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Validation of Rapid Radiochemical Method for Radium-226 in Brick Samples for Environmental Remediation Following Radiological Incidents

U.S. Environmental Protection Agency

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This report was prepared for the National Analytical Radiation Environmental Laboratory of the Office of Radiation and Indoor Air and the National Homeland Security Research Center of the Office of Research and Development, United States Environmental Protection Agency (EPA). It was prepared by Environmental Management Support, Inc., of Silver Spring, Maryland, under contract EP-W-13-016, Task Order 0014, managed by Dan Askren. This document has been reviewed in accordance with EPA policy and approved for publication. Note that approval does not signify that the contents necessarily reflect the views of the Agency. Mention of trade names, products, or services does not convey EPA approval, endorsement, or recommendation.

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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
DL ....discrimination level
dpm ....disintegrations per minute
dps..................disintegrations per second
DQO...............data quality objective
DRP................discrete radioactive particle
EPA................U.S. Environmental Protection Agency
FRMAC..........Federal Radiological Monitoring and Assessment Center
ft.....................foot
FWHM...........full width at half maximum
g......................gram
gal...................gallon
G-M...............Geiger-Muller [counter or probe]
GEL………….General Engineering Laboratories
Gy...................gray
h......................hour
ICP-AES ....inductively coupled plasma – atomic emission spectrometry
ID ....identifier/identification number
IND ....improvised nuclear device
IUPAC............International Union of Pure and Applied Chemistry
kg....................kilogram (10^3 gram)
L ....liter
Lc ....critical level
LCS ....laboratory control sample
m ....meter
M ....molar
MARLAP.......*Multi-Agency Radiological Laboratory Analytical Protocols Manual*
MDA ....minimum detectable activity
MDC ....minimum detectable concentration
MeV ....mega electron volts (10^6 electron volts)
mg ....milligram (10^{-3} gram)
min ....minute
mL…………...milliliter (10^{-3} liter)
mm ....millimeter (10^{-3} meter)
MQO ....measurement quality objective
MVRM...........method validation reference material
µCi..................microcurie (10^{-6} curie)
µm ....micrometer (10^{-6} meter)

NAREL..........EPA's National Analytical Radiation Environmental Laboratory, Montgomery, AL
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 Radiation and Indoor Air
φ_{MR}..........................required relative method uncertainty
pCi..................picocurie (10^{-12} curie)
PPE.................personal protective equipment
ppm ....parts per million
PT...................proficiency test or performance test
QAPP ....quality assurance project plan
R.....................Roentgen – unit of X or γ radiation exposure in air
rad ....unit of radiation absorbed dose in any material
RDD...............radiological dispersal device
rem ....roentgen equivalent: man
ROI.................region of interest
s......................second
SI....................International System of Units
Sv ....sievert
u_{MR} ....required method uncertainty
wt% ....percent by mass
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/kilogram (kg) Bq/cubic meters (m^3) Bq/m^3	picocuries (pCi) pCi/gram (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)	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

The U.S. Environmental Protection Agency's (EPA's) Office of Radiation and Indoor Air's (ORIA) National Analytical Radiation Environmental Laboratory (NAREL), in conjunction with the EPA Office of Research and Development's National Homeland Security Research Center (NHSRC) developed this method validation report. Dr. John Griggs served as project lead. Several individuals provided valuable support and input to this document throughout its development. Special acknowledgment and appreciation are extended to Kathleen M. Hall, of NHSRC.

We also wish to acknowledge the valuable suggestions provided by the staff of NAREL, who conducted the method validation studies. Dr. Keith McCroan, of NAREL, provided significant assistance with the equations used to calculate minimum detectable concentrations and critical levels. Numerous other individuals, both inside and outside of EPA, provided comments and criticisms of this method, and their suggestions contributed greatly to the quality, consistency, and usefulness of the final method. Environmental Management Support, Inc. provided technical support.

1. Introduction

Rapid methods need to be developed and validated for processing samples taken in response to a radiological incident. In order to address this need, EPA initiated a project to develop rapid methods that can be used to prioritize environmental sample processing as well as provide quantitative results that meet measurement quality objectives (MQOs) that apply to the intermediate and recovery phases of an incident.[1] Similar to the rapid method project initiated in 2007 for radionuclides in water (EPA 2008), this rapid method development project for a brick matrix addressed four different radionuclides in addition to ^{226}Ra: ^{241}Am, ^{nat}U, ^{90}Sr, and $^{239/240}$Pu. Each of these radionuclides will have separate method validation reports for the brick matrix. The methodology used for this validation process makes use of ^{225}Ra tracer (validated for water matrices) and a new process for fusing brick samples. The combination of these two techniques provides a unique approach for rapid analysis of brick samples.

The method validation plan developed for the rapid methods project follows the guidance in *Method Validation Guide for Qualifying Methods Used by Radiological Laboratories Participating in Incident Response Activities* (EPA 2009), *Validation and Peer Review of U.S. Environmental Protection Agency Radiochemical Methods of Analysis* (2006), and Chapter 6 of *Multi-Agency Radiological Laboratory Analytical Protocols Manual* (MARLAP) (EPA 2004). The method was evaluated according to MARLAP method validation "Level C" (see MARLAP Sections 6.1 and 6.6.3.5). The method formulated was preliminarily tested at a government laboratory and refinements to the method were made according to the feedback from the laboratory and the quality of the generated results. For the method validation process, the laboratory analyzed several sets of blind proficiency test (PT) samples according to specifications that meet established MQOs and guidance outlined in *Radiological Sample Analysis Guide for Incident Response – Radionuclides in Soil* (EPA 2012).

The proposed MQO specification for the required method uncertainty at the analytical action level (AAL) was based on a ^{226}Ra concentration of approximately 5.0 pCi/g. Performance test samples were prepared to meet this proposed AAL, and the final tested AAL value was 4.755 pCi/g. This value is the combined ^{226}Ra spike value of the soil plus the inherent ^{226}Ra in the soil of 1.025 ± 0.027 pCi/g (standard error) as determined from ten blank brick samples. The required method uncertainty at this AAL was calculated to be 0.62 pCi/g.

This report provides a summary of the results of the method validation process for a combination of two methods; *Rapid Method for Sodium Hydroxide Fusion of Concrete and Brick Matrices Prior to Americium, Plutonium, Strontium, Radium, and Uranium Analyses for Environmental Remediation Following Radiological Incidents* (Attachment II) and *Rapid Radiochemical Method for Ra-226 in Building Materials for Environmental Remediation Following Radiological Incidents* (Attachment III). In this document, the combined methods are referred to as "combined rapid ^{226}Ra - Brick method." The method validation process is applied to the fusion dissolution of brick using sodium hydroxide and the subsequent separation and quantitative analysis of ^{226}Ra using alpha spectrometry to detect the 4.60- and 4.78-million

[1] ORIA and the Office of Research and Development jointly undertook the rapid methods development projects. The MQOs were derived from Protective Action Guides determined by ORIA.

electron volt (MeV) alpha particles from the decay of ^{226}Ra and the 7.07-MeV alpha particle from ^{217}At (progeny of ^{225}Ra) that is used as the tracer yield monitor. The laboratory's complete report, including a case narrative and a compilation of the reported results for this study, can be obtained by contacting EPA's National Analytical Radiation Environmental Laboratory (NAREL) (http://www.epa.gov/narel/contactus.html).

2. Radioanalytical Methods

The combined rapid ^{226}Ra - Brick method was written in a format consistent with EPA guidance and conventions. The rapid method was formulated to optimize analytical throughput for sample preparation, chemical processing, and radiation detection.

Specifications for sample processing were incorporated into the combined rapid ^{226}Ra - Brick method. These specifications are reflected in the scope and application and in the body of the methods. The specifications include the use of a radiotracer yield monitor and the required method uncertainty. Known interferences are addressed in Section 4 of the attached method (Attachment III). For this validation study, the laboratory used a 1,000-minute counting time for three test level samples for the method uncertainty evaluation and an 800-minute counting time for the required minimum detectable concentration (MDC) samples. A 1-g sample size was processed by the rapid method for both the method uncertainty and required MDC evaluations. A summary of the rapid method is presented in Section 8.1 prior to presenting the experimental results of the method validation analyses.

The combined rapid ^{226}Ra - Brick method used for rapid analysis of ^{226}Ra in brick samples is included in Attachments II and III of this report. Although this final method is a departure from the originally tested method, the incorporated revisions are significant improvements and do not change the general methodology. The validation process was performed using this final combined method in the attachments.

3. Method Validation Process Summary

The method validation plan for the combined rapid ^{226}Ra - Brick method follows the guidance provided in *Method Validation Guide for Qualifying Methods Used by Radiological Laboratories Participating in Incident Response Activities* (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 method validation 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 2011). The method was evaluated according to MARLAP method validation "Level C" (see Section 6.1 and MARLAP Section 6.6.3.5). More specifically, the method was validated against acceptance criteria for the required method uncertainty (u_{MR}) at a specified AAL concentration and the required MDC. In addition, analytical results were evaluated for radiochemical yield (as a characteristic of method ruggedness), and relative bias at each of the three test-level radionuclide activities. The absolute bias of the method was evaluated using the laboratory's reagent blanks because the brick used as the method validation reference material (MVRM) had native ^{226}Ra that was not removed prior to spiking the MVRM.

The method validation process was divided into four phases:

1. Phase I
    a. Laboratory familiarization with the methods for brick samples.
    b. Set-up of the laboratory and acquisition of reagents, standards and preparation of in-house PT samples.
    c. Perform preliminary tests of the new fusion method and continue the analysis using the dissolved flux from that process with the existing combined rapid ^{226}Ra - Brick method, having the brick samples spiked with ^{226}Ra and the ^{225}Ra tracer.
    d. Make changes to improve the method based on consultation with Environmental Management Support, Inc. consultants and the results of the preliminary tests.
2. Phase II
    a. Conduct blank sample analyses to assess the method's critical level concentration.
    b. Conduct method validation test for required method uncertainty.
3. Phase III
    a. Conduct verification of the required MDC
4. Phase IV
    a. Report results.
    b. Laboratory writes report to describe the process and narratives on the method.
    c. Review and comment on method.
    d. Environmental Management Support, Inc., writes method validation report, which is reviewed by laboratory.

During Phases I, II, and III, the laboratory processed and evaluated batch quality control samples according to their laboratory quality manual, including an analytical reagent blank, laboratory control sample (LCS), and a sample duplicate.[2]

The dual objectives of the first (preliminary) phase were to familiarize the laboratory with the formulated rapid method and then gain hands-on experience using the rapid method to identify areas that might require optimization. During this phase, the laboratory processed samples of blank brick material and blank brick that was spiked in-house with ^{226}Ra activities consistent with evaluating the required method uncertainty at the AAL and the required MDC (see "^{226}Ra Method Validation Test Concentrations and Results," Table 1; see footnote 3 on the next page). The blank and laboratory spiked samples used in Phase I were made by the laboratory in order to assess the original feasibility of the proposed method. Based on information and experience gained during Phase 1 practice runs, the rapid ^{226}Ra method was optimized without compromising data collected during the validation process in Phases II and III.

During Phases II and III of the method validation process, the laboratory analyzed PT samples (consisting of MVRMs) provided by an external, National Institute of Standards and Technology (NIST)-traceable source manufacturer (Eckert & Ziegler Analytics, Atlanta, GA). The MVRM was brick prepared and homogenized prior to spiking by Eckert and Ziegler (see Attachment IV). The laboratory was instructed to analyze specific blind PT samples having concentration levels

[2] During the validation study, the laboratory prepared an LCS, substituted PT blanks for their lab blank and used replicate PT samples for their lab duplicates.

consistent with validation test levels for the required method uncertainty and the required MDC. The test levels of the PT samples are listed in Tables 1 and 2. Following completion of the method validation studies, comments from the labs were evaluated and the method revised to conform to the documented “as-tested” conditions in Phases II and III. Thus, the validation data presented in this report reflect the combined final method included in the attachments to this document.

4. Participating Laboratory

NAREL validated the combined rapid ^{226}Ra - Brick method using NIST-traceable test samples prepared in a brick medium.

5. Measurement Quality Objectives

The combined rapid ^{226}Ra - Brick method was developed to meet MQOs for the rapid methods project. The selected MQOs included the radionuclide concentration range, the required method uncertainty at a specified radionuclide concentration (e.g., AAL), and the required MDC. The required relative method uncertainty (φ_{MR}) for the combined rapid ^{226}Ra method was set at 13%[3] at an AAL equal to 4.755 pCi/g, which is approximately the 1×10^{-5} risk concentration for a 50-year exposure period for a soil matrix. This brick concentration value is based on guidance found in Federal Radiological Monitoring and Assessment Center (FRMAC) for soil.[4] This particular value is consistent with the concentration limit for site cleanup activities. This value is about five times greater than ^{226}Ra concentrations that commonly exist in brick (~ 1 pCi/g). Specific action levels for ^{226}Ra in soil are provided in the *Radiological Sample Analysis Guide for Incidents of National Significance – Radionuclides in Soil* (draft EPA 2012). The exact values for the target concentrations as tested had ^{226}Ra concentrations that were based on the addition of the inherent ^{226}Ra in the blank brick matrix plus the ^{226}Ra that was spiked in the sample (see Attachment IV for the chemical composition of the brick matrix). Table 1 summarizes the targeted MQOs for the method validation process, the calculated known values (which includes the inherent ^{226}Ra in the blank material) for the samples analyzed, and the average measured values as determined by this method. The AALs for the four other radionuclides are ^{241}Am (1.570 pCi/g), $^{239/240}$Pu (1.890 pCi/g), ^{238}U (12.35 pCi/g), and ^{90}Sr (2.440 pCi/g). The PT sample supplier provided test data for ten 1-gram (g) samples that documents the spread in the spike in the samples as a 1.59% standard deviation in the distribution of results.

[3] Type I and II decision error rates were set at $z_{1-\alpha}$= 0.01 and $z_{1-\beta}$= 0.05. The required method uncertainty is calculated using the formula, u_{MR} = (AAL-DL)/[$z_{1-\alpha} + z_{1-\beta}$] where the analytical action level (AAL) is as noted above and the discrimination level (DL) is ½ the AAL.

[4] Federal Radiological Monitoring and Assessment Center. Appendix C of the FRMAC Manual (FRMAC 2010) or calculated using TurboFRMAC 2010 available from Sandia National Laboratory.

Table 1 – ^{226}Ra Method Validation Test Concentrations and Results

	Target Value, pCi/g	Calculated Known Value [1]	Average Measured Value	Required Method Uncertainty (u_{MR})	Combined Uncertainty
MDC	Inherent Ra-226	1.025 ± 0.027	1.000	—	± 0.045
½ × AAL SO-U1	2.5	2.385 ± 0.035	2.427	0.62	± 0.027
AAL SO-U2	5.0	4.755 ± 0.053	4.73	0.62	± 0.37
3 × AAL SO-U2	15.0	15.03 ± 0.23	15.4	2.0[2]	± 1.1

[1] The calculated known values listed here are the sum of the spike value added by Eckert & Ziegler Analytics plus the measured inherent native ^{226}Ra in the brick of 1.025 ± 0.027 pCi/g. The uncertainties for the spike and the standard uncertainty from the blank brick analysis have been calculated in quadrature.

[2] The value of 2.0 pCi/g is the relative required method uncertainty and represents 13% of 15.03 pCi/g.

6. Method Validation Plan

The combined rapid ^{226}Ra - Brick method was evaluated for the six 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 2011). These characteristics include method uncertainty, detection capability, bias, analyte activity range, method ruggedness, and method specificity. A summary of the manner in which these performance characteristics were evaluated is presented below. The chemical yield of the method, an important characteristic for method ruggedness, was also evaluated.

6.1 Method Uncertainty

The method uncertainty of the combined rapid ^{226}Ra - Brick method was to be evaluated at a proposed AAL concentration (5.0 pCi/g) specified in the MQOs presented in Table 1. However, since there was a known inherent ^{226}Ra in the brick of 1.025 pCi/g and the source supplier spiked at 3.730 pCi/g, the "as tested" AAL was found to be less than the proposed AAL by approximately 0.24 pCi/g or a final value of 4.755 pCi/g. In accordance with MARLAP method validation "Level C," this method was a new application and was evaluated at each of three test concentration levels. The laboratory analyzed five replicate external PT samples containing ^{226}Ra activities at approximately one-half the AAL, the AAL, and three times the AAL. The method was evaluated against the required method uncertainty (u_{MR} = 0.62 pCi/g), at and below the "as tested" AAL, and against the required relative method uncertainty (φ_{MR} = 13% of the known test value) above the AAL. The test level concentrations analyzed are listed in Table 1.

6.2 Detection Capability

In the statement of work to the laboratory, the detection capability of the combined rapid ^{226}Ra - Brick method was to be evaluated to meet a MDC of approximately 1.0 pCi/g, which was the measured inherent[5]radium in the blank brick material. The laboratory estimated the counting time, chemical yield and sample size to meet this 1.0 pCi/g MDC. The final MDC known value was 1.025 pCi/g as presented in Table 2. In accordance with the guidance provided in *Method Validation Guide for Qualifying Methods Used by Radiological Laboratories Participating in Incident Response Activities* (EPA 2009), the laboratory estimated the critical net concentration based on the results of seven reagent blank samples. Results from ten replicate MDC brick samples at the required MDC concentration were to be compared to the critical net concentrations to determine method detection capability. For this validation study, the laboratory used a 1000-minute counting time for three test level samples, allowing sufficient time for ingrowth of ^{217}At from ^{225}Ra while starting the sample counts the same day as the column separation, instead of waiting 24 hours before counting as in the concrete validation study (EPA 2014). This approach allowed sufficient ingrowth of tracer counts with an earlier completion of sample counting. Both the reagent blank samples and the MDC brick test samples were to be counted for a length of time (800 minutes) to meet the proposed MDC requirement.

Table 2 – Sample Identification and Test Concentration Level for Evaluating the Required Minimum Detectable Concentration

Test Sample Designation	Number of Samples Prepared	Nuclide	Calculated Known Value for MDC (pCi/g)[1]	Mean Measured Concentration (pCi/g)
1 – 10 (Brick MDC samples)	10	^{226}Ra	1.025 ± 0.027	1.000 ± 0.045
RS41 – R47 (Reagent blanks)	7	^{226}Ra	—	.0.045 ± 0.015
R41 – R47 (Brick[2] matrix blanks)	7	^{226}Ra	1.025 ± 0.027	1.12 ± 0.13

[1] Weighted mean and weighted standard deviation of 10 separate blank brick samples analyzed prior to the method validation.

[2] Blank brick matrix supplied by Eckert & Ziegler Analytics, Atlanta, Georgia.

6.3 Method Bias

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

Absolute Bias

The blank brick material used for this method validation study contained ^{226}Ra (See Attachment IV). Therefore, the absolute bias for the method was determined using the reagent method blanks that were put through the entire process.

The results from the seven blank samples for the required MDC evaluation were assessed 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;

[5] The inherent ^{226}Ra content of the brick matrix was estimated by analyzing 10 replicate samples and determining the weighted mean and weighted standard deviation of the results.

however, there was no acceptance limit for bias established for the method in the validation process.

The following protocol was used to test the method blanks for ^{226}Ra for absolute bias:

1. Calculate the mean ($\overline{X}$) and estimated standard deviation (s_x) for "N" (at least seven) blank sample net results.

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 $t_{1-\alpha/2}$ (N-1) represents the (1 - α/2)-quantile of the t-distribution with N-1 degrees of freedom. For seven blanks, an absolute bias is identified at a significance level of 0.05, when |T| > 2.447.

Relative Bias

The results from the seven samples for each of the three test levels and the 10 MDC samples were evaluated for relative bias according to the protocol and equation presented in the *Method Validation Requirements for Qualifying Methods Used by Radioanalytical Laboratories Participating in Incident Response Activities* (EPA 2009). No acceptable relative bias limit was specified for this method validation process.

The following protocol was used to test the combined rapid ^{226}Ra - Brick method for relative bias:

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

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

$$|T| = \frac{|\overline{X} - K|}{\sqrt{s_X^2 / N + u^2(K)}} \tag{3}$$

where:

$\overline{X}$ 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:

$$|T| > t_{1-\alpha/2(\nu_{eff})} \tag{3a}$$

The number of *effective degrees of freedom* for the *T* statistic is calculated as follows:

$$\nu_{\text{eff}} = (N-1)\left(1+\frac{u^2(K)}{s_X^2/N}\right)^2 \tag{4}$$

ν_{eff}, as calculated by the equation, generally is not an integer so ν_{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 $t_{1-\alpha/2(\nu\text{eff})}$, the (1 - α/2)-quantile of the *t*-distribution with ν_{eff} degrees of freedom (see MARLAP Appendix G, Table G.2).

6.4 Analyte Concentration Range

The combined rapid ^{226}Ra - Brick method was evaluated for the required method uncertainty at three test level activities. The five replicate PT samples from each test level concentration were analyzed. The proposed (target) and "as tested" (calculated known) test level activities are presented in Table 1. Note that the final test concentration values for the PT samples varied from the proposed test levels because of the inherent ^{226}Ra in the blank brick matrix.

6.5 Method Specificity

The method is specific for ^{226}Ra by collecting and purifying ^{226}Ra through a series of column separations after sample digestion. The brick sample is fused with sodium hydroxide in zirconium crucibles for ~15 minutes at 600 °C in a furnace. The fused material is dissolved using water and transferred to a centrifuge tube. A preconcentration step using a calcium carbonate precipitation is used to remove all isotopes of Ra from the alkaline matrix. The precipitate is dissolved in dilute acid and loaded onto cation resin to remove calcium (Ca) ions. After elution from the cation resin, barium (Ba) ions present in brick are removed using Sr Resin to prevent Ba interference on alpha peak resolution. This step eliminates concern about sample size and native Ba content adversely affecting alpha peak resolution. The sample is then passed through Ln (lanthanide) Resin to remove actinium-225 (^{225}Ac) and any residual Ca ions. Ra-226 in the purified sample is precipitated using barium sulfate microprecipitation in the presence of isopropanol to prepare sources for alpha counting.

6.6 Method Ruggedness

The rapid sodium hydroxide fusion is very rugged and will dissolve refractory particles present. The series of column separations removes alpha-emitting interferences and results in very good alpha peak resolution and spectra free from interferences. The sodium hydroxide fusion has been used successfully on the U.S. Department of Energy's Mixed Analyte Performance Evaluation

Program soil samples containing refractory actinides. When brick or soil samples are digested in an alkaline matrix, iron hydroxide precipitates, resulting in Ra loss in that precipitate. If the sample were passed through MnO_2 resin, for example, at an alkaline to neutral pH, there would be loss of Ra in that iron hydroxide precipitate. A MnO_2 precipitation can also collect unwanted Ca present in the sample. With this approach, any Ra that precipitates with the iron hydroxide present is also captured in the calcium carbonate precipitate, thus providing significant method ruggedness. The use of ^{225}Ra as a tracer also provides method ruggedness, providing an improved measurement of chemical yield versus ^{133}Ba, which may or may not behave identically to Ra. The use of ^{133}Ba tracer would also preclude use of Sr Resin to remove native Ba in the brick samples.

7. Techniques Used to Evaluate the Measurement Quality Objectives for the Rapid 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, the bias, and the radiochemical yield is presented in this section.

7.1 Required Method Uncertainty

The combined rapid ^{226}Ra - Brick method was evaluated following the guidance presented for "Level C" 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* (EPA 2004).

MARLAP "Level C" method validation requires the laboratory to conduct a method validation study wherein five replicate samples from each of the three concentration levels are analyzed according to the method. The concentration test levels analyzed are listed in Table 1. For validation "Level C," externally prepared PT samples consisting of NIST-traceable ^{226}Ra were used to spike the MVRM. In order to determine if the proposed method met the rapid methods development project MQO requirements for the required method uncertainty (u_{MR} = 0.62 pCi/g), each external PT sample result was compared with the method uncertainty acceptance criteria listed in the table below. The acceptance criteria stated in Table 3 for "Level C" validation stipulate that, for each test sample analyzed, the measured value had to be within ± 2.9 u_{MR} (required method uncertainty) for test level activities at or less than the AAL, or ± 2.9 φ_{MR} (required relative method uncertainty) for test level activities above the AAL.

Table 3 – MARLAP "Level C" Acceptance Criteria

MARLAP Validation Level	Application	Sample Type [1]	Acceptance Criteria [2]	Number of Test Levels	Number of Replicates	Total Number of Analyses
C	New Application	Method Validation Reference Materials	Measured value within ± 2.9 u_{MR} or ± 2.9 φ_{MR} of validation value	3	5	15

[1] "Method Validation Reference Materials" is not a requirement of MARLAP for these test levels. However, in order to assure laboratory independence in the method validation process, a NIST- traceable source manufacturer was contracted to produce the testing materials for Phases II and III of the project.

[2] The measured value must be within ± 2.9 u_{MR} for test level concentrations at or less than the AAL and within ± 2.9 φ_{MR} for a test level concentration above the AAL. It was assumed that the uncertainty of a test sample concentration will be negligible compared to the method uncertainty acceptance criteria and was not incorporated in the acceptance criteria.

7.2 Required Minimum Detectable Concentration

The analytical results reported for the PT samples having a ^{226}Ra concentration at the tested MDC of 1.025 ± 0.027 pCi/g 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). NAREL analyzed the external PT samples in accordance with the proposed rapid method.

Critical Net Concentration

In order to evaluate whether the combined method can meet the required MDC (1.025 pCi/g), the critical net concentration, as determined from the results of method reagent blanks, must be calculated. The critical net concentration (CL_{NC}) with a Type I error probability of $\alpha = 0.05$ was calculated using the following equation (consistent with MARLAP, Chapter 20, Equation 20.35):

$$CL_{NC}(\text{pCi}) = t_{1-\alpha}(n-1) \times s_{Blanks} \quad (5)$$

where s_{Blanks} is the standard deviation of the n blank-sample net results (corrected for instrument background) in radionuclide concentration units of pCi/g, 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 validation study a Type I error rate of 0.05 was chosen.

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

$$CL_{NC}(\text{pCi/g}) = 1.94 \times s_{Blanks} \quad (6)$$

Verification of Required MDC

Each of the 10 analytical results reported for the PT samples having a concentration at the required MDC for ^{226}Ra (1.025 pCi/g) was 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 reagent blank sample net results, calculate the estimated *Critical Net Concentration*, CL_{NC}.

III. Analyze 10 replicate samples spiked at the required MDC.

IV. From the results of the 10 replicate samples spiked at the required MDC, determine the number (Y) of sample results at or below the estimated CL_{NC}.

V. If Y ≤ 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.

8. Evaluation of Experimental Results

Only the experimental results for Phases II and III of the method validation process are reported and evaluated in this study. Information presented in this section will include results for Sections 6 and 7. The ^{226}Ra analytical results were evaluated for the required method uncertainty, required MDC, and bias. In addition, the mean radiochemical yield for the method for Phases II and III is reported to provide the method user the expected mean and range of this method performance characteristic.

8.1 Summary of the Method

The brick sample is fused with sodium hydroxide in zirconium crucibles for ~15 minutes at 600 °C in a furnace. The fused material is dissolved using water and transferred to a centrifuge tube. The sample is digested using sodium hydroxide fusion and the Ra is preconcentrated from the alkaline fusion matrix using calcium carbonate precipitation. Calcium ions are effectively removed using cation exchange separation, native Ba in the samples is removed using Sr Resin, and a final removal of ^{225}Ac and Ca ions is performed using Ln Resin. Radium is precipitated using barium sulfate microprecipitation in the presence of isopropanol for alpha spectrometry counting.

8.2 Required Method Uncertainty

Table 4A summarizes the ^{226}Ra results and the acceptability of each result compared to the acceptance criteria presented in Section 7.1. Based on the results of the individual analyses counted for 1,000 minutes, it may be concluded that combined rapid ^{226}Ra - Brick method is capable of meeting a required method uncertainty of 0.62 pCi/g at and below the AAL of 4.755 pCi/g, and a relative method uncertainty of 13% above the AAL.

Table 4A – Ra-226 Analytical Results for Required Method Uncertainty Evaluation

Nuclide: ^{226}Ra   Matrix: Brick   AAL Tested: 4.755 pCi/g

Proposed Method: *Rapid Method for Ra-226 in Brick for Environmental Restoration Following Homeland Security Events*

Required Method Validation Level: MARLAP "C"

Required Method Uncertainty, u_{MR}: 0.62 pCi/g at and below AAL; 13% of the known value above AAL

Acceptance Criteria:

Test Levels 1 and 2: $2.9 \times u_{MR} = \pm$ 1.8 pCi/g of quoted known value of sample in test level

Test Level 3: $2.9 \times \varphi_{MR} = \pm$ 37.7% of quoted known value of sample in test level

Test Level 1

Sample	pCi/g Known	CSU [1] (pCi/g)	pCi/g Measured	CSU [2] (pCi/g)	Allowable Range [3] (pCi/g)	Acceptable Y/N
R01	2.385	0.035	2.45	0.15	0.59 – 4.2	Y
R02			2.40	0.15		Y
R03			2.39	0.15		Y
R04			2.44	0.15		Y
R05			2.45	0.15		Y

Test Level 2

Sample	pCi/g Known	CSU [1] (pCi/g)	pCi/g Measured	CSU[2] (pCi/g)	Allowable Range [3] (pCi/g)	Acceptable Y/N
R06	4.755	0.053	5.18	0.30	3.0 – 6.5	Y
R07			4.30	0.24		Y
R08			5.00	0.28		Y
R09			4.75	0.26		Y
R10			4.43	0.24		Y

Test Level 3

Sample	pCi/g Known	CSU [1] (pCi/g)	pCi/g Measured	CSU[2] (pCi/g)	Allowable Range [3] (pCi/g)	Acceptable Y/N
R11	15.03	0.23	15.97	0.77	9.4 – 21	Y
R12			15.78	0.75		Y
R13			16.63	0.80		Y
R14			14.99	0.70		Y
R15			13.77	0.65		Y

[1] Quoted combined standard uncertainty (CSU; one sigma) determined by combining in quadrature the standard error of the mean inherent ^{226}Ra in blank brick and the reported uncertainty (coverage factor k=1) by the radioactive source manufacturer.

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

[3] Because the test level is actually above the proposed action level, the relative required method uncertainty was used to calculate the acceptable range.

As a measure of the expected variability of results for a test level, the calculated standard deviation of the seven measurements of each test level is provided in Table 4B. The standard deviation of the analytical results for a test level was much smaller than the required method uncertainty.

Table 4B – Experimental Standard Deviation of the Five PT Samples by Test Level

Test Level	Mean Concentration Measured (pCi/g)	Standard Deviation of Measurements (pCi/g)	Required Method Uncertainty
1	**2.427**	**0.027**	0.62
2 (AAL)	**4.73**	**0.37**	0.62
3	**15.4**	**1.1**	2.0 [1]

[1] This figure represents the absolute value of the required method uncertainty, calculated by multiplying the mean known value of Test Level 3 by the required relative method uncertainty (13%).

8.3 Required Minimum Detectable Concentration

The rapid ^{226}Ra method was validated for the required MDC using the methods identified in Attachments II and III and MDC samples counted for 800 minutes.

Tables 5, 5A, and 6 summarize the ^{226}Ra results and the acceptability of the method's performance specified in Section 7.2 to meet the tested required MDC of 1.025 ± 0.027 pCi/g.

Table 5 documents that the reported CSUs for the blank reagent sample measurements were similar in magnitude as the calculated standard deviation of the seven sample results, indicating that the inputs into the calculation of the CSU were properly estimated.

Table 5 – Reported ^{226}Ra Concentration Reagent Blank Samples

Sample ID [1]	Concentration (pCi/g)	CSU [2] (pCi/g)
RS41	0.076	0.020
RS42	0.032	0.013
RS43	0.035	0.015
RS44	0.038	0.014
RS45	0.046	0.016
RS46	0.047	0.016
RS47	0.044	0.015
Mean [3]	**0.045**	0.016
Standard Deviation	**0.015**	
Critical Net Concentration (pCi/g)	**0.028**	

[1] These samples were prepared at NAREL in demineralized water.
[2] Combined standard uncertainty (CSU), coverage factor *k*=1.
[3] Mean and standard deviation were calculated before rounding.

In order to determine the inherent ^{226}Ra in the blank brick material, 10 additional blank brick samples were processed prior to the method evaluation process and the weighted mean and weighted standard uncertainty (standard error of the mean) of the 10 results calculated. Table 5A provides the results of these measurements.

Table 5A –Concentrations of the Blank Brick Samples Used to Determine the Inherent ^{226}Ra

Sample ID [1]	Concentration (pCi/g)	CSU [1] (pCi/g)
1	1.17	0.13
2	0.90	0.11
3	0.990	0.065
4	1.063	0.069
5	1.12	0.13
6	0.945	0.070
7	1.11	0.12
8	1.002	0.069
9	0.90	0.11
10	1.167	0.082
Weighted Mean	**1.025**	
Weighted Standard Deviation [2]	0.027	

[1] Combined standard uncertainty (CSU), coverage factor *k*=1.
[2] Standard error (*k*=1).

In additional to the seven reagent blanks, seven blank brick samples were also processed as part of the method validation process. These blank brick samples were processed to determine if the inherent ^{226}Ra concentration in the brick material was consistent in a separate set of brick aliquants. Table 5B presents the results for these seven blank samples. The mean and standard deviation of the reported seven values were 1.12 ± 0.13 pCi/g. As indicated in Table 7, there was no bias between the results in Table 5A and 5B.

Table 5B – Reported ^{226}Ra Concentration of Blank Brick Samples

Sample ID [1]	Concentration (pCi/g)	CSU [2] (pCi/g)
R41	1.153	0.099
R42	1.29	0.12
R43	0.921	0.076
R44	0.964	0.088
R45	1.188	0.097
R46	1.20	0.11
R47	1.117	0.094
Mean [3]	**1.12**	**0.097[4]**
Standard Deviation	0.13	

[1] These samples were prepared at Eckert & Ziegler Analytics and analyzed by NAREL using the proposed combined radium method.
[2] Combined standard uncertainty (CSU), coverage factor k=1.
[3] Mean and standard deviation were calculated before rounding.
[4] Mean of reported CSU values.

Critical Net Concentration

The critical net concentration for reagent blanks for the method under evaluation was calculated using Equation 6 from Section 7.2. Based on the results of the seven analytical blanks (Table 5), the critical net concentration for the combined method was estimated to be 0.028 pCi/g. Although there was a bias in the reagent blank sample results (Table 7), the bias would not significantly affect the estimate of the net critical concentration. The bias may be attributed to trace ^{226}Ra contamination in the sodium carbonate used (25 mL, 2M sodium carbonate). Based on limited testing at NAREL, it may be possible to lower ^{226}Ra blank measurements by lowering the excess carbonate levels to 10–15 mL, 2M sodium carbonate, but this approach was not formerly validated in this study.

Required MDC

A summary of the reported results for samples containing ^{226}Ra at the required MDC (1.025 pCi/g) is presented in Table 6. The mean measured value for ^{226}Ra in the 10 MDC test samples was calculated as 1.000 ± 0.045 pCi/g (k=1). Based on the analytical results, the combined rapid ^{226}Ra - Brick method is capable of meeting a required MDC of 1.0 pCi/g. As a matter of interest, the average *a priori* MDC reported for the reagent blank, blank brick and MDC samples was of the order of 0.02 to 0.03 pCi/g for a 800 minute counting time. A much shorter count could be used to meet a MDC of 1 pCi/g. The count time, however, was designed to allow sufficient ingrowth of ^{217}At while allowing the count time to begin late in the same day as the column separation instead of waiting 24 hours to begin the count. Therefore, decreasing the count time would have to take the ingrowth of ^{217}At tracer counts into account.

Table 6 – Reported Results for Samples Containing ^{226}Ra at the As-Tested MDC Value (1.025 pCi/g)

Sample ID	Concentration (pCi/g)	CSU [1] (pCi/g)	Test Result ≤ Reagent Blank CL_{NC} [3]
R30	0.994	0.086	N
R31	1.099	0.090	N
R32	0.989	0.083	N
R33	0.978	0.084	N
R34	1.052	0.091	N
R35	0.941	0.083	N
R36	0.982	0.082	N
R37	0.963	0.081	N
R38	1.009	0.086	N
R39	0.993	0.086	N
Mean [2]	**1.000**		—
Standard Deviation of Results	**0.045**		
	CL_{NC}	—	0.028 pCi/g
	Acceptable maximum values ≤ CL_{NC}	—	**2**
	Number of results > CL_{NC}	—	10
	Number of results ≤ CL_{NC}	—	0
		Evaluation	**Pass**

[1] Combined standard uncertainty (CSU), coverage factor k=1.
[2] Mean and standard deviation were calculated before rounding.
[3] Critical net concentration.

8.4 Evaluation of the Absolute and Relative Bias

The ^{226}Ra results for the seven reagent blank samples (Table 5), seven blank brick samples (Table 5B), 10 MDC samples (Table 6), and five replicate PT samples on the three test levels (Table 4A) were evaluated for bias according to the equations presented in Section 6.3. The results and interpretation of the evaluation are presented below in Table 7.

Table 7 – Relative Bias Evaluation of the Rapid ^{226}Ra Brick Method

Type of Bias	Test Level	Calculated Known Value ± CSU (k=1) (pCi/g) [1]	Mean of Measurements ± Standard Deviation [2] (pCi/g)	Difference from Known	Number of Measurements/Degrees of Freedom	|T|	t_{df}	Bias Yes/No
Absolute	Method reagent blanks	0.0000	0.045 ± 0.015	0.045	7/6	8.22	2.45	Y
Relative	Brick Blanks	1.025 ± 0.027	1.12 ± 0.13	0.10	7/10	1.65	2.23	N
Relative	MDC	1.025 ± 0.027	1.000 ± 0.045	-0.025	10/>100	0.82	1.97	N
Relative	1	2.385 ± 0.035	2.427 ± 0.027	0.042	5/>100	1.13	1.97	N
Relative	2 – AAL	4.755 ± 0.053	4.73 ± 0.37	-0.025	5/4	0.14	2.78	N
Relative	3	15.03 ± 0.23	15.4 ± 1.1	0.37	5/5	0.75	2.57	N

[1] The stated CSU includes the uncertainty in the ^{226}Ra reference standard used to prepare the samples and the standard uncertainty of the measurement results for the test samples.
[2] Standard deviation of the measurements.

Only the method reagent blank samples prepared by NAREL using method reagents could be evaluated for absolute bias since the blank brick had inherent ^{226}Ra as part of its makeup. These method reagent blank samples were taken through the entire method described in Attachment II and III. Based on a statistical analysis of the results shown in Table 7, an absolute bias exists for the reagent blanks. Since the observed sample results of the seven measurements were of the same magnitude, most likely there was inherent ^{226}Ra in the reagents, notably the Na_2CO_3 used in the pre-concentration of radium from the hydroxide matrix. Limited testing with less sodium carbonate at NAREL did lower blank activity levels, but the level of sodium carbonate was kept the same as the concrete validation study for consistency. The magnitude of the ^{226}Ra content in the reagents, however, is very low and would not affect the method validation evaluation results.

Measurement results for the 10 blank brick samples (Table 5A) used to estimate the inherent ^{226}Ra in the blank brick material had a weighted mean and weighted standard uncertainty of 1.025 ± 0.027 pCi/g. This inherent concentration of ^{226}Ra was added to the spike values certified by Eckert & Ziegler Analytics for the MDC and the three method uncertainty test levels. The stated uncertainty for these calculated known values was determined by summing, in quadrature, the uncertainty of the spiked value and the standard uncertainty (standard error) in the inherent ^{226}Ra mean blank value.

The 10 MDC test level samples were also blank brick samples that had a final calculated known value of 1.025 ± 0.027 pCi/g. The mean measured concentration of these MDC samples was 1.000 ± 0.045 pCi/g. As determined by the paired *t*-test described in Section 7, no relative bias was indicated for the MDC samples. In addition, no relative bias was determined for the sample results of the three test levels for the method uncertainty evaluation. The relative percent difference for the mean of the MDC samples and the mean of method uncertainty test level samples compared to the known values was:

- MDC: -2.4%

- Test Level 1: 1.8%.
- Test Level 2: -0.53%.
- Test Level 3: 2.5%.

The small average bias versus reference values at the 3 test levels, as well as the MDC study, indicates a very robust, reliable rapid method to determine ^{226}Ra in brick samples.

8.5 Method Ruggedness and Specificity

The results summarized in Table 8 represent the radiochemical yields for all three test levels, the reagent and brick blanks, the LCSs, and the MDC samples that were processed in accordance with the final method identified in Attachments II and III. The observed radiotracer yield results for the 50 analyses were evaluated and the mean and standard deviation of the distribution were calculated to be 71.0 ± 8.6%.

Table 8 – Summary of ^{225}Ra Radiochemical Yield Results for Test and Quality Control Samples

Number of Samples	50
Mean Radiochemical Yield	71.0%
Standard Deviation of Distribution (1σ)	8.6%
Median	70.6%
Minimum Value	38.5%
5^{th} Percentile	58.7%
95^{th} Percentile	86.4%
Maximum Value	87.2%

The yields for samples evaluated using this method are shown on Figure 1. The mean yield and standard deviation of the results were within expected values. The reagent blank samples had the highest yields (samples 10 – 17).

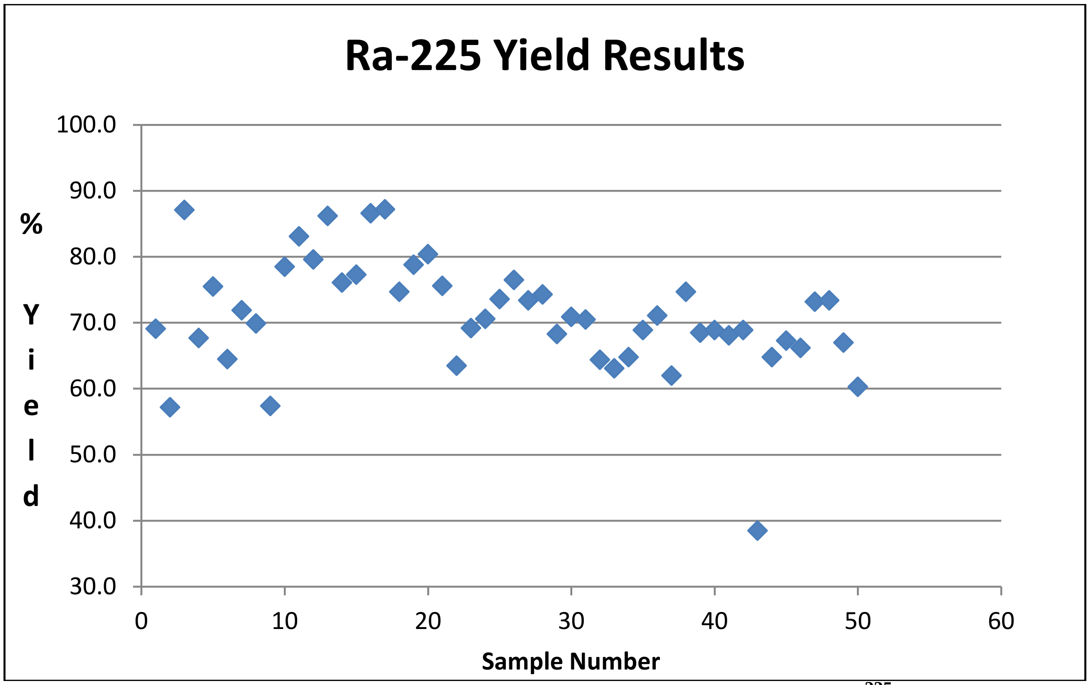

Figure 1 – Yields for Method Based on Measurement of ^{225}Ra

9. Timeline to Complete a Batch of Samples

NAREL kept a timeline log on processing a batch of samples and associated internal quality control samples. The total time to process a batch of samples, including counting of the samples and data review and analysis, was about 17 hours, excluding a ~ 6 hour wait time to allow additional ingrowth of ^{217}At. The amount of ingrowth time can be varied depending on the amount of tracer used and the number of tracer counts desired. NAREL's breakdown of the time line by method-process step is presented in Attachment I (this information is also presented in more detail in the method flow chart in Attachment III, Section 17.5).

10. Reported Modifications and Recommendations

NAREL performed the rapid ^{226}Ra method validation and made a minor modification to the method prior to analyzing samples for Phases II and III of the project. Selected modifications and recommendations provided by NAREL are listed below.

<u>Modifications of the Method During Phases II and III</u>:

Rapid Radiochemical Method for Ra-226 in Building Materials for Environmental Remediation Following Radiological Incidents (Attachment III):

11.2.8 Transfer each sample solution from Step 11.2.3.12 into the appropriate column at ~1-1.5 mL/min.

NOTE: It is important to load samples rapidly enough (1–1.5 mL/min) to avoid any retention of Ra on Ln Resin, but not so fast that Ac-225 breaks through resin and causes erroneously high tracer yields.

11. Summary and Conclusions

The combined rapid ^{226}Ra - Brick method was successfully validated according to "*Method Validation Requirements for Qualifying Methods Used by Radioanalytical Laboratories Participating in Incident Response Activities*" and Chapter 6 of *Multi-Agency Radiological Laboratory Analytical Protocols Manual* (EPA 2004). The method was evaluated using well-characterized brick analyzed for its macro-constituents by an independent laboratory[6] and for its radiological constituents (Attachment IV) using the combined rapid ^{226} Ra - Brick method by NAREL.

The pulverized brick samples were spiked with three ^{226}Ra concentrations consistent with a concentration range that incorporated the 10^{-5} exposure risk contaminant level in soil in the presence of low-level concentrations of ^{241}Am, ^{239}Pu, ^{90}Sr, and uranium (Table 1). The combined rapid ^{226}Ra - Brick method met MARLAP Validation Level "C" requirements for required method uncertainty of 0.62 pCi/g at and below the AAL, and for the required relative method uncertainty of 13% above the AAL concentration of 4.755 pCi/g. A 1-g sample aliquant and a 1,000-minute counting time were used for the method uncertainty evaluation.

For a reagent blank matrix containing no ^{226}Ra, the critical net concentration for the method was estimated to be 0.028 pCi/g for an 800-minute counting time. The mean reported MDC value for the reagent blank and MDC test samples was ~ 0.02 – 0.03 pCi/g or 1/40 the theoretical *a priori* MDC for blank samples of ~1 pCi/g, indicating the method passed the MDC capability test.

Predicated on the statistical tests provided in the *Method Validation Guide for Qualifying Methods Used by Radiological Laboratories Participating in Incident Response Activities* (EPA 2009), the combined rapid ^{226}Ra - Brick method was found to have an absolute bias for the reagent blank matrix. The mean and standard error of the seven reagent blank samples were calculated as 0.0455 ± 0.0057 pCi/g. It was suspected that inherent ^{226}Ra in the Na_2CO_3 reagent used in the pre-concentration of radium from the hydroxide matrix was the cause of the bias. No relative bias was noted for the measurements performed on the 10 MDC test level samples. The mean concentration of 1.000 ± 0.045 pCi/L for the 10 MDC test samples falls within -0.025 pCi/g of the calculated known value.

No bias was noted for the three test levels for the method validation evaluation samples. The percent difference of the mean measured value and the known value for the three test levels was 1.8%, -0.53% and 2.5%, respectively. The excellent results at the three test levels demonstrate that the rapid method for ^{226}Ra in brick samples is both rugged and robust under the conditions tested.

The chemical interferences that were present in the brick matrix, plus those noted in the Method Ruggedness section of this report, were tested during this method development.

[6] Wyoming Analytical Laboratories, Inc. of Golden, Colorado performed the macro analysis.

The observed radiotracer yield results for the 50 analyses was evaluated and the mean and standard deviation of the distribution were calculated to be 71.0 ± 8.6%. Chemical yields that were lower tended to be reagent blank samples rather than actual brick samples. The brick matrix components tend to facilitate higher chemical yields, presumably due to more efficient recovery across the calcium carbonate precipitation step, presumably aided by iron hydroxide precipitation that also occurs due to Fe in the brick matrix under alkaline conditions

The laboratory provided a minor modification and recommendations to clarify and improve the rapid ^{226}Ra method. The modifications were applied to the analyses of samples during Phases II and III of the method validation process. The method is rapid and the validation study indicates it can be used with confidence after a radiological incident for the analysis of emergency brick samples.

12. References

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

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Attachment I:

Estimated Elapsed Times

Step	Elapsed Time (hours)
Rapid Fusion	3
Vacuum Box Setup	3.5
Load Sample to cation resin columns	5
Transfer Ra eluate to 150mL glass beakers	5.75
Load sample to Sr Resin cartridge for Ba removal	6.25
Transfer Ra eluate to 100mL glass beakers	7.5
Load sample to Ln Resin cartridges	8
Microprecipitation	9
Count sample test source (16.7 hours)**	13 – 22

*These estimates depend on the number of samples which can be processed simultaneously. These estimates are based on ~15-20 samples.

** An *a priori* MDC of ~0.02 to 0.03 pCi/g can be obtained for a counting time of 800 minutes. Shorter counting times can be used to obtain MDC values of greater magnitudes.

Attachment II:

Rapid Method for Sodium Hydroxide Fusion of Concrete[7] and Brick Matrices Prior to Americium, Plutonium, Strontium, Radium, and Uranium Analyses for Environmental Remediation Following Radiological Incidents

1. Scope and Application

1.1. The method is applicable to the sodium hydroxide fusion of concrete and brick samples, prior to the chemical separation procedures described in the following procedures:

1.1.1. Rapid Radiochemical Method for Americium-241 in Building Materials for Environmental Remediation Following Radiological Incidents (Reference 16.1).

1.1.2. Rapid Radiochemical Method for Plutonium-238 and Plutonium-239/240 in Building Materials for Environmental Remediation Following Radiological Incidents (Reference 16.2).

1.1.3. Rapid Radiochemical Method for Radium-226 in Building Materials for Environmental Remediation Following Radiological Incidents (Reference 16.3).

1.1.4. Rapid Radiochemical Method for Total Radiostrontium (Sr-90) in Building Materials for Environmental Remediation Following Radiological Incidents (Reference 16.4).

1.1.5. Rapid Radiochemical Method for Isotopic Uranium in Building Materials for Environmental Remediation Following Radiological Incidents (Reference 16.5).

1.2. This general method for concrete and brick building material applies to samples collected following a radiological or nuclear incident. The concrete and brick samples may be received as core samples, pieces of various sizes, dust or particles (wet or dry) from scabbling, or powder samples.

1.3. The fusion method is rapid and rigorous, effectively digesting refractory radionuclide particles that may be present.

1.4. Concrete or brick samples should be ground to at least 50–100 mesh size prior to fusion, if possible.

1.5. After a homogeneous, finely ground sample is obtained, the dissolution of concrete or brick matrices by this fusion method is expected to take approximately 1 hour per batch of 20 samples. This method assumes the laboratory starts with a representative, finely ground, 1–1.5-g aliquant of sample and employs simultaneous heating in multiple furnaces. The preconcentration steps to eliminate the alkaline fusion matrix and collect the radionuclides are expected to take approximately 1 hour.

1.6. As this method is a sample digestion and pretreatment technique, to be used prior to other separation and analysis methods, the user should refer to those individual methods

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[7] U.S. Environmental Protection Agency (EPA). 2014. *Rapid Radiochemical Method for Plutonium-238 and Plutonium-239/240 in Building Materials for Environmental Remediation Following Radiological Incidents*, Office of Air and Radiation, Washington, DC, EPA 402-R-07-007, April 2014. Unpublished.

and any project-specific requirements for the determination of applicable measurement quality objectives (MQOs).

1.7. Application of this method by any laboratory should be validated by the laboratory using the protocols provided in *Method Validation Guide for Qualifying Methods Used by Radioanalytical Laboratories Participating in Incident Response Activities* (Reference 16.6), or the protocols published by a recognized standards organization for method validation.

1.7.1. In the absence of project-specific guidance, MQOs for concrete or brick samples may be based on the Analytical Action Levels (AALs), the Required Method Uncertainty (u_{MR}) and the Required Relative Method Uncertainty (φ_{MR}) found in the *Radiological Laboratory Sample Analysis Guide for Incident Response — Radionuclides in Soil* (Reference 16.7).

2. Summary of Method

2.1. The method is based on the rapid fusion of a representative, finely ground 1–1.5-g aliquant using rapid sodium hydroxide fusion at 600 °C.

2.2. Pu, U, and Am are separated from the alkaline matrix using an iron/titanium hydroxide precipitation (enhanced with calcium phosphate precipitation) followed by a lanthanum fluoride matrix removal step.

2.3. Sr is separated from the alkaline matrix using a carbonate precipitation, followed by a calcium fluoride precipitation to remove silicates.

2.4. Ra is separated from the alkaline matrix using a carbonate precipitation.

3. Definitions, Abbreviations and Acronyms

3.1. Discrete Radioactive Particles (DRPs or “hot particles”). Particulate matter in a sample of any matrix where a high concentration of radioactive material is present as a tiny particle (µm range).

3.2. *Multi-Agency Radiological Analytical Laboratory Protocols (MARLAP) Manual* (Reference 16.8).

3.3. The use of the term concrete or brick throughout this method is not intended to be limiting or prescriptive, and the method described herein refers to all concrete or masonry-related materials. In cases where the distinction is important, the specific issues related to a particular sample type will be discussed.

4. Interferences and Limitations

NOTE: Large amounts of extraneous debris (pebbles larger than ¼", non-soil related debris) are not generally considered to be part of a concrete or brick matrix. When consistent with data quality objectives (DQOs), materials should be removed from the sample prior to drying. It is recommended this step be verified with Incident Command before discarding any materials.

4.1. Concrete or brick samples with larger particle size may require a longer fusion time during Step 11.1.8.

4.2. As much information regarding the elemental composition of the sample should be obtained as possible. For example some concrete or brick may have native concentrations of uranium, radium, thorium, strontium or barium, all of which may have an effect on the chemical separations used following the fusion of the sample. In some cases (e.g., radium or strontium analysis), elemental analysis of the digest prior to chemical separations may be necessary to determine native concentrations of carrier elements present in the sample.

NOTE: In those samples where native constituents are present that could interfere with the determination of the chemical yield (e.g., strontium for ^{90}Sr analysis) or with the creation of a sample test source (e.g., Ba for ^{226}Ra analysis by alpha spectrometry), it may be necessary to determine the concentration of these native constituents in advance of chemical separation (using a separate aliquant of fused material) and make appropriate adjustments to the yield calculations or amount of carrier added.

4.3. Matrix blanks for these matrices may not be practical to obtain. Efforts should be made to obtain independent, analyte-free materials that have similar composition as the samples to be analyzed. These blanks will serve as process monitors for the fusion, and as potential monitors for cross contamination during batch processing.

4.4. Uncontaminated concrete or brick material may be acceptable blank material for Pu, Am, and Sr analyses, but these materials will typically contain background levels of U and Ra isotopes.

4.4.1. If analyte-free blank material is not available and an empty crucible is used to generate a reagent blank sample, it is recommended that 100–125 milligram (mg) calcium (Ca) per gram of samples be added as calcium nitrate to the empty crucible as blank simulant. This step facilitates Sr/Ra carbonate precipitations from the alkaline fusion matrix.

4.4.2. Tracer yields may be slightly lower for reagent blank matrices, since the concrete and brick matrix components typically enhance recoveries across the precipitation steps.

4.5. Samples with elevated activity or samples that require multiple analyses from a single concrete or brick sample may need to be split after dissolution. In these cases the initial digestate and the split fractions should be carefully measured to ensure that the sample aliquant for analysis is accurately determined.

4.5.1. Tracer or carrier amounts (added for yield determination) may be increased where the split allows for the normal added amount to be present in the subsequent aliquant. For very high activity samples, the addition of the tracer or carrier may need to be postponed until following the split, in which case special care must be taken to ensure that the process is quantitative until isotopic exchange with the yield monitor is achieved. This deviation from the method should be thoroughly documented and reported in the case narrative.

4.5.2. When this method is employed and the entire volume of fused sample is processed in the subsequent chemical separation method, the original sample size and units are used in all calculations, with the final results reported in the units requested by the project manager.

4.5.3. In cases where the sample digestate is split prior to analysis, the fractional aliquant of the sample is used to determine the sample size. The calculation of the appropriate sample size used for analysis is described in Section 12, below.

4.6. In the preparation of blank samples, laboratory control samples (LCSs) and duplicates, care should be taken to create these quality control samples as early in the process as possible, and to follow the same tracer/carrier additions, digestion process, and sample splitting used for the field samples. In the case of this method, quality control samples should be initiated at the point samples are aliquanted into crucibles for the fusion.

4.7. Although this method is applicable to a variety of subsequent chemical separation procedures, it is not appropriate where the analysis of volatile constituents such as iodine or polonium is required. The user of this method must ensure that analysis is not required for any radionuclide that may be volatile under these sample preparation conditions, prior to performing this procedure.

4.8. Zirconium crucibles used in the fusion process may be reused.

4.8.1. It is very important that the laboratory have a process for cleaning and residual contamination assessment of the reused zirconium crucibles. The crucibles should be cleaned very well using soap and water, followed by warm nitric acid and then water. Blank measurements should be monitored to ensure effective cleaning.

4.8.2. Segregation of crucibles used for low and high activity samples is recommended to minimize the risk of cross-contamination while maximizing the efficient use of crucibles.

4.9. Centrifuge speed of 3500 rpm is prescribed but lower rpm speeds (>2500 rpm) may be used if 3500 rpm is not available.

4.10. Titanium chloride ($TiCl_3$) reductant is used during the co-precipitation step with iron hydroxide for actinides to ensure tracer equilibrium and reduce uranium from U^{+6} to U^{+4} to enhance chemical yields. This method adds 5 mL 10 percent by mass (wt%) $TiCl_3$ along with the Fe. Adding up to 10 mL of 10 wt% $TiCl_3$ may increase uranium chemical yields, but this will need to be validated by the laboratory.

4.11. Trace levels of ^{226}Ra may be present in Na_2CO_3 used in the ^{226}Ra pre-concentration step used in this method. Adding less 2M Na_2CO_3 (<25 mL used in this method) may reduce ^{226}Ra reagent blank levels, while still effectively pre-concentrating ^{226}Ra from the fusion matrix. This will need to be validated by the laboratory.

4.12. La is used to pre-concentrate actinides along with LaF_3 in this method to eliminate matrix interferences, including silica, which can cause column flow problems. La follows Am in subsequent column separations and must be removed. Less La (2 mg) was used for brick samples to minimize the chance of La interference on alpha spectrometry peaks. While this may also be effective for concrete samples, this will have to be validated by the laboratory.

5. Safety

5.1. General

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

5.1.2. Refer to your laboratory's chemical hygiene plan (or equivalent) for general safety rules regarding chemicals in the workplace.

5.2. Radiological

5.2.1. Discrete Radioactive Particles (DRPs or "hot particles")

5.2.1.1. Hot particles will be small, on the order of 1 millimeter (mm) or less. DRPs are typically not evenly distributed in the media and their radiation emissions are not uniform in all directions (anisotropic).

5.2.1.2. Concrete/brick media should be individually surveyed using a thickness of the solid sample that is appropriate for detection of the radionuclide decay particles.

NOTE: The information regarding DRPs should accompany the samples during processing as well as be described in the case narrative that accompanies the sample results.

5.3. Procedure-Specific Non-Radiological Hazards:

5.3.1. The sodium hydroxide fusion is performed in a furnace at 600 °C. The operator should exercise extreme care when using the furnace and when handling the hot crucibles. Long tongs are recommended. Thermal protection gloves are also recommended when performing this part of the procedure. The fusion furnace should be used in a ventilated area (hood, trunk exhaust, etc.).

5.3.2. Particular attention should be paid to the use of hydrofluoric acid (HF). HF is an extremely dangerous chemical used in the preparation of some of the reagents and in the microprecipitation procedure. Appropriate personal protective equipment (PPE) must be used in strict accordance with the laboratory safety program specification.

6. Equipment and Supplies

6.1. Adjustable temperature laboratory hotplates.

6.2. Balance, top loading or analytical, readout display of at least ± 0.01 g.

6.3. Beakers, 100 mL, 150 mL capacity.

6.4. Centrifuge able to accommodate 225 mL tubes.

6.5. Centrifuge tubes, plastic, 50 mL and 225 mL capacity.

6.6. Crucibles, 250 mL, zirconium, with lids.

6.7. 100 µL, 200 µL, 500 µL, and 1 mL pipets or equivalent and appropriate plastic tips.

6.8. 1-10 mL electronic/manual pipet(s).

6.9. Drill with masonry bit (¼-inch carbide bit recommended).

6.10. Hot water bath or dry bath equivalent.

6.11. Ice bath.

6.12. Muffle furnace capable of reaching at least 600 °C.

6.13. Tongs for handling crucibles (small and long tongs).

6.14. Tweezers or forceps.

6.15. Sample size reduction equipment (ball mill, paint shaker, etc.) and screens. The necessary equipment will be based on a laboratory's specific method for the process of producing a uniformly ground sample from which to procure an aliquant.

NOTE: See appendix for a method for ball-milling and homogenization of concrete or brick.

6.16. Vortex stirrer.

7. Reagents and Standards

NOTES:

Unless otherwise indicated, all references to water should be understood to mean Type I reagent water (ASTM D1193; Reference 16.9).

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

7.1. Type I reagent water as defined in ASTM Standard D1193 (Reference 16.9).

7.2. Aluminum nitrate ($Al(NO_3)_3 \cdot 9H_2O$)

7.2.1. Aluminum nitrate solution (2M): Add 750 g of aluminum nitrate ($Al(NO_3)_3 \cdot 9H_2O$) to ~700 mL of water and dilute to 1 L with water. Low-levels of uranium are typically present in $Al(NO_3)_3$ solution.

NOTE: Aluminum nitrate reagent typically contains trace levels of uranium concentration. To achieve the lowest possible blanks for isotopic uranium measurements, some labs have removed the trace uranium by passing ~250 mL of the 2M aluminum nitrate reagent through ~7 mL TRU® Resin or UTEVA® Resin (Eichrom Technologies), but this will have to be tested and validated by the laboratory.

7.3. Ammonium hydrogen phosphate (3.2M): Dissolve 106 g of $(NH_4)_2HPO_4$ in 200 mL of water, heat on low to medium heat on a hot plate to dissolve and dilute to 250 mL with water.

7.4. Boric Acid, H_3BO_3.

7.5. Calcium nitrate (1.25M): Dissolve 147 g of calcium nitrate tetrahydrate ($Ca(NO_3)_2 \cdot 4H_2O$) in 300 mL of water and dilute to 500 mL with water.

7.6. Iron carrier (50 mg/mL): Dissolve 181 g of ferric nitrate ($Fe(NO_3)_3 \cdot 9H_2O$) in 300 mL water and dilute to 500 mL with water.

7.7. Hydrochloric acid (12M): Concentrated HCl, available commercially.

7.6.1. Hydrochloric acid (0.01M): Add 0.83 mL of concentrated HCl to 800 mL of water and dilute with water to 1 L.

7.6.2. Hydrochloric acid (1.5M): Add 125 mL of concentrated HCl to 800 mL of water and dilute with water to 1 L.

7.8. Hydrofluoric acid (28M): Concentrated HF, available commercially.

7.9. Lanthanum carrier (1.0 mg La^{3+}/mL): Add 1.56 g lanthanum (III) nitrate hexahydrate [$La(NO_3)_3 \cdot 6H_2O$] in 300 mL water, diluted to 500 mL with water.

7.10. Nitric acid (16M): Concentrated HNO_3, available commercially.

7.10.1. Nitric acid (3M): Add 191 mL of concentrated HNO_3 to 700 mL of water and dilute to 1 L with water.

7.10.2. Nitric acid–boric acid solution (3M-0.25M): Add 15.4 g of boric acid and 190 mL of concentrated HNO_3 to 500 mL of water, heat to dissolve, and dilute to 1 liter with water.

7.10.3. Nitric acid (7M): Add 443 mL of concentrated HNO_3 to 400 mL of water and dilute to 1 L with water.

7.10.4. Nitric acid (8M): Add 506 mL of concentrated HNO_3 to 400 mL of water and dilute to 1 L with water.

7.11. Sodium carbonate (2M): Dissolve 212 g anhydrous Na_2CO_3 in 800 mL of water, then dilute to 1 L with water.

7.12. Sodium hydroxide pellets.

7.13. Titanium (III) chloride solution ($TiCl_3$), 10 wt% solution in 20–30 wt% hydrochloric acid.

7.14. Radioactive tracers/carriers (used as yield monitors) and spiking solutions. A radiotracer is a radioactive isotope of the analyte that is added to the sample to measure any losses of the analyte. A carrier is a stable isotope form of a radionuclide (usually the analyte) added to increase the total amount of that element so that a measureable mass of the element is present. A carrier can be used to determine the yield of the chemical process and/or to carry the analyte or radiotracer through the chemical process. Refer to the chemical separation method(s) to be employed upon completion of this dissolution technique. Tracers/carriers that are used to monitor radiochemical/chemical yield should be added at the beginning of this procedure. This timing allows for monitoring and correction of chemical losses in the combined digestion process, as well as in the chemical separation method. Carriers used to prepare sample test sources but not used for chemical yield determination (e.g., cerium added for microprecipitation of plutonium or uranium), should be added where indicated.

8. Sample Collection, Preservation, and Storage

Not Applicable.

9. Quality Control

9.1. Where the subsequent chemical separation technique requires the addition of carriers and radioactive tracers for chemical yield determinations, these are to be added prior to beginning the fusion procedure, unless there is good technical justification for doing otherwise.

9.2. Batch quality control results shall be evaluated and meet applicable analytical protocol 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's Quality Manual and procedures shall be used to determine acceptable performance for this method.

9.2.1. An exception to this approach may need to be taken for samples of exceptionally high activity where human safety may be involved.

9.3. Quality control samples are generally specified in the laboratory's Quality Manual or in a project's APS. At the very minimum the following are suggested:

9.3.1. A laboratory control sample (LCS), which consists solely of the reagents used in this procedure and a known quantity of radionuclide spiking solution, shall be run with each batch of samples. The concentration of the LCS should be at or near the action level or level of interest for the project

9.3.2. One reagent blank shall be run with each batch of samples. The blank should consist solely of the reagents used in this procedure (including tracer or carrier from the analytical method added prior to the fusion process).

9.3.3. A sample duplicate that is equal in size to the original aliquant should be analyzed with each batch of samples. This approach provides assurance that the laboratory's sample size reduction and sub-sampling processes are reproducible.

10. Calibration and Standardization

10.1. Refer to the individual chemical separation and analysis methods for calibration and standardization protocols.

11. Procedure

11.1. Fusion

11.1.1. In accordance with the DQOs and sample processing requirements stated in the project plan documents, remove extraneous materials from the concrete or brick sample using a clean forceps or tweezers.

11.1.2. Weigh out a representative, finely ground 1-g aliquant of sample into a labeled crucible (1.5-g aliquants for ^{90}Sr analysis).

NOTES:

It is anticipated that concrete or brick powder sample material will be dry enough to aliquant without a preliminary drying step. In the event samples are received that contain moisture, the samples may be dried in a drying oven at 105 °C prior to taking the aliquant.

For Sr and Ra analyses, a reagent blank of 100–150 mg calcium per gram of sample (prepared by evaporating 2.5 mL of 1.25M calcium nitrate, $Ca(NO_3)_2$, for radium and 3 mL of 1.25M $Ca(NO_3)_2$ for strontium) should be added to the crucible as a blank simulant to ensure the blank behaves like the concrete or brick samples during the precipitation steps.

11.1.3. Add the proper amount of tracer or carrier appropriate for the method being used and the number of aliquants needed.

11.1.4. Place crucibles on a hot plate and heat to dryness on medium heat.
NOTE: Heat on medium heat to dry quickly but not so high as to cause splattering.

11.1.5. Remove crucibles from hot plate and allow to cool.

11.1.6. Add the following amounts of sodium hydroxide based on the aliquant size/analysis required.

1 g for Pu, Am, U:	15 g NaOH
1.5 g for Sr:	15 g NaOH
1 g for Ra:	10 g NaOH

11.1.7. Place the crucibles with lids in the 600 °C furnace using tongs.

11.1.8. Fuse samples in the crucibles for ~15 minutes.

NOTE: Longer times may be needed for larger particles.

11.1.9. Remove hot crucibles from furnace very carefully using tongs, and transfer to hood.

11.1.10. Add ~25-50 mL of water to each crucible ~8 to 10 minutes (or longer) after removing crucibles from furnace, and heat on hotplate to loosen/dissolve solids.

11.1.11. If necessary for dissolution, add more water, and warm as needed on a hotplate.

11.1.12. Proceed to Section 11.2 for the actinide preconcentration procedure, 11.3 or 11.4 for Sr preconcentration, or 11.5 for Ra preconcentration steps.

11.2. Preconcentration of Actinides (Pu, U, or Am) from Hydroxide Matrix

11.2.1. Pipet 2.5 mL of iron carrier (50 mg/mL) into a labeled 225-mL centrifuge tube for each sample.

11.2.2. Add La carrier to each 225-mL tube as follows:

Concrete: 5 mL of 1 mg La/mL for Pu, Am, U
Brick: 5 mL of 1 mg La/mL for Pu, and U; 2 mL 1 mg La/mL for Am

11.2.3. Transfer each fused sample to a labeled 225 mL centrifuge tube, rinse crucibles well with water, and transfer rinses to each tube.

11.2.4. Dilute each sample to approximately 180 mL with water.

11.2.5. Cool the 225 mL centrifuge tubes in an ice bath to approximately room temperature as needed.

11.2.6. Pipet 1.25M $Ca(NO_3)_2$ and 3.2M $(NH_4)_2HPO_4$ into each tube as follows:

Pu, Am:	2 mL 1.25M $Ca(NO_3)_2$ and 3 mL 3.2M $(NH_4)_2HPO_4$
U:	3 mL 1.25M $Ca(NO_3)_2$ and 5 mL 3.2M $(NH_4)_2HPO_4$

11.2.7. Cap tubes and mix well.

11.2.8. Pipet 5 mL of 10 wt% $TiCl_3$ into each tube, and cap and mix immediately.

11.2.9. Cool the 225 mL centrifuge tubes in an ice bath for ~10 minutes.

11.2.10. Centrifuge tubes for 6 minutes at 3500 rpm.

11.2.11. Pour off the supernate, and discard to waste.

11.2.12. Add 1.5M HCl to each tube to redissolve each sample in a total volume of ~60 mL.

11.2.13. Cap and shake each tube to dissolve solids as well as possible.

NOTE: There will typically be undissolved solids, which is acceptable.

11.2.14. Dilute each tube to ~170 mL with 0.01M HCl. Cap and mix.

11.2.15. Pipet 1 mL of 1.0 mg La/mL into each tube.

11.2.16. Pipet 3 mL of 10 wt% $TiCl_3$ into each tube. Cap and mix.

11.2.17. Add 22 mL of concentrated HF into each tube. Cap and mix well.

11.2.18. Place tubes to set in an ice bath for ~10 minutes to get the tubes very cold.

11.2.19. Centrifuge for ~10 minutes at 3000 rpm or more, as needed.

11.2.20. Pour off supernate, and discard to waste.

11.2.21. Pipet 5 mL of 3M HNO_3 - 0.25M boric acid into each tube.

11.2.22. Cap, mix and transfer contents of the tube into a labeled 50 mL centrifuge tube.

11.2.23. Pipet 6 mL of 7M HNO_3 and 7 mL of 2M aluminum nitrate into each tube, cap and mix (shake or use a vortex stirrer), and transfer rinse to 50-mL centrifuge tube.

11.2.24. Pipet 3 ml of 3M HNO_3 directly into the 50 mL centrifuge tube.

11.2.25. Warm each 50 mL centrifuge tube in a hot water bath for a few minutes, swirling to dissolve.

11.2.26. Remove each 50 mL centrifuge tube from the water bath and allow to cool to room temperature

11.2.27. Centrifuge the 50 ml tubes at 3500 rpm for 5 minutes to remove any traces of solids (may not be visible prior to centrifuging), and transfer solutions to labeled beakers or tubes for further processing. Discard any solids.

11.2.28. Proceed directly to any of those methods listed in Sections 1.1.1, 1.1.2, or 1.1.5 (for Pu, U, or Am).

11.3. Preconcentration of ^{90}Sr from Hydroxide Matrix (Concrete)

NOTE: The preconcentration steps for ^{90}Sr in this section can also be applied to brick samples, but this will have to be validated by the laboratory. See Section 11.4 for steps validated for ^{90}Sr in brick samples.

11.3.1. Transfer each fused sample to a 225-mL centrifuge tube, rinse crucibles well with water, and transfer rinses to each tube.

11.3.2. Dilute to approximately 150 mL with water.

11.3.3. Add 15-mL concentrated HCl to each tube.

11.3.4. Cap and mix solution in each tube.

11.3.5. Pipet 1-mL of 1.25M $Ca(NO_3)_2$ into each tube.

11.3.6. Add 2-mL of 50-mg/mL iron carrier into each tube.

11.3.7. Add 25-mL of 2M Na_2CO_3 to each tube.

11.3.8. Cap tubes and mix well.

11.3.9. Cool the 225-mL centrifuge tubes in an ice bath for ~10 minutes.

11.3.10. Centrifuge tubes for 5 minutes at 3500 rpm.

11.3.11. Pour off the supernate, and discard to waste.

11.3.12. Add 1.5M HCl to each tube to redissolve each sample in a total volume of ~50 mL.

11.3.13. Cap and shake each tube to dissolve solids as well as possible.

11.3.14. Dilute each tube to ~170 mL with 0.01M HCl. Cap and mix.

11.3.15. Add 22 mL of concentrated HF into each tube. Cap and mix well.

11.3.16. Place tubes to set in an ice bath for ~10 minutes to get the tubes very cold.

11.3.17. Centrifuge for ~6 minutes at 3500 rpm.

11.3.18. Pour off supernate, and discard to waste.

11.3.19. Pipet 5 mL of concentrated HNO_3 and 5 mL of 3M HNO_3 - 0.25M boric acid into each 225 mL tube to dissolve precipitate.

11.3.20. Cap and mix well. Transfer contents of the tube into a labeled 50-mL centrifuge tube.

11.3.21. Pipet 5 mL of 3M HNO_3 and 5 mL of 2M aluminum nitrate into each tube, cap tube and mix.

11.3.22. Transfer rinse solutions to labeled 50-mL centrifuge tubes and mix well (shake or use vortex stirrer).

11.3.23. Centrifuge the 50 mL tubes at 3500 rpm for 5 minutes to remove any traces of solids.

11.3.24. Transfer solutions to labeled beakers or new 50 mL tubes for further processing.

11.3.25. If solids remain, add 5 mL 3M HNO_3 to each tube, cap, and mix well, centrifuge for 5 minutes and add the supernate to the sample solution. Discard any residual solids.

11.3.26. If solids remain in the original 50 mL tubes (step 11.3.23), add 5 mL of 3M HNO3 to each tube containing solids, cap, and mix well, Centrifuge for 5 minutes and add the supernate to the sample solution from step 11.3.24. Discard any remaining solids.

11.4. Preconcentration of ^{90}Sr from Hydr*oxide Matrix (Brick)*

NOTE: *The preconcentration steps for ^{90}Sr in this section, using calcium phosphate instead of calcium carbonate, can also be* applied to concrete samples but this will have to be validated by the laboratory. See Section 11.3 for steps validated for ^{90}Sr in concrete samples.

11.4.1. Transfer each fused sample to a labeled 225-mL centrifuge tube, rinse crucibles well with water, and transfer rinses to each tube.

11.4.2. Dilute to approximately 150 mL with water.

11.4.3. Pipet 2 mL 1.25M $Ca(NO_3)_2$ into each tube.

11.4.4. Add 1 mL 50-mg/mL iron carrier into each tube.

11.4.5. Add 5 mL 3.2M $(NH_4)_2HPO_4$ to each tube.

11.4.6. Cap tubes and mix well.

11.4.7. Centrifuge tubes for 5 minutes at 3500 rpm.

11.4.8. Pour off the supernate and discard to waste.

11.4.9. Add 1.5M HCl to each tube to redissolve each sample in a total volume of ~60 mL.

11.4.10. Cap and shake each tube to dissolve solids as well as possible.

11.4.11. Dilute each tube to ~170 mL with 0.01M HCl. Cap and mix.

11.4.12. Add 22 mL of concentrated HF into each tube. Cap and mix well.

11.4.13. Place tubes to set in an ice bath for ~10 minutes to get the tubes very cold.

11.4.14. Centrifuge for ~6 minutes at 3500 rpm.

11.4.15. Pour off supernate and discard to waste.

11.4.16. Pipet 5 mL of concentrated HNO_3 and 5 mL of 3M HNO_3 – 0.25M boric acid into each 225 mL tube to dissolve precipitate.

11.4.17. Cap and mix well. Transfer contents of the tube into a labeled 50-mL centrifuge tube.

11.4.18. Pipet 5 mL of 3M HNO_3 and 5 mL of 2M aluminum nitrate into each tube, cap tube and mix.

11.4.19. Transfer rinse solutions to labeled 50 mL centrifuge tubes and mix well (shake or use vortex stirrer).

11.4.20. Centrifuge the 50 mL tubes at 3500 rpm for 5 minutes to remove any traces of solids.

11.4.21. Transfer solutions to labeled beakers or new 50 mL tubes for further processing.

11.4.22. If solids remain in the original 50 mL tubes (step 11.4.20), add 5 mL of 3M HNO3 to each tube containing solids, cap, and mix well, Centrifuge for 5 minutes and add the supernate to the sample solution from step 11.4.21. Discard any remaining solids.

11.4.23. Set aside for ^{90}Sr analysis using *Rapid Radiochemical Method for Total Radiostrontium (Sr-90) In Building Materials for Environmental Remediation Following Radiological Incidents* (Reference 16.4).

11.5. Preconcentration of ^{226}Ra from Hydroxide Matrix

11.5.1. Transfer each sample to a labeled 225 mL centrifuge tube, rinse crucibles well with water, and transfer rinses to each tube.

11.5.2. Dilute to approximately 150 mL with water.

11.5.3. Add 10 mL of concentrated HCl to each tube.

11.5.4. Cap and mix each tube well.

11.5.5. Pipet 0.5 mL of 1.25M $Ca(NO_3)_2$ into each tube.

11.5.6. Add 25 mL of 2M Na_2CO_3 to each tube.

11.5.7. Cap tubes and mix.

11.5.8. Cool the 225-mL centrifuge tubes in an ice bath for ~5–10 minutes.

11.5.9. Centrifuge tubes for 6 minutes at 3500 rpm.

11.5.10. Pour off the supernate, and discard to waste.

11.5.11. Pipet 10 mL 1.5M HCl into each tube to dissolve precipitate. Cap and mix.

11.5.12. Transfer sample solution to a labeled 50-mL centrifuge tube.

11.5.13. Pipet 10 mL 1.5M HCl into each 225-mL tube to rinse. Cap and rinse well.

11.5.14. Transfer rinse solution to 50 mL-tube and mix well.

NOTE: Typically the HCl added to dissolve the carbonate precipitate is sufficient to acidify the sample. If the precipitate was unusually large and milky suspended solids remain, indicating additional acid is needed, the pH can be checked to verify it is pH 1 or less. To acidify the pH <1, 1 or 2 mL of concentrated hydrochloric acid may be added to acidify the solution further and get it to clear. Undissolved solids may be more likely to occur with brick samples. Tubes may be warmed in a water bath to help dissolve samples.

11.5.15. If solids remain in the original 225 mL tubes, add 5 mL of 1.5M HCl to each tube containing solids, cap, and mix well. Centrifuge for 5 minutes and add the supernate to the sample solution from step 11.5.14. Discard any remaining solids.

11.5.16. Set aside for ^{226}Ra analysis using *Rapid Radiochemical Method for Radium-226 in Building Materials for Environmental Remediation Following Radiological Incidents* (Reference 16.3).

12. Data Analysis and Calculations

12.1. Equations for determination of final result, combined standard uncertainty, and radiochemical yield (if required) are found in the corresponding chemical separation and analysis methods, with the project manager providing the units.

12.2. In cases where samples have elevated activity, smaller initial sample aliquants may be taken from the original sample. Alternately, smaller aliquant volumes may be taken from the final sample volume containing the dissolved precipitate (digestate). Aliquants should be removed carefully and accurately from this final sample volume.

NOTE: Small aliquants taken from the final sample digestate for Sr and Ra analysis may be used in the respective analytical procedures as is. Smaller aliquants for actinide analysis should be diluted to a 15 mL total volume with 3M HNO_3 so that load solution acidity is maintained when valence adjustment reagents are added.

For a single split, the effective size of sample is calculated:

$$W_a = W_s \frac{D_a}{D_s} \qquad (1)$$

Where:

W_s = original sample size, in the units designated by the project manager (e.g., 1 g, etc.)

D_s = mass or volume of the entire final digestate, (e.g., 20 mL, etc.).

D_a = mass or volume of the aliquant of digestate used for the individual analyses, (e.g., 5.0 mL, etc.). Note that the values for D_a must be in the same units used in D_s.

W_a = sample aliquant size, used for analysis, in the units designated by the project manager (e.g., kg, g, etc.).

NOTE: For higher activity samples, additional dilution may be needed. In such cases, Equation 1 should be modified to reflect the number of splits and dilutions performed. It is also important to measure the masses or volumes, used for aliquanting or dilution, to enough significant figures so that their uncertainties have an insignificant impact on the final uncertainty budget. In cases where the sample will not be split prior to analysis, the sample aliquant size is simply equal to the original sample size, in the same units requested by the project manager.

13. Method Performance

13.1. Report method validation results.

13.2. The method performance data for the analysis of concrete and brick by this dissolution method may be found in the attached appendices.

13.3. Expected turnaround time per sample

13.3.1. For a representative, finely ground 1-g aliquant of sample, the fusion should add approximately 2 hours per batch to the time specified in the individual chemical separation methods.

13.3.2. The preconcentration steps should add approximately 2 to 2.5 hours per batch.

NOTE**: Processing times for the subsequent chemical separation methods are given in those methods for batch preparations.**

14. Pollution Prevention

This method inherently produces no significant pollutants. The sample and fusion reagents are retained in the final product and are carried into the ensuing chemical separation techniques, which marginally increases the salt content of the effluent waste. It is noted that if the sampled particulates include radionuclides that may be volatile under the fusion conditions, these constituents will be exhausted through the fume hood system.

15. Waste Management

15.1. Refer to the appropriate chemical separation methods for waste disposal information.

16. References

Cited References

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16.9. ASTM D1193, "Standard Specification for Reagent Water" ASTM Book of Standards 11.01, current version, ASTM International, West Conshohocken, PA.

Other References

16.10. Maxwell, S., Culligan, B. and Noyes, G. 2010. Rapid method for actinides in emergency soil samples, *Radiochimica Acta*. 98(12): 793-800.

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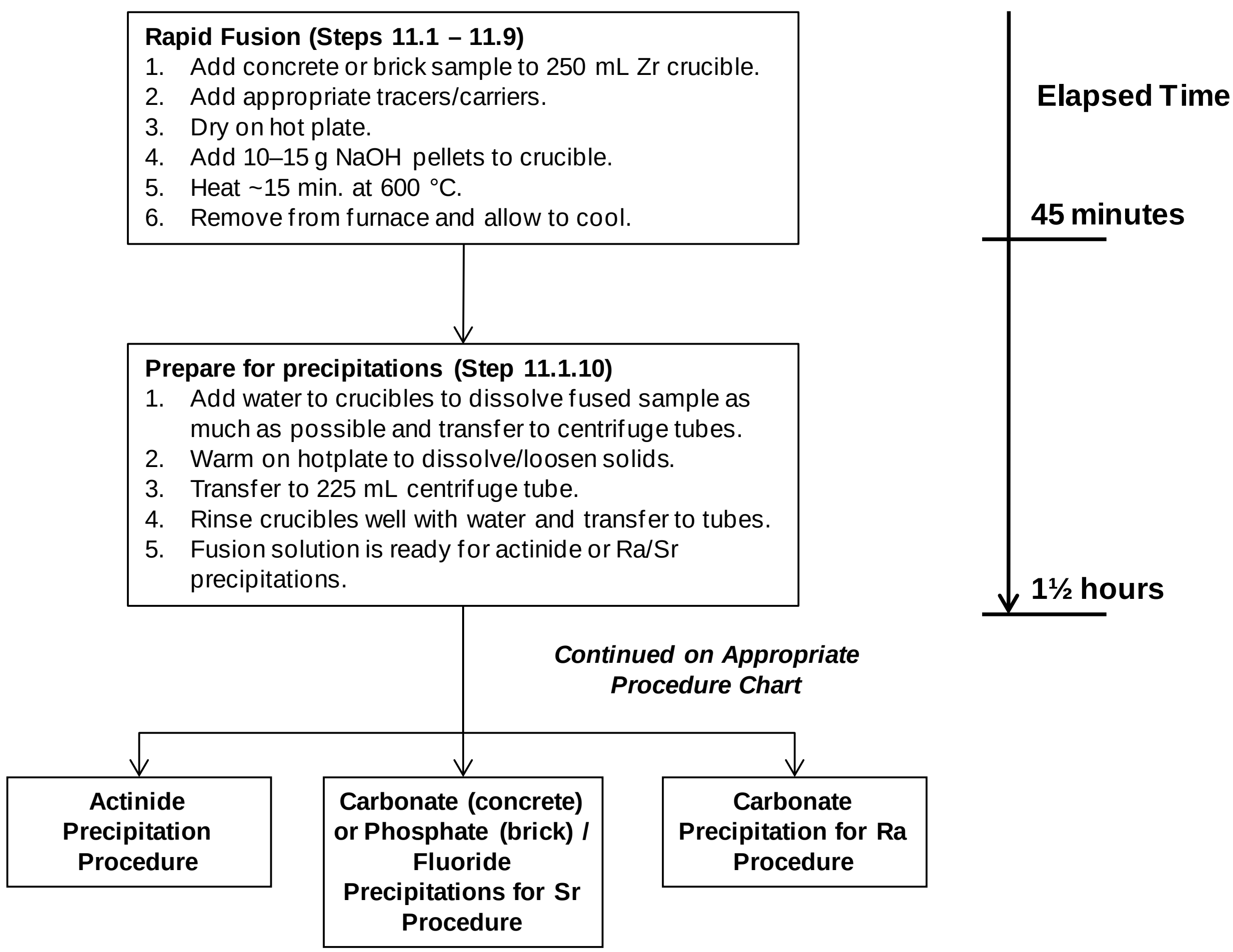
16.12. U.S. Environmental Protection Agency (EPA). 2010. *Rapid Radiochemical Methods for Selected Radionuclides in Water for Environmental Restoration Following Homeland Security Events*, Office of Air and Radiation. EPA 402-R-10-001, February. Revision 0.1 of rapid methods issued October 2011. Available at: www.epa.gov/narel/.

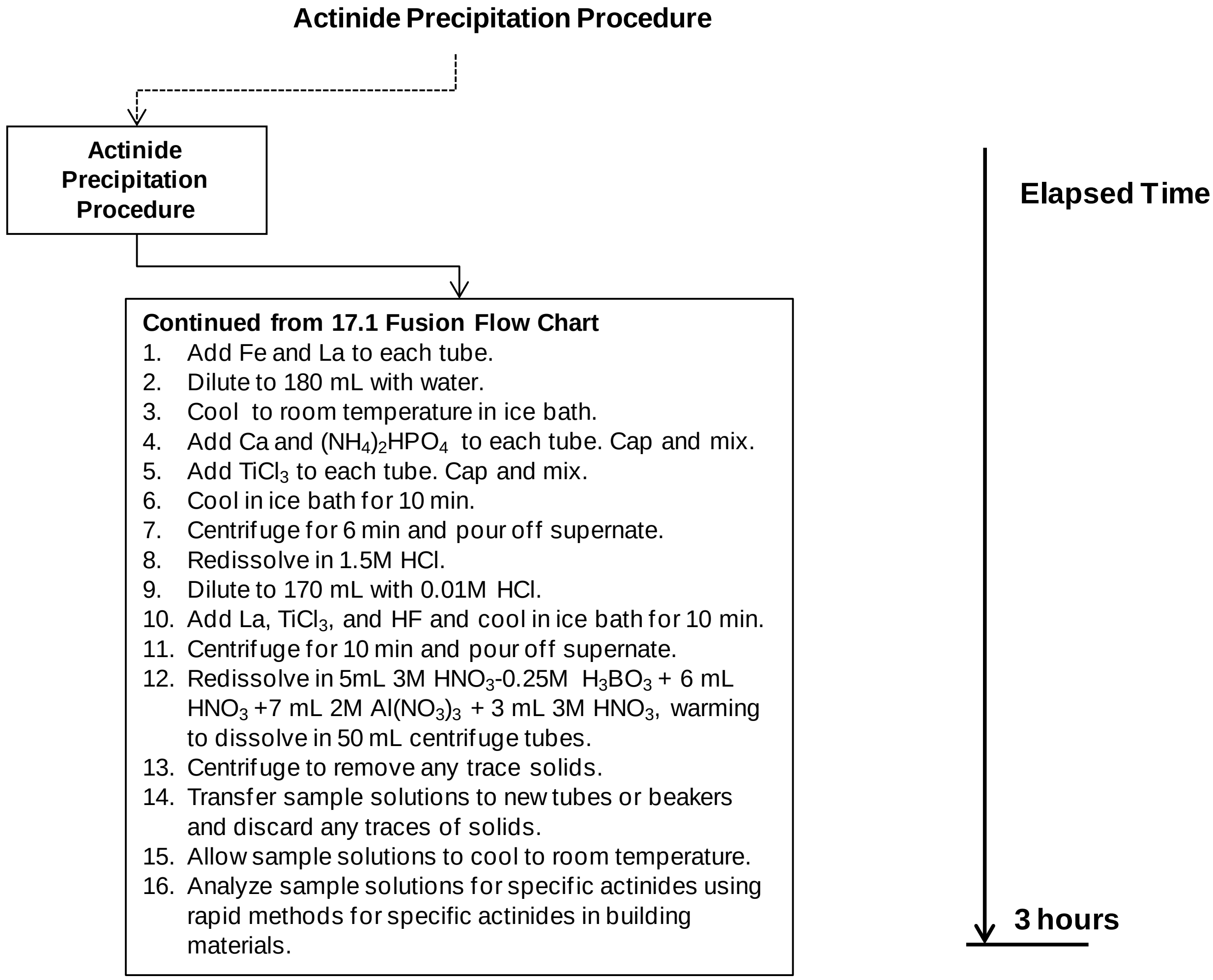
17. Tables, Diagrams, and Flow Charts

17.1. Fusion Flow Chart

Timeline for Rapid Fusion and Preparation of Building Materials Samples for Precipitation and Analysis



17.2. Actinide Precipitation Flow Chart



17.3. Strontium Precipitation Flow Chart

Strontium Precipitation Procedure (Concrete)

$CaCO_3$ / CaF_2 Precipitation for Sr in Concrete Procedure

Continued from 17.1 Fusion Flow Chart

1. Dilute to 150 mL with water.
2. Add 15 mL of concentrated HCL to each tube.
3. Add 1 mL 1.25M Ca $(NO_3)_2$, 100 mg Fe and 25 mL 2M Na_2CO_3 to each tube.
4. Cool 10 min in ice bath.
5. Centrifuge for 5 min. and pour off supernate.
6. Add 1.5M HCl to each tube to redissolve each sample.
7. Dilute each tube to ~170 mL with 0.01M HCl.
8. Add 22 mL concentrated HF and cool in ice bath for 10 min.
9. Centrifuge for 6 min and pour off supernate.
10. Redissolve in 5 mL 3M HNO_3-0.25M H_3BO_3 + 5 mL concentrated HNO_3 +5 mL 2M $Al(NO_3)_3$ + 5 mL 3M HNO_3.
11. Cap and mix using shaking or vortex stirrer.
12. Centrifuge for 5 min and discard trace solids.
13. Analyze sample solutions for ^{90}Sr using ^{90}Sr method for building materials.

Elapsed Time

2½ hours

Strontium Precipitation Procedure (Brick)

$Ca_3(PO_4)_2$ / CaF_2 Precipitation for Sr in Brick Procedure

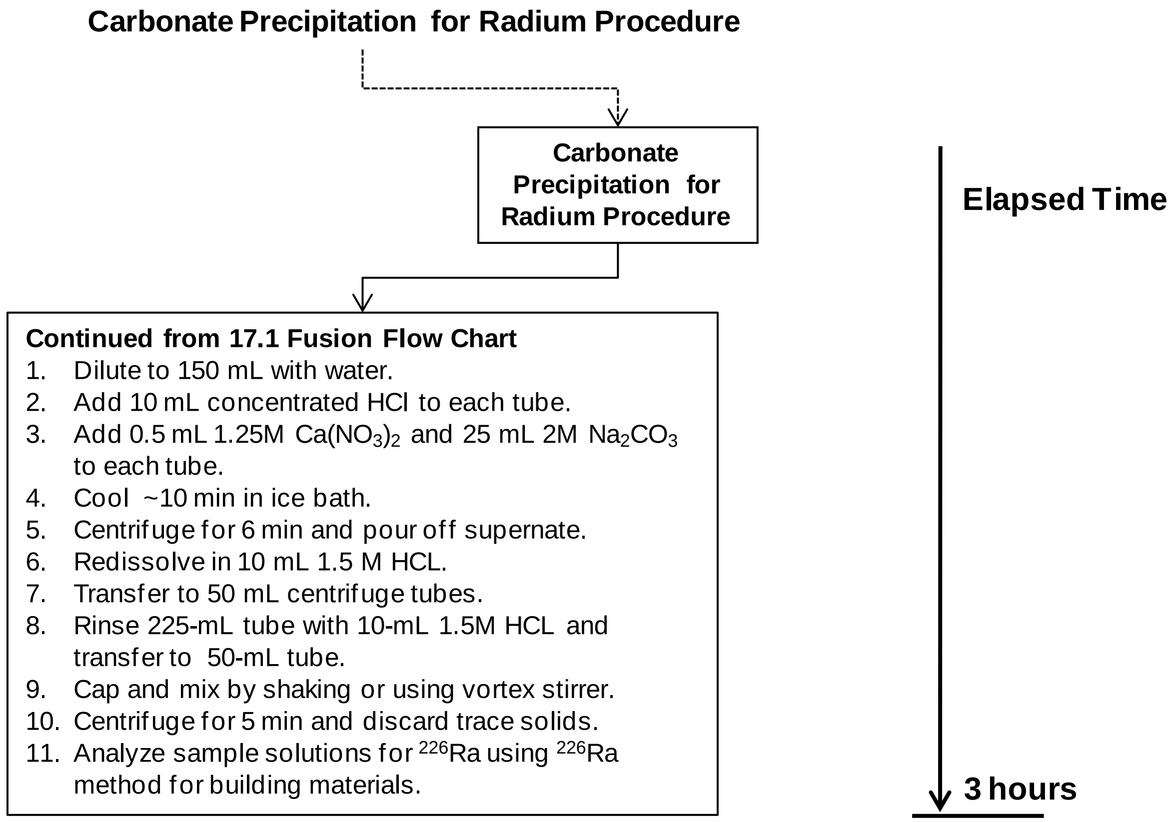
Elapsed Time

Continued from 17.1 Fusion Flow Chart

1. Dilute to 150 mL with water.
2. Add 2 mL 1.25M $Ca(NO_3)_2$, 50 mg Fe, and 5 mL 3.2M $(NH_4)_2HPO_4$ to each tube.
3. Centrifuge for 5 min and pour off supernate.
4. Redissolve in ~60 mL1.5M HCL.
5. Dilute to 170 mL with 0.01M HCl.
6. Add 22 mL Concentrated HF and wait 10 min.
7. Centrifuge for 6 min and pour off supernate.
8. Redissolve in 5 mL 3M HNO_3-0.25M H_3BO_3 + 5 mL concentrated HNO_3 +5 mL 2M $Al(NO_3)_3$ + 5 mL 3M HNO_3.
9. Cap and mix using vortex stirrer.
10. Centrifuge for 5 min and discard trace solids.
11. Analyze sample solutions for ^{90}Sr using ^{90}Sr method for building materials.

2½ hours

17.4. Radium Precipitation Flow Chart



Appendix:

Rapid Technique for Milling and Homogenizing Concrete and Brick Samples

A1. Scope and Application

A1.1. Concrete or brick samples may be received as powder, core samples or other size pieces or chunks. The goal is to obtain representative sample aliquants from homogeneous amounts of sample.

A1.2. The ball mill method describes one approach for the rapid, gross preparation of concrete or brick samples to yield representative 1–2-g aliquant for radiochemical analysis of non-volatile radionuclides. The method addresses steps for splitting, drying, and milling of 50–2,000 g concrete or brick samples. The concrete or brick sample must be reduced to pieces or fragments less than ~25 mm in diameter prior to using the ball mill. This can be done with a hydraulic press or mallet.

A1.3. The method is designed to be used as a preparatory step for the attached methods for fusion of concrete or brick for ^{241}Am, $^{239/240}$Pu, U, ^{90}Sr, and ^{226}Ra. It may also be applied to other matrices whose physical form is amenable to pulverization in the ball mill.

A1.4. If the levels of activity in the sample are low enough to permit safe radiological operations, up to 2 kg of concrete or brick can be processed.

A1.5. For smaller amounts of concrete or brick samples, a drill with masonry bit can be used in a lab hood inside a plastic bag to collect the powder that results.

A2. Summary of Methods

A2.1. This method uses only disposable equipment to contact the sample, minimizing the risk of contamination and cross-contamination and eliminating concerns about adequate cleaning of equipment.

A2.2. Extraneous material, such as rocks or debris, may be removed prior to processing the sample unless the project requires that they be processed as part of the sample.

NOTE: The sample mass is generally used for measuring the size of solid samples. The initial process of acquiring a representative aliquant uses the volume of the sample, as the total sample size is generally based on a certain volume of concrete or brick (e.g., 500 mL).

A2.3. The entire sample as received (after reducing fragment size to less than ~25 mm diameter) is split by coning and quartering until 75-150 mL of concrete or brick are available for subsequent processing. If less than 450 mL of concrete or brick is received, the entire sample is processed.

A2.4. The concrete or brick is transferred to a paint can or equivalent. Percent solids are determined, if required, by drying in a drying oven. A mallet and plastic bag or hydraulic press may be needed to break up larger pieces.

A2.5. Grinding media (stainless steel or ceramic balls or rods) are added, and the sample is milled to produce a finely-ground, well-homogenized, powder with predominant particle size less than 250 micrometers (µm).

NOTE: A mortar and pestle may also be used as needed to grind the sample further.

A2.6. If the sample may contain discreet radioactive particles (DRPs), particles larger than a nominal size of 150 µm are screened for radioactivity, and further milled, or processed with another appropriate method to ensure that they will be chemically available for subsequent processing.

A2.7. The resulting milled sample is stored in, and aliquanted directly from, the container used for pulverization.

A2.8. The drill bit method involves drilling into the sample using a drill bit. The operation is performed inside a disposable plastic bag in a hood so that the drilled out sample is caught within the plastic bag (this approach also minimizes the spread of contamination). A drill bit such as a ¼-inch carbide bit is recommended. The holes should be drilled in such a way as to obtain representative powdered samples. The drill bit should be cleaned between uses on different samples using soap and water.

A3. Definitions, Abbreviations, and Acronyms

A3.1. Discrete Radioactive Particles (DRPs or "hot particles"). Particulate matter in a sample of any matrix where a high concentration of radioactive material is contained in a tiny particle (µm range).

A3.2. *Multi-Agency Radiological Analytical Laboratory Protocols (MARLAP) Manual* (Reference A16.3).

A3.3. *ASTM C999 Standard Practice for Soil Sample Preparation for the Determination of Radionuclides* (Reference A16.4).

A4. Interferences

A4.1. Radiological Interferences

A4.1.1. Coning and quartering provides a mechanism for rapidly decreasing the overall size of the sample that must be processed while optimizing the representativeness of the subsampling process. By decreasing the time and effort needed to prepare the sample for subsequent processing, sample throughput can be significantly improved. Openly handling large amounts of highly contaminated materials, however, even within the containment provided by a fume hood, may pose an unacceptable risk of inhalation of airborne contamination and exposure to laboratory personnel from radioactive or other hazardous materials. Similarly, it may unacceptably increase the risk of contamination of the laboratory.

A4.1.2. In such cases, the coning and quartering process may be eliminated in lieu of processing the entire sample. The time needed to dry the sample will increase significantly, and the container size and the number and size of grinding media used will need to be adjusted to optimize the milling process. See *ASTM C999* for an approach for homogenization and milling of larger soil samples.

A4.1.3. The precise particle size of the milled sample is not critical to subsequent processes. However, milling the sample to smaller particle sizes, and thorough mixing, both facilitate representative sub-sampling by minimizing the amount of sample that is not pulverized to fine mesh and must be discarded. Additionally, subsequent fusion and digestion processes are more effective when performed on more finely milled samples.

A4.1.4. This method assumes that radioactivity in the sample is primarily adsorbed onto the surface of particles, as opposed to being present as a hot particle (see discussion of DRPs below). Thus, nearly all of the activity in a sample will be associated with sample fines. By visually comparing the sample to a qualitative standard of 50–100 mesh size particles, it is possible to rapidly determine whether the sample is fine enough to facilitate the subsequent fusion or digestion. This method assumes that when greater than 95% of the sample is as fine or finer than the 50–100 mesh sample, bias imparted from losses of larger particles will be minimal.

A4.1.5. If the sample was collected near the epicenter of a radiological dispersal device (RDD) or improvised nuclear device (IND) explosion, it may contain millimeter- to micrometer-sized particles of contaminant referred to as “discrete radioactive particles” or DRPs. DRPs may consist of small pieces of the original radioactive source and thus may have very high specific activity. They may also consist of chemically intractable material and present special challenges in the analytical process. Even when the size is reduced to less than 50-100 mesh, these particles may resist fusion or digestion of the solids into ionic form that can be subjected to chemical separations.

A4.1.6. When DRPs may be present, this method isolates larger particles by passing the sample through a disposable 50-mesh screen after which they can be reliably checked for radioactivity. DRPs may reliably be identified by their very high specific activity, which is readily detectable, since they show high count rates using hand-held survey equipment such as a thin-window Geiger-Muller (G-M) probe.

A4.1.7. When present, DRPs may be further milled and then recombined with the original sample. Alternatively, the particles, or the entire sample may need to be processed using a different method capable of completely solubilizing the contaminants such that the radionuclides they contain are available for subsequent chemical separation.

A5. Safety

A5.1. General

A5.1.1. Refer to your safety manual for concerns of contamination control, personal exposure monitoring, and radiation dose monitoring.

A5.1.2. Refer to your laboratory's chemical hygiene plan (or equivalent) for general safety rules regarding chemicals in the workplace.

A5.2. Radiological

A5.2.1. Refer to your radiation safety manual for direction on working with known or suspected radioactive materials.

A5.2.2. This method has the potential to generate airborne radioactive contamination. The process should be carefully evaluated to ensure that airborne contamination is maintained at acceptable levels. This should take into account the activity level, and physical and chemical form of contaminants possibly present, as well as other engineering and administrative controls available.

A5.2.3. Hot Particles (DRPs)

A5.2.3.1. Hot particles will usually be small, on the order of 1 mm or less. Typically, DRPs are not evenly distributed in the media, and their radiation emissions are not uniform in all directions (anisotropic). Filtration using a 0.45 µm or smaller filter may be needed following subsequent fusion to identify the presence of smaller DRPs.

A5.2.3.2. Care should be taken to provide suitable containment for filter media used in the pretreatment of samples that may have DRPs, because the particles become highly statically charged as they dry out and will "jump" to other surfaces potentially creating contamination-control issues.

A5.3. Method-Specific Non-Radiological Hazards

A5.3.1. This method employs a mechanical shaker and should be evaluated for personnel hazards associated with the high kinetic energy associated with the milling process.

A5.3.2. This method employs a mechanical shaker and involves vigorous agitation of steel or ceramic balls inside steel cans. The process should be evaluated to determine whether hearing protection is needed to protect the hearing of personnel present in the area in which the apparatus is operated.

A6. Equipment and supplies

A6.1. Balance, top-loading, range to accommodate sample size encountered, readability to ±1%.

A6.2. Drying oven, at 110 ± 10 ºC.

A6.3. Steel paint cans and lids (pint, quart, 2-quart, 1-gallon, as needed).

A6.4. Steel or ceramic grinding balls or rods for ball milling, ~15–25 mm diameter. The size and number of grinding media used should be optimized to suit the types of concrete or brick, the size of the can, and the volume of sample processed.

A6.5. Disposable wire cloth – nominal 48 mesh size (~300 µm).

A6.6. Disposable sieves, U.S. Series No. 50 (300 µm or 48 mesh) and U.S. Series No. 100 (150 µm or 100 mesh).

A6.7. Red Devil 5400 mechanical paint shaker or equivalent.

A6.8. Disposable scoop, scraper, tongue depressor or equivalent.

A7. Reagents and Standards

No reagents needed.

A8. Sample Collection, Preservation and Storage

A8.1. Samples should be collected in appropriately sized plastic, metal or glass containers.

A8.2. No sample preservation is required. If samples are to be held for an extended period of time, refrigeration may help minimize bacterial growth in the sample.

A8.3. Default sample collection protocols generally provide solid sample volumes equivalent to approximately 500 mL of sample. Such samples will require two splits to obtain a ~100 mL sample.

A9. Quality Control

A9.1. Batch quality control results shall be evaluated and meet applicable Analytical Protocol 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.

A9.2. Quality control samples should be initiated as early in the process as possible. Since the risk of cross-contamination using this process is relatively low, initiating blanks and laboratory control samples at the start of the chemical separation process is acceptable. If sufficient sample is available, a duplicate sample should be prepared from the two discarded quarters of the final split of the coning and quartering procedure.

A10. Procedure

NOTE: This method ensures that only disposable equipment comes in contact with sample materials to greatly minimize the risk of sample cross-contamination and concerns about adequate cleaning of equipment. Under certain circumstances (disposable sieves are not available, for example), careful, thorough cleaning of the sieves with water and the ethanol may be an option.

A10.1. If necessary, reduce the concrete or brick particle diameter to less than ~25 mm using a hydraulic press, mallet, or alternate equipment capable or reducing the fragment size.

A10.2. Estimate the total volume of sample, as received.

NOTE: If the sample is dry, the risk of resuspension and inhalation of the solids may be determined to be unacceptable. In such cases, the entire sample may be processed in a larger can. The drying and milling time will be increased, and more grinding media will be required to obtain a satisfactory result.

NOTE: The next step uses absorbent paper in the reverse fashion for the normal use of this type of paper; it allows for a smooth division of the sample and control of contamination.

A10.2.1. Spread a large piece of plastic backed absorbent paper, plastic side *up* in a hood.

A10.2.2. If the sample volume is less than 450 mL, there is no benefit to coning and quartering.[8]

A10.2.2.1. Carefully pour the sample onto the paper.

A10.2.2.2. Remove extraneous material, such as rocks or debris, unless the project requires that such material be processed as part of the sample. Continue with Step A10.2.5.

A10.2.3. If the sample volume is greater than ~450 mL, carefully pour the entire sample into a cone onto the paper.

Remove extraneous material, such as rocks or debris unless the project requires that such material be processed as part of the sample.

A10.2.4. If levels of gross activity in the sample permit, the sample is split at least twice using the coning and quartering steps that follow.

NOTE: Unused quarters are considered representative of the original sample and may be reserved for additional testing. The process should be carried out expediently to minimize loss of volatile components in the sample, especially if volatile components or percent solids are to be determined.

A10.2.4.1. Spread the material into a flat circular cake of soil using a tongue depressor or other suitable disposable implement. Divide the cake radially and return two opposing quarters to the original sample container.

A10.2.4.2. Reshape the remaining two quarters into a smaller cone, and repeat Step A10.2.2.1 until the total volume of the remaining material is approximately 100-150 mL.

NOTE: Tare the can and lid together. Do not apply an adhesive label. Rather, label the can with permanent marker since the can will be placed in a drying oven. The lid should be labeled separately since it will be removed from the can during drying.

A10.2.5. Transfer the coned and quartered sample to a tared, labeled 1-pint paint can. If the total volume was less than ~450 mL, transfer the entire sample to a tared, labeled 1-quart paint can.

NOTE: Constant mass may be determined by removing the container from the oven and weighing repeatedly until the mass remains constant with within 1% of the starting mass of the sample. This determination may also be achieved

[8] International Union of Pure and Applied Chemistry (IUPAC). 1997. Compendium 1675 of Chemical Terminology, 2nd ed. (the "Gold Book"). Compiled by A. D. (Reference A16.1).

operationally by observing the time needed to ensure that 99% of the samples will obtain constant mass.

A10.3. Place the can (without lid) in an oven at 110 ± 10 ºC and dry the concrete or brick to constant mass.

NOTE: **Concrete or brick samples may be dry enough such that heating prior to homogenizing the sample is not required.**

A10.4. Weigh the combined mass of the can, sample, and lid. If the percent solids are required see Section A12.1 calculations. Remove can from oven and allow to cool.

A10.5. Add five 1.5 cm stainless steel or ceramic balls or rods to the can. Replace the lid and seal well.

A10.6. Shake the can and contents for 5 minutes, or longer, as needed to produce a finely-milled, well-homogenized, sample.

NOTE: **Although the precise particle size of the milled sample is not critical, complete pulverization and fine particle size facilitates representative sub-sampling and subsequent fusion or digestion processes. A qualitative standard can be prepared by passing quartz sand or other milled material through a 50-mesh and then a 100-mesh screen. The portion of the sample retained in the 100 mesh screen can be used as a qualitative visual standard to determine if samples have been adequately pulverized.**

A10.7. Visually compare the resulting milled sample to a qualitative 50–100 mesh pulverized sample (~150–300 µm or 50–100 mesh using the Tyler screen scale). The process is complete once 95% of the sample (or greater) is as fine, or finer, than the qualitative standard. If, by visual estimation, more than ~5% of total volume of the particles in the sample appear to be larger than the particle size in the standard, return the sample to the shaker and continue milling until the process is complete.

A10.8. Following milling, a small fraction of residual larger particles may remain in the sample.

A10.8.1. If the sample was collected close to the epicenter of an RDD or IND explosion, it may also contain particles of contaminant referred to as "discrete radioactive particles" or DRPs. In such a case, the larger particles should be isolated by passing through a disposable 48 mesh screen and checked for radioactivity. DRPs are readily identified by their very high specific activity which is detectable using hand-held survey equipment such as a thin-window G-M probe held within an inch of the particles.

A10.8.1.1. If radioactivity is clearly detected, the sieved material is returned to the can and ball milled until the desired mesh is obtained. In some cases, these materials may be resistant to further pulverization and may need to be processed according to a method specially designed to address highly intractable solids.

A10.8.1.2. If the presence of DRPs is of no concern, the larger particles need not be included in subsequent subsamples taken for analysis. It may be possible to easily avoid including them during aliquanting with a disposable scoop. If not, however, they should be removed by sieving through a nominal 50 mesh screen (disposable) prior to further subsampling for subsequent analyses.

A10.9. Sample fines may be stored in, and aliquanted directly from, the container used for drying and pulverization.

A11. Calibration and Standardization

A11.1. Balances used shall be calibrated using National Institute of Standards and Technology (NIST)-traceable weights according to the process defined by the laboratory's quality manual.

A12. Data Analysis and Calculations

A12.1. The percent solids (dry-to-as-received mass ratio) for each sample is calculated from data obtained during the preparation of the sample as follows:

$$\%\,\text{Solids} = \frac{M_{dry} - M_{tare}}{M_{as\,rec} - M_{tare}} \times 100$$

Where:

M_{dry} = mass of dry sample + labeled can + lid (g)
M_{tare} = tare mass of labeled can + lid (g)
$M_{as\,rec}$ = mass of sample as received + labeled can + lid (g)

A12.2. If requested, convert the equivalent mass of sample, as received, to dry mass. Dry mass is calculated from a measurement of the total as received mass of the sample received as follows:

$$\text{Dry Sample Equivalent} = M_{\text{total-as rec.}} \times \frac{\%\,\text{Solids}}{100}$$

Where:

$M_{\text{total-as rec.}}$ = total mass of sample, as received (g)

A12.3. Results Reporting

A12.3.1. The result for percent solids and the approximate total mass of sample as received should generally be reported for each result.

A13. Method Performance

A13.1. Results of method validation performance are to be archived and available for reporting purposes.

A13.2. Expected turnaround time is about 3 hours for an individual sample and about 4 hours per batch.

A14. Pollution Prevention.

Not applicable

A15. Waste Management

A15.1. All radioactive and other regulated wastes shall be handled according to prevailing regulations.

A16. References

A16.1. International Union of Pure and Applied Chemistry (IUPAC). 1997. Compendium of Chemical Terminology, 2nd ed. (the "Gold Book"). Compiled by A. D. McNaught and A. Wilkinson. Blackwell Scientific Publications, Oxford. XML on-line corrected version: http://goldbook.iupac.org/C01265.html. (2006) created by M. Nic, J. Jirat, B. Kosata; updates compiled by A. Jenkins. Last update: 2010-12-22.

A16.2. ALS Laboratories, Fort Collins, SOP 736.

A16.3. MARLAP. *Multi-Agency Radiological Laboratory Analytical Protocols Manual.* 2004. Volumes 1 – 3. Washington, DC: EPA 402-B-04-001A-C, NUREG 1576, NTIS PB2004-105421, July. Available at: www.epa.gov/radiation/marlap.

A16.4. ASTM C 999-05, "Standard Practice for Soil Sample Preparation for the Determination of Radionuclides," Volume 12.01, ASTM, 2005.

Attachment III:

Rapid Radiochemical Method for Ra-226 in Building Materials for Environmental Remediation Following Radiological Incidents

1. Scope and Application
   1.1. The method will be applicable to samples where contamination is either from known or unknown origins.
   1.2. This method uses rapid radiochemical separations techniques for the isotopic determination of ^{226}Ra in building materials samples, such as concrete and brick, following a nuclear or radiological incident.
   1.3. The method is specific for ^{226}Ra. It uses 50WX8 cation resin to separate radium from concrete or brick matrix constituents, followed by additional separation steps using Sr Resin and Ln Resin to remove interferences.
   1.4. The method is capable of satisfying a required method uncertainty for ^{226}Ra of 0.62 pCi/g at an analytical action level (AAL) of 4.76 pCi/g, a required relative method uncertainty (φ_{MR}) of 13% above the AAL and a MDC of <<1.0 pCi/g. To attain the required method uncertainty at the AAL, a sample aliquant of approximately 1 g and count time of 8 hours (or longer) are recommended. Application of the method must be validated by the laboratory using the protocols provided in *Method Validation Guide for Qualifying Methods Used by Radiological Laboratories Participating in Incident Response Activities* (EPA 2009, Reference 16.1). The sample turnaround time and throughput may vary based on additional project MQOs, the time for analysis of the sample test source, and initial sample weight/volume.
   1.5. The rapid ^{226}Ra method was initially validated for concrete building materials following the guidance presented for “Level E Method Validation: Adapted or Newly Developed Methods, Including Rapid Methods” in *Method Validation Guide for Qualifying Methods Used by Radiological Laboratories Participating in Incident Response Activities* (EPA 2009, Reference 16.1) and Chapter 6 of *Multi-Agency Radiological Laboratory Analytical Protocols Manual* (EPA 2004, Reference 16.2). Subsequent building material matrices were validated at Level C (“Similar Matrix/New Application”).
   1.6. Other solid samples such as soil can be digested using the rapid sodium hydroxide fusion procedure as an alternative to other digestion techniques, but the laboratory will have to validate this procedure.

2. Summary of Method
   2.1. A known quantity of ^{225}Ra is used as the yield tracer in this analysis. The sample is fused using procedure, *Rapid Method for Sodium Hydroxide Fusion of Concrete and Brick Matrices Prior to Americium, Plutonium, Strontium, Radium, and Uranium Analyses* (Reference 16.3), and then the radium isotopes are removed from the fusion matrix using a carbonate precipitation step. The sample is acidified and loaded onto 50WX8 cation resin to remove sample interferences such as calcium. The radium is eluted from the cation resin with 8M nitric acid. After evaporation of the eluate, the sample is dissolved and passed through Sr Resin to remove Ba. This solution is

evaporated to dryness, redissolved in 0.02M HCl and passed through Ln Resin to remove interferences such as residual calcium and to remove the initial ^{225}Ac present. The radium (including ^{226}Ra) is prepared for counting by microprecipitation with $BaSO_4$.

2.2. Low-level measurements are performed by alpha spectrometry. The activity measured in the ^{226}Ra region of interest is corrected for chemical yield based on the observed activity of the alpha peak at 7.07 MeV (^{217}At, the third progeny of ^{225}Ra). See Table 17.1 for a list of alpha particle energies of the radionuclides that potentially may be seen in the alpha spectra.

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 decisionmaker to choose one of the alternative actions.

3.3. Discrete Radioactive Particles (DRPs or Hot Particles). Particulate matter in a sample of any matrix where a high concentration of radioactive material is contained in a tiny particle (micron range).

3.4. *Multi-Agency Radiological Analytical Laboratory Protocols Manual* (MARLAP) provides guidance for the planning, implementation, and assessment phases of those projects that require the laboratory analysis of radionuclides (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. Radiological Dispersal Device (RDD), i.e., a "dirty bomb." This device is an unconventional weapon constructed to distribute radioactive material(s) into the environment either by incorporating them into a conventional bomb or by using sprays, canisters, or manual dispersal.

3.7. 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.

3.8. 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 AAL.

3.9. Sample Test Source. 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. Unless other radium isotopes are present in concentrations greater than approximately three times the ^{226}Ra activity concentration, interference from other radium alphas will be resolved when using alpha spectrometry. Method performance may be compromised if samples contain high levels of radium isotopes due to ingrowth of interfering decay progeny, but this interference will depend on the actual spectral resolution.

4.1.2. Radionuclides with overlapping alpha energies such as ^{229}Th, ^{234}U, and ^{237}Np will interfere if they are not removed effectively. The method removes these radionuclides.

4.1.3. Decay progeny from the ^{225}Ra tracer will continue to ingrow as more time elapses between the separation of radium and the count of the sample. Delaying the count significantly longer than a day may introduce a possible positive bias in results near the detection threshold. When MQOs require measurements close to detection levels, and coordinating sample processing and counting schedules is not conducive to counting the sample within ~36 hours of the separation of radium, the impact of tracer progeny tailing into the ^{226}Ra may be minimized by reducing the activity of the ^{225}Ra tracer that is added to the sample. This approach will aid in improving the signal-to-noise ratio for the ^{226}Ra peak by minimizing the amount of tailing from higher energy alphas of the ^{225}Ra progeny.

4.1.4. There is also a possibility that the higher energy peaks associated with the ^{225}Ra progeny may result in energy-attenuated counts that show up in the lower energy ^{226}Ra alpha spectra region, so reducing the ^{225}Ra tracer while still achieving enough ^{217}At counts to minimize tracer uncertainty may be optimal.

4.1.4.1. The amount of ^{225}Ra added to the samples may be decreased, and the time for ingrowth between separation and counting increased, to ensure that sufficient ^{225}Ac, ^{221}Fr, and ^{217}At are present for yield corrections at the point of the count. Although this detracts from the rapidity of the method, it does not detract significantly from the potential for high throughput.

4.1.5. A purified ^{225}Ra tracer solution may be used when performing this method (See Appendix).

4.1.5.1. When using a purified source of ^{225}Ra, the beginning of decay for ^{225}Ra is the activity reference date established during standardization of the ^{225}Ra solution.

4.1.6. It is also possible to use ^{225}Ra in equilibrium with ^{229}Th for convenience, which may be added to each sample as a tracer.[1] This allows use of ^{229}Th without purification and therefore is a simpler approach. This approach requires complete decontamination of a relatively high activity of ^{229}Th in

[1] The single-laboratory validation for this method was performed successfully by adding ^{225}Ra in secular equilibrium with ^{229}Th tracer. See Appendix of this method for a method for separating (and standardizing) ^{225}Ra tracer from ^{229}Th solution.

the later steps in the method, since the spectral region of interest (ROI) for ^{229}Th slightly overlaps that of ^{226}Ra.

4.1.7. ^{229}Th is removed during the cation exchange step (retained), and the ^{225}Ra is unsupported from this point on in the method (retained on the cation resin). If the time delay between the cation exchange step and the Ln Resin separation of ^{229}Th is 6 hours or less the error associated with the ^{225}Ra reference value is ≤ 1.2% due to ^{225}Ra decay. A correction for this decay can also be made by recording the cation exchange elution time, and decaying ^{225}Ra from this point until the Ln Resin separation time to eliminate this relatively small bias.

4.1.8. The method provides effective removal of ^{229}Th. Inadequate decontamination of ^{229}Th may lead to high bias in the ^{226}Ra result especially when the levels of ^{226}Ra in the sample are below 1 pCi/g. The spectral region above ^{226}Ra corresponding to ^{229}Th should be monitored routinely to identify samples where ^{229}Th interference may impact compliance with project MQOs. If problematic levels of ^{229}Th are identified in spectra, measures must be taken to address the interference. These might include:

4.1.8.1. Separating ^{225}Ra from ^{229}Th prior to its use as a tracer.

4.1.8.2. Increasing the sample aliquant size without changing the amount of tracer added will increase the analyte signal and reduce the relative impact of the interference to levels that may be amenable with project MQOs.

4.1.8.3. The absolute amount of ^{229}Th added to the samples may be decreased, as long as the time for ingrowth between separation and counting is increased to ensure that sufficient ^{217}At is present for yield corrections at the point of the count. Although this approach detracts from the rapidity of the method, it allows more flexibility in the timing of the count and does not detract from the potential for high throughput.

4.1.8.4. The samples may be counted as early as about 8 hours after separation time with an 8-hour count time if ~100 pCi ^{229}Th is added, but separation times and counting time midpoints must be recorded carefully and precisely.

4.1.9. When a solution containing ^{225}Ra in equilibrium with ^{229}Th is used as a tracer, thorium is removed during the processing of the sample. The equilibrium between the ^{225}Ra and ^{229}Th is essentially maintained until the cation exchange elution step is performed. At this point, the ^{225}Ra activity in the eluate is unsupported and begins to decay. ^{225}Ac is removed during the Ln Resin separation.

4.1.10. Ascorbic acid is added to the sample load solution to reduce Fe^{3+} present to Fe^{2+}, which has less retention on cation resin than Fe^{3+}.

4.1.11. Trace levels of ^{226}Ra may be present in Na_2CO_3 used in the ^{226}Ra pre-concentration step of the fusion method. Adding less 2M Na_2CO_3 (<25 mL used in this method) may reduce ^{226}Ra reagent blank levels, while still effectively pre-concentrating ^{226}Ra from the fusion matrix. This will need to be validated by the laboratory.

4.2. Non-radiological

4.2.1. The amount of inherent stable (non-radioactive) barium in the sample that may be carried through the processes prior to microprecipitation should not significantly exceed the amount of the barium carrier (50 µg), which is added for microprecipitation. Microprecipitates on the sample test source greater than 50 µg Ba may severely degrade the resolution of alpha spectra.

4.2.1.1. In this procedure, barium is removed using Sr Resin and alpha peak resolution is typically very good. It is important for the total volume of 3M HNO_3 passed through Sr Resin to be kept relatively small per procedure to remove Ba effectively. It is likely that Sr Resin can be washed and reused to reduce resin costs, but this will have to be validated by the laboratory.

4.2.1.2. The removal of Ba allows larger aliquant sizes of concrete, brick or soil to be analyzed that could not typically be tolerated in methods that do not remove Ba, allowing shorter count times and lower minimum detectable activity (MDA) levels.

4.2.2. Ca can also cause alpha peak resolution problems and needs to be effectively removed. Most of the Ca ions are removed using the initial cation exchange separation. A small amount is removed during the final Ln Resin purification step.

4.2.3. A smaller sample size may need to be selected when these interferences cannot be removed adequately.

4.2.4. After initial separations using cation resin and Sr Resin, the sample eluent solution is evaporated to dryness. This heating to dryness just prior to redissolution in very dilute HCl must be performed at very low heat (removed from hot plate just prior to going to dryness) to avoid formation of any oxides that may not dissolve well in the very dilute HCL just prior to loading on Ln Resin. This is important to maximize chemical yields.

4.2.5. It may be possible to skip the HCl/H_2O_2 evaporation step after evaporating the 3M HNO_3 to reduce sample preparation time, but this would have to be validated by the laboratory.

4.2.6. The Ln Resin step provides a final purification for the Ra-225 tracer. If the flow rate is too fast (>1.5 drops/second) and Ac-225 is present prior to the final separation time breaks through the resin, a high bias in the tracer yield will occur.

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 your laboratory's chemical hygiene plan for general chemical safety rules.

5.2. Radiological

5.2.1. Hot Particles (DRPs)

5.2.1.1. Hot particles, also termed "discrete radioactive particles" (DRPs), will be small, on the order of 1 mm or less. Typically, DRPs are not evenly distributed in the media and their radiation emissions are not uniform in all directions (anisotropic).

5.2.2. For samples with detectable activity concentrations of these radionuclides, labware should be used only once due to the potential for cross contamination.

5.3. Procedure-Specific Non-Radiological Hazards:

5.3.1. Solutions of 30% H_2O_2 can rapidly oxidize organic materials and generate significant heat. Do not mix large quantities of peroxide solution with solutions of organic solvents as the potential for explosion and conflagration exists.

6. Equipment and supplies

6.1. Alpha spectrometer calibrated for use over the range of ~3.5-7.5 MeV.

6.2. Cartridge reservoirs, 10 or 20 mL syringe style with locking device, or reservoir columns (empty luer tip, CC-10-M) plus 12 mL reservoirs (CC-06-M), Image Molding, Denver, CO, or equivalent.

6.3. Centrifuge tubes, polypropylene, 50 mL, disposable or equivalent.

6.4. Chromatography columns, polypropylene, disposable:

6.4.1. 1.5 cm inner diameter × 15 cm or equivalent (Environmental Express, Mount Pleasant, SC).

6.4.2. Additional frits for 1.5 cm inner diameter × 15 cm columns (Environmental Express, Mount Pleasant, SC).

6.5. Filter funnels.

6.6. Filter manifold apparatus with 25 mm-diameter polysulfone. A single-use (disposable) filter funnel/filter combination may be used, to avoid cross-contamination.

6.7. 100 µL, 200 µL, 500 µL and 1 mL pipets or equivalent and appropriate plastic tips.

6.8. 1-10 mL electronic pipet or manual equivalent.

6.9. Glass beaker, 50 mL and 150 mL capacity.

6.10. Heat lamp.

6.11. Hot plate.

6.12. Graduated cylinders, 500 mL and 1000 mL.

6.13. 25 mm polypropylene filter, 0.1 µm pore size, or equivalent.

6.14. pH paper.

6.15. Stainless steel planchets or other adhesive sample mounts (Environmental Express, Inc. P/N R2200) able to hold the 25 mm filter.

6.16. Tips, white inner, Eichrom part number AC-1000-IT, or PFA 5/32" × ¼" heavy-wall tubing connectors, natural, Ref P/N 00070EE, cut to 1 inch, Cole Parmer, or equivalent

6.17. Tips, yellow outer, Eichrom part number AC-1000-OT, or equivalent.

6.18. Tweezers.

6.19. Vacuum box, such as Eichrom part number AC-24-BOX, or equivalent.

6.20. Vacuum pump or laboratory vacuum system.

6.21. Vortex mixer.

6.22. Heat lamp.

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 16.4). For microprecipitation, all solutions used in microprecipitation should be prepared with water filtered through a 0.45 µm (or smaller) filter.

7.1. Type I reagent water as defined in ASTM Standard D1193 (Reference 16.4).

7.2. Ammonium sulfate, solid $(NH_4)_2SO_4$.

7.3. Barium carrier (1000 µg/mL as Ba^{2+}). May be purchased as an inductively coupled plasma – atomic emission spectrometry (ICP-AES) standard and diluted, or prepared by dissolving 0.90 g reagent grade barium chloride, dihydrate ($BaCl_2{\cdot}2H_2O$) in water and diluting to 500 mL with water.

7.4. Calcium nitrate (1.25M): Dissolve 147 g of calcium nitrate tetrahydrate ($Ca(NO_3)_2{\cdot}4H_2O$) in 300 mL of water and dilute to 500 mL with water.

7.5. Cation resin, 50WX8, 200–400 µm mesh size (available from Eichrom Technologies, Lisle, IL).

7.6. Ethanol, reagent (C_2H_5OH): Available commercially (or mix 95 mL 100% ethanol and 5 mL water).

7.7. Hydrochloric acid (12M): Concentrated HCl, available commercially.

7.7.1. Hydrochloric acid (3.0M): Add 250 mL of concentrated HCl to 600 mL of water and dilute to 1.0 L with water Hydrochloric acid (1.5M): Add 125 mL of concentrated HCl to 800 mL of water and dilute to 1.0 L with water.

7.7.2. Hydrochloric acid (1.5M): Add 125 mL of concentrated HCl to 800 mL of water and dilute to 1.0 L with water.

7.7.3. Hydrochloric acid (1M): Add 83 mL of concentrated HCl to 800 mL of water and dilute to 1.0 L with water.

7.7.4. Hydrochloric acid (0.1M): Add 8.3 mL of concentrated HCl to 950 mL of water and dilute to 1.0 L with water.

7.7.5. Hydrochloric acid (0.02M): Add 1.66 mL of concentrated HCl to 950 mL of water and dilute to 1.0 L with water

7.8. Hydrogen peroxide, H_2O_2 (30 % weight/weight): Available commercially.

7.9. Isopropanol, 2-propanol, (C_3H_7OH): Available commercially.

7.9.1. Isopropanol (2-propanol), 20% (volume/volume) in water: Mix 20 mL of isopropanol with 80 mL of water.

7.10. Ln Resin cartridges, 2 mL, small particle size (50–100 μm), in appropriately sized column pre-packed cartridges.

7.11. Methanol (CH_3OH): Available commercially

7.12. Nitric acid (16M): Concentrated HNO_3, available commercially.

7.13. Ra-225 tracer in 1M HCl solution in a concentration amenable to accurate addition of about 180 dpm per sample (generally about 150–600 dpm/mL).

7.13.1. Ra-225 may be purified and standardized using a ^{229}Th/^{225}Ra generator as described in the Appendix of this method.

7.13.2. Th-229 (~70–100 pCi) containing an equilibrium concentration of ^{225}Ra has been successfully used without prior separation of the ^{225}Ra.

7.13.3. The tracer activity added and the sample count time should be sufficient to obtain a combined standard uncertainty of less than 5% for the chemical yield measurement.

7.14. Sr Resin cartridges, 2 mL, small particle size (50–100 μm), in appropriately sized column pre-packed cartridges.

7.15. Yttrium carrier (10 mg/mL as Y^{3+}) for use in Appendix Step A4.2: May be purchased as an inductively coupled plasma – atomic emission spectrometry standard and diluted, or prepared by dissolving 4.3 g of yttrium nitrate hexahydrate ($Y(NO_3)_3 \cdot 6 H_2O$) in water and diluting to 100 mL in water.

8. Sample Collection, Preservation, and Storage

Not Applicable.

9. Quality Control

9.1. Batch quality control results shall be evaluated and meet applicable Analytical Protocol 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.

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

9.1.2. One method blank shall be run with each batch of samples. The laboratory blank should consist of an acceptable simulant or empty crucible blank processed through the fusion procedure. If an empty crucible is used to generate a reagent blank sample, it is recommended that 150 mg Ca be added as calcium nitrate to the empty crucible as blank simulant. This addition facilitates Ra carbonate precipitations from the alkaline fusion matrix.

9.1.3. 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.

9.1.4. 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.

9.2. Sample-specific quality control measures

9.2.1. Limits and evaluation criteria shall be established to monitor each alpha spectrum to ensure that spectral resolution and peak separation is adequate to provide quantitative results. When ^{229}Th/^{225}Ra solution is added directly to the sample, the presence of detectable counts between ~5.0 MeV and the upper boundary established for the ^{226}Ra ROI generally indicates the presence of ^{229}Th in the sample, and in the ^{226}Ra ROI. If the presence of ^{229}Th is noted and the concentration of ^{226}Ra is determined to be an order of magnitude below the AAL or the detection threshold of the method, take corrective actions to ensure that MQOs have not been compromised (e.g., clean-up ^{225}Ra tracer before adding, or re-process affected samples and associated quality control samples. See interferences sections Steps 4.1.4 – 4.1.5 for discussion).

10. Calibration and Standardization

10.1. Set up, operate, calibrate and perform quality control for alpha spectrometry units in accordance with the laboratory's quality manual and standard operating procedures and consistent with ASTM Standard Practice D7282, Sections 7-13, 18, and 24 (Reference 16.5).

NOTE: The calibrated energy range for the alpha spectrometer for this method should be from ~3.5 to 7.5 MeV.

10.2. If ^{225}Ra is separated and purified from ^{229}Th for use as a tracer, the activity reference date established during standardization of the tracer is used as the ^{225}Ra activity reference date (see the appendix of this method).

10.3. When using ^{229}Th containing an equilibrium concentration of ^{225}Ra, the time of most recent separation/purification of the ^{229}Th standard solution must be known in order to determine the extent of secular equilibrium between ^{229}Th and its ^{225}Ra progeny. Verify the date of purification by examining the Certificate of Analysis, or other applicable documentation, for the standard.

10.4. When using ^{229}Th containing an equilibrium concentration of ^{225}Ra, ^{225}Ra is separated from its ^{229}Th parent in the solution during the cation exchange elution step. This is the beginning of ^{225}Ra decay and the date and time used for decay correction of the tracer. This time must be known and recorded precisely.

10.4.1. If the purification date of the ^{229}Th is not documented, at least 100 days must have elapsed between separation and use to ensure that ^{229}Th, and its progeny ^{225}Ra are in full secular equilibrium (i.e., >99%. See Table 17.3).

11. Procedure

11.1. Initial Sample Preparation for Radium

11.1.1. Ra isotopes are preconcentrated from building material samples using procedure *Rapid Method for Sodium Hydroxide Fusion of Concrete and Brick Matrices Prior to Americium, Plutonium, Strontium, Radium, and Uranium Analyses* (Reference 16.3), which fuses the samples using rapid NaOH fusion followed by carbonate precipitation to preconcentrate Ra isotopes from the hydroxide matrix.

11.1.2. The carbonate precipitate is dissolved in an HCl solution and additional separation steps to purify the radium isotopes are performed using this procedure.

11.1.3. A smaller volume of the total load solution may be taken and analyzed as needed for very high activity samples, with appropriate dilution factor calculations applied.

11.1.4. This separation can be used with other solid sample matrices dissolved in 0.1M to 1.5M HCl.

11.2. Initial Matrix Removal Using 50WX8 Cation Resin

11.2.1. Prepare sample solution

11.2.1.1. Add 3 mL of 1.5M ascorbic acid to each sample solution to reduce any Fe present to Fe^{2+}. Mix and wait ~3 minutes.

11.2.2. Set up vacuum box

NOTE: More than one vacuum box may be used to increase throughput as needed.

11.2.2.1. For each sample solution, place the empty large columns (15 cm columns or equivalent) on the vacuum box.

11.2.2.2. Add a water slurry (or weigh out the solid resin) of cation resin 50WX8 (200-400 mesh) into each column equivalent to 5 g of resin.

11.2.2.3. Turn the vacuum on and ensure proper fitting of the lid.

IMPORTANT: The unused openings on the vacuum box should be sealed. Yellow caps (included with the vacuum box) can be used to plug unused white tips to achieve a good seal during the separation. Alternately, plastic tape can be used to seal the unused lid holes as well.

11.2.2.4. After the water has passed through, place a frit down on top of the resin bed.

11.2.2.5. Add additional water (~10–15 mL) to rinse the resin and remove fine resin particles.

11.2.2.6. Add 10 mL of 1M HCl to the column to precondition the resin.

11.2.2.7. Press frit down tightly on resin bed.

NOTE: It is important to control flow rates such that they are not too fast. Gravity flow (no vacuum) may be adequate, although a small amount of vacuum may be needed to get the flow started.

11.2.2.8. Adjust the vacuum (or use no vacuum) to achieve a flow-rate of ~1 mL/min (roughly ~1 drop/sec).

11.2.2.9. Discard column rinses.

11.2.2.10. Load sample solution slowly to each column at ~1 mL/min.

NOTE: It is likely that the ~1 mL/min flow rate can be achieved with no vacuum at all. The frit should be pressed down tightly to prevent too fast a flow rate.

11.2.2.11. Add 5mL of 1.5M HCl to rinse each sample solution tube and add to column at ~1–2 mL/min. Discard eluate.

11.2.2.12. Press frit down on resin bed.

11.2.2.13. Add 30 mL of 3M HCl to each column at ~1–2 mL/min. Discard rinse.

NOTE: The flow rate should not be too fast to ensure effective removal of Ca and other interferences.

11.2.2.14. Press frit down tightly on resin bed.

11.2.2.15. Place clean 50 mL centrifuge tubes beneath the columns to catch the eluate.

11.2.2.16. Press frit down tightly on resin bed.

11.2.2.17. Add 25 mL of 8M HNO_3 to each column to elute Ra at ~1mL/min. Record the date and time as the date and time of separation of ^{225}Ra and thorium to account for the decay of unsupported ^{225}Ra.

NOTE: Date and time need only be recorded if the ^{225}Ra was in equilibrium with ^{229}Th tracer.

11.2.2.18. Transfer the eluate solution to 150-mL glass beakers. Rinse tubes with ~3 mL of 8M HNO_3 and add to beaker.

11.2.2.19. Add 2 mL of 30 wt% H_2O_2 to each beaker and evaporate on medium heat to dryness on a hotplate being very careful not to bake material into the beaker. Samples should be taken off hotplate prior to going dry and allowed to go to dryness as the beaker cools.

11.2.2.20. Add 5 mL of 3M HNO_3 to redissolve each sample, warming slightly on hotplate as needed.

NOTE: Barium in the sample can interfere with the ^{226}Ra alpha peak resolution. Sr Resin is used to remove Ba in the sample. The volume of 3M HNO_3 must be kept small to remove Ba effectively.

11.2.3. Sr Resin Separation of Barium

11.2.3.1. Place a 2-mL Sr Resin cartridge on the vacuum box.

11.2.3.2. Condition each Sr Resin cartridge with 5 mL of 3M HNO_3 at 1 mL/min. Discard rinse.

11.2.3.3. Ensure that clean, labeled plastic tubes are placed in the tube rack under each cartridge.

11.2.3.4. Transfer each sample solution from Step 11.2.2.20 into the appropriate Sr Resin cartridge at a flow rate of ~1 mL/min or less.

11.2.3.5. Add 3 mL of 3M HNO_3 to each beaker (from Step 11.2.2.20) as a rinse and transfer each solution into the appropriate column at ~1 mL/min.

11.2.3.6. Add 3 mL of 3M HNO_3 into each reservoir as a column rinse (flow rate ~1–2 mL/min).

11.2.3.7. Turn off vacuum. Discard Sr Resin.

11.2.3.8. Remove tubes and transfer sample solution to 100-mL glass beakers.

11.2.3.9. Add 2 mL of 30 wt% H_2O_2 and evaporate solutions on medium heat to dryness on a hot plate being very careful not to bake material into the beaker. Samples should be taken off the hotplate prior to going dry and allowed to go to dryness as the beaker cools

NOTE: The method has been performed in some labs without the following evaporation step with HCl and H_2O_2 to save time but the laboratory will have validate this.

11.2.3.10. Add 2 mL of 1M-HCl and 2 mL of 30% H_2O_2 and evaporate solutions carefully to dryness on low heat and evaporate solutions on medium heat to dryness on a hot plate being very careful not to bake material into the beaker. Samples should be taken off the hotplate prior to going dry and allowed to go to dryness as the beaker cools.

NOTE: Heating to dryness on very low heat and allowing to dry just after coming off the hotplate with low heat is very important to prevent oxide formation, which can be difficult to redissolve in low acid and cause lower yields.

11.2.3.11. Add 2 mL of 0.1M HCl to each beaker, warming on a hotplate to dissolve.

11.2.3.12. Add 8 mL water and swirl to mix. Warm to ensure sample is dissolved.

11.2.4. Final Purification Using Ln Resin.

11.2.5. Place a 2 mL Ln Resin cartridge on the vacuum box.

11.2.6. Add 5 mL of 0.02M HCl into each column to precondition resin at ~1 mL/min. Discard rinse.

11.2.7. Ensure that clean, labeled plastic tubes are in the tube rack below each cartridge.

11.2.8. Transfer each sample solution from Step 11.2.3.12 into the appropriate column at ~1–1.5 mL/min.

NOTE: It is important to load sample rapidly enough (1–1.5 mL/min) to avoid any retention of Ra on Ln Resin.

11.2.9. Add 5 mL of 0.02M HCl to each beaker (from Step 11.2.3.12) as a rinse and transfer each solution into the appropriate reservoir at ~1–2 mL/min).

11.2.10. Add 5 mL of 0.02M HCl into each column to rinse at ~1–2 mL/min.

11.2.11. Record the date and time of the last rinse (Step 11.3.6) as the date and time of separation of radium from progeny. This time is also the beginning of ingrowth of ^{225}Ac (and ^{221}Fr and ^{217}At).

NOTE: If purified ^{225}Ra tracer is added to the sample (see the appendix), the ^{225}Ra activity was unsupported before the tracer solution was added to the sample. The activity reference date and time established during standardization of the ^{225}Ra tracer is used as the reference date for the ^{225}Ra solution.

NOTE: If ^{225}Ra at some degree of secular equilibrium with ^{229}Th is added as tracer in the initial step, the activity of ^{225}Ra is dependent upon the total amount of time between the last ^{229}Th purification and cation exchange elution step (Step 11.2.2.17). The decay of ^{225}Ra starts at the ^{229}Th removal step and is decayed to the Ln Resin separation time, where ^{225}Ac is removed, to determine the reference activity of the ^{225}Ra tracer at that point.

11.2.12. Remove tubes from vacuum box and add 3 mL concentrated HCl to each tube. Cap and mix.

11.2.13. Discard Ln Resin.

11.3. Barium sulfate micro-precipitation of ^{226}Ra

11.3.1. Add ~3.0 g of $(NH_4)_2SO_4$ to the purified sample solution. Mix well using a vortex stirrer to completely dissolve the salt.

11.3.2. Add 50 µg of Ba carrier (50 µL of 1000 µg Ba/mL) into each tube. Cap and mix well with vortex stirrer.

11.3.3. Add 5.0 mL of isopropanol and mix well using a vortex stirrer.

11.3.4. Place each tube in an ice bath filled with cold tap water for at least 15 minutes, periodically stirring on vortex stirrer (before placing in ice, midway, and after icing).

11.3.5. Pre-wet a 0.1-micron filter using methanol or ethanol. Filter the suspension through the filter using vacuum. The precipitate *will not be* visually apparent.

11.3.6. Rinse the sample container with 3 mL of 20% isopropanol solution.

11.3.7. Rinse the filter apparatus with about 2 mL of methanol or ethanol to facilitate drying. Turn off vacuum and discard rinses.

11.3.8. Mount the filter on a labeled adhesive mounting disk (or equivalent) ensuring that the filter is not wrinkled and is centered on mounting disk.

11.3.9. Place the filter under a heat lamp for ~5 minutes or more until it is completely dry.

11.3.10. Store the filter for ~24 hours to allow sufficient ^{217}At (third progeny of ^{225}Ra) to ingrow into the sample test source allowing a measurement uncertainty for the ^{217}At of < ~5 %.

11.3.11. Count by alpha spectrometry. The count times should be adjusted to meet the uncertainties and detection capabilities identified in Step 1.4.

12. Data Analysis and Calculations

12.1. The final sample test source (filter mounted on a planchet) will likely need to have approximate ingrowth period of 18 to 24 hours for ^{225}Ac (and ^{221}Fr and ^{217}At) to meet Analytical Protocol Specifications for chemical yield with a counting time of 4 to 8 hours. At-217 (third progeny of ^{225}Ra) has a single, distinct alpha peak with a centroid at 7.067 MeV and is used for determining the yield.

12.2. The following equation can be used to calculate the radiochemical yield:

$$RY = \frac{R_t - R_b}{\varepsilon \times A_t \times I_t} \qquad (1)$$

Where:

RY	=	Fractional radiochemical yield based on ^{225}Ra (from ingrown ^{217}At at 7.07 MeV)
R_t	=	Total count rate beneath the ^{217}At peak at 7.07 MeV, cpm
R_b	=	Background count rate for the same region, cpm
ε	=	Efficiency for the alpha spectrometer
I_t	=	Fractional abundance for the 7.07 MeV alpha peak counted (= 0.9999)

NOTE: If ^{225}Ra is separated from ^{229}Th for use as a purified tracer, the ^{225}Ra activity is unsupported and begins to decay at time of prior separation from ^{229}Th. The reference date and time established when the tracer is standardized is used for decay correction of the ^{225}Ra activity. If ^{229}Th solution (with ^{225}Ra in full secular equilibrium) is added to the sample, the ^{225}Ra activity is equal to the ^{229}Th activity added and only begins to decay at the point of separation of ^{225}Ra from ^{229}Th during the sample preconcentration steps (cation exchange elution step).

A_t	=	Activity of ^{217}At at midpoint of the count (the target value that should be achieved for 100% yield), in dpm
		$= 3.0408\left(I_t\right)\left(A_{^{225}\text{Ra}}\right)\left[e^{\lambda_1 d} - e^{\lambda_2 d}\right]$
$A_{^{225}\text{Ra}}$	=	Activity in dpm of ^{225}Ra tracer added to the sample decay corrected to the date and time of radium separation in Step 11.3.6.[2]

[2] **Unsupported ^{225}Ra**: When separated ^{225}Ra tracer is added to the sample, its initial activity, $A_{225\text{Ra-initial}}$, must be corrected for decay from the reference date established during standardization of the tracer to the point of separation of ^{225}Ra and ^{225}Ac as follows:

$$A_{^{225}Ra} = \left(A_{^{225}Ra-initial}\right)\left(e^{-\lambda_1 d_t}\right)$$

where: λ_1 = decay constant for ^{225}Ra (0.04652 d^{-1}); and d_t = time elapsed between the activity reference date for the ^{225}Ra tracer solution added to the sample and the separation of ^{225}Ra and ^{225}Ac in Step 11.3.6 (days).

^{229}Th/^{225}Ra added in equilibrium: When ^{229}Th containing ingrown ^{225}Ra is added directly to the sample, the amount of ^{225}Ra ingrown since purification of the ^{229}Th solution up until ^{229}Th removal point during the method is calculated as:

$$A_{^{225}Ra} = \left(A_{^{229}Th}\right)\left(1 - e^{-\lambda_1 d_i}\right)$$

where: $A_{229\text{Th}}$ = Activity of the ^{229}Th standard on the date of the separation of Th and Ra (cation exchange elution step); λ_1 = decay constant for ^{225}Ra (0.04652 d^{-1}); and d_i = time elapsed between the purification of ^{229}Th solution

d	=	Elapsed ingrowth time for ^{225}Ac [and the progeny ^{217}At], in days from the date and time of Ra separation to the midpoint of the sample count
λ_1	=	0.04652 d^{-1} (decay constant for ^{225}Ra – half-life = 14.9 days)
λ_2	=	0.06931 d^{-1} (decay constant for ^{225}Ac) – half-life = 10.0 days)
I_t	=	Fractional abundance for the 7.07 MeV alpha peak counted (= 0.9999)
3.0408	=	$\lambda_2/(\lambda_2+\lambda_1)$ [a good approximation as the half lives of ^{221}Fr and ^{217}At are short enough so that secular equilibrium with ^{225}Ac is ensured]

12.3. The activity concentration of an analyte and its combined standard uncertainty are calculated using the following equations:

$$AC_a = \frac{A_t \times R_{na}}{W_a \times R_{nt} \times D_a \times I_a \times 2.22} \tag{2}$$

and

$$u_c(AC_a) = \sqrt{u^2(R_{na}) \times \frac{A_t^2}{W_a^2 \times R_{nt}^2 \times D_a^2 \times I_a^2 \times 2.22^2} + AC_a^2 \times \left(\frac{u^2(A_t)}{A_t^2} + \frac{u^2(W_a)}{W_a^2} + \frac{u^2(R_{nt})}{R_{nt}^2}\right)} \tag{3}$$

where:

AC_a	=	activity concentration of the analyte at time of count, (pCi/g)
A_t	=	activity of ^{217}At at midpoint of the count (the target value that should be achieved for 100% yield), in dpm (see Step 12.2 for detailed calculation)
R_{na}	=	net count rate of the analyte in the defined region of interest (ROI), in counts per minute (Note that the peaks at 4.784 and 4.602 MeV are generally included in the ROI for ^{226}Ra)
R_{nt}	=	net count rate of the tracer in the defined ROI, in counts per minute
W_a	=	weight of the sample aliquant (g)
D_a	=	correction factor for decay of the analyte from the time of sample collection (or other reference time) to the midpoint of the counting period, if required
I_a	=	probability of α emission for ^{226}Ra (*The combined peaks at 4.78 and 4.602 MeV are generally included in the ROI with an abundance of 1.00.*)[3]
$u_c(AC_a)$	=	combined standard uncertainty of the activity concentration of the analyte (pCi/L)
$u(A_t)$	=	standard uncertainty of the activity of the tracer added to the sample (dpm)
$u(W_a)$	=	standard uncertainty of the volume of sample aliquant (g)

added to the sample and the separation of ^{225}Ra and ^{229}Th (days). The ^{225}Ra is then corrected for decay to the ^{225}Ac removal separation time (Step 11.3.6) using the first equation above.

[3] If the individual peak at 4.78 MeV used, *and completely resolved from the 4.602 MeV peak*, the abundance would be 0.9445.

$u(R_{na})$	=	standard uncertainty of the net count rate of the analyte in counts per minute
$u(R_{nt})$	=	standard uncertainty of the net count rate of the tracer in counts per minute

NOTE: The uncertainties of the decay-correction factors and of the probability of decay factors are assumed to be negligible.

NOTE: The equation for the combined standard uncertainty ($u_c(AC_a)$) calculation is arranged to eliminate the possibility of dividing by zero if $R_a = 0$.

NOTE: The standard uncertainty of the activity of the tracer added to the sample must reflect that associated with the activity of the standard reference material and any other significant sources of uncertainty such as those introduced during the preparation of the tracer solution (e.g., weighing or dilution factors) and during the process of adding the tracer to the sample.

12.3.1. The net count rate of an analyte or tracer and its standard uncertainty can be calculated using the following equations:

$$R_{nx} = \frac{C_x}{t_s} - \frac{C_{bx}}{t_b} \tag{4}$$

and

$$u(R_{nx}) = \sqrt{\frac{C_x + 1}{t_s^2} + \frac{C_{bx} + 1}{t_b^2}} \tag{5}$$

where:

R_{nx}	=	net count rate of analyte or tracer, in counts per minute[4]
C_x	=	sample counts in the analyte or the tracer ROI
t_s	=	sample count time (min)
C_{bx}	=	background counts in the same ROI as for x (x refers to the respective analyte or tracer count)
t_b	=	background count time (min)
$u(R_{nx})$	=	standard uncertainty of the net count rate of tracer or analyte, in counts per minute

12.3.2. If the critical level concentration (L_c) or the minimum detectable concentration (MDC) are requested (at an error rate of 5%), they can be calculated using the following equations.[5]

[4] For methods with very low counts, MARLAP Section 19.5.2.2 recommends adding one count each to the gross counts and the background counts when estimating the uncertainty of the respective net counts. This approach minimizes negative bias in the estimate of uncertainty and protects against calculating zero uncertainty when a total of zero counts are observed for the sample and background.

[5] The formulations for the critical level and minimum detectable concentrations are based on the Stapleton Approximation as recommended in MARLAP Section 20A.2.2, Equations 20.54 and 20A.3.2, and Equation 20.74, respectively. The formulations presented here assume an error rate of $\alpha = 0.05$, $\beta = 0.05$ (with $z_{1-\alpha} = z_{1-\beta} = 1.645$), and $d = 0.4$. For methods with very low numbers of counts, these expressions provide better estimates than do the traditional formulas for the critical level and MDC.

$$L_c = \frac{\left[0.4 \times \left(\frac{t_s}{t_b} - 1\right) + 0.677 \times \left(1 + \frac{t_s}{t_b}\right) + 1.645 \times \sqrt{\left(R_{ba} t_b + 0.4\right) \times \frac{t_s}{t_b} \times \left(1 + \frac{t_s}{t_b}\right)}\right] \times A_a \times D_a \times I_a}{t_s \times W_a \times R_t \times D_a \times I_a} \tag{6}$$

$$\text{MDC} = \frac{\left[2.71 \times \left(1 + \frac{t_s}{t_b}\right) + 3.29 \times \sqrt{R_{ba}\, t_s \times \left(1 + \frac{t_s}{t_b}\right)}\right] \times A_t}{t_s \times W_a \times R_{nt} \times D_a \times I_a \times 2.22} \tag{7}$$

where:

R_{ba} = background count rate for the analyte in the defined ROI, in counts per minute

12.4. Results Reporting

12.4.1. The following data should be reported for each result: weight of sample used; yield of tracer and its uncertainty; and full width at half maximum (FWHM) of each peak used in the analysis.

12.4.2. The following conventions should be used for each result:

12.4.2.1. Result in scientific notation ± combined standard uncertainty.

13. Method Performance

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

13.2. Expected sample preparation time for a batch of 15 samples is ~9 hours. Total processing time is dependent on actual wait time for ^{217}At ingrowth (~16–24 hours) and count times (~6 hours).

14. Pollution Prevention

14.1. The use of 50WX8 cation resin, Sr Resin and Ln Resin reduces the amount of solvents that would otherwise be needed to co-precipitate and purify the final sample test source.

15. Waste Management

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

15.2. All final precipitated materials contain tracer and should be dealt with as radioactive waste and disposed of in accordance with the restrictions provided in the facility's NRC license.

15.3. It may be advisable to rinse the cation resin columns with water to remove strong nitric acid prior to resin disposal.

16. References

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Other References

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17. Tables, Diagrams, and Flow Charts

17.1. Tables

Table 17.1 – Alpha Particle Energies and Abundances of Importance

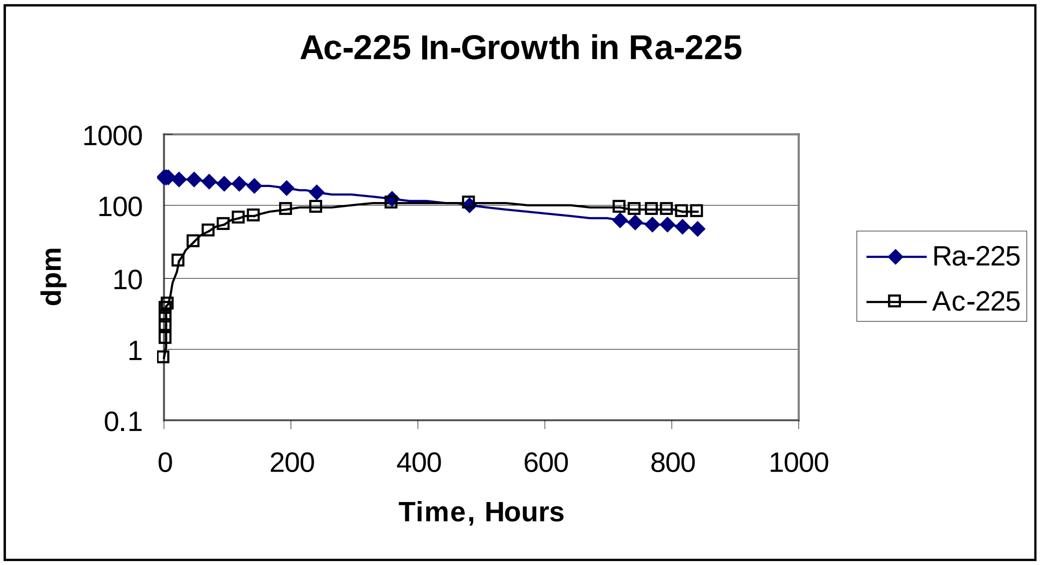
Energy (MeV)	Abundance (%)	Nuclide	Energy (MeV)	Abundance (%)	Nuclide
4.601	5.6	Ra -226	5.791	8.6	Ac -225
4.784	94.5	Ra -226	5.793	18.1	Ac -225
4.798	1.5	Th -229	5.830	50.7	Ac -225
4.815	9.3	Th -229	5.869	1.9	Bi -213
4.838	5.0	Th -229	6.002	100.0	Po -218
4.845	56.2	Th -229	6.051	25.1	Bi -212
4.901	10.2	Th -229	6.090	9.8	Bi -212
4.968	6.0	Th -229	6.126	15.1	Fr -221
4.979	3.2	Th -229	6.243	1.3	Fr -221
5.053	6.6	Th -229	6.278	16.2	Bi -211
5.434	2.2	Ra -223	6.288	99.9	Rn -220
5.449	5.1	Ra -224	6.341	83.4	Fr -221
5.489	99.9	Rn -222	6.425	7.5	Rn -219
5.540	9.0	Ra -223	6.553	12.9	Rn -219
5.580	1.2	Ac -225	6.623	83.5	Bi -211
5.607	25.2	Ra -223	6.778	100.0	Po -216
5.609	1.1	Ac -225	6.819	79.4	Rn -219
5.637	4.4	Ac -225	7.067	99.9	At -217
5.682	1.3	Ac -225	7.386	100.0	Po -215
5.685	94.9	Ra -224	7.450	98.9	Po -211
5.716	51.6	Ra -223	7.687	100.0	Po -214
5.724	3.1	Ac -225	8.376	100.0	Po -213
5.732	8.0	Ac -225	8.525	2.1	Po -212
5.732	1.3	Ac -225	11.660	96.8	Po -212
5.747	9.0	Ra -223			

(light shading)	- Analyte
(hatched)	- ^{217}At (3rd progeny of ^{225}Ra tracer)
(dark shading)	- ^{229}Th (Check ROI for indications of inadequate clean-up)

[1] Includes only alpha particles emissions with abundance > 1% from radionuclides commonly present in the sample test source.

Reference: NUDAT 2.4, Radiation Decay National Nuclear Data Center, Brookhaven National Laboratory; Available at: www.nndc.bnl.gov/nudat2/indx_dec.jsp; Queried: November 11, 2007.

17.2. Ingrowth curves and Ingrowth factors



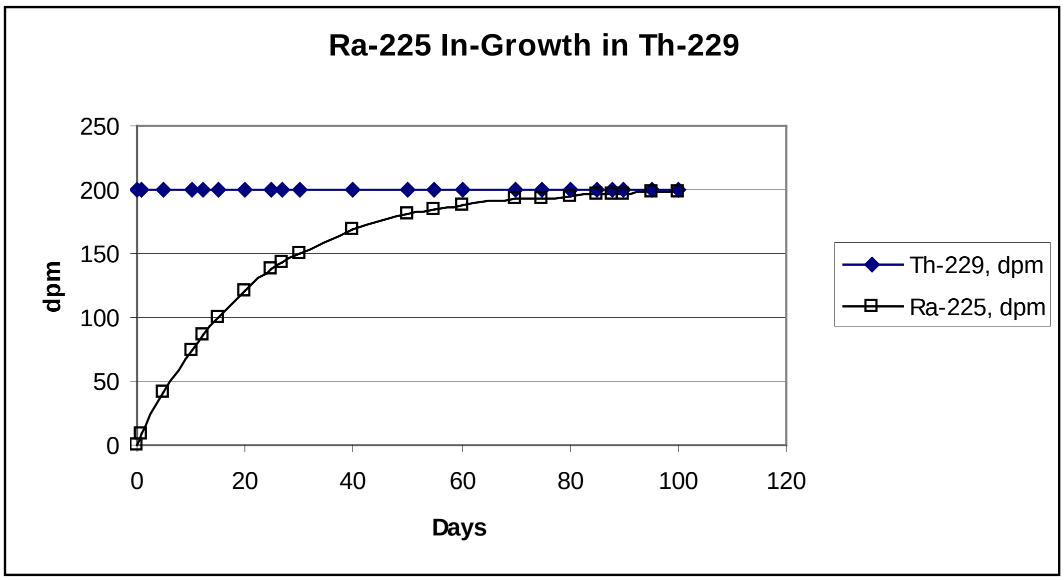


Table 17.2 – Ingrowth Factors for ^{217}At in ^{225}Ra

Time elapsed between separation of Ra and midpoint of count in hours	1	2	3	4	5	6	24	48
Ingrowth Factor*	0.002881	0.005748	0.008602	0.01144	0.01427	0.01708	0.06542	0.1235
Time elapsed between separation of Ra and midpoint of count in hours	**72**	**96**	**120**	**144**	**192**	**240**	**360**	**480**
Ingrowth Factor*	0.1748	0.2200	0.2596	0.2940	0.3494	0.3893	0.4383	0.4391

**Ingrowth Factor represents the fraction of ^{217}Ac activity at the midpoint of the sample count relative to the ^{225}Ra activity present at the date/time of Ra separation. These ingrowth factors may be closely approximated (within a fraction of a percent) using the expression for A_t in Step 12.2.*

Table 17.3 – Ingrowth Factors for ^{225}Ra in ^{229}Th

Time elapsed between purification of the ^{229}Th standard and date of Ra separation in days	1	5	10	12	15	20	25	27	30	40
Ingrowth Factor*	0.04545	0.2075	0.3720	0.4278	0.5023	0.6056	0.6875	0.7152	0.7523	0.8445
Time elapsed between purification of the ^{229}Th standard and date of Ra separation in days	**50**	**55**	**60**	**70**	**80**	**90**	**100**	**130**	**160**	**200**
Ingrowth Factor*	0.9023	0.9226	0.9387	0.9615	0.9758	0.9848	0.9905	0.9976	0.9994	0.9999

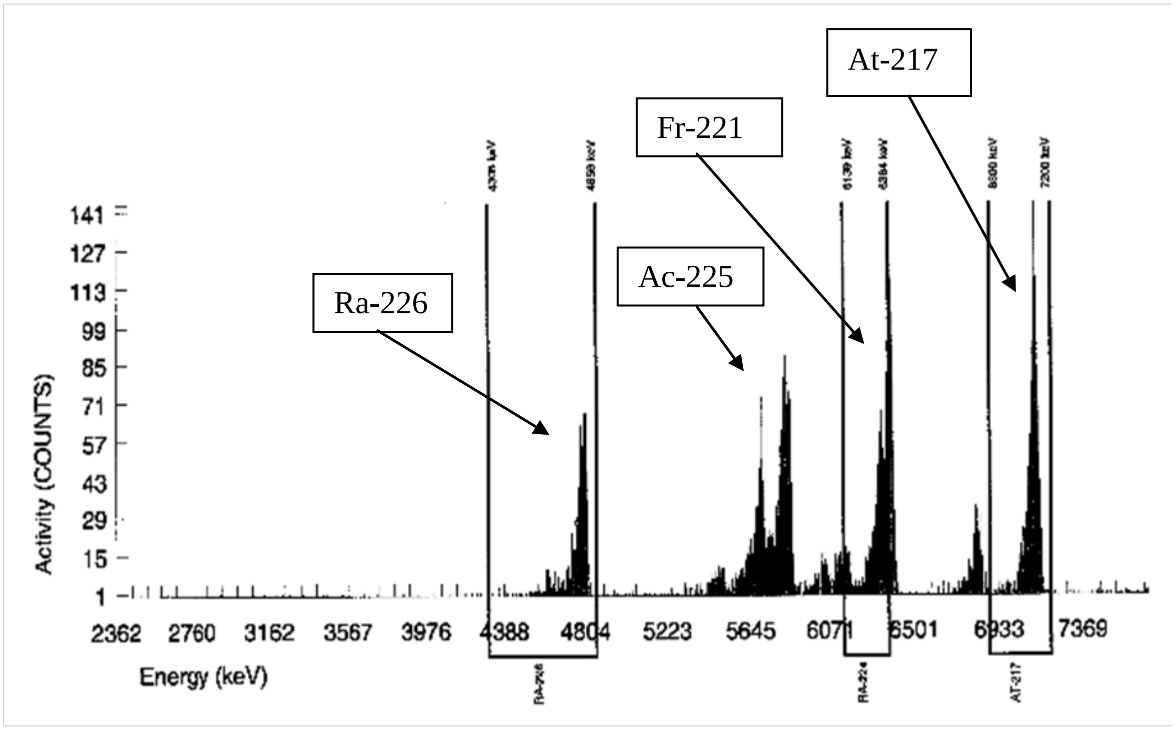
**Ingrowth Factor represents the fraction ^{225}Ra activity/^{229}Th activity at the time of Ra separation.*

Table 17.4 Decay Factors for Unsupported ^{225}Ra

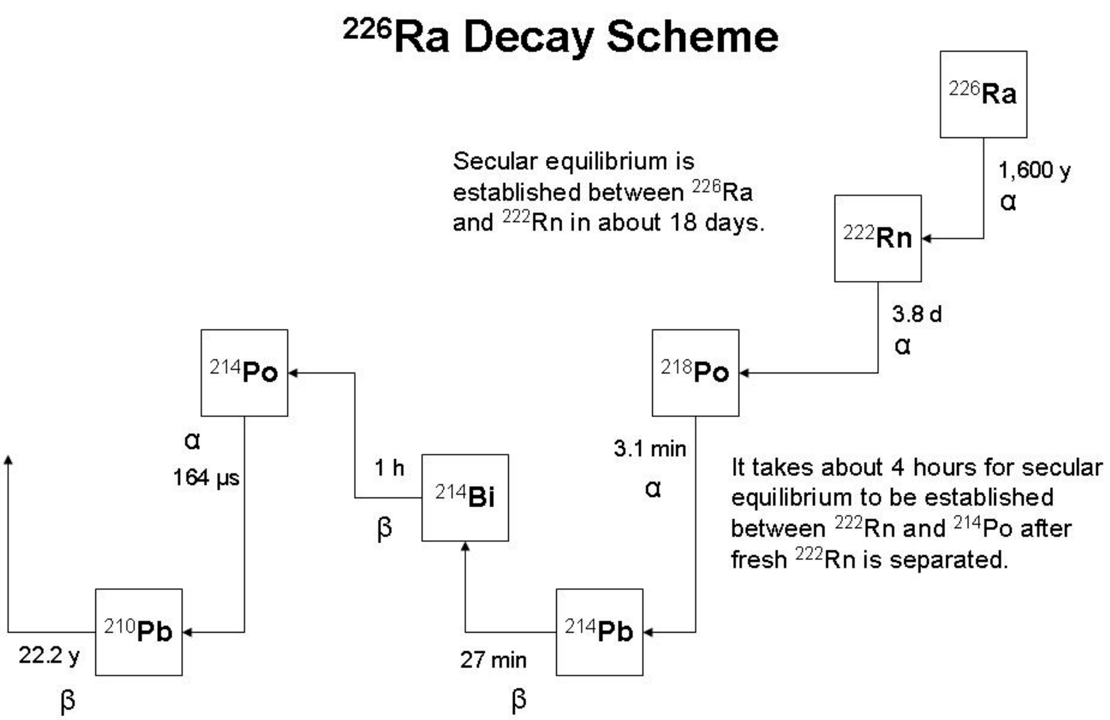
Time elapsed between separation of ^{229}Th and ^{225}Ra in days	1	5	10	12	15	20	25	27	30	40
Decay Factor*	0.9545	0.7925	0.6280	0.5722	0.4977	0.3944	0.3125	0.2848	0.2477	0.1555
Time elapsed between separation of ^{229}Th and ^{225}Ra in days	**50**	**55**	**60**	**70**	**80**	**90**	**100**	**130**	**160**	**200**
Decay Factor*	0.09769	0.07741	0.06135	0.03853	0.02420	0.01519	0.00954	0.00236	0.00059	0.00009

**Decay Factor represents the fraction ^{225}Ra activity remaining as calculated using the equation in Footnote 2.*

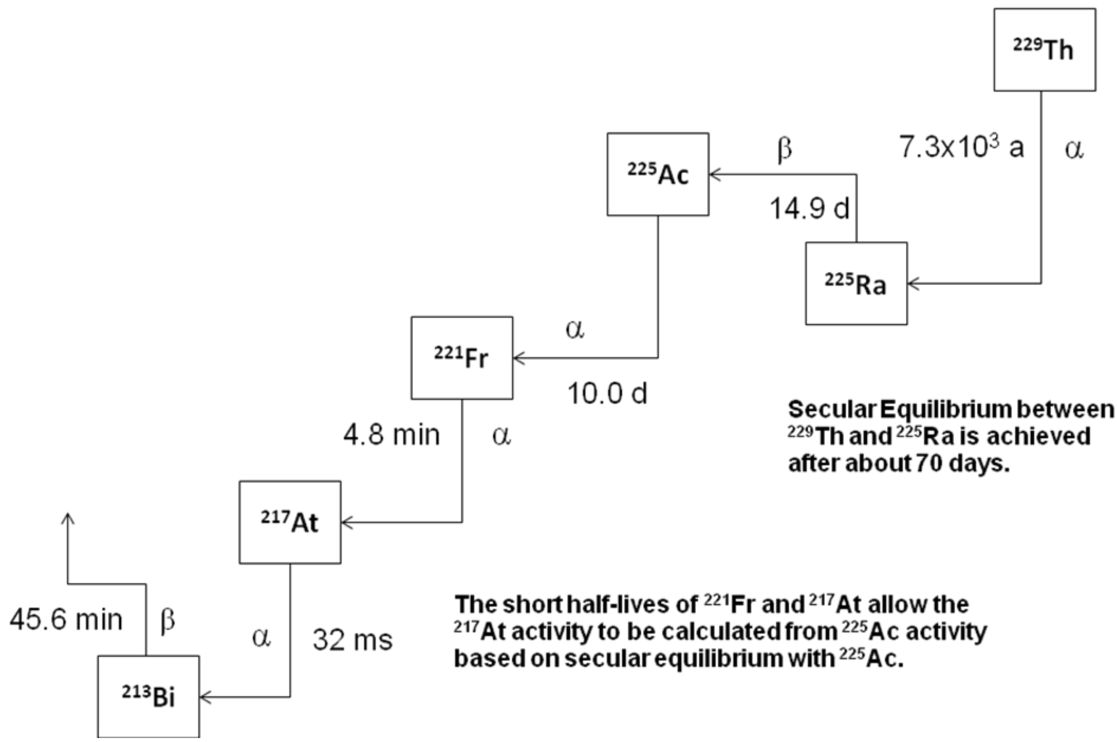
17.3. Example Alpha Spectrum from a Processed Sample



17.4. Decay Schemes for Analyte and Tracer

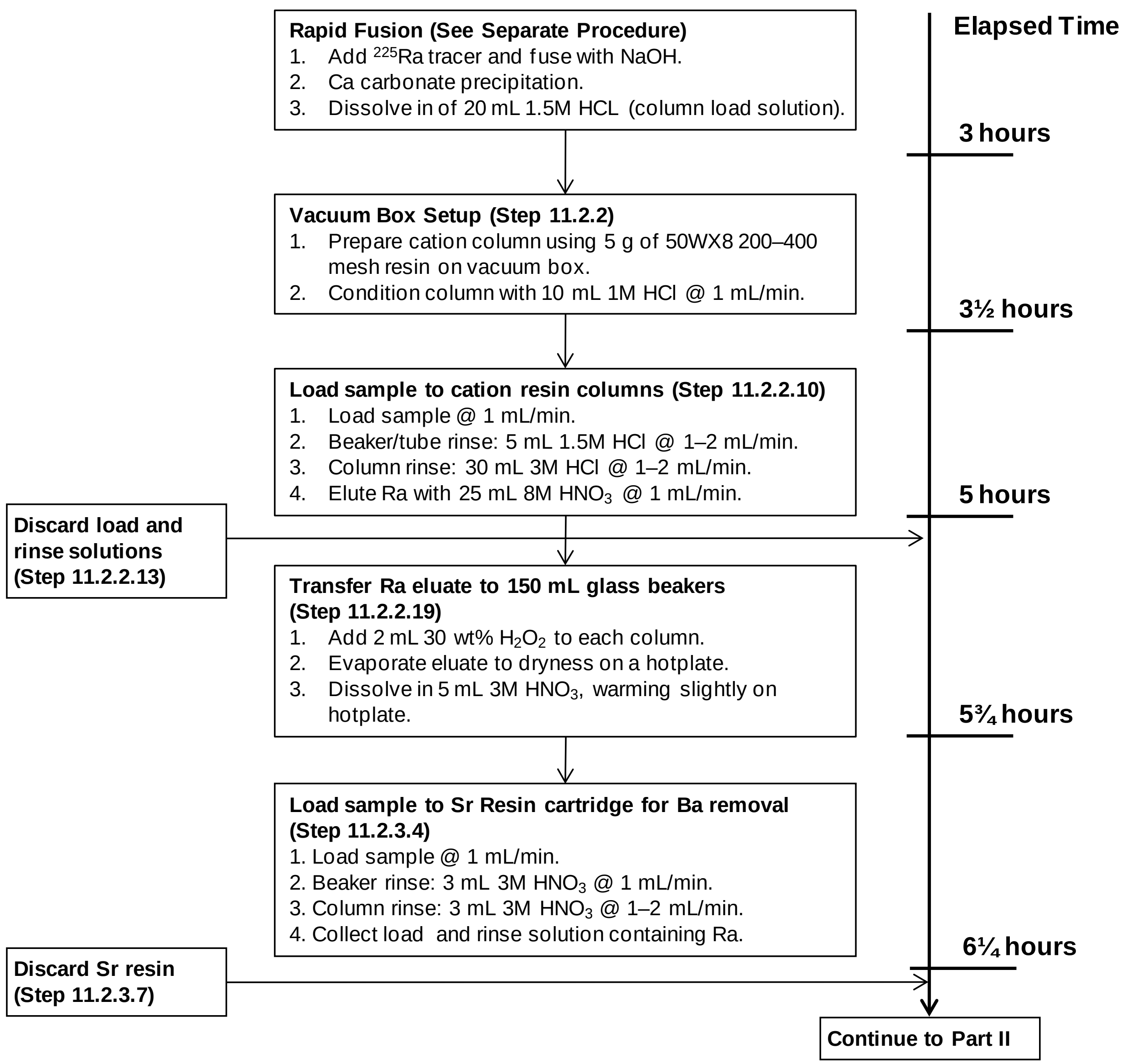


^{225}Ra (Including Parent) Decay Scheme

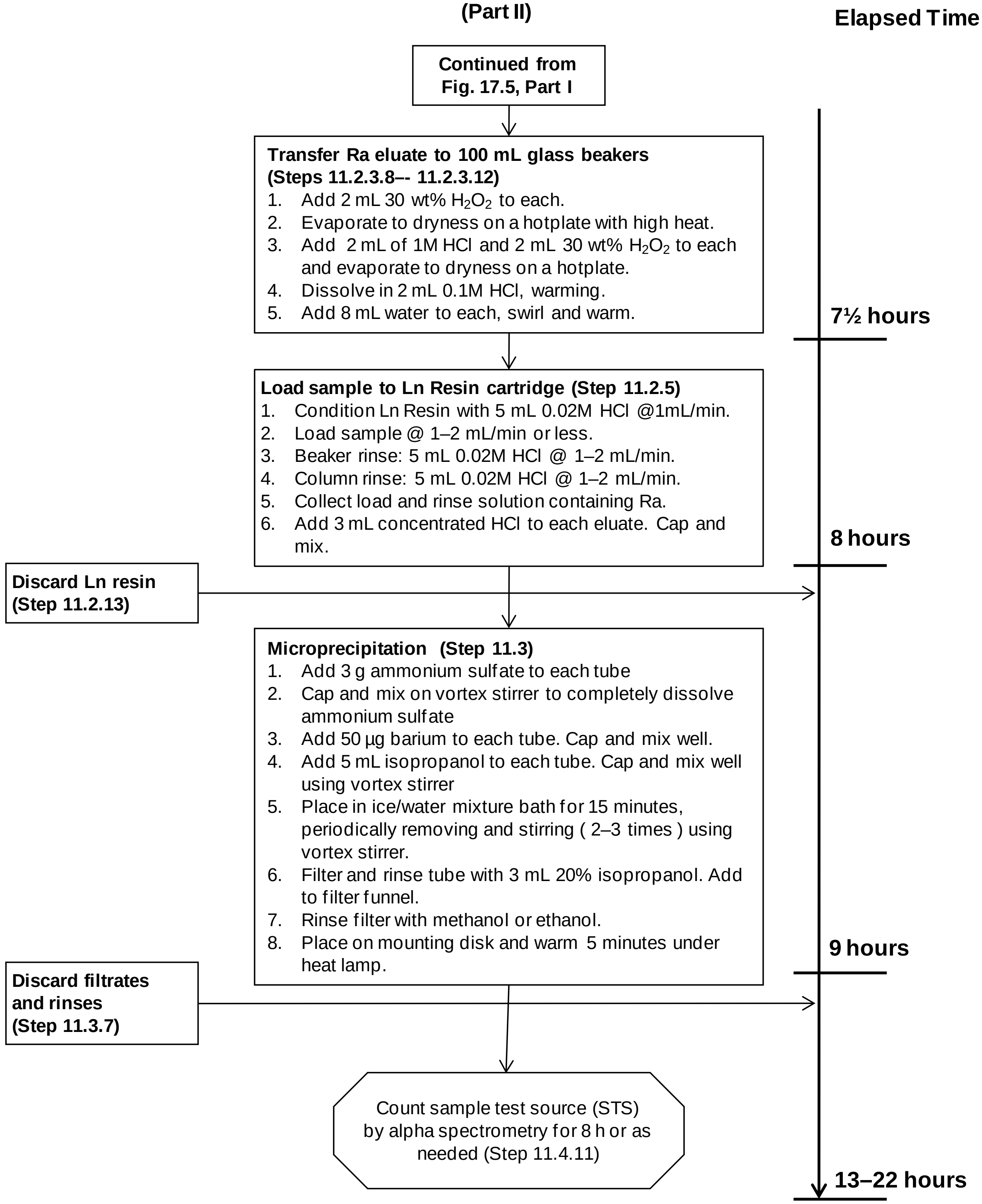


17.5. Flow Chart

Separation Scheme and Timeline for Determination of Ra-226 in Building Materials Samples (Part I)



Separation Scheme and Timeline for Determination of Ra-226 in Building Materials Samples (Part II)



Appendix:

Preparation and Standardization of ^{225}Ra Tracer Following Separation from ^{229}Th

A1. Summary Description of Procedure

This procedure describes a ^{225}Ra generator to make tracer amounts of ^{225}Ra using a ^{229}Th solution. ^{229}Th is separated from ^{225}Ra using $Y(OH)_3$ co-precipitation. ^{229}Th is carried in the precipitate and most of the ^{225}Ra remains in solution. Centrifugation to remove ^{229}Th in the precipitate and filtration of the supernate produces the ^{225}Ra tracer solution. The ^{225}Ra activity of the tracer solution is standardized by counting sample test sources prepared from at least five replicate aliquants of the ^{225}Ra solution, each spiked with a known quantity of a ^{226}Ra standard. This standardized activity concentration, referenced to the date and time of the ^{225}Ra separation described in Step A4.10.9 below, is then decay-corrected to the date and time of subsequent sample analyses.

The Y[Th]$(OH)_3$ precipitate may be stored and re-used later to generate more ^{225}Ra tracer solution. ^{225}Ra ingrows in the ^{229}Th fraction ($Y(OH)_3$ precipitate) and after 50 days will be about 90% ingrown. After sufficient ingrowth time ^{225}Ra may be harvested to make a fresh ^{225}Ra tracer solution by dissolving the precipitate and re-precipitating $Y(OH)_3$ to separate ^{229}Th from ^{225}Ra. Multiple ^{225}Ra generators may be prepared to ensure that ^{225}Ra tracer will be continuously available. The ^{225}Ra tracer solution produced is usable for 2–3 half-lives (~30–45 days). To minimize effort involved with standardization of the ^{225}Ra solution, it is recommended that the laboratory prepare an amount of ^{229}Th sufficient to support the laboratory's expected workload for 3-5 weeks. Since the ^{229}Th solution is reused, and the half-life of ^{229}Th is long (7,342 years), the need to purchase a new certified ^{229}Th solution is kept to a minimum.

A2. Equipment and Supplies

A2.1. Refer to Section 6 of the main procedure.

A3. Reagents and Standards

A3.1. Refer to Section 7 of the main procedure.

A4. Procedure

A4.1. Add a sufficient amount of ^{229}Th solution (that which will yield at least 150–600 dpm/mL of the ^{225}Ra solution) to a 50 mL centrifuge tube.[1]

A4.2. Add 20 mg yttrium (Y) (2 mL of 10 mg/mL Y metals standard stock solution).

A4.3. Add 1 mg Ba (0.1 mL of 10 mg/mL Ba metals standard stock solution).

A4.4. Add 4 mL of concentrated ammonium hydroxide to form $Y(OH)_3$ precipitate.

A4.5. Centrifuge and decant the supernatant into the open barrel of a 50 mL syringe, fitted with a 0.45-µm syringe filter. Hold the syringe barrel over a new 50-mL centrifuge tube while decanting. Insert the syringe plunger and filter the supernatant into the new centrifuge tube. Discard the filter as potentially contaminated rad waste.

[1] For example, if 40 mL of a ^{229}Th solution of 600 dpm/mL is used, the maximum final activity of ^{225}Ra will be ~510 dpm/mL at Step B4.8. This solution would require about 1.4 mL for the standardization process and about 8 mL for a batch of 20 samples.

A4.6. Cap the centrifuge tube with the precipitate, label clearly with the standard ID, precipitation date, and the technician's initials and store for future use.

A4.7. Properly label the new centrifuge tube with the supernate. This is the ^{225}Ra tracer solution.

A4.8. Add 3 mL of concentrated HCl to ^{225}Ra tracer solution. Cap centrifuge tube and mix well.

A4.9. Prepare the following solutions in 10 mL of 2M HCl for standardization of ^{225}Ra tracer.

Solution	**Spike(s)**
Standardization Replicates (5 replicates)	~80 dpm of the ^{225}Ra tracer solution, and ~8 dpm of a ^{226}Ra standard traceable to the National Institute of Standards and Technology (NIST) or equivalent
Blank	~80 dpm of the ^{225}Ra tracer solution *(the blank should be evaluated to confirm that ^{226}Ra is not detected in the ^{225}Ra tracer solution at levels that may compromise sample results when used in the method)*
Standardization Control Sample	~80 dpm of the ^{225}Ra tracer solution, and ~8 dpm of a second source independent traceable ^{226}Ra standard (the Standardization Control Sample should be evaluated to confirm that the standardization process does not introduce significant bias into the standardized value for the ^{225}Ra tracer).

A4.10. Process the solutions to prepare sources for alpha spectrometry as follows:

A4.10.1. Evaporate aliquants in 50 mL glass beakers on a hot plate.

A4.10.2. Add 2 mL of 0.1M HCl to each beaker, warming on hot plate to dissolve.

A4.10.3. Add 8 mL water and swirl to mix. Warm to ensure sample is dissolved.

A4.10.4. Place a 2 mL Ln Resin cartridge on the vacuum box.

A4.10.5. Add 5 mL of 0.02M HCl into each column to precondition resin at ~1 mL/min. Discard rinse.

A4.10.6. Transfer each sample solution from Step A4.10.3 into the appropriate reservoir. Allow solution to pass through the Ln Resin cartridge at a flow rate of ~1 mL/min.

A4.10.7. Add 5 mL of 0.02M HCl to each beaker (from Step A4.10.3) as a rinse and transfer each solution into the appropriate reservoir at ~1 mL/min.

A4.10.8. Add 5 mL of 0.02M HCl into each column to rinse at ~1 mL/min.

A4.10.9. Record the date and time of the last rinse as the date and time of separation of radium (beginning of ^{225}Ac ingrowth).

NOTE: The activity reference date and time established during standardization of the ^{225}Ra tracer is used as the reference date for the ^{225}Ra solution.

A4.10.10. Remove tubes from vacuum box and add 3 mL concentrated HCl to each tube. Cap and mix.

A4.10.11. Add ~3.0 g of $(NH_4)_2SO_4$ to the purified sample solution Mix well to completely dissolve the salt (dissolves readily).

A4.10.12. Add 75 µg of Ba carrier (75 µL of 1000 µg Ba/mL) into each tube. Cap and mix well with vortex stirrer.

A4.10.13. Add 5.0 mL of isopropanol and mix well using a vortex stirrer.

A4.10.14. Place each tube in an ice bath filled with cold tap water for at least 20 minutes, periodically stirring on vortex stirrer.

NOTE: Sonication may be used instead of occasional stirring using a vortex stirrer.

A4.10.15. Pre-wet a 0.1-micron filter using methanol or ethanol. Filter the suspension through the filter using vacuum. The precipitate *will not be* visually apparent.

A4.10.16. Rinse the sample container with 3 mL of 20% isopropanol solution.

A4.10.17. Rinse the filter apparatus with about 2 mL of methanol or ethanol to facilitate drying. Turn off vacuum.

A4.10.18. Mount the filter on a labeled adhesive mounting disk (or equivalent) ensuring that the filter is not wrinkled and is centered on mounting disk.

A4.10.19. Place the filter under a heat lamp for ~5 minutes or more until it is completely dry.

A4.10.20. Count filters for an appropriate period of time by alpha spectrometry.

A4.10.21. Mount the dried filter on a support appropriate for the counting system to be used.

A4.10.22. Store the filter for at least 24 hours to allow sufficient ^{217}At (third progeny of ^{225}Ra) to ingrow into the sample test source allowing a measurement uncertainty for the ^{217}At of < ~5 %.

A4.10.23. After allowing about 24-hours ingrowth, count the standardization sources by alpha spectrometry.

A4.11. Calculate the activity of ^{225}Ra, in units of dpm/mL, in the standardization replicates, at the ^{225}Ra time of separation as follows:

$$A_{^{225}Ra} = \frac{\left(\dfrac{N_{^{217}At}}{t_{^{217}At}} - \dfrac{N_b}{t_b}\right) \times \left(A_{^{226}Ra}\right) \times \left(V_{^{226}Ra}\right)}{\left(\dfrac{N_{^{226}Ra}}{t_a} - \dfrac{N_b}{t_b}\right) \times \left[(3.0408)(I_t)\ \left(e^{-\lambda_1 d} - e^{-\lambda_2 d}\right)\right] \times V_{^{225}Ra}}$$

where:

$A_{^{225}Ra}$ = Activity concentration of ^{225}Ra, in dpm/mL [at the time of separation from ^{229}Th, Step B4.4.10]

$N_{^{217}At}$ = Total counts beneath the ^{217}At peak at 7.07 MeV

$N_{^{226}Ra}$ = Total counts beneath the ^{226}Ra peak at 4.78 MeV

N_b = Background count rate for the corresponding region of interest,
t_a = Duration of the count for the sample test source, minutes
t_b = Duration of the background count, minutes
$A_{^{226}Ra}$ = Activity of ^{226}Ra added to each aliquant, in dpm/mL
$V_{^{226}Ra}$ = Volume of ^{226}Ra solution taken for the analysis (mL)
$V_{^{225}Ra}$ = Volume of ^{225}Ra solution taken for the analysis (mL)
d = Elapsed ingrowth time for ^{225}Ac [and the progeny ^{217}At], from separation to the midpoint of the sample count, days
λ_1 = 0.04652 d^{-1} (decay constant for ^{225}Ra – half-life = 14.9 days)
λ_2 = 0.06931 d^{-1} (decay constant for ^{225}Ac) – half-life = 10.0 days)
I_t = Fractional abundance for the 7.07 MeV alpha peak counted (= 0.9999)
3.0408 = $\lambda_2 d / (\lambda_2 d - \lambda_1 d)$ [a good approximation as the half lives of ^{221}Fr and ^{217}At are short enough so secular equilibrium with ^{225}Ac is ensured]

NOTE: The activity of the separated A_{225Ra} will need to be decay corrected to the point of separation in the main procedure (Step 11.3.6) so that the results can be accurately determined.

A4.12. Calculate the uncertainty of the activity concentration of the ^{225}Ra tracer at the reference date/time:

$$u_c(AC_{^{225}Ra}) = \sqrt{\frac{\left(\frac{N_{^{217}At}}{t_a^2} + \frac{N_b}{t_b^2}\right) \times AC_{^{226}Ra}^2 \times I_{^{226}Ra}^2 \times V_{^{226}Ra}^2}{\left(\frac{N_{^{226}Ra}}{t_a} - \frac{N_b}{t_b}\right)^2 \times \left[3.0408 \times I_{^{217}At} \times \left(e^{-\lambda_1 d} - e^{-\lambda_2 d}\right)\right]^2 \times V_{^{225}Ra}^2} + AC_{^{225}Ra}^2 \times \left(\frac{u^2(AC_{^{226}Ra})}{AC_{^{226}Ra}^2} + \frac{u^2(V_{^{225}Ra})}{V_{^{225}Ra}^2} + \frac{u^2(V_{^{226}Ra})}{V_{^{226}Ra}^2} + \frac{u^2(R_{^{226}Ra})}{R_{^{226}Ra}^2}\right)}$$

where:

$u(AC_{^{225}Ra})$ = Standard uncertainty of the activity concentration of ^{225}Ra, in dpm/mL
$N_{^{217}At}$ = Total counts beneath the ^{217}At peak at 7.07 MeV,
$N_{^{226}Ra}$ = Total counts beneath the ^{226}Ra tracer peak at 4.78 MeV
N_b = Background count rate for the corresponding region of interest,
t_a = Duration of the count for the sample test source, minutes
t_b = Duration of the background count, minutes
$AC_{^{226}Ra}$ = Activity of ^{226}Ra added to each aliquant, in dpm/mL
$u(AC_{^{226}Ra})$ = Activity of ^{225}Ra, in dpm/mL
$V_{^{226}Ra}$ = Volume of ^{226}Ra solution taken for the analysis (mL)
$u(V_{^{226}Ra})$ = Volume of ^{226}Ra solution taken for the analysis (mL)
$I_{^{226}Ra}$ = Fractional abundance for the ^{226}Ra peak at 4.78 MeV (= 1.000)
$V_{^{225}Ra}$ = Volume of ^{225}Ra solution taken for the analysis (mL)
$u(V_{^{225}Ra})$ = Volume of ^{225}Ra solution taken for the analysis (mL)
d = Elapsed ingrowth time for ^{225}Ac [and the progeny ^{217}At], from separation to the midpoint of the sample count, days
λ_1 = 0.04652 d^{-1} (decay constant for ^{225}Ra – half-life = 14.9 days)
λ_2 = 0.06931 d^{-1} (decay constant for ^{225}Ac) – half-life = 10.0 days)
$I_{^{225}Ra}$ = Fractional abundance for the 7.07 MeV alpha peak counted (= 0.9999)

3.0408 = $\lambda_2 d / (\lambda_2 d - \lambda_1 d)$ *[a good approximation as the half lives of ^{221}Fr and ^{217}At are short enough so secular equilibrium with ^{225}Ac is ensured]*

$u(R_{^{226}\text{Ra}})$ = Standard uncertainty of net count rate for ^{226}Ra, in cpm

$R_{^{226}\text{Ra}}$ = Net count rate for ^{226}Ra, in cpm

NOTE: The **uncertainty of half-lives and abundance values are a negligible contributor to the combined uncertainty and are considered during the evaluation of combined uncertainty.**

A4.13. Calculate the mean and standard deviation of the mean (standard error) for the replicate determinations, to determine the acceptability of the tracer solution for use. The calculated standard deviation of the mean should be equal to or less than 5% of the calculated mean value.

A4.14. Store the centrifuge tube containing the $Y(OH)_3$/$Th(OH)_4$ precipitate. After sufficient time has elapsed a fresh ^{225}Ra tracer solution may be generated by dissolving the precipitate with 40 mL of 0.5M HNO_3 and repeating Steps A4.4 through A4.10 of this Appendix.

Attachment IV:

Composition of Brick Used for Spiking in this Study

Metals by ICP-AES [4]	Concentration (ppm) [1]
Silicon Dioxide	721,700
Aluminum	78,700
Barium	400
Calcium	1,600
Iron	40,000
Magnesium	4,600
Potassium	15,300
Sodium	1,500
Titanium	4,400
Manganese	600
Strontium	100
Uranium	<30
Thorium	<30
Non-Metals	
Chloride	—
Sulfur	5,600
Phosphorus	1,500
Radionuclide	**Concentration (pCi/g) [2, 3]**
Uranium 238, 234	1.054 ± 0.020, 1.102 ± 0.021
Plutonium 239/240	-0.0003 ± 0.0041
Americium 241	0.048 ± 0.039
Strontium 90	0.119 ± 0.077
Radium 226	1.025 ± 0.027

NOTE: Analyses conducted by an independent laboratory.

[1] Values below the reporting level are presented as less than (<) values. No measurement uncertainty was reported with the elemental analysis values. Parts per million (ppm).

[2] Reported values represent the average value of seven blank samples analyzed except for ^{226}Ra and U by NAREL. Ten blank brick samples were analyzed for ^{226}Ra. Sixteen blank brick samples were analyzed for the uranium isotopes.

[3] Reported uncertainty is the standard deviation of the results (k=1).

[4] ICP-AES=Inductively Coupled Plasma – Atomic Emission Spectrometry