Preparation and Standardization of ^{229}Th SRM 4328d

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Abstract

The certified massic activity for ^{229}Th in SRM 4328d was obtained by $4\pi\alpha\beta$ liquid scintillation (LS) counting by comparative measurements in 2022 against SRM 4328c. Both SRMs were prepared from the identical 2007 ^{229}Th stock solution. SRM 4328c was standardized in 2007 by live-timed anticoincidence counting (a primary standardization method) with confirmatory measurements by four other methods. The comparative measurements were performed using two different commercial LS counters and with LS counting sources prepared with two different cocktail compositions. Homogeneity of SRM 4328d was confirmed by photonic emission spectrometry of the SRM ampoules with a NaI(Tl) well counter. The certified massic activity of ^{229}Th in SRM 4328d, based on the decay-corrected certified value for SRM 4328c, is (41.19 ± 0.41) Bq·g^{-1} at $k = 2$ as of 1200 EST, 14 July 2022. This report documents the preparation, standardization, and certification of SRM 4328d.

Keywords

Activity; Liquid Scintillation (LS); Metrology; Radioactivity: Standard Reference Material (SRM); Thorium-229.

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Acknowledgments

Author Contributions

By Taxonomy

Collé: Conceptualization, Formal analysis, Investigation, Methodology, Supervision, Validation, Visualization, Writing - original draft, Writing – review & editing; **Laureano-Pérez**: Conceptualization, Investigation, Supervision, Visualization, Writing – review & editing; **DiGiorgio:** Formal analysis, Investigation, Validation, Visualization, Writing – review & editing.

By Roles

Preparation of the SRM 4328d dispensing solution was performed by **Laureano-Pérez** with the assistance of **Collé.** Ampoule dispensing and sealing was performed by **Collé** with the assistance of **Laureano-Pérez.** LS counting sources were prepared by **Laureano-Pérez** and **Collé**. LS measurements were performed by **Laureano-Pérez.** Analyses of the LS data. including statistical analyses, were performed by **Collé** and **DiGiorgio** with the assistance of **Laureano-Pérez.** Homogeneity testing was performed by **Laureano-Pérez, DiGiorgio** and **Collé.** Overall technical direction was provided by **Collé** and **Laureano-Pérez. Collé** wrote the first draft and all authors participated in reviewing and editing the final version.

1.   Introduction

A high-purity ^{229}Th standard is needed as a tracer for alpha- and mass-spectrometry methods, such as ^{234}U/^{230}Th radiochronometry [Inn, et al., 2008], as well as for nuclear forensic analyses [Essex, et al., 2017]. As a result, ^{229}Th Standard Reference Materials (SRM) have been developed and disseminated by the National Institute of Standards and Technology (NIST) since the 1980s. The current standard (SRM 4328d) was preceded by four earlier issues, *viz*.: SRM 4328 in 1984; SRM 4328a in 1994; 4328b in 1996; and SRM 4328c in 2007. The first three were standardized by defined solid-angle alpha counting with a scintillation detector. The primary standardization of SRM 4328c was based on live-timed 4πβ-γ anticoincidence counting (LTAC) of the equilibrium solution for the nine-member ^{229}Th decay chain [Fitzgerald, et al., 2010]. SRM 4328c was also used for a massic activity comparison with a high-purity ^{229}Th molality reference material that resulted in a new ^{229}Th half-life determination [Essex, et al., 2018].

2. ^{229}Th Stock Material

The ^{229}Th stock material was received from Oak Ridge National Laboratory (ORNL) as solid salt of Th(NO$_3$)$_4$·nH$_2$O. The material was known to contain a small ^{228}Th impurity, which was later quantified, as detailed in Section 10 below. The source material, containing about 1 MBq of ^{229}Th, was dissolved in 1 mol·L^{-1} HNO$_3$ to make a "stock solution" with a massic activity of approximately 13 kBq·g^{-1}. The density of the HNO$_3$ diluent was determined to be (1.031 ± 0.002) g·mL^{-1} at 21 °C.[1] The entire stock solution was dispensed, for subsequent use, into 18 glass ampoules, each containing about 5 mL of solution, and flame sealed. Two of these stock solution ampoules were used to prepare SRM 4328c in 2007 and SRM 4328d in 2022. See Fig. 1.

3.   Overview and Calibration Scheme

Figure 1 shows an overview of the preparation of SRM 4328c and SRM 4328d from the same stock solution prepared in 2007. The SRM 4328c and SRM 4328d dispensing solutions were linked to the stock solution through gravimetrically-determined dilution factors (DF), that were determined to approximately ± 0.04 % at $k = 2$. Comparative liquid scintillation measurements to standardize SRM 4328d against SRM 4328c were simplified because both SRMs were prepared from the same stock solution. The LS comparisons were made with aliquants from one ampoule of SRM 4328c and from two randomly selected ampoules of SRM 4328d. All aliquots for the LS counting sources were linked to the dispensing solutions by gravimetric determinations with a microbalance. The LS counting sources were made with two different LS cocktail compositions (labeled "HF" and "UGAB" in Fig. 1) and measurements were performed with two different commercial LS counters.

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[1] Unless otherwise noted, all uncertainties given in this report 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. The treatment and reporting of uncertainties follows NIST policy and international conventions given in Taylor and Kuyatt (1994) and JCGM (2008).
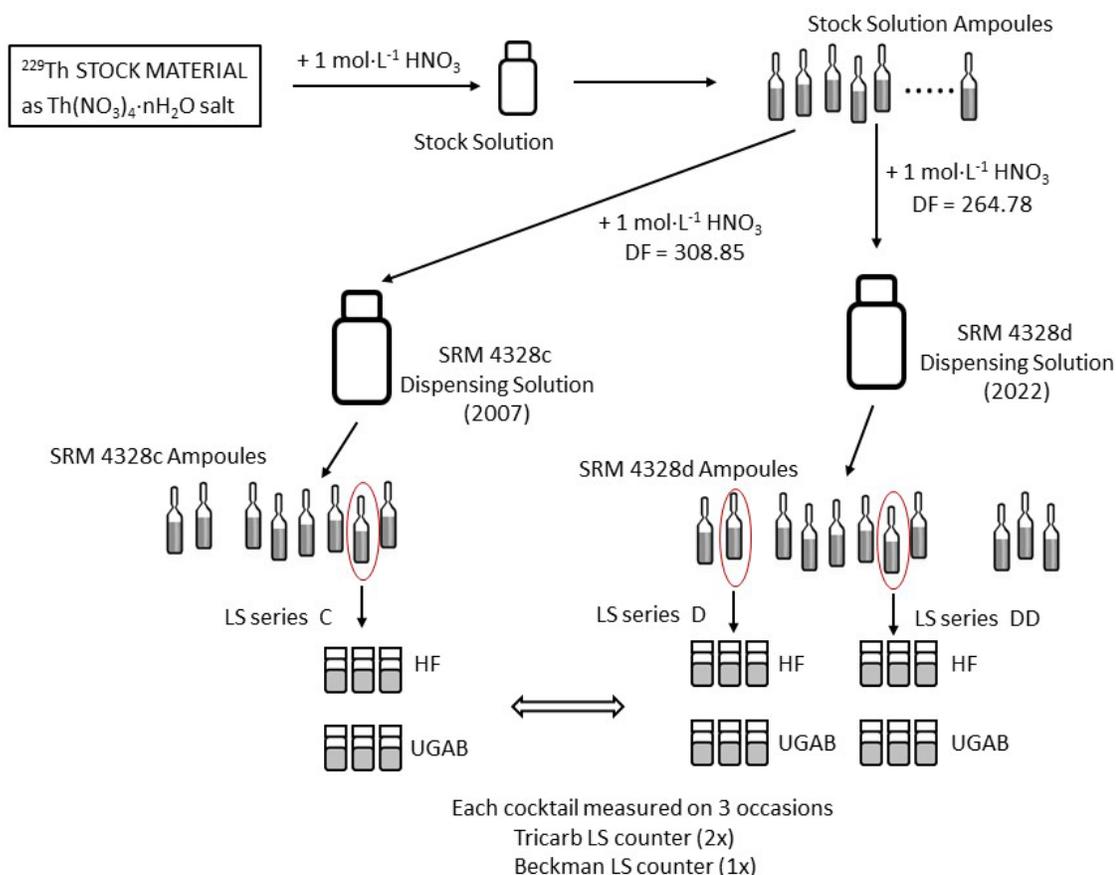
Fig. 1. General scheme used for the production of SRM 4328c in 2007 and SRM 4328d in 2022, and for the comparative LS measurements. Refer to text for further details.

4.   Standardization of SRM 4328c

The standardization of ^{229}Th for SRM 4328c has been described in detail by Fitzgerald, et al [2010]. The certified massic activity of SRM 4328c was determined by live-timed $4\pi\alpha\beta$-γ anticoincidence counting (LTAC) to be (35.29 ± 0.11) Bq·g^{-1} at a reference time of 1200 EST, 31 December 2008. This combined standard uncertainty of 0.3 % leads to an expanded uncertainty of 0.6 % for a coverage factor of $k = 2$. Confirmatory results by four other methods showed good agreement with this value, as shown in Fig. 2. The other methods used were: liquid-scintillation-based CIEMAT/NIST efficiency tracing method [Laureano-Perez, 2007; Zimmerman et al, 1997; Collé, et al., 1997] using ^{3}H as the efficiency monitor (LS CNET)[2]; liquid-scintillation-based triple-to-double coincidence counting (TDCR) [Zimmerman, et al., 2004a, 2004b] using a custom-made NIST TDCR spectrometer (LS TDCR); $2\pi\alpha$ multi-wire proportional counting ($2\pi\alpha$ PC); and Si surface-barrier detector alpha spectrometry with isotope dilution with an aliquant of a standard of ^{230}Th, *viz.*, SRM 4342a (α SPEC).

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[2] The acronym CNET refers to the CIEMAT/NIST Efficiency Tracing method. CIEMAT/NIST refers to the two laboratories that collaborated in developing the protocol for this LS tracing methodology, i.e., the Centro de Investigaciones Energéticas, Medioambientales y Tecnológicas (CIEMAT) and the National Institute of Standards and Technology (NIST).
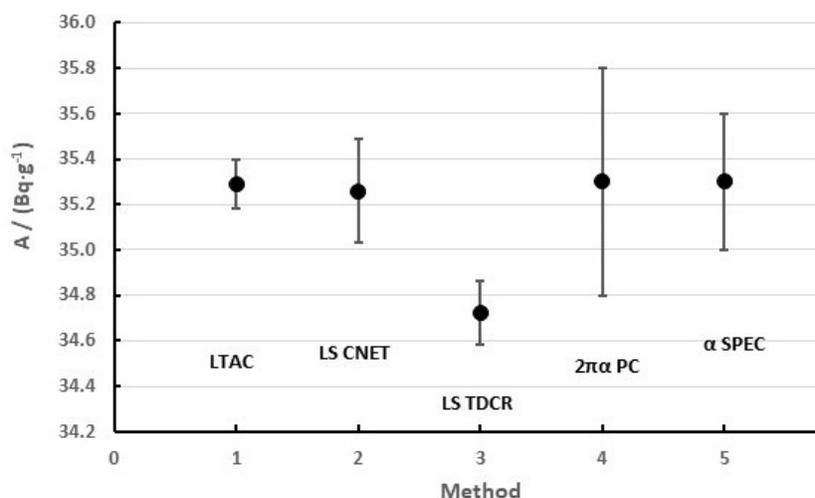
Fig. 2. Measurement results for the ^{229}Th massic activity A in units of Bq·g^{-1} in SRM 4328c as reported by Fitzgerald [2010]. The uncertainty intervals for each value corresponds to a combined standard uncertainty on the measurement. The NIST certified value for SRM 4328c is based on only the anticoincidence (LTAC) value.

5. Evaluation of the ^{229}Th half-life

Inasmuch as there is no available and tabulated half-life for ^{229}Th in the Decay Data Evaluation Project (DDEP), an evaluation of the half-life was made for the standardization of SRM 4328d. The adopted ^{229}Th half-life was based on the unweighted average of the four determinations made by Goldstein, et al. [1989], Kikunaga, et al. [2011], Varga, et al. [2014], and Essex, et al. [2018]. A weighted average was not used because of the inconsistent and unequal uncertainty treatments for the determinations. The value of (7889 ± 76) a was adopted for this work. The stated uncertainty is the standard deviation of the mean for 3 degrees of freedom expanded by $k = 3.179$.

6. SRM 4328d Ampoule Preparation

The SRM 4328d dispensing solution (see Fig.1) was dispensed into 145 borosilicate ampoules using a Microlab 620 single-syringe automatic dispenser (Hamilton Company, Reno, NV, USA)[3]. The ampoules used are designated as NIST-3 ampoules [Collé, 2019]. The solution consisted of carrier-free thorium in 1.0 mol·L^{-1} HNO$_3$, with a density of (1.032 ± 0.001) g·mL^{-1} at 20 °C ($k = 2$). Fifteen ampoules, roughly every tenth one that was filled, were weighed before and after they were filled to obtain an estimate of the dispensing precision and contained mass. Weighing was performed with an electronic analytical balance (Mettler AE240). The average mass was 5.1490 g with a relative standard deviation of 0.028 % for the $n = 15$ sample distribution. The data were

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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.

tested and found to fit a normal distribution. Figure 3 shows the relative invariance of the solution mass with sample filling order. After filling and weighing, all 145 ampoules were: (1) flame sealed using the Ampulmatic-10 automatic sealer (Bioscience, Inc, Bethlehem, PA, USA); (2) visually inspected for flaws; (3) tested for leakage of radioactivity by ampoule inversion and surveys for radioactive contamination; (4) physically tested for seal integrity by vacuum pumping on the seal; and (5) labelled.
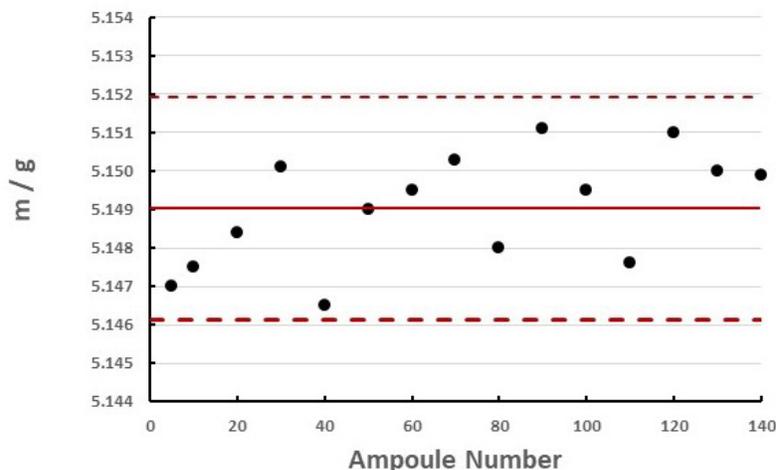
Fig.3. Dispensed masses of the SRM 4328d dispensing solution *m* (in units of grams) in 5 mL aliquants as a function of filling order. The solid horizontal line corresponds to the mean mass (5.1490 g) and the dashed lines represent the upper and lower limits for the ± 2*s* about the mean, where *s* = 0.0015 g is the standard deviation for the *n* = 15 distribution.

7.   LS Comparative Measurements

Comparative measurements for the massic activity of ^{229}Th in SRM 4328d against the known ^{229}Th content of SRM 4328c were performed by 4παβ LS counting. Three measurement trials were conducted using the same six sets of LS counting sources. Each set of sources was measured on two different LS counters: (i) Packard Tricarb A2500 TR (Perkin-Elmer, Wesley, MA, USA) and (ii) Beckman LS 6500 (Beckman Coulter, Fulleron, CA, USA). 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 (QIP) to monitor quenching. The Beckman counter 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 Tricarb counter uses a parameter called the "Transformed Spectral Index of the External Standard" (*tSIE*), which utilizes a proprietary calculation to sum the individual channels starting at the end of the Compton spectrum over the entire ^{133}Ba external source spectrum to calculate a transformed spectrum from which the *tSIE* is extracted from two points (a 20 % and 10 % point of all counts) on the transformed spectrum. Monitoring of the QIPs helps to ensure that counting sources are well matched for comparison measurements.

Six different sets of LS counting sources were, in all cases, gravimetrically prepared in 20 mL glass LS vials with Ultima Gold AB (UGAB) and Hionic Fluor (HF) scintillation fluids (PerkinElmer, Waltham, MA, USA). These two scintillants are based on very different principal solvents, *viz.,* DIPN (2,6-Diisopropylnapthalene) for UGAB and pseudocumene for HF. The sets were: CU and CH prepared from one stored ampoule of SRM 4328c (# 260) with UGAB (CU) and HF (CH), respectively; DU and DH prepared from one randomly selected ampoule of SRM 4328d (# 45) with UGAD (DU) and HF (DH), respectively; and DDU and DDH prepared from a second randomly selected ampoule of SRM 4328d (# 92) with UGAB (DDU) and HF (DDH), respectively. Aliquants from the SRM 4328c and SRM 4328d ampoules, 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 AE240). Blank sources (for subsequent background subtraction) of similar composition over the same quench range were also prepared using the $1 \ mol \cdot L^{-1}$ HNO_3 diluent used to prepare the SRM 4328d dispensing solution. Composition of the LS cocktails was typically 9.8 g of the scintillant (UGAB or HF) with 0.85 g of the ^{229}Th SRM solutions with 60 mg of HDEHP (Di-(2-ethylhexyl)phosphoric acid), which serves as a complexing agent for Th^{+4} ions in the cocktails.

The LS counting data as collected by the LS counters contain: (1) start time of measurements; (2) live time duration; (4) counting rate (usually in units of counts per minute) in a given window; (5) quench indicating parameter (QIP). Options for other instrument quantities, such as luminescence detection and correction, homogeneity monitoring, etc., are available, but are generally not used. Collection and storage of the LS spectra may or may not be employed.

All subsequent calculations were performed manually with spreadsheets and extensive graphical analyses. The LS counter's software is not used for calculations.

Massic counting rates for each source for each measurement were calculated by subtracting that measurement cycle's background (or average background for the entire measurement trial), correcting for radioactive decay to the 1200 EST, 14 July 2022 Reference Time and normalizing by the mass of the radioactive solution in the vial.

All sets of sources were measured on two occasions with the Tricarb counter with midpoint counting times of 1.31 days and 19.35 days after the 14 July 2022 Reference Time and once on the Beckman counter at 5.18 days after the Reference Time. Five replicate measurements of 1800 s live time counting intervals (with the CU, CH, DU, DH, DDU and DDH sources interspersed) were made for each of the three measurement occasions. Each measurement occasion was over a period of about 2.5 days.

8.   Results for the LS Comparative Measurements

The results of the three LS comparative measurement trials are summarized in Tables, 1, 2, and 3. Different scintillators generally have substantially different detection efficiencies, which is observed in the massic counting rate differences between UGAB and HF. It is also not surprising that the counting rates for the same source varies with the LS counter used considering that the nine member ^{229}Th decay chain involves a wide energy range of radiations and that the counters have very different operating characteristics that affect the detection efficiencies. For the analysis of each trial, the five replicate measurements on a given counting source, after corrections for background and decay, were averaged to give a mean massic counting rate R. The five values were also used to calculate the relative standard deviation of the mean s_m. The average of the mean and

median of the three s_m values for the three sources in each set is taken as an estimator of the typical within-source variation, $\overline{s}_m$. The three R values for the three sources for a given series were also averaged to obtain a grand mean $\overline{R}$. Its relative standard deviation is taken to be an estimator of the between-source variation, s_b, for that set. An estimator of the LS measurement precision of $\overline{R}$ as a relative standard uncertainty, S, is given by $S = (\overline{s}_m{}^2 + s_b{}^2)^{1/2}$.

9.   Solution Stability and Homogeneity Evaluation

The SRM 4328d solution is believed to be indefinitely homogeneous and stable based on the known chemical behavior of carrier free thorium in 1 mol·L-1 nitric acid. This is the same chemical composition as that used for calibration standards for the quantitative determination of thorium (e.g., SRM 3159). In addition, comparison of the decay-corrected $4\pi\alpha\beta$ LS counting rate for SRM 4328c over a 14.5 year period from 2007 initial standardization to the remeasurement in 2022 exhibited an agreement to 0.19 % with LS measurement uncertainties of approximately 0.3 % (k = 2).

Homogeneity of the SRM 4321d dispensing 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 141 ampoules were measured in 7 batches and were loaded into the well by the automatic sample changer using custom-built centering tubes. Each batch contained 24 ampoules, including blanks for background subtraction. The ampoules for the first three measurement batches were sampled by taking every fourth or fifth ampoule in the filling order. The remaining batches counted the sources in the ampoule 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 230 known γ transitions in the ^{229}Th decay chain, 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 Ac, Fr, At, Bi, and Po, along with only some weak higher-energy lines, principally from ^{229}Th, ^{225}Ac, ^{221}Fr, and ^{213}Bi. The spectrum for each measurement was accumulated for an interval of 1800 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 and normalized by the background-corrected counting rate for the ^{129}I check source. The relative Poisson statistical counting error on any one measurement was 0.14 %. The mean counting rate ratio R (^{229}Th) / R (^{129}I) from 171 measurements was 0.203, with a relative standard deviation of 0.22 % over a period of 8 days and for a mean ^{129}I counting rate R (^{129}I) of 43.438 s^{-1} with a relative standard deviation of 0.031 %. The average relative difference between 28 duplicate measurements on the same ampoules, randomly sampled from the entire set, was 0.20 %. Approximately 10 % of the initial measurements were excluded from the results and were remeasured because of evident ampoule positioning errors in the detector, and four ampoules were not included in the results because of known total solution mass differences. The positioning errors were a result of insufficiently taking care to ensure that all of the solution in the ampoules were in the ampoule bodies and not trapped in the narrow necks of the NIST-3 ampoules. The necks of NIST-3 ampoules are somewhat narrower compared to that of NIST-1 ampoules., and great care

must be exercised to ensure that no solution is above the neck for any measurements with NIST-3 ampoules.

The individual results for these homogeneity measurements are displayed in Fig. 4. Interestingly, but not surprisingly, 96 % of the values lie within the mean $\pm 2s$ interval, with only 6 of the 171 values falling outside. The normality of the homogeneity data was verified with a probability plot correlation coefficient (PPCC) test ($p \approx 0.50$). The data also passed both an Anderson-Darling goodness-of-fit test ($p \approx 0.16$) and a Wilk-Shapiro test for normality ($p \approx 0.42$)

Table 1. Tricarb 1: Summary of the LS comparative measurement data for the first measurement trial with the Tricarb LS counter. Refer to text for definition and descriptions of the series and LS sources.

Series	LS Sources	(a) R $s^{-1}g^{-1}$ $n = 5$	(b) s_m % $n = 5$	(c) $\overline{s}_m$ % $n = 3$	(d) $\overline{R}$ $s^{-1}g^{-1}$ $n = 3$	(e) s_b % $n = 3$	(f) S %
CU	CU1	252.04	0.057				
	CU2	250.67	0.12	0.065	251.51	0.29	0.30
	CU3	251.81	0.043				
CH	CH1	253.04	0.13				
	CH2	252.97	0.12	0.13	253.11	0.075	0.15
	CH3	253.33	0.18				
DU	DU1	294.86	0.038				
	DU2	294.76	0.069	0.080	294.88	0.044	0.091
	DU3	295.02	0.16				
DH	DH1	295.03	0.080				
	DH2	294.79	0.14	0.11	294.74	0.11	0.16
	DH3	294.38	0.11				
DDU	DDU1	293.69	0.080				
	DDU2	294.53	0.13	0.080	294.31	0.19	0.20
	DDU3	294.72	0.029				
DDH	DDH1	295.08	0.069				
	DDH2	294.92	0.028	0.072	294.93	0.085	0.011
	DDH3	294.79	0.13				

[a] R = Mean massic counting rate
[b] s_m = Relative standard deviation of the mean for R values
[c] $\overline{s}_m$ = Typical relative standard deviation of the mean for s_m values (average of mean and median of s_m values)
[d] $\overline{R}$ = Grand mean massic counting rate of R values
[e] s_b = Relative standard deviation of the R values
[f] S = Relative standard uncertainty on grand mean $\overline{R}$; $(\overline{s}_m^2 + s_b^2)^{1/2}$

Table 2. Beckman: Summary of the LS comparative measurement data for the second measurement trial with the Beckman LS counter. Refer to text for definition and descriptions of the series and LS sources.

Series	LS Sources	(a) R $s^{-1}g^{-1}$ $n = 5$	(b) s_m % $n = 5$	(c) $\overline{s}_m$ % $n = 3$	(d) $\overline{R}$ $s^{-1}g^{-1}$ $n = 3$	(e) s_b % $n = 3$	(f) S %
CU	CU1	244.91	0.030				
	CU2	243.13	0.051	0.036	244.33	0.42	0.42
	CU3	244.94	0.033				
CH	CH1	244.36	0.12				
	CH2	244.63	0.050	0.061	244.81	0.23	0.24
	CH3	245.45	0.044				
DU	DU1	286.35	0.046				
	DU2	286.37	0.028	0.043	286.15	0.018	0.047
	DU3	286.28	0.049				
DH	DH1	285.70	0.046				
	DH2	285.38	0.042	0.042	285.63	0.065	0.078
	DH3	285.37	0.039				
DDU	DDU1	285.41	0.038				
	DDU2	286.26	0.034	0.033	285.96	0.17	0.17
	DDU3	286.22	0.025				
DDH	DDH1	285.82	0.042				
	DDH2	285.73	0.029	0.029	285.78	0.014	0.032
	DDH3	285.78	0.016				

[a] R = Mean massic counting rate
[b] s_m = Relative standard deviation of the mean for R values
[c] $\overline{s}_m$ = Typical relative standard deviation of the mean for s_m values (average of mean and median of s_m values)
[d] $\overline{R}$ = Grand mean massic counting rate of R values
[e] s_b = Relative standard deviation of the R values
[f] S = Relative standard uncertainty on grand mean $\overline{R}$; $(\overline{s}_m{}^2 + s_b{}^2)^{1/2}$

Table 3. Tricarb 2: Summary of the LS comparative measurement data for the third measurement trial with the Tricarb LS counter. Refer to text for definition and descriptions of the series and LS sources.

Series	LS Sources	(a) R $s^{-1}g^{-1}$ $n = 5$	(b) s_m % $n = 5$	(c) $\overline{s}_m$ % $n = 3$	(d) $\overline{R}$ $s^{-1}g^{-1}$ $n = 3$	(e) s_b % $n = 3$	(f) S %
CU	CU1	251.66	0.060				
	CU2	250.30	0.11	0.10	251.24	0.32	0.34
	CU3	251.75	0.11				
CH	CH1	252.26	0.12				
	CH2	252.41	0.16	0.12	252.59	0.18	0.22
	CH3	253.11	0.10				
DU	DU1	294.83	0.11				
	DU2	294.34	0.080	0.10	294.86	0.18	0.21
	DU3	295.40	0.10				
DH	DH1	294.43	0.080				
	DH2	294.63	0.12	0.083	294.54	0.033	0.089
	DH3	294.56	0.056				
DDU	DDU1	293.91	0.13				
	DDU2	294.14	0.041	0.098	294.12	0.071	0.12
	DDU3	294.32	0.10				
DDH	DDH1	294.65	0.074				
	DDH2	294.73	0.017	0.060	294.61	0.047	0.076
	DDH3	294.46	0.068				

[a] R = Mean massic counting rate
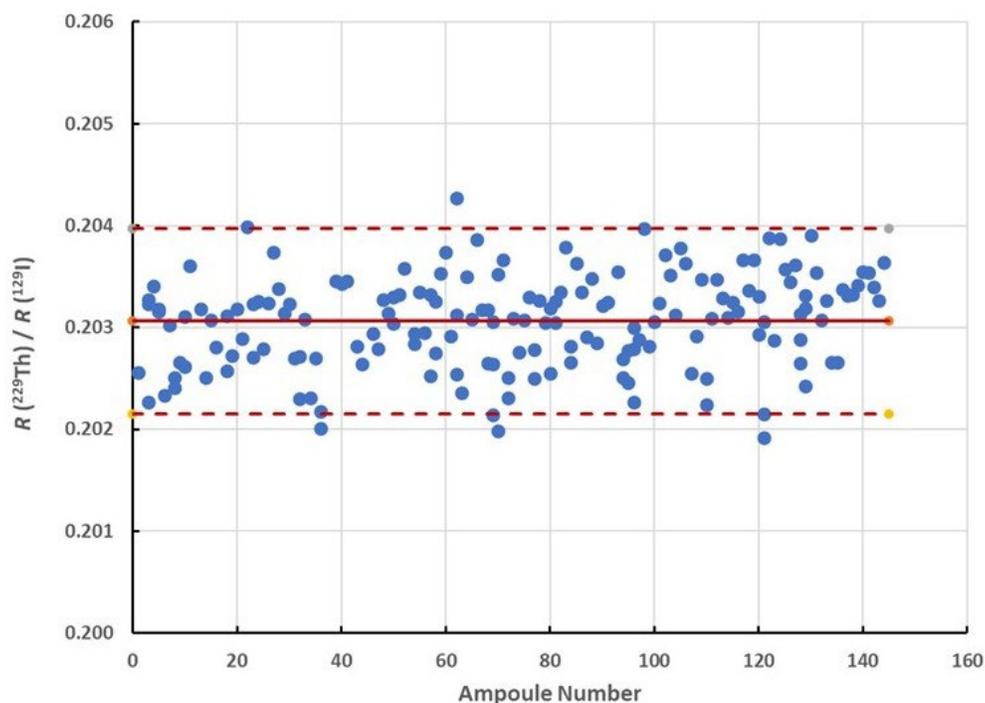[b] s_m = Relative standard deviation of the mean for R values
[c] $\overline{s}_m$ = Typical relative standard deviation of the mean for s_m values (average of mean and median of s_m values)
[d] $\overline{R}$ = Grand mean massic counting rate of R values
[e] s_b = Relative standard deviation of the R values
[f] S = Relative standard uncertainty on grand mean $\overline{R}$; $(\overline{s}_m^2 + s_b^2)^{1/2}$

Fig. 4 The background-corrected mean counting ratio R (^{229}Th) / R (^{129}I) for the integral counting rates from 171 measurements on 137 ampoules of SRM 4328d plotted versus ampoule number (filling order) as measured in a NaI(Tl) well counter. The dashed lines show the mean ± 2s interval, where s is the standard deviation of the distribution for the n = 171 measurements. Twenty-eight ampoules were measured in duplicate, with a 0.20 % average relative difference.

10. Radionuclidic Impurity Analysis

Fitzgerald, et al. [2010] reported in detail on impurity analysis for the ^{229}Th stock solution used to prepare both SRM 4328c and SRM 4328d. Oak Ridge National Laboratory (ORNL) had reported a ^{228}Th/^{229}Th impurity ratio, based on their γ-ray analysis of the stock material sent to NIST. They also reported other radionuclidic impurities, as obtained by mass spectrometry, including ratios for ^{230}Th/^{229}Th, ^{232}Th/^{229}Th, and ^{233}U/^{229}Th. The isotopes ^{239}Th, ^{240}Th, ^{242}Th, ^{234}U, ^{235}U, ^{236}U and ^{238}U were not detected. Each of these had a lower limit of detection of $< 2 \cdot 10^{-5}$ in terms of the mass ratio to ^{229}Th [ORNL, 2007]. The ORNL value for the ^{228}Th impurity was not used for SRM 4328c. Instead, Fitzgerald, et al. [2010] determined the impurity by two separate methods, *viz*., by HPGe γ-ray spectrometry and by alpha spectrometry following a Th separation. The results of the two NIST determinations for the ^{228}Th impurity were averaged and reported as (0.60 ± 0.07) Bq·g^{-1} as of 1200 EST, 31 December 2007 SRM 4328c Reference Time.

The ^{228}Th impurity in SRM 4328d was evaluated by decay correcting the ^{228}Th impurity in SRM 4328c as reported in the 2007 determination by Fitzgerald, et al. [2010] and normalizing by the two dilution factors of the stock solution. The result for the ^{228}Th impurity in SRM 4328d at the 1200 EST, 14 July 2022 Reference Time was (0.097 ± 0.011) Bq·g^{-1}.

Impurity analyses of the SRM 328d solution addition were also performed by high-resolution photonic emission spectrometry using high-purity germanium (HPGe) detectors. For this, the contents of one ampoule of SRM4328d in a NIST-3 ampoule was quantitatively transferred into a NIST-1 ampoule, which is the "standard ampoule" used to define the geometry and attenuation for all ionization chamber measurements and the γ-ray spectrometry performed at NIST [Collé, 2019], for the impurity analysis. The NIST-1 ampoule containing the SRM 4328d solution ampoule was measured on NIST "Detector B" at a solid angle distance of 5 cm for 607400 s of livetime counting (roughly 7 days). The detectors and spectrometry procedures used by the NIST Radioactivity Group have been described by Pibida et al, [2006a, 2006b].

No photon emitting impurities were detected. Gamma-ray lines for only radionuclides in the ^{229}Th decay chain were observed. The detection limits for other potential γ-rays were

$$15 \text{ keV} < E < 100 \text{ keV} \qquad 0.041 \text{ s}^{-1}\text{g}^{-1}$$

$$105 \text{ keV} < E < 430 \text{ keV} \qquad 0.036 \text{ s}^{-1}\text{g}^{-1}$$

$$450 \text{ keV} < E < 1450 \text{ keV} \qquad 0.039 \text{ s}^{-1}\text{g}^{-1}$$

$$1470 \text{ keV} < E < 2000 \text{ keV} \qquad 0.036 \text{ s}^{-1}\text{g}^{-1}$$

The transferred NIST-1 ampoule of SRM 4328d was also assayed by γ-ray spectrometry and found to contain a ^{229}Th activity of (44.4 ± 6.2) Bq·g^{-1} at $k = 2$ on the 1200 EST, 14 July 2022 Reference Time. This differs from the LS comparative measurement result by + 7.9 %, although the γ-ray spectrometry result has a large $k = 2$ combined standard uncertainty of ± 14 %.

11.   Assignment of ^{229}Th Massic Activity and Uncertainty Assessment

The massic counting rates R and their associated standard uncertainties S, as given in Tables 1, 2, and 3 for the six measurements, were used to derive a ratio $\overline{D}/C$ of the counting rates from SRM 4328d and SRM 4328c. The rates for the sources in the DU and DDU series and in the DH and DDH series were averaged to obtain mean massic counting rates $\overline{D}$ that was used to form the $\overline{D}/C$ ratio. The ratios when multiplied by the decay-corrected, certified massic activity of SRM 4328c at the 14 July 2022 Reference Time $[(35.24 \pm 0.21)$ Bq·g^{-1} at $k = 2]$ yield massic activity values for SRM 4328d. These results are shown in Table 4. This table summarizes the six determinations of the massic activity A for SRM 4328d. The mean A is 41.186 Bq·g^{-1} with a typical within-value S_m of 0.16 % and a between-value S_b of 0.26, which gives a combined standard uncertainty S of 0.31 %.

Table 4. Summary of the six massic activity determinations from the LS comparative measurements for the three trials. The massic count rates are the grand means R as given in Tables 1, 2, and 3. Values in parentheses are relative standard uncertainties S as also given in Tables 1, 2, and 3.

	Grand mean massic count rate $\overline{R}$ (s⁻¹g⁻¹)				$\overline{D}/C$ ratio	A Massic Activity Bq·g⁻¹
	C	D	DD	$\overline{D}$		
Tricarb #1 UGAB	251.51 (0.30 %)	294.88 (0.091 %)	294.31 (0.20 %)	294.60 (0.16 %)	1.1713 (0.18 %)	41.277
Tricarb #1 HF	253.11 (0.15 %)	294.74 (0.16 %)	294.93 (0.11 %)	294.83 (0.14 %)	1.1648 (0.21 %)	41.048
Beckman UGAB	244.33 (0.42 %)	286.15 (0.047 %)	285.96 (0.17 %)	286.06 (0.12 %)	1.1708 (0.13 %)	41.259
Beckman HF	244.81 (0.24 %)	285.63 (0.078 %)	285.78 (0.032 %)	285.70 (0.060 %)	1.1670 (0.098 %)	41.126
Tricarb #2 UGAB	251.24 (0.34 %)	294.86 (0.21 %)	294.12 (0.12 %)	294.49 (0.17 %)	1.1721 (0.27 %)	41.307
Tricarb #2 HF	252.59 (0.22 %)	294.54 (0.089 %)	294.61 (0.076 %)	294.58 (0.083 %)	1.1662 (0.12 %)	41.097
					Mean A	41.186 Bq·g⁻¹
					Within-value (typical) S_m	0.16 %
					Between-values S_b	0.26 %
					Combined S	0.31 %

The dependence of the LS counter (Tricarb or Beckman) and chosen scintillant (UGAB or HF) on A is shown in Table 5. As seen, the values of A are largely invariant on LS counter and have a positive bias for UGAB compared to HF. The surprisingly large difference between UGAB and HF may result from different detection efficiencies for the x rays and low-energy conversion electrons in the decay chain for the two scintillants.

Table 5. Two-variable data table showing the effect of scintillant and LS counter on the massic activity A given in Table 4.

	Massic Activity A in Bq·g⁻¹			% Difference Tricarb-Beckman
	Tricarb #1	Beckman	Tricarb #2	
UGAB	41.277	41.259	41.307	0.08
HF	41.048	41.126	41.097	-0.13
% Difference UGAB-HF	0.56	0.33	0.51	

The LS comparative measurement data was examined for both within-source and between-source components of variance for a given LS counter, as well as between-counter components of variance for a given source. This is the typical analysis procedure for all Radioactivity SRM standardizations.

Each counting source was measured five times in each LS counter on each measurement occasion. The five decay- and background-corrected counting rates R were averaged and used to calculate a relative standard deviation of the mean s_m. For a given set of three sources (for the same cocktail and counter) the "typical" within-source variation, $\overline{s}_m$ is taken to be the average of the mean and median of the three s_m values. These within-source variations are shown in Tables 1, 2, and 3 (column 5) and typically are in the range of 0.1 %. For the same given set of three sources in the series, the three massic counting rate R values were averaged to give a grand mean $\overline{R}$ and its standard deviation is taken to be the between-source variation s_b for the series. Tables 1, 2, and 3 (columns 6 and 7) give the $\overline{R}$ and s_b values for each series. The standard uncertainty $\overline{R}$ (as a measure of the LS measurement precision S) is given by the quadratic combination of $\overline{s}_m$ and s_b. As shown in column 8 of Tables 1, 2, and 3, the S values are in the range of 0.1 % to 0.3 %.

For a given trial and series of sources (same scintillant and counter) to compare SRM 4328c and SRM 4328d, the uncertainty in the ratio of the grand means $\overline{D}/C$ was taken as the combination of the two S values (Table 4).

The values of A from the six determinations (Table 4, column 7) were averaged (unweighted) to obtain the assigned massic activity of 4328d. The combined standard uncertainty of 0.31 % for the LS measurement precision was obtained by considering the within-value and between-values variations.

Other uncertainty components that affect the LS measurement results for the massic activity are:

(1) Background and cocktail stability and mismatch effects, which were considered to be wholly embodied in the LS measurement precision estimator.
(2) LS counter dependence was considered to be negligible and was also partially embodied in the LS measurement precision.
(3) Scintillator dependence that was observed was estimated to have a relative standard uncertainty of 0.24 %.
(4) Live time determinations for the LS counting time intervals were taken to have a relative standard uncertainty of 0.07 % based on the 0.1 % tolerance limits on the two counter's gated oscillators.
(5) Aliquant mass determinations for preparation of the counting sources were estimated to have a relative standard uncertainty of 0.02 %, with the mass measurement precision partially embodied in the LS measurement precision.

One of the most critical uncertainty components is, of course, the uncertainty in the certified massic activity of SRM 4328c since the standardization of SRM 4328d was based on comparative measurements against the earlier [229]Th issue. This was reported by Fitzgerald, et al. [2010] as 0.30 % ($k = 1$).

Decay corrections for both the SRM 4328c to the 2022 Reference Time as well as for the LS measurement data were rather negligible (< 0.0004 %) considering the long [229]Th half-life.

Any potential radionuclidic impurity effects due to solution differences were also assumed to be non-existent or negligible considering that both SRM 4328c and SRM 4328d were prepared from the same ^{229}Th stock solution, and that any effects may have also been covered by the comparative LS measurement precision.

Table 2 in the SRM 4328d Certificate tabulates this uncertainty assessment.

12.   Certification of SRM 4328d and Summary

The prepared SRM 4328d solution standards were certified for the massic activity of the ^{229}Th on the basis of comparative LS measurements against SRM 4328c that had been standardized in 2007 by live-timed anticoincidence counting with confirmation by four other methods [Fitzgerald, 2010].

The standardization results for SRM 4328d were obtained from six trials using counting sources prepared with two different LS scintillants and measured in two different commercial LS counters. SRM 4328d was certified and will be disseminated with the following specifications (refer to Certificate):

Radionuclide:	Thorium-229
Reference time:	1200 EST, 14 July 2022
Massic activity of the solution:	41.19 Bq·g^{-1}
Relative combined standard uncertainty ($k = 2$):	1.0 %

A NIST SRM certified value, as used within the context of the SRM certification, is a value for which NIST has the highest confidence in its uncertainty assessment. It is a "measurement result" [JCGM 200 ,2012] obtained directly or indirectly from a "primary reference measurement procedure" [JCGM 200, 2012]. Given that the standardization of SRM 4328c had been standardized by live-timed anticoincidence, a primary standardization method, SRM4328d is indirectly traceable to the derived SI unit, becquerel (Bq).

The solution was also characterized in terms of the following uncertified information (refer to Appendix A in Certificate):

Source description:	Liquid in flame-sealed 5 mL borosilicate NIST-3 ampoule
Solution composition:	1.0 mol·L^{-1} HNO$_3$ with carrier-free ^{229}Th
Solution density:	(1.032 ± 0.001) g·mL^{-1} at 20 °C ($k = 2$)
Solution mass:	(5.149 ± 0.002) g
Radionuclidic impurity:	^{228}Th, (0.097 ± 0.019) Bq·g^{-1} ($k = 2$)
Half-lives used:	^{229}Th (7889 ± 24) a ($k = 1$)
	^{228}Th, (1.9126 ± 0.0009) a ($k = 1$)

The uncertainty assessment for the certified massic activity is summarized in Section 11, as well as in Table 2 of Certificate.

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Appendix A. SRM 4328d Certificate

The certificate follows.

National Institute of Standards and Technology
U.S. Department of Commerce

Standard Reference Material® 4328d

Thorium-229 Radioactivity Standard

CERTIFICATE

Purpose: The certified value delivered by this Standard Reference Material (SRM) is intended primarily for the calibration of instruments that are used to measure radioactivity and for the monitoring of radiochemical procedures.

Description: A unit of SRM 4328d consists of approximately 5 mL of a solution of a standardized and certified quantity of radioactive thorium-229 in a suitably stable and homogeneous matrix, contained in a flame-sealed borosilicate-glass ampoule [1].

Certified Values: A NIST certified value, as used within the context of this certificate, is a value for which NIST has the highest confidence in its uncertainty assessment. It is a "measurement result" [2] obtained directly or indirectly from a "primary reference measurement procedure" [3]. Uncertainties for the certified quantities are expanded ($k = 2$). The uncertainties are calculated according to the ISO/JCGM and NIST Guides [4,5]. The certified value is traceable to the derived SI unit, becquerel (Bq).

Table 1. Certified Massic Activity of SRM 4328d

Radionuclide	Thorium-229
Reference time	1200 EST, 14 July 2022
Massic activity of the solution	41.19 Bq·g^{-1}
Relative expanded uncertainty ($k = 2$) [a]	1.0 %

[a] The uncertainties on certified values are expanded uncertainties, $U = ku_c$. The quantity u_c is the combined standard uncertainty calculated according to the ISO/JCGM and NIST Guides [4,5]. The combined standard uncertainty is multiplied by a coverage factor of $k = 2$ and was chosen to obtain an approximate 95 % level of confidence.

Non-Certified Values: Non-certified values and additional information are provided in Appendix A.

Period of Validity: The certification of **SRM 4328d** is valid indefinitely, within the measurement uncertainty specified, provided that the SRM is handled and stored properly and that no evaporation or change in composition has occurred. The certification is nullified if the SRM is damaged, contaminated, or otherwise modified. Periodic recertification of this SRM is not required.

Maintenance of Certification: NIST will monitor this SRM over the period of its validity. If substantive technical changes occur that affect the certification, NIST will issue an amended certificate through the NIST SRM website (https://www.nist.gov/srm) and notify registered users. SRM users can register online from a link available on the NIST SRM website or fill out the user registration form that is supplied with the SRM. Registration will facilitate notification. Before making use of any of the values delivered by this material, users should verify they have the most recent version of this documentation, available through the NIST SRM website (https://www.nist.gov/srm).

James M. Adams, Chief
Radiation Physics Division

Steven J. Choquette, Director
Office of Reference Materials

Table 2. Uncertainty Evaluation for the Massic Activity of SRM 4328d

	Uncertainty component	Assessment Type[a]	Relative standard uncertainty contribution on massic activity of ^{229}Th (%)
1	Liquid scintillation (LS) comparative measurement precision; relative standard deviation of the mean on the great grand mean for six LS measurement trials, considering all within-trial and between-trial components of variance. Each of the six grand mean values was based on five replicate measurements on each of three LS sources for SRM 4328c and six LS sources for 4328d. The sources were prepared with two different LS cocktail compositions and each source was measured in two different LS counters (on three separate measurement occasions). The typical within-trial relative standard deviation of the mean (considering the variations for the between five measurements and the between three or six sources) for each trial was 0.16 %. The between-trial relative standard deviation across the six trials was 0.26 %. The individual values for each data set fit Normal distributions. The relative standard deviation of the mean from the six trials was 0.11 % with a 95 % confidence interval about the mean of ±0.28 %.	A	0.31
2	Background; LS measurement variability, cocktail mismatch effects and cocktail composition stability; wholly embodied in component 1.	A	--
3	LS counters dependencies; wholly embodied in component 1.	A	--
4	Uncertainty on the standardization of SRM 4328c	A	0.30
5	Potential undetected alpha- and photon emitting impurity differences in SRM 4328c and 4328d; wholly embodied in component 1	B	--
6	Scintillator dependence (absolute difference of 0.49 %); partially embodied in component 1	B	0.24
7	Live time determinations for LS counting time intervals; includes uncorrected deadtime effects.	B	0.07
8	Aliquant mass determination by gravimetric measurements for preparation of LS counting sources; includes mass measurement precision partially embodied in component 1.	B	0.02
9	Decay correction for ^{229}Th for a half-life uncertainty of 0.30 %.	B	0.0004
Relative combined standard uncertainty			**0.50**
Relative expanded uncertainty ($k = 2$)			**1.0**

[a] Letter A denotes evaluation by statistical methods; Letter B denotes evaluation by other methods.

Safety: Consult the Safety Data Sheet (SDS) enclosed with the SRM shipment, for radiological and chemical hazard information.

Storage and Handling: SRM 4328d should be stored and used at a temperature between 5 °C and 65 °C. The ampoule (or any subsequent container) should always be clearly marked as containing radioactive material. If the ampoule is transported, it should be packed, marked, labeled, and shipped in accordance with the applicable national, international, and carrier regulations. This is **not** a pre-scored ampoule; **the gold color band is only for identification**. The solution in the ampoule is a dangerous good (hazardous material) because of both the radioactivity and the strong acid. The ampoule should be opened only by persons qualified to handle both radioactive material and alkaline and/or acidic solutions. Appropriate shielding and/or distance should be used to minimize personnel exposure. Refer to the SDS for further information.

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Certain commercial equipment, instruments, or materials may be identified in this Certificate to adequately specify the experimental procedure. 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.

Users of this SRM should ensure that the Certificate in their possession is current. This can be accomplished by contacting the Office of Reference Materials 100 Bureau Drive, Stop 2300, Gaithersburg, MD 20899-2300; telephone (301) 975-2200; e-mail srminfo@nist.gov; or the Internet at https://www.nist.gov/srm.

* * * * * * * * * * * End of Certificate * * * * * * * * * * * *

APPENDIX A

This SRM was prepared by the NIST Physical Measurement Laboratory, Radiation Physics Division, under the direction of B.E. Zimmerman, Group Leader of the Radioactivity Group. Overall technical direction and physical measurement leading to certification were provided by R. Collé and L. Laureano-Pérez of the NIST Radiation Physics Division, Radioactivity Group. Photon-emitting-impurity analyses were provided by L. Pibida of the NIST Radiation Physics Division, Radioactivity Group. Support aspects involved in the issuance of this SRM were coordinated through the NIST Office of Reference Materials.

Non-Certified Values: Non-certified values are suitable for use in method development, method harmonization, and process control but do not provide metrological traceability to the International System of Units (SI) or other higher-order reference system. Non-certified values are provided in Table A1.

Table A1. Non-Certified Values for SRM 4328d[a]

Source description	Liquid in a flame-sealed 5 mL borosilicate-glass ampoule [1]
Solution composition	(1.00 ± 0.03) mol•L^{-1} HNO$_3$[b]
Solution density	(1.032 ± 0.001) g•mL^{-1} at 20.0 °C[b]
Solution mass	(5.149 ± 0.002) g[b]
Alpha-particle-emitting impurities	^{228}Th: (0.097 ± 0.011) Bq•g^{-1}[b, c]
Photon-emitting impurities	None detected [d]
Half-lives used	^{229}Th: (7889 ± 24) a[e] ^{228}Th: (1.9126 ± 0.0009) a[f]
Calibration methods (and instruments)	The certified massic activity for ^{229}Th was obtained by $4\pi\alpha\beta$ LS counting by comparative measurements against SRM 4328c[g] using two different LS measurement systems (with varying operating systems) and two different LS cocktail compositions. Solution homogeneity measurements were made with a NaI(Tl) well counter.

[a] References on page 3.

[b] The stated uncertainty is two times the standard uncertainty [5].

[c] The ^{228}Th impurity was based on 2π alpha-emission rate measurements with Si surface barrier detectors following chemical separations, and by photon-emission rate measurements by HPGe detectors. The former was performed on 17 March 2008 and the latter on 01 March 2008. The ^{228}Th / ^{229}Th activity ratio, decay-corrected to 31 December 2007, as reported by the source supplier (Oak Ridge National Laboratory), based on γ-ray spectrometry, was 0.014.

[d] The estimated limits of detection for photon-emitting impurities as of August 2022, expressed as massic photon emission rates (numbers of photons per second per gram), are:

0.041 s^{-1}•g^{-1} for energies between 15 keV and 100 keV,

0.036 s^{-1}•g^{-1} for energies between 105 keV and 430 keV,

0.039 s^{-1}•g^{-1} for energies between 450 keV and 1450 keV, and

0.036 s^{-1}•g^{-1} for energies between 1470 keV and 2000 keV,

provided that the photons are separated in energy by 4 keV or more from photons emitted in the decay chain of ^{229}Th.

[e] The ^{229}Th half-life was based on the unweighted average of the four determinations made by Goldstein, et al. (1989), Kikunaga, et al. (2011), Varga, et al. (2014), and Essex, et al. (2018). A weighted average was not used because of the inconsistent and unequal uncertainty treatments for the determinations. The cited uncertainty is the standard deviation of the mean for 3 degrees of freedom expanded by k = 3.179. See references 6-9.

[f] The stated uncertainty is the standard uncertainty. See reference 10.

[g] SRM 4328c was standardized in 2007 by live-timed anticoincidence counting (a primary standardization method), which is traceable to the derived SI unit, Becquerel (Bq) [11].

Maintenance of Non-Certified Values: NIST will monitor this material to the end of its period of validity. If substantive technical changes occur that affect the non-certified values during this period, NIST will update this Certificate and notify registered users. SRM users can register online from a link available on the NIST SRM website or fill out the user registration form that is supplied with the SRM. Registration will facilitate notification. Before making use of any of the values delivered by this material, users should verify they have the most recent version of this documentation, available through the NIST SRM website (https://www.nist.gov/srm).

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