Evaluation of Ultra-Low Background Materials for U and Th using ICP-MS

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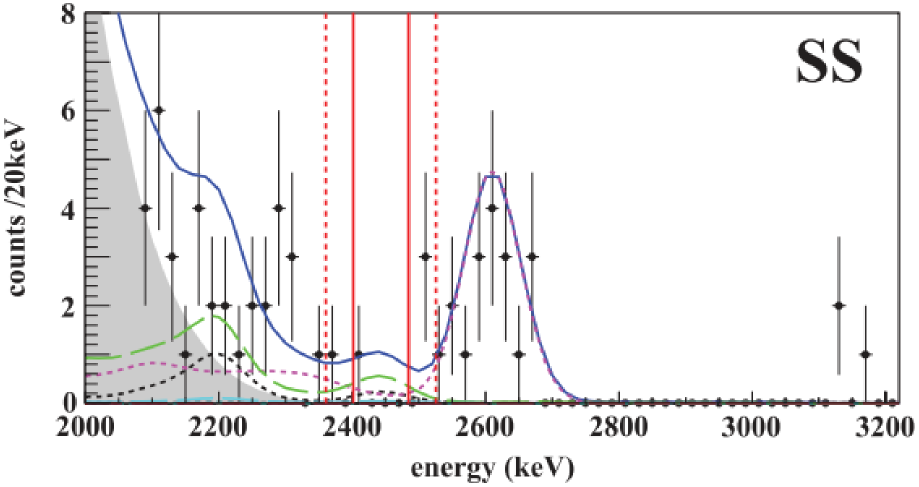
Outline

- Examples of assay need
- Material assay challenges
- Assay of copper using ICP-MS
- Assay of polymers
- Assay of fused silica
- General low background assay requirements
- Conclusions

Examples of Assay Need

- EXO – 200 kg liquid Xe TPC
  - Require <20 events per year from radioactive contamination in the signal region of 2420-2500 keV
- Started a comprehensive assay program to qualify materials
  - Followed with a screening program to confirm materials

M. Auger et al., PRL 109, 032505 (2012)



Examples of Assay Need

- Variety of techniques used to measure U, Th, K contamination (D.S. Leonard et al., NIM A591, 490 (2008) for a table of 225 samples)
  - Low-background Ge
  - Neutron activation analysis
  - Mass spectrometry
- Worked with industry (Applied Plastics Technology) to develop clean plastics through the DOE-SBIR program
- Met their goal, first results showed 5 events in the signal region in 120 days

Examples of Assay Need:

The MAJORANA DEMONSTRATOR Background Budget

Material	Part of DEMONSTRATOR	Decay Chain	Purity Goals		Achieved Assay	
			[µBq/kg]	[c/ROI/t/y]	[µBq/kg]	[c/ROI/t/y]
EFCu	Inner Cu Shield, Cryostat, Coldplate, Thermal Shield, Detector Mounts	Th	0.3	0.76	0.7 ± 0.3	1.8 ± 0.7
		U	0.3	0.12	<1.3	<0.52
OFHC	Outer Copper Shield	Th	0.9	0.19	<9.7	<1.9
		U	3	0.10	<36	<1.2
Pb	Lead Shield	Th	3	0.13	<140	<6.2
		U	10	0.06	<370	<2.3
PTFE	Detector Supports	Th	0.1	≤0.01	0.1 ± 0.01	≤0.01
		U	5	0.01	<5	<0.01
PEEK	Cross Arm Support	Th	1600	<0.01	<1600	<0.01
		U	63000	<0.01	<63000	<0.01
Vespel	Cold Plate Support	Th	12	<0.01	<12	<0.01
		U	1000	<0.01	<1000	<0.01
Parylene	Cu Coating, Cryostat Seals	Th	200	0.01	3800	0.16
		U	370	<0.01	4400	0.05
Silica / Au, Epoxy	Front-End Electronics	Th	4000	0.10	<4000	<0.10
		U	2300	0.09	<2300	<0.09
Cu Wire + PFA	Signal /HV Cable and Connectors	Th	350	0.14	<1200	<0.48
		U	500	0.08	<3700	<0.59
Stainless Steel	Service Body	Th	18000	<0.04	$(18 \pm 3) \times 10^3$	<0.04
		U	5000	<0.03	<5000	<0.03

(**MJD Final Design Report;** MAJORANA Collaboration [M-ADMDOCREVS-2012-048])

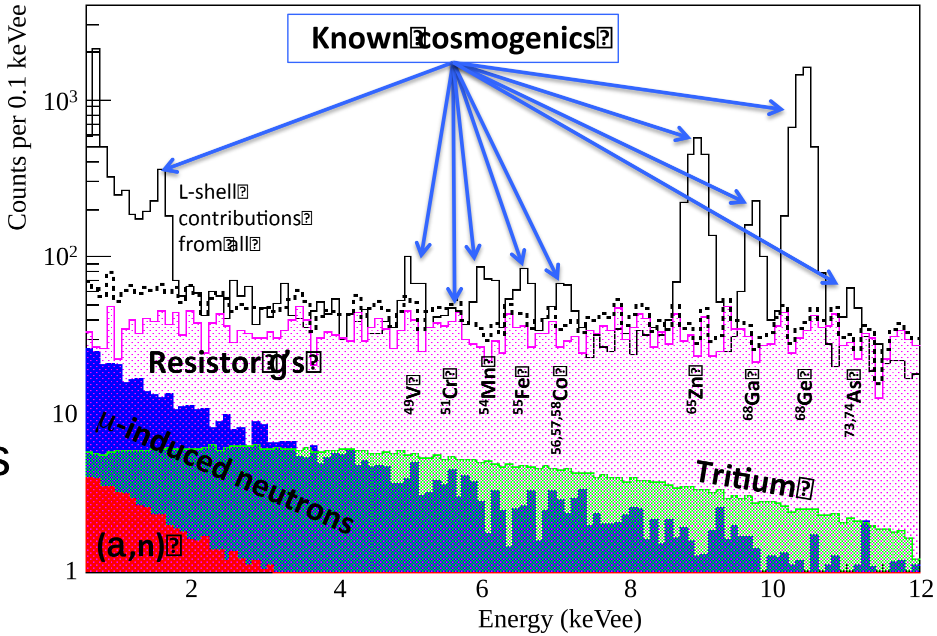
Examples of Assay Need

- Comprehensive background analysis in low energy region:

Source	Events in **CoGeNT** dataset (0.5 – 3 keVee)
Resistor backgrounds	~324
Muon induced events in shielding	339 +/- 68
Tritium b-decay	<150
Cavern neutrons from radioactivity	<54
U and Th backgrounds in copper	<9
External cavern neutrons (μ-induced)	<1.4
Old lead (^{210}Pb + daughters)	<0.6
Spontaneous fission neutrons in lead	<0.5
SF neutrons in HDPE	<0.2
HDPE (a,n)	<0.03
^{8}B solar neutrinos	<0.014

Examples of Assay Need

- Interplay between material assay results and analysis
  - Use assay results:
    - Input to design
    - Used to fix background model
  - Rapidly identify discrepancies
    - Only *un*-assayed materials are potential culprits…



Examples of Assay Need

- Searches for WIMP dark matter are currently pushing the state of the art in terms of neutrons from radioactivity
  - Currently detector limits of 0.01 event per kilogram of target matter per year
  - Long term goal is 0.1 event / ton / year, a 100 fold reduction of current backgrounds

Assay Performance Requirements

- Example Challenge: FET for use on front end board electronics must be < 1 mBq U or Th/kg. The FET mass is ~0.025 g and cost $11 each.
  - Option 1, purchase 250 g of FETs @ $110,000 and count for 4 months on a world leading radioassay detector

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  - Option 3, purchase 0.10 g of FETs @$44 and analyze by ICP-MS and results available in 30 days

    (requires dissolution and analysis, this could be done on a single FET and the analysis completed in a day if necessary)

Assay Performance Requirements

- Example Challenge: Evaluate purity of copper anode stock prior to use in electroforming

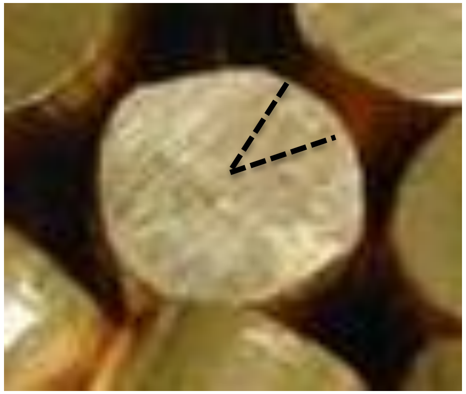
Sample: 24.23 kg OFHC Cu nuggets, 2009

GeMPI-2 at LNGS
(4 month count or 8 kg-yr):

- ^{40}K 190 ± 60 μBq/kg
- ^{232}Th (as ^{228}Th) 30 ± 10 μBq/kg
- ^{238}U (as ^{226}Ra) 20 ± 10 μBq/kg

(many thanks to M. Laubenstein)

Sample 0.01 kg OFHC Cu nugget, 2009



ICP-MS at PNNL
(1 week):

- ^{40}K <500 μBq/kg
- ^{232}Th 1.3 ± 0.6 μBq/kg
- ^{238}U <30 μBq/kg

Combined results provides most useful information:

- ^{40}K 190 ± 60 μBq/kg
- ^{232}Th 1.3 ± 0.6 μBq/kg
- ^{238}U 20 ± 10 μBq/kg

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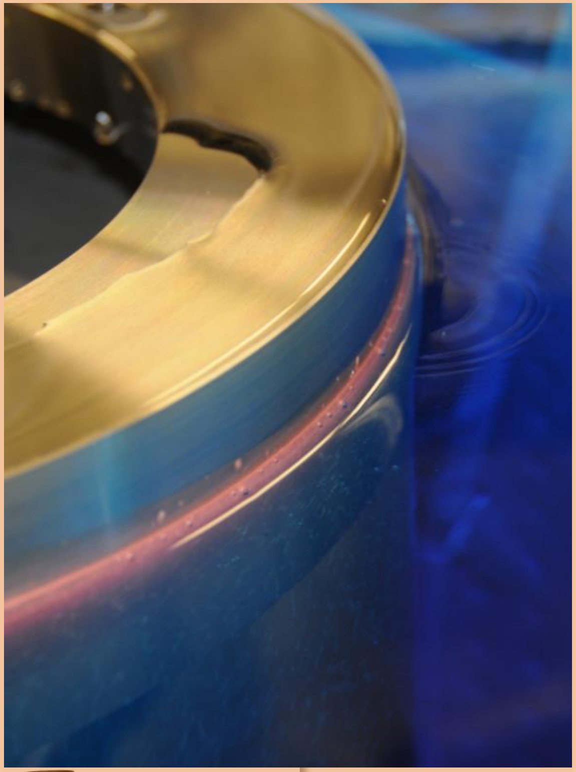
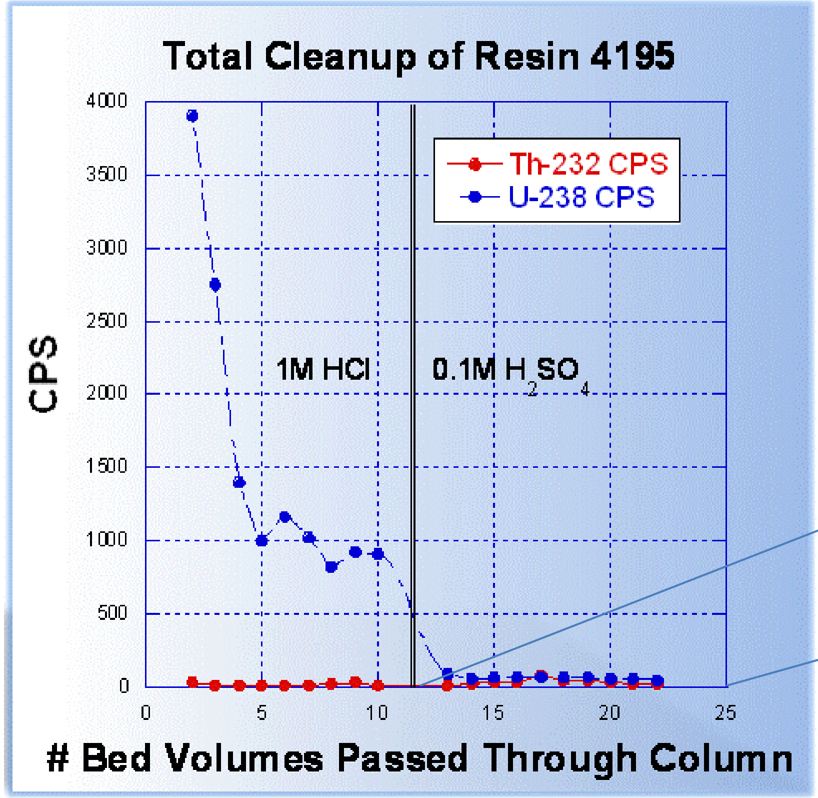
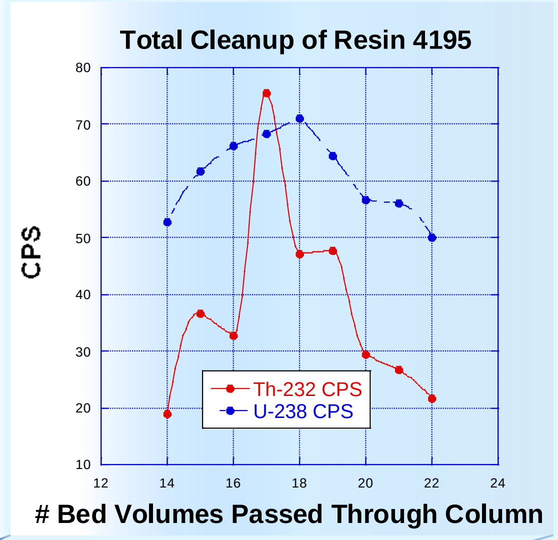
Assay of Cu for Th and U by ICP-MS

- Older ICP-MS lacked matrix tolerance (ion suppression) and sensitivity
  - Result of ~42 µBq ^{238}U/kg Cu (3.33 x 10^{-12} g ^{238}U/g Cu) by ICP-MS in 2005 by dilution only, no ion exchange
  - Ion exchange blanks were too high to be useful
- Purchased new ICP-MS 2009
  - Installed in class 1000 cleanroom
  - Greater matrix tolerance
  - Dedicated to low-background measurements only
  - Quickly obtained result of ~30 µBq ^{238}U/kg Cu (2.4 x 10^{-12} g ^{238}U/g Cu) by ICP-MS in 2010 by dilution only



Extensive investigation of ion exchange resins for use in copper assay





Resin continues to give off U and Th

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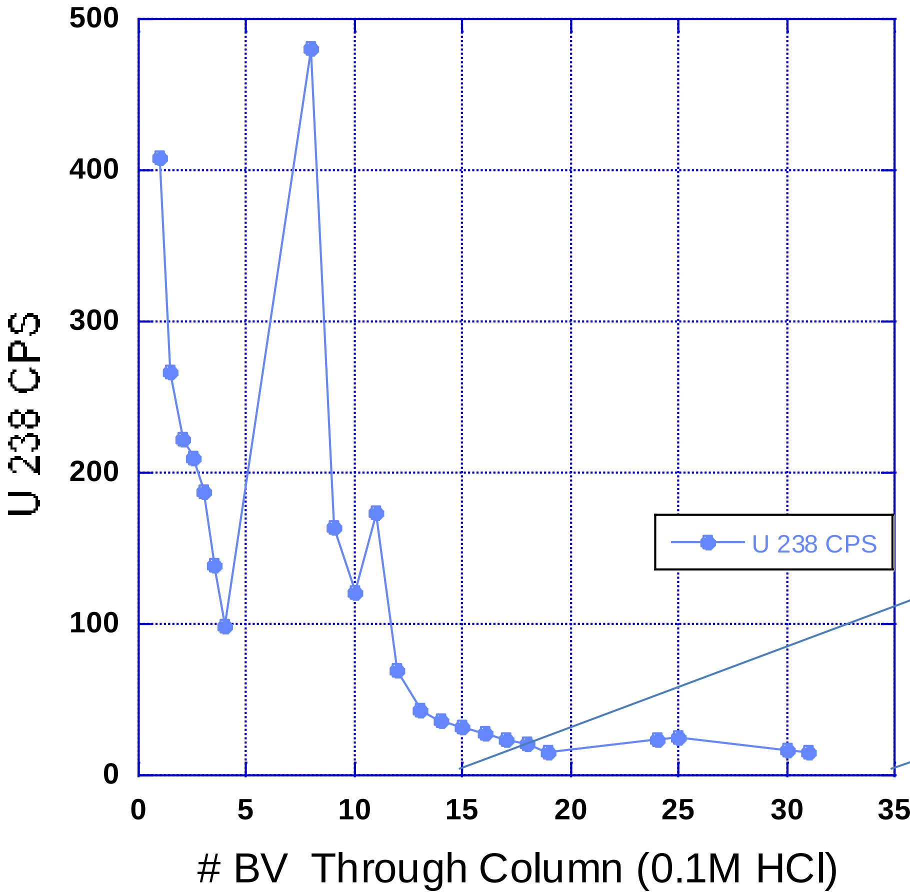

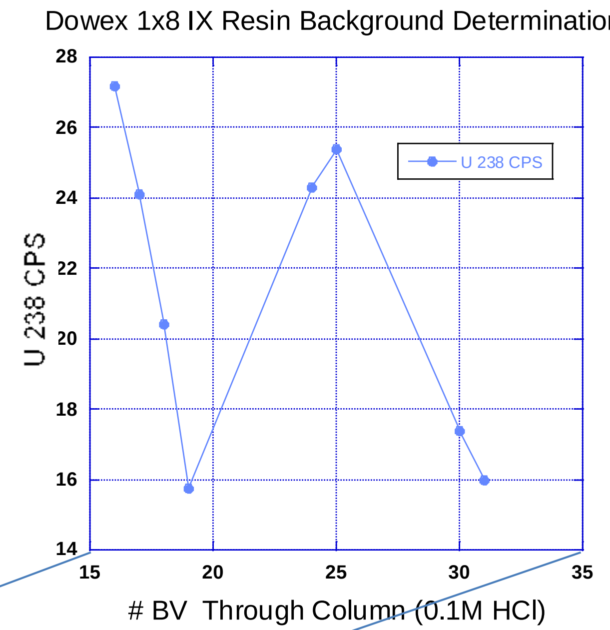

Resin continues to give off U and Th, seemingly forever!

Extensive investigation of ion exchange resins for use in copper assay

- Best Method Detection Limits (MDL) for Th and U in copper obtained by 2012 using ion exchange
  - 0.6 µBq ^{232}Th/kg Cu (0.15 x 10^{-12} g Th/g Cu)
  - 1.3 µBq ^{238}U/kg Cu (0.10 x 10^{-12} g U/g Cu)
- Estimated Quantitation Limit (EQL) is typically 3 -10 times the MDL
- Still short of Majorana goal of 0.3 µBq Th and U/kg Cu (EQL) by a factor of 6 to 43

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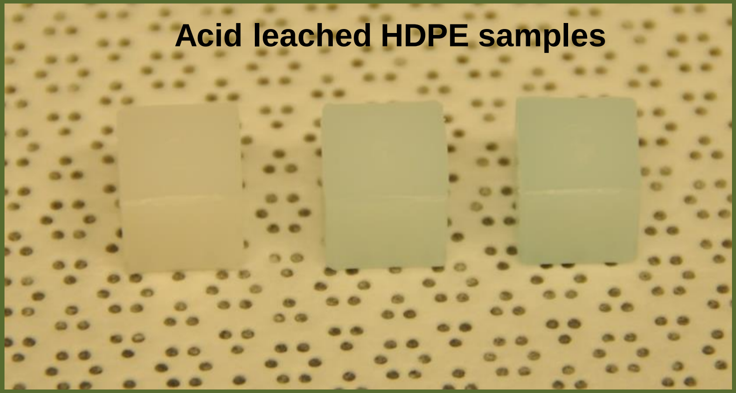
Challenge

Measure trace inorganic compounds in polymer matrices to determine suitability for use "as-is" and, if not, to study contaminant pathways into polymers used within ultra-low background detectors



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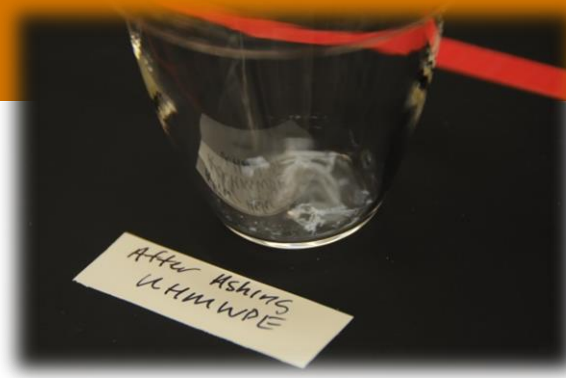
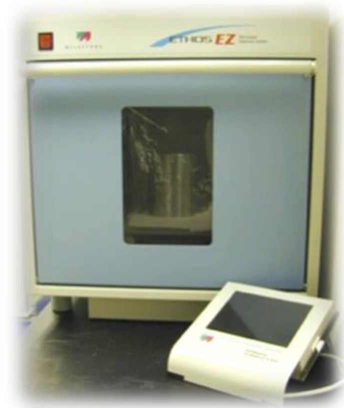
Polymer Analysis

- Developed an assay technique to measure trace inorganic compounds in polymer matrices
- Combined digestion methodologies as needed to create an acid soluble residue from the polymer
- Utilized ICP-MS capabilities to perform analysis on the resulting residue for Th and U with detection limits <µBq/kg





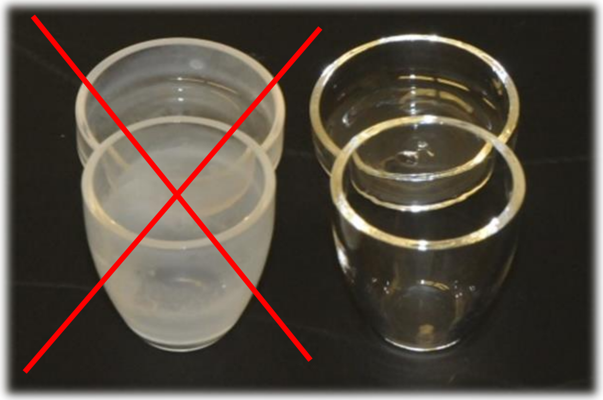
(Overman NR, et. al. 2012. "Surface Cleaning Techniques: Ultra-Trace ICP-MS Sample Preparation and Assay of HDPE." Jrnl of Radioanalytical and Nuclear Chemistry. doi:10.1007/s10967-012-2301-1)

Polymer Analysis

			µBq ^{232}Th/kg	µBq ^{238}U/kg
Vendor A	PEEK	Sample A	67	1689
		Sample B	67	4878
	UHMWPE	Sample A	22	5852
		Sample B	31	10489
		Sample C	61	6137
Vendor B	UHMWPE	Sample A	68	12266
		Sample B	163	19181
		Sample C	153	29093
	HDPE	Sample A	29	354
Detection Limit (based on 1-g sample)			0.4	1.2

Example results

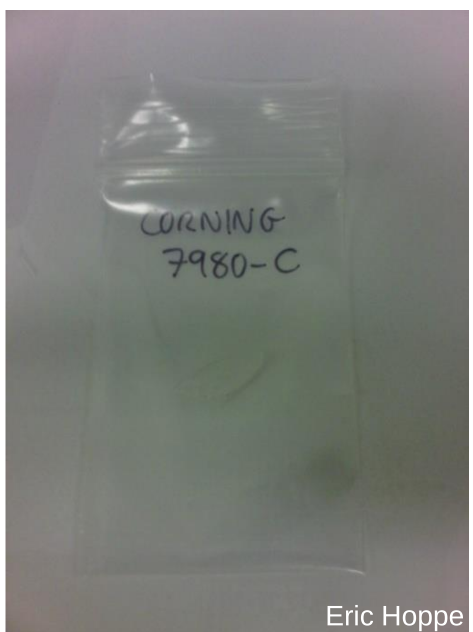
Larger sample size possible



Fluorinated polymer reacts with quartz surface during high temperature ashing, searching for more appropriate low background crucible material

Analysis of High Purity Fused Silica

- Samples not always received in ideal condition (applies to all sample types, in this case written on with a black marker)
- May also digest entire front end electronics board (FET, resistor, gold traces, etc. on fused silica wafer)
- Requires change-out of some ICP-MS components prior to HF use
- Assay detection limits for Th and U is µBq/kg, although materials not found that clean to date



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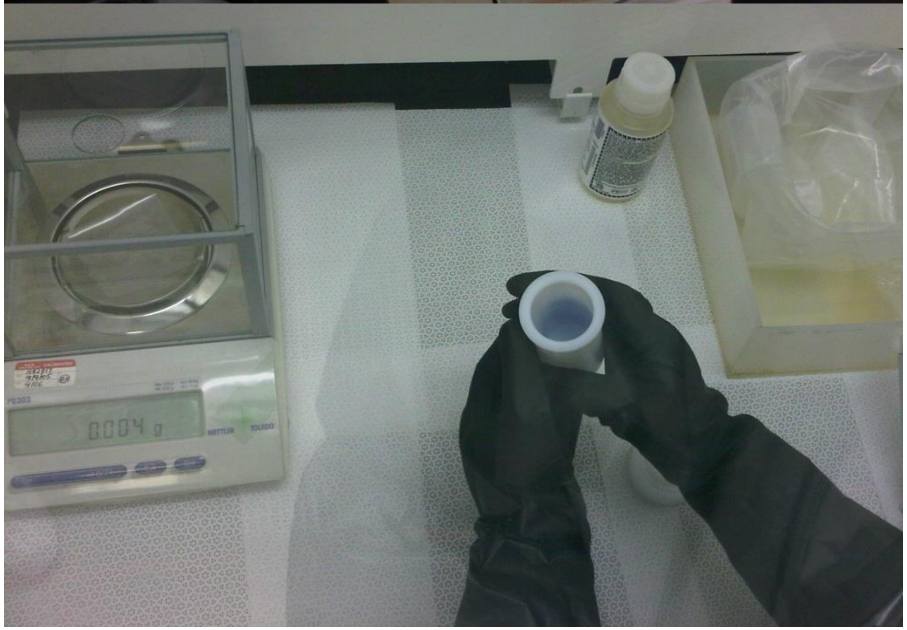

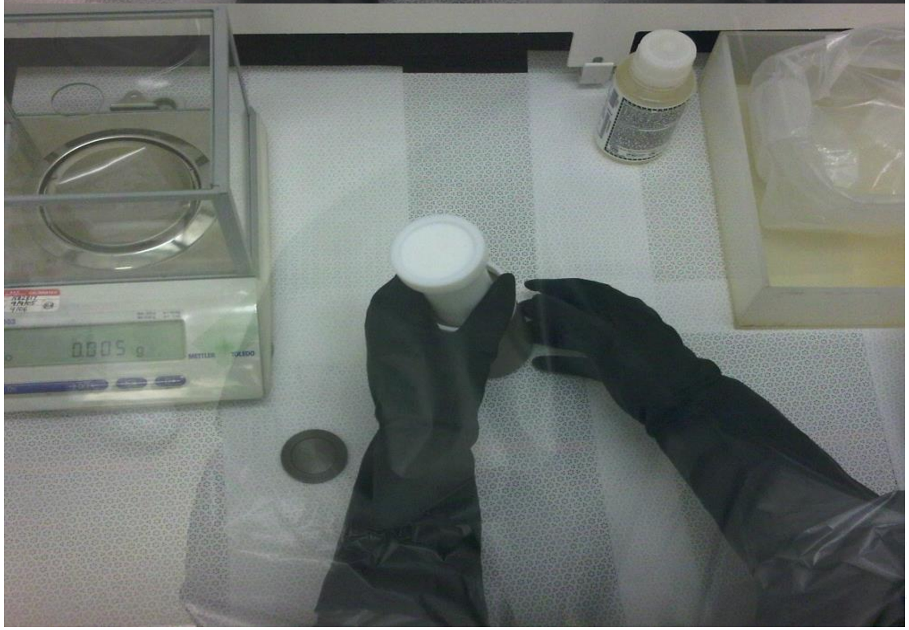

Fused Silica/Front End Electronics Board Analysis

	Fused Silica	μBq ^{232}Th/kg	μBq ^{238}U/kg
Vendor A	Sample A	1552	54780
Vendor B	Sample A	9653	85099
	Sample B	1233	56141
Vendor C	Sample A	802	22376
	Sample B	627	6362
	Sample C	413	3524
	Sample D	<345	6006
Detection limit		1	3
Entire front end electronics board		51237	342204

General sample preparation comments to keep backgrounds low

- Preparation in clean environment (cleanroom, glovebox, etc.) essential
- Must have well trained, meticulous individuals performing all steps of analysis
- All lab ware is leached thoroughly (Overman NR, et. al. 2012. "Surface Cleaning Techniques: Ultra-Trace ICP-MS Sample Preparation and Assay of HDPE." Journal of Radioanalytical and Nuclear Chemistry. doi:10.1007/s10967-012-2301-1)
- Lab ware is dedicated to low-background measurements
- Use of highest grade acids obtainable, even then additional distillation helpful

Conclusions

- ICP-MS increasingly becoming analytical tool of choice for low activity radionuclides, low background materials characterization
  - Sample preparation methods for low-background materials analysis improving
  - Low blank levels continue to be difficult to obtain
  - Broad spectrum analysis (similar to gamma assay) is preferred but not usually performed using ICP-MS (such as by employing highly selective ion exchange preparation)
  - Analysis using ICP-MS demands meticulous sample preparation

Acknowledgements

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