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CHEMICAL PRODUCTION OF COPPER STANDARD  
TARGET FOR ASSAY OF  $^{233}\text{U}/^{229}\text{Th}$

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README

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This work was done over the 2020 summer for 3 months from May 1st to July 31st. Due to the effect of COVID-19 most work was done from home as the laboratory was inaccessible. My research position is supervised by Dr. Razvan Gornea from Carleton University's Physics Department. I am working with Dr. Carlos Vivo-Vilches and Dr. Razvan Gornea. For our project, we are collaborating with Liam Keiser from André E. Lalonde AMS Laboratory at the University of Ottawa. Ottawa University's laboratory is very well equipped for the chemical preparations necessary for our work as well as housing the AMS. For this reason, all laboratory work was done at the University of Ottawa.

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## 1 Introduction

Radioactive elements are everywhere in our environment. For the most pressing physics mysteries of our half-century, low energy particle physicists have had to develop techniques to make the most sensitive of detectors. This largely involves protecting the detector from any type of radiation which would create a background in the detector. From this, solutions have been provided, such as clean rooms, sonification cleaning, and building detector deep underneath the earth's surface. Billions of dollars are put into researching ways to prevent this radiation from creating background noise in the detector. The specific detector which we are applying this novel method towards is the next Enriched Xenon Observatory (nEXO) attempting to observe neutrinoless double-beta decay. Every material used must be investigated to ensure it contributes the least amount of background to the detector. For this reason, many materials such as copper, sapphire and Kapton are being assayed by the collaboration for various radioactive elements. Ensuring that the materials used for the detector contain minimal radioactive impurities that would undergo alpha decays at energies problematic to the detector is also a prominent field of investigation and it the topic of my current work.

An Accelerator Mass Spectrometer (AMS) can determine the isotopic ratio of an element in a material. It is often used for radiocarbon dating of items with extreme sensitivity observing the  $^{14}\text{C}/^{12}\text{C}$  isotopic ratio. Importantly, it can accelerate any molecular ion to MeV energies forcing collision resulting in the molecules breaking into their elemental compositions. This is advantageous as other assaying techniques are greatly impacted by molecular background. The sensitivity of the machine is comparable to being able to detect 1 specific grain of sand in  $100\text{km}^2$  of desert.

We are developing novel technology to assay  $^{233}\text{U}$  and  $^{229}\text{Th}$  by AMS in copper. The largest challenge is to produce standard targets for the calibration of the measurements. This involves making sintered copper targets with known  $^{233}\text{U}$  and  $^{229}\text{Th}$  concentrations for the creation of such standards. A detailed procedure is outlined and various investigation into the topic of interest are outlined in the following section.

## 2 Chemical procedure for standard targets

Starting with a solution containing a known amount of  $\text{Cu}(\text{NO}_3)_2$ , known amounts of  $^{233}\text{U}$  and  $^{229}\text{Th}$  are added to the solution. The addition of basic  $\text{NH}_3$  causes the formation of  $\text{Cu}(\text{OH})_2$ , which is insoluble and will precipitate. In the same step, we expect our actinide to precipitate as well. We are precipitating two ions at the same time,  $\text{Cu}^{2+}$  and trace amounts of  $\text{UO}^{2+}/\text{Th}^{4+}$ . This process is done by coprecipitation which is discussed in detail.

Our initial chemical preparation procedure attempted to react the precipitated  $\text{Cu}(\text{OH})_2$  heating to 650C inducing thermal decomposition to create  $\text{CuO}$ . Then by annealing at 673K with  $\text{N}_2$ , creating solid copper. At temperatures lower than 1173K we expected to see formation  $\text{CuO}$ .

Tests in the lab showed that annealing with  $\text{N}_2$  did not cause the thermal decomposition of copper oxide. We believe that the reason why our method did not work was that the mechanism relied on total pressure and not just partial pressure of oxygen. The next steps are to try in a vacuum.

## 2.1 Coprecipitation Percent Yield

Since the trace amounts of  $^{233}\text{U}$  and  $^{229}\text{Th}$  added are too dilute to precipitate by conventional means, it is typically coprecipitated with a carrier ( $\text{Cu}(\text{OH})_2$ ), a substance that has a similar crystalline structure that can incorporate the desired element. There are three types of coprecipitation. (i) Incorporated in the lattice (homogeneous) (ii) Absorbed during lattice growth (homogeneous) (iii) Absorbed on the surface of the lattice (inhomogeneous). Since inhomogeneity of the actinide in the precipitate would be detrimental to the calibration we must ensure that we do not have such a case. This third case mostly only happens when the coprecipitate is a colloidal particle in solution which is not the case in this procedure. Further proof of homogeneity may be done by laser ablation ICP-MS.

The coprecipitation yield is the percent incorporation of the actinide into the carrier. Coprecipitation of U/Th has been done in literature with  $\text{Fe}(\text{OH})_3$ . Two factors can play a potentially critical role in the coprecipitation yield during the  $\text{Fe}(\text{OH})_3$  and  $\text{UO}^{2+}$  co-precipitation process. (i) The concentration of Fe(III) in the sample. Coprecipitation yield increases to 140mg/L and then follows an asymptotic trend. We will be using much greater concentrations than this. (ii) The total volume of processed solution. Less volume of the solution means better yield.

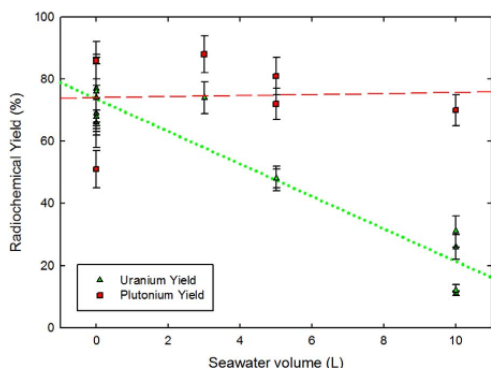


Fig. 3. Radiochemical yields for uranium and plutonium isotopes obtained for different volumes of processed seawater.

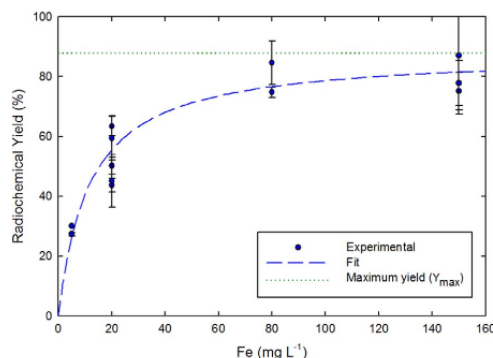


Fig. 4. Uranium radiochemical yield of the coprecipitation process obtained by ICP-MS for different Fe(III) concentrations. All the experimental point came from one litre sea-water samples.

Coprecipitation yield of  $\text{UO}^{2+}$  was from 30% – 80%. For  $\text{Th}^{4+}$  ion, factors such as the amount of Fe used and concentration of Th were measured however no correlation with a percent yield of coprecipitation was observed. The coprecipitation yield was  $\text{Th}^{4+}$  28% – 93%.

(Informal citing: <https://www.osti.gov/etdeweb/servlets/purl/587828>)

The viability of using  $\text{Cu}(\text{OH})_2$  as our carrier was investigated comparing it too  $\text{Fe}(\text{OH})_2$ . The ionic radius of  $\text{Cu}^{2+}$  is 0.91 Angstrom,  $\text{Fe}^{3+}$  is 0.63 Angstrom. The larger copper ions would mean greater coprecipitation of larger ions like  $\text{UO}^{2+}$  (3.5 Angstroms) and  $\text{Th}^{4+}$  (1.08 Angstroms). The 2+ charge for  $\text{Cu}^{2+}$  and  $\text{UO}^{2+}$  will give greater coprecipitation as we can expect incorporation into lattice than Fe(III). However, for  $\text{Th}^{4+}$  the effect of 4+ charge may result in lower yields than with  $\text{Fe}^{3+}$ . Conveniently, we will be using low volume and a higher concentration of precipitate which should give higher yields. The conclusion is that the coprecipitation yield will be unknown unless measured. Therefore we need to assay the coprecipitation yields by alpha spectrometry.

### 3 Alpha counting determination of coprecipitation yields of $^{232}\text{U}$ and $^{228}\text{Th}$ in chemically prepared sintered copper samples

#### 3.1 Method

The chemical preparations needed for the assay of  $^{233}\text{U}$  and  $^{229}\text{Th}$  in copper will involve the coprecipitation of the actinide along with  $\text{Cu}(\text{OH})_2$ . Since the trace element ( $^{233}\text{U}/^{229}\text{Th}$ ) is too dilute to precipitate by conventional means, it is coprecipitated with the carrier ( $\text{Cu}(\text{OH})_2$ ). The carrier substance's crystalline structure will incorporate the actinide. The effectiveness of the coprecipitation or coprecipitation yield with the chosen carrier has not been measured in literature. The yield will affect the AMS measurements and therefore we need to assay the coprecipitation yields by alpha spectrometry.

Our proposed method is to make a copper sample as we would for AMS and determine the concentrations of U and Th by alpha spectrometry. This will allow us to get the coprecipitation yield. Instead of using the isotopes under investigation in AMS, we propose using  $^{232}\text{U}$  and  $^{228}\text{Th}$  as they have much lower half-lives which is advantageous for alpha counting. Isotopic differences will not influence the coprecipitation yields.

The sintered copper sample will be made using  $^{232}\text{U}$  solution, which is in secular equilibrium with its daughters, including  $^{228}\text{Th}$ . We expect a lower coprecipitation yield from  $\text{Th}^{4+}$  due to its  $4+$  state in solution compared to the  $2+$  charge state from  $\text{UO}^{2+}$ . This will result in the secular equilibrium being broken in the final precipitate. Since the half-life of  $^{228}\text{Th}$  is comparatively short, it will reach secular equilibrium with its daughters in a month. Therefore we will assume secular equilibrium with the daughters of  $^{228}\text{Th}$  but not secular equilibrium with  $^{232}\text{U}$ . The alpha counting will be done multiple times weeks apart to observe changes in any secular equilibrium. We will be able to measure the concentration and thus the coprecipitation yields of both U and Th with just one sample.

We will make a copper sintered target with a maximum concentration of 0.1ppt  $^{232}\text{U}$  using the spike solution. For the AMS measurements, in same sample we add  $^{233}\text{U}$  and  $^{229}\text{Th}$  to 0.1ppt. We then modify the target to be compatible with the alpha counter and wait 30 days. Secular equilibrium will be achieved with  $^{228}\text{Th}$  but not with  $^{232}\text{U}$ . We then will measure by alpha counting and get both concentrations of  $^{232}\text{U}$  and  $^{228}\text{Th}$ . We can then measure the 0.1ppt  $^{233}\text{U}$  and 0.1ppt  $^{229}\text{Th}$  by AMS to calibrate our measurements. Another sample will be made to only be measured by AMS with 1ppt  $^{233}\text{U}$  and 1ppt  $^{229}\text{Th}$  to aid in the calibration. The same coprecipitation yield measured by alpha spectrometry will be applied to this sample for calibration.

#### 3.2 Feasibility Investigation for Alpha Counting Method

Since alpha particles are charged particles, they lose energy in the medium, therefore most of them are absorbed by the material itself and not emitted out of the material. Energy deposition of the emitted alpha particles for each atom in the decay chain was simulated in SRIM using the most prevalent alpha decay energy. This was simulated in pure copper with a density of  $8.92\text{g}/\text{cm}^3$ . Sintered copper is expected to have a slightly lower density.

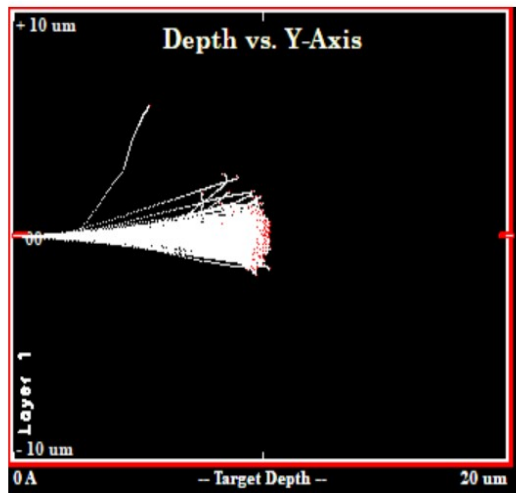


Figure 1: Simulated alpha particles in copper

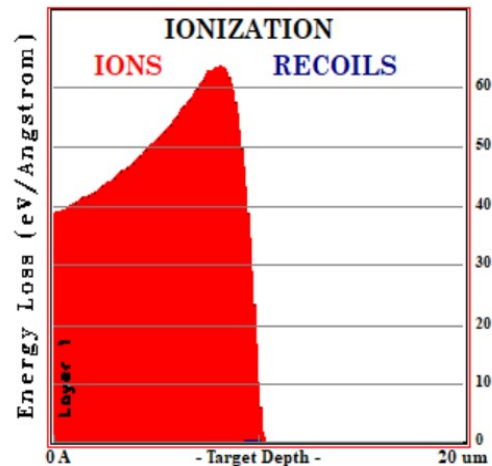


Figure 2: Energy deposition over depth of emitted alpha particle simulated using SRIM

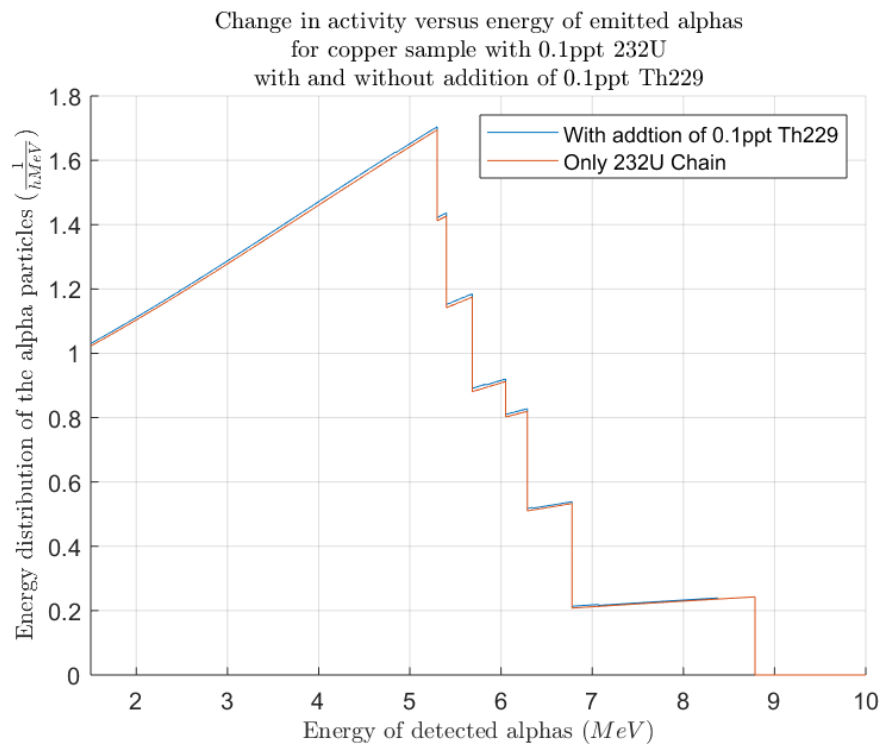
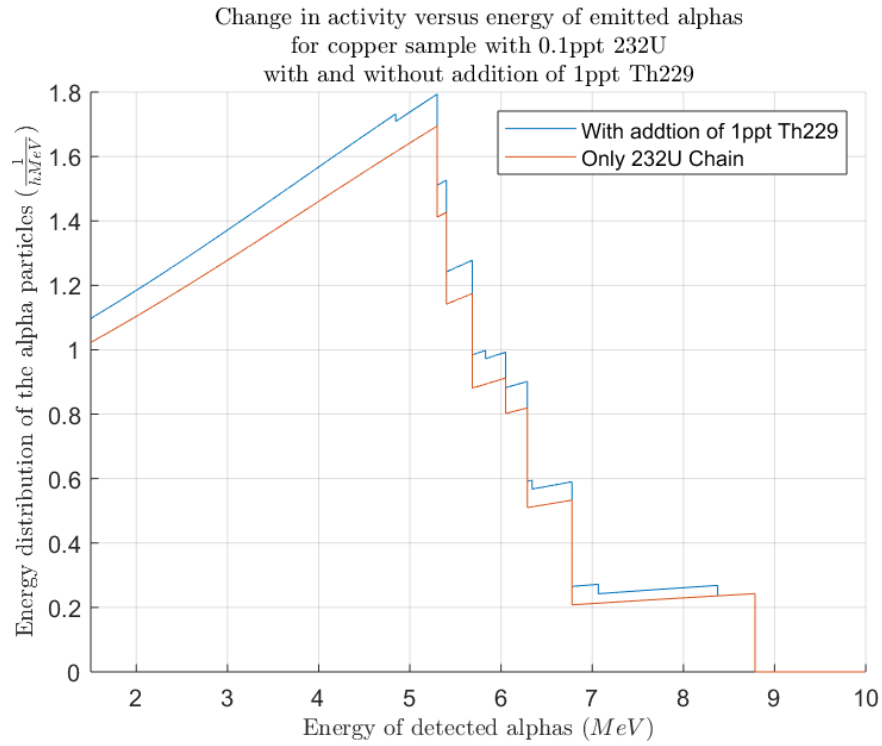
The integral of the energy deposition over the depth provides the energy lost by the alpha particle. Subtracting the energy lost from the initial energy of the alpha's we obtain the energy distribution which we will observe in the alpha counter. Since this counter has a minimum observable energy of 1.5MeV we take the distance for the alpha particles to reach that energy as the max range in which the particle can traverse through the copper and still be counted by the detector. This allows us to determine the volume of the sample which contains the radionuclides we observe by the detector.

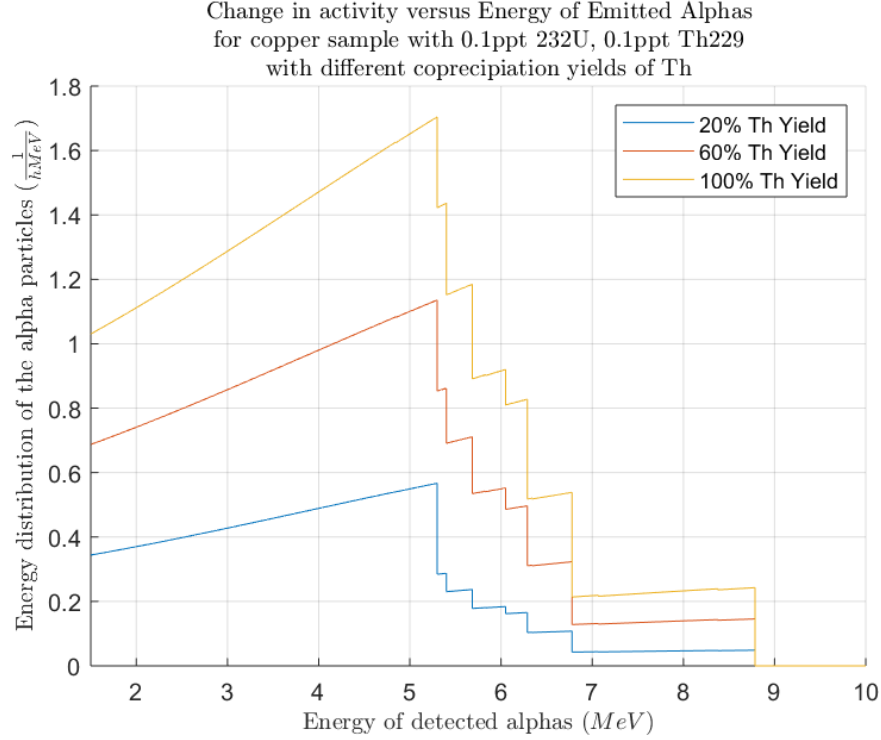
If  $N_{actinide}$  is the number of actinide atoms present and  $T_{\frac{1}{2}}$  is the half-life of the associated actinide, the activity is given by

$$A = \frac{\ln(2)N_{actinide}}{T_{\frac{1}{2}}} \quad (1)$$

The distance between the sample and the detector can be approximated to be 0 since the distance is so short meaning that the activity observed by the detector is one half of the total activity.

Using the surface area of the target multiplied by the max range of the alpha particles allows us to get the activity observed for each radionuclide in the chain. The alpha per hour for each daughter in the chain with 1ppt concentration starting with  $^{232}\text{U}$  is 8.7129, 8.9204, 9.7502, 11.6172, 13.2768, 3.8835, 13.0113. These activities are then divided by their respective maximum alpha range to give activity per target depth  $\frac{dA}{dx}$  which is constant. The depth over energy data was then fitted with a 4th order polynomial. The derivative was then calculated yielding  $\frac{dx}{dE}$ . The result of multiplying the two is a function  $\frac{dA}{dE}(E)$  for each actinide. Summing each of the function gives the prediction for what we will observe by the detector. Multiplying each of the daughters of  $^{232}\text{U}$  by a yield factor allows us to see the difference that the  $^{228}\text{Th}$  coprecipitation yield will give.





1ppt concentration of  $^{229}\text{Th}$  would impact the alpha energy spectrum. However, as can be seen, the addition of 0.1ppt  $^{229}\text{Th}$  would result in minimal background. Any background which is a result of  $^{229}\text{Th}$  could be accounted for.

### 3.3 Relationship between Observed Alpha Particles and Radionuclides Concentrations

This data was used to calculate two constants to determine the specific alpha particles coming from  $^{232}\text{U}$  and  $^{228}\text{Th}$  from the entire decay chain alpha particles. The alpha energy of the  $^{232}\text{U}$  nuclide is 5.3MeV and is the lowest of the energies in the decay chain. From the alpha counting measurement, we will know the total rate of alpha particles reaching the detector,  $\alpha_{Total}$ , and the alpha per hour which hit the detector with greater energy than 7.5MeV,  $\alpha_{E>7.5\text{MeV}}$ . We chose 7.5MeV as it is 6.8MeV is the second-highest emitted alpha energy of all the radionuclides in the chain, and we account for the 9% energy resolution of the alpha counter. The rate of alpha particles from the  $^{232}\text{U}$  decay reaching the detector is

$$\begin{aligned}\alpha_{^{232}\text{U}} &= \alpha_{Total} - \alpha_{^{228}\text{Th}Chain} \\ &= \alpha_{Total} - (20.0781)\alpha_{E>7.5\text{MeV}}\end{aligned}\tag{2}$$

where alpha  $^{228}\text{Th}$  Chain is the rate of alpha particles from the  $^{228}\text{Th}$  decay chain reaching the detector.

$$\alpha_{^{228}\text{Th}} = (2.9481)\alpha_{E>7.5\text{MeV}}\tag{3}$$

The concentration for  $^{232}\text{U}$  can be calculated by the following

$$C_{^{232}\text{U}} = \alpha_{^{232}\text{U}} \frac{M_{^{232}\text{U}} T_{\frac{1}{2}}}{\rho S R_{^{232}\text{U}}} \frac{1}{\ln(2) 6.022 \times 10^{23}}\tag{4}$$

Where  $S$  is the surface of the copper disk, and  $R_{^{232}\text{U}}$  is the range of alpha particles from the  $^{232}\text{U}$  decay in copper. To conclude, we expect to be able to measure the coprecipitation yields of both uranium and thorium by alpha spectrometry using one sample.