COMPLEX-MATRIX RADIONUCLIDE STANDARD REFERENCE MATERIALS

Purpose

This document describes the production, measurement, and reporting procedures for the massic activity or mass fraction of radionuclides in Complex-Matrix Radionuclide Standard Reference Materials (referred to here as Complex-Matrix SRMs). Included within this document are the procedures for preparation and calibration of the Complex-Matrix SRMs. SRMs developed under this procedure are intended to comply with the requirements outlined in NIST Quality Manual for Measurement Services (NIST-QM-I) [1] and the Radiation Physics Division Quality Manual (RPD-QM-II) [2] thereby satisfying international standards for reference material producers [3].

Background

One of the missions of the Radiation Physics Division is to provide standards containing radionuclides for research, commerce, and industry. Generally, the SRMs that are available from NIST are provided for one of several reasons: (a) they are not available from outside commercial suppliers, (b) commercially-produced standards may not be traceable to national standards, (c) the accuracy of commercially-produced standards is not adequate for a significant number of users, or (d) there are enough requests from the user community for a standard not otherwise available. The Complex-Matrix SRM program seeks to quantify radionuclide massic activity or mass fraction in complex matrix materials such as soils, sediments, biological specimens, or synthetic mixtures (representing construction or industrial materials). The radionuclides present in these matrices have both natural and anthropogenic origins. Complex-Matrix SRMs provide the metrology community with means by which they can: a) validate radioanalytical methods, b) control the quality of measurement process, c) compare measurement results within projects and programs (both within a laboratory and between laboratories) over an extended time period, and d) support the traceability and credibility of measurement results [4].

NIST issues a wide array of Complex-Matrix SRMs for measurements of radioactivity or amount of radioactive nuclide (Appendix 1A). There are approximately 10 such SRMs in stock with the number of calibrated radionuclides ranging from 3 to 13 depending on the material. A total of 42 different radionuclide calibrations have been performed across these materials. These Complex-Matrix SRMs are frequently a result of a collaboration of national and international environmental and radiochemistry laboratories. Calibrations at NIST and the collaborating laboratories use various radiometric techniques and several mass spectrometric methods. SRM units of these materials are distributed as ground, homogenized powders containing between 15 g and 300 g depending on matrix material. Radionuclides are generally present at low massic activities (< 1.0 Bq g^{-1}) and/or trace mass fractions (<100 ppm).

Scope

This procedure discusses:
- the selection of material matrices;
- processing them into final form;
- the interlaboratory comparisons used to develop the data files from which the certified radionuclide massic activity will be derived;
- the NIST radiochemical analysis process to contribute to the data file;
- the data evaluation process; and
- the preparation of supporting documentation and the SRM certificate.

Safety

The processes for production and characterization of the Complex-Matrix SRMs involve working with radioactive materials (sometimes at moderate levels of activity and dose rate), with biological materials, with various acids and other chemicals, with dispersible powders, and with potentially dangerous equipment. Safe work practices are an essential part of the production process. See Subsection 6 of the Procedures section.

Radiation safety-general: Users of radioactive materials at NIST must complete Radiation Safety Training and should only be handling materials in accordance with active procedures that have approved Safety Evaluations (SEs). Handling and processing of the radioactive materials shall be performed in rooms that have been designated as Radiation Facilities by the Gaithersburg Radiation Safety Division (GRSD) and are marked with magenta and yellow strip tape and/or placards. Specific requirements for entry and exit from the rooms are provided by the GRSD. Source acquisition proposals are submitted using the NIST 364 Form (“Radioactive Material Request”) in the context of approved SEs. In addition, safety protocols are posted in the laboratories.

Chemical safety-general: Chemical safety and training operations are provided by the NIST Gaithersburg Office of Safety, Health, and Environment (OSHE). GRSD is a sub-group within the OSHE.

Equipment

The production and characterization of the Complex-Matrix SRMs may involve a large number of different machines and measuring instruments. See Appendix A2 and Subsection 8 of the Procedure section.

Uncertainty Analysis

A measurement result is complete only when accompanied by a quantitative statement of its uncertainty. The uncertainty often determines the usefulness of the measurement result. The analysis and reporting of measurement uncertainties is an essential step in the production process. See Subsection 18 of the Procedures section.

Records

Production records should be complete enough so that anyone who is reasonably familiar with the SRM production process can reproduce any or all of the calculations that lead to the final measurement results and uncertainties for the SRM (i.e., the certified values) and evaluate and reproduce the production process (e.g., for the next batch of that SRM). See Subsection 21 of the Procedures section.

Filing and Retention

The radioactivity SRM production records are stored in the SRM Records Storage Room. The production records are retained for as long as the SRM is available for sale to the public, plus at least an additional 10 years. See Subsection 21 of the Procedures section.

The Radiation Physics Division (RPD) Quality Manager shall maintain the original and past versions of this RPD Procedure as specified in RPD-QM-II.

Definitions and Abbreviations

Organizations:
- NIST – National Institute of Standards and Technology
  - GRSD – Gaithersburg Radiation Safety Division, NIST
  - OSHE – Office of Safety, Health and Environment
  - ORM – Office of Reference Materials
  - PML – Physical Measurement Laboratory
    - RPD - Radiation Physics Division (Division 682 of PML)
    - RG – Radioactivity Group (Group 4 of RPD)
    - PI – Principal Investigator: the NIST employee primarily responsible for the development of the reference material project.

SRM Coordinator: The PML staff member with primary responsibility for and oversight of the development of SRMs within the Radioactivity Division

SED – Statistical Engineering Division

Concepts and Units:

Becquerel (Bq) – SI unit of radioactivity equal to one nuclear transformation per second

Curie (Ci) – unit of radioactivity equal to 3.70E+10 nuclear transformations per second (originally based on the nuclear transformation rate of 1 gram of ^{226}Ra)

CRM – certified reference material

Gray (Gy) – SI unit of absorbed dose equal to 1 joule/kilogram

QC – quality control

SI – the International System of units (metric)

Traceability of measurement – establishment of an unbroken chain of measurements, with uncertainties, linked to a fundamental SI unit

Processes:

Bateman equations – solutions to systems of differential equations governing the ingrowth and decay as a function of time of radioactive progeny of a given radioactive parent progenitor.

Carrier – a stable element, usually added in the form of a salt, to facilitate the stability of a solution of or separation of a particular radionuclide. An isotopic carrier is the same element as the radionuclide (e.g., stable Sr added to ^{90}Sr). A non-isotopic carrier is a different element from the radionuclide (e.g., stable Ba added to ^{226}Ra).

Chemical equilibration – any chemical process which causes the tracer/carrier and the analyte to assume the same chemical state (e.g., oxidation, reduction, complexation, solvation, hydration, etc.).

Combined standard uncertainty – standard measurement uncertainty that is obtained using the individual standard measurement uncertainties associated with the input quantities in a measurement model.

Electrodeposition – a method of producing a nearly massless source containing radionuclides intended for alpha spectrometry measurement with optimum spectral resolution. The radionuclides are typically deposited as an oxide layer onto a stainless steel or platinum disk from a solution in an electrochemical cell with the passage of an electric current under controlled conditions.

Isotope dilution – the use of an added isotopic tracer or carrier in known amount to facilitate the measurement of one or more analytes (e.g., addition of ^{242}Pu tracer to facilitate the mass spectrometric measurement of ^{239}Pu and ^{240}Pu).

Leaching – a chemical process intending to selectively dissolve a particular component of interest (e.g., Pu) from a matrix (e.g., soil) without requiring total dissolution of the matrix (e.g., digestion of soil with strong acids, singly or in combination).

Lyophilization – freeze-drying.

Micro co-precipitation – a method of producing a source with mass typically less than 500 µg containing radionuclides intended for alpha spectrometry measurement. For example, actinides in their tri- and tetravalent oxidation states can crystallize essentially quantitatively within a matrix of freshly precipitated rare earth fluoride (e.g., NdF_3) due to the similarity of their ionic radii. The rare earth fluoride precipitate is filtered onto a membrane filter of 0.1 µm porosity, washed and dried to produce the source. It is an alternative to the electrodeposition method but typically has poorer spectral resolution.

Radioactive equilibrium – the state where the rate of ingrowth of the decay product of a specific radionuclide equals the rate of decay of its radioactive daughter nuclide of shorter half-life than its parent. At this point, the ratio of daughter to parent atoms (and therefore the activity ratio) remains constant.

Sample decomposition – any process that alters the chemical or physical state of a sample with the objective of analyzing for one or more components (in the present case, amounts of selected radionuclides).

Sample dissolution – the process of dissolving a sample, sometimes after a preliminary sample decomposition, in order to prepare a solution from which one or more components (radionuclides) may be chemically separated.

Total dissolution – a chemical process intending to completely dissolve a sample matrix in order to ensure that all of the desired analyte is brought into solution for subsequent chemical separation steps. High temperature molten-salt fusion is one example of this approach.

Tracer – a radionuclide added to follow the chemical behavior of the particular radionuclide to be analyzed and often to facilitate the quantitative measurement of that radionuclide. An isotopic tracer is the same element as the analyte radionuclide (e.g., ^{243}Am tracer added to ^{241}Am analyte), whereas a non-isotopic tracer is a different element (e.g., ^{133}Ba tracer added to ^{226}Ra analyte).

Procedures

The need for a new SRM largely derives from advice from the radioactivity user community. Interactions with this community include the annual CIRMS (Council on Ionizing Radiation Measurements and Standards) meeting; the NIST Radioactivity Measurement Assurance Program (NRMAP) Inc. steering committees; focused workshops; and personal interactions with users within other laboratories, academia, and industry. This need is usually identified by the principal investigator responsible for producing, calibrating, and certifying the SRM. A need could also be identified by other Radioactivity Group (RG) members.

The responsibilities of the RG Leader, SRM Coordinator, and Principal Investigator (PI) as well as the coordination of SRM activities among them, is described in RPD-QM-II.

Below is a sequence of general steps that describe the process for production, characterization, and certification of a Complex-Matrix SRM.

1.0 *Determine the intended use, the requirements, and the demand for the SRM.*

1.1 Each NIST Complex-Matrix SRM must be of the highest metrological quality and be fit for purpose. To achieve these goals requires more than defining certified values and an associated uncertainty. It also requires that the form, chemical composition, homogeneity, size, activity, and packaging of the SRM are such that the user can easily make correct and accurate measurements. In order to help insure that these requirements are met, guidance may be sought from relevant regulatory bodies or specialized technical organizations in addition to the requests and suggestions of individual customers.

1.2 If an SRM is a renewal (i.e., the production of a new batch of an already existing, but presently out-of-stock, SRM), the previous sales record is also considered. If there is some question about the continued need for a particular Complex-Matrix SRM, previous customers for that SRM are usually consulted to obtain their comments and suggestions.

2.0 *Select the chemical and physical properties of the SRM and select the chemical and physical attributes that are to be quantified and/or certified.*

2.1 There are three basic guidelines for the selection of the chemical and physical properties of a Complex-Matrix SRM:

2.1.1 Provided that the material is properly stored, the Complex-Matrix SRM should be stable for a period of at least at least 20 years (i.e. no chemical or physical change to the SRM, other than the intrinsic radioactive decay, that make the material unsuitable for analysis or alters a certified value by more than 25 percent of its stated uncertainty).

2.1.2 The Complex-Matrix SRM should be as similar as is practical to the sample(s) that the customer will measure. This helps reduce or eliminate additional uncertainties due to dilution or due to corrections for different preparation requirements (particularly decomposition/dissolution behavior if destructive analysis is applied), different sample geometries, different photon absorptions, etc.

2.1.3 The Complex-Matrix SRM should be in a form and quantity that is useable by as many customers as possible.

2.2 There are two basic guidelines for the selection of the chemical and physical properties whose values are to be quantified:

2.2.1 All of the properties that are essential to the proper use of the Bulk SRM must be described quantitatively. For example, the major element composition of the matrix and minimum sample size for certified values must be indicated so that the user can best determine how to process the bulk material for analysis.

2.2.2 The precision of contributing measurements should be considered such that the expanded uncertainty of the Complex-Matrix SRM remains low enough to be satisfactory for the majority of users.

3.0 *Select a suitable container and packaging for the SRM.*

3.1 Containers for Complex-Matrix SRMs must be selected based on 4 criteria which will vary depending on the properties of the material:

3.1.1 Containers should have sufficient volume to hold the chosen mass of Complex-Matrix SRM without compressing the material.

3.1.2 The container geometry should be such that material can be readily dispensed or retrieved (e.g. with a spatula); generally, wide-mouth glass or polyethylene bottles.

3.1.3 The container should be sufficiently impermeable to protect the material from alteration due to diffusion of gas or vapor phase (e.g. moisture during storage or oxygen for biological samples).

3.1.4 The container should be sufficiently robust to resist degradation due to aging or chemical interaction with the Complex-Matrix material (massic activities for Complex-Matrix SRMs are typically very low, so long-term radiation damage to containers from the material itself is not a significant factor).

3.2 Materials such as soils, sediments, or synthetic material can be packaged in polyethylene bottles. Potentially light- and air-sensitive biological materials are packaged in amber or clear glass bottles under dry nitrogen or vacuum. Additionally, the latter may be stored in deep freezers until shipped to customers.

3.3 As part of the production process, additional packaging may be placed around the container of the Complex-Matrix SRM. When necessary, this packaging is designed to protect the SRM during handling and long-term storage. Packaging for the Radioactivity SRMs is designed to pass the performance tests for Type-A packages of radioactive material. Complex-Matrix SRMs will, however, generally ship as “Excepted” packages so outer packaging may not be required to meet Type-A criteria. See Section 20 for more detailed requirements. The packaging currently in use for the Complex-Matrix SRMs has proven satisfactory over decades of use.

4.0 *Select a measurement model, suitable sampling and measurement method (experimental design), including the sequence of operations for the production process.*

4.1 Complex-Matrix SRMs are generally certified as consensus standards that include results from measurements performed outside of the PML RG and measurements performed by the RG. Planning for sampling and analysis are generally in accordance with concepts outlined in [5] and [6].

4.2 For measurements outside of the PML RG, leading experienced international radiochemical metrology laboratories are invited to participate in a “best effort” replicate analysis interlaboratory comparison to obtain the most accurate and consistent radionuclide concentration data possible.

- 4.2.1 The laboratories are selected through their reputations and demonstrated capabilities evidenced by past participation in comparisons and publications in peer reviewed literature
- 4.2.2 All laboratories agree to participate without anonymity.
- 4.2.3 Chemical yield monitors quantitatively diluted from SRMs are typically provided by NIST to the participants.
- 4.2.4 Each laboratory uses the radioanalytical methodology for which they are most expert and selects the radionuclide results that are returned to NIST.
- 4.2.5 At least one measurement from each of the SRM units is requested for each reported radionuclide. The laboratory also has the option of reporting at least three measurement results from each of the SRM units for assessment of between-bottle and within-bottle heterogeneity.
- 4.2.6 The laboratories are requested to report their results within one year of receiving the SRM units.
- 4.2.7 The information requested for reported analytical results includes: five massic activity results for each radionuclide with the associated combined standard uncertainties, the reference date, and a brief description of the analytical method used.

4.3 For measurements within the PML RG, the selection of primary and confirmatory measurement methods depends primarily on the decay mode of the primary radionuclide and on the activity and physical form of the sample(s) to be measured. The general criteria for the selection of a measurement method are:

- 4.3.1 Ease of measurement.
- 4.3.2 Ease of sample preparation.
- 4.3.3 Low measurement uncertainty.
- 4.3.4 Selectivity (if more than one radionuclide is present).
- 4.3.5 High detection efficiency (especially important for typically low massic activities).

4.4 There are presently 5 basic methods (alpha spectrometry, gamma spectrometry, liquid scintillation and beta gas-flow proportional counting, and mass spectrometry), some with many variations, used within the PML RG for primary, confirmatory, and/or impurity measurements of the Complex-Matrix SRMs. See Section 14 for a description of the various measurement methods and sample preparation techniques used for Complex-Matrix SRMs.

4.5 Statistical evaluation of the measurement data is described in Section 15.

5.0 *Draft a project plan and have the proposed production process reviewed and approved.*

5.1 The project plan shall include the sequence in which the required project activities are to be carried out. Proposed attributes for characterization, participating laboratories, required facilities, equipment, personnel, supplies, and funding should be documented in whatever form is satisfactory for the purpose, such as lists, tables, drawings, flow charts, Gantt diagrams, etc.

5.2 The review and approval of the SRM production plan are carried out by the RG Leader and the SRM Coordinator. A record of this review shall be maintained with the SRM documentation.

6.0 *Have the proposed safety measures reviewed and approved by Gaithersburg Radiation Safety Division and* the NIST Office of Safety, Health and Environment.

6.1 The acquisition and use of radioactive material, or a Complex-Matrix material known to contain radionuclides, at NIST must be approved by the GRSD, in advance, in the context of an Ionizing Radiation Safety Committee (IRSC)-approved SE. For the Complex-Matrix SRM production process, this is done by submitting a Proposed Use Request for approval under a specific SE, along with a NIST 364 “Radioactive Material Request” (signed by the RG Leader or RPD Chief). Once approved by GRSD, the proposed use is assigned an identification number and can be referenced in future production processes.

6.2 Preparation of Complex-Matrix SRMs may require the handling of biological materials and dispersible powders, both of which may require special safe handling procedures. These activities will be reviewed by the NIST Office of Safety, Health and Environment under a specific SE.

7.0 *Obtain the necessary funding.*

This step is normally carried out by the RG SRM Coordinator together with the RG leader. Funding of a radioactivity SRM production from the SRM Working Capital Fund requires the approval of the RPD Administrative Officer, the RPD Chief, the Director of the Physical Measurement Laboratory, and the NIST Comptroller.

8.0 *Arrange for the use of the necessary facilities, equipment, and personnel*

8.1 Use of necessary facilities and equipment is normally arranged by, or in cooperation with, the PI for the Complex-Matrix SRM production and with the concurrence of the RG leader and staff with primary responsibility for the facilities or equipment.

8.2 The production of the NIST Complex-Matrix SRMs may involve a large number of different machines and measuring instruments. Measurement instruments and other equipment are described in Appendix A2.

8.3 Suitable general-purpose radiochemistry laboratories are available in the NIST Radiation Physics Division/Radioactivity Group (RPD/RG) for the preparation of Complex-Matrix SRMs and measurement of samples. Use and preparation of these facilities will be determined based on the facility capabilities and specific production needs associated with the SRM. The SOPs, SEs, and hazard reviews under which SRM work is performed state where specific work will occur.

9.0 *Acquire suitable materials.*

9.1 As used here, materials include

9.1.1 Stock quantities of complex-matrix material.

9.1.2 Radioactive materials, if these are going to be added to the bulk materials.

9.1.3 Chemical reagents and other consumable materials.

9.1.4 SRM containers, glassware, and other laboratory supplies.

9.2 Bulk-matrix materials for preparation of SRMs are highly specific matrices chosen to represent a type of complex matrix that would be encountered by measurement facilities making radioactivity measurements. These materials are not, in general, commercially mass-produced. As such, they are provided as a custom order from a vendor to meet project-specific requirements; they are obtained from a specific source known to have desired characteristics for the SRM; or they are synthetically produced to meet project-specific requirements. If a matrix is going to be obtained by collection, the procedures for collection will be consistent with NIST-QM-I. Once the radionuclide composition and massic activity characteristics of the target matrix and potential collection sites are identified, cost estimates are obtained from personal contacts with access to the collection sites.

9.3 Many of the Complex-Matrix SRM materials are produced from material specifically chosen for known content of radioactive nuclides. In some cases, however, radionuclides may be added to a bulk material to prepare the matrix standard. To the extent possible, any radionuclides used for this purpose will be NIST radioactivity SRMs, calibrated SRM master solutions, or CRMs from other suppliers. If it is necessary to obtain radionuclides from a commercial supplier, suitable radioactive starting materials that do not require any additional chemical purification will be purchased. Radionuclidic purity and carrier concentration can vary so chemical purification may be necessary to improve the calibration accuracy.

9.4 Chemical reagents used as solvents and non-radioactive carriers are at least Analytical Grade reagents, and each bottle/unit is provided with a lot analysis. Spectroscopic Grade reagents or Trace Element Grade reagents are preferred. Purchased chemical reagents will be inspected and their identity confirmed prior to use. The quality of the laboratory reagents will be confirmed during the analysis of reagent blanks to check the titer of the reagents, as well as any significant contribution to the blank signal. Any failure of the reagent's titer or indication of contamination will result in the suspension of use of the material and a suitable replacement will be obtained to carry out the requested measurements.

9.3 Purchasing documents shall include technical specifications for all quality-critical labware, reagents and instrumentation. Quality-critical purchased items will be inspected and evaluated against the purchasing technical specifications

9.4 Critical consumables such as unit containers will be purchased based on project specific technical requirements. Borosilicate glass, quartz glass, or Teflon containers are normally used for solution chemistry associated with Complex-Matrix SRM preparation and characterization. The SRM containers, glassware, and other laboratory supplies are prepared, as necessary, using standard analytical laboratory techniques for washing, rinsing, drying, labeling, etc.

10.0 *Addition of radionuclides to Complex-Matrix (as necessary).*

10.1 For some Complex-Matrix materials it may be necessary to add known amounts of radionuclides to the bulk material. There are two primary methods for adding radionuclides; as a chemical component in a synthetically produced Complex-Matrix or as a physical mixture with a previously prepared bulk material. For either method, a known quantity of nuclide (as determined based on mass and/or massic activity) is added to the matrix.

10.2 For radionuclides that are a chemical component of a synthetic material, the nuclides are added prior to final preparation of reference material units (see section 11.0).

10.3 For nuclides added as physical mixture, the material is added to the complex-matrix material prior to the blending step in the material preparation (see Section 11.5) or may be added as a quantitatively known amount of solution to individual units. For the latter case, the radionuclide-bearing solution shall be characterized for massic activity and a unit must be processed in its entirety for a single analysis.

11.0 *Prepare the materials (as necessary).*

11.1 <u>SRM Unit size determination</u>: The minimum unit size for most Complex-Matrix SRMs is chosen to be at least three times the typical sample size used by the metrology community for an analysis of the matrix. Typically, the maximum sample size for soils and sediments is 10 g; for biological materials, it is the amount of material that would result in 10 g of ash.

11.2 <u>Matrix drying</u>: When economically feasible, the preferred method of initially drying the matrix is by lyophilization. In cases where lyophilization is not possible, air drying is acceptable. If possible, the drying is done at NIST, but otherwise is done externally when appropriate facilities are not present at NIST.

11.3 <u>Initial Matrix Size Reduction</u>: If necessary, the initial matrix size reduction and processing (milling) are most often carried out at a facility external to NIST. NIST is often present at the external facility to monitor the processing of the material insofar as is possible during real time. It is during this initial matrix size reduction step when, if two or more sources of materials are to be combined to yield the desired SRM characteristics, the materials are initially mixed.

11.4 <u>Pulverization</u>: To minimize heterogeneity and separation due to particle size differences, the material must be pulverized to micrometer-size dimensions with a narrow particle size dispersion. Air-jet pulverization is the method of choice for dry, friable materials with the average particle size typically about 10 μm. Despite its inherent advantages, there is no guarantee that radioactively “hot” particles will be absent in the final product. Alternatively, for organic materials of relatively high oil content, cryogenic hammer-milling is more appropriate. The same concerns about "hot" particles apply here as well.

11.5 Blending: To further minimize heterogeneity, materials are thoroughly mixed, particularly to evenly disperse "hot" particles. Ideally, the material is blended as one batch. In cases where the capacity of the blender is insufficient to blend the entire amount of material, sub-batches are blended. In this case, additional blending of the split sub-batches is necessary. It is recommended that a three-level cross blending approach provides sufficient mixing of the final material.

11.6 Final Drying: Biologically-derived materials require final drying to remove moisture absorbed during material processing and to increase shelf-life. Lyophilization is usually the method of choice prior to final packaging.

12.0 *Dispensing and Packaging*

12.1 Environmental materials such as soils and sediments and inert synthetic matrices are packaged in polyethylene bottles. Potentially light- and air-sensitive biological materials are packaged in amber or clear glass bottles under dry nitrogen or vacuum. Additionally, the latter may be stored in deep freezers until shipped to customers.

12.2 The amount of bulk material dispensed to unit containers is determined by mass. Distribution is typically performed by placing a unit container on a calibrated balance, taring the container wait and then manually adding the complex matrix material until the desired mass is achieved (within a predetermined range).

12.3 Sterilization of the final SRM product is necessary to satisfy export requirements of environmental and biological materials, and to increase shelf life. The materials are irradiated with ^{60}Co gamma rays to an absorbed dose in excess of 40 kGy. This absorbed dose is confirmed by dosimetry traceable to NIST provided by the vendor. The excessive sterilization provided by the 40 kGy absorbed dose precludes the need for microbiological analysis. The container materials are selected to avoid potentially deleterious effect of radiation damage to the bottles and caps.

13.0 *Distribution of Analysis Samples for Characterization*

13.1 Sample units for analysis are selected based on a stratified random sampling routine with the "strata" corresponding to criteria such a unit filling order or the container from which the starting material was obtained (when more than one container of stock material is necessary).

13.2 Multiple samples are transferred to a laboratory participating in the characterization analyses (See section 4.2) with the number sent to each laboratory based on statistical sampling model and factors such as number of units in the production run, the size of the sample units, and the need for between-unit and within-unit replicate measurements.

13.3 Typically it is requested that the laboratory report 5 massic activity results for each radionuclide with the associated combined standard uncertainties, the reference date, and a brief description of the analytical method used. For assessment of between bottle and within bottle heterogeneity, the laboratory also has the option of reporting three measurement results from each of the SRM units provided.

14.0 *Characterization analyses by the NIST Radiation Physics Division, Radioactivity Group*

14.1 Gamma Ray Measurements:

14.1.1 Assessment of heterogeneity.

14.1.1.a The heterogeneity of the bulk material is initially evaluated by gross gamma-ray measurements using a 12.7 cm diameter NaI(Tl) detector. The detection system is set for a broad (e.g., 50 keV to 1350 keV) energy window. An experimental plan is developed in consultation with NIST's Statistical Engineering Division (SED) to decide the appropriate sample size and number of samples to be measured for a desired confidence level. Glass or plastic cylindrical counting containers having high dimensional uniformity, preferably with flat-plate bottoms, are used. The sample material is weighed, tamped to a selected height, then sealed in the container. If electrostatic charge is not a problem keeping the material at the bottom of the counting container, Plexiglas is the preferred material for the container to minimize the ^{40}K contribution to the gamma-ray Compton background. A waiting time of 3 to 4 weeks is allowed for the sample to attain radioactive equilibrium (e.g., ingrowth of radon-222 and its daughters) in the container before measurement.

14.1.1.b Each sample is then placed in a counting jig to assure that each sample is counted in the same geometry with respect to the detector. Each sample is counted for the same amount of live time, generally one day to one week per sample.

14.1.1.c Check sources and blank sample containers are generally counted before, between samples and after the last sample is counted to evaluate the stability of the counting system during the measurement schedule.

14.1.2 HPGE Gamma Ray Measurements: Quantitative Measurements

14.1.2.a Gamma-ray measurements using high purity germanium (HPGe) detectors provide nuclide-specific measurement, and HPGe systems are used for quantifying the gamma-ray emitting radionuclides. Providing there is sufficient radioactivity, the same samples used for the heterogeneity assessment in 14.1 can be used for massic activity quantification.

14.1.2.b HPGe instrument stabilities are monitored with check sources and blank determinations during the scheduled sample measurements. The check sources are counted in a reproducible geometry and are used to check that the energy and efficiency responses of the detectors have been maintained and are under control. The absolute values of the QC source emission rates need not be known so long as they are predictable (e.g., have a stable physical/chemical form and can be decay-corrected).

14.1.2.c Each sample is placed in a counting jig to assure that each sample is counted in the same geometry with respect to the detector. Each sample is counted for the same amount of live time, which is dependent upon the activity concentrations of the nuclides of interest and may be for as long as 2 to 4 weeks per sample.

14.1.2.d Check sources and blank sample containers are counted before, between samples and after the last sample is counted to evaluate the stability of the counting system during the measurement schedule.

14.1.2.e The HPGe instruments are calibrated for energy response and efficiency with a sample of the matrix of interest that has been quantitatively spiked with SRM radionuclides of interest and thoroughly blended [7, 8, & 9]. The thoroughness of blending is verified by measuring a set of sub-samples (typically 5 g to 15 g) from the blended material. This method of calibrating the detector avoids the added uncertainty contributions that affect interpolation of efficiencies from an experimentally determined calibration curve.

14.1.3 NaI(Tl) Gamma Ray Measurements: Quantitative Measurements

14.1.3.a Sodium iodide instrument stabilities are monitored with check sources and blank determinations during the scheduled sample measurements. The check sources are counted in a reproducible geometry and are used to check that the energy and efficiency responses of the detectors have been maintained and are under control. The absolute values of the QC source emission rates need not be known so long as they are predictable (e.g., have a stable physical/chemical form and can be decay-corrected).

14.1.3.b The instrument blanks are empty counting bottles that are measured in the same geometry as the samples.

14.1.3.c These determinations are done at the beginning of the schedule, between samples, and after the final sample is counted

14.1.4 Gamma Ray Data Analysis

14.1.4.a Background corrected NaI(Tl) spectra counts are manually summed over broad peaks, generally over the 50 keV to 2000 keV region of interest.

14.1.4.b Spectra from HPGe spectrometry are analyzed for net peak area above the Compton background often using numeric methods that incorporate the assessment of peak shape and peak overlap but manual integration methods are sometimes used when the photopeak is well-resolved from others [10 & 11].

14.1.4.c For each instance when software is changed, it is verified by comparing computational results against previously validated results and the change is recorded in the instrument's log book, which is located with the instrument and is accessible to all staff. The instrument log books notes the current software version being used or acceptable for use.

14.1.5 Gamma Ray Data Computations

14.1.5.a The NaI(Tl) net region of interest count rates for each peak from the replicate samples are compared using a Normal Probability Plot to evaluate the normality of the distribution of the data. When the probability plot correlation coefficient is greater than the statistical critical value, it is judged that the data distribution is consistent with a normal distribution and that the energy window's heterogeneity can be estimated using its relative standard deviation.

14.1.5.b Massic activity determinations from the HPGe spectra are determined from the appropriate formula that includes contributions from the net peak counts, counting time, blank correction, mass of the sample, calibration based on the spiked standard sample, emission probability, and radioactive decay from the reference date. Uncertainties in the massic activities are propagated from the uncertainties in each component of the formula used to calculate them.

14.2 Alpha- and Beta-particle Emitting Radionuclide Measurements:

14.2.1 Isotope Dilution.

14.2.1.a Measurement of alpha-particle emitting radionuclides requires radiochemical separation and purification from the host matrix prior to measurement. The generally complicated chemical purification steps that are used result in varying degrees of loss of the target radionuclides. Addition of a known amount of an isotope of extremely low abundance (isotope dilution) into the sample matrix provides a means for monitoring the loss of the analyte during the chemical processing steps.

14.2.1.b The fundamental requirement is that the added traceable SRM isotope be chemically and physically equilibrated with the analyte radionuclide prior to any losses. The first step of this requirement is generally satisfied by total dissolution of the sample in an appropriate solvent (usually an acid solution) containing the tracing isotope (also called "tracer"). Further steps are necessary to ensure chemical equilibrium of analyte and tracer after dissolution and most often include the use of strong oxidizing or reducing agents

14.2.1.c Losses of pure beta-particle emitting radionuclides, such as ^{90}Sr, can be traced using isotopes such as ^{85}Sr. Alternatively, addition of a known amount of the non-radioactive element of interest can be used as a "chemical yield monitor". Stable (non-radioactive) strontium is used to trace the ^{90}Sr losses during chemical purification steps. The amount of stable strontium recovered at the end of the radiochemical procedure is gravimetrically compared to the known amount originally added at the beginning of the procedure to determine the chemical yield. A correction to the amount of recovered stable element at the end of the chemical procedure is needed when the sample contains any of the stable elements in the matrix.

14.2.2 Alpha- and Beta-particle Measurement QC.

14.2.2.a As in the case of gamma-ray spectrometry, it is necessary to ensure that the radioactivity measurement instrumentation is functioning correctly. This can be done by measurement of known “check sources” with reproducible geometry and predictable alpha and beta emission rates (e.g., have a stable physical/chemical form and can be decay-corrected). For example, electrodeposited sources containing deposits of long-lived actinides (e.g., ^{232}Th, ^{230}Th, natural U, ^{237}Np, ^{238}Pu, ^{239}Pu, ^{240}Pu, ^{241}Am, ^{243}Am, ^{243}Cm, ^{244}Cm), either singly or in combination, can be used to examine the response of solid-state Si alpha-detectors and their associated electronics in terms of count rate (in a reproducible geometry), energy calibration, signal resolution and sometimes detection efficiency (if the source activity is well-known). Blanks are measured for long periods (weeks – month) when samples are not being measured to observe any changes in the so-called background spectrum that might be associated with contamination of the detector and/or counting chamber.

14.2.2.b Similarly, for beta-particle measurements with a gas-flow proportional counter, $SrCO_3$ sources containing ^{90}Sr in radioactive equilibrium with its ^{90}Y daughter are useful for establishing the long-term beta proportional counter behavior and especially to identify significant deviation from normal operation. Blank sources (e.g., membrane filter with or without $SrCO_3$ prepared from Sr carrier solution) are measured regularly to check for possible contamination of the detectors and source holders.

14.2.2.c Liquid scintillation counting (for ^{3}H, ^{14}C, ^{90}Sr/^{90}Y, ^{99}Tc, ^{241}Pu) QC is managed with commercially available sealed liquid scintillation vials with cocktails containing ^{3}H, ^{14}C and blank material.

14.3 Inductively Couple Plasma Mass Spectrometry Measurements:

14.3.1 Isotope Dilution.

14.3.1.a Mass spectrometric analysis of radionuclides frequently requires radiochemical separation and purification from the host matrix to maximize detection efficiency and to prevent isobaric interference from other elements. The generally complicated chemical purification steps that are used can result in varying degrees of loss of the target radionuclides. Addition of a known amount of an isotope of extremely low abundance (isotope dilution) into the sample matrix provides a means for monitoring the loss of the analyte during the chemical processing steps.

14.3.1.b Mass spectrometric techniques are used to make accurate and precise measurements of the relative proportions of isotopes of the element for which an isotopic spike was added. Based on the known quantity of added spike and the ratio of spike to sample isotopes the original amount of the target isotope in the sample can be calculated.

14.3.2 Elemental mass fraction analysis: inductively couple plasma – mass spectrometry (ICP-MS) can be used to determine the element mass fraction of many major and trace constituents of a Bulk Matrix SRM. There 2 primary methods for these analyses: standard addition and external calibration.

14.3.1.a Standard addition analysis requires the complete dissolution of the SRM material, then several aliquot of the dissolved solution are taken and different quantities of a known amount of a target element are added to the aliquots. These aliquots are analyzed along with an undoped aliquot and the amount of target element is determined by a regression through the instrument signal intensity response for the element versus the proportion of unknown sample to added target element.

14.3.1.b External calibration mass fraction determinations are performed by creating a set of sample solutions with known but different amounts of target elements (and if possible a matched dissolved matrix) and analyzing those solutions to generate a signal intensity versus element concentration curve. The unknown is then analyzed and compared to the response curve to determine the mass fraction of the target element(s) in the unknown.

14.4 Micro X-ray Fluorescence Measurements (micro-XRF): This technique is a nondestructive technique, advantageous for pre-digestion characterization of samples.

14.4.1 Elemental Analysis.

14.4.1.a Micro-XRF derived homogeneity characterization: Micro XRF can be used to assess the heterogeneity of a material. A particulate sample is pressed into a pellet (preferable) or sandwiched into a special Mylar-covered holder to present a flat surface to the incident X-rays. The calibrated instrument analysis routine is set to take a ~10,000 spatially-random set of analyses. Every pixel contains an X-ray spectrum from which elemental concentrations per pixel are extracted. A principal component analysis (PCA) is performed and, using estimated X-ray penetration thicknesses verses the calculated homogeneity, a minimum sample size per element is calculated. The calculated minimum sample size of the most heterogeneous element desired to be certified is the minimum sample size for further bulk characterization.

14.4.1.b Bulk Elemental characterization: The micro-XRF elemental analysis can be also used to certify the elemental composition of a bulk material. Using methodology from NIST Special Publication 260-172 (which has been used to certify SRM 2709a, 2710a, and 2711a), the elemental concentration of major and minor elements can be characterized. This methodology is usually used a secondary method of characterization (except for major elements), as mass spectrometric results are more robust and produce lower uncertainty.

14.5 Sample Dissolution: It is necessary to achieve complete dissolution of the Complex-Matrix SRM for most analysis routines including for radiochemical separations for counting measurements, isotope dilution, measurements, and ICP-MS measurements. There are 3 primary dissolution techniques used for Complex-Matrix SRMs: high temperature molten salt fusion; acid dissolution; and microwave-assisted acid dissolution. The method or combination of methods used is dependent on the nature of the Complex-Matrix SRM material and in some cases the elements or nuclides of interest for analysis [12-16].

14.5.1.a The sample matrix (e.g., a mineral or inorganic remainder from ignition) is mixed with a selected salt “flux” (both typically in powder form) in a crucible or dish (e.g., platinum, graphite or zirconium) and subjected to temperatures at which the flux melts (often ~1000°C) by means of an electric muffle furnace or gas-fired torch. Under proper conditions, the molten flux dissolves the sample completely. Isotope dilution tracers and carriers are added as chemical yield monitors to the sample-flux mixture before the fusion takes place. This method is especially useful in the decomposition of refractory materials which dissolve only slowly and with difficultly in hot, concentrated acids.

14.5.1.b Sample size can be as much as 10g, although smaller amounts are more easily managed. The resulting fusion cake, after cooling, is then dissolved to produce an aqueous solution from which the radionuclide(s) of interest must be chemically separated after radiochemical equilibrium of analytes and tracers has been achieved (see 14.2.1).

14.5.2 Acid dissolution (e.g., $HF + HNO_3 + HClO_4$, or $HNO_3 + HCl$)

14.5.2.a This method of sample decomposition uses hot, concentrated acids to dissolve the sample matrix and analytes. Isotope dilution tracers and carriers are introduced at the beginning of the sample digestion as chemical yield monitors. Often several different acids are used successively or in combination. Hydrofluoric acid (HF) is well known for its ability to dissolve silica and refractory oxides of transition metals and actinides. Hydrochloric and nitric acids are commonly employed. Conversion from a hydrochloric acid solution to a nitric acid solution can be achieved by several successive evaporations with added excess nitric acid. The reverse process (conversion from nitric to hydrochloric) can be accomplished similarly by successive evaporations with added excess hydrochloric acid.

14.5.2.b An advantage of the acid dissolution method is the ability to remove excess acid by evaporation. For samples with high silica content, several evaporations with concentrated HF can remove a large fraction of the silica as the volatile silicon tetrafluoride. However, complete dissolution of 10g of a complex matrix (e.g., soil ash) often requires many successive digestions over extended time periods (days). Some material may fail to dissolve and would require additional assay (e.g., by molten salt fusion) to determine if it contains significant analyte of interest. Final solutions must be treated to ensure radiochemical equilibrium of analytes and tracers before undergoing chemical separation operations.

14.5.3 Microwave dissolution

14.5.3.a Samples difficult to digest via open beaker or which molten salt fusion would introduce unacceptable impurities can be dissolved via microwave digestion. The user places the powdered analyte and reagent (for example, nitric acid, hydrofluoric acid, and a small amount of boric acid to dissolve a silica rich sample) into a Teflon lined cell. The mixture is heated via microwave in a programmed (monitoring time, power, temperature, and pressure) sequence to digest the material under high temperature and pressures.

14.6 Radiochemical Separations:

14.6.1 Radiochemical separations are developed specifically for each natural-matrix SRM analysis [17-25]. The objective of the separation process is to produce counting sources of high radionuclide purity or highly purified samples for mass spectrometric analysis. To achieve this objective, a series of element-specific chemical steps are employed that can include co-precipitation, solvent extraction, chromatography, ion exchange, and redox techniques. The effectiveness of the separation procedure is monitored by the isotopic purity of the resulting measured alpha- or gamma-spectrum, confirmation of radioactive half-life for pure beta-emitters, or through yield monitors. An overall validation of the procedure is done by running control samples of reference materials of similar matrix with well-known massic activities of the radionuclides of interest.

14.6.2 A radiochemical blank is typically included with each batch of samples. The blank samples consist of all tracers, chemical yield monitors, and chemicals (except for the matrix material), and are subjected to the same radiochemical processing and measurement as the matrix samples.

14.6.3 Radiochemical blank samples (i.e., all components other than the original matrix material) are used to determine the amount of analyte contributed by the chemical reagents and physical processes used. Corrections for this amount of analyte radionuclide in the gross radionuclide determinations from the matrix samples are needed to determine the analyte radionuclide content from the sample exclusively.

14.7 Measurement Sample Preparation for Radioactivity/Amount Measurement:

14.7.1 Purified alpha-emitting radionuclide solutions are prepared for counting by either electrodeposition [26a,b] or micro co-precipitation methods [27a,b]. In general, electrodeposition of the alpha-emitting radionuclides is preferred on the basis of its usually better spectral resolution. On the other hand, some counting sources (e.g. americium) are often prepared by micro co-precipitation because of the added selectivity introduced by the fluoride precipitation step.

14.7.2 Purified ^{90}Sr is precipitated with stable strontium carrier as strontium carbonate, filtered on a washed and pre-weighed filter, washed with distilled water and 95 % ethyl alcohol, vacuum dried, weighed to determine the Sr chemical recovery, center-mounted on 5 cm steel disc, and covered with a ¼-mil Mylar film [28].

14.7.3 Sample preparation for analysis by ICP-MS is dependent on the type of measurements being performed. Sample preparation for isotopic ratio measurements, standard addition measurements, and externally calibrated elements measurements are somewhat different.

14.7.3.a For determining the isotopic ratio of a target element for isotope dilution mass spectrometry (IDMS) or to quantify the relative activity contribution of isotopes of an element (e.g. ^{239}Pu and ^{240}Pu) it is generally necessary to perform careful radiochemical separations (See section 14.6) to obtain relatively pure solution containing the target element. The purified element is dissolved in an appropriate carrier solution (2% HNO_3 or 2% HNO_3 and 0.05% HF) and, if necessary, diluted to a concentration suitable for measurement (typically ≤ 1 to 2 ppb of target element).

14.7.3.b For standard addition, similar sized aliquots of dissolved sample are prepared by dissolving them in an appropriate carrier solution and then adding different but known amounts of the target element to each sample. The samples are diluted to the same proportion of sample to final mass/volume of solution and to a concentration appropriate for analysis.

14.7.3.c For externally calibrated elemental analysis an aliquot of the sample is prepared in the appropriate carrier solution and diluted to a concentration (or more often concentrations) suitable for analysis of major or trace elements.

14.7.3.d For all three analysis methods the solutions may be spiked with known amounts of an element such as indium or rhodium to allow for monitoring of ionization efficiency and instrument drift during or between analyses.

14.7.4 Sample preparation for analysis by XRF analysis depends upon the characteristics of the sample.

14.7.4.a A reliable technique, if the sample will remain cohesive, is to press it into briquettes using a hydraulic press and sample dies. The goal is to present the X-ray beam with a compact material with a homogeneously flat surface.

14.7.4.b A secondary sample preparation technique is to carefully sandwich the samples into a plastic cup with Mylar surface. As with pressing particulate samples into briquettes, the goal is to create a homogenously smooth surface that is also calculated to be infinitely thick to the beam (please refer to the SOP for more information).

14.7.4.c Another sample preparation method involves creating a solid fused surface, for example through borate fusion. The sample, which should be quite homogeneous as it is digested first, is ground flat to present the beam with a flat surface.

14.7.4d Other sample types (solids, chips, thin films, foils, liquid-soaked filter paper) are also possible if care is taken to be certain that the instrument will not be contaminated, and that the measurement will be repeatable and under calibration.

14.8 Instrumentation, Counting, and Measurements:

14.8.1 Alpha-emitting sources for counting are measured under vacuum and typically in close geometry (< 10 mm) to ion-implanted, planar silicon detector spectrometers [28]. Measurement times are dependent on the signal strength of the source. Energy calibrations of each alpha detector are determined by counting sources of alpha-emitting radionuclides with well-known alpha-particle emission energies. In most cases, no absolute detector efficiency determinations are needed because of the use of an isotopic alpha-emitting dilution tracer. Extended detector background measurements are made prior to and after measurements.

14.8.2 Strontium-90 beta-particle emitting counting sources have traditionally been measured using thin-window, gas-flow proportional counters [29-31]. Sources are typically counted continuously for approximately two weeks, with counting data stored in electronic files on a periodic basis to observe the in-growth of the ^{90}Y daughter. Measurements are made after the ^{90}Y daughter has reached radioactive equilibrium with its ^{90}Sr parent. Often measurements are performed 1 year or more later to confirm that the beta activity is decaying in accordance with the known ^{90}Sr half-life (a test of radioactive purity). Each detector is calibrated using a set of strontium carbonate standards containing ^{90}Sr in equilibrium with ^{90}Y in the same geometry as counting samples. The set of $SrCO_3$ standards are of varying masses, to determine the appropriate counting efficiency as a function of source mass for sample sources. Extended detector background measurements are made prior to and after measurement of samples.

14.8.3 Alternatively, liquid scintillation counting methods of ^{90}Sr analysis can be used which offer some advantages over the proportional counting method (e.g., nearly 100 % counting efficiency for both ^{90}Sr and ^{90}Y) but may suffer from higher background rates.

14.8.4 ICP-MS measurements are performed using the Element 2, a mass spectrometer with a double-focusing magnetic sector mass analyzer and a single secondary electron multiplier detector. Operating parameters (gas flows, ion optics, RF power, etc.) are checked prior to measurement and adjusted when needed to ensure sensitivity and stability. In cases where the instrument has been run recently, typically only minor modifications are necessary. Samples are to be diluted to a mass fraction of approximately 1 ng g^{-1} or less for the target analytes using 2% (*v*/*v*) nitric acid where possible to ensure that the detector can operate in pulse-counting mode and in the range of signal intensity where response increases approximately linearly with concentration. Signal intensities are measured using ratios (most abundant sample and spike isotopes for IDMS, relative to an internal standard such as ^{115}In for other methods) to correct for drift in signal intensity. When deemed necessary, sample introduction methods including use of a desolvating nebulizer and/or Peltier cooling of the sample introduction are used to reduce polyatomic ion formation and enhance sensitivity.

14.8.4.a In Low Resolution mode, where the peak shape is flat-topped, typically the list of m/z values is scanned through quickly, acquiring only one data point for each peak to minimize the elapsed time between any two measurements. Typically, dwell times of 10-20 ms are used for peaks with strong signals, although comparatively weak peaks may be measured for longer periods. The brief integration time on any one run through the scan list is counterbalanced by acquiring a large number of measurement cycles for each sample.

14.8.4.b In Medium and High Resolution modes, the peak shape is not flat-topped, but closer to triangular in shape. A single measurement point for each peak is not adequate in this case; instead the entire area under the peak must be integrated. For this reason, the higher resolution modes are not typically used unless there is an interfering species that cannot be resolved or corrected for while measuring in Low Resolution mode.

14.8.5 Micro X-ray Fluorescence

14.8.4.a Samples, whether for heterogeneity analysis or for elemental characterization are analyzed under vacuum, if possible, to reduce blank. The instrument must be calibrated before measurement using written instrumental protocols and results (and corrections) noted. For heterogeneity analysis, 5-10 k random points are analyzed to reduce spatial-drift effects, and a modified PCA method determines minimal sample size. For elemental analysis, raster imagery is possible to access hot spots, but data must be drift-corrected to determine the elemental mass fraction for each element.

14.9 Data Analysis: Peak Deconvolution Analysis, Interferences, Corrections:

14.9.1 Alpha spectra are analyzed for net peak area above the background using manual and numeric methods that incorporate the assessment of peak shape and peak overlap. Care is taken to account for radioactive impurities detected in the spectrum when determining the net peak areas.

14.9.2 Most often the beta measurements taken when ^{90}Y is in equilibrium with ^{90}Sr are used for the ^{90}Sr activity evaluation. As a test of the radioactive purity, the ^{90}Sr/^{90}Y in-growth curve may be evaluated using the two component Bateman solution to the parent-daughter system [32-34]

14.9.3 Analysis of ICP-MS data requires accounting for possible isobaric interferences. These include both atomic isobars and polyatomic compounds formed *in situ* while the sample is introduced to the ICP-MS. Typically, these interferences are corrected by measuring another isotope of the interfering element in the case of atomic isobars, which cannot be resolved even in High Resolution mode. Corrections for polyatomic species often require experimental determination of the hydride or oxide formation rate for the offending element under the experimental conditions, or else changing to a higher resolution to resolve the target peak from its interference. When high precision isotope amount-ratios are required, mass fractionation must be corrected, typically by either normalizing to a known isotope amount-ratio for the element being analyzed, or by the use of isotopic reference materials as standards to determine empirical correction factors. Acid blanks are usually run prior to each sample; additionally, process blanks and/or matrix-matched process blanks are run when deemed necessary. Provided there is no significant process blank, the acid blank measured prior to each sample is used to perform the correction; if the process blank is significant, a correction for this quantity is applied as well.

14.9.4 Quantitative Micro-XRF data must undergo background, calibration, and drift corrections. Furthermore, it is advantageous to analyze a complex (natural matrix) SRM for further potential elemental corrections. As the Micro-XRF delivers elemental—not isotopic—data, no reference date corrections generally apply.

14.10 Final Value Computation:

14.10.1 Massic activity determinations from the alpha spectra are derived from the measurements taking into consideration the net peak counts, counting time, blank correction, activity of the tracer added to the sample, impurity corrections, emission probability, and radioactive decay corrections from the reference date.

14.10.2 Massic activity determinations from the ^{90}Sr data are derived from the measurements taking into consideration the net counts, counting time, blank correction, Sr chemical yield (e.g., determined from the amount of stable Sr carrier initially added to the sample), impurity corrections, emission probability, counting efficiency calibrations, and radioactive decay corrections from the reference date.

14.10.3 Determination of the final mass fraction value obtained from ICP-MS measurements involves application of a number of corrections and attendant uncertainties. Corrections for blank and interfering peaks are applied to individual measurements. Uncertainties for blank and interference corrections are then added after the fact. Further corrections must be applied in some cases, including for dark noise (spurious counts due to electrical noise in the detector), for the tails of more abundant adjacent peaks, and, when necessary, for cross-calibration of values measured in counting mode and analog mode.

14.10.3.a For IDMS experiments, the value is determined from the mass and concentration of the spike solution, the mass of the unknown solution, the isotopic compositions of the spike solution and the unknown solution, and finally the measured isotope amount-ratio (after accounting for mass fractionation and the various corrections described above) for the sample-spike mixture.

14.10.3.b For standard addition and external calibration measurements, the same corrections are applied to the instrument output. Value determination is then based on a linear regression of the external calibration curve, or in the case of standard addition, on the x-intercept of a linear regression through the signal intensities of the unspiked sample and the spiked sample solutions.

14.10.4 Micro XRF calibration curves depend upon the instrument X-ray tube used (W or Rh), and the line used (K, L, or M—the selection which depends upon the element's characteristics and interferences), and element choice. Depending upon element, either gross or net counts are used. Data is deconvoluted to calculate the mass fraction of each element. Final values depend upon using other methods to determine or estimate the light elements for which the micro-XRF is less sensitive (for example, F, O, N, and C) or the micro-XRF simple cannot measure (B, Be, Li, and gases like He, and H.

15.0 *Interlaboratory Comparison Data and Statistical Analysis*

15.1 Resulting data from participating laboratories are carefully evaluated for systematic bias and material heterogeneity with the full participation of NIST's Statistical Engineering Division (SED) [5]. All data are accepted as valid unless there are strong scientific reasons that justify treating any identified datum as an outlier for rejection. The protocol for data evaluation for each radionuclide typically includes the following considerations:

15.1.1 Data normalization.

Reference Date
Units
Expanded Uncertainty

15.1.2 Data Screening.

≥ 3 Laboratories
Between-Laboratory Mean and Uncertainty (Mean Plot)
Between-Laboratory Data Distribution (Normal Probability Plot)
Distribution of Lab Means (Normal Probability Plot)
Resolve Interlaboratory Method Discrepancies
Laboratory Homogeneity (Normal Probability Plot)

15.1.3 Data Certification.

Combined Data (Normal Probability Plot)
Bottle Number Heterogeneity (Curve Fitting)
Sample Size (*F*-Test)
Between-Bottle vs. Within Bottle Heterogeneity (*F*-test, ANOVA)
Distribution: Probability Plot Correlation Coefficient (PPCC)
Define Purposes for Material Use: Mean (e.g., Methods Development/validation), Tolerance (e.g., Proficiency Testing)
Bootstrap: Robustness Testing and data distribution characterization
Uncertainty Summary, including heterogeneity
Mean or median (depending on the data distribution characteristics)

16.0 *Certified and Uncertified Radionuclide Values:*

16.1 The protocol for evaluation of the interlaboratory comparison data had been carefully developed over the history of the SRM program e.g., [6 and 35] in collaboration with the NIST Statistical Engineering Division. Acceptable data from a minimum of three laboratories are required to provide sufficient confidence for radionuclide massic activity certification. When there are statistically significant discrepancies among data sets, an "uncertified" mean value is provided, for information only, on the certificate.

16.2 The major evaluation issues that the radionuclide certification protocol focuses on include:

16.2.1 Systematic difference among analytical methodologies.

16.2.2 Consistency among the distributions of results from each laboratory

16.2.3 Characterization of the distribution of the pooled results (including material heterogeneity and minor interlaboratory biases) by characterizing the mean or median value with its uncertainty.

16.3 While normal probability plots allow identification of discrepant laboratory results, it is only through extensive personal contacts with the laboratory and additional constrained experiments that these discrepancies can be revealed and resolved.

16.4 Once the data are carefully screened, probability plot correlation coefficients are used to evaluate the robustness of characterizing the data with a number of distributional models and their family members. The criterion for the robustness of the data characterization is convergence of fit simulations, i.e., nearly identical results for the estimated mean and tolerance limit values, independent of the fit model chosen

17.0 *Establishing Traceability*:

17.1 Each participating laboratory establishes traceability to the SI through appropriate calibration of instruments and the use of gravimetrically diluted and verified tracers obtained from NIST SRMs, other National Metrology Institute Certified Reference Materials (CRMs), or NIST-traceable commercial providers.

17.2 For Complex-Matrix SRMs the necessary measurements for characterization include:

17.2.1 Sample Mass
17.2.2 Radionuclide(s)
17.2.3 Massic Activity(ies) (or in some cases, mass fraction)
17.2.4 Expanded Uncertainty(ies),
17.2.5 Reference Time

17.3 Associated measurements made at NIST as part of the calibration of a Complex-Matrix SRM are traceable as follows:

17.3.1 Mass - Balances and scales used to measure the mass of the SRM are serviced and calibrated at least once per year using masses (weight sets) directly traceable to NIST.

17.3.2 Time - Measurements of clock time are made using direct time transmissions from NIST Boulder. Counting time increments obtained with calibration instruments are measured by counting the number of cycles from temperature compensated crystal oscillators whose frequencies are measured using a frequency meter traceable to NIST.

17.3.3 Temperature / Pressure / Relative Humidity - The manufacturer's stated accuracy for instruments used to measure temperature, pressure and relative humidity are sufficient.

17.4 Radionuclide Measurement Duration: The determination of activity requires that the number of radioactive decays that occur during a finite time interval be counted. If practical, a time interval will be chosen so as to minimize its uncertainty contribution.

17.5 Sample yield for radiochemical processing: For accurate measurement of the radioactivity (alpha and beta emissions) or mass fraction of radionuclides it is often necessary to perform extensive radiochemical separations of the target elements from the Complex-Matrix material and to create specially prepared measurement sources. These processes can result in variable losses of the target nuclides. The relative proportion of material successfully measured to the amount initially present referred to as the yield. Yield is monitored by use of certified nuclide tracers (i.e. isotope dilution), by mass (carrier recovery), or by quantification of yield for reproducible processes using other certified standards.

17.6 Detector efficiency for the radioactive decays: Every radioactivity detector has some intrinsic inefficiency, has a finite size (and hence boundaries), cannot detect radioactive decays that deposit less than some minimum amount of energy in the detector (threshold), and gives some count rate even in the absence of radioactive decays in the source (background count rate). The efficiency of a single detector (decays detected/total decays) must be verified using well established theoretical methods [36, 37, and 38], prepared test material with known activity, or by use of a yield monitor.

18.0 *Attribute Uncertainty*

18.1 Measurement uncertainty is evaluated in accordance with the *Guide to the Expression of Uncertainty in Measurement* [39] and the *Guidelines for Evaluating and Expressing the Uncertainty of NIST*

Measurement Results [40]. The bootstrap method [41] has been used to estimate the uncertainty for the Complex-Matrix SRM radionuclide's certified massic activities produced thus far. Appropriate methods for SRMs currently in development are to be determined in consultation with SED.

19.0 *Certificate.*

19.1 Before a final certificate is issued for each natural matrix SRM, there is an official technical review by persons familiar with the scientific aspects of the radioactivity measurements and with the statistical evaluation of the results obtained by the participants in the interlaboratory exercise. Prior to issuance, the certificate undergoes a final technical review. The technical review must be approved (and signed) by the principal investigator, RG leader, the RPD chief and the SRM coordinator. An example of an approval form for the internal technical review of the SRMs is given in Appendix B.

19.2 The NIST Certificate for a Complex-Matrix SRM is intended to conform with the requirements of ISO 17034. The certificate contains information about the composition, the properties, and the proper use of the SRM, and additional required information as stated in NIST-QM-I. For an example of a previously issued certificates, see Appendix C. Information on the SRM certificate typically includes:

19.2.1 SRM number (inclusive of batch number) and name
19.2.2 Description of the SRM and the intended and correct use of the material
19.2.3 Unit mass
19.2.4 Reference time
19.2.5 Parties responsible for the preparation of material
19.2.6 Source and preparation of the material
19.2.7 Instructions for preparation
19.2.8 Radionuclide leachability
19.2.9 Application of the certified values
19.2.10 Uncertainties
19.2.11 Heterogeneity determinations
19.2.12 Notice and warning to users
- Stability and expiration of certification (period of validity)
- Radiological hazards
- Storage and handling

19.1.13 Contact persons
19.1.14 Certified massic activities for radionuclides and uncertainties
- Radionuclide
- Certified value + U (Bq g^{-1})
- Number of assays
- Half lives used
- Methods
- Contributing laboratories

19.1.15 Notes
- Analytical methods
- Participating laboratories

19.1.16 Uncertified massic activities
19.1.17 Semi-quantitative trace element analysis
19.1.18 Major elements recalculated as oxides

20.0 *Label, package, and store the SRM containers.*

20.1 As part of the production process, additional packaging may be placed around the container for the radioactivity SRM.

20.2 When shipping additional packaging is placed around the container. This packaging is designed to protect the SRM during handling.

20.3 For those complex-matrix SRMs that are considered radioactive for shipping purposes, the US Department of Transportation (USDOT) and the US Nuclear Regulatory Commission (USNRC) require that personnel that label and package radioactive material for shipping be certified to do so. USDOT certification is available through training by the NIST GRSD.

20.4 The Office of Reference Material (ORM) provides support services in the production and delivery of SRMs. These services include: label research and design, SDS development for the SRMs, pricing for materials, order processing, and documentary support necessary for delivering the SRMs

21.0 *Collect and store the production records.*

21.1 The primary record of the radioactivity SRM production plan, detailed descriptions of the certification methods and procedures, methods of validation, measurement uncertainty, and sampling plans are archived together in individual file boxes.

21.2 These documents and records are stored in SRM Records Storage Room.

21.3 The production information is retained for as long as the SRM is available for sale to the public, plus at least an additional 10 years.

21.4 A list of the typical contents of the Record File is presented below:

21.4.1 Preparatory

- Justification for SRM production. This is a simple statement as to why the SRM is being produced; e.g., reissue of previous one, new demand for new one and justification, etc. The SRM coordinator can assist in the justification.
- Funding request to and approval from the SRM Program Office. This is largely handled by the SRM coordinator.
- Approval for acquisition and use of radioactive materials by GRSD (NIST 364).
- Description of the experimental design/plans (i.e., list, table, diagrams, outline, flowchart, etc.), which may include measurement methods, sequence of steps to be used, facilities, equipment, supplies, personnel, counting source preparation details, etc.
- Production approval by SRM coordinator, including number to be produced, activity levels, composition, etc.
- Purchase order for radioactive material (if necessary).
- Acquisition of material explanation (if not purchased).

21.4.2 Production (as applicable)

- Any relevant technical information of the material provided by the manufacturer or from previous production.
- Material Safety Data Sheet (MSDS; if material presents a physical, chemical or biological hazard).
- Preparation of carrier solution data (if applicable).
- Preparation of master solution or mixture data (if applicable).
- Dispenser test data (if applicable).
- SRM dispensing data (if applicable).

- Statement of SRM sterilization and independent documentation if available (e.g., radiation sterilization for natural matrix SRM).

- Preparation of counting sources/samples data (if applicable).

21.4.2 Data and Analyses (for standardization). Analytical records used for a project shall be sufficiently detailed to repeat analyses, investigate discrepancies, troubleshoot methodologies, and should include:

- Principal investigator’s name.
- Appropriate project identification.
- Description of the type of item to be tested or calibrated.
- Parameters or quantities and ranges to be determined.
- Equipment, including technical performance requirements.
- Reference standards and reference materials utilized.
- Environmental conditions during work and record of any stabilization period needed. - Description of the procedure, including:
  - checks to be made before the work is started;
  - checks that the equipment is working properly;
  - Where required, calibration and adjustment of the equipment before each use;
  - the method of recording the observations and results.
  - criteria and/or requirements for approval/rejection;
  - notations of any equipment and instruments settings (as needed)

- Hardcopies of all data analysis records (electronic version is acceptable to include, but hardcopy is needed), including all analysis software output, all spreadsheets, all summary tables, graphs, etc.

- Any calculations performed, e.g., for corrected masses, solution composition, decay corrections, decay-corrected K values for appropriate RRS (see RPD Procedure 01), LS detection efficiencies, etc.

- Explanation of any calculation assumptions.

- Uncertainty analysis records (including basis, assumptions, and derivations as needed).

21.4.2 Certification and Transfer

- Summary statement(s) – in short paragraph or tabular form-- regarding the basis for the certified values and how they were determined.

- Production/calibration schedule of all principal steps (from the initial design and lab set up through the certification) with a listing of the responsible person(s) and dates.

- All the drafts of the certificate and revisions (see NIST-QM-I for everything that the certificate must contain at a minimum).

- Packaging information and a sample of the SRM label.

- All packaging inserts; user notes, MSDS, etc.

- Technical review sheet (signed).

- Transfer form(s) to SRM stock or inventory control. This is largely handled by the SRM coordinator.

References

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Appendix A1: Complex-Matrix Radionuclide Standard Reference Materials

	SRM 4350B	**SRM 4351**	**SRM 4352**	**SRM 4353A**
Complex-Matrix	Powdered river sediment	Freeze dried human lung	Dried & ground human liver	Dried and powdered soil
Unit Mass	85 g	45 g	45 g	75 g
Unit Container	polethylene bottle	125 mL glass bottle	125 mL glass bottle	polethylene bottle
Sampling Size	≥ 5 g	45 g	45 g	5 g - 10 g and ≥ 30 g for γ
Special Storage	not applicable	store at ≤0 °C	store at ≤0 °C	not applicable
Expiration	indefinite	indefinite	indefinite	indefinite
Certified and Reported Radionuclides C = Certified Value *I* = Information Value				
Ac-228	---	---	---	---
Am-241	C	*I*	C	*I*
Bi-214	---	---	---	*I*
B1-212	---	---	---	---
C-14	---	---	---	---
Cm-242	---	---	---	---
Cm-244	---	---	---	---
Cm-243+244	---	---	---	---
Co-60	C	---	---	---
Cs-137	C	---	---	C
Eu-152	C	---	---	---
Eu-154	C	---	---	---
Eu-155	---	---	---	---
Fe-55	*I*	---	---	---
H-3	---	---	---	---
I-129	---	---	---	---
K-40	*I*	---	---	*I*
Np-237	---	---	---	---
Ra-224	---	---	---	---
Ra-226	C	---	---	*I*
Ra-228	---	---	---	C
Pb-210	---	---	---	C
Pb-212	---	---	---	*I*
Pb-214	---	---	---	*I*
Po-210	---	---	---	---
Pu-238	C	---	C	C
Pu-239+240	C	C	C	C
Pu-239	C	---	---	---
Pu-240	C	---	---	---
Pu-241	---	---	---	*I*
Sb-125	---	---	---	---
Sr-90	*I*	---	---	C
Tc-99	---	---	---	---
Th-228	*I*	*I*	*I*	*I*
Th-230	*I*	*I*	*I*	*I*
Th-232	*I*	C	*I*	*I*
Th-234	---	---	---	*I*
Tl-208	---	---	---	*I*
U-234	*I*	C	*I*	C
U-235	*I*	---	*I*	C
U-236	---	---	---	---
U-238	*I*	C	*I*	C
Certified Values	10	4	3	9
Info Values	9	3	6	12

	SRM 4354	**SRM 4355**	**SRM 4356**	**SRM 4357**
Complex-Matrix	Powdered lake sediment	Dried and powdered soil	Ashed human & bovine bone	Powdered ocean sediment
Unit Mass	25 g	75 g	15 g	85 g
Unit Container	polethylene bottle	polethylene bottle	glass bottle	polethylene bottle
Sampling Size	≥ 2 g	not specified	≥ 5 g	≥ 10 g
Special Storage	not applicable	not applicable	not applicable	not applicable
Expiration	indefinite	indefinite	indefinite	indefinite
Certified and Reported Radionuclides C = Certified Value *I* = Information Value				
Ac-228	---	---	*I*	---
Am-241	C	C	*I*	*I*
Bi-214	---	*I*	---	*I*
B1-212	---	---	---	---
C-14	---	---	---	---
Cm-242	---	---	---	---
Cm-244	---	---	---	---
Cm-243+244	---	---	C	---
Co-60	C	C	---	---
Cs-137	C	C	C	---
Eu-152	---	C	---	---
Eu-154	---	C	---	---
Eu-155	---	C	---	*I*
Fe-55	---	*I*	---	---
H-3	---	---	---	---
I-129	---	---	---	*I*
K-40	---	*I*	*I*	C
Np-237	---	---	---	*I*
Ra-224	---	---	---	---
Ra-226	*I*	---	C	C
Ra-228	---	---	*I*	C
Pb-210	*I*	---	*I*	*I*
Pb-212	---	---	---	*I*
Pb-214	---	---	---	---
Po-210	---	---	*I*	*I*
Pu-238	C	*I*	C	C
Pu-239+240	C	C	C	C
Pu-239	---	---	---	---
Pu-240	---	---	---	---
Pu-241	---	---	---	---
Sb-125	---	C	---	---
Sr-90	C	*I*	C	C
Tc-99	---	---	---	---
Th-228	C	C	*I*	C
Th-230	*I*	C	C	C
Th-232	C	C	C	C
Th-234	---	---	---	---
Tl-208	---	*I*	---	---
U-234	*I*	---	C	*I*
U-235	C	---	*I*	*I*
U-236	---	---	---	---
U-238	C	---	C	*I*
Certified Values	10	11	10	9
Info Values	4	6	8	11

	SRM 4358	**SRM 4359**	**SRM 4600**	**SRM 4601**
Complex-Matrix	Freeze dried shellfish	Freeze dried seaweed powder	Silicate glass powder	Silicate glass powder
Unit Mass	150 g	300 g	25 g	26 g
Unit Container	polethylene bottle	glass bottle	polyethylene bottle	polyethylene bottle
Sampling Size	≥ 30 g	≥ 10 g and ≥ 30 g for γ	to be deternined	to be deternined
Special Storage	not applicable	not applicable	not applicable	not applicable
Expiration	indefinite	indefinite	indefinite	indefinite
Certified and Reported Radionuclides C = Certified Value *I* = Information Value				
Ac-228	---	---	---	---
Am-241	C	C	---	---
Bi-214	*I*	---	---	---
B1-212	---	*I*	---	---
C-14	---	*I*	---	---
Cm-242	*I*	---	---	---
Cm-244	*I*	---	---	---
Cm-243+244	---	---	---	---
Co-60	---	---	---	---
Cs-137	C	C	---	---
Eu-152	---	---	---	---
Eu-154	---	---	---	---
Eu-155	---	---	---	---
Fe-55	---	---	---	---
H-3	---	*I*	---	---
I-129	---	*I*	---	---
K-40	C	C	---	---
Np-237	---	*I*	---	---
Ra-224	---	*I*	---	---
Ra-226	*I*	*I*	---	---
Ra-228	C	C	---	---
Pb-210	C	C	---	---
Pb-212	*I*	*I*	---	---
Pb-214	*I*	---	---	---
Po-210	---	C	---	---
Pu-238	C	---	---	---
Pu-239+240	C	C	---	---
Pu-239	---	C	---	---
Pu-240	---	*I*	---	---
Pu-241	*I*	---	---	---
Sb-125	---	---	---	---
Sr-90	*I*	*I*	---	---
Tc-99	---	*I*	---	---
Th-228	C	*I*	---	---
Th-230	C	*I*	---	---
Th-232	C	C	---	---
Th-234	---	*I*	---	---
Tl-208	*I*	---	---	---
U-234	C	C	C	C
U-235	C	C	C	C
U-236	---	---	---	C
U-238	C	C	C	C
Certified Values	13	12	3	4
Info Values	9	14	0	0

Appendix A2: Radionuclide measurement and balance equipment

Sodium Iodide Detectors:
12.7 cm (5 inch) NaI(Tl) detectors (245/C15) in operation; Detector “D” = 5 cm well, Detector “E” = 2.5 cm well

HPGe detectors, < 3 keV FWHM, in operation:
(245/C13) = Detector “K”, PGT model NIGC23185 [NIST #519933], n-type coaxial, 24 % efficiency relative to 3” x 3” NaI(Tl)
(245/C17) = Detector “P”, PGT model IGP510 [no NIST#]
(245/C17) = Detector “A”, Canberra model GR7023 [NIST #627278], p-type coaxial, 70 % efficiency relative to 3” x 3” NaI(Tl)

Alpha spectrometers (245/C13); <25 keV FWHM:
Seven EG&G Ortec 8-unit Octete alpha spectrometers [NIST #569445, 574836, 589621, 632424 and 627318 (3 Octetes)] in operation
Two EG&G Ortec 8-unit Octete alpha spectrometers [NIST #N103747 and N103747] awaiting installation

Gas-flow proportional counters (245/B001), low background (<0.5 cpm beta background) in operation:
Berthold model LB 770-2 [NIST #520379] 10-channel low-level counter
Three Protean model 9604 Ultra Low-Level α/β Counter units [NIST #619065 and 618773]

Liquid scintillation analyzers:
Perkin Elmer Quantulus 1220 Ultra Low Level Liquid Scintillation Spectrometer (245/C17) [NIST #640959] in operation
Two Ordela PERALS model 8100AB photon-electron rejecting alpha liquid scintillation spectrometers (245/C15), [NIST #646165] in operation and [NIST #647434] awaiting installation

Inductive Couple Plasma Mass Spectrometer:
Thermo Scientific Element II (245/C10).

Micro X-ray Fluorescence:
Bruker M4 Tornado (245/C10)

Laboratory Microwave System
Anton Paar Microwave Reaction System Multiwave Pro (245/C10)

Balances (all with yearly service and calibration using weights traceable to NIST):
Mettler-Toledo model AX26, 6-place, 22 g capacity, (245/B152)
Mettler model B6, 4-place, 100 g capacity, (245/C135) [NIST #95568]
Mettler-Toledo model XP205, 5-place, 205 g capacity, (245/C135) and (245/B152), [NIST #632835]
Mettler model B4C1000, 3-place, 1000 g capacity, (245/C135) [NIST #526540]
Voland model Jupiter, 3-place, 3000 g capacity, (245/B152) [NIST #526518]

Appendix B

TECHNICAL REVIEW – SRM CERTIFICATES

REVIEW THE ATTACHED DRAFT CAREFULLY. ANY SUGGESTIONS OR CHANGES SHOULD BE MADE ON THIS DRAFT FORWARD DRAFT AND APPORVAL RECORD TO THE NEXT INDIVIDUAL INDICATED.

RETURN TO: SRM Coordinator

SRM: XXXX

TITLE: Complex-Matrix Radionuclide Standard Reference Material

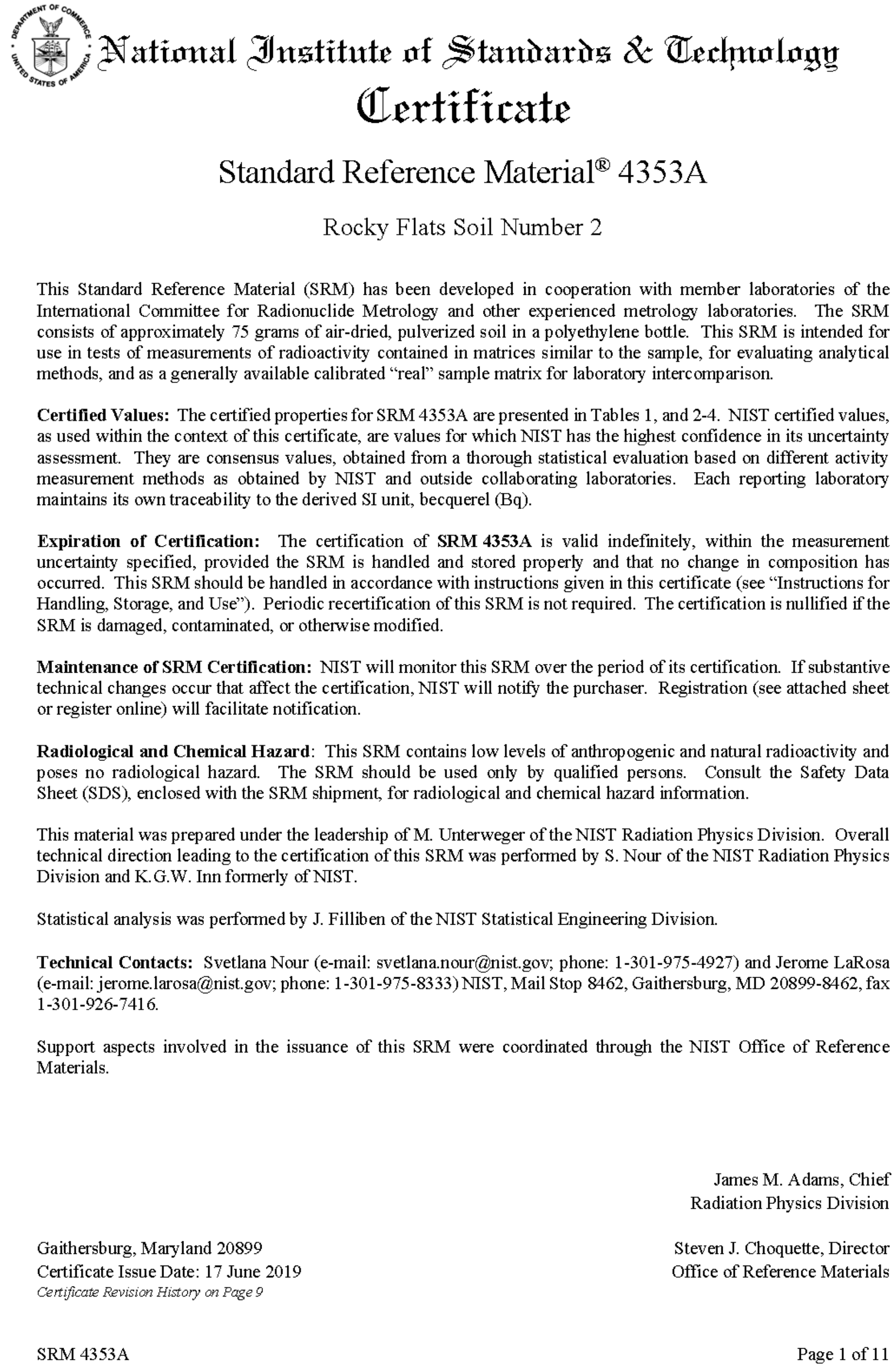
DATE: December 31, 1999

PROJECT MANAGER: Principal Investigator

TELEPHONE: XXXX

ROUTING				APPROVAL
NAME (REVIEWER)	BLDG ROOM	DIV. SEC.	INITIALS	DATE
P. Investigator	245 XXX	846 04		
Co-Investigator 1	245 XXX	846 04		
Co-Investigator 2	245 XXX	846 04		
Group Leader	245 XXX	846 04		
James Adams	245 XXX	846 00		
L. Laureano-Perez	245 XXX	846 04		
R. Collé	245 XXX	846 04		

Appendix C:



National Institute of Standards & Technology
Certificate

Standard Reference Material® 4353A

Rocky Flats Soil Number 2

This Standard Reference Material (SRM) has been developed in cooperation with member laboratories of the International Committee for Radionuclide Metrology and other experienced metrology laboratories. The SRM consists of approximately 75 grams of air-dried, pulverized soil in a polyethylene bottle. This SRM is intended for use in tests of measurements of radioactivity contained in matrices similar to the sample, for evaluating analytical methods, and as a generally available calibrated "real" sample matrix for laboratory intercomparison.

Certified Values: The certified properties for SRM 4353A are presented in Tables 1, and 2-4. NIST certified values, as used within the context of this certificate, are values for which NIST has the highest confidence in its uncertainty assessment. They are consensus values, obtained from a thorough statistical evaluation based on different activity measurement methods as obtained by NIST and outside collaborating laboratories. Each reporting laboratory maintains its own traceability to the derived SI unit, becquerel (Bq).

Expiration of Certification: The certification of **SRM 4353A** is valid indefinitely, within the measurement uncertainty specified, provided the SRM is handled and stored properly and that no change in composition has occurred. This SRM should be handled in accordance with instructions given in this certificate (see "Instructions for Handling, Storage, and Use"). Periodic recertification of this SRM is not required. The certification is nullified if the SRM is damaged, contaminated, or otherwise modified.

Maintenance of SRM Certification: NIST will monitor this SRM over the period of its certification. If substantive technical changes occur that affect the certification, NIST will notify the purchaser. Registration (see attached sheet or register online) will facilitate notification.

Radiological and Chemical Hazard: This SRM contains low levels of anthropogenic and natural radioactivity and poses no radiological hazard. The SRM should be used only by qualified persons. Consult the Safety Data Sheet (SDS), enclosed with the SRM shipment, for radiological and chemical hazard information.

This material was prepared under the leadership of M. Unterweger of the NIST Radiation Physics Division. Overall technical direction leading to the certification of this SRM was performed by S. Nour of the NIST Radiation Physics Division and K.G.W. Inn formerly of NIST.

Statistical analysis was performed by J. Filliben of the NIST Statistical Engineering Division.

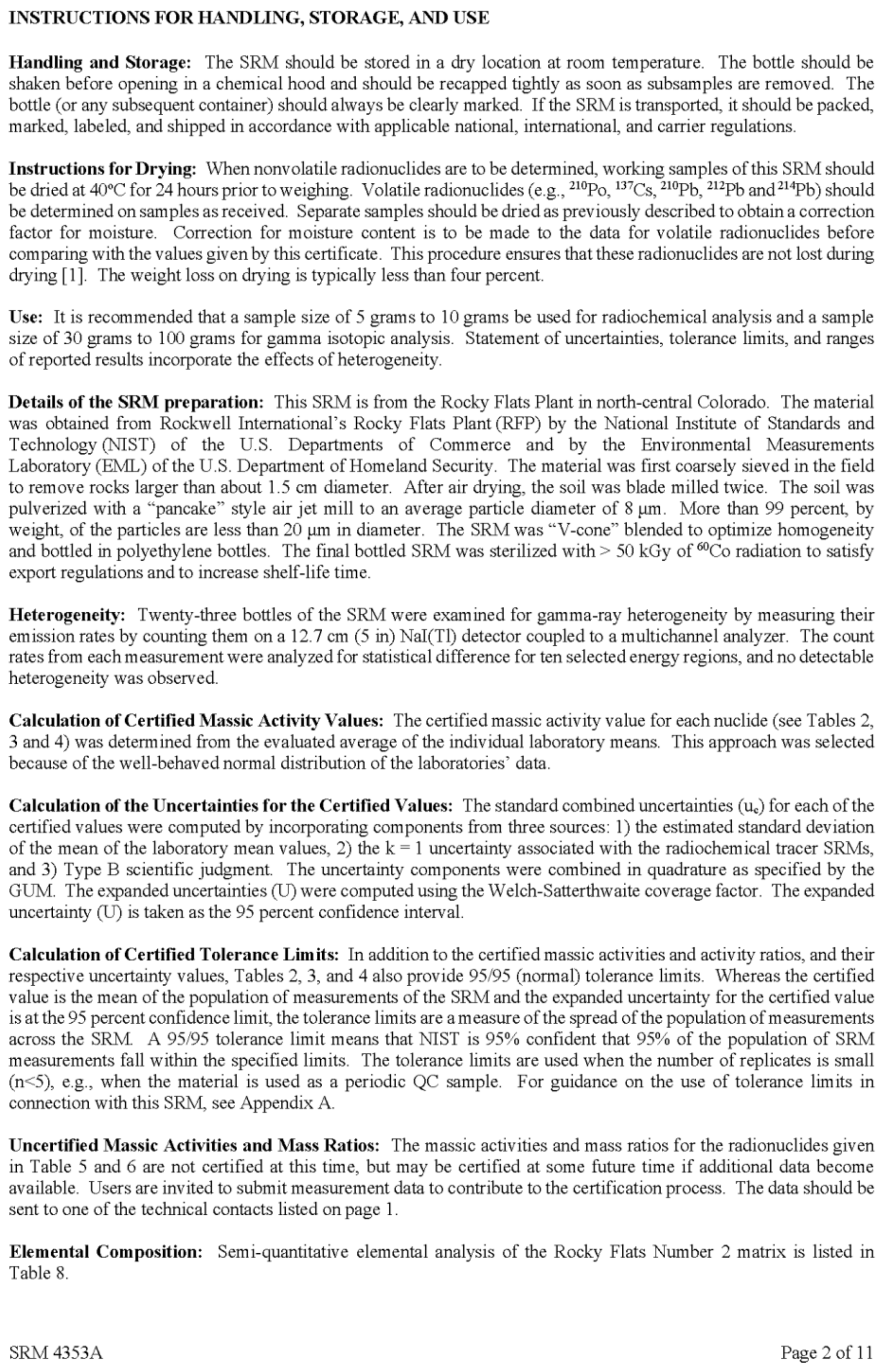
Technical Contacts: Svetlana Nour (e-mail: svetlana.nour@nist.gov; phone: 1-301-975-4927) and Jerome LaRosa (e-mail: jerome.larosa@nist.gov; phone: 1-301-975-8333) NIST, Mail Stop 8462, Gaithersburg, MD 20899-8462, fax 1-301-926-7416.

Support aspects involved in the issuance of this SRM were coordinated through the NIST Office of Reference Materials.

James M. Adams, Chief
Radiation Physics Division

Gaithersburg, Maryland 20899
Certificate Issue Date: 17 June 2019
Certificate Revision History on Page 9

Steven J. Choquette, Director
Office of Reference Materials



INSTRUCTIONS FOR HANDLING, STORAGE, AND USE

Handling and Storage: The SRM should be stored in a dry location at room temperature. The bottle should be shaken before opening in a chemical hood and should be recapped tightly as soon as subsamples are removed. The bottle (or any subsequent container) should always be clearly marked. If the SRM is transported, it should be packed, marked, labeled, and shipped in accordance with applicable national, international, and carrier regulations.

Instructions for Drying: When nonvolatile radionuclides are to be determined, working samples of this SRM should be dried at 40°C for 24 hours prior to weighing. Volatile radionuclides (e.g., ^{210}Po, ^{137}Cs, ^{210}Pb, ^{212}Pb and ^{214}Pb) should be determined on samples as received. Separate samples should be dried as previously described to obtain a correction factor for moisture. Correction for moisture content is to be made to the data for volatile radionuclides before comparing with the values given by this certificate. This procedure ensures that these radionuclides are not lost during drying [1]. The weight loss on drying is typically less than four percent.

Use: It is recommended that a sample size of 5 grams to 10 grams be used for radiochemical analysis and a sample size of 30 grams to 100 grams for gamma isotopic analysis. Statement of uncertainties, tolerance limits, and ranges of reported results incorporate the effects of heterogeneity.

Details of the SRM preparation: This SRM is from the Rocky Flats Plant in north-central Colorado. The material was obtained from Rockwell International's Rocky Flats Plant (RFP) by the National Institute of Standards and Technology (NIST) of the U.S. Departments of Commerce and by the Environmental Measurements Laboratory (EML) of the U.S. Department of Homeland Security. The material was first coarsely sieved in the field to remove rocks larger than about 1.5 cm diameter. After air drying, the soil was blade milled twice. The soil was pulverized with a "pancake" style air jet mill to an average particle diameter of 8 µm. More than 99 percent, by weight, of the particles are less than 20 µm in diameter. The SRM was "V-cone" blended to optimize homogeneity and bottled in polyethylene bottles. The final bottled SRM was sterilized with > 50 kGy of ^{60}Co radiation to satisfy export regulations and to increase shelf-life time.

Heterogeneity: Twenty-three bottles of the SRM were examined for gamma-ray heterogeneity by measuring their emission rates by counting them on a 12.7 cm (5 in) NaI(Tl) detector coupled to a multichannel analyzer. The count rates from each measurement were analyzed for statistical difference for ten selected energy regions, and no detectable heterogeneity was observed.

Calculation of Certified Massic Activity Values: The certified massic activity value for each nuclide (see Tables 2, 3 and 4) was determined from the evaluated average of the individual laboratory means. This approach was selected because of the well-behaved normal distribution of the laboratories' data.

Calculation of the Uncertainties for the Certified Values: The standard combined uncertainties (u_c) for each of the certified values were computed by incorporating components from three sources: 1) the estimated standard deviation of the mean of the laboratory mean values, 2) the k = 1 uncertainty associated with the radiochemical tracer SRMs, and 3) Type B scientific judgment. The uncertainty components were combined in quadrature as specified by the GUM. The expanded uncertainties (U) were computed using the Welch-Satterthwaite coverage factor. The expanded uncertainty (U) is taken as the 95 percent confidence interval.

Calculation of Certified Tolerance Limits: In addition to the certified massic activities and activity ratios, and their respective uncertainty values, Tables 2, 3, and 4 also provide 95/95 (normal) tolerance limits. Whereas the certified value is the mean of the population of measurements of the SRM and the expanded uncertainty for the certified value is at the 95 percent confidence limit, the tolerance limits are a measure of the spread of the population of measurements across the SRM. A 95/95 tolerance limit means that NIST is 95% confident that 95% of the population of SRM measurements fall within the specified limits. The tolerance limits are used when the number of replicates is small (n<5), e.g., when the material is used as a periodic QC sample. For guidance on the use of tolerance limits in connection with this SRM, see Appendix A.

Uncertified Massic Activities and Mass Ratios: The massic activities and mass ratios for the radionuclides given in Table 5 and 6 are not certified at this time, but may be certified at some future time if additional data become available. Users are invited to submit measurement data to contribute to the certification process. The data should be sent to one of the technical contacts listed on page 1.

Elemental Composition: Semi-quantitative elemental analysis of the Rocky Flats Number 2 matrix is listed in Table 8.

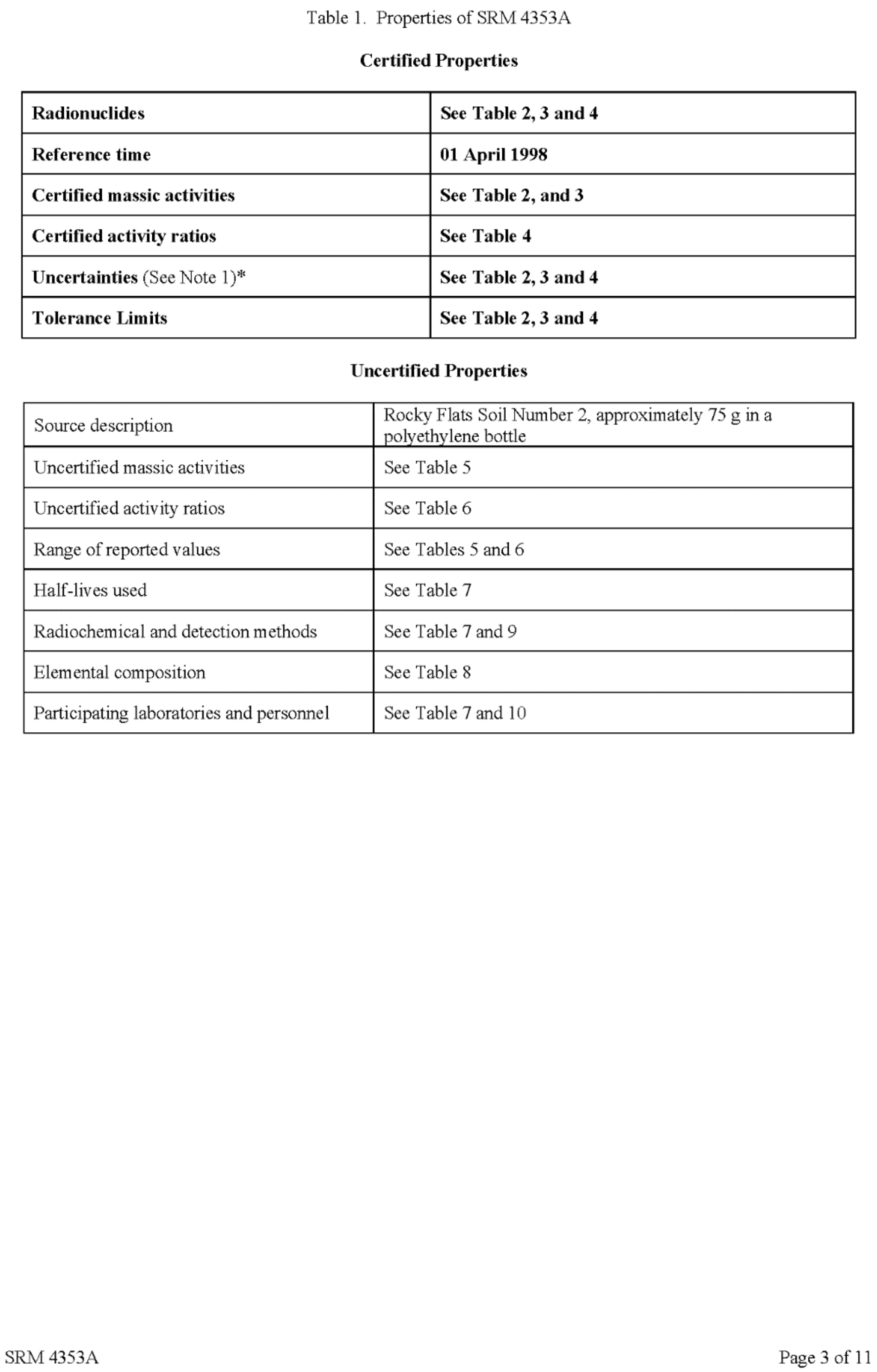


Table 1. Properties of SRM 4353A

Certified Properties

Radionuclides	**See Table 2, 3 and 4**
Reference time	**01 April 1998**
Certified massic activities	**See Table 2, and 3**
Certified activity ratios	**See Table 4**
Uncertainties (See Note 1)*****	**See Table 2, 3 and 4**
Tolerance Limits	**See Table 2, 3 and 4**

Uncertified Properties

Source description	Rocky Flats Soil Number 2, approximately 75 g in a polyethylene bottle
Uncertified massic activities	See Table 5
Uncertified activity ratios	See Table 6
Range of reported values	See Tables 5 and 6
Half-lives used	See Table 7
Radiochemical and detection methods	See Table 7 and 9
Elemental composition	See Table 8
Participating laboratories and personnel	See Table 7 and 10

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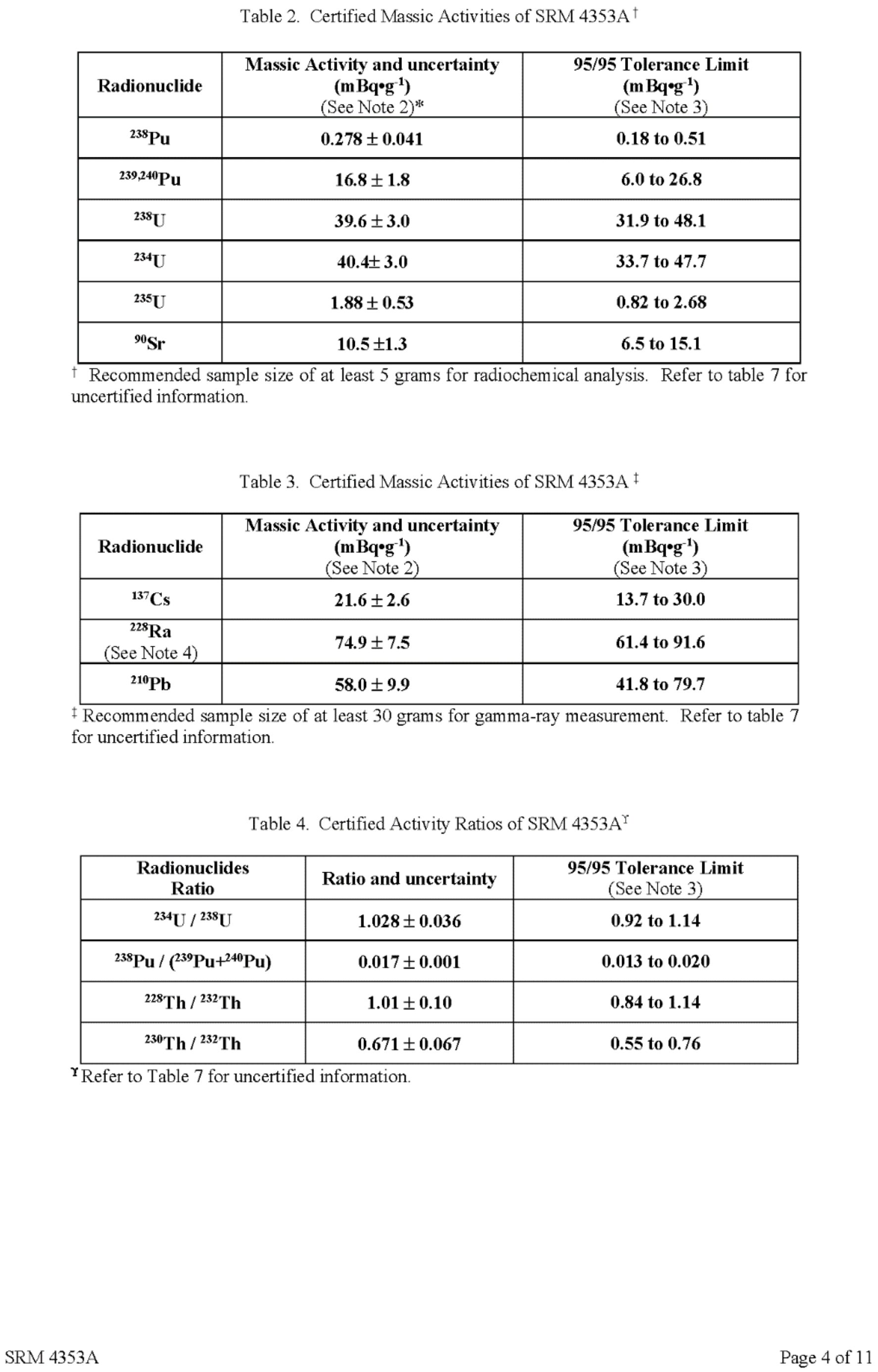

Table 2. Certified Massic Activities of SRM 4353A †

Radionuclide	**Massic Activity and uncertainty ($mBq \cdot g^{-1}$)** (See Note 2)*	**95/95 Tolerance Limit ($mBq \cdot g^{-1}$)** (See Note 3)
^{238}Pu	**0.278 ± 0.041**	**0.18 to 0.51**
^{239,240}Pu	**16.8 ± 1.8**	**6.0 to 26.8**
^{238}U	**39.6 ± 3.0**	**31.9 to 48.1**
^{234}U	**40.4± 3.0**	**33.7 to 47.7**
^{235}U	**1.88 ± 0.53**	**0.82 to 2.68**
^{90}Sr	**10.5 ±1.3**	**6.5 to 15.1**

† Recommended sample size of at least 5 grams for radiochemical analysis. Refer to table 7 for uncertified information.

Table 3. Certified Massic Activities of SRM 4353A ‡

Radionuclide	**Massic Activity and uncertainty ($mBq \cdot g^{-1}$)** (See Note 2)	**95/95 Tolerance Limit ($mBq \cdot g^{-1}$)** (See Note 3)
^{137}Cs	**21.6 ± 2.6**	**13.7 to 30.0**
^{228}Ra (See Note 4)	**74.9 ± 7.5**	**61.4 to 91.6**
^{210}Pb	**58.0 ± 9.9**	**41.8 to 79.7**

‡ Recommended sample size of at least 30 grams for gamma-ray measurement. Refer to table 7 for uncertified information.

Table 4. Certified Activity Ratios of SRM 4353Aϒ

Radionuclides Ratio	**Ratio and uncertainty**	**95/95 Tolerance Limit** (See Note 3)
^{234}U / ^{238}U	**1.028 ± 0.036**	**0.92 to 1.14**
^{238}Pu / (^{239}Pu+^{240}Pu)	**0.017 ± 0.001**	**0.013 to 0.020**
^{228}Th / ^{232}Th	**1.01 ± 0.10**	**0.84 to 1.14**
^{230}Th / ^{232}Th	**0.671 ± 0.067**	**0.55 to 0.76**

ϒ Refer to Table 7 for uncertified information.

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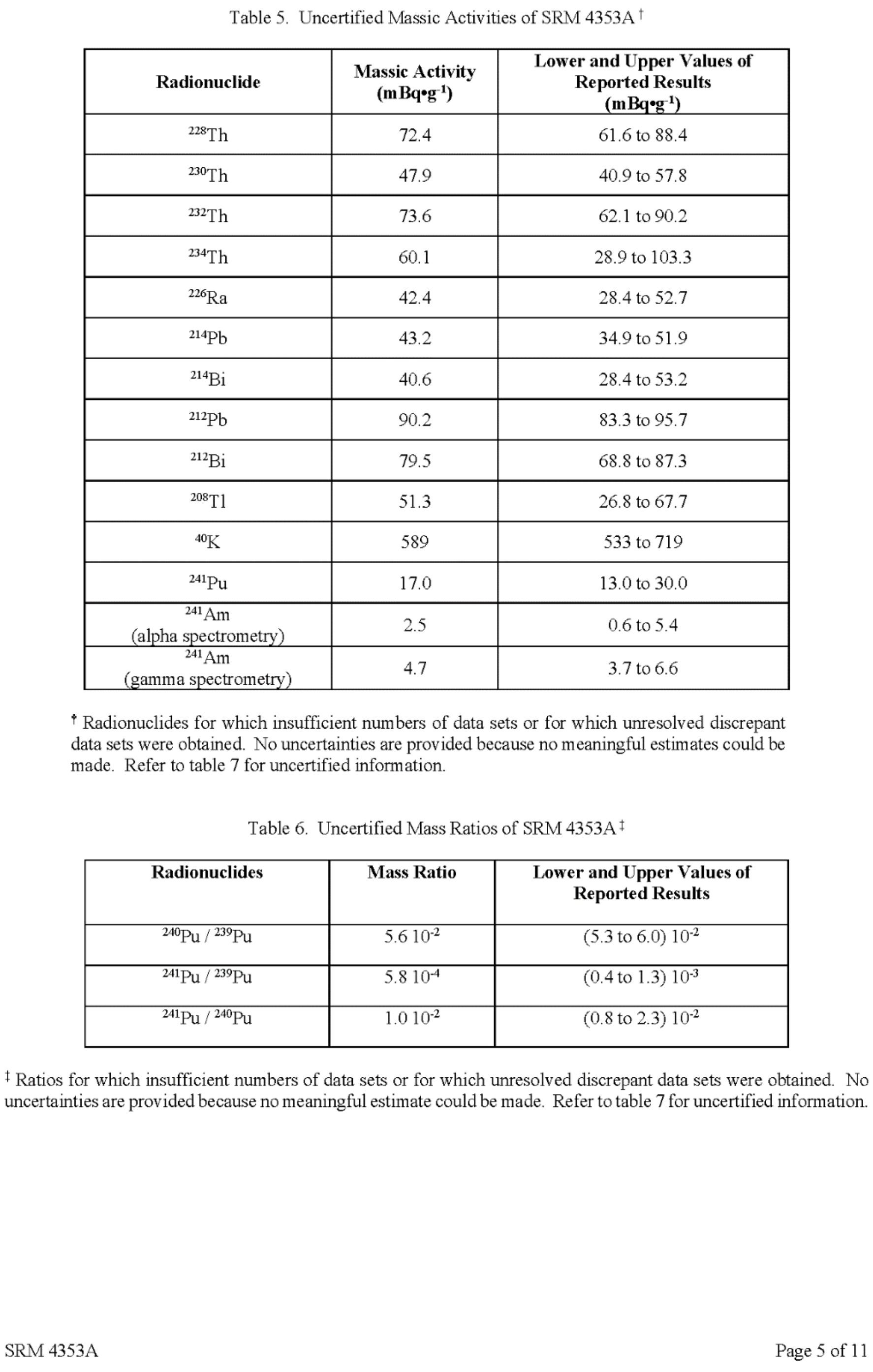

Table 5. Uncertified Massic Activities of SRM 4353A †

Radionuclide	Massic Activity (mBq•g^{-1})	Lower and Upper Values of Reported Results (mBq•g^{-1})
^{228}Th	72.4	61.6 to 88.4
^{230}Th	47.9	40.9 to 57.8
^{232}Th	73.6	62.1 to 90.2
^{234}Th	60.1	28.9 to 103.3
^{226}Ra	42.4	28.4 to 52.7
^{214}Pb	43.2	34.9 to 51.9
^{214}Bi	40.6	28.4 to 53.2
^{212}Pb	90.2	83.3 to 95.7
^{212}Bi	79.5	68.8 to 87.3
^{208}Tl	51.3	26.8 to 67.7
^{40}K	589	533 to 719
^{241}Pu	17.0	13.0 to 30.0
^{241}Am (alpha spectrometry)	2.5	0.6 to 5.4
^{241}Am (gamma spectrometry)	4.7	3.7 to 6.6

† Radionuclides for which insufficient numbers of data sets or for which unresolved discrepant data sets were obtained. No uncertainties are provided because no meaningful estimates could be made. Refer to table 7 for uncertified information.

Table 6. Uncertified Mass Ratios of SRM 4353A ‡

Radionuclides	Mass Ratio	Lower and Upper Values of Reported Results
^{240}Pu / ^{239}Pu	5.6 10^{-2}	(5.3 to 6.0) 10^{-2}
^{241}Pu / ^{239}Pu	5.8 10^{-4}	(0.4 to 1.3) 10^{-3}
^{241}Pu / ^{240}Pu	1.0 10^{-2}	(0.8 to 2.3) 10^{-2}

‡ Ratios for which insufficient numbers of data sets or for which unresolved discrepant data sets were obtained. No uncertainties are provided because no meaningful estimate could be made. Refer to table 7 for uncertified information.

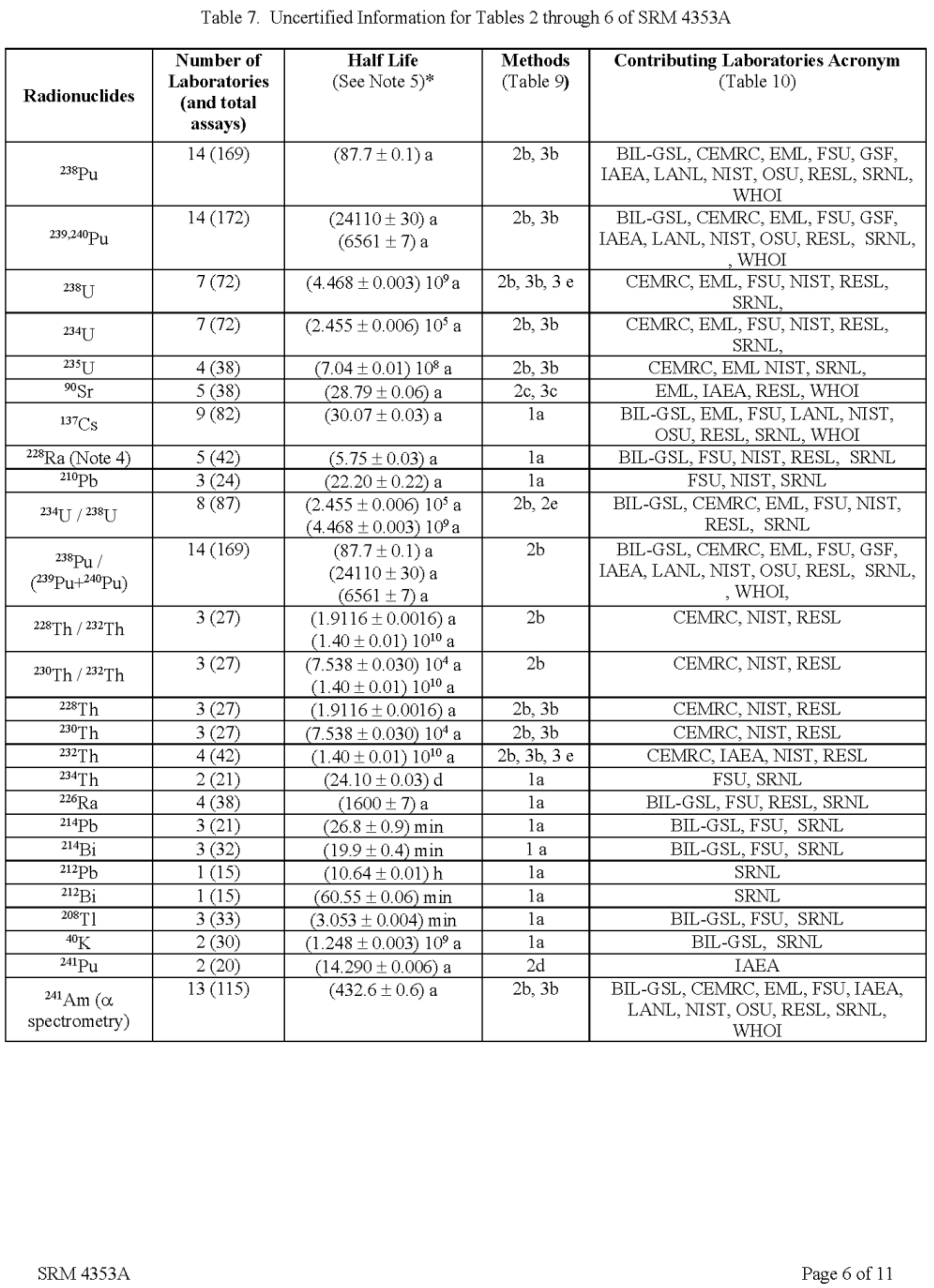

Table 7. Uncertified Information for Tables 2 through 6 of SRM 4353A

Radionuclides	**Number of Laboratories (and total assays)**	**Half Life** (See Note 5)*	**Methods** (Table 9**)**	**Contributing Laboratories Acronym** (Table 10)
^{238}Pu	14 (169)	(87.7 ± 0.1) a	2b, 3b	BIL-GSL, CEMRC, EML, FSU, GSF, IAEA, LANL, NIST, OSU, RESL, SRNL, WHOI
^{239,240}Pu	14 (172)	(24110 ± 30) a (6561 ± 7) a	2b, 3b	BIL-GSL, CEMRC, EML, FSU, GSF, IAEA, LANL, NIST, OSU, RESL, SRNL, , WHOI
^{238}U	7 (72)	$(4.468 \pm 0.003)\ 10^{9}$ a	2b, 3b, 3 e	CEMRC, EML, FSU, NIST, RESL, SRNL,
^{234}U	7 (72)	$(2.455 \pm 0.006)\ 10^{5}$ a	2b, 3b	CEMRC, EML, FSU, NIST, RESL, SRNL,
^{235}U	4 (38)	$(7.04 \pm 0.01)\ 10^{8}$ a	2b, 3b	CEMRC, EML NIST, SRNL,
^{90}Sr	5 (38)	(28.79 ± 0.06) a	2c, 3c	EML, IAEA, RESL, WHOI
^{137}Cs	9 (82)	(30.07 ± 0.03) a	1a	BIL-GSL, EML, FSU, LANL, NIST, OSU, RESL, SRNL, WHOI
^{228}Ra (Note 4)	5 (42)	(5.75 ± 0.03) a	1a	BIL-GSL, FSU, NIST, RESL, SRNL
^{210}Pb	3 (24)	(22.20 ± 0.22) a	1a	FSU, NIST, SRNL
^{234}U / ^{238}U	8 (87)	$(2.455 \pm 0.006)\ 10^{5}$ a $(4.468 \pm 0.003)\ 10^{9}$ a	2b, 2e	BIL-GSL, CEMRC, EML, FSU, NIST, RESL, SRNL
^{238}Pu / (^{239}Pu+^{240}Pu)	14 (169)	(87.7 ± 0.1) a (24110 ± 30) a (6561 ± 7) a	2b	BIL-GSL, CEMRC, EML, FSU, GSF, IAEA, LANL, NIST, OSU, RESL, SRNL, , WHOI,
^{228}Th / ^{232}Th	3 (27)	(1.9116 ± 0.0016) a $(1.40 \pm 0.01)\ 10^{10}$ a	2b	CEMRC, NIST, RESL
^{230}Th / ^{232}Th	3 (27)	$(7.538 \pm 0.030)\ 10^{4}$ a $(1.40 \pm 0.01)\ 10^{10}$ a	2b	CEMRC, NIST, RESL
^{228}Th	3 (27)	(1.9116 ± 0.0016) a	2b, 3b	CEMRC, NIST, RESL
^{230}Th	3 (27)	$(7.538 \pm 0.030)\ 10^{4}$ a	2b, 3b	CEMRC, NIST, RESL
^{232}Th	4 (42)	$(1.40 \pm 0.01)\ 10^{10}$ a	2b, 3b, 3 e	CEMRC, IAEA, NIST, RESL
^{234}Th	2 (21)	(24.10 ± 0.03) d	1a	FSU, SRNL
^{226}Ra	4 (38)	(1600 ± 7) a	1a	BIL-GSL, FSU, RESL, SRNL
^{214}Pb	3 (21)	(26.8 ± 0.9) min	1a	BIL-GSL, FSU, SRNL
^{214}Bi	3 (32)	(19.9 ± 0.4) min	1 a	BIL-GSL, FSU, SRNL
^{212}Pb	1 (15)	(10.64 ± 0.01) h	1a	SRNL
^{212}Bi	1 (15)	(60.55 ± 0.06) min	1a	SRNL
^{208}Tl	3 (33)	(3.053 ± 0.004) min	1a	BIL-GSL, FSU, SRNL
^{40}K	2 (30)	$(1.248 \pm 0.003)\ 10^{9}$ a	1a	BIL-GSL, SRNL
^{241}Pu	2 (20)	(14.290 ± 0.006) a	2d	IAEA
^{241}Am (α spectrometry)	13 (115)	(432.6 ± 0.6) a	2b, 3b	BIL-GSL, CEMRC, EML, FSU, IAEA, LANL, NIST, OSU, RESL, SRNL, WHOI

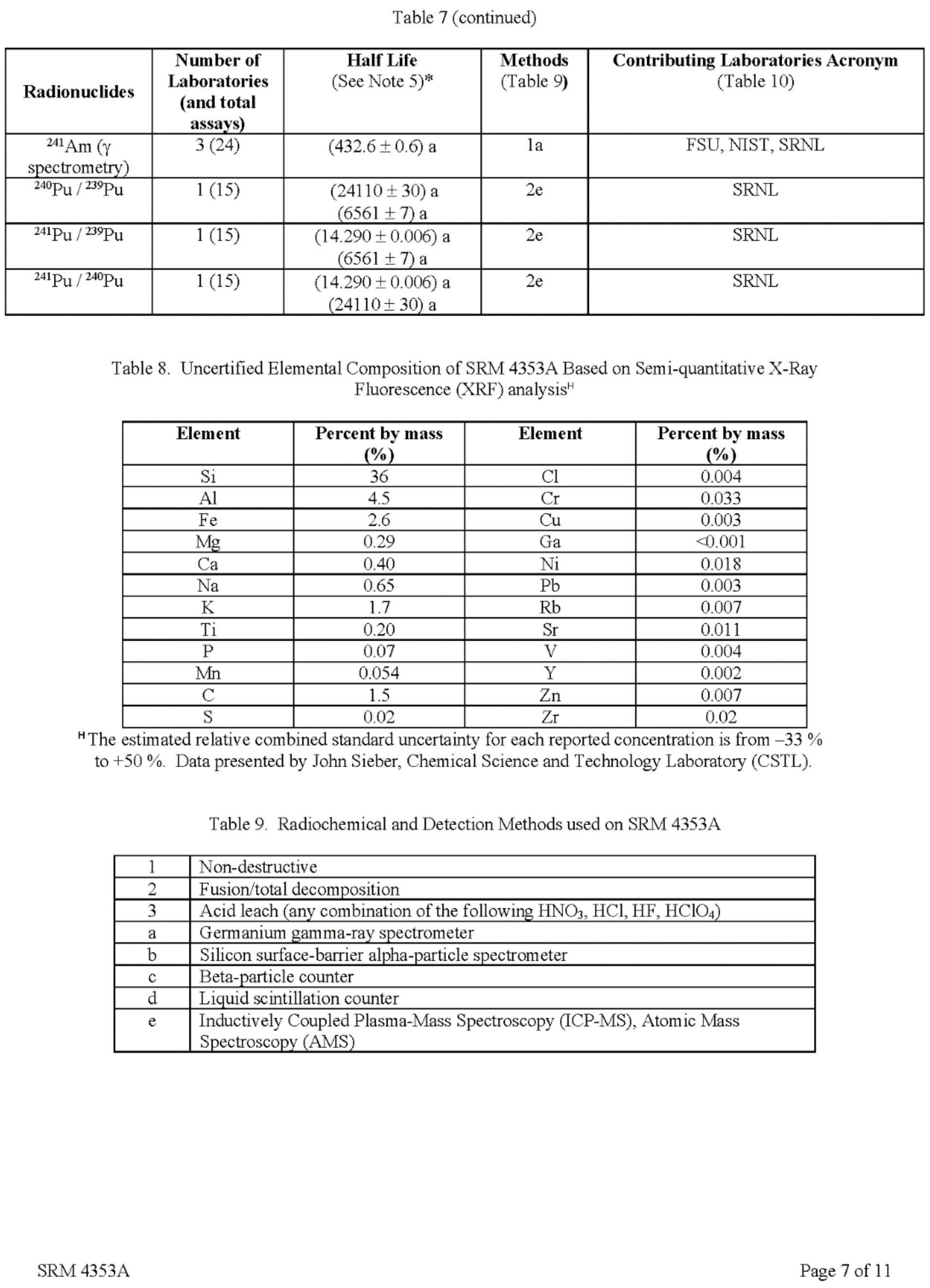

Table 7 (continued)

Radionuclides	Number of Laboratories (and total assays)	Half Life (See Note 5)*	Methods (Table 9)	Contributing Laboratories Acronym (Table 10)
^{241}Am (γ spectrometry)	3 (24)	(432.6 ± 0.6) a	1a	FSU, NIST, SRNL
^{240}Pu / ^{239}Pu	1 (15)	(24110 ± 30) a (6561 ± 7) a	2e	SRNL
^{241}Pu / ^{239}Pu	1 (15)	(14.290 ± 0.006) a (6561 ± 7) a	2e	SRNL
^{241}Pu / ^{240}Pu	1 (15)	(14.290 ± 0.006) a (24110 ± 30) a	2e	SRNL

Table 8. Uncertified Elemental Composition of SRM 4353A Based on Semi-quantitative X-Ray Fluorescence (XRF) analysis[H]

Element	Percent by mass (%)	Element	Percent by mass (%)
Si	36	Cl	0.004
Al	4.5	Cr	0.033
Fe	2.6	Cu	0.003
Mg	0.29	Ga	<0.001
Ca	0.40	Ni	0.018
Na	0.65	Pb	0.003
K	1.7	Rb	0.007
Ti	0.20	Sr	0.011
P	0.07	V	0.004
Mn	0.054	Y	0.002
C	1.5	Zn	0.007
S	0.02	Zr	0.02

[H] The estimated relative combined standard uncertainty for each reported concentration is from –33 % to +50 %. Data presented by John Sieber, Chemical Science and Technology Laboratory (CSTL).

Table 9. Radiochemical and Detection Methods used on SRM 4353A

1	Non-destructive
2	Fusion/total decomposition
3	Acid leach (any combination of the following HNO$_3$, HCl, HF, HClO$_4$)
a	Germanium gamma-ray spectrometer
b	Silicon surface-barrier alpha-particle spectrometer
c	Beta-particle counter
d	Liquid scintillation counter
e	Inductively Coupled Plasma-Mass Spectroscopy (ICP-MS), Atomic Mass Spectroscopy (AMS)

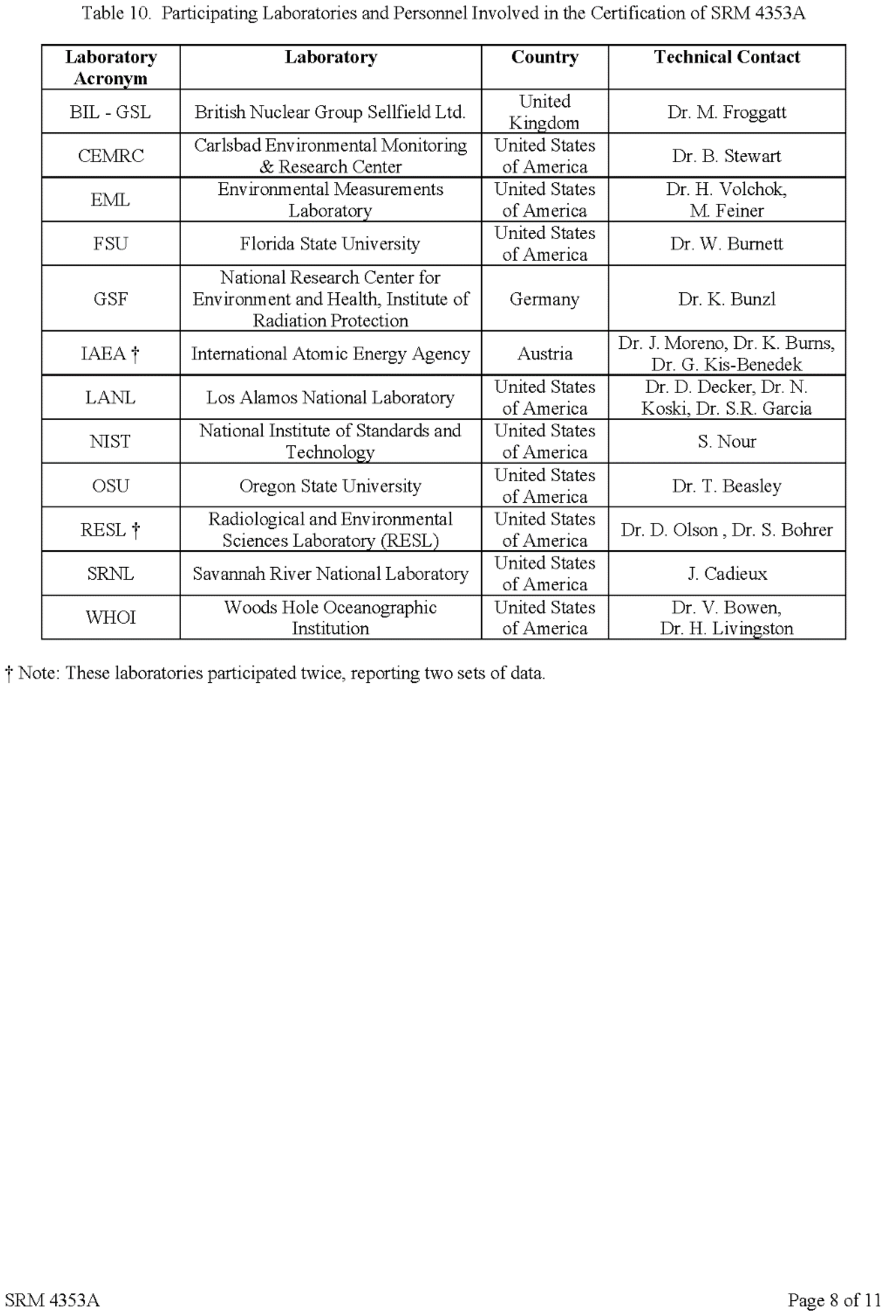

Table 10. Participating Laboratories and Personnel Involved in the Certification of SRM 4353A

Laboratory Acronym	Laboratory	Country	Technical Contact
BIL - GSL	British Nuclear Group Sellfield Ltd.	United Kingdom	Dr. M. Froggatt
CEMRC	Carlsbad Environmental Monitoring & Research Center	United States of America	Dr. B. Stewart
EML	Environmental Measurements Laboratory	United States of America	Dr. H. Volchok, M. Feiner
FSU	Florida State University	United States of America	Dr. W. Burnett
GSF	National Research Center for Environment and Health, Institute of Radiation Protection	Germany	Dr. K. Bunzl
IAEA †	International Atomic Energy Agency	Austria	Dr. J. Moreno, Dr. K. Burns, Dr. G. Kis-Benedek
LANL	Los Alamos National Laboratory	United States of America	Dr. D. Decker, Dr. N. Koski, Dr. S.R. Garcia
NIST	National Institute of Standards and Technology	United States of America	S. Nour
OSU	Oregon State University	United States of America	Dr. T. Beasley
RESL †	Radiological and Environmental Sciences Laboratory (RESL)	United States of America	Dr. D. Olson , Dr. S. Bohrer
SRNL	Savannah River National Laboratory	United States of America	J. Cadieux
WHOI	Woods Hole Oceanographic Institution	United States of America	Dr. V. Bowen, Dr. H. Livingston

† Note: These laboratories participated twice, reporting two sets of data.

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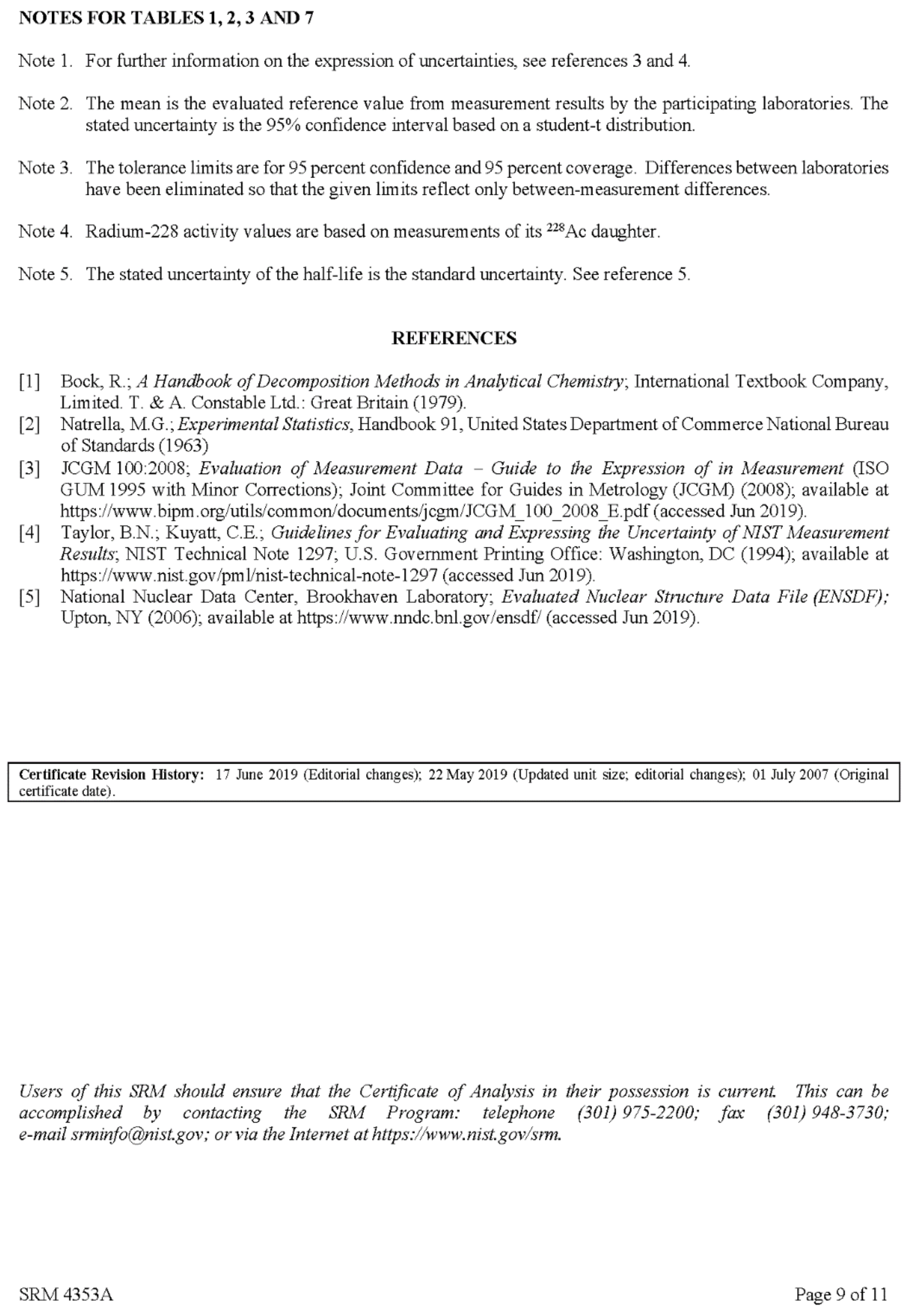


NOTES FOR TABLES 1, 2, 3 AND 7

Note 1. For further information on the expression of uncertainties, see references 3 and 4.

Note 2. The mean is the evaluated reference value from measurement results by the participating laboratories. The stated uncertainty is the 95% confidence interval based on a student-t distribution.

Note 3. The tolerance limits are for 95 percent confidence and 95 percent coverage. Differences between laboratories have been eliminated so that the given limits reflect only between-measurement differences.

Note 4. Radium-228 activity values are based on measurements of its ^{228}Ac daughter.

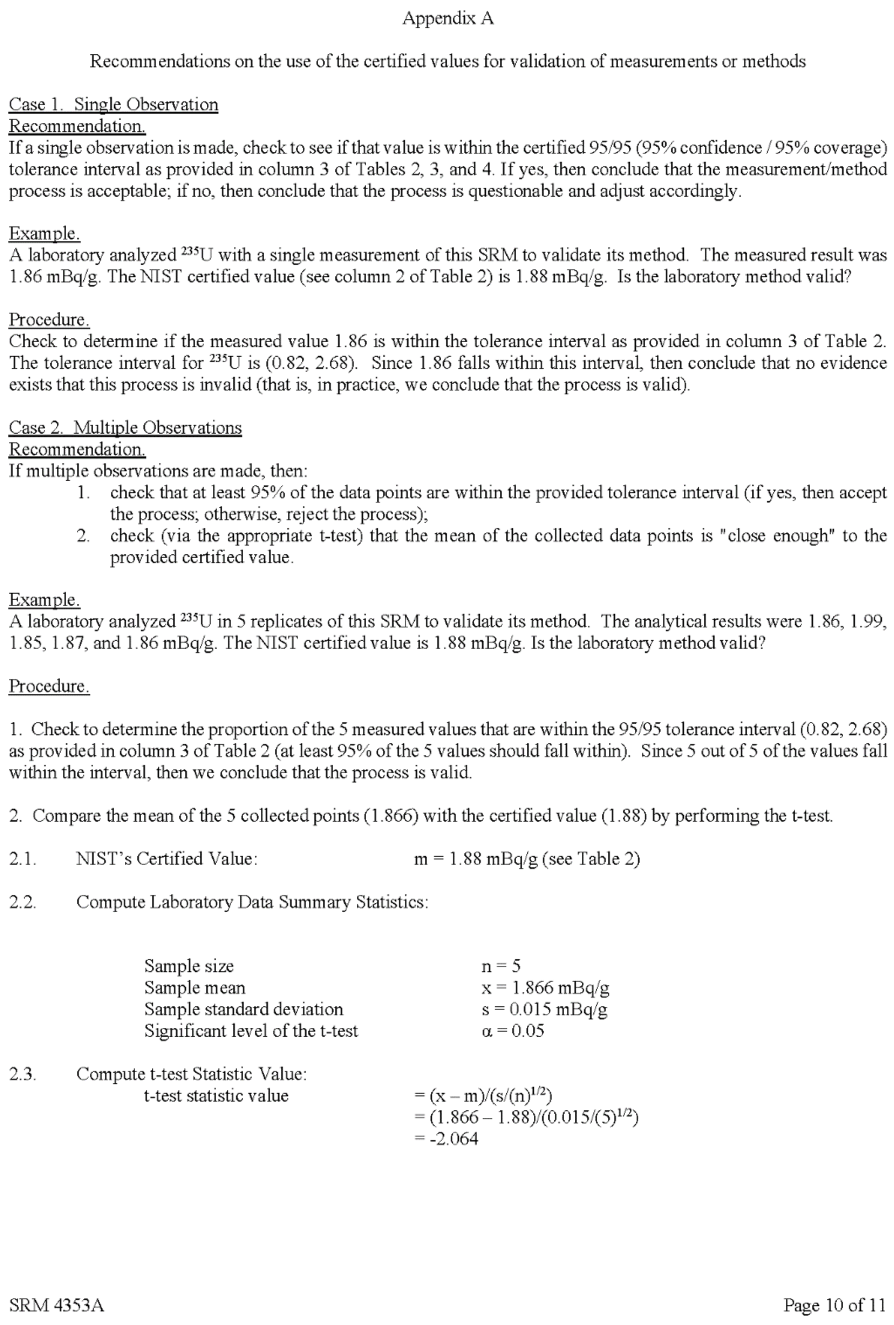
Note 5. The stated uncertainty of the half-life is the standard uncertainty. See reference 5.

REFERENCES

[1] Bock, R.; *A Handbook of Decomposition Methods in Analytical Chemistry*; International Textbook Company, Limited. T. & A. Constable Ltd.: Great Britain (1979).
[2] Natrella, M.G.; *Experimental Statistics*, Handbook 91, United States Department of Commerce National Bureau of Standards (1963)
[3] JCGM 100:2008; *Evaluation of Measurement Data – Guide to the Expression of in Measurement* (ISO GUM 1995 with Minor Corrections); Joint Committee for Guides in Metrology (JCGM) (2008); available at https://www.bipm.org/utils/common/documents/jcgm/JCGM_100_2008_E.pdf (accessed Jun 2019).
[4] Taylor, B.N.; Kuyatt, C.E.; *Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results*; NIST Technical Note 1297; U.S. Government Printing Office: Washington, DC (1994); available at https://www.nist.gov/pml/nist-technical-note-1297 (accessed Jun 2019).
[5] National Nuclear Data Center, Brookhaven Laboratory; *Evaluated Nuclear Structure Data File (ENSDF);* Upton, NY (2006); available at https://www.nndc.bnl.gov/ensdf/ (accessed Jun 2019).

Certificate Revision History: 17 June 2019 (Editorial changes); 22 May 2019 (Updated unit size; editorial changes); 01 July 2007 (Original certificate date).

Users of this SRM should ensure that the Certificate of Analysis in their possession is current. This can be accomplished by contacting the SRM Program: telephone (301) 975-2200; fax (301) 948-3730; e-mail srminfo@nist.gov; or via the Internet at https://www.nist.gov/srm.



Appendix A

Recommendations on the use of the certified values for validation of measurements or methods

Case 1. Single Observation

Recommendation.

If a single observation is made, check to see if that value is within the certified 95/95 (95% confidence / 95% coverage) tolerance interval as provided in column 3 of Tables 2, 3, and 4. If yes, then conclude that the measurement/method process is acceptable; if no, then conclude that the process is questionable and adjust accordingly.

Example.

A laboratory analyzed ^{235}U with a single measurement of this SRM to validate its method. The measured result was 1.86 mBq/g. The NIST certified value (see column 2 of Table 2) is 1.88 mBq/g. Is the laboratory method valid?

Procedure.

Check to determine if the measured value 1.86 is within the tolerance interval as provided in column 3 of Table 2. The tolerance interval for ^{235}U is (0.82, 2.68). Since 1.86 falls within this interval, then conclude that no evidence exists that this process is invalid (that is, in practice, we conclude that the process is valid).

Case 2. Multiple Observations

Recommendation.

If multiple observations are made, then:

1. check that at least 95% of the data points are within the provided tolerance interval (if yes, then accept the process; otherwise, reject the process);
2. check (via the appropriate t-test) that the mean of the collected data points is "close enough" to the provided certified value.

Example.

A laboratory analyzed ^{235}U in 5 replicates of this SRM to validate its method. The analytical results were 1.86, 1.99, 1.85, 1.87, and 1.86 mBq/g. The NIST certified value is 1.88 mBq/g. Is the laboratory method valid?

Procedure.

1. Check to determine the proportion of the 5 measured values that are within the 95/95 tolerance interval (0.82, 2.68) as provided in column 3 of Table 2 (at least 95% of the 5 values should fall within). Since 5 out of 5 of the values fall within the interval, then we conclude that the process is valid.

2. Compare the mean of the 5 collected points (1.866) with the certified value (1.88) by performing the t-test.

2.1. NIST's Certified Value: $m = 1.88$ mBq/g (see Table 2)

2.2. Compute Laboratory Data Summary Statistics:

Sample size	$n = 5$
Sample mean	$x = 1.866$ mBq/g
Sample standard deviation	$s = 0.015$ mBq/g
Significant level of the t-test	$\alpha = 0.05$

2.3. Compute t-test Statistic Value:

t-test statistic value

$$= (x - m)/(s/(n)^{1/2})$$
$$= (1.866 - 1.88)/(0.015/(5)^{1/2})$$
$$= -2.064$$

2.4. Determine Cutoff Values for 95 % Confidence:

Upper 2.5% point of $t_{(n-1)}$ distribution = 2.776 (See Table A1)
Lower 2.5% point of $t_{(n-1)}$ distribution = -2.776 (See Table A1)

3. Conclusions:

3.1 If test statistic value < lower cutoff value, then conclude method is invalid with negative bias relative to the certified value.

3.2 If test statistic value > upper cutoff value, then conclude method is invalid with positive bias relative to the certified value.

3.3 If neither of the above, then conclude method is valid.

Example's Conclusion: Since the laboratory's test statistic value of -2.064 is neither > the upper cutoff value of 2.776 nor < the lower cutoff value of -2.776, case 3 applies and it can be concluded that the laboratory's method for ^{235}U analysis is valid.

Table A1: Probability points of the t distribution with (n-1) degrees of freedom.

Degrees of freedom	Tail area probability, $t_{(n-1)}$ (cutoff values)	
(n-1)	Upper 2.5 %	Lower 2.5 %
1	12.706	-12.706
2	4.303	-4.303
3	3.182	-3.182
4	2.776	-2.776
5	2.571	-2.571
6	2.447	-2.447
7	2.365	-2.365
8	2.306	-2.306
9	2.262	-2.262
10	2.228	-2.228