Analytical Challenges of Precise Ra Measurements in Brine

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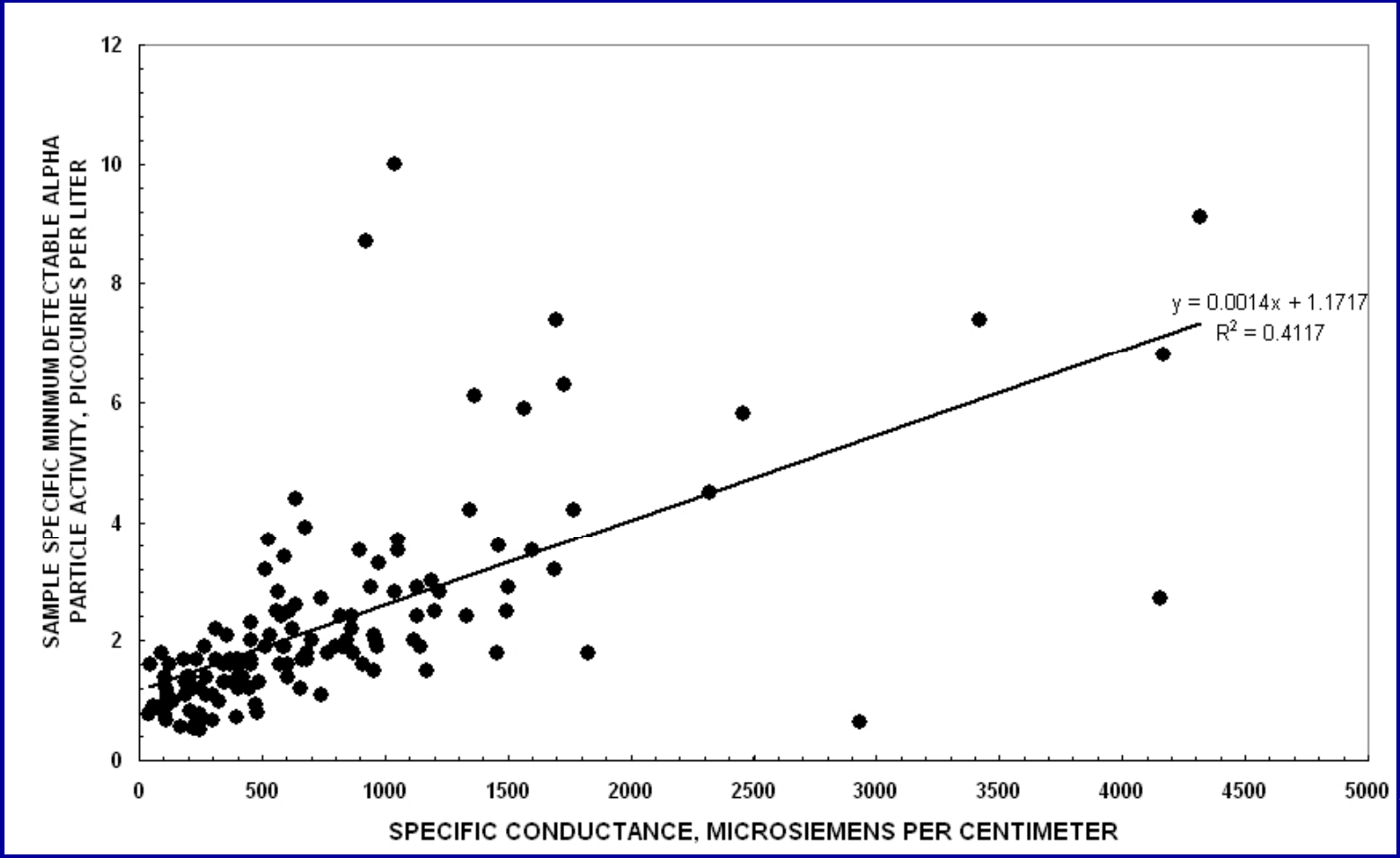
NORM in Produced Waters: Process-based studies need precise enough characterization of radionuclides that mechanisms of mobility and progressive changes can be determined

- Characterizing U, Ra, other isotope ratios and mixtures in the produced waters. What level of precision and detection capability is needed?
- To determine solely whether activity level is too high to be acceptable likely does not need high precision or detection capacity, at least at a “screening” level?
- For isotopic forensics for studying waste-products generation during the fracturing process, analyses require high precision and accuracy to study progressive changes
- Analytical challenges need to be overcome
- Build an Approach:
  - Evaluate and troubleshoot existing analytical methods
  - Identify matrix interferences and how they can be removed
  - Refine or modify analytical methods as needed

Notes of concern for using "indicators" for NORM in produced waters

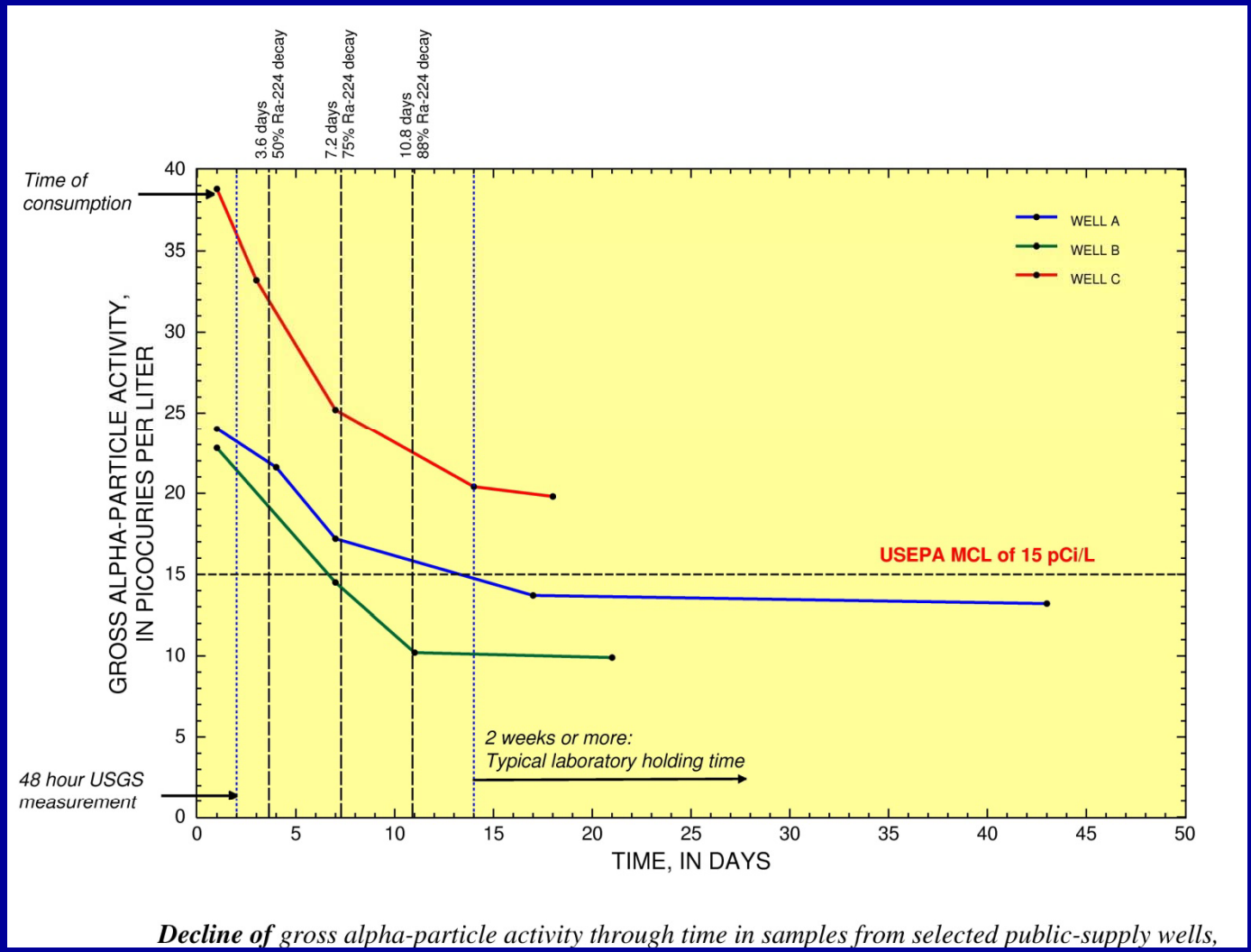
- Isotopic forensics required for comprehensive characterization of the wastes
- Once the nature of the isotope mixtures has been characterized by direct analyses, the more generalized gross gamma and alpha activity measurements may be enough (with care!) for screening purposes to indicate those drilling and waste products of concern.
- Characterize and monitor radionuclides in other wastes: pipe scale, sludges, salts. For workers or residents, might there be gamma exposure concerns? (Likely Yes). Gamma spectroscopy techniques ought to provide enough sensitivity for determining concentrations in these waste products of concern.

Detection of gross alpha is extremely limited in water with increasing TDS (or SC) as illustrated below for drinking water samples. Co-precipitation methods with dilution and/or some ion-exchange clean-up needed



Szabo et al., in review

NORM in produced waters: Isotope characterization is a must! Gross alpha varies considerably with time of measurement after sample collection on basis of mix of short-lived isotopes. Ra-224 occurrence is common, here see effect in drinking-water supply).



Decline of *gross alpha-particle activity through time in samples from selected public-supply wells,*

(Szabo et al in review)

Analyses for Ra with High Precision, Low MDC (Process based studies or precise verification needs)

- Radioactivity Counting
- -Radon emanation (Rn-em): Ra-226
- -Alpha spectrometry, direct or of progeny (AS): Ra-226, Ra-224, Ra-223
- -Gamma spectrometry (GS): All
- -Delayed Coincidence counting (DCC): All, mostly for Ra-223, Ra-224
- Atom (Mass) Counting
- -Thermal Ionization Mass Spectrometry (TIMS): Ra-226
- -Multiple Ion Counting Plasma Mass Spectrometry (MC-ICP-MS): Ra-226, possibly Ra-228

Precision, Background

$$\text{Activity} = \frac{\text{(Net (= Total-Background) counts/time)}}{\text{(Yield)(Volume)(Detector Efficiency)(Branching Factor)}}$$

Maximize total counts relative to background, yield, efficiency

For efficient laboratory operations: minimize time, volume

Minimize background plus matrix interference

Critical level (instrument response) is defined for a method based on a distribution of blank samples and a probability of Type I error (false detection).

Clean-up/Extraction necessary to remove interferences, and maintaining high yield is necessary. These need to be assessed independently of “blank” samples.

$$u_c^2(c_\alpha) = \frac{\left(N_S \times t_B^2 - N_B \times t_S^2\right)}{t_S^2 \times t_B^2 \times \varepsilon^2 \times V^2} + \frac{\left(\frac{N_S}{t_S} - \frac{N_B}{t_B}\right)}{\varepsilon^2 \times V^2} \times \left[\frac{u^2(\varepsilon)}{\varepsilon^2} + \frac{u^2(V)}{V^2}\right] \qquad (6)$$

Precision or Uncertainty

Net combined uncertainty becomes the square root of variances for the already considered terms; that is of Net Count rates (= Total-Background count rates), of Yield, Volume, and Detector Efficiency.

Atomic counting minimizes, relative to activity counting, variances in total counts by avoiding random radioactivity count errors. relative to background, yield, efficiency

Still need to minimize variances in background and efficiency. Still necessary to remove interferences and to maintaining high yield.

Barium (lead, strontium) sulfate co-precipitation

- Used typically with all counting techniques except DCC
- Poor yield with high Ca, Sr waters (problem, all techniques): needs ion-exchange and/or EDTA addition to supernatant
- Uneven crystal size and heterogeneous planchet distribution (problem, especially AS): seeding solutions, slow precipitation, Empore disk as precipitation surface
- Thorium interference (problem, especially GS): anion-exchange pretreatment
- For atomic counting, extraction is more difficult, usually requiring a carbonate matrix precipitation and anion- and cation-exchange resin purifications

Manganese Dioxide or Other Resin Extraction (usually completed directly in the field)

- Mostly used for DCC, but has been tested with success for all counting techniques
- Yield often estimated by comparing relative concentrations on successive resin cartridges
- Spiking directly of cartridges with Ra, Th isotope solutions added to cartridge with slow drip
- Acidic and reducing waters (deep brines?) are limited by the properties of the manganese oxide; Oxic and alkaline waters are optimal
- Isotope specific resins being developed are more expensive –yields from brines would still need to be demonstrated

Yield Monitoring

- Ba-133 for any sulfate salt co-precipitate counted by Gamma-spectroscopy

-Decreased yield with high Ca, Sr waters; also divergent from Ra yield in such waters

- Ra-228 and Th-229 tracers for Ra-226 and Th-228 for atom counting (TIMS, MC-ICP-MS)

-Ba interference: no easy fix

-organic compounds could be especially a problem for the brines; needs additional periods of thermal degassing for TIMS

Challenges for Precise Radium Analysis in Brine

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For detailed evaluation of changes in radionuclide concentrations and isotopic ratios for studying waste-products generation during the fracturing process, analyses require high precision and accuracy to study progressive changes. For high precision determinations of the concentrations of Ra-226 with low minimum critical detection levels (MDLs), the most commonly used technique is the USEPA-approved (Method 903.1) radon (Rn) de-emanation technique, with scintillation counting of the Rn-222 progeny after cold-trapping on charcoal. Alpha spectrometry has become increasingly commonly used to determine concentrations of Ra-226 and Ra-224. A 100-minute count for a 1 L (liter) sample is typically long enough to achieve detection of 1 pCi/L or less for aliquots with simple matrices. Spectral analysis can also explicitly include short-lived progeny for verification and improved quantification (example, polonium-216 progeny for Ra-224). The gamma-spectrometric analytical technique (Standard Method 7500-E of the American Public Health Association, 2005) has become more commonly used, though it has a precision and MDL that is higher by factors of 2 to 5 times that of the alpha-spectrometry technique using reasonable operating parameters. The strong benefit of the technique is that it can determine all four of the naturally occurring Ra isotopes, but the background gamma count cannot be maintained at levels as low as those achievable for measurements of alpha particles, thus is also more imprecise under comparable optimal operating conditions. The counting time required for alpha-spectrometric or Rn de-emanation technique is shorter (60 or 100 minutes as opposed to 1000 minutes), the sample volume required for achieving low MDL is smaller (1 L as opposed to 4 to 20 L), and the instrumentation is less bulky and expensive than that required for gamma-spectrometric determination. Delayed coincidence counting has also allowed for an increase in precision and level of detection for multiple isotopes at once.

Multiple-counting inductively coupled plasma mass spectrometry (MC-ICP-MS) and thermal ionization mass spectrometry (TIMS) for U and Th isotopes and for Ra-226 have increased the level of available precision and detection substantially. The limitation to these atom-counting techniques remains the ability to effectively extract and purify the isotopes from brine. One option in using TIMS is once the Ra-226 is precisely quantified, other techniques such as gamma spectroscopy that define the ratios of Ra isotopes relative to each other can be used on remaining sample aliquots to provide a reasonable estimation of the other Ra isotope levels.

Extraction, purification, and pre-concentration along with successful yield monitoring are critical steps in achieving low detection levels and high precision. Chemical separation by forming a Ba-Ra-sulfate precipitate is most commonly used to extract Ra isotopes from sample

aliquots for Ra-226 and Ra-224 analyses by the Rn de-emanation technique, by alpha spectrometry, and by gamma spectroscopy. Cation-exchange chromatography (Bio-Rad AG 50W-X8 resin) is typically used to first separate the Ra and Ba, which are then eluted with 8-molar HNO_3, and are co-precipitated with barite using a seeding suspension. The seeding suspension is needed to ensure the formation of uniform fine-grained crystals of the barite that is required for efficient counting by alpha spectrometry, which is most sensitive of the techniques to variable geometry of the Ra-bearing precipitate crystals. Experimentation is ongoing with forming the precipitate on Sr-specific resin filter plates. Using a bed of previously precipitated microcrystalline barite as the seeding agent has also been tried to improve the precipitate formation. A widely used approach is to improve barium-specific precipitation performance by using ethylenediaminetetraacetic acid **(**EDTA) as a complexing agent to limit co-precipitation of impurities. The Ra isotopes can also be extracted using Mn-coated fibers (prepared in various forms: in tubes, filters, or disks). Oxic and alkaline waters are optimal for use with the Mn-coated fibers, however, in acidic and especially in reducing waters such as might be encountered in deep brines extraction efficiency is limited by the properties of manganese oxide. Numerous element-specific resins have been developed for Ra, Pb, U, Th that may allow for efficient extraction of the target radionuclide from briney solution. The issue is cost, as the more specialized extraction resins are expensive.

A radioactive tracer (Ba-133) is added to the samples during precipitation of the Ra-bearing barium sulfate to determine yield. The Ba-133 is analyzed by gamma spectroscopy after sample purification. The Ba-133 tracer on occasion exhibits variable and low recoveries in Ca- and Sr-rich waters, and in these cases, may not match Ra recovery quantitatively; thereby, cation-exchange removal or EDTA-complexing of the competing divalent cations is helpful. For atom counting techniques, a mixture containing Ra-228 and Th-229 can be added to monitor recovery of Ra-226 and Th-228. The use of these tracers more precisely quantify Ra yield, which is appropriate for the more precise measurements possible with atom counting as opposed to activity counting techniques. Organic compounds provide interference for TIMS analysis, Ba for MC-ICP-MS analysis, and Th-228 interferes with yield tracing with Ra-228; of these, limiting Ba poses the greatest challenge. The MDLs and precision for all analysis types are influenced by dilution, interference effects, temperature or pressure that need to be understood and minimized.