National Institute of Standards & Technology

Certificate

Standard Reference Material® 4353A

Rocky Flats Soil Number 2

This Standard Reference Material (SRM) has been developed in cooperation with member laboratories of the International Committee for Radionuclide Metrology and other experienced metrology laboratories. The SRM consists of approximately 90 grams of air-dried, pulverized soil in a polyethylene bottle. The SRM 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 intercomparison.

Radiological Hazards: This SRM contains low levels of anthropogenic and natural radioactivity and poses no radiological hazard. The SRM should be used only by qualified persons.

Chemical Hazards: The SRM is a dried sterilized soil and poses no chemical or 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 opening in a chemical hood and 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 under the leadership of the Physics Laboratory, Ionizing Radiation Division, Radioactivity Group, Michael Unterweger, Acting Group Leader. The overall technical direction leading to the certification of this SRM was provided by Svetlana Nour and Kenneth G.W. Inn of the Radioactivity Group.

Statistical support was provided by James 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 NIST Measurement Services Division.

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Details of the SRM preparation: This SRM is from the Rocky Flats Plant in north-central Colorado. The material was obtained from Rockwell International's Rocky Flats Plant (RFP) by the National Institute of Standards and Technology (NIST) of the U.S. Departments of Commerce and by the Environmental Measurements Laboratory (EML) of the U.S. Department of Homeland Security. The material was first coarsely sieved in the field to remove rocks larger than about 1.5 cm diameter. After air drying, the soil was blade milled twice. The soil was pulverized with a "pancake" style air jet mill to an average particle diameter of 8 µm. More than 99 percent, by weight, of the particles are less than 20 µm in diameter. The SRM was "V-cone" blended to optimize homogeneity and bottled in polyethylene bottles. The final bottled SRM was sterilized with > 50 kGy of ^{60}Co radiation to satisfy export regulations and to increase shelf-life time.

Instructions for Drying: When nonvolatile radionuclides are to be determined, working samples of this SRM should be dried at 40°C for 24 hours prior to weighing. Volatile radionuclides (e.g., ^{210}Po, ^{137}Cs, ^{210}Pb, ^{212}Pb and ^{214}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 with the values given by this certificate. This procedure ensures that these radionuclides are not lost during drying (see Reference [1]*). The weight loss on drying is typically less than 4 percent.

Heterogeneity: Twenty-three bottles of the SRM were examined for gamma-ray heterogeneity by measuring their emission rates by counting them on a "5-in" (12.7 cm) NaI(Tl) detector coupled to a multichannel analyzer. The count rates from each measurement were analyzed for statistical difference for ten selected energy regions, and no detectable heterogeneity was observed.

This material has also been measured for alpha-particle emitting radionuclides using sample sizes of 1 gram to 100 grams. There are variations of results due to sample size. Based on over 100 plutonium and ^{241}Am measurements it was concluded that the material contains "hot" particles, and it is recommended that a sample size of 5 grams to 10 grams be used for radiochemical analysis and a sample size of 30 grams to 100 grams for gamma isotopic analysis. Statement of uncertainties, tolerance limits, and ranges of reported results incorporate the effects of heterogeneity.

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 certification to the purchaser. Return of the enclosed registration card is mandatory to receive such notifications. The properties of the SRM are given in Table 1.

Calculation of Certified Massic Activity Values: The certified massic activity value for each nuclide (see Tables 2, 3 and 4) was determined from the evaluated average of the individual laboratory means. This approach was selected because of the well-behaved normal distribution of the laboratories' data.

Calculation of the Uncertainties for the Certified Values: The standard combined uncertainties (u_c) for each of the certified values were computed by incorporating components from three sources: 1) the estimated standard deviation of the mean of the laboratory mean values, 2) the $k = 1$ uncertainty associated with the radiochemical tracer SRMs, and 3) Type B scientific judgment. The uncertainty components were combined in quadrature as specified by the GUM. The expanded uncertainties (U) were computed using the Welch-Satterthwaite coverage factor. The expanded uncertainty (U) is taken as the 95 percent confidence interval.

 *Notes and references are on page 11

Calculation of Certified Tolerance Limits: In addition to the certified massic activities and activity ratios, and their respective uncertainty values, Tables 2, 3, and 4 also provide 95/95 (normal) tolerance limits. Whereas the certified value is the mean of the population of measurements of the SRM and the expanded uncertainty for the certified value is at the 95 percent confidence limit, the tolerance limits are a measure of the spread of the population of measurements across the SRM. A 95/95 tolerance limit means that NIST is 95% confident that 95% of the population of SRM measurements fall within the specified limits. The tolerance limits are used when the number of replicates is small (n<5), e.g., when the material is used as a periodic QC sample. For guidance on the use of tolerance limits in connection with this SRM, see Appendix 1.

Uncertified Massic Activities and Mass Ratios: The massic activities and mass ratios for the radionuclides given in Table 5 and 6 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 to contribute to the certification process. The data should be sent to one of the technical contacts listed on page 1.

Elemental Composition: Semi-quantitative elemental analysis of the Rocky Flats Number 2 matrix is listed in Table 8.

Table 1: Properties of SRM 4353A.

Certified Properties

Radionuclides	**See Table 2, 3 and 4**
Reference time	**1 April 1998**
Certified massic activities	**See Table 2, and 3**
Certified activity ratios	**See Table 4**
Uncertainties (See Note 1)*	**See Table 2, 3 and 4**
Tolerance Limits	**See Table 2, 3 and 4**

Uncertified Properties

Source description	Rocky Flats Soil Number 2, approximately 90 g in a polyethylene bottle
Uncertified massic activities	See Table 5
Uncertified activity ratios	See Table 6
Range of reported values	See Tables 5 and 6
Half-lives used	See Table 7
Radiochemical and detection methods	See Table 7 and 9
Elemental composition	See Table 8
Participating laboratories and personnel	See Table 7 and 10

 *Notes and references are on page 11

Table 2: Certified Massic Activities.†

Radionuclide	**Massic Activity and uncertainty ($mBq•g^{-1}$)** (See Note 2)*	**95/95 Tolerance Limit ($mBq•g^{-1}$)** (See Note 3)
^{238}Pu	**0.278 ± 0.041**	**0.18 to 0.51**
^{239,240}Pu	**16.8 ± 1.8**	**6.0 to 26.8**
^{238}U	**39.6 ± 3.0**	**31.9 to 48.1**
^{234}U	**40.4± 3.0**	**33.7 to 47.7**
^{235}U	**1.88 ± 0.53**	**0.82 to 2.68**
^{90}Sr	**10.5 ±1.3**	**6.5 to 15.1**

† Recommended sample size of at least 5 grams for radiochemical analysis. Refer to table 7 for uncertified information.

Table 3: Certified Massic Activities.‡

Radionuclide	**Massic Activity and uncertainty ($mBq•g^{-1}$)** (See Note 2)	**95/95 Tolerance Limit ($mBq•g^{-1}$)** (See Note 3)
^{137}Cs	**21.6 ± 2.6**	**13.7 to 30.0**
^{228}Ra (See Note 4)	**74.9 ± 7.5**	**61.4 to 91.6**
^{210}Pb	**58.0 ± 9.9**	**41.8 to 79.7**

‡ Recommended sample size of at least 30 grams for gamma-ray measurement. Refer to table 7 for uncertified information.

Table 4: Certified Activity Ratios.ϒ

Radionuclides Ratio	**Ratio and uncertainty**	**95/95 Tolerance Limit** (See Note 3)
^{234}U / ^{238}U	**1.028 ± 0.036**	**0.92 to 1.14**
^{238}Pu / (^{239}Pu+^{240}Pu)	**0.017 ± 0.001**	**0.013 to 0.020**
^{228}Th / ^{232}Th	**1.01 ± 0.10**	**0.84 to 1.14**
^{230}Th / ^{232}Th	**0.671 ± 0.067**	**0.55 to 0.76**

ϒ Refer to table 7 for uncertified information.

 *Notes and references are on page 11

Table 5: Uncertified Massic Activities.†

Radionuclide	Massic Activity ($mBq \cdot g^{-1}$)	Lower and Upper Values of Reported Results ($mBq \cdot g^{-1}$)
^{228}Th	72.4	61.6 to 88.4
^{230}Th	47.9	40.9 to 57.8
^{232}Th	73.6	62.1 to 90.2
^{234}Th	60.1	28.9 to 103.3
^{226}Ra	42.4	28.4 to 52.7
^{214}Pb	43.2	34.9 to 51.9
^{214}Bi	40.6	28.4 to 53.2
^{212}Pb	90.2	83.3 to 95.7
^{212}Bi	79.5	68.8 to 87.3
^{208}Tl	51.3	26.8 to 67.7
^{40}K	589	533 to 719
^{241}Pu	17.0	13.0 to 30.0
^{241}Am (alpha spectrometry)	2.5	0.6 to 5.4
^{241}Am (gamma spectrometry)	4.7	3.7 to 6.6

† Radionuclides for which insufficient numbers of data sets or for which unresolved discrepant data sets were obtained. No uncertainties are provided because no meaningful estimates could be made. Refer to table 7 for uncertified information.

Table 6: Uncertified Mass Ratios.‡

Radionuclides	Mass Ratio	Lower and Upper Values of Reported Results
^{240}Pu / ^{239}Pu	5.6 10^{-2}	(5.3 to 6.0) 10^{-2}
^{241}Pu / ^{239}Pu	5.8 10^{-4}	(0.4 to 1.3) 10^{-3}
^{241}Pu / ^{240}Pu	1.0 10^{-2}	(0.8 to 2.3) 10^{-2}

‡ Ratios for which insufficient numbers of data sets or for which unresolved discrepant data sets were obtained. No uncertainties are provided because no meaningful estimate could be made. Refer to table 7 for uncertified information.

Table 7: Uncertified Information for Tables 2 through 6.

Radionuclides	**Number of Laboratories (and total assays)**	**Half Life** (See Note 5)*	**Methods** (Table 9)	**Contributing Laboratories Acronym** (Table 10)
^{238}Pu	14 (169)	(87.7 ± 0.1) a	2b, 3b	BIL-GSL, CEMRC, EML, FSU, GSF, IAEA, LANL, NIST, OSU, RESL, SRNL, WHOI
$^{239,240}Pu$	14 (172)	(24110 ± 30) a (6561 ± 7) a	2b, 3b	BIL-GSL, CEMRC, EML, FSU, GSF, IAEA, LANL, NIST, OSU, RESL, SRNL, , WHOI
^{238}U	7 (72)	(4.468 ± 0.003) 10^9 a	2b, 3b, 3 e	CEMRC, EML, FSU, NIST, RESL, SRNL,
^{234}U	7 (72)	(2.455 ± 0.006) 10^5 a	2b, 3b	CEMRC, EML, FSU, NIST, RESL, SRNL,
^{235}U	4 (38)	(7.04 ± 0.01) 10^8 a	2b, 3b	CEMRC, EML NIST, SRNL,
^{90}Sr	5 (38)	(28.79 ± 0.06) a	2c, 3c	EML, IAEA, RESL, WHOI
^{137}Cs	9 (82)	(30.07 ± 0.03) a	1a	BIL-GSL, EML, FSU, LANL, NIST, OSU, RESL, SRNL, , WHOI
^{228}Ra (Note 4)	5 (42)	(5.75 ± 0.03) a	1a	BIL-GSL, FSU, NIST, RESL, SRNL
^{210}Pb	3 (24)	(22.20 ± 0.22) a	1a	FSU, NIST, SRNL
^{234}U / ^{238}U	8 (87)	(2.455 ± 0.006) 10^5 a (4.468 ± 0.003) 10^9 a	2b, 2e	BIL-GSL, CEMRC, EML, FSU, NIST, RESL, SRNL
^{238}Pu / (^{239}Pu+^{240}Pu)	14 (169)	(87.7 ± 0.1) a (24110 ± 30) a (6561 ± 7) a	2b	BIL-GSL, CEMRC, EML, FSU, GSF, IAEA, LANL, NIST, OSU, RESL, SRNL, , WHOI,
^{228}Th / ^{232}Th	3 (27)	(1.9116 ± 0.0016) a (1.40 ± 0.01) 10^{10} a	2b	CEMRC, NIST, RESL
^{230}Th / ^{232}Th	3 (27)	(7.538 ± 0.030) 10^4 a (1.40 ± 0.01) 10^{10} a	2b	CEMRC, NIST, RESL
^{228}Th	3 (27)	(1.9116 ± 0.0016) a	2b, 3b	CEMRC, NIST, RESL
^{230}Th	3 (27)	(7.538 ± 0.030) 10^4 a	2b, 3b	CEMRC, NIST, RESL
^{232}Th	4 (42)	(1.40 ± 0.01) 10^{10} a	2b, 3b, 3 e	CEMRC, IAEA, NIST, RESL
^{234}Th	2 (21)	(24.10 ± 0.03) d	1a	FSU, SRNL
^{226}Ra	4 (38)	(1600 ± 7) a	1a	BIL-GSL, FSU, RESL, SRNL
^{214}Pb	3 (21)	(26.8 ± 0.9) min	1a	BIL-GSL, FSU, SRNL
^{214}Bi	3 (32)	(19.9 ± 0.4) min	1 a	BIL-GSL, FSU, SRNL
^{212}Pb	1 (15)	(10.64 ± 0.01) h	1a	SRNL
^{212}Bi	1 (15)	(60.55 ± 0.06) min	1a	SRNL
^{208}Tl	3 (33)	(3.053 ± 0.004) min	1a	BIL-GSL, FSU, SRNL
^{40}K	2 (30)	(1.248 ± 0.003) 10^9 a	1a	BIL-GSL, SRNL
^{241}Pu	2 (20)	(14.290 ± 0.006) a	2d	IAEA
^{241}Am (α spectrometry)	13 (115)	(432.6 ± 0.6) a	2b, 3b	BIL-GSL, CEMRC, EML, FSU, IAEA, LANL, NIST, OSU, RESL, SRNL, , WHOI

Table 7 (cont.): Uncertified Information for Tables 2 through 6.

Radionuclides	Number of Laboratories (and total assays)	Half Life (See Note 5)*	Methods (Table 9)	Contributing Laboratories Acronym (Table 10)
^{241}Am (γ spectrometry)	3 (24)	(432.6 ± 0.6) a	1a	FSU, NIST, SRNL
^{240}Pu / ^{239}Pu	1 (15)	(24110 ± 30) a (6561 ± 7) a	2e	SRNL
^{241}Pu / ^{239}Pu	1 (15)	(14.290 ± 0.006) a (6561 ± 7) a	2e	SRNL
^{241}Pu / ^{240}Pu	1 (15)	(14.290 ± 0.006) a (24110 ± 30) a	2e	SRNL

Table 8: Elemental Composition Based on Semi-quantitative X-Ray Fluorescence (XRF) analysis[¤]. These values are not certified.

Element	Percent by mass (%)	Element	Percent by mass (%)
Si	36	Cl	0.004
Al	4.5	Cr	0.033
Fe	2.6	Cu	0.003
Mg	0.29	Ga	<0.001
Ca	0.40	Ni	0.018
Na	0.65	Pb	0.003
K	1.7	Rb	0.007
Ti	0.20	Sr	0.011
P	0.07	V	0.004
Mn	0.054	Y	0.002
C	1.5	Zn	0.007
S	0.02	Zr	0.02

[¤] The estimated relative combined standard uncertainty for each reported concentration is from -33 % to +50 %. Data presented by John Sieber, Chemical Science and Technology Laboratory (CSTL).

Table 9: Radiochemical and Detection Methods.

1	Non-destructive
2	Fusion/total decomposition
3	Acid leach (any combination of the following HNO_3, HCl, HF, $HClO_4$)
a	Germanium gamma-ray spectrometer
b	Silicon surface-barrier alpha-particle spectrometer
c	Beta-particle counter
d	Liquid scintillation counter
e	Inductively Coupled Plasma-Mass Spectroscopy (ICP-MS), Atomic Mass Spectroscopy (AMS)

Table 10: Participating Laboratories and Personnel.

Laboratory Acronym	Laboratory	Country	Technical Contact
BIL - GSL	British Nuclear Group Sellfield Ltd.	United Kingdom	Dr. M.Froggatt
CEMRC	Carlsbad Environmental Monitoring & Research Center	United States of America	Dr. B. Stewart
EML	Environmental Measurements Laboratory	United States of America	Dr. H. Volchok, M. Feiner
FSU	Florida State University	United States of America	Dr. W. Burnett
GSF	National Research Center for Environment and Health, Institute of Radiation Protection	Germany	Dr. K.Bunzl
IAEA †	International Atomic Energy Agency	Austria	Dr. J. Moreno, Dr. K.Burns, Dr. G. Kis-Benedek
LANL	Los Alamos National Laboratory	United States of America	Dr. D. Decker, Dr. N. Koski, Dr. S.R. Garcia
NIST	National Institute of Standards and Technology	United States of America	S. Nour, Dr. K. Inn
OSU	Oregon State University	United States of America	Dr. T. Beasley
RESL †	Radiological and Environmental Sciences Laboratory (RESL)	United States of America	Dr. D. Olson , Dr. S. Bohrer
SRNL	Savannah River National Laboratory	United States of America	J. Cadieux
WHOI	Woods Hole Oceanographic Institution	United States of America	Dr. V. Bowen, Dr. H. Livingston

† Note: These laboratories participated twice, reporting two sets of data.

Appendix 1

Recommendations on the use of the certified values for validation of measurements or methods

Case 1. Single Observation
Recommendation.
If a single observation is made, check to see if that value is within the certified 95/95 (95% confidence / 95% coverage) tolerance interval as provided in column 3 of Tables 2, 3, and 4 . If yes, then conclude that the measurement/method process is acceptable; if no, then conclude that the process is questionable and adjust accordingly.

Example.
A laboratory analyzed ^{235}U with a single measurement of this SRM to validate its method. The measured result was 1.86 mBq/g. The NIST certified value (see column 2 of Table 2) is 1.88 mBq/g. Is the laboratory method valid?

Procedure.
Check to determine if the measured value 1.86 is within the tolerance interval as provided in column 3 of Table 2. The tolerance interval for ^{235}U is (0.82, 2.68). Since 1.86 falls within this interval, then conclude that no evidence exists that this process is invalid (that is, in practice, we conclude that the process is valid).

Case 2. Multiple Observations
Recommendation.
If multiple observations are made, then:

1. check that at least 95% of the data points are within the provided tolerance interval (if yes, then accept the process; otherwise, reject the process);
2. check (via the appropriate t-test) that the mean of the collected data points is "close enough" to the provided certified value.

Example.
A laboratory analyzed ^{235}U in 5 replicates of this SRM to validate its method. The analytical results were 1.86, 1.99, 1.85, 1.87, and 1.86 mBq/g. The NIST certified value is 1.88 mBq/g. Is the laboratory method valid?

Procedure.
1. Check to determine the proportion of the 5 measured values that are within the 95/95 tolerance interval (0.82, 2.68) as provided in column 3 of Table 2 (at least 95% of the 5 values should fall within). Since 5 out of 5 of the values fall within the interval, then we conclude that the process is valid.

2: Compare the mean of the 5 collected points (1.866) with the certified value (1.88) by performing the t-test .

2.1. NIST's Certified Value: m = 1.88 mBq/g (see Table 2)

2.2. Compute Laboratory Data Summary Statistics:

Sample size	$n = 5$
Sample mean	$x = 1.866$ mBq/g
Sample standard deviation	$s = 0.015$ mBq/g
Significant level of the t-test	$\alpha = 0.05$

2.3. Compute t-test Statistic Value:

t-test statistic value $= (x - m)/(s/(n)^{1/2})$

$= (1.866 - 1.88)/(0.015/(5)^{1/2})$

$= -2.064$

2.4. Determine Cutoff Values for 95 % Confidence:

Upper 2.5% point of $t_{(n-1)}$ distribution = 2.776 (See Table A1)
Lower 2.5% point of $t_{(n-1)}$ distribution = -2.776 (See Table A1)

3. Conclusions:

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

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

3.3 If neither of the above, then conclude method is valid.

Example's Conclusion: Since the laboratory's test statistic value of -2.064 is neither > the upper cutoff value of 2.776 nor < the lower cutoff value of -2.776, case 3 applies and it can be concluded that the laboratory's method for ^{235}U analysis is valid.

Table A1: Probability points of the t distribution with (n-1) degrees of freedom.

Degrees of freedom	Tail area probability, $t_{(n-1)}$ (cutoff values)	
(n-1)	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

NOTES FOR TABLES 1, 2, 3 AND 7

Note 1. For further information on the expression of uncertainties, see references [3] and [4].

Note 2. The mean is the evaluated reference value from measurement results by the participating laboratories. The stated uncertainty is the 95% confidence interval based on a student-t distribution.

Note 3. The tolerance limits are for 95 percent confidence and 95 percent coverage. Differences between laboratories have been eliminated so that the given limits reflect only between-measurement differences.

Note 4. Radium-228 activity values are based on measurements of its ^{228}Ac daughter.

Note 5. The stated uncertainty of the half-life is the standard uncertainty. See reference [5].

REFERENCES

[1] R. Bock, *A Handbook of Decomposition Methods in Analytical Chemistry*, International Textbook Company, Limited. T. & A. Constable Ltd., Great Britain, 1979.

[2] M. G. Natrella, Experimental Statistics, Handbook 91, 1963, United States Department of Commerce National Bureau of Standards

[3] 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, USA. 1-212-642-4900. (Listed under ISO miscellaneous publications as "ISO Guide to the Expression 1993".)

[4] 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, USA.

[5] Evaluated Nuclear Structure Data File (ENSDF), online database, National Nuclear Data Center, Brookhaven Laboratory (Upton, NY), November 2006. Refer to http://www.nndc.bnl.gov/ensdf/