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Copper electroplating for background suppression in the NEWS-G experiment

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Abstract

New Experiments with Spheres-Gas (NEWS-G) is a dark matter direct detection experiment that will operate at SNOLAB (Canada). Similar to other rare-event searches, the materials used in the detector construction are subject to stringent radiopurity requirements. The detector features a 140-cm diameter proportional counter comprised of two hemispheres made from commercially sourced 99.99% pure copper. Such copper is widely used in rare-event searches because it is readily available, there are no long-lived Cu radioisotopes, and levels of non-Cu radiocontaminants are generally low. However, measurements performed with a dedicated ²¹⁰Po alpha counting method using an XIA detector confirmed a problematic concentration of ²¹⁰Pb in bulk of the copper. To shield the proportional counter's active volume, a low-background electroforming method was adapted to the hemispherical shape to grow a 500-µm thick layer of ultra-radiopure copper to the detector's inner surface. In this paper the process is described, which was prototyped at Pacific Northwest National Laboratory (PNNL), USA, and then conducted at full scale in the Laboratoire Souterrain de Modane in France. The radiopurity of the electroplated copper was assessed through inductively coupled plasma mass spectrometry (ICP-MS). Measurements of samples from the first (second) hemisphere give 68% confidence upper limits of $<0.58 \ \mu Bq/kg$ ($<0.24 \ \mu Bq/kg$) and $<0.26 \ \mu Bq/kg$ ($<0.11 \ \mu Bq/kg$) on the ²³²Th and ²³⁸U contamination levels, respectively. These results are comparable to previously reported measurements of electroformed copper produced for other rare-event searches, which were also found to have low concentration of ²¹⁰Pb consistent with the background goals of the NEWS-G experiment.

Keywords: Dark matter, Direct detection, Rare Event, Electroforming, Copper, Low background

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1. Introduction

Direct searches for dark matter (DM) and neutrinoless double-beta decay [1, 2, 3, 4] have strict requirements on the experimental background to ⁵ achieve their targeted sensitivities. While such experiments are generally carried out in underground laboratories and in specifically designed shielding to suppress backgrounds from external sources, one of the main remaining sources arises from radioac-

tive decays in the detector's construction materials, including the gaseous target. The effort to procure materials with the lowest possible radioactivity has driven significant improvements in the techniques and facilities used to assay and prepare radiopure materials [5, 6, 7, 8].

A common choice for a high-purity material is commercially sourced copper [9, 10, 11], because it is readily available and there are no long-lived Cu radioisotopes—with a half-life of 61.8 hours [12],

- 20 ⁶⁷Cu is the longest-lived. For this reason, the NEWS-G collaboration [13] chose C10100 (99.99% pure) copper² to construct a \emptyset 140 cm spherical proportional counter [14], which will be housed in the compact shielding shown in Fig. 1, to perform a di-
- ²⁵ rect DM search at SNOLAB, Canada. Along with this outer spherical shell, which is grounded, the detector is composed of a central electrode set at high voltage. To first approximation, this produces a radial $1/r^2$ electric field in the detector. The in-
- teractions of a particle with the gas, such as a DM particle elastically interacting and resulting in a nuclear recoil, may cause ionisation. The resulting primary electrons drifting under the electric field until within approximately 1 mm of the central electrode,
- ³⁵ where the electric field becomes large enough that the primary electrons gain sufficient energy to cause secondary ionisation. This results in a Townsend avalanche, thus providing signal amplification. Due to it's proximity to the active medium and it's size,
 ⁴⁰ the radiopurity of the spherical shell is of critical

importance.

Even without long-lived Cu radioisotopes, a copper sample will have some (non-Cu) radiogenic

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Figure 1: Schematic diagram of the NEWS-G detector and shielding. The \emptyset 140 cm spherical proportional counter is shown at the centre, surrounded by 3 cm of archaelogical lead, followed by 22 cm of low radioactivity lead in a stainless steel skin. The outer-most part of the shielding comprises 40 cm of high-density polyethylene (HDPE).

contamination resulting from cosmogenic activation and industrial production processes. For example, cosmic-ray neutrons interacting with copper through the (n, α) reaction can produce ⁶⁰Co. The half-life of the produced ⁶⁰Co is approximately 5.3 years, making it a long-lived background relative to the typical time scale of direct DM detection experiments. At the surface of the Earth, the added activity due to ⁶⁰Co is approximately 0.4 µBq/kg/day [15]. Other cosmogenic contaminants with shorter half-lives are also produced, e.g. ⁵⁹Fe. These contributions can be suppressed by minimising the copper's exposure to cosmic rays. Other radiocontaminants primarily originate from the 238 U and 232 Th decay chains. The 238 U decay chain is shown in Fig. 2. This contamination is inherent to the raw material and a result of the manufacturing and handling processes. An established technique is to directly measure the uranium and thorium levels with inductively coupled plasma mass spectrometry (ICP-MS), which has been demonstrated to have sensitivity better than 30 fg/g to these contaminants [6, 16, 17]. The progeny activities can also be inferred and used to estimate background contributions to experiments, under the assumption of secular equilibrium.

However, ²²²Rn, which is part of the ²³⁸U decay chain, is a gaseous isotope. As a result, ²²²Rn may deposit its decay products on the copper surface or into the copper bulk at the raw-ore stage or during manufacturing. This contribution adds to the contamination and may break the secularequilibrium assumption. The longest-lived isotope

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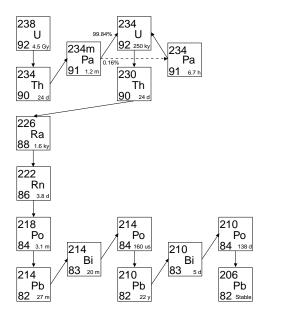


Figure 2: 238 U decay chain. All daughters are solid at room temperature and pressure except 222 Rn, which is a gas. Only decays with a branching fraction greater than 0.05% are shown [12].

in the ²²²Rn decay chain is ²¹⁰Pb with a half-life of 22.2 years [18]. Accumulation of ²¹⁰Pb from ²²²Rn deposits can result in experiment backgrounds that cannot be inferred by ICP-MS measurements of the ²³⁸U measurements of the

²³⁸U progenitor. One method to assess this contamination is by directly measuring the 5.3 MeV α particles from the ²¹⁰Po decays [19, 20, 8], using a highsensitivity XIA UltraLo-1800 spectrometer, which

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- has a sensitivity of 0.0001 $\alpha/\text{cm}^2/\text{hour}$ [21]. The XMASS collaboration has established a method to estimate very low ²¹⁰Pb contamination in copper bulk, having demonstrated the ability to distinguishing the contamination in bulk from that on
- ⁹⁰ the surface [20]. For oxygen-free copper (at least 99.96% pure by weight³) the ²¹⁰Pb contamination in the bulk is estimated to be in the range of 17– 40 mBq/kg [20]. The corresponding value for the C10100 copper procured by the NEWS-G collabo-
- ration is 29^{+8+9}_{-8-3} mBq kg⁻¹, the estimation of which is discussed in Section 2.

The measured level of ²¹⁰Pb in the C10100 copper bulk and the corresponding contamination of its progeny in the bulk of the NEWS-G detector's copper sphere would represent approximately 72%

of the experimental background [15] below 1 keV

as estimated by means of a Geant4 [22] simulation. The second largest contribution to the experimental background is cosmogenic activation of the copper resulting from a 93-day exposure of the copper to surface-level cosmic muon fluxes, which is anticipated for manufacturing the detector and transporting it from France to Canada, followed by 1 year of being in an underground laboratory. This contribution accounts for approximately 11% of the anticipated background below 1 keV. An additional contribution from the copper, of 2.7%, comes from trace amounts of 238 U, 232 Th and 40 K contamination. Finally, the remaining approximately 13.9% of the expected background below 1 keV originates from the following sources, listed from largest to smallest contribution: ²³⁸U, ²³²Th and ⁴⁰K contamination of the lead shielding; ³H and ²²²Rn contamination of the gas mixtures used; γ rays and neutrons from the cavern; and cosmic muons.

An approach to suppress the background from ²¹⁰Pb contamination is to grow a layer of ultraradiopure copper onto the inner surface of the detector sphere. This layer acts as an internal shield to suppress backgrounds, e.g. from β -decays of ²¹⁰Pb and accompanying X-rays and Auger electrons, and its progeny ²¹⁰Bi, originating from the bulk of the commercially sourced C10100 copper. It is estimated that a 500 µm-thick layer of ultraradiopure copper will suppress this background contribution below 1 keV by a factor of 2.6which constitutes 49.5% of the total background in that region [15].

A method to deposit ultra-radiopure copper is potentiostatic electroforming [20, 23]. This method takes advantage of electrochemical properties to produce copper with reduced impurities. The process is discribed in Section 3. This method was previously used to produce a variety of detector components, including those requiring extreme radiopurity such as for the Majorana Demonstrator [24]. Internal fittings were fabricated from electroformed copper with ²³⁸U and ²³²Th levels less than 0.099 and 0.119 $\mu Bq/kg^4$ at 68% confidence, respectively—limited by the ICP-MS assay precision [17]. In order to apply this process to a hemispherical surface, a scale model was produced and used to determine the operating conditions. This is described in Section 4. The electroplating procedure used on the NEWS-G detector and the results

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³Japanese Industrial Standard, JIS:C1020

 $[\]frac{4 \text{For } ^{238}\text{U}, 1 \ \mu\text{Bq/kg} \approx 0.081 \ \text{pg/g}. \text{ For } ^{232}\text{Th}, \\ 1 \ \mu\text{Bq/kg} \approx 0.244 \ \text{pg/g}$

of a subsequent radioisotope assay of the produced copper are detailed in Section 5 and Section 6, respectively.

2. Assessment of the ²¹⁰Pb Contamination ¹⁵⁵ in NEWS-G Copper

To assess the level of ²¹⁰Pb contamination in the C10100 copper used to produce the detector, samples were taken from the same batch of copper after casting. The α particles from ²¹⁰Po decays were measured using an XIA UltraLo-1800 [21] ionisation chamber, which uses an active veto to obtain a second complementary signal arising from cases where the α particle does not originate from the sample under test. This is used to suppress back-

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- ¹⁶⁵ ground coming from the detector's own construction materials. The sample is placed in the detector which is flushed with argon gas to minimise ²²²Rn contamination. In this measurement, the ²¹⁰Po content of the bulk of the copper sample is of
- ¹⁷⁰ interest. The observable energy of 5.30 MeV α particles emerging from the bulk of the copper sample was estimated with a Geant4 simulation. An energy window of 2.5 MeV to 4.8 MeV was used to primarily select α particle originating from a depth
- ¹⁷⁵ of approximately 2 µm to 8 µm. This improves the signal-to-noise ratio for selecting bulk α particle events. The conversion factor for measured counts to bulk activity was estimated from Geant4 to be 2.7×10^2 (Bq/kg)/(α /cm²/hour) [20].
- ²¹⁰Po has a half-life of approximately 138 days, which is significant shorter than the approximately 22 years of the progenitor ²¹⁰Pb. As a result, the activities of ²¹⁰Po and ²¹⁰Pb may be different due to different contamination amounts at the produc-
- tion phase. Therefore, the activities of the two isotopes may be out of secular equilibrium; however, the ²¹⁰Po activity in a sample will evolve over time until it matches that of ²¹⁰Pb. Therefore, multiple measurements of the ²¹⁰Po activity over time are
- ¹⁹⁰ required to accurately infer the activity of ²¹⁰Pb in the copper. Four measurements of the α particles from the sample were made over the course of approximately one year, each lasting between 12 and 23 days. Table 1 shows the results of the four measurements.
- A joint likelihood fit of all measurements was performed and is shown in Figure 3 along with the measurements. From this fit, it was estimated that the 205 210 Pb activity in the sample is 29^{+8+9}_{-8-3} mBqkg⁻¹,
- 200 where the statistical and systematic uncertainties

Table 1: Measurements of the α particles in a 2.5 MeV to 4.8 MeV energy window originating from ²¹⁰Po decays in a C10100 copper sample.

Citito copper sample.			
Date	Measurement		
	$[10^{-4} \alpha/\mathrm{cm}^2/\mathrm{hour}]$		
Jul. 2 - 25, 2018	2.3 ± 0.4		
Oct. 5 - 17, 2018	2.2 ± 0.4		
Dec. 28, 2018 - Jan. 9, 2019	1.4 ± 0.3		
Apr. 19 - May 7, 2019	1.4 ± 0.3		

are given separately. This is consistent with other copper samples with similar purity [20].

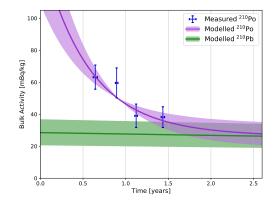


Figure 3: Measurements of the α particles from the decay of 210 Po in a sample of C10100 copper used in the production of the NEWS-G detector. Time is measured from the estimated production date of the copper. The purple (green) line shows the fitted 210 Po (210 Pb) activity over time, with the bands showing the $\pm 1\sigma$ region.

3. Electroplating

Electroplating is carried out through the use of an electrolytic cell, which consists of an anode and a cathode separated by an electrolyte, as illustrated in Fig. 4. A current is used to supply electrons to the cathode where an ion undergoes a reduction reaction (gain of electrons) to form an atom deposited on the surface, while oxidation reactions (loss of electrons) occur at the anode. The reactions occurring at each of the electrodes will be of the general form:

$$A^{(y+z)+} + ze^{-} \leftrightarrows A^{y+}, \qquad (1)$$

where A is the molecular species, y is its ionic charge and z is the number of electrons required for the reduction reaction (reading left-to-right) or the number of electrons released in the oxidation

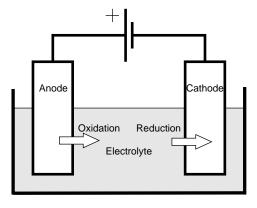


Figure 4: Schematic diagram of a simple electrolytic cell. Arrows indicate the motion of ions, which are released into the electrolyte by oxidation reactions at the anode and then deposited on the cathode in reduction reactions.

reaction (reading right-to-left). Reading this equation in one direction gives the "half-cell reaction", where the anode and cathode half-cell reactions are not necessarily the same; e.g., in the case where one species is oxidized at the cathode but a different species is reduced at the anode.

A current I flows through the circuit and electrolyte. As the reduction reactions require electrons, the number of moles of reduced atoms during electroplating is proportional to the total supplied charge: $Q(t) = \int I dt$. The number of moles n of ions reduced in time t is given by

$$n(t) = \frac{Q(t)}{zF}, \qquad (2)$$

where $F = eN_A$ is the Faraday constant, and e^{-2} and N_A are the elementary charge and the Avogadro constant, respectively. The resulting deposited mass as a function of time is

$$M(t) = m_r n(t)$$
, (3) ²⁴⁰

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where m_r is the molecular mass of the deposited species. When the current is reversed the process is called electropolishing, which is a technique used to remove material from a surface.

There will be several species of ions in the electrolyte available to electroplate to the cathode. The tendency of an ion species to be reduced is quantified by the reduction potential E^0 . Examples are shown in Table 2 for copper and radioisotope contaminants. A greater value of E^0 indicates a species that is more easily reduced. Each half-cell reaction will have its own reduction potential. The standard cell potential E_{cell}^0 of the electrolytic cell is defined as the difference between the reduction potentials of the half-cell reactions at the anode E_{A} and cathode E_{C} :

$$E_{\rm cell}^0 = E_{\rm C}^0 - E_{\rm A}^0 \,. \tag{4}$$

For $E_{\text{cell}}^0 < 0$, additional energy will be required for the reaction to proceed [25]. For $E_{\text{cell}}^0 \ge 0$, the reaction is spontaneous (or in chemical equilibrium in the case of equality). For a given species being oxidized at the anode, the reaction will only proceed when the cathode half-cell reaction has a higher reduction potential. In the case of a copper anode being oxidized, only ion species in the electrolyte with a reduction potential greater than that of copper will reduce. The relatively high reduction potential of copper compared to many radioisotopes means that it is purified during electroplating. However, other factors, such as mass transport of contaminant ions, can cause species with lower reduction potentials to be deposited with the copper in small amounts [23].

Table 2: Reduction potential for copper and possible radiocontaminants.

Reductants		Oxidants	E^0 (V)	
$Cu^{2+} + 2e^-$		Cu	+0.34	[26]
$Pb^{2+} + 2e^{-}$	—	Pb	-0.13	[27]
$U^{3+} + 3e^{-}$	\leftrightarrows	U	-1.80	[28]
$\mathrm{Th}^{4+} + 4e^{-}$	\rightleftharpoons	Th	-1.90	[28]
$K^+ + e^-$	\rightleftharpoons	Κ	-2.93	[29]

In this work, a copper anode is used to provide Cu^{2+} ions to the electrolyte. For Cu^{2+} ions reducing at the cathode, the system will have $E_{cell}^0 = 0$ V. Thus, to drive the reaction and overcome energy loss mechanisms in the system, the electrodes are kept at a potential difference of 0.3 V [30].

It has been shown that applying a time-varying potential difference between the electrodes can have several benefits compared to a constant potential difference [31]. During electroplating, the region of the electrolyte at the surface of the cathode becomes depleted of Cu^{2+} relative to the bulk electrolyte. This slows down the rate of electroplating and affects the properties of the deposited copper [31]. The waveform of the time-varying potential difference allows this region to be replenished by allowing diffusion from the bulk electrolyte when no voltage is applied and by reintroducing more ions from the surface during the reverse-voltage part of

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the waveform. Also, differences in current density can arise due to differences in the distance be-

tween the anode and cathode surfaces (e.g. a surface $_{290}$ rough point). High current density regions of the electrolyte are more depleted of Cu²⁺ than lower density regions. When no voltage is applied, ions can diffuse between two such regions and thus lead

- to a more uniform overall current density, while 295 the reverse-voltage part of the waveform prevents a thick layer forming in the high current density regions [31]; both effects promote more uniform growth of the electroplated copper layer. The re-
- versing of polarity also allows for release of contaminant ions that may have been entrapped during the high mass transport portion of the forward plating. The waveform used for the electroplating is shown in Fig, 5. Note that while the potential is applied in Fig. 5. Note that while the potential is applied
- 270 it is potentiostatic at a level that favors the oxida- 305 tion/reduction of copper.

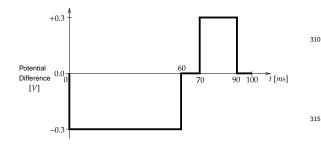


Figure 5: Waveform used in the electroplating. The negative terminal was attached to the cathode.

4. Scale Model

The copper electroplating procedure described ³²⁵ in the previous section is a well-established and ²⁷⁵ successful method that has existed for over a decade [23]. However, this method must meet fairly rigid operational conditions to produce optimal material. Failure to meet these conditions can not only produce copper of poor radiopurity but often results

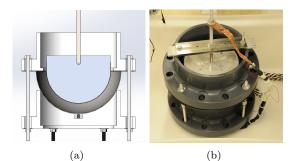
- in deposits with poor physical properties as well. For NEWS-G the initial loading of copper into solution would need to be generated from an initial electropolishing step, because commercially available copper sulfate is not sufficiently pure. How-
- ever, for traditional electroforming, the amount of copper required in the electrolyte is too great to achieve through electropolishing. As a result, the

plating conditions for the NEWS-G hemispheres required a major deviation in the concentration of copper sulfate ($CuSO_4$) in the electrolyte.

Not all parameters have a well-studied effect on growth, especially when multiple parameters are outside of their established optimal operating ranges. Prior experience has shown that electrolyte with a low copper-ion concentration can produce dendritic copper deposition. In the absence of accurate deposition models it was necessary to run a scaled experiment prior to plating the fullsized \emptyset 140 cm sphere underground in Laboratoire Souterrain de Modane (LSM). Key growth parameters were identified and an experiment was designed based on those that could be adjusted *in situ* at LSM and projected onto a scale model.

The key independent and adjustable variables were determined to be the concentration of copper and overall conductivity of the electrolyte, and the current based on the limiting set of voltage conditions. Control of the CuSO₄ concentration is limited by the amount of copper that can be dissolved during an initial electropolishing step, which serves two purposes: a) expose the underlying bulk crystal structure to prepare the copper surface for electroplating; and b) load the electrolyte with copper. During this step, the \emptyset 140 cm hemisphere will act as the anode and careful control of the potential is not as important, whereas subsequently copper will be plated to the \emptyset 140 cm hemisphere which will then be serving as the cathode. During the latter step, the voltage control and deposition rate are critical. As a result, establishing how the plating responds to small changes in $CuSO_4$ is crucial. As such, three variations of $CuSO_4$ concentration, three conductivities, and three voltage settings were identified for experimentation on the scale model.

A stainless steel spherical float with a diameter of 30 cm was cut in half and used as a stand-in for the full-scale \emptyset 140 cm copper hemisphere. A smaller hemisphere was machined from aluminum and plated with copper to serve as the anode after the initial electropolishing step. Figure 6 shows the experimental setup of the scale model. Although the transport dynamics involved are not fully understood, previous experience has shown that the electrode gap (path length) has an effect on plating, regardless of CuSO₄ concentration and conductivity. So, while the spacing between the two electrodes was scaled, the impedance needed to be matched to that of the full-scale setup. This required the electrolyte conductivity to be reduced



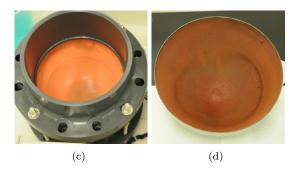


Figure 6: (a) CAD model of the small-scale setup; (b) the assembled scale-model experiment; (c) copper plated onto the scale model's stainless steel hemisphere; and (d) the final scale-model growth of copper.

to compensate for the reduced electrode spacing in the model.

A bath, shown in Fig. 6(a) and Fig. 6(b), was designed to hold and stabilize the stainless steel hemisphere, and several iterations of plating were

- performed to cycle through the plating variations and determine the optimal electroplating conditions. Based on these trials, the parameters chosen for plating copper onto the full-scale hemispheres are a CuSO₄ concentration of 0.03 mol L^{-1} , a con-
- ductivity of 91.9 mS cm⁻¹ (corresponding to a fullscale conductivity of 300 mS cm⁻¹), and a potential of 0.35 V. Using these parameters, the estimated time to electroplate each full-scale hemisphere is ~ 8 days to attain a thickness of 500 µm. The result-
- ing growth for the small-scale model is shown in ³⁹⁰ Fig. 6(c) and Fig. 6(d).

5. Electroplating NEWS-G Detector

The electroplating was conducted at LSM at a

depth of 4800 m water equivalent to reduce cosmogenic activation. The detector outer shell is comprised of two Ø140 cm hemispheres, produced by a spinning technique using C10100 copper. The 400



Figure 7: A detector hemisphere following (a) initial cleaning with detergent and (b) chemical etching with an acidified hydrogen peroxide solution.

result after cleaning with commercial detergent is shown in Figure 7(a). The hemispheres were then sanded to produce a smooth surface and subsequently chemically etched using an acidified hydrogen peroxide solution [32, 8]. The result of this preparation is shown in Figure 7(b).

A smaller C10100 copper hemisphere was produced to act as the anode for electroplating and was cleaned in the same way as the detector hemispheres. It was suspended inside the detector, separated by an electrolyte comprised of deionized water (18 Mohm), Optima[®] grade sulphuric acid (Fisher Scientific), and copper sulphate produced by a previous electroplating. A pump provided mechanical mixing with a filter removing particulates greater than 1 µm in size from the electrolyte. The anode and cathode were connected to a pulse-reverse power supply (Dynatronix, Amery, WI, USA), which could supply up to 80 A. The whole set-up was contained in a temporary purposeconstructed cleanroom to prevent particulates entering the electrolyte and subsequently providing nucleation sites for nodule-like copper growth [33]. The setup is shown in Fig. 8.

Prior to electroplating, each hemisphere was electropolished to remove a layer of material from the surface. This exposes the underlying crystalline structure and provides an ultraclean surface prior to deposition. Furthermore, this process enhances the amount of Cu^{2+} in the electrolyte. A higher voltage was used for this process to extract all species from the surface. During electropolishing, $(21.2 \pm 0.1) \ \mu m$ and $(28.2 \pm 0.1) \ \mu m$ were removed from the first and second detector hemispheres, respectively. This was estimated from the integrated current and Eq. 3, assuming uniform polishing. Following this process, the electrolyte circulated through the filter for several days prior to

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electroplating to remove particulates released from 420 the copper surface.

The electroplating procedure used the reversepulse plating waveform shown in Fig. 4. The cur-

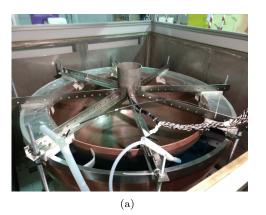
rent and voltage were monitored throughout, and 405

the conductivity and temperature were recorded us- 425 ing a HACH inductive conductivity sensor. Electroplating continued for a total of 19.8 days and 21.0 days for the first and second hemispheres, re-

- spectively. The process took longer than estimated 410 based on the small-scale experiments due to power 430 supply current limitations, plating at slightly lower potential and a slightly lower electrolyte conductivity. The process was only interrupted for short
- periods to perform checks or due to power outages. 415 The thickness of the deposited layer, which is shown 435 as a function of time in Fig. 9, was estimated from the integrated current assuming a uniform deposition. Total copper thicknesses of $(502.1 \pm 0.2) \ \mu m$

and (539.5 ± 0.2) µm were plated onto the first and second detector hemispheres, respectively. The achieved plating rate corresponds to approximately 1.3 cm/year. A photo of the finished plating is shown in Fig. 10.

After removing the hemispheres from the setup, they were rinsed with deionized water and the surface passivated with a 1% citric-acid solution to prevent surface oxidation [32]. Following the welding of the hemispheres together, a final stage of surface etching using an acidified-peroxide solution will be undertaken in order to mitigate the surface contamination caused by contact with the air. This etching technique has been shown to reduce the surface contamination of ²¹⁰Pb on electroformed copper to the background level of the XIA UltraLo-1800, which is used in these assays [8]. This process will be conducted under a nitrogen cover gas to mitigate possible surface recontamination following the etching. Following this stage, the inner detector surface will not be exposed to air again.



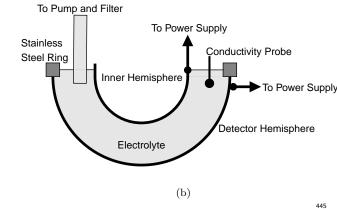


Figure 8: (a) Electroplating setup showing the detector hemisphere, anode, support structures, and fixtures. (b) Schematic diagram of the setup.

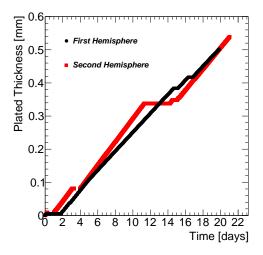


Figure 9: Estimated thickness of the electroplated copper for both detector hemispheres.

6. Radioisotope Assay Results

Samples of the electroplated copper were used to assess its ²³⁸U and ²³²Th concentrations. Samples were taken from copper plated on the stainless steel ring, shown in Fig. 8, to avoid damaging the detector cladding. These samples originate from near the electrolyte-air interface and from the stainless steel surface; thus, they represent a worst case scenario

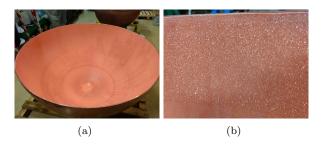


Figure 10: (a) The inner surface of the second hemisphere after electroplating and (b) a close-up of the surface.



with respect to contamination. The samples collected from each hemisphere are shown in Fig. 11.

Figure 11: Samples of electroplated copper, taken from the stainless steel ring shown in Fig. 8.

The samples were shipped to Pacific Northwest National Laboratory and analysed using ICP-MS following the methods described in Refs. [6, 16]. The results are summarized in Table 3, along with representative examples of electroformed and com-455 mercially sourced (machined) copper. A substantial improvement over the latter is observed, with radiopurity levels comparable to previously measured 490 electroformed copper. The measurement sensitiv-

ity for the two hemispheres is limited by the mass 460 of the available samples. Previous samples of electroformed copper have exhibited a bulk contamination of ²¹⁰Pb compatible with the background of the XIA UltraLo-1800, and are often used for blank measurements or for the construction of the sample 465 tray inside the device [20, 8].

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7. Summary

The NEWS-G collaboration has utilized recent advances in high-purity copper electroforming to

Table 3: ICP-MS results for ²³⁸U and ²³²Th contamination in samples of the electroplated copper layer, along with representative examples of electroformed and commercially sourced copper [17]. These are quoted as 68% upper confidence limits, where the measurement sensitivity was limited by the available sample mass.

	Weight	²³² Th	²³⁸ U
Sample	[g]	$[\mu Bq/kg]$	$[\mu Bq/kg]$
C10100 Cu (Machined)	-	8.7 ± 1.6	27.9 ± 1.9
Cu Electroformed	-	< 0.119	< 0.099
Hemisphere 1	0.256	< 0.58	< 0.26
Hemisphere 2	0.614	< 0.24	< 0.11

produce a layer of copper on the inner surface of the 470 \emptyset 140 cm detector. This layer will act as a shield to mitigate background from ²¹⁰Pb in the bulk of the detector's commercially sourced C10100 copper. This is the largest surface to be plated with ultra-radiopure copper in an underground laboratory. This operation has demonstrated the feasibility of plating onto the surface of a large hemisphere. The radiopurity of the plated copper was assessed using ICP-MS and found to be comparable to other electroformed copper. A copper deposition rate of approximately 1.3 cm/year was achieved, which is promising for fabrication of a fully electroformed copper sphere in the future.

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References

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- 510 [1] R. Agnese, et al. (SuperCDMS Collaboration), Projected Sensitivity of the SuperCDMS SNOLAB experiment, Phys. Rev. D 95 (2017) 082002.
 - [2] M. Agostini, et al., Background-free search for neutrinoless double-β decay of ⁷⁶Ge with GERDA, Nature 544 (2017) 47–52.
 - [3] P. Agnes, et al. (DarkSide Collaboration), DarkSide-50 532-day dark matter search with low-radioactivity argon, Phys. Rev. D 98 (2018) 102006.
 - [4] C. Alduino, et al. (CUORE Collaboration), First Results from CUORE: A Search for Lepton Number Violation via 0νββ Decay of ¹³⁰Te, Phys. Rev. Lett. 120 (2018) 132501.
 - [5] P. Scovell, et al., Low-background gamma spectroscopy at the Boulby Underground Laboratory, Astropart. Phys. 97 (2018) 160–173.
 - [6] B. LaFerriere, T. Maiti, I. Arnquist, E. Hoppe, A novel assay method for the trace determination of Th and U in copper and lead using inductively coupled plasma mass spectrometry, Nucl. Instrum. Methods Phys. Res. A 775 (2015) 93–98.
- [7] W. K. Warburton, B. Dwyer-McNally, M. Momayezi, J. E. Wahl, Ultra-low background alpha particle counter using pulse shape analysis, in: IEEE Symposium Conference Record Nuclear Science 2004., volume 1, 2004, pp. 577–581. doi:10.1109/NSSMIC.2004.
 - [8] R. Bunker, et al., Evaluation and mitigation of trace ²¹⁰Pb contamination on copper surfaces, Nucl. Instrum. Meth. A 967 (2020) 163870.
- [9] C. Bucci, et al., First results from the Cuoricino experiment, Nucl. Instrum. Methods Phys. Res. A 520 (2004) 132–134. Proceedings of the 10th International Workshop on Low Temperature Detectors.
- [10] E. Armengaud, et al., First results of the EDELWEISS II WIMP search using Ge cryogenic detectors with in terleaved electrodes, Phys. Lett. B 687 (2010) 294–298.
 - [11] C. E. Aalseth, et al., DarkSide-20k: A 20 tonne twophase LAr TPC for direct dark matter detection at LNGS, Eur. Phys. J Plus 133 (2018).
- 550 [12] National Nuclear Data Center, information extracted ⁶¹⁵ from the Chart of Nuclides database, 2020. Accessed: 10-02-2020.
- [13] Q. Arnaud, et al., First results from the NEWS-G direct dark matter search experiment at the LSM, Astropart.
 Phys. 97 (2018) 54–62.
 - [14] I. Giomataris, et al., A Novel large-volume Spherical Detector with Proportional Amplification read-out, JINST 3 (2008) P09007.
- [15] A. Brossard, Optimization of spherical proportional counter backgrounds and response for low mass dark matter search, Ph.D. thesis, Queen's University, Kingston, Ontario, Canada and Université Paris-Saclay, Saint-Aubin, France, 2020. http://hdl.handle.net/ 1974/27649.

- [16] I. Arnquist, M. di Vacri, E. Hoppe, An automated ultracleanion exchange separation method for the determinations of ²³²Th and ²³⁸U in copper using inductively coupled plasma mass spectrometry, Nucl. Instrum. Methods Phys. Res. A 965 (2020) 163761.
- [17] N. Abgrall, et al., The Majorana Demonstrator radioassay program, Nucl. Instrum. Methods Phys. Res. A 828 (2016) 22–36.
- [18] M. Shamsuzzoha Basunia, Nuclear Data Sheets for A = 210, Nuclear Data Sheets 121 (2014) 561–694.
- [19] G. Zuzel, K. Pelczar, M. Wójcik, Studies of surface and bulk ²¹⁰Po in metals using an ultra-low background large surface alpha spectrometer, Appl. Radiat. Isot. 126 (2017) 165–167. Proceedings of the 7th International Conference on Radionuclide Metrology – Low-Level Radioactivity Measurement Techniques.
- [20] K. Abe, et al., Identification of ²¹⁰Pb and ²¹⁰Po in the bulk of copper samples with a low-background alpha particle counter, Nucl. Instrum. Methods Phys. Res. A 884 (2018) 157–161.
- [21] XIA Ultra-Lo1800, 2020. URL: https://www.xia.com/ ultralo.html, Accessed: 02-03-2020.
- [22] S. Agostinelli, et al. (GEANT4), GEANT4: A Simulation toolkit, Nucl. Instrum. Meth. A 506 (2003) 250– 303.
- [23] E. W. Hoppe, et al., Use of electrodeposition for sample preparation and rejection rate prediction for assay of electroformed ultra high purity copper for ²³²Th and ²³⁸U prior to inductively coupled plasma mass spectrometry (ICP/MS), J. Radioanal. Nucl. Chem. 277 (2008) 103–110.
- [24] N. Abgrall, et al. (Majorana Collaboration), The Majorana Demonstrator neutrinoless double-beta decay experiment, Adv. High Energy Phys. 2014 (2014) 365432.
- [25] W. Greiner, L. Neise, H. Stöcker, Thermodynamics and statistical mechanics, Classical theoretical physics, Springer-Verlag, 1995. URL: https://books.google. co.uk/books?id=V6zvAAAAMAAJ.
- [26] A. Bard, R. Parsons, J. Jordan, Standard Potentials in Aqueous Solution, Monographs in Electroanalytical Chemistry and Electrochemistr, Taylor & Francis, 1985. URL: https://books.google.co.uk/books? id=fuJV1H18KtEC.
- [27] P. Atkins, Physical Chemistry, 6th edition, W.H. Freeman and Company, New York, 1997.
- [28] D. Lide, CRC Handbook of Chemistry and Physics, 87th Edition, Taylor & Francis, 2006. URL: https: //books.google.co.uk/books?id=yTTUQgAACAAJ.
- [29] W. Haynes, CRC Handbook of Chemistry and Physics, 92nd Edition, CRC Press, 2011. URL: https://books. google.co.uk/books?id=pYPRBQAAQBAJ.
- [30] E. W. Hoppe, et al., Microscopic evaluation of contaminants in ultra-high purity copper, J. Radioanal. Nucl. Chem. 282 (2009) 315.
- [31] M. Chandrasekar, M. Pushpavanam, Pulse and pulse reverse plating - conceptual, advantages and applications, Electrochim. Acta 53 (2008) 3313–3322.
- [32] E. Hoppe, et al., Cleaning and passivation of copper surfaces to remove surface radioactivity and prevent oxide formation, Nucl. Instrum. Methods Phys. Res. A 579 (2007) 486–489. Proceedings of the 11th Symposium on Radiation Measurements and Applications.
- [33] N. Overman, et al., Majorana Electroformed Copper Mechanical Analysis, Technical Report PNNL-21315, Pacific Northwest National Laboratory, 2012. doi:10.

620

590

2172/1039850.