National Institute of Standards and Technology

Certificate

Standard Reference Material® 4359

Seaweed Radionuclide Standard

This Standard Reference Material (SRM) is a blend of seaweed collected off the coast of Ireland and the White Sea. The SRM has been developed in cooperation with member laboratories of the International Committee for Radionuclide Metrology (ICRM) and experienced metrology laboratories. The SRM is intended for use in tests of measurements of radioactivity contained in matrices similar to the sample; the evaluation of analytical methods and as a generally available calibrated "real" sample matrix for laboratory inter-comparison.

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 quality control persons.

Chemical Hazards: The SRM is a dried sterilized seaweed 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 then 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 Iisa Outola and Kenneth 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 NIST Measurement Services Division.

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*Notes and references on page 8.

Details of the SRM preparation: This SRM is a blend of three different seaweed species, which were collected off the western coast of Ireland and the White Sea: *Fucus vesiculosus*, *Laminaria saccharina*, *and Ascophyllum nodosum.* The material was provided by International Specialty Products (ISP) Alginates Ltd. (UK), and Scientific Association "Typhoon" (Russia). The material was first warm-air dried and blade milled. By dry sieving, it was determined that 98 % of particles were smaller than 180 µm. The material was then freeze-dried to a residual moisture below 5 %. It was subsequently blended, pulverized, reblended, freeze-dried and bottled. The seaweed was packaged in 625 mL amber glass bottles with polypropylene-lined caps. The final bottled SRM was sterilized with > 50kGy 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 in air at 60°C for 24 hours prior to weighing. Volatile radionuclides should be determined on samples as received. Separate samples should be dried as previously described to obtain a correction factor for moisture. This correction factor should be applied to the data for volatile radionuclides before comparing the measurement results to that given in this certificate. This procedure ensures that these radionuclides are not lost during drying [1]*. The weight loss on drying is typically less than 4 percent.

Heterogeneity: This material has been measured using sample sizes of 5 grams to 300 grams. The variation of measurements due to sample size was not statistically significant. It is recommended that a sample size of 10 grams or larger be used for radiochemical analysis and a sample size of 30 grams or larger for isotopic analysis based on gamma-ray spectrometry**.**

Radionuclide Disequilibrium: Because of the fractionation caused by natural processes, disequilibrium was found in the decay chain of ^{238}U - ^{234}U - ^{230}Th - ^{226}Ra - ^{210}Pb - ^{210}Po and ^{232}Th - ^{228}Ra - ^{228}Th. Compared with the natural decay chain of ^{238}U and ^{232}Th, this material contains excess amount of ^{210}Pb, ^{210}Po, ^{228}Ra and ^{228}Th. Because the decay chains of ^{238}U and ^{232}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 monitor this material and will report any substantive changes in certification to the purchaser. Should any of the certified values change, purchasers will be notified by NIST. Return of the attached registration card is mandatory to receive such notifications.

*Notes and references on page 8**.**

Table 1: Properties of SRM 4359

Source identification number	NIST SRM 4359
Physical Properties:	
Source description	Freeze dried radiation-sterilized seaweed powder in glass bottle
Mass	Approximately 300 g
Radiological and Chemical Properties:	
Radionuclides	See Tables 2 and 3
Reference time	1 January 2002
Massic activities [a]*	See Tables 2, 3 and statement below
Relative uncertainties [b]	See Table 2 and statement below
Half lives used	See Tables 2 and 3
Measuring instruments and methods	See Tables 2, 3 and 4
Elemental composition	See Table 5

Calculation of the Massic Activity Value: The central value chosen to report the massic activity value for each nuclide (see Tables 2 and 3) was the median of the individual laboratory means. The median was chosen due to its superior robust statistical properties.

Calculation of the Uncertainty for the Certified Value: A general closed-form formula approach does not exist for calculation of the uncertainty for a median (see Table 2). To circumvent this problem, the "bootstrap" statistical method was utilized. The bootstrap method is a general, computationally-intensive procedure for estimating and computing the uncertainty of a statistic whose form is complicated and/or whose underlying assumptions are non-standard. The virtue of the procedure is that it provides a straightforward, rigorous methodology for computing uncertainties that would have otherwise been difficult or impossible to obtain. For specific bootstrap information as related to this SRM, see Appendix 1. For general bootstrap information, see reference 2. Combined expanded (k = 2) uncertainties were calculated by combining the calculated bootstrap uncertainties with the type B uncertainties. The type B uncertainties were based on the uncertainties of diluted NIST SRM solutions that were used as tracers for actinide measurements, and on scientific judgment.

Calculation of Tolerance Limits: In addition to the certified massic activity value and the uncertainty of the certified value, Table 2 also provides 95/95 (normal) tolerance limits. Whereas the certified value is a statistical estimate for the "center" of the population of measurements of SRM bottles, and whereas the uncertainty for the certified value is a statistically-based measure of NIST's confidence in that center point estimate, the tolerance limits are rather a measure of the spread of the population of measurements across SRM bottles themselves. The 95/95 tolerance limits means that NIST is 95 % confident that 95 % of the population of SRM bottle measurements fall within the specified limits. To compute such limits, the lab means were assumed to be normally distributed. For guidance on the use of tolerance limits in connection with this SRM, see Appendix 2.

*Notes and references on page 8.

Table 2: Certified Massic Activities

Radio-nuclide	Median ± U (k=2) [c]* [mBq•g^{-1}]	95/95 Tolerance Limits [d]* (mBq•g^{-1})	Number of laboratories (and total assays)	Half Life[e]* (k=1)	Methods (See Table 4)	Contributing Laboratories (See Table 6)
^{40}K	734 ± 44	685 - 783	14 (70)	(1.248 ± 0.003) 10^9 a	1a, 1b	CEFAS, IFE, IRI, IRSN, ITU, LUND, NLH, NPL, NRPB, PTB, RISØ, STUK, TYPHOON
^{137}Cs	0.933 ± 0.075	0.63 - 1.23	14 (72)	(30.07 ± 0.03) a	1a	IRSN, UAB, IFE, IAEA, ITU, NLH, NIST, LUND, STUK, RISØ, PTB, NRPB, TYPHOON
^{210}Pb	21.0 ± 3.0	11.8 - 30.2	9 (39)	(22.20 ± 0.22) a	1a	ANSTO, CIEMAT, IRSN, KORDI, NPL, PTB, RISØ, TYPHOON, UAB
^{210}Po	20.6 ± 1.5	18.8 - 22.3	5 (19)	(138.376 ± 0.002) d	2d, 3d	ANSTO, KORDI, LUND, UAB
^{228}Ra [f]*	4.32 ± 0.60	2.90 - 5.74	7 (40)	(5.75 ± 0.03) a	1a	IRSN, ITU, KORDI, NIST, NPL, PTB, TYPHOON
^{232}Th	2.40 ± 0.30	1.91 - 2.88	8 (41)	(1.405 ± 0.006) 10^{10} a	1a, 2d, 4d	IAEA, INER, IRI, KORDI, LUND, NIST, RISØ, SOC
^{234}U	9.5 ± 1.1	8.1 - 10.8	10 (64)	(2.455 ± 0.006) 10^5 a	2d, 4d	IAEA, INER, KORDI, LUND, NIST, NLH, PTB, RESL, RISØ, SOC
^{235}U	0.400 ± 0.047	0.285 - 0.514	9 (59)	(7.04 ± 0.01) 10^8 a	2d, 4d	IAEA, INER, KORDI, NIST, NLH, PTB, RESL, RISØ, SOC
^{238}U	8.67 ± 0.54	7.0 - 10.3	12 (70)	(4.468 ± 0.003) 10^9 a	1a, 1b, 2d, 4d	IAEA, INER, IRI, KORDI, LUND, NIST, NLH, NPL, PTB, RISØ, RESL, SOC
^{238}Pu	0.00606 ± 0.00025	0.0034 - 0.0088	6 (39)	(87.7 ± 0.1) a	2d, 3d, 4d	CEFAS, IAEA, IRSN, NIST, PTB, RISØ
^{239}Pu	0.0840 ± 0.0033	0.066 - 0.10	3 (16)	(24110 ± 30) a	2f, 3f	ANU, IRSN, RISØ
^{239,240}Pu	0.1296 ± 0.0075	0.095 - 0.165	16 (100)	(24110 ± 30) a (6561 ± 7) a	2d, 3d, 4d	CEFAS, CIEMAT, IAEA, IFE, INER, IRSN, KORDI, LUND, NIST, NLH, PTB, RESL, RISØ, STUK, UAB
^{241}Am [g]*	0.0432 ± 0.0064	0.029 - 0.057	10 (63)	(432.2 ± 0.7) a	2d, 4d	CEFAS, IRSN, LUND, STUK, RISØ, ITU, RESL, NIST, IAEA, KORDI

*Notes and references on page 8.

Table 3: Uncertified Massic Activities

Radio-nuclide	Median ($mBq \cdot g^{-1}$)	Range of Reported Results ($mBq \cdot g^{-1}$)	Number of laboratories (and total assays)	Half Life [e]* (k=1)	Analytical Methods (See Table 4)	Contributing Laboratories (See Table 6)
^{3}H	1.1		1 (1)	(12.32 ± 0.02) a	5e	IRSN
^{14}C	250[#]		1 (1)	(5700 ± 30) a	5e	IRSN
^{90}Sr	0.26	0.10 - 0.51	5 (25)	(28.79 ± 0.06) a	2c, 3c, 4c, 4e	IAEA, KORDI, PTB, RISØ, TYPHOON
^{99}Tc	38	17 - 48	5 (23)	(2.111 ± 0.012) 10^{5} a	2c, 3c, 2e, 3e	CEFAS, LUND, RISØ, SOC, STUK
^{129}I	0.0149	0.0148 – 0.0151	1 (5)	(1.57 ± 0.04) 10^{7} a	5f	IsoTrace
^{208}Tl	1.3	1.1 - 1.5	2 (6)	(3.053 ± 0.004) min	1a	IRSN, ITU
^{212}Bi	4.5	3.7 - 6.2	2 (6)	(60.55 ± 0.06) min	1a	IRSN, ITU
^{212}Pb	4.0	3.6 - 4.5	2 (6)	(10.64 ± 0.01) h	1a	IRSN, ITU
^{224}Ra	3,8		1 (1)	(3.66 ± 0.04) d		IRSN
^{226}Ra [f]*	5.7	3.8 – 9.5	7 (66)	(1600 ± 7) a	1a	ANSTO, IRSN, ITU, KORD, NPL, PTB, RISØ
^{228}Th	3.6	1.0 - 4.8	8 (46)	(1.9116 ± 0.0016) a	1a, 2d, 4d	IAEA, INER, KORDI, LUND, NIST, NPL, PTB, RISØ
^{230}Th	3.3	1.3 - 4.6	7 (40)	(75380 ± 300) a	2d, 4d	IAEA, INER, KORDI, LUND, NIST, RISØ, SOC
^{234}Th	7.9		1 (1)	(24.10 ± 0.03) d	1a	IRSN
^{237}Np	0.173	0.152 - 0.198	1 (10)	(2.144 ± 0.007) 10^{6}	2f	RISØ
^{240}Pu	0.06	0.049 - 0.070	3 (16)	(6561 ± 7) a	2f, 3f	ANU, IRSN, RISØ

[#] mBq/g carbon

The data are provided for information only.

*Notes and references on page 8.

Table 4: Radiochemical and Detection Methods

1	Non-destructive
2	Calcinations, acid leach (any combination of the following HNO_3, HCl, HF, $HClO_4$)
3	Acid leach (any combination of the following HNO_3, HCl, HF, $HClO_4$)
4	Fusion/total decomposition
5	Combustion
a	Germanium gamma-ray spectrometer
b	Neutron activation analysis
c	Beta-particle counter
d	Silicon surface-barrier alpha-particle spectrometer
e	Liquid scintillation counter
f	ICP-MS, AMS

Table 5: Semi-quantitative composition of SRM 4359, expressed as common oxides % determined by X-ray fluorescence analysis from ashed seaweed material. These values are not certified.

Oxide	%	Oxide	%
F	<0.01	Cr_2O_3	<0.002
Na_2O	18.0	MnO	0.085
MgO	7.0	Fe_2O_3	1.6
Al_2O_3	1.4	NiO	0.015
SiO_2	5.5	CuO	<0.002
P_2O_5	1.5	ZnO	0.012
SO_3	26.7	Br	0.44
Cl	14.2	SrO	0.31
K_2O	13.1	Y_2O_3	0.31
CaO	10.0	I	<0.002
TiO_2	0.12	BaO	0.038

Table 6: Participating Laboratories and Personnel

Abbreviation	Laboratory	Country	Personnel
ANSTO	Australian Nuclear Science and Technology Organization	Australia	G.A. Peck, J. Twining
ANU	Australian National University	Australia	S.G. Tims, L.K. Fifield
CEFAS	The Centre for Environment, Fisheries and Aquaculture Science	United Kingdom	P. Smedley
CIEMAT	Centro de Investigaciones Energeticas, Mediambientales y Tecnologicas	Spain	M.P. Antón, C. Cascó
IAEA	IAEA Marine Laboratory	Monaco	J. La Rosa, M. K. Pham, P. Povinec, J.A. Sanchez
IFE	Institute for Energy Technology	Norway	A. Raaum
INER	Institute of Nuclear Energy Research	Republic of China	H.-J. Wei
IRI	Interfaculty Reactor Institute	The Netherlands	G.C. Krijger
IRSN	Institut de Radioprotection et de Sûreté Nucléaire	France	P. Bouisset
IsoTrace	IsoTrace Laboratory	Canada	A.E. Litherland, W.E. Kieser
ITU	Institute for Transuranium Elements	Germany	M. Betti, L. Aldave de las Heras
KORDI	Korea Ocean Research and Development Institute	Korea	G.H. Hong
LUND	Department of Radiation Physics, Lund University	Sweden	E. Holm
NIST	National Institute of Standards and Technology	United States of America	I. Outola, K. Inn, C.A. McMahon
NLH	Agricultural University of Norway	Norway	L. Skipperud
NPL	National Physical Laboratory	United Kingdom	A.V. Harms, A. Arinc
NRPB	National Radiological Protection Board	United Kingdom	M. Youngman
PTB	Physikalisch-Technische Bundesanstalt	Germany	D. Arnold, H. Wershofen
RESL	Radiological and Environmental Sciences Laboratory	United States of America	D.S. Sill, S. Bohrer
RISO	Risø National Laboratory	Denmark	H. Dahlgaard
SOC	Southampton Oceanography Centre	United Kingdom	I.W. Croudace, P.E. Warwick
STUK	Radiation and Nuclear Safety Authority	Finland	T.K. Ikäheimonen, S. Klemola
TYPHOON	Scientific Production Association "Typhoon"	Russia	S.M. Vakulovsky
UAB	Universitat Autonoma de Barcelona	Spain	J.A. Sanchez-Cabeza

NOTES FOR TABLE 1, 2 AND 3

[a] "**Massic activity**" is the preferred name for the quantity activity divided by the total mass of the sample. See appendix 1 and reference [3].

[b] For further information on the expression of uncertainties, see references [4] and [5].

[c] The median reflects the best consensus value over participating laboratories. The stated uncertainty is obtained by multiplying the combined uncertainty by a coverage factor, k = 2.

[d] The tolerance limits are for 95 percent confidence and 95 percent coverage. Between laboratory differences have been eliminated so that the given limits reflect only between bottle differences.

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

[f] The ^{228}Ra massic activity is based on measurements of its short-lived daughter, ^{228}Ac; and ^{226}Ra activity values are based on measurements of ^{214}Bi and ^{214}Pb.

[g] The ^{241}Am massic activity is certified as of the reference date. No certified ^{241}Pu massic acitivity values are currently available.

[h] The uncertified massic activities in Table 3 are for radionuclides for which insufficient numbers of data sets, or for which discrepant data sets were obtained. No uncertainties are provided because no meaningful estimates could be made. The data 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.

REFERENCES

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

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

[3] 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, USA. 1-212-642-4900

[4] 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".)

[5] 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. Goverment Printing Office, Washington, DC 20402 (USA).

[6] Evaluated Nuclear Structure Data File (ENSDF), April 2005.

Appendix 1

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

1. From the original sample of *n* observations (that is, the *n* laboratory means), compute the statistic of interest (e.g., the median of the means).

2. Compute a bootstrap sample – that is a random sample -- with replacement -- from the original *n* points. The bootstrap sample is constructed to also be of size *n*. The bootstrap sample will be similar to – but not identical to – the original sample of *n* laboratory means.

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

Appendix 2

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

If a single observation is made, that value should be within the certified tolerance interval (see Table 2) 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.

An example on the use of tolerance limits follows:

Question: A laboratory analyzed ^{235}U in 5 replicates of this SRM to validate its method. The analytical results were 0.30, 0.35, 0.40, 0.39, and 0.47 mBq/g. The NIST certified value is 0.40 mBq/g. Is the laboratory method valid?

The simplest t-test to address this question would treat the NIST value as a reference constant, to which the laboratory measurements are to be compared. We performed this t-test as follows:

1. NIST's Certified Value: m = 0.400 mBq/g (see Table 2)

2. Laboratory Data Summary Statistics:

Sample size	$n = 5$
Sample mean	$x = 0.382$ mBq/g
Sample standard deviation	$s = 0.063$ mBq/g
Significant level of the t-test	$\alpha = 0.05$

3. t-Test Statistic Value:

t-Test statistic value $= (x - m)/(s/(n)^{1/2})$
$= (0.38 - 0.40)/(0.063/(5)^{1/2})$
$= -0.710$

4. Cutoff Values:

Upper 2.5 % point of $t_{(n\text{-}1)}$ distribution = 2.776 (See Table A2)
Lower 2.5 % point of $t_{(n\text{-}1)}$ distribution = -2.776 (See Table A2)

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 -0.710 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 A2: Probability points of the t distribution with (*n*-1) degrees of freedom

Degrees of freedom	Tail area probability (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