Reductions of Radioactive Backgrounds in Ultra-High Purity Electroformed Copper

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Outline

▶ Brief history of Electroforming

▶ Future needs from electroformed materials

▶ Capabilities

▶ Underground EF facilities in the US

▶ Assay methods

▶ Ion exchange sample preparation for Th

▶ ICP-MS for Th and U and detection limits

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Electroforming Copper

▶ Ultra High Purity Copper with ever increasing purity is needed for a wide variety of experiments including those for the next generation of neutrino physics, dark matter, and material sciences
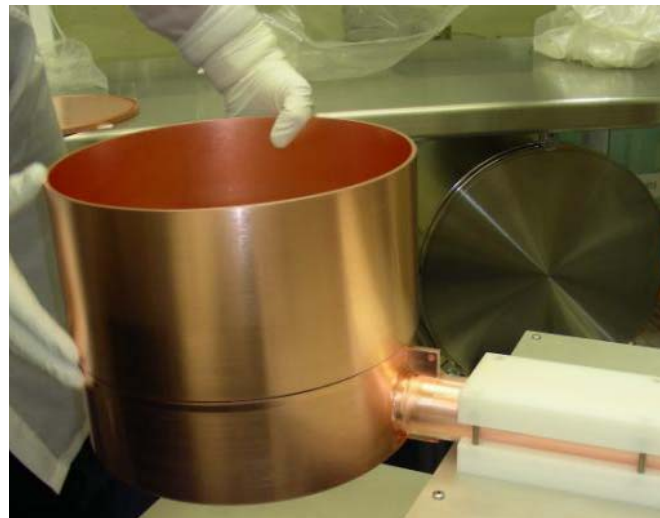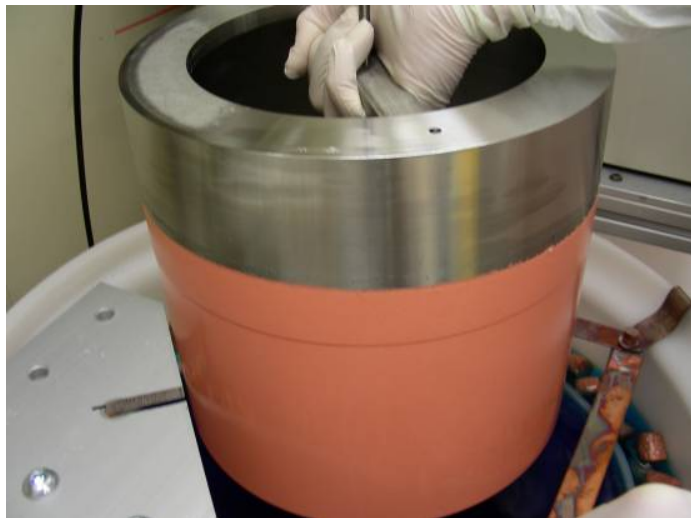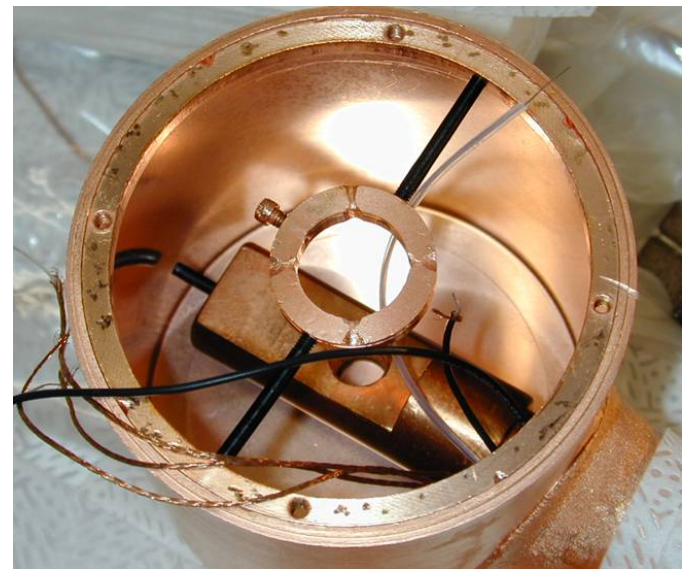

Journal of Radioanalytical and Nuclear Chemistry 282(3):703-708

High Purity Low-Background Electroformed Copper

- Has been formed into a variety of thin, low-mass parts, or thick, high heat transfer and shielding parts
- Has exhibited strength equal to or better than OFHC
- Free standing electroformed parts ranging from 0.150 to 15 mm thick

Electroformed Copper / Clean Fabrication

▶ Next generation experiments require material production

- ❑ of even greater purity

- ❑ maintains it's purity using clean fabrication and material surface cleanup techniques

- ❑ with little or no cosmogenic exposure

- ❑ larger dimensions/greater throughput which maintains or improves physical properties

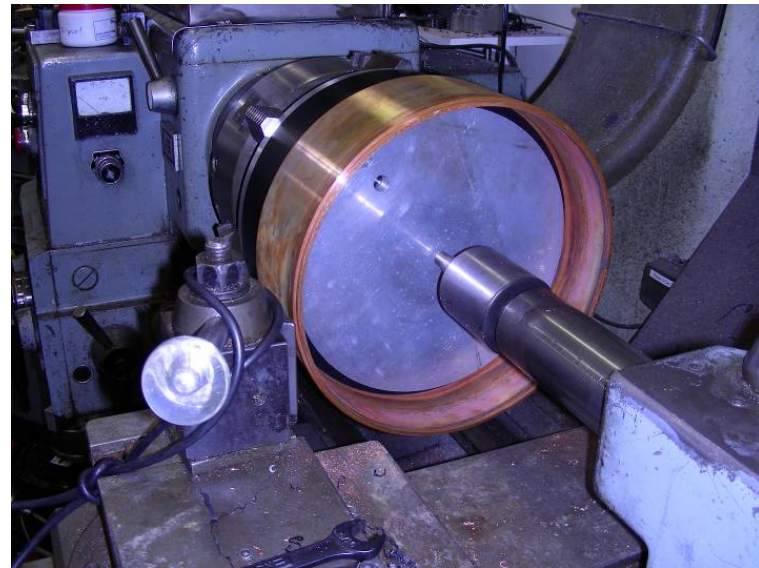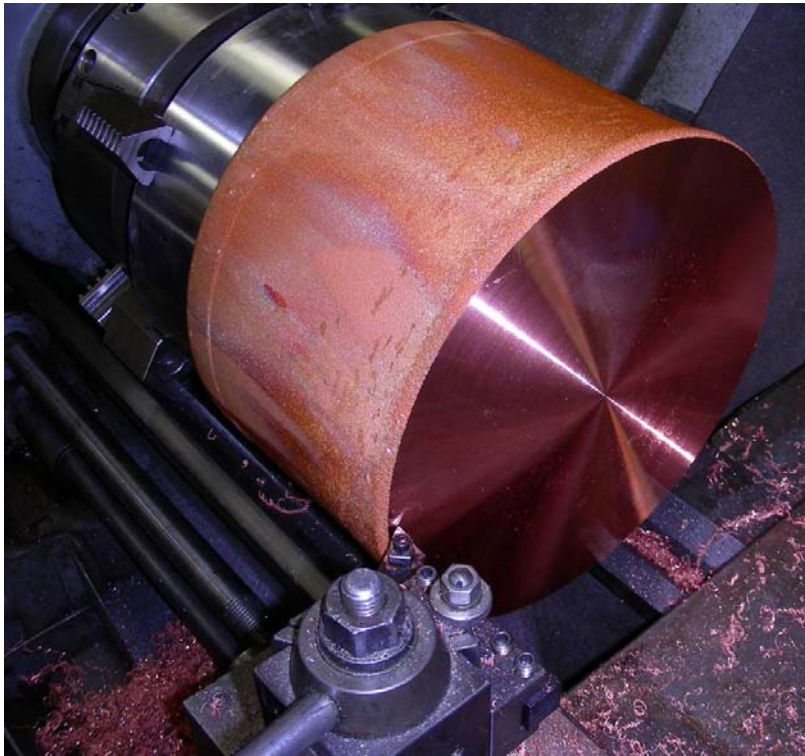Large parts produced with ultra-pure Cu

Fabrication

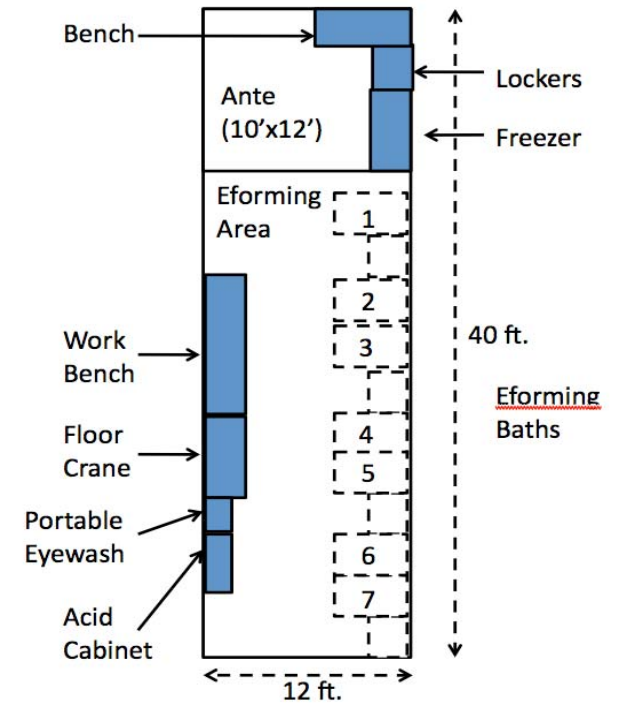Significant experience machining electroformed parts. Majorana will conduct these activities underground

Deep Underground Electroforming Facilities in US

electroforming

machine shop
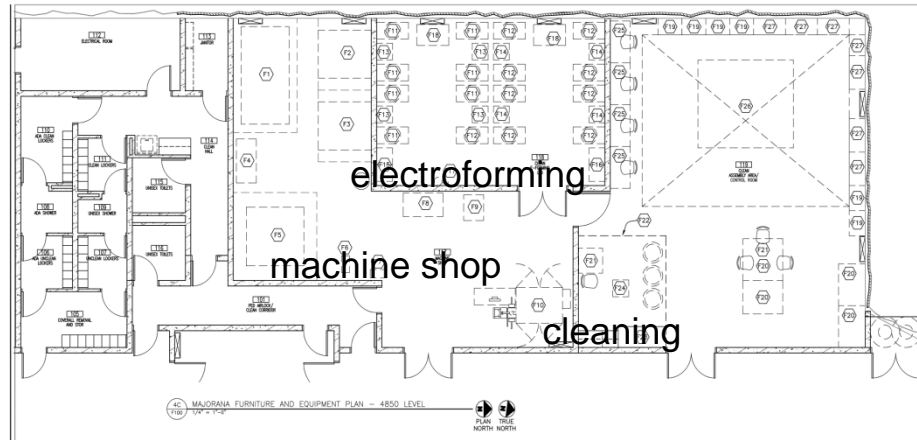
cleaning

Majorana at Sanford/DUSEL

Bench
Ante (10'x12')
Lockers
Freezer
Eforming Area
Work Bench
Floor Crane
Portable Eyewash
Acid Cabinet
40 ft.
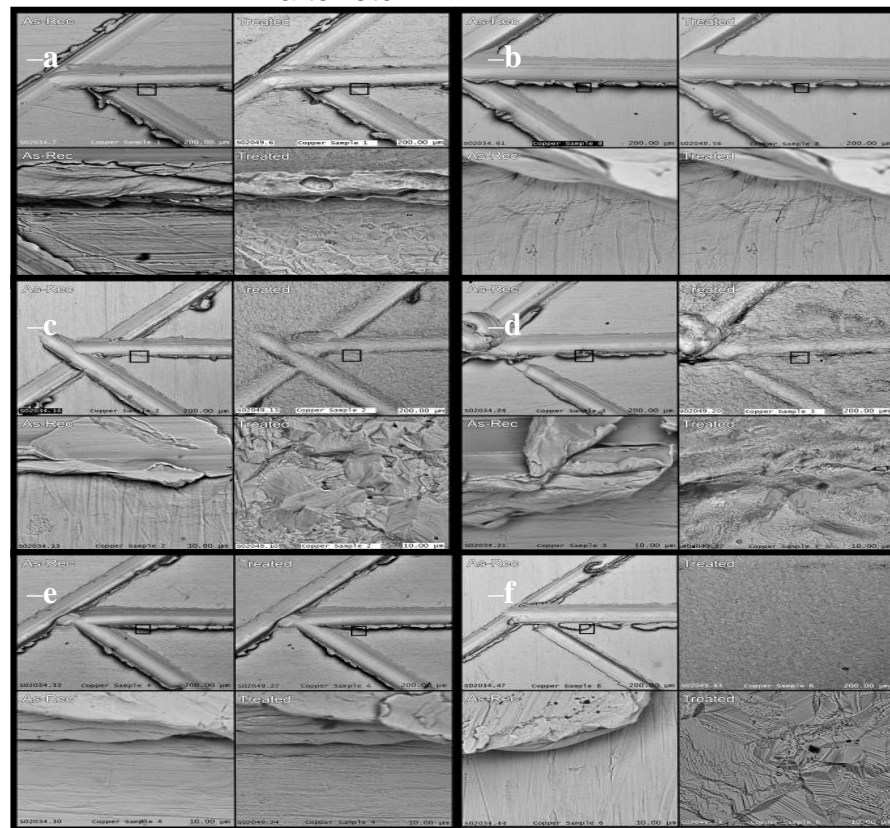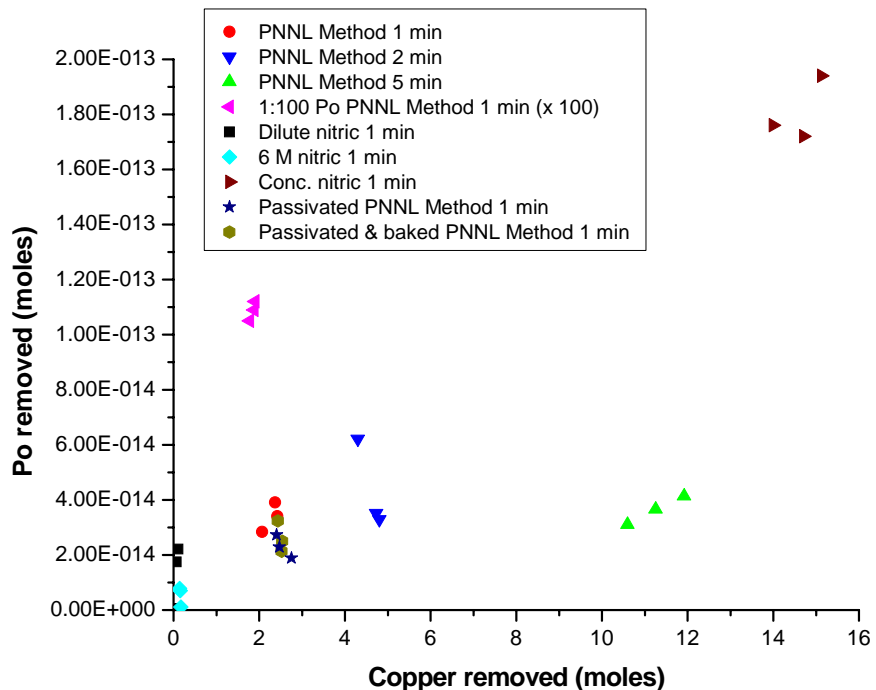Eforming Baths
1
2
3
4
5
6
7
12 ft.

Soudan Mine
(Reeves and Sons)

Cleaning and passivation techniques have been developed and proven effective

copper surfaces   before etch   after etch

▶ Evaluated removal of electrochemically difficult species such as polonium from copper surfaces

Legend:
- ● PNNL Method 1 min
- ▼ PNNL Method 2 min
- ▲ PNNL Method 5 min
- ◀ 1:100 Po PNNL Method 1 min (x 100)
- ■ Dilute nitric 1 min
- ◆ 6 M nitric 1 min
- ▶ Conc. nitric 1 min
- ★ Passivated PNNL Method 1 min
- ⬠ Passivated & baked PNNL Method 1 min

Y-axis: Po removed (moles)
X-axis: Copper removed (moles)

▶ Conducted numerous studies to determine the optimum surface cleaning and passivation of copper and other surfaces

Increasing dimensional requirements and greater throughput needed

Prototype MAJORANA electroforming bath, power supply, and mandrel are currently running at PNNL
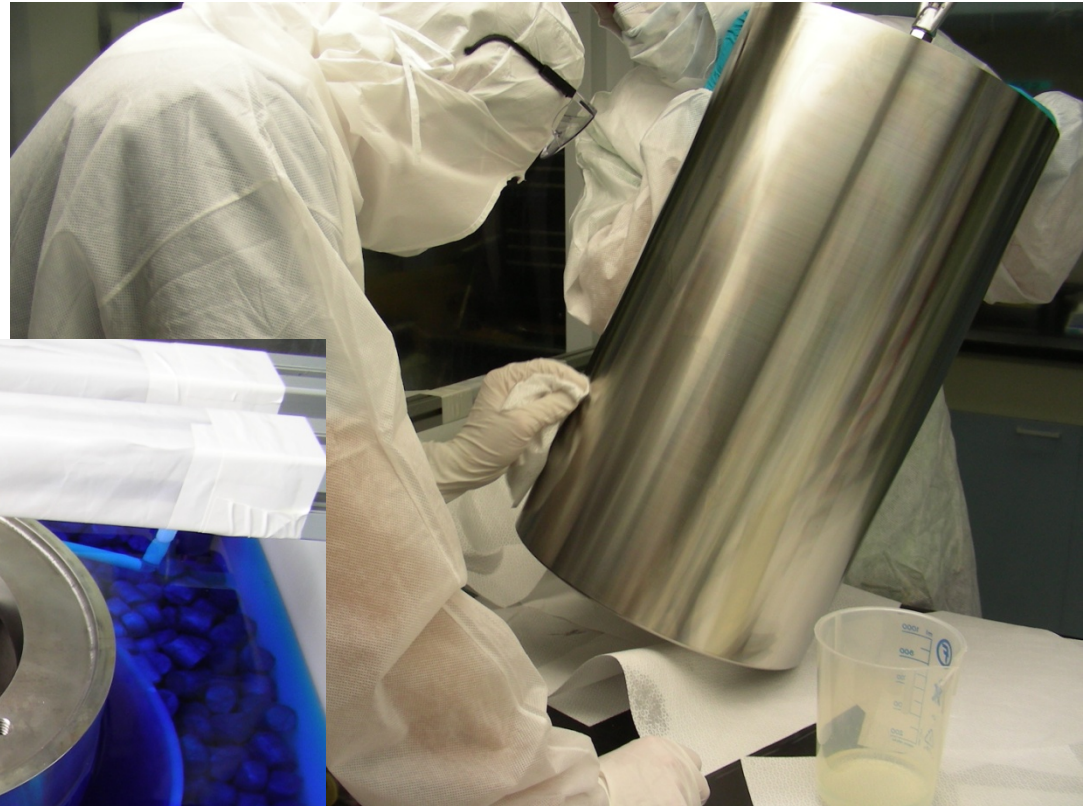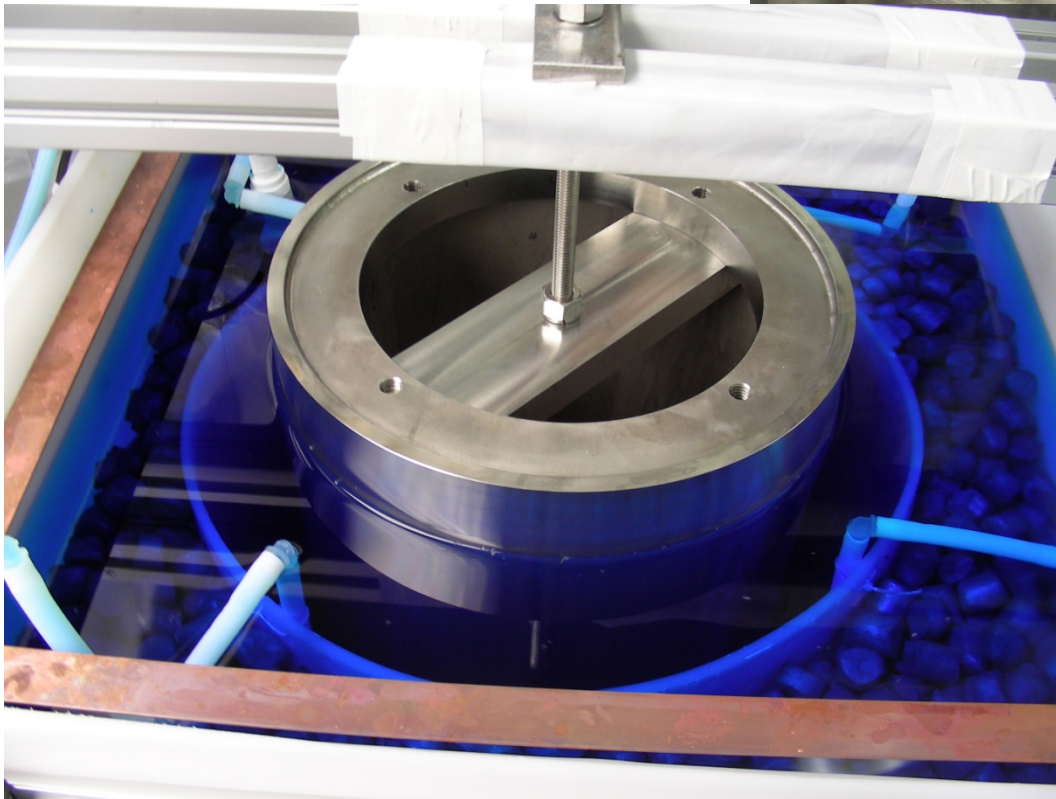
Each bath can produce ~100kg/yr on mandrel shown above (13" diameter x 23" height)

Undergound Laboratory at PNNL

Underground Laboratory at PNNL

Essential to maintain satisfactory physical properties
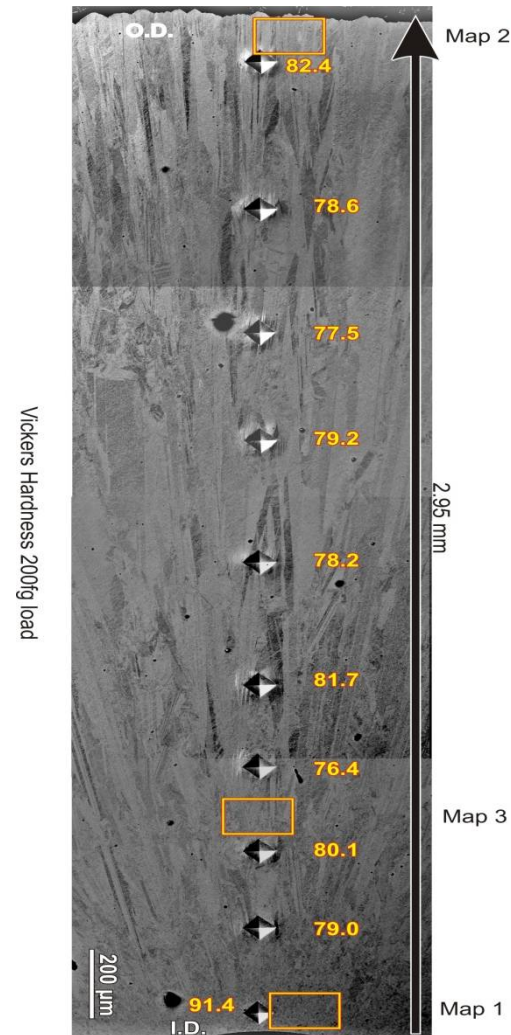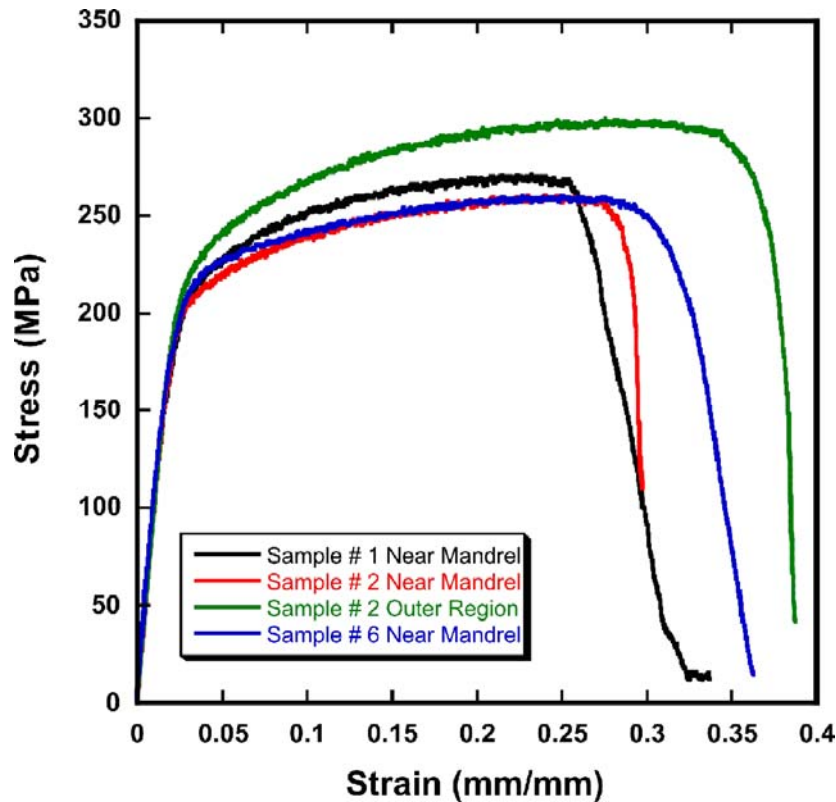
Electroformed Copper / Clean Fabrication
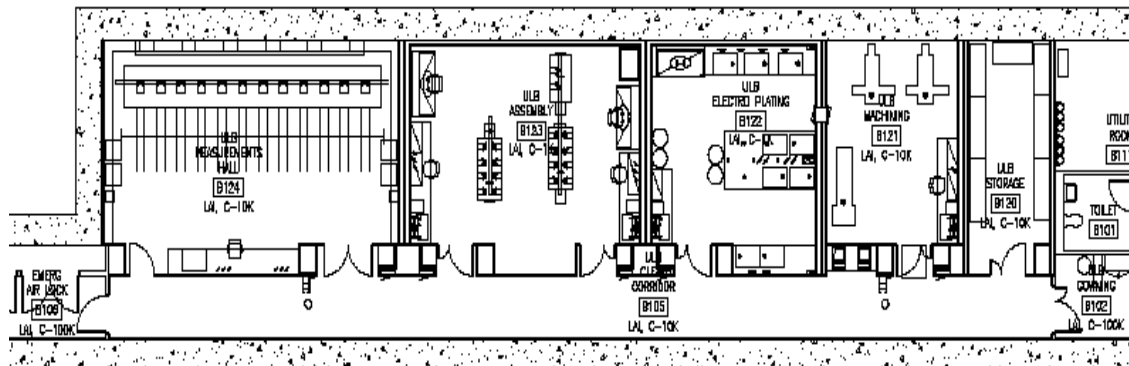
▶ Next generation experiments require material production

❑ of even greater purity

✓ maintains it's purity using clean fabrication and surface cleanup techniques

✓ with little or no cosmogenic exposure

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Large parts produced with ultra-pure Cu

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Assay Performance Requirements

▶ Most stringent copper radiopurity specified by the Majorana project background budget

- Most stringent material goal is 0.3 μBq ^{232}Th and ^{238}U/kg Cu

- To ensure proper confidence in the result an assay capable of at least 1/3 of the goal is needed. Therefore we need an assay with detection limits of 0.10 μBq ^{232}Th and ^{238}U/kg Cu (~0.03 and 0.008 x 10^{-12} g ^{232}Th and ^{238}U/g Cu)

- Must be produced underground to maintain purity due to reactions with cosmic secondary neutrons (e.g. ^{63}Cu(n,α)^{60}Co)

Radioassay impractical

▶ More sensitive assays are certainly necessary to meet Majorana goals

Results:
^{226}Ra   <25 µBq/kg
^{228}Th   9 µBq/kg
(Brodzinski et al, Journal of Radioanalytical and Nuclear Chemistry, 193 (1) 1995 pp. 61-70)

LNGS NOSV High-Purity Cu:
^{226}Ra   <18 µBq/kg
^{228}Th   <12 µBq/kg
(M. Laubenstein et al, Applied Radiation and Isotopes, 61 (2004) 167-172)

6 kg-yr GeMPI assay of anode Cu provides similar results in 2009
(not published, thanks to M. Laubenstein)

~22 kg of starting anode material (99.995% Cu) prepared for radioassay at Gran Sasso in 2008

Other assay methods considered reasonable candidates for U and Th in copper

▶ Laser Excitation/MS

- Can be very selective and could be made very sensitive. Initial investment is high (required specific lasers) and is required for each analyte (element and isotope). Sample must be in gas phase (DL~10^{-8}-10^{-14}g).

▶ Accelerator Mass Spectroscopy

- Insufficient dynamic range to handle direct analysis of copper (DL~10^{-12}-10^{-14}g)

▶ Neutron Activation Analysis

- Post activation products of copper requires significant separation chemistries must be employed (DL based on a variety of factors)

Attempts to exploit the higher concentration of contaminants expected at the grain boundaries to improve assay sensitivity

Locations where increased contaminant levels expected
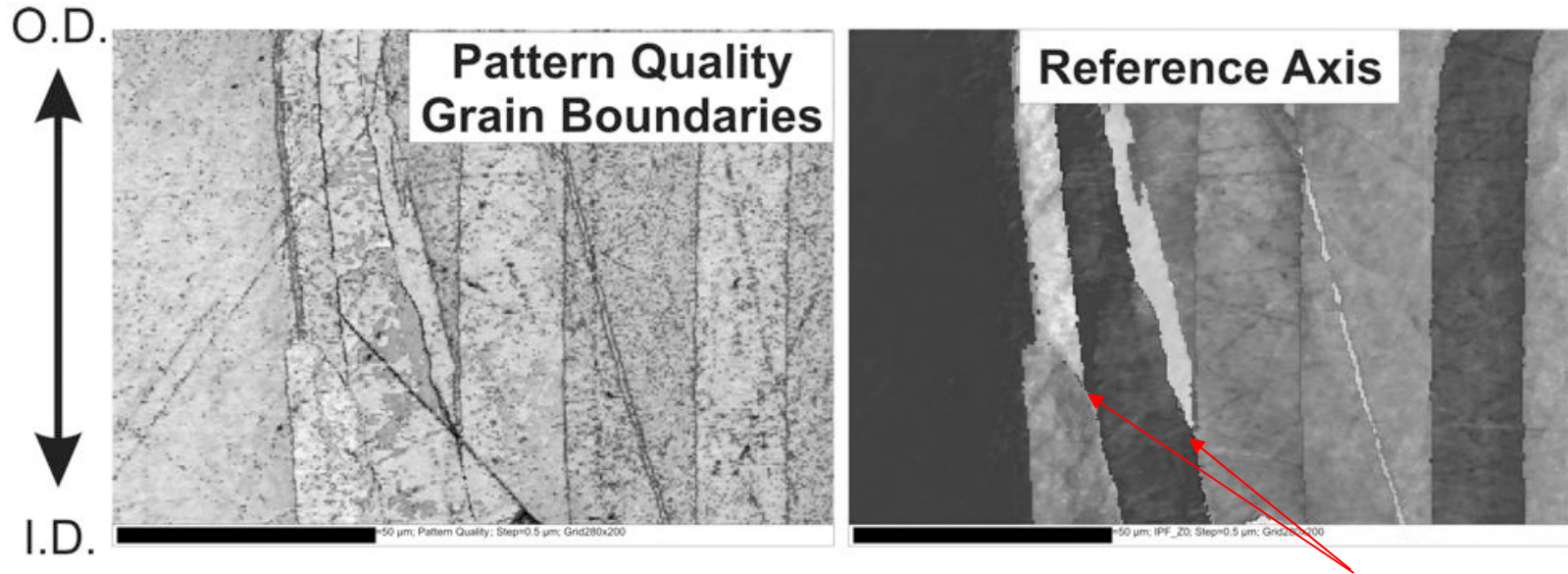
▶ The gain in sensitivity depends on the ratio of grain boundary volume to that of the crystal volume

▶ EDS run during SEM examination yielded no signal other than copper

SIMS demonstrates that as expected contaminants appear to be present at the grain boundaries
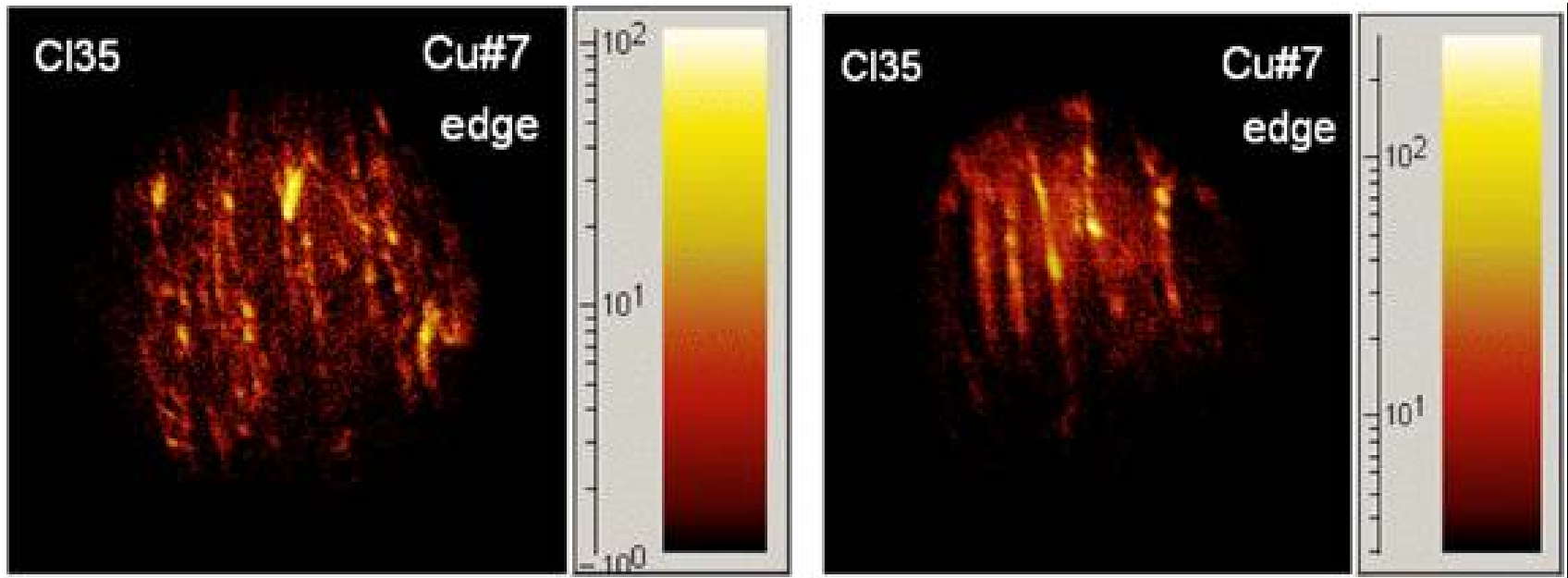
SIMS ion images showing the localization of chlorine contamination (Negative ion mode, 10 kV Cs+ primary ion beam)

SIMS also demonstrates that contaminant concentration varies with depth
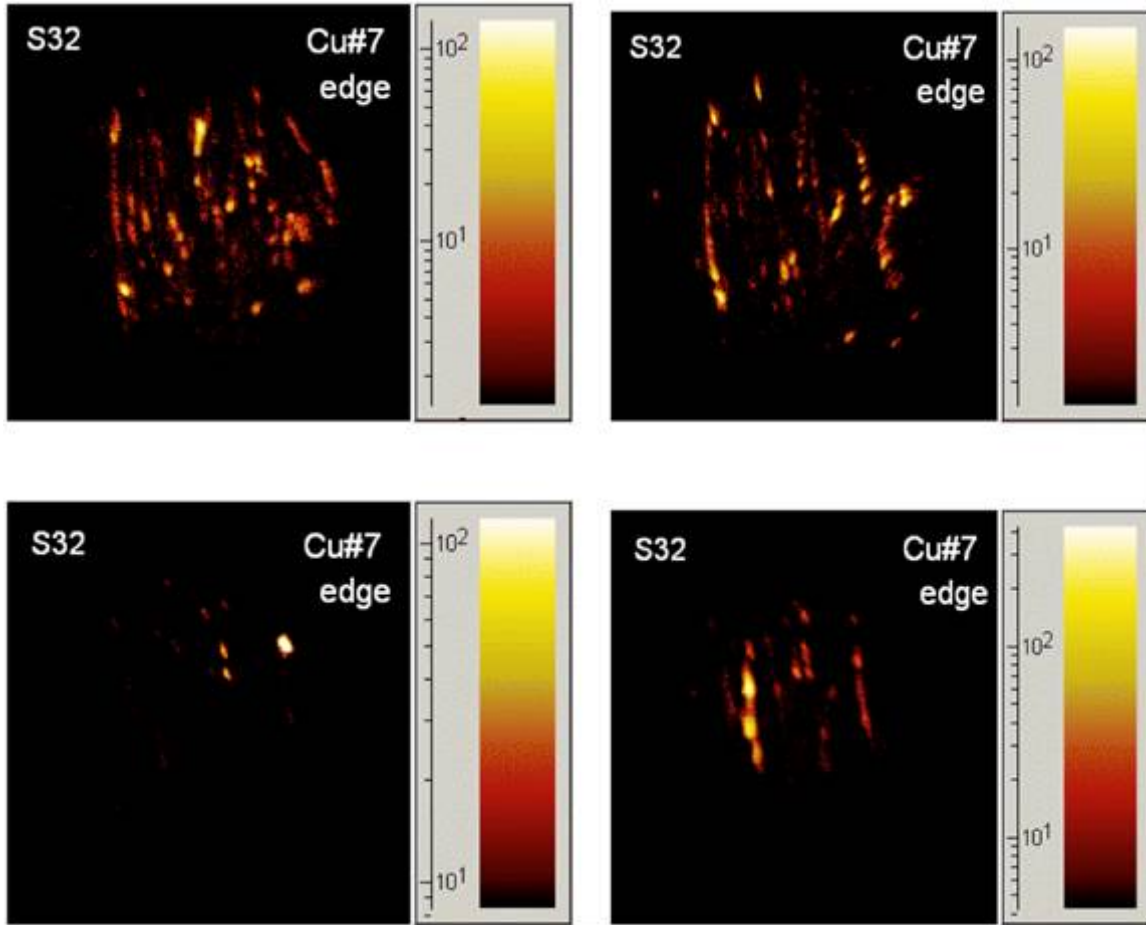
Series of SIMS ion images using the ion beam to remove sample material exhibiting the depth of contamination and localization of sulfur in copper

Unfortunately, no significant signal was found for Th or U. Detection limit estimated ~1ppb

LA-ICP-MS: Demonstrates co-deposition of contaminants but without quantitation
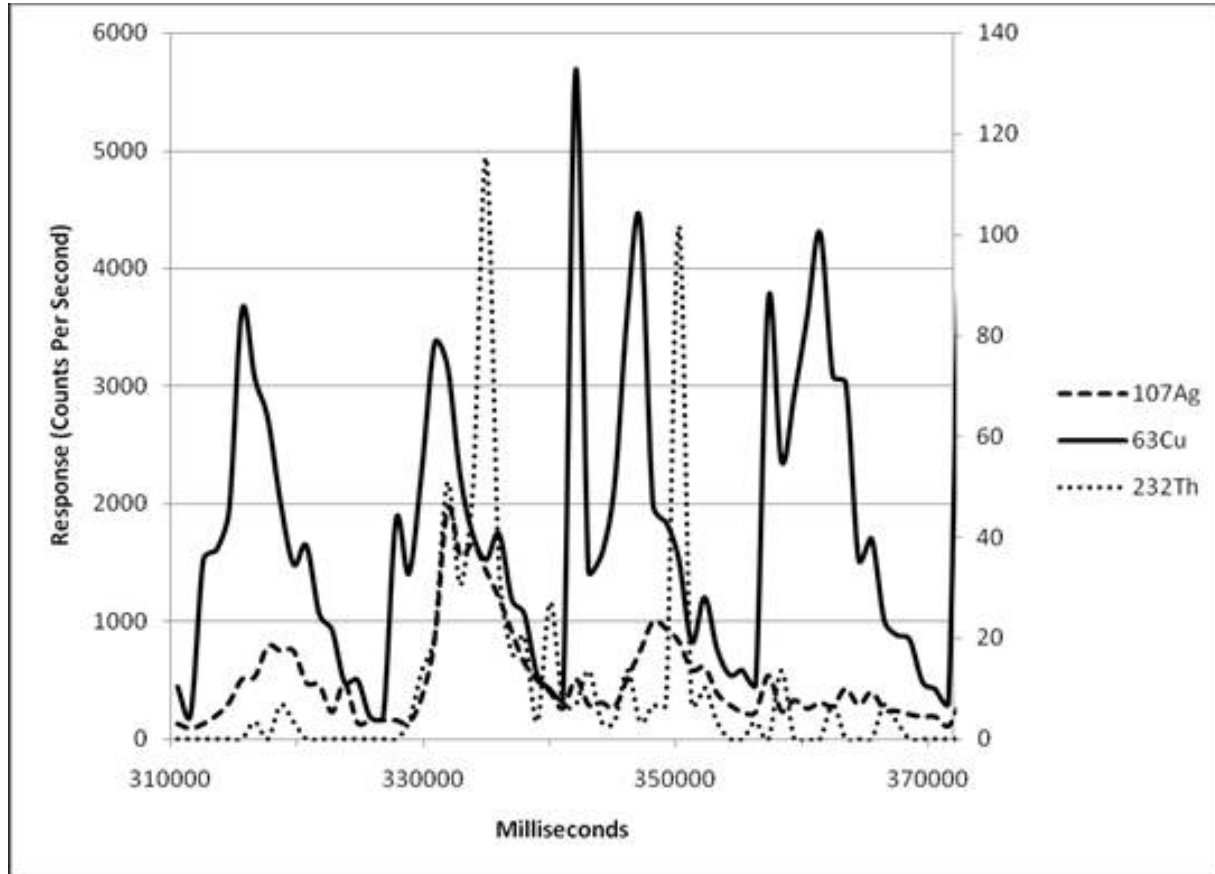
Electrochemical
Potentials:
Ag 0.80 V
Cu 0.34
Th -1.9

Similar inhomogeneity
seen in NIST 1252a
SRM for Th, U
(not certified for these
components)

LA-ICP-MS (10 Hz for 5 sec) trace showing co-localization of Ag and Th
contaminants although they have vastly differing electrochemical potentials.
(Cu matrix rejected, response on the primary y-axis with Ag, Th is on the secondary y-axis)

Journal of Radioanalytical and Nuclear Chemistry 282(1):315-320. doi:10.1007/s10967-009-0241-1

Assay of Cu for Th using ion exchange sample preparation, ICP-MS
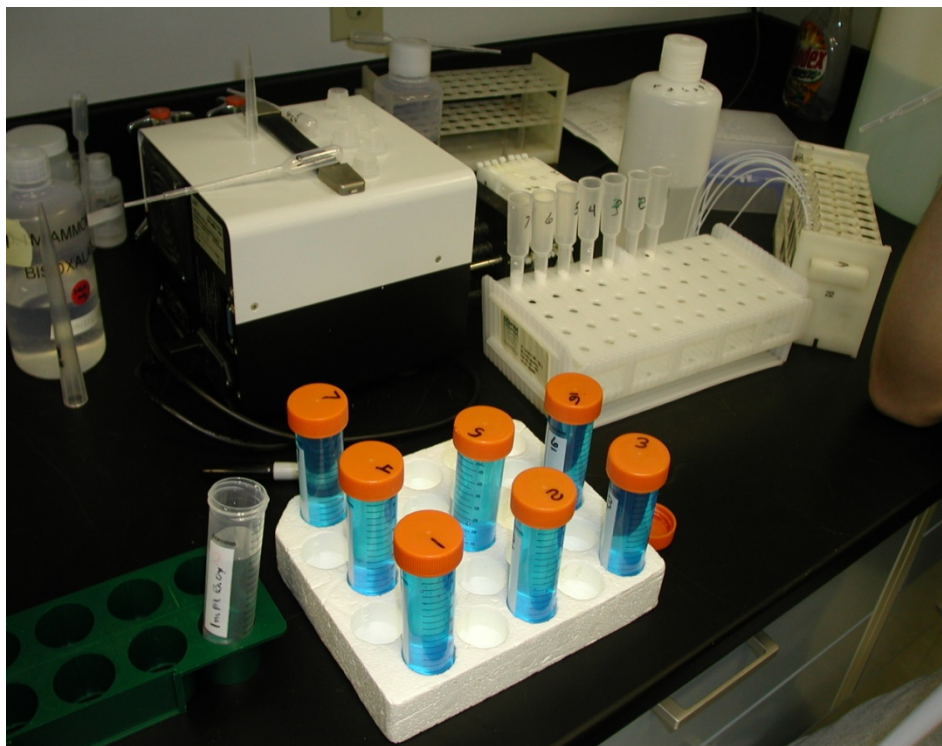
- Analysis of 7 aliquots from a single copper sample dissolved in nitric acid

- 10 ml columns loaded with 0.8 ml of TRU resin using Millipore LC 10 μm filter to retain resin

- Work performed manually on bench top with open columns

Copper Assay Ion Exchange Process
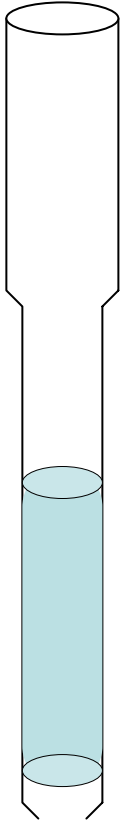
1. Condition column
   - 1.0ml of 2.5M nitric acid

2. Load the sample
   - 50ml total volume comprised of 25ml of 15M nitric acid, 25ml DI water, and 0.1ml of 10^{-12} g/ml ^{229}Th tracer

3. Wash the column
   - 2.0ml of 2.5M nitric acid

4. Strip column
   - 5 aliquots of 0.5ml 1mM Bioxalate
   - Save and combine aliquots
   - Acidify with 0.025 ml of 15M nitric acid
   - Analyze solution by ICP/MS

5. Wash the column
   - 30 ml DI water to remove any bioxalate

Results from Copper Samples using Ion Exchange Sample Processing

	Ave of μBq ^{232}Th/kg in Blanks	μBq ^{232}Th/kg of Starting Anode Cu	μBq ^{232}Th/kg of PNNL Electroformed Cu
Column 1	1.0	1.7	1.6
Column 2	0.5	1.6	1.2
Column 3	0.6	1.4	0.9
Column 4	0.5	1.5	2.0
Column 5	0.5	1.8	1.5
Column 6	0.4	1.0	1.3
Column 7	0.6	1.3	0.9
Ave	0.6	1.5	1.3
Std Dev	0.2	0.2	0.4
% Std Dev	34.9	16.8	30.2

Ratio between starting to electroformed copper was expected to be much larger!

Analysis of electroforming bath solution using precipitation techniques found ave 77μBq ^{232}Th/liter

Indicated rejection ratio of ~10^2-10^3 which is consistent with Journal of Radioanalytical and Nuclear Chemistry 277(1):103, 110. doi:DOI: 10.1007/s10967-008-0716-5

▶ ~0.6 μBq ^{232}Th/kg Cu DL (0.15 x 10^{-12} pgTh/gCu)

Assay of Cu for U by ICP-MS

- ► Older ICP-MS lacking matrix tolerence and sensitivity
  - ■ Result of ~42 µBq ^{238}U/kg Cu (3.33 x 10^{-12}g^{238}U/gCu) by ICP-MS in 2005 without ion exchange
  - ■ Ion exchange blanks currently too high to be useful
- ► Purchased new ICP-MS in 2009
- ► Installed in class 1000 cleanroom
- ► Greater matrix tolerance
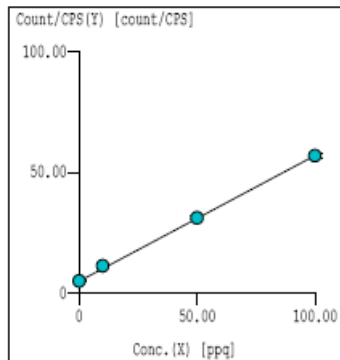- ► Dedicated to low-background measurements

New ICP-MS instrument

▶ Detection limit optimistically ~10^{-16} g/ml U obtainable

▶ Without significant matrix present

Instrument response with constant quantity of analyte

~1000 ppm background matrix

~10 ppm background matrix

Increasing quantity of matrix
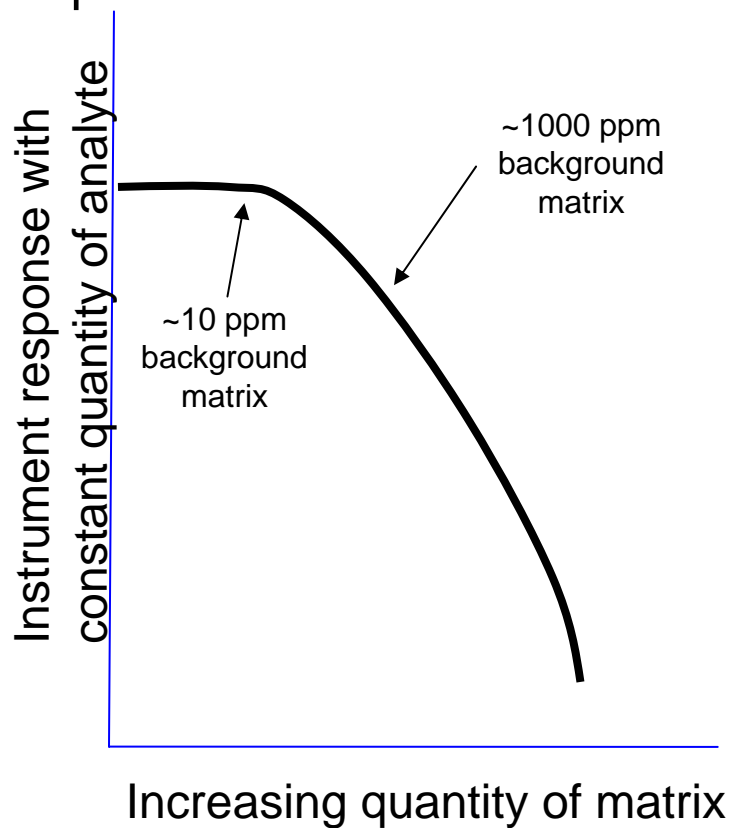
=== Graph Detail ===

Step Mass Element   ISTD   Unit
(1) 232 Th   ---   ppq

Count/CPS(Y) [count/CPS]

	Rjct	Conc		Calc Conc	CPS/Count	Ratio		RSD [%]
1		0.000		0.000	4.800	---	P	6.054
2		10.00		12.08	11.10	---	P	2.267
3		50.00		50.25	31.01	---	P	2.299
4		100.0		99.67	56.79	---	P	1.415
5		---		---		---		
6		---		---		---		
7		---		---		---		
8		---		---		---		
9		---		---		---		
10		---		---		---		
11		---		---		---		
12		---		---		---		
13		---		---		---		
14		---		---		---		
15		---		---		---		
16		---		---		---		
17		---		---		---		
18		---		---		---		
19		---		---		---		
20		---		---		---		

Conc. (X) [ppq]

Curve Fit: Y=aX+[blank]
r = 0.9998
Y = 5.216E-001*X +4.800E+000
X = 1.917E+000*Y -9.202E+000
DL = 1.671 ppq
BEC = 9.202 ppq

Weight: OFF
Min Conc: 0.000

Step Mass Element   ISTD   Unit
(1) 238 U   ---   ppq

Count/CPS(Y) [count/CPS]
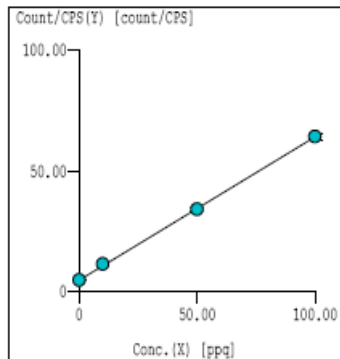
	Rjct	Conc		Calc Conc	CPS/Count	Ratio		RSD [%]
1		0.000		0.000	4.822	---	P	1.740
2		10.00		11.16	11.46	---	P	7.896
3		50.00		49.39	34.18	---	P	1.531
4		100.0		100.2	64.37	---	P	1.943
5		---		---		---		
6		---		---		---		
7		---		---		---		
8		---		---		---		
9		---		---		---		
10		---		---		---		
11		---		---		---		
12		---		---		---		
13		---		---		---		
14		---		---		---		
15		---		---		---		
16		---		---		---		
17		---		---		---		
18		---		---		---		
19		---		---		---		
20		---		---		---		

Conc. (X) [ppq]

Curve Fit: Y=aX+[blank]
r = 0.9999
Y = 5.943E-001*X +4.822E+000
X = 1.683E+000*Y -8.114E+000
DL = 4.234E-01 ppq
BEC = 8.114 ppq

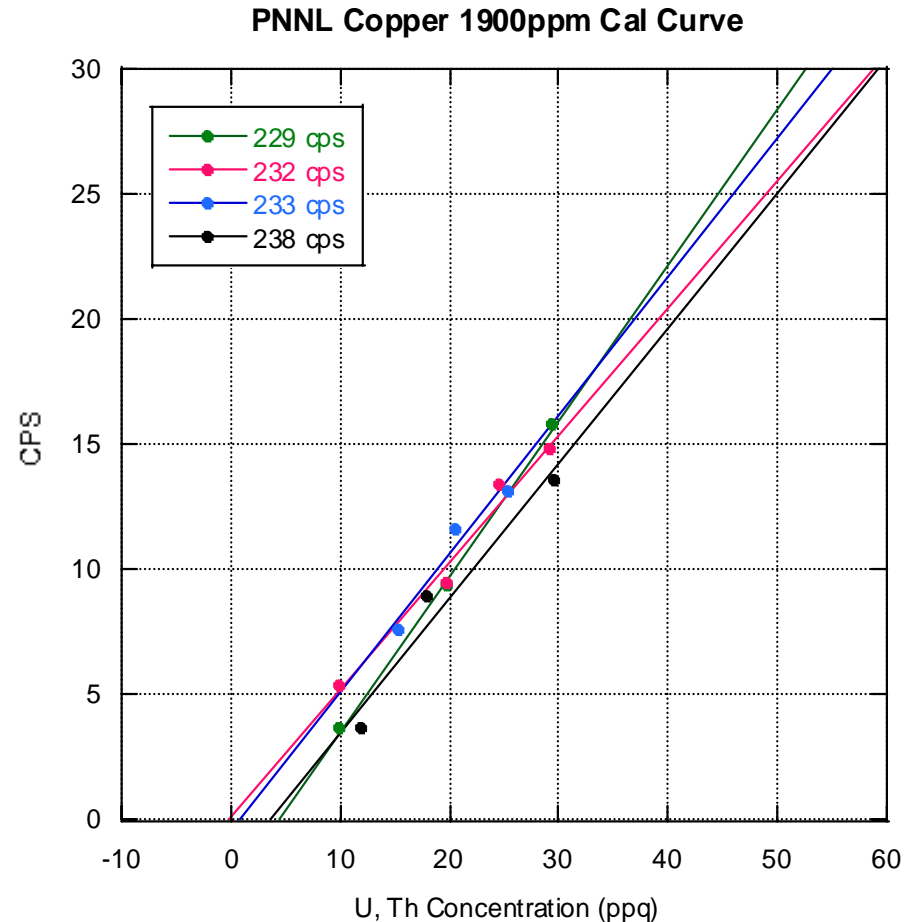# Assay using standard addition ICP-MS

• Standard additions method for quantifying the ^{238}U is difficult to interpret from spikes of 10-30 ppq

• The standard deviation (SD) can be used to approximate the detection limit
(Title 40 part 136 CFR)

• The SD of the 20 ppq spiked copper solution was calculated to be 0.707 CPS

• **Approximate detection limit = 3*SD**

• Detection limit = 2.12 CPS corresponding to 4.7 x 10^{-15}g ^{238}U in 1900 ppm copper matrix

**= 2.4 x 10^{-12} g^{238}U/g Cu
   (~30 µBq ^{238}U/kg Cu)**
achieved without significant sample preparation

PNNL Copper 1900ppm Cal Curve

Legend:
- 229 cps
- 232 cps
- 233 cps
- 238 cps

Axis labels: CPS (y-axis), U, Th Concentration (ppq) (x-axis)

$y = -2.6013 + 0.62154x \quad R^2 = 0.99758$

$y = 0.17355 + 0.50809x \quad R^2 = 0.97765$

$y = -0.47462 + 0.555x \quad R^2 = 0.94235$

$y = -1.9299 + 0.54027x \quad R^2 = 0.94917$

Conclusions

▶ ICP-MS appears to be analytical tool of choice for low activity, low background materials characterization

  ▪ Sample preparation methods for low-background materials analysis lacking for ICP-MS

  ▪ Wide analytical spectrum and low blank levels extremely difficult to obtain (certainly not by employing ion exchange methodologies)

  ▪ Analysis using ICP-MS demands meticulous sample preparation

  ▪ Assay development and purity concerns must stay on the "to-do" list

Conclusions: Projected assay detection limits for U and Th in Cu
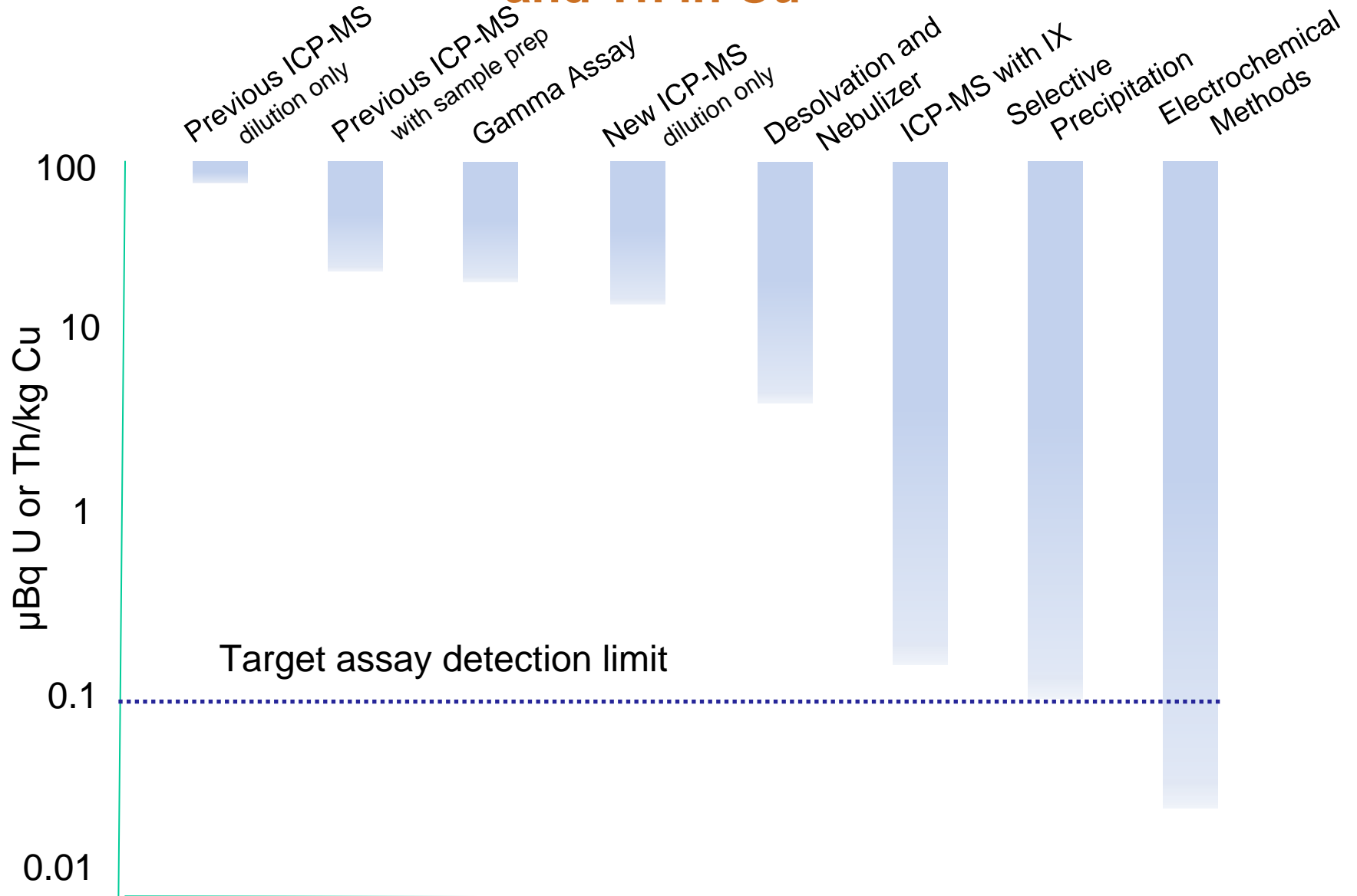
Acknowledgements

▶ Nicole Overman, Jason Merriman, Brian LaFerriere, Heather Hamilton, Kira Shevchenko, Brian Whitehead

▶ DOE and NSF for funding the development activities

▶ SNOLAB for being incredible hosts with an impressive facility. Make sure you take advantage of the tour opportunity