Difficulties with Accurately
Quantifying Radionuclide
Activities in Oil and Gas
Wastewater Utilizing Current
Methodology

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Topics to be Addressed

- Difficult and high total solids (TS) matrices
- Lower Limit of Detection
- Limitations of current EPA radiochemical methods
 - Gross Alpha (EPA 900.0)
 - Radium 228 (EPA 904.0)
- Dilutions to mitigate TS interference
 - Impacts of dilutions to results
 - Elevated lower limits of detection and measurement error



Topics to be Addressed

- Inter-Lab Study
 - Samples run for
 - Ra-228 via EPA 904.0
 - Ra-226 via EPA 903.1
 - Gross Alpha/Beta via EPA 900.0
 - Results and additional information of study
- Use of Gamma Spectroscopy for quantifying isotopes in high TS samples
- Questions



High TS Matrices

- Come from many sources
 - Oil and gas exploration and recovery
 - Uranium Mining and Milling
 - High saline waters
 - Produced water from hydraulic fracturing
- \bullet Have TS values > 5,000 mg/L
- Elevated TS can also impact sample preservation criteria



High TS Matrices

- Impacts on sample results
 - Inconsistent reproducibility
 - Elevated Lower Limits of Detection (LLD)
 - Elevated measurement error
 - May require significantly longer count times
 - Unstable reactions with the addition of acids
 - Data is heavily qualified
 - End user confusion with results



Common Types of Oil & Gas Samples with Elevated TS





Lower Limit of Detection (LLD)

The Lower Limit of Detection (LLD), as defined in NRC Regulatory Guide 4.14 Appendix, is "the smallest concentration of radioactive material sampled that has a 95% probability of being detected, with only a 5% probability of being undetected, with only a 5% probability that a blank sample will yield a response interpreted to mean that radioactive material is present."



LLD Equation (USNRC 4.14)

LLD pCi/L =
$$\frac{4.66 \text{ (S}_{b}) 1000}{2.22 \text{ (Eff) (V) (Y)}}$$

Where:

4.66 = critical value of confidence (USNRC)

 $S_b = STDEV$ of background

1000 = Conversion to liquid

 $2.22 = \overline{DPM/pCi}$

Eff = counting efficiency (counts per disintigration)

V = volume of sample (mL)

Y= fractional chemical yield (Barium and Yttrium, when applicable)



LLD cont.

- Ways to reduce the LLD include increasing any variable in the denominator
 - Volume
 - Efficiency
 - Count time included in denominator for other LLD equations
 - Chemical yield recovery included in denominator for other LLD equations



EPA Method Limitations — Gross Alpha EPA 900.0/9310

- Highly impacted by elevated TS
- Target of residue densities of 5mg/cm²
- Self attenuation of alpha particles
 - Large particles
 - Low energy
- Calibrations
 - Aimed at correcting for attenuations and calculating detector efficiency



High TS Gross Alpha Samples with ImL of Sample Volume



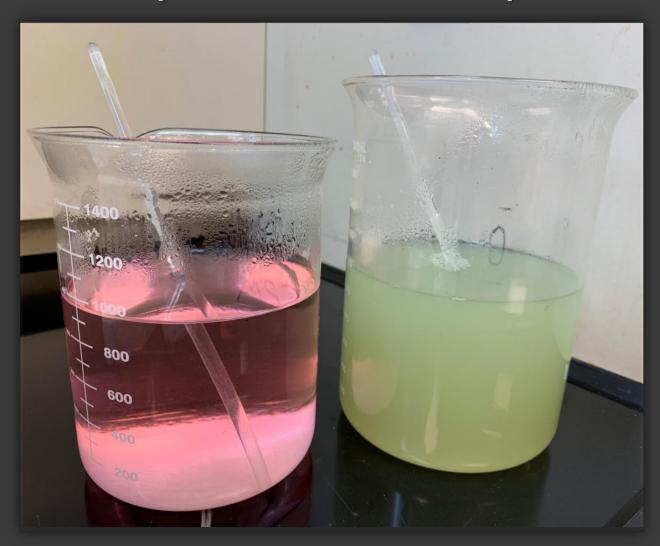


EPA Method Limitations – Radium-228 EPA 904.0/9320

- High TS samples require large dilutions
 - To achieve usable co-precipitation values for Yttrium and Barium carriers
 - To account for possible chemical reactions during sample prep addition of strong acids/bases
- Large dilutions, >10x, increase measurement error and may cause LLD's to be unusable
- Small sample volumes can cause reproducibility issues



Comparison of High TS Sample vs. Drinking Water Sample at Barium Precipitation Step



Sample Dilutions

- Most efficient way to reduce matrix interference
- Impacts measurement error
 - Can raise error due to lower sample volume
 - Increases Barium and Yttrium Recovery which reduces error
- Increases Lower Limit of Detections often significantly



Inter-Lab Study

- 15 labs participated in the study
- 3 O&G liquid samples from the Appalachian Basin were distributed to labs
- Samples analyzed for metals, cations, anions, Radium
- Goal was to evaluate quality of data and accuracy of measurements.
- Inter-lab Manuscript Information
 - Tasker, Travis L. et al. "Accuracy of methods for reporting inorganic element concentrations and radioactivity in oil and gas wastewaters from the Appalachian Basin, U.S. based on an inter-laboratory comparison." Environ. Sci.: Processes & Impacts, 2019,21, 224-241



Inter-Lab Study

- ACZ Labs participated in the inter-lab comparison on chemical characterization in 3
 O&G wastewaters and 4 solids
- Results in wastewaters for Ra-226 and Ra-228 showed activities at ± 50% and ± 30%, of the most probable value (MPV), respectively
- Results for Radium in solid matrices showed less variability, ±20% of MPV



What about Gamma Spec?

- Gamma Spectroscopy is a viable option for reducing impacts of high TS samples
 - Pros
 - Non destructive
 - Minimal interference from TS
 - Reproducible
 - No strong acids or bases used during prep
 - Cons
 - Long turn around times
 - Particular isotopes requiring >20 days of ingrow
 - o Long count times to achieve usable LLD's, >24hrs
 - Requires large lab spaces and several detectors to be commercially viable
 - Matching sample geometry



Conclusions

- High TS samples from the oil and gas industry pose issues with usable LLD's and reproducibility
- Diluting samples does help at the sacrifice of LLD's and measurement error
- EPA radiochemical methods need to be scrutinized when applied to high TS samples
- Gamma Spec is an option for reducing matrix interferences
- I believe more studies should be conducted on the viability of EPA methods to offer continuous accuracy when quantifying radionuclides



Questions?

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