Savannah River National Laboratory®

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We put science to work.™

Applications of Eichrom Resins to Savannah River Site Highly Radioactive Sample Matrices

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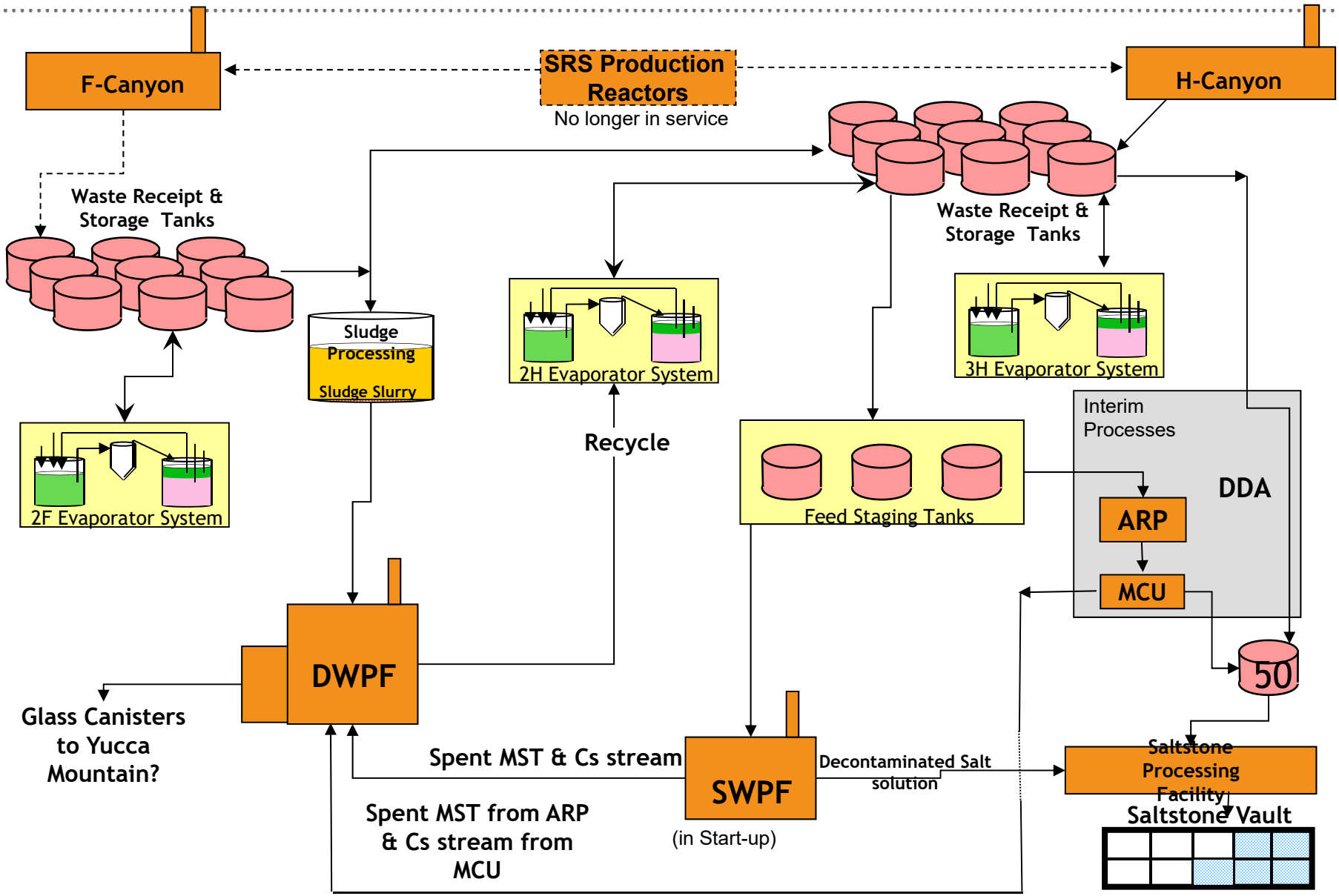
Nuclear Measurements Group/Analytical Development Section

Eichrom UGM RRMC 2019

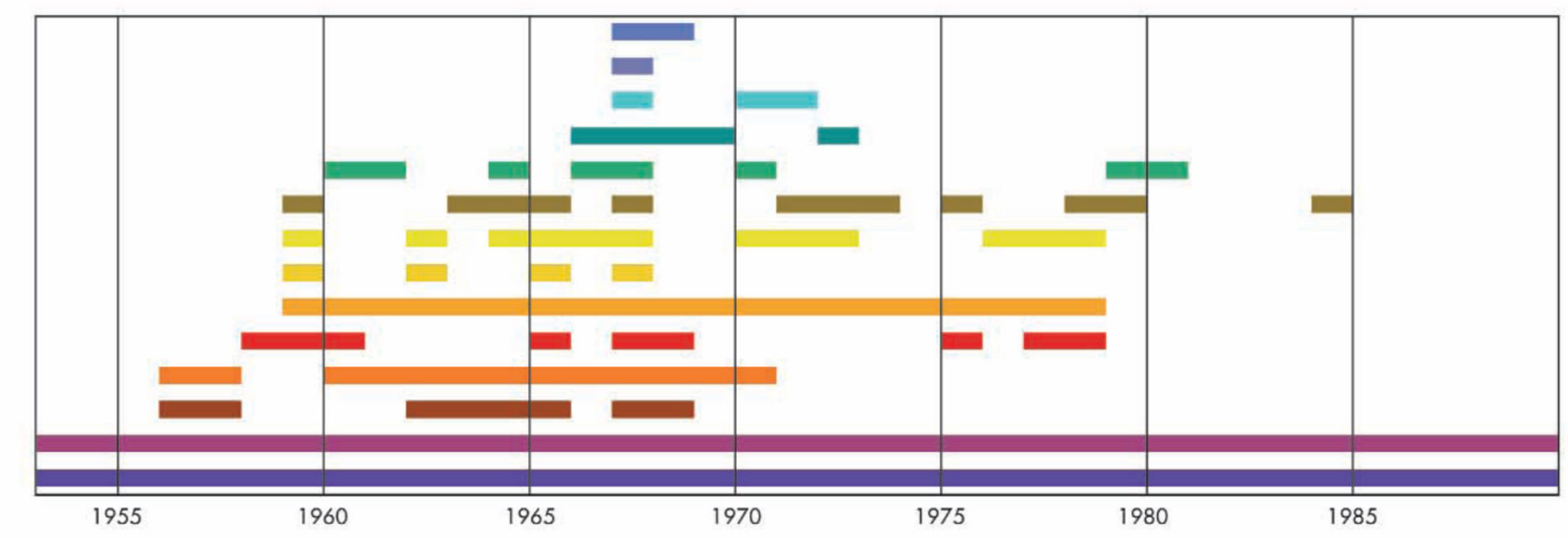
Savannah River NUCLEAR SOLUTIONS℠

FLUOR • NEWPORT NEWS NUCLEAR • HONEYWELL

Savannah River Site High Level Waste Flowsheet

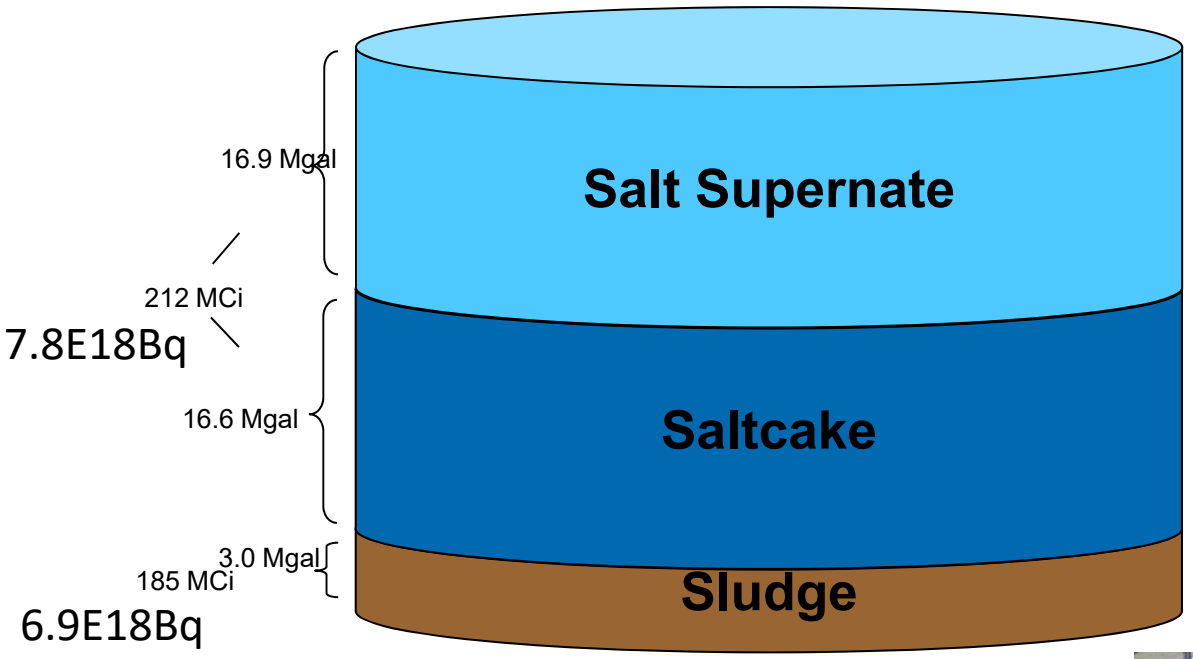


Radionuclides Produced at SRS



- thulium-170
- europium-152
- californium-252
- polonium-210
- special programs, other isotopes
- plutonium-242
- curium-244
- americium-243
- plutonium-238
- plutonium-240
- cobalt-60
- uranium-233
- tritium
- plutonium-239

F and H Tank Farms



Dominant chemical & radiological constituents

Sodium nitrate
Sodium nitrite
Sodium hydroxide
Sodium aluminate
Cs-137

Crystallized sodium nitrate
Cs-137

Metal (Fe, Mn, Al) oxides & hydroxides
Sr-90, actinides

Two tank farms

49 waste tanks

- **22 "old-style" tanks**
- **27 "new-style" tanks**

Approximately 37 million gallons of waste

Nuclear Measurements Group

STAFFING

4 PhD Nuclear Chemists 2 PhD Nuclear Engineers

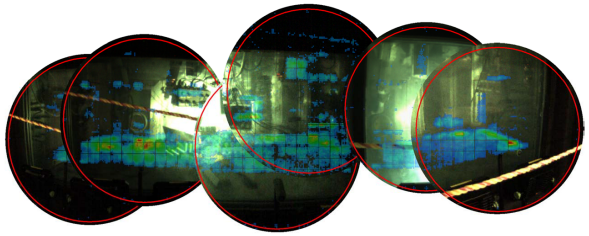
4 BS Chemists 1 BS Physicist

2 Specialists 1 Laboratory Technician

Customized Radiochemistry

H-3	C-14	Al-26	Cl-36	K-40	Ca-41	Ni-59	Co-60	Ni-63	Se-79	Rb-87
Sr-90	Y-90	Mo-93m	Nb-93m	Zr-93	Nb-94	Zr-95	Tc-99	Ru-103	Ru-106	Pd-107
Ag-108m	Ag-110m	Sn-121m	Sb-125	Te-125m	Sb-126	Sn-126	I-129	I-131	Ba-133	Cs-134
Cs-135	Ba-137m	Cs-137	Ba-140	Ce-141	Ce-144	Nd-147	Pm-147	Sm-151	Eu-152	Eu-154
Eu-155	Pt-193m	Bi-207	Tl-208	Bi-210	Pb-210	Pb-210	Po-210	Po-210	Bi-212	Pb-212
Po-212	Bi-214	Pb-214	Po-214	Po-216	Po-218	Rn-220	Rn-222	Ra-224	Ra-226	Ac-227
Ac-228	Ra-228	Th-228	Th-229	Th-230	Pa-231	Th-231	Th-232	U-232	U-233	Pa-234
Th-234	U-234	U-235	U-236	Np-237	Pu-238	U-238	Pu-239	Pu-240	Am-241	Pu-241
Am-242m	Cm-242	Pu-242	Am-243	Cm-243	Cm-244	Pu-244	Cm-245	Cm-246	Bk-247	Cm-247
		Cm-248	Bk-249	Cf-249	Cf-250	Cm-250	Cf-251	Cf-252		

Non-Destructive Assay



Gamma Imaging
Neutron Multiplicity Counting
Field Radiological Assays
Calorimetry

Instrument Development

University Collaborations

Energy Frontier Research Center

CENTER FOR HIERARCHICAL WASTEFORM MATERIALS
CHWM

Nuclear Measurements Group - Radiochemistry

H-3	C-14	Al-26	Cl-36	K-40	Ca-41	Ni-59	Co-60	Ni-63	Se-79	Rb-87
Sr-90	Y-90	Mo-93m	Nb-93m	Zr-93	Nb-94	Zr-95	Tc-99	Ru-103	Ru-106	Pd-107
Ag-108m	Ag-110m	Sn-121m	Sb-125	Te-125m	Sb-126	Sn-126	I-129	I-131	Ba-133	Cs-134
Cs-135	Ba-137m	Cs-137	Ba-140	Ce-141	Ce-144	Nd-147	Pm-147	Sm-151	Eu-152	Eu-154
Eu-155	Pt-193m	Bi-207	Tl-208	Bi-210	Pb-210	Pb-210	Po-210	Po-210	Bi-212	Pb-212
Po-212	Bi-214	Pb-214	Po-214	Po-216	Po-218	Rn-220	Rn-222	Ra-224	Ra-226	Ac-227
Ac-228	Ra-228	Th-228	Th-229	Th-230	Pa-231	Th-231	Th-232	U-232	U-233	Pa-234
Th-234	U-234	U-235	U-236	Np-237	Pu-238	U-238	Pu-239	Pu-240	Am-241	Pu-241
Am-242m	Cm-242	Pu-242	Am-243	Cm-243	Cm-244	Pu-244	Cm-245	Cm-246	Bk-247	Cm-247
		Cm-248	Bk-249	Cf-249	Cf-250	Cm-250	Cf-251	Cf-252		

- NMG develops customized radiochemical separations and analyses upon request
  - SRS conducted diverse radioisotope production campaigns,
    - The remnants of these programs remain scattered across SRS's waste tank farms, providing a constant radioanalytical challenges
  - Sample types range from
    - Various high activity waste matrices from SRS as well as other DOE Sites
    - forensic analyses i.e. FBI's NFAC samples, WIPP fire, INL drum explosion, PORTS Off-Site Contamination question,
    - environmental samples for which SRS's production environmental and off-site commercial laboratories cannot provide services
  - Particular expertise involves measuring trace radiological isotopes in the presence of 10 or more orders of magnitude of interfering isotopes
  - The Nuclear Measurements Group fills in the gap for any emergent radioanalytical request that production or commercial radioanalytical laboratories will not support

Radiochemistry Preparation Laboratories

- **5 Laboratory Modules**
  - 2 Chemical Hoods
  - 3 Gloveboxes
    - *Ability to work with up to 400 grams Plutonium*
  - 10 Radiological Hoods, 3 Radiobenches
    - *Routinely work with samples containing up to 1E+10 dpm (1.67E+8 Bq) alpha and beta*
    - *Routinely work with samples having up to 10 mRem/h (0.1 mSv/h) whole body dose @ 30cm*
    - *Routinely work with samples having up to 2000 mRem/h (20 mSv/h) contact dose*

- **SRNL Shielded Cells Facility utilized for initial separation steps of high-activity samples**

Nuclear Measurement Counting Instrumentation

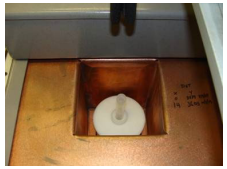
- 4 counting rooms contain nuclear measurement instrumentation
- In addition, the radiochemistry group leverages additional ADS instrumentation for radiochemical analyses
  - i.e. ICP-MS, ICP-AES

Beta Spectrometry - Triple, double, single PMT LSC counters, cosmic suppressed LSC, Portable beta spectrometers, conversion electron spectrometer, GFPCs, beta PIPS

Alpha Spectrometry
~100 alpha PIPS + portable alpha spectrometers

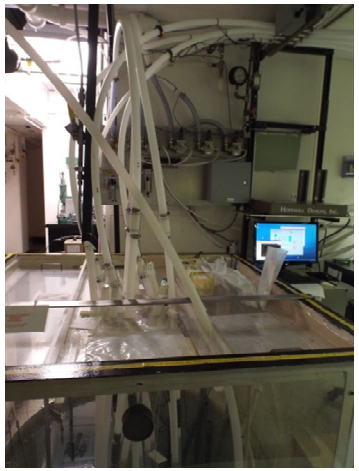
Gamma Spectrometry

- 15 shielded spectrometers ranging from planar to coaxial to well HPGe
- 4 automated systems
- Numerous field deployable x-ray and gamma-ray spectrophotometers
- Calibrations generated with NIST traceable standards, Canberra LABSOCS/ISOCS, or with Customized MCNP Models

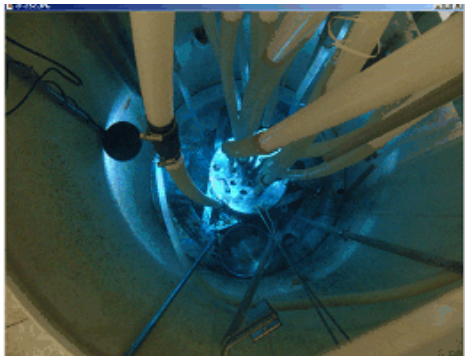


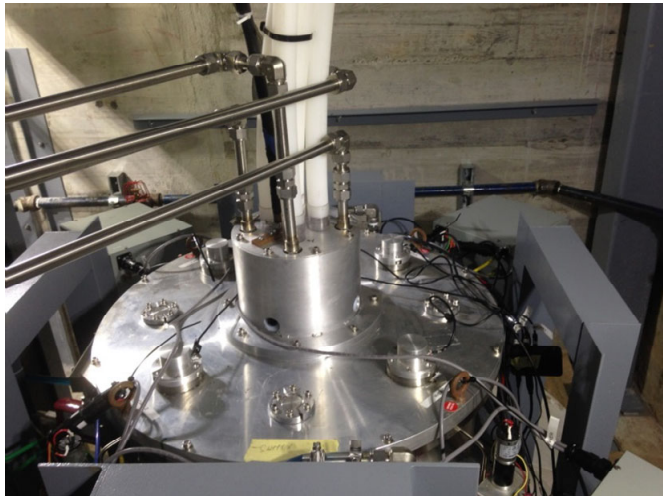
Neutron Activation Analysis Facilities

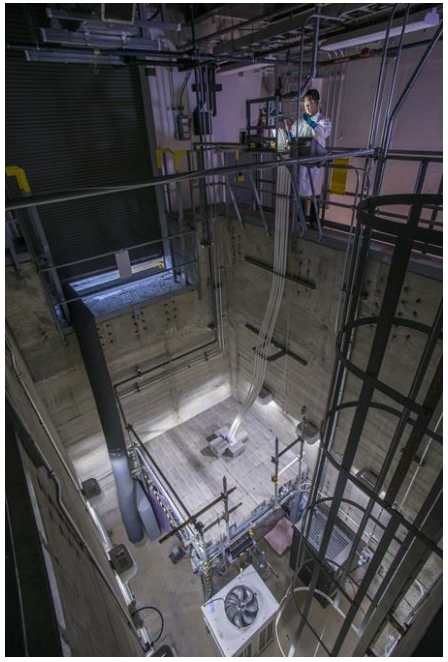
- Supports radiological tracer production (i.e. Tc-99m)
- Supports radiochemical separation tracer recovery measurements
  - Iodine, selenium, strontium, samarium



- ~2mg (decayed from ~60mg in 2003) Cf-252 generates ~1E7 n/s/cm^2 thermal neutron flux
- Pneumatic system allows for repeated irradiations
- System being replaced with an Adelphi D-D neutron generator with ~5E7 n/s/cm^2 thermal neutron flux







Tank Closure Campaigns

Pictures of 2 SRS Waste Tanks Following Mechanical Cleaning

H-3	C-14	Ni-59	Ni-63	Co-60	Se-79
Sr-90	Y-90	Tc-99	Sn-126	Sb-126	Cs-135
Cs-137	Ba-137m	Sm-151	Eu-152	Eu-154	Eu-155
Th-229	Th-230	U-232	U-233	U-234	U-235
U-236	U-238	Np-237	Pu-238	Pu-239	Pu-240
Pu-241	Pu-242	Pu-244	Am-241	Am-242m	Am-243
Cm-243	Cm-244	Cm-245	Cm-247	Cm-248	Cf-249
Pa-231	Ra-226	Pm-147	Ac-227	Al-26	Zr-93
Nb-94	I-129	Cl-36	K-40	Pd-107	Pt-193m

Tasked to conduct radiological characterizations on SRS Waste Tanks slated for closure

- Waste tanks slated for closure have been mechanically or chemically cleaned
- Residues are highly radioactive, as high as 1.3E9 Bq/g Beta, 1.7E7 Bq/g Alpha
- Required analyses for trace radionuclides (as low as 0.37 Bq/g) in the presence of gross levels of interfering radionuclides
- Large list of analytes requested for numerous samples of Tank Waste (up to 40 in recent campaigns)
- Cs-137 is the main contributor to whole body dose
- Sr-90/Y-90 main contributor to Extremity Dose
- Radiochemical separations run much more efficiently in radiohoods as opposed to the Shielded Cells

Tank 19 & 18 54 Radio-isotopes Requiring Characterization

H-3	C-14	Ni-59	Ni-63	Co-60	Se-79
Sr-90	Y-90	Tc-99	Sn-126	Sb-126	Cs-135
Cs-137	Ba-137m	Sm-151	Eu-152	Eu-154	Eu-155
Th-229	Th-230	U-232	U-233	U-234	U-235
U-236	U-238	Np-237	Pu-238	Pu-239	Pu-240
Pu-241	Pu-242	Pu-244	Am-241	Am-242m	Am-243
Cm-243	Cm-244	Cm-245	Cm-247	Cm-248	Cf-249
Pa-231	Ra-226	Pm-147	Ac-227	Al-26	Zr-93
Nb-94	I-129	Cl-36	K-40	Pd-107	Pt-193m

Every Waste Tank often has unique challenges even for routine analyses

Target typically to measure down to the 0.37 Bq/g neighborhood, Tank Waste in the 2.5E7 Bq/g activity range

Question becomes how many analytes will actually be present at much higher levels (makes for a much easier analysis), and how many will require procedures to get down to the 0.37 Bq/g levels, and then, can we even do it in this time frame

54 Radio-isotopes' Origins

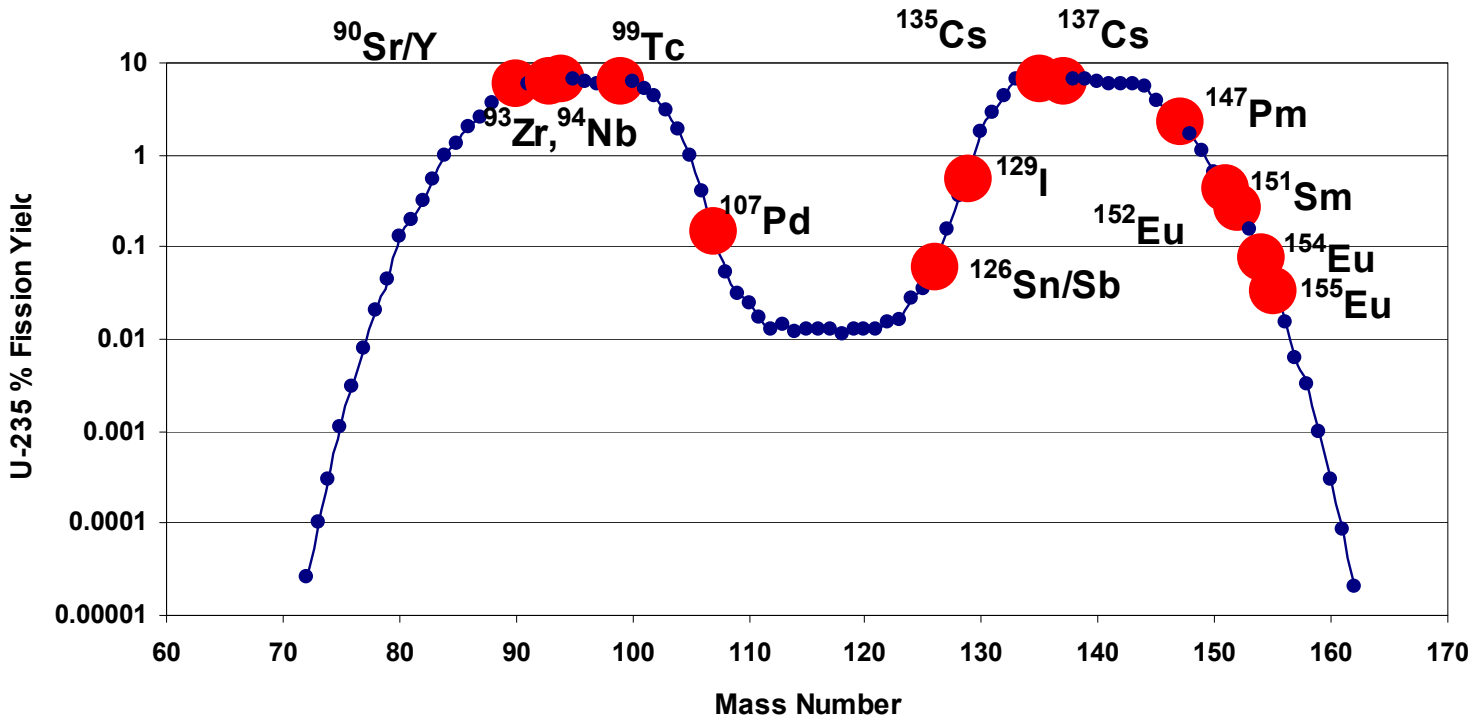
H-3	C-14	Ni-59	Ni-63	Co-60	Se-79
Sr-90	Y-90	Tc-99	Sn-126	Sb-126	Cs-135
Cs-137	Ba-137m	Sm-151	Eu-152	Eu-154	Eu-155
Th-229	Th-230	U-232	U-233	U-234	U-235
U-236	U-238	Np-237	Pu-238	Pu-239	Pu-240
Pu-241	Pu-242	Pu-244	Am-241	Am-242m	Am-243
Cm-243	Cm-244	Cm-245	Cm-247	Cm-248	Cf-249
Pa-231	Ra-226	Pm-147	Ac-227	Al-26	Zr-93
Nb-94	I-129	Cl-36	K-40	Pd-107	Pt-193m

From Fission Products

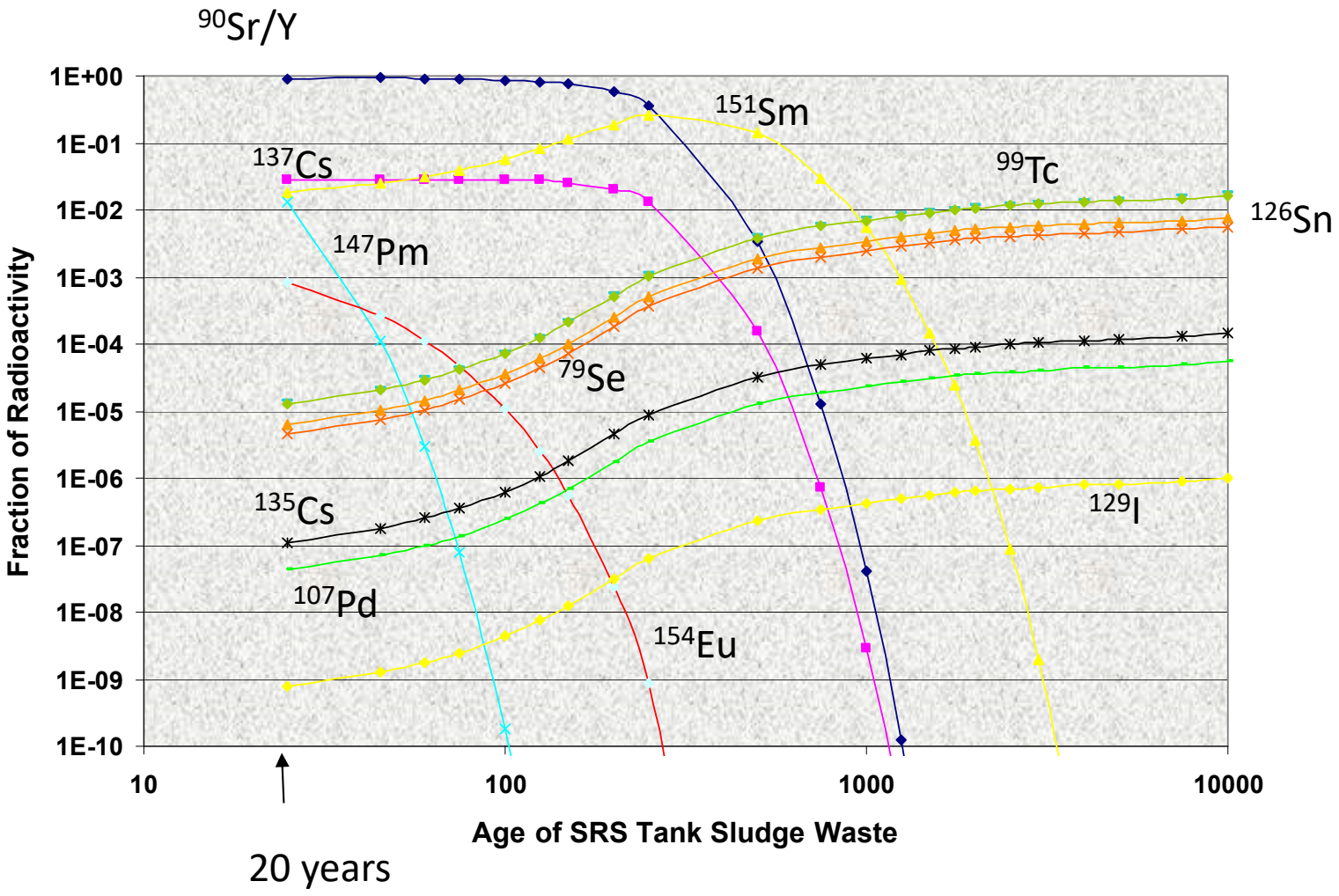
From Activation Products

Natural

Fission Products – Fission Yield Curve



Fission Product Distribution Over Time



Activation Products

H-3	C-14	Ni-59	Ni-63	Co-60	
Th-229		U-232	U-233		
U-236		Np-237	Pu-238	Pu-239	Pu-240
Pu-241	Pu-242	Pu-244	Am-241	Am-242m	Am-243
Cm-243	Cm-244	Cm-245	Cm-247	Cm-248	Cf-249
				Al-26	
		Cl-36			Pt-193m

- Was the precursor present to be exposed to a neutron flux to generate levels having current activities >0.37 Bq/g ?
- i.e. H-2(n,γ)H-3, or N-14(n,p)C-14 Probably so
- i.e. Cl-35(n,γ)Cl-36 or Pt-192(n,γ)Pt-193m Probably not

Looking at Isotopes on the List That Use Eichrom Resins

Isotopes in blue make use of Eichrom Products

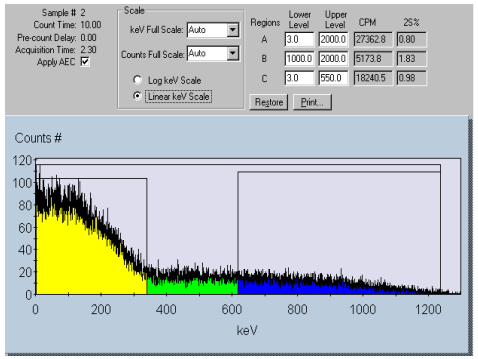
H-3	C-14	Ni-59	Ni-63	Co-60	Se-79
Sr-90	Y-90	Tc-99	Sn-126	Sb-126	Cs-135
Cs-137	Ba-137m	Sm-151	Eu-152	Eu-154	Eu-155
Th-229	Th-230	U-232	U-233	U-234	U-235
U-236	U-238	Np-237	Pu-238	Pu-239	Pu-240
Pu-241	Pu-242	Pu-244	Am-241	Am-242m	Am-243
Cm-243	Cm-244	Cm-245	Cm-247	Cm-248	Cf-249
Pa-231	Ra-226	Pm-147	Ac-227	Al-26	Zr-93
Nb-94	I-129	Cl-36	K-40	Pd-107	Pt-193m

Sr-90/Y-90

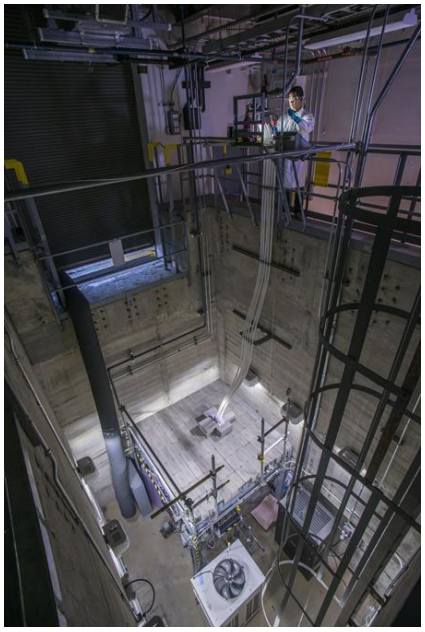
Peroxide Fusion Digestion in Shielded Cells

Eichrom Sr resin Extraction

For HLW supernate we do 2 Sr extractions, for HLW sludge we do 1



Liquid Scintillation Counting for Sr-90



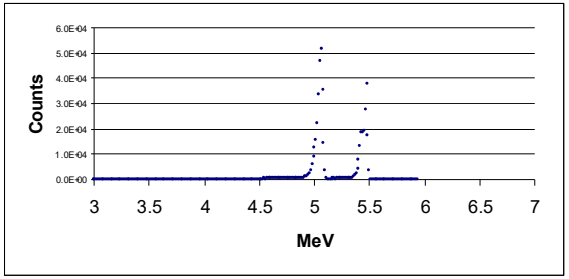
Neutron Activation Analysis to determine Sr Carrier yields

Pu-238, 239, 240, 241, 242, 244

Peroxide Fusion Digestion in Shielded Cells

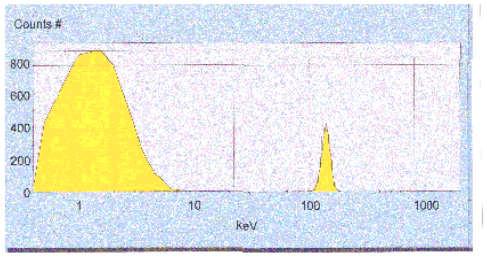
Thenoyltrifluoroacetone (TTA) solvent-solvent extraction for Pu

For Pu-238, and Pu-239/240, traced with Pu-236



Eichrom TEVA resin Extraction

Eichrom TEVA resin Extraction



Liquid Scintillation Counting for Pu-241 to Pu Alpha ratio

ICP-MS for Pu-239, 240, 242, 244

Tc-99

Pressurized Mixed Acid Digestion in Shielded Cells

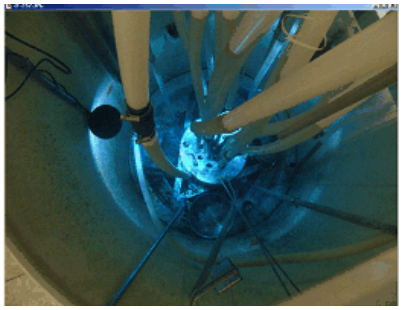
Eichrom TEVA resin Extraction

Eichrom TEVA filter Extraction

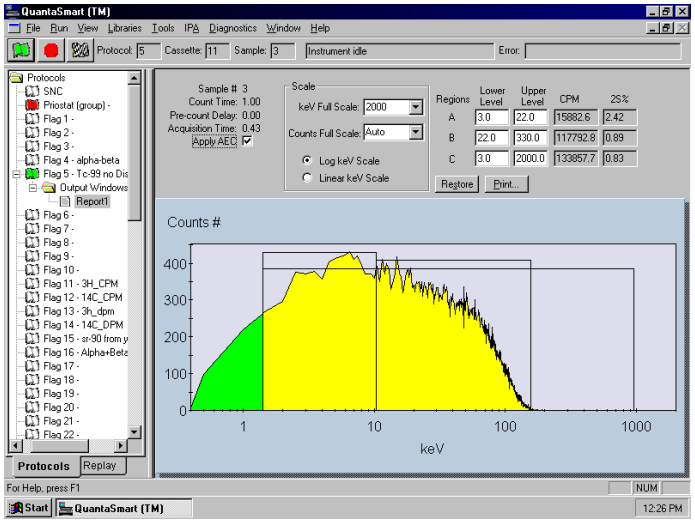
3x3 NaI Well gamma spectrometer for Tc-99m

Tc-99m Tracer Generation

Mo-99 + n > Tc-99m



MIK extraction of Tc-99m tracer



Liquid Scintillation Counting for Tc-99

Th-229, Th-230, Ac-227

Peroxide Fusion Digestion in Shielded Cells → ICP-MS for Th-232 among other things

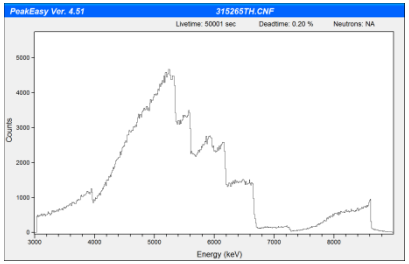
↓

Eichrom TEVA resin Extraction

↓

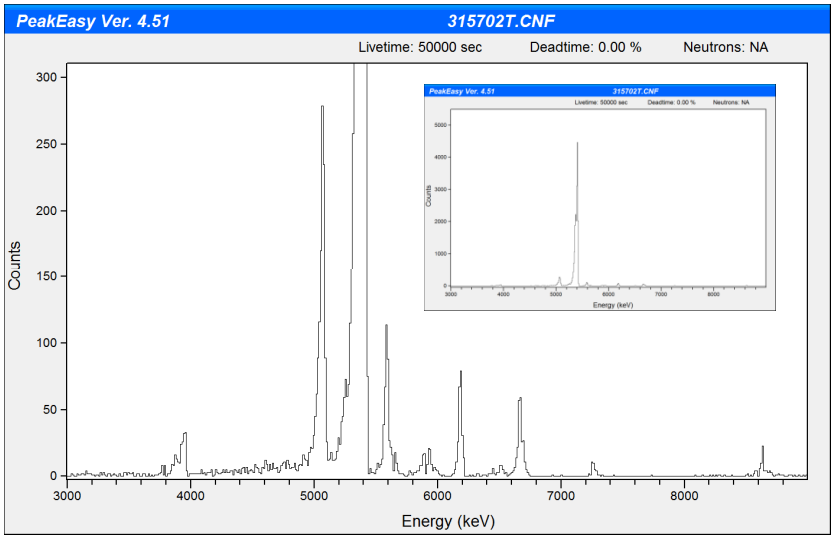
Cerium Co-Precipitation

↓



Occasionally unexpectedly high in Thorium

- We yield from Th-229 or Th-228 tracers or from Th-232 measured from ICP-MS
- Calculate Ac-227 from measured Th-227



Alpha Spectrometry for Th-227, 229 and 230

Am-241, 242m, 243, Cm-242, 243, 244, 245, 248, Cf-249

Peroxide Fusion Digestion in Shielded Cells

↓

Eichrom DGA resin extraction of Trivalent actinides in Shielded Cells

↓ 2 week cool to let Y-90 decay

Eichrom RE resin extraction of Trivalent actinides in radiohoods

→

Eichrom Ln resin extraction of Trivalent actinides in radiohoods

↙

Alpha Spectrometry for Am-241, Am-243, Cm-242/Am-242m, Cm-244

↓

Gamma Spectrometry for Am-241, Am-243, Cm-243, Cm-245, Cf-249

↘

ICP-MS for Am-241, Cm-244, Cm-245, Cm-247, Cm-248

Peroxide Fusion Digestion in Shielded Cells

↓

Gamma and or Cesium removed gamma analysis for Am-241 or Am-243

U-232, U-233, U-234, U-235, U-236, U-238

Peroxide Fusion Digestion in Shielded Cells

ICP-MS for U-235, U-238 among other isotopes

Eichrom U-TEVA resin Extraction

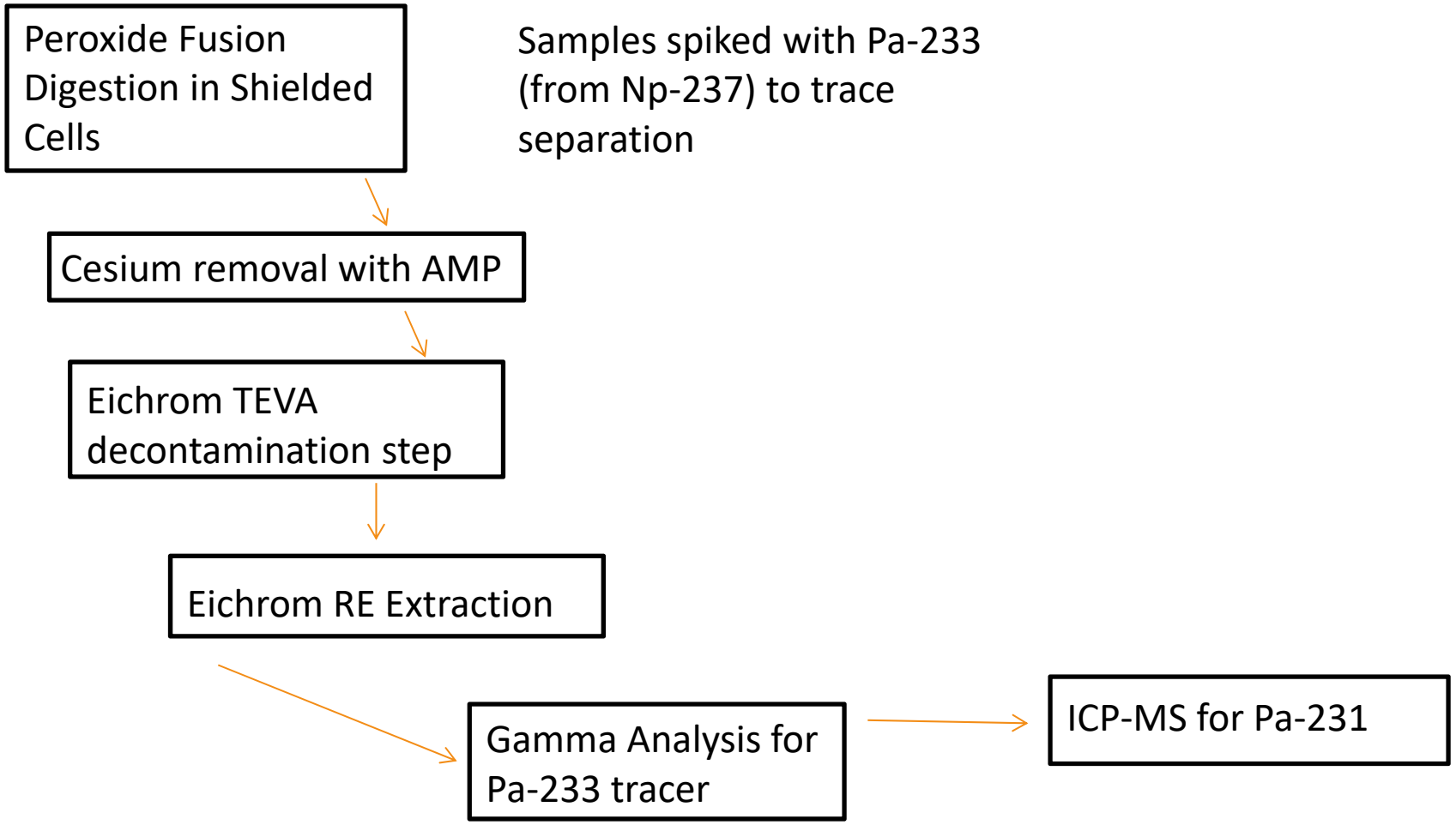
Cerium Co-Precipitation

Eichrom U-TEVA resin Extraction

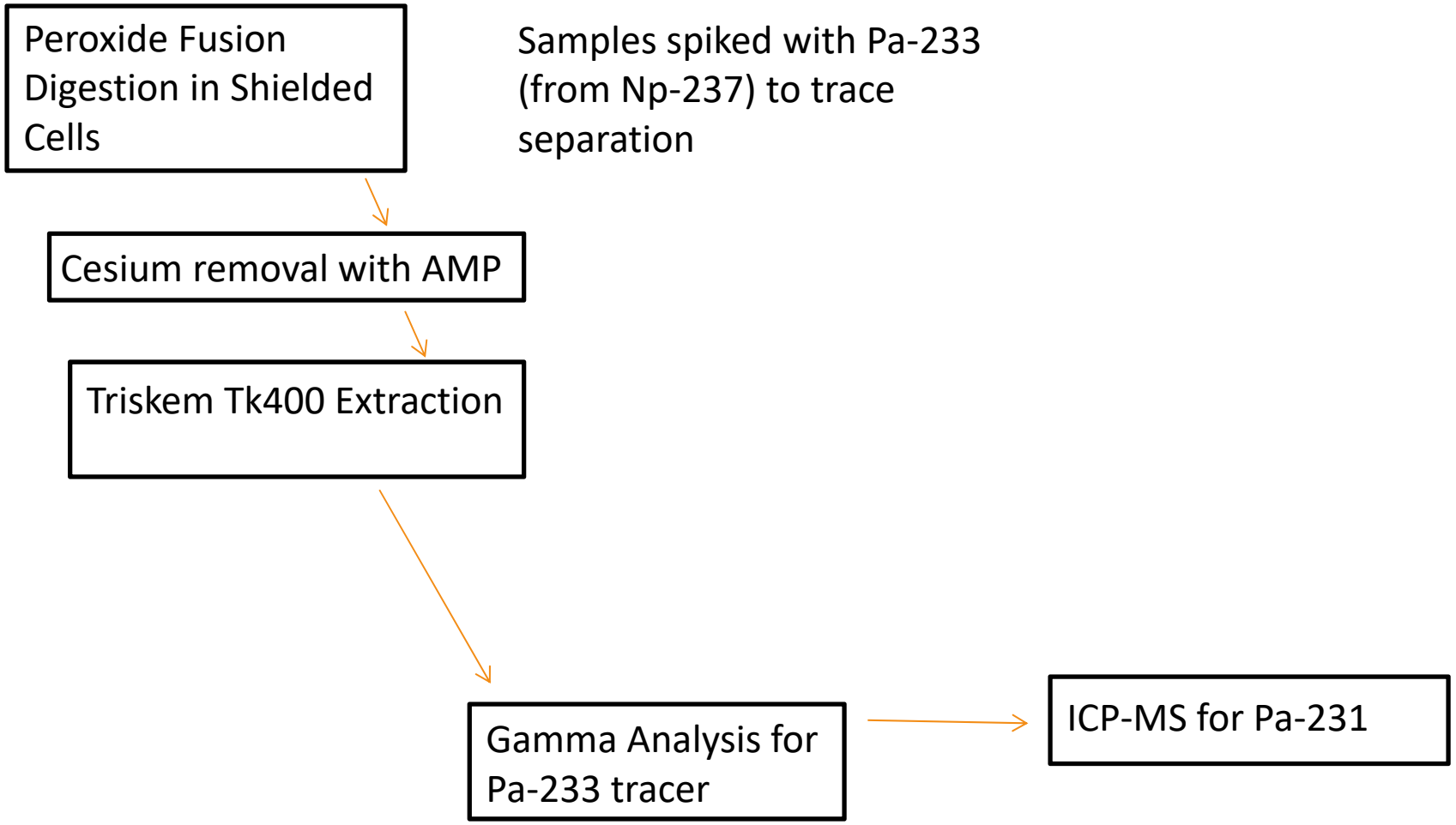
ICP-MS for U-233, U-234, U-236

Alpha Spectrometry for U-232, traced with U-233 or ratioed to U-238 measured by ICP-MS

Pa-231 – Old Method



Pa-231 – New Method



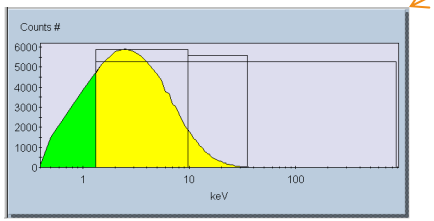
Ni-59/63

Pressurized Mixed Acid Digestion in Shielded Cells

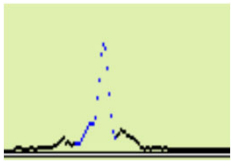
Eichrom Ni resin Extraction

Bio-RAD AMP Strike

Eichrom Ni resin Extraction



Liquid Scintillation Counting for Ni-63



Be windowed Semi-planar HPGe for Ni-59

ICP-AES for Ni Carrier Recovery

Pt-193m

Peroxide Fusion Digestion in Shielded Cells

Pt carrier added for tracing

Bio-RAD AMP Strike

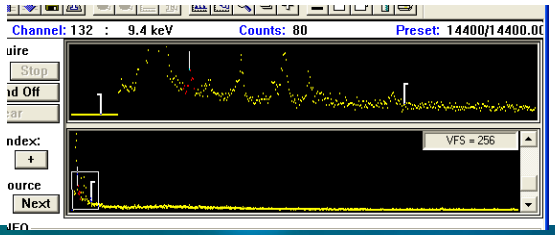
Eichrom TEVA resin Extraction

Bio-RAD AMP Strike

Eichrom TEVA resin Extraction

ICP-AES for Pt Carrier Recovery

Be-windowed Semi-planar HPGe for Pt-193m



Pd-107

Peroxide Fusion Digestion in Shielded Cells

Spike aliquot with stable Pd if measurable stable Pd hasn't already been measured

↓

Eichrom Ni resin Extraction

↓

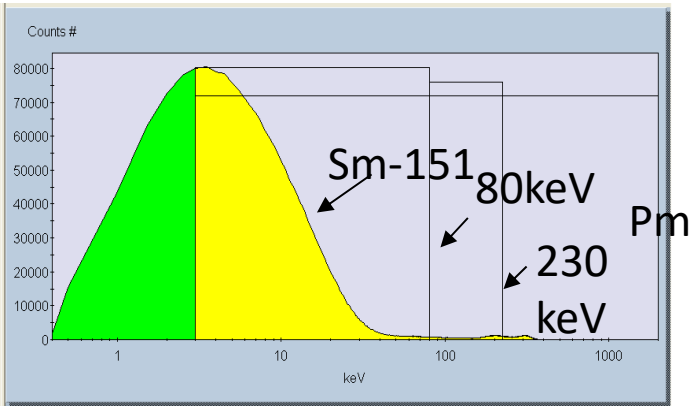
Eichrom Ni resin Extraction

↓

ICP-MS for Pd-107 and Pd Carrier Recovery

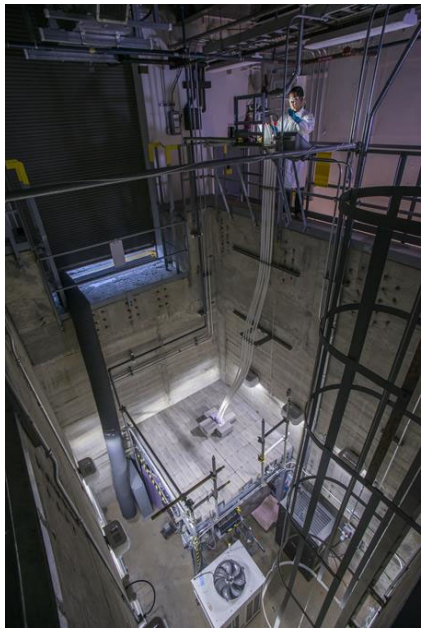
Pm-147/Sm-151

Peroxide Fusion Digestion in Shielded Cells → Eichrom RE resin Extraction → Eichrom Ln resin Extraction



Liquid Scintillation Counting for Sm-151 and Pm-147

Neutron Activation Analysis to determine Sm Carrier yields



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