A Comparison of EPA Method 908.0 and ASTM D6239 for Uranium in Hard Water Matrices

Robert L. Metzger & Pierre Pouquette

Radiation Safety Engineering, Inc.

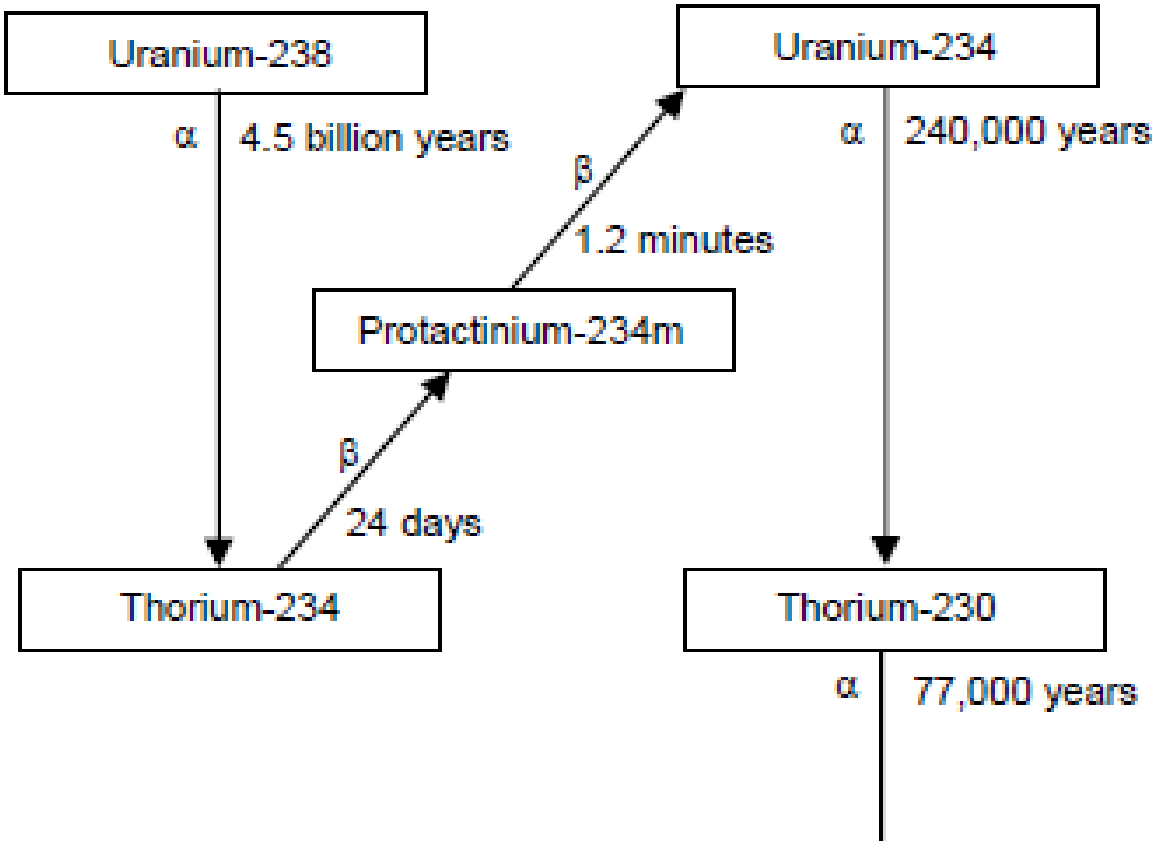
Maximum Contaminate Levels (EPA)

- Adjusted Gross Alpha – 15 pCi/L
- Adjusted Gross Alpha = Gross Alpha – Uranium Activity
- Uranium – 30 µg/L
- Uranium, in its soluble form, is nephrotoxic, so the MCL is correctly listed in units of mass.
- For Uranium laden waters, uranium must be defined in units of mass and activity.
- Since two parameters with MCLs are determined from the measurement, errors (low or high) in the Uranium analysis invariably affect both results.

Uranium Methods

- Most Uranium methods measure either the mass (e.g. EPA 200.8, ICP-MS), or the activity of the uranium (e.g. EPA 908.0).
- Almost all of the Uranium mass is provided by the ^{238}U.
- Isotopic Methods provide results in both activity and mass. The activity by uranium isotope or the $^{234}U/^{238}U$ ratio is needed to have an accurate conversion from mass to activity, or vice versa.
- The $^{234}U/^{238}U$ isotopic ratio varies widely in natural waters.

Uranium Decay Series

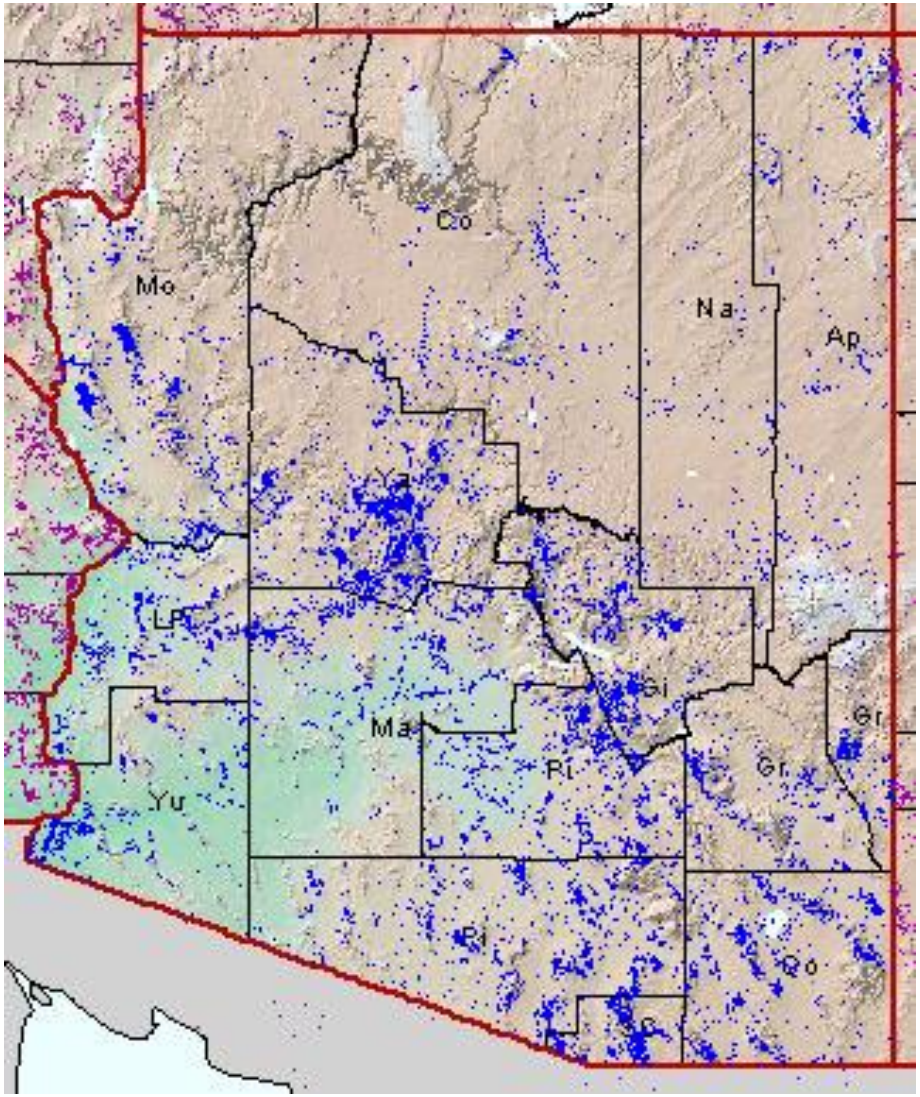


Uranium in Natural Waters

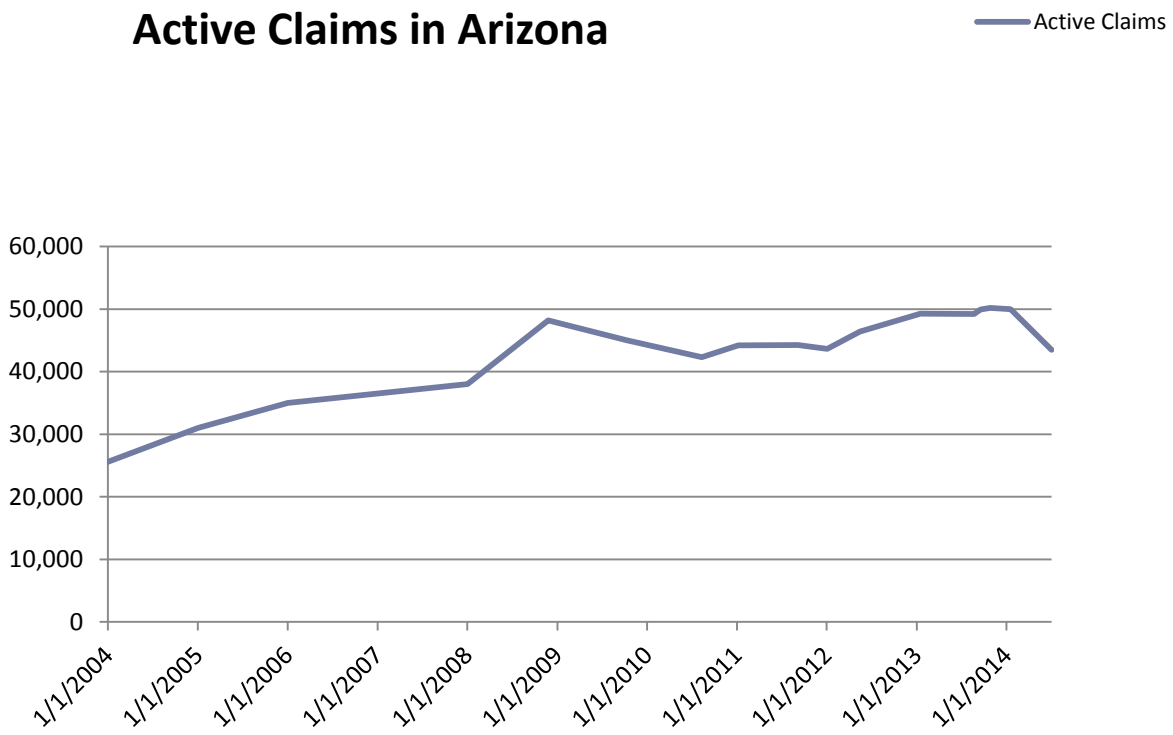
- Actual $^{234}U/^{238}U$ isotopic ratios in Arizona waters range from 1:1 (secular equilibrium), to 10:1.
- Isotopic ratios as high as 20:1 have been reported in other areas of the country.
- Uranium mass methods (e.g. 200.8) provide no information about the total uranium activity.
- Total Uranium activity methods (e.g. 908.0) provide no information about the mass.
- EPA has published several "conversions" based on an assumed isotopic ratio to solve this problem.
- EPA mandates a "conversion" of 0.67 for 200.8 to get activity. It assumes a $^{234}U/^{238}U$ ratio of 1:1.

Mineralization in Arizona

Each blue dot in the image represents a mine. In 2013, USGS reported that Arizona produced over 7.5 billion dollars in non-fuel minerals. It is second only to Nevada (where there are a lot of gold properties)



Mining Claims in Arizona over Time



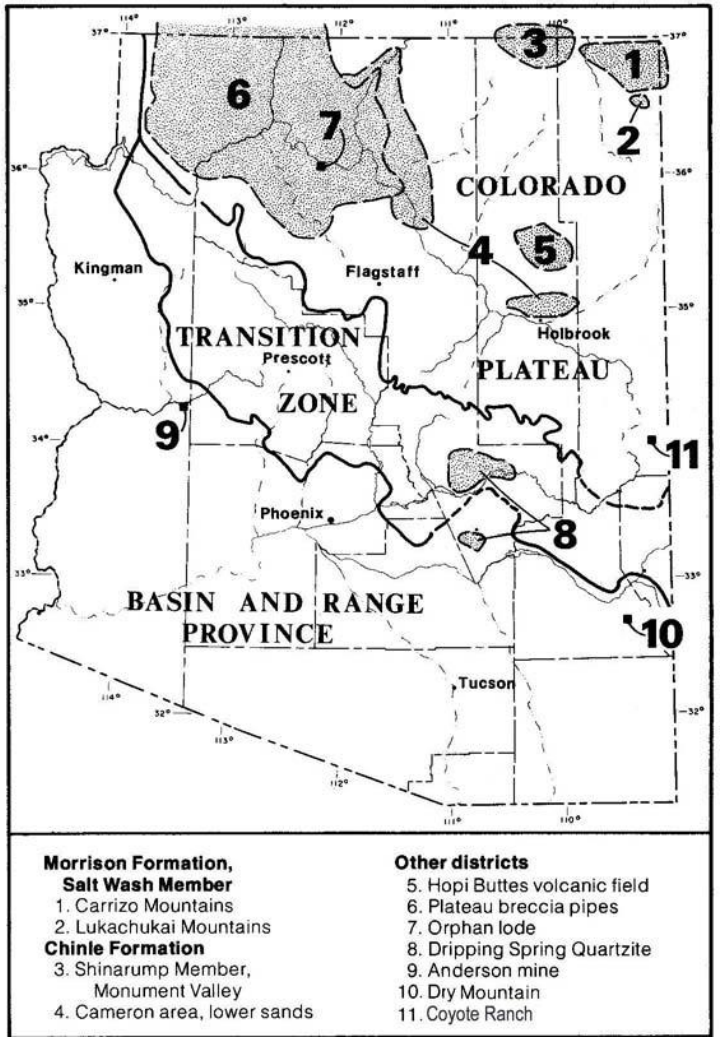
Arizona Geologic Survey

Uranium in Arizona

- Uranium is prevalent throughout Arizona
- Well water ranges from <1 pCi/L to over 200 pCi/L.
- Non-detects for U in water are uncommon.
- The $^{234}U/^{238}U$ isotopic ratio varies from 1:1 to 10:1.
- All of the water is hard, with total dissolved solids of 200 to over 2,000 ppm.
- While wells with Radium concentrations of concern exist, they are far less common. Ra-228 wells also exist, but are rare.
- Water sources impacted by mining activities are also uncommon; the vast majority of U in water is natural.

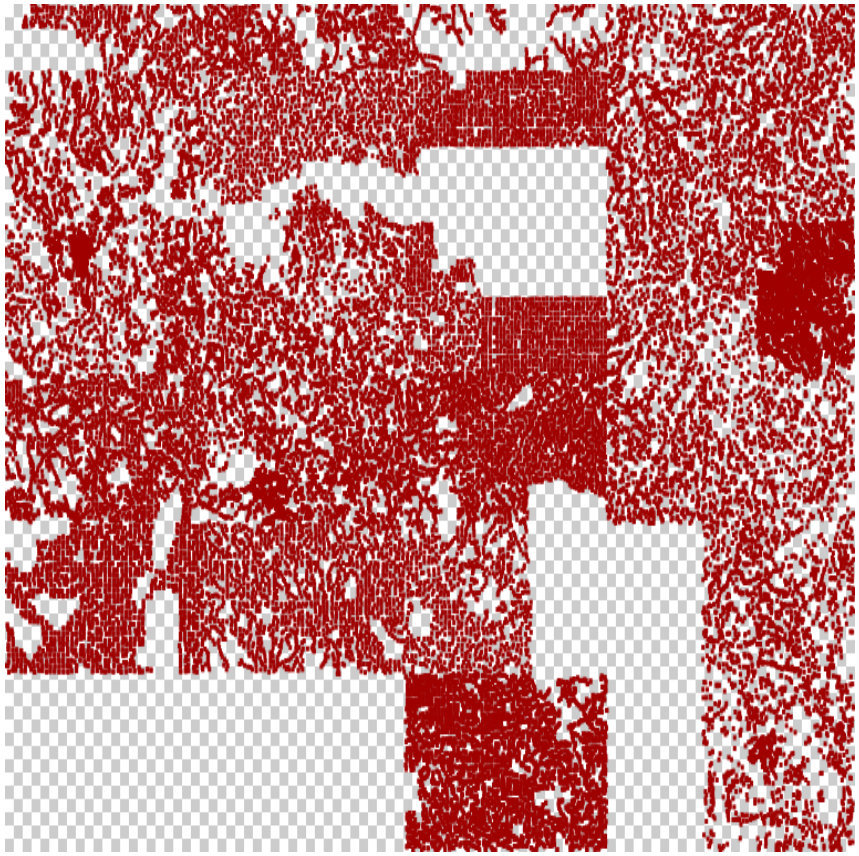
Major Uranium Districts in Arizona

- Major Uranium Districts in AZ are shown on the right.
- In addition, low grade deposits and outcroppings exist throughout the state.
- Thorium deposits are also present, but thorium and thorium chain radionuclides are far less soluble in neutral pH waters.



NURE Uranium Data for Arizona

- National Uranium Resource Evaluation program from USGS shows the following uranium concentration map for Arizona. The blank areas were not sampled.



A Comparison of Uranium Methods

- The traditional U activity method, 908.0 was compared to a new ASTM solvent extraction method, D6239 using excess water from samples provided by clients.
- Each sample was run by both methods, and the total dissolved solids in the sample was determined.
- The ^{232}U tracer in the D6239 method was used to determine the recovery of the uranium from both methods (908.0 has no tracer).
- The performance of the method (recovery) was plotted as a function of TDS.

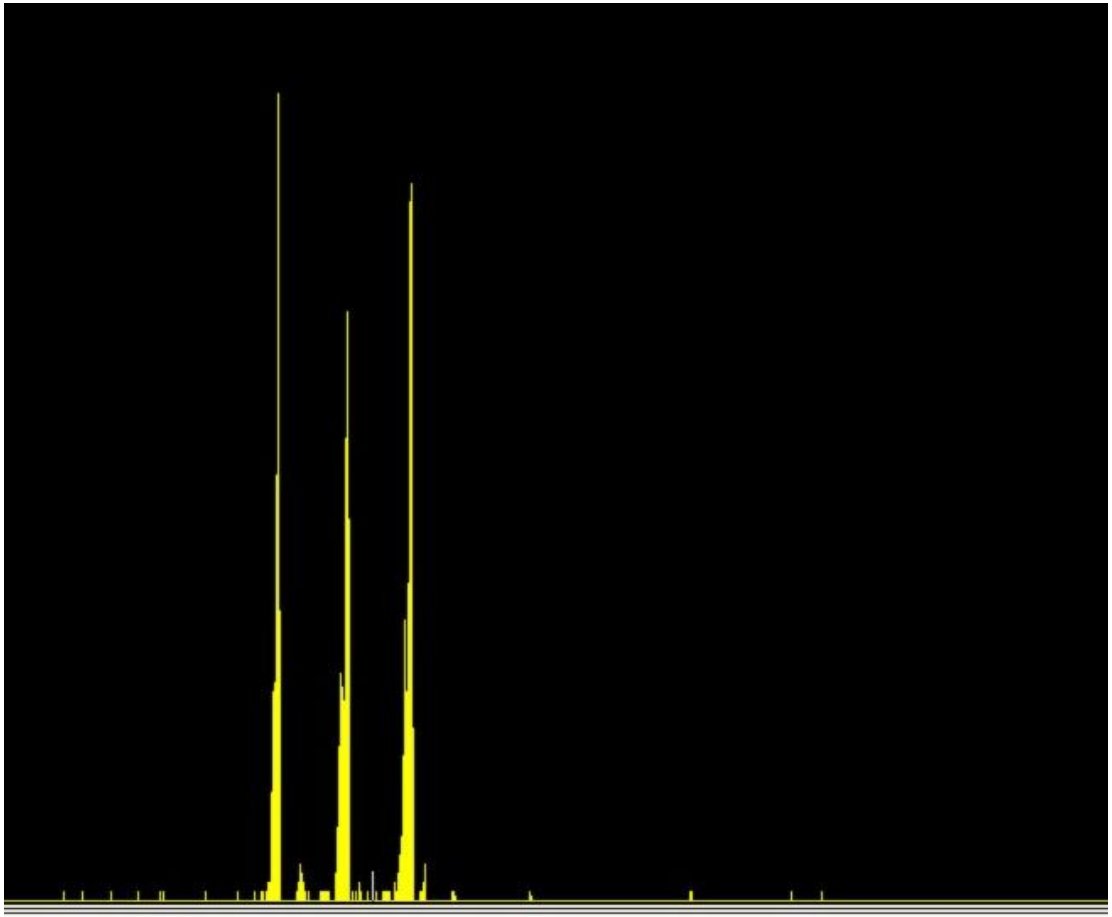
EPA 908.0 for Uranium Activity

- Precipitates Uranium with Ferric Hydroxide.
- Redissolve precipitate and pass through an anion exchange column.
- Strip with HCL.
- Convert to a nitrate system.
- Evaporate into a planchet.
- Count with a proportional counter.
- The method is not traced.
- Results are total U activity.

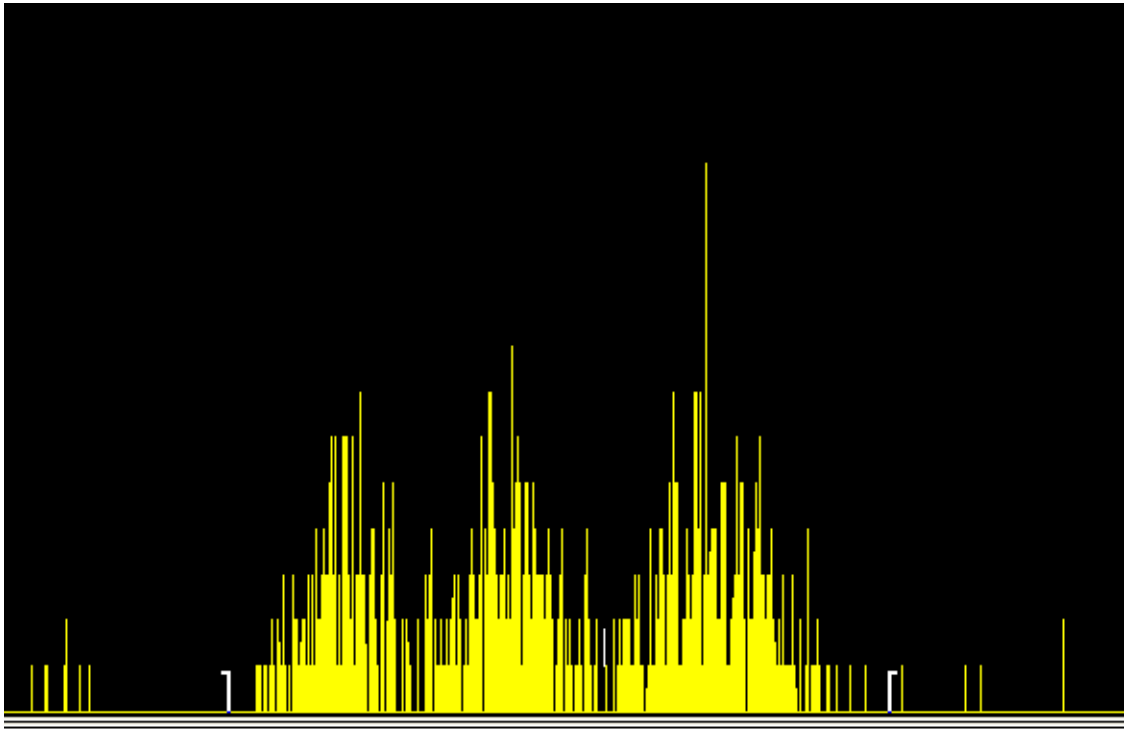
ASTM D6239

- Solvent extraction method using a (bis) 2-ethylehexyl hydrogen phosphate based extractive scintillator.
- Other natural chain radionuclides are chelated with DTPA prior to extraction leaving only the linear uranium ion visible to the extractant.
- Ascorbic acid is used to reduce Fe^{3+} to Fe^{2+}
- Counted on a PERALS spectrometer
- Traced with ^{232}U to determine recovery for each sample.
- $^{234}U/^{238}U$ isotopic ratios are easily determined from the alpha spectra.

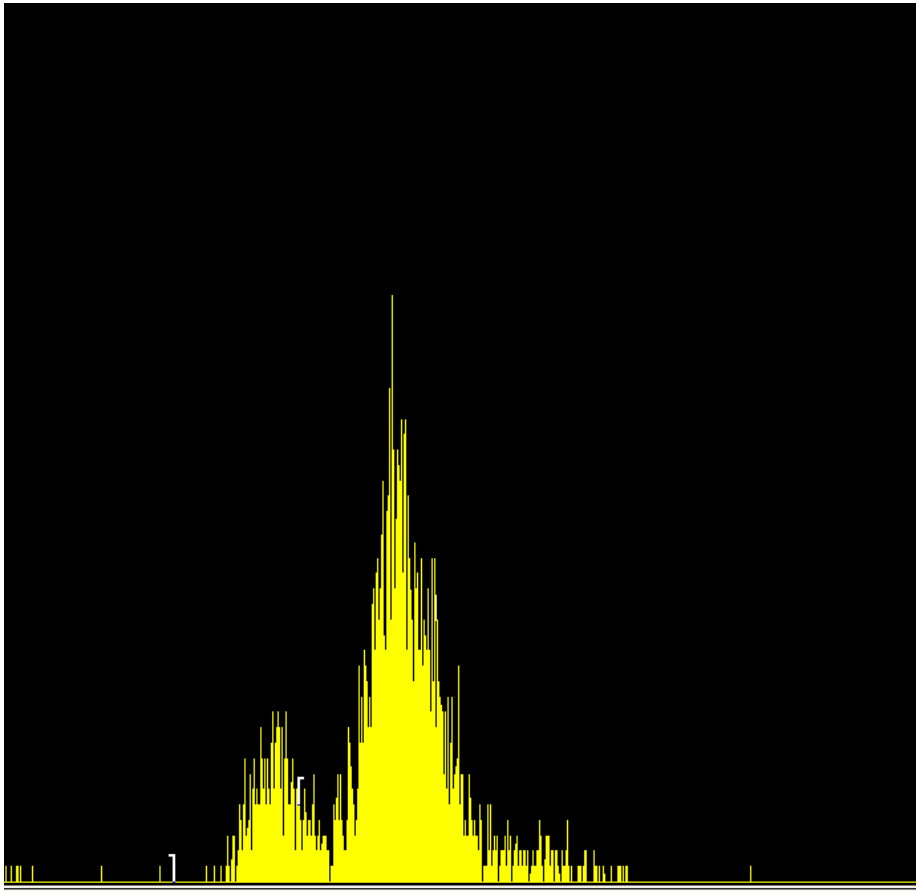
Alpha Spectrum of Natural Uranium



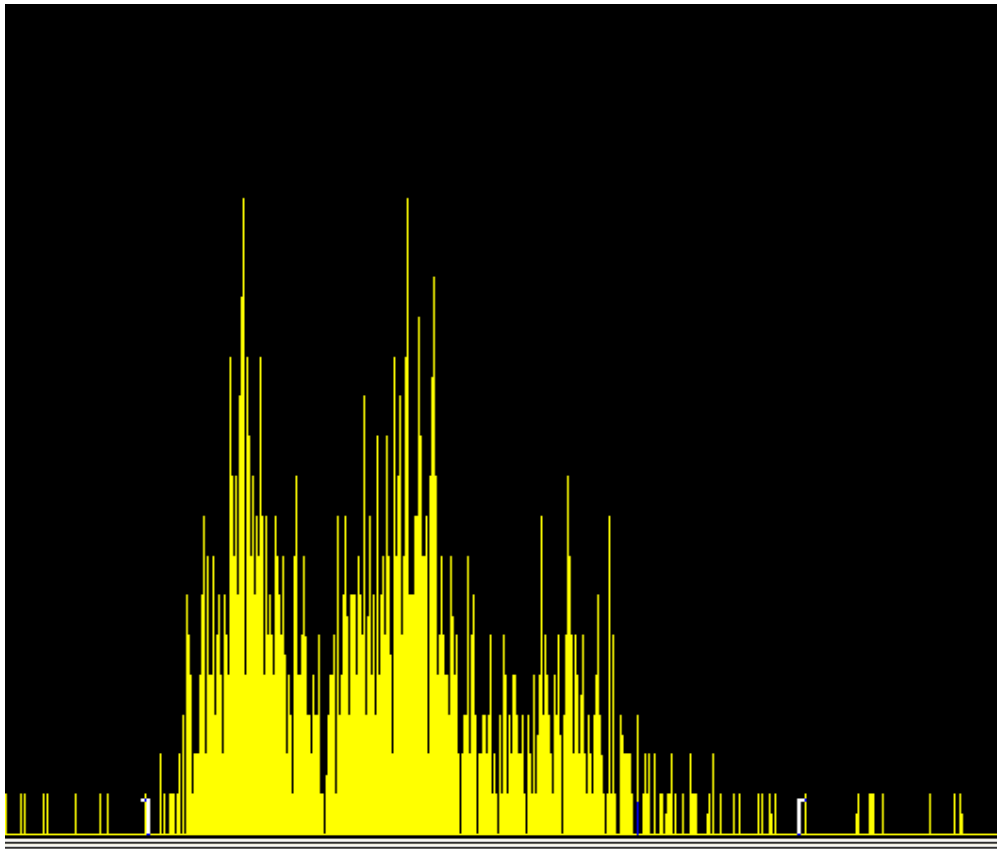
PERALS Spectrum of Natural Uranium



Uranium Disequilibrium Spectrum



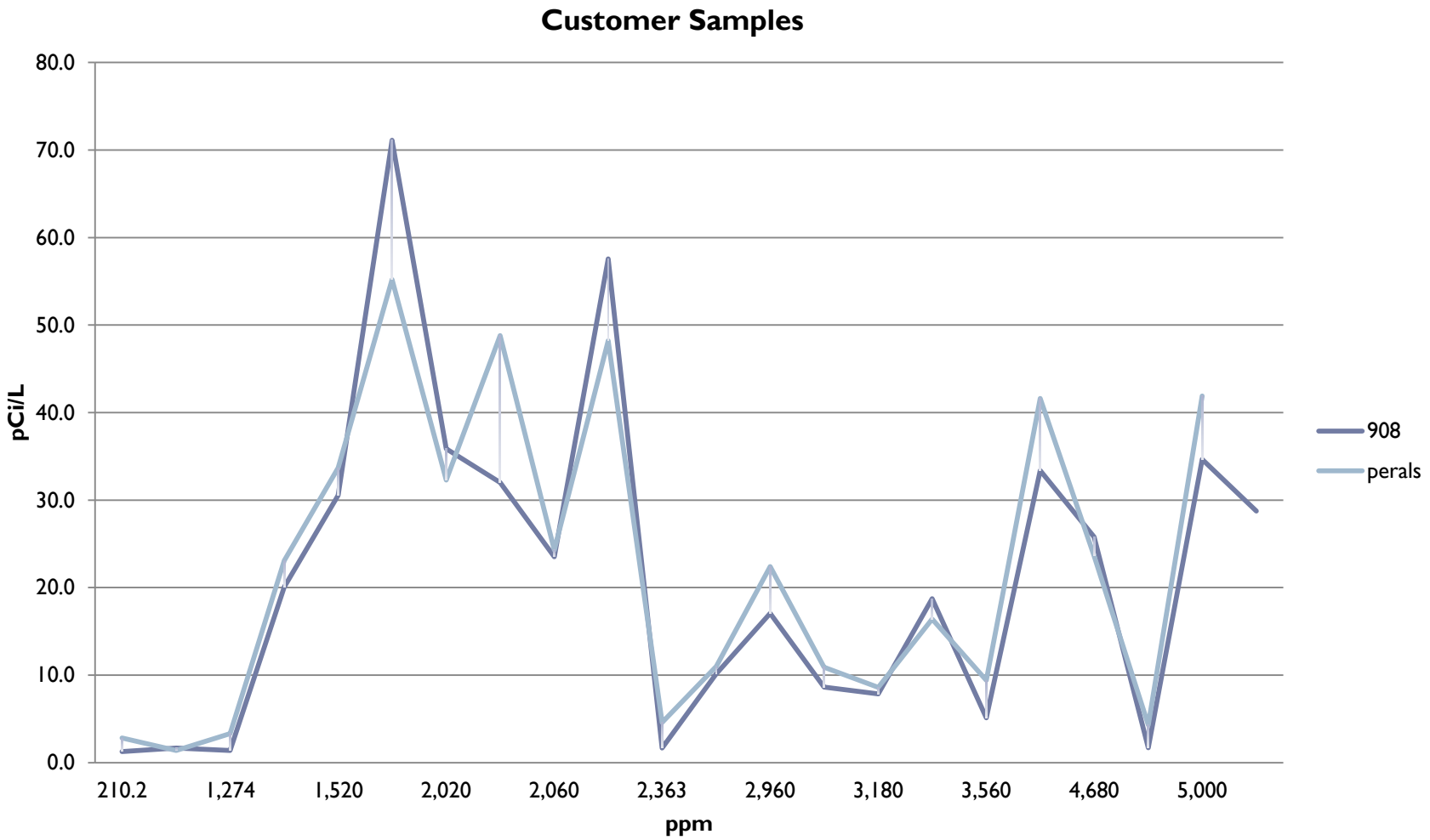
Equilibrium Uranium PERALS Spectrum



The Problem with 908 in Hard Waters

- Isolated hard water samples exhibited poor recoveries, resulting in an underestimate of the U concentration, and an abnormally high adjusted gross alpha.
- Since 908 is not traced, the failures were impossible to spot.
- Hypothesis: Unknown anions from hard water samples in mineralized areas saturated the anion column and the uranium broke through, resulting in low recoveries in isolated samples.

D6239 vs 908 as a Function of TDS



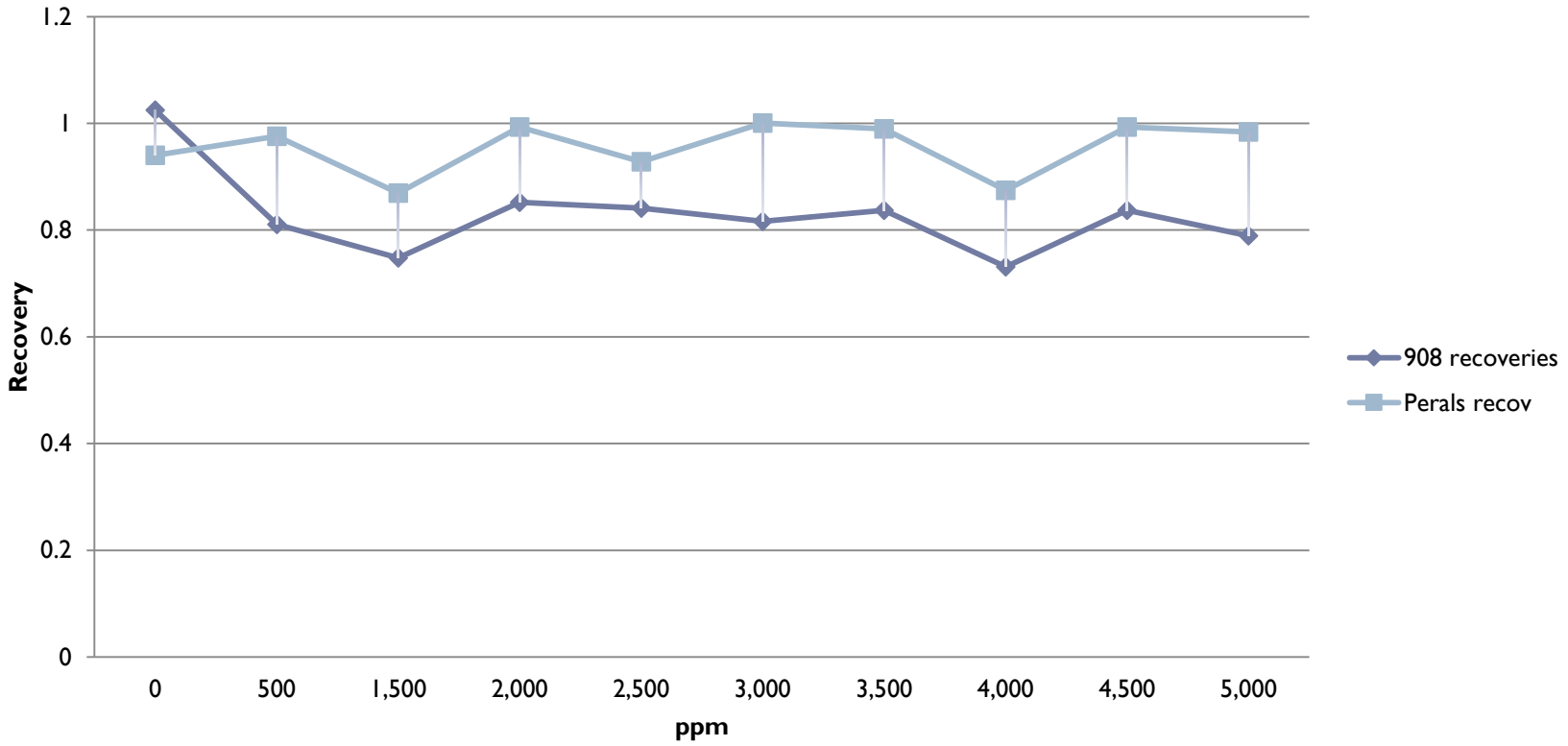
Method

- Attempt to find the component of the hard waters that was producing the abnormally low recoveries for the 908 method in isolated samples.
- Use a combination of split samples from various regions of the state and samples spiked with known quantities of cations and anions.
- Use the D6239 tracer to determine recoveries for both methods.
- Comparisons of mass estimates made from spectral analysis in D6239 to those made using the EPA assumed isotopic ratio were not performed.

Water Samples from Alluvial Fill

- Ground waters from the flat parts of Arizona (e.g. Phoenix and Tucson), are hard, but the total dissolved solids are primarily salts of calcium and magnesium.
- Water samples of various degrees of hardness were run by both methods and the percent recovery was plotted as a function of TDS.
- Both methods were shown to be quite robust across the entire range of solids concentrations.

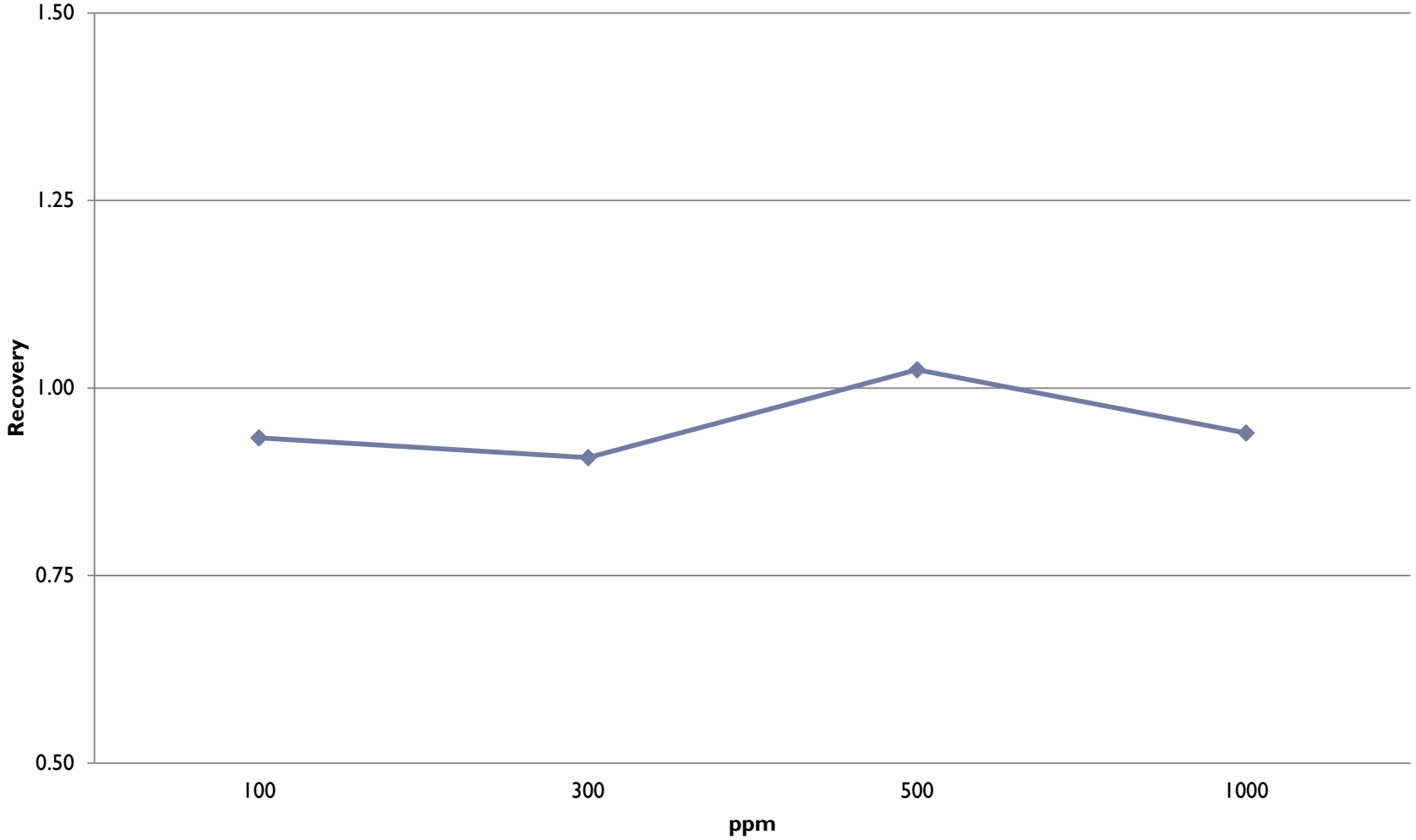
Recovery of D6239 vs 908 - Cations



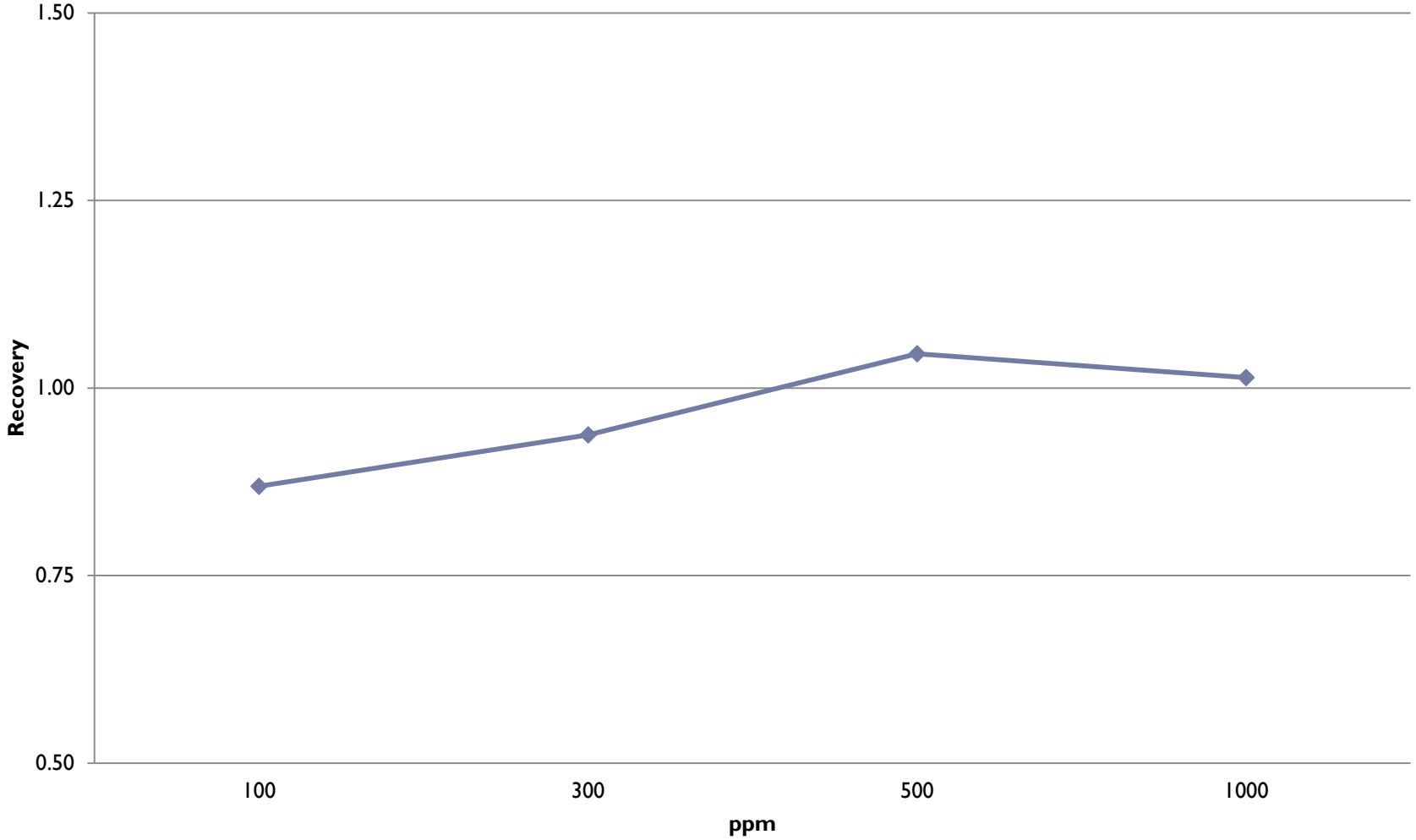
Results – D6239

- Both methods exhibited good recoveries from 200 through 5,000 ppm TDS.
- Recovery was easily determined from the ^{232}U tracer.
- There was good agreement with the gross alpha performed on the samples where Radium isotopes were not present (not shown).
- The aqueous/organic phase separation is slower at high TDS and sometimes needs to be centrifuged to get a clean layer. Note: we use a "safe" scintillator for our work; the xylene based scintillator (Alphaex) has a faster phase separation.

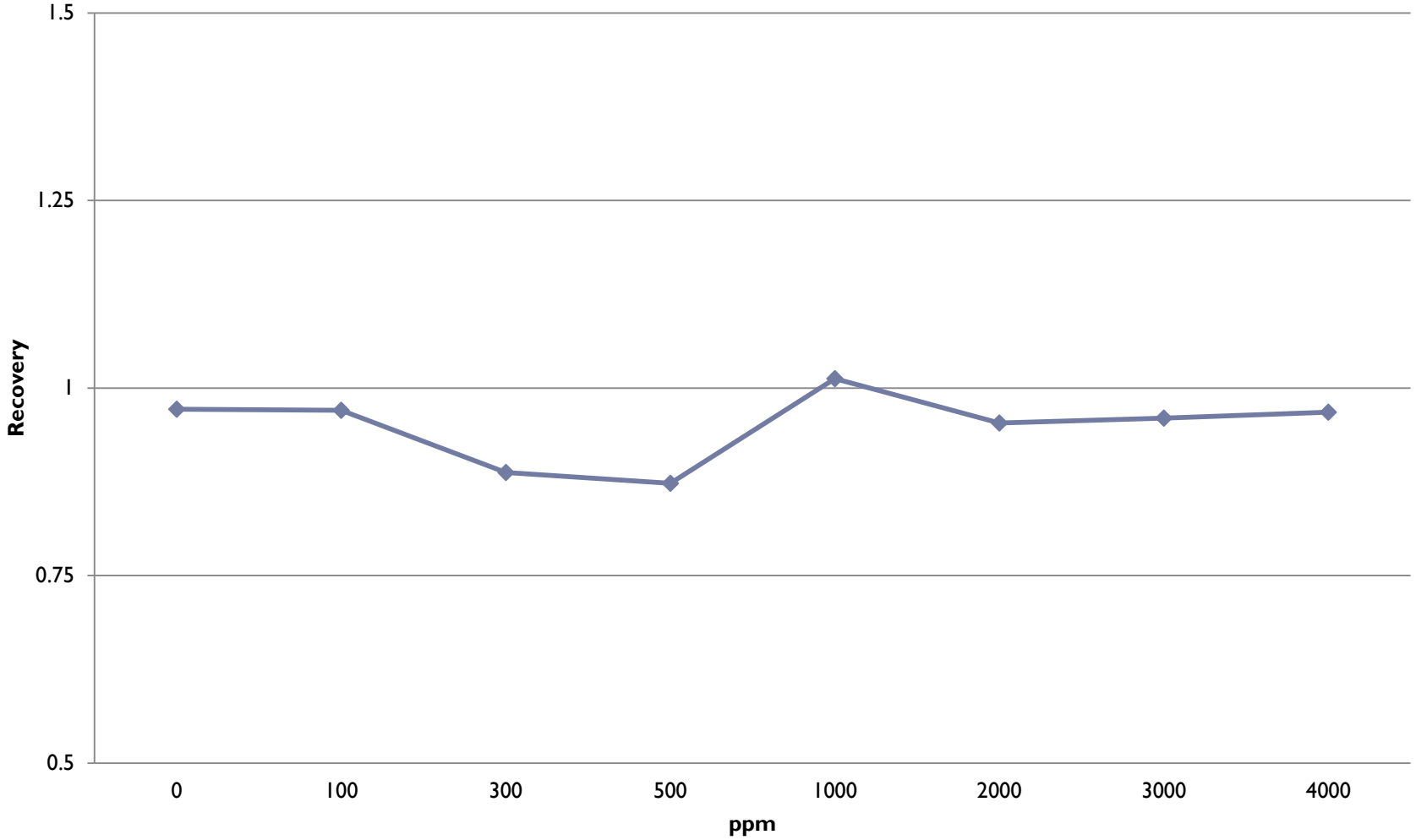
908 Recovery as a Function of TDS: Nitrite Anion



908 Recovery as a Function of TDS: Nitrate Anion

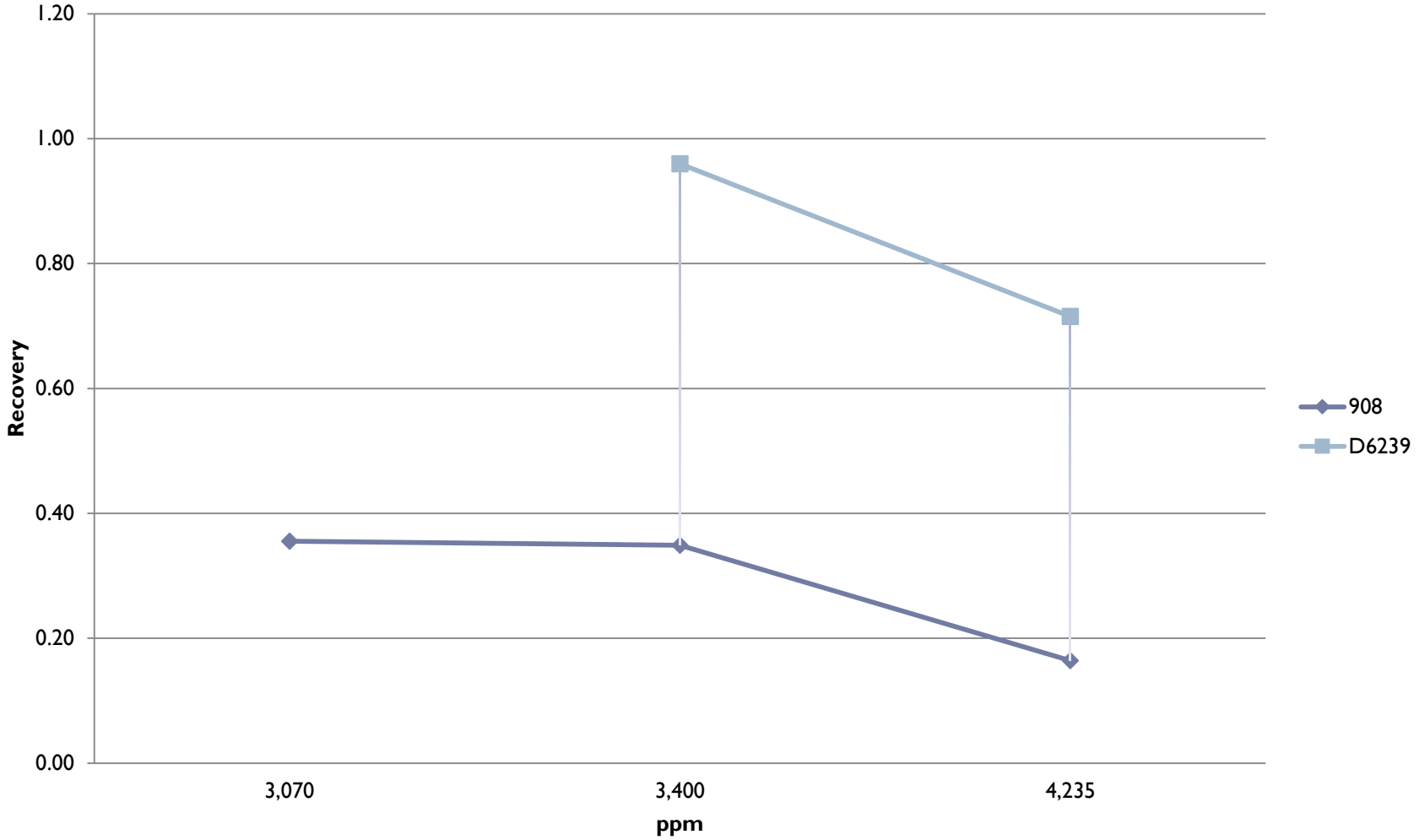


908 Recovery as a Function of TDS: Sulfite Anion



908 Recovery as a Function of TDS: Sulfate Anion

D6239 vs 908 Recoveries: Fe Cation



EPA 908.0 Results

- EPA 908.0 exhibited good recoveries for samples over a wide range of TDS comprised of both cations and anions. The hypothesized column breakthrough did not materialize.
- The observed failure of the method in random hard water samples was due to iron fouling of the anion resin.
- Iron is found in some water supplies both as an anion organo/iron complex which is removed from the solution by the resin, and in several cation forms.
- All will foul the resin and produce breakthrough of the uranium, resulting in a low recovery.