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Development of the NIST Rocky Flats Soil Standard

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The National Institute of Standards and Technology (NIST) Rocky Flats Soil-II Standard reference material (SRM) is being certified through a statistical analysis of results from an interlaboratory comparison of fourteen laboratories from four countries. Mean values were calculated as the most robust and reliable certified values for each of the radionuclides. Twenty two radionuclides and four isotopes ratios were evaluated based on reported data. This article describes the approach for establishing the certified values and uncertainties for the radionuclides in the Rocky Flats Soil II SRM.

Introduction

Standard reference materials (SRMs) are needed for method validation, quality control, calibration of measuring devices, and for data comparability of low-level radioactivity measurements. A new radionuclide natural matrix SRM is being developed from low organic-low carbonate soil collected at the former Rocky Flats Plant in north-central Colorado. The area around the Rocky Flats Plant has been studied over many years because it was contaminated with transuranic elements during its operation. Previous studies identified considerable contamination of the soil.[1,2,5–7]

Over 1000 bottles of RFS-II were produced to provide the radiochemistry community with an anticipated 20-year supply of the SRM. The certification of the soil standard reference material is being accomplished through an intercomparison with fourteen participating highly experienced laboratories from four different countries (Table 1) who volunteered to participate in this project.

This paper discusses the statistical approach used to derive the certified values for the SRM.

Material characterization

More than 100 kg of soil was collected from the western part of the Rocky Flats Plant and labeled Rocky Flats Soil II (RFS-II) that will be certified as SRM 4353A. The material was collected by Rockwell International's Rocky Flats Plant (RFP), the National Institute of Standards and Technology (NIST) of the US Department of Commerce, and the Environmental Measurements Laboratory (EML) of the US Department of Energy (DOE). Initially, the material was first coarsely sieved in the field to remove rocks larger than about 1.5 cm diameter. The soil was air dried, and then blade milled twice and air-jet pulverized. The SRM was "V-cone" blended with an intensifier bar to assure homogeneity, bottled in polyethylene bottles, and sterilized with >50 kGy of ^{60}Co gamma-radiation to satisfy export regulations and to increase shelf-life.[6]

X-ray fluorescence analysis (XRF) for the RFS-II showed a high content of silicates (36%) and low content of carbonates (1.5%).

In order to assess the sample heterogeneity twenty-three randomly chosen 90-g bottles containing RFS-II randomly selected were examined for their gamma-ray-emission rates by counting them in a 5 in. (12.5 cm) NaI(Tl) detector coupled to a multichannel analyzer. The count rates from each measurement were analyzed for statistical differences for ten selected energy regions, and no detectable heterogeneity was observed. This test was conducted before the bottles were shipped to the laboratory participants. Additional tests of heterogeneity were performed for radionuclide-specific content in the soil. Normal probability plots were used to evaluate the laboratory data sets for heterogeneity. Non-normal character of the data would have suggested either sample heterogeneity or that the analyses were not under control. The Analysis of Variance (ANOVA) test was used to evaluate the within versus between bottles differences.

Interlaboratory measurements

Interlaboratory comparisons are used to certify NIST natural-matrix radionuclide SRMs. Fourteen laboratories who were involved in the Rocky Flats Soil SRM project reported radioanalytical results for a total of 22 radionuclides. Each laboratory received five bottles of soil and NIST tracer solutions for ^{243}Am, ^{242}Pu, ^{232}U, and ^{229}Th to provide a common reference base for actinide measurements. The participants used radioanalytical methodologies for which they had the most experience. The participating laboratories were

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asked to provide at least one result for each of the five bottles for each of the analyzed radionuclides. Eight laboratories reported three replicates values for each bottle of material for certain radionuclides.

Data analysis

A minimum criteria for certifying a radionuclide is to have essential agreement between results reported by at least three laboratories. Statistical analyses of the data provided the assessment of sample homogeneity, sample size effects, and radioanalytical methodology bias.

Figure 1 shows the procedure for the statistical evaluation of the reported data. All data were screened by laboratory for each radionuclide using descriptive statistical tools[4] that include normal probability plot, box and whisker plot, analysis of variance (ANOVA), means plot, *t*-test, *F*-test, and Outlier-tests. The data from each laboratory was evaluated for potential outlying values (e.g., for ^{239}Pu + ^{240}Pu, Figs 2–5).

Heterogeneity and sample size effects

For each laboratory that had reported replicate results the difference of within versus between bottles was evaluated: eight laboratories analyzed three replicates within each of their five bottles for Pu isotopes, five laboratories for ^{241}Am, four laboratories for U isotopes, three laboratories for ^{137}Cs, two laboratories for Th isotopes, ^{228}Ra, and ^{214}Bi, and one laboratory for ^{90}Sr, ^{226}Ra, ^{210}Pb, and ^{214}Pb. ANOVA, *F*-test, and *t*-test were used for the evaluation of radionuclide specific heterogeneity estimation (Fig. 6). Although no significant evidence of heterogeneity was found between bottles, within bottle heterogeneity was detected.

Two laboratories performed analyses on different sample sizes for ^{238}Pu, ^{239,240}Pu, and ^{241}Am. Using ANOVA and the *F*-test, a difference between the reported mean values for the two sets of sample size data was found (Fig. 7). Furthermore, data for smaller sample size have more variability than bigger sample size, which leads to the recommendation that sample sizes of more than five grams should be used for actinide radiochemical analyses.

Table 1. Participating laboratories and personnel

Abbreviation	Laboratory	Country
FSU	Florida State University	USA
GSF	National Research Center for Environment and Health, Institute of Radiation Protection	Germany
IAEA*-1998	International Atomic Energy Agency, Seibersdorf	Austria
RESL*-2004	Radiological and Environmental Sciences Laboratory	USA
LANL	Los Alamos National Laboratory	USA
CEMRC	Carlsbad Environmental Monitoring & Research Center	USA
IAEA*-2004	International Atomic Energy Agency, Seibersdorf	Austria
NIST	National Institute of Standards and Technology	USA
SRNL	Savannah River National Laboratory	USA
EML	Environnemental Monitoring Laboratory	USA
RESL*-80s*	Radiological and Environmental Sciences Laboratory	USA
WHOI	Woods Hole Oceanographic Institution	USA
OSU	Oregon State University	USA
BIL-GSL	British Nuclear Fuels (BNFL) Geoffrey Schofield Laboratory (GSL).	UK

* Laboratories performed the analysis in different times (RESL and IAEA).

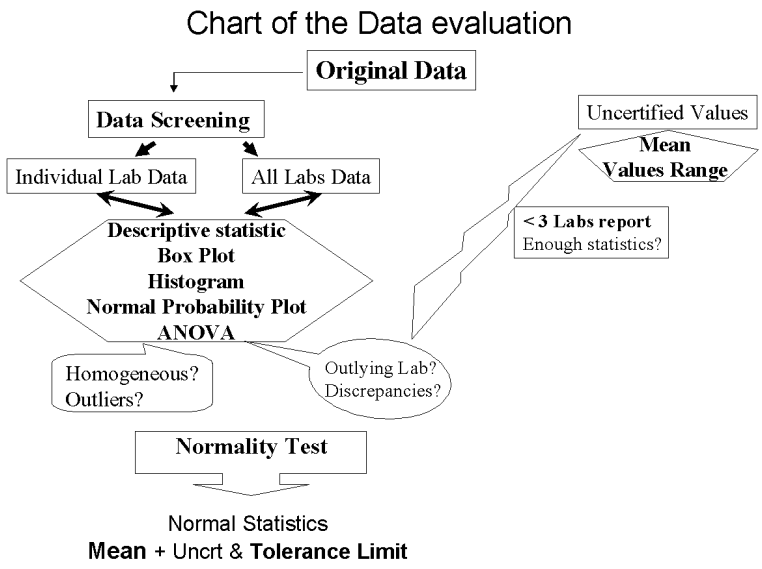

Fig. 1. Procedure for the statistical analyses of the intercomparison project

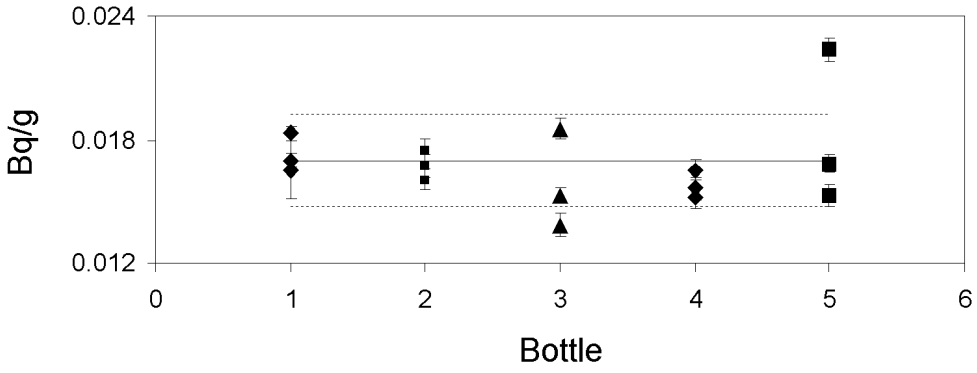

Fig. 2. Replicate massic activity ^{239,240}Pu determinations from RFS-II for one laboratory. The solid line represents the massic activity mean value and the dotted lines indicate the expanded uncertainty ($k = 2$) of the mean

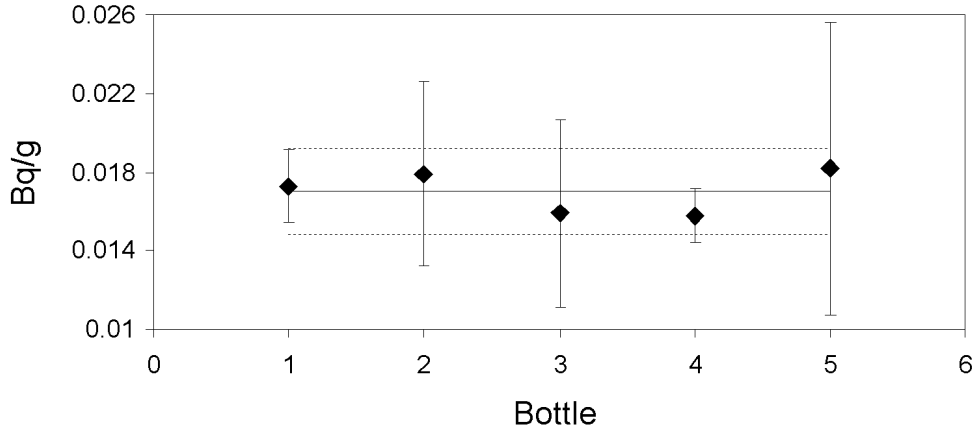

Fig. 3. Mean bottle massic activity ^{239,240}Pu from RFS-II for one laboratory. The solid line represents the massic activity mean value and the dotted lines indicate the expanded uncertainty ($k = 2$)

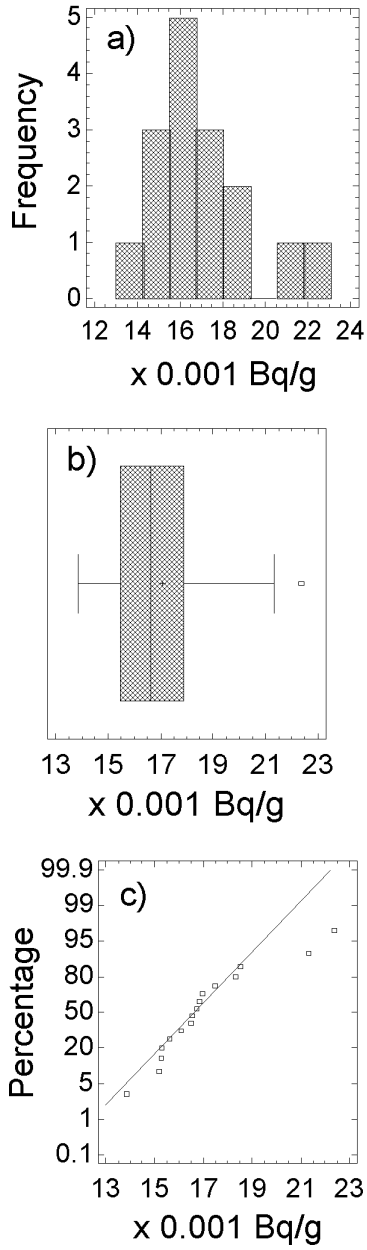

Fig. 4. Histogram (a), box-and-whisker plot (b), and normal probability plot (c) techniques for $^{239}Pu+^{240}Pu$ massic activity values to test for potential outlying values within a laboratory's replicates data set

Radioanalytical methodology bias

Laboratories used different matrix decomposition methodologies such as acid leaching, total dissolution, fusion, or non-destructive methods. They also used gamma-, alpha-, beta-spectroscopy or else, liquid scintillation counting (LSC) measurement methods. ANOVA analyses shows that there is no difference between the means, medians, and distributions of the leaching and fusion dissolution methods for $^{239,240}Pu$ data at the 95% confidence level, and there was only a slight difference between the standard deviations of measurement results from these two dissolution methods (Fig. 8).

Thirteen laboratories analyzed the soil for ^{241}Am. Eleven laboratories used alpha spectrometry, and three laboratories used gamma-spectrometry. A significant difference between the measuring techniques was detected by ANOVA. The difference is due to influences from sample decomposition techniques, instrument calibration, sample size, and inter-laboratory differences.

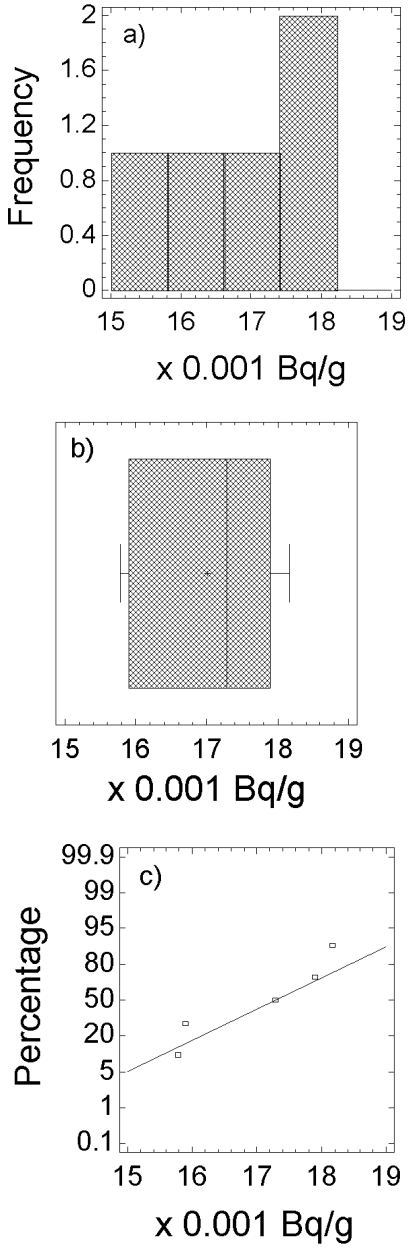

Fig. 5. Histogram (a), box-and-whisker plot (b), and normal probability plot (c) for $^{239,240}Pu$ massic activity values to test for outlying values amongst a laboratory's bottles mean values

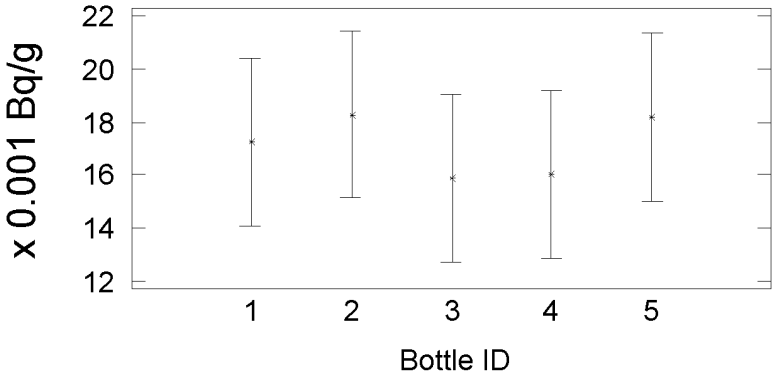

Fig. 6. Graphical view of massic activity difference between bottles based on ^{239,240}Pu data as an example

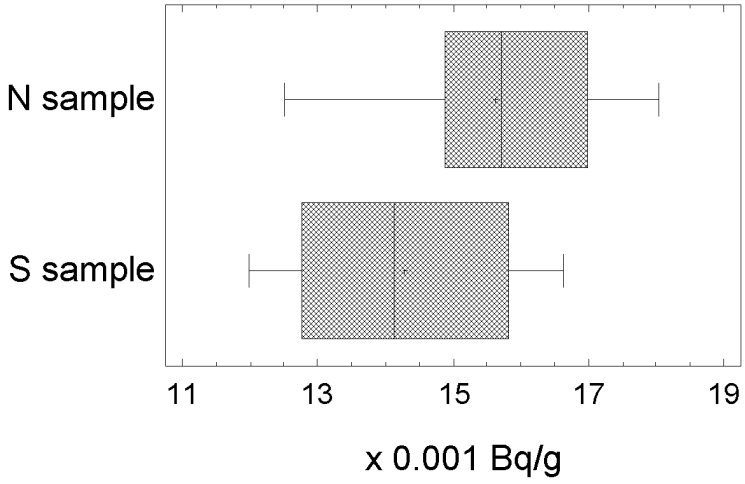

Fig. 7. Graphical view of the effect of sample size on ^{239,240}Pu massic activity within one laboratory that had two sets of data: for normal size samples (N sample = 10 g) and for small size samples (S sample = 1 g)

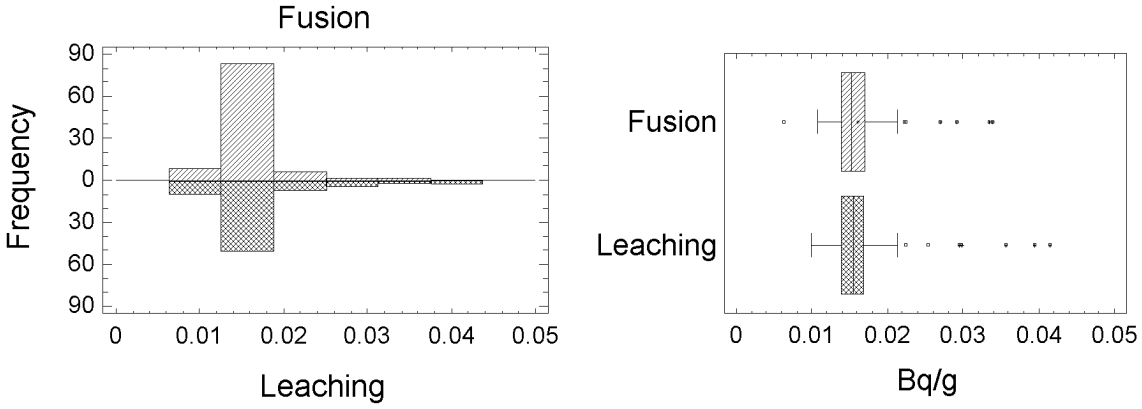

Fig. 8. Box-and-whisker plot (a) and frequency distribution (b) of ^{239,240}Pu massic activity for leaching and fusion methods of sample dissolution for difference of dissolution methods

Because of the 50% relative difference between alpha spectrometry (2.49 mBq/g±0.53 mBq/g, $k=2$) and gamma-spectrometry (4.75 mBq/g±0.85 mBq/g, $k=2$) measurements, all of the data were not combined into an overall mean (2.91 mBq/g±0.69 mBq/g). Two uncertified ^{241}Am values, based on alpha- and gamma-measurements, will be reported in the RFS-II certificate as information values.[8]

Hot particles

The data from each laboratory was plotted for each radionuclide on normal probability plots to test the distribution of the data. Any non-normal characteristics of the data in this type of plot would suggest either sample heterogeneity or that the analyses were not under control. Results from the normal probability tests are shown in Table 2. The values in the table are the ratio, n, between the observed normal probability plot correlation coefficient, $PPCC$,[3] and the expected theoretical critical value, CV, ($n=PPCC/CV$). The data set is considered to be normally distributed (95% confidence) if $n>1$. From 48 sets of data sets with replicate values, twelve were found to be non-normally distributed: one data set each for ^{238}U and ^{241}Am, six data sets for ^{238}Pu, and four data sets for $^{239,\,240}$Pu. From the mean values of 99 data sets of bottles two data sets for $^{239,\,240}$Pu, one for ^{90}Sr, and one for ^{241}Am are not normally distributed. Based on the previous discussion on the heterogeneity evaluations, the non-normal data sets for ^{238}U and ^{90}Sr are likely due to the lack of statistical control. However, the non-normal character of the data for ^{238}Pu, $^{239,\,240}$Pu, and ^{241}Am are more complicated. The ANOVA tests showed that there is no difference between bottles within each laboratory's results, but there is within bottle heterogeneity. The transuranium contamination at the Rocky Flats was distributed on the soil particles called 'hot particles'. These 'hot particles' (non-refractory) are distributed uniformly between the bottles, but the particles are heterogeneously distributed over small sample masses. The certificate will contain explicit recommendations regarding the sub-sampling the soil from the SRM bottle, i.e., mixing the bottle before sampling, and using a sample size of at least five grams for radiochemical actinide analysis.

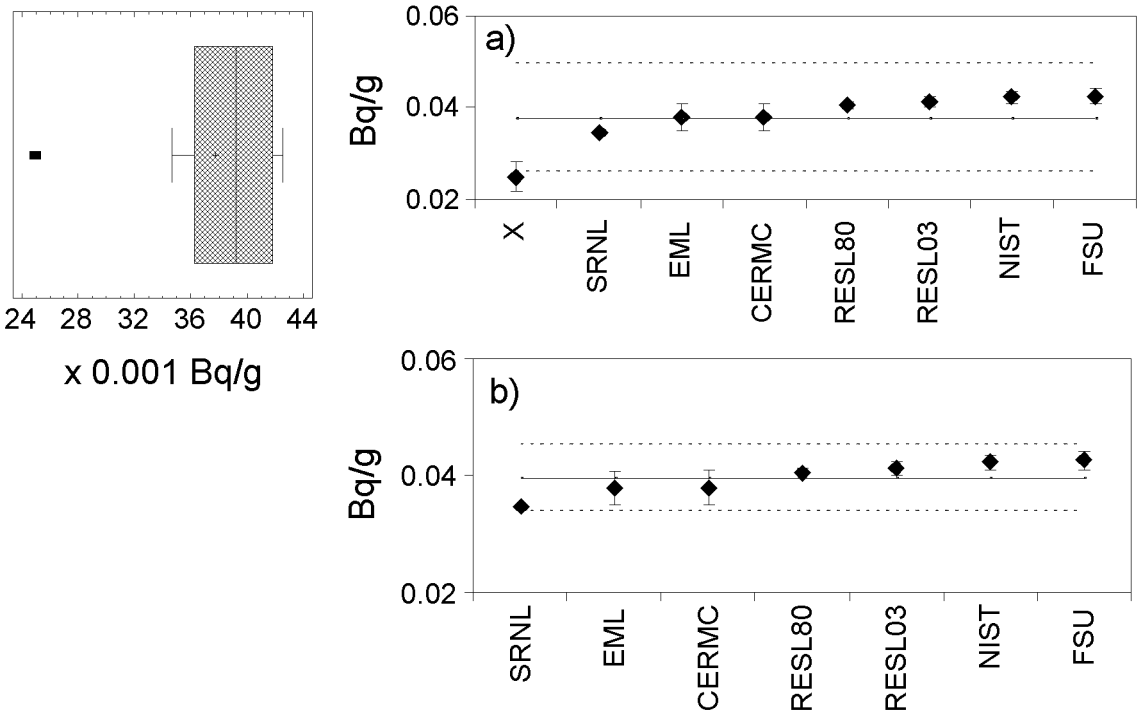

Fig. 9. Massic activities of ^{238}U in RFS-II of laboratories' mean values and their expanded uncertainty ($k=2$) for: (a) – eight laboratories mean values with an outlier (the box-and-whisker plot test indicating an outlier is shown on the upper left side of the figure; and (b) – seven laboratories mean values excluding the outlier. The solid line represents the mean for the radionuclide and the dotted lines indicate the expanded uncertainty ($k=2$) of the mean

Table 2. Ratio of *PPCC/CV* (observed/theoretical) from the normality test

Lab	Estimate	^{137}Cs	^{210}Pb	^{214}Pb	^{214}Bi	^{228}Ra	^{226}Ra	^{234}U	^{235}U	^{238}U	^{238}Pu	^{239,240}Pu	^{90}Sr	^{228}Th	^{230}Th	^{232}Th	^{241}Am alpha
FSU	**1**	>1*	>1*	>1*	>1*	>1*	>1*	1.04		1.10	1.08	1.08					
	2							1.04		**0.85**	**0.95**	**0.96**					
GSF	**1**										1.11	1.07					
	2										1.04	**0.90**					
IAEA98	**1**										1.04	1.09	1.13				1.12
	2										**0.98**	**0.89**	1.05				**0.99**
RESL03	**1**							1.12		1.15	1.11	1.11					1.12
	2							1.05		1.04	1.05	1.04					1.04
LANL	**1**	1.11									1.00	1.01					1.03
	2	1.01									**0.96**	1.02					1.04
CERMC	**1**							1.13	1.06	1.09	1.02	1.01		1.01	1.07	1.05	1.07
IAEA04	**1**										1.11	**0.94**	**0.96**			1.06	
NIST	**1**	1.09	1.09			1.07		1.10	1.08	1.10	1.1	1.08		1.11	1.10	1.06	1.09
	2							1.04	0.96	1.05	**0.98**	1.00		1.04	1.03	1.02	1.04
SRNL	**1**	1.10	1.10	1.06	1.05	1.09		1.12	1.04	1.07	1.11	1.05					
	2	0.99	1.05	1.04	1.03	1.04		1.05	1.03	1.04	**0.92**	**0.94**					
EML	**1**	>1*						>1*		>1*	1.01	1.1	1.13				1.08
RESL80	**1**	>1*		>1*		>1*	1.04	>1*	>1	>1*	1.07	**0.98**	1.10	1.09	1.07	1.09	**0.92**
WHOI	**1**	1.08									1.02	1.06	1.10				1.03
OSU	**1**	>1*									>1*	>1*					
UK-BIL-GSL	**1**	1.11			1.10	1.10	1.10				1.01	1.09		1.12	1.10	1.10	1.05
	2	1.04			1.03	1.05	1.03				**0.96**	1.04		1.05	1.03	1.05	1.06

1 – Estimation of bottle means (5 values).

2 – Estimation of all the replicates (>15 values).

* There are 3 values in the data set.

The values in the table are the ratio between the observed normal probability plot correlation coefficient (PPCC)[3] and the expected theoretical critical value (*CV*) ($n = PPCC/CV$).

The data set is considered to be normally distributed (95% confidence) if $n>1$.

Resolving discrepant laboratory results

The certified value for each radionuclide was calculated based on the evaluated mean of the laboratories' bottle means. After a detailed statistical data analyses, the results were discussed with all the participants to resolve inter-laboratory discrepancies. After self re-evaluation, each laboratory had the opportunity to voluntarily withdraw data and one laboratory decided to withdraw its U results. When the inter-laboratory discrepancies could not be resolved, no data were discarded without strong scientific justification. The resulting U data set with and without the withdrawn result is shown in Fig. 9. The discrepant laboratory's measurement ratio of $^{234}U/^{238}U$ was unaffected by its analytical bias, and was included in the certification of the $^{234}U/^{238}U$ ratio.

Results and conclusions

All the laboratories mean data are normally distributed after the withdrawal of one U result. The certified values will be derived from the mean of the laboratories means and the expanded uncertainty will be estimated based on the standard deviation of these means ($k=2$). Based on the statistical data analyses eleven radionuclides and four isotopes ratios will be certified: ^{238}Pu, $^{239,240}Pu$, ^{238}U, ^{234}U, ^{235}U, ^{228}Th, ^{230}Th, ^{232}Th, ^{228}Ra, ^{137}Cs, ^{90}Sr, $^{234}U/^{238}U$, $^{238}Pu/^{239,240}Pu$, $^{228}Th/^{232}Th$, and $^{230}Th/^{232}Th$. An uncertainty for a certified radionuclide will be provided only where the "true value" is asserted to lie with 95% confidence. Data for eleven radionuclides will be reported in the certificate as information values because there is either insufficient data, unresolved inter-laboratory discrepancies, or the uncertainty of the value is so large that it diminishes the purpose of a certified value. Uncertified values will consist of the mean value of the data and the range of the reported values for the radionuclide; no uncertainty estimations will be provided. The certificate will recommend using a sample size for analyses not less than five grams for actinide radiochemical measurements.

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