Natural-Matrix Radionuclide Standard Reference Materials

1 Purpose

This document describes the production, measurement and reporting procedures for the massic activity of radionuclides in Natural-Matrix Standard Reference Materials (SRMs).

2 Framework

One of the missions of the Radiation Physics Division is to provide radioactivity standards for research, commerce and industry. The Natural-Matrix SRM program seeks to quantify radionuclide concentrations in complex, environmental materials such as soils, sediments and biological specimens. The radionuclides present in these materials have both natural and anthropogenic origins.

Natural-Matrix SRMs provide the metrology community with means by which they can: 1) validate radioanalytical methods, 2) control the quality of measurement process, 3) compare measurement results within projects and programs (both within a laboratory and between laboratories) over an extended time period, and 4) support the traceability and credibility of measurement results [1].

3 Scope

This procedure discusses the selection of material matrices, processing them into final form, the interlaboratory comparisons used to develop the data file from which the certified radionuclide massic activity will be derived, the data evaluation process, the NIST radiochemical analysis process to contribute to the data file, and the writing of the certificate.

4 Definitions

Organizations:

- IAEA – International Atomic Energy Agency (United Nations)
- NMI – national metrology institute
- NIST - National Institute of Standards and Technology
    - GRSD – Gaithersburg Radiation Safety Division, NIST
    - OSHE – Office of Safety, Health and Environment
    - PML – Physical Measurement Laboratory

    - RPD - Radiation Physics Division (Division 682 of PML)
    - RG – Radioactivity Group (Group 4 of RPD)
- 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
- GUM – guide to the expression of uncertainty in measurement
- QC – quality control
- QM – quality manual
- 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:

- Lyophilization – freeze-drying
- 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
- 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).
- Tracer – a radionuclide added to follow the chemical behavior of a 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).
- 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)
- 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.)

- Radioactive equilibrium – the situation where the rate of ingrowth equals the rate of decay of a 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.
- 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
- 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)
- 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.
- 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.
- 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 inherently has poorer spectral resolution.

5 Safety

Radiation safety: Rooms marked by the Gaithersburg Radiation Safety Division (GRSD) with magenta and yellow strip tape have been designated as Radiation Areas. 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 Safety Evaluations (SEs). In addition, safety protocols are posted in the laboratories.

Chemical safety: Chemical safety and training operations are provided by the NIST Gaithersburg Office of Safety, Health, and Environment (OSHE).

6 Procedures

6.1 Quality Control

6.1.1 Document Change

Laboratory books shall be amended according to the policies set forth in Guide RPD-G-06.

6.1.2 Subcontracting

Reference materials certifications are not subcontracted (see NIST-QM-I Section 4.4.4).

6.1.3 Purchasing Services and Supplies

Purchased supplies 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 blank contamination will result in the suspension of use of the material, and a suitable replacement will be obtained to carry out the requested measurements.

Failures of a reagent’s titer or blank contamination shall be noted in the investigator’s laboratory notebook. Resolution of the failure will also be noted in the investigator’s laboratory notebook.

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

Quality-critical consumables of suppliers will be evaluated against technical specifications. Those suppliers which can supply consumables of adequate quality will be listed for the NIST purchasing agent to contact for bids.

6.1.4 Records

Analytical procedures, instrument and software laboratory books and manuals shall be readily available (at workstations, labs, offices)as resources. , Hardcopy resources shall be stored in nearby drawers that have been designated for such use. Electronic storage will be utilized whenever possible.

Analytical records used for a project shall be sufficiently detailed to repeat analyses, investigate discrepancies, troubleshoot methodologies, and should include:

A. investigator’s name
B. appropriate identification;

C. scope;
D. description of the type of item to be tested or calibrated;
E. parameters or quantities and ranges to be determined;
F. equipment, including technical performance requirements;
G. reference standards and reference materials required;
H. environmental conditions required and any stabilization period needed;
I. description of the procedure, including:
    a. affixing of identification marks, handling, transporting, storing and preparation of items,
    b. checks to be made before the work is started,
    c. checks that the equipment is working properly and, where required, calibration and adjustment of the equipment before each use,
    d. the method of recording the observations and results, and
    e. any safety measures to be observed;
J. criteria and/or requirements for approval/rejection;
K. data to be recorded and method of analysis and presentation; and
L. the uncertainty or the procedure for estimating uncertainty.

Old records are exclusively hardcopies, whereas new ones include electronic storage of measurement data and results as files on password-protected individual and common-access computers with supported by PML backup shared drives located in building 245, rooms C106, C112, C115, and C117.

6.1.5 Technical Requirements

6.1.5.1 Accommodation and environmental conditions

Environmental conditions are not critical factors that affect the quality of analyses. Laboratory activities will cease when the electricity goes out, a water pipe bursts, or temperature varies by more than ambient tolerance (i.e., < 15 $^{\circ}$C or > 32 $^{\circ}$C).

Tests and calibrations shall be stopped when the environmental conditions jeopardize the safety of the investigators.

Work is segregated among specified laboratories based on low (μBq/g - mBq/g), intermediate ($\geq$ Bq/g) and high ($\geq$ kBq/g) levels of sample radioactivity to prevent cross-contamination. Swipes of intermediate and high level laboratories are taken to confirm the absence of contamination at the conclusion of the sample preparation stage, and results are posted for all users of common area laboratories to determine the acceptability of the laboratory for use.

6.1.5.2 Methods

Radioanalytical methods use a blend of techniques to provide samples appropriate for alpha-, beta- and gamma-ray measurements. The particular selection of radiochemical techniques is from among standard methodologies and techniques described in evaluated literature citations. In cases where no standard methods are deemed appropriate, in-house methods are developed, verified against SRMs, certified reference materials (CRMs), interlaboratory comparisons or proficiency testing results, and proficiency of use by each person involved in the project, and are verified to fit the need and purpose of the measurement. These in-house methods are described in project files that should include:

A. investigator's name
B. appropriate identification;
C. scope;
D. description of the type of item to be tested or calibrated;
E. parameters or quantities and ranges to be determined;
F. equipment, including technical performance requirements;
G. reference standards and reference materials required;
H. environmental conditions required and any stabilization period needed;
I. description of the procedure, including:
    a. affixing of identification marks, handling, transporting, storing and preparation of items,
    b. checks to be made before the work is started,
    c. checks that the equipment is working properly and, where required, calibration and adjustment of the equipment before each use,
    d. the method of recording the observations and results, and
    e. any safety measures to be observed;
J. criteria and/or requirements for approval/rejection;
K. data to be recorded and method of analysis and presentation; and
L. the uncertainty or the procedure for estimating uncertainty.

6.1.5.3 Estimation of uncertainty of measurement

Guidance for combining and estimating uncertainties is provided in the *ISO Guide to the Expression of Uncertainty in Measurement* (1993) and in NIST Technical Note 1297 *Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results* (1994) and NIST Technical Note 1900 Simle Guide for Evaluating and Expressing the Uncertainty of NIST Measurement Results (2015).

Electronic data collection, data transfers, appropriate use of software, and contributions by impurities are evaluated during spectral evaluations, quality control checks and statistical evaluations of the results. Any suspect results are investigated for root cause for adjustment, re-measurement, or classified as a marked error.

Old, hardcopy measurement results are stored in file cabinets in building 245, room E103 that are secured from intrusion by key-access locked room doors (when unattended),

badge-only access locked building doors, and the NIST physical security system. Electronic storage of measurement data and results as files on password-protected individual and common-access computers with supported by PML backup shared drives will be maintained and are located in building 245, rooms C106, C112, C115, and C117.

6.1.5.4 Equipment

All radiation measurement instruments in Building 245, Rooms B001, C10, C13, C15, and C17 have met purchasing technical specifications and are sufficiently shielded to minimize the influence of background radiation on the quality of the measurements. They are regularly monitored for stability of background, energy calibrations and efficiency calibrations to assure that they do not impact the quality of the measurements. The instruments are safeguarded from unauthorized adjustments by locking the rooms when unattended, badge-only access locked building doors, and the NIST physical security system.

Alpha-particle detectors are regularly calibrated for energy response after checking/adjustment of electronic settings using single or multi-nuclide electrodeposited or co-precipitated sources, often before use. High-purity germanium gamma-ray detectors are energy calibrated using single- and multi-gamma-ray line sources, and are calibrated for efficiency using gravimetrically spiked matrix sources (see also section 5.8.1.2). In general, it is necessary that only the gain for the sodium iodide detectors be adjusted using gamma-ray emitting sources of known energy so that all gamma-ray energy lines of interest from samples are included for relative wide-open energy window analysis. Gas-flow beta-particle detectors are efficiency calibrated using gravimetrically prepared traceable sources as described in section 5.8.2.1. Background and quality control samples are measured for each specific project. All results are recorded and entered in the project folder.

All users of the instrumentation and associated software are expert with their operations.

A laboratory book shall be kept with each set of instruments that include information on:

A) manufacturer's name, type identification and NIST property number;
B) history of background and check source measurement;
C) location;
D) history of calibrations, adjustments, critical parameter settings; and
E) history of damage, malfunction, modification or repair.

6.1.5.5 Measurement traceability

All radiation measurement instruments are calibrated with NIST SRM-traceable sources, gravimetrically prepared, that match the counting geometry, z_{eff}, self-absorption and scattering of measurement samples (see section 5.7.1.2 and 5.7.2.2).

Criteria for acceptable verification of traceability of derived sources are 1 % u_c, and percent difference limited to 3 %.

Alpha-, beta- and gamma-emitting calibration and check reference sources are stored in Building 245, rooms B001 and C13 for limited access and safety.

6.1.5.6 Sampling

Sampling protocols are developed in consultation with NIST's Statistical Engineering Division (SED) and are based on the type of SRM material being certified.

Statistical tools traditionally used to assess measurements of solutions and spiked samples include mean, standard deviation, and normal probability plots. SED will select and employ appropriate methods for data evaluation together with input from the Radioactivity Group experts. Additional considerations for assessing natural-matrix radionuclide reference materials are discussed in section 6.7.

6.1.5.7 Assuring the quality of measurement results

Measurements of test samples are planned to include the following operations: sample handling, sub-sampling, standard tracers, traceability, blank and background controls, sample dissolution options, radiochemical cleanup options, counting source preparation, measurement optimization, data analysis and reporting of results. The dissolution, cleanup, and measurement technique options are balanced to obtain an acceptable measurement uncertainty against time and cost considerations.

Control over the measurement process includes analysis of blanks, comparison against reference values, interlaboratory comparisons, decay curve and spectral analyses for impurities, spectral resolution, inter-nuclide systematics, and statistical identification and investigation of suspect results and method bias.

6.1.5.8 Reporting the results

A structured format for reporting results facilitates the transfer of information and provides a mechanism to minimize misinterpretation of data. Electronic data reporting is the method of choice. It allows the results to be compiled into digital spreadsheets that are readily processed by reliable computer programs for data reduction and analysis.

6.2 Process Control

The responsibilities of the Radioactivity Group Leader, SRM Coordinator and SRM principal investigator, as well as the coordination of SRM activities among them, is described in RPD-QM-II Sections 4.2.3.2.2 and 4.2.3.2. The natural-matrix SRM principal investigator relies on the SRM Coordinator to provide non-technical support services for the SRM such as development and production funding, labeling and storage of the SRM units, pricing, and advertising and marketing.

Throughout the following SRM matrix preparation procedures, each step is carefully considered and planned to maintain control. It is recognized that the preparation procedure will result in material alteration; however, it is desirable that the material characteristics and radionuclide speciation are preserved as much as possible. Care is taken to minimize contamination of the material by foreign sources (equipment wear, equipment cleanliness), and undue heating (e.g., flash evaporation instead of controlled freeze drying). As much as possible, a NIST representative accompanies the material when it is sent for commercial processing to inspect the equipment before use for cleanliness and after processing for equipment wear and to obtain temperature charts and particle size information to assure that the material is processed as expected. By careful process control during the preparation of the material, it is expected that there will be minimal effects on the final certified values which are mainly derived from the measurement process of the packaged material.

6.3 Matrix Selection

Needs expressed by the global radiochemical community are the primary reason for matrix selection. A number of conditions must be met for consideration of a natural matrix SRM development:

1. There has to be a great enough demand.
2. The basic material (soil, sediment, biota) for development must be available.
3. Resources for the collection and processing of this material must be provided.
4. Coordination with other reference material producers (e.g., IAEA's Analytical Quality Control Services) is required to prevent duplication.
5. The quantity of potential SRM material must be sufficient for a 10-year supply. .

6.4 Matrix Collection

Matrix collection procedures are consistent with 5.7.2 of 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. At times, several tons of wet material need to be collected, shipped and processed to end up with the anticipated 10 year supply of the reference material. These factors are weighed to select the "best" material for the amount of money allotted for the development of the material into an SRM.

Purchase Orders are sent to the collection contacts to collect and send the material to NIST for processing and, when necessary, to field screen and dry the material prior to shipment.

6.5 Matrix Preparation

6.5.1 Size of SRM Unit

The minimum SRM unit size 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.

6.5.2 Drying

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.

6.5.3 Matrix Size Reduction

The actual matrix size reduction and processing (milling, pulverizing, blending) 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.

6.5.4 Pulverization

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.

6.5.5 Blending

To further minimize heterogeneity, materials are thoroughly mixed, particularly to evenly disburse "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.

6.5.6 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 (see also 6.5.2).

6.5.7 Packaging

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

6.5.8 Sterilization

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.

6.6 Interlaboratory Comparison

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. The laboratories are selected through their reputations for excellence in scientific measurements. All

laboratories agree to participate without anonymity. Chemical yield monitors quantitatively diluted from SRMs are typically provided by NIST to the participants. Each laboratory uses the radioanalytical methodology for which they are most expert, and selects the radionuclide results that are returned to NIST. At least one measurement from each of the SRM units is requested for each reported radionuclide. The laboratory also has the option of reporting three measurement results from each of the SRM units for assessment of between bottle and within bottle heterogeneity. The laboratories are requested to report their results within one year of receiving the SRM units.

The information requested for reported analytical results include: five massic activity results for each radionuclide with the associated standard combined uncertainties, the reference date, and a brief description of the analytical method used.

6.7 Measurement Traceability

Each participating laboratory establishes traceability to the SI through appropriate calibration of instruments (e.g., high-purity germanium spectrometers) and the use of gravimetrically diluted and verified tracers obtained from NIST SRMs and/or National Metrology Institute Certified Reference Materials (CRMs).

6.8 NIST Analysis

6.8.1 Gamma Ray Measurements

6.8.1.1 Assessment of heterogeneity

The heterogeneity of the environmental material is initially evaluated by gross gamma-ray measurements using a 12.7 cm diameter NaI(Tl) detector in 245/C15. 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.

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.

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.

6.8.1.2 Quantitative Measurements

Gamma-ray measurements using high purity germanium (HPGe) detectors provide nuclide-specific measurement, and HPGe systems in building 245 rooms C13 and C17 are used for quantifying the gamma-ray emitting radionuclides. Providing there is sufficient radioactivity, the same samples used for the heterogeneity assessment in 6.8.1.1 can be used for massic activity quantification.

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.

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.

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 [2-4]. 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.

6.8.1.3 Gamma-ray Measurement Quality Control (QC)

Sodium iodide and 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). The instrument blanks are empty counting bottles that are measured in the same geometry as the samples. These determinations are done at the beginning of the schedule, between samples and after the final sample is counted.

6.8.1.4 Data Analysis

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

Spectra from HPGe spectrometry are analyzed for net peak area above the Compton background using numeric methods that incorporate the assessment of peak shape and peak overlap [5-6]. For each instance 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 accessible to all staff. The instrument log books note the current software version being used or acceptable for use.

6.8.1.5 Computations

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.

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.

6.8.2 Alpha- and Beta-particle Emitting Radionuclide Measurements

6.8.2.1 Isotope Dilution

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.

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.

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.

6.8.2.2 Alpha- and Beta-particle Measurement QC

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.

Similarly, for ^{90}Sr 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.

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.

6.8.2.3 Sample Dissolution and Radiochemical Separations

High temperature, molten salt fusions (e.g., lithium metaborate, sodium carbonate, potassium fluoride) or repeated treatments with hot, aggressive acid mixtures (e.g., HF + HNO_3 + $HClO_4$) are used to achieve total dissolution and homogeneous mixing of the target radionuclides and their tracer(s) [7-11]. Final equilibration is achieved when analyte and tracer species in true solution are chemically manipulated into the same oxidation state (e.g., by appropriate reducing or oxidizing agents) and chemical environment.

Radiochemical separations are developed specifically for each natural-matrix SRM analysis [12-20]. The objective of the separation process is to produce counting sources of high radionuclide purity. To achieve this objective, a series of element-specific chemical steps are employed that 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, or confirmation of radioactive half-life for pure beta-emitters. 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.

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 of this amount of analyte radionuclide to the gross radionuclide determinations from the matrix samples are needed to determine the analyte radionuclide content from only the sample.

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.

6.8.2.4 Source Preparation for Radioactivity Measurement

Purified alpha-emitting radionuclide solutions are prepared for counting by either electrodeposition [21a,b] or micro co-precipitation methods [22a,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.

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 [23].

6.8.2.5 Instrumentation and Counting

Alpha-emitting sources for counting are measured under vacuum and typically in close geometry (< 10 mm) to ion-implanted, planar silicon detector spectrometers [24]. 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 measurement of samples.

Strontium-90 beta-particle emitting counting sources have traditionally been measured using thin-window, gas-flow proportional counters [25-26]. 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 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.

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.

6.8.2.6 Data Analysis: Peak Deconvolution Analysis, Interferences

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 [6]. Care is taken to account for radioactive impurities detected in the spectrum when determining the net peak areas.

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 [27-29].

6.8.2.7 Computations

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 [e.g., 30].

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 [e.g., 23].

6.9 Interlaboratory Comparison Data and Statistical Analysis

Resulting data from participating laboratories are carefully evaluated with the full participation of NIST's Statistical Engineering Division (SED) for systematic bias and material heterogeneity [31]. 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:

DATA NORMALIZATION
Reference Date
Units
Expanded Uncertainty
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)
DATA CERTIFICATION
Combined Data (Normal Probability Plot)
Bottle Number Heterogeneity (Curve Fitting)
Sample Size (*F*-Test)
Between-Bottle vs. Within Bottle Heterogeneity (*F*-test)
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)

6.10 Certified and Uncertified Radionuclide Values

The protocol for evaluation of the interlaboratory comparison data had been carefully developed over the history of the SRM program [e.g., 32-33] 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.

The major evaluation issues that the radionuclide certification protocol focuses on include: a) systematic difference among analytical methodologies; b) consistency among the distributions of results from each laboratory; c) 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. While normal probability

plots allow identification of discrepant laboratory results, it is only through extensive personal contacts with the laboratory and additional revealing experiments that these discrepancies can be unfolded and resolved. 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.

A summary of the radionuclides and their massic activities in the natural matrix series SRMs 4350B through 4359 is presented in Appendix A.

6.11 Certificate

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. An example of such an approval form for SRMs in given in Appendix B.

The information on the SRM certificate includes,

- SRM number (inclusive of batch number) and name
- Description of the SRM and the intended and correct use of the material
- Unit mass
- Reference time
- Parties responsible for the preparation of material
- Source and preparation of the material
- Instructions for drying
- Radionuclide leachability
- Application of the certified values
- Uncertainties
- Heterogeneity determinations
- Notice and warning to users
    - Stability and expiration of certification (period of validity)
    - Radiological hazards
    - Storage and handling
- Contact persons
- Certified massic activities for radionuclides and uncertainties
    - Radionuclide
    - Certified value + U (Bq g^{-1})
    - Number of assays
    - Half lives used
    - Methods
    - Contributing laboratories

- Notes
  - Analytical methods
  - Participating laboratories
- Uncertified massic activities
- Semi-quantitative trace element analysis
- Major elements recalculated as oxides

Appendix C provides a completely reproduced sample certificate for SRM 4357 Ocean Sediment Radionuclide Standard.

7 Uncertainty Analysis

The bootstrap method [34] has been used to estimate the uncertainty for the natural-matrix SRM radionuclides certified massic activities produced thus far. Appropriate methods for SRMs currently in development are to be determined in consultation with SED.

8 Equipment

Radionuclide measurement and balance equipment (specified by NIST inventory number or equivalent) include:

- 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
- 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]

Calibrations of radionuclide measurement equipment are discussed in sections 5.7.1.2 and 5.7.2.2.

9 Records

Data, analysis printouts, and copies of the SRM certificate are stored in folders within file boxes identified by SRM number and held in the custody of the principle investigator. Supporting documentation for older SRMs is in the form of hardcopies. This information is currently located in 245/E103.

SRM certificates are maintained as hardcopies in 245/E103 and are available through the NIST external website during the time of the SRM's availability. When the SRM becomes unavailable, at least one copy of the SRM certificate remains in 245/E103 and an archived certificate is maintained electronically on the NIST external website.

Instrument calibration logs relevant to SRM measurements are maintained by the principle investigators in folders identified by SRM number in 245/E103. General instrument calibration records are maintained electronically and in log books located in the same room as the instrument.

Quality control logs relevant to SRM measurements are maintained by the principle investigators in folders identified by SRM number in 245/E103. Past and current quality control measurements are entered into the instrument QC data book in the same room as the instrument.

10 Filing and Retention

Data, analysis printouts and copies of the SRM certificate are stored electronically and/or as hardcopies (pre-computer information) in folders identified by SRM number and held in the custody of the principle investigator.

The RPD Quality Manager shall maintain the original and all past versions of this RPD Procedure.

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Appendix A:	**Radionuclides and Massic Activities in the Natural Matrix radioactivity SRMs**				
SRM Number	4350B	4351	4352	4353A	4354
Description	River Sediment	Human Lung	Human Liver	RF Soil II	Lake Sediment
Reference Date	09 Sep 1981	01 Oct 1982	01 Jun 1982	1 Apr 1998	14 Feb 1986
Radionuclide	Massic Activity ($mBq \cdot g^{-1}$) **Certified values are in bold type**.				
^{40}K	560.	-	-	589	-
^{55}Fe	17.	-	-	-	-
^{60}Co	**4.64**	-	-	-	**320.**
^{90}Sr	5.3	-	-	**10.5**	**1090.**
^{129}I	-	-	-	-	-
^{137}Cs	**29.0**	-	-	**21.6**	**59.2**
^{152}Eu	**30.5**	-	-	-	-
^{154}Eu	**3.78**	-	-	-	-
^{155}Eu	-	-	-	-	-
^{208}Tl	-	-	-	51.3	-
^{210}Po	-	-	-	-	-
^{210}Pb	-	-	-	**58.0**	120.
^{212}Pb	-	-	-	90.2	-
^{214}Bi	-	-	-	40.6	-
^{226}Ra	**35.8**	-	-	42.4	30.
^{228}Ra	-	-	-	**74.9**	-
^{228}Ac	-	-	-	-	-
^{228}Th	33.5	0.22	0.51	72.4	**28.6**
^{230}Th	29.5	0.20	0.20	47.9	13.
^{232}Th	33.2	**0.21**	0.058	73.6	**26.8**
^{234}U	33.2	**0.100**	0.10	**40.4**	19.
^{235}U	1.7	-	0.009	**1.88**	**0.75**
^{238}U	30.8	**0.101**	0.088	**39.6**	**17.4**
^{237}Np	-	-	-	-	-
^{238}Pu	**0.013**	**0.017**	**0.055**	**0.278**	**0.26**
$^{239+240}Pu$	**0.508**	**1.1**	**2.06**	**16.8**	**4.00**
^{241}Am	**0.150**	-	**0.15**	2.5, 4.7	**1.1**
$^{243+244}Cm$	-	0.11	-	-	-

Appendix A:	**Radionuclides and Massic Activities in the Natural Matrix radioactivity SRMs**				
SRM Number	4355	4356	4357	4358	4359
Description	Peruvian Soil	Ashed Bone	Ocean Sediment	Ocean Shellfish	Seaweed
Reference Date	1 Jun 1982	31 Dec 1995	16 Feb 1994	16 Feb 1998	1 Jan 2002
Radionuclide	Massic Activity ($mBq \cdot g^{-1}$) **Certified values are in bold type**.				
^{40}K	585.	49.	**225.**	**160**	**734**
^{55}Fe	2.	-	-	-	-
^{60}Co	<0.016	-	-	-	-
^{90}Sr	0.22	**42.6**	**4.4**	**0.092**	0.26
^{129}I	-	-	0.009	-	0.0149
^{137}Cs	**0.33**	-	**12.7**	**0.254**	0.933
^{152}Eu	<0.23	-	-	-	-
^{154}Eu	<0.2	-	-	-	-
^{155}Eu	<0.2	-	1.4	-	-
^{208}Tl	12.,15.	-	-	0.89	1.3
^{210}Po	-	13.	14.	-	**20.6**
^{210}Pb	-	20.	24.	**6.5**	**21.0**
^{212}Pb	-	-	14.1	1.48	4.0
^{214}Bi	42.,39.	-	15.	0.32	-
^{226}Ra	-	**14.5**	**12.7**	0.34	5.7
^{228}Ra	-	6.1	**13.3**	**1.41**	**4.32**
^{228}Ac	-	6.9	-	-	-
^{228}Th	**42.2**	7.1	**12.1**	**1.35**	3.6
^{230}Th	**39.7**	**0.52**	**12.0**	**0.41**	3.3
^{232}Th	**43.0**	**0.98**	**13.0**	**0.64**	**2.40**
^{234}U	-	**0.64**	12.	**1.56**	**9.5**
^{235}U	-	0.028	0.6	**0.061**	**0.400**
^{238}U	-	**0.63**	12.	**1.46**	**8.67**
^{237}Np	-	-	0.007	-	0.000173
^{238}Pu	3.,3.27	**0.86**	**2.29**	**0.009**	**0.00606**
$^{239+240}Pu$	**0.0076**	**1.26**	**10.4**	**0.055**	**0.1296**
^{241}Am	**0.004**	9.98	10.	**0.101**	**0.0432**
$^{243+244}Cm$	-	**0.12**	-	0.012	-

Appendix B: Approval Form for SRMs

Technical Review - SRM Certificates

Please review the attached draft carefully. Any suggestions or changes should be made clearly on this draft. Forward this draft and approval record to the next individual indicated. The Measurement Services Division (MSD) has listed potential reviewers from names contained in the SRM documentation. Please feel free to add or remove names as you see fit.

Return to the MSD Documentation Contact (Stop 2300) within **TEN (10)** WORKING days.

NOTE: Signatures on certificate record signify that the Reviewer/Division is assenting only to the aspects of the certification analysis and those parts of the certification that pertain to the Reviewer/Division's involvement with the SRM(s).

Final approval of SRM certificates and certificates of analysis is delegated jointly to the Chief of MSD and the Chief of the initiating technical division by NIST Lab Council Policy.

SRM(s)/RM(s): 4226d **DRAFT # or Version Date: March 29, 2010**

Title: Nickel-63 Radioactivity Standard

MSD Documentation Contact: Dinis Camara **Telephone: x2205**

Date Sent: **Date of Expected Return:**

Name (Suggested Reviewers)	Mail Stop	Division	Signature	Date
L. Laureano-Perez	8462	846		
J. LaRosa	8462	846		
M.P. Unterweger	8462	846		
R. Collé	8462	846		
Statistician: S.D. Leigh	8980	898		
Tech. Div. Chief: L.R. Karam	8460	846		
MSD Documentation Contact:				

MSD-21
Revision date: 2007.01.18

Appendix C:

National Institute of Standards and Technology

Certificate

Environmental Radioactivity

Standard Reference Material 4357

Ocean Sediment Radionuclide Standard

Description of the Standard and Intended Use: This Standard Reference Material (SRM) has been developed in cooperation with member laboratories of the International Committee for Radionuclide Metrology and expert national laboratories. The SRM is intended for use in tests of measurements of environmental radioactivity contained in matrices similar to field samples. Uses of the material include: 1) development of radiochemical procedures, 2) test of radiochemical procedures already in use for environmental and biokinetic evaluations, 3) calibration of instruments, 4) interlaboratory comparison materials for radiochemical methods evaluation, 5) test for competency of technicians to do radiochemical assays, and 6) demonstration that data output is reliable.

Unit Mass: 85 g Nominal
Reference Time: 16 February 1994

Preparation of Material: This Standard Reference Material was prepared in the Physics Laboratory, Ionizing Radiation Division, Radioactivity Group, J.M.R. Hutchinson, Group Leader. The overall technical direction leading to certification was provided by Kenneth G.W. Inn of the Radioactivity Group.

Statistical support was provided by Drs. James J. Filliben, Eric S. Lagergren, Walter S. Liggett, Nien-Fan Zhang, and Keith R. Eberhardt.

The support aspects involved in the preparation, certification, and issuance of this SRM were coordinated through the Standard Reference Materials Program by Nancy M. Trahey.

Gaithersburg, Maryland 20899
January 1996

Thomas E. Gills, Chief
Standard Reference Materials Program

Source and Preparation of Material: The sediment is a blend of material collected off the coast of Sellafield, UK, and in the Chesapeake Bay, USA, in the weight ratio of 1:200, respectively. A. Knight and M. Measures of the National Radiological Protection Board, UK, collected, sieved to -200 mesh, dried and analyzed the Sellafield Sediment before sending it to NIST. The Chesapeake Bay sediment was freeze dried, blended with the Sellafield sediment, sterilized with 50 kGy of ^{60}Co radiation and pulverized with a "pancake"-style air-jet mill. The average particle diameter for the resulting powder is approximately 6 μm, and more than 99 percent, by weight, of the particles are less than 20 μm in diameter.

Instructions for Drying: When nonvolatile radionuclides are to be determined, working samples of this SRM should be dried in air at 40 °C for 24 hours prior to weighing. Volatile radionuclides (e.g., ^{137}Cs, ^{210}Pb and ^{212}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 to the certified values. This procedure ensures that these radionuclides are not lost during drying. The weight loss on drying is typically less than 2 percent.

Radionuclide Leachability: All actinides and their daughters are approximately 87 percent removed from the sample by normal HNO_3 or HNO_3-HCl leaching procedures. Total sample digestion or non-destructive analysis is required to produce results that can be compared to those listed in this certificate.

Application of the Certified Values: When 5 or more measurements are available, compute the sample mean and ascertain that the mean falls within the certified mean plus uncertainties interval. When 4 or fewer measurements are available, then ascertain that all of the individual values are within the certified tolerance limits interval.

Uncertainties: The bootstrap is a computationally-intensive, statistical procedure for estimating and computing the uncertainty of a statistic whose form is complicated and/or whose underlying assumptions (e.g., normality) are non-standard. The virtue of the procedure is that it provides a straightforward, rigorous methodology for computing uncertainties that would otherwise have been difficult to obtain.

The bootstrap was utilized here for the median calculations and for the tolerance limit calculations -- these statistics are distributionally complicated; also, the underlying normality of some of the data is suspect. The usual underlying assumptions do not hold due to a variety of experimental conditions, including interlaboratory biases, within-laboratory methodology differences, and material heterogeneity.

Procedurally, the bootstrap estimate for the uncertainty of a statistic (e.g., the median) is obtained as follows:

1. From the original sample of n observations, compute the statistic of interest (e.g., the median).

2. From the original n data points, extract a random sample -- with replacement -- of n points (this becomes the "bootstrap sample").

3. Compute the statistic of interest (e.g., the median) from this bootstrap sample (this will be the bootstrap statistic).

4. Repeat steps 2 and 3 a large number of times (e.g., 1000 times); the bootstrap statistic will, of course, change from one bootstrap sample to the next.

5. Compute the standard deviation of the statistic by applying the usual standard deviation formula to the 1000 bootstrap statistics.

Reference: Efron B. and Tibshirani, R.J. (1993). An Introduction to the Bootstrap. Monographs on Statistics & Applied Probability 57, Chapman and Hall, New York.

Heterogeneity Determinations: The material has been tested for sample sizes of 10 to 100 g, for which the heterogeneity of gamma-ray-emitting radionuclides have been detectable. Furthermore, material heterogeneity has been detected at a sample size of 10 g for ^{90}Sr and actinide radionuclides. The expected variation of measurements due to heterogeneity has been incorporated in the certified tolerance limits and uncertainty of mean concentration values. The certified values for radionuclides with normal distribution of analytical measurements are listed in Table 1. Table 2 lists the certified values for radionuclides with non-normal distribution of analytical measurements. It is recommended that a sample sizes of 10 g or larger be used for radiometric and radiochemical analysis.

Notice and Warnings to Users:

Stability and Expiration of Certification: This matrix is considered to be stable; however, its stability has not been rigorously assessed. NIST will monitor this material and will report any substantive changes in certification to the purchaser. Should any of the certified values change, purchasers will be notified by NIST. Return of the attached registration card is mandatory to receive such notifications.

Radiological Hazards: The SRM contains low levels of anthropogenic and natural radioactivity. The SRM poses no radiological hazard. The SRM should be used only by qualified quality control persons.

Chemical Hazards: The SRM is a dried and sterilized sediment that poses no chemical hazard. However, inhalation or ingestion of the material is not recommended.

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

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Table 1: Certified Massic Activities for Radionuclides with Normal Distribution of Results

Radio-nuclide	Mean $\pm$ $2s_m$* ($mBq \cdot g^{-1}$)	2.5 to 97.5 Percent Tolerance Limit** ($mBq \cdot g^{-1}$)	Number of Assays	Half Lives Used (a)***	Methods	**Contributing Laboratories**
^{40}K	225 $\pm$ 5	190 - 259	31	1.277×10^9 $\pm$ 8×10^6	3a	KU, MAFF, NIR, NPL, YAEL
^{226}Ra	12.7 $\pm$ 0.4	10.3 - 15.0	21	1600 $\pm$ 7	3a	EML, IT, KU, NPL
^{228}Ra	13.3 $\pm$ 0.8	9.2 - 17.4	20	5.75 $\pm$ 0.03	3a	IT, KU, NPL
^{228}Th	12.1 $\pm$ 0.3	9.7 - 14.6	40	1.9131 $\pm$ 0.0009	3a +1c	EML, KU, LGC, MAFF, NIST, NPL, OSUH, YAEL
^{230}Th	12.0 $\pm$ 0.5	9.6 - 14.4	18	75380 $\pm$ 300	1c	LGC, NIST, OSUH
^{232}Th	13.0 $\pm$ 0.3	11.6 - 14.3	18	1.405×10^{10} $\pm$ 6×10^7	1c	LGC, NIST, OSUH

* Two standard deviations of the Mean

** Normal Tolerance Limit for 95 percent confidence and 95 percent coverage.

*** Evaluated Nuclear Data Structure File (ENSDF), January 1996. The stated uncertainty is the standard uncertainty.

Table 2: Certified Massic Activities for Radionuclides with Non-Normal Distribution of Results

Radio-nuclide	Mean ± $2s_m$* ($mBq \cdot g^{-1}$)	2.5 to 97.5 Percent Tolerance Limit** ($mBq \cdot g^{-1}$)	Number of Assays	Half Lives Used (a)***	Methods	Contributing Laboratories
^{90}Sr	4.4 ± 0.3	2.1 - 8.4	49	28.78 ± 0.04	1b, 2d	EML, LGC, MAFF, NE, NRPB, YAEL
^{137}Cs	12.7 ± 0.2	10.8 - 15.9	76	30.07 ± 0.03	3a	EML, IT, KU, LGC, MAFF, NE, NIR, NPL, ORNL, OSUB, YAEL
^{238}Pu	2.32 ± 0.06	2.01 - 3.02	53	87.7 ± 0.3	1c	EML, LGC, MAFF, NIST, OSUB
^{239}Pu + ^{240}Pu	10.4 ± 0.2	9.2 - 13.3	72	24110 ± 30 6564 ± 11	3a +1c	EML, IT, LGC, MAFF, NIST, OSUB, OSUH

* Two standard deviations about the Weibull Mean

** Weibull Tolerance Limit for 95 percent confidence and 95 percent coverage

*** Evaluated Nuclear Data Structure File (ENSDF), January 1996. The stated uncertainty is the standard uncertainty.

NOTES:

Analytical Methods:

1. HF-HNO_3 or HF-HNO_3-$HClO_4$ Dissolution
2. NaOH-HCl Leach
3. Non-Destructive Analysis

a. Germanium Gamma-ray Spectrometer
b. Thin-Window Beta-Particle Geiger Counter
c. Silicon Surface-Barrier Alpha-Particle Spectrometer
d. Plastic-Phosphor Beta-Particle Scintillation Counter

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Uncertified Massic Activities: Radionuclides for which insufficient numbers of data sets, or for which discrepant data sets were obtained, are listed in Table 3. No uncertainties are provided because insufficient bases upon which meaningful estimates could be determined.

Table 3: Uncertified Massic Activities

Radionuclide	Massic Activity ($mBq \cdot g^{-1}$)	Methods	Contributing Laboratories
^{129}I	0.009	3a +1c	NIR
^{155}Eu	1.4	3a	MAFF
^{210}Po	14	3a	OSUH
^{210}Pb	24	3a	IT, ORNL
^{212}Pb	14	3a	MAFF
^{214}Bi	14.5	3a	MAFF
^{234}U	12	3a +1c	AWE, IT, LGC, OSUH, NIST
^{235}U	0.40	3a +1c	AWE, LGC, NIST, NPL
^{238}U	12	3a +1c	IT, LGC, NIST, OSUH
^{237}Np	0.007	3a +1c	LRM, KU
^{241}Am	10	3a +1c	AWE, BNF, IT, KU, LGC, MAFF, NIST, NPL, ORNL, OSUB

Semi-Quantitative Trace Element Analysis:

Tables 4 and 5 are intended for information only. The values given are not certified.

Table 4: Semi-quantitative Emission Spectrographic Analysis for SRM 4357

Element	**µg ·g^{-1}**	Element	µg ·g^{-1}	Element	µg ·g^{-1}
Ag	0.12	Al	24700	As	<100
Au	<6.8	B	34	Ba	143
Be	<0.1	Bi	<10	Ca	6267
Cd	<32	Ce	<43	Co	2.9
Cr	27	Cu	82	Dy	<22
Er	<4.6	Eu	<2.2	Fe	10700
Ga	3.5	Gd	<32	Ge	<4.6
Hf	<150	Ho	<6.8	In	<10
Ir	<15	K	5070	La	25
Li	<68	Lu	<15	Mg	3930
Mn	163	Mo	1.8	Na	4000
Nb	10	Nd	<32	Ni	97
Os	<15	P	<680	Pb	12
Pd	<1.0	Pr	<100	Pt	<2.2
Re	<10	Rh	<2.2	Ru	<2.2
Sb	<68	Sc	2.8	Si	>340000
Sm	<10	Sn	<4.6	Sr	64
Ta	<320	Tb	<32	Th	<46
Tl	<10	Tm	<4.6	U	<220
V	21	W	<15	Y	12
Yb	1.8	Zn	45	Zr	540

Table 5: Major Elements Recalculated as Oxides

Oxide	Weight Percent	Oxide	Weight Percent
SiO_2	>73	Al_2O_3	4.7
Fe_2O_3	1.5	MgO	0.65
CaO	0.88	Na_2O	0.54
K_2O	0.5	TiO_2	0.42
P_2O_5	<0.16	MnO	0.021