Natural Uranium Radioactivity Solution Standard: SRM 4321d

Ronald Collé, Lizbeth Laureano-Pérez, Svetlana Nour, Jerome J. La Rosa, Brian E. Zimmerman, Leticia Pibida, and Denis E. Bergeron

National Institute of Standards and Technology,
Gaithersburg, MD 20899-8462, USA

ronald.colle@nist.gov
lizbeth.laureano-perez@nist.gov
svetlana.nour@nist.gov
jerome.larosa@nist.gov
brian.zimmerman@nist.gov
leticia.pibida@nist.gov
denis.bergeron@nist.gov

A new natural uranium solution standard has been produced and will be disseminated by the National Institute of Standards and Technology (NIST) as Standard Reference Material 4321d. The standard is certified for the massic activities of ^{234}U, ^{235}U, and ^{238}U in solution, and it is based on isotopic mass data for the metallic Certified Reference Material (CRM) 112-A (originally issued as SRM 960) that was obtained from THE U.S. Department of Energy, New Brunswick Laboratory. The metallic CRM was chemically cleaned, dissolved, and gravimetrically diluted to prepare a master solution, which was quantitatively dispensed into 5 mL aliquots that were contained within flame-sealed glass ampoules for each SRM unit. Homogeneity among SRM units, verifying solution homogeneity, was substantiated by photonic-emission integral counting with a NaI(Tl) well counter. Confirmatory measurements were performed by liquid scintillation counting for the total massic activity, and by isotope dilution α spectrometry for the ^{234}U and ^{238}U massic activities.

1. Introduction

Natural uranium refers to the element of atomic number $Z = 92$ (uranium) in the same isotopic ratios of ^{234}U, ^{235}U, and ^{238}U as found in nature. All three isotopes are primordial radionuclides with half-lives ranging from 10^5 years to 10^9 years. There are three naturally occurring radioactive series, and two of these series, termed the "actinium series" and "uranium series," are headed by ^{235}U and ^{238}U, respectively. The shorter-lived ^{234}U isotope is a decay product in the ^{238}U uranium series. Figure 1 shows the initial and relevant parts of these decay chains that lead to ^{230}Th and ^{231}Pa, with half-lives of $> 10^4$ years. The isotopic ratios in natural uranium, in terms of radioactivity, correspond to approximately 49 % ^{234}U, 2 % ^{235}U, and 49 % ^{238}U.
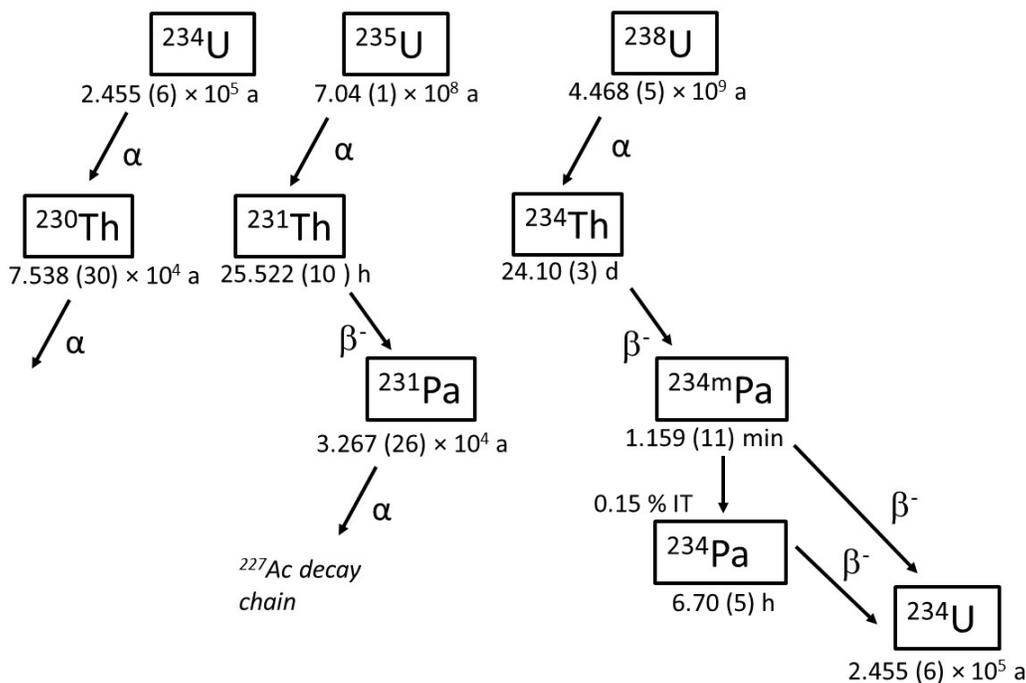
Fig. 1. Decay chain of the natural uranium isotopes [234]U, [235]U, and [238]U. The half-life for each nuclide was obtained from the Decay Data Evaluation Project (DDEP) [1].

A natural uranium radioactivity solution standard was last issued by the National Institute of Standards and Technology (NIST) nearly 20 years ago as a Standard Reference Material (SRM)[1] and has been out of stock and unavailable for many years. Previous issues, all derived from the same stock uranium metal isotopic standard, were: SRM 4321 in 1986, SRM 4321b in 1992, and SRM 4321c in 1997 [2]. These standards are used for calibrating α-particle counting instruments, for monitoring of radiochemical procedures, and for testing measurement proficiency by laboratories. They are needed by wide segments of the environmental measurement community and for geophysical research, particularly in examining uranium series disequilibrium and for [230]Th/U dating methods. For example, SRM 4321b was recently used to calibrate and make corrections for uranium-series isotope analysis by thermal-ionization mass spectrometry that was part of a study of a 130 000 year old archaeological site in southern California, USA [3], showing evidence of human manipulation of broken stones and mastodon bone fractures. Even critics of the study's conclusions concur that the geochronology dating of the site was flawless [4]. If correct, the study indicates that some unknown species of *Homo* was in North America over 100 000 years earlier than previously believed. This species would be ancestors of Neanderthals or members of some other extinct human lineage, unrelated to any living group of people. The dating of this remarkable archeological finding can in part be attributed to the availability of a natural uranium radioactivity solution standard.

This paper describes the production of a new issue of a natural uranium radioactivity solution standard by NIST, *viz.*, SRM 4321d.

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2. Overview, Experimental Design, and Production

2.1 CRM 112-A Stock Material

The standardization of SRM 4321d for the massic activities of [234]U, [235]U, and [238]U is linked, both in terms of origin and certified values, to an isotopic mass standard, Certified Reference Material (CRM) 112-A [5], which was obtained from the U.S. Department of Energy, New Brunswick Laboratory (NBL). This CRM consists of a natural uranium metal bar having an assay purity of (99.975 ± 0.006) % by mass and a relative atomic mass of 238.028 918 ± 0.000 012, with certified values for atom percentages of [234]U, [235]U, and [238]U isotopes (given in the second column of Table 1),[2] as obtained from mass spectrometry. Each unit consists of a metal bar of nominal mass, ranging from 4 g to over 25 g, as listed on the container. The CRM has a significant amount of surface oxide that requires chemical cleaning before use.

Table 1. Calculation of the activity per unit mass of the CRM 112-A metal for each uranium isotope, as obtained from the atom percentages given in the CRM 112-A Certificate of Analysis [5] and the DDEP-evaluated half-lives [1]. Numbers in parentheses represent the numerical value of the uncertainty and refer to the corresponding last digits of the quoted result. The atom percent uncertainty is two times the standard uncertainty, as given in the CRM Certificate, while those for the half-life and activity per unit mass are standard uncertainties.

Uranium isotope	Atom percent of isotope (%), I	Half-life (a), T	Activity per unit mass of CRM 112-A (Bq g^{-1}), A
[234]U	0.005 245 8 (81)	$2.455\ (6) \times 10^5$	$1.187\ 1\ (30) \times 10^4$
[235]U	0.72 017 (39)	$7.04\ (1) \times 10^8$	$5.683\ 4\ (82) \times 10^2$
[238]U	99.247 48 (39)	$4.468\ (5) \times 10^9$	$1.234\ 4\ (14) \times 10^4$

The provenance of the CRM 112-A material is convoluted. The history is summarized in NIST and NBL certificates [1, 5]. The material was produced by Mallinckrodt Chemical Works (St. Louis, MO, USA) using the direct-ingot or "dingot" technique, which produces high-purity massive uranium metal with low carbon content. The ingot was shipped to New Brunswick Laboratory in 1959 and was subsequently processed and cut into smaller bars at National Lead of Ohio (Fernald, OH, USA). Production details are available in a NBL report [8]. Measurements and certification of the uranium assay were performed at the National Bureau of Standards (NBS, now NIST), and the material was originally issued in 1972 by NBS as SRM 960 [9]. All technical and administrative aspects of the NBS special nuclear material SRMs, including SRM 960, were transferred to the NBL program in 1987. In 1998, NBL repackaged the material and verified the uranium assay and atomic mass. In 2010, NBL again repackaged the material and performed isotopic certification and assay verification measurements.

The relation between activity A and number of atoms N for a radionuclide is directly proportional, with the decay constant λ as proportionality constant, leading to A being inversely proportional to the radionuclide's half-life T, i.e., $A = N\,\lambda = N\,\frac{\ln 2}{T}$. With this, the activity per gram, A_i, in units of Bq g^{-1}, for each of the three isotopes in CRM 112-A was calculated using

$$A_i = \frac{P}{W} L\, I_i\, \frac{\ln 2}{T_i},\qquad(1)$$

where
P is the fractional uranium assay (purity) certified for CRM 112-A (given above);
W is the relative atomic mass for CRM 112-A (given above);
L is the Avogadro constant taken to be 6.022 140 857 (74) × 10^{23} mol^{-1};
I_i is the isotopic atom ratio for the isotope in CRM 112-A (Table 1, col. 2); and

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[2] The stated uncertainties are two times the standard uncertainty. Unless otherwise noted, all uncertainties given in the paper correspond to standard uncertainties multiplied by a coverage factor of $k = 2$. Certain nuclear data (e.g., half-lives) and fundamental physical constants (e.g., Avogadro number) are given, by convention, only as standard uncertainties. At times, uncertainties may be given as numbers in parentheses, which represent the numerical value of the uncertainty and refer to the corresponding last digits of the quoted result. The treatment and reporting of uncertainties follows NIST policy and international conventions given in Taylor and Kuyatt [6] and JCGM [7].

T_i is the half-life of the isotope (Table 1, col. 3) in seconds using a conversion of 31 556 926 s a^{-1} for the mean solar year.

The results for the calculated individual isotopic activities per gram of CRM 112-A metal from Eq. (1) are given in Table 1. These values served as the basis for linking a measured mass of the CRM to the massic activities for the SRM 4321d solution standard.

The overall scheme to produce SRM 4321d is illustrated in Fig. 2. As indicated, the CRM metal was first chemically cleaned, rinsed, and dried, and its mass was determined by two independent gravimetric measurements. Second, the metal was dissolved in nitric acid and subsequently diluted to form a large-volume master solution, after an acidity adjustment. The master solution was dispensed in 5 mL aliquots into borosilicate glass ampoules, which were then flame-sealed.
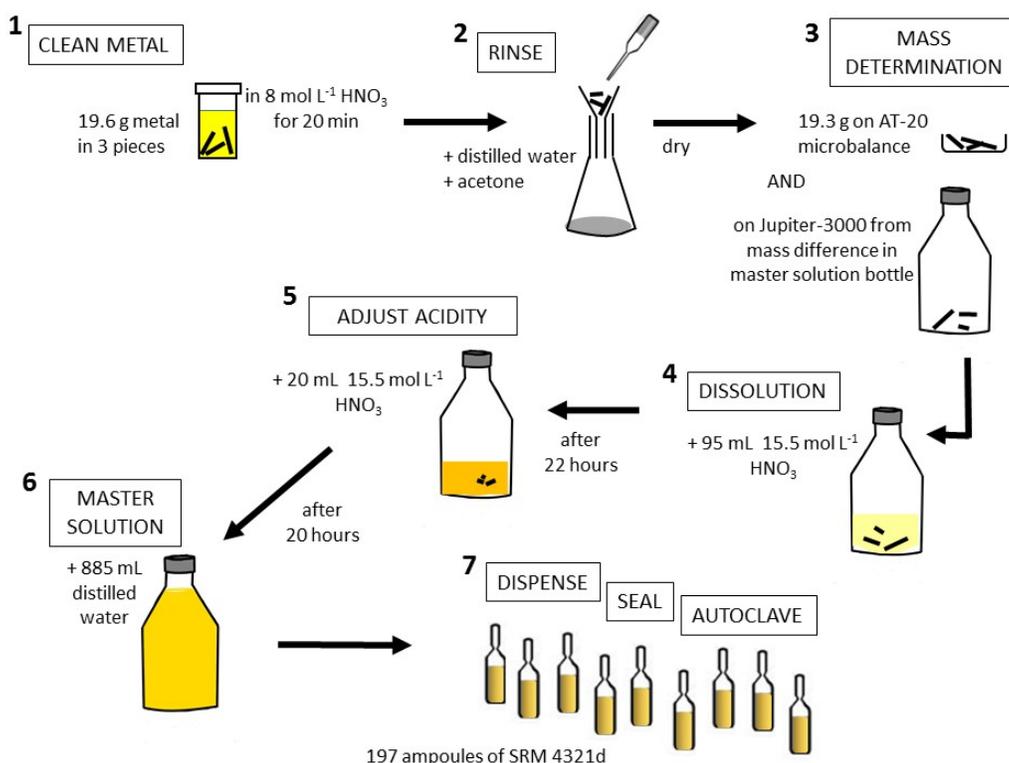
Fig. 2. General scheme used for the production of SRM 4321d. Refer to text for details.

2.2 Chemical Cleaning and Gravimetry of Metal

Before initiating the gravimetry and dissolution of CRM 112-A, the metal bar required cleaning. The material was acquired in 1997, and the 26 g bar had been cut into smaller sections for more convenient handling. Three pieces in the range of 5 g to 7 g were used for this work. As recommended by NBS for the original SRM 960 [9], the chemical cleaning procedure used to remove the UO_2 surface contamination from the metallic bar consisted of the following steps:

a) metal was immersed in 8 mol L^{-1} HNO$_3$ for 20 min, which removed all visible black, dusty surface oxides;
b) cleaned metal was rinsed with deionized, distilled water to remove residual HNO$_3$;
c) metal was rinsed with pure acetone to wash off residual water;
d) acetone was evaporated for 90 s; and

e) on immediately weighing the metal, readings were observed as a function of time until constant mass was reached.

Mass differences from weighing the metal before and after cleaning indicated that approximately 300 mg of mass were removed in the cleaning (about 1.6 % of the initial mass).

Figure 3 displays the results of the gravimetric determinations of the mass of CRM 112-A used for the dissolution and for the total solution mass. The mass of the cleaned metal was determined first by quickly weighing the metal in a weighing boat with a Mettler AT20 electronic microbalance (Mettler-Toledo, Columbus, OH., USA).[3] The mass was also determined with a large-capacity (3 kg) mechanical balance with optical scale (Voland Jupiter 3000)[4] from the mass difference of a 1 L master solution reagent bottle before and after the metal was added to the bottle. The relative difference in the two mass determinations was 0.04 %.

Fig. 3. Gravimetric determinations of the mass of the CRM 112-A cleaned uranium metal used for the dissolution and the total solution mass. The mass of the U metal was obtained by two independent determinations using the AT-20 microbalance and the large-capacity Jupiter balance. The two results given, with a relative difference of 0.042 %, include air buoyancy corrections. The total mass of the master solution was obtained from the mass difference readings between the empty and filled bottle. This difference was multiplied by the air buoyancy correction shown. The balance was checked with added standardized weights (with the sum of the weight corrections δ for the added weights) at values bracketing each of the two readings. The numbers in parentheses represent the replication precision of the observed mass readings, given as ts_m (product of Student's t value for $n = 3$ with $p = 0.95$ and the standard deviation of the mean), and refer to the corresponding last digits of the quoted result.

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[3] Certain commercial equipment, instruments, or materials are identified in this paper to foster understanding. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.
[4] Voland & Sons, Inc., formerly of New Rochelle, NY, USA.

2.3 Dissolution and Solution Gravimetry

Prior to the initiation of this work, there was an element of uncertainty in the dissolution of uranium with nitric acid. Given that the final master solution was intended to have an acid amount-of-substance concentration (molarity) of about 1 mol L^{-1}, it was important to know the required HNO$_3$:U amount-of-substance (mole) ratio needed to dissolve the metal. This would determine the amount of HNO$_3$ to be used for the dissolution. The stoichiometry was conflicting. None of the major references on uranium chemistry [10–12] addressed the issue. A paper by Larsen [13] reported that the dissolution reaction with nitric acid is "complicated, with the acid reduction products varying from nitrogen dioxide to ammonia." In generalizing, Larsen concluded that at acidities of less than 8 mol L^{-1}, nitrous oxide was the principal gaseous product, while at higher acidities, nitrogen dioxide is the principal product. Balanced chemical reactions or amount-of-substance (mole) ratios were not given. Conflicting NIST laboratory records and anecdotal information [14] suggested that the dissolution of uranium with concentrated nitric acid had an HNO$_3$:U amount-of-substance ratio in the range of 3 to 4 with the evolution of H$_2$. It subsequently became apparent that this was in error. Yet, based on the report by Larsen [13], the balanced reactions yielding either NO or NO$_2$ were derived to be:

$$U + 4\ HNO_3 \rightarrow UO_2(NO_3)_2 + 2\ H_2O + 2\ NO,$$
and
$$U + 8\ HNO_3 \rightarrow UO_2(NO_3)_2 + 4\ H_2O + 6\ NO_2,$$
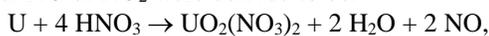
indicating that the dissolution either required a 4:1 or 8:1 amount-of-substance ratio for HNO$_3$:U. A conservative 4:1 choice was initially chosen for the amount of concentrated HNO$_3$ to add, knowing that an acidity adjustment could be subsequently made if necessary.

Dissolution of the nominal 19.3 g of the cleaned metal was made with 95 mL of 15.5 mol L^{-1} HNO$_3$. It was soon readily apparent that the 8:1 amount-of-substance ratio was operative, given that huge volumes of the characteristic reddish-brown NO$_2$ were observed. To ensure that the final master solution had a desired 1 mol L^{-1} HNO$_3$ amount-of-substance concentration, an additional 20 mL of 15.5 mol L^{-1} HNO$_3$ was added after 22 h of dissolution. Minute particulate matter was observed in the master solution bottle, so the dissolution in the concentrated solution was allowed to continue for another 20 h until there was no further evidence of any remaining particulate matter. After expelling all excess NO$_2$, the resulting solution was diluted with a nominal 885 mL of distilled water to form the SRM 4321d master solution. Figure 3 shows the careful gravimetric determination of the total master solution mass on the Jupiter-3000 balance. The mass of the empty bottle at about 607.8 g and the mass of the filled bottle at about 1648.4 g were closely bracketed by balance checks with OIML Class E1 standard weights.[5] The relative differences between the standard weights and mass measurements for these balance checks were in the range of 10^{-4} % to 10^{-6} % in all cases.

2.4 Ampoule Preparation

The resulting SRM 4321d master solution was dispensed into 197 borosilicate glass ampoules using a Microlab 620 single-syringe automatic dispenser (Hamilton Company, Reno, NV, USA). The deeply yellow-colored uranyl nitrate solution consisted of 21 mg UO$_2^{+2}$ per gram of solution in (1.06 ± 0.01) mol L^{-1} HNO$_3$ with a density of (1.057 ± 0.001) g mL^{-1} at 21.6 °C. Fourteen ampoules, roughly every fifteenth one that was filled, were weighed before and after they were filled to obtain an estimate of the dispensing precision and contained solution mass. Weighing was performed with an electronic analytical balance (Mettler AE240). The average mass was 5.284 3 g, with a relative standard deviation of 0.11 % for the $n = 14$ sample distribution. Figure 4 shows the relative invariance in the solution mass with the ampoule filling order. After filling and weighing, the ampoules were (1) flame-sealed with a natural gas/O$_2$ torch on the Collé-Cavallo NIST-custom sealer, (2) inspected for flaws, (3) autoclaved in a pressure vessel for 20 min at 0.10 MPa (≈15 psi) and about 120 °C, and (4) labelled.

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[5] Organisation Internationale de Métrologie (OIML), which defines the requirements for various classes of weights, classifies E1 as a mass standard one level below E0, the national primary mass standard.
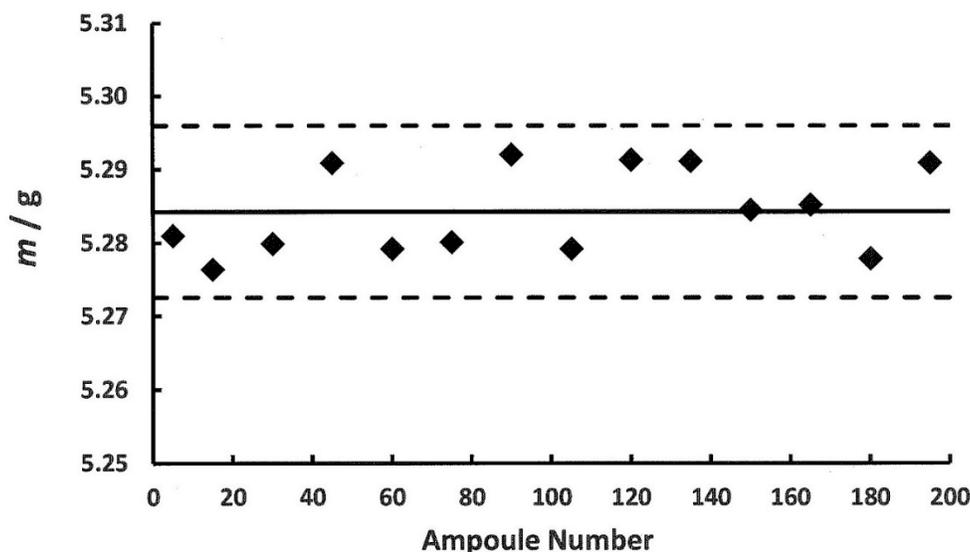
Fig. 4. Dispensed mass of master solution m (in units of grams) in 5 mL aliquots of SRM 4321d as a function of ampoule filling order. The solid horizontal line corresponds to the mean mass (5.284 3 g), and the dashed lines represent the lower and upper limits for the $\pm$ $2s$ about the mean, where s is the standard deviation for the $n = 14$ distribution.

3.   Solution Massic Activities for SRM 4321d

The massic activities in units of Bq g^{-1} for the ^{234}U, ^{235}U, and ^{238}U isotopes in SRM 4321d were obtained from the values of the activity per unit mass of CRM 112-A (Table 1, col. 4) on multiplication by the mass ratio m_u/M_s, where m_u is the mass of the cleaned uranium metal, and M_s is the total solution mass. Refer to Fig. 3. Table 2 provides the certified values for the massic activities of the three uranium isotopes in the SRM solution along with their respective relative expanded uncertainties. A tabulation for the uncertainty assessment is given in Table 3. As indicated, the uncertainty in the respective half-life values dominates the massic activity uncertainties.

Table 2. Certified massic activities of ^{234}U, ^{235}U, and ^{238}U in the natural uranium solution standard SRM 4321d. The uncertainties on these certified values are expanded uncertainties, $U = k\,u_c$. The quantity u_c is the combined standard uncertainty that was calculated according to NIST and JCGM guidelines [5, 6]. To obtain U, the combined standard uncertainty u_c was multiplied by a coverage factor of $k = 2$, which was chosen to obtain an approximate 95 % level of confidence. The uncertainty components that comprise U are given in Table 3.

Uranium isotope	Massic activity of isotope in SRM 4321d	Relative expanded uncertainty, U ($k = 2$)
^{234}U	220.16 Bq g^{-1}	0.52 %
^{235}U	10.540 Bq g^{-1}	0.31 %
^{238}U	228.93 Bq g^{-1}	0.25 %

Table 3. Uncertainty assessment for the massic activities of ^{234}U, ^{235}U, and ^{238}U in the natural uranium solution standard SRM 4321d, where u in percent is the relative standard uncertainty for each component. All uncertainty components were evaluated by Assessment Type B, which denotes an evaluation by methods other than statistical methods [6, 7].

	Uncertainty component	u (%)		
		^{234}U	^{235}U	^{238}U
1	Uranium mass fraction in CRM 112-A, from CRM 112-A Certificate [5]	0.003	0.003	0.003
2	Isotopic uranium atom fraction in CRM 112-A, from CRM 112-A Certificate [5]	0.077	0.027 1	0.000 20
3	Half-life [4] used for conversion of number of atoms to activity	0.244	0.142	0.112
4	Mass of CRM 112-A uranium metal used	0.05	0.05	0.05
5	Quantitative dissolution of metal	0.05	0.05	0.05
6	Mass of SRM 4321d master solution	0.005	0.005	0.005
Relative combined standard uncertainty, u_c		**0.261**	**0.153**	**0.123**
Relative expanded uncertainty ($k = 2$), U		**0.52**	**0.31**	**0.25**

4.   Experimental Measurements Aspects

4.1   Homogeneity

Homogeneity of the SRM 4321d master solution and among the filled and sealed ampoules was checked by photonic emission integral counting. Each and every ampoule was measured on one or two occasions in a NaI(Tl) well counter; *viz.*, a PerkinElmer (Waltham, MA, USA) 2480 WIZARD2 Automatic Gamma Counter. The detector crystal was 75 mm diameter with 80 mm height and shielded with a minimum of 50 mm of lead. The 197 ampoules were measured in eight batches and were loaded into the well by the automatic sample changer using custom-built centering tubes. Each batch contained 30 ampoules, including blanks for background subtraction. The ampoules for a given batch were sampled by taking every fourth or fifth ampoule in the filling order. Stability amongst batches on the different measurement occasions was monitored with a 1.97 kBq ^{129}I check source (1.6×10^7 a half-life). Although there are over 250 known γ transitions in the three uranium isotopes and the three β^--emitting daughters (^{231}Th, ^{234}Th, and ^{234m}Pa), the NaI(Tl) spectra are rather uninteresting, with the decay fractionated through many weak transitions and dominated by the K and L X-rays of Th and Pa, along with only some weak higher-energy lines, principally from ^{234m}Pa decay. The spectrum for each measurement was accumulated for an interval of 2700 s (live time), and the region from nominal 20 keV to 2000 keV was integrated to obtain an integral counting rate that was corrected for background. The Poisson counting statistics on any one measurement were 0.15 %. The mean counting rate from 223 measurements was 191.89 s^{-1}, with a relative standard deviation of 0.21 %. The average relative difference between 28 duplicate measurements on the same ampoules, randomly sampled from the entire set, was 0.16 %. The individual results are displayed in Fig. 5. Interestingly, but not surprisingly, 96 % of the values lie within the mean $\pm 2s$ interval, with only 8 of the 223 values falling outside. The normality of the homogeneity data was verified with a probability plot correlation coefficient (PPCC) test ($p \approx 0.64$) [15]. The data also passed both an Anderson-Darling goodness-of-fit test ($p \approx 0.28$) and a Wilk-Shapiro test for normality ($p \approx 0.31$).

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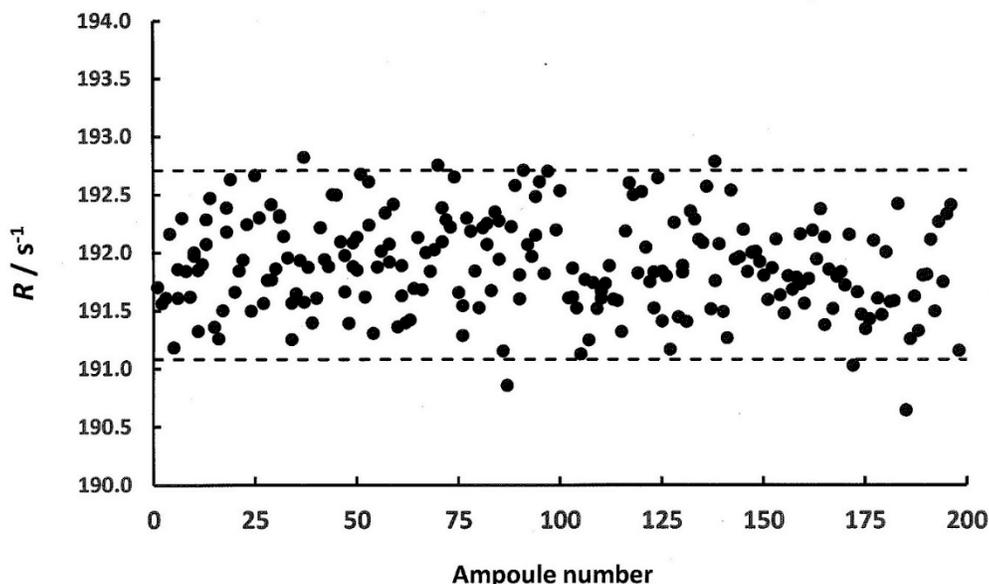
Fig. 5. The background-corrected integral counting rate *R* (in units of counts per second) for each of 195 SRM 4321d ampoules plotted versus ampoule number (filling order) as measured in a NaI(Tl) well counter. The dashed lines show the mean $\pm\,2s$ interval, where *s* is the standard deviation of the distribution for the $n = 223$ measurements. Twenty-eight ampoules were measured in duplicate, with a 0.16 % average relative difference.

4.2   Impurities

The CRM 112-A stock metal was certified to have an elemental purity of (99.975 ± 0.006) % on a mass basis [5]. Also, as reported, ^{233}U and ^{236}U "were not detected" [5], and the limit of detection of uranium ratios for the techniques that were used was stated to be 5×10^{-9}.

Impurity analyses of the SRM 4321d solution were also performed by high-resolution photonic emission spectrometry using high-purity germanium (HPGe) detectors. For this, the contents of one of the SRM ampoules were transferred gravimetrically to a NIST "standard ampoule," which is used to define the geometry and attenuation for all ionization chamber and γ-ray spectrometry measurements performed at NIST. Measurements, ranging in length between 1 d and 2 d, were made with three detectors (*viz.*, "T," "B," and "X") in different geometries. The detectors and spectrometry procedures used by NIST have been described by Pibida et al. [16, 17].

No photon-emitting impurities were observed in any of the measurements. The estimated lower limits of detection for the X detector, expressed as massic photon emission rate, as of April 2017, were:

$1.4\ \mathrm{s^{-1}\,g^{-1}}$ for 15 keV $< E <$ 20 keV;

$0.36\ \mathrm{s^{-1}\,g^{-1}}$ for 25 keV $< E <$ 105 keV;

$0.25\ \mathrm{s^{-1}\,g^{-1}}$ for 110 keV $< E <$ 490 keV; and

$0.32\ \mathrm{s^{-1}\,g^{-1}}$ for 500 keV $< E <$ 2000 keV.

These limits are in the range of 0.03 % to 0.15 % relative to the total massic activity of the three uranium isotopes and their daughters, assuming an impurity with 100 % emission of a single photon.

These impurity analyses were formidable tasks, given the large number of weak γ transitions and intense Th and Pa K and L X-rays. Similarly, it was difficult to perform accurate assays of the three uranium isotopes from the γ-ray spectrometry. The assays had estimated relative standard uncertainties in the range of 15 % to 30 %, and the ^{238}U and ^{234}U results compared to the certified massic activities were consistent to only 7.4 % and 29 %, respectively. By fortuity, the assay result for ^{235}U, with lowest massic activity, agreed with the certified value to better than 0.1 %! The large measurement uncertainties are not

from the uncertainties in the nuclear decay data, but rather they come from the low counting statistics resulting from the very small magnitudes in the probabilities per decay for the photons.

Alpha spectrometry for impurities was also performed as a part of the isotope dilution analysis. No impurities were detected, as considered and discussed in Sec. 4.3.2.

4.3 Confirmatory Measurements on SRM 4321d

4.3.1 Liquid Scintillation Counting

Confirmatory measurements for the total massic activity in SRM 4321d were performed by $4\pi\alpha\beta$ liquid scintillation (LS) counting. Two separate trials were conducted. Each set of sources for the trials was measured on two different LS counters; *viz.*, Beckman LS 6500 (Beckman Coulter, Fullerton, CA, USA), designated as counter "B"; and Hitachi Accuflex LSC-8000 (Hitachi Aloka Medical, Ltd., Tokyo, Japan), designated as counter "H." More than one LS counter is typically used in our laboratory for any given set of experiments to hopefully demonstrate that results are independent of the operating characteristics of a particular instrument (detection threshold, photomultiplier efficiency, deadtime, amplification, signal conversion, *etc.*). In addition to our laboratory's common practice of closely matching quenching conditions and cocktail compositions in counting sources, both instruments use quench indicating parameters (QEP) to monitor quenching. The Beckman counter "B" uses a Horrocks Number *H#* to monitor the quench level, which is based on the downward spectrum shift of the Compton edge of an external ^{137}Cs source with increasing quenching in the cocktail, while the Hitachi counter "H" uses the less reliable external standard channel ratio (*ESCR*) quench parameter, which relates quenching to the ratio of two counting windows in the Compton spectrum of [133]Ba.

The LS counting sources were in all cases gravimetrically prepared in 20 mL glass LS vials with Ultima Gold AB (UGAB) scintillation fluid (PerkinElmer, Waltham, MA, USA). Aliquots from randomly selected ampoules of SRM 4321d as dispensed with a polyethylene aspirating pycnometer were measured on an electronic microbalance (Mettler AT20). Other cocktail components were weighed with a mechanical analytical balance (Mettler B5). To match aqueous mass fractions, f_{aq}, additional amounts of nominal 1 mol L^{-1} HNO_3 were added to some cocktails. Blank sources (for subsequent background subtraction) of similar composition over the same quench range were also prepared.

The LS rate from a counting source of natural uranium must be considered before addressing the details for the two trials. To a very good, first approximation, the LS counting rate *R* for cocktails of the SRM 4321d uranium solution, integrated over the entire spectrum, can be estimated to be:

$$R = m_U \left[A_{234U}\varepsilon_{234U} + A_{235U}(\varepsilon_{235U} + \varepsilon_{231Th}) + A_{238U}(\varepsilon_{238U} + \varepsilon_{234Th} + \varepsilon_{234mPa}) \right], \qquad (2)$$

where m_U is the aliquot mass of the uranium solution in the source; A_{234U}, A_{235U}, and A_{238U} are the massic activities of the [234]U, [235]U, and [238]U isotopes, respectively; and ε_{234U}, ε_{235U}, ε_{231Th}, ε_{238U}, ε_{234Th}, and ε_{234mPa} are the respective LS detection efficiencies for [234]U, [235]U, [231]Th, [238]U, [234]Th, and [234m]Pa. Refer to Fig. 1 for placement of these nuclides in the decay chains.

The efficiency for each of the three α-emitting uranium isotopes can be taken to be unity, since the α particles are detected with 100 % efficiency in 4π geometry, and it has been demonstrated by Fitzgerald [18] that there is negligible, < 0.01 %, wall effect loss in LS counting with α emitters.

The three β⁻-emitting radionuclides were expected to have reasonably high detection efficiencies, but they still required separate evaluations and determinations. This can be achieved by efficiency calculations with free-parameter models using computational codes that are employed for the CNET[6] method [19]. Generally, the efficiency calculations for a given radionuclide are linked through the free parameter to that for ^{3}H as an efficiency monitor. The [231]Th, [234]Th, and [234m]Pa nuclides all have extremely complicated decay schemes, with many β⁻ branches and numerous γ transitions and crossovers, all of which requires

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considerable input data; e.g., the branching ratios and β^- spectrum for each branch, along with the probability per decay and conversion coefficients for each γ, and accompanying atomic data for the conversion electrons and rearrangement processes. In order to create manageable input data files, the decay scheme for each of the three nuclides was simplified by considering only branches with greater than 1 % probability of the total decay, with renormalizations of the probabilities per decay for the simplification.

For these calculations, the LS counting efficiencies for ^{231}Th, ^{234}Th, and ^{234m}Pa were calculated for an assumed cocktail of 1 mL of water in 10 mL of Ultima Gold using the 2011 version of the MICELLE2 code [20, 21] with Birks parameter, kB, of 0.0075 MeV cm^{-1}. The composition of the scintillator and functional form of the electron stopping power for Ultima Gold were used as given in the data files that accompany the MICELLE2 code. The nuclear decay data used as input were derived from simplified level schemes as mentioned above, using DDEP recommended data files [1] for each nuclide. Individual L-shell and total M-shell conversion probabilities were calculated using the BrICC code using the frozen orbital approximation [22]. In all, a single β^- branch was calculated for ^{234m}Pa, whereas one β^-, two $\beta^-\gamma$, and two $\beta^-\gamma\gamma$ cascades were calculated for ^{234}Th, and four $\beta^-\gamma$ and two $\beta^-\gamma\gamma$ cascades were considered for ^{231}Th. The efficiencies for the individual results were renormalized and summed to give a total efficiency for each isotope. The computational results for these efficiencies as a function of the ^{3}H efficiency are shown in Fig. 6. For comparison, at a relatively unquenched level of 50 % ^{3}H efficiency ($\varepsilon_3 = 0.50$), the corresponding efficiencies for ^{231}Th, ^{234}Th, and ^{234m}Pa are 0.901, 0.916, and 0.998, respectively. Because of the decay scheme simplifications, the calculated efficiencies are not expected to be accurate to better than 1 % to 2 %.
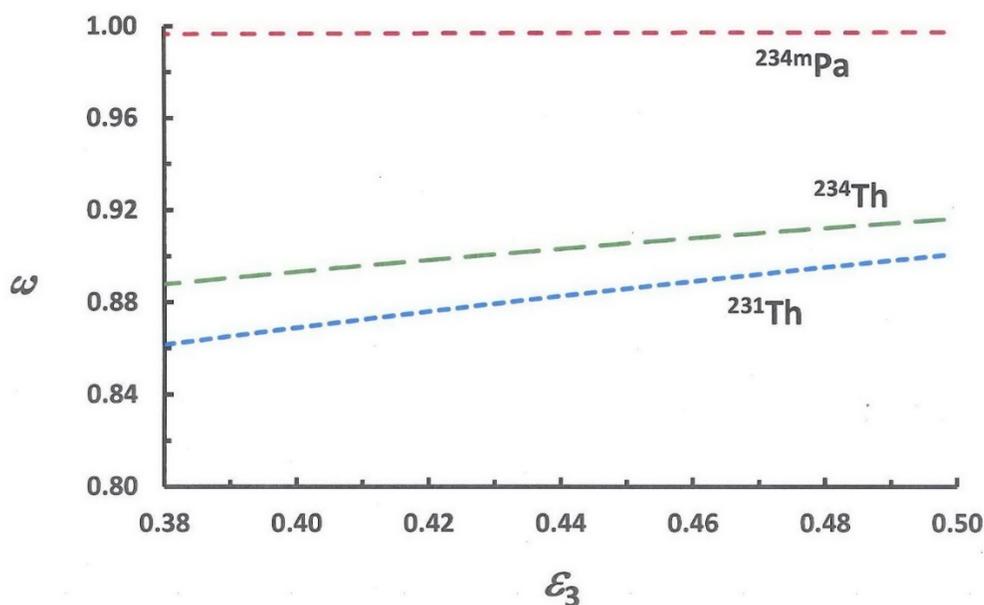
Fig. 6. Computed LS detection efficiencies ε for the uranium-isotope daughters, ^{234m}Pa, ^{234}Th, and ^{231}Th, as a function of the efficiency for ^{3}H as obtained with the MICELLE2 code.

For the first trial, a preliminary evaluation of the total massic activity of the SRM solution by LS spectrometry was performed using three different cocktail compositions with UGAB scintillation fluid. This was intended to evaluate the effects of chemical quenching by varying aqueous fractions f_{aq} (by the addition of dilute HNO$_3$), and the effects of color quenching by varying the mass of the yellow SRM solution. Three replicate sources were prepared for each of the three series, along with matched blanks for background subtraction. Each source consisted of a cocktail with about 9.8 g of UGAB, an aliquot of the SRM solution, and blank HNO$_3$ with the approximate amount-of-substance concentration of the SRM solution. In addition, approximately 60 mg of di-(2-ethylhexyl)phosphoric acid (DEHPA or HDEHP),

$(C_8H_{17}O)_2PO_2H$, which is a complexing agent, was added to each cocktail. Its use here was intended to complex the uranyl ions in the cocktail. The total cocktail mass for each source was held constant.

These sources were measured in both LS spectrometers, for $n = 4$ cycles in counter "B" and $n = 3$ cycles in counter "H." Each measurement was conducted for a live-time interval of 3600 s, with a relative Poisson statistical "counting error" in the range of 0.08 % to 0.12 %. These results are tabulated in Table 4, showing the grand mean averages of the massic counting rates (R_U/m) for the three series in the two counters. The computed relative precision estimator S considers both within-source and between-source components of variance. The within-source component is a "typical" value of the standard deviation of the mean, s_m, on the $n = 4$ or $n = 3$ replicate measurements of a given source, where the typical value is taken to be the average of the mean and median of the n s_m values. The between-source component is the standard deviation for the mean values of the three sources. The two components are combined in quadrature to form S. Quenching, as reflected in the average quench-indicating parameter $H\#$, maps with the source composition variations shown in Table 5 and clearly scales more strongly with the aliquot mass (affecting color and UO_2^{+2} ion content) than with the aqueous fraction. Nevertheless, the massic counting rates are not strongly influenced by quenching because of the efficiency invariance for the three α emitters and the high detection efficiencies for the ^{231}Th, ^{234}Th, and ^{234m}Pa β$^-$ emitters.

Table 4. LS counting results for the first trial as obtained in the two counters. The average quench-indicating parameter $H\#$ (measured in counter "B") maps with the composition variations shown in Table 5. Values for the massic counting rate R_U/m are grand mean averages for the three sources for each series and across the $n = 4$ (for "B") or $n = 3$ (for "H") replicate measurements for each source. The relative measurement precision estimator S is the combination in quadrature of the typical within-source standard deviation of the mean for the three sources and the between-source standard deviation of the three mean values.

Series	Average $H\#$	"B" counter		"H" counter	
		R_U/m (s^{-1} g^{-1})	S (%)	R_U/m (s^{-1} g^{-1})	S (%)
A	104.2	905.5	0.17	906.9	0.56
B	120.0	904.5	0.10	905.0	0.14
C	122.9	903.9	0.11	905.0	0.62

It was estimated that the equivalent ^{3}H efficiency in the three series is in the range of about 40 % to 45 %. From the MICELLE2 calculations (Fig. 6), the efficiencies are estimated to be $\varepsilon_{231Th} = 0.869$, $\varepsilon_{234Th} = 0.893$, and $\varepsilon_{234mPa} = 0.997$ at a tritium efficiency $\varepsilon_3 = 0.40$; and $\varepsilon_{231Th} = 0.886$, $\varepsilon_{234Th} = 0.906$, and $\varepsilon_{234mPa} = 0.997$ at a tritium efficiency of $\varepsilon_3 = 0.45$. Using these values in Eq. (2) along with the certified massic activities for each of the three uranium isotopes (Table 2) gives calculated values of

$(R_U/m)_{calc} = 901.5$ s^{-1} g^{-1} at equivalent $\varepsilon_3 = 0.40$, and

$(R_U/m)_{calc} = 904.6$ s^{-1} g^{-1} at equivalent $\varepsilon_3 = 0.45$,

which can be compared to the average measured values in Table 4, which range from 904 s^{-1} g^{-1} to 907 s^{-1} g^{-1}. The agreement is substantial, which confirms the total massic activity in SRM 4321d as derived from the isotopic atom percentages for metallic CRM 112-A.

Table 5. Characteristics of the LS counting sources for the first LS trial in terms of preparation details. Each series consisted of three replicate sources. The three series include variations in mass of the SRM aliquot (affecting UO_2^{+2} ion content and color) and the aqueous fraction f_{aq}. The aqueous part of f_{aq} consisted of a nominal 1 mol L^{-1} HNO$_3$ in all cases. The values for the masses and f_{aq} are averages for the three sources in the series. Each cocktail also contained approximately 60 mg of the HDEHP complexing agent.

Series	Mass of UGAB (g)	Mass of blank HNO$_3$ (g)	Aliquot mass of SRM solution (g)	Total cocktail mass (g)	f_{aq} (%)
A	9.804	0.620	0.221	10.70	7.86
B	9.804	0.483	0.424	10.77	8.43
C	9.629	0.619	0.419	10.72	9.67

The second LS counting trial was designed to more definitely determine the efficiencies of the three β$^-$-emitting nuclides in prepared cocktails. In order to link the efficiencies of these nuclides to a ^{3}H efficiency, ε_3, it was necessary to know what ε_3 would be in a uranium cocktail at its level of quenching, i.e., to determine the tritium efficiency in a cocktail with a composition matching that in a uranium

counting source with large UO_2^{+2} ion loading and color quenching. This was achieved by preparing a mixed U/^{3}H cocktail using measured aliquots of the natural uranium SRM solution and a tritiated water standard (SRM 4926e) [23]. The counting rate R_{UT} for this mixed cocktail can be given by

$$R_{UT} = m_U \left(\frac{R_u}{m}\right) + \varepsilon_T m_T A_T \,, \tag{3}$$

where m_U is the mass of the uranium aliquot, (R_U/m) is the massic counting rate for a matched pure uranium cocktail, and ε_T, m_T, and A_T are the ^{3}H counting efficiency, the mass of the ^{3}H standard aliquot, and the massic activity of the ^{3}H standard in the mixed cocktail, respectively. Rearrangement gives

$$\varepsilon_T = \frac{R_{UT} - m_U\left(\frac{R_u}{m}\right)}{m_T A_T}. \tag{4}$$

With this, it is possible to obtain the equivalent tracing efficiency for ^{3}H, which can be used to determine the LS detection efficiencies for the ^{231}Th, ^{234}Th, and ^{234m}Pa β^- emitters from the MICELLE2 calculations. This value of ε_T is the equivalent ^{3}H efficiency in a cocktail of composition matching the uranium cocktails.

Table 6 provides the characteristics of the sources used for this second LS trial to obtain ε_T in a quenched uranium cocktail. The counting results for these sources, given in Table 7, could in turn be used to calculate the detection efficiencies for the ^{231}Th, ^{234}Th, and ^{234m}Pa β^- emitters using the MICELLE2 calculations (Fig. 6).

Table 6. Characteristics of the LS counting sources for the second LS trial in terms of preparation details. There were three replicate cocktails for the uranium sources. The masses given here for them are the averages for the three, and the values in parentheses correspond to their standard deviation of the means. Only one source was prepared for each tritium cocktail (T), the mixed uranium U/^{3}H cocktail (UT), and for a blank (B). Each cocktail also contained approximately 60 mg of the HDEHP complexing agent.

Cocktail	Mass of UGAB (g)	Mass of blank HNO$_3$ (g)	Aliquot mass of SRM solution (g)	Aliquot mass of ^{3}H standard (g)	Total cocktail mass (g)	f_{aq} (%)
U ($n = 3$)	9.849 5 (28)	0	0.213 2 (12)	0	10.175 8 (19)	2.638 (10)
T	9.857 3	0.225 1	0	0.047 01	10.137 7	2.684
UT	9.845 8	0	0.208 8	0.047 05	10.109 8	2.531
B	9.858 3	0.250 5	0	0	10.219 2	2.960

Table 7. LS counting results for the second trial as obtained in the two counters. The *H#* quench-indicating parameter (measured in counter "B") maps with the composition variations given in Table 6 and shows the close matching between the three uranium U cocktails (U) and the mixed U/^{3}H cocktail (UT). The pure ^{3}H cocktail (T) is less quenched because of the absence of uranyl nitrate ions and the yellow coloring present in the other cocktails. It also reflects a higher tritium efficiency. Values for the massic counting rate (R_U/m) are grand mean averages for the three U sources, and the values in parentheses are the standard deviations of the mean for the $n = 3$ sources. The values of R_{UT}, m_U, m_{at}, and ε_T for the UT cocktail were used to obtain ε_T from Eq. (4). The efficiencies for the three β^--emitting isotopes were obtained from the MICELLE2 calculations (Fig. 6) for the determined value of ε_T. The calculated value of $(R_U/m)_{calc}$ was in turn obtained from Eq. (2) using these efficiencies and the certified isotopic massic activities (Table 2). The relative difference between the measured (R_U/m) value and calculated $(R_U/m)_{calc}$ value is given as δ

Cocktails	*H#*	Quantity	"B" counter	"H" counter
U ($n = 3$)	78.6 (8)	(R_U/m)	910.70 (34) s^{-1} g^{-1}	910.16 (29) s^{-1} g^{-1}
T	59.5	ε_3	0.490 6	0.475 5
UT		R_{UT}	276.61 s^{-1}	225.54 s^{-1}
UT		m_U	0.208 83 g	0.208 83 g
UT		$m_T A_T$	82.471 Bq	82.471 Bq
UT	77.7	ε_T	0.442	0.431
UT		ε_{231Th}	0.883	0.880
UT		ε_{234Th}	0.904	0.901
UT		ε_{234mPa}	0.997	0.997
UT		$(R_U/m)_{calc}$	904.1 s^{-1} g^{-1}	903.4 s^{-1} g^{-1}
U/UT	—	δ	0.73 %	0.75 %

The three uranium U cocktails (U) and the mixed U/^{3}H cocktail (UT) were closely matched, as reflected in the compositions given in Table 6 and the *H#* quench-indicating parameters, thus validating the

approach. The pure ^{3}H cocktail (T), prepared merely for comparison purposes, was less quenched because of the absence of uranyl nitrate ions and the yellow coloring that was present in the other cocktails, and this is also reflected in its greater detection efficiency. With these reasonably well determined efficiencies, values of $(R_U/m)_{calc}$ obtained for the certified isotopic massic activities could be compared to measured values of (R_U/m), as shown in Table 7. The agreement is about 0.75 %, which is about as good as could be expected given the assumptions for the MICELLE2 calculations.

4.3.2 Isotope Dilution Analysis

A more rigorous confirmation of the certified massic activity values for SRM 4321d was performed by α-particle spectrometry using an isotope dilution analysis procedure, with a ^{232}U standard as a tracer to determine ^{234}U and ^{238}U.

The solution used for the isotope dilution procedure was a gravimetric dilution of one randomly selected SRM 4321d ampoule. A dilution factor of $D = 6.7148 \pm 0.0026$ was determined by measuring both the dispensed and contained masses of the SRM solution and a nominal 1.8 mol L^{-1} HNO$_3$ diluent. The resulting solution had a density of (1.062 ± 0.005) g mL^{-1} and an amount-of-substance concentration of about 1.8 mol L^{-1} HNO$_3$, and it contained about 3.1 mg UO$_2^{+2}$ per gram of solution. The preparation was performed with a polyethylene aspirating pycnometer, and both components were weighed with a Mettler AT20 electronic microbalance. The relative difference in contained and dispensed masses for the SRM aliquot was 0.017 %, and that for the total solution mass was 0.007 %.

Four replicate counting sources were prepared as follows:

Aliquots of the SRM 4321d dilution, in the range of 26 mg to 28 mg, were gravimetrically added to 20 mL glass vessels, adding an approximately equal mass of ^{232}U standard tracer (SRM 4324B) [24]. The massic activities of ^{232}U, ^{234}U, and ^{238}U were all in the 32 Bq g^{-1} to 34 Bq g^{-1} range. One blank with the same ^{232}U tracer was also prepared. Another sample of the diluted SRM solution without ^{232}U tracer was prepared to check for α-emitting impurities. Each sample then received about 90 mg of 0.42 mol L^{-1} NaHSO$_4$ and 1 mL of 2 mol L^{-1} HNO$_3$ to prevent the formation of insoluble oxides that can be difficult to re-dissolve in a subsequent evaporation step. All samples were evaporated to dryness and re-dissolved with heating in about 5 mL of a nominal 3 mol L^{-1} HNO$_3$ solution. The ^{232}U tracer solution contains its decay product ^{228}Th, which has α-particle energies close to those of ^{232}U, in radioactive equilibrium; *viz.*, 5436 keV (26 %) and 5520 keV (73 %) for ^{228}Th, and 5355 keV (31 %) and 5413 keV (69 %) for ^{232}U [4]. To diminish the overlapping of the detection signals of ^{232}U and ^{228}Th in the α spectra, a purification of the uranium fraction was necessary to eliminate the ^{228}Th.

Uranium was separated from thorium using extraction chromatography with UTEVA (Uranium und TEtraValents Actinides) resin (EiChrom, Inc., Lisle, IL, USA). About 125 mg of a Zr(IV) solution (100 µg Zr/mL as nitrate in 2 mol L^{-1} HNO$_3$) were added as a nonisotopic carrier for ^{228}Th to the 5 mL of 3 mol L^{-1} HNO$_3$ sample solution to facilitate the ^{228}Th separation [25]. Each sample solution containing the ^{232}U tracer was passed through a UTEVA column with 2 mL bed volume, preconditioned with 3 mol L^{-1} HNO$_3$. The resin (retaining uranium and thorium) was rinsed with 20 mL of 3 mol L^{-1} HNO$_3$ (with excess Zr and ^{228}Th progeny being eluted), and then 20 mL of 6 mol L^{-1} HCl was passed to elute ^{228}Th. The uranium fraction was subsequently stripped from the column with 20 mL to 25 mL of 0.01 mol L^{-1} HCl. After addition of 2 mL of 0.42 mol L^{-1} NaHSO$_4$ to the uranium strip solutions, and evaporation and fuming with concentrated HNO$_3$ and HClO$_4$ to decompose the resin's organic matter, the purified uranium fractions were electrodeposited onto stainless-steel disks from an electrolyte of sodium hydrogen sulfate–sodium sulfate buffer (NaHSO$_4$/Na$_2$SO$_4$ amount-of-substance ratio = 0.194, pH = 2.6).

The electrodeposited uranium sources were measured with EG&G Ortec Octete alpha spectrometers (Oak Ridge TN, USA), having 450 mm^2 planar, ion-implanted Si detectors. Thin films prepared from collodion were interposed between sources and detectors to prevent recoil contamination of the detectors by ^{232}U progeny [26]. The sample sizes were chosen to produce sources with approximately 1 Bq each of ^{234}U and ^{238}U and a source deposit thickness (as uranium oxide) of no more than about 60 µg cm^{-2}, to minimize α energy straggling in the source. The samples were typically counted for about 2 d to obtain good Poisson counting statistics (of about 0.5 %) in all α-spectral peaks, except that for ^{235}U. Two software programs were used for the spectrum analysis; *viz.*, Maestro-32 (Ortec-Ametek Advanced Measurement

Technology, Oak Ridge, TN, USA) and Genie 2000 (Canberra Industries, Inc., Meriden, CT, USA). Typical spectra for the unspiked and spiked sources are shown in Fig. 7. In all, eight spiked spectra were accumulated from the four independent replicate sources, with each source measured at two source-detector counting distances. These eight spectra were analyzed using the Genie program. Another collaborator independently analyzed four of the spectra from one counting position with the Maestro software.
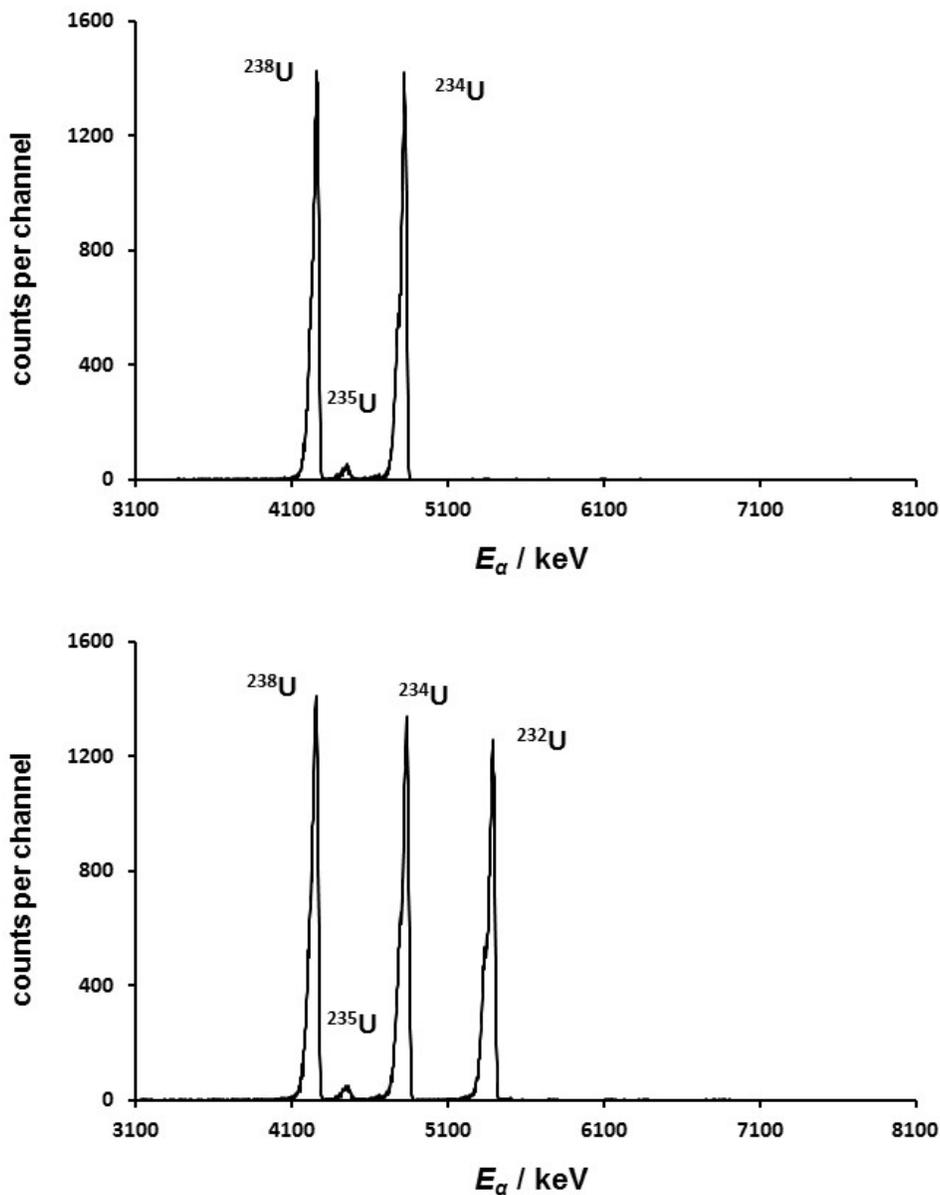
Fig. 7. Alpha-particle spectra from the isotope dilution analysis. Upper trace: typical spectrum for an unspiked natural uranium electrodeposited source, showing the peaks for ^{238}U and ^{234}U, along with that for the weaker ^{235}U. Lower trace: typical spectrum for a natural uranium electrodeposited source spiked with ^{232}U tracer (following chemical purification to remove the ^{228}Th daughter of ^{232}U). Both spectra were accumulated for about 1.71 d with planar ion-implanted silicon detectors. No impurities were detected.

Figure 8 shows the collective results for the twelve determinations. The results are summarized in Table 8, along with a comparison with the certified massic activities for ^{234}U and ^{238}U. Both the ^{234}U and

[238]U massic activity data sets (for $n = 12$), along with the A_{238U}/A_{234U} activity ratios were found to be normally distributed based on PPCC tests [15], with p values of 0.31, 0.76, and 0.24, respectively. These data sets also passed a Wilks-Shapiro test for normality, with p values of 0.53, 0.13, and 0.85, respectively. The relative difference in mean values for the two counting positions by the analyses using Genie was 0.03 % for [234]U and 0.17 % for [238]U. The relative difference between independent use of Genie and Maestro (and by different collaborators) in analyses of the same collected spectra was about 0.9 % for both [234]U and [238]U, corresponding to an estimated relative standard uncertainty of 0.25 % uncertainty from the systematic difference in the two spectral analysis approaches. The main uncertainty components (> 0.1 % on relative basis) for the average massic activity of [234]U and [238]U were the measurement precision, Poisson counting statistics, massic activity for the [232]U tracer, and the correction for the ingrown [228]Th contribution into the [232]U α peak. The uncertainty assessment is outlined in Table 9.
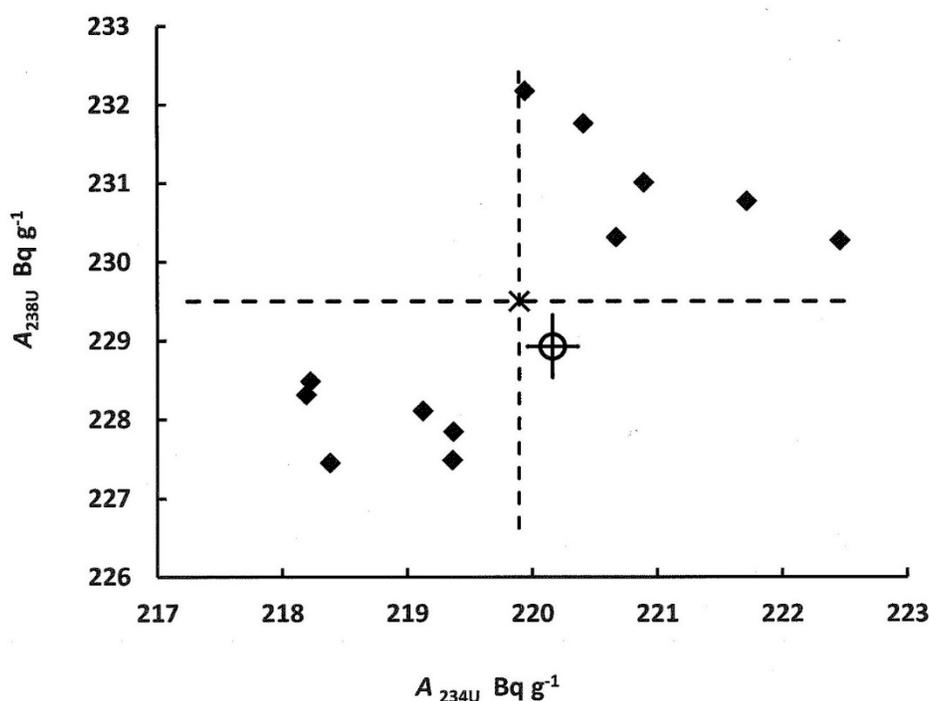
Fig. 8. Results showing the twelve determinations of the paired values for the massic activities of [234]U and [238]U as obtained from the isotope dilution α spectrometry. The cross represents the measured average values for A_{234U} and A_{238U}. The lengths of the dashed horizontal and vertical lines correspond to expanded uncertainties ($k = 2$) on A_{234U} and A_{238U}, respectively. The circle with solid horizontal and vertical bars represents the certified massic activities for A_{234U} and A_{238U} in SRM 4321d.

Table 8. Results of the isotope dilution analysis by α-particle spectrometry using a [232]U tracer (SRM 4324B). The measurement values are based on twelve determinations of [234]U and [238]U obtained from four replicate counting sources in two geometries (eight spectra), where four spectra were independently analyzed by two independent spectral analysis procedures. The certified massic activities for SRM 4321d are taken from Table 2. Numbers in parentheses represent the numerical values of the expanded uncertainties (for $k = 2$) and refer to the corresponding last digits of the quoted result. The uncertainty components that comprise the standard uncertainty for the measured values are given in Table 9.

	Massic activity (Bq g^{-1})	
	A_{234U}	A_{238U}
Measured value	219.9 (2.7)	229.5 (2.9)
Certified value for SRM 4321d	220.2 (1.1)	228.93 (57)
Relative difference	−0.12 %	+0.25 %

Table 9. Uncertainty assessment for the massic activities of ^{234}U and ^{238}U in standard SRM 4321d, as determined by isotope dilution analysis with α-particle spectrometry, where u (in percent) is the relative standard uncertainty for each component, as obtained from either a type A (evaluation by statistical methods) or type B (evaluation by other methods) assessment [6, 7].

	Uncertainty component	Assessment type	u (%)	
			^{234}U	^{238}U
1	Measurement precision; standard deviation of the mean for $n = 12$ determinations on four counting sources in two counting geometries (8 spectra)	A	0.26	0.31
2	Massic activity of ^{232}U tracer from SRM 4324B Certificate [24]	B	0.41	0.41
3	Poisson statistics "counting error"; partially embodied in component 1	B	0.18	0.18
4	^{228}Th ingrowth correction in ^{232}U peak analysis; varies in range 0.1 % to 0.3 % depending on measurement time	B	0.2	0.2
5	Gravimetric mass measurements	B	0.05	0.05
6	Spectral analysis for peak determinations	B	0.25	0.25
7	Gravimetric dilution factor	B	0.02	0.02
Relative combined standard uncertainty, u_c			**0.61**	**0.63**
Relative expanded uncertainty ($k = 2$), U			**1.22**	**1.26**

As seen in Fig. 8, the paired results for the measured massic activities for ^{234}U and ^{238}U are highly correlated. The correlation coefficient for A_{238U} as a function of A_{234U} is $r^2 = 0.45$, and the differences in both A_{234U} and A_{238U} from either of the measured mean values of certified values are either both positive (quadrant I of that shown) or both negative (quadrant III), meaning that the measured values for ^{234}U and ^{238}U scale in the same direction within the same spectrum.

No α-emitting impurities were detected by way of the following evaluations. One aliquot of the SRM 4321d dilution (identified as source U5) that had not been spiked with ^{232}U was directly electrodeposited without any previous UTEVA extraction chromatography separation. Under the electrodeposition conditions, actinides ($Z = 89$ to $Z = 96$) as well as Bi and Po were expected to be deposited with high yield on the stainless-steel disk. Radium would not deposit. In the resulting 147 ks α spectrum of source U5, no peaks (channels with more than 4 counts per channel) were observed in the regions 3.1 MeV to 4.0 MeV and 4.8 MeV to 8.2 MeV (i.e., those regions below and above the 4.1 MeV to 4.7 MeV range of the ^{238}U, ^{235}U, and ^{234}U peaks). The 3.1 MeV to 4.0 MeV region had counts that were attributable to "low-energy peak tailing" from the large ^{238}U peak. The 4.8 MeV to 8.2 MeV region had only scattered counts, the sum of which was not statistically different from that of background measurements in that region. The estimated lower limits of detection for α-emitting impurities (excluding radium) relative to the ^{238}U signal in source U5 were 0.2 % and 0.06 % for regions 3.1 MeV to 4.0 MeV and 4.8 MeV to 8.2 MeV, respectively. In addition, the ratio of the ^{234}U to ^{238}U α peak counts in source U5 were compared to the corresponding ratio in the spiked samples. The difference of 0.5 % was not significant when compared to the uncertainty from Poisson statistics "counting error" arising from the integral counts in the α peaks. This suggested that there were no interferences in the 4.2 MeV and 4.7 MeV α lines of ^{238}U and ^{234}U, respectively, that could be attributed to (1) isotopic or nonisotopic impurities that were present in the directly electrodeposited U5 source or (2) any isotopic impurities in the ^{232}U spike that were not removed by the UTEVA column.

5. Certification of SRM 4321d and Summary

The prepared natural uranium solution standards were certified for massic activities of ^{234}U, ^{235}U, and ^{238}U on the basis of the isotopic atom percentages for metallic CRM 112-A, as obtained from mass spectrometry. The standards will be disseminated as NIST SRM 4321d with the following specifications [27]:

Radionuclides: Natural uranium (mixture of ^{234}U, ^{235}U, and ^{238}U)
Reference time: 1200 h EST, 15 March 2017
Massic activities of the solution: ^{234}U: 220.16 Bq g^{-1}; ^{235}U: 10.540 Bq g^{-1}; ^{238}U: 228.93 Bq g^{-1}
Relative expanded uncertainties ($k = 2$): ^{234}U: 0.52 %; ^{235}U: 0.31 %; ^{238}U: 0.25 %
The solution was also characterized in terms of the following uncertified information:

Source description: Liquid in flame-sealed, 5 mL borosilicate glass ampoule
Solution composition: (1.06 ± 0.06) mol L^{-1} HNO_3 with 21 mg UO_2^{+2} per gram of solution
Solution density: (1.057 ± 0.001) g mL^{-1} at 21.6 °C
Solution mass: (5.284 ± 0.001) g
Radionuclidic impurities, including other uranium isotopes: none; ^{233}U and ^{236}U were not detected
Half-lives [4]:

^{234}U: $(2.455 \pm 0.006) \times 10^5$ a
^{235}U: $(7.04 \pm 0.01) \times 10^8$ a
^{238}U: $(4.468 \pm 0.005) \times 10^9$ a

The uncertainty assessments for the certified massic activities are summarized in Table 3. Confirmatory measurements by LS counting and by α-spectrometry isotope dilution analysis verified the quantitative dissolution, dilution, and preparation of suitable 5 mL aliquots of the SRM. Experimental work also demonstrated SRM solution homogeneity and equivalence between SRM units, as well as consistency with the absence of radionuclidic impurities.

Acknowledgments

6.   References

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About the authors: All authors are members of the Radioactivity Group in the Radiation Physics Division of the NIST Physical Measurement Laboratory. These seven collaborators collectively represent 132 years of experience in radionuclidic metrology at NIST. The National Institute of Standards and Technology is an agency of the U.S. Department of Commerce.