A Novel Assay Method for the Trace Determination of Th and U in Copper and Lead Using Inductively Coupled Plasma Mass Spectrometry

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Abstract

This study describes a novel sample preparation and assay method developed, primarily in support of the MAJORANA DEMONSTRATOR neutrinoless double-beta decay experiment, for the determination of extremely low levels of Th and U in copper and lead shielding components. Meticulously clean sample preparation methods combined with anion exchange separations for analyte pre-concentration and matrix removal were developed. Quantification was performed by isotope dilution inductively coupled plasma mass spectrometry. Detection limits of 0.0084 pg $^{232}\text{Th/g}$ (0.034 $\mu\text{Bq }^{232}\text{Th/kg}$) and 0.0106 pg $^{238}\text{U/g}$ (0.131 $\mu\text{Bq }^{238}\text{U/kg}$) were determined for copper, while detection limits of 0.23 pg $^{232}\text{Th/g}$ (0.94 $\mu\text{Bq }^{232}\text{Th/kg}$) and 0.46 pg $^{238}\text{U/g}$ (5.7 $\mu\text{Bq }^{238}\text{U/kg}$) were achieved for lead. These methods allow the Majorana Collaboration to accurately assay detector components and ensure that the experiment's stringent radiopurity requirements are met.

Keywords: Ultratrace, U, Th, Radiopurity Assay, ICP-MS, Majorana, Copper, Lead

1. Introduction

As part of the Majorana collaboration, the study described herein was motivated by the need to perform ultra-low radiopurity assays of detector materials in support of the MAJORANA DEMONSTRATOR experiment [1]. The MAJORANA DEMONSTRATOR will search for the neutrinoless double-beta ($\beta\beta(0\nu)$) decay of ^{76}Ge in a mixed detector array of natural and enriched germanium detectors. The observation of this rare decay would indicate that the lepton number is violated, that the neutrino is a Majorana particle, and yield information on the absolute mass of the neutrino. Currently, the MAJORANA DEMONSTRATOR experiment is under construction at the Sanford Underground Research Facility (SURF) in Lead, South Dakota.

Along with the MAJORANA DEMONSTRATOR experiment, there are an increasing number of physics experiments requiring ultra-low background materials for their construction; *e.g.*, neutrino [1; 2; 3; 4; 5] and dark matter studies [6; 7]. While backgrounds stemming from cosmic rays can be mitigated through the use of deep underground laboratories [8; 9; 10] (SURF is at 4850 m level), considerable effort is required to limit and account for intrinsic radioisotopes in the manufacturing of the detector. The extremely low background and costly manufacturing required for these experiments stipulates detector components that have been validated for their radiopurity [5; 11]. With knowledge of radioactive contaminant levels in components, background contributions can be accounted for using powerful computer modeling and background rejection techniques [12; 13].

Several well established quantitative analytical techniques exist for radiopurity material assay, including gamma spectroscopy, neutron activation analysis (NAA), and inductively coupled plasma mass spectrometry (ICP-MS) [5; 14]. Gamma ray spectroscopy proves impractical in many cases because it requires large quantities of material—frequently many kilograms—and prolonged counting times (often months). While NAA can accommodate smaller samples (*ca.* 1

g) and is often non-destructive, the analysis can be expensive and create further complications by the formation of unwanted radionuclides. Recent advances in ICP-MS have increased its sensitivity, particularly in the elemental high-mass range of U and Th, making it more useful than gamma ray spectroscopy or NAA for ultra-low radiopurity assays.

In contrast to direct radioassay, ICP-MS is a destructive technique, as it requires the sample to be vaporized, atomized, and ionized in a high-temperature plasma before concomitant ions are resolved by the mass analyzer. ICP-MS analysis is relatively quick and inexpensive. It is a very robust and sensitive technique, typically requiring <0.5 g sample of material and offering parts-per-trillion (pg/g) detection limits for a large number of elements. However, a major drawback of this technique, at the ultra-trace level, is the need for assiduous sample preparation prior to analysis. With regards to material assay, the solid sample typically undergoes acid digestion. Further, while the instrument is very robust, it is not tolerant to high matrices (>0.1%) of dissolved solids and typically subsequent dilution is needed to preserve the functional integrity of the skimmer cones and ion optics in order to maintain adequate performance. For routine analysis, a simple dilution can be used to reduce the dissolved solids while still achieving required detection limits. However, when working in the ultra-trace regime required for sensitive radiopurity assays, alternative methods that involve the separation of the matrix element, pre-concentration of the analyte, or both may be necessary.

Separation of the matrix and analyte can be performed using a variety of methods including electrochemical techniques, selective precipitation, and ion exchange, among others. A recent review [15] highlights a wide range of sample preparation strategies for Th and U determination. One study [16] has examined the utilization of various resins, including UTEVA (Eichrom), TRU (Eichrom), and AMBERLITE CG-400 (Sigma-Aldrich) for the separation of Th and U in natural samples. Furthermore, Grinberg and co-workers developed a sample preparation method for the analysis of lead using the UTEVA resin that achieved detection limits of 1.5 pg Th/g lead and 0.5 pg U/g lead [17]. The procedure consisted of a concentrated nitric acid digestion followed by evaporation, reconstitution in 3 M HNO₃ and loading on UTEVA resin. The Th and U were then eluted separately, evaporated, reconstituted and analyzed via ICP-MS. This procedure produced detection limits that nearly met the Majorana target of 1 pg/g lead of Th and U, but the procedure is also more cumbersome than the method developed here, and contains a larger number of steps and reagents.

In this work, a novel sample preparation and assay method was developed as part of the Majorana Collaboration's effort to determine the amount of Th and U in copper and lead materials. The germanium array detectors are housed in, and partly composed of, in-lab electroformed ultra-pure copper [18] and positioned within lead and polyethylene shields. Based on calculations performed by the MAJORANA DEMONSTRATOR simulations task group, the most stringent radiopurity goal applies to the copper used in the inner shield and detector components. The required purity level for Th is <0.3 $\mu\text{Bq } ^{232}\text{Th/kg}$ copper, which is equivalent to 0.075 pg $^{232}\text{Th/g}$ copper. For U, the purity level required is also <0.3 $\mu\text{Bq } ^{238}\text{U/kg}$ copper or 0.024 pg

^{238}U /g copper [1]. Limits of radioimpurities for the lead shielding bricks (*ca.* 1 pg/g Pb) are not as stringent as those for the copper material due to the greater distance between the bricks and the detector and the shielding between them. This paper discusses the meticulous sample preparation and assay methods developed to meet the low detection limits needed for ultra-low background physics experiments.

2. Experimental Section

Facilities. All laboratory work was performed in a Class 10,000 clean-room at Pacific Northwest National Laboratory (PNNL). Samples were prepared using a laminar flow hood, providing a Class 10 clean-room environment.

Instrumentation. All analyses were performed using an Agilent 7700x series ICP-MS (Agilent Technologies) with an integrated auto-sampler equipped with an Agilent microflow nebulizer and standard quartz double-pass spray chamber. Plasma, ion optics, and mass analyzer settings were tuned to maximize sensitivity for high m/z species (specifically Th and U) at the expense of lower m/z signals. Oxides were monitored and kept at a minimum (typically <2%). Daily tuning and optimization was performed as needed. In order to improve instrumental precision, data acquisition times were lengthened to 6 s for each analyte and repeated in triplicate. The Agilent 7700x is equipped with a reaction cell, but it was not employed.

Preparation of Reagents and Labware. All vials, containers, lids, and pipette tips were cleaned with Micro-90 detergent (Cole-Parmer) and triply rinsed with 18.2 M Ω ·cm Milli-Q (Millipore Corp) deionized water, followed by three overnight leaches in 6 M HNO₃ [19]. The last leach bath took place in Optima grade 6 M HNO₃ (Fisher Scientific). Apart from the initial nitric leaches and the Micro-90, all reagents were of Optima grade purity. All water used was 18.2 M Ω ·cm Milli-Q water. Before use, all cleaned labware went through a precautionary rinse with 6 M HNO₃ followed by a rinse with water. Moreover, following leaching, all sample vessels underwent a validation, which consisted of a 5% nitric acid rinse followed by ICP-MS analysis of the rinse volume to verify that Th and U levels were sufficiently near or below background. If labware failed validation, an additional cycle of leaching and validation was performed until the material was sufficiently clean.

2.1. Analysis of Copper

Sample Origins. The *ca.* 80-g copper sample used for analysis was cut from a piece of electroformed copper produced at PNNL or in the Temporary Clean Room at SURF for the MAJORANA DEMONSTRATOR experiment.

Sample Cleaning & Digestion. To remove machining lubricant used during the material cutting process, the sample was cleaned in an aqueous solution of *ca.* 2% Micro-90 (Cole-Parmer), followed by a thorough rinsing with water. To remove surface contaminants, the surface was then etched in 6 M HNO₃ reducing the sample mass by *ca.* 3%. The remaining sample was

completely dissolved in 8 M HNO₃. The final solution (ca. 0.12 g Cu/g) was spiked with ²²⁹Th and ²³³U to ca. 0.035 pg/g sample solution. This spiked solution was then used for all separations and analyses.

Column Preparation. All columns were prepared to a bed volume of ca. 0.5 mL using AG 1×4, 100-200 anion exchange resin (Bio-Rad Corp). Columns of 7.1-mm i.d. and 93.6-mm length with a 2.5-mL bed capacity were used (Environmental Express, Charleston, SC). All columns and frits were leached at room temperature for at least 72 hours in 6 M HNO₃ prior to use.

Cleaning columns to the desired background levels proved to be more difficult than anticipated. Initially, resin was cleaned by passing 2 mL 8 M HNO₃ through the column, followed by 2 mL deionized water, 2 mL concentrated HCl, and 8 mL 0.1 M HCl. To check the efficacy of this procedure, a final 4 mL of 0.1 M HCl was passed through, collected and analyzed. Analysis revealed that while this cleaning procedure had significantly reduced the column background, the standard deviation of the background was well above that needed to achieve detection limits in the realm required for the MAJORANA DEMONSTRATOR. To further reduce the backgrounds of Th and U from the anion exchange columns, tests were conducted using acids that had been “cleaned” from previous passes through the column. Sufficient cleaning of the resin was obtained by performing a loading and elution cycle, using 3.5 mL of the “cleaned” 0.1 g Cu/g 8 M HNO₃ solution followed by 8 mL of 0.1 M HCl. This procedure repeatedly produced sufficiently low background levels and was also satisfactory for re-cleaning used columns. This procedure indicated that the columns become cleaner after each use. Therefore, columns were re-used throughout the copper assay method development.

Sample loading. Immediately prior to loading, sample columns were conditioned with 2 mL “cleaned” 8 M HNO₃. This conditioning ensured that the column was at the optimum nitric acid concentration for the adsorption of Th and U. After conditioning, 5.0 mL of the sample was loaded on the column in 0.5-mL increments. Additions of 0.5-mL increased recoveries by reducing the flow rate of the sample through the column. After sample loading, adsorbed copper remaining on the column was removed by washing with 0.6 mL “cleaned” 8 M HNO₃. Th and U were then eluted together with 1.2 mL of 0.1 M HCl and collected in validated 5-mL vials (Savillex Corp, Bloomington, MN). Samples were then analyzed via ICP-MS and quantified using isotope dilution ICP-MS.

2.2. Analysis of Lead

Sample Origins. Five- to ten-gram lead samples were obtained from cleaned bricks to be used as shielding for the MAJORANA DEMONSTRATOR.

Leaching of Vials for Lead Dissolution. Labware cleaning for the analysis of lead followed the same procedure as was used for copper, varying only in the cleaning of the digestion vessels.

These vessels were 20-mL polyethylene liquid scintillation counting (LSC) screw-cap vials (PerkinElmer). The vials were cleaned by filling with 15 mL of 6 M HNO₃, capping, heating for three days in an 80° C oven, and then rinsing three times with water. Before use, the LSC vials were rinsed once with 6 M HNO₃, then three times with water, and dried with filtered nitrogen gas.

Sample Dissolution and Preparation. Lead samples were dissolved as received by PNNL without any pre-cleaning or rinsing. Dissolution was performed by removing small aliquots (*ca.* 1 g) of lead from the received samples using a clean stainless steel razor blade. The aliquot was then placed in 10 mL of 1.5 M HNO₃, which was spiked to *ca.* 0.20 pg ²²⁹Th/mL and 0.35 pg ²³³U/mL in LSC vials. To accelerate the dissolution process the solutions were heated overnight in an oven at 80° C. After dissolution, an aliquot of the sample was brought up to 5.0 mL for column loading, within a final acid concentration of 6 M HNO₃ and a final lead concentration of no more than 17,000 µg Pb/mL. Greater concentrations of lead in solution were attempted; however, when carryover of lead through the ion exchange column exceeded *ca.* 10 ppm in the final solution, a significant interference at *m/z* 238 was observed, likely due to formation of polyatomic PbO₂⁺ species. Attempts to reduce the interference using the collision cell were successful but also reduced the sensitivity for the analyte therefore the collision cell was not employed. Maintaining a relatively low final lead concentration to prevent the formation of the polyatomic interference turned out to be the most expedient solution to ensure adequate detection limits.

Column and Resin Preparation. The required detection limits for Th and U were not as stringent for lead as for copper; therefore the resin cleaning process was simplified. Instead of using “cleaned” solutions to lower the column background contribution, stock Optima-grade reagents were used. Furthermore, this allowed the ion exchange resin to be cleaned in batches (*ca.* 10 mL bed volumes). These were prepared through a series of conditioning and rinse washes, in the following order: 24 mL 8 M HNO₃, 16 mL DI water, 16 mL concentrated HCl, 16 mL DI water, 24 mL 8 M HNO₃, and 80 mL 0.1 M HCl. The cleaned resin was then carefully loaded into individual columns with 0.5 mL resin bed volumes. A validation of the columns’ cleanliness was performed by passing 8 mL of 0.1 M HCl through the columns, followed by 4 mL of 0.1 M HCl, which was collected and analyzed for contaminants via ICP-MS. Columns were not re-used due to the difficulty of removing lead after a single use.

Sample loading. Columns were conditioned with 2 mL 6 M HNO₃ just prior to loading the sample. The 5.0 mL 6 M HNO₃ sample solution was then loaded onto the column. To remove lead remaining on the column, 1.8 mL of 6 M HNO₃ were passed through it. Th and U were then eluted together with 1.2 mL of 0.1 M HCl and samples were analyzed via ICP-MS. Figure 1 illustrates the column preparation steps for column validation, sample separation and collection.

3. Results and Discussion

Separation. In high concentrations of nitric acid (*e.g.*, 8 M HNO₃), copper and lead exist as their neutral nitrate salts, while Th is in the form of Th(NO₃)₆²⁻ and U is in the form of UO₂(NO₃)₄²⁻ [20]. This makes the anion exchange resin AG 1×4 ideal for separation away from bulk matrix elements.

Th has a large K_d value (weight distribution coefficient, mL/g) of approximately 323, while U has a less favorable K_d of 16 in 8 M HNO₃ [21]. The anion exchange reactions are shown below, where R is the anion exchange resin:

Both the Th and U anionic species can be co-eluted in a chloride matrix according to the following reactions:

Because the K_d value for U is relatively low, it has a lower propensity to adsorb to the resin. Therefore, resin wash volumes must be limited to reduce the amount of prematurely eluted U while still maximizing the removal of matrix copper or lead. Washing columns with a large volume (>1 mL) of 8 M HNO₃ would remove some U from the resin, resulting in lower recoveries.

Th and U can be eluted using 0.1 M HCl. The elution profiles for Th and U were obtained by loading four columns with 5 mL of *ca.* 100,000 µg/mL copper solution, followed by a 0.2 mL wash (one displacement volume) with 8 M HNO₃. The columns were then eluted with 4 mL of 0.1 M HCl, which was collected in 1-mL increments and analyzed. It should be noted that with only a 0.2-mL wash step, significant amounts of copper were still retained on the column. The first 1-mL collection fraction contained >20,000 µg/mL copper, which is significantly greater than the upper matrix tolerance limit (1000 µg/mL) preferred for introduction into the instrument, and required a 20-fold dilution prior to analysis. Consequently, a larger 8 M HNO₃ wash volume (0.6 mL) was used for method validation experiments to ensure removal of copper from the

column prior to collection for analysis. The tracer recoveries as a function of fraction collected are plotted in Figure 2. As the figure shows, most of the Th and U elutes in the first milliliter.

3.1. Method Results, Copper

The method detection limit (MDL) evaluation for a high-copper matrix was performed using a broadly accepted U.S. Environmental Protection Agency (EPA) process [22]. Instrument background was determined from seven replicate analyses of the 0.1 M HCl solution used for the elution of the analytes from the column. Tracer recoveries were calculated using a linear external calibration while ^{232}Th and ^{238}U concentrations were determined by isotope dilution using the following equation:

$$\text{Concentration} = \frac{A_{\text{analyte}} \times C_{\text{tracer}}}{A_{\text{tracer}}},$$

where A_{analyte} is the instrument response for the analyte to be measured, A_{tracer} is the instrument response for the tracer/internal standard, and C_{tracer} is the concentration of the tracer in the sample. Per the EPA method, the MDL was calculated as the standard deviation of eight replicate sample analyses multiplied by the student's t value for the 99% confidence level. Due to the extreme radiopurity of the copper electroformed by PNNL, the sample stock solution needed to be spiked with 22.8 fg ^{238}U /g copper to bring the ^{238}U into the desired range of 3-10 times the MDL. The results of the method validation are shown in Table 1.

Tests were also performed to demonstrate the recovery of the tracers over a number of repetitive column uses. These tests followed the same column loading and elution procedure as used for the method validation, in which 5 mL of *ca.* 100,000 $\mu\text{g/mL}$ copper solution was used. Four columns were loaded and eluted 3 times. The tracer recoveries averaged 66% for Th and 80% for U (Figure 3). Although there appears to be an improvement in the recovery of Th with use, the results demonstrate that there is no significant variation in tracer recoveries over multiple column uses indicating columns can be used multiple times.

3.2. Method Results, Lead

Unlike copper, large amounts of lead cannot be dissolved in 8 M HNO_3 due to the formation of a passivation layer of lead oxide in high nitric-acid matrices [23]. Therefore, digestion was performed in 1.5 M HNO_3 .

Initially, aliquots of the lead samples in a 1.5 M HNO_3 matrix were diluted using concentrated nitric acid to a final concentration of 8 M HNO_3 ; subsequently these aliquots underwent the same anion exchange separation procedure as copper samples. Upon analysis interferences at 220 m/z (attributed to PbO^+) and 238 m/z (attributed to PbO_2^+) were observed. Consequently, wash volumes were increased to remove more lead from the columns. Low U recoveries with higher wash volumes prompted a study comparing 6 M HNO_3 to 8 M HNO_3 as the sample loading

matrix. Using 8 M HNO₃, lead could not be removed sufficiently without also eluting U. However, with 6 M HNO₃, lead could be removed much more effectively (see Figures 4 and 5). It was determined that an acid wash of 1.8 mL with 6 M HNO₃ (compared to 0.6 mL 8 M HNO₃ for lead matrices) would sufficiently remove problematic matrix lead for the U analysis.

Absolute detection limits of 0.24 pg Th and 0.48 pg U were approximated using 3 times the standard deviation of 8 process blanks, shown in Figure 6. Average tracer recoveries of 49% and 13% were obtained for ²²⁹Th and ²³³U in the process blanks respectively, while lead samples resulted in 45% and 12% for ²²⁹Th and ²³³U, respectively. The consistency of the recovery between the blanks and samples indicates that the sample preparation procedure is not significantly impacted by the presence of the lead matrix. The reduced recoveries for the lead samples relative to the copper samples is attributed to the larger rinse volume of nitric acid that was required to sufficiently reduce the remaining lead on the column.

The digestion method allowed for the dissolution of 0.10 g Pb/g solution in 1.5 M HNO₃, giving relative detection limits of 0.23 pg Th/g lead and 0.46 pg U/g lead. This is a factor of two to three better than those reported in the study by Grinberg et al. [17], for which detection limits of 0.5 pg U/g lead and 1.5 pg Th/g lead were achieved using UTEVA resin. Many additional steps were required in the UTEVA method, such as decomposition of the oxalic acid used for elution of Th and reconstitution in nitric acid. The method described in this paper avoids many of these additional steps by co-eluting Th and U in a matrix that is acceptable for analysis on the ICP-MS. This simplified sample preparation may have contributed to the lower detection limits obtained by requiring less sample handling and fewer reagents. While our determined detection limits are adequate for the needs of the MAJORANA DEMONSTRATOR experiment, there is opportunity for further improvement if necessary through the use of validated perfluoroalkoxy (PFA) vials for lead digestion and collection uses rather than the LSC vials used. Use of a different resin may also provide improvements in U recoveries and could eliminate the need to make up samples in 6M HNO₃. For example, U can be effectively loaded on TRU resin in lower nitric acid concentrations and effectively eluted using hydrofluoric acid [16; 24].

4. Conclusion

Anion exchange is an effective preparation method for concentrating analytes while also removing unwanted sample matrix. The preparation method described achieved extremely low detection limits of 0.0084 pg Th/g copper and 0.0106 pg U/g copper. Furthermore, with minor modifications, this method proved viable for the determination of Th and U in lead samples, achieving detection limits of 0.23 pg Th/g lead and 0.46 pg U/g lead. There are still improvements to be made in the resin preparation and column configuration. Smaller-diameter columns have the potential to improve separation and thereby increase recoveries, pushing detection limits even lower—particularly in the case of lead analysis, where the matrix interferences played a significant role. The further purification of Optima-grade acids through distillation or ion exchange column scavenging would also further lower backgrounds. Lastly,

the development of an automated separation scheme in line with the ICP-MS would allow for a more consistent, less time-consuming approach. The reproducibility of automation would likely lower the detection limits even further.

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Figure 1. Flow diagram for column preparation and separation steps. Cleaned columns and resins were validated for their purity by passing 0.1 M HCl through the resin and collecting for analysis using ICP-MS (step #1). After ensuring the column and resin were sufficiently clean, the resin was conditioned using 2 mL of nitric acid (step #2). The concentration of the conditioning HNO₃ matched that of the acid matrix of the sample (*i.e.*, 8 M HNO₃ for copper samples and 6 M HNO₃ for lead samples). Five milliliters of sample were then loaded onto the columns (step #3). A wash step (step #4) of 0.6 mL 8 M HNO₃ for copper samples or 1.8 mL 6 M HNO₃ for lead samples was used to further reduce the background before elution using 1.2 mL 0.1 M HCl (step #5). Eluted solutions were collected in cleaned vials only during steps #1 and #5 for analysis on the ICP-MS, otherwise eluted solutions went to waste.

Figure 2. Tracer recoveries as a function of elution volume. One milliliter fractions were collected and quantified using ICP-MS. ■ ^{229}Th ■ ^{233}U

Figure 3. Recoveries of ^{229}Th and ^{233}U after three successive column uses. ■ ^{229}Th ■ ^{233}U

Figure 4. Elution of lead from the column using 6 M HNO_3 eluent after loading 5 ml of 6 M HNO_3 lead solution.

Figure 5. Elution of lead from column using 8 M HNO₃ eluent after loading 5 ml of 8 M HNO₃ lead solution.

Figure 6. Picograms of analyte in the process blanks from lead analysis. ■ ^{232}Th ■ ^{238}U

Table 1. Summary of Method Validation Data for Copper Analysis

Determination #	pg ^{232}Th /g Cu	pg ^{238}U /g Cu
1	0.0268	0.0466
2	0.0233	0.0442
3	0.0256	0.0408
4	0.0289	0.0449
5	0.0311	0.0510
6	0.0269	0.0440
7	0.0236	0.0412
8	0.0236	0.0402
Average	0.0262	0.0441
Spike Subtracted Average	0.0262	0.0213
Standard Deviation	0.0028	0.0036
MDL (2.998*Standard Dev.)	0.0084	0.0106
	Tracer Recoveries (%)	
	^{229}Th	^{233}U
Average	69.9	79.4