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

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34

35 **Abstract**

36 A new determination of the ^{229}Th half-life was made based on measurements of the ^{229}Th massic
37 activity of a high-purity solution for which the ^{229}Th molality had previously been measured.
38 The ^{229}Th massic activity was measured by direct comparison with SRM 4328C using $4\pi\alpha\beta$
39 liquid scintillation counting, NaI counting, and standard addition liquid scintillation counting.

40 The ^{229}Th massic activity was confirmed by isotope dilution alpha spectrometry measurements.

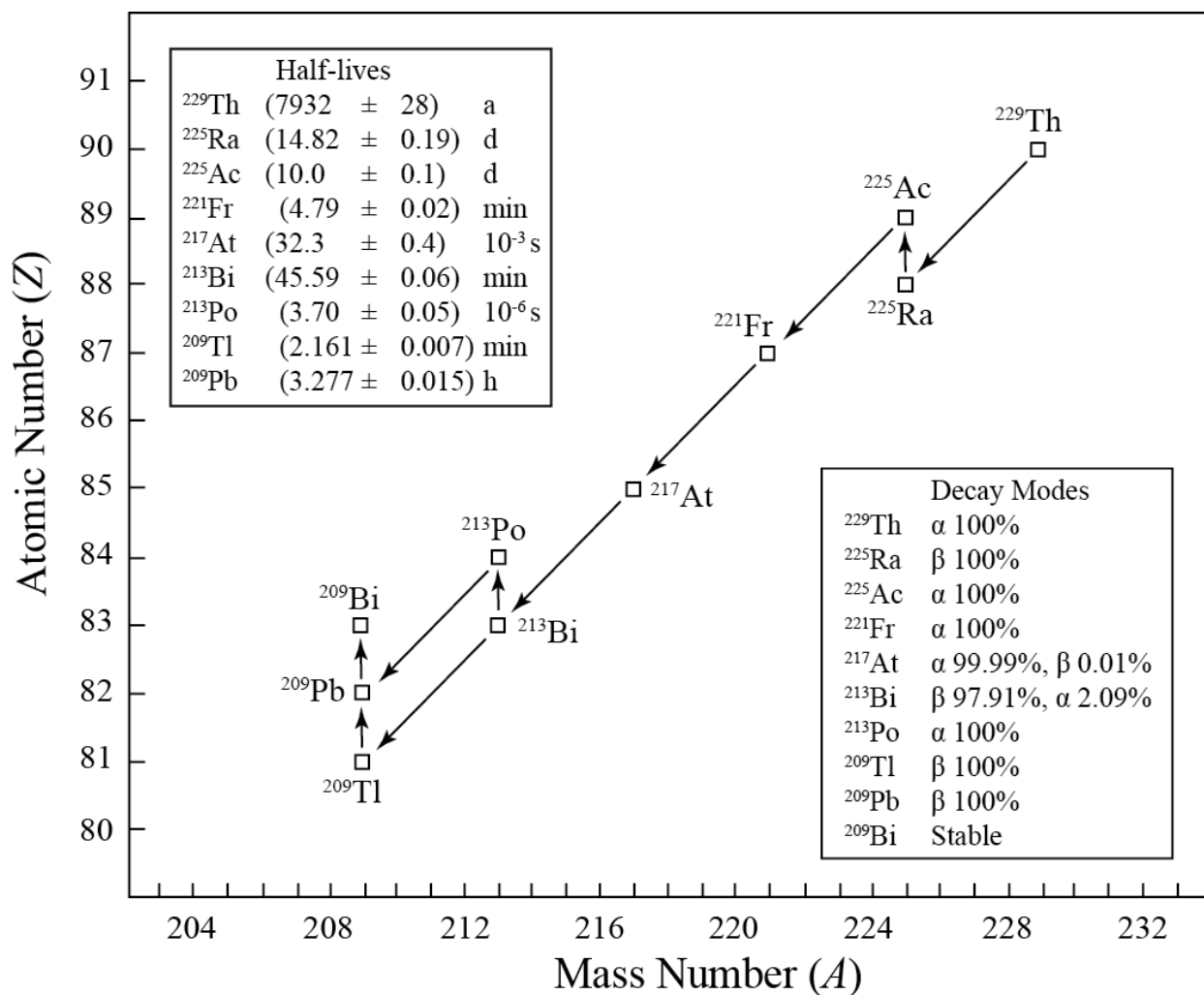
41 The ^{229}Th half-life calculated from the activity measurements is (7825 ± 87) years ($k = 2$).

42 **Key Words**

43 ^{229}Th , half-life, liquid scintillation counting, NaI counting, isotope dilution alpha spectrometry

44 **Introduction**

45 The ^{229}Th isotope is a relatively long-lived nuclide in the ^{237}Np decay series and primarily occurs
46 as a decay product of ^{233}U [1]. The isotope decays by α emission to ^{225}Ra which, in turn, decays
47 to ^{225}Ac followed by a series of short-lived nuclides to ^{209}Bi (Fig. 1). The ^{229}Th isotope does not
48 occur in nature making it useful to the environmental and geological sciences where it is used as
49 a yield tracer for thorium α spectrometry [2] and as an isotope dilution mass spectrometry
50 (IDMS) spike for thorium amount measurements [3]. In addition, ^{229}Th is a source of high-purity
51 ^{225}Ac for research in nuclear medicine [4] and is being evaluated for use as a high accuracy
52 nuclear clock [5]. The nuclide is particularly important for nuclear forensics where it is used as
53 an IDMS spike for ^{230}Th “dating” of uranium materials associated with the nuclear fuel cycle,
54 e.g. [6,7]. Due to ongoing interest in the radionuclide, the National Institute of Standards and
55 Technology (NIST) has produced four issues of ^{229}Th Standard Reference Material (SRM)
56 certified for massic activity (Bq g^{-1}). These standards are SRM 4328 issued in 1984, SRM
57 4328A issued in 1995, SRM 4328B issued in 1996, and SRM 4328C issued in 2008 [8-11].



58

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

62

63 To date, four half-life measurements have been published for ^{229}Th , but these values have been
 64 somewhat inconsistent. Hagemann *et al.* [1] published a ^{229}Th half-life of $(7340 \pm 160)^1$ years as
 65 part of a study of the ^{233}U decay chain. This value is significantly shorter than subsequent

¹Uncertainties 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 ($U = k u_c$).

66 measurements ($\approx 7\%$) with the discrepancy attributed to a combination of factors including a
67 biased ^{233}U half-life value used to calculate the quantity of ^{229}Th in the analysis samples, a
68 possible underestimate of ^{228}Th contributions to ^{229}Th activity measurements, or ^{233}U
69 interference in ^{229}Th activity measurements [14-15]. Goldstein *et al.* [14] performed a study to
70 refine the ^{229}Th half-life value by measuring the molality of ^{229}Th in a solution with a well-
71 characterized massic activity, SRM 4328. The resulting measurement indicated a half-life of
72 (7880 ± 120) years ($k = 2$). More recently, Kikunaga *et al.* [15] calculated a half-life of $(7932 \pm$
73 $55)$ years ($k = 2$) based on measured $A(^{233}\text{U})/A(^{232}\text{U})$ and $A(^{229}\text{Th})/A(^{228}\text{Th})$ activity ratios.
74 Finally, Varga *et al.* [16] measured the molality of the SRM 4328C massic activity standard by
75 IDMS using two different Th spikes. One spike was a commercially prepared natural Th solution
76 [Method A: (7889 ± 32) years] and the second spike was a high purity U material with a
77 calculated quantity of ingrown ^{230}Th [Method B: (7952 ± 36) years]. The half-lives calculated for
78 each set of IDMS measurements were combined for a reported half-life value of (7917 ± 48)
79 years ($k = 2$).

80 Fitzgerald *et al.* [17] describe a massic activity calibration for the ^{229}Th Master (M) solution used
81 to prepare SRM 4328C. To produce the stock solution for the SRM, an aliquot of the M solution
82 was quantitatively diluted by a factor (D_S) of 308.85 ± 0.09 . The ^{229}Th massic activity of the M
83 solution was then measured by live-timed $4\pi\alpha\beta$ - γ anticoincidence counting. The massic activity
84 of the SRM solution was calculated using the measured massic activity of the M solution and the
85 gravimetrically determined dilution factor. Relative liquid scintillation (LS) counting of the M
86 and SRM 4328C solutions was used to verify the gravimetric dilution factor for the SRM, with
87 the relative difference between the activity ratio and the dilution factor of 0.04 % and a
88 combined standard uncertainty of about 0.4 % in the activity ratio. The calculated activity value

89 for the SRM was also confirmed by four additional radioactivity measurement methods,
90 including LS counting with ^3H CIEMAT/NIST efficiency tracing², triple-to-double coincidence
91 counting (LS TDCR), $2\pi\alpha$ proportional counting, and α spectrometry.

92 In a separate project, two ampoules of the M solution were combined and diluted by a factor (D_X)
93 of approximately 56.0^3 to produce a new reference material that was characterized for ^{229}Th
94 molality ($^{229}\text{Th mol g}^{-1}$) and Th isotopic composition [18]. The ^{229}Th molality of the new
95 reference material was measured by IDMS on a total of 14 sample units in two measurement
96 campaigns. To minimize potential systematic bias, three separate ^{232}Th IDMS spike solutions
97 were prepared for the measurements and mass spectrometric analyses were distributed between
98 three different laboratories. The resulting ^{229}Th molality value for the reference material solution,
99 $(0.11498 \pm 0.00008) \text{ nmol g}^{-1}$, was verified using the SRM 4342A ^{230}Th massic activity standard
100 as an independent IDMS spike.

101
102 The following describes the determination of the massic activity of the new ^{229}Th molality
103 reference material (referred to here as $^{229}\text{Th RM}$) by direct comparison with the SRM 4328C
104 massic activity standard and the confirmation of the measured value by isotope dilution alpha
105 spectrometry (IDAS). A new value for the ^{229}Th half-life is calculated from the measured ^{229}Th
106 massic activity and the previously measured ^{229}Th molality.

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 $^{229}\text{Th RM}$ (D_X) is only used for comparison purposes. During the dilution of the M solution to create the $^{229}\text{Th RM}$ 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.

107

108 **Direct Activity Comparison**

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

117 **Relative LS Counting**

118 The ^{229}Th decay series consists of a seven-nuclide-long decay chain (Fig. 1) with an LS
119 efficiency of $> 6.9 \text{ s}^{-1} \text{ Bq}^{-1}$. To achieve accurate results for the comparative LS counting
120 measurements, it is imperative that the two ^{229}Th solutions are in identical states of radioactive
121 equilibrium and that the solutions were counted with identical detection efficiency. Nearly
122 identical counting efficiency was achieved by gravimetrically determining all of the components
123 in the counting source cocktails to assure similar quenching. Identical radioactive equilibrium is
124 also a reasonable assumption when the history and handling of the solutions are considered.
125 Both ^{229}Th solutions were prepared from quantitative dilutions of aliquots from the same M
126 solution; both solutions were diluted with $1 \text{ mol L}^{-1} \text{ HNO}_3$; and no additional separations or
127 processing were performed on either solution prior to sealing in glass ampoules. Ampoules of
128 both reference materials were opened specifically for the activity measurements performed in

129 April 2017, however, the SRM 4328C solution was prepared, dispensed into ampoules, and
130 sealed in October 2007 while the ^{229}Th RM was prepared and sealed in March 2012. Although it
131 is not possible to categorically rule out chemical fractionation of the sealed M solution aliquots
132 over the 4.5 year period between preparation of the ^{229}Th solutions (e.g., preferential adsorption
133 or precipitation of an element in the ^{229}Th decay chain), there is no *a priori* reason to suspect a
134 difference in the radioactive equilibrium of the two solutions.

135 Counting sources for high precision LS were prepared from the ^{229}Th RM and SRM 4328C
136 solutions (Table 1). Two different scintillation fluids were used to create liquid scintillation
137 sources for both ^{229}Th solutions, Ultima Gold AB⁴ (PerkinElmer, Waltham, MA) and Ecoscint
138 (National Diagnostics, Tampa, FL). Three sources were gravimetrically prepared in 20 mL glass
139 LS vials for each scintillant- ^{229}Th solution combination, resulting in a total of 12 sources. To
140 prepare the sources, aliquots from ampoules of the SRM and ^{229}Th RM were dispensed using
141 polyethylene aspirating pycnometers with masses measured on an electronic microbalance
142 (AT20, Mettler Toledo, USA). Other cocktail components were weighed with a mechanical
143 analytical balance (Mettler B5, Mettler Toledo, USA). Close matching of the aqueous mass
144 fraction in the sets of cocktails was achieved by the addition of 1 mol L^{-1} HNO_3 to some of the
145 sources. In addition, each cocktail contained approximately 60 mg of di-(2-ethylhexyl)
146 phosphoric acid (DEHPA or HDEHP), $(\text{C}_8\text{H}_{17}\text{O})_2\text{PO}_2\text{H}$, which is a complexing agent. Matched
147 blank sources of similar composition over the same quench range were also prepared for
148 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.

149 Each source was counted in triplicate on a LS 6500 counter (Beckman Coulter, Fullerton, CA,
 150 USA) and on an Accuflex LSC-8000 (Hitachi Aloka Medical Ltd., Tokyo, Japan). Two LS
 151 counters were used for this set of experiments to demonstrate that results are independent of the
 152 operating characteristics of a particular instrument (detection threshold, photomultiplier
 153 efficiency, deadtime, amplification, signal conversion, etc.). Individual LS measurements
 154 consisted of integrating the entire LS spectrum, and were of sufficient duration to accumulate
 155 over 10^6 counts, such that the relative Poisson counting statistics on each was $< 0.1\%$. In
 156 addition to closely matching quenching conditions and cocktail compositions in counting
 157 sources, both instruments use quench indicating parameters (QIP) to monitor quenching. The
 158 Accuflex LSC-8000 (Counter H) uses the External Standard Channel Ratio (*ESCR*) quench
 159 parameter, which relates quenching to the ratio of two counting windows in the Compton
 160 spectrum of ^{133}Ba . The Beckman LS 6500 (Counter B) uses a Horrocks Number (*H#*) to monitor
 161 the quench level, which is based on the downward spectrum shift of the Compton edge of an
 162 external ^{137}Cs source with increasing quenching in the cocktail.

163

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} (%)	<i>H#</i>
^{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)

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

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

171

172 **Relative Photon Emission**

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

184 **Results for LS and Photon Emission Counting Rates**

185 The measurement results are provided in terms of grand-means and great-grand-means of the
186 massic count ratios (Table 2). The measured count rates from the LS and NaI(Tl) experiments
187 are proportional to the massic activity of the respective solutions. Therefore, if ^{229}Th decay chain
188 equilibrium is the same for both solutions, then the ratio of the massic count rates is equivalent to
189 the ^{229}Th relative activity ratio (A_X/A_S) which, in turn is equivalent of the inverse ratio of M

190 solution dilution factors (D_S/D_X) for the two reference materials. The uncertainty values for the
 191 grand-mean massic count ratios in Table 2 are computed precision estimators, equivalent to a
 192 standard deviation of the mean ($S_{\bar{x}}$), that consider both the within-source and between-source
 193 components of variance. The within-source component is a “typical” (i.e., average) value for the
 194 standard deviation of the replicate source measurements and the between-source component is
 195 the standard deviation of the mean values for the three sources. The two variance components are
 196 combined in quadrature to calculate the standard deviation of the mean for each counter-
 197 scintillant combination. Separate great grand-means are calculated for the LS and Na(Tl)
 198 measurements with a relative precision estimator calculated as described above.

199

Counter	LS Counters			Scintillant	NaI(Tl) Counter	
	Scintillant	Grand Mean Massic Count Ratio	$S_{\bar{x}}$		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

200 **Table 2** Count Ratios of ^{229}Th RM - SRM 4328C as measured by LS and NaI(Tl) counters.

201 Counters H and B are as described in the text. UGAB and ECOS are as previously defined. $S_{\bar{x}}$ is
 202 a relative precision estimator equivalent to the standard deviation of the mean.

203 **Activity Ratio by LS Standard Addition**

204 A LS standard addition experiment was performed using a series of counting sources prepared as
 205 scintillation cocktails that contain mixtures of SRM 4328C and the ^{229}Th RM in varying
 206 proportions (Table 3). A total of five standard addition LS sources were prepared using the

207 Ecosint scintillation solution. Aliquots of both SRM 4328C and the ^{229}Th RM were added to
208 each source but source preparation was, otherwise, as previously described. The LS counting
209 rate (R_c) for the mixtures of the SRM 4328C, with massic activity (A_S), and the ^{229}Th RM, with
210 massic activity (A_X), can be given by

$$211 \quad R_c = \varepsilon (m_S A_S + m_X A_X) \quad (1)$$

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

$$215 \quad \frac{R_c}{m_S} = \varepsilon A_S + \varepsilon A_X (m_X / m_S) \quad (2)$$

216 with intercept εA_S and slope εA_X . From a series of matched counting sources with rates R_c for
217 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
218 intercept parameters whose ratio gives A_X / A_S . Additionally, the linear equation, in two
219 independent variables of Eq. (1), can be fit by multiple regression to yield εA_S and εA_X directly.
220 The two calculational approaches give identical results, though extraction of the covariance
221 between εA_S and εA_X from the covariance matrix is easier with multiple regression.

222 Ten (10) replicate measurements of the five sources were made in both Counter B and Counter
223 H. The counting rates for the sources integrated over the entire LS spectrum ranged from about
224 520 s^{-1} to 950 s^{-1} . So, a duration of 3600 s was used for the measurements in order to accumulate
225 approximately $1.9 \cdot 10^6$ to $3.4 \cdot 10^6$ integral counts in each spectrum (corresponding to relative
226 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)	<i>f</i> _{aq} (%)	<i>H</i> # 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)

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

233

234 Results for LS Standard Addition Measurement

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

$$241 \quad S = \left[\left(\frac{S_X}{A_X} \right)^2 + \left(\frac{S_S}{A_S} \right)^2 - 2 \frac{S_{XS}}{A_X A_S} \right]^{1/2} \quad (3)$$

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

244 for $\nu = 3$ degrees of freedom were 3.1 and 0.61, with corresponding percentile points of $p =$
 245 0.024 and $p = 0.61$ for Counters B and H data, respectively.

246

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

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

251

252

253 **Isotope Dilution Alpha Spectrometry**

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

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

261 The IDAS analysis samples were prepared by transferring aliquots of the SRM 4342A ^{230}Th
262 activity standard to 5 separate beakers as an isotope dilution spike, followed by aliquots of the
263 ^{229}Th RM (Table 5). The masses of the SRM 4342A and ^{229}Th RM aliquots were measured by
264 difference on XP 205 balance (Mettler, Toledo USA). Approximately 2 mL of 0.4 mol L⁻¹
265 NaHSO₄ (Fisher Scientific, Hampton, NH) and 2 mL 2 mol L⁻¹ HNO₃ were also added to sample
266 beakers which were then refluxed on a hotplate for roughly 1 hour. Additional 2 mol L⁻¹ HNO₃
267 was added to each beaker, as necessary, to yield 10 mL of solution in preparation for ion
268 exchange separation using UTEVA resin (Eichrom Technologies, Chicago, USA). Prior to
269 loading, approximately 1 mg of Zr in a 4 mol L⁻¹ nitrate solution (SPEX Industries, Metuchen,
270 NJ) was added to each sample to assist in the recovery of Th from the UTEVA columns. The Th
271 was eluted from the columns into a beaker using 20 mL of 6 mol L⁻¹ HCl. Approximately 1 mL
272 concentrated H₂SO₄ was added to the samples to break down any organic compounds that may
273 have washed through the UTEVA column during elution and the solution was heated until the
274 sulfuric acid was completely fumed off. Once dry, the samples were cooled and then re-
275 dissolved in 10 mL of 2 mol L⁻¹ HNO₃. Preparation of the samples for counting on the alpha
276 spectrometer entailed co-precipitation of the Th with ≈ 50 μg of NdF₃, (Lindsay Rare Earth
277 Chemicals, West Chicago, IL) in 1 mol L⁻¹ HCl and collection of the sample on a 0.1 μm
278 Metricel filter (Pall Corp. Baltimore, USA). The α -decays from ^{230}Th and ^{229}Th were counted
279 for approximately 10^6 seconds on an Ortec Octete alpha spectrometer (Ortec, Oak Ridge, USA)
280 with silicon detectors. The measured α activities for ^{230}Th and ^{229}Th were corrected for peak
281 tailing, background, and decay probability. The ratio of the corrected activities in conjunction

282 with the known aliquot weights were then used to calculate the ^{229}Th massic activity using a
 283 standard isotope dilution algorithm.

284

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

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

286 Results from IDAS

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

292

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 %)	

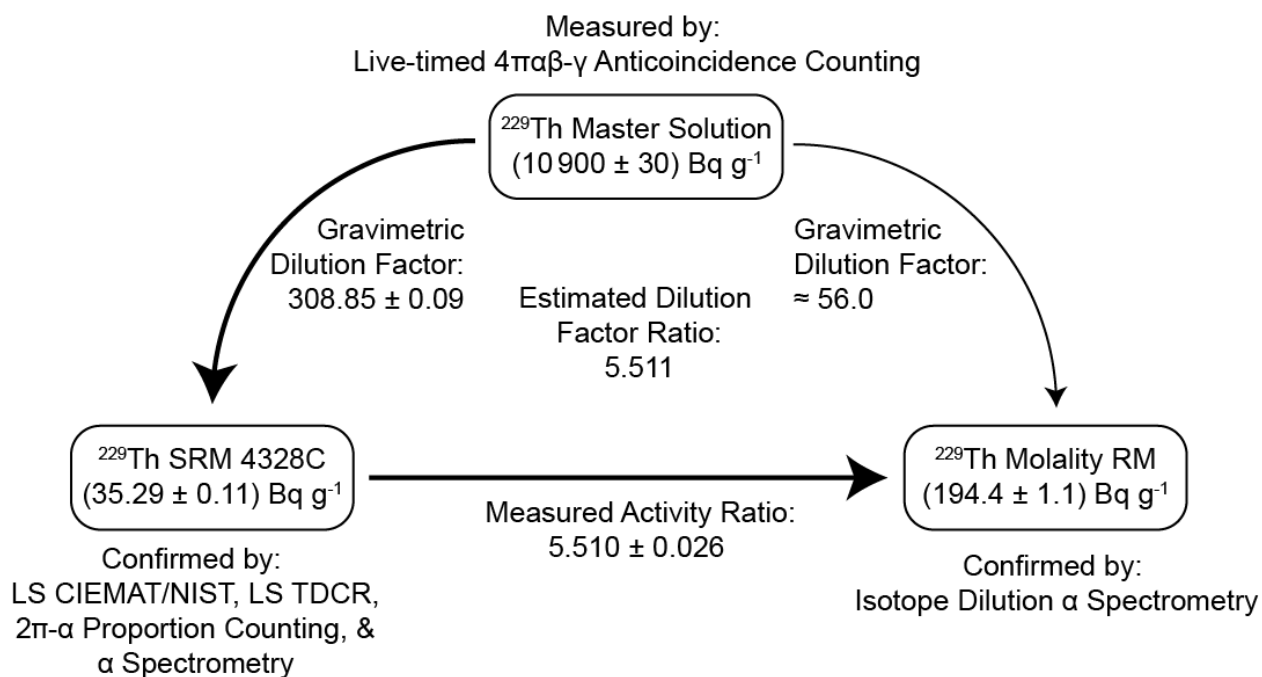
293 **Table 6** Uncertainty Budget for ²²⁹Th massic activity by IDAS. The uncertainty estimate for the
 294 half-life was calculated in accordance with Taylor and Kuyatt, [20] and GUM protocols [21]
 295 using the GUM Workbench software [22]. u_i % represents the relative standard uncertainty for
 296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

299 Discussion

300 The physical and analytical linkages between the M solution, SRM 4328C, and the ²²⁹Th RM
 301 allow for the measurement of the ²²⁹Th RM massic activity through a direct comparison to SRM
 302 4328C (Fig. 2). The three counting methods used to measure the activity ratios of the ²²⁹Th RM
 303 and SRM 4328C should yield the same values, within uncertainties. Results from the LS and
 304 NaI(Tl) relative counting methods are consistent among all three counters and both scintillation
 305 cocktails used to prepare the sources (Table 2). The LS standard additions results are also
 306 consistent for both LS counters (Table 4) but the relative difference between the standard
 307 addition and the relative counting methods (δ) is 0.7 %, while the relative standard deviation for
 308 the results of the two standard addition measurements are both approximately 0.16 %. No clear
 309 explanation for the apparent discrepancy between the A_X / A_S ratio for the methods has been
 310 identified. Firstly, the composition matching of the five standard addition sources dictated nearly
 311 identical detection efficiencies across the series. Secondly, the quality of the fits, as reflected in
 312 the adjusted R^2 , reduced χ^2 , and F -values (for ANOVA ratio of variances), suggests that there

313 should have been better agreement. The 95.4 % coverage factor on the standard deviation S_X and
314 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 %
315 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
316 of identifiable analytical problems for the three activity ratio measurement methods, the overall
317 mean values for each method were averaged to yield a combined activity ratio $(A_X / A_S)_c$ of 5.510
318 with a standard uncertainty of 0.026. This standard uncertainty is calculated by adding, in
319 quadrature, two variance components. These components are the within-method variability,
320 represented by the typical standard deviation of the mean for the great-grand-means multiplied
321 by the Student's T distribution for 2 degrees of freedom ($n = 3$ measurement methods), and the
322 between-method variability represented by the standard deviation of the 3 activity ratio values.

323



324

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

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

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

$$339 \quad A_X = \frac{A_m (A_X/A_S)_c}{D_S} \quad (4)$$

340 The resulting massic activity value for the ^{229}Th RM is $(194.4 \pm 1.1) \text{ Bq g}^{-1}$. For comparison, the
341 ^{229}Th massic activity measured by IDAS can be corrected to the reference date for SRM 4328C
342 (December 31, 2007). The resulting massic activity value is 196.0 Bq g^{-1} with an expanded
343 uncertainty of 3.2 Bq g^{-1} ($k = 2$). The relative difference between the activity measurements is
344 0.8 % which is well within the 1.6 % relative uncertainty of the IDAS measurement.

345 The massic activity from Eq. 4 (A_X) and the ^{229}Th molality (b_X) of $(0.11498 \pm 0.00008) \text{ nmol g}^{-1}$,
346 as measured for the ^{229}Th RM in [18], can then be used to calculate a decay constant (λ) for ^{229}Th

347 but a decay correction for the (4.7 ± 0.25) year interval between the reference dates for the
 348 massic activity and the molality measurements (t) must also be incorporated into the calculation
 349 (Eq. 5).

$$350 \quad \lambda e^{\lambda t} = \frac{A_X}{b_X L} \quad (5)$$

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

$$354 \quad T = \frac{\ln(2)}{\lambda} \quad (6)$$

355 The best-fit decay constant for the ^{229}Th data is $8.858 \cdot 10^{-5} \text{ a}^{-1}$ with a combined standard
 356 uncertainty of $0.049 \cdot 10^{-5} \text{ a}^{-1}$ which corresponds to a half-life and expanded uncertainty of $(7825$
 357 $\pm 87)$ years ($k = 2$). The uncertainty for the half-life determination is dominated by components
 358 from the M solution activity measurement and the measured activity ratio for the ^{229}Th RM (see
 359 Table 7). The uncertainties for the measured molality of the ^{229}Th RM solution, the SRM 4328C
 360 dilution factor, and the decay interval between the SRM reference date and the ^{229}Th molality
 361 measurements represent minor contributions to the overall uncertainty for the half-life.

362

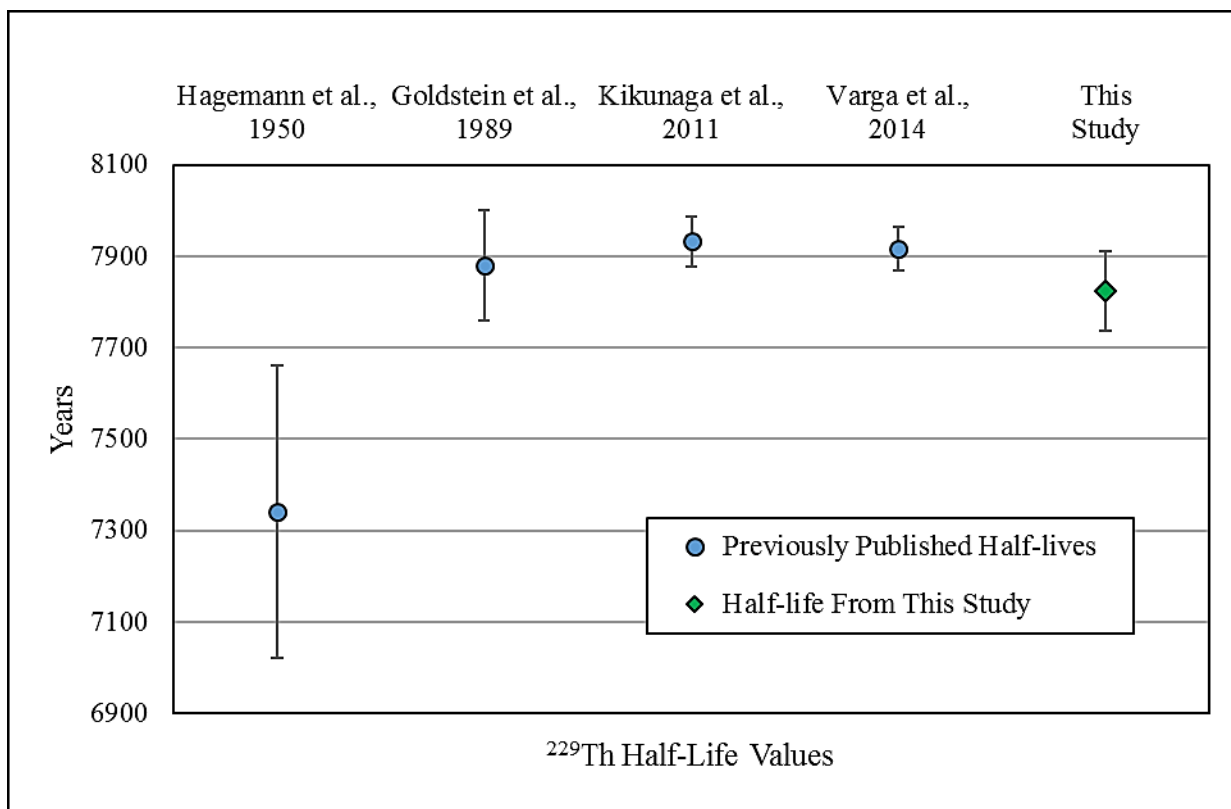
Component	Comment	Type	$u_i \%^2$
Activity Ratio	Standard uncertainty of combined activity ratio measurements from this study	A	0.48
LTAC ^{229}Th Activity	Standard Uncertainty of the M solution massic activity	B	0.28
^{229}Th Molality	Combined standard uncertainty of the measured ^{229}Th molality	B	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 %)

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

369 The ^{229}Th half-life measured in this study is largely consistent with previous determinations (Fig.
 370 3) with the exception of the first published half-life for the isotope presented in Hagemann *et al.*
 371 [1]. As previously discussed, the value from Hagemann *et al.* is significantly shorter than
 372 subsequent half-life measurement and is probably erroneous. The present half-life measurement
 373 is consistent with the published half-life reported by Goldstein *et al.* [14] but is only marginally
 374 consistent with the values of Varga, *et al.* [16] and Kikunaga *et al.* [15] as indicated by
 375 overlapping expanded uncertainty envelopes. Pommé [23] noted that discrepancies between half-
 376 life measurements for the same nuclide are common and speculated that a major cause for the
 377 apparent differences is underestimated measurement uncertainty. It is not possible to assess the
 378 uncertainty cited by Hagemann *et al.* [1] and the uncertainty cited by Goldstein *et al.* [14]
 379 appears to be reasonably conservative. The uncertainty of the half-lives from Kikunaga *et al.*
 380 [15] and Varga *et al.* [16], however, may be underestimated.

381



382

383 **Fig. 3** Reported half-lives for ^{229}Th . Error bars are expanded uncertainties ($k = 2$).

384 Kikunaga *et al.* measured the half-life by an indirect method based on known ingrowth periods
 385 for Th in a high purity ^{233}U material that also contains a small proportion of ^{232}U . In their study,
 386 the measured α count ratios of $A(^{233}\text{U})/A(^{232}\text{U})$ and $A(^{229}\text{Th})/A(^{228}\text{Th})$ and the half-lives of ^{232}U
 387 and ^{228}Th were used to calculate a ^{229}Th half-life without the necessity of measuring the absolute
 388 amount or activity for the nuclide. Accordingly, their calculations are highly sensitive to the
 389 ^{228}Th half-life and the measured ^{229}Th to ^{228}Th count ratio, for which they indicate an average
 390 uncertainty of 0.2 %. The ^{228}Th half-life appears to be well constrained [21], and Kikunaga, *et*
 391 *al.* addressed potential sources for significant bias in their data such as corrections for
 392 background and interferences in the α spectra. However, the combined alpha spectra for ^{229}Th
 393 and ^{228}Th are complex and there is potential that their choice of region-of-interest for the

394 nuclides, the magnitude of applied corrections, and/or uncertainties in decay data for the nuclides
395 could result in a bias that is not covered by the 0.15 % relative “systematic” uncertainty cited for
396 their measurements.

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

407 **Conclusion**

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

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