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Development of Rapid Radiochemical Method for Gross Alpha and Gross Beta Activity Concentration in Flowback and Produced Waters from Hydraulic Fracturing Operations

R E S E A R C H   A N D   D E V E L O P M E N T

Validation of Rapid Radiochemical Method for Gross Alpha and Gross Beta Activity Concentration in Flowback and Produced Waters from Hydraulic Fracturing Operations

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Acronyms, Abbreviations, Units, and Symbols

AAL ....analytical action level

ACS...............American Chemical Society

APS ....analytical protocol specification

Bq..................becquerel

CL_{NC} ....critical net concentration

CSU...............combined standard uncertainty

Ci...................curie

d....................day

EPA...............U.S. Environmental Protection Agency

ESD...............Environmental Sciences Division

FPWHFO… ...Flowback and Produced Waters from Hydraulic Fracturing Operations

g....................gram

GPC...............gas-flow proportional counter

h....................hour

ID ....[identifier] [identification number]

L ....liter

LCS ....laboratory control sample

LSC ....liquid scintillation [count] [cocktail]

m ....meter

M .... [molar]

MARLAP.......*Multi-Agency Radiological Laboratory Analytical Protocols Manual*

MD................method development

MDA ....minimum detectable activity

MDC ....minimum detectable concentration

MDRM...........method development reference material

min ....minute

MQO ....measurement quality objective

MVG ....*Method Validation Guide for Qualifying Methods Used by Radiological Laboratories Participating in Incident Response Activities*

NAREL ....EPA's National Analytical Radiation Environmental Laboratory, Montgomery, AL

NERC.............National Exposure Research Center

NHSRC ....EPA's National Homeland Security Research Center, Cincinnati, OH

NIST..............National Institute of Standards and Technology

ORD ..............U.S. EPA Office of Research and Development

ORIA.............U.S. EPA Office of Indoor Air and Radiation

φ_{MR}.........................required relative method uncertainty

PT...................proficiency testing

QA..................quality assurance

QAPP ....quality assurance project plan

QC..................quality control

STS................sample test source

u_{MR} ....required method uncertainty

y......................year

Radiometric and General Unit Conversions

To Convert	To	Multiply by	To Convert	To	Multiply by
years (y)	seconds (s) minutes (min) hours (h) days (d)	3.16×10^7 5.26×10^5 8.77×10^3 3.65×10^2	s min h d	Y	3.17×10^{-8} 1.90×10^{-6} 1.14×10^{-4} 2.74×10^{-3}
disintegrations per second (dps)	becquerels (Bq)	1	Bq	dps	1
Bq Bq/kg Bq/m^3 Bq/m^3	picocuries (pCi) pCi/g pCi/L Bq/L	27.0 2.70×10^{-2} 2.70×10^{-2} 10^{-3}	pCi pCi/g pCi/L Bq/L	Bq Bq/kg Bq/m^3 Bq/m^3	3.70×10^{-2} 37.0 37.0 10^3
microcuries per milliliter (µCi/mL)	pCi/L	10^9	pCi/L	µCi/mL	10^{-9}
disintegrations per minute (dpm)	µCi pCi	4.50×10^{-7} 4.50×10^{-1}	pCi	dpm	2.22
cubic feet (ft^3)	cubic meters (m^3)	2.83×10^{-2}	m^3	ft^3	35.3
gallons (gal)	liters (L)	3.78	L	gal	0.264
gray (Gy)	Rad	10^2	rad	Gy	10^{-2}
roentgen equivalent man (rem)	sievert (Sv)	10^{-2}	Sv	rem	10^2

NOTE: Traditional units are used throughout this document instead of the International System of Units (SI). Conversion to SI units will be aided by the unit conversions in this table.

Acknowledgments

1.0   Introduction

This report summarizes the development and testing of an improved method for the Determination of Gross Alpha and Gross Beta Activity in Flowback and Produced Waters from Hydraulic Fracturing Operations (FPWHFO). Flowback and produced waters are characterized by high concentrations and complex mixtures of inorganic salts, organic compounds and other materials. They may commonly contain concentrations of naturally-occurring radionuclides from the uranium and thorium decay chains as high as 10^3–10^4 times the level of activity routinely observed in environmental water samples. The complex nature and high concentration of matrix constituents in these water samples present significant technical challenges especially for gross alpha and gross beta determinations in such samples.

It is critical when working with gross alpha and gross beta measurements that one understand what the screening results represent. These measurements are not nearly as simple as many people may believe. There is a relatively a short list of natural chain radionuclides. Uranium and thorium chain radioactivity (i.e., ^{238}U and ^{232}Th, and progeny), and ^{40}K, usually account for >95% of the naturally occurring alpha and beta activity. A relatively small amount of actinium (Ac) chain activity may also be present (less than 5% of total activity is associated with the Ac chain, i.e., ^{235}U and its decay progeny). Thus, five radioelements in the sample either directly comprise or indirectly support the naturally occurring activity of the sample:

- uranium (^{238}U; ^{235}U; ^{234}U);
- thorium (^{232}Th; ^{230}Th; ^{228}Th; ^{234}Th and its short-lived decay progeny ^{234m}Pa)
- radium
    - ^{228}Ra and its short-lived decay progeny ^{228}Ac;
    - ^{226}Ra and its short-lived decay progeny ^{222}Rn, ^{218}Po, ^{214}Pb, ^{214}Bi, ^{214}Po;
    - ^{224}Ra and its short-lived decay progeny ^{220}Rn, ^{216}Po, ^{212}Pb, ^{212}Bi, ^{212}Po, ^{208}Tl;
- lead (^{210}Pb and its short-lived decay progeny ^{210}Bi; and
- polonium (^{210}Po).

Method 900.0 is the benchmark method for gross alpha and gross beta determinations. Method 900.0 involves evaporating the sample to a thin layer of solid residue in a stainless-steel planchet and analyzing alpha and beta particles emitted from the source using gas-flow proportional counting. The benefit of this method is its rapidity and relatively low-cost in comparison to performing radionuclide specific testing. This method focuses heavily on identifying ^{226}Ra, with a secondary concern on natural uranium and thorium chain activity. This method will identify some non-volatile man-made radionuclides that are present as environmental contaminants.

Method 900.0 has several notable limitations that impact the reliability and intercomparability of gross alpha and beta measurements, especially for naturally occurring radioactivity. The method under-responds to low-energy beta emitters such as ^{210}Pb and ^{228}Ra. Lax control of the timing of the count relative to preparation and collection of the sample may cause the method to dramatically over-respond, or to completely fail to detect radionuclides

present at the point of collection. For example, the gross alpha activity of samples containing ^{226}Ra will increase following the preparation with the count stabilizing at 400% of the actual ^{226}Ra activity 3–4 weeks after preparation.[1] In contrast, delaying the analysis of the sample for more than two weeks after collection will lead to a failure to detect ^{224}Ra or its decay progeny that were present at the time of collection. Finally, the method is not applicable for the determination of analytes that are volatile under the conditions of analysis. This would potentially impact ^{210}Po.

Finally, Method 900.0 is designed for low-solids samples such as drinking water. This is because alpha and beta particles are severely attenuated by matter they encounter as they travel to the detector (including "self-absorption" by the solids in the sample test source). The amount of solids in a sample limits the size of sample that can be processed and thereby the sensitivity of the measurement. Method 900.0 restricts residue thickness for gross alpha measurements to a maximum of 5 mg/cm^2. In a 50-mm diameter stainless-steel planchet, this is equivalent to 100 milligrams of solid residue. While this method is applicable to drinking water samples which generally have solids content under 500 mg/L, FPWHFO samples may have solids content in the hundreds of thousands of mg/L and sample sizes would be restricted to a small fraction of a milliliter. Since the sensitivity of the measurement is inversely proportional to the size of sample processed, the capability of the method to detect activity could be decreased by a factor of a one-thousand and the ability of the evaporation approach to detect radioactivity in FPWHFO becomes questionable at best.

One approach to addressing this limitation would involve using a measurement technique that is not sensitive to the solids content of the sample being analyzed. Gamma spectrometry, for example, is capable of determining isotope specific gamma-ray emissions from samples of 3 - 5 kg or larger. Unfortunately, this technique is not as sensitive as techniques such gas-flow proportional counting (GPC) or liquid scintillation counting (LSC). Gamma spectrometry cannot detect pure alpha and beta emitters, of which there are several of concern for FPWHFO samples. Liquid scintillation spectrometry is a technique that is capable of sensitive measurements of alpha and beta particle emissions and can tolerate somewhat larger amounts of solids (up to about ½ gram in the sample test source) than can GPC.

A second approach can be taken to improve the sensitivity of gross alpha and gross beta measurements. This involves developing chemical separation methods to remove non-radioactive constituents from the sample thereby allowing the radioactive constituents to be concentrated into a source that can be measured using a method sensitive to alpha and beta particle emissions (e.g., gas-flow-proportional counting or liquid scintillation spectrometry). Method 900.0 relies on evaporation to accomplish this. Water, which is not in itself radioactive, is removed from the sample by evaporation. For this reason, Method 900.0 is limited to determining non-volatile constituents in samples.[2]

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[1] This is due to ingrowth of short-lived alpha-emitting decay progeny ^{222}Rn, ^{218}Po, and ^{214}Po. Similar effects are noted with beta-emitting decay progeny of ^{226}Ra, ^{224}Ra, ^{238}U, and ^{210}Pb with time frames ranging from days to months.

[2] This raises questions about whether Po can be reliably determined using method 900.0.

As a result of these considerations, method development efforts in Phase 1 of this project focused on exploring:

- Detection methods that are less subject to self-absorption (e.g., gamma spectrometry or liquid scintillation), and if possible, less sensitive to differences in the energy of the decay particle;

- The viability of using chemical separation methods that selectively isolate longer-lived radionuclides of concern from non-radioactive constituents that may be present in high enough concentrations to limit sample size *(i.e., U, Th, Ra, Pb, and* Po need to be separated from *Ca, Sr, Ba, Mg, Na, K, Fe)*; and

- Preparation methods that are less subject to losses due to analyte volatility.

- Developing and validating a method that could rapidly achieve detection limits *in the range* of those recognized for gross alpha and gross beta in drinking water.

Since each FPWHF sample matrix is different, it is important to initially characterize whether or not U/Th isotopes may be present prior to validating any method. This will ensure that necessary chemistry is addressed for each radionuclide.

Another important aspect of gross alpha and gross beta determinations needs to be considered. As mentioned above, the time elapsed between collection of the sample and the sample preparation, and the time between the preparation of the sample and the count, significantly impact the final result. While it is not practicable to simulate this during the development process, the theoretical impact of decay and ingrowth is well established and should be addressed in the scope and applicability and interferences statements when a laboratory adopts this method and validates it in their method format. Failure to delineate these concerns may result in a failure of users to recognize that results may vary by a factor of two or more, and that delay in analysis may result in complete failure of the method to detect short-lived radionuclides such as ^{224}Ra, present in significant quantities at the time of sample collection.

2.0　　Characterization of the Sample Matrix

Per instruction by the Environmental Protection Agency (EPA), the method development and testing targeted a single FPWHFO sample from the Marcellus shale region of Pennsylvania. A 55-gallon drum of the water was received at the National Analytical and Radiation Environmental Laboratory (NAREL) in Montgomery, Alabama in late April, 2013. At the beginning of May 2013, it was then transferred to the State Hygienic Laboratory at the University of Iowa for method development and testing studies.

The sample was described by the Iowa laboratory as a clear, light amber liquid, of high specific gravity (~1.25 g/cc) with less than ~0.5% by volume (by visual inspection) of a light, suspended reddish-brown precipitate. The sample was not preserved prior to receipt at the laboratory. After the sample arrived at the laboratory, the drum was mixed to ensure homogeneity and two carboys of the water withdrawn. No sample filtering or preservation was performed.

Preliminary analytical work was performed to characterize the major non-radiological (i.e., chemical) composition of the water. These analyses provided perspective on the matrix so that one could assess how best to configure a method as well as to help understand difficulties encountered while developing the method. The data were also used to create a surrogate sample for the method development process whose composition was very similar to that of the sample. The chemical analyses of the field sample and the surrogate solutions are shown in Table 1.

Table 1 – Non-Radiological Analysis of FPWHFO and Surrogate Sample

Analyte	Concentration (mg/L) Field Sample	LOD [1] (mg/L)	Concentration in Surrogate (mg/L)	LOD [1] (mg/L)	Method
Chloride (Cl⁻)	147,000±6,000	1	100,000	1	Chloride, EPA 300.0
Strontium (Sr)	36,000±2,000	200	34,000	0.10	Metals, EPA 200.7
Sodium (Na)	29,000±1,000	5,000	30,000	2.5	Metals, EPA 200.7
Calcium (Ca)	13,000±1,000	10,000	12,000	5.0	Metals, EPA 200.7
Barium (Ba)	9,000±400	500	8,500	0.25	Metals, EPA 200.7
Magnesium (Mg)	850±40	120	850	2.5	Metals, EPA 200.7
Potassium (K)	160±10	2.5	160	5.0	Metals, EPA 200.7
Manganese (Mn)	3.4±0.2	1	—	—	Metals, EPA 200.7
Iron (Fe)	43±2	5	23	0.10	Metals, EPA 200.7
Lead (Pb)	1.0±0.1	0.5	—	—	Metals, EPA 200.7
Aluminum (Al)	LOD	5	—	—	Metals, EPA 200.7
Fluoride (F⁻)	LOD	0.1	—	—	Fluoride, SM 4500-F C 18th
Sulfate (SO_4^{2-})	LOD	40	—	—	Sulfate, EPA 300.0
Nitrate nitrogen as N (NO_3^-)	LOD	10	—	—	Anions, EPA 300.0
Nitrite nitrogen as N (NO_2^-)	LOD	5	—	—	Anions, EPA 300.0
Ortho-phosphate as P (PO_4^{3-})	8±1	0.02	—	—	ortho-Phosphate as P, LAC 10-115-01-1A
Alkalinity	10	1	—	—	Alkalinity as CaCO3, SM 2320 B 18th
Bicarbonate alkalinity (HCO_3^-)	10	1	—	—	Alkalinity as CaCO3, SM 2320 B 18th
Carbonate alkalinity (CO_3^{2-})	LOD	1	—	—	Alkalinity as CaCO3, SM 2320 B 18th
Silicon (Si)	3.7±0.3	2.5	—	—	Silicon, EPA 200.7
Total Solids (TS)	278,000±6,000	1	—	—	Total Solids (Dried at 103°C), SM 2540 B 18th
Total Suspended Solids (TSS)	780	1	—	—	Total Suspended Solids (Dried at 103 °C) USGS 1-3765-85
Total Extractable Hydrocarbons (TEH)[2]	2.3±0.1	0.1	—	—	Total Extractable Hydrocarbons, Iowa OA-2

[1] LOD – Limit of Detection at 99% confidence determined per 40 CFR Part 136, Appendix B Definition and Procedure for the Determination of the Method Detection Limit (MDL).

[2] Chromatographic patterns do not conform to fuel standards for this range.

A radiological characterization of the water was also conducted during the preliminary phase to determine the radionuclides present in the sample. Gamma spectrometric analysis of raw FPW showed high levels of activity for the ^{226}Ra sub-chain of ^{238}U with a ^{226}Ra concentration of 17,600 ± 1,400 pCi/L (k=1). Significantly elevated activity of ^{228}Ra (1,950 ± 110 pCi/L) was also noted with no indication of significant levels of ^{224}Ra which may be present in freshly collected samples containing ^{228}Ra. This indicates that activity concentrations of ^{228}Th were likely low and that the sample had probably aged enough that ^{224}Ra and ^{212}Pb had decayed prior to receipt at the laboratory (longer than one month). The activity concentrations of ^{238}U (^{234}Th, and ^{234m}Pa), and ^{235}U were not detectable using gamma spectrometry.[3] Thus, it is possible to make theoretical conclusions about the state of equilibrium at the time of sampling. Since the gross radioactivity of naturally-occurring decay chains changes with time, control of time elapsed between sampling and preparation of the sample, and the preparation and analysis will be factors that will significantly impact gross alpha and gross beta measurements and which will need to be closely controlled.

Based on the elevated levels of radioactivity in the sample received, it became apparent that a method development reference material (MDRM) would need to be created that closely matched the composition of the FPWHFO but did not contain significant concentrations of naturally occurring radionuclides. In previous method development studies of matrices such as air filters and soil, low concentrations of naturally occurring radionuclides were present that could easily be accounted for when creating test samples of low activity. However with the high concentrations of the naturally occurring radionuclides in this sample, an effective measure of uncertainty at low activities, or of a minimum detectable concentration (MDC), would not be possible.

Reproducing the predominant non-radioactive constituents in the sample, Cl, Ca, Ba, Sr, Mg, Na, K, and total solids in the test samples was critical both for the method development and testing process. Based on the non-radiological analysis of the sample, a "surrogate" method development reference material (MDRM) solution composition was formulated. It was evident from some of the first attempts at gross radioactivity analysis that minimum detectable concentrations would be much higher than that for drinking water.

The elevated concentrations of solids in the sample meant ordering very large quantities of the soluble salts needed to make the surrogate used to prepare development process blank, MDC and spiked samples.

The extremely high levels most particularly of Ca, Sr, and Ba, all Group II chemical analogues for Ra, placed into question the initially proposed analytical approach and required significant modification of the techniques used. While the procurement of salts was in process, laboratory staff attempted several gross separation and analysis processes (noted below) on the real sample to see how they would fare as preparation for the method development process.

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[3] Informal alpha spectrometry results obtained from personnel working with NAREL staff in May 2013 indicated that no ^{238}U or ^{234}U was detected in the sample at the 0.1 pCi/L level.

Once created, the surrogate matrix was spiked with ^{226}Ra, ^{230}Th and ^{228}Ra based on the magnitude of blank analyses to create MDRMs at three levels for testing of the required method uncertainty and one MDRM for verification of the required minimum detectable concentration. The radionuclides for spiking differed from the outline in the method development plan.

3.0   Initial Radioanalytical Methods

A series of different approaches were explored for the gross alpha and gross beta analysis to identify an approach optimized to accommodate the matrix of the FPWHFO sample received from the EPA. While the testing matrix used was quite challenging, these results may or may not be applicable to matrices that differ from this sample matrix. Approaches explored ranged from tests of EPA Method 900.0 through attempts to explore different detection techniques, to approaches to separate/concentrate radioactive constituents of the sample. Several examples include:

- The Method 900.0 approach failed to produce a usable test source with an extremely small 0.1 mL aliquant.

- Direct addition of the sample to liquid scintillation cocktail resulted in precipitation of matrix components and failure to produce a useable test source.

- Gamma spectrometry analysis provided results for a number of the natural emitters in the sample. This approach to quantitation is not based on measurement of alpha emissions, but the results are radionuclide specific and can be used to calculate the total gross alpha activity associated with a radionuclide such as [226]Ra in a sample when it is in secular equilibrium[4] with its progeny (that are gamma emitters).

Attachment I provides additional details on these and other attempts to processing the FPWHFO sample, as well as testing if the relative robustness of several techniques for chemical separation of key radionuclides (Th, U, and Po).

The goal of developing a rapid, and economically viable approach for isolating and analyzing alpha emitting radionuclides (Ra, Th, U and Po) in a single test source and determining gross alpha activity using a single sensitive measurement of alpha emissions, however, has yet to be realized. This is due to the complex matrix composition, and the levels of Group II elements (Mg, Ca, Sr, and Ba) in the FPWHFO matrix. Group II constituents were present in overwhelming amounts (gram/liter concentrations) in this sample. The chemical behavior of these elements closely mimics that of radium, which foiled all attempts to achieve a group separation of Ra, Th, U, and Po.

As a result, the most viable approach for gross alpha analysis involved the use of two physical determinations of alpha activity. The first of these determinations involves a group separation of Th, U, and Po using a rapid solid-phase extraction chromatographic separation technique[5] followed by liquid scintillation analysis of alpha emissions. This technique is described in greater detail below. The other contributor to gross alpha, [226]Ra (+progeny) is

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[4] If secular equilibrium is to be assumed steps need to be taken in a laboratory's method that indicates how this will be controlled. If secular equilibrium cannot be assured then the measured values should be qualified noting that these activity concentrations maybe larger.

[5] This involves the use of a commercial solid phase extraction resin such as Eichrom™. This material has a very high selectivity coefficient for U, Th and Po (and other high atomic number radionuclides) over first second and third row transition series elements.

determined by high purity germanium (HPGe) gamma spectrometric measurement of gamma emissions from the sample.

Since the gamma spectrometric determination of ^{226}Ra has very different levels of measurement uncertainty than does the liquid scintillation approach for thorium, uranium, and polonium, it was necessary to establish separate measurement quality objectives (MQOs) for required method uncertainty for each of the two analyses. The results of the analyses may be used separately as the individual results are quite informative about radioactivity in the sample, or the two results and their respective uncertainties mathematically combined to yield a single combined activity and standard uncertainty for gross alpha activity in the sample.

Attempts to perform gross beta in a method along the lines of Method 900.0 also proved fruitless as extremely elevated solids in the sample produced unacceptably high-levels of self-attenuation or resulted in sample aliquants that were far too small to provide meaningful detection levels. Preparation of a reproducible test source proved to be unsuccessful due to non-uniform drying and spattering of sample solids. While a chemical separation of naturally occurring beta emitting members and progeny of the uranium and thorium decay chains may theoretically be possible, there would still be concern about significant differences in decay energy of the beta emitters that could negatively impact quantitation. Using gamma emissions from the radionuclides, however, permits use of a non-destructive method that avoids lengthy separations, and minimizes time performing the separations. The trade-off, however, is that the counting times for samples can be significant (6 hours or more) depending upon the gamma detector efficiency.

While each gamma ray detected can be ascribed to a specific radionuclide and the activities of these radionuclides and their progeny are easily summed, an assessment of the total uncertainty can only account for the uncertainty of those beta-gamma emitters identified. It will not account for beta-gamma emitters present at low, sub-detectable levels. This is a more significant issue for low-activity samples where no gamma rays are detected. Based on the high activity of radium in this type of sample matrix, this seems to be a more remote possibility.

4.0   Method Development Process Summary

The method development (MD) plan for gross alpha and gross beta analysis of FPWHFO follows the guidance provided in *Method Validation Guide for Qualifying Methods Used by Radiological Laboratories Participating in Incident Response Activities* [MVG] (EPA 2009), *Validation and Peer Review of U.S. Environmental Protection Agency Radiochemical Methods of Analysis* (EPA 2006), and Chapter 6 of MARLAP (2004). This MD process was conducted under the generic *Quality Assurance Project Plan Validation of Rapid Radiochemical Methods for Radionuclides Listed in EPA's Standardized Analytical Methods (SAM) for Use During Homeland Security Events* (EPA 2012). This method is considered a "first time approach." Therefore, the method needed to be evaluated according to MARLAP method validation "Level D" or "Level E."

The proposed method, for both gross alpha and gross beta, in the MD plan was validated against acceptance criteria for the required method uncertainty about a specified analytical action level (AAL) concentration and at the required MDC. After several modifications to the MD plan, and due to significant challenges related to the matrix of the sample, the technique used for gross beta analysis was changed from the traditional screening using beta particle emission counting (gas-flow proportional counting or liquid scintillation counting) to an inferential gamma spectrometric analysis method. Since the gamma spectrometry allows the determination of several beta-gamma emitters, the overall relative required method uncertainty for beta-gamma emitters was expanded to 50% to accommodate the increased uncertainties of the multiple measurements needed.

In addition to determination of the required method uncertainty and verification of the required minimum detectable concentration, analytical results were evaluated for statistical bias, absolute bias for blank samples and relative bias at each of the three test level radionuclide activities. The radiochemical yield of the method was also evaluated as a characteristic of method ruggedness.

The method development process was divided into four phases as follows:

1. Phase 1
   a. Laboratory familiarization with the method concept.
   b. Set-up of the laboratory and acquisition of reagents, standards and preparation of in-house performance test (PT) samples.
   c. Perform preliminary tests of the methods on an actual sample.
   d. Make changes to improve the method based on the preliminary tests.
2. Phase 2
   a. Conduct method testing for required method uncertainty using internal PT samples.
3. Phase 3
   a. Conduct verification of the required MDC using internal PT samples.

4. Phase 4
   a. Report results.
   b. Written report and narratives by laboratory describing the process/method.
   c. Feedback comments on the method.
   d. Method development report written by EMS and reviewed by laboratory.

The objective of Phase 1 was to have the laboratory become familiar with the draft method. While the laboratory obtained hands-on experience, areas of the method that required optimization were identified. Based on the information and experience gained during Phase 1 runs, the analysis method was optimized and modified prior to initiating the formal testing process in Phases 2 and 3.

The draft method was run (see Attachment I for description of Radionuclide: ^{226}Ra and Radionuclides: U, Th, and Po) with the field sample obtained from the EPA using the innate ^{226}Ra as a measure of the success of each purported separation step. The laboratory also prepared blank and spiked surrogate solutions (as described in the introduction above) to assess the feasibility of the draft method with elements representing the longer-lived U and Th decay chain radionuclides (i.e., ^{230}Th, natural uranium, ^{209}Po) since these radionuclides and their short-lived progeny comprise the alpha radioactivity of the sample. Sample test sources were prepared after the separation of the respective alpha emitters for alpha spectrometric analysis. The radionuclide specific testing also allowed assessment of the robustness of the method to recover the added radionuclides from the matrix. Attachment 1 presents data on the recovery of these radionuclides/radioelements. Due to the challenging matrix, quantitative recovery was neither expected nor was it achieved, but the final method was effective and obtained recoveries that approached 80–90% for the targeted analytes. As a gross screening method, this is deemed to be acceptable.

The initial objective for detection levels was aimed at drinking water MPC concentrations. However, the difficulties encountered in this initial evaluation of the proposed methods with the matrix evoked a reevaluation of what could be the attainable action levels and detectability concentrations. The values that are found in Tables 2 and 3 were based on this reevaluation.

During Phases 2 and 3 of the MD process, the laboratory analyzed in-house PT samples consisting of method development reference materials [MDRM] prepared from the surrogate solution (described in the introduction above) spiked with known amounts of ^{230}Th, ^{226}Ra and ^{228}Ra. The laboratory was instructed to spike the PT samples with concentrations consistent with test levels for the required method uncertainty and the required MDC. The targeted test levels and applicable MQOs for Phases 2 and 3 are listed in Table 2.

Following completion of the method developpkment studies, comments from the laboratories were evaluated per guidance in the MVG. The final method was finalized to conform to the documented "as-tested" conditions in Phases 2 and 3. The report was also edited to ensure clarity based on comments received from the laboratories. Thus, the test data presented in this report reflect the final method included in the attachments to this document.

5.0   Participating Laboratories

The State Hygienic Laboratory and at the Radiology and Radiation Oncology Free Radical and Radiation Biology Program Laboratory, both at the University of Iowa, performed all of the analyses (radiological as well as non-radiological).

6.0   Measurement Quality Objectives

The gross alpha and gross beta analysis method was developed to meet MQOs established for the project. The MQOs selected include the radionuclide concentration range, the required method uncertainty at a specified radionuclide concentration (i.e., AAL), and the required MDC. Since the EPA did not provide regulatory action levels, MQOs were defined in the method development plan based on the presumed sensitivity of the techniques to be used. Once the sample was received and initial testing proved how challenging nature of the matrix would be, new technical approaches were needed and MQOs were updated to maintain consistency with the capabilities of the techniques being used. The AAL for ^{226}Ra by gamma spectrometry is higher than initially envisioned while that for gross alpha by liquid scintillation is somewhat lower. Gross beta MQOs are based on gamma spectrometric analysis (see Attachment 1 descriptions for not using traditional gross beta analysis) with separate MQOs for ^{228}Ra (for gross beta analysis) and ^{226}Ra (contribution to gross alpha and gross beta activity), based on the relative sensitivity for these radionuclides using gamma spectrometry. The targeted test levels and applicable MQOs for Phases 2 and 3 are listed in Table 2.

The required method uncertainty for gross alpha (liquid scintillation count [LSC] contribution) assumes tolerable error rates of 10% ($z_{1-\alpha} = z_{1-\beta} = 1.282$) for Type I and Type II errors. It is calculated for gross alpha using the following equation:

$$u_{MR} \text{ , } \text{Goss Alpha}_{LSC}, \frac{pCi}{L} = \frac{(AAL - DL)}{(z_{1-\alpha} + z_{1-\beta})} = \frac{(30 - 5)}{(1.282 + 1.282)}$$

$$= \frac{25}{2.564} = 9.8 \text{ pCi/L}$$

Where AAL is the analytical action level and DL is the discrimination level for gross alpha analysis.

And the value for the relative required method uncertainty is:

$$\varphi_{MR}, \text{Gross Alpha}_{LSC}, = 100 \times u_{MR} / (AAL) = (9.8 / 30) = 33\%$$

The required method uncertainty for gross alpha (gamma spectrometry contribution) is:

$$\varphi_{MR}, \text{Gross Alpha}_{gamma\ spectrometry}, u_{MR} = 33\%$$

as determined by the gamma spectrometry software algorithm.

The potential contributors to the gross beta activity are ^{234}Th, ^{234m}Pa, ^{214}Pb, ^{214}Bi, ^{212}Pb, ^{212}Bi, ^{208}Tl, ^{228}Ra, ^{228}Ac, ^{210}Pb, and ^{210}Bi.

Several of these are linked in shorter decay chains so contributions to the gross beta at full ingrowth can be calculated by measuring one of the radionuclides and assuming secular equilibrium with the others in the respective decay chain. These would be summarized as follows:

^{234}Th = **^{234m}Pa** *(full secular equilibrium within 10 minutes)*

^{214}Pb = ^{214}Bi *(full secular equilibrium within 3 hours, Rn-222 is in secular equilibrium with Ra-226)*

^{212}Pb = **^{212}Bi** = **^{208}Tl** / 0.36 *(full secular equilibrium 72 hours after separation)*

^{228}Ra = **^{228}Ac** *(full secular equilibrium 36 hours)*

^{210}Pb = ^{210}Bi *(full secular equilibrium 15–25 days after collection)*

Since only the non-bolded radionuclides are measured, the bolded radionuclides are determined inferentially. The activity and uncertainty of the measured values will be used as the values for the inferred radionuclides ^{234}Th/ ^{234m}Pa, ^{214}Pb/ ^{214}Bi, ^{212}Pb/ ^{212}Bi/ ^{208}Tl/, ^{228}Ra/ ^{228}Ac, and ^{210}Pb/ ^{210}Bi.

The gross beta activity of samples is calculated based on the gamma spectrometric measurement of beta-gamma emitting radionuclides from the uranium and thorium chains that are present in detectable levels in the sample. The concentration of beta emitters that are detected may be calculated by inference when their gamma-emitting parents or progeny where these are present at detectable levels. Gamma emitting radionuclides are considered to be detectable when the relative combined standard uncertainty of the radionuclide is determined by the gamma spectrometry software to be less than or equal to 50%. The overall beta uncertainty is calculated as the quadratic sum of the uncertainties of the detected radionuclides contributing to the total gross beta activity.[6]

Ra-228, based on the gamma emission of its short-lived progeny ^{228}Ac, was chosen *in lieu* of other naturally occurring beta-gamma emitters to determine action levels and MDC for gross beta analysis. This choice is based on three factors:
- The abundance of the ^{228}Ac gamma ray at 911 keV is 25.8%. The abundance of the ^{214}Bi at 609 keV peak is 45.9% and that of ^{212}Pb at 238 keV is 43.6%.
- The efficiency of the 911 keV peak is lower than the other two gamma ray peaks.
- The abundance of ^{228}Ra in many geologic formations used for oil and gas production is much lower than that of Ra-226 or their respective progeny.

This provides assurance that if the ^{228}Ac action levels and MDC can be confirmed that those for the other principal naturally occurring beta-gamma chains can also be achieved.

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[6] The exception for this will be for ^{226}Ra with a u_{MR} = 9.8 pCi/L and a φ_{MR} = 33%.

The targeted required method uncertainty for each of the beta-gamma emitters that will be measured by gamma spectrometry is 50% at the AAL of 60 pCi/L.

$$\varphi_{MR}, Gross\ Beta_{gamma\ sectrometry}, = 50\%$$

Although the evaluations for the other beta/gamma emitters were not performed pending development of the gamma spectrometry measurement, further work needs to be performed with the ^{224}Ra and ^{226}Ra progeny fully ingrown to assess the achievable MDC and AALs. Table 2 also presents targeted values that will be evaluated once a gamma spectrometry method for a broader list of analytes has been fully developed.

Table 2 – MQOs Targeted for Gross Alpha and Gross Beta in FPWHFO

Measurement	Matrix[1]	AAL	Required MDC/MDA[2]	u_{MR}[3]	φ_{MR}[4]
Gross Alpha		pCi/L	pCi/L	pCi/L	(%)
^{230}Th (liquid scintillation)	FPWHFO	30	5	9.8	33%
^{226}Ra (based on the 186 keV gamma emission)	FPWHFO	150	55	50	33%
Gross Beta[4]					
^{228}Ra (^{228}Ac)	FPWHFO	60	30	30	50%
Beta-emitting progeny of ^{226}Ra (^{214}Pb/^{214}Bi) and other gamma emitters in sample[5]	FPWHFO	--	--	--	50%
Beta-emitting progeny of ^{224}Ra[5] (inferred based on gamma emissions of ^{212}Pb)	FPWHFO	--	--	--	50%
Th-234[5] (and inferred ^{234m}Pa)	FPWHFO	--	--	--	50%

[1] A single sample of flowback and produced water supplied by EPA was used as the prototype for a surrogate matrix for method testing. The method development reference material (MDRM) consisted of aliquants of the surrogate matrix spiked with radionuclide solutions traceable to the National Institute of Standards and Technology (NIST).

[2] The MDC represents the value for the individual measurement. A combined MDC for gross alpha or beta will not be determined due to significant differences in the sensitivity of the respective measurement techniques.

[3] Required method uncertainty at and below the AAL.

[4] Relative required method uncertainty above the AAL.

[5] Preliminary development of the method for gross beta is based on measurement of ^{228}Ac (gamma emitting decay progeny of ^{228}Ra). Final testing will be conducted pending further refinement of the gamma spectrometry measurement technique.

A synopsis of the final method testing results for all three test levels and the MDC is found in Table 3. The ^{230}Th values represent the results by chemical separation and liquid scintillation counting. The results for ^{226}Ra and ^{228}Ra are from direct sample analysis by gamma ray spectrometry.

Table 3 – Method Development As-Spiked Concentrations, MQOs and Mean Measured Results

Concentration Relative to Action Level	Isotope	Targeted PT Activity (pCi/L)	Known Value[1] ± CSU[2] (pCi/L)	Measured Mean ± SD[3] (pCi/L)	Required Method Uncertainty[4] u_{MR} (pCi/L)	Required Relative Method Uncertainty φ_{MR}	Measured Relative Standard Deviation (k=1)
MDC	^{230}Th	15	12.45±0.79	10.2 ±1.9	5	n/a	19 %
MDC	^{226}Ra	60	55.2±1.5	85±28	55	n/a	33 %
MDC	^{228}Ra	30	30.4±0.2	39±12	30	n/a	31 %
½ × AAL	^{230}Th	20	22.5 ± 1.2	14.9 ± 2.2	12 pCi/L	n/a	15%
½ × AAL	^{226}Ra	90	75.0 ± 2.0	94 ± 32	54 pCi/L	n/a	34%
½ × AAL	^{228}Ra	30	41.4 ± 0.65	43.2 ± 9.8	22 pCi/L	n/a	23%
AAL	^{230}Th	40	37.5 ± 2.1	31.4 ± 4.2	12 pCi/L	n/a	13%
AAL	^{226}Ra	180	164.9 ± 4.5	138 ± 18	54 pCi/L	n/a	13%
AAL	^{228}Ra	60	62.47 ± 0.99	74 ± 12	31 pCi/L	n/a	16%
3 × AAL	^{230}Th	120	104.9 ± 6.3	73 ± 12	n/a	33%	16%
3 × AAL	^{226}Ra	540	449 ± 12	431 ± 52	n/a	33%	12%
3 × AAL	^{228}Ra	90	180.1 ± 2.8	199.3 ± 6.8	n/a	50%	3.4%

[1] The known values were calculated by dilution of the tracers added to the surrogate matrix.

[2] CSU – combined standard uncertainty (k=1).

[3] SD – Standard deviation of the observed measurements

[4] u_{MR} = φ_{MR} × as-spiked concentration of the test sample at the AAL

All of the measurement quality objectives in the method development plan were achieved. The details of the measurement synopses in Table 3 are found in Section 9.

7.0   Method Development Plan

The methods for gross alpha and gross beta activity were evaluated for four important performance characteristics for radioanalytical methods specified in *Quality Assurance Project Plan Validation of Rapid Radiochemical Methods for Radionuclides Listed in EPA's Standardized Analytical Methods (SAM) for Use During Homeland Security Events* (EPA 2012). These include method uncertainty, detection capability, bias, and analyte activity range. A summary of the manner in which these performance characteristics were evaluated is presented below. Chemical yield of the method, an important characteristic for method ruggedness, is not specifically evaluated on an ongoing basis as this method is not radionuclide specific. Tracers were used in method development to assess recovery, however, to provide information on method ruggedness. See Attachment I for further discussion.

Three counting methods were evaluated during the method development to determine the counting method to be used for method testing. Gas proportional counting was eliminated as a method of gross alpha or beta analysis because the high concentration of dissolved solids prevented the achievement of activity concentration detection limits that were reasonable due to self-attenuation and due to challenges encountered in preparing the test source. The final method utilizes liquid scintillation counting and high purity germanium gamma spectrometry. The proposed testing combinations are shown in Table 4.

Table 4 – Proposed Sample Processing and Counting Combinations

Method	Processing Method	Gamma Spectrometry	Liquid Scintillation Counting	Gas Proportional Counting [1]
Gross Alpha	Chemical Separation		X	X
Gross Beta	Non-destructive Count	X		

[1]   *Eliminated from final testing.*

7.1   Method Uncertainty

The method uncertainty for gross alpha and gross beta activity was initially estimated based on the gamma analysis of the untreated field sample and spiked demineralized water and surrogate MDRM sample spikes. Based on those trials, sample target concentrations were derived and finalized as noted in Table 5.

Table 5 – Actual Sample Concentrations Used for MD Process

Sample Type	Minimum Number Analyzed	Spike Concentration	Gross Alpha by LSC (as fraction of the AAL) AAL = 37.5 pCi/L	[226]Ra by Gamma Spectrometry (as fraction of the AAL) AAL = 164.9 pCi/L	[228]Ra by Gamma Spectrometry (as fraction of the AAL) AAL = 62.47 pCi/L
Demineralized Water Blanks	7	Blank	0	0	0
Surrogate MDRM Blanks	7	Blank	0	0	0
Surrogate MDRM Spikes	10	MDC	0.33	0.33	0.49
Surrogate MDRM Spikes	7	½ × AAL	0.60	0.45	0.65
Surrogate MDRM Spikes	7	AAL	1.0	1.0	1.0
Surrogate MDRM Spikes	7	3 × AAL	2.8	2.7	2.9

Internal MDRM proficiency test samples were prepared:

- The performance of gross alpha as evaluated using two difference radioelements as follows:
  - Thorium, uranium, and polonium: the performance of the chemical separation / LSC approach was evaluated based on recovery of [230]Th added to the MDRMs since characterization of the method in Phase 1 demonstrated that Th, U, and Po behave similarly using this method.
  - [226]Ra: The alpha activity as determined by gamma spectrometry was used to validate the method based on recovery of [226]Ra. This MDRM contained the alpha-emitting radionuclide [226]Ra.
- Gross beta as determined by gamma spectrometry reflects the activity of beta-emitting decay progeny of [226]Ra and [228]Ra and the progeny of the [228]Ra.

The respective concentrations for the test samples are noted in Table 5. The method was evaluated against the required method uncertainty values identified in Table 2.

7.2   Detection Capability

The detection capability for gross alpha by LSC (Th/U/Po) was estimated at 10 pCi/L. For ^{226}Ra by gamma spectrometry, it was estimated at 60 pCi/L, and for gross beta based on ^{228}Ra[7] for all significant beta emitters was estimated at 30 pCi/L. In accordance with the guidance provided in the MVG, the critical net concentration (CL$_{NC}$) of the method was to be estimated based on the results of at least seven blank samples. Results from ten replicate samples having an "as tested" concentration at the required MDC being tested were compared to the critical net concentration to determine method detection capability. It should be noted that the verification of the required MDC for gross beta failed to meet criteria when tested at the 15 pCi/L level. The test was repeated using test samples spiked at twice the initial activity indicating that the method is capable of meeting a required minimum detectable concentration value at the 30 pCi/L level.

7.3   Method Bias

Two types of method bias were evaluated, absolute and relative.

Absolute Bias

Absolute bias was determined as a method performance parameter. The results from the seven blank samples for the required MDC evaluation were evaluated for absolute bias according to the protocol and equation presented in the *Method Validation Guide for Qualifying Methods Used by Radiological Laboratories Participating in Incident Response Activities* (EPA 2009). Absolute bias was to be determined as a method performance parameter; however, there was no acceptance limit for bias established for the method in this method development process.

The following protocol was used to test the gross alpha water method for absolute bias:

1. Calculate the mean ($\overline{X}$) and estimated standard deviation (s_x) for "N" (at least seven) blank sample net results (in the case of gamma spectrometry measurements 13 were used as the demineralized water blank and the blank surrogate were indistinguishable from each other)

2. Use the equation below to calculate the |T| value:

$$|T| = \frac{|\overline{X}|}{s_X / \sqrt{N}} \tag{1}$$

3. An absolute bias in the measurement process is indicated if:

$$|T| > t_{1-\alpha/2}(N-1) \tag{2}$$

    where:

    $|T|$ represents the absolute value of the statistical t-value determined from analysis of the samples analyzed, and

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[7] The analysis for ^{228}Ra was performed using the gamma ray emissions of its first progeny, ^{228}Ac, which emits a gamma ray at 911 keV. See discussion at the end of Section 6.1.

$t_{1-\alpha/2}$ (N–1) represents the (1 – α/2)-quantile of the t-distribution with N–1 degrees of freedom.

For seven blanks (or in the case of gamma spec 13 blanks), an absolute bias is identified at a significance level of 0.05, when $|T| > t_{1-\alpha/2}$.

Relative Bias

The results from the replicate samples for each of the three test levels and at the MDC level were evaluated for relative bias according to the protocol and equation presented in the *Method Validation Guide for Qualifying Methods Used by Radioanalytical Laboratories Participating in Incident Response Activities* (EPA 2009). No acceptable relative bias limit was specified for this MD process.

The following protocol was used to test the gross alpha method for relative bias:

1. Calculate the mean ($\overline{X}$) and estimated standard deviation (s_x) of the replicate results for each method test level.

2. Use the equation below to calculate the |T| value:

$$|T| = \frac{\left|\overline{X} - K\right|}{\sqrt{s_X^2 / N + u^2(K)}}$$

(3)

where:
  $|T|$ is the average measured value
  s_x is the experimental standard deviation of the measured values
  N   is the number of replicates
  K   is the reference value
  u(K)   is the standard uncertainty of the reference value

A relative bias in the measurement process is indicated if:

$$|T| > t_{1-\alpha/2(v_{eff})}$$

(3a)

The number of effective degrees of freedom for the t-statistic is calculated as follows:

$$v_{eff} = (N-1)\left(1 + \frac{u^2(K)}{s_X^2 / N}\right)^2$$

(4)

Where v_{eff} as calculated by the equation generally is not an integer so v_{eff} should be truncated (rounded down) to an integer. Then, given the significance level, 0.05, the critical value for |T| is defined to be $t_{1-\alpha/2(veff)}$, the (1 – α/2)-quantile of the t-distribution with v_{eff} degrees of freedom (see MARLAP Appendix G, Table G.2).

7.4   Analyte Concentration Range

The gross alpha method was evaluated for the required method uncertainty at three test level activities. The seven replicate PT samples from each test level concentration were analyzed. The three "targeted" and "known" test level activities are presented in Table 3. Note that the final test concentration values for the PT samples varied from the proposed test levels but that these values were within the sample preparation specifications provided to the laboratory.

The gross beta method was evaluated for required method uncertainty using the gamma spectrometry software criterion of $\leq 50\%$ and the combined standard uncertainty as calculated by the gamma spectrometry software.

7.5   Method Specificity

The purpose of this method is to perform a gross activity measurement. The specificity relates only to gross alpha or gross beta analysis. The separation steps employed were intended to isolate groups of radionuclides that were either alpha or beta emitters. In the development of the final method, certain tracers were used to follow the separation of the surrogate radionuclides used for the analysis.

7.6   Method Ruggedness

Method ruggedness was evaluated primarily in Phase 1 of the MD process for the effects that the extreme combination of chemical compounds and high dissolved solids content would have on the method. In this phase, the method was modified to use a general chemical separation process for isotopes of uranium, thorium and polonium, and gamma spectrometry was selected for analysis of beta emitting radionuclides and ^{226}Ra. The ruggedness of the method was testing during Phase 1 using the EPA provided sample and with different radionuclides spiked into the surrogate matrix. See Attachment 1 for details on this testing.

8.0 Techniques Used to Evaluate the Measurement Quality Objectives for Methods Development Project

A general description of the specifications and techniques used to evaluate the required method uncertainty, required MDC and bias was presented in Section 6. The detailed method evaluation process for each MQO and bias is presented in this section.

8.1 Required Method Uncertainty

The gross alpha and gross beta activity method was evaluated following the guidance presented for "Level E Method Validation: Adapted, Newly Developed Methods, Including Rapid Methods" in *Method Validation Guide for Qualifying Methods Used by Radiological Laboratories Participating in Incident Response Activities* (EPA 2009) and Chapter 6 of Multi-Agency Radiological Laboratory Analytical Protocols Manual (MARLAP 2004).

MARLAP "Level E" method validation requires the laboratory to conduct a method development study wherein seven (or more) replicate samples from each of the three concentration levels are analyzed according to the method. The concentration test levels analyzed are listed in Table 3. For validation "Level E," internally prepared PT samples consisting of NIST-traceable ^{230}Th, ^{228}Ra and ^{226}Ra spiked into the surrogate matrix to create a method development reference material (MDRM). In order to determine if the proposed method met the project MQO requirements for the required method uncertainty, each PT sample result was compared with the method uncertainty acceptance criteria listed in Tables 6A, 6B, and 6C. "Level E" validation stipulates that for each test sample analyzed, the measured value must be within ± 3.0 u_{MR}[8] for test level activities at or less than the AAL, or ± 3.0 φ_{MR}[9] for test level activities above the AAL.

8.2 Required Minimum Detectable Concentration

The analytical results reported for the PT samples having a gross alpha and gross beta activity at the tested MDCs (Th/U/Po by LSC alpha at 12 pCi/L; ^{226}Ra alpha by gamma spectrometry at 55 pCi/L; ^{228}Ra beta at 30 pCi/L) were evaluated according to Sections 5.5.1 and 5.5.2 of Testing for the Required MDC in *Method Validation Guide for Qualifying Methods Used by Radiological Laboratories Participating in Incident Response Activities* (EPA 2009). For this method development process, the terms "MDC" and "Critical Net Concentration" are used. The State Hygienic Laboratory at the University of Iowa analyzed the prepared PT samples in accordance with the final proposed method.

Critical Net Concentration

In order to evaluate whether the combined method can meet the required MDC (Th/U/Po by LSC alpha at 12 pCi/L; ^{226}Ra alpha by gamma spectrometry at 55 pCi/L; ^{228}Ra beta at 30 pCi/L), the critical net concentration, as determined from the results of analytical blanks, must be calculated. The critical net concentration (CL$_{NC}$) with a Type I error probability of $\alpha =$

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[8] u$_{MR}$ is the required method uncertainty

[9] φ_{MR} is the required relative method uncertainty

0.05, was calculated using the following equation (consistent with MARLAP, Chapter 20, Equation 20.35):

$$CL_{NC}(pCi) = t_{1-\alpha}(n-1) \times S_{Blanks} \tag{7}$$

Where:

S_{Blanks} is the standard deviation of the n blank-sample net results (corrected for instrument background) in radionuclide concentration units of pCi/L, and

$t_{1-\alpha(n-1)}$ is the $(1-\alpha)$-quantile of the t-distribution with n–1 degrees of freedom (see MARLAP Table G.2 in Appendix G). For this method development study, a Type I error rate of 0.05 was chosen.

For example, for seven (minimum) blank results (six degrees of freedom) and a Type I error probability of 0.05, the previous equation reduces to:

$$CL_{NC}(pCi) = 1.94 \times S_{Blanks} \tag{8}$$

The use of the above equations assumes that the method being evaluated has no bias.

Required MDC

Each of the analytical results reported for the PT samples having concentration at the required MDC (Th/U/Po by LSC alpha at 12 pCi/L; ^{226}Ra alpha by gamma spectrometry at 55 pCi/L; ^{228}Ra beta at 30 pCi/L) were compared to the estimated critical net concentration for the method. The following protocol was used to verify a method's capability to meet the required method MDC for a radionuclide-matrix combination:

I.   Analyze a minimum of seven matrix blank samples for the radionuclide.

II.   From the blank sample net results, calculate the estimated Critical Net Concentration, CL_{NC}.

III.   Analyze ten replicate samples spiked at the required MDC.

IV.   From the results of the ten replicate samples spiked at the required MDC, determine the number (Y) of sample results at or below the estimated CL_{NC}.

V.   If $Y \leq 2$, the method evaluated at the required MDC passes the test for the required MDC specification.

VI.   If $Y > 2$, the method evaluated at the required MDC fails the test for the required MDC specification.

9.0   Evaluation of Experimental Results

Only the experimental results for Phases 2 and 3 of the MD process are reported and evaluated in this study. Information presented in this section will include results for Sections 6 and 7. The gross alpha and gross beta activity concentration results were evaluated for the required method uncertainty, required MDC, and bias.

9.1   Summary of the Method

The full method for the analysis is located in Attachment III. A brief description of each part of the method is described here.

Th, U, Po Gross Alpha by LSC

A 300 mL sample is treated with permanganate in ammonaical solution to coprecipitate all radionuclides in the naturally occurring series. The mixture is settled and the supernatant solution discarded. The residue is dissolved in hydrochloric acid and passed through a TRU Resin™ column. [10] Thorium, uranium and polonium are eluted from the resins using ammonium oxalate. The eluent is transferred to a liquid scintillation vial as the final sample test source and counted in the alpha emission region of the liquid scintillation spectrum. The final sample test source is counted for 30 minutes.

^{226}Ra Alpha by Gamma Spectrometry

A sample test source of 3 L is counted directly by gamma ray spectrometry. The activity concentration of ^{226}Ra is determined by gamma ray analysis using the 186 keV gamma ray region (assumes no significant amount of ^{235}U compared to the amount of ^{226}Ra in the sample). The sample is counted for 12 hours or long enough to achieve the required method uncertainty.

^{228}Ra Beta by Gamma Spectrometry

The sample test source of 3 L is counted directly by gamma ray spectrometry. In addition to ^{228}Ra being determined indirectly by analysis of its first progeny ^{228}Ac (911 or 338 keV) several other radionuclides are determined directly by their gamma ray emission and others may be determined indirectly through analysis of a parent or progeny radionuclide that is a gamma ray emitter. The sample is counted for 12 hours or long enough to achieve the required method uncertainty.

9.2   Required Method Uncertainty

Tables 6A through 6C show the measured results for each of the samples analyzed and the testing requirements for each level. The "known" values and combined standard uncertainty of the known values ("CSU known") are based on the amount of NIST-traceable standards added to the samples. The allowable range of results is calculated by taking the known

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[10] Eichrom Technologies, LLC, Lisle, IL.

value and adding (to get the upper value of the range) and subtracting (to get the lower value of the range)

three times the required method uncertainty ($3.0 \times u_{MR}$). For example, in Table 6A, the allowable range for gross alpha for Test Level 2 is $37.5 \pm (3.0 \times 12)$ pCi/L or 1.5 to 74 pCi/L (rounded to two significant figures).

Table 6A – Th, U. Po Gross Alpha by LSC—Analytical Results for Required Method Uncertainty Evaluation

Nuclide: Gross Alpha (Th-230)   Matrix: FWHFPO   AAL Tested: 37.5 pCi/L

Proposed Method: U, Th, Po Gross Alpha by LSC

Required Method Validation Level: MARLAP "E"

Required Method Uncertainty, u_{MR}: 12 pCi/L at and below AAL; 33% above AAL

Acceptance Criteria:
Test Levels 1 and 2: $3.0 \times u_{MR}$ = known value of sample in test level ± 36 pCi/L

Test Level 3: $3.0 \times \varphi_{MR}$ = quoted known value of sample ± 99% of known value of sample (pCi/L)

Test Level 1 Test Value = 22.5 ± 1.2 pCi/L						
Sample #	pCi/L Known	CSU* Known	pCi/L Measured	CSU** Measured	Allowable Range (pCi/L)	Acceptable Y/N
1			13.68	0.96		Y
2			18.1	1.1		Y
3			14.93	0.99		Y
4	22.5	1.2	11.74	0.92	-14 to 59	Y
5			15.7	1.0		Y
6			13.45	0.96		Y
7			16.9	1.0		Y

Test Level 2 Test Value = 37.5 ± 2.1 pCi/L						
Sample #	pCi/L Known	CSU* Known	pCi/L Measured	CSU** Measured	Allowable Range (pCi/L)	Acceptable Y/N
1			31.0	1.3		Y
2			38.8	1.5		Y
3			32.8	1.3		Y
4	37.5	2.1	32.0	1.3	1.5 to 74	Y
5			24.8	1.2		Y
6			33.0	1.4		Y
7			27.2	1.2		Y
8			31.5	1.3		Y

Test Level 3 Test Value = 104.9 ± 6.3 pCi/L						
Sample #	pCi/L Known	CSU* Known	pCi/L Measured	CSU** Measured	Allowable Range (pCi/L)	Acceptable Y/N
1			72.6	2.0		Y
2			60.7	1.8		Y
3			67.5	1.9		Y
4	104.9	6.3	60.2	1.8	1.0 to 210	Y
5			76.5	2.1		Y
6			86.5	2.2		Y
7			89.3	2.3		Y

*   *Quoted uncertainty (one sigma)*

**   *Combined standard uncertainty, k = 1*

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Table 6B – ^{226}Ra Alpha by Gamma Spectrometry - Analytical Results for Required Method Uncertainty Evaluation

Nuclide: Gross Alpha (^{226}Ra)   Matrix: FWHFPO   AAL Tested: 164.9 pCi/L

Proposed Method: ^{226}Ra Alpha by Gamma Spectrometry

Required Method Validation Level: MARLAP "E"

Required Method Uncertainty, u_{MR}: 54 pCi/L at and below AAL; 33% above AAL

Acceptance Criteria:
Test Levels 1 and 2: $3.0 \times u_{MR}$ = known value of sample in test level ± 162 (pCi/L)

Test Level 3: $3.0 \times \varphi_{MR}$ = quoted known value of sample ± 99% of known value (pCi/L)

Sample #	pCi/L Known	CSU* Known	pCi/L Measured	CSU** Measured	Allowable Range (pCi/L)	Acceptable Y/N
Test Level 1 Test Value = 75.0 ± 2.0 pCi /L						
1			58.55	18.1		Y
2			93.7	41.8		Y
3			107.3	36.45		Y
4	75.0	2.0	101	41.8	-87 to 240	Y
5			153	42.8		Y
6			62.5	19.5		Y
7			84.1	33.2		Y
Test Level 2 Test Value = 164.9 ± 4.5 pCi/L						
1			125.8	22		Y
2			140	21.6		Y
3			144	22.2		Y
4			110	22.6		Y
5	164.9	4.5	167	43.6	2.9 to 330	Y
6			131	22.9		Y
7			150	22.7		Y
8			125.8	22		Y
Test Level 2 Test Value = 37.5 ± 2.1 pCi/L						
1			31.0	1.3		Y
2			38.8	1.5		Y
3			32.8	1.3		Y
4			32.0	1.3		Y
5	37.5	2.1	24.8	1.2	1.5 to 74	Y
6			33.0	1.4		Y
7			27.2	1.2		Y
8			364	32.2		Y

*   *Quoted uncertainty (one sigma)*

**   *Combined standard uncertainty, k=1.*

Table 6C – ^{228}Ra Beta by Gamma Spectrometry—Analytical Results for Required Method Uncertainty Evaluation

Nuclide: Gross Beta (^{228}Ra)   Matrix: FWHFPO   AAL Tested: 62.47 pCi/L

Proposed Method: ^{228}Ra Beta by Gamma Spectrometry

Required Method Validation Level: MARLAP "E"

Required Method Uncertainty, u_{MR}: 31 pCi/L at and below AAL; 50% above AAL

Acceptance Criteria:
Test Levels 1 and 2: $3.0 \times u_{MR}$ = known value of sample in test level ± 93 pCi/L

Test Level 3: $3.0 \times \varphi_{MR}$ = quoted known value of sample ± 150% of known value (pCi/L)

Test Level 1 **Test Value = 41.4 ± 0.65 pCi/L**						
Sample #	**pCi/L Known**	**CSU* Known**	**pCi/L Measured**	**CSU** Measured**	**Allowable Range pCi/L**	**Acceptable Y/N**
1			44.9	6.03		Y
2			50.2	7.13		Y
3			54	6.46		Y
4	41.40	0.65	39.2	4.61	-52 to 130	Y
5			52.2	5.08		Y
6			30.6	5.07		Y
7			31.1	5.5		Y
Test Level 2 **Test Value = 62.47± 0.99 pCi/L**						
Sample #	**pCi/L Known**	**CSU***	**pCi/L Measured**	**CSU****	**Allowable Range pCi/L**	**Acceptable Y/N**
1			77.2	6.67		Y
2			80.2	8.44		Y
3			53.2	6.13		Y
4			82.4	10.5		Y
5	62.47	0.99	85.3	10.5	-31 to 160	Y
6			62.3	6.52		Y
7			76.7	9.17		Y
8			77.2	6.67		Y
Test Level 2 **Test Value = 37.5 ± 2.1 pCi/L**						
Sample #	**pCi/L Known**	**CSU* Known**	**pCi/L Measured**	**CSU** Measured**	**Allowable Range (pCi/L)**	**Acceptable Y/N**
1			31.0	1.3		Y
2			38.8	1.5		Y
3			32.8	1.3		Y
4	37.5	2.1	32.0	1.3	1.5 to 74	Y
5			24.8	1.2		Y
6			33.0	1.4		Y
7			27.2	1.2		Y

*   *Quoted uncertainty (one sigma)*

**   *Combined standard uncertainty, k=1.*

Based on the results in Tables 6A to 6C it may be concluded that:

- A required method uncertainty of 12 pCi/L can be achieved at an action level of 38 pCi/L for gross alpha analysis using LSC

- A required method uncertainty of 54 pCi/L can be achieved at an action level of 165 pCi/L for ^{226}Ra analysis using gamma spectrometry

- A required method uncertainty of 31 pCi/L can be achieved at an action level of 62 pCi/L for ^{228}Ra analysis using gamma spectrometry.

These results meet the measurement quality objectives from the method development plan.

Tables 7A to 7C provide summary information regarding the expected variability of the results for an individual analysis and test level. In each case, the experimental standard deviation was considerably less than the required method uncertainty indicated that the method is capable of meeting the method uncertainty MQO.

Table 7A – Th, U, Po Gross Alpha by LSC—Experimental Standard Deviation of the Seven PT Samples by Test Level (^{230}Th)

Test Level	Mean Concentration Measured (pCi/L)	Experimental Standard Deviation[1] (pCi/L)	Required Method Uncertainty (pCi/L)
1	14.9	2.2	12
2 (AAL)	31.4	4.2	12
3	73	12	35[2]

[1] *Standard deviation of the seven measurements.*

[2] *Calculated by multiplying the known value of Test Level 3 by the required relative method uncertainty.*

Table 7B – ^{226}Ra Alpha by Gamma Spectrometry—Experimental Standard Deviation of the Seven PT Samples by Test Level

Test Level	Mean Concentration Measured (pCi/L)	Experimental Standard Deviation[1] (pCi/L)	Required Method Uncertainty (pCi/L)
1	94	32	54
2 (AAL)	138	18	54
3	431	52	150[2]

[1] *Standard deviation of the seven measurements.*

[2] *Calculated by multiplying the known value of Test Level 3 by the required relative method uncertainty.*

Table 7C – [228]Ra Beta by Gamma Spectrometry—Experimental Standard Deviation of the Seven PT Samples by Test Level

Test Level	Mean Concentration Measured (pCi/L)	Experimental Standard Deviation[1] (pCi/L)	Required Method Uncertainty (pCi/L)
1	43.2	9.8	31
2 (AAL)	74	12	31
3	199.3	6.8	90[2]

[1] *Standard deviation of the seven measurements.*

[2] *Calculated by multiplying the known value of Test Level 3 by the required relative method uncertainty.*

9.3   Required Minimum Detectable Concentration

Critical Net Concentration

The method for Th, U, Po gross alpha by LSC in an FWHFO matrix was evaluated for a required MDC using surrogate water blanks that were taken through the analytical processes of gross alpha chemical separation and LSC. Ra-226 and Ra-228 were evaluated for the MDC by direct analysis of the MDC verification samples by gamma counting.

Demineralized water blanks for the gross alpha determination by LSC yielded an expected blank value of zero since the average of these blanks was used to determine the background subtraction value, while surrogate samples yielded values greater than zero. The elevated result for surrogates is likely due to the contribution of low levels of naturally occurring radionuclides in the reagents used to make the surrogate. Thus, the surrogate water blanks were used to determine a matrix appropriate critical net concentration for the verification of the MDC. The results of the demineralized water and surrogate blanks for gross alpha are shown in Tables 8A and 8B.

Table 8A – Th, U, Po Gross Alpha by LSC—Blank Water Samples

Sample ID	Concentration (pCi/L)	CSU* (pCi/L)
DI Water Blank 1	0.07	0.69
DI Water Blank 2	-0.12	0.68
DI Water Blank 3	0.54	0.71
DI Water Blank 4	-0.12	0.68
DI Water Blank 5	-0.59	0.66
DI Water Blank 6	0.07	0.69
DI Water Blank 7	0.15	0.69
*Mean** (pCi/Liter)*	*0.00*	
*Standard Deviation ** (pCi/Liter)*	*0.34*	
Critical Net Concentration (pCi/Liter)	*0.66*	

*   *Combined standard uncertainty, k=1 or coverage factor of 1.*

**   *Mean and standard deviation were calculated before rounding.*

Table 8B – Th, U, Po Gross Alpha by LSC—Surrogate Water Samples

Sample ID	Concentration (pCi/L)	CSU* (pCi/L)
Surrogate Blank 1	8.86	0.85
Surrogate Blank 2	6.95	0.85
Surrogate Blank 3	7.92	0.83
Surrogate Blank 4	6.53	0.79
Surrogate Blank 5	7.81	0.82
Surrogate Blank 6	7.03	0.80
Surrogate Blank 7	7.03	0.80
*Mean** (pCi/Liter)*	*7.45*	
*Standard Deviation ** (pCi/Liter)*	*0.79*	
Critical Net Concentration (pCi/Liter)	*1.5*	

*   *Combined standard uncertainty, k=1 or coverage factor of 1.*

**   *Mean and standard deviation were calculated before rounding.*

The results for the demineralized water blanks and surrogate blanks measured by gamma ray spectrometry were indistinguishable from each other (i.e., statistically the same). Therefore these data were pooled and used to calculate the critical level net concentration for the ^{226}Ra and ^{228}Ra measurements. The pooled results are shown in tables 8C and 8D.

Table 8C – ^{226}Ra Alpha by Gamma Spectrometry in Demineralized and Surrogate Water Samples

Sample ID	Concentration (pCi/L)	CSU* (pCi/L)
Surrogate 1	-12.6	17.3
Surrogate 2	-17.9	18.3
Surrogate 4	-15.78	34
Surrogate 5	-8.99	19.5
Surrogate 6	14.3	24.5
Surrogate 7	-12.1	17.4
Surrogate 8	-6.73	22.9
DM Water Blank 1	53.5	26
DM Water Blank 2	-6.4	17.8
DM Water Blank 3	-1.94	28.6
DM Water Blank 5	-45	30.7
DM Water Blank 6	-18.3	24.8
DM Water Blank 7	-9.94	21.3
*Mean** (pCi/Liter)*	*-7*	
*Standard Deviation ** (pCi/Liter)*	*22*	
Critical Net Concentration (pCi/Liter)	*40*	

*   *Combined standard uncertainty, k=1 or coverage factor of 1.*

** *Mean and standard deviation were calculated before rounding.*

Table 8D – ^{228}Ra Gross Beta by Gamma Spectrometry in Demineralized and Surrogate Water Samples

Sample ID	Concentration (pCi/L)	CSU* (pCi/L)
Surrogate 1	11.8	5.24
Surrogate 2	13.3	6.62
Surrogate 4	14.9	5.7
Surrogate 5	-9.54	11.1
Surrogate 6	-16.2	23.8
Surrogate 7	5.65	4.24
Surrogate 8	-11.8	8.19
DM Water Blank 1	-10.7	13.4
DM Water Blank 2	-1.87	1.2
DM Water Blank 3	-17.1	34.1
DM Water Blank 5	-9.42	10.1
DM Water Blank 6	-3.08	4.34
DM Water Blank 7	-11.7	13.2
*Mean** (pCi/Liter)*	**-4**	
*Standard Deviation ** (pCi/Liter)*	**11**	
Critical Net Concentration (pCi/Liter)	**20**	

* *Combined standard uncertainty, k=1 or coverage factor of 1.*

** *Mean and standard deviation were calculated before rounding.*

Required MDC

The method development plan based the estimated MDC values for gross alpha and gross beta on demineralized water blanks. The initial estimates of the MDCs targeted for ^{226}Ra and ^{228}Ra proved to be too low and were adjusted to a higher concentration during the method development process. The most likely reason for this was increased background counts from low activity concentration of natural radioactivity in the surrogate matrix.

The MDC data for each of the three evaluations are shown in Tables 9A through 9C. The determination of gross alpha using ^{226}Ra as the radionuclide and gamma spectrometry as the measurement technique is not as sensitive as using liquid scintillation as the measurement technique.[11] For this reason, the two different techniques for the gross alpha measurement have different MDC values. This is highlighted in the MDC results shown in Tables 9A and 9B.

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[11] The abundance of the 186 keV gamma ray for ^{226}Ra is only 3.3 % while the abundance of the alpha particle emission is 100 %.

Table 9A – Reported Results for Samples Containing Th, U, Po Gross Alpha by LSC[1] at the As-Tested MDC Value (12.45 pCi/L)

Sample ID	Concentration (pCi/L)	CSU[2] (pCi/L)	Test Result $\leq CL_{NC}$ (Y/N)
MDC 1	12.08	0.93	N
MDC 2	7.73	0.82	N
MDC 3	13.72	0.96	N
MDC 4	9.05	0.85	N
MDC 5	11.89	0.92	N
MDC 6	8.97	0.85	N
MDC 7	8.62	0.84	N
MDC 8	10.10	0.88	N
MDC 9	10.57	0.89	N
MDC 10	9.21	0.86	N
Mean [3] (pCi/L)			10.2
Standard Deviation of Results [3] (pCi/L)			1.9
CL_{NC} [4] (pCi/L)			1.5
Acceptable maximum values ≤ CL$_{NC}$			2
Number of results > CL$_{NC}$			10
Number of results ≤ CL$_{NC}$			0
Evaluation			PASS

[1]   Samples spiked with ^{230}Th.

[2]   Combined standard uncertainty, coverage factor k=1.

[3]   Mean and standard deviation were calculated before rounding.

[4]   Critical net concentration. CL_{NC} based on the water blanks taken through the entire method.

Table 9B – Reported Results for ^{226}Ra Alpha[1] by Gamma Spectrometry at the As-Tested MDC Value (55.2 pCi/L)

Sample ID	Concentration (pCi/L)	CSU[2] (pCi/L)	Test Result $\leq CL_{NC}$ (Y/N)
MDC 1	148	42.1	N
MDC 2	99.6	42.4	N
MDC 3	79.2	34.13	N
MDC 4	51.7	17	N
MDC 5	102	44.9	N
MDC 6	74.7	31.8	N
MDC 7	72.8	36.6	N
MDC 8	68	33.2	N
MDC 9	58.9	25.4	N
MDC 10	98.1	34	N
Mean [3] (pCi/L)			**85**
Standard Deviation of Results [3] (pCi/L)			**28**
CL_{NC} [4] (pCi/L)			40
Acceptable maximum values $\leq CL_{NC}$			2
Number of results $> CL_{NC}$			10
Number of results $\leq CL_{NC}$			0
Evaluation			**PASS**

[1]   Samples spiked with ^{226}Ra.

[2]   Combined standard uncertainty, coverage factor k=1.

[3]   Mean and standard deviation were calculated before rounding.

[4]   Critical net concentration. CLNC based on the water blanks taken through the entire method.

The initial MDC verification PTs for gross beta using gamma spectrometry turned out to be below the detection capability of the method as was demonstrated when an initial run failed to meet the acceptance criteria. It was determined that the samples initially counted for the ½ AAL uncertainty determination (30.4 pCi/L) provided a more representative estimate of the MDC. Additional MDC test samples were prepared and counted and the results are reported in Table 9C. A new set of samples was also prepared for testing of uncertainty at the "½ AAL" (approximately 65% of the AAL) and counted with results reported in Table 6C (41.4 pCi/L). The results for ^{228}Ra (^{228}Ac) as a measure of the gross beta activity were very reproducible. However, further work on other gamma ray emitters in the natural decay series needs to be performed to provide better estimation for the detection limits using this method.

Table 9C – Reported Results for ^{228}Ra Beta[1] by Gamma Spectrometry at the As-Tested MDC Value (30.4 pCi/L)

Sample ID	Concentration (pCi/L)	CSU [2] (pCi/L)	Test Result $\leq CL_{NC}$ (Y/N)
MDC 1	35.8	6.03	N
MDC 2	44.2	5.45	N
MDC 3	57.9	5.55	N
MDC 4	35.5	5.59	N
MDC 5	58.3	6.6	N
MDC 6	40.5	4.53	N
MDC 7	26.2	5.06	N
MDC 8	34	3.52	N
MDC 9	30.8	4.02	N
MDC 10	26.2	5.31	N
Mean [3] (pCi/L)			39
Standard Deviation of Results [3] (pCi/L)			12
CL_{NC} [4] **(pCi/L)**			20
Acceptable maximum values $\leq CL_{NC}$			2
Number of results > CL_{NC}			10
Number of results $\leq CL_{NC}$			0
Evaluation			**PASS**

[1]   *Samples spiked with ^{228}Ra.*

[2]   *Coverage factor k=1.*

[3]   *Mean and standard deviation were calculated before rounding.*

[4]   *Critical net concentration. CL_{NC} based on the water blanks taken through the entire method.*

9.4   Evaluation of the Absolute and Relative Bias

Test results for verification of the MDC and test levels 1–3 were evaluated for absolute and relative bias using the test process described in Section 7.3 above.[12] The bias test results are summarized in Table 10. It should be noted that the presence of detectable levels of bias is not a criterion for the method development until the magnitude of the bias is significant enough to cause results to fall outside the acceptance criteria of the required method uncertainty. In most cases bias was detected across the range of concentrations tested with highest levels of relative bias generally being associated with the lowest activity concentration samples. For example, the largest relative bias (percent) was observed for MDC samples for gross beta using ^{228}Ra as a tracer. Please see further discussion of the bias in Section 9.5.

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[12] For more complete treatments of the statistical detection and evaluation for absolute and relative bias see *Method Validation Guide for Qualifying Methods Used by Radiological Laboratories Participating in Incident Response Activities* (EPA 2009) and *Quality Assurance of Chemical Measurements* (Taylor 1987).

Table 10 – Absolute and Relative Bias for Gross Alpha and Gross Beta by the Three Measurements

Type of Bias	Gross Measurement (Radionuclide Measured)	Known Value ± CSU ($k=1$), pCi/L	Mean of Measurement ± SD ($k=1$), pCi/L	Difference from Known, pCi/L (%)	Number of Measurements/ (Effective) Degrees of Freedom[1]	│T│[1]	t_{df}[1]	Bias[2] (Y/N)?
Absolute	Gross Alpha (^{230}Th, LSC)	–	7.45 ± 0.79	7.45	7/6	2.447	24.8	Y
	Gross Alpha (^{226}Ra, GS)	–	-7 ± 22	7	13/12	2.179	1.09	N
	Gross Beta (^{228}Ra/^{228}Ac, GS)	–	-4 ± 11	4	13/12	1.12	2.179	N
MDC	Gross Alpha (^{230}Th, LSC)	12.45±0.79	10.2 ±1.9	2.25 (-18)	10/70	2.28	1.99	Y
	Gross Alpha (^{226}Ra, GS)	55.2±1.5	85±28	27.2 (54)	10/9	3.36	2.26	Y
	Gross Beta (^{228}Ra/^{228}Ac, GS)	30.4±0.2	39±12	8.6 (28)	10/9	2.32	2.26	Y
Level 1	Gross Alpha (^{230}Th, LSC)	22.5±1.2	14.9±2.2	7.6 (-34)	7/64	5.05	2.00	Y
	Gross Alpha (^{226}Ra, GS)	75.0±2.0	94±32	19 (25)	7/6	1.59	2.45	N
	Gross Beta (^{228}Ra/^{228}Ac, GS)	41.40±0.65	43.2±9.8	1.8 (4.3)	7/6	0.47	2.45	N
Level 2	Gross Alpha (^{230}Th, LSC)	37.5±2.1	31.4±4.2	6.1 (-16)	8/61	2.39	2.00	Y
	Gross Alpha (^{226}Ra, GS)	164.9±4.5	138±18	26.9 (-16)	8/12	3.23	2.18	Y
	Gross Beta (^{228}Ra/^{228}Ac, GS)	62.47±0.99	74±12	11.5 (18)	8/6	2.52	2.45	Y
Level 3	Gross Alpha (^{230}Th, LSC)	104.9±6.3	73±12	31.9 (-30)	7/55	4.14	2.00	Y
	Gross Alpha (^{226}Ra, GS)	449±12	431±52	18 (-4.0)	8/11	0.76	2.20	N
	Gross Beta (^{228}Ra/^{228}Ac, GS)	180.1±2.8	199.3±6.8	19.2 (11)	8/28	5.06	2.05	Y

[1] Assessment of relative bias was performed at MDC and Levels 1, 2, and 3.

[2] │T│ is the absolute value of the *t*-statistic, and t_{df} is the effective degrees of freedom of the *t*-statistic. They are defined in Section 7.3 and represent the statistical factors for the actual measurement data and for data from a normal distribution.

9.5 Method Ruggedness

Ruggedness represents the ability of a method to be unaffected by changes in the components of the sample or the measurement system. The matrix selected for this project was based on that of a single sample of FPWHFO and will not necessarily represent method performance in samples of significantly different composition such as FPWHFO collected at different times in the life of a well or from different wells or regions. Nonetheless, this matrix is considered to be a particularly challenging one due to its extremely high dissolved solids content and its complexity (very elevated levels of divalent cations). This affected the bias and detectability of each of the three measurements associated with the method.

Based on testing performed at the end of the method development process, gross alpha activity determined by liquid scintillation counting of the separated U, Th, and Po fraction of the sample was measured with recoveries ranging from 84–96 % of the expected value (see Section 11 and Attachment II, "Flow Chart for the Alpha Beta Methods Attempted " and Figure 6). The low bias was confirmed during formal development testing with an average gross alpha recovery for the 14 test measurements at test levels 2 and 3 of 77±11% (k=1) of the known value and results ranging from 57–104 %.[13] Although these results easily meet testing acceptance criteria, the systematic low bias and the observation that quantitative (or near-quantitative) recovery of ^{230}Th is not achieved raises concerns about the ruggedness of the chemical separation method. Final method testing was performed using ^{230}Th, which had the lowest recovery of the three radioelements evaluated in final preliminary tests, but not uranium or polonium. Since uranium and polonium were not quantitatively recovered in preliminary testing, it is reasonable to expect similar low bias for these elements with real test samples.

Gamma spectrometry, by its nature as a non-destructive method, is more rugged than methods that rely on chemical separations since there can be no losses prior to the analytical measurement and variability of the matrix will have less potential to impact analytical results. The average recovery calculated from values presented in Table 6B for the 14 test-level-2 and 3 analytical measurements of ^{226}Ra was 90±13% (k=1) with individual values ranging from 67–108%. The average recovery calculated from values presented in Table 6C for the 14 analytical measurements of ^{228}Ra spikes at test levels 2 and 3 was 114±14% (k=1) with individual values ranging from 85–137%. While it likely would be possible to improve the process used for the gamma spectrometry measurement, better control of the sample (i.e., no introduction of added variability from chemical separations) makes gamma spectrometry a very rugged technique. Thus, there is little concern that measured values will adequately reflect the performance of the gamma spectrometry technique on real-world samples.

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[13] Note that the level of uncertainty for samples for the verification of the MDC and test level 1 due to the low concentrations in these samples.

10.0   Timeline to Complete a Batch of Samples

It is important for the laboratory to know how long an analysis will take so that they can provide timely results back to their clients. Historically a batch of gross alpha and gross beta analyses will take on the order of 3–4 days (based on the SDWA methods). There are two separate timelines for the analysis based on the two different analytical methods that are used for measuring the gross alpha and gross beta activity concentrations. Gross Th, U, and Po using gross alpha analysis by LSC, from sample preparation to final results reporting, can take place in 3 hours for a single sample, or approximately one day for a batch of 20 samples (assuming a single LSC is available). The gamma spectrometry count for ^{228}Ra beta and ^{226}Ra alpha can require about 12 hours for a single sample and can process about 2 samples per day per spectrometer. Assuming a single gamma ray spectrometer is available, a batch of 20 samples would require 10 days for analysis. Laboratories will need to judge their processing times for a batch of samples based on the number of instruments they have available.

See Attachment II for a breakdown of the times for the individual steps shown in the flowchart in Section 17.4.

11.0 Reported Modifications During Development and Recommendations for Future Work

The development of a straight-forward, inexpensive, single measurement method for gross alpha and gross beta screening of FPWHFO samples was hampered by the complexity of the matrix itself. Significant preliminary effort was spent in Phase 1 modifying the approach initially conceived to accommodate a FPWHFO matrix which turned out to be particularly challenging. The development process will be briefly summarized here to provide perspective. Attachment I is a more complete presentation of various trials and modification that had to be made during the Phase 1 method development process that preceded the final method development process.

Several classic water methods for gross activity testing were explored in hopes that a simple non-destructive analysis (i.e., an analysis without chemical separation) could be performed. Unfortunately solids content in the gram per liter range is 200–1000 times above the range that Method 900.0 evaporation or direct counting by liquid scintillation (e.g., ASTM D7282) can accommodate. Digestion and fusion techniques were considered but in view of the high non-volatile solids content of the sample matrix, would not have made the matrix more amenable to processing. All attempts to use these classic approaches failed to yield acceptable results.

A variety of classic chemical separation techniques were explored for chemically isolating radium, thorium, uranium, or polonium. Among the approaches explored were barium sulfate precipitation techniques (e.g., EPA Method 900.1 or 903.0, SM 7110C), barium chromate precipitations (e.g., EPA Method 905.0) and solid phase extraction with chelating agents, such as Empore™ Radium RadDisks. Again, the gram per liter levels of barium, strontium, and calcium interfered with every attempt to chemically isolate radium (also a divalent cation) together with thorium, uranium, and polonium.

A radon deemanation method (Rad7™ electronic radon detector) proved to be reasonably successful but this approach had to be abandoned due to concerns about foaming of the sample and extended turn-around times as long as 7–21 days (required for ingrowth of ^{222}Rn). Other radon emanation techniques, such as mineral oil extraction of radon with liquid scintillation counting or radon deemanation similar to the classic approach used in EPA Method 903.1 could be considered as possible avenues for future exploration for more sensitive radionuclide-specific determinations of ^{226}Ra.

One of the methods used to initially characterize the sample, gamma spectrometry, proved to be one of the most viable, attractive, and rugged alternatives for the analysis of FPWHFO. The primary advantage of gamma spectrometry is its ability for simultaneous measurement of all gamma emitters present in the sample together with its nominal insensitivity to solids in the sample. In contrast to alpha and beta emissions, where sample solids above 100–200 mg interfere with measurements, the highly penetrating nature of gamma rays allows measurement of solid samples in the 3–5 kg range without chemical separations. The response of gamma spectrometers is also limited relative to that of liquid scintillation counters. Gamma

detection efficiencies are generally less than 10% of the efficiency for either alpha or beta emissions by liquid scintillation. Similarly, the gamma emission rate associated with natural chain alpha and beta emitters (3% to 45%) is low relative to the corresponding alpha and beta particle emission rates (nearly 100%). By increasing the size of the aliquant and the count time, however, it is possible to compensate, as least in part, for low response in the gamma detector. As a result, detection capabilities may be obtained for gamma spectrometry that are generally within a factor of 10–50 of those possible by direct measurement of alpha and beta emissions. Gamma spectrometry was ultimately the technique chosen to perform determinations of ^{226}Ra and gross beta.

Efforts were focused on finding a group chemical separation for thorium, uranium and polonium. Iron hydroxide coprecipitation was initially explored as a preconcentration technique but due to the possibility of high iron content in samples that would interfere with chemical separations and subsequent liquid scintillation measurements, the decision was made to use a manganese dioxide coprecipitation in reducing environment (i.e., to remove iron). A number of extraction chromatographic techniques were tested including a stacked TEVA-TRU followed by Sr Resin approach. Sr Resin is effective only for polonium and would be overwhelmed by barium resulting in low yields. Testing of the TRU Resin alone, however, showed excellent uptake of thorium, uranium, and polonium from a 4 M HCl load solution (containing ascorbic acid to reduce iron) and effective retention of the analytes during 4 M HCl rinse steps. Elution profiles (see Attachment 1, Figure 5) indicated that the three analytes could effectively be stripped from the column with 5 mL of ammonium bioxalate. Analysis of subsequent data indicated that a more complete recovery of analytes, especially uranium, was obtained by modifying the single 5-mL elution to five sequential 1-mL additions of bioxalate.

Source preparation techniques were also investigated. A number of coprecipitation techniques were explored but obtaining quantitative coprecipitation for all three radioelements in a single step proved to be elusive. In the end, a simple technique was chosen - direct addition of the eluent to liquid scintillation cocktail.

Pulse-shape discrimination liquid scintillation analysis is an attractive option because it was less sensitive to solids in the sample than gas flow proportional counting, has very high detection efficiencies due to the 4π counting geometry (~90%), and reasonably low backgrounds. The result was reasonably short count times (e.g., 30 minutes) and good detection capabilities.

The final method for gross alpha (Th, U, and Po) by liquid scintillation was thus assembled based on the most successful approaches identified: manganese dioxide coprecipitation followed by group separation of thorium, uranium and polonium on TRU Resin, stripping with ammonium bioxalate, and pulse-shape discrimination liquid scintillation analysis. The draft method was tested using ^{230}Th, ^{232}U, and ^{209}Po tracers and recoveries of ~89% and above were obtained for each of the three elements with ^{230}Th, the test isotope selected for testing, showing the lowest recoveries (See Attachment 1, Figure 6).

Gamma spectrometry was selected for the ^{226}Ra alpha measurement and the gross beta measurement. Beyond ensuring that solids remained suspended using an agar gelling technique, the classic technique for gamma spectrometry was used without significant modification.

No technical changes were made to the final measurement techniques following the initiation of development testing. Since the technical content of the method was finalized prior to Phase 2 and 3 testing, the data obtained in Phases 2 and 3 alone should be used reflect the performance of the final method as presented in Attachment III.

The method validated for gross alpha by LSC measures the activity of isotopes of thorium, uranium and polonium. Alpha-emitting radium isotopes, which are likely to be more prevalent in these samples (in terms of activity concentration), could not be easily or economically incorporated into a single-step gross alpha method at this time. The uncertainty for alpha-emitting radium isotopes determined by gamma spectrometry is much larger than that for the liquid scintillation analysis for the other alpha-emitting isotopes.[14] This result complicates the reporting process, and the determination of uncertainty, and prevents calculation of a single meaningful value for gross alpha detection capability.

While radionuclide-specific determinations of the naturally occurring progeny of uranium and thorium decay chain members are possible by gamma spectrometry, the same differences in efficiency and abundance will result in counting times that are significantly longer than that for the alpha analyses. As mentioned in Section 1, gross alpha and beta activity is temporally dependent due to the inherent complexity of radioactive ingrowth and decay in the uranium and thorium decay chains. As a result of this, the physical activity of some of the radionuclides being measured will change over time such that the results at the beginning of an analysis sequence may not be comparable to those at the end of the run. Although the activity of long-lived radionuclides such as ^{226}Ra would not be impacted, delaying count times for measurements of shorter-lived beta-emitters such as ^{212}Pb, ^{214}Pb, and ^{214}Bi will have an impact on the activity measured.

Overall the detection limits achieved, the MDC target and the action levels that were used were based on the results of the preliminary testing. These values were not as low as had originally been hoped for and can be improved upon with further analysis and development studies.

Thus, two sets of recommendations follow for use of this method and possible further development. The first set of recommendations falls within the scope of the current method and possible improvements (recommendation 8) on it:

1. Sample results using this method should be reported separately as:

    a. Gross alpha (U, Th, Po) – LSC

    b. Gross alpha (^{226}Ra) – Gamma Spectrometry[15]

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[14] The magnitude of differences in uncertainty and counting time is attributable to the relative detection efficiency of liquid scintillation and gamma spectrometry instruments and differences in the abundance of decay particle emission rates (i.e., abundance) for the radionuclides. The detection efficiency of gamma spectrometry instruments is generally less than 10% of that for liquid scintillation counters. The abundance for gamma rays is often significantly less than 100%, but for radionuclides that decay by alpha emission the abundance is close to 100%.

[15] Combined gross alpha results provide no information about the radionuclides present. For example, it is not uncommon to find high levels of radium in FPWHFO samples even though there may be next to no U, Th, or Po present. By separately screening samples for Ra-226, and for alpha activity associated with U, Th, or Po, it may be possible to decide there is no need for radionuclide-specific testing for U, Th, or Po. This strategy can be used to streamline the characterization of samples.

      c.   Gross beta – Gamma Spectrometry

2.   In principal, a screening test should be designed to minimize the risk of not detecting analyte present at the analytical action level to a rate that is acceptable in the decisionmaking process. Low bias in a screening measurement may be tolerable as long as the criteria used to decide that the analytical action level has been exceeded take into account uncertainty and the bias associated with the measurement. Thus, additional work is needed to estimate the bias and uncertainty associated with the Th, U, Po gross alpha measurement, and to propose decision rules that ensure that measurements will reliably identify samples with activity that exceeds the specified analytical action level.[16]

3.   Although testing criteria were met, an observed low bias raises questions about the ruggedness of the gross alpha measurement, especially with regard to analysis of FPWHFO of different compositions, from different regions, or at different times in the hydraulic fracturing life cycle. Future work should be done to explore the chemical separation scheme to improve the individual recoveries for Th, U, and Po, and to test the approach using FPWHFO of varying compositions such as will be encountered in samples resulting from routine hydraulic fracturing operations.

4.   Additional work is needed to validate the gamma spectrometry measurement for each of the longer-lived beta-emitting members of the natural decay chains used to quantify gross beta activity by gamma spectrometry (in addition to ^{228}Ra).

5.   Additional work is needed to optimize the data inputs (e.g., libraries), analysis parameters (i.e., spectrum analysis parameters) and calculations used for the gamma spectrometry analysis of ^{226}Ra and radionuclides of interest to the gross beta analysis with a goal of minimizing levels of bias and uncertainty in the measurement.

6.   Additional work is needed to explore options for optimizing the preparation of the gamma spectrometry sample so that the radioelements can be concentrated, thereby improving measurement sensitivity and reducing the sample counting time.

7.   Additional work would be needed if all four of the long-lived radioelements (Ra, U, Th, and Po) associated with natural decay chain alpha-emissions are to be included in a single separation and analysis.

8.   Build on experience gained in this project in the area of chemical separations in FPWHFO samples to develop sensitive radionuclide-specific testing methods including: ^{226}Ra, ^{228}Ra, ^{210}Pb, ^{228}Th, ^{230}Th, ^{232}Th, ^{238}U, ^{235}U, ^{234}U, and ^{210}Po.

       The second set of recommendations has to do with temporally dynamic processes of radioactive decay and decay-progeny relationships is common to all gross alpha and beta

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[16] See Appendix VI of *Radiological Laboratory Sample Analysis Guide for Incidents of National Significance – Radionuclides in Water* (EPA 2008) for a discussion of the directed planning process (DQOs/MQOs) and guidance on controlling decision errors with analytical decision levels (ADLs). In this case, there is an additional concern about low bias in the measurement that must be worked out.

measurements of natural decay chain radioactivity. As discussed above in Section 1, the activity of samples containing natural decay chain activity, especially ^{226}Ra and ^{224}Ra, changes over time due to radioactive ingrowth and decay processes. Specifically, the activity physically present in the sample test source and the interpretation of gross alpha and gross beta results, depend on the timing of processes preceding the sample collection, the elapsed time between sample collection and preparation, and the elapsed time between sample preparation and the count. Parameters that either must be controlled, or at least taken into consideration, to ensure reliable interpretation of results include:

1. How long did FPWHFO fluids recirculate in the geologic formation prior to discharge to a settling pond, basin or waterway?

2. Does the activity present in the FPWHFO at the time of the sample measurement reflect that at key points in the life cycle of the FPWHFO (e.g., time of discharge, point of full ingrowth, point of transport or release of fluids)?

3. How does the time elapsed between collection, preparation and counting of the samples impact results. Can the timing of event be managed to minimize variability of results and provide useful and intercomparable measurements for gross alpha and beta.

4. Does the use of ^{230}Th or ^{210}Po for LSC provide the best method isotope for gross alpha activity?

5. The analysis of treated FPWHFO may prove to be a completely different matrix where some radionuclides have been removed (e.g., Ra). Thus future work should also examine these types of treated matrices.

Addressing these questions as part of the entire process, or identifying individual times for each of the separate steps until the laboratory receives the samples will ensure that the analytical results support defensible decisionmaking regarding the handling and disposition of the fluids.

12.0 Summary and Conclusions

Three parts of The *Gross Alpha and Gross Beta Method in FPWHFO* were tested using a matrix based on the composition of a FPWHFO sample received from the EPA to determine whether they would satisfy method development guidelines outlined in the *Method Validation Guide for Qualifying Methods Used by Radiological Laboratories Participating in Incident Response Activities* (EPA, 2009). Two of the three parts comprise measurements of alpha emitters in the sample while the third is designed to measure beta emitters.

The MQOs for each of the three parts differed based on the matrix complexity, the instruments used for analyses, and the nuclear constants associated with the principal radionuclides used for the development process, and variation associated with preparation of the test samples. The as-tested MQOs and measured results are presented in Table 3. The final method with flow diagram used in this method development study is presented in Attachment III.

Each of the three parts of the method validated met all of the acceptance criteria for method uncertainty as shown in Tables 6A, 6B, and 6C. A summary of the observed levels of uncertainty at each of three activity levels is summarized in Tables 7A, 7B, and 7C. Detectable levels of bias were observed across the activity levels for each of the three measurements as summarized in Table 10. The levels of bias, however, were so large that they compromised the determinatoin of method uncertainty. The detection capability for each of the three parts was successfully verified as summarized in 9A, 9B, and 9C.

Although all testing criteria were met as described in this report, the complexity of the matrix prevented development of a single-measurement method for gross alpha and beta in FPWHFO samples that will be simple, economical, and sufficiently rugged in matrices beyond the one used for the testing. Performing this analysis required a level of effort that was much different from previous analytical methods in other water matrices for alpha or beta emitters. Several unique approaches were attempted in order to identify an analytical approach that would accommodate this particularly challenging matrix. Section 11 provides a brief synopsis of development activities and Attachment 1 provides additional detail supporting the method development activities preliminary to final testing.

The final approach for gross alpha requires two measurements. The first measurement involves gross alpha by liquid scintillation counting following chemical separation to isolate thorium, uranium and polonium from the matrix. Method testing in the surrogate matrix indicates that a measureable bias is associated with the technique. Average recovery were 74±11% (*k*=1) of the known concentration of ^{230}Th. Recoveries ranged from 57–104%. Although all of the testing criteria were met, the observed low bias raises possible questions about the ruggedness of the technique, especially with regard to use of the method for analyzing of FPWHFO of different compositions, from different regions or different times in the hydraulic fracturing life cycle. Possible future work should be done to improve the ruggedness of the method and to develop

estimates of uncertainty and decision criteria that would protect against decision errors using this screening technique.[17] See Section 11 for recommendations for possible future work in this area.

The second measurement for alpha activity associated with ^{226}Ra is performed by gamma spectrometry. The gamma spectrometry measurement is used to simultaneously determine the activity of longer-lived members of the thorium and uranium decay chains for calculation of gross beta activity. Although the development process detected bias in the gamma spectrometry measurements at some levels, the magnitude of the bias is lower than that observed for the alpha and there is no need for concern about the ruggedness of the non-destructive measurement technique since there are no variables such chemical separations that will introduce variable levels of bias into the method. Section 11 suggests the possibility of future work to improve the sensitivity of the gamma spectrometry measurement.

Due to the physics of the measurement technologies, radionuclide determinations performed by gamma spectrometry are generally less sensitive and have higher uncertainty that those performed by the liquid scintillation counting. This complicates the reporting process, the determination of uncertainty, and prevents calculation of a single meaningful value for gross alpha detection capability. Section 11 recommends that measurements of gross alpha by LSC and of ^{226}Ra be reported and interpreted separately and suggests the possibility of future work that would improve the sensitivity of the gamma spectrometry measurement thereby minimize the disparity in the sensitivity of the two techniques.

Finally, as mentioned in the introduction in Section 1, all gross alpha and beta measurements are limited by the complexities of radioactive decay and ingrowth in the uranium and thorium decay chains which causes the alpha and beta activity physically present in the sample to change over time. Thus gross alpha and beta measurements are often not (inter-) comparable from measurement to measurement or laboratory to laboratory. This significantly complicated the interpretation of gross alpha and beta results. Section 11 recommends that future work explore the impact of timing on the performance of the method and the interpretation of results, a project that would benefit gross alpha and beta measurements of natural products in all water matrices.

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[17] A screening test should generally be designed to minimize the risk of not detecting analyte when it is present at some action level to a rate tolerable to the data end user. For this reason, screening tests tend to be structured to deliver results that systematically bias high. Low bias in a screening measurement may be tolerable as long as the criteria used to decide whether the action level has been exceeded take into account uncertainty and bias associated with the measurement.

13.   References

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Attachment I:

Method Development Trials

Classic Approach to Gross Alpha Beta: Evaporation and Gas Proportional Counting

One ml of the field sample (no dilution or treatment) was evaporated directly onto a planchet. The dry weight was 260.3 mg and 276.4 mg for replicate samples. These values were well outside the efficiency calibration curves for either gross beta or gross alpha. Spattering of the material was significant which would lead to an underestimate of the count rate. Based on these two significant issues no further analysis by this method was deemed to be fruitful.

Radionuclide: ^{226}Ra

Precipitation of $BaSO_4$ to coprecipitate radium was tried once. It was evident that too much precipitate formed (other solids besides the barium/radium precipitate salt out and provide too heavy a matrix for gross analysis by GPC). The resulting precipitate could not be processed any further, even when small sample volumes (< 100 mL) were used.

A more selective precipitation using barium chromate was attempted. This process yielded similar problems to using $BaSO_4$ with a large mass of other salts precipitating, forming a black/green 'dusty' precipitate that could not be loaded onto a planchet for gas flow proportional counting. Using this material for liquid scintillation analysis yielded severe color quench[18]. Radium recovery was only about 1%.[19]

Replicate aliquants of the sample (6×250 mL and 6×40 mL) were analyzed for ^{222}Rn following a period for ingrowth to assess ^{226}Ra concentration using a Durridge Rad7™ electric radon detector. This method provides high quality and consistent results, when the foaming of samples, relative humidity is controlled. Some issues where encountered with foaming of the FPWHFO samples. Methods could be developed for unsupported ^{222}Rn/ ^{220}Rn as well. The success of this approach indicates that a radon de-emanation approach to the analysis of ^{226}Ra (direct analysis of 50 mL of sample without prior chemical concentration) would be capable of a reasonably sensitive determination of ^{226}Ra with MDCs of ~10 pCi/L or less. The method would require waiting several days allowing the ^{222}Rn to ingrow into the sample. This approach was not pursued further, however, because it would require significant additional development and would not provide the longer list of beta-emitting analytes possible for gamma spectrometry analysis.

Radionuclides: U, Th, and Po

A classical approach was attempted to obtain a gross separation of uranium and thorium by $Fe(OH)_3$ precipitation. The iron hydroxide precipitate was dissolved in hydrochloric acid and loaded onto an Eichrom TRU/TEVA column for separation of the U/Th, and then eluted through a SR Resin™ for polonium.

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[18] Quench refers to any process that reduces the production of, or transmission of light from the sample to the photomultiplier detector. If a correction cannot be applied, quench may result in questionable results.

[19] The recovery of ^{226}Ra in this attempt was based on the analysis of the original sample for ^{226}Ra by gamma spectrometry.

In order to assess the success of the gross alpha attempts, the sample test sources were analyzed by alpha spectrometry. This not only helped to quantify yields but also to determine the effectiveness of separation of the alpha emitters.

The recovery for the radionuclides was assessed using alpha spectrometry and was as follows:

- Th recovery indeterminate due to ^{228}Th ingrowth

- Po recovery ~29.6 ± 1.7%

- U recovery ~26-49 ± 11%

Po can be selectively electroplated onto a silver disk. However, it must be isolated first with SR Resin™. Attempts to electrodeposit without a SR Resin clean-up resulted in no recovery with significant Th/Th-daughter contamination (as determined by alpha spectrometry). Figure 1 shows the alpha spectrum for the separated polonium (most abundant alpha in the spectrum at channel number ~ 950 is 4.88 MeV.

Figure 1 – Po-209 Alpha Spectrum
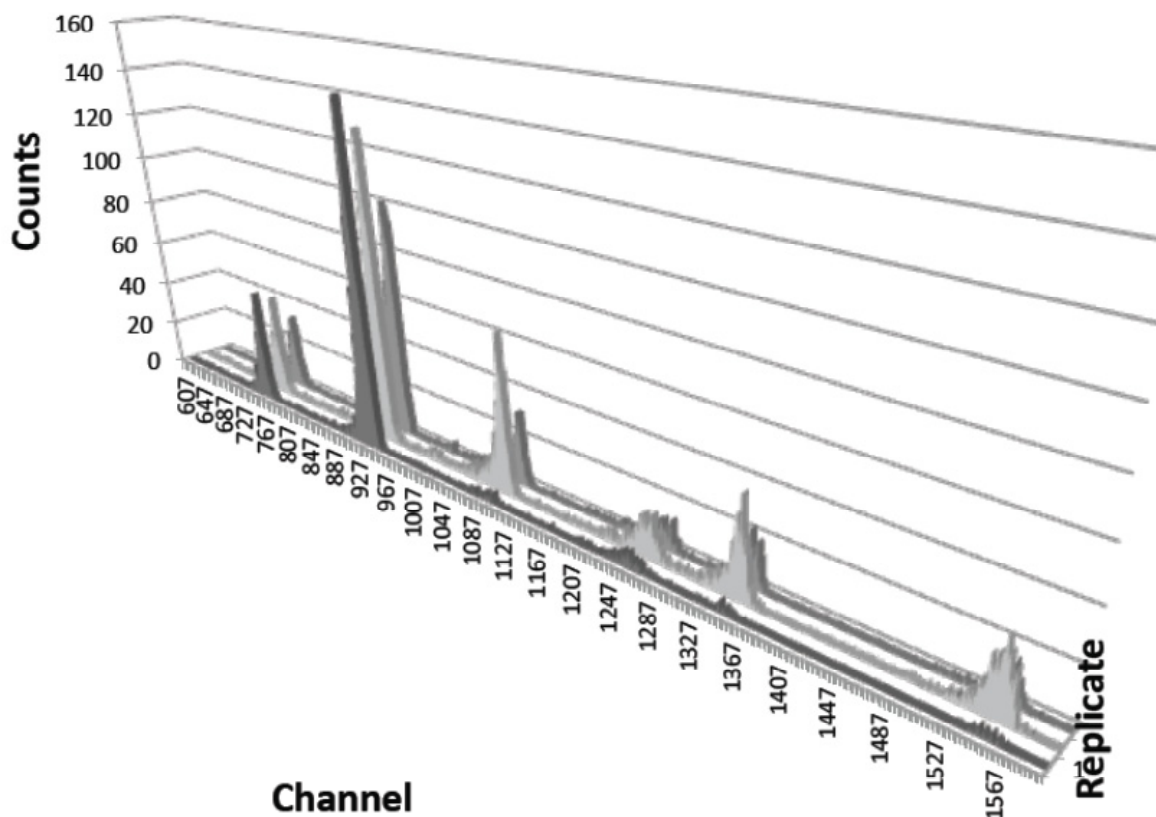
Group Separation Using MnO₂/Fe(OH)₃ Precipitation

This is a non-specific precipitation technique for radionuclide separation. The $MnO_2/Fe(OH)_3$ precipitate is dissolved in hydrochloric acid followed by TRU/TEVA group separation of actinides and SR-Resin for Po (U/Th). Run in quadruplicate.

Adding MnO_2 substantially increases recovery of U. Note that [228]Th cannot be used as a tracer since it may be present in the sample as an ingrowth product from [228]Ra; this provides an interesting possibility for dating of flowback waters. Natural [230]Th and its parents are generally not detectable in samples. As such, [230]Th may be a suitable candidate as a Th tracer for yield calculations. The U recovery for this mixed precipitate was 71.7±4.8%.

Thorium recovery from the field sample was indeterminate due to [228]Th ingrowth[20] from [228]Ra Analysis for either radium isotope was not attempted. When the surrogate solution was used with added [230]Th tracer, the alpha spectrum in Figure 2 was obtained (the most abundant alpha at channel number ~ 970 is 4.688 MeV).

Figure 2 – Alpha Spectrum of Separated [230]Th

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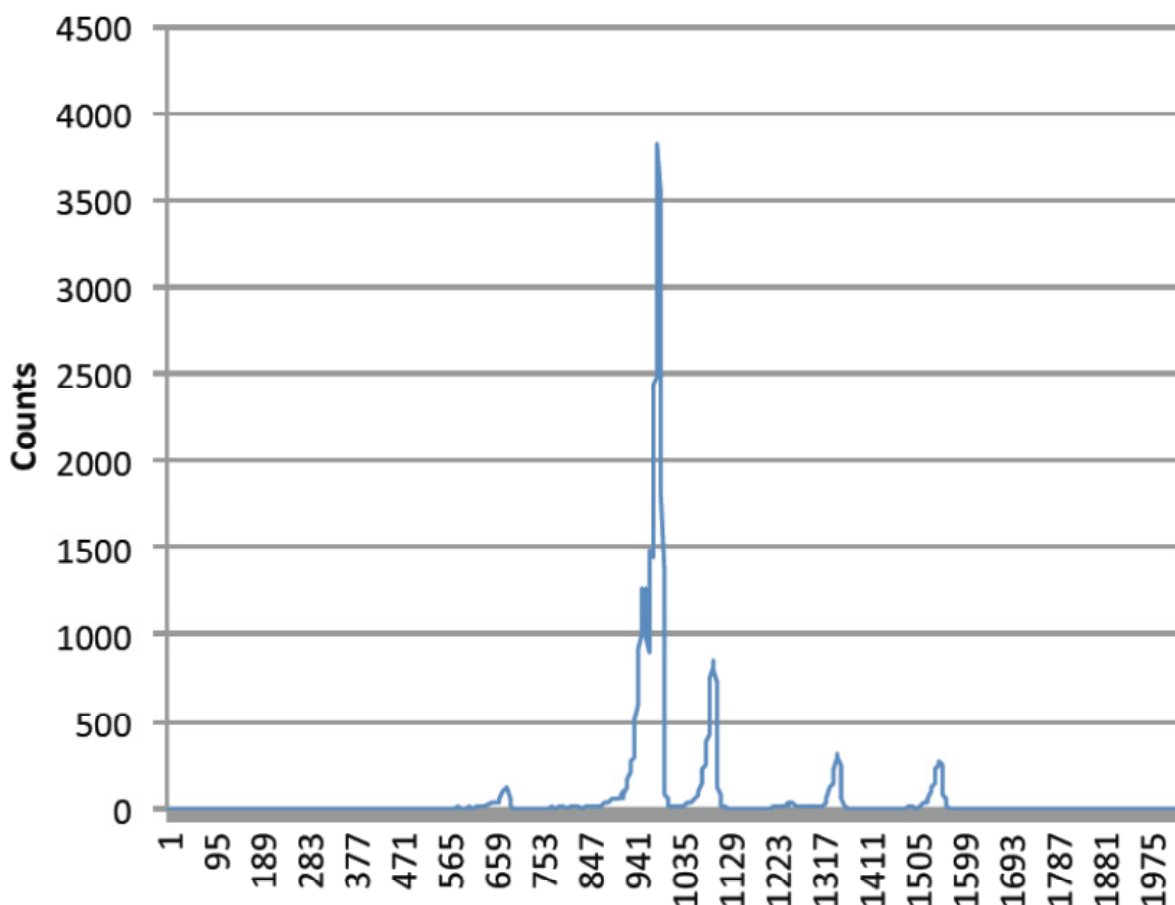
[20] Initially the concentration of [228]Th may have been very low. However the age of the sample (at least 3 months) and the high concentration of [226]Ra (determined by gamma spectrometry) have allowed significant ingrowth of the [228]Th.

Empore™ RAD Disks

This method of radionuclide concentration from water is used for several different radionuclides. The disadvantage is that disk material shows significant uptake of barium. Additionally, high concentrations of non-radionuclides, such as Ca and Sr, can outcompete Ra and significantly decrease retention on the disk. The recovery for radium was low, ~13.0 ± 1.1%, even with volumes as low as 50 mL of field sample diluted ten-fold to reduce the concentration of the non-radionuclide ions. There was too much competition for the exchange sites from non-radiological elements, and in particular for this sample, from barium. Therefore the use of the Empore disks was abandoned because of the significant non-radiological interfering ions.

Direct Addition to LS Cocktail

Addition of 0.10 to 10 mL aliquants of the field sample to liquid scintillation cocktail were used to determine the feasibility of performing direct gross alpha analysis. Even less than 0.1 mL led to salting out in the cocktail yielding a two-phase mixture with a high quench. Although liquid scintillation measurement remained attractive, this experience indicated that analysis of the sample would only be possible after clean-up from the FPWHFO matrix (i.e., chemical separations).

Gamma Spectrometry

Gamma spectrometry was one of the first analyses to be performed to assess the level of beta-gamma-emitting radionuclides native to the sample. A 3-L Marinelli beaker was counted in three different manners: for 17 hours as a straight sample, for 6 hours as a straight sample, and for 17 hours with agar added to ensure that settling of suspended solids did not occur.

^{226}Ra and ^{228}Ra (or their progeny) were detectable; however, no peaks were observed for ^{238}U (^{234}Th, ^{234m}Pa) or ^{235}U or ^{228}Th (^{224}Ra). The low concentration of ^{235}U in the sample, allowed for straightforward analysis of ^{226}Ra using the 186 keV peak.

Acid Digests Prior to Separations

Gross alpha analysis was attempted using 10–100 mL of sample following digestion in nitric acid. However, the amount of residue formed from this digest clogged the TRU Resin preventing completion of preparation for analysis by alpha spectrometry. In the case of LSC, the final digestate resulted in unacceptably high amounts of color quench.

Platinum Crucible

Initially acid digestion or fusion techniques were considered as an initial step in the process. The quantities of dissolved solids in the field sample limit the size of the aliquant making the fusion method using platinum crucibles unfeasible.

Polonium by Sulfide Precipitation

A method of isolating polonium from the bulk solution used CuS precipitation under acidic conditions was attempted as PoS will coprecipitate with CuS. Figure 3 shows the liquid scintillation spectrum from that gross separation. However, this separation technique was not

used in the final method as it caused an unacceptable level of quench in the liquid scintillation spectrum which would degrade the measurement sensitivity and reliability of the method.

Figure 3 – Liquid scintillation Spectrum of ^{209}Po
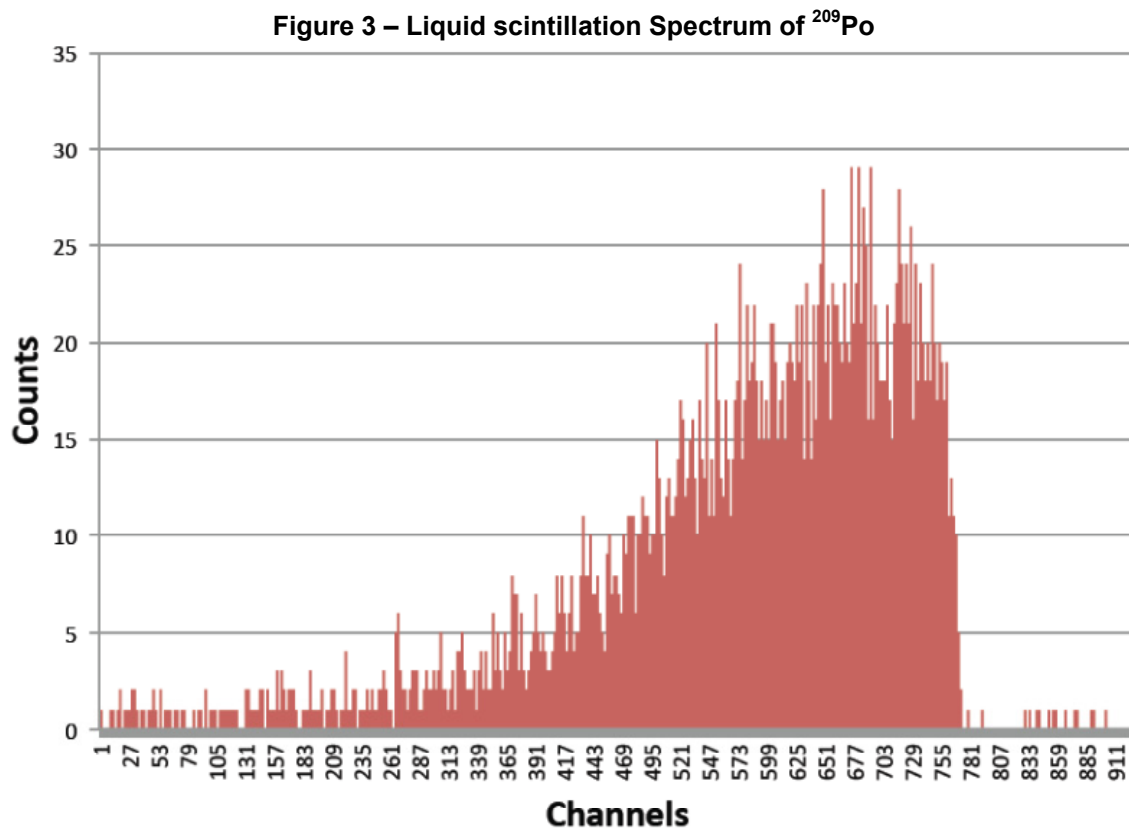
   While this separation technique was fairly specific for polonium, the low yield and the quantity of salts (high quench) made this separation technique undesirable.

Thiacalix Resins

   Thiacalix resins initially appeared to be a possibility for ^{226}Ra separation since they are the most selective of Ra resins. However at a Ba: Ra mass ratio of 10^4, recovery drops to 20%. The field sample obtained had a mass ratio for Ba: Ra of 10^9. Furthermore, these resins experience interference from other divalent cations such as Mg, Ca, Sr, which are present in similar concentrations to Ba in our sample. Therefore this method of radium separation was not used.

Flow Chart for the Alpha Beta Methods Attempted

   Figure 4 shows the flow chart for the methods attempted for the analysis of gross alpha and gross beta. In this instance, tracers were used with the surrogate solution to assess the viability of these separations. The combined iron hydroxide manganese dioxide precipitate, combined with the elution of the dissolved precipitate through a TRU column provided a good separation of the alpha emitters uranium, polonium and thorium. Figure 5 shows that with a few milliliters of bioxalate solution (0.1 molar), the major alpha contributors are eluted together.

Figure 6 shows the recovery of three radioelements (U, Th, Po) using the optimized method prior to method testing.

Figure 4 – Flow Chart for Method Development Using Tracers
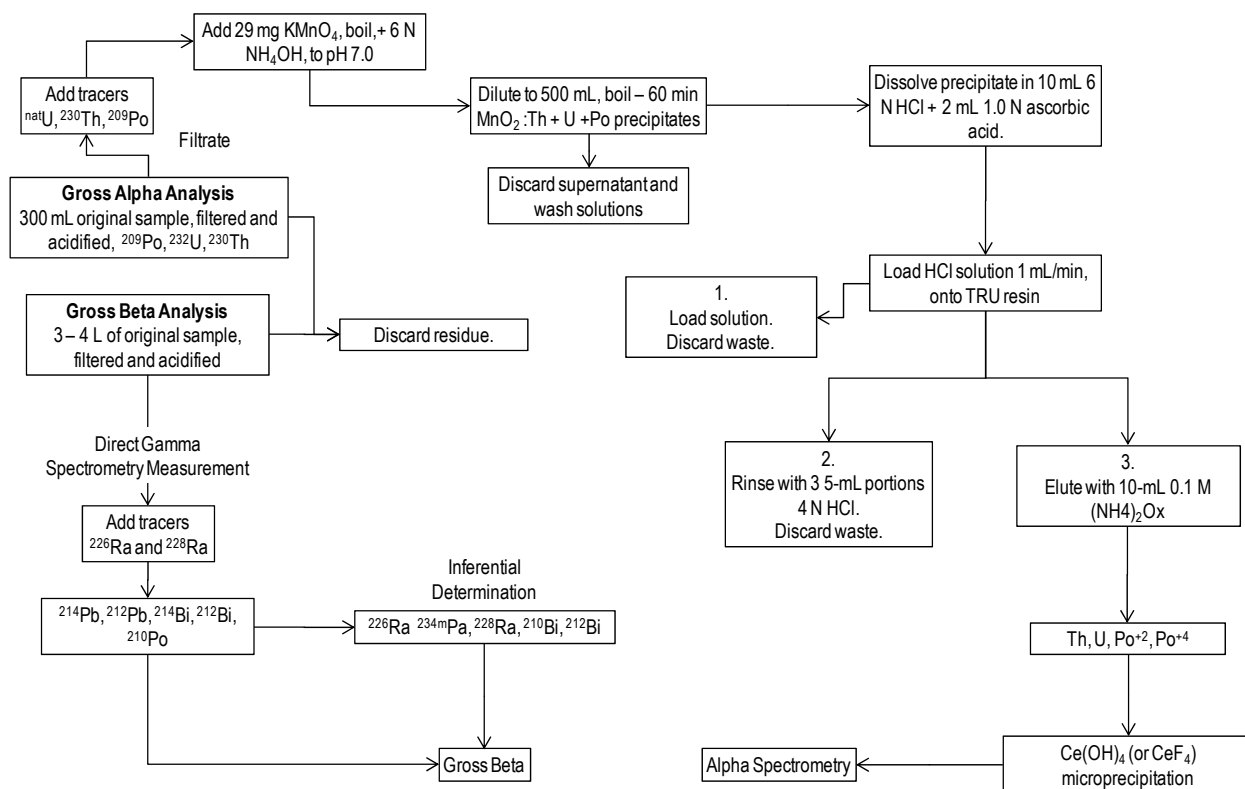
Figure 5 – Elution Profile for Traced solution with 0.1 M Ammonium Bioxalate in 4 M HCl
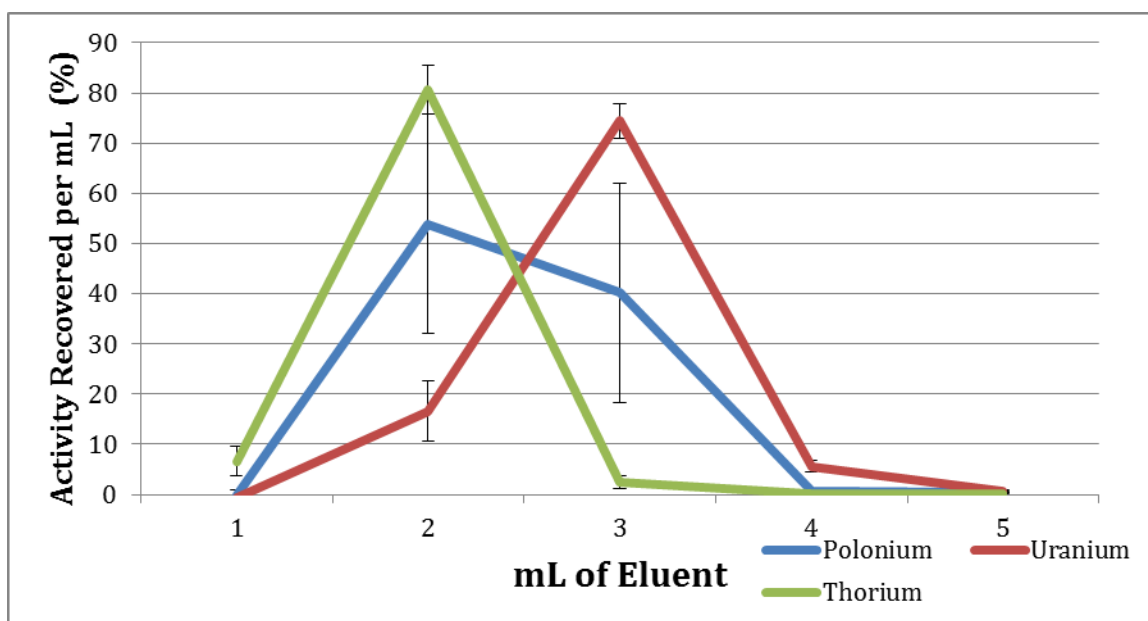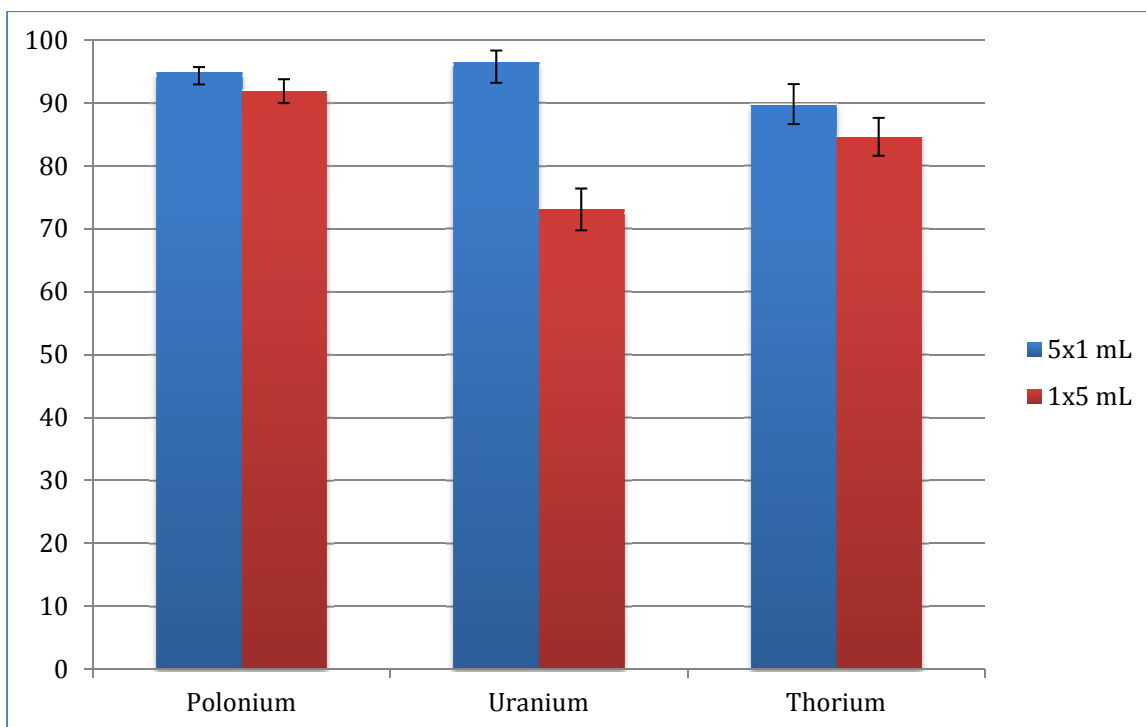
Figure 6 – Total Recovery of Tracers (%) with (0.1 M Ammonium Bioxalate in 4 M HCl)

Note: These elutions were performed with 5 -1 mL (blue) volumes or 1- 5 mL volume (red).

These final results of the tracer trials provided evidence that the proposed methods of chemical separation for the gross alpha (for Th, U, and Po) would be successful.

Attachment II:

Time Lapse

Table 11 – Estimated Elapsed Times for Gross Alpha Analysis

Gross Alpha Analysis Step	Time for 1 Sample (min.)	Time for Batch of 20 (min.)
Measure aliquant, take "initial" volume of sample	2	20
Precipitation and removal of supernatant	90	200
Redissolution	5	50
Loading and elution of sample through TRU Resin	30	300
Perform eluate transfer to LSC vial	2	20
Count samples (maximum count time)	30	600[*]
Data analysis and review	20	300
Total Time	179	1490

Assumes only one LSC unit is used

Table 12 – Estimated Elapsed Times for Gross Beta Analysis

Gross Beta Analysis Step	Time for 1 sample (min.)	Time for Batch of 20 (min.)
Measure aliquant, take "initial" volume of sample	4	40
Count samples (maximum count time)	720	14400[*]
Data analysis and review	20	300
Totals	744	14740

Assumes only one gamma-ray spectrometer is used.

Attachment III:

Rapid Radiochemical Method for Gross Alpha and Gross Beta Activity in Flowback and Produced Waters from Hydraulic Fracturing Operations (FPWHFO)

1. Scope and Applicability

    1.1. This method was developed for flowback and produced water from hydraulic fracturing (FPWHF) operations. This type of sample will contain several radionuclides from any of the three natural decay chains. However, based on the variability in of chemical compounds in the fracturing fluid, the geologic formation that is being developed and other environmental factors, no assumptions about radioactive equilibrium should be made when performing the analyses.

    1.2. The following alpha and beta activity is determined in this method:

        1.2.1. All alpha radioactivity in a hydraulic fracturing sample is associated with naturally occurring uranium, thorium and radium, short-lived progeny of these radioelements, and ^{210}Po. The gross alpha screen is accomplished with two measurements.

            1.2.1.1. The first involves a group separation of U, Th, and Po followed by liquid scintillation counting for gross alpha. This approach quantifies gross alpha activity associated with uranium isotopes (^{238}U, ^{235}U , ^{234}U), thorium isotopes, (^{232}Th ^{230}Th , ^{228}Th), short-lived progeny from ^{228}Th as may have ingrown following the separations, and ^{210}Po.

            1.2.1.2. A non-destructive gamma spectrometry screen is used to determine alpha-emitting radium activity, primarily associated with ^{226}Ra.

            1.2.1.3. The results of the two measurements may be used, either individually, or the measurements may be mathematically summed and their uncertainties combined to yield an estimate the combined gross alpha activity of the sample.

        1.2.2. Gross beta screening is accomplished by gamma spectrometry measurement of radium isotopes (^{226}Ra, ^{228}Ra, ^{224}Ra) and other gamma-emitting natural chain radionuclides. The beta activity of Ra and its short-lived progeny (assuming equilibrium ingrowth) are summed and uncertainties combined to yield a result for the gross beta screen.

        1.2.3. The gamma spectrometry measurement also achieves a definitive determination of the isotopic activity of gamma-emitting tracers used to assess the efficacy of the hydraulic fracturing process that have not decayed between collection and the gamma spectrometric measurement.

    1.3. The gross alpha and beta screening results are not corrected for decay.

Development of Rapid Radiochemical Method for Gross Alpha and Gross Beta Activity in FPWHFO

1.4. The method is not intended to demonstrate compliance with the requirements of the Safe Drinking Water Act (SDWA).

1.5. FPWHFO matrices may contain different chemical mixtures. Method validation may need to be performed for mixtures that significantly differ in composition from a fluid matrix that has been previously validated.

1.6. The method is capable of achieving the following MQOs:

    1.6.1. Gross alpha screen consisting of the following two components:

        1.6.1.1. Gross Alpha by liquid scintillation counting for Th, U, and Po and decay progeny. A 300 mL sample can achieve a required method uncertainty of 9.0 pCi/L at less than or equal to an Analytical Action Level (AAL) of 40 pCi/L. This result is referenced to the radionuclide used for calibration of the detection system, ^{230}Th, or ^{210}Po.

        1.6.1.2. ^{226}Ra alpha by gamma spectrometry: A 3.0 L sample can achieve a required method uncertainty of 33% (relative), at less than or equal to an AAL of 165 pCi/L.

    1.6.2. ^{228}Ra beta by gamma spectrometry: A 3-L sample can achieve a relative required method uncertainty of 50%, at less than or equal to an AAL of 60 pCi/L.

    1.6.3. Application of the method must be validated by the laboratory using the protocols provided in Reference 16.1. The sample turnaround time and throughput may vary based on additional project MQOs, the time for analysis of the final counting form and initial sample volume.

2. Summary of Method

2.1. See Section 17.4 for a flow chart overview of the process.

2.2. Gross Alpha

    2.2.1. The sample is treated with potassium permanganate and ammonia to coprecipitate radionuclides. The alpha emitting radionuclides are separated using a TRU™ resin. The activity of the eluate from the resin is determined using a liquid scintillation counter.

    2.2.2. Ra-226 is determined by direct counting of the 186 keV photopeak using gamma-ray spectrometry. It may also be used to determine the activity of its beta-gamma emitting progeny.

2.3. Gross Beta

    2.3.1. A 3L aliquant of the sample is counted directly using gamma ray spectrometry. Gross beta activity is determined by summing the gamma emitters activity plus those beta only-emitters that are progeny or parents of gamma emitters detected with less than 50% relative CSU (see Step 2.2.2 and 2.3.2).

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2.3.2.   Ra-228 is determined by direct counting of the 911 or 338 keV photopeak using gamma ray spectrometry.

3. Definitions, Abbreviations and acronyms

3.1.   Analytical Protocol Specifications (APS). The output of a *directed planning process* that contains the project's analytical data needs and requirements in an organized, concise form.

3.2.   Analytical Action Level (AAL). The term "analytical action level" is used to denote the value of a quantity that will cause the decision maker to choose one of the alternative actions.

3.3.   Flowback and Produced Water from Hydraulic Fracturing (FPWHF) Operations. A fluid used when gas or oil is extracted from shale rock formations. The produced water from fracking operations contains up to 200 different chemicals that comprise the solution, plus any minerals that are extracted from the shale formation during the process. Each type of FPWHF may be unique in its chemical and physical properties.

3.4.   *Multi-Agency Radiological Analytical Laboratory Protocols Manual* (MARLAP) (see Reference 16.2).

3.5.   Measurement Quality Objective (MQO). The analytical data requirements of the data quality objectives that are project- or program-specific and can be quantitative or qualitative. These analytical data requirements serve as measurement performance criteria or objectives of the analytical process.

3.6.   Required Method Uncertainty (u_{MR}). The required method uncertainty is a target value for the individual measurement uncertainties and is an estimate of uncertainty (of measurement) before the sample is actually measured. The required method uncertainty as an absolute value is applicable at or below an AAL.

3.7.   Relative Required Method Uncertainty (φ_{MR}). The relative required method uncertainty is the u_{MR} divided by the AAL and is typically expressed as a percentage. It is applicable above the action level.

3.8.   Sample Test Source (STS). This is the final form of the sample that is used for nuclear counting. This form is usually specific for the nuclear counting technique in the method, such as a solid deposited on a filter for alpha spectrometry analysis.

4. Interferences

4.1.   Radiological:

4.1.1.   The elapsed time between sampling and arrival at the laboratory and the start of the analytical process to the counting time should be recorded for each sample. These time frames can have significant effects on the final activity concentrations determined. This is due to the various radiochemical equilibria that exist for the naturally occurring radionuclides. It will be important for the laboratory to know at which point in time (e.g., sample time, arrival at laboratory, time of discharge) the client desires to have the activity concentrations corrected to so that they can meet the needs of the project.

4.2. Non-radiological:

    4.2.1. FPWHFO samples will be high in dissolved solids content as well as having a high concentration of other ionic substances not usually encountered in surface or drinking water samples (e.g., barium, strontium, and silica).

    4.2.2. Although the method has been designed to accommodate high levels of solids, including Group II elements, concentrations of non-radioactive barium in the grams/L range may require a decreased sample size (i.e., smaller) to be selected.

    4.2.3. Similarly, high concentrations of non-radioactive calcium, magnesium or strontium in the sample may require the use of a decreased sample size.

5. Safety

  5.1. General

    5.1.1. Refer to your safety manual for concerns of contamination control, personal exposure monitoring and radiation dose monitoring.

    5.1.2. Refer to the laboratory chemical hygiene plan for general chemical safety rules.

  5.2. Procedure-Specific Non-Radiological Hazards:

    5.2.1. Solutions of potassium permanganate can rapidly oxidize organic materials and generate significant heat. Do not mix large quantities of permanganate solution with solutions of organic solvents as the potential for conflagration exists.

6. Equipment and Supplies

  6.1. Toploader balance with a 0.1-g readability.

  6.2. Beakers, Pyrex®: 250, 400 mL.

  6.3. Centrifuge capable of holding 300 mL vessels (optional).

  6.4. Hot plate, or other suitable device for heating ammoniated sample volume.

  6.5. Glass stirring rods.

  6.6. Graduated cylinders: 500, 1000, 4000 mL capacities.

  6.7. Scintillation vials: 22 mL glass.

  6.8. pH paper; range 5.0–9.0 pH units.

7. Reagents and Standards

    NOTES: All reagents are American Chemical Society (ACS) reagent grade or equivalent unless otherwise specified.

    Unless otherwise indicated, all references to water should be understood to mean Type I Reagent water (ASTM D1193, Reference 16.3).

  7.1. Potassium Permanganate, ($KMnO_4$)

  7.2. Ammonium Hydroxide (NH_4OH): Concentrated (15 M)

    7.2.1. Ammonium Hydroxide (NH_4OH): (6 M); dilute 40 mL of concentrated ammonium hydroxide to 100 mL with water.

7.3.   Hydrochloric Acid (HCl): Concentrated (12 M)

    7.3.1.   Hydrochloric Acid (HCl): (6 M); dilute 50 mL of concentrated hydrochloric to 100 mL with water.

    7.3.2.   Hydrochloric Acid (HCl): (4 M); dilute 33 mL of concentrated hydrochloric to 100 mL with water.

7.4.   Ascorbic Acid, crystals

    7.4.1.   Ascorbic Acid (1 M); dissolve 176 g of dried crystals in 100 mL of water

7.5.   Ammonium Bioxalate, crystals

    7.5.1.   Ammonium Bioxalate (0.1 M); dissolve 12.4 g of dried crystals in 100 mL of demineralized water

7.6.   UltimaGold AB™ scintillation cocktail, (available from PerkinElmer Inc.) or equivalent.

7.7.   TRU Resin™ (Eichrom Technologies, LLC.); 100-150 micron

7.8.   Calibration sources, Traceable to a national standards body such as the National Institute of Standards and Technology (NIST) in the U.S.

    7.8.1.   For liquid scintillation: ^{230}Th or ^{210}Po in a counting configuration that matches that of the sample test source as closely as possible. If sample quench varies enough that the efficiency varies by more than 10%, prepare standards with varying levels of quench that span the range of efficiencies encountered during the analysis of samples.

    7.8.2.   For gamma spectrometry: Either ^{228}Ra and ^{226}Ra or a mixed gamma source with energies spanning the entire range of energies to be used during analysis of samples. The geometry of the calibration standard shall match that of the sample test source as closely as possible (e.g., Marinelli beaker 3000-mL volume, density, average "z", etc.). See Section 11.1.3 for a description of preparation of the sample test source.

8.   Sample Collection, Preservation and Storage

8.1.   None recommended

9.   Quality Control

9.1.   Batch quality control results shall be evaluated and meet applicable Analytical Project Specifications (APS) prior to release of unqualified data. In the absence of project-defined APS or a project-specific quality assurance project plan (QAPP), the quality control sample acceptance criteria defined in the laboratory quality manual and procedures shall be used to determine acceptable performance for this method.

9.2.   A laboratory control sample (LCS) shall be run with each batch of samples. The concentration of the LCS should be at or near the action level or a level of interest for the project.

9.3.   One method blank shall be run with each batch of samples. The laboratory blank should consist of demineralized water.

9.3.1.   If possible a matrix blank that includes a surrogate solution made from reagent grade chemicals should be analyzed.

9.4.   One laboratory duplicate shall be run with each batch of samples. The laboratory duplicate is prepared by removing an aliquant from the original sample container after mixing/stirring.

9.5.   A matrix spike sample may be included as a batch quality control sample if there is concern that matrix interferences, such as the presence of elemental barium in the sample, may compromise chemical yield measurements, or overall data quality.

9.5.1.   Matrix spike added activity may be difficult to estimate unless there is prior historical data to identify an existing concentration of some of the radionuclides.

10. Calibration and Standardization

10.1.   The liquid scintillation counter is set-up, calibrated, verified, quality controls performed according to manufacturer's specifications for alpha/beta discrimination, and as specified in ASTM D7282 Sections 9, 12, 13, 19, and 25.

10.1.1.   Set up the scintillation counter to discriminate between alpha and beta pulses according to manufacturer's specifications. Samples are counted in an energy window that encompasses the alpha peak observed in the middle section of the alpha spectrum.

10.1.2.   Calibrate the LSC for alpha efficiency in the same energy window of the alpha spectrum used to count samples.

10.1.3.   Use standard ^{230}Th or ^{210}Po incorporated in the same counting configuration used for samples (i.e., vial type, cocktail, chemical make-up of the aqueous matrix, sample to cocktail ratio, and quench levels should match that of the samples as closely as possible). See Sections 11.1.2.9 and 11.1.2.10 for a description of preparation of the sample test source.

10.1.4.   The subtraction background is determined in the same energy window of the alpha spectrum used to count samples using a background sample that matches that of samples being analyzed.

10.2.   The gamma spectrometer is set-up, calibrated, verified, quality controls performed according to manufacturer's specifications for alpha/beta discrimination, and as specified in ASTM D7282 Sections 9, 12, 13, 17, and 23.

10.2.1.   Calibrate the gamma spectrometer across the entire energy range to be used during analysis of samples.

10.2.2.   Count the calibration standard (Section 7.1.2) in the same juxtaposition to the detector as the samples.

11. Procedure

11.1.   Water Sample Preparation

11.1.1.   A well-mixed portion of the sample is taken for each of the separate analysis flow paths:

NOTE: The sample is not filtered.

11.1.1.1. 300 mL for gross alpha analysis

11.1.1.2. 3.0 L for gamma spectrometry analysis

11.1.2. Gross Alpha Analysis

11.1.2.1. Add 29 mg of $KMnO_4$ and bring the solution to a boil.

11.1.2.2. Add enough concentrated ammonium hydroxide to bring the solution into a pH range of 5.0 to 9.0.

11.1.2.3. Dilute the solution to 500 mL with demineralized water and bring to a boil for approximately 60 minutes.

11.1.2.4. When the solution has cooled, and settled, decant off and discard the supernatant solution

11.1.2.5. To the residue after decantation add approximately 10 mL of 6 M HCl and 2 mL of 1.0 M ascorbic acid.

NOTE: this is the load solution for the solid phase extraction column and should be kept to a minimum. Fresh ascorbic acid should be used to ensure all the Fe^{+3} have been reduced to Fe^{+2}.

11.1.2.6. Load the solution in 11.1.2.5 onto a TRU Resin column at the rate of 1 mL/min

11.1.2.7. Discard the eluate from the load solution

11.1.2.8. Rinse the TRU Resin column with three 5-mL portions of 4M HCl at a flow rate of 1 mL/min. Discard the wash solutions.

11.1.2.9. Elute the radionuclides using 10 mL of 0.1 M ammonium bioxalate solution

11.1.2.10. Add the entire eluate to 15 mL of UltimaGold AB cocktail in a 22-mL scintillation vial. This is the sample test source (STS) for the gross alpha measurement.

11.1.2.10.1. Liquid Scintillation Counting

After dark adaptation, the sample is counted for approximately 30 minutes or long enough to meet the MQOs noted in Step 1.6.

11.1.3. Determination of Gross Beta and Radium 226 activity by gamma spectrometry

11.1.3.1. If necessary to prevent settlement of solids during the counting time either:

11.1.3.1.1. Acidify the solution with 16 M nitric acid until solids dissolve, or

11.1.3.1.2. Add sufficient agar to suspend any solid materials.

11.1.3.2. Count the sample on a gamma ray spectrometer for approximately 6–12 hours or until the MQO's noted in Step 1.6 can be achieved.

NOTE: The exact time to count the sample will depend upon the exact sample size taken and the efficiency of the detectors used for the analysis. In either case the counting time should be adjusted so that the MQOs noted in Step 1.6 can be achieved.

11.1.3.3. Using the information in Figure 17.1:

11.1.3.3.1. Determine which radionuclides that are to be inferentially determined will be in secular equilibrium based on the time between sampling and analysis.

11.1.3.3.2. Sum the activities of the radionuclides that have a CSU of less than 50% and those inferred assuming secular equilibrium.

11.1.3.3.3. Review the gamma-ray spectrum report for any gamma rays that are unidentified and ascribe identities to them.

Determine if these activities need to be added to the sum in Step 11.1.3.3.2.

11.1.3.3.4. The gross beta activity is estimated by the sum of Steps 11.1.3.3.2 and 11.1.3.3.3 (See Section 12)

12. Data Analysis and Calculations

12.1. Results are reported as gross alpha and gross beta activity as follows:

12.1.1. Gross Alpha Activity

$$Gross\ Alpha\ Activity_{LSC}, \frac{pCi}{L} = \frac{(cpm_s - cpm_b)}{(V \times 2.22 \times \epsilon)} \tag{1}$$

Where:

cpm_s is the sample gross count rate, in counts per minute

cpm_b is the instrument background count rate in counts per minute

ϵ is the detector efficiency based on the instrument quench curve and a ^{230}Th or ^{210}Po calibration source

V is the sample volume used in liters

$$Gross\ Alpha\ Activity_{gamma\ spec}, \frac{pCi}{L} = \sum_1^n (I_{\alpha-\gamma})_n \tag{2}$$

Where:

$I_{\alpha-\gamma}$ are the individual radium alpha emitter activities inferred from gamma-emitting counterparts (usually only ^{226}Ra)

12.1.2. Gross Beta Activity

$$Gross\ beta\ activity_{gamma\ spec}, \frac{pCi}{L} = \sum_1^j (M_\gamma)_j + \sum_1^k (I_\gamma)_k \tag{3}$$

Where:

M_γ is the activity of each measured gamma-ray emitting radionuclides

I_γ are the activities of the non-gamma, beta- emitting radionuclides that are inferred.

12.1.3. Measurement uncertainty

NOTE: The uncertainty for the indirectly measured radionuclides should be made equal to the uncertainty from their gamma-emitting parent or progeny (for either the alpha-only or beta only emitters). Since this is a gross analysis this approximation should be satisfactory.

12.1.3.1. Gross alpha

$$Gross\ Alpha\ Uncertainty_{LSC}, 1s = \frac{\left\{\frac{cpm_s}{t_s} + \frac{cpm_b}{t_b}\right\}^{1/2}}{(2.22 \times \epsilon \times V)} \tag{3}$$

$$Gross\ Alpha\ Uncertainty_{gamma\ spec}, 1s = \sqrt{\Sigma_1^n u_{I_{\alpha-\gamma}^n}^2} \tag{4}$$

Where:

$u_{I_{\alpha-\gamma}^n}$ is the uncertainty of an individual gamma emitter that is used to determine the alpha activity.

12.1.3.2. Gross Beta

$$Gross\ Beta\ Uncertainty_{gamma\ spec}, 1s = \sqrt{\Sigma_1^{j,k}\left[u^2{}_{M_{\gamma_j}} + u^2{}_{I_{\gamma_k}}\right]} \tag{5}$$

Where:

$$u_{M_{\gamma_j}} = 1\ \sigma\ from\ \gamma - spectrum\ report\ for\ directly\ measured\ radionuclides \tag{6}$$

and

$$u_{I_{\gamma_k}} = 1\ \sigma\ for\ indirectly\ measured\ radionuclides \tag{7}$$

13. Method Performance

13.1.   Results of method validation performance are to be archived and available for reporting purposes.

13.2.   Expected turnaround times are:

13.12.1   Gross alpha ~3 hours for an individual sample and ~25 hours per batch (see Section 17.2).

13.12.2   Gross beta ~13 hours for an individual sample and ~10 days per batch (see Section 17.3).

14. Pollution Prevention

14.1.   The use of potassium permanganate to produce MnO_2 and a TRU® resin reduces the amount of solvents that would otherwise be needed to co-precipitate and purify the final sample test source.

14.2.   Ultima Gold AB is a non-hazardous waste after it is used.

15. Waste Management

15.1.   Nitric acid and hydrochloric acid wastes should be neutralized before disposal and then disposed of in accordance with local ordinances.

16. References

16.1.   U.S. Environmental Protection Agency (EPA). 2009. *Method Validation Guide for Radiological Laboratories Participating in Incident Response Activities*. Revision 0.

Office of Air and Radiation, Washington, DC. EPA 402-R-09-006, June. Available at: www.epa.gov/narel/incident_guides.html.

16.2. *Multi-Agency Radiological Laboratory Analytical Protocols Manual* (MARLAP). 2004. EPA 402-B-1304 04-001A, July. Volume I, Chapters 6, 7, 20, Glossary; Volume II and Volume III, Appendix G. Available at: www.epa.gov/radiation/marlap/index.html.

16.3. ASTM D1193, "Standard Specification for Reagent Water," ASTM Book of Standards 11.02, current version, ASTM International, West Conshohocken, PA.

16.4. NNDC, Brookhaven National Laboratory, sonzogni@bnl.gov.

16.5. Data Source: National Nuclear Data Center, Brookhaven National Laboratory, based on ENSDF and the Nuclear Wallet Cards (2014); http://www.nndc.bnl.gov/chart/.

16.6. ASTM D7282 "Standard Practice for Set-up, Calibration, and Quality Control of Instruments Used for Radioactivity Measurements," ASTM Book of Standards 11.02, current version, ASTM International, West Conshohocken, PA.

17. Tables, Diagrams and Flow Charts

17.1. Table of Direct and Inferential Determinations for Gamma Ray Emitters

Radionuclide	Gamma Ray Energy, keV	Abundance,%	Half-Life, Days	Time from Sampling to Counting, Days	Inferred Activity
^{208}Tl [1]	583	85.0	2.1×10^{-3}	< 0.1	^{212}Bi
^{210}Pb	46.5	4.25	$8.1 \times 10^{+3}$	365	^{210}Po
				30	^{210}Bi
^{212}Pb	238	43.6	4.4×10^{-1}	2	^{224}Ra
^{212}Bi	727	6.67	4.2×10^{-2}	2	^{224}Ra
^{214}Pb	295	18.4	1.9×10^{-2}	18	^{226}Ra
	352	35.6	1.9×10^{-2}	18	^{226}Ra
^{214}Bi	609	45.5	1.4×10^{-2}	18	^{226}Ra
	1120	14.9	1.4×10^{-2}	18	^{226}Ra
^{226}Ra [2]	186	3.64	$5.8 \times 10^{+5}$	—	—
^{228}Ac	338	11.3	2.6×10^{-1}	1.5	^{228}Ra
	911	25.8	2.6×10^{-1}	1.5	^{228}Ra
^{234}Th	93	4.2	$2.4 \times 10^{+1}$	< 0.1	^{234m}Pa
	63	3.7	$2.4 \times 10^{+1}$	< 0.1	^{234m}Pa

[1] Tl-208 also has a gamma at 2615 keV that is 99% abundant.

[2] Note that this gamma ray is interfered with by the gamma ray from ^{235}U at 185. The ^{226}Ra can be determined directly if no ^{235}U is present or if the ^{235}U peak issued to subtract out the interference at 186 keV. See Reference 16.5.

17.2. Estimated Elapsed Times for Gross Alpha Analysis

| Gross Alpha Analysis Step	Time for 1 Sample, Minutes	Time for Batch of 20, Minutes
Measure aliquant, take "initial" volume of sample	2	20
Precipitation and removal of supernatant	90	200
Redissolution	5	50
Loading and Elution of sample through TRU resin columns	30	300
Perform eluate transfer to LSC vial	2	20
Count samples (maximum count time)	30	600[*]
Data analysis and review	20	300
Total Time	179	1,490

*Assumes only one LSC unit is used.

17.3. Estimated Elapsed Times for Gross Beta Analysis

Gross Beta Analysis Step	Time for 1 Sample, minutes	Time for Batch of 20, minutes
Measure aliquant, take "initial" volume of sample	4	40
Count samples (maximum count time)	720	14,400[*]
Data analysis and review	20	300
Totals	744	14,740

*Assumes only one gamma ray spectrometer is used.

17.4.   Sample Processing for FPWHFO

EPA
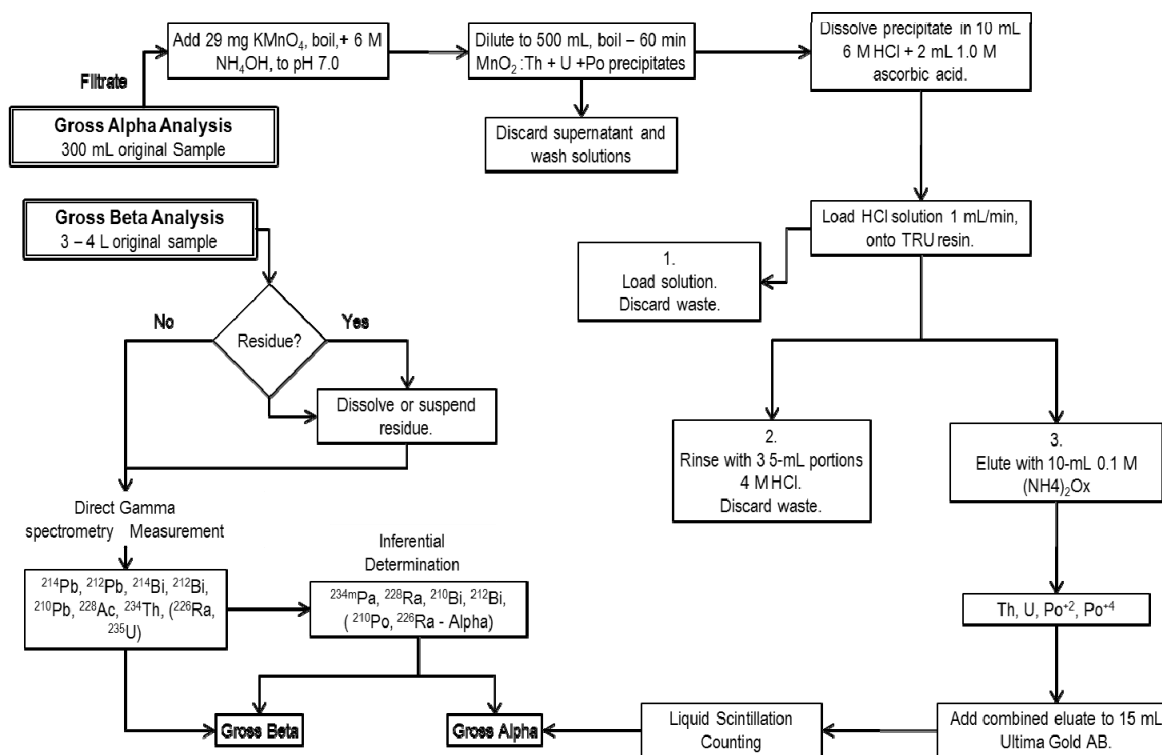
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