National Institute of Standards & Technology

Certificate

Standard Reference Material 4357
Ocean Sediment Environmental Radioactivity Standard

This Standard Reference Material (SRM) is a blend of ocean sediments collected off the coast of Sellafield, UK, and in the Chesapeake Bay, USA. The SRM has been developed in cooperation with member laboratories of the International Committee for Radionuclide Metrology and expert national laboratories. The SRM is intended for use in tests of measurements of environmental radioactivity contained in matrices similar to the sample, for evaluating analytical methods, and as a generally available calibrated "real" sample matrix for interlaboratory intercomparisons.

Radiological Hazard

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

Chemical Hazard

The SRM is a dried sterilized sediment and poses no chemical 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 opening 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 the applicable national, international, and carrier regulations.

Preparation

This Standard Reference Material was prepared in the Physics Laboratory, Ionizing Radiation Division, Radioactivity Group, J.M.R. Hutchinson, Group Leader. The overall technical direction leading to certification was provided by K.G.W. Inn of the Radioactivity Group.

Statistical support was provided by J.J. Filliben, E.S. Lagergren, W.S. Liggett, N.F. Zhang, and K.R. Eberhardt 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 N.M. Trahey.

Gaithersburg, Maryland 20899
March 1997

Thomas E. Gills, Chief
Standard Reference Materials Program

Details of the SRM Preparation

This SRM is a blend of material collected off the coast of Sellafield, UK, and in the Chesapeake Bay, USA, in the weight ratio of 1:200, respectively. A. Knight and M. Measures of the National Radiological Protection Board, UK, collected, sieved to -200 mesh, dried and analyzed the Sellafield Sediment before sending it to NIST. The Chesapeake Bay sediment was freeze dried, blended with the Sellafield sediment, sterilized with 50 kiloGrays of ^{60}Co radiation, and pulverized with a "pancake-style" air-jet mill. The average particle diameter for the resulting powder is approximately 6 µm and more than 99 percent, by weight, of the particles are less than 20 µm in diameter.

Instructions for Drying

When nonvolatile radionuclides are to be determined, working samples of this SRM should be dried in air at 40°C for 24 hours prior to weighing. Volatile radionuclides (e.g., ^{137}Cs, ^{210}Pb and ^{212}Pb) 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 certified values This procedure ensures that these radionuclides are not lost during drying. The weight loss on drying is typically less than 2 percent.

Heterogeneity

This material has been measured using sample sizes of 10 grams to 100 grams, for which heterogeneity of gamma-ray-emitting radionuclides has been detectable. Furthermore, heterogeneity has been detected at a sample size of 10 grams for ^{90}Sr and transuranium radionuclides. The expected variation of measurements due to heterogeneity has been incorporated in the certified tolerance limits and in the uncertainty of mean concentration values. The certified values for radionuclides with a normal distribution of analytical measurements are listed in Table 1. Table 2 lists the certified values for radionuclides with a non-normal distribution of analytical measurements. It is recommended that a sample size of 10 grams or larger be used for radiometric and radiochemical analysis.

Radionuclide Leachability

All actinides and their daughters are approximately 87 percent removed from the sample by HNO_3 or HNO_3-HCl leaching procedures. Total sample digestion or non-destructive analysis is required to produce results that can be compared to those listed in this certificate.

Application of the Certified Values

When 5 or more measurements are available, compute the sample mean and ascertain that the mean falls within the certified mean plus uncertainties interval. When 4 or fewer measurements are available, then ascertain that all of the individual values are within the certified tolerance limits interval.

Material Stability and Changes in Certified Values

This matrix is considered to be stable; however, its stability has not been rigorously assessed. NIST will monitor this material and will report any substantive changes in certified values to the purchaser. The attached registration card must be returned in order to receive such notifications.

Technical Contacts

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PROPERTIES OF SRM 4357

Source identification number	NIST SRM 4357
Physical Properties:	
Source description	Powder in polyethylene bottle
Mass	Approximately 85 g
Radiological Properties:	
Radionuclides	See Tables 1, 2, and 3
Reference time	16 February 1994
Massic activities [a]*	See Tables 1, 2, and 3
Relative uncertainties [b]	See Tables 1 and 2
Half lives used in the decay corrections	See Tables 1, 2, and 3
Measuring instruments and methods	See Tables 1, 2, and 3

Calculation of the Uncertainties

The bootstrap is a computationally-intensive statistical procedure for estimating and computing the uncertainty of a statistic whose form is complicated and/or whose underlying assumptions (e.g., normality) are non-standard. The virtue of the procedure is that it provides a straightforward, rigorous methodology for computing uncertainties that would otherwise be difficult to obtain. See reference [4].

The bootstrap was utilized here for calculation of the mean and the tolerance limits. The calculations of these statistics are complicated because the normality of some of the data is suspect. The usual underlying assumptions do not hold due to a variety of experimental conditions, including interlaboratory biases, within-laboratory methodology differences, and material heterogeneity.

Procedurally, the bootstrap estimate for the uncertainty of a statistic (e.g., the mean) is obtained as follows:

1. From the original sample of n observations, compute the statistic of interest (e.g., the mean).

2. From the original n data points, extract a random sample (with replacement) of n points (this becomes the bootstrap sample).

3. Compute the statistic of interest (e.g., the mean) 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.

*Notes and references are on pages 9 and 10.

Table 1: Certified Massic Activities for Radionuclides with a Normal Distribution of Measurement Results

Radio-nuclide	Mean ± $2s_m$ [c]* ($mBq \cdot g^{-1}$)	2.5 to 97.5 Percent Tolerance Limit [d] ($mBq \cdot g^{-1}$)	Number of Assays	Half Life (a) [f]	Analytical Method(s) See page 7	Contributing Laboratories
^{40}K	225 ± 5	190 - 259	31	$(1.277 \pm 0.008) \times 10^{9}$	3a	KU, MAFF, NIR, NPL, YAEL
^{226}Ra	12.7 ± 0.4	10.3 - 15.0	21	1600 ± 7	3a	EML, IT, KU, NPL
^{228}Ra	13.3 ± 0.8	9.2 - 17.4	20	5.75 ± 0.03	3a	IT, KU, NPL
^{228}Th	12.1 ± 0.3	9.7 - 14.6	40	1.9131 ± 0.0009	1c,3a	EML, KU, LGC, MAFF, NIST, NPL, OSUH, YAEL
^{230}Th	12.0 ± 0.5	9.6 - 14.4	18	75380 ± 300	1c	LGC, NIST, OSUH
^{232}Th	13.0 ± 0.3	11.6 - 14.3	18	$(1.405 \pm 0.006) \times 10^{10}$	1c	LGC, NIST, OSUH

Table 2: Certified Massic Activities for Radionuclides with a Non-Normal Distribution of Measurement Results

Radio-nuclide	Mean ± $2s_m$ [c] ($mBq \cdot g^{-1}$)	2.5 to 97.5 Percent Tolerance Limit [e] ($mBq \cdot g^{-1}$)	Number of Assays	Half Life (a) [f]	Analytical Method(s) See page 7	Contributing Laboratories
^{90}Sr	4.4 ± 0.3	2.1 - 8.4	49	28.78 ± 0.04	1b,2d	EML, LGC, MAFF, NE, NRPB, YAEL
^{137}Cs	12.7 ± 0.2	10.8 - 15.9	76	30.07 ± 0.03	3a	EML, IT, KU, LGC, MAFF, NE, NIR, NPL, ORNL, OSUB, YAEL
^{238}Pu	2.29 ± 0.05	1.96 - 2.98	65	87.7 ± 0.3	1c,4c	EML, GAU, LGC, MAFF, NIST, OSUB, RESL
^{239}Pu + ^{240}Pu	10.4 ± 0.2	9.3 - 13.2	84	24110 ± 30 6564 ± 11	1c,3a,4e	EML, GAU, IT, LGC, MAFF, NIST, OSUB, OSUH, RESL

*Notes and references are on pages 9 and 10.

Table 3: 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 ($mBq \cdot g^{-1}$)	Range of Reported Results ($mBq \cdot g^{-1}$)	Number of Assays	Half Life (a) [f]*	Analytical Method(s) See page 7	Contributing Laboratories
^{129}I	0.009	0.006 - 0.012	6	$(1.57 \pm 0.04) \times 10^{7}$	5a	NIR
^{155}Eu	1.4	1.2 - 1.5	2	4.68 ± 0.05	3a	MAFF
^{210}Po	14	12 - 15	5	138.376 ± 0.002 d	3a	OSUH
^{210}Pb	24	14 - 35	19	22.3 ± 0.2	3a	IT, ORNL
^{212}Pb	14	13 - 14	5	10.64 ± 0.01 h	3a	MAFF
^{214}Bi	15	9 - 20	5	19.9 ± 0.4 m	3a	MAFF
^{234}U	12	9 - 15	68	$(2.45 \pm 0.02) \times 10^{5}$	1c,3a	AWE, IT, LGC, OSUH, NIST, RESL
^{235}U	0.6	0.1 - 1.4	63	$(7.038 \pm 0.006) \times 10^{8}$	1c,3a,4c	AWE, GAU, IT, NIST, NPL, RESL
^{237}Np	0.007	0.004 - 0.009	9	$(2.14 \pm 0.01) \times 10^{6}$	1c,3a	LRM, KU
^{238}U	12	7 - 16	76	$(4.468 \pm 0.003) \times 10^{9}$	1c,3a,4c	AWE, GAU, IT, LGC, NIST, OSUH, RESL
^{241}Am	10	7 - 18	97	432.7 ± 0.6	1c,3a	AWE, BNF, IT, KU, LGC, MAFF, NIST, NPL, ORNL, OSUB, RESL

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 2.

*Notes and references are on pages 9 and 10.

Table 4: Semi-quantitative Emission Spectrographic Analysis of SRM 4357. These values are not certified. [g]

Element	$\mu g \cdot g^{-1}$	Element	$\mu g \cdot g^{-1}$	Element	$\mu g \cdot g^{-1}$
Ag	0.12	Ho	<6.8	Re	<10
Al	24700	I	3.1 [h]	Rh	<2.2
As	<100	In	<10	Ru	<2.2
Au	<6.8	Ir	<15	Sb	<68
B	34	K	5070	Sc	2.8
Ba	143	La	25	Si	>340000
Be	<0.1	Li	<68	Sm	<10
Bi	<10	Lu	<15	Sn	<4.6
Ca	6267	Mg	3930	Sr	64
Cd	<32	Mn	163	Ta	<320
Ce	<43	Mo	1.8	Tb	<32
Co	2.9	Na	4000	Th	<46
Cr	27	Nb	10	Tl	<10
Cu	82	Nd	<32	Tm	<4.6
Dy	<22	Ni	97	U	<220
Er	<4.6	Os	<15	V	21
Eu	<2.2	P	<680	W	<15
Fe	10700	Pb	12	Y	12
Ga	3.5	Pd	<1.0	Yb	1.8
Gd	<32	Pr	<100	Zn	45
Ge	<4.6	Pt	<2.2	Zr	540
Hf	<150				

*Notes and references are on pages 9 and 10.

Analytical Methods

1. HF-HNO_3 or HF-HNO_3-$HClO_4$ dissolution
2. NaOH-HCl leach
3. Non-destructive analysis
4. Fusion
5. Heat oxidation and charcoal-filter trapping

a. Germanium gamma-ray spectrometer
b. Thin-window beta-particle geiger counter
c. Silicon surface-barrier alpha-particle spectrometer
d. Plastic-phosphor beta-particle scintillation counter
e. Thermal-ionization mass spectrometer

Participating Laboratories and Personnel

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*Notes and references are on pages 9 and 10.

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*Notes and references are on pages 9 and 10.

NOTES

[a] **Massic activity** is the preferred name for the quantity activity divided by the total mass of the sample. See reference [1].

[b] For further information on the expression of uncertainties, see references [2] and [3].

[c] The stated uncertainty is two time the standard deviation of the mean.

[d] Normal tolerance limit for 95 percent confidence and 95 percent coverage. See reference [5].

[e] Weibull tolerance limit for 95 percent confidence and 95 percent coverage.

[f] The stated uncertainty is the standard uncertainty. See reference [6].

[g] Data provided by United States Department of the Interior, Geological Survey, Reston, Virginia.

[h] Data provided by Niedersachsisches Institut fur Radiookologie (NIR), Hannover, GE.

[j] Retired

[k] Now at the U.S. Department of Energy, Richland, Washington.

[m] Independent consultant.

[n] EIChroM Industries, Inc.

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REFERENCES

[1] 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.

[2] 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".)

[3] 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.

[4] B. Efron and R.J. Tibshirani, *An Introduction to the Bootstrap*, Monographs on Statistics & Applied Probability 57, 1993, Chapman and Hall, New York.

[5] M.G. Natrella, *Experimental Statistics*, National Bureau of Standards Handbook 91, 1963. Available from the Superintendent of Documents, U.S. Government Printing Office, Washington, DC 20402, U.S.A.

[6] Evaluated Nuclear Structure Data File (ENSDF), January 1996.