New Determination of the 229Th Half-life

R. M. Essex, J. L. Mann, R. Colle, L. Laureano-Perez, M. E. Bennett, H. Dion, R. Fitzgerald, A. M. Gaffney, A. Gourgiotis, A. Hubert, K. G. W. Inn, W. S. Kinman, S. P. Lamont, R. Steiner, R. W. Williams

August 10, 2018

Journal of Radioanalytical and Nuclear Chemistry

Disclaimer

Manuscript Title Page

Names of authors: Richard M. Essex[1], Jacqueline L. Mann[1], Ronald Collé[1], Lizbeth Laureano-Perez[1], Megan E. Bennett [2], Heather Dion[3], Ryan Fitzgerald[1], Amy M. Gaffney[4], Alkiviadis Gourgiotis[5], Amélie Hubert[6], Kenneth G. W. Inn[7], William S. Kinman[3], Stephen P. Lamont[3], Robert Steiner[3], Ross W. Williams[4]

Title: New determination of the ^{229}Th half-life

Affiliation and addresses of authors:

[1] National Institute of Standards and Technology, 100 Bureau Drive, Mail Stop 8462,
Gaithersburg, MD 20899, USA

[2] Shine Medical Technologies, 101 East Milwaukee Street, Janesville, WI 53545, USA

[3] Los Alamos National Laboratory, Los Alamos, NM 87545, USA

[4] Lawrence Livermore National Laboratory, P.O. Box 808, L-231, Livermore, CA 94551-0808,
USA

[5] Institut de Radioprotection et de Sûreté Nucléaire (IRSN), PSE-ENV/SEDRE/LELI, 31 avenue
de la Division Leclerc, Fontenay-aux-Roses

[6] CEA/DAM-Ile de France, Bruyères-le-Châtel, 91297 Arpajon Cedex, France

[7] K&E Innovations, Ewa Beach, HI 96706, USA

Corresponding Author: Richard.essex@NIST.gov

New determination of the ^{229}Th half-life

Richard M. Essex[1], Jacqueline L. Mann[1], Ronald Collé[1], Lizbeth Laureano-Perez[1], Megan E. Bennett [2], Heather Dion[3], Ryan Fitzgerald[1], Amy M. Gaffney[4], Alkiviadis Gourgiotis[5], Amélie Hubert[6], William S. Kinman[3], Stephen P. Lamont[3], Robert Steiner[3], Ross W. Williams[4]

[1] National Institute of Standards and Technology, 100 Bureau Drive, Mail Stop 8462, Gaithersburg, MD 20899, USA

[2] Shine Medical Technologies, 101 East Milwaukee Street, Janesville, WI 53545, USA

[3] Los Alamos National Laboratory, Los Alamos, NM 87545, USA

[4] Lawrence Livermore National Laboratory, P.O. Box 808, L-231, Livermore, CA 94551-0808, USA

[5] Institut de Radioprotection et de Sûreté Nucléaire (IRSN), PSE-ENV/SEDRE/LELI, 31 avenue de la Division Leclerc, Fontenay-aux-Roses

[6] CEA/DAM-Ile de France, Bruyères-le-Châtel, 91297 Arpajon Cedex, France

Abstract

A new determination of the ^{229}Th half-life was made based on measurements of the ^{229}Th massic activity of a high-purity solution for which the ^{229}Th molality had previously been measured. The ^{229}Th massic activity was measured by direct comparison with SRM 4328C using 4παβ liquid scintillation counting, NaI counting, and standard addition liquid scintillation counting. The ^{229}Th massic activity was confirmed by isotope dilution alpha spectrometry measurements. The ^{229}Th half-life calculated from the activity measurements is (7825 ± 87) years ($k = 2$).

Key Words

^{229}Th, half-life, liquid scintillation counting, NaI counting, isotope dilution alpha spectrometry

Introduction

The ^{229}Th isotope is a relatively long-lived nuclide in the ^{237}Np decay series and primarily occurs as a decay product of ^{233}U [1]. The isotope decays by α emission to ^{225}Ra which, in turn, decays to ^{225}Ac followed by a series of short-lived nuclides to ^{209}Bi (Fig. 1). The ^{229}Th isotope does not occur in nature making it useful to the environmental and geological sciences where it is used as a yield tracer for thorium α spectrometry [2] and as an isotope dilution mass spectrometry (IDMS) spike for thorium amount measurements [3]. In addition, ^{229}Th is a source of high-purity ^{225}Ac for research in nuclear medicine [4] and is being evaluated for use as a high accuracy nuclear clock [5]. The nuclide is particularly important for nuclear forensics where it is used as an IDMS spike for ^{230}Th "dating" of uranium materials associated with the nuclear fuel cycle, e.g. [6,7]. Due to ongoing interest in the radionuclide, the National Institute of Standards and Technology (NIST) has produced four issues of ^{229}Th Standard Reference Material (SRM) certified for massic activity (Bq g^{-1}). These standards are SRM 4328 issued in 1984, SRM 4328A issued in 1995, SRM 4328B issued in 1996, and SRM 4328C issued in 2008 [8-11].

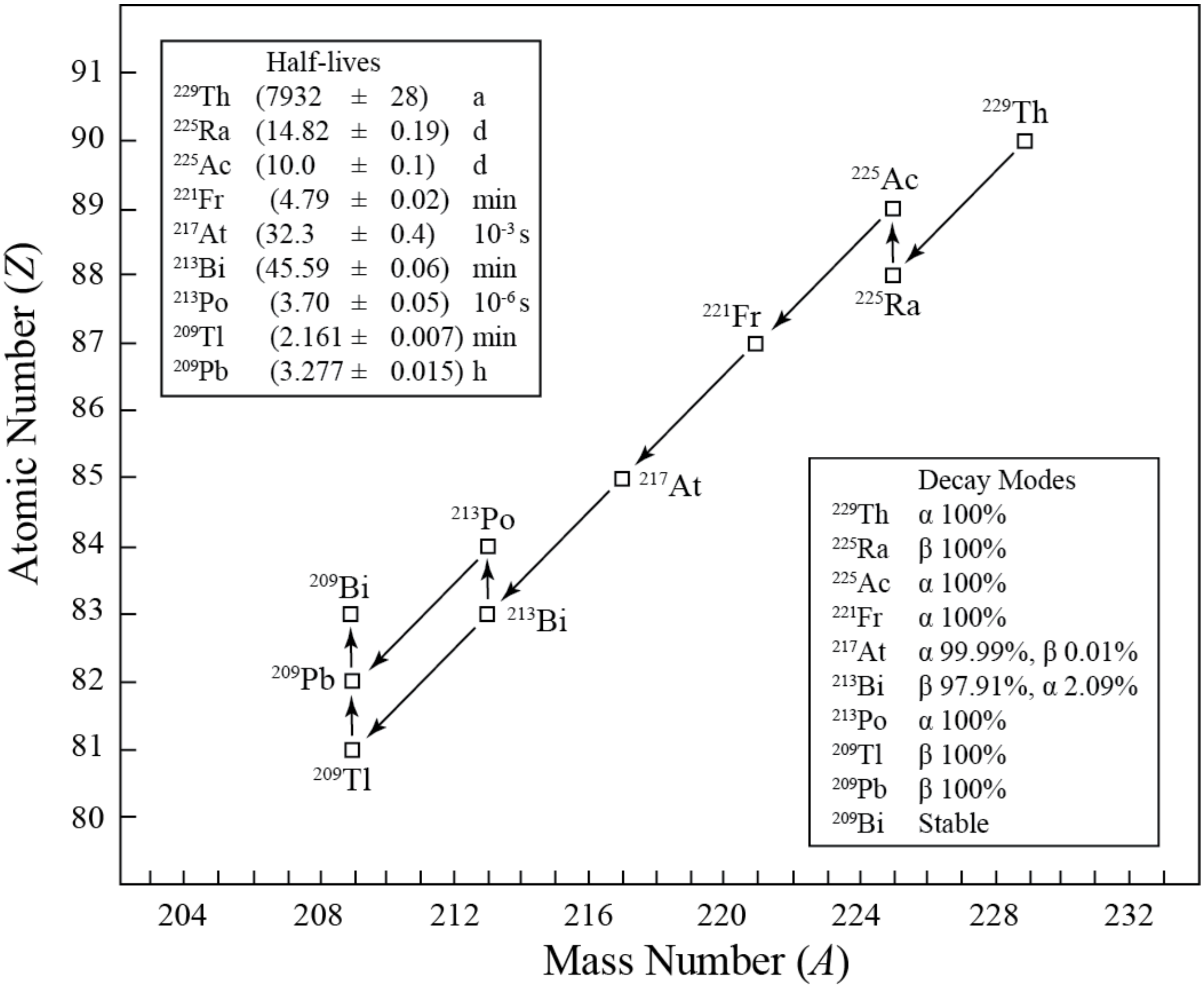

Fig 1. Simplified decay scheme for ^{229}Th. The uncertainties for the half-lives are standard uncertainties. Half-life and decay mode data for ^{229}Th are from [12]. Half-life and decay mode data for all other isotopes are from [13].

To date, four half-life measurements have been published for ^{229}Th, but these values have been somewhat inconsistent. Hagemann *et al.* [1] published a ^{229}Th half-life of (7340 ± 160)[1] years as

---

[1] Uncertainties for values in text are combined standard uncertainties (u_c) unless otherwise indicated with a coverage factor value (k) of 2 or greater for the expanded uncertainties ($U = k\,u_c$).

part of a study of the ^{233}U decay chain. This value is significantly shorter than subsequent measurements (≈ 7%) with the discrepancy attributed to a combination of factors including a biased ^{233}U half-life value used to calculate the quantity of ^{229}Th in the analysis samples, a possible underestimate of ^{228}Th contributions to ^{229}Th activity measurements, or ^{233}U interference in ^{229}Th activity measurements [14-15]. Goldstein *et al.* [14] performed a study to refine the ^{229}Th half-life value by measuring the molality of ^{229}Th in a solution with a well-characterized massic activity, SRM 4328. The resulting measurement indicated a half-life of (7880 ± 120) years ($k = 2$). More recently, Kikunaga *et al.* [15] calculated a half-life of (7932 ± 55) years ($k = 2$) based on measured $A(^{233}\mathrm{U})/A(^{232}\mathrm{U})$ and $A(^{229}\mathrm{Th})/A(^{228}\mathrm{Th})$ activity ratios. Finally, Varga *et al.* [16] measured the molality of the SRM 4328C massic activity standard by IDMS using two different Th spikes. One spike was a commercially prepared natural Th solution [Method A: (7889 ± 32) years] and the second spike was a high purity U material with a calculated quantity of ingrown ^{230}Th [Method B: (7952 ± 36) years]. The half-lives calculated for each set of IDMS measurements were combined for a reported half-life value of (7917 ± 48) years ($k = 2$).

Fitzgerald *et al.* [17] describe a massic activity calibration for the ^{229}Th Master (M) solution used to prepare SRM 4328C. To produce the stock solution for the SRM, an aliquot of the M solution was quantitively diluted by a factor (D_S) of 308.85 ± 0.09. The ^{229}Th massic activity of the M solution was then measured by live-timed 4παβ-γ anticoincidence counting. The massic activity of the SRM solution was calculated using the measured massic activity of the M solution and the gravimetrically determined dilution factor. Relative liquid scintillation (LS) counting of the M and SRM 4328C solutions was used to verify the gravimetric dilution factor for the SRM, with the relative difference between the activity ratio and the dilution factor of 0.04 % and a combined standard uncertainty of about 0.4 % in the activity ratio. The calculated activity value for the SRM was also confirmed by four additional radioactivity measurement methods, including LS counting with ^{3}H CIEMAT/NIST efficiency tracing[2], triple-to-double coincidence counting (LS TDCR), 2πα proportional counting, and α spectrometry.

In a separate project, two ampoules of the M solution were combined and diluted by a factor (D_X) of approximately 56.0[3] to produce a new reference material that was characterized for ^{229}Th molality (^{229}Th mol g^{-1}) and Th isotopic composition [18]. The ^{229}Th molality of the new reference material was measured by IDMS on a total of 14 sample units in two measurement campaigns. To minimize potential systematic bias, three separate ^{232}Th IDMS spike solutions were prepared for the measurements and mass spectrometric analyses were distributed between three different laboratories. The resulting ^{229}Th molality value for the reference material solution, (0.11498 ± 0.00008) nmol g^{-1}, was verified using the SRM 4342A ^{230}Th massic activity standard as an independent IDMS spike.

The following describes the determination of the massic activity of the new ^{229}Th molality reference material (referred to here as ^{229}Th RM) by direct comparison with the SRM 4328C massic activity standard and the confirmation of the measured value by isotope dilution alpha

---

[2] The acronym CIEMAT/NIST refers to the two laboratories that collaborated in developing the protocol for this LS tracing methodology; viz., the Centro de Investigaciones Energéticas, Medioambientales y Tecnológicas (CIEMAT) and the National Institute of Standards and Technology (NIST).

[3] The dilution factor for the ^{229}Th RM (D_X) is only used for comparison purposes. During the dilution of the M solution to create the ^{229}Th RM stock solution, the masses measured on a large-capacity Jupiter 3000 balance appear to be inconsistent with normal operation of the balance. Accordingly, the calculated dilution factor value is an approximation.

spectrometry (IDAS). A new value for the ^{229}Th half-life is calculated from the measured ^{229}Th massic activity and the previously measured ^{229}Th molality.

Direct Activity Comparison

A massic activity value for ^{229}Th in the ^{229}Th RM was determined by measuring the ratio of relative activities (i.e. activity per gram solution) for the ^{229}Th RM solution and the SRM 4328C activity standard. Three counting methods were used to make the relative activity measurements. The first method compared the relative LS counting rates for carefully prepared sources of the two solutions. Then, the relative integral photon emission rates of the LS counting sources were directly compared using a NaI(Tl) well counter. Finally, a standard addition LS counting method was used to determine the activity ratio from a series of mixtures of the two reference materials.

Relative LS Counting

The ^{229}Th decay series consists of a seven-nuclide-long decay chain (Fig. 1) with an LS efficiency of > 6.9 s^{-1} Bq^{-1}. To achieve accurate results for the comparative LS counting measurements, it is imperative that the two ^{229}Th solutions are in identical states of radioactive equilibrium and that the solutions were counted with identical detection efficiency. Nearly identical counting efficiency was achieved by gravimetrically determining all of the components in the counting source cocktails to assure similar quenching. Identical radioactive equilibrium is also a reasonable assumption when the history and handling of the solutions are considered. Both ^{229}Th solutions were prepared from quantitative dilutions of aliquots from the same M solution; both solutions were diluted with 1 mol L^{-1} HNO_3; and no additional separations or processing were performed on either solution prior to sealing in glass ampoules. Ampoules of both reference materials were opened specifically for the activity measurements performed in April 2017, however, the SRM 4328C solution was prepared, dispensed into ampoules, and sealed in October 2007 while the ^{229}Th RM was prepared and sealed in March 2012. Although it is not possible to categorically rule out chemical fractionation of the sealed M solution aliquots over the 4.5 year period between preparation of the ^{229}Th solutions (e.g., preferential adsorption or precipitation of an element in the ^{229}Th decay chain), there is no *a priori* reason to suspect a difference in the radioactive equilibrium of the two solutions.

Counting sources for high precision LS were prepared from the ^{229}Th RM and SRM 4328C solutions (Table 1). Two different scintillation fluids were used to create liquid scintillation sources for both ^{229}Th solutions, Ultima Gold AB[4] (PerkinElmer, Waltham, MA) and Ecoscint (National Diagnostics, Tampa, FL). Three sources were gravimetrically prepared in 20 mL glass LS vials for each scintillant-^{229}Th solution combination, resulting in a total of 12 sources. To prepare the sources, aliquots from ampoules of the SRM and ^{229}Th RM were dispensed using polyethylene aspirating pycnometers with masses measured on an electronic microbalance (AT20, Mettler Toledo, USA). Other cocktail components were weighed with a mechanical analytical balance (Mettler B5, Mettler Toledo, USA). Close matching of the aqueous mass fraction in the sets of cocktails was achieved by the addition of 1 mol L^{-1} HNO_3 to some of the sources. In addition, each cocktail contained approximately 60 mg of di-(2-ethylhexyl) phosphoric acid (DEHPA or HDEHP), $(C_8H_{17}O)_2PO_2H$, which is a complexing agent. Matched blank sources of similar composition over the same quench range were also prepared for background subtraction.

---

[4] Certain commercial equipment, instruments, software, 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.

Each source was counted in triplicate on a LS 6500 counter (Beckman Coulter, Fullerton, CA, USA) and on an Accuflex LSC-8000 (Hitachi Aloka Medical Ltd., Tokyo, Japan). Two LS counters were used for this set of experiments to demonstrate that results are independent of the operating characteristics of a particular instrument (detection threshold, photomultiplier efficiency, deadtime, amplification, signal conversion, etc.). Individual LS measurements consisted of integrating the entire LS spectrum, and were of sufficient duration to accumulate over 10^6 counts, such that the relative Poisson counting statistics on each was < 0.1 %. In addition to closely matching quenching conditions and cocktail compositions in counting sources, both instruments use quench indicating parameters (QIP) to monitor quenching. The Accuflex LSC-8000 (Counter H) uses the 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 Beckman LS 6500 (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.

LS Source Series	Mass of Scintillant (g)	Mass of ^{229}Th Solution Aliquot (g)	Mass of Blank HNO_3 (g)	Total Mass Cocktail (g)	f_{aq} (%)	*H#*
^{229}Th RM UGAB	9.850 (3)	0.2039 (9)	0.798 (23)	10.912 (19)	9.18 (19)	89.0 (3)
4328C UGAB	9.852 (1)	0.9909 (10)	---	10.906 (11)	9.09 (8)	91.2 (5)
^{229}Th RM ECOS	8.916 (17)	0.1993 (40)	0.790 (26)	9.969 (42)	9.92 (2)	118.4 (3)
4328C ECOS	8.910 (7)	1.0103 (26)	---	9.987 (8)	10.12 (2)	121.1 (3)

Table 1 ^{229}Th RM and SRM 4328C LS source preparation details and characteristics. Each LS Source Series consisted of 3 separately prepared counting sources. UGAB and ECOS refer to the Ultima Gold AB and Ecoscint scintillation solutions, respectively. The values for the masses (g) and aqueous mass fraction f_{aq} (in %) are averages for the three sources in the series with the values

in parentheses representing the standard deviation of the means. *H#* is the average quench indicating parameter (as measured in Counter B) which is an additional indicator of the close composition matching.

Relative Photon Emission

As an independent measurement of the ^{229}Th RM and SRM 4328C activity ratio, relative photon emission rates were measured on the LS sources described above. Six replicate measurements of each source were made on a NaI (Tl) well-type counter (2480 WIZARD2, PerkinElmer, Waltham, MA). The detector crystal is 75 mm in diameter with a height of 80 mm and is shielded with a minimum of 50 mm of lead. A total of 6 trials for each source were measured sequentially, alternating between SRM and ^{229}Th RM vials and the spectrum for each measurement was accumulated for an interval of 10800 s (live time). Stability between trials was monitored with a 1.97 kBq ^{129}I check source (Half-life = 1.6 x 10^7 years). The region from, nominally, 20 keV to 2000 keV was integrated to obtain an integral counting rate that was corrected for background. The Poisson counting statistics on any single measurement was approximately 0.13 %.

Results for LS and Photon Emission Counting Rates

The measurement results are provided in terms of grand-means and great-grand-means of the massic count ratios (Table 2). The measured count rates from the LS and NaI(Tl) experiments are proportional to the massic activity of the respective solutions. Therefore, if ^{229}Th decay chain equilibrium is the same for both solutions, then the ratio of the massic count rates is equivalent to the ^{229}Th relative activity ratio (A_X / A_S) which, in turn is equivalent of the inverse ratio of M solution dilution factors (D_S / D_X) for the two reference materials. The uncertainty values for the grand-mean massic count ratios in Table 2 are computed precision estimators, equivalent to a standard deviation of the mean ($S_{\bar{x}}$), that consider both the within-source and between-source components of variance. The within-source component is a "typical" (i.e., average) value for the standard deviation of the replicate source measurements and the between-source component is the standard deviation of the mean values for the three sources. The two variance components are combined in quadrature to calculate the standard deviation of the mean for each counter-scintillant combination. Separate great grand-means are calculated for the LS and Na(Tl) measurements with a relative precision estimator calculated as described above.

LS Counters				NaI(Tl) Counter		
Counter	Scintillant	Grand Mean Massic Count Ratio	$S_{\bar{x}}$	Scintillant	Grand Mean Massic Count Ratio	$S_{\bar{x}}$
B	UGAB	5.5186	0.0121	UGAB	5.5148	0.0143
B	ECOS	5.5199	0.0155			
H	UGAB	5.5216	0.0088	ECOS	5.5303	0.0166
H	ECOS	5.5301	0.0166			
Great Grand Mean		**5.5226**	**0.0109**		**5.5226**	**0.0170**

Table 2 Count Ratios of ^{229}Th RM - SRM 4328C as measured by LS and NaI(Tl) counters. Counters H and B are as described in the text. UGAB and ECOS are as previously defined. $S_{\bar{x}}$ is a relative precision estimator equivalent to the standard deviation of the mean.

Activity Ratio by LS Standard Addition

A LS standard addition experiment was performed using a series of counting sources prepared as scintillation cocktails that contain mixtures of SRM 4328C and the ^{229}Th RM in varying proportions (Table 3). A total of five standard addition LS sources were prepared using the Ecosint scintillation solution. Aliquots of both SRM 4328C and the ^{229}Th RM were added to each source but source preparation was, otherwise, as previously described. The LS counting rate (R_c) for the mixtures of the SRM 4328C, with massic activity (A_S), and the ^{229}Th RM, with massic activity (A_X), can be given by

$$R_c = \varepsilon\ (m_S\, A_S + \ m_X\, A_X\ ) \tag{1}$$

where m_S and m_X are the respective aliquot masses of the two solutions in the cocktail and where ε is the overall ^{229}Th decay chain detection efficiency for the mixture in matched cocktails. Simple rearrangement, by normalization of each term in Eq. (1) by m_S, yields a linear function

$$\frac{R_c}{m_S} = \varepsilon\, A_S \ + \ \varepsilon\, A_X(m_X/m_S) \tag{2}$$

with intercept $\varepsilon\, A_S$ and slope $\varepsilon\, A_X$. From a series of matched counting sources with rates R_c for varying m_S and m_X, a linear fit of $R_c\,/\,m_S$ as a function of $m_X\,/\,m_S$ will determine slope and intercept parameters whose ratio gives A_X/A_S. Additionally, the linear equation, in two independent variables of Eq. (1), can be fit by multiple regression to yield $\varepsilon\, A_S$ and $\varepsilon\, A_X$ directly. The two calculational approaches give identical results, though extraction of the covariance between $\varepsilon\, A_S$ and $\varepsilon\, A_X$ from the covariance matrix is easier with multiple regression.

Ten (10) replicate measurements of the five sources were made in both Counter B and Counter H. The counting rates for the sources integrated over the entire LS spectrum ranged from about 520 s^{-1} to 950 s^{-1}. So, a duration of 3600 s was used for the measurements in order to accumulate approximately 1.9 10^6 to 3.4 10^6 integral counts in each spectrum (corresponding to relative Poisson counting statistics of about 0.07 % to 0.05 % for each of the 10 measurements).

Source ID	Mass of Scintillant (g)	Mass of ^{229}Th RM Aliquot (g)	Mass of SRM 4328C Aliquot (g)	Mass of Blank HNO_3 (g)	Total Mass Cocktail (g)	f_{aq} (%)	$H\#^{2}$
SA1	13.5365	0.076775	1.697757	0	15.3669	11.54	123.5 (5)
SA2	13.5657	0.201698	1.304430	0.2647	15.3962	11.50	123.2 (4)
SA3	13.5808	0.348458	0.995254	0.4289	15.416	11.50	123.6 (4)
SA4	13.5832	0.476746	0.600704	0.6948	15.4124	11.50	122.9 (4)
SA5	13.5711	0.632714	0.327851	0.8073	15.4002	11.48	123.1 (3)

Table 3 Standard Addition Source Preparation Details and Characteristics. Mass values have a standard uncertainty of < 0.01 %. *H#* is a quench indicating parameter (as measured in Counter B for $n = 10$ replications) which is an additional indicator of the close composition matching. The values in parentheses represent the numerical values of the standard deviation of the mean for the quoted H#.

Results for LS Standard Addition Measurement

The standard deviation of the mean for the average of the 10 replicate measurements of a source on Counter B ranged from 0.25 % to 0.37 %, and from 0.060 % to 0.083 % on Counter H. Multiple regressions of the Counter B and Counter H data sets for the R_c (m_X, m_S) two-independent-variable function of Eq. (3) were performed with the LAB Fit code [19]. Table 4 summarizes the results of these regressions. The ratio A_X/A_S was obtained from the fitted parameters εA_X and εA_S and its relative standard deviation was computed from

$$S = \left[\left(\frac{S_X}{A_X}\right)^2 + \left(\frac{S_S}{A_S}\right)^2 - 2\,\frac{S_{XS}}{A_X\,A_S} \right]^{1/2} \tag{3}$$

where S_X and S_S are the standard deviations on A_X and A_S, respectively, and where S_{XS} is the covariance between A_X and A_S (refer to Table 4). The reduced χ^2 values for the two regressions for

$\nu = 3$ degrees of freedom were 3.1 and 0.61, with corresponding percentile points of $p = 0.024$ and $p = 0.61$ for Counters B and H data, respectively.

Quantities	Counter B	Counter H
εA_X	1347.9	1369.4
εA_S	245.57	249.98
S_X^2	0.08892	0.6583
S_S^2	0.008953	0.03474
S_{XS}	-0.01646	-0.07668
A_X / A_S	5.4888	5.4780
S	0.0030	0.0067
Grand Mean	**Massic Activity Ratio** **5.4834**	**Standard Deviation** **0.0087**

Table 4 Standard Addition Activity Ratio Measurement Results. The fitted parameters εA_X and εA_S are for the ^{229}Th RM and SRM 4328C solutions, respectively, with corresponding variances S_X^2 and S_S^2 and covariance S_{XS}. The estimator S is the propagated standard deviation of the A_X / A_S massic activity ratio.

Isotope Dilution Alpha Spectrometry

The massic activity of the ^{229}Th RM was measured on five subsamples that were prepared for IDAS from a single unit of the reference material. This measurement method is independent of the three activity ratio methods and is not reliant upon comparison with SRM 4328C. The IDAS analysis is a nuclide-specific measurement of ^{229}Th activity so any perturbation of the radioactive equilibrium of the decay chain for the isotope will not bias the measurement results.

Accordingly, the analyses represent a robust verification of massic activity calculated from the previously described relative activity measurements.

The IDAS analysis samples were prepared by transferring aliquots of the SRM 4342A ^{230}Th activity standard to 5 separate beakers as an isotope dilution spike, followed by aliquots of the ^{229}Th RM (Table 5). The masses of the SRM 4342A and ^{229}Th RM aliquots were measured by difference on XP 205 balance (Mettler, Toledo USA). Approximately 2 mL of 0.4 mol L^{-1} $NaHSO_4$ (Fisher Scientific, Hampton, NH) and 2 mL 2 mol L^{-1} HNO_3 were also added to sample beakers which were then refluxed on a hotplate for roughly 1 hour. Additional 2 mol L^{-1} HNO_3 was added to each beaker, as necessary, to yield 10 mL of solution in preparation for ion exchange separation using UTEVA resin (Eichrom Technologies, Chicago, USA). Prior to loading, approximately 1 mg of Zr in a 4 mol L^{-1} nitrate solution (SPEX Industries, Metuchen, NJ) was added to each sample to assist in the recovery of Th from the UTEVA columns. The Th was eluted from the columns into a beaker using 20 mL of 6 mol L^{-1} HCl. Approximately 1 mL concentrated H_2SO_4 was added to the samples to break down any organic compounds that may have washed through the UTEVA column during elution and the solution was heated until the sulfuric acid was completely fumed off. Once dry, the samples were cooled and then re-dissolved in 10 mL of 2 mol L^{-1} HNO_3. Preparation of the samples for counting on the alpha spectrometer entailed co-precipitation of the Th with ≈50 µg of NdF_3, (Lindsay Rare Earth Chemicals, West Chicago, IL) in 1 mol L^{-1} HCL and collection of the sample on a 0.1 µm Metricel filter (Pall Corp. Baltimore, USA). The α-decays from ^{230}Th and ^{229}Th were counted for approximately 10^6 seconds on an Ortec Octete alpha spectrometer (Ortec, Oak Ridge, USA) with silicon detectors. The measured α activities for ^{230}Th and ^{229}Th were corrected for peak tailing, background, and decay probability. The ratio of the corrected activities in conjunction with the known aliquot weights were then used to calculate the ^{229}Th massic activity using a standard isotope dilution algorithm.

Source ID	^{229}Th Aliquot (g)	4342A aliquot (g)	^{229}Th corrected counts	^{230}Th corrected counts	Massic activity (Bq g^{-1})
1A	0.04681	0.23224	201134	208015	195.7
2A	0.03359	0.23442	146521	214837	194.2
3A	0.04935	0.22853	193851	187416	195.5
4A	0.03323	0.21738	121015	160688	201.0
5A	0.03362	0.23496	138180	203920	193.2

Table 5 ^{229}Th IDAS sample data. Mass values have a relative standard uncertainty of 0.3 %.

Results from IDAS

The combined IDAS measurement data indicate a ^{229}Th massic activity of (195.9 ± 3.2) Bq g^{-1} (k = 2) for a measurement date of March 5, 2012. The uncertainty of the measured value is dominated by the variability of the replicate massic activity measurements (Table 6) with the uncertainty for solution masses, the SRM 4342A tracer, and peak tail corrections representing minor contributions.

Component	Comment	Type	u_i %
Massic Activity	Standard uncertainty of replicate IDAS measurements of ^{229}Th massic activity	A	0.69
Weighing	Estimated relative uncertainty for potential bias in mass of IDAS solution aliquots	B	0.30
Peak Tail	Estimated uncertainty of ^{229}Th peak tail correction applied to the α count data	B	0.21
^{230}Th Spike	Combined standard uncertainty of the massic activity for SRM 4342A	B	0.20
Background	Estimated uncertainty of ^{229}Th and ^{230}Th background corrections	B	0.04

Relative combined standard uncertainty (u_c)	0.81 %

^{229}Th Massic Activity (Bq g^{-1})	Expanded Uncertainty (Bq g^{-1})
195.9	3.2 (Relative: 1.6 %)

Table 6 Uncertainty Budget for ^{229}Th massic activity by IDAS. The uncertainty estimate for the half-life was calculated in accordance with Taylor and Kuyatt, [20] and GUM protocols [21] using the GUM Workbench software [22]. u_i % represents the relative standard uncertainty for the listed components. The expanded uncertainty ($U = k \times u_c$) for the massic activity value is the product of the combined standard uncertainty (u_c) and a coverage factor (k), with $k = 2$ to achieve an approximately 95 % level of confidence.

Discussion

The physical and analytical linkages between the M solution, SRM 4328C, and the ^{229}Th RM allow for the measurement of the ^{229}Th RM massic activity through a direct comparison to SRM 4328C (Fig. 2). The three counting methods used to measure the activity ratios of the ^{229}Th RM and SRM 4328C should yield the same values, within uncertainties. Results from the LS and NaI(Tl) relative counting methods are consistent among all three counters and both scintillation cocktails used to prepare the sources (Table 2). The LS standard additions results are also consistent for both LS counters (Table 4) but the relative difference between the standard addition and the relative counting methods (δ) is 0.7 %, while the relative standard deviation for the results of the two standard addition measurements are both approximately 0.16 %. No clear explanation for the apparent discrepancy between the A_X / A_S ratio for the methods has been identified. Firstly, the composition matching of the five standard addition sources dictated nearly identical detection efficiencies across the series. Secondly, the quality of the fits, as reflected in the adjusted R^2, reduced χ^2, and F-values (for ANOVA ratio of variances), suggests that there should have been better agreement. The 95.4 % coverage factor on the standard deviation S_X and S_S for A_X and A_S is $k = 3.31$, such that the expanded relative uncertainties kS on A_X / A_S of 0.18 % and 0.40 % are roughly a factor of 2 to 3 smaller than the δ from the A_X / A_S ratio. In the absence of identifiable analytical problems for the three activity ratio measurement methods, the overall mean values for each method were averaged to yield a combined activity ratio $(A_X / A_S)_c$ of 5.510 with a standard uncertainty of 0.026. This standard uncertainty is calculated by adding, in quadrature, two variance components. These components are the within-method variability, represented by the typical standard deviation of the mean for the great-grand-means multiplied by the Student's T distribution for 2 degrees of freedom (n = 3 measurement methods), and the between-method variability represented by the standard deviation of the 3 activity ratio values.

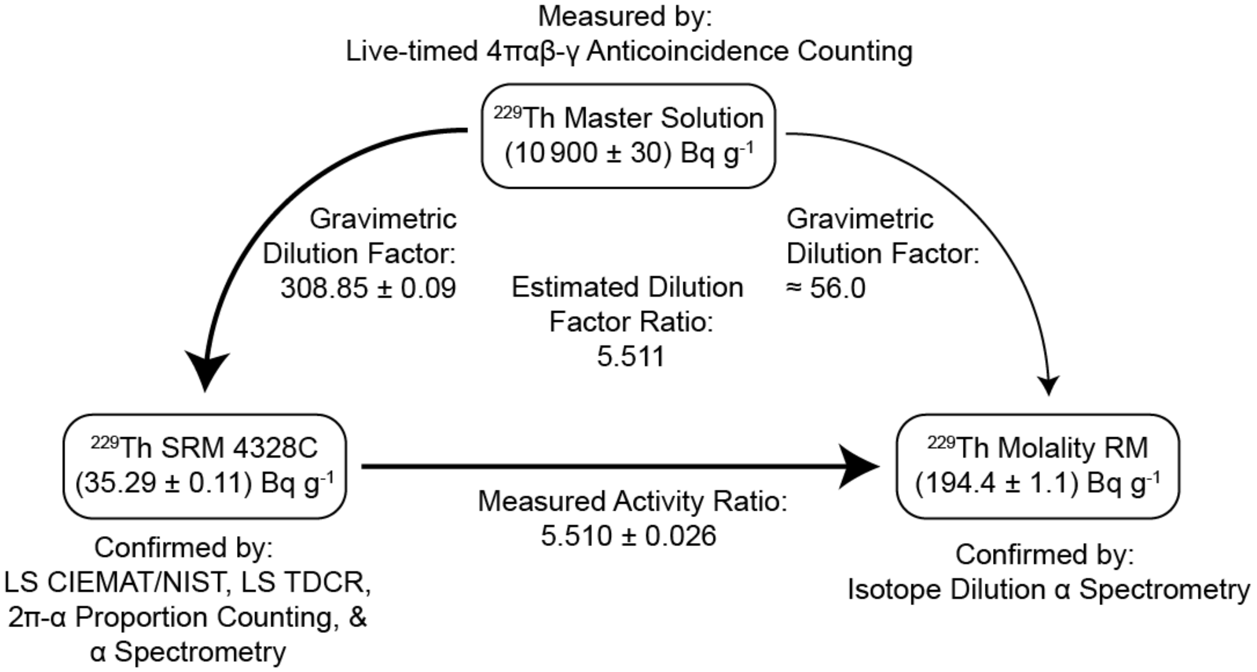

Fig. 2 Schematic of material and analytical linkages between the M solution, SRM 4328C, and the ^{229}Th RM. Bold arrows indicate the activity measurement linkages. The lighter arrow indicates direct production of the ^{229}Th RM from the M solution. Activity values shown in the figure are for the December 31, 2007 reference date of the massic activity value of the M solution. All uncertainties are combined standard uncertainties.

As previously described, the inverse ratio of dilution factors (D_S / D_X) for the two reference materials should be identical to the ^{229}Th activity ratio, representing an independent confirmation of the measured ratio. Although the dilution factor for the ^{229}Th RM is an approximation, a calculated D_S / D_X of 5.511 is essentially indistinguishable from the measured activity ratio value indicating the measured ratio is consistent with the values expected based on preparation of the reference material from the M solution.

The massic activity of the ^{229}Th RM solution (A_X) can be calculated (Eq. 4) from the combined activity ratio $(A_X / A_S)_c$, as described above, and the measured activity of the M solution (A_m) and the dilution factor for production of SRM 4328C stock solution (D_S), as reported in [17].

$$A_X = \frac{A_m \, (A_X/A_S)_c}{D_S} \tag{4}$$

The resulting massic activity value for the ^{229}Th RM is (194.4 ± 1.1) Bq g^{-1}. For comparison, the ^{229}Th massic activity measured by IDAS can be corrected to the reference date for SRM 4328C (December 31, 2007). The resulting massic activity value is 196.0 Bq g^{-1} with an expanded uncertainty of 3.2 Bq g^{-1} ($k = 2$). The relative difference between the activity measurements is 0.8 % which is well within the 1.6 % relative uncertainty of the IDAS measurement.

The massic activity from Eq. 4 (A_X) and the ^{229}Th molality (b_X) of (0.11498 ± 0.00008) nmol g^{-1}, as measured for the ^{229}Th RM in [18], can then be used to calculate a decay constant (λ) for ^{229}Th but a decay correction for the (4.7 ± 0.25) year interval between the reference dates for the massic activity and the molality measurements (*t*) must also be incorporated into the calculation (Eq. 5).

$$\lambda e^{\lambda t} = \frac{A_X}{b_X\ L} \tag{5}$$

Where *L* is the Avogadro's Constant. This function is solved for the decay constant by numerical iteration, which converges rapidly because of the small magnitude of the exponential term. A half-life (*T*) is then calculated from the decay constant (Eq. 6).

$$T = \frac{\ln(2)}{\lambda} \tag{6}$$

The best-fit decay constant for the ^{229}Th data is 8.858 10^{-5} a^{-1} with a combined standard uncertainty of 0.049 10^{-5} a^{-1} which corresponds to a half-life and expanded uncertainty of (7825 ± 87) years ($k = 2$). The uncertainty for the half-life determination is dominated by components from the M solution activity measurement and the measured activity ratio for the ^{229}Th RM (see Table 7). The uncertainties for the measured molality of the ^{229}Th RM solution, the SRM 4328C dilution factor, and the decay interval between the SRM reference date and the ^{229}Th molality measurements represent minor contributions to the overall uncertainty for the half-life.

Component	Comment	Type	$u_i\,\%^2$
Activity Ratio	Standard uncertainty of combined activity ratio measurements from this study	A	0.48
LTAC ^{229}Th Activity	Standard Uncertainty of the M solution massic activity	B	0.28
^{229}Th Molality	Combined standard uncertainty of the measured ^{229}Th molality	B	0.07
Dilution Factor	Standard uncertainty of the dilution factor for production of SRM 4328C from the M solution	B	0.03
Decay Interval	Relative uncertainty associated with the interval between the M solution reference date and molality measurements	B	0.00

Relative combined standard uncertainty (u_c)	0.56 %
^{229}Th Half-life (a)	Expanded Uncertainty[3] (a)
7825	87 (Relative: 1.1 %)

Table 7 Uncertainty budget for ^{229}Th half-life determination. The uncertainty estimate for the half-life was calculated in accordance with Taylor and Kuyatt, [20] and GUM protocols [21] using the GUM Workbench software [22]. u_i *%* represents the relative standard uncertainty for the listed components. The expanded uncertainty ($U = k \times u_c$) for the half-life value is the product of the combined standard uncertainty (u_c) and a coverage factor (k), with $k = 2$ to achieve an approximately 95 % level of confidence.

The ^{229}Th half-life measured in this study is largely consistent with previous determinations (Fig. 2) with the exception of the first published half-life for the isotope presented in Hagemann *et al.* [1]. As previously discussed, the value from Hagemann *et al.* is significantly shorter than subsequent half-life measurement and is probably erroneous. The present half-life measurement is consistent with the published half-life reported by Goldstein *et al.* [14] but is only marginally consistent with the values of Varga, *et al.* [16] and Kikunaga *et al.* [15] as indicated by overlapping expanded uncertainty envelopes. Pommé [23] noted that discrepancies between half-life measurements for the same nuclide are common and speculated that a major cause for the apparent differences is underestimated measurement uncertainty. It is not possible to assess the uncertainty cited by Hagemann *et al*. [1] and the uncertainty cited by Goldstein et al. [14] appears to be reasonably conservative. The uncertainty of the half-lives from Kikunaga *et al.* [15] and Varga *et al.* [16], however, may be underestimated.

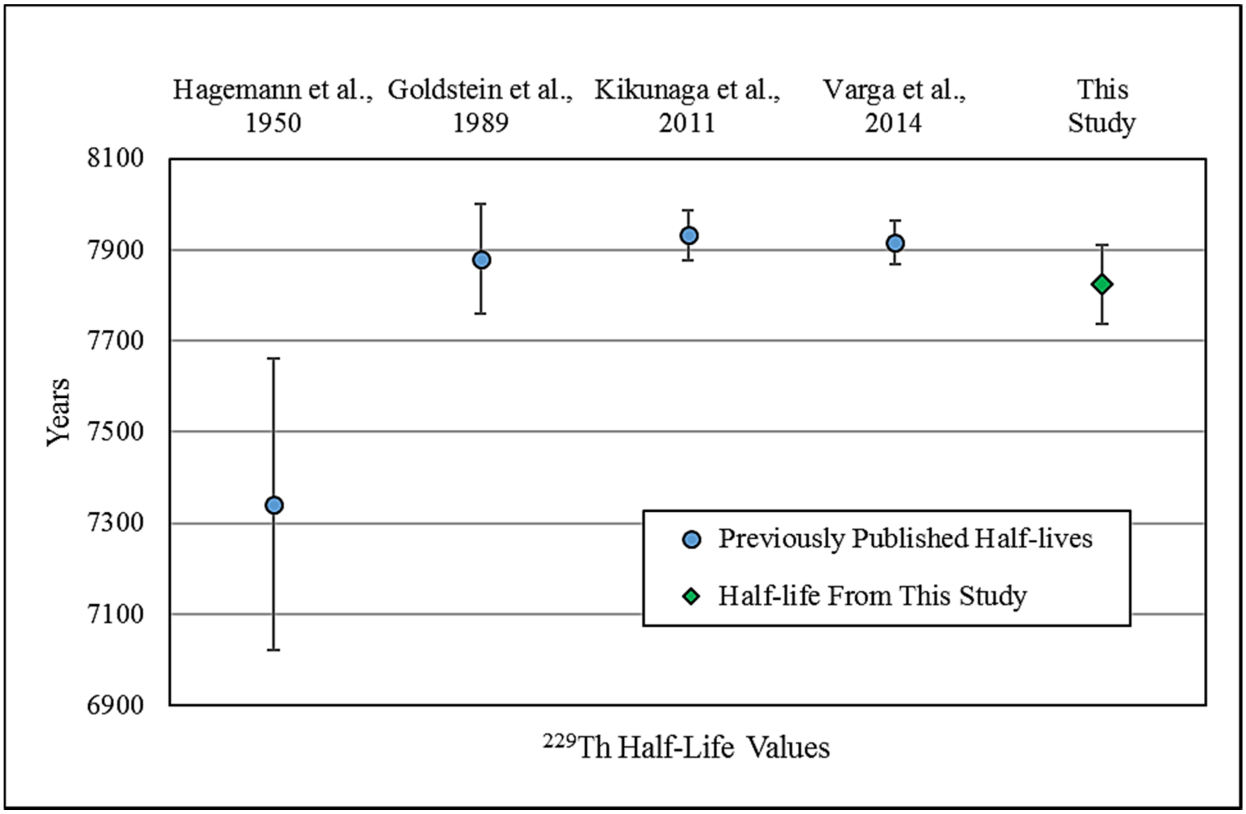

Fig. 2 Reported half-lives for ^{229}Th. Error bars are expanded uncertainties ($k = 2$).

Kikunaga *et al.* measured the half-life by an indirect method based on known ingrowth periods for Th in a high purity ^{233}U material that also contains a small proportion of ^{232}U. In their study, the measured α count ratios of $A(^{233}\mathrm{U})/A(^{232}\mathrm{U})$ and $A(^{229}\mathrm{Th})/A(^{228}\mathrm{Th})$ and the half-lives of ^{232}U and ^{228}Th were used to calculate a ^{229}Th half-life without the necessity of measuring the absolute amount or activity for the nuclide. Accordingly, their calculations are highly sensitive to the ^{228}Th half-life and the measured ^{229}Th to ^{228}Th count ratio, for which they indicate an average uncertainty of 0.2 %. The ^{228}Th half-life appears to be well constrained [21], and Kikunaga, *et al*. addressed potential sources for significant bias in their data such as corrections for background and interferences in the α spectra. However, the combined alpha spectra for ^{229}Th and ^{228}Th are complex and there is potential that their choice of region-of-interest for the nuclides, the magnitude of applied corrections, and/or uncertainties in decay data for the nuclides could result in a bias that is not covered by the 0.15 % relative "systematic" uncertainty cited for their measurements.

Varga *et al.* [13] provided detailed uncertainty budgets for each of the measurement methods used for their half-life determination (Methods A and B). The uncertainties for each method is dominated by the Type B uncertainties for SRM 4328C massic activity. Three replicates of the ^{229}Th molality measurement were performed for each method but no variability component associated with the replicate IDMS measurements was specified. Varga et al. then combined the two measured half-lives to obtain a weighted mean value of 7917 years with an expanded uncertainty of only 48 years ($k = 2$), despite a 63 year difference in the half-lives for the two methods. It appears that the combined measurement uncertainty did not incorporate a component for the variability evident between measurement methods and it is unclear whether the type B uncertainty components shared by the methods were appropriately propagated.

Conclusion

A new measured half-life of (7825 ± 87) years ($k = 2$) is reported for ^{229}Th. This value is based on the previously determined ^{229}Th molality of a new thorium IDMS reference material and the detailed characterization of the massic activity value for the reference material, presented here. The measured massic activity is tied directly to the SRM 4328C activity standard through multiple replicate activity ratio measurements using three independent methods and was also independently confirmed by IDAS measurements. This new ^{229}Th half-life measurement is between 0.7 % and 1.4 % shorter than other modern half-life determinations but is otherwise consistent with these values (overlapping uncertainties at the 95 % level of confidence).

Acknowledgements

Project activities at NIST were supported by the United States Department of Homeland Security Countering Weapons of Mass Destruction Office. Lawrence Livermore National Laboratory is operated by Lawrence Livermore National Security, LLC, for the U.S. Department of Energy, National Nuclear Security Administration under Contract DE-AC52-07NA27344. LLNL-JRNL-756361.

References

1. Hagemann F, Katzin L I, Studier M H, Seaborg G T, Ghiorso A (1950) The 4n + 1 radioactive series: The decay products of U^{233}*. Phys Rev. 79(3):435-443

2. de Lavison P, Husband L J, Jerome S M, Keightley J D, Woodman A P, Woods D H, Woods S A (2000) The standardization of the ^{229}Th for an environmental yield tracer. Appl Rad Iso. 53:243-249

3. Aggarwal S K (2016) A review on the mass spectrometric analysis of thorium. Radiochim Acta, 104 (7):445-456.

4. Apostolidis C, Molinet R, Rasmussen G, Morgenstern A (2005) Production of Ac-225 from Th-229 for targeted alpha therapy. Anal Chem. 77:6288-6291

5. Campbell C J, Radnaev A G, Kuzmich A, Dzuba V A, Flambaum V V, Derevianko A (2012) A Single-Ion Nuclear Clock for Metrology at the 19th Decimal Place. Phys Rev Lett. 108 (120802):1-5

6. Lamont S P, Hall G J (2005) Uranium age determination by measuring the ^{230}Th/^{234}U ratio. Radioanal Nuc Chem. 264:423-427

7. Williams R W, Gaffney A M (2011) ^{230}Th-^{234}U model ages of some uranium standard reference materials. Proc Radiochim Acta, 1:31-35

8. NBS (1984) Standard Reference Material 4328 Radioactivity Standard, National Bureau of Standards, Gaithersburg, MD, certificates available at https://www.nist.gov/srm

9. NIST (1995) Standard Reference Material 4328A Thorium-229 Radioactivity Standard, National Institute of Standards and Technology, Gaithersburg, MD, certificate available at https://www.nist.gov/srm

10. NIST, (1996) Standard Reference Material 4328B Thorium-229 Radioactivity Standard, National Institute of Standards and Technology, Gaithersburg, MD, certificate available at https://www.nist.gov/srm

11. NIST (2008) Standard Reference Material 4328C Thorium-229 Radioactivity Standard, National Institute of Standards and Technology, Gaithersburg, MD, certificate available at https://www.nist.gov/srm

12. Tuli J K (2011) Nuclear Wallet Cards, Nation Nuclear Data Center, https://www.nndc.bnl.gov. Accessed 1 Jan 2018

13. BIPM (2013) Monograph 5: Table of Radionuclides, 7-A:14-245.

14. Goldstein S J, Murrell M T, Williams R W (1989) Half-life of ^{229}Th. Phys Rev C. 40(6): 2793-2795.

15. Kikunaga H, Suzuki T, Nomura M, Mitsugashira T, Shinohara A (2011) Determination of the half-life of the ground state of ^{229}Th by using ^{232}U and ^{233}U decay series. Phys Rev C. 84 (014316): 1-6

16. Varga Z, Nicholl A, Mayer K, (2014) Determination of the ^{229}Th half-life. Phys Rev C. 89 (064310): 1-6

17. Fitzgerald R, Collé R, Laureano-Pérez L, Pibida L, Hammond M M, Nour S, Zimmerman B E (2010) A new primary standardization of ^{229}Th. Appl Radiat Iso. 68:1303-1308

18. Essex R M, Mann J L, Williams R W, Kinman W S, Hubert A, Bennett M E, Alkiviadias G (2018) A new thorium-229 reference material. Appl Rad Iso. 134:23-31

19. da Silva W, da Silva C P (2011) Lab Fit Curve Fitting Software. Universidade Federal de Campina Grande, Campina Grande, Brazil, zeus.df.ufcg.edu.br/labfit/.

20. Taylor B N, Kuyatt C E (1994) Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results: NIST Technical Note 1297. National Institute of Standards and Technology, Gaithersburg, MD

21. JCGM (2008) Evaluation of measurement data — Guide to the expression of uncertainty in measurement. JCGM 100, (E/F).

22. Metrodata GmbH, (2009) GUM Workbench. Weil am Rhein, Germany.

23. Pomme S (2015) The uncertainty of the half-life. Metrologia, 52:S51-S65.