US-Japan Seminar on
Double-Beta Decay
and Neutrino Mass

Materials Purity: Ultra-Low-Background Copper, ICP-MS Assay, and Lead Surface Preparation for the Majorana Project

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Outline

- Motivation
- Electroformed Copper
- ICP-MS Copper Assay
- Lead Surface Preparation
- Summary

Materials are Critical

- Depth is only part of the equation
- Must also have
  - Pure materials
  - Environmental gamma shielding
  - Environmental neutron shielding
  - Residual muon shielding
- Muon-induced secondary neutrons can dominate under good conditions

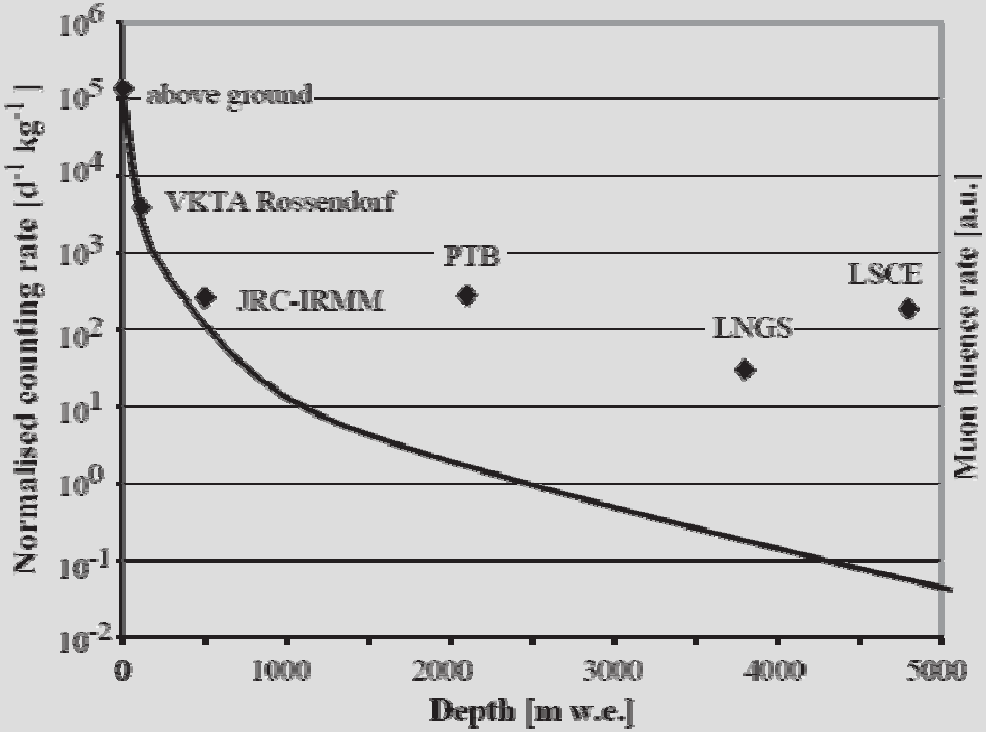


Fig. 1. The integral background counting rate from 40 to 2700 keV divided by the mass of the Ge-crystal for the best HPGe-detectors in some CELLAR laboratories. The solid line shows the muon fluence rate in arbitrary units normalised to the background counting rate above ground. All detectors have only passive shielding.

M. Laubenstein et al. / Applied Radiation and Isotopes 61 (2004) 167–172

Estimated backgrounds in the 0νββ-decay ROI

Majorana Example

Background Source		Gross and Net Rates for Important Isotopes			Total Est. Background (per t-y)
		Counts in ROI per t-y			Counts in ROI
		^{68}Ge	^{60}Co		
Germanium (100 day exp)	Gross	2.54	1.22		
	Net	0.01	0.02		0.03
		^{208}Tl	^{214}Bi	^{60}Co	
Inner Mount	Gross	0.12	0.03	0.26	
	Net	0.01	0.00	0.00	0.01
Cryostat	Gross	0.77	0.16	0.58	
	Net	0.22	0.04	0.00	0.26
Copper Shield	Gross	2.28	0.30	0.02	
	Net	0.64	0.06	0.00	0.70
Small Parts	Gross	0.18	0.04	0.34	
	Net	0.02	0.01	0.00	0.03
External Sources (6000 mwe)		muons	cosmic activity	(α,n)	
	Gross	0.03	1.33	0.003	
	Net	0.003	0.18	0.003	0.18
2ν ββ -decay					< 0.01
		TOTAL SUM			1.21

Crystals are clean

Dominated by ^{232}Th in Cu

See talk by T. Hossbach

Must go deep

- "Gross" indicates level of activity before any analysis cuts are applied.
- "Net" indicates level of activity after cuts have been applied.

Copper Motivation

- Commercial high-purity copper is an attractive material for constructing ultra-low-background spectrometers.
- Thermal, mechanical, electrical, and vacuum properties enable vacuum cryostats, crystal mounts, heat conductors, electrical interconnects, etc.
- When even higher purity is required, additional electrolytic and chemical purification can be combined with the final fabrication step, resulting in “electroformed” copper parts of extreme purity.
- This process can be done underground, providing a potential way to eliminate cosmogenic activation products seen in copper with above-ground exposure.
- Additional purity improvements seem possible with modest additional chemistry.

Ultra-Low-Background Electroformed Copper

Electroformed cups shown have wall thickness of only 250 μm!

- Strength equal to OFHC
- Technology has small physical footprint for production
- Can be easily formed into thin, low-mass parts
- Purity established with IGEX* experience, development continues

*(International Germanium EXperiment)

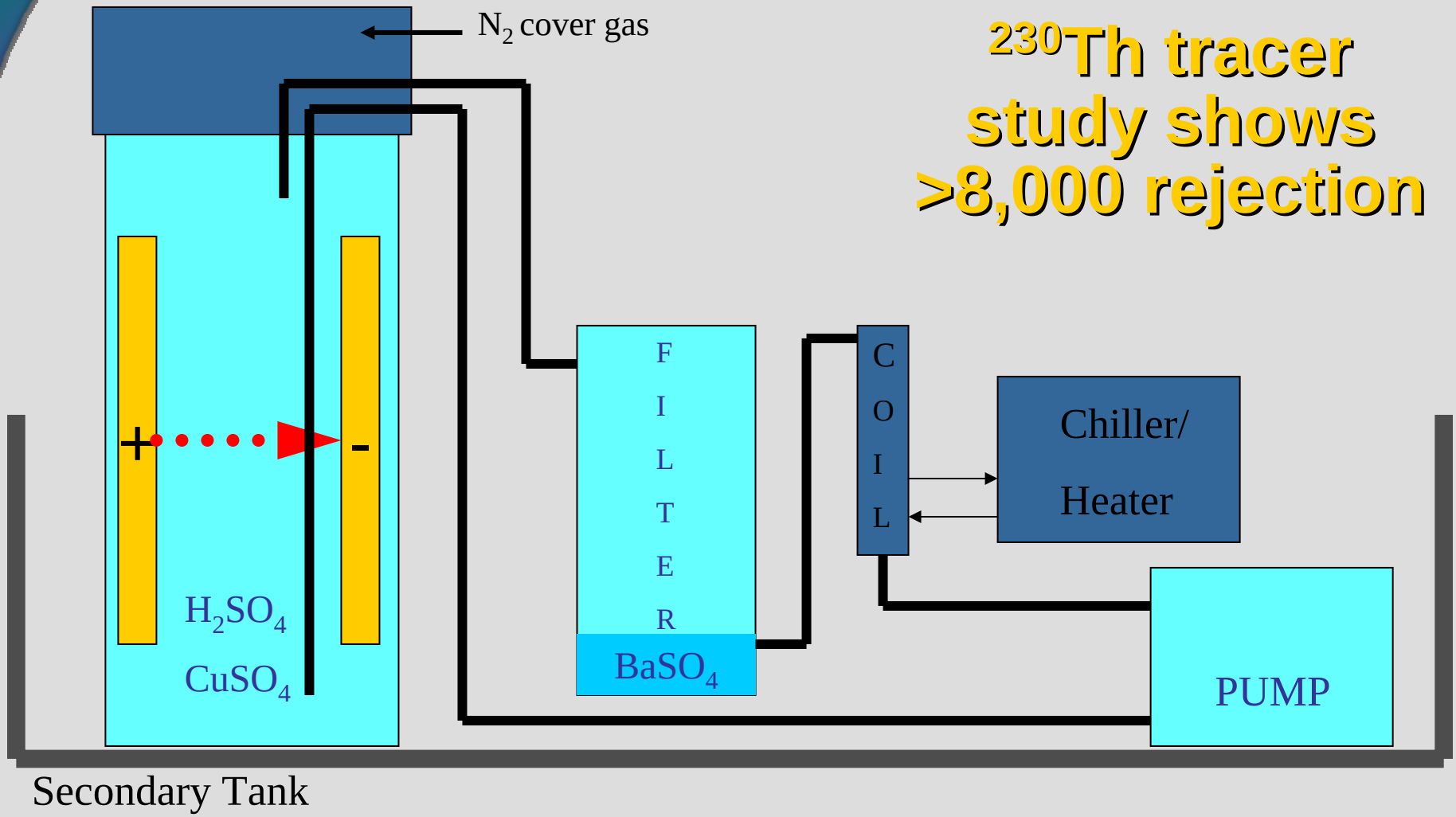
Low-Background Electroformed Copper Key Elements

Low-background detector and electroformed cryostat during assembly

- Semiconductor-grade acids
- Glassware-free handling
- Copper sulfate purified by recrystallization
- Baths circulated with continuous microfiltration to remove oxides and precipitates
- Continuous barium scavenge removes radium
- Cover gas in plating tanks reduces oxide formation
- Periodic surface machining during production minimizes dendritic growth

Electroforming Overview

^{230}Th tracer study shows >8,000 rejection



Plating Bath Process Parameters

- Plating is done onto polished, cleaned, stainless steel mandrels in the shape of the desired parts
- Current density is ~40 mA/cm^2
- Plating rate is ~0.05 mm/h
- $BaSO_4$ collects in the micro-filtration stage and acts as radium scavenge
- $CoSO_4$ was added as a holdback carrier for the cosmogenic $^{56,57,58,60}Co$ present in the starting copper
- HCl and Thiourea affect copper crystal nucleation and grain size

Constituent	Concentration
$CuSO_4$	188 g/l
H_2SO_4	75 g/l
HCl	30 mg/l
Thiourea	3 mg/l
$CoSO_4$	1 mg/l
$BaSo_4$	~1 mg/l

C. E. Aalseth *et al.*, Phys. Rev. C **59**, 2108 (1999).

Chemistry & Cosmogenics

- Further improvements were made in the chemistry for electroformed Cu production
- U, Th progeny reduced substantially (100x, 10x) over early work [Bro95]
- Underground production would totally eliminate cosmogenic ^{60}Co, other less-important cosmogenics
- Current chemistry development continues (tracer studies, mass balance, etc.)

~1995 to present
Electroformed copper radiochemistry gains:

- **H_2SO_4 Purity**
- **Recrystalized $CuSO_4$**
- **Barium scavenge**

Results:

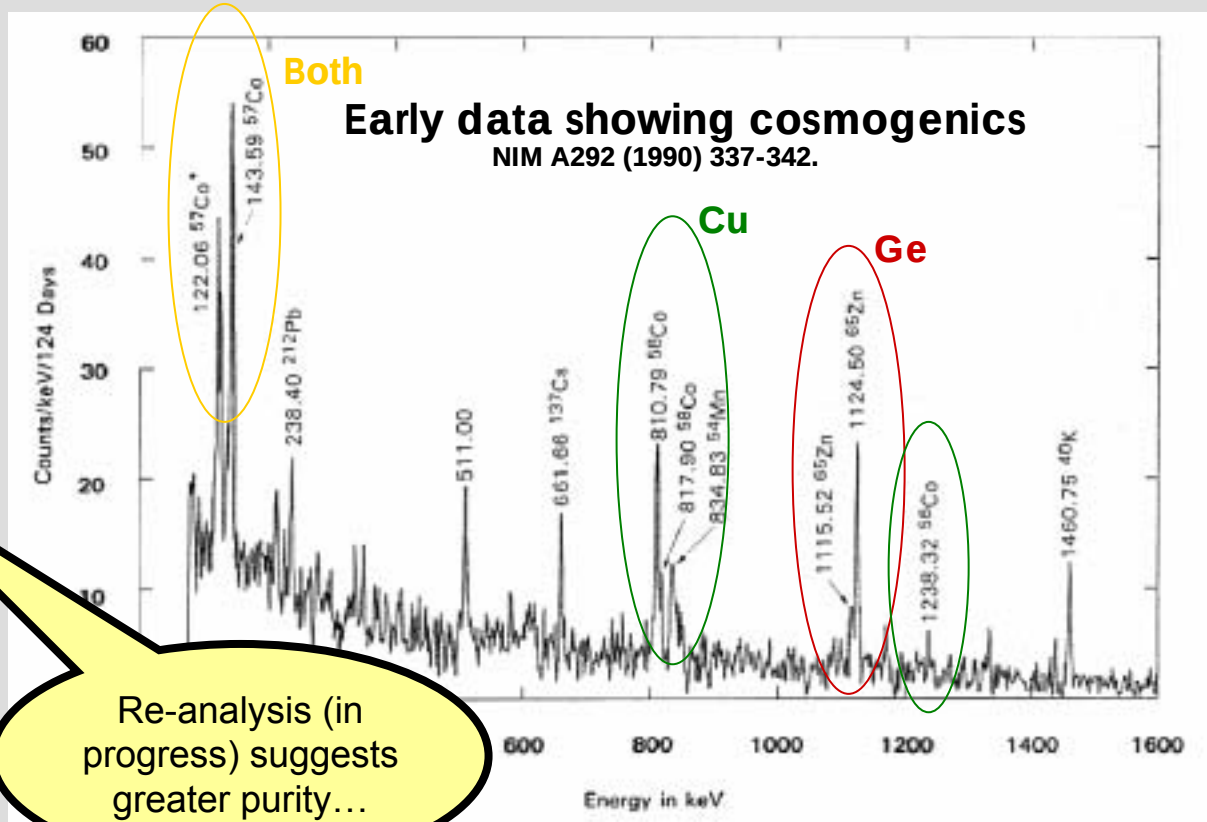
^{226}Ra	**<25 μBq/kg**
^{228}Th	**9 μBq/kg**

(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**

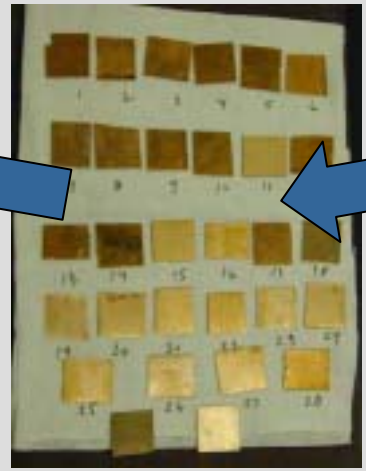
(M. Laubenstein et al, Applied Radiation and Isotopes, 61 (2004) 167-172)

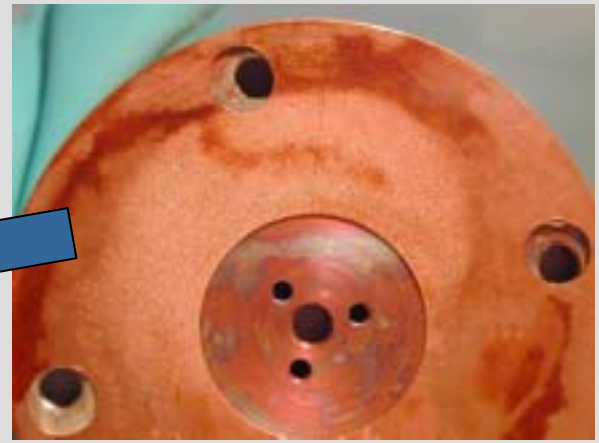


Re-analysis (in progress) suggests greater purity…

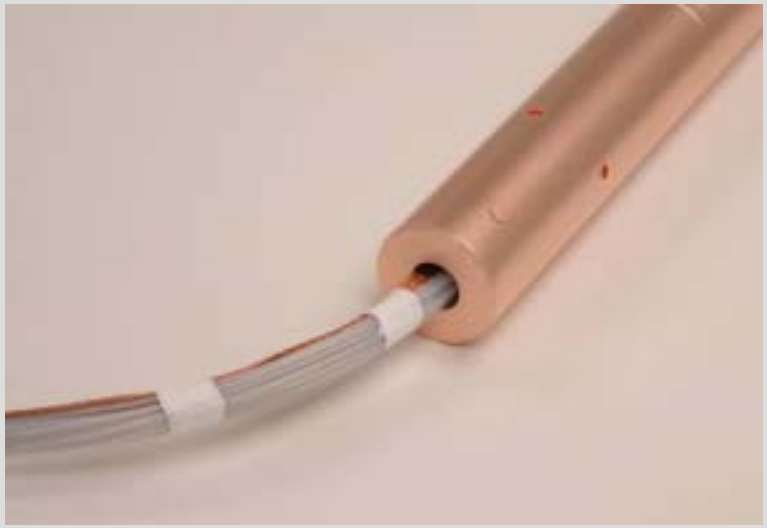
Electroformed Copper Surface Cleaning & Passivation

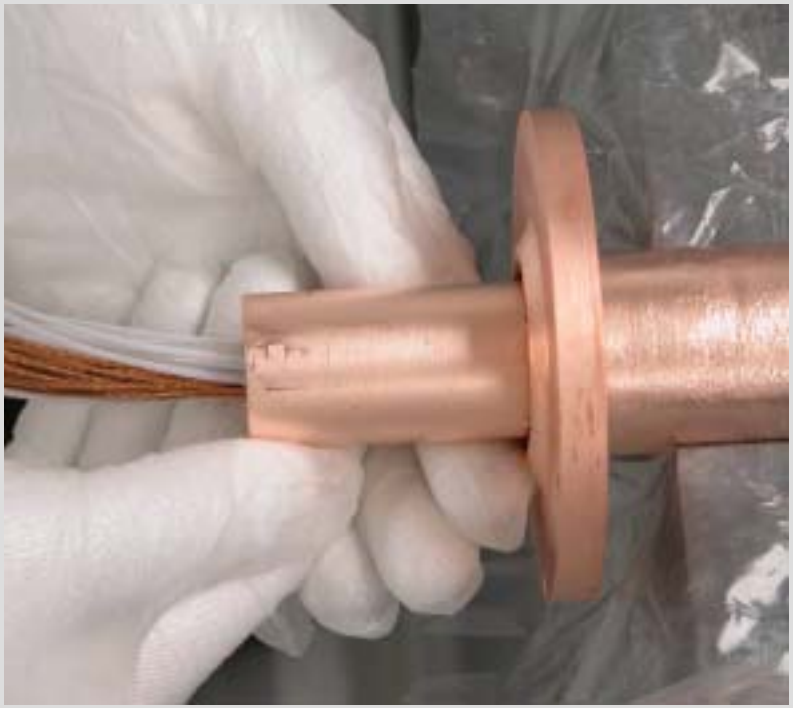
- Goal was to find copper cleaning process to replace destructive nitric acid etch
- Surface passivation was also desired
- Experiments inspired by CUORE conversations
- Tested several oxide removal methods
- Tested ~30 passivation chemistries
- H_2O_2-based cleaning & citric acid passivation were final result





Examples from MEGA Detector





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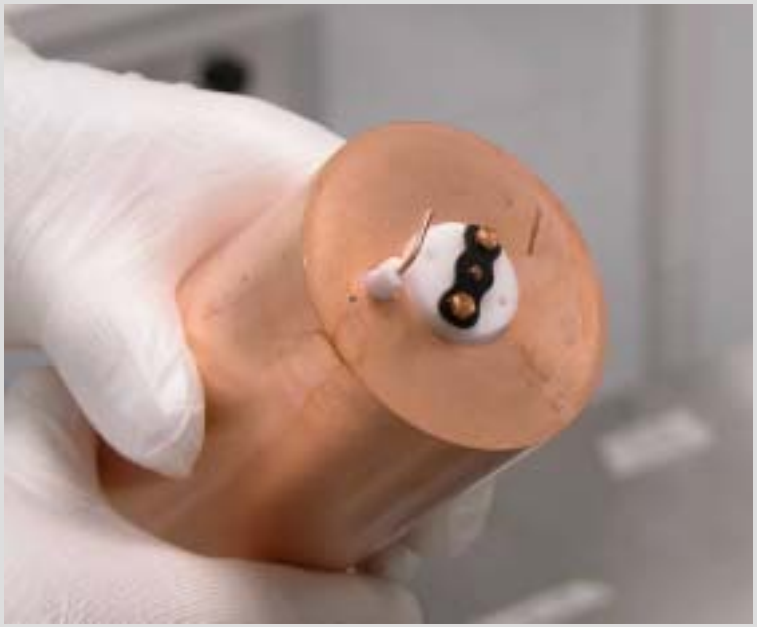
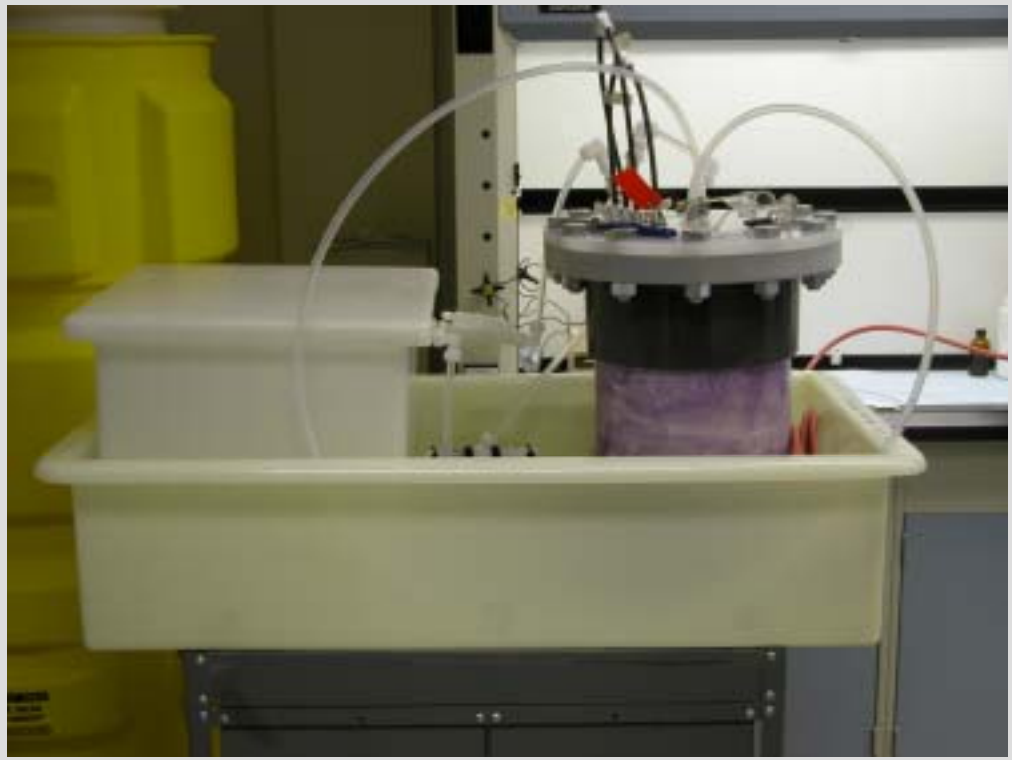


Electroforming R&D is Ongoing

LANL-PNNL Underground Cu Experiment

- Equipment underground at WIPP
- LANL, Majorana team will operate
- Will demonstrate cosmogenic suppression



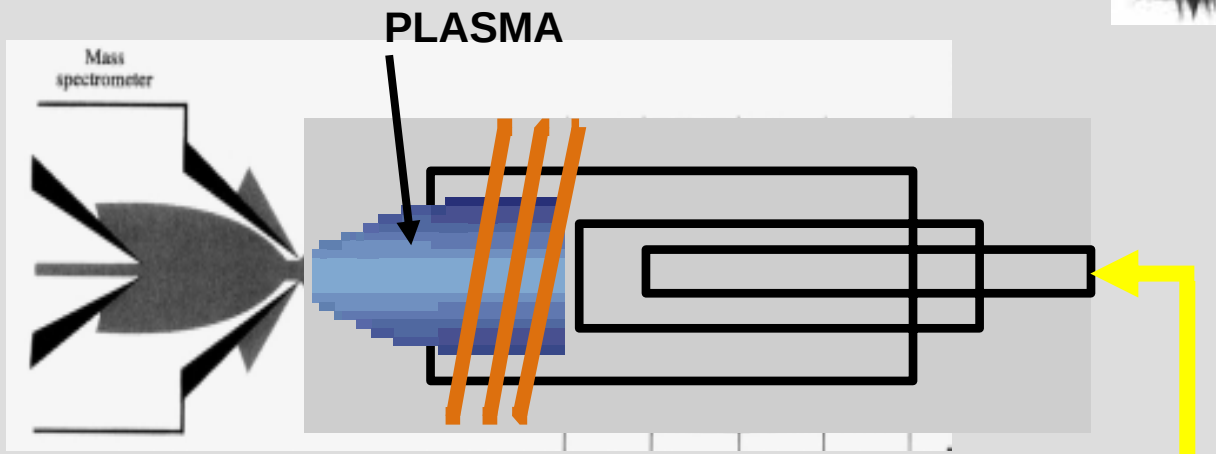
ICPMS Copper Purity Assay

Motivation

- Direct radiometric methods require large sample mass (~10 kg), long count time (~3 months), have reached limit
- Producing material for next-generation detector (Majorana) will require careful QA of even small parts
- Inductively-Coupled Plasma – Mass Spectrometry (ICP-MS) has good potential for reaching radiopurity goals

Basic ICP/MS

mass spectrometer
Quadrupole

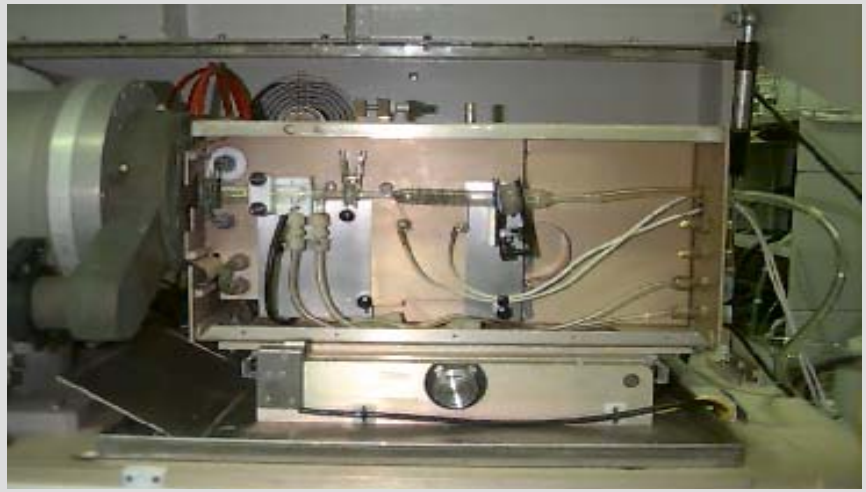


ion detection
EM
FC
Daly
ASAT

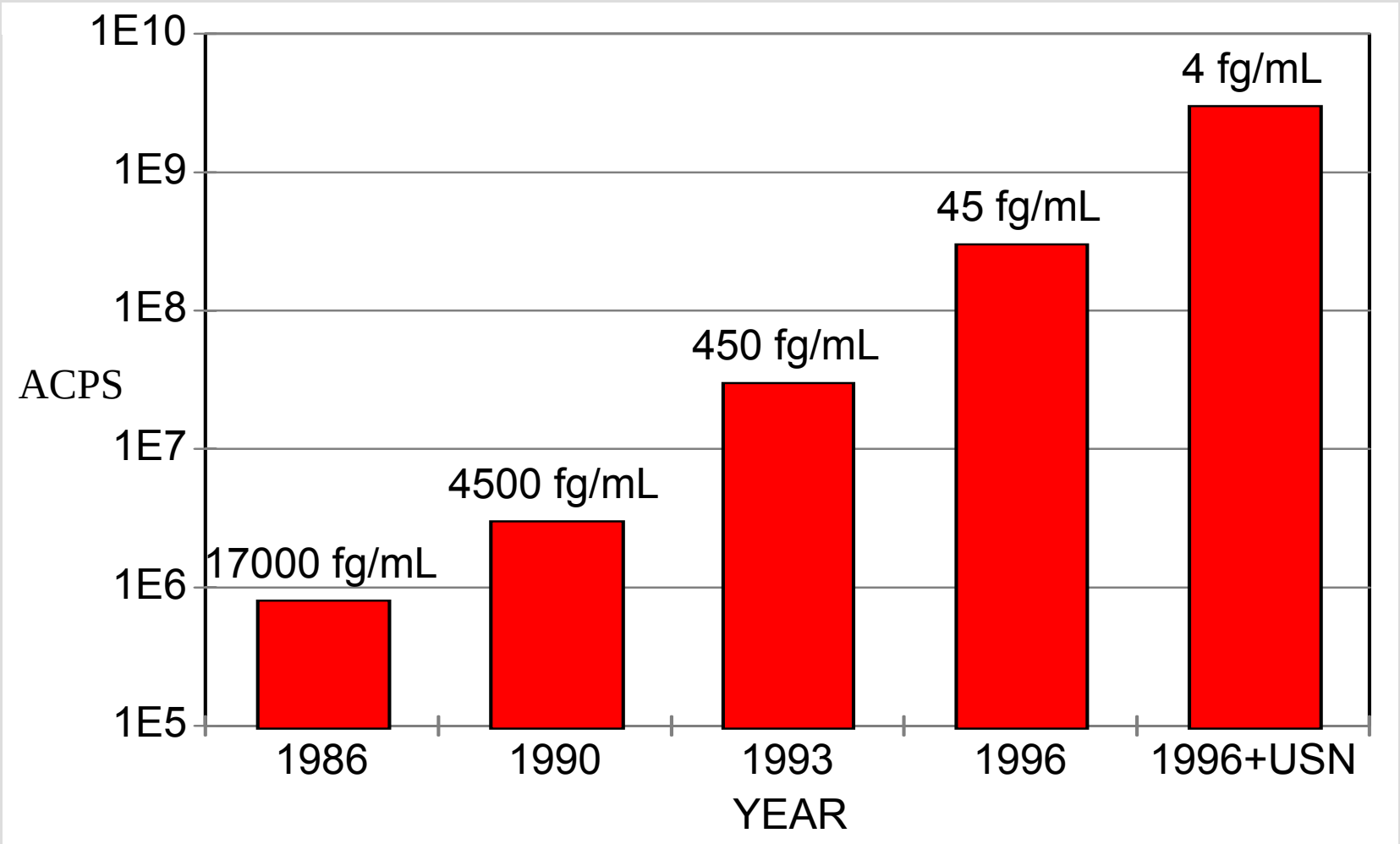
sample & aerosols:
liquid
gases
solids

PNNL ICP/MS Equipment

Sample Introduction Methodologies



DETECTION IMPROVEMENT IN ICP/MS



ICP-MS DETECTION RANGES

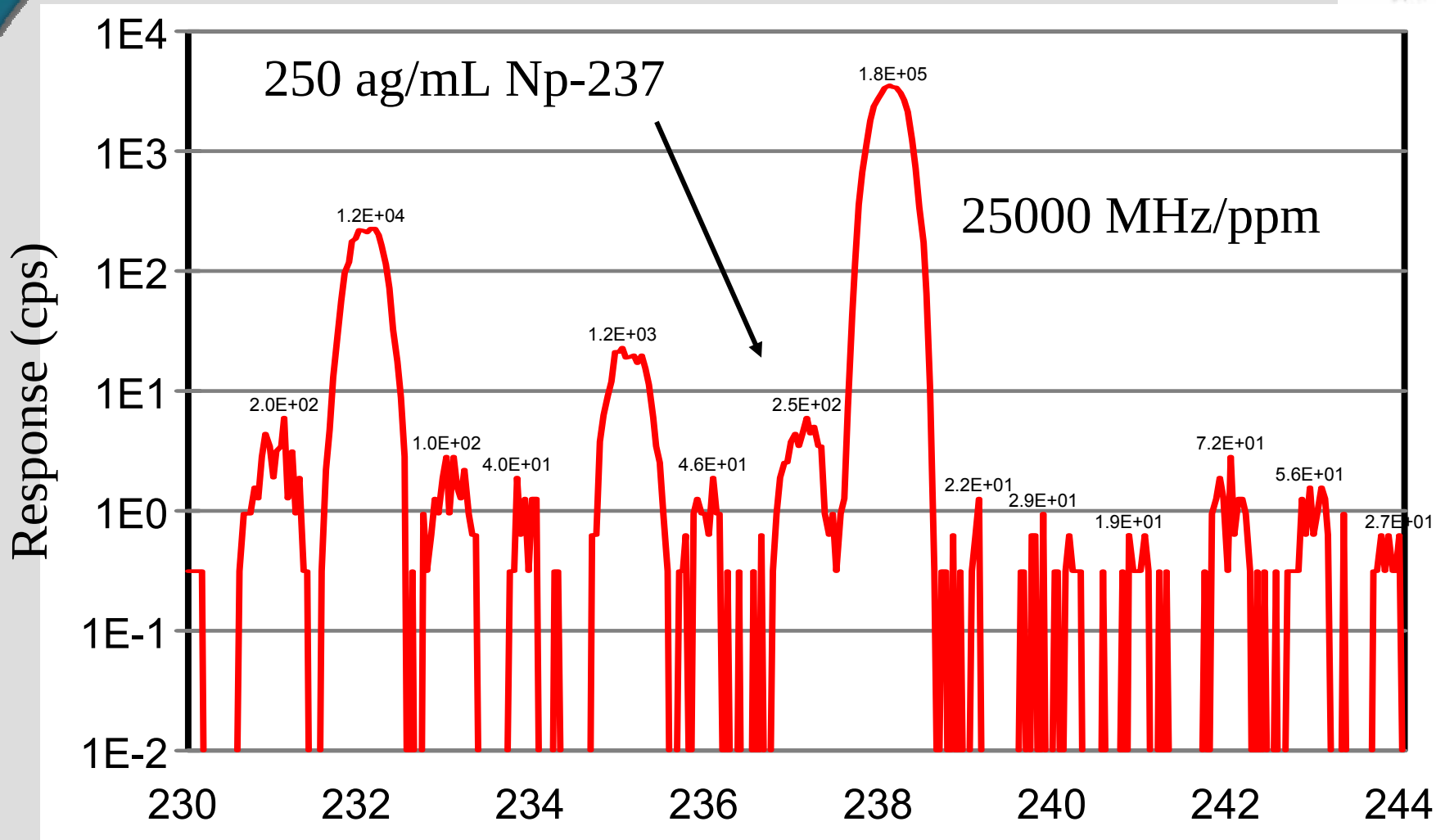
Aqueous Standards

WEIGHT	PREFIX	^{238}U ATOMS/ml
10^{-3} (ppt)	Milli	2.53×10^{18}
10^{-6} (ppm)	Micro	2.53×10^{15}
10^{-9} (ppb)	Nano	2.53×10^{12}
10^{-12} (ppt)	Pico	2.53×10^{9}
10^{-15} (ppq)	Femto	2.53×10^{6}
10^{-18} (pp?)	Atto	2530
10^{-21} (pp??)	Zepto	2.53
10^{-24} (pp???)	Guaca	0.00253

NORMAL ICP-MS RANGE

THIS WORK

Direct Atto-gram/mL Detection

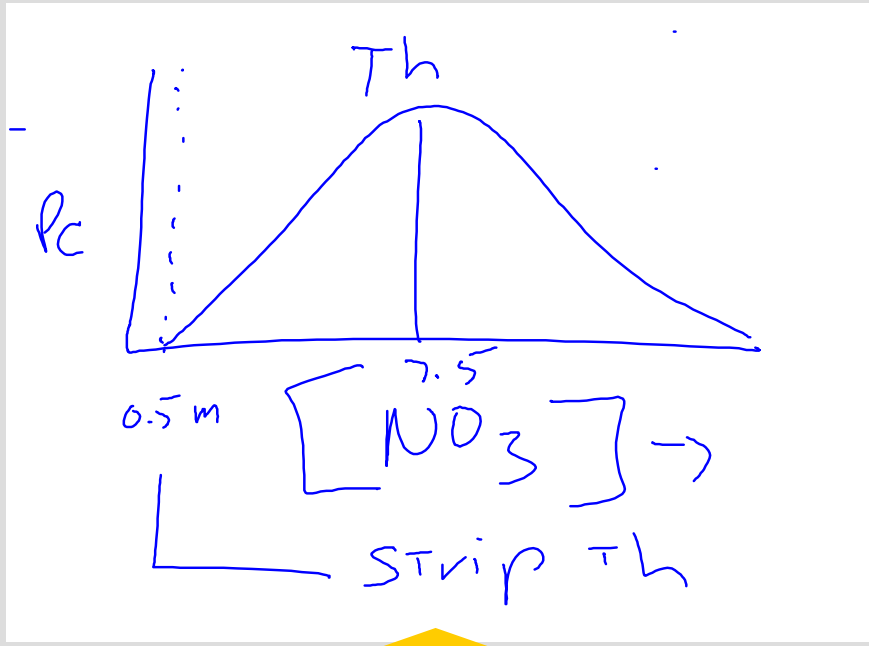


Copper Sample Preparation

- Nominal 1g copper sample is placed in 75ml clear Teflon bottle
- 20ml 7.5M HNO_3 (<0.05pg/ml) is added
- Tracer (^{229}Th or ^{230}Th) is added at about 10% of expected ^{232}Th value
- Gentle heat is applied until dissolution is complete
- Copper goes to +2 state

Thorium Separation

- Column is 200-400 mesh anion resin
- Column is first washed with H_2O
- Column is conditioned with 7.5M HNO_3
- Sample is loaded (20 ml 7.5M HNO_3)
- Wash copper from column void volume (7.5M HNO_3)
- Elute (strip) thorium with 0.5M HNO_3
  - Elute in 3 ml directly to MS



chemist explains to me how this works on my whiteboard…

ICP-MS Instrument

- Condition instrument with 0.5M HNO_3 until stable background is achieved
- Switch in eluent (also 0.5M HNO_3) and wait for signal to stabilize
- Measure (integrate) mass response during eluent ionization
  - Typically ~6 integration periods of 30 seconds each
  - Provides 10 seconds on each of three mass peaks (230.0, 230.5, 232.0) for each integration period

Data Reduction

- Subtract instrument background from eluent signal
  - This is from 0.5M HNO_3 reagent and is small
- Subtract process blank from eluent signal
  - This is from an eluent blank prepared without copper and is larger
- Quote result (pg/g) based on tracer
- Convert to μBq/kg equivalent ^{232}Th (4x multiplier)

First Copper Result

- Two 1-g samples of MEGA inner-can copper were analyzed
- Sample #1 (0.882 g)
  - The process blank was 6.0±0.3 pg/g
  - The sample yielded a value of
    - 7.3±0.7 pg/g (gross)
    - or 1.2±0.8 pg/g (net)
  - This is a net ^{232}Th activity of 4.9±2.9 μBq/kg
- Sample #1 (0.936 g)
  - The process blank was 5.7±0.3 pg/g
  - The sample yielded a value of
    - 7.0±0.6 pg/g (gross)
    - or 1.3±0.7 pg/g (net)
  - This is a net ^{232}Th activity of 5.2±2.8 μBq/kg

Cu ICP-MS Next Steps

- Sensitivity
  - Preliminary result appears to be first positive indication of Th in Cu
  - Anion column cleanup of 7.5M HNO_3 planned
  - Sub-boiling distillation to further clean HNO_3 if necessary
  - Instrument background now 6x lower
- Documentation
  - Process will eventually transition into “service center” activity
  - Will benefit from QA, standardized reporting
- Priority
  - Repeat process blanks
  - Repeat and extend copper measurements (starting stock, other Cu)
  - Test reagent cleanup chemistry

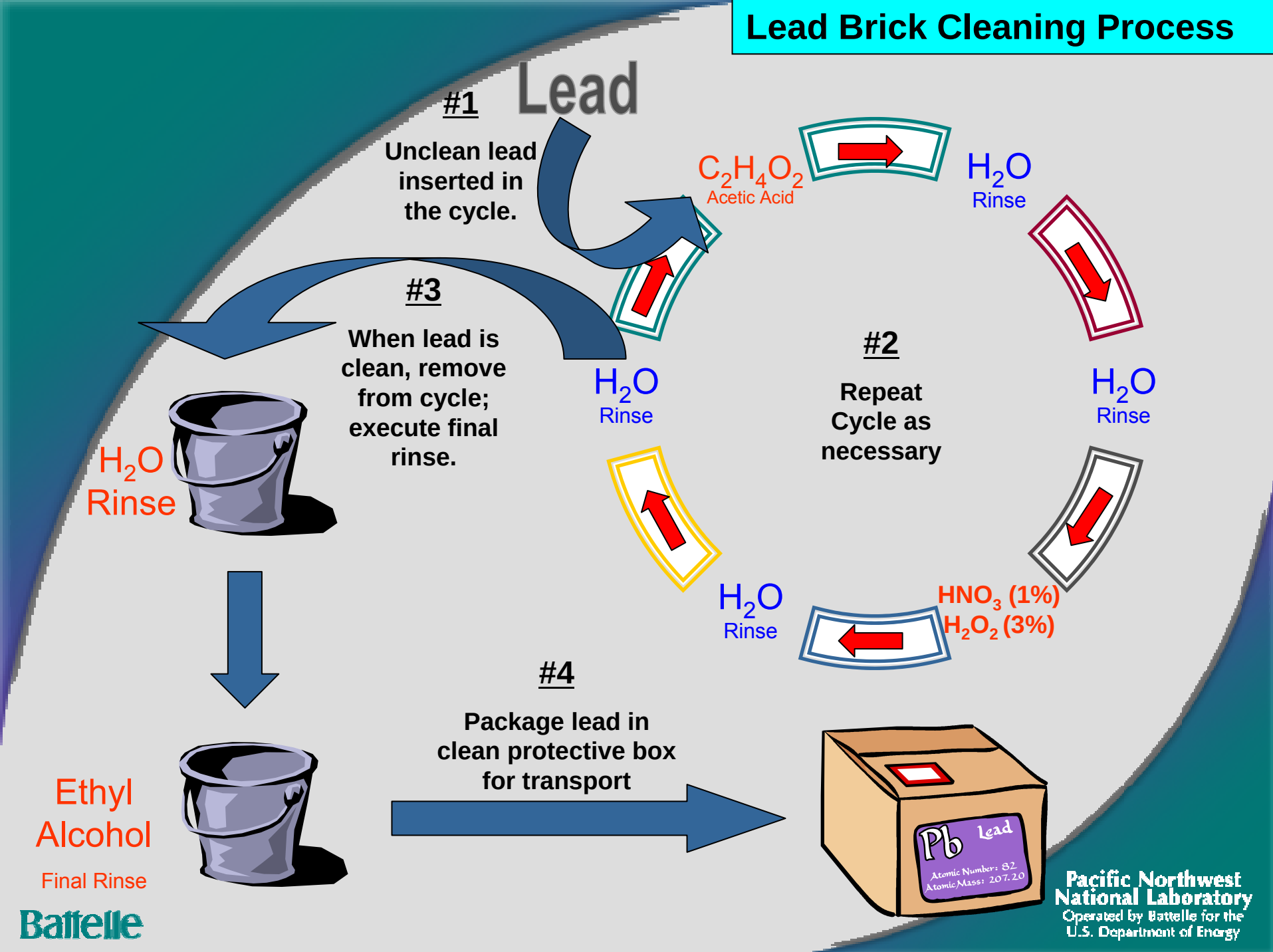
Pb Cleaning

- Ancient lead is desired to avoid ^{210}Pb backgrounds, present in all modern lead
- Materials are usually recovered needing extensive surface cleaning
- Even new lead may need oxide removal for safety reasons

"Spanish" Lead~1542

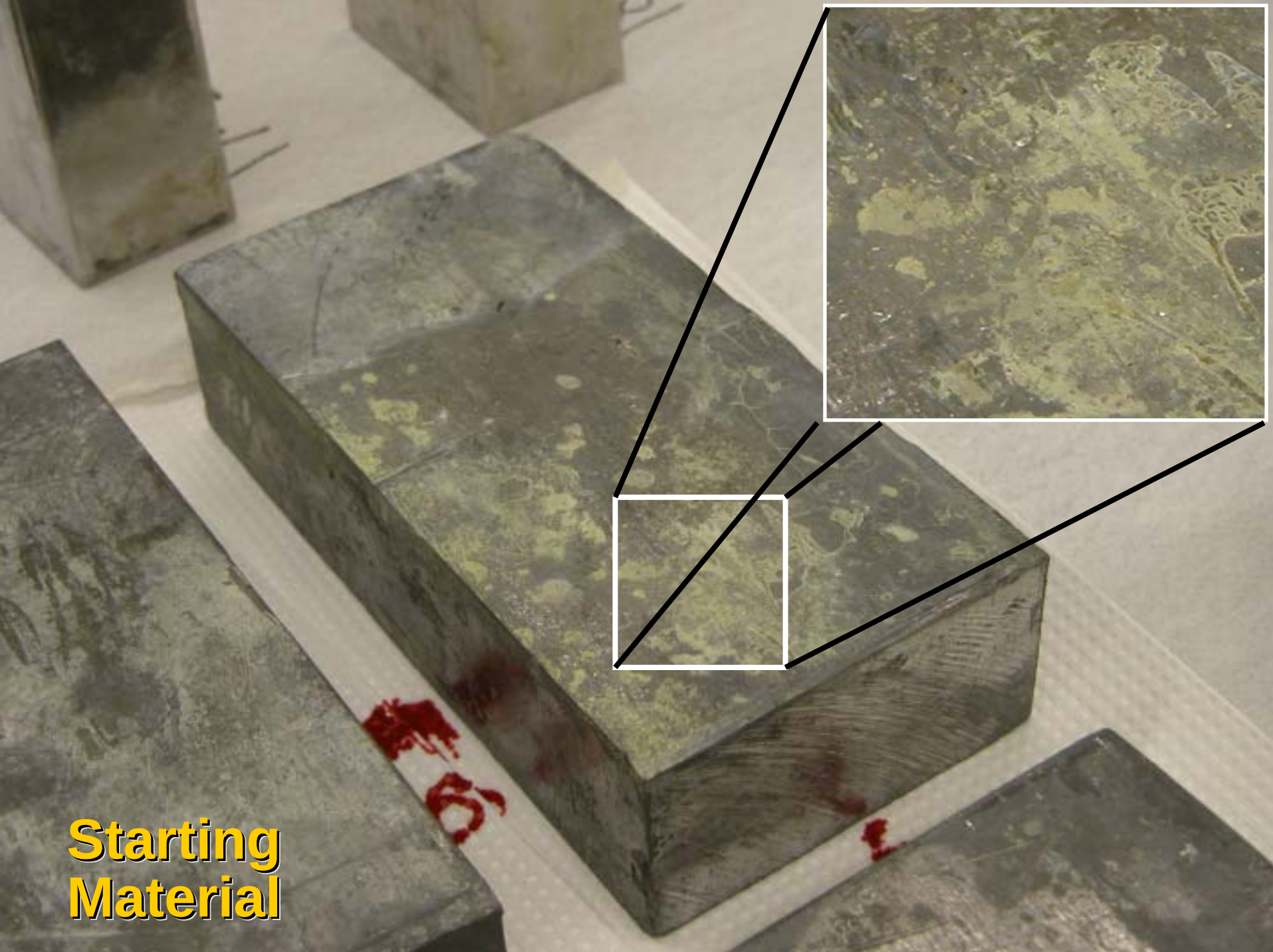
"New" Lead ~1950 to ~1980

Lead Brick Cleaning Process



Battelle

Pacific Northwest National Laboratory
Operated by Battelle for the U.S. Department of Energy


Starting
Material

Acetate Formation

Acetate Removal

Final Result

Summary

- Ultra-Low-Background Electroformed copper is an established technology, improvements continue
- R&D to reach Majorana assay targets underway
  - ICP-MS expected to reach Majorana target sensitivity for ^{232}Th in copper
  - Surface α, β assay for Pb and Cu are planned
- Underground electroforming R&D in progress in two underground locations
  - Soudan (SBIR partner Jim Reeves)
  - WIPP (LANL Majorana team, Steve Elliott, et al.)
- Surface preparation chemistry being developed for lead

Acknowledgements

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