



# National Institute of Standards & Technology

## Certificate

### Standard Reference Material 4356 Ashed Bone Environmental Radioactivity Standard

This Standard Reference Material (SRM) is an ashed blend of contaminated human bone and diluent bovine bone. The SRM has been developed in cooperation with member laboratories of the International Committee for Radionuclide Metrology and expert national laboratories. It is intended for use in tests of measurements of radioactivity contained in matrices similar to the sample, for evaluating analytical methods, and as a generally available calibrated "real" sample matrix for laboratory intercomparisons.

**Radiological Hazard:** This SRM contains low levels of anthropogenic and natural radioactivity and poses no radiological hazard. The SRM should be used only by qualified quality control personnel.

**Chemical Hazard:** The SRM is dried sterilized bone ash and poses no chemical nor biological hazard. However, inhalation or ingestion of the material should be avoided.

**Storage and Handling:** The SRM should be stored in a dry location at room temperature. The bottle should be shaken before being opened in a chemical hood, and the bottle should be recapped tightly as soon as subsamples are removed.

The bottle (or any subsequent container) should always be clearly marked. If the SRM is transported, it should be packed, marked, labeled, and shipped in accordance with applicable national, international, and carrier regulations.

**Preparation:** This Standard Reference Material was prepared in the Physics Laboratory, Ionizing Radiation Division, Radioactivity Group, Lisa Karam, Group Leader. The overall technical direction leading to certification of this material was provided by Z.C. Lin and K.G.W. Inn of the Radioactivity Group.

Statistical support was provided by J.J. Filliben of the Information Technology Laboratory, Statistical Engineering Division.

The support aspects involved in the preparation, certification, and issuance of this SRM were coordinated through the Standard Reference Materials Program by J.W.L. Thomas.

**Technical Contacts:**

Zhichao Lin (email: zhichao.lin@nist.gov, telephone: 1-301-975-5645; facsimile: 1-301-926-7416) or  
Kenneth G.W. Inn (e-mail: kenneth.inn@nist.gov, telephone: 1-301-975-5541, facsimile: 1-301-926-7416),  
NIST, 100 Bureau Drive, Mail Stop 8462, Gaithersburg, Maryland 20899-8462 USA.

Bert M. Coursey, Chief  
Ionizing Radiation Division

Gaithersburg, Maryland 20899  
January 2000

Thomas E. Gills, Director  
Office of Measurement Services

**Details of the SRM Preparation:** This SRM is a composite material of contaminated human bone and bovine bone in a weight ratio of 1:22. De-fleshed human bone with marrow and elevated radionuclide concentration from the inventory of the U.S. Transuranium and Uranium Registries (USTUR) was selected by Los Alamos National Laboratory (LANL). The U.S. Department of Energy's Environmental Measurements Laboratory (EML) collected de-fleshed bovine leg bones from a local supplier in New York. Using the LANL ashing procedure, all collected human and bovine bones were ashed step-wise to 450 °C at EML, crushed, blended, and pulverized with an air-jet pulverizer. The median particle diameter of the resulting powder is 1.8 µm with a range of 0.7 to 10 µm. The resulting powder was re-blended at EML and sent to the National Institute of Standards and Technology (NIST). The powder was sterilized using 60 kGy of <sup>60</sup>Co radiation and then packaged. All pathogens in the material matrix are expected to have been destroyed during the ashing and irradiation processes.

**Instructions for Drying:** When nonvolatile radionuclides are to be determined, working samples of this SRM should be dried in air at 60°C for 24 hours prior to weighing. Volatile radionuclides (e.g., Rn and daughters) should be determined on samples as received; separate samples should be dried as previously described to obtain a correction factor for moisture. Correction for moisture content is to be made to the data for volatile radionuclides before comparing to the values given by this certificate. This procedure ensures that these volatile radionuclides are not lost during drying [1]\*. The weight loss on drying is typically less than 2 percent.

**Heterogeneity:** This material has been measured using sample sizes of 5 grams to 15 grams. The variation of measurements due to sample size was not statistically significant. It is recommended that a sample size of 5 grams or larger be used for radiometric and radiochemical analysis. Because of the complicated behavior of <sup>222</sup>Rn in the SRM bottle, the homogeneity of <sup>210</sup>Pb and <sup>210</sup>Po in the material may change over time.

**Radionuclide Disequilibrium:** Because of the way the composite material was prepared and because of the fractionation caused by internal biological processes, disequilibrium was found in the decay chain of <sup>234</sup>U - <sup>230</sup>Th - <sup>226</sup>Ra - <sup>210</sup>Pb - <sup>210</sup>Po and <sup>232</sup>Th - <sup>228</sup>Ra - <sup>228</sup>Ac - <sup>228</sup>Th. Compared with the natural decay chain of <sup>234</sup>U and <sup>232</sup>Th, this material contains excess amounts of <sup>210</sup>Pb, <sup>210</sup>Po, <sup>226</sup>Ra, <sup>228</sup>Ra, <sup>228</sup>Ac, and <sup>228</sup>Th. Because the decay chains of <sup>234</sup>U and <sup>232</sup>Th in the material are not in equilibrium, any measurement based on parent - daughter relationships should be avoided unless the massic activity of all the members in the chain are certified.

**Material Stability and Changes in Certified Values:** This matrix is considered to be stable; however, its stability has not been rigorously assessed. NIST will continue to monitor this material and will report any substantive changes in certified values to the purchaser.

PROPERTIES OF SRM 4356

Source identification number	NIST SRM 4356
Physical Properties:	
Source description	Freeze-dried radiation-sterilized pulverized ashed bone powder
Mass	Approximately 15 g
Radiological and Chemical Properties:	
Radionuclides	See Tables 1 and 2
Reference time	1200 EST, 31 December 1995
Massic activities [a]*	See Tables 1 and 2
Uncertainties [b]	See Table 1
Half-lives used	See Tables 1 and 2
Measuring instruments and methods	See Tables 1 and 2
Elemental composition	See Table 3

**Calculation of the Tolerance Limits:** In order to compute tolerance limits, a common robust data distribution across all 9 radionuclides was sought. A set of 47 possible distributions and distributional families was analyzed and the lognormal distribution provided such a robust distributional fit [2]. This distribution was then used to certify the 2.5% and 97.5% massic activity tolerance limits (at 95% confidence). The combined uncertainty is an inseparable contribution of factors that include interlaboratory variance, material heterogeneity, counting statistics, and analytical methodologies. Because of this complexity, the calculations of the tolerance limits require the utilization of the bootstrap method (see below) for the lognormal distribution.

The bootstrap is a computationally-intensive statistical procedure for estimating and computing the uncertainty of a statistic whose form is complicated or non-standard. The virtue of this procedure is that it provides a straightforward, rigorous methodology for computing uncertainties that would otherwise be difficult to obtain. See reference [3]. Procedurally, the bootstrap estimate for the uncertainty of a statistic (e.g., the 2.5% point) is obtained as follows:

1. From the original sample of  $n$  observations, compute the statistic of interest (e.g., the 2.5% point).
2. From the original  $n$  observations, extract a random sample (with replacement) of  $n$  observations (this becomes the bootstrap sample).
3. Compute the statistic of interest (e.g., the 2.5% point) from this bootstrap sample (this will be the bootstrap statistic).
4. Repeat steps 2 and 3 a large number of times (e.g., 1000 times); the bootstrap statistic will, of course, change from one bootstrap sample to the next.
5. Compute the standard deviation of the statistic by applying the usual standard deviation formula to the 1000 bootstrap statistics, and compute a lower 5% confidence value which 95% of the 1000 bootstrap values exceed.

Table 1: Certified Massic Activities.

Radio-nuclide	Mean $\pm 2s_m$ [c]* (mBq·g <sup>-1</sup> )	2.5% to 97.5% Tolerance Limit [d] (mBq·g <sup>-1</sup> )	Number of Assays	Half Life [e]	Analytical Method(s) See page 6	Contributing Laboratories
<sup>90</sup> Sr	42.6 $\pm$ 0.9	36.4 - 49.5	32	(28.78 $\pm$ 0.04) a	3b, 5b, 3d	IRMM, JCAC, MAFF, NIST, NRPB
<sup>226</sup> Ra	14.5 $\pm$ 1.1	8.7 - 20.5	21	(1600 $\pm$ 7) a	1a, 5d, 3e	IRMM, JCAC, JSI, MAFF, PTB
<sup>230</sup> Th	0.52 $\pm$ 0.03	0.34 - 0.89	45	(75380 $\pm$ 300) a	2c, 3c, 6c	IRMM, JCAC, MAFF, NIST, WSU
<sup>232</sup> Th	0.98 $\pm$ 0.03	0.85 - 1.46	48	(1.405 $\pm$ 0.006) $\times 10^{10}$ a	2c, 3c, 6c	IRMM, JCAC, MAFF, NIST, WSU
<sup>234</sup> U	0.64 $\pm$ 0.02	0.49 - 0.89	60	(2.45 $\pm$ 0.02) $\times 10^5$ a	2c, 3c, 6c	IRMM, JCAC, LDMC, LDML, MAFF, NIST, PTB
<sup>238</sup> U	0.63 $\pm$ 0.02	0.48 - 0.86	60	(4.468 $\pm$ 0.003) $\times 10^9$ a	2c, 3c, 6c	IRMM, JCAC, LDMC, LDML, MAFF, NIST, PTB
<sup>238</sup> Pu	0.86 $\pm$ 0.01	0.73 - 1.0	79	(87.7 $\pm$ 0.3) a	2c, 3c, 6c, 7c	ARPA, IRMM, JCAC, LDMC, LDML, MAFF, NIST, NRPB, PTB, WSU
<sup>239</sup> Pu + <sup>240</sup> Pu	1.26 $\pm$ 0.03	1.09 - 1.65	86	(24110 $\pm$ 30) a (6564 $\pm$ 11) a	2c, 3c, 6c, 7c	ARPA, IRMM, JCAC, LDMC, LDML, MAFF, NIST, NRPB, PTB, WSU
<sup>243</sup> Cm + <sup>244</sup> Cm	0.12 $\pm$ 0.01	0.07 - 0.18	26	(29.1 $\pm$ 0.1) a (18.10 $\pm$ 0.02) a	3c, 6c	JCAC, LDMC, LDML, MAFF

Table 2: Uncertified Massic Activities. Radionuclides for which there are insufficient numbers of data sets or for which discrepant data sets were obtained. No uncertainties are provided because no meaningful estimates could be made.

Radio-nuclide	Mean (mBq·g <sup>-1</sup> )	Range of Reported Results (mBq·g <sup>-1</sup> )	Number of Assays	Half Life [e]*	Analytical Method(s) See page 6	Contributing Laboratories
<sup>40</sup> K	49	41 - 55	10	(1.277 ± 0.008) × 10 <sup>9</sup> a	1a	JCAC, PTB
<sup>210</sup> Pb	20	12 - 33	21	(22.3 ± 0.2) a	1a, 3b, 3c	IRMM, JCAC, JSI, MAFF, PTB
<sup>210</sup> Po	13	11 - 16	5	(138.376 ± 0.002) d	4c	NRPB
<sup>228</sup> Ac	6.9	4.7 - 8.1	10	(6.15 ± 0.2) h	1a	JCAC, PTB
<sup>228</sup> Ra	6.1	5.8 - 6.3	5	(5.75 ± 0.03) a	1a	JSI
<sup>228</sup> Th	7.1	6.0 - 9.2	57	(1.9131 ± 0.0009) a	1a, 2c, 3c, 6c	IRMM, JCAC, JSI, MAFF, NIST, PTB, WSU
<sup>235</sup> U	0.028	0.018 - 0.055	35	(7.038 ± 0.006) × 10 <sup>8</sup> a	2c, 3c, 6c	JCAC, MAFF, NIST, PTB
<sup>241</sup> Am	9.98	8.76 - 13.6	88	(432.7 ± 0.6) a	1a, 2c, 3c, 6c, 7c	ARPA, IRMM, JCAC, JSI, LDMC, LDML, MAFF, NIST, NRPB, PTB, WSU

Data for these radionuclides are provided for information only. The massic activities are not certified at this time, but may be certified at some future time if additional data become available. Users are invited to submit measurement data that they think might contribute to the certification process. The data should be sent to one of the technical contacts listed on page 1.

Table 3: Uncertified Elemental Composition. Semi-quantitative Inductively-Coupled Plasma Mass Spectrometric Analysis of SRM 4356.

Element	mg·g <sup>-1</sup>	Element	mg·g <sup>-1</sup>	Element	mg·g <sup>-1</sup>
Al	0.11	Cu	0.004	Ni	0.003
Ba	0.15	Fe	0.86	Pb	0.0007
Ca	416	La	0.0003	Sr [f]	0.173
Ce	0.0004	Mg	17	V	0.01
Cr	0.011	Mn	0.003	Zn	0.2

### **Radiochemical and Detection Methods:**

1. Non-destructive
  2. HNO<sub>3</sub>-H<sub>2</sub>O<sub>2</sub>-HF-HClO<sub>4</sub>
  3. HNO<sub>3</sub>
  4. HNO<sub>3</sub>-HCl
  5. HNO<sub>3</sub>-HF
  6. HNO<sub>3</sub>-H<sub>2</sub>O<sub>2</sub>
  7. Calcination at 500 °C followed by addition of 8 M HNO<sub>3</sub>
- 
- a. Germanium gamma-ray spectrometer
  - b. Beta-particle Geiger counter
  - c. Silicon surface-barrier alpha-particle spectrometer
  - d. Liquid scintillation counter
  - e. Lucas Emanation

### **Participating Laboratories and Personnel:**

Agenzia Regionale per la Protezione Ambientale (ARPA)  
Mauro Magnoni  
Via Lago San Michele, 11, 10015 Ivrea (TO), Italy

Environmental Measurements Laboratory (EML)  
Phillip Krey (Retired)  
New York, NY, USA

Institute for Reference Materials and Measurements (IRMM)  
Timos Altitzoglou  
EC - JRC, Retieseweg, B-2440 Geel, Belgium

Japan Chemical Analysis Center (JCAC)  
Yoshinori Takata  
Chiba-shi, Chiba 263, Japan

Josef. Stefan Institute (JSI)  
Matjaz Korum  
Ljubljana, Slovenia

Laboratoire d'Analyses Medicales (LDMC)  
COGEMA-MARCOULE  
Didier Cavadore  
BP 170 - 30206 Bagnols Sur Ceze Cedex, France

Laboratoire d'Analyses Medicales (LDML)  
COGEMA-La HAGUE  
L. Exmelin  
50440 - Beaumont Hague Cedex, France

Los Alamos National Laboratory (LANL)  
James McInroy (Retired)  
Los Alamos, NM, USA

Ministry of Agriculture, Fisheries, and Food (MAFF)  
B. R. Harvey  
Parkfield Road, Lowestoft, Suffolk, NR33 0HT, UK

National Radiological Protection Board (NRPB)  
G. J. Ham  
Chilton, Didcot, Oxon, OX11 0RQ, UK

Physikalisch-Technische Bundesanstalt (PTB)  
H. Wershofen  
Postfach 33 45, 38023 Braunschweig, FRG

U.S. Transuranium and Uranium Registries (USTUR)  
Ronald Kathren (Retired)  
Richland, WA, USA

Washington State University (WSU)  
Sam Glover  
Pullman, WA 99164-1300 USA

## NOTES

- [a] **Massic activity** is the preferred name for the quantity activity (Bq) divided by the total mass of the sample. See Appendix and reference [4].
- [b] For further information on the expression of uncertainties, see references [5] and [6].
- [c] Based upon a normal distribution. The expanded uncertainty is two times the standard deviation of the mean ( $k=2$ ).
- [d] The tolerance limits are computed by the bootstrap method in concert with the lognormal distribution. The tolerance limits define an interval in which 95% of the values lie at a 95% confidence level.
- [e] The stated uncertainty is the standard uncertainty. See reference [7].
- [f] The concentration of stable Sr in the matrix was quantitatively determined by both NIST and IRMM. The mean is 0.173 mg·g<sup>-1</sup>. One standard uncertainty is 0.015 mg·g<sup>-1</sup>.

## REFERENCES

- [1] Bock, R., *A Handbook of Decomposition Methods in Analytical Chemistry*, International Textbook Company, Limited. T. & A. Constable Ltd., Great Britain, 1979.
- [2] Alan Heckert and J. J. Filliben, *DATAPLOT Reference Manual and Updates*, 1995. Available from the National Institute of Standards and Technology, Statistical Engineering Division, Gaithersburg, MD 20899. U.S.A.
- [3] B. Efron and R.J. Tibshirani, *An Introduction to the Bootstrap*, Monographs on Statistics & Applied Probability 57, 1993, Chapman and Hall, New York.
- [4] International Organization for Standardization (ISO), *ISO Standards Handbook - Quantities and Units*, 1993. Available from the American National Standards Institute, 11 West 42nd Street, New York, NY 10036, U.S.A. 1-212-642-4900.
- [5] International Organization for Standardization (ISO), *Guide to the Expression of Uncertainty in Measurement*, 1993. Available from the American National Standards Institute, 11 West 42nd Street, New York, NY 10036, U.S.A. 1-212-642-4900. (Listed under ISO miscellaneous publications as "ISO Guide to the Expression 1993".)
- [6] B. N. Taylor and C. E. Kuyatt, *Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results*, NIST Technical Note 1297, 1994. Available from the Superintendent of Documents, U.S. Government Printing Office, Washington, DC 20402, U.S.A.
- [7] Evaluated Nuclear Structure Data File (ENSDF), January 1996.

## Appendix

Recommendations on the use of the certified values for validation of measurements or procedures:

If a single observation is made, that value should be within the certified tolerance interval with 95 percent probability and 95 percent confidence. If multiple observations are made, then approximately 95% of the observed data values should be within the certified tolerance interval; in addition, the normal *t*-test should be employed which will compare the "location" of the observed data to the NIST certified mean value and validate the measurements.

Example of performing this *t*-test:

**Question:** A laboratory analyzed Pu-238 in 5 replicates of this SRM to validate its method. The analytical results were 0.823, 0.845, 0.875, 0.831, and 0.891 mBq/g. The NIST certified value is 0.864 mBq/g. Is the laboratory method valid?

Perform a *t*-test to the data:

1. NIST's Certified Value:  $m_0 = 0.864$  mBq/g

2. Laboratory Data Summary Statistics:

Sample size	$n = 5$
Sample mean	$\bar{x} = 0.853$ mBq/g
Sample standard deviation:	$s = 0.029$ mBq/g
Significant level of the <i>t</i> -test:	$\alpha = 0.05$

3. *t*-Test Statistic Value:

$$\begin{aligned}t\text{-Test statistic value} &= (\bar{x} - m_0)/(s/\sqrt{n}) \\ &= (0.853 - 0.864)/[0.029/\sqrt{5}] \\ &= -0.1696\end{aligned}$$

4. Cutoff Values:

Upper 2.5% point of  $t_{(n-1)}$  distribution = 2.776 (See Table A-1 on page 10)

Lower 2.5% point of  $t_{(n-1)}$  distribution = -2.776 (See Table A-1 on page 10)

Case 1: If test statistic value < lower cutoff value, then conclude method is invalid with negative bias relative to the certified value.

Case 2: If test statistic value > upper cutoff value, then conclude method is invalid with positive bias relative to the certified value.

Case 3: If neither of the above, then conclude method is valid.

**Answer:** Since the laboratory's test statistic value of -0.1696 is neither > the upper cutoff value of 2.776 nor < the lower cutoff value of -2.776, then conclude: the laboratory's method for Pu-238 analysis is valid.

Table A-1. Probability points of the  $t$  distribution with  $(n-1)$  degrees of freedom.

degrees of freedom ( $n-1$ )	tail area probability (cutoff values)	
	Upper 2.5%	Lower 2.5%
1	12.706	-12.706
2	4.303	-4.303
3	3.182	-3.182
4	2.776	-2.776
5	2.571	-2.571
6	2.447	-2.447
7	2.365	-2.365
8	2.306	-2.306
9	2.262	-2.262
10	2.228	-2.228