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

Mark McNeal
QA/QC Coordinator
Radiochemistry Technical Director

ACZ LABORATORIES

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

ACZ LABORATORIES

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

ACZ LABORATORIES

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
- Have TS values > 5,000 mg/L
- Elevated TS can also impact sample preservation criteria

ACZ LABORATORIES

High TS Matrices

- Impacts on sample results
  - Inconsistent reproducibility
  - Elevated Lower Limits of Detection (LLD)
  - Elevated measurement error
  - May require longer significantly 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

ACZ LABORATORIES

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."

ACZ LABORATORIES

LLD Equation (USNRC 4.14)

$$\text{LLD pCi/L} = \frac{4.66\,(S_b)\,1000}{2.22\,(Eff)\,(V)\,(Y)}$$

Where:

4.66 = critcal value of confidence (USNRC)

S_b = STDEV of background

1000 = Conversion to liquid

2.22 = DPM/pCi

Eff = counting efficiency (counts per disintigration)

V = volume of sample (mL)

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

ACZ LABORATORIES

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

ACZ LABORATORIES

EPA Method Limitations – Gross Alpha EPA 900.0/9310

- Highly impacted by elevated TS
- Target of residue densities of $5 mg/cm^2$
- Self attenuation of alpha particles
  - Large particles
  - Low energy
- Calibrations
  - Aimed at correcting for attenuations and calculating detector efficiency

ACZ LABORATORIES

High TS Gross Alpha Samples with 1mL of Sample Volume

ACZ LABORATORIES

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

ACZ LABORATORIES

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

ACZ LABORATORIES

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

ACZ LABORATORIES

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

ACZ LABORATORIES

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
    - Long count times to achieve usable LLD's, >24hrs
    - Requires large lab spaces and several detectors to be commercially viable
    - Matching sample geometry

ACZ LABORATORIES

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

ACZ LABORATORIES

Questions?

My contact information:

Mark McNeal

Markm@acz.com

970-879-6590 x584

ACZ LABORATORIES