Measurement of Gross Alpha: Application, Interpretation and New Method Options

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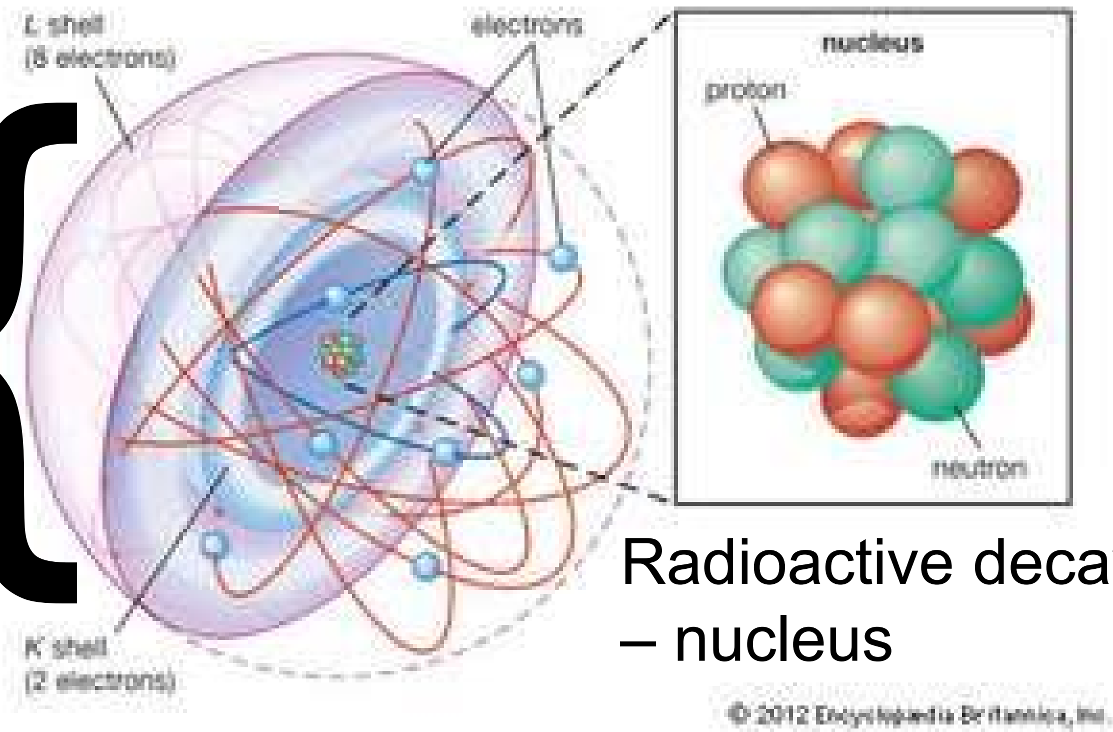
Some fundamentals

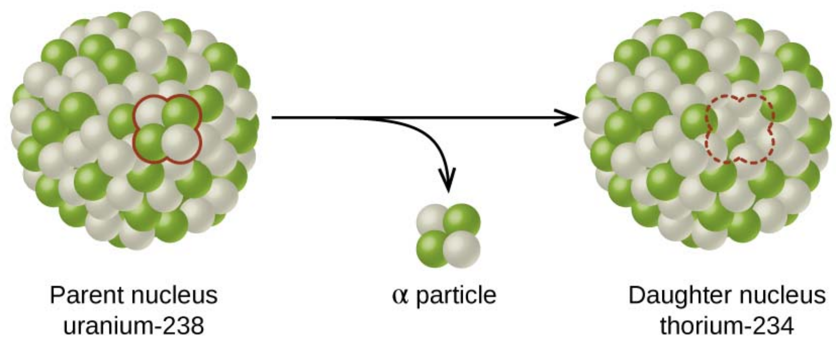
Chemical bonding/breaking/ ionic interactions – electron shells



Radioactive decay – nucleus

Some fundamentals

- All elements above atomic number 83 (bismuth) are radioactive
- Release of alpha particle (helium nucleus) results in a decay product with reduced atomic number (-2) and mass (-4).



Source: opentextbc.ca

Some fundamentals

- Activity ~ degree of radioactivity = decays/time
  - picocurie, pCi = 2.22 disintegrations/min
  - becquerel, Bq = 27.03 pCi

- Half-life ($t_{1/2}$) = time it takes the number of radioactive atoms to be reduced to one-half the original amount
  - Each radioactive isotope has its own characteristic half-life

- Activity is inversely proportional to half-life

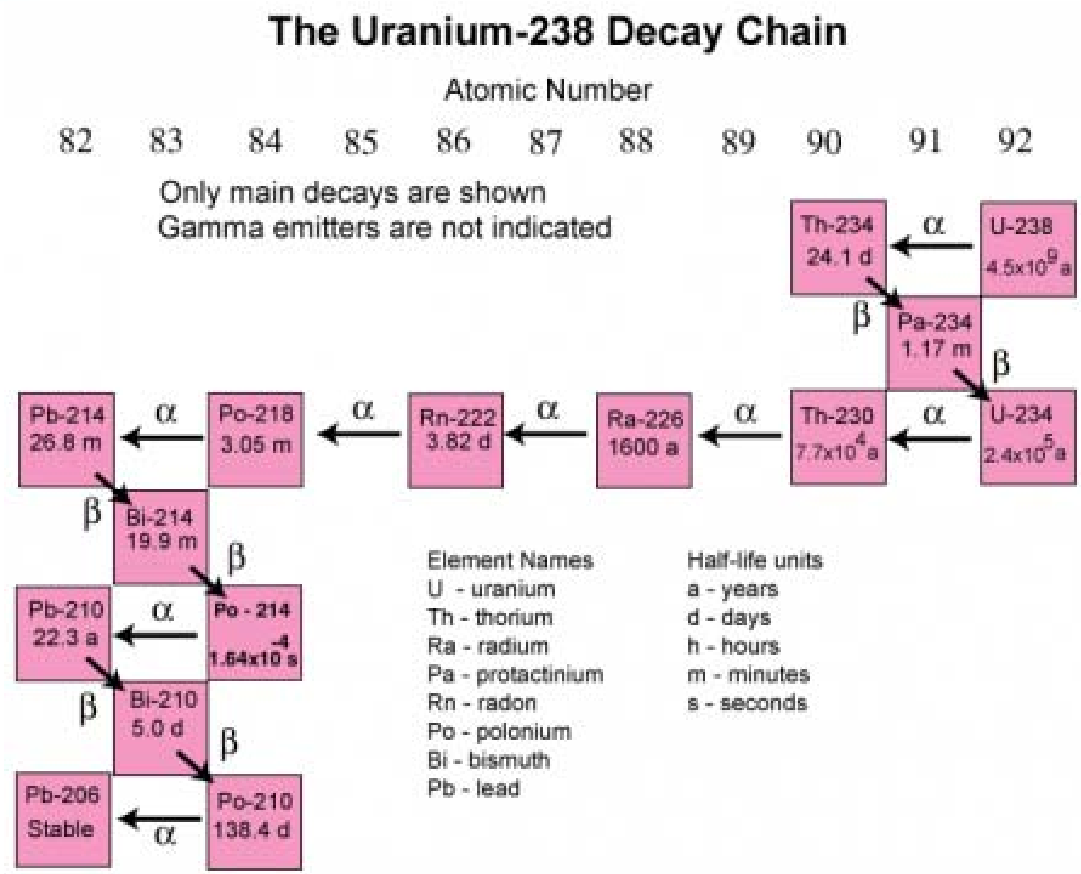
  Shorter half-life means higher activity

Background

- Many groundwaters contain measurable amounts of naturally occurring alpha particle-emitting radionuclides
- Gross alpha analysis provides a measurement estimate of alpha particle activity
- Gross alpha analysis cannot discriminate among all possible alpha emitters or their energies

Background: Decay Chains

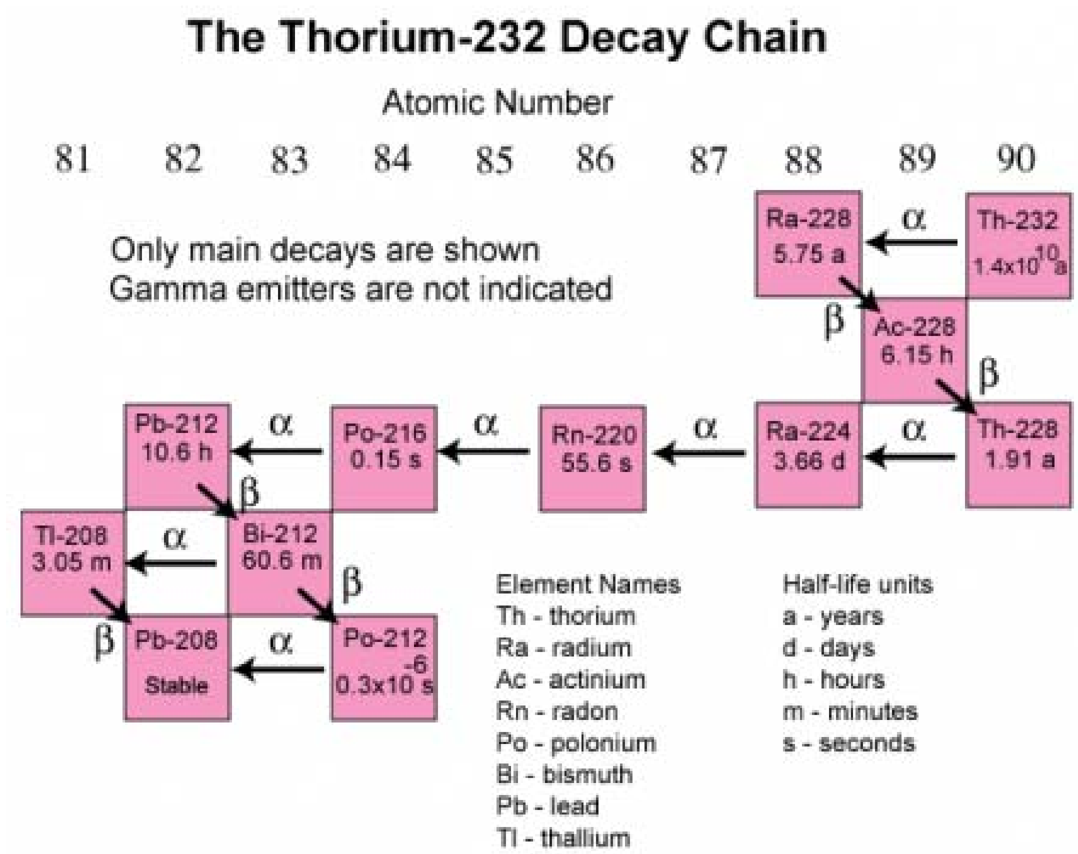
Most naturally occurring alpha emitters arise from two decay chains. Uranium-238 decay chain includes U-238, U-234, Th-230, Ra-226, Rn-222, Po-218, Po-214, Po-210



Source: U.S. Geological Survey (USGS)

Background: Decay Chains

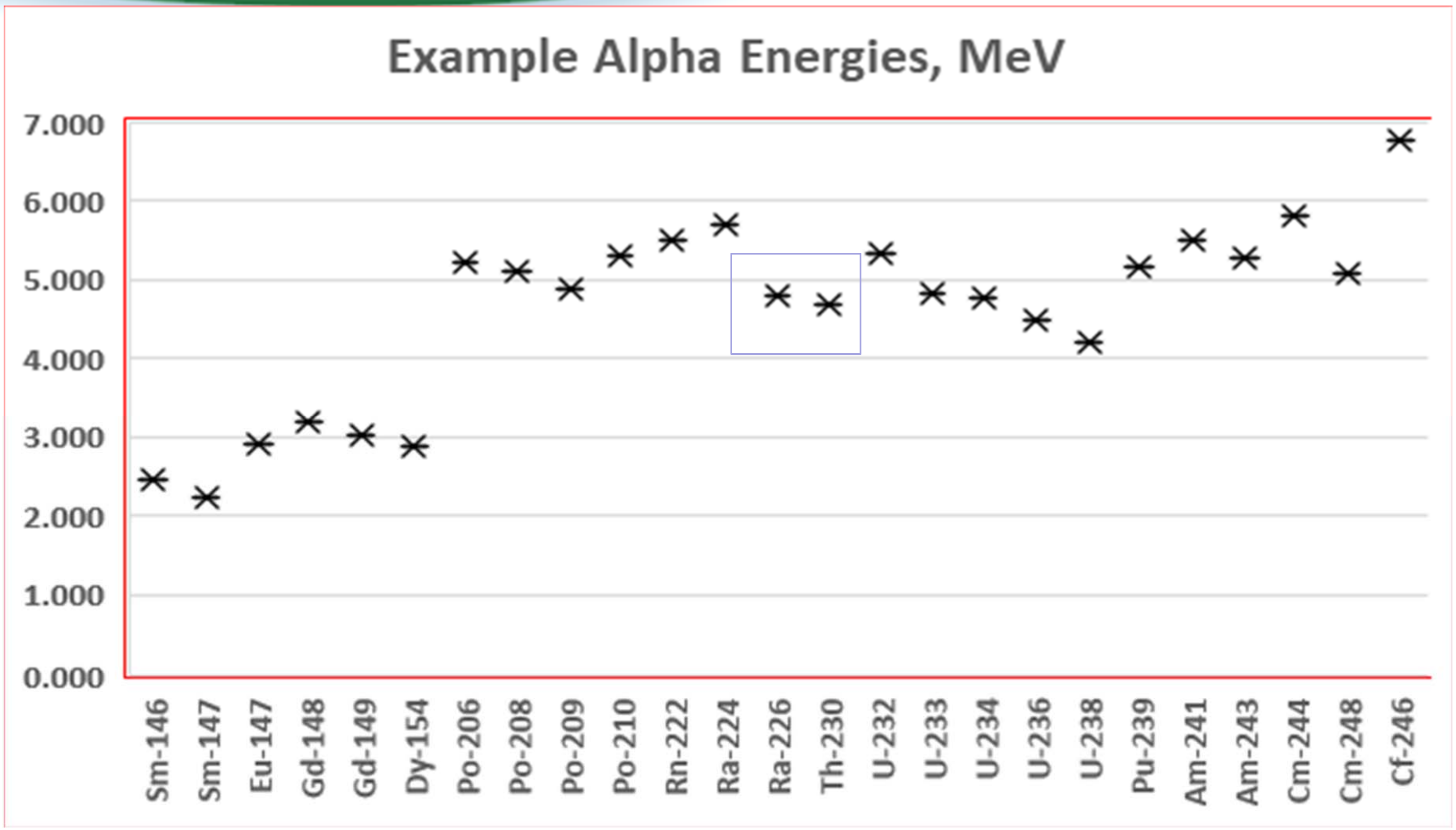
The Thorium-232 decay chain includes Th-232, (Ra-228 a beta-emitter), Th-228, Ra-224, Rn-220, Po-216, Bi-212, Po-212



Source: U.S. Geological Survey (USGS)

Assumptions

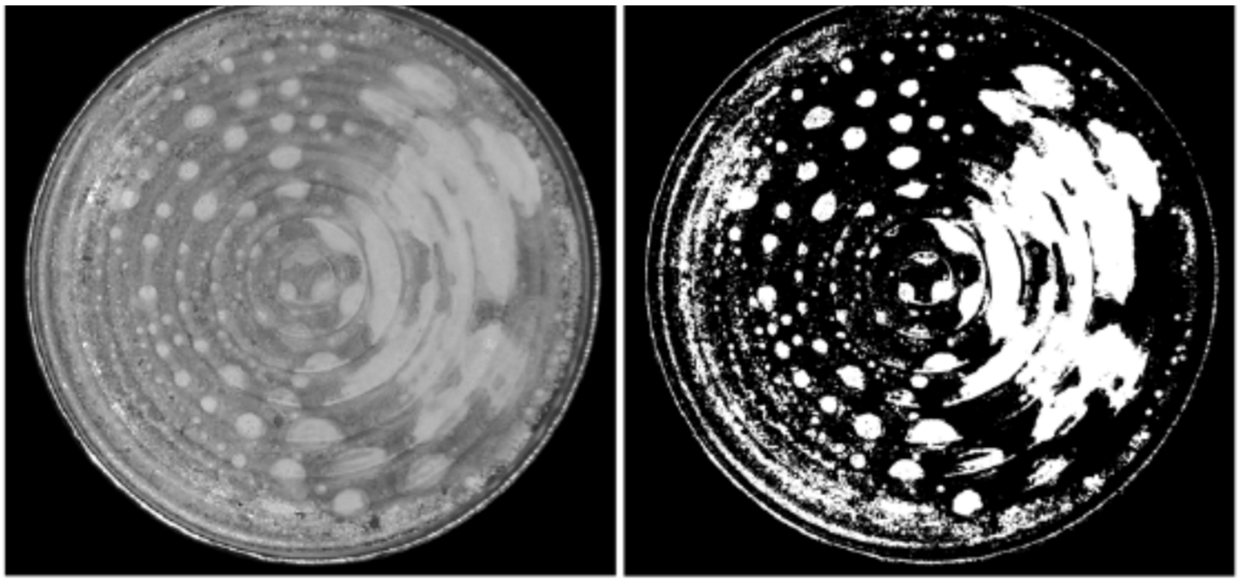
- Cannot calibrate detector for every possible alpha particle emitter
  - Calibrate with a "reference radionuclide"
  - Approved drinking water reference radionuclides (40 CFR 141.25(a))
    - Gross alpha evaporation methods (e.g. EPA Method 900.0): Th-230, U-nat (not Am-241)
    - Gross alpha co-precipitation methods (e.g. Standard Method 7110 C): Th-230, U-nat, and Am-241
- Gross alpha analysis implicitly assumes that all alpha particle emitters are detected with the same efficiency as the reference radionuclide.



MeV: Mega-electron volts

Limitations - Geometry

- Geometry is critical!



Source: Arndt and West. 2007. *Health Physics*, 92, 148-156

Limitations - Geometry

- Consistent preparation of uniform sample residues is key!
  - Alpha particle energy emission reduced by any kind of barrier
  - Good sensitivity only possible at low total solids levels
    - Limited to samples that yield < 100 mg solid residue in a 20 cm^2 counting planchet (i.e. < 5 mg/ cm^2)
  - “Patchy” residues inhibit alpha particle energy emission more than uniform residues
  - Emissions from center of planchet are more likely to be captured by detector than those from edges

Gross Alpha Variability – Timing Events

When is the best time to count? Depends on what you want to know!

- Radium-224 (half-life 3.66 days)
  - Samples containing radium-228 activity can contain comparable radium-224 activity at the time of collection (remember the thorium-232 decay chain – radium-224 is one of the progeny of radium-228)
  - Radium-224 produces four short-lived alpha particle emitters: Rn-220, Po-216, Bi-220, and Po-212
  - Radium-224 activity is rarely determined (except in some states), but if a sample is prepared and counted within one week of collection, radium-224 and its progeny can have a significant impact on gross alpha activity
  - If radium-224 contribution to gross alpha activity is not required by your state, hold samples 2-3 weeks before preparing/counting to allow radium-224 and its progeny to decay away.

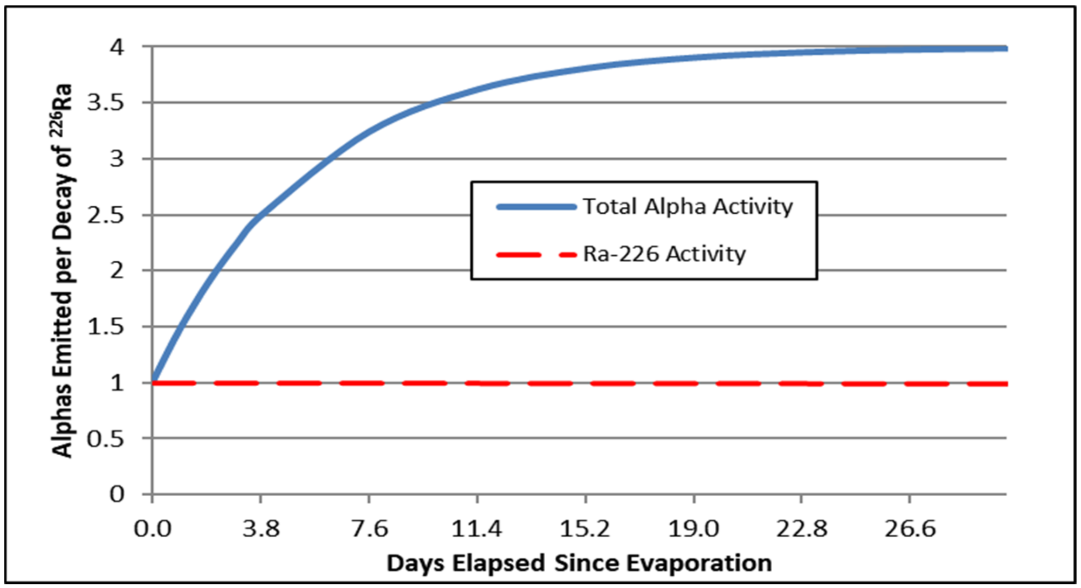
Gross Alpha Variability – Timing Events

40 CFR 141.66(c): Gross alpha particle activity MCL is 15 pCi/L (including radium-226, but excluding radon and uranium)

- Screen water samples for radium-226 at levels that may exceed the combined radium MCL of 5 pCi/L
- The most accurate screening for radium-226: delay sample preparation for 2-3 weeks (allow radium-224 and progeny to decay), then prepare and count *right away*.
- If radium-226 is present in a sample, the time between sample preparation and counting can significantly impact gross alpha. Why? Radon!
- Radon is removed when the sample is prepared. But sample residue forms a thin film. As radium-226 decays, radon-222 is formed and trapped in the solid residue.

Gross Alpha Variability – Timing Events

As radon-222 and its short-lived alpha-emitting progeny polonium-218 and polonium-214 build up within the prepared evaporated sample, alpha activity increases. In 3-4 weeks after sample preparation, activity quadruples!



Eaton and Shannon. 2015. AWWA. Radionuclide Rule Compliance: Utility Guidance on Analytical Methods

Gross Alpha Variability – Timing Events

EPA Method 900.0, Sect. 8.4: After drying (the sample) "alpha counting should be delayed at least 72 hours until equilibrium has occurred." No consensus on what 'equilibrium' means.

If radium-226 is present (and radium-224 is not considered), 72 hours allows two things to happen:

- When sample is prepared, radon-222 is removed but alpha-emitting progeny remain. Decay of the unsupported progeny will occur within ~ 8 hours
- Partial ingrowth of radon-222 and its supported progeny from radium-226 begins

Specifying that prepared samples be held at least 72 hours can result in inter-laboratory inconsistencies. Consider what happens if one lab counts after 72 hours and another lab waits a week or two.

What's with Gross Alpha and Uranium?

- Uranium is regulated as a heavy metal (MCL = 30 µg/L), but it is also an alpha particle-emitting radionuclide
- Radionuclide Rule specifies conversion factor of 0.67 pCi/µg to convert uranium mass concentration in µg/L to an <u>estimated</u> activity concentration in pCi/L
  - 0.67 pCi/µg based on activity ratio in uranium-bearing minerals (not water)
  - Yields a <u>conservative</u> estimation of uranium activity from a public health protection standpoint, i.e. calculated uranium alpha emission activity will be biased low, resulting in a higher adjusted gross alpha (gross alpha minus uranium contribution)
  - If adjusted gross alpha based on converting uranium mass to activity exceeds 15 pCi/L MCL, determine a more accurate uranium activity using a radiochemical method (e.g. alpha spectrometry)

What's Being Done to Reduce Gross Alpha Variability?

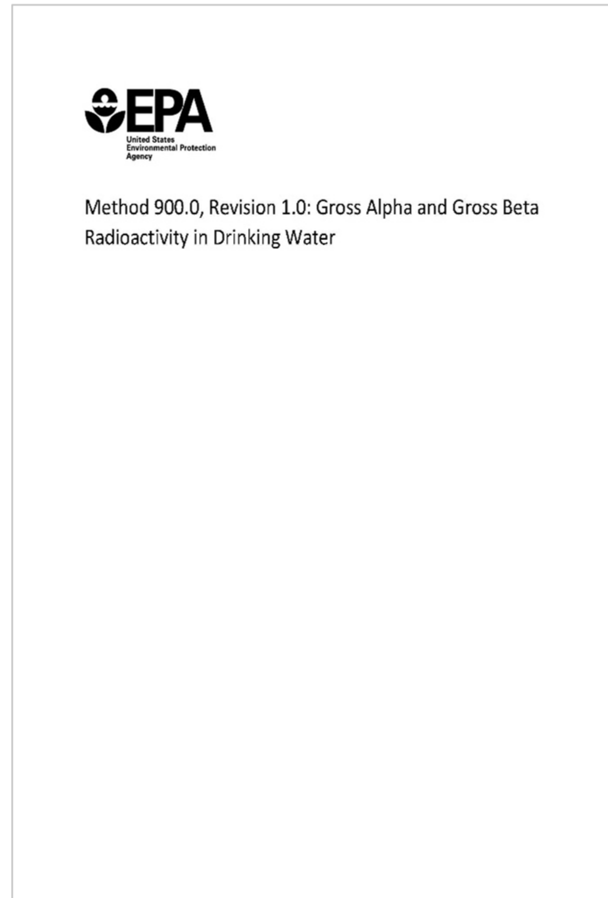
- Still a screening method and some limitations will exist (e.g. calibration reference radionuclide)

- But variability in some factors can be controlled:
  - Revising the 900-Series EPA Methods
  - Approving new methodologies for gross alpha analysis

EPA Method 900.0, Rev. 1.0 (Feb. 2018)

EPA Doc. 815-B-18-002; Approved Oct. 12, 2018 (83 FR 51636)

- Updated for simultaneous alpha/beta counting and addresses spillover (crosstalk)
- Details efficiency calibration and QC specifications
- Details the importance of timing events and removes the minimum 72-hour hold time between sample preparation and counting


EPA
United States Environmental Protection Agency

Method 900.0, Revision 1.0: Gross Alpha and Gross Beta Radioactivity in Drinking Water

ASTM D7283-17 and Standard Method 7110 D-17

Approved July 27, 2017 (82 FR 34861)

- Gross alpha and gross beta by liquid scintillation counting (LSC)
  - Simultaneous alpha/beta counting with pulse height discrimination
  - Consensus organizations followed the EPA Drinking Water Radiochemistry Alternate Test Procedure (ATP) Protocol to set up multi-lab validation study, QC and acceptance criteria
  - Newer scintillation cocktails provide homogeneous sample dissolution
    - Minimizes matrix solids effects
    - LSC provides higher detection efficiencies

SDWA Radionuclide Detection Limit

EPA Doc. 815-B-17-003; Published April 2017

- DL defined at 40 CFR 141.25(c)
- SDWA DL ≠ MDA, MDC or MDL
- Derives equation for reporting:

$$DL = \frac{\frac{1.96^2}{2t_s} \times \left[1 + \sqrt{1 + \frac{4t_s^2}{1.96^2} \times B \times \left(\frac{1}{t_s} + \frac{1}{t_B}\right)}\right]}{\varepsilon \times V \times 2.22}$$

Summary

- Several sources of variability can bias gross alpha results:
  - Reference radionuclide used for calibration
  - Different energies of alpha emitters
  - Uniformity of prepared sample residues
  - Timing intervals between collection and preparation of sample, and between preparation and counting of sample
- Improving consistency through new methods:
  - Current analytical technology
  - Quality control criteria
  - Clearly discuss the importance of timing events

References for Help

- Approved analytical drinking water methods https://www.epa.gov/dwanalyticalmethods/approved-drinking-water-analytical-methods.
  - Select Radionuclides
  - Table of approved methods with links to the approved versions (including EPA Method 900.0, Rev. 1.0). Table is current as of April 2019
- Radionuclide DL document and radiochemistry training modules https://www.epa.gov/dwlabcert.
  - Under "Certification, Monitoring and Analysis Requirements" select the Procedure for Safe Drinking Water Act Program Detection Limits for Radionuclides
  - Under "Certification Process and Training" select Radiochemistry Training for Drinking Water Compliance

Questions

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