THE CHEMISTRY OF ULTRA-RADIOPURE MATERIALS

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1 INTRODUCTION

Ultra-pure materials are needed for the construction of the next generation of ultra-low level radiation detectors. These detectors are used for environmental research as well as rare nuclear decay experiments, e.g. probing the effective mass and character of the neutrino. Unfortunately, radioactive isotopes are found in most construction materials, either primordial isotopes, activation/spallation products from cosmic-ray exposure, or surface deposition of dust or radon progeny.

Copper is an ideal candidate material for these applications. High-purity copper is commercially available and, when even greater radiopurity is needed, additional electrochemical purification can be combined with the final construction step, resulting in "electroformed" copper of extreme purity. Copper also offers desirable thermal, mechanical, and electrical properties.

To bridge the gap between commercially-available high purity copper and the most stringent requirements of next-generation low-background experiments, a method of additional chemical purification is being developed based on well-known copper electrochemistry. This method is complemented with the co-development of surface cleaning techniques and more sensitive assay for both surface and bulk contamination. Developments in the electroplating of copper, assay of U and Th in the bulk copper, and the removal and prevention of residual surface contamination will be discussed relative to goals of less than 1 microBq/kg Th.

2 MOTIVATION

A germanium crystal must be kept cold and free from light to function as a gamma-ray spectrometer. This is usually accomplished with an Al or SS vacuum cryostat and numerous small parts for support, electrical connection, and conduction of heat to a liquid nitrogen reservoir. To lower the ambient background of such a spectrometer, enabling the detection and quantification of much lower quantities of radionuclides, these materials have been gradually replaced with copper and carefully selected plastics. (See Figure 1.) Further, the copper itself has undergone a transformation, from a common commercially supplied material to a carefully selected and chemically transformed material. The specific

design of such a Ge spectrometer incorporates one or more kg of Cu structural material per kg of detector mass. Even low levels of contamination in this mass of copper could easily dominate the background for a specialized measurement such as double-beta decay of ^{76}Ge, in which the crystal provides both the sample and the measurement device.

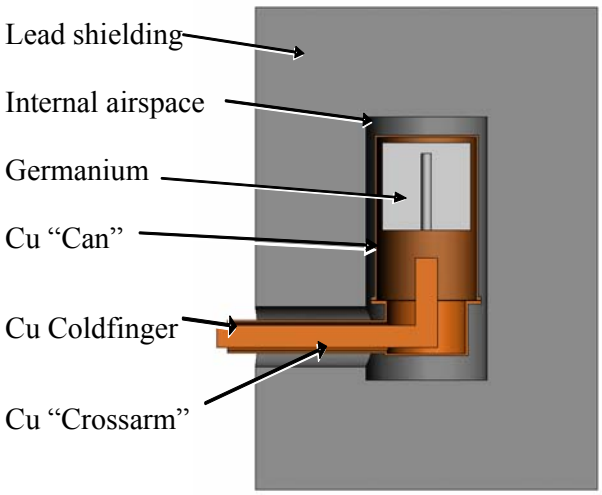

Figure 1 Design of a typical Ge spectrometer with about 2.7 kg of Cu per 1 kg of Ge

Frequently, the cosmic-ray related signals in a low background spectrometer will necessitate placement in an underground location. In addition, this system may require some consideration to the reduction of sample-associated backgrounds, either through decay, chemical separation, or coincidence techniques, listed in increasing order of expense.

The sensitivity of a Ge spectrometer will then depend on several factors, including depth and the purity of construction and shielding materials. Example background spectra obtained with several detectors are shown in Figure 2. However, it has recently been reported by Laubenstein et al[1] that several systems background spectra are not dependant on depth below perhaps 1000 meters water equivalent (mwe) of cosmic-ray shielding. Since the effect of cosmic-ray secondary muons is well known to continue decreasing, this suggests that materials effects became dominant at that depth. In fact, it suggests that material backgrounds could be reduced by a factor of 1000 before the cosmic ray associated backgrounds would be dominant again at depths of 4000-5000 meters water equivalent.

As an example, an assay conducted several years ago[3] on electroformed copper presented ~8 kg of Cu to a specially produced germanium gamma-ray spectrometer at ~4000 mwe over a ~100 day period. Through observation of the ^{228}Th and ^{226}Ra daughters the authors concluded that if the ^{232}Th chain were it in equilibrium, it would correspond to ~9 microBq/kg, and similarly, the ^{238}U chain concentration would have been <26 microBq/kg. A subsequent analysis by the authors has indicated[3,4] that the ~9 microBq/kg activity should be considered <9 microBq/kg based on the fact that the introduction of the 8 kg of Cu did not cause increased activity in the ^{228}Th chain, pointing to the activity being in small parts within the cryostat or surface activity on the Ge crystal itself. Thus, the key limits obtained by gamma-ray assay are <9 and <26 microBq/kg for the Th and U chains, respectively.

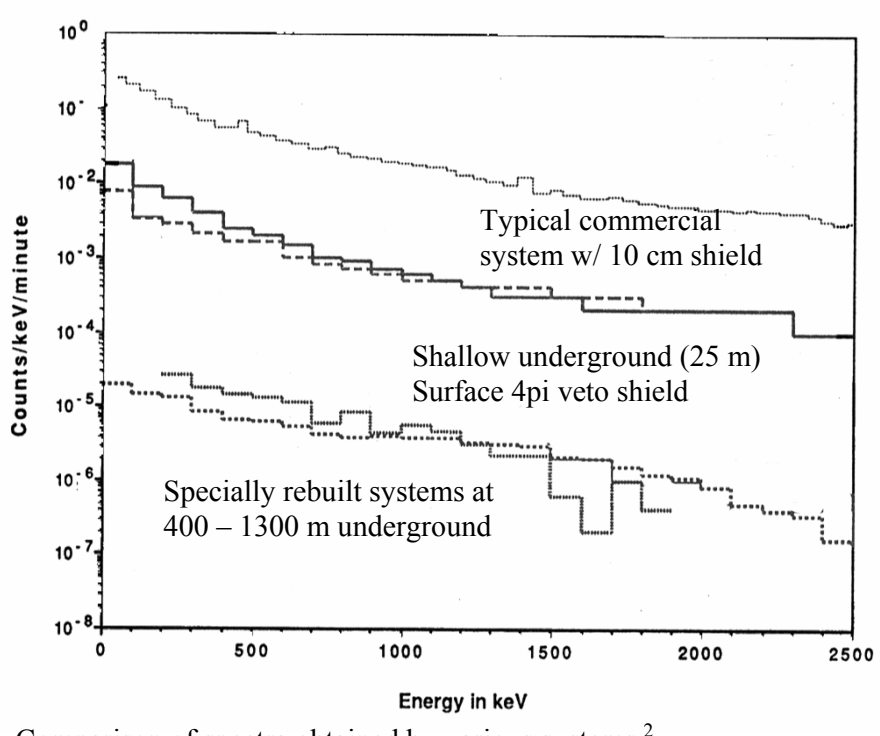

Figure 2 Comparison of spectra obtained by various systems.[2]

Other authors have recently reported different limits on different sources of Cu via gamma-ray spectroscopy, as shown in Table 1.

Table 1 Recently published gamma-ray-based assay limits for Th and U in electrolytic copper.

^{228}Th (^{232}Th)	^{226}Ra (^{238}U)	**Comment**
$< 1\times10^{-6}$ Bq/kg	$< 1\times10^{-6}$ Bq/kg	Goal of this research
$< 9\times10^{-6}$ Bq/kg	$< 26\times10^{-6}$ Bq/kg	In-house electroformed Cu discussed above
$< 28\times10^{-6}$ Bq/kg	$< 25\times10^{-6}$ Bq/kg	Commercially obtained electrolytic Cu Motta, et al.[5]
$< 12\times10^{-6}$ Bq/kg		Commercially obtained electrolytic Cu Rugel, et al.[6]
$< 19\times10^{-6}$ Bq/kg	$< 16\times10^{-6}$ Bq/kg	Commercially obtained electrolytic Cu Heusser, et al.[7]

While it may be tempting to draw conclusions about the quality of the various samples from the values in Table 1, it must be remembered that any of these materials may be orders of magnitude purer than these limits might suggest. However, these values do provide the introduction to an effort to document and achieve lower levels of contamination based on the ability to assay well below the limits afforded by gamma-ray spectroscopy.

3 ELECTROFORMED COPPER

Copper benefits from the "electrowinning" process used during refinement. This processing step electroplates the material from a sulfate solution onto cathodes. Most contaminants do not follow copper in this step by virtue of their negative electrochemical values as compared to copper, which has a cell potential of 0.342 V, and the resulting material, known as "electrolytic tough pitch" copper, is rather pure. Commercial high-purity copper usually undergoes further processing, including smelting to improve purity and hot rolling to improve density and mechanical properties.

Additional electrolytic and chemical purification can be combined with a final fabrication step, resulting in "electroformed" copper parts of extreme purity. In this process copper is electrodeposited onto forms, usually made of stainless steel in the shape of the desired final part. An example of an electroforming system is shown in Figure 3. This electroforming process can even be done underground, providing a potential way to eliminate cosmogenic activation products seen in copper that has had above-ground exposure, e.g. ^{60}Co.

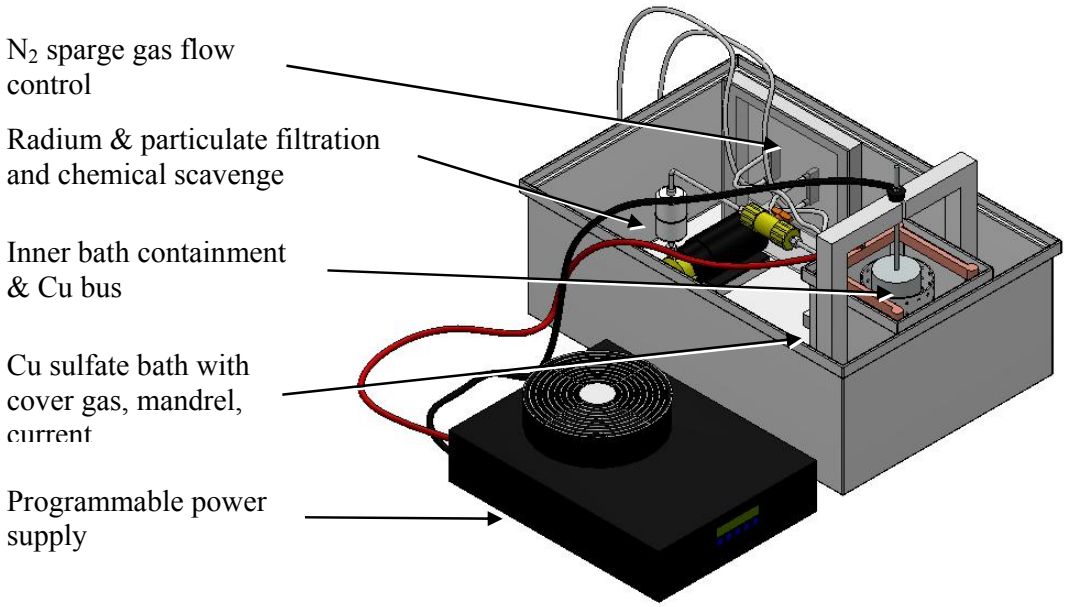

Figure 3 Schematic of the electroforming system.

3.1 Electrochemical Purity Considerations

The Nernst equation describes the tendency of an electrochemical reaction to go to the right, and can be used to model the behavior of ions in an electrochemical cell when that cell is in equilibrium.

For the generalized reaction

$$aA + bB + \ldots + ne^- \leftrightarrow cC + dD + \ldots, \quad (1)$$

the classic Nernst equation is given by

$$E_{cell} = E^0 - (RT/nF)*\ln([C]^c[D]^d/[A]^a[B]^b). \quad (2)$$

The more positive electrochemical values favor the formation of reduced species. For example, the Nernst equation predicts that thorium with a half cell potential of E^o Th = -1.9 V, would have to be at a concentration of over 10^{150} M before it would plate out at the half-cell potential of copper, E^o Cu = 0.34 V. Even when a reverse pulse plating process is employed to create level, and polycrystalline, copper, the Nernst equation predicts thorium would still have to be at a concentration of over 10^{100} M before it would plate out at -0.34 V. One would expect to obtain extreme copper purity from contaminants such as Th when electroplating at the voltages required for copper plating.

However, at high ionic strengths such as those used in most electroplating baths, activity coefficients cannot be calculated for the reactant and product species, leading to error in the Nernst-calculated value of E_{cell}. Also, as previously stated, the cell must be in equilibrium for the Nernst equation to hold. Any electrochemical cell under applied voltage is a dynamic system, where the concentrations of species are dramatically different surrounding the anode than they are surrounding the cathode. Ions are continuously being formed at the anode and reduced at the cathode. Given efficient mass transport, the concentration gradient is lessened, but the system remains in disequilibrium. Also, plating at rates of industrial practicality results in notable disequilibrium. A more accurate model would assume at least three different "zones" of equilibrium: one about the anode, one about the cathode, and one in the bulk of the plating bath. Ultimately, the presence of impurities in electroplated copper such as thorium which possess a very negative cell potential, indicates that the Nernst equation does not accurately model most real-world plating systems. In fact, it has been found by Hoppe, et al.[8] that at low concentrations in a copper sulfate bath, Th is only rejected at rates of 10^3 to 10^4, rather than 10^{100}. Obviously, mass transport and other factors dominate the behavior of contaminants regardless of redox potentials.

3.2 Cleaning Copper and Surface Treatments

Many low-background experiments which employ high-purity copper, e.g. Cuoricino,[9] have observed that surface contamination emerges as the dominant background. Radon daughters plate out on exposed surfaces, leaving a residual ^{210}Pb background that is difficult to avoid. Dust is also a problem; even under cleanroom conditions, the amount of U and Th deposited on surfaces can represent the largest remaining background.

Radiopurity is not the only motivation for surface cleaning; final machining processes also leave unwanted residues and copper fragments that make assembly difficult. Additionally, copper oxides can remain, creating unwanted additional infrared absorptive surface area. Surface cleaning is thus critical to ensuring high purity copper parts.

To address all these factors, an improved copper cleaning chemistry has been developed by Hoppe, et al.[10] Designed to replace an effective, but overly aggressive concentrated nitric acid etch, this peroxide-based method allows for more controlled cleaning of surfaces.

In an effort to keep the copper surfaces clean, passivation strategies have been developed to inhibit the reformation of oxides on the surface in an effort to minimize recontamination. The performance of the cleaning process and subsequent passivation were investigated by Hoppe, et al.[11]

4 PHYSICAL PROPERTIES OF ELECTROFORMED COPPER

4.1 Emissivity

Emissivity of both passivated and bare electroformed copper has been determined based on radiative thermal transfer. Electroformed copper cans at room temperature were fitted onto a cryostat, with a large thermal absorber (having a high emissivity coating), held near 80°K. Total heat transport was determined based on the rate of mass loss for the liquid nitrogen filled Dewar. Heat transport from the surface of interest was estimated by subtracting the heat transport of the cryostat alone (1.54 ± 0.06 W) from the total heating (ranging between 1.72 ± 0.05 W and 2.06 ± 0.07 W, depending on the surface of interest). Surface emissivity values were then extracted, using an analytic model for heat transfer between concentric convex shapes. Two samples of the passivated copper were examined, and were found to have emissivities, expressed as a percentage, of 2.7 ± 1.3 % and 2.8 ± 1.2 %, the stated errors representing statistical variations. These values are in reasonably good agreement with published values, which range from 1% up through 5% at room temperature, depending on preparation.[12-14] For bare cleaned copper, emissivity was estimated to be 8.0 ± 1.5 %. This is somewhat higher than published values; however, some small amount of oxidation or staining was observed, indicating that protocols to prevent exposure to oxygen may have been insufficient. The emissivity of a machined aluminum tube was also measured, and found to have a value of 5.3 ± 1.5 %, again in agreement with established values ranging from 3 to 10%.[14]

4.2 Mechanical Strength

The mechanical properties of electroformed copper can vary drastically depending on the conditions under which it was formed. Conditions that favor high purity can form large crystalline structures with poor mechanical strength. Small polycrystalline formations can exhibit adequate tensile strength but lower purities. Reverse pulse plating has allowed the growth of larger polycrystalline forms with the average hardness of 105-108 Vickers using 100 grams of force. This translates to approximately 300-340 MPa tensile strength.

5 STRATEGIES TO IMPROVE COPPER PURITY

Our current practice in preparing an electrochemical bath utilizes the highest purity acids commercially available to us. We have verified the concentration of contaminants stated by the vendor-supplied assay. We are also satisfied with the purity of water obtained from the output of laboratory grade ion exchange water treatment systems. We currently recrystallize all copper sulfate from saturated aqueous systems. The electrochemical baths are constantly circulated and filtered at 0.2 micron using a fluoropolymer cartridge. The bath is sparged with nitrogen boil-off from a stainless steel Dewar. This same nitrogen serves as a cover gas for the plating bath. A small amount of barium sulfate is loaded onto the filter to act as a radium scavenge.

In the future, we intend to perform the electroforming underground to limit the formation of cosmogenic species. We may need to take additional steps to improve the purity and quality of the copper such as electroforming our own anode material, which may also be formed underground. The exact waveform we use in the reverse pulse may be altered in order to offer an additional opportunity for those electronegative species, such as Th or U which may have been encapsulated during the forward portion of the plating

process, to detach from the plate and be re-entrained into the bulk solution. Scrubbing of the bulk solution may be necessary using ion exchange, secondary electrogravimetric methods, or other processes. Use of the rejection rate information obtained from assay development work[8] will serve as a useful forecasting tool to determine what purity of copper can be expected from an electrochemical bath increasingly contaminated by the dissolution of anode material.

In order to determine if some of these improvements to the electroforming process are necessary, either additional rejection rate information must be obtained so that predictive models can be developed or more sensitive assays must be developed, which will be capable of measuring contaminants such as Th at our goal of less than 1 microBq/kg Th (0.25×10^{-12}g/g Cu). We plan to resume our work determining the rejection values using ^{228}Th as a tracer in the electroforming process.

6 ISSUES IN COPPER ASSAY

Concentrations of contaminants to meet our purity goal are far below the detection limits of many current analytical methods. As stated previously, radiometric assays require impractical amounts of material and exceedingly long counting times. Other analytical tools, such as Secondary Ion Mass Spectrometry (SIMS), lack adequate sensitivity or, such as Inductively-Coupled Plasma Mass Spectrometry (ICP/MS), lack the dynamic range to perform direct assays. ICP/MS, however, can detect many contaminants at or below these levels, including Th or U, if the bulk species of Cu can be reduced, since sensitivity of this assay is diminished by high copper concentration in the sample. Removal of the bulk species has been successful using ion exchange.[15] Unfortunately, the ion exchange resins are contaminated with the target species at levels that create significant background. We have confirmed the same contamination issues in our attempts to analyze samples using ion exchange to concentrate Th or U species from the bulk copper.

We have also pursued electrochemically back-plating of the copper sample to reduce the copper ion concentration and leave in solution impurities such as thorium and uranium, which should not plate out at the half-cell potential of copper.[8] Theoretically, the amount of sample that can be processed in this manner is not limited. All materials including any non-sample electrodes must not add contamination and must be of extreme purity. Also, the amount of copper remaining in solution must be back-plated to <10 μg/ml, and if a sulfate system is used, which is useful in support of further developing the predictive rejection rate information, then the sulfate ion should be <10 mmol as well. This approach hinges on the rejection rate remaining sufficiently high as to not introduce an undue amount of error. We have measured rejection rates as low as ~10^3 but even at 10^2 this would only represent a 1% error in the assay result.

7 CONCLUSIONS

In order to build a radiation detector capable of extreme sensitivity, historical copper electroforming has produced copper of < 9 microBq/kg ^{232}Th , and < 26 microBq/kg ^{238}U. However, future systems require levels below 1 microBq/kg. To achieve this, a new copper plating procedure has been devised and will be modified as needed to achieve the goal using ideas presented above. However, a copper assay capability below this level is desired. Limiting features of ion exchange plus ICP/MS approaches have been discussed. A new approach is being developed to produce samples of the copper to be assayed which

are both low in Cu, to work within the dynamic range of the ICP/MS, and which have Th and U only from the original source of copper, not from the preparation materials or process. Fortunately, the current assay capability, 2-4 microBq/kg ^{232}Th, is not that far from the goal. Given that several useful reduction strategies exist, the authors feel it is likely that the sensitivity goal can be reached and that the rejection of Th and U by the electroforming process can be documented on a part-by-part basis. In any case, a one-time test to demonstrate Th rejection should be possible using ^{228}Th in the near future.

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