STANDARD OPERATING PROCEDURE
USGS-DRIL-01, R0
Uranium-Thorium Disequilibrium Studies

1. INTRODUCTION:

The USGS Denver Radiogenic Isotope Laboratory (DRIL) located in Building 21 of the Denver Federal Center obtains geochemical and isotope data from rock and water samples for characterization studies. This document describes standard procedures for the collection of uranium (U) and thorium (Th) isotope data. Resulting data are used for (1) estimating ages and initial uranium isotopic compositions ($^{234}U/^{238}U$) of surficial and hydrogenic deposits, (2) determining the $^{234}U/^{238}U$ composition of uranium dissolved in water samples to help trace water sources and flowpaths, or (3) evaluating degrees of water/rock interaction in whole rock and other geologic material as a proxy for recent (last several hundred thousand years) fracture flow and weathering. The procedure describes methods used for chemical processing and isotope analysis that can be applied to rock, mineral, and water samples. Samples are prepared for isotope analysis using chemical digestion or evaporation followed by purification of U and Th salts and subsequent mass spectrometric analyses. Procedures described here use standard methods for U-Th disequilibrium analysis found in published literature (Lally, 1982; Faure, 1986; Ludwig and Paces, 2002; Paces et al., 2002).

2. RESPONSIBILITIES:

2.1 **Principal Investigator (PI)** is responsible for assuring compliance with this procedure and for conducting the activities described in this procedure.

2.2 **Operator** is a USGS employee or contractor who is trained to this procedure and conducts activities described herein.

3. QUALIFICATIONS AND TRAINING:

Personnel working on this procedure will be qualified and knowledgeable about the chemical processes and isotopic principles described herein. Personnel in the process of being trained as operators will be closely supervised by the PI or qualified delegate. Operators will also be authorized to handle radioactive materials in accordance with the USGS Denver-based NRC broad-scope license.

4. ASSOCIATED WORK ACTIVITIES:

There are no other work activities or procedures associated with implementation of this procedure. There are no conflicts, impacts, or coordination issues known to exist with other work activities.

5. METHODS:

5.1 The general principles of isotope dilution techniques are presented in Faure (1986). Laboratory procedures are performed under clean-bench conditions (HEPA-filtered laminar air). In order to minimize the amount of uranium and thorium contributed through chemical processing, acids and other reagents added to samples are of a purity equivalent to that obtained through sub-boiling distillation. All volumes, temperatures, times, and acid concentrations given below are approximate and do not need independent calibration. Successful application of chemical processes and isotopic determinations does not demand strict adherence to specific steps or recipes. The range of materials requires some flexibility in order to obtain purified salts of U and Th that are analyzed by mass spectrometry. Ultimately, successful application of chemical procedures are verified by analytical runs with

ion yields sufficient to measure the minor isotope peaks (^{234}U and ^{230}Th) at counts-per-second-level intensities and by total system verification described in section 10.5.

5.1.1 Preparation of Solid Samples: Rock and mineral samples can be treated in a variety of ways prior to digestion depending on sample size, type of material, U and Th concentrations, and goals for the analysis. Samples with low ^{232}Th contents (Th/U ratios less than about 1) may need no special preparation besides obtaining the appropriate-sized aliquot without contamination from other sources. Pulverization of samples, either by hand using a mortar and pestle or in a ceramic or tungsten carbide shatterbox, aids in digestion, but is not required. For bulk-rock analysis, pulverization of the sample is the only preparation step required. For U-series dating of soils, secondary minerals, or other deposits, authigenic materials precipitated from aqueous solutions having the highest uranium concentrations and lowest thorium concentrations are targeted. To obtain this material, bulk samples can be subsampled using a variety of methods including mineral separation by crushing and handpicking, micro-milling of target material under binocular magnification, or in-situ sequential microdigestion (Paces et al., 2004) if applicable. In general, chemical separation of the readily-soluble carbonate component of many deposits is avoided because of the potential for laboratory fractionation of uranium from thorium. However, treatment of silicate minerals and well-formed opal with dilute nitric or acetic acid to remove unwanted surface contamination or calcite does not significantly impact the U/Th ratios of the remaining residue. In some cases, quantification of the uranium isotopic composition inherent in different components of a rock is desired. If so, different leachate mediums (for example, de-ionized water, acetic acid, sodium acetate, nitric acid, or other) may be used for selective uranium extraction followed by complete dissolution of the residue remaining after leaching steps. Methods used to prepare samples prior to chemical processing are recorded in laboratory notebooks along with names that uniquely identify individual samples or subsamples.

5.1.2 Preparation of Water Samples: Samples of groundwater or surface water are collected in acid-washed, polyethylene bottles (or equivalent). If possible, water is filtered in the field using barrel- or plate-type filters capable of removing 0.45-micrometer-diameter, or finer, particles. If sufficient quantities of water are available, sample bottles are rinsed at least two times with the same filtered water that will be collected. Samples require no other special preservation, handling, or storage procedures. In the laboratory, water samples are acidified to an approximate pH of 3 or less using high-purity concentrated nitric acid so that any precipitates formed within the bottle at higher pH are re-dissolved. Samples that have not been filtered in the field should be noted as such and analyzed twice if the pH is above 4 and if solids are visible to compare the potential contributions from particulate matter; once by acidification before laboratory filtration, and once with acidification after laboratory filtration. Samples of pore water extracted by centrifugation or pore-water salts extracted by leaching with de-ionized water are also filtered and acidified if sufficient material is available.

5.1.3 Weighing of Samples: Samples of solid materials are weighed into appropriate-sized Teflon digestion container. Sample size is dictated by uranium concentration. The total amount of uranium needed to determine isotopic compositions by mass spectrometry can vary from approximately 1×10^{-6} to 1×10^{-9} grams. Given the range of U concentrations found in many natural rocks and minerals, sample weights of solid materials range

between 0.001 and 0.20 grams. Uranium concentrations are typically several orders of magnitude lower in natural water samples compared to rock or mineral samples and require larger sample sizes. Sample weights for water samples typically range from 1 to 500 grams. Samples are weighed in appropriate beakers or jars (preferably Teflon if heating is required) that are closed or covered to minimize interactions between the sample and atmosphere. Sample weights are recorded in laboratory notebooks.

5.1.4 Leaching of Whole-Rock Samples: Leachate analyses of whole-rock samples are performed by weighing a known amount of sample into an appropriately sized leaching vessel and adding a known weight of leaching media to the rock sample. The mixture is gently agitated to wet all surfaces and left to react. Reaction times can vary from 1 hour to several days depending on the intent of the experiment. The supernatant is removed by filtration on a pre-weighed filter. The rock and filter are then dried to determine the mass removed by leaching. All sample weights, leachate weights, reaction times, and residue weights are recorded in laboratory notebooks.

5.1.5 Weighing of Isotopic Spikes: In order to determine uranium and thorium concentrations by isotope dilution, a solution enriched with non-natural isotopes of uranium and thorium is added to the sample. This isotopic "spike" consists of a solution containing highly purified ^{236}U and ^{229}Th tracers with known concentrations such that the amount of these anthropogenic isotopes added to each sample is known. "Spike" solution is weighed into the same vessel containing the weighed solid or solution sample prior to further digestion or chemical processing. Spike weights are recorded in laboratory notebooks. After spiking, solid samples undergo further chemical digestion: water samples are placed on hotplates protected from atmospheric dust and evaporated to dryness.

5.1.6 Digestion of Solid Samples: Samples are digested using an appropriate combination of inorganic acids (typically hydrofluoric, nitric, and hydrochloric). Teflon digestion vials are sealed and heated either by placing on a hot plate set to 130° to 150°C, or by placing sample vials into high-pressure digestion vessels that are then placed in an oven set to approximately 190°C. The digestion period can range from overnight to several days. After initial acid attack, samples are taken to dryness. The remaining salts are dissolved in 7N nitric acid and centrifuged to separate the supernatant from any remaining residue or precipitate. Solids are transferred to the original containers and redigested using additional acids. These dry-down, dissolution, centrifugation, and acid attack steps are repeated until the sample is completely dissolved in 7N nitric acid, or until no further reduction in insoluble solids is achieved. At this point, the digested sample is contained within a single vial and is ready for extraction of U and Th.

5.1.7 Uranium and Thorium Extraction and Purification: Uranium and thorium are extracted and purified by standard anion-exchange chromatographic methods (Lally, 1982). Chromatographic columns use between 0.5 and 2 milliliters (mL) of commercially available AG1x8 resin (or equivalent) that has been cleaned using at least 20 column volumes of water and dilute acid (typically 0.05N HNO_3) to reduce U and Th in the blank.

To increase the efficiency of the chromatographic separation, U and Th can be co-precipitated along with iron or aluminum hydroxide, although this step is optional. Co-precipitation is performed by adding ammonium hydroxide (NH_4OH) to the digested

sample until the pH reaches between 9 and 10. Iron and aluminum hydroxides will form if Fe^{+++} and Al^{+++} are naturally present. An iron nitrate solution can be added to the original acidified solution prior to adding NH_4OH if the sample does not contain sufficient natural Fe^{+++}. The iron or aluminum hydroxide precipitate is separated from the supernatant by centrifugation and the supernatant is discarded. The precipitate is washed with water adjusted to a pH of 8 to 10 using purified NH_4OH, agitated well, and centrifuged again. After discarding the supernatant, the precipitate containing the uranium and thorium from the sample is dissolved in nitric acid and taken to dryness. Any remaining SiO_2 or Al_2O_3 is dissolved using concentrated hydrofluoric acid. Salts should go into solution completely in 7 N nitric acid for loading onto chromatographic columns.

Separation of uranium and thorium from the digested chemical matrix is required for mass spectrometric determinations, unless the matrix is high-purity silica that can be removed by digestion with hydrofluoric acid (for instance, microdigestion of hyalitic opal; Paces et al., 2004). Furthermore, U is typically separated from Th, prior to mass spectrometric analysis, but can be left together or recombined and run on the same filament if desired. Column size and resin volume vary depending on sample size and matrix. Because of the nature of the ion exchange process on the chromatographic columns, chemical protocols are flexible, and acid concentrations and volumes can vary. Acceptable procedures involve an initial clean-up column using AG1×8, 200-400 mesh, anion-exchange resin cleaned as above and conditioned with ~7 N nitric acid to retain Th. The sample solution is added to the column and allowed to elute. Matrix ions are eluted using approximately 4 column volumes of 7 N nitric acid. The waste container is then replaced with the original sample vial, and Th is eluted using 4 to 5 column volumes of 6 to 8 N hydrochloric acid. The Th vial is then replaced with a separate clean vial, and U is eluted using a series of 5 to 10 column volumes of 0.05 N nitric acid and water. Multiple passes in smaller columns may be needed to adequately purify uranium and thorium separates.

5.1.8 Filament loading and Mass Spectrometry: Uranium or thorium isotopic ratios are determined by thermal-ionization mass spectrometry. Purified U and Th salts are loaded onto vacuum-outgassed rhenium filaments, typically as either single, graphite-doped loads or directly onto side (evaporation) filaments if both ionization and evaporation filaments are being used. Other methods of loading also may produce adequate ionization. Filaments are loaded into the source of a thermal-ionization mass spectrometer equipped with an ion-counter or electron multiplier. Appropriate data acquisition routines supplied by the instrument manufacturer, or equivalent, are used to obtain uranium and thorium isotopic compositions. In addition to directly measured $^{236}U/^{238}U$, $^{234}U/^{238}U$, $^{230}Th/^{229}Th$, $^{232}Th/^{229}Th$, and $^{230}Th/^{232}Th$ atomic ratios, $^{230}Th/^{238}U$, and $^{232}Th/^{238}U$ atomic ratios are calculated using the abundance of the added spike isotopes and the measured uranium and thorium isotopic ratios. Analytical precisions of less than 0.5% are optimal, but less-precise data may be obtained when only small amounts of U are available, or for ^{230}Th of young materials. These less precise data may still provide useful information. Isotope ratios and associated analytical errors are recorded by the instrument software. Atomic ratios are converted to activity ratios by either using known decay constants or by ratioing the measured U and Th isotopic ratios to those of a secular equilibrium standard measured on the same instrument under the same running conditions.

5.2 Materials and Testing Equipment (M&TE): Materials and equipment needed to perform this work include:

- Analytical balance capable of accurately weighing samples and spikes to better than 1.0 % of measured weight
- NIST-traceable standard weights for operational checks of analytical balances
- Non-reactive (Teflon, platinum, or other) digestion containers
- High-purity acids: nitric (HNO_3), hydrofluoric (HF), hydrochloric (HCl), perchloric ($HClO_4$), acetic (CH_3CO_2H)
- High-purity de-ionized water
- Solutions of high-purity salts used for leaching: sodium acetate (CH_3CO_2Na), magnesium chloride ($MgCl_2$), or others
- Hot plate
- High-pressure, Teflon-lined digestion vessels
- Isotopically-enriched uranium and thorium tracer solutions (such as ^{236}U, ^{233}U, ^{229}Th, or equivalent)
- Iron solution for co-precipitation: iron nitrate [$Fe(NO_3)_3$]
- Ammonium hydroxide (NH_4OH)
- Centrifuge
- Chromatographic columns
- Anion exchange chromatographic resins (AG1×8)
- Rhenium ribbon welded onto filament holders
- Graphite colloidal suspension
- Thermal-ionization mass spectrometer with mass resolution of >300, abundance-sensitivity of <10 ppm at 1/238 mass offset for natural uranium, and ion counting or electron multiplier detection capabilities
- Primary NIST-traceable uranium and thorium isotope and concentration standards: SRM4321B, SRM950a, SRM U500, SRM 3159, or equivalents
- Secular equilibrium standard: Schwartzwalder uranium ores D1, D3, D9, C4-6, or C1-7 (Ludwig et al., 1985), or equivalent natural uranium-rich material in secular equilibrium between ^{238}U, ^{234}U, and ^{230}Th.

Data collected under this procedure will be traceable to calibrated or certified equipment by recording unique M&TE identifiers in laboratory notebooks. Calibrated or certified M&TE includes:

- Analytical balances, calibrated by operational checks (section 10.2 of this procedure)
- NIST-traceable standard weights, certified by a qualified vendor
- Isotopically-enriched uranium and thorium spike solutions, calibrated using NIST-certified concentration standards (section 10.3 of this procedure)
- Thermal ionization mass spectrometers, calibrated using NIST- (or equivalent) certified U-isotope standards (section 10.4 of this procedure)

6. **ANALYTICAL PREREQUISITES, LIMITS, PRECAUTIONS, AND ENVIRONMENTAL CONDITIONS**:

6.1 Prerequisites: Knowledge of the chemistry and natural radioactive decay of uranium and thorium, as well as availability of the appropriate laboratory facilities and mass spectrometer operation are prerequisites to the successful implementation of this procedure

6.2 Limits: The limitations of this procedure are (a) the skill and care of the operator in performing the sample preparation and chemical procedures, and (b) the performance of the electronic devices (analytical balances, mass spectrometers, and computer systems). Problems arising from either of these categories are indicated by inadequate ion beam

intensities, abnormally imprecise isotope measurements, or incorrect measured values for isotope standards. These problems are readily identifiable by a qualified operator. If any of these problems are suspect, data will be flagged and not released unless an adequate justification is provided. If the acquired data indicate an instrumental problem, analyses of unknown samples are suspended until the problem is rectified

6.3 Precautions: Uranium and thorium solutions exhibit low-level radioactivity and need to be handled in a manner consistent with requirements dictated by USGS radiation safety policies. Also, these solutions need to be stored and handled in a way that minimizes evaporation and contamination.

6.4 Environmental Conditions: Clean-lab conditions are used to minimize the amount of U and Th added from environmental sources.

7. **ACCEPTANCE CRITERIA, PRECISION, ACCURACY AND COMPLETENESS:** Data quality indicators against which job performance or completion can be evaluated are derived from replicate analytical results on NIST- (or equivalent) certified isotope standards, in-house age or secular equilibrium standards, or replicate analyses of unknown samples. If any of the criteria identified in this section cannot be met, no further data will be collected on samples until the problem is identified, rectified, and the standards reanalyzed to obtain acceptable results. All data released will be collected with appropriately calibrated or certified M&TE.

7.1 Mass Spectrometer Calibration: Operation of the thermal ionization mass spectrometer is considered acceptable if individual measurements of the atomic $^{234}U/^{238}U$ ratio in NIST isotope standard SRM 4321 have a within-run analytical error of better than 1% (two sigma) and a resulting $^{234}U/^{238}U$ atomic ratio that is within 2% (two sigma) of the NIST-certified value of $(5.29\pm0.02)\times10^{-5}$ (equal to a $^{234}U/^{238}U$ activity ratio of 0.963±0.003). At least one position in each multi-sample magazine/turret contains a filament loaded with SRM 4321 which is analyzed several times during analysis of unknown samples included in the magazine. If other internationally accepted isotope standards are used in place of SRM 4321, measured U-isotope ratios will be within 2% of their certified values, as above.

7.2 Total System Verification: Operation of the entire U-Th disequilibrium system (chemistry, mass spectrometry, and data reduction) is considered acceptable and verified if (1) measured $^{234}U/^{238}U$ and $^{230}Th/^{238}U$ ratios in the secular equilibrium standard (section 10.5.1) have within-run analytical errors of better than 2% (two sigma), and resulting ratios that are within 2% (two sigma) of the secular equilibrium values of 1.00, or if (2) $^{230}Th/U$ ages for the known-age standard (section 10.5.2) calculated from measured $^{234}U/^{238}U$ and $^{230}Th/^{238}U$ ratios are within 2% (two sigma) of the accepted value.

7.3 Precision: Replicate samples of homogeneous materials (water samples, whole-rock powders) will be analyzed at least every 20-50 samples. Isotope ratios will be reproducible within 2% (two-sigma) of the values obtained. In addition, replicate analyses of standards are used to evaluate external analytical uncertainty by descriptive statistical treatments. If precision criteria are not met, the data shall be evaluated for usability based on the data purpose and reasons for the reduction in precision.

7.4 Accuracy: Accuracy will be assessed by replicate analyses of standards with known isotopic compositions. In particular, $^{234}U/^{238}U$ and $^{230}Th/^{238}U$ activity ratios for a secular equilibrium or known-age standards (section 10.5.2) will give values that are between 1.02 and 0.98 (i.e., within 2% of secular equilibrium values given at the 95% confidence level) or within 2% (2σ) of the accepted age. Other standards can also be used if certified isotopic values are

available. Values exceeding the acceptance criteria for accuracy must be evaluated prior to release of data for project use.

7.5 Completeness: The number of samples sufficient to meet data requirements is identified in planning documents developed to meet Project needs. DRIL receives and analyzes most samples from external participants. Any data losses from handling, shipping, and analytical problems will be documented in data packages.

8. **SAMPLES**: Sample collection is not controlled by this procedure; however, subsampling of samples obtained through other procedures may be required.

8.1 Identification and Traceability: All samples will have a unique identification number issued by the DRIL or the PI who collected the sample. Samples may also have a unique identifier assigned by users of this procedure that may include additional information on the sample site, sample type, borehole footage, date of collection, or other. A further identifier will be appended to subsamples that maintains the identity of the source sample as well as the individual subsample. Sample and subsample identification will be maintained on original containers and laboratory notebooks. Furthermore, unique identification numbers are engraved on all Teflon jars, beakers, vials, digestion vessels, and other labware that are used to contain sample solutions during chemical processing. Tables cross referencing unique sample identifiers and labware numbers are recorded in laboratory notebooks.

8.2 Control, Storage, and Disposition: Samples and subsamples, both pre-processed and processed, are stored in a secured areas at the Denver Federal Center, Denver, CO. Final disposition of individual samples, is determined by the DRIL PI.

8.3 Special Treatment: No special treatment of rock or water samples is required. If samples or subsamples require shipment, packing and labeling will be done to ensure that sample integrity and traceability is maintained.

9. **SOFTWARE:** Software programs used to implement this procedure are an integral part of the mass spectrometric equipment (and thus proprietary) or are commercially available off-the-shelf products that use simple mathematical calculations. Software functionality is verified by analysis of standards and total system verification as described in section 10.5. No other controls are required.

10. **MEASURING AND TEST EQUIPMENT (M&TE):** Calibration of selected equipment is required. All necessary calibrations and acceptance criteria are documented in this section. Any M&TE that does not comply with calibration criteria will be removed from service until the item can be repaired and recalibrated. Measuring and test equipment (M&TE) that requires calibration includes:

M&TE Item	Calibration/check frequency	Procedure
Certified weights	Prior to initial use or if suspected of damage	USGS-DRIL-01, sec. 10.2
Analytical balances	Each use	USGS-DRIL-01, section 10.2
Spike solutions	At least once every two years	USGS-DRIL -01, Section 10.3
Thermal-ionization mass spectrometer	Each use	USGS-DRIL -01, Section 10.4

10.1 Standard Weights: High-quality, stainless steel, weights are used to calibrate analytical balances. Each weight or weight set has a unique serial number. All standard weights have weight values that have been certified against NIST-traceable sources, either upon purchase from the vendor or subsequently by calibration from a NIST-compliant vendor. Standard weights are maintained under controlled environmental conditions and do not drift over time. However, if weights become damaged, they are recertified by a NIST-compliant vendor or replaced.

10.2 Calibration of Analytical Balances: Analytical balances are calibrated at each use by performing the manufacture's internal auto-calibrate routine followed by checking a series of NIST-traceable standard weights in the range representing the samples being weighed. Measured values are documented in a laboratory notebook and compared to certified values. If the balance readings are off by more than the amount listed in the following table, the balance will be removed from service until it can be adjusted and rechecked to ensure compliance:

Acceptable deviations from calibrated weight values or balances with different sensitivities.

Minimum weight reading of balance	Acceptable deviation from certified weight
0.00001 g	≤ 0.0005 g
0.0001 g	≤ 0.001 g
0.001 g	≤ 0.005 g
0.01 g	≤ 0.05 g

10.3 Calibration of Spike Solutions: Calibration of the uranium and thorium isotopic spikes is determined by isotope dilution techniques using certified NIST-traceable concentration standards ("shelf solutions"), such as SRM4321B, SRM950a, SRM3164 or equivalent, for uranium and SRM3159 or equivalent for thorium. Alternatively, concentration standards can be prepared gravimetrically from purified metals or oxides of uranium or thorium, such as SRM U500, SRM 950a, or equivalent. Measured isotope ratios of the equilibrated spike-shelf mixture are then used to calculate the concentrations of the spike isotopes by standard isotope dilution calculations (Faure, 1986) based on the known concentrations of uranium and thorium in the shelf solutions. Calibration of the U/Th concentration ratio in the spike solution is further verified as part of the System Calibration by analyzing solutions of geologic material known to be in secular equilibrium or having known age (section 10.5.2). Spike solutions are calibrated whenever new stocks of spike solution are prepared, or whenever the System Calibration indicates that the spike concentrations may have shifted.

10.4 Calibration of Mass Spectrometer: Thermal ionization mass spectrometers are calibrated by analyzing NIST, or equivalent, standards with certified U-isotopic compositions. A standard (NIST SRM 4321, or equivalent) is included in each multi-sample magazine and is analyzed

during the course of isotope measurements to ensure proper operation of the instrument. Acceptance criteria are given in section 7.1.

10.5 Total System Verification: The overall procedure for uranium-thorium disequilibrium studies is verified as a coherent and complete laboratory system by analysis of known geologic materials in a state of radioactive secular equilibrium (section 10.5.1) or materials with known age (section 10.5.2). The resulting $^{234}U/^{238}U$ and $^{230}Th/^{238}U$ atomic ratios for these materials will give values that are consistent accepted values within 2% at the 95% confidence level. This verification represents they entire process because the standard materials undergo all processing steps (weighing, spiking, chemical separation, mass spectrometry, data reduction). Successful replication of the expected $^{234}U/^{238}U$ and $^{230}Th/^{238}U$ ratios ensures that the entire data collection system is operating as expected. Analysis of verification standards will be performed during the same period of time that U-Th samples are run. If the resulting $^{234}U/^{238}U$ and $^{230}Th/^{238}U$ ratios are not within the limits defined above, data collection operations on samples will be suspended until problems can be rectified and the standards rerun.

10.5.1 Secular Equilibrium Standard: A material (typically a natural uranium mineral or ore) shall qualify as a secular equilibrium standard if 1) U-Pb age determinations have shown that the age of the material is greater than five million years, 2) the $^{206}Pb/^{238}U$ and $^{207}Pb/^{235}U$ ages of the material are concordant to within 5%, and 3) $^{234}U/^{238}U$ and $^{230}Th/^{238}U$ ratios are shown to be within 1% (determined by alpha-decay counting) or 0.5% (determined by mass spectrometry) of values expected for secular equilibrium material ($^{234}U/^{238}U$atomic = 5.4891×10^{-5} and $^{230}Th/^{238}U$atomic = 1.6939×10^{-5} given in Cheng et al., 2000, pages 24 and 27, respectively). Natural uranium ores from the Schwartzwalder Mine (D1, D3, D9, C4-6, and C1-7; Ludwig et al., 1985) meet these criteria, and have $^{234}U/^{238}U$ ratios that are consistent with known decay constants. Solutions of these uranium ores also exhibit $^{234}U/^{238}U$ and $^{230}Th/^{238}U$ ratios that are identical within analytical uncertainties, and are identical, within error, to other secular equilibrium standards.

10.5.2 Known-Age Standard: Analysis of a natural material with known Pleistocene age can be used to verify reliable operation of the total U-series dating system. In the 1980s, the USGS developed an in-house U-series dating standard consisting of large sample of Acropora coral that was cleaned, powdered, and homogenized. Repeat analysis of this standard yields a $^{230}Th/U$ age of 119.6 ±1.9 ka (n=17, Watanabe and Nakai, 2006) and a calculated initial $^{234}U/^{238}U$ value consistent with seawater value of 1.1496 ±0.0060 (Delanghe et al., 2002). Analysis of this material along with unknown samples provides robust evidence that the entire U-series dating process including digestion, weighing, spiking, chemical separation, mass spectrometry, and data reduction is functioning properly providing the resulting age calculated for the standard is within error of the known age (i.e., 119.6 ±1.9 ka).

10.6 Calibration Records: Calibration records generated as a result of this technical procedure are documented in laboratory notebooks, spectrometer output, and spreadsheet or database calculations. Total System Verification results will be documented in a similar manner. Records documenting calibrations shall be maintained by the PI or delegate. Calibration records will be submitted along with data packages.

11. **HANDLING, STORAGE AND SHIPPING OF EQUIPMENT AND CONSUMABLES:** Equipment and consumable materials will be handled and stored in a manner consistent with USGS chemical- and

radiation-safety policies. Access to chemistry labs are limited to authorized users only. Use of acid-storage cabinets, secondary containment, personal protective equipment, and limited access practices will be used as appropriate. Bench-top chemistry is performed under HEPA-filtered air flow in temperature-controlled laboratories. Cleanliness of the labware, lab environment, and consumable reagents is monitored by routine inclusion of total-process blanks (pure spike solution that undergoes the entire chemical digestion and separation processes). No shipping of equipment or consumables is required.

12. **PROCUREMENT:** No contracts or agreements are required to implement this procedure. Consumable materials are procured from commercial sources using normal credit card purchases or through the USGS procurement process. All USGS procurements of goods or equipment include technical specifications that vendors must meet and demonstrate acceptability before goods or equipment are used. Quality-affecting materials are inspected on receipt and are verified as part of the analyses and calibration/verification using NIST-traceable isotope standards.

13. **ELECTRONIC MANAGEMENT OF INFORMATION:** Data generated by this procedure consist of isotope ratios that are generated by proprietary commercial software controlling the mass spectrometer. Original data files are maintained on the computer controlling the instrument and are copied to several other USGS-DRIL computers in Building 21 of the Denver Federal Center. All computers are password protected.

14. **RECORDS:**

    14.1 **Records Packages:** The completed analytical data set consists of uranium and thorium concentrations, activity ratios ($^{234}U/^{238}U$, $^{230}Th/^{238}U$, $^{232}Th/^{238}U$, $^{230}Th/^{232}Th$), and errors. Only uranium concentrations and $^{234}U/^{238}U$ activity ratios and the associated uncertainties are required for analyses of water samples or samples of solids where Th results were not analyzed. In addition to a table of data, a Data Summary Sheet containing supporting information (description of intended use, as well as results of calibrations, analyses of standard materials, and appropriate data quality indicators) will be included along with individual records sheets for each sample.

    14.2 **Individual Records:** Pertinent analytical and calibration information will be transcribed from chemistry laboratory notebooks, mass spectrometer logbooks, and instrument output sheets into records of individual analyses. Information includes sample and spike identification, sample and spike weights, dates of analysis, identification of the instrument used for analysis, and resulting atomic ratios for the isotopes of interest. Concentrations along with activity ratios calculated from these data will also be included.

15. **REFERENCES:**

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APPROVALS AND EFFECTIVE DATE:

EFFECTIVE DATE:

December 16, 2011

CONCURRENCE:

James B. Paces
Principal Investigator, USGS

16 December 2011
Date

William L. Dam
Technical Reviewer, USGS

December 16, 2011
Date

APPROVAL:

Bonnie K. Thompson
NNSA Program Manager, USGS

12/16/2011
Date