



A reference material for evaluation of ^{137}Cs radiochronometric measurements

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Abstract

A new nuclear forensic reference material has been characterized as a standard for radiochronometric determination of the model purification date for ^{137}Cs sources. The purification date of a radioactive source is a potentially diagnostic nuclear forensic signature for determining the provenance of a radioactive material. Reference values have been measured for the attributes needed to use the $^{137}\text{Cs}/^{137}\text{Ba}$ chronometer: the molality (reported here as nmol g^{-1}) of ^{137}Cs and of the radiogenic portion of ^{137}Ba in the material (hereafter referred to as $^{137}\text{Ba}^*$). All measurement results were decay-corrected to represent the composition of the material on the reference date of July 7, 2011. The molality of ^{137}Cs is $(0.7915 \pm 0.0073) \text{ nmol g}^{-1}$; this value was calculated from the massic activity of ^{137}Cs , $(348.4 \pm 3.0) \text{ kBq g}^{-1}$, as measured in the NIST $4\pi\text{-}\gamma$ secondary standard ionization chamber (previously calibrated by $4\pi\text{-(e+x)-}\gamma$ -coincidence efficiency extrapolation counting) and the evaluated half-life of ^{137}Cs , $(30.05 \pm 0.08) \text{ years}$. The molality of $^{137}\text{Ba}^*$, $(1.546 \pm 0.024) \text{ nmol g}^{-1}$, was measured by isotope dilution mass spectrometry using the measured relative proportion of ^{138}Ba in the material to apply a correction for the ^{137}Ba contribution from natural Ba. A model age of $(47.04 \pm 0.56) \text{ years}$, corresponding to a model purification date of June 22, 1964 with an expanded uncertainty of 200 days is calculated from the reference material values. This age is consistent with the date engraved on the capsule that contained the ^{137}Cs starting material and with a prior independent determination of the model purification date. A full discussion of the uncertainties of the reference material values is included.

Keywords Radiochronometry · Cesium-137 · Nuclear forensics · Reference materials · Mass spectrometry · Radiological forensics

Introduction

Ensuring the availability of appropriate, fit-for-purpose reference materials is of great importance to the field of nuclear forensics. High quality, metrologically-traceable reference materials are necessary due to the need to demonstrate the accuracy of measurements and methodologies and due to the need to meet legal standards for

quality of analytical measurements in a courtroom setting [1]. Certified reference materials currently available from national metrological institutions and commercial sources do not meet these needs for some specialized nuclear forensic measurements, such as purification age determinations for radiological materials of interest to the nuclear forensics community. For this reason, the United States Department of Homeland Security has supported a program for the production and distribution of reference materials intended specifically for nuclear forensic applications. This program has sponsored production of a reference material for the radiochronometric age-dating of ^{137}Cs sources.¹ This work reports on the production and characterization of

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¹ Development of the Cs–Ba radiochronometry reference material was sponsored by Department of Homeland Security and the material is available on a case-by-case basis. Requests to obtain units of this material can be sent to DHSCRMInfo@hq.dhs.gov.

a ^{137}Cs – ^{137}Ba radiochronometric reference material (hereafter abbreviated as “Cs–Ba RM”) characterized for molality of ^{137}Cs and of radiogenic ^{137}Ba (hereafter referred to as “ $^{137}\text{Ba}^*$ ”).

The scope of the field of nuclear forensics is typically defined to include radiological materials as well as special nuclear materials, e.g., [2]. Although much of the effort in the field of nuclear forensics has been focused on special nuclear materials due to the severity of potential consequences associated with them, nuclear forensic measurements capabilities for radiological materials are also needed. With the exception of short-lived isotopes used in nuclear medicine, radiological materials are primarily used in sealed radioactive sources. These sources are manufactured using a variety of radionuclides, are intended for a wide variety of purposes, and are distributed widely around the globe [3]. The locations and ownership of these sources are often not closely tracked in the manner that special nuclear materials are, nor is their ownership as tightly restricted. As a result of the availability and the inconsistent levels of accountability for sealed sources, the risk associated with misuse of radiological materials is relatively high. Furthermore, many sources, particularly those prepared for certain medical or industrial applications, contain quantities of material with activity levels that pose a serious threat to human health.

The nuclide ^{137}Cs is a widely used material for applications including teletherapy sources, flow gauges, and other industrial equipment. ^{137}Cs decays with a half-life of (30.05 ± 0.08) years [4] to either the ^{137}Ba ground state, with emission of a β particle ($Q = 1176$ keV, 5.3%), or to $^{137\text{m}}\text{Ba}$ ($Q = 514$ keV, 94.7%) which rapidly ($t_{1/2} = 2.552$ min) decays to the ^{137}Ba ground state with emission of a 661.7 keV γ photon. It is this relatively clean γ emission that has made ^{137}Cs one of the more commonly used radiological materials for sealed sources [5]. ^{137}Cs sealed sources are of concern both because of their ubiquity and because many of these are defined by the International Atomic Energy Agency as Category 1 sources [6], indicating the highest risk based on the potential for delivering a dose large enough to cause acute deterministic health effects [7]. There have already been several significant incidents involving lost or stolen ^{137}Cs sources. In fact, mishandling and dismantling of stolen sources in Goiânia, Brazil in 1987 [8] and in Estonia in 1994 [9] resulted in multiple confirmed deaths due to radiation exposure; in Goiânia, ^{137}Cs contamination was also spread over a large area.

In the event of a nuclear forensic investigation involving a ^{137}Cs source, identifying the origin of the radioactive material will be a high priority. Answering this question would be particularly challenging if the material has been separated from its shielded container, making it impossible to use information including serial numbers or other

markings. An important piece of information that could constrain the range of possible origins is the age of the radioactive material. Radiochronometry can be used to measure the age of a material or, more precisely, a model purification date. The model purification date represents an estimate of the last time a radionuclide was purified from its decay product. Determination of a model purification date is greatly simplified for a closed system where neither nuclide enters or leaves the system during the time between purification and analysis.

^{137}Cs sealed sources are produced using Cs recovered as a fission product from nuclear fuel or fissile material irradiated specifically for isotope production. In fission products, the primary Cs isotopes are stable ^{133}Cs , long-lived ^{135}Cs ($t_{1/2} = 2.3 \times 10^6$ years), and ^{137}Cs ; the other Cs isotopes either have negligible fission yields or they are short-lived and will have decayed away on the timescale of the sealed source production process. This leaves two radioactive Cs isotopes and three potential chronometers. The first radiochronometer involves comparing the proportion of ^{135}Cs – ^{137}Cs , which can be used to estimate the time since the fuel used to produce the source was removed from the reactor. However, use of this chronometer requires independent knowledge of reactor conditions and fuel to estimate fission yields. This makes the $^{135}\text{Cs}/^{137}\text{Cs}$ chronometer of limited usefulness for the case of a sealed source of unknown origin. The second radiochronometer involves comparison of the amount of ^{135}Cs present in a material to the amount of its decay product, ^{135}Ba . Due to the long half-life of ^{135}Cs , age measurements made using this radiochronometer are analytically difficult and have large uncertainties. The third radiochronometer has the highest potential of yielding age data that does not require extensive knowledge of the production history, and that will have relatively small uncertainties. This radiochronometer involves comparison of the amount of ^{137}Cs to ingrown ^{137}Ba . In order to maximize specific activity and to minimize radioactive impurities, preparation of ^{137}Cs for sealed source applications requires separation of Cs from nuclear material, activation products, and other fission products including alkali earth elements such as Sr and Ra. Therefore, the assumption that the Cs is effectively separated from Ba during processing is reasonable in the case of ^{137}Cs sealed sources. The assumption of a closed system is also reasonable for sealed sources since they are, by definition, sufficiently sealed off from the broader environment to prevent appreciable gain or loss of ^{137}Cs or ^{137}Ba . Isotopically natural Ba is, however, a ubiquitous trace constituent in air, water, and soil [10], so a correction of analytical results for some component of natural Ba will frequently be required. This is relatively easily achieved since Ba produced within the source by radioactive decay should be composed almost entirely of ^{137}Ba , while ^{138}Ba , the most abundant naturally occurring Ba isotope, should be absent.

The primary purpose of the Cs–Ba RM is to be a well-characterized “known” material for development and quality control of ^{137}Cs – ^{137}Ba radiochronometric measurements. The Cs–Ba reference material was produced as a solution standard using starting material recovered from a ^{137}Cs sealed source of known age and provenance. Production activities were performed taking precautions to avoid contamination with exogenous material to ensure that it is suitable for the application. A model purification age is readily calculated from the characterized values for molality of ^{137}Cs and of $^{137}\text{Ba}^*$. Accordingly, this reference material can be used to demonstrate accuracy of ^{137}Cs – $^{137}\text{Ba}^*$ model age measurements and for validation of methods developed with this application in mind. Additional information about the material that was determined during characterization, namely the ^{137}Cs massic activity and the Cs isotopic composition of the material, are also provided for informational purposes.

Materials and methods

Unit production and sample analysis preparation

The target mass fraction (at the time of unit production) of ^{137}Cs was 100 ng g^{-1} (equivalent to massic activity of 0.32 MBq g^{-1}), corresponding roughly to a nominal 500 ng (equivalent to activity of 1.6 MBq) of ^{137}Cs in each unit containing 5 mL of solution. This quantity of material was chosen as a compromise between providing a sufficient quantity to allow for accurate amount measurements of both ^{137}Cs and ingrown ^{137}Ba on one hand and having activity levels low enough to avoid a significant dose of radioactivity to the user on the other hand. The relatively low molality of ^{137}Cs planned for the reference material and the correspondingly low levels of $^{137}\text{Ba}^*$ mean that even a small quantity of contamination could make accurate measurement of the isotope amounts more difficult with a resulting increase in uncertainty. Furthermore, any introduction of variable contamination could result in a heterogeneous product unsuitable for use as a reference material. To minimize the potential for contamination with natural Ba, special precautions were incorporated into the production and characterization processes.

Where possible, the material was handled in cleanroom facilities and only high purity reagents suitable for trace analysis were used (i.e. sub-boiling distilled mineral acids and $18.2\text{ M}\Omega\text{ cm}$ ultrapure water). Thorough cleaning of labware was required prior to use and the ampoules used to contain the material were fabricated from Suprasil high-purity quartz (Heraeus, Germany).² Prior to filling, the

ampoules were also subjected to a rigorous cleaning procedure. A leaching study was performed in which 53 ampoules were filled with ultra-high purity 3 mol L^{-1} nitric acid and allowed to soak for several days, after which the acid solution was removed and its Ba content was determined via mass spectrometry. The results of this study verified that the Suprasil material was not a contributor of Ba contamination, as both the average observed Ba mass concentration of $(0.09 \pm 0.14)\text{ ng mL}^{-1}$ (corresponding to 0.010 ng mL^{-1} ^{137}Ba) and the maximum observed mass concentration of 0.54 ng mL^{-1} of isotopically natural Ba were well below the estimated 200 ng g^{-1} $^{137}\text{Ba}^*$ planned for the source.

Production of material

The ^{137}Cs material used to produce the Cs–Ba RM was removed from a sealed capsule stamped with an encapsulation date of October 27, 1965 and initial activity of 0.74 TBq (20 Ci) [11]. A CsCl pellet was extracted from the sealed source capsule and crushed at the Idaho National Laboratory’s (INL) Hot Fuel Examination Facility. A small quantity of the crushed pellet material was sampled using a glass capillary tube and dissolved in 3 mol L^{-1} nitric acid to create a ^{137}Cs master solution. An aliquot of the master solution was transferred out of the Hot Fuel Examination Facility and diluted using 3 mol L^{-1} nitric acid to produce a solution with a nominal ^{137}Cs mass fraction of 100 ng g^{-1} . For unit production, 200 quartz ampoules were each filled with 5 mL of solution using an autotitrator. Six Savillex vials (for characterization measurements) and five borosilicate glass ampoules (for activity measurements) were also filled interspersed at random intervals between the quartz ampoules. Five additional quartz ampoules of the solution were filled and prepared for analysis at the conclusion of the production run. All of the borosilicate ampoules and a subset of the quartz ampoules were weighed using an XS205DR (Mettler Toledo, USA) balance before and after filling. The ampoules were then flame-sealed immediately following filling (and weighing, if weighed) of the filled ampoule.

Distribution

Cs–Ba RM units and aliquots of the stock solution were selected for characterization analyses and distributed as described in Table 1. The five borosilicate glass ampoules were sent to the National Institute of Standards and Technology (NIST) where ^{137}Cs activity measurements were

Footnote 2 continued

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.

² Certain commercial equipment, instruments, software, or materials are identified in this paper to foster understanding. Such identification

Table 1 Characterization and verification samples

Sample designation (fill order in parentheses)	Container type	Measured attributes	Intended data usage
NIST 1 (3) NIST 2 (155) NIST 3 (173) NIST 4 (177) NIST 5 (204)	Borosilicate ampoule	^{137}Cs massic activity	Molality of ^{137}Cs characterization
INL S1 (1)	Savillex vial	Molality of ^{137}Cs Cs isotopic composition Molality of $^{137}\text{Ba}^*$ Ba isotopic composition	Value verification Information values Characterization IDMS calculations
INL37 (39) INL101 (104) INL153 (157) INL10-1 (207) INL10-2 (208) INL10-3 (209) INL10-4 (210) INL10-5 (211)	Quartz ampoule		
ORNL S4 (144) ORNL S6 (206)	Savillex vial	Ba isotopic composition	Value verification
ORNL 82 (85) ORNL 178 (182)	Quartz ampoule		
ORNL S3 (73) ORNL 59 (61) ORNL 178 (182)	Savillex vial Quartz ampoule	Molality of $^{137}\text{Ba}^*$	Value verification

performed to characterize the molality of ^{137}Cs . The five quartz ampoules that were filled following the conclusion of the production run, one of the Savillex vials, and three randomly selected ampoules from the production run were retained at INL for characterization of molality of $^{137}\text{Ba}^*$ as well as measurements of Cs isotopic composition, molality of ^{137}Cs , and Ba isotopic composition. Finally, three Savillex vials and three ampoules from the production run were selected for Ba analyses at Oak Ridge National Laboratory (ORNL). These samples were prepared for verification of the Ba isotope dilution mass spectrometry (IDMS) and isotopic measurements performed at INL. Prior to analysis at INL or transfer to ORNL, all samples were spiked as appropriate for the planned analyses, then separated into Cs and Ba fractions at INL using gas pressurized extraction chromatography [11]. The reported results and recommended reference values calculated from these measurements have all been decay-corrected to represent their values as of a common reference date of July 7, 2011, in order to account for changes due to radioactive decay of ^{137}Cs and ingrowth of $^{137}\text{Ba}^*$ because of differences in when the various characterization and verification measurements were performed.

Molality of ^{137}Cs determination

The molality of ^{137}Cs was determined by measurement of gamma activity using the NIST “ 4π ”- γ ionization

chamber. This instrument is a well-type pressurized re-entrant ionization chamber primarily used at NIST for calibration of gamma-emitting radionuclides [12]. Characterization samples were measured alternating with blanks and a ^{226}Ra reference source. A total of 40 replicate activity measurements were made for each of the samples. The average blank-corrected sample response relative to the reference source was then used to determine activity via a calibration factor previously determined for a primary ^{137}Cs standard with known activity measured by a direct method (4π -($e+x$)- γ -coincidence efficiency extrapolation counting) [12]. The 5 samples for gamma activity measurement (NIST 1 through NIST 5) were sealed in borosilicate ampoules produced to NIST specifications for dimensions and composition to ensure correct measurement geometry and to control for gamma interactions with the container material. However, the ampoules sent to NIST were sealed with necks too long to fit in the sample holder for the ionization chamber, so each sample had to be transferred to a new ampoule and resealed. The post-transfer masses were recorded and used for calculation of massic activity. A single ampoule had a sufficiently short neck to measure in the ionization chamber before transfer, and this sample’s activity was measured both before and after transfer to a new ampoule. Prior to measurement in the ionization chamber, additional measurements were performed using a high-purity germanium detector to

establish that no photon-emitting impurities existed in quantities that could bias the ionization chamber measurement result. The decay constant ($\lambda_{137\text{Cs}}$) derived from the most recent evaluated ^{137}Cs half-life (30.05 ± 0.08 years) [4] and the measured activity ($A_{137\text{Cs}}$) were used to determine the amount of ^{137}Cs ($n_{137\text{Cs}}$) in the sample solutions (Eq. 1), which was then converted to molality of ^{137}Cs .

$$A_{137\text{Cs}}/\lambda_{137\text{Cs}} = n_{137\text{Cs}} \quad (1)$$

The accuracy of the radiometrically determined molality of ^{137}Cs was verified by Cs IDMS measurements performed at INL. Two sets of IDMS measurements were made: One set was composed of aliquots from the five ampoules filled following the completion of the production run (INL 10-1 through INL 10-5); the other set consisted of one Savillex vial (INL S1) and three ampoules randomly selected from the production units (INL 37, 101, and 153) that were measured at a later time. Prior to IDMS analyses, the isotopic composition of the unspiked material was determined by measuring the $n(^{135}\text{Cs})/n(^{133}\text{Cs})$ and $n(^{137}\text{Cs})/n(^{133}\text{Cs})$ isotope ratios.

A Thermo Finnigan Triton (ThermoFisher Scientific, USA) thermal ionization mass spectrometer (TIMS) was used for all of the Cs measurements performed at INL. Natural Cs is monoisotopic, so mass bias corrections were performed using NIST Standard Reference Material (SRM) 3104a (Barium Standard Solution, lot no. 070222) and correction factors were determined using an exponential law [13]. SRM 3104a does not have certified values for isotopic composition, so the isotopic abundances for naturally occurring Ba recommended by the International Union of Pure and Applied Chemistry (IUPAC) [14] were used to calculate isotope amount ratios for SRM 3104a. Molality of ^{137}Cs measurements were performed using SRM 3111a (Cesium Standard Solution, lot no. 492909) as a reverse isotope dilution spike added to IDMS samples prior to Cs–Ba separation. For the samples INL S1, 37, 101, and 153, two separate aliquots were taken and used to prepare separate sample-spike mixtures. For preparation of sample and spike dilutions, as well as preparation of sample-spike mixtures for IDMS analyses, masses were measured using a calibrated XS205DR balance.

Molality of radiogenic ^{137}Ba determination

The molality of $^{137}\text{Ba}^*$ was determined by IDMS with the isotopic analyses performed using a Triton TIMS at INL. As was the case with Cs measurements, prior to the isotope dilution assay, the non-natural isotopic composition of the material was determined by measurement of the Ba isotope

amount ratios $n(^{130}\text{Ba})/n(^{137}\text{Ba})$, $n(^{132}\text{Ba})/n(^{137}\text{Ba})$, $n(^{134}\text{Ba})/n(^{137}\text{Ba})$, $n(^{135}\text{Ba})/n(^{137}\text{Ba})$, $n(^{136}\text{Ba})/n(^{137}\text{Ba})$, and $n(^{138}\text{Ba})/n(^{137}\text{Ba})$. The signal at m/z 133 was also monitored to confirm the separation of Cs and Ba was sufficient to ensure that the Ba isotopic composition measurements were not biased by residual Cs. Isotopic composition measurements were performed on the Ba fraction of the unspiked samples collected from three ampoules and one Savillex vial, which are the counterparts to the second set of samples used in the Cs isotopic composition measurements. As with Cs isotopic composition determination, SRM 3104a was used in conjunction with the IUPAC abundances to determine mass bias correction factors using an exponential law.

The determination of molality of $^{137}\text{Ba}^*$ was performed using SRM 3104a as a reverse isotope dilution spike in addition to its use as mass bias standard. All mass measurements taken during sample and spike preparation were performed using a calibrated XS205DR balance. The molality of ^{137}Ba was determined using the $n(^{138}\text{Ba})/n(^{137}\text{Ba})$ isotope amount ratio measured in the IDMS mixtures, with mass bias correction factor determined as described above for isotopic composition characterization. To calculate a model age, it is necessary to correct for non-radiogenic ^{137}Ba contributed by isotopically natural Ba contamination present in the samples. To perform this correction, it was assumed that all ^{138}Ba present in each sample was from natural Ba. The amount of non-radiogenic ^{137}Ba was then determined by multiplying the abundance of ^{138}Ba by the $n(^{137}\text{Ba})/n(^{138}\text{Ba})$ isotope amount ratio calculated using the IUPAC abundances for barium. The calculated non-radiogenic ^{137}Ba was then subtracted from the measured ^{137}Ba to determine the radiogenic ^{137}Ba .

Verification of the molality of $^{137}\text{Ba}^*$ was provided by an independent set of isotopic measurements performed using a Thermo Finnigan Neptune inductively coupled plasma mass spectrometer (ICP-MS) at ORNL. Samples of unspiked material for isotopic composition characterization and samples spiked with SRM 3104a for IDMS were purified at INL using the gas pressurized extraction chromatography method described above, and the Ba fractions were sent to ORNL for analysis. Instrumental mass bias correction factors at ORNL were determined using SRM 3104a and IUPAC isotopic abundances. Corrections were made for isobaric interference due to Xe present in the plasma gas (^{130}Xe , ^{132}Xe , ^{134}Xe , and ^{136}Xe corrections were performed) based on the measured ^{129}Xe intensity. Screening measurements indicated that Ce and La concentrations are negligible, making corrections for Ce (^{136}Ce , ^{138}Ce) and La (^{138}La) unnecessary.

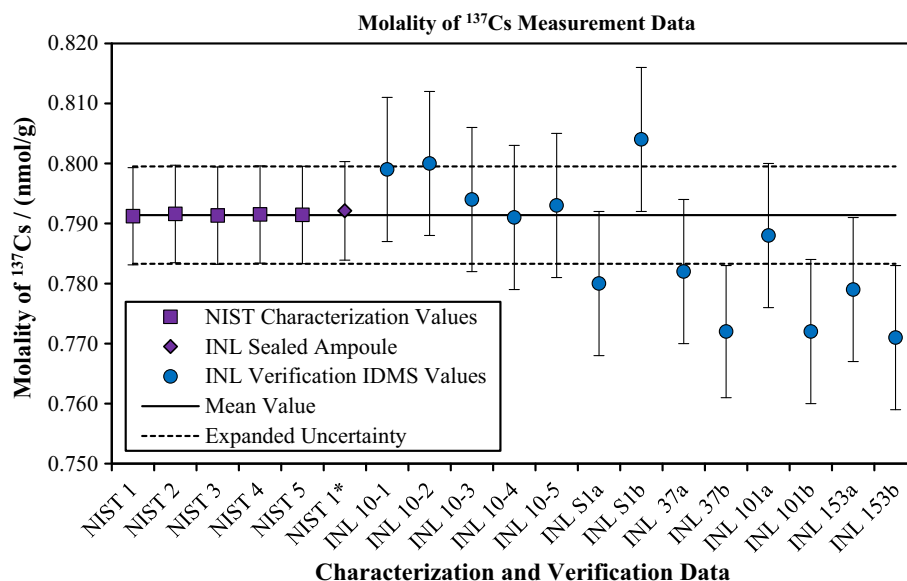


Fig. 1 Measured molality of ^{137}Cs in the Cs–Ba RM. All values are decay-corrected to the reference date of July 7, 2011. The first set of data points (purple squares) represent the molality of ^{137}Cs obtained from the massic activity measured at NIST. The purple diamond data point is the activity measured in the ampoule received from INL prior to transfer into a new ampoule. The blue circles represent measurements obtained by Cs IDMS at INL. The solid horizontal line

represents the reference value and dashed horizontal lines show the expanded uncertainty envelope of the reference value. Note that the reference value and uncertainty are based on the γ activity measurements only. Error bars on individual data points represent an estimate of expanded uncertainty for each individual measurement and were calculated separately from the reference value uncertainty. (Color figure online)

Results and discussion

Cs measurements

Results for the measurement of molality of ^{137}Cs in the Cs–Ba reference material made using the $4\pi\text{-}\gamma$ ionization chamber are displayed in Fig. 1.³ A single sample (corresponding to “NIST-1”), was measured both before and after transferring the material from the received ampoule to a new ampoule. The massic activity measured before and after transfer for this sample differ by less than 0.4 kBq g^{-1} , (0.11%), well within the 0.86% relative uncertainty of the aggregated measurements (Table 2), demonstrating that the required transfer of the samples to new ampoules before counting did not significantly influence the measurement result.

The mean measured massic activity at the reference date (determined using only measurements obtained after transfer to new ampoules) was 348.4 kBq g^{-1} with an expanded uncertainty of 3.0 kBq g^{-1} . This corresponds to

a molality of ^{137}Cs of $0.7915 \text{ nmol g}^{-1}$ with an expanded uncertainty (corresponding to an approximate 95% level of confidence) of $0.0073 \text{ nmol g}^{-1}$. The uncertainty in the molality of ^{137}Cs was determined using a Bayesian observation equation method [15]. The Bayesian observation equation method allows for a more precise characterization of the probability distribution of the modeled value than that which is provided by the approach to uncertainty analysis prescribed in the *Guide to the expression of uncertainty in measurement* (GUM) [16] (hereafter referred to as the “GUM uncertainty framework”) and was therefore chosen as the basis for the recommended reference values and uncertainties for this reference material. This analysis was performed by generating a posterior distribution for the measurand with the Markov Chain Monte Carlo (MCMC) [17] method, using OpenBUGS [18] and R [19]. The standard deviation of the posterior probability distribution can be interpreted as corresponding to the standard uncertainty. The recommended expanded uncertainty was determined using the smallest symmetrical interval that completely encompasses 95% of the posterior probability distribution for molality of ^{137}Cs ; due to slight asymmetry in the posterior distribution, this means that the expanded uncertainty is slightly more conservative than the 95% credible interval. Although the Bayesian model represents a statistically more rigorous uncertainty estimate than a traditional GUM uncertainty framework approach,

³ Except where otherwise noted, measurement uncertainties are quoted as expanded uncertainties corresponding to an approximate 95% level of confidence. This corresponds either to a coverage factor of $k = 2$ or, for values determined using the Observation Equation method, the smallest symmetrical interval covering a minimum of 95% of the measurand posterior probability distribution (also referred to as a 95% credible interval).

Table 2 Primary ^{137}Cs $4\pi\text{-}\gamma$ ionization chamber activity measurements and calculated molality of ^{137}Cs

Sample ID	^{137}Cs massic activity (kBq g^{-1})	Molality of ^{137}Cs (nmol g^{-1})
<i>NIST-1</i> ^a	348.7 (31)	0.7921 (81)
NIST-1	348.3 (30)	0.7912 (81)
NIST-2	348.4 (31)	0.7916 (81)
NIST-3	348.3 (31)	0.7913 (81)
NIST-4	348.4 (30)	0.7915 (81)
NIST-5	348.4 (31)	0.7914 (81)
Average value	348.4 (30)	0.7915 (73)

^a Activity measurement of sample NIST-1 before transfer to a new ampoule at NIST. This measurement was not included in the calculations of values or uncertainties because the experimental conditions for the measurement may have deviated slightly from the prescribed counting geometry and because it is not a unique sample. Expanded uncertainties are shown in parenthesis for all measurements. Uncertainties for individual data points represent an estimate of expanded uncertainty for each individual measurement and were calculated independently from the reference (or information) value uncertainty. All results have been decay-corrected to reference date of July 7, 2011

Table 3 Uncertainty budget for molality of ^{137}Cs

Component	Comment	Type	% Relative contribution ^a
Calibration factor	Ratio relating ionization chamber signal response for ^{137}Cs primary standard to ^{226}Ra reference source	B	39
Calibration source position correction	Correction for change in source holder position between time of calibration factor determination and measurement	B	30
^{137}Cs half-life	Evaluated half-life of ^{137}Cs	B	27
Calibration source positioning	Uncertainty in calibration source position	B	4
Measurement precision	Variability of activity measurements on five ampoules	A	< 0.5
Combined standard uncertainty (u_c)		0.0036	
Molality of ^{137}Cs (nmol g^{-1})		0.7915	
Expanded uncertainty (nmol g^{-1})		0.0073	

^aRelative contributions for individual uncertainty components represent an estimate of their percentage contribution to the overall measurement uncertainty. The expanded uncertainty corresponds to an approximate 95% level of confidence

an uncertainty model was also generated in accordance with the GUM uncertainty framework using the software package GUM Workbench [20] for comparison purposes. Little difference was observed between the results generated by the two approaches. Due to the fact that a straightforward determination of relative uncertainty contributions is not possible when modeling uncertainty using Monte Carlo methods [21], an uncertainty budget was generated based on the sensitivity factors calculated using the GUM uncertainty framework (Table 3). Note that this budget is only an approximation of the relative contributions of uncertainty components within the Bayesian model, but that it is useful for discussion of uncertainty drivers for the attribute value. The measurement variability, with uncertainty determined by Type A evaluation, makes only a small contribution. Instead, the measurement

uncertainty is primarily driven by several other factors whose uncertainties were determined by Type B evaluation. The largest contributors to the uncertainty are the calibration coefficient relating the ionization chamber response for ^{137}Cs to that for ^{226}Ra (39% relative contribution to the uncertainty) and a correction made to account for the change in the height of the sample holder between the time of the ionization chamber calibration and the time of measurement (30% relative contribution) [22]. The uncertainty in the half-life of ^{137}Cs (27% relative contribution) associated with the conversion from massic activity to molality of ^{137}Cs is also a significant uncertainty component.

For verification of the accuracy of the reference value for molality of ^{137}Cs , confirmatory measurements were performed by IDMS. Since knowledge of the isotopic

Table 4 Cs isotope amount ratios in Cs–Ba RM

Sample ID	$n(^{135}\text{Cs})/n(^{133}\text{Cs})$	$n(^{137}\text{Cs})/n(^{133}\text{Cs})$
INL10-1	0.3453	0.2693
INL10-2	0.3449	0.2686
INL10-3	0.3451	0.2690
INL10-4	0.3449	0.2687
INL10-5	0.3451	0.2690
INL S1a	0.3447	0.2684
INL S1b	0.3450	0.2688
INL 37a	0.3451	0.2689
INL 37b	0.3449	0.2687
INL 101a	0.3449	0.2687
INL 101b	0.3459	0.2703
INL 153a	0.3450	0.2689
INL 153b	0.3453	0.2693
Average isotope amount ratios	0.3451 (11)	0.26897 (84)

All results are decay-corrected to reference date of July 7, 2011. Expanded uncertainties associated with average isotope ratios were calculated based on variability in the measured results plus uncertainties associated with the mass bias correction and decay correction. All measurements were performed at INL

composition of the unspiked Cs–Ba RM is required for determination of concentration by IDMS, the isotopic composition of the material was also measured. $n(^{135}\text{Cs})/n(^{133}\text{Cs})$ and $n(^{137}\text{Cs})/n(^{133}\text{Cs})$ isotope amount ratio measurement results for the Cs–Ba RM are shown in Table 4. The measurements were acquired in two sets taken at different times, with samples INL10-1 through INL10-5 comprising the first set, with the remaining samples belonging to a second set measured later. The results indicate that ^{133}Cs is the most abundant isotope, with significant proportions of ^{135}Cs and ^{137}Cs also present. This distribution is roughly consistent with what would be expected for Cs recovered from fission products and the age of the material. The two sets of samples analyzed at different times show good agreement for both isotope amount ratios measured. At the reference date, the ratio $n(^{135}\text{Cs})/n(^{133}\text{Cs})$ had a mean value of 0.3451 with an expanded uncertainty of 0.0011 and the ratio $n(^{137}\text{Cs})/n(^{133}\text{Cs})$ had a mean value of 0.26897 with an expanded uncertainty of 0.00084. Measurement variability played a relatively small role in the uncertainty of the isotope ratio measurement results. The uncertainty is instead dominated primarily by the uncertainty in the mass bias correction factor, which is a combination of uncertainties in the IUPAC isotopic abundances for Ba and variability in the measured isotope ratio for the mass bias standard. The Cs isotope ratios for the individual measurements appear to show a small degree of between-sample variability. The

Table 5 IDMS verification measurements of molality of ^{137}Cs

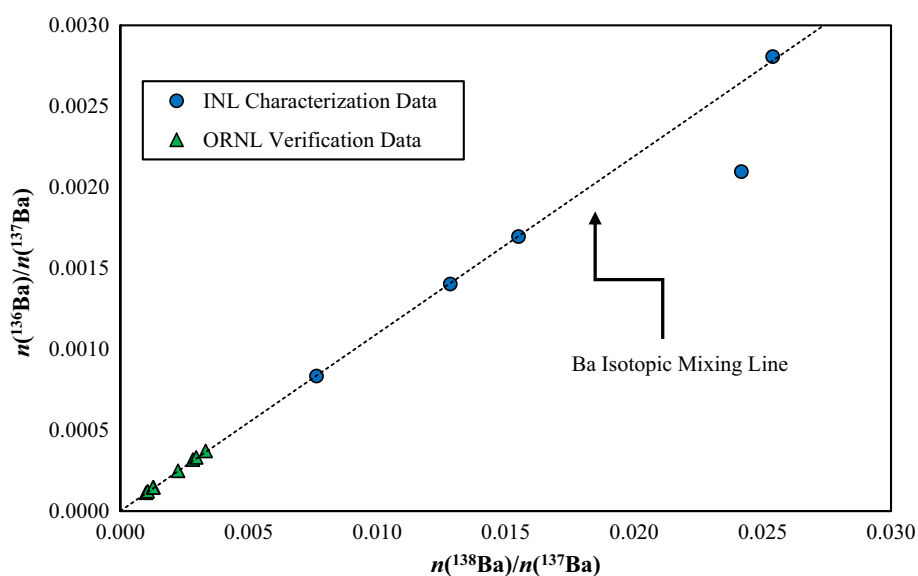
Sample ID	Molality of ^{137}Cs (nmol g ⁻¹)
INL 10-1	0.794 (13)
INL 10-2	0.796 (13)
INL 10-3	0.790 (13)
INL 10-4	0.787 (13)
INL 10-5	0.789 (13)
INL S1a	0.784 (13)
INL S1b	0.802 (13)
INL 37a	0.786 (13)
INL 37b	0.776 (12)
INL 101a	0.792 (13)
INL 101b	0.776 (12)
INL 153a	0.783 (12)
INL 153b	0.775 (12)
Verification data set average molality	0.787 (14)

All values have been decay-corrected to the reference date of July 7, 2011. Expanded uncertainties are shown for all measurements. Uncertainties for individual data points represent an estimate of expanded uncertainty for each individual measurement and were calculated independently from the uncertainty in the average value

measured $n(^{135}\text{Cs})/n(^{133}\text{Cs})$ and $n(^{137}\text{Cs})/n(^{133}\text{Cs})$ ratios for each sample are strongly correlated, which suggests much of this variation is due to differing amounts of ^{133}Cs present in the samples. This most likely represents variable contamination with natural Cs occurring during sample processing or Cs interference during mass spectrometric analysis.

The results of the IDMS measurements performed for verification of the reference value are presented in Table 5. The uncertainties for individual measurements represent a reasonably conservative estimate of expanded uncertainty calculated using the GUM uncertainty framework. There are, however, experimental factors that could represent sources of variability or bias that are difficult to quantify and may be underrepresented in the uncertainty model. The first of these factors is the fact that ^{133}Cs is both the most abundant isotope in the samples and also the only Cs isotope available for use as an IDMS spike. Accordingly, the potential effect of variability in IDMS isotopic ratio measurements can be amplified. The second factor is that a multi-isotopic Cs mixture for mass bias correction is not available, so the mass bias correction factor was determined based on measurements of a Ba standard. Although the Ba material is within an appropriate mass range for Cs, it is not clear to what extent the mass fractionation behavior of the two elements differ. The potential that uncertainties are slightly larger than the quoted values for the IDMS molality of ^{137}Cs measurements should be

Fig. 2 The measured isotopic composition of Ba in the Cs–Ba radiochronometric reference material. Data points represent the measured Ba isotopic composition for samples analyzed by TIMS at INL (blue circles) and by ICP-MS at ORNL (green triangles). Expanded uncertainties for individual data points are smaller than the data symbols. A mixing line is plotted between a point representing an IUPAC natural Ba composition (6.383, 0.699; outside of chart area) and the origin (i.e. pure ^{137}Ba). (Color figure online)



considered when comparing the results of these verification measurements to the reference value.

Ba measurements

Ba isotope ratio measurements were made on unspiked aliquots of the Cs–Ba RM to obtain isotope abundance values to be used in isotope dilution calculations and to assess the homogeneity of the reference material. As expected, the isotopic composition measurements performed by INL and ORNL indicate the predominance of ^{137}Ba produced by the decay of ^{137}Cs , but the relative abundances of the various Ba isotopes are highly variable (Fig. 2). The measurements performed at ORNL consistently indicate significantly lower $n(^{138}\text{Ba})/n(^{137}\text{Ba})$ and $n(^{136}\text{Ba})/n(^{137}\text{Ba})$ ratios than the INL data, which also show a greater degree of variability.

A three-isotope plot comparing the $n(^{138}\text{Ba})/n(^{137}\text{Ba})$ and $n(^{136}\text{Ba})/n(^{137}\text{Ba})$ ratios (Fig. 2) shows that the measured isotope ratios reported by both labs fall along a mixing line with end member compositions consistent with natural Ba and pure ^{137}Ba . This suggests that the highly dispersed $n(^{138}\text{Ba})/n(^{137}\text{Ba})$ ratios are the result of variable contamination with natural Ba. Since sample preparation processes, including spiking of IDMS samples and Cs–Ba separations for all samples, were performed by INL, the higher relative abundance of ^{138}Ba measured in the INL dataset indicates that significant contamination with natural Ba probably took place in association with the isotopic analysis. This discrepancy underscores the need for a correction to the measured quantity of ^{137}Ba to ensure that only the quantity of radiogenic Ba present in the material is used for the model age calculation.

The results of measurements of the molality of $^{137}\text{Ba}^*$ for each sample are shown in Fig. 3; again, both the primary IDMS measurements performed at INL and the verification measurements performed at ORNL are shown. Uncertainties for individual data points in the later set of INL characterization samples (INLS1, INL37, INL101, INL153) are larger because different sample to spike ratios were used than for the earlier INL set composed of samples INL10-1 through INL10-5 (Table 6). The lower spike-to-sample ratio in the second INL data set resulted in larger relative correction for the poorly constrained initial $n(^{137}\text{Ba})/n(^{138}\text{Ba})$ isotopic ratio of 51 with an expanded uncertainty of 17. The second sample set is also more variable and results in a slightly lower mean than the earlier measurements, but both sets agree with each other within uncertainty. The two sets of characterization measurements combined result in a recommended reference value for molality of $^{137}\text{Ba}^*$ of $1.546 \text{ nmol g}^{-1}$ with an expanded uncertainty (corresponding to an approximate 95% level of confidence) of $0.024 \text{ nmol g}^{-1}$ for the Cs–Ba RM. The mean of the verification measurements of molality of $^{137}\text{Ba}^*$ performed at ORNL of $1.536 \text{ nmol g}^{-1}$, with expanded uncertainty of $0.014 \text{ nmol g}^{-1}$, is in agreement with the recommended reference value. The recommended value and uncertainty were determined using the same Bayesian Observation Equation method used for the determination of molality of ^{137}Cs . The standard uncertainty determined using the Bayesian method was slightly lower than indicated by the model generated using the GUM uncertainty framework and the expanded uncertainty based on the 95% credible interval was comparable to that determined using the GUM uncertainty framework. The verification IDMS measurements

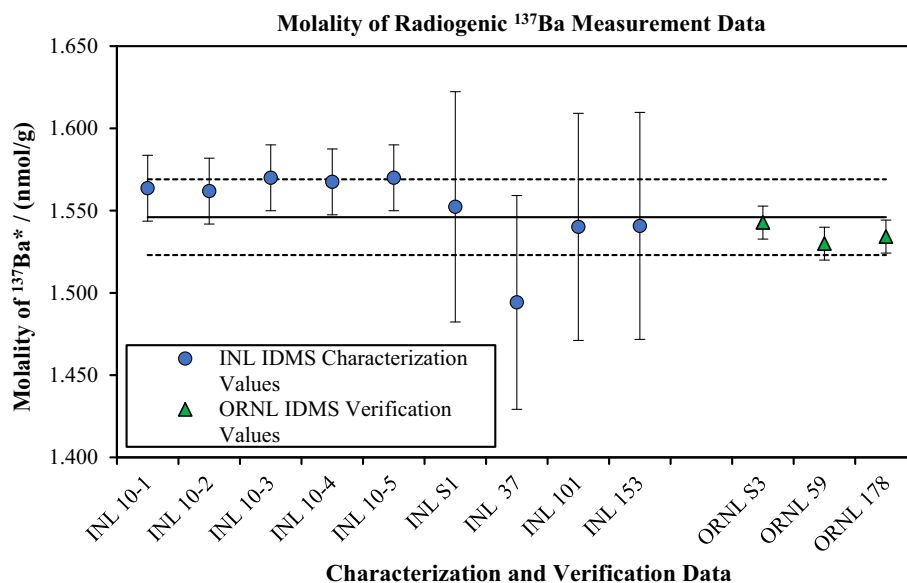


Fig. 3 Measured molalities of radiogenic ^{137}Ba in the Cs–Ba RM. IDMS characterization measurements performed at INL are shown as blue circles. IDMS verification measurements performed at ORNL are green triangles. The solid horizontal line indicates the reference value for the molality of $^{137}\text{Ba}^*$. The dashed horizontal lines indicate

the expanded uncertainty envelope (corresponding to an approximate 95% level of confidence) for the reference value. Error bars on individual data points represent an estimate of expanded uncertainty for each individual measurement and were calculated independently from the reference value uncertainty. (Color figure online)

Table 6 Measurements of molality of $^{137}\text{Ba}^*$

Sample ID	Molality of $^{137}\text{Ba}^*$ (nmol g $^{-1}$)
<i>Primary characterization measurements (INL)</i>	
INL 10-1	1.564(17)
INL 10-2	1.562(17)
INL 10-3	1.570(17)
INL 10-4	1.567(17)
INL 10-5	1.570(17)
INL S1	1.552(40)
INL 37	1.494(38)
INL 101	1.540(40)
INL 153	1.541(40)
Weighted average molality of $^{137}\text{Ba}^*$	1.546(24)
<i>Verification measurements (ORNL)</i>	
ORNL S3	1.543(12)
ORNL 59	1.530(12)
ORNL 178	1.534(12)
Verification data set average molality of $^{137}\text{Ba}^*$	1.536(14)

All results have been decay-corrected to the reference date of July 7, 2011. Values in parentheses represent expanded uncertainties. Uncertainties for individual data points represent an estimate of expanded uncertainty for each individual measurement and were calculated independently from the reference value uncertainty

performed, also shown in Fig. 3, agree well with the recommended value.

The uncertainty budget for the molality of $^{137}\text{Ba}^*$ in the Cs–Ba RM shown in Table 7 is an approximation (as described for the Molality of ^{137}Cs budget) of the relative contribution of uncertainty components to the Bayesian uncertainty model. The largest contributors are the uncertainty in the isotopic composition of the unspiked material (48% relative contribution to the overall uncertainty) and the variability in the IDMS measurements (46% relative contribution). Other minor contributors include uncertainty in the mass bias correction factor (2% relative contribution) and in the concentration of the spike solution (4% relative contribution). The mass bias correction uncertainty is a combination of the uncertainty in the IUPAC abundances of the Ba isotopes measured and variability in the measurements performed on the mass bias standard.

Determination of model purification date

The model purification date is a derived value that is readily determined from the values for the molalities of ^{137}Cs and $^{137}\text{Ba}^*$ (Eq. 2). The model age at time t after purification can be determined from the ratio of remaining ^{137}Cs to its decay product:

$$\text{Model Purification Date} = \text{Date}_{\text{Ref}} - \ln\left(\frac{^{137}\text{Ba}^*}{^{137}\text{Cs}} + 1\right) / \lambda_{^{137}\text{Cs}} \quad (2)$$

Table 7 Uncertainty budget for molality of $^{137}\text{Ba}^*$

Component	Comment	Type	% Relative contribution ^a
IDMS measurements	Variability of nine IDMS measurements of $^{137}\text{Ba}^*$ molality	A	46
Ba isotopic composition	Standard uncertainty for the unspiked Ba-isotopic composition as measured at INL	B	48
Mass bias correction	Estimated uncertainty in value of mass bias correction factor	B	2
Spike concentrations	Combined standard uncertainty in certified value of SRM 3104a	B	4
Weighing	Estimated relative uncertainty for potential bias in mass of solution aliquots	B	< 0.5
Combined standard uncertainty (u_c)		0.0115	
Molality of $^{137}\text{Ba}^*$ (nmol g^{-1})		1.546	
Expanded uncertainty (nmol g^{-1})		0.024	

^aRelative contributions for individual uncertainty components represent an estimate of their percentage contribution to the overall measurement uncertainty. The expanded uncertainty corresponds to an approximate 95% level of confidence

where ^{137}Cs and $^{137}\text{Ba}^*$ are the molalities of the respective nuclides at the reference date (Date_{Ref}) and $\lambda_{^{137}\text{Cs}}$ is the decay constant for ^{137}Cs .

Calculation of the model age for the Cs–Ba RM using the recommended molalities for ^{137}Cs and $^{137}\text{Ba}^*$ of $(0.7915 \pm 0.0073) \text{ nmol g}^{-1}$ and $(1.546 \pm 0.023) \text{ nmol g}^{-1}$, respectively, gives a result of (47.04 ± 0.56) years ($k=2$) prior to the reference date, corresponding to a model purification date of June 22, 1964 and an expanded uncertainty of 200 days. This model purification date falls more than one year before the encapsulation date of October 27, 1965 that represents the latest possible time of purification. The model date is also in agreement with previous independent determinations of the model purification date for this source [11, 23].

Calculated model ages based on determinations of molality of $^{137}\text{Ba}^*$ for individual samples and using the recommended molality of ^{137}Cs are shown in Fig. 4. Use of the molality of ^{137}Cs measured by IDMS for individual samples to calculate model age result in model ages that agree within uncertainty with those calculated using the reference value for molality of ^{137}Cs . The largest contributor to uncertainty in the model age is the molality of $^{137}\text{Ba}^*$ (57% relative contribution to the overall uncertainty), due to its larger relative uncertainty, followed by the molality of ^{137}Cs (22% relative contribution), and uncertainty in the half-life of ^{137}Cs (20% relative contribution).

Suitability as a reference material

For a reference material to be fit for its intended use it must be stable and homogenous and characterized values should be reproducible and traceable to the base units as defined by the international system of units (SI). They must also have uncertainties calculated using methods that are

consistent with international standards [24–26]. The Cs–Ba RM was planned to meet accepted international standards for the designation of ‘certified reference material’ [25]. The following discussion will outline how the production and characterization of the Cs–Ba RM has ensured that it conforms to criteria including stability, homogeneity, traceability, and uncertainty estimation.

Long-term stability of the Cs–Ba RM material is expected. Both Cs and Ba are readily soluble in the 3 mol L^{-1} nitric acid solution used to create the reference material units. No change in molalities of ^{137}Cs and $^{137}\text{Ba}^*$ due to evaporation is anticipated due to the production of the reference material units as flame-sealed quartz ampoules. The use of pre-cleaned high-purity quartz ampoules is expected to prevent the leaching of Ba from the ampoules affecting the composition of the Cs–Ba RM solution and the leach-testing performed on the ampoules indicates that the potential contamination should be minimal. These precautions ensure that over the lifetime of the reference material (10–20 years), the only change in composition occurring within a sealed unit will be the decay of the Cs radioisotopes present in the solution.

Careful preparation of the quartz ampoules also serves to ensure the homogeneity of individual units by minimizing the potential for differential contamination. The ampoule-filling process for the units was also designed to assure homogeneity, with all units produced in one run from a single batch of master solution dispensed using an autotitrator to assure consistent aliquot size. Small variations in aliquot size do not affect the uncertainty in the reference values since they are presented in terms of molality. During filling, all ampoules were covered with a plastic cap immediately following filling and flame-sealed promptly thereafter to prevent evaporation and contamination. Characterization of the Cs–Ba reference material included sampling of both reference material ampoules and aliquots of stock Cs–Ba RM solution that were not

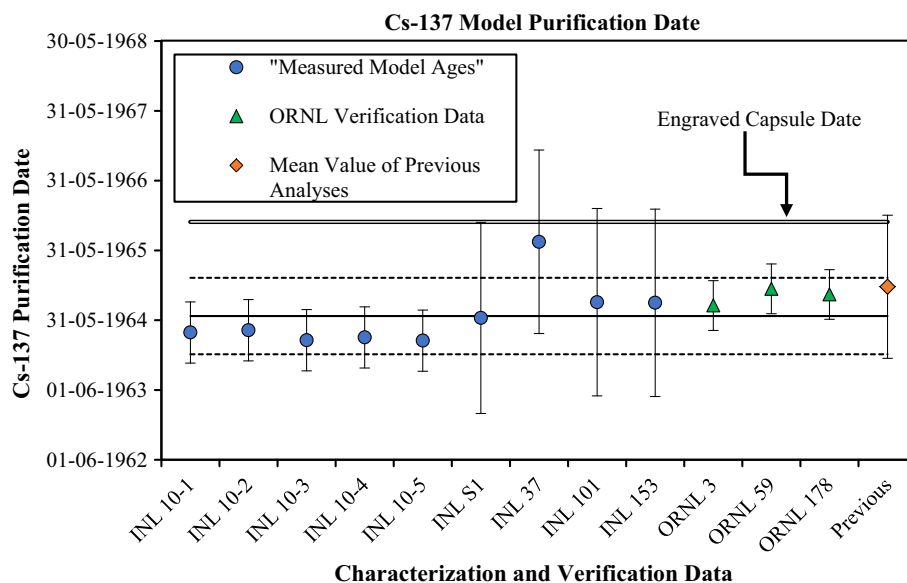


Fig. 4 Model purification dates derived from characterization of the Cs–Ba RM. All values were calculated using the molality of ^{137}Cs derived from radiometric measurement, with each data point representing the result of a unique $^{137}\text{Ba}^*$ measurement. Blue circle symbols indicate $^{137}\text{Ba}^*$ INL characterization measurements. Green triangle symbols represent $^{137}\text{Ba}^*$ ORNL verification measurements. A mean value for model purification dates of previous analyses of the same source [11, 23] is also shown (orange diamond). The horizontal

single solid line represents the model age derived from the recommended values for the molalities of ^{137}Cs and $^{137}\text{Ba}^*$ and the dashed lines represent the envelope of the expanded uncertainty. The double line represents the date engraved on the capsule that contained the starting material. Error bars for individual data points represent the combination of the expanded uncertainty of the reference value for ^{137}Cs and the individual expanded uncertainty estimates for each $^{137}\text{Ba}^*$ measurement. (Color figure online)

dispensed to ampoules (i.e. Savillex vials). Cs characterization included five ampoules characterized radiometrically as well as an additional eight ampoules and one Savillex vial of the material characterized by IDMS as verification measurements and to assess the magnitude of variation in composition despite the precautions taken. Likewise, Ba characterization measurements were performed on the same eight ampoules and one Savillex vial on which Cs measurements were performed, and an additional three ampoules and three Savillex vials were measured for verification of the primary Ba measurement. As discussed above, some variable contamination of some samples with isotopically natural Ba was observed; however, this variability was much smaller for the verification units measured at ORNL (Fig. 2). Since sample preparation and separations chemistry for all samples were done in tandem at INL, this natural Ba contamination is not believed to represent heterogeneity in the composition of the Cs–Ba RM units themselves, but rather foreign material introduced during the process of mass spectrometry measurements.

The recommended values for molality of ^{137}Cs (and the related value for ^{137}Cs massic activity) and molality of $^{137}\text{Ba}^*$ were determined using methods and standards that are traceable to the SI. Since the model purification date is derived from these two values, its value is also traceable. Figure 5 is a schematic illustrating the chain of

measurements and calibrations used to establish traceability of the measured molalities of ^{137}Cs and $^{137}\text{Ba}^*$ and by extension the traceability of the model purification date. The ^{137}Cs activity measurement was performed using an ionization chamber at NIST previously calibrated with a primary ^{137}Cs standard for which activity had been determined using a direct method. From activity, the molality of ^{137}Cs was calculated using the evaluated half-life [4]. The molality of $^{137}\text{Ba}^*$ was determined by IDMS using a NIST Standard Reference Material (SRM 3104a) as both isotope dilution spike and mass bias standard. The isotopic composition of Ba in the Cs–Ba RM was also determined by mass spectrometry using SRM 3104a as mass bias standard. For the isotopic composition of SRM 3104a, IUPAC isotopic abundances and uncertainties for natural Ba were used.

As previously discussed, the uncertainty models for the molalities of ^{137}Cs and $^{137}\text{Ba}^*$ were not derived using the GUM uncertainty framework. These uncertainty estimates, however, do incorporate all significant sources of measurement uncertainty and are statistically rigorous. Furthermore the models yield uncertainty estimates that are largely consistent with those that were generated in compliance with the GUM uncertainty framework [16] and are in accordance with NIST Technical Note 1297 [27].

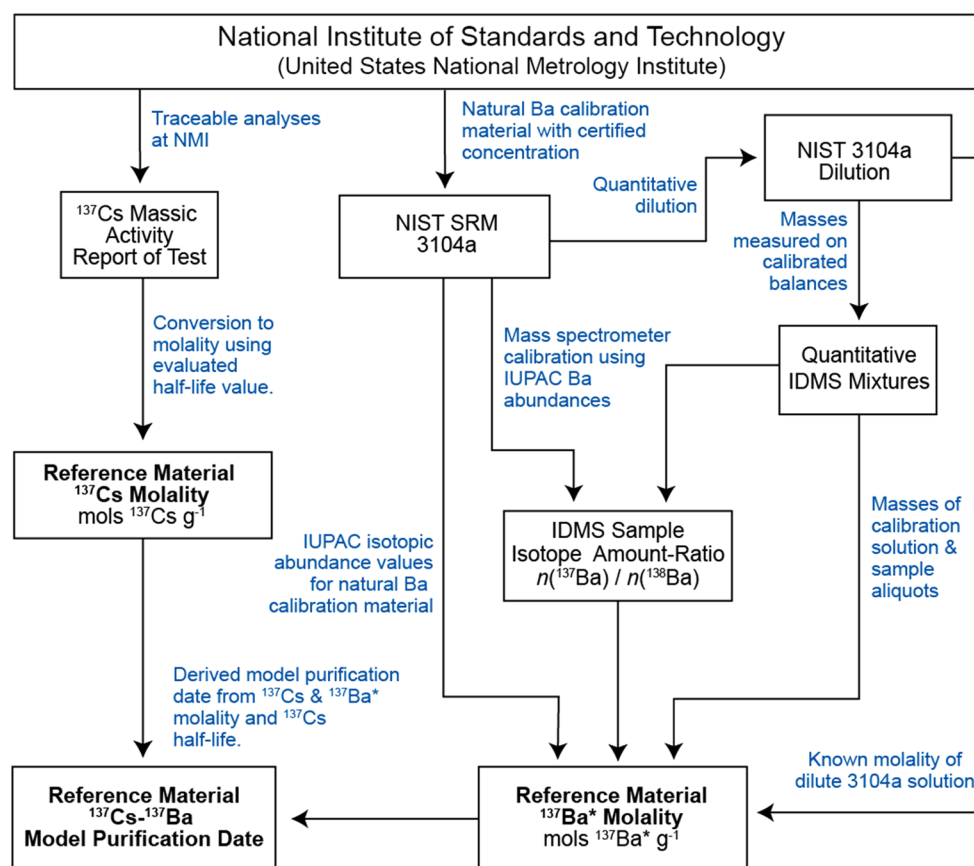


Fig. 5 Traceability schematic for the radiochronometric reference material

Conclusions

The Cs–Ba RM is fit for the purpose of radiochronometric age dating for nuclear forensics. Recommended values for ^{137}Cs and $^{137}\text{Ba}^*$ molalities of (0.7915 ± 0.0073) nmol g⁻¹ and (1.546 ± 0.024) nmol g⁻¹, respectively, at the reference date of July 7, 2011 have been determined on the basis of traceable amount and radiometric measurement techniques. These values, in turn, indicate a model purification date of June 22, 1964, with an expanded uncertainty of 200 days. This model purification date agrees with prior independent determinations made for the same material and is consistent with the encapsulation date stamp for the ^{137}Cs source used to create the reference material. Supporting data including the isotopic composition of Cs and the massic activity of ^{137}Cs in the material have also been provided. This new reference material will enhance the nuclear forensics analysis capability of labs engaged in the age-dating of sealed ^{137}Cs sources using the Cs–Ba radiochronometer to demonstrate the quality of their methods and measurement results.

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References

- Leggitt J, Inn K, Goldberg S, Essex R, LaMont S, Chase S (2009) Nuclear forensics—metrological basis for legal defensibility. *J Radioanal Nucl Chem* 282(3):997. <https://doi.org/10.1007/s10967-009-0293-2>
- Nuclear Forensics Support Reference Manual (2006). International Atomic Energy Agency, Vienna
- Varga Z, Krajcók J, Peňkin M, Novák M, Eke Z, Wallenius M, Mayer K (2017) Identification of uranium signatures relevant for nuclear safeguards and forensics. *J Radioanal Nucl Chem*:1–16. <https://doi.org/10.1007/s10967-017-5247-5>
- Bé M-M, Chisté V, Dulieu C, Browne E, Baglin C, Chechev V, Kuzmenko N, Helmer R, Kondev F, MacMahon D, Lee KB (2006) Table of radionuclides (Vol. 3: A = 3 to 244). International Bureau of Weights and Measures (BIPM)
- Ferguson CD, Kazi T, Perera J (2003) Commercial radioactive sources: surveying the security risks. Monterey Institute of International Studies, Center for Nonproliferation Studies, Monterey
- Categorization of Radioactive Sources (2003) IAEA TECDOC 1344. International Atomic Energy Agency, Vienna
- Shin H, Kim J (2009) Development of realistic RDD scenarios and their radiological consequence analyses. *Appl Radiat Isot* 67(7–8):1516–1520

8. The Radiological Accident in Goiânia (1988). International Atomic Energy Agency, Vienna
9. Croft JR (1999) Summary of major accidents with radiation sources and lessons learned. International Atomic Energy Agency, Vienna
10. Toxicological Profile for Barium (2007). Agency for Toxic Substances and Disease Registry (ATSDR), Atlanta
11. Sommers J, Cummings D, Giglio J, Carney K (2009) “Age” determination of irradiated materials utilizing inductively coupled plasma mass spectrometric (ICP-MS) detection. *J Radioanal Nucl Chem* 282(2):591. <https://doi.org/10.1007/s10967-009-0210-8>
12. Calhoun JM (1987) NBS measurement services: radioactivity calibrations with the “4 π ” gamma ionization chamber and other radioactivity calibration capabilities. Government Printing Office, Washington, D.C.
13. Russell WA, Papanastassiou DA, Tombrello TA (1978) Ca isotope fractionation on the Earth and other solar system materials. *Geochim Cosmochim Acta* 42(8):1075–1090. [https://doi.org/10.1016/0016-7037\(78\)90105-9](https://doi.org/10.1016/0016-7037(78)90105-9)
14. Berglund M, Wieser ME (2011) Isotopic compositions of the elements 2009 (IUPAC Technical Report). *Pure Appl Chem* 83(2):397–410
15. Antonio P, Blaza T (2007) Assessment of measurement uncertainty via observation equations. *Metrologia* 44(6):464
16. JCGM (2008) Evaluation of measurement data—guide to the expression of uncertainty in measurement. JCGM 100:2008
17. Gelman A, Carlin JB, Stern HS, Rubin DB (2013) Bayesian data analysis, (Chapman & Hall/CRC Texts in Statistical Science), CRC Press, Boca Raton
18. Lunn D, Spiegelhalter D, Thomas A, Best N (2009) The BUGS project: evolution, critique and future directions. *Stat Med* 28(25):3049–3067. <https://doi.org/10.1002/sim.3680>
19. R Development Core Team (2017) R: a language and environment for statistical computing. R Foundation for Statistical Computing, Vienna
20. Metrodata GmbH (2009) GUM workbench. Weil am Rhein
21. JCGM (2008) Evaluation of measurement data—Supplement 1 to the “Guide to the expression of uncertainty in measurement”—propagation of distributions using a Monte Carlo method. JCGM 101:2008
22. Fitzgerald R (2012) NIST ionization chamber “A” sample-height corrections. *J Res Natl Inst Stand Technol* 117:80–95. <https://doi.org/10.6028/jres.117.003>
23. Cummings DG, Sommers JD, Adamic ML, Jimenez M, Giglio JJ, Carney KP, Grimm K (2009) Characterization of sealed radioactive sources: uncertainty analysis to improve detection methods. *J Radioanal Nucl Chem* 282(3):923. <https://doi.org/10.1007/s10967-009-0368-0>
24. JCGM (2008) International vocabulary of metrology—basic and general concepts and associated terms (VIM). JCGM 200:2008
25. ISO Guide 35 (2006) Reference materials—general and statistical principles for certification. International Organization for Standardization (ISO), Geneva
26. ISO Guide 34 (2009) General requirements for the competence of reference material producers. International Organization for Standardization (ISO), Geneva
27. Taylor BN, Kuyatt CE (1994) NIST technical note 1297: guidelines for evaluating and expressing the uncertainty of NIST measurement results. Government Printing Office, Washington, D.C.