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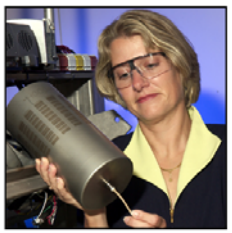
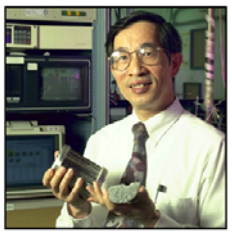
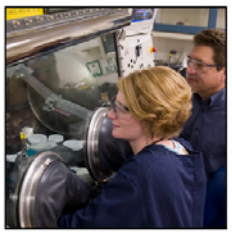
Tanks 18/19: Sample Characterization, Method Development and Statistical Sampling

Frank Pennebaker, Larry Oji, David DiPrete, Thomas White, Steve Harris, and Andrew Tisler

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Outline

- **Background – Tank 18/19 and Characterization**
- **Sampling – Sample types and technique**
- **Characterization Process**
- **Development of new methods**
- **Statistical Evaluation**
- **Conclusions**

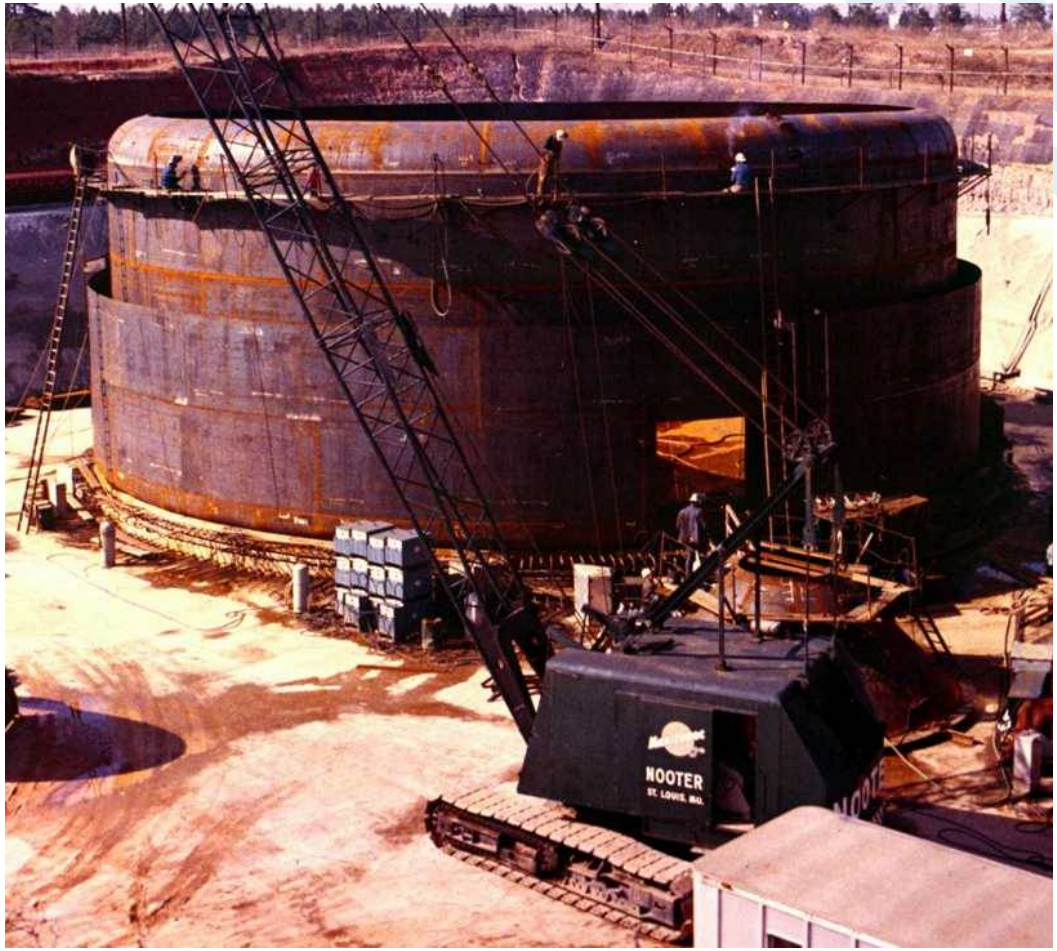
Tank 18/19 Characterization

This presentation is focused on the sampling process and characterization of residual material in the tanks.

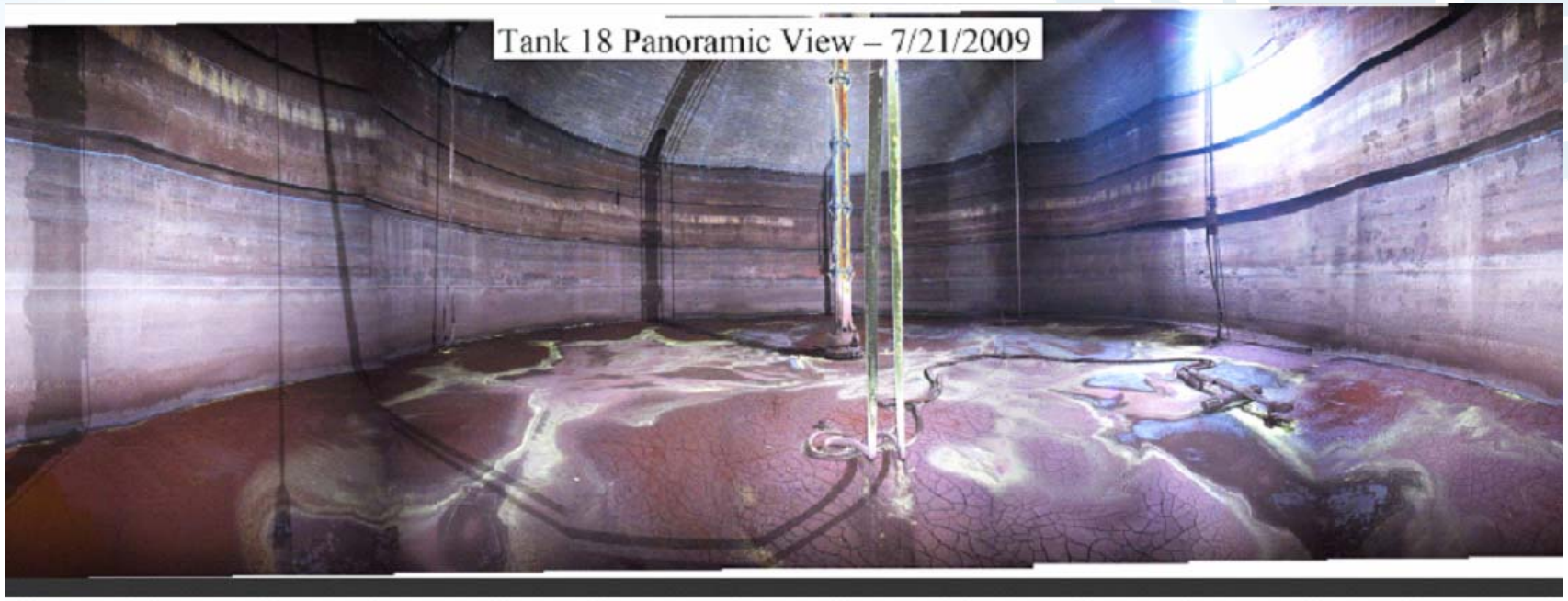
- **Measurement of non-radioactive constituents in tank.**
- **Measurement of radioactive constituents in tank.**
- **Statistical evaluation of data with UCL determination for individual constituents.**

This data can be combined with the tank volume to calculate total inventory.

SRS Waste Tank

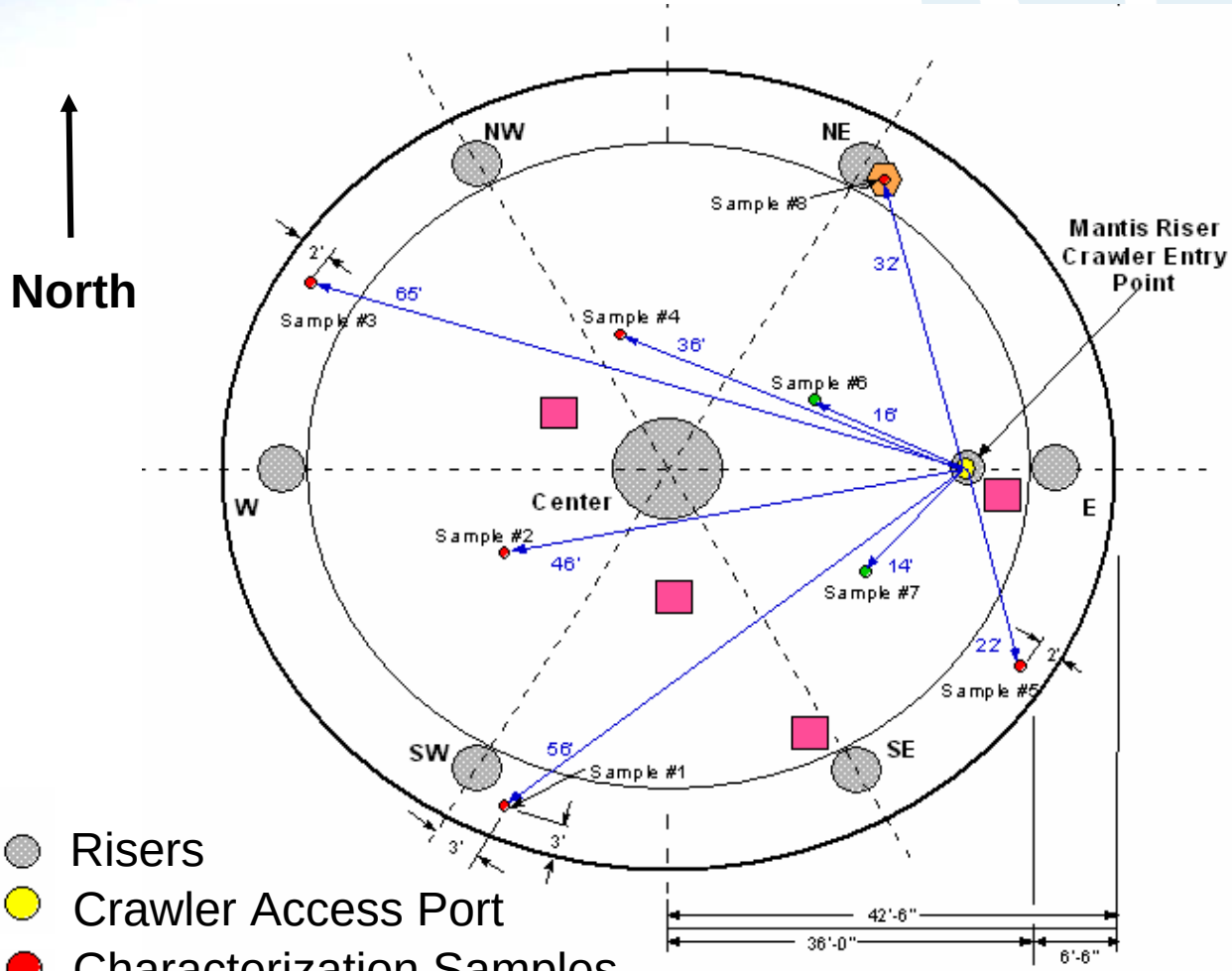


Tank 18 Residual Material



Tank 18 residual material for characterization.

Tank 18 Sample Locations



- Risers
- Crawler Access Port
- Characterization Samples
- Archive Sample Locations

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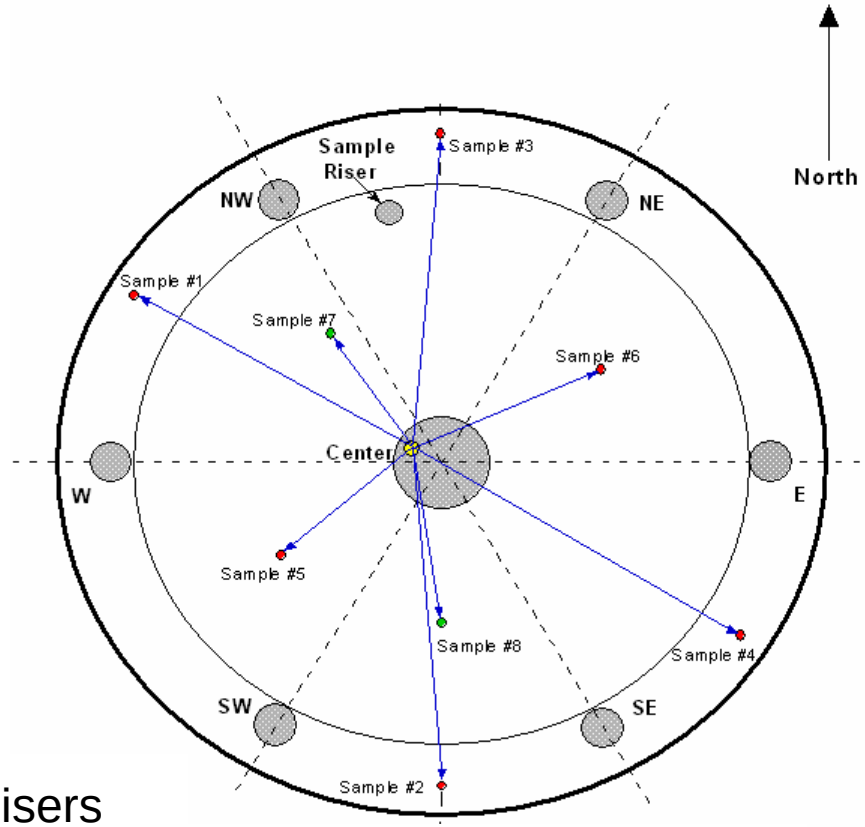
Tank 19 Sample Locations



- Risers
- Crawler Access Port
- Characterization Samples
- Archive Sample Locations

Tank 18/19 Sampling - Crawler

Tank 18/19 Sampling - Crawler

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Tank 18/19 Sampling - Crawler

Tank 18 Characterization Samples

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Tank 19 Characterization Samples

The white color in the samples is caused by the presence of IE-95 (zeolite) in the samples. The northeast corner of the tank contained an ion exchange Cs removal column.

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Radiochemistry Characterization Challenges

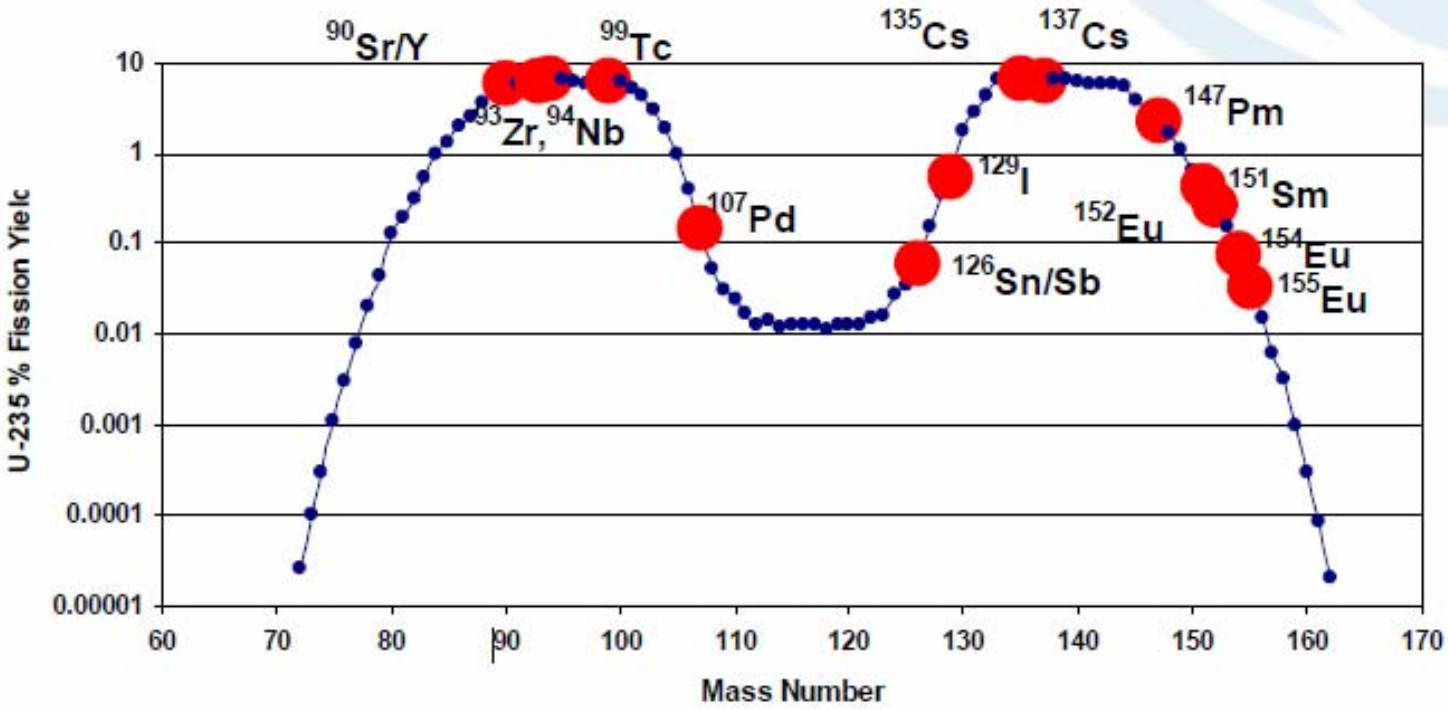
- Residues were highly radioactive - Nominally $1.5*10^{9}$ dpm/g beta/gamma, $1*10^{8}$dpm/g alpha.
- Our challenge was to analyze for trace radionuclides ($5*10^{-5}$ μCi/g or 22 dpm/g) in the presence of gross levels of interfering radionuclides.
- Large list of methods (~40 different radiochemical methods) for customer.
- Aggressive measurement schedule considering number and type of measurements.

Radiological Constituents

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
Naturally Occurring

Fission Products



Sample Preparation and Characterization

- **Initial Preparation**
  - **Density measurement – for volume conversion.**
  - **Raw samples were air dried, ground and sieved to 30 mesh (~600 micron).**

- **Digestion**
  - **Peroxide Fusion – most aggressive**
  - **Sealed vessel aqua regia – volatile elements**
    - **HF acid also utilized for IE-95**
  - **Water leach – anions, etc.**

- **Characterization – variety of analytical techniques.**

- **Special Analyses – bulk of radionuclides – C-14, Se-79, etc.**

Items in green performed in SRNL Shielded Cells due to high levels of contamination.

Low Level Measurements

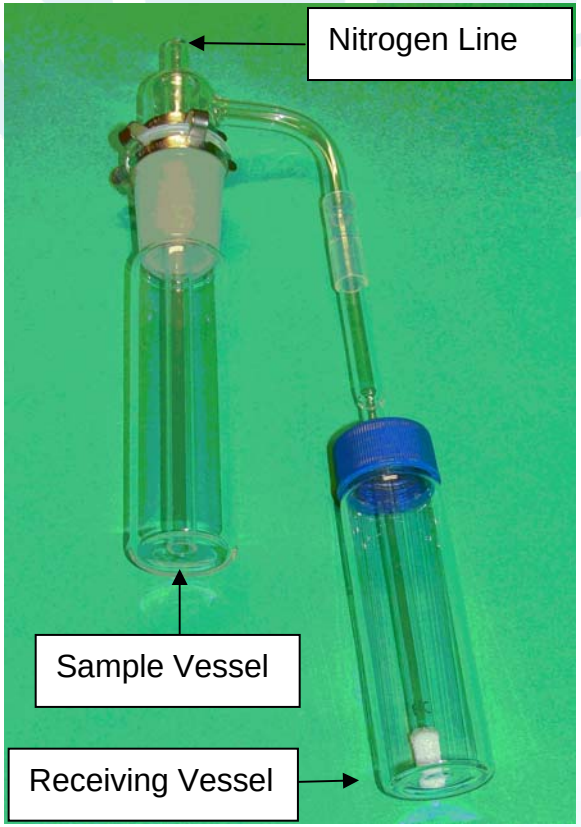
Cm-243	Cm-244	Cm-245	Cm-247	Cm-248	Cf-249
Pa-231	Ra-226	Pm-147	Ac-227	Al-26	Zr-93
Nb-94	I-129	Cl-36	K-40	Pd-107	Pt-193m

- Detection Limit targets were very aggressive, considering high concentrations of interfering radionuclides.
  - Cs-137 approximately $1*10^9$ dpm.
  - Significant concentrations of Eu and actinides.
- Combination of separations, ICP-MS, beta and gamma measurements.
- Develop of new methods or significant modifications for items in yellow.
- X-Ray measurement method developed for Pt-193.

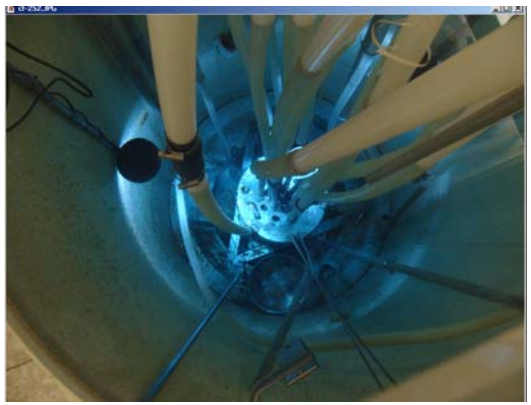
Radionuclide	Target (µCi/g)
Ac-227	$5*10^{-5}$
Pa-231	$5*10^{-5}$
Al-26	$5*10^{-5}$
Zr-93	$5*10^{-5}$
Nb-94	$5*10^{-5}$
K-40	$5*10^{-5}$
Cl-36	$5*10^{-5}$
Pd-107	$5*10^{-5}$
Pt-193	$5*10^{-5}$
Ra-226	$1*10^{-4}$

Characterization of Cl-36

- Long half-life – 3E5 years, beta emitter (709 keV end point), no gamma emitters
- Volatile analyte – requires a traced digestion
- Activation product, but not expected.
- Initial approach chosen was decontamination by resins and distillation.



Cl-36 Distillation Apparatus



Cf-252 NAA Facility

Cl-36 Measurement

Digestion
HNO_3 and HCl

Solubilize Cl-36 and provide Cl tracer

→

Sample Clean-up

Cs-137 removal
Actinides, Lanthanides, and Y-90 removal
Cation removal
Sr-90 removal

→

Distillation

1

Additional Clean-up

1) Tc and Cation removal 2

2) Precipitation with silver 3

Measurement by LSC

Measurement of Cl by NAA

Target = 22 dpm

1 ~1000 dpm/g

2 ~200 dpm/g

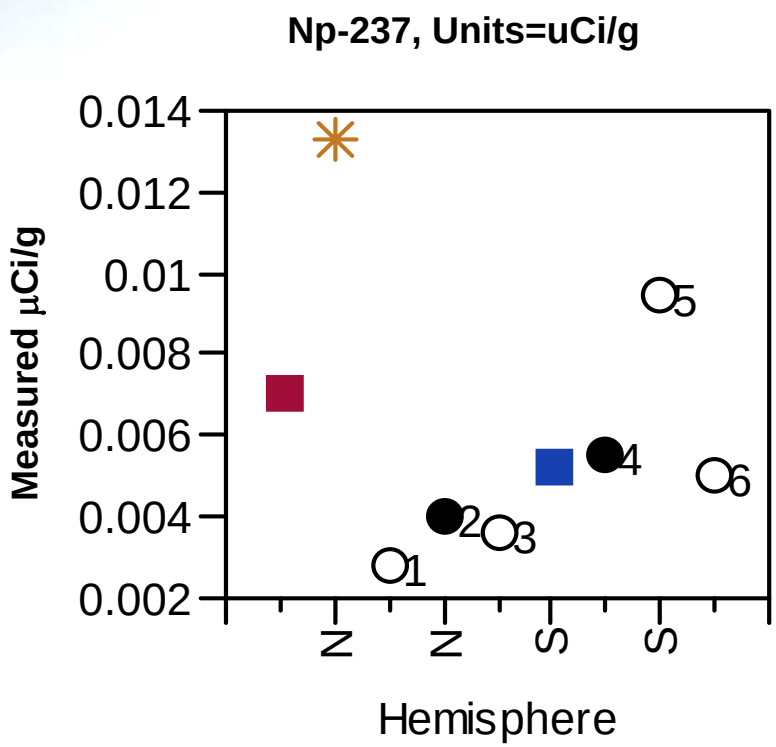
3 Low level

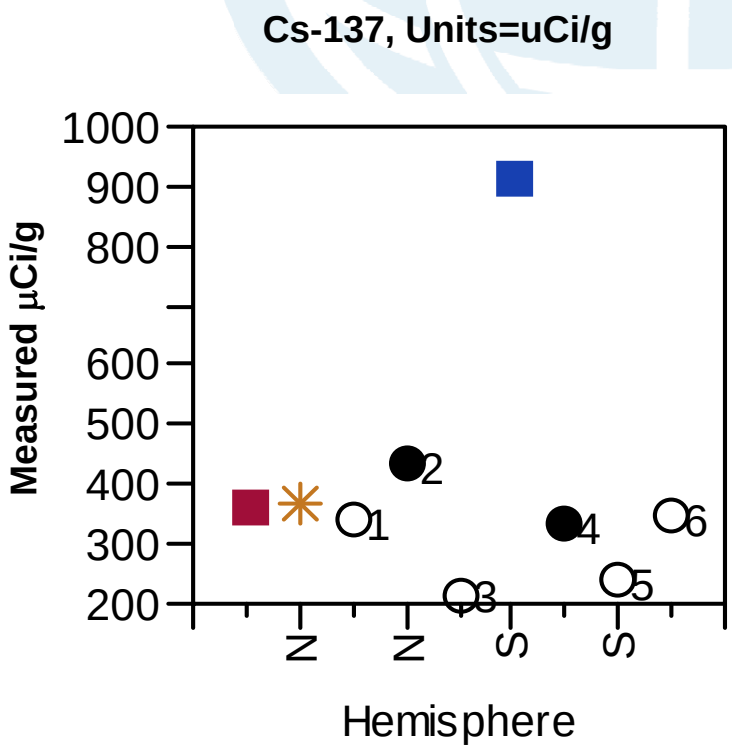
Cl-36 Measurement

- **Treating the distillate with silver nitrate lowered the detection limit to acceptable levels**

Cust ID	***Cl-36 (uCi/g)***		
Tank 19 Position 4	< 1.38E-05	MDA	
Tank 18 Position 2	< 1.06E-05	upper limit	

Tank 18 Results

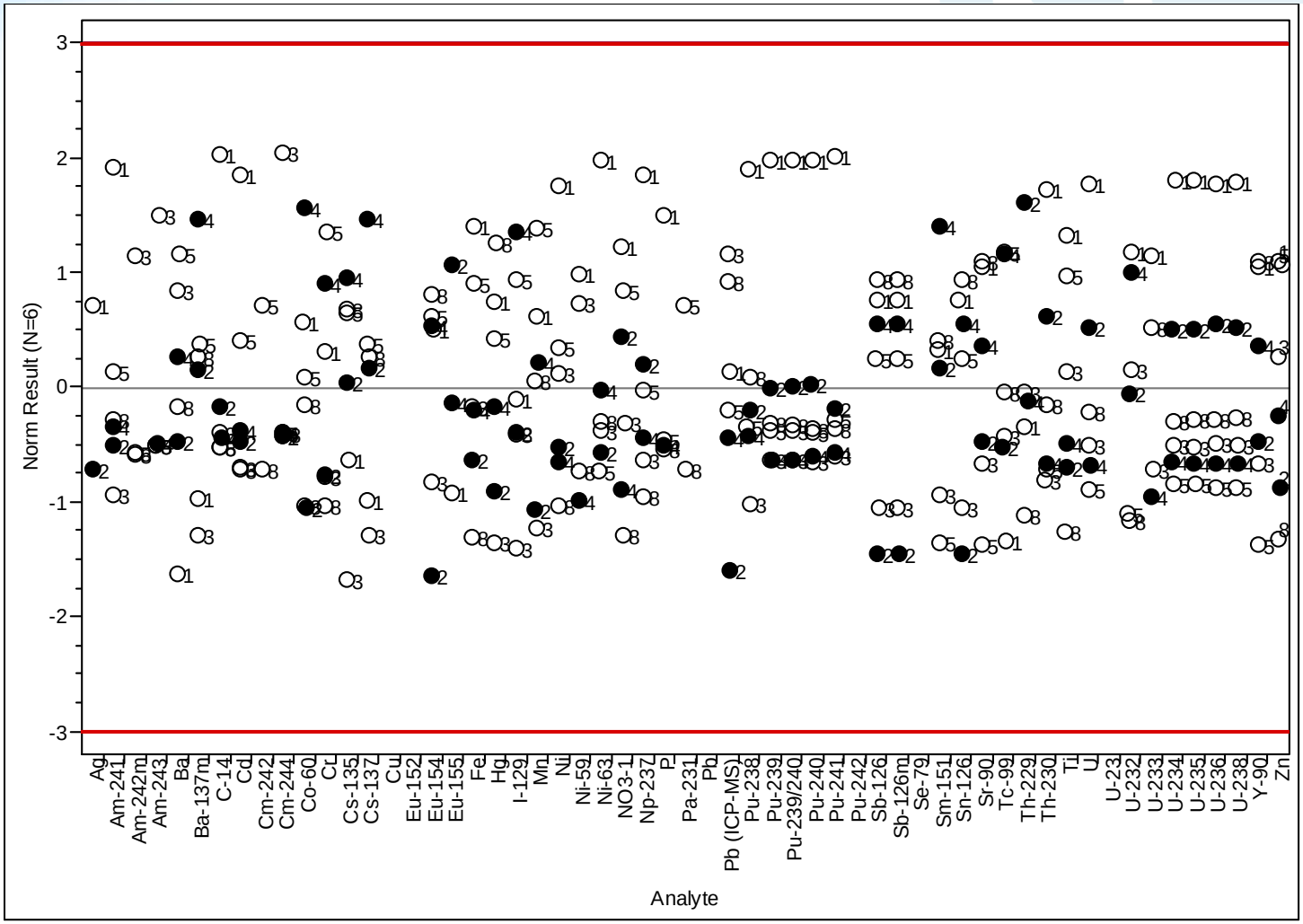




Note: Red and blue boxes and brown stars are from previous tank measurements. Numbered samples indicate sampling region except 6.

● Outer Region
○ Inner Region

Tank 18 Statistical Analysis



3 sigma

3 sigma

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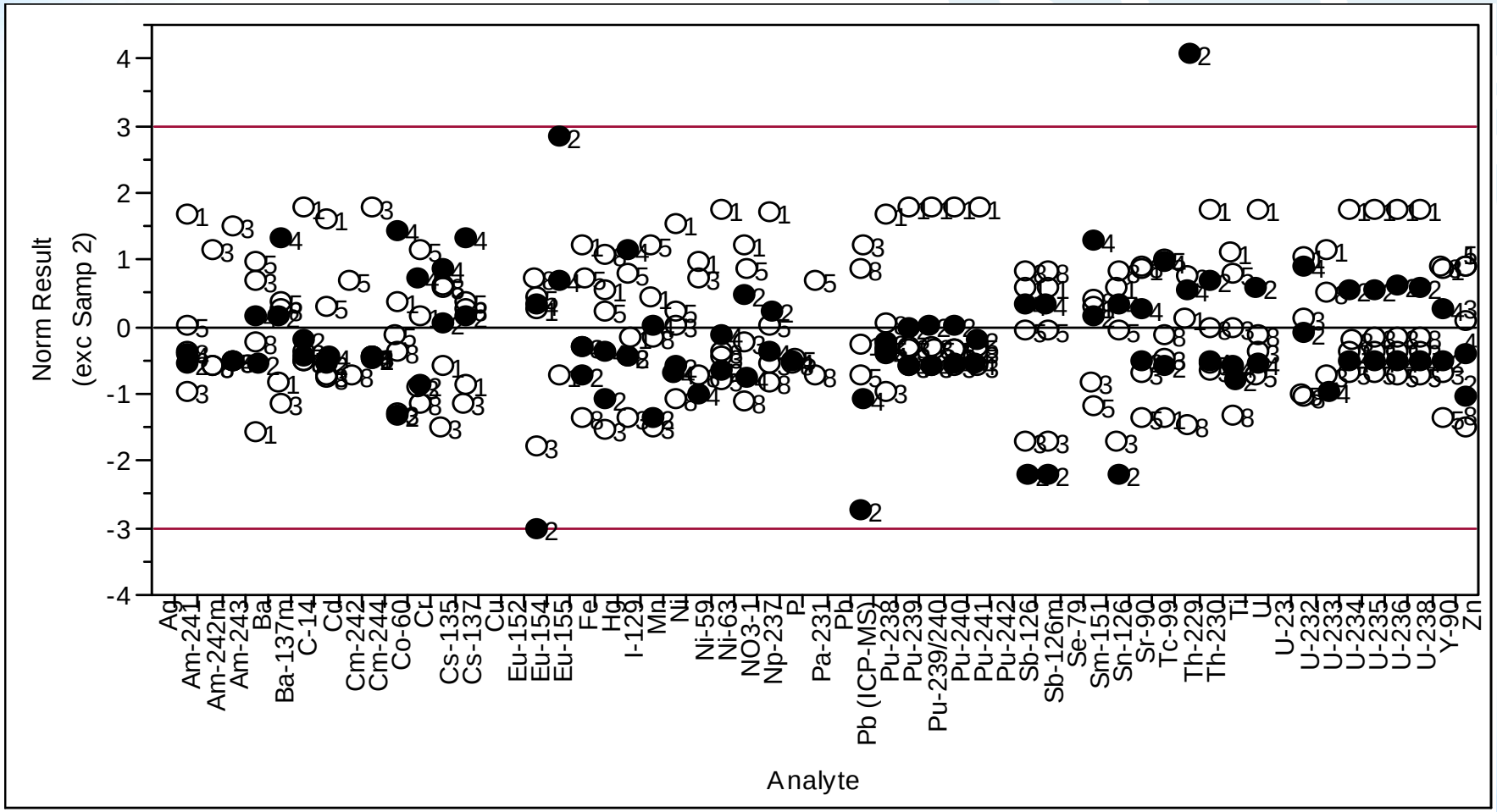
Tank 18 Statistical Analysis



Statistical plot with average derived from all samples except sample location 2.

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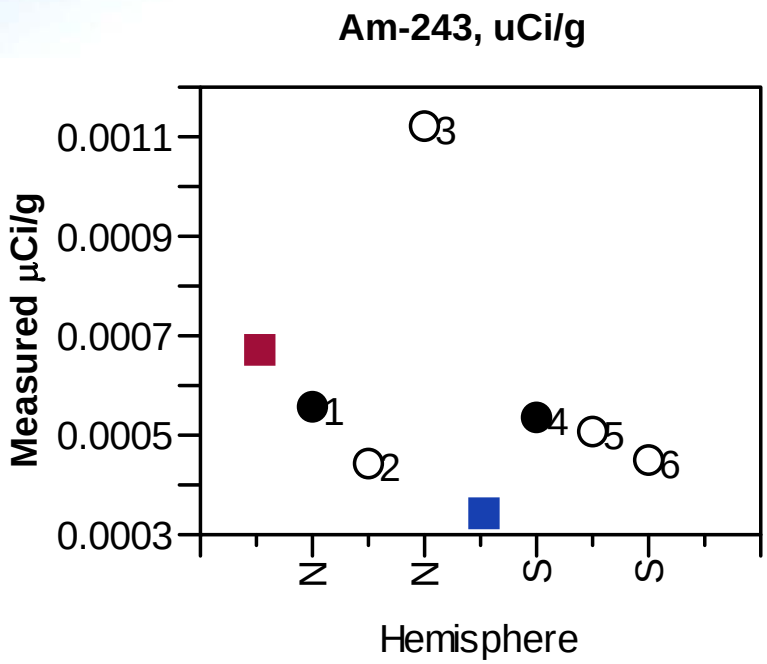
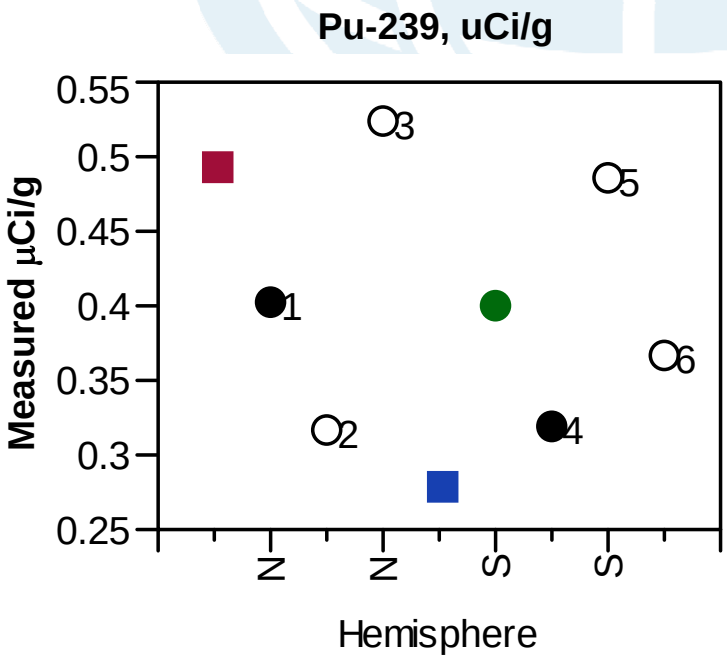
Tank 19 Results – Selected Analytes





Note: Red, blue and green boxes are from previous tank measurements.
Numbered samples indicate sampling region from map.

● Outer Region
○ Inner Region

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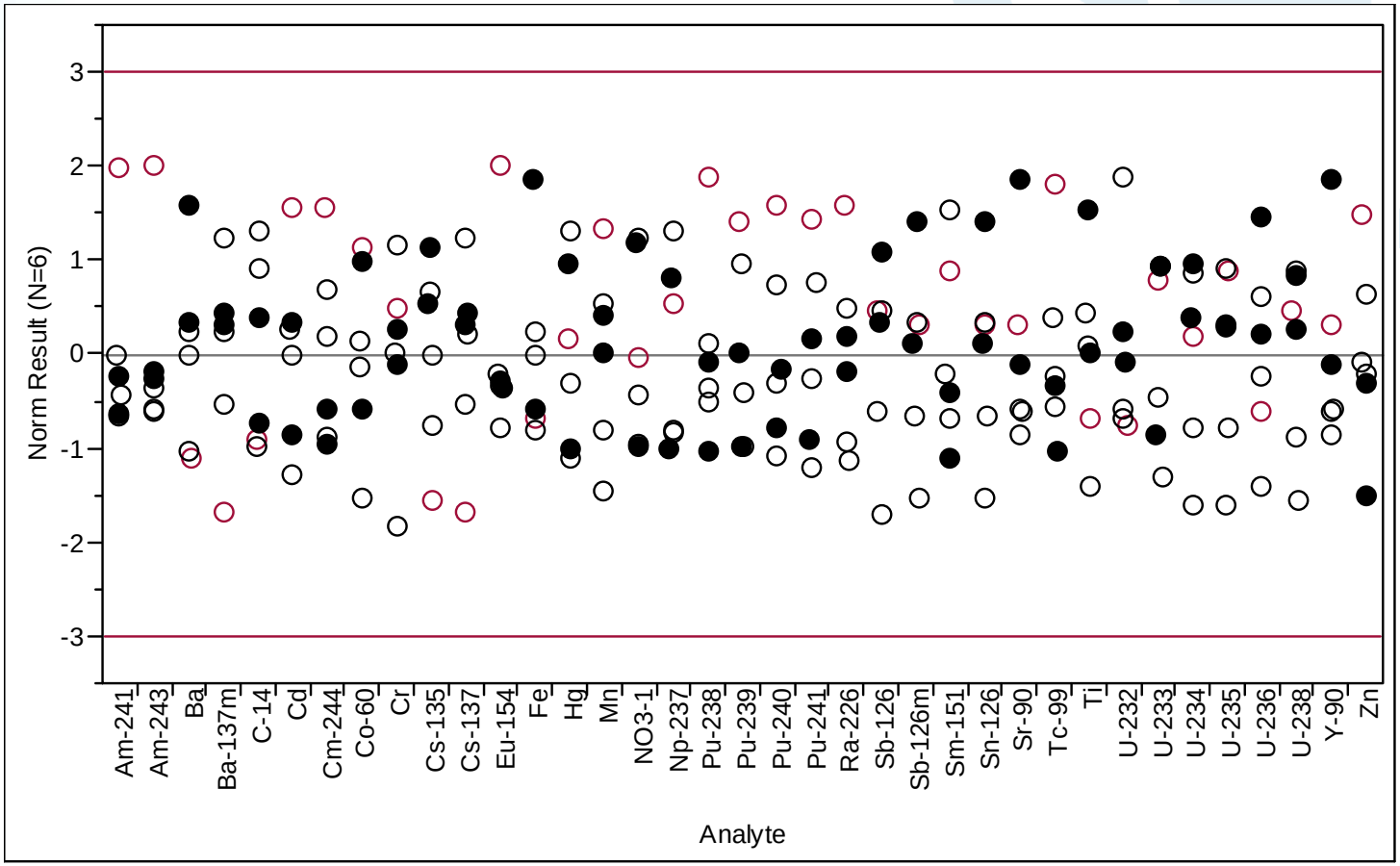
Tank 19 Results – Statistical Analysis



	Inner/Outer	Sample
1	Outer	1
2	Outer	2, 3, 4
3	Inner	5, 6

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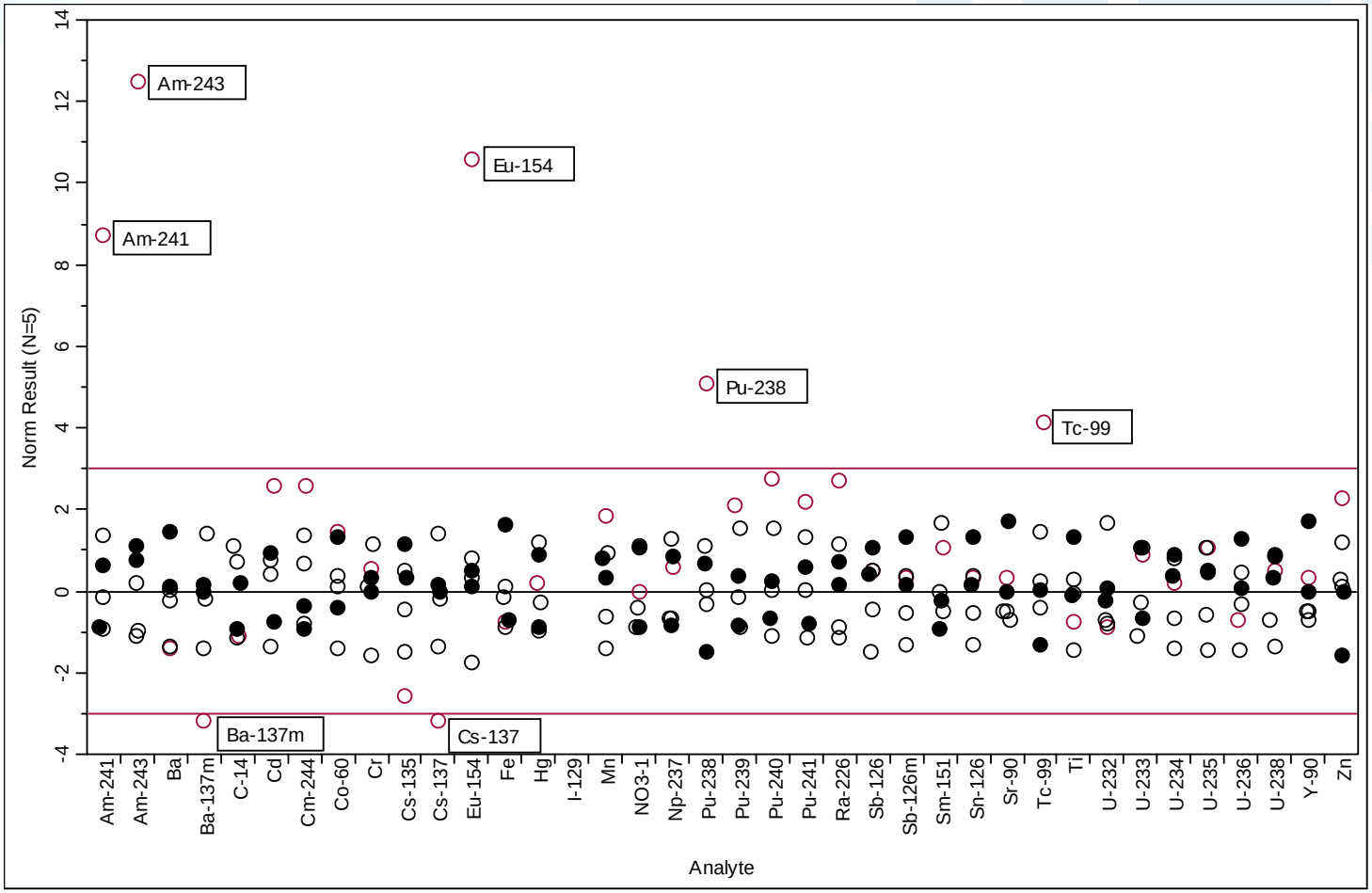
Tank 19 Results – Statistical Analysis



Statistical plot with average derived from all samples except sample location 3.

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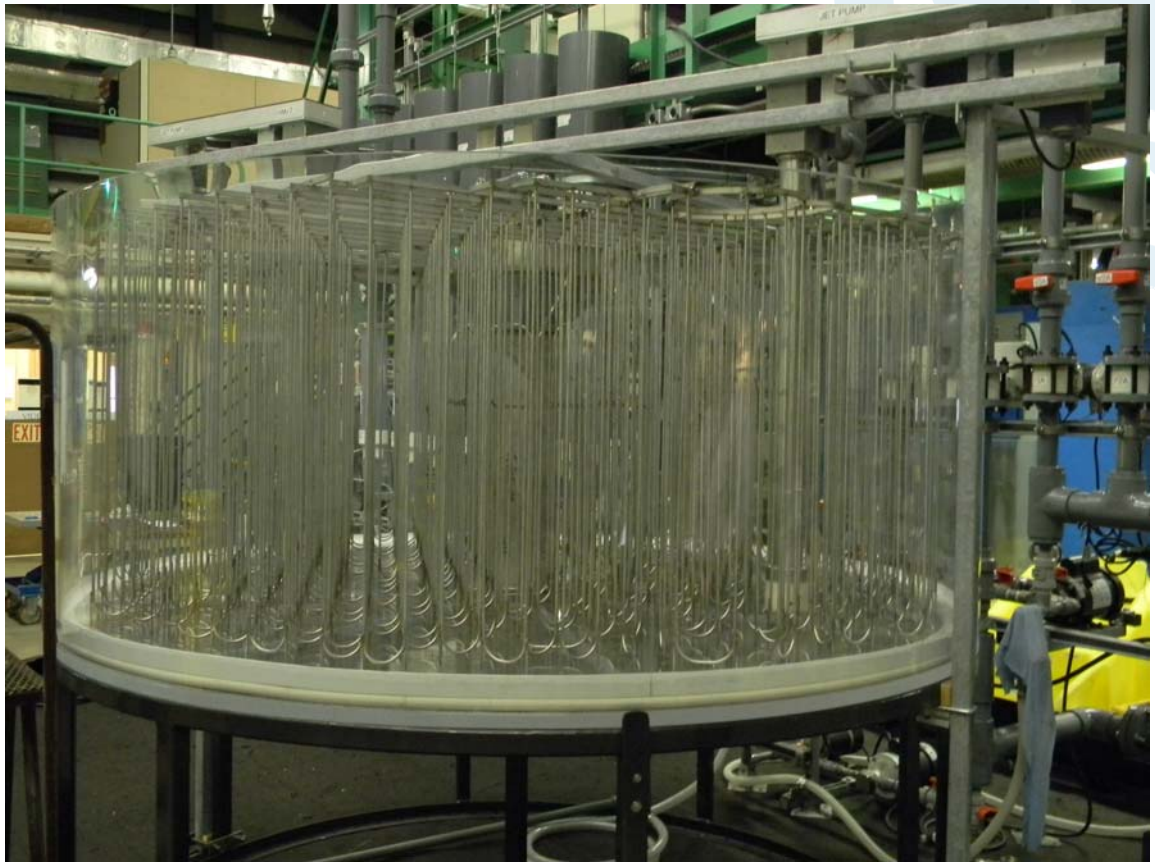
Conclusions

- **Samples were taken and measured from 6 distinct areas within Tanks 18 and 19.**
- **SRNL developed new methodology to determine low activities of new isotopes.**
- **Sample measured were statistically evaluated and produced reasonably similar results between different locations.**
- **Characterization of floor samples have been provided for all isotopes to determine inventory.**

Future



A majority of tanks remaining at SRS will contain cooling coils, which provides an additional sampling challenge.