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Determination of Method Detection Limits for Trace 232-Thorium and 238-Uranium in Copper using Ion Exchange and ICPMS

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April 2014

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Executive Summary

Based on the MAJORANA DEMONSTRATOR (MJD) simulations task group calculations, the copper used in the inner shield and detector components require purity levels of <0.3 µBq ^{238}U/kg Cu and <0.3 µBq ^{232}Th/kg Cu [1]. The MAJORANA Collaboration is endeavoring to achieve this goal by electroforming copper using ultra-clean materials in facilities at PNNL and SURF. In this document, a broadly accepted U.S. Environmental Protection Agency method is used to evaluate an ion exchange technique, developed at PNNL, for determining sensitivity in the assay of copper for trace levels of thorium and uranium [2]. These data indicate that, in all cases, the assay sensitivity and material limits are being met.

Acronyms and Abbreviations

ICP-MS	inductively coupled plasma mass spectroscopy
MJD	MAJORANA DEMONSTRATOR
PNNL	Pacific Northwest National Laboratory
SURF	Sanford Underground Research Facility
MDL	method detection limit
TCR	Temporary Clean Room

Contents

1.0 Introduction

Based on the MAJORANA DEMONSTRATOR (MJD) simulations task group calculations [1], the most stringent radiopurity goal is that for copper used in the inner shield and detector components. The required purity level for uranium is <0.3 µBq ^{238}U/kg copper or 0.024 x 10^{-12} g ^{238}U/g Cu. For thorium, the purity level required is also <0.3 µBq ^{232}Th/kg Cu although this is equivalent to 0.075 x 10^{-12} g ^{232}Th/g Cu. At these levels, the electroformed copper is estimated to contribute ≤ 0.9 counts/ROI/tonne/year. The MAJORANA Collaboration is endeavoring to achieve this goal by electroforming copper using ultra-clean materials in facilities at Pacific Northwest National Laboratory (PNNL) and the Sanford Underground Research Facility (SURF).

Here we evaluate the method developed at PNNL for sensitivity in the assay of copper for trace levels of thorium and uranium. The method detection limit (MDL) evaluation was performed using a broadly accepted U.S. Environmental Protection Agency technique [2].

2.0 Sample Preparation

Copper samples were selected at random from the first round of production runs at the Temporary Clean Room (TCR) in SURF.in August 2013. About 10 grams of each copper sample were dissolved using ultra clean nitric acid and tracers of ^{229}Th and ^{233}U at approximately 100 femtograms/ml of each added. Aliquots of these solutions were used for the replicate analysis. In December 2013, ~80 grams of another copper sample was dissolved; otherwise, the preparations were the same. For separation of U and Th from each copper sample, seven replicate pre-leached columns were used and packed with 0.5 ml AG IX4 100-200 mesh (Bio-Rad, Inc.) ion exchange resin. Before sample loading, all columns were cleaned using a series of acid washes. To verify that the acid washes effectively removed all U and Th present, the resin was rinsed with dilute HCl, which was collected and analyzed using an Agilent 7700 series inductively coupled plasma mass spectroscopy (ICP-MS). The anion exchange separation was performed by loading 5ml of sample solution followed by a wash with ultra clean nitric acid to remove any residual copper left on the column. Uranium and thorium were then eluted using dilute hydrochloric acid. The eluent was collected and analyzed via ICP-MS.

3.0 Experimental and Results

Assay of the samples was performed using an Agilent 7700x ICP-MS instrument. Samples were prepared and analyzed in a class 10000 clean room and using a laminar flow hood providing a class 10 environment. All vials were validated prior to use. Instrument detection limits were calculated at approximately 2 ppq for both ^{238}U and ^{232}Th in a 5% nitric acid matrix. Uranium and thorium calibration solutions ranged from a 15 ppq concentration to 700 ppq.

Two analysts performed the MDL determinations. The first analyst performed analysis in August 2013 using two electroformed copper samples and these results are shown in Tables 1 and 2. The second analyst performed two separate MDL determinations in December 2013 with one of the same electroformed copper samples used in August. The samples were freshly prepared in December using a much larger sample. These results are summarized in Table 3.

Table 1: Results for Sample P37WT and the Method Detection Limits Derived From Replicate Analysis in August 2013

Sample ID	^{232}Th (µBq/kg Cu)	^{238}U (µBq/kg Cu)
P37WT_1	0.095	0.194
P37WT_2	0.066	0.113
P37WT_3	0.068	0.155
P37WT_4	0.050	0.137
P37WT_5	0.038	0.190
P37WT_6	0.061	0.198
P37WT_7	0.057	0.179
average	0.062	0.167
Standard deviation	0.018	0.032
MDL	0.053	0.097

Table 2: Results for Sample P34MQ and the Method Detection Limits Derived From Replicate Analysis in August 2013

Sample ID	^{232}Th (µBq/kg Cu)	^{238}U (µBq/kg Cu)
P34MQ_1	0.115	0.174
P34MQ_2	0.120	0.226
P34MQ_3	0.146	0.185
P34MQ_4	0.112	0.233
P34MQ_5	0.164	0.187
P34MQ_6	0.090	0.263
P34MQ_7	0.115	0.234
average	0.123	0.215
Standard deviation	0.024	0.033
MDL	0.073	0.098

Table 3: Method Detection Limits Determined by Analyst 2 for Two Separate Analysis Dates

Sample P34MQ	^{232}Th (µBq/kg Cu)	^{238}U (µBq/kg Cu)
MDL (12/18/2013)	0.045	0.267
MDL (12/23/2013)	0.043	0.164

4.0 Conclusion

These data indicate there is likely a slight systematic high bias for the analysis of ^{232}Th by analyst 1 although the difference between the analysts is within one standard deviation. There is a high bias for ^{238}U by analyst 2 and although a separate lot of ion exchange resin was used between the two analysts, the MDL was notably lower for the second attempt by this analyst indicating it may be associated with technique. Additional data will be obtained and MDLs updated as needed. These data indicate that in all cases the assay sensitivity and material limits required for MJD are being met.

5.0 References

1. J. A. Detwiler, “Demonstrator Background Calculations Spreadsheet”, M-TECHODOCPHYS-2010-024 (2010).

2. CFR 2012 Title 40, vol. 24, part 136, Appendix B, Definition and Procedure for the Determination of Method Detection Limit-Rev 1.11

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