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Interlaboratory Comparison Radionuclides in Irish Sea Water

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Interlaboratory Comparison Radionuclides in Irish Sea Water IAEA-443



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> INTERLABORATORY COMPARISON RADIONUCLIDES IN IRISH SEA WATER IAEA-443

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FOREWORD

Our society is giving increasing importance to the study and assessment of the state and health of the environment. Organizations involved in such activities rely on the quality of the information provided and, ultimately, on the precision and accuracy of the data on which the information is based. Many laboratories are involved in the production of environmental data, in many cases leading to wider assessments. These laboratories may develop and validate new analytical methods, study the environmental impact of human activities, provide services to other organizations, etc. In particular, laboratories are providing data on levels of radioactivity in a variety of marine matrixes such as water, suspended matter, sediments and biota. Because of the need to base scientific conclusions on valid and internationally comparable data, the need to provide policy makers with correct information and the need for society to be informed of the state of the environment, it is indispensable to ensure the quality of the data produced by each laboratory.

Principles of good laboratory practice require both internal and external procedures to verify the quality of the data produced. Internal quality is verified in a number of ways, such as the use of laboratory information systems, keeping full records of equipment performance and standardization of analytical procedures. External quality can also be ascertained in a number of ways, notably accreditation by an external body under a defined quality scheme but also, amongst others, the use of internationally accepted calibration standards that are traceable to the SI international system of units, the participation in interlaboratory comparisons or the regular use of Reference Materials to test laboratory performance.

The Radiometrics Laboratory of the International Atomic Energy Agency's Marine Environment Laboratories has been providing quality products for the last 40 years, which include the organization of interlaboratory comparisons, production of Reference Materials and Certified Reference Materials, and training. More than 40 Reference Materials have been produced, which include a wide range of marine sample matrices and radionuclide concentrations.

As part of these activities, a new interlaboratory comparison was organized to provide the participating laboratories with the possibility of testing the performance of their analytical methods on a seawater sample with elevated radionuclide levels due to discharges from a nuclear facility. The material was designed for the analysis of anthropogenic and natural radionuclides in sea water. It is expected that the sample, after successful certification, will be issued as a Certified Reference Material for radionuclides in sea water.

Laboratories were informed that, after the completion of the exercise, an IAEA report describing the results of the interlaboratory comparison would be issued, including their identities, but that the results would not be associated with each laboratory's identity.

The IAEA officers responsible for this publication were M.K. Pham and J.-A. Sanchez-Cabeza of the IAEA Marine Environment Laboratories in Monaco.

EDITORIAL NOTE

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1. INTRODUCTION

The accurate and precise determination of radionuclide concentrations in marine samples are important aspects of marine radioactivity assessments and the use of radionuclides in studies of oceanographic processes. To address the problem of data quality, the IAEA Marine Environment Laboratories (IAEA-MEL) in Monaco regularly conduct interlaboratory comparisons of radionuclides in marine samples as part of its contribution to the IAEA's Programme of Analytical Quality Control Services (AQCS) [1-2].

In collaboration with IAEA-MEL, the Federal Maritime and Hydrographical Agency, Hamburg, Germany (BSH) collected sea water from the Irish Sea in 1993. A part of the sample was forwarded to IAEA-MEL and was used for the IAEA-381 interlaboratory comparison on anthropogenic and natural radionuclides. The results obtained from 28 laboratories were reported [3-4] and the IAEA-381 Certified Reference Material was issued. In 2005, 1100L of this sample, kept by the Risø National Laboratory, Denmark (Risø), was provided to IAEA-MEL. This sample was used to organize, in collaboration with the Oslo-Paris Commission (OSPAR), an interlaboratory comparison for OSPAR laboratories (13 laboratories from 10 OSPAR contracting parties) to test their performance in analysing radionuclides in sea water. The results of this exercise will allow IAEA-MEL to produce a new Reference Material (RM), replacing IAEA-381 (out of provision) and to test the stability of the sample after 15 years' conservation in high density polyethylene container.

As the sample was collected in the Irish Sea, elevated levels of anthropogenic radionuclides were expected due to discharges from the Sellafield reprocessing plant. Participants were informed that the expected activities for anthropogenic radionuclides would be in the ranges $(mBq kg^{-1})$:

$${}^{90}{\rm Sr} : 50{-}500 \\ {}^{137}{\rm Cs} : 100{-}1000 \\ {}^{239{+}240}{\rm Pu} : 1{-}50 \\ {}^{241}{\rm Am} : 1{-}50$$

This report describes the results obtained from 12 laboratories on anthropogenic and natural radionuclide determinations in sea water.

2. SCOPE OF THE INTERLABORATORY COMPARISON

This interlaboratory comparison was organized to provide the participating laboratories with the possibility to test the performance of their analytical methods on a seawater sample with elevated radionuclide levels due to discharges from a nuclear facility.

The intercomparison material was designed for the analysis of anthropogenic and natural radionuclides. Participating laboratories were requested to determine as many radionuclides as possible by gamma spectrometry, transuranium radionuclides and other radionuclides requiring radiochemical separation and alpha or beta counting.

It is expected that the sample, after successful certification, will be issued as a Certified Reference Material for radionuclides in sea water [5].

3. DESCRIPTION OF THE MATERIAL

About 3600 litres of surface water were collected by BSH on September 7, 1993, onboard the Research Vessel *Valdivia*. Sampling was performed during a transect between two shallow (*circa* 20 m water depth) stations located at 54°24,89' N - 3°33,62' W and 54°23,2'N - 3°33,45'W. Water was sampled from 5 m water depth, stored in 600 L containers and acidified to pH<1 immediately without prior filtration.

4. HOMOGENEITY TESTS

The sample received in 2005 was transferred into a container of 1500 L and mixed for 4 hours using two pumps, aliquoted into 5 L cubitainers and coded as IAEA-443. Sample homogeneity was checked by measuring ¹³⁷Cs, ⁴⁰K ⁹⁰Sr, ²³⁸Pu and ²³⁹⁺²⁴⁰Pu activities (by using high resolution low background gamma spectrometry, low level beta proportional counter and alpha spectrometry) in 2 L aliquots from 5 cubitainers chosen at random. Homogeneity was tested by using one-way analysis of variance. The coefficient of variation was below 10% for all radionuclides analysed (Table 1, Appendix I). On the basis of the homogeneity tests (Figs 1 and 2, Appendix II for ¹³⁷Cs and ²³⁹⁺²⁴⁰Pu, for instance), the sample could be considered sufficiently homogeneous for the assayed radionuclides for volumes of over 2 L.

5. SAMPLE DISPATCH AND DATA RETURN

Each participant received 5 L of the seawater sample. For each radionuclide analysed, the following information was requested:

- Average weight of sample
- Number of analyses
- Massic activity calculated in net values (i.e. corrected for blank, background etc.)
- and expressed in Bq kg⁻¹
- Estimate of the total uncertainty (counting and other uncertainties)
- Description of chemical procedures and counting equipment
- Reference standard solutions used
- Chemical recoveries, counting time, half-life.

The reference date for reporting activities was 1 January 2007.

The samples were distributed to 13 laboratories in June 2007. The deadline for reporting data was set for 1 January 2008. A reminder was sent to late participants. A total of 12 laboratories sent their reports. The list of reported radionuclides is given in Table 2, Appendix I.

Laboratories were informed that, after the completion of the exercise, an IAEA report describing the results of the interlaboratory comparison would be issued, including their identities, but that the results would not be associated to each laboratory identity.

6. EVALUATION OF RESULTS

6.1. DATA TREATMENT

The submitted results are shown under their laboratory code numbers in Tables 3 to 8, Appendix I. Laboratory means were calculated when necessary from individual results and are given either as arithmetic means with corresponding uncertainties when more than two

results were reported, or as weighted means with weighted uncertainties in the case of only two results reported. All values have been rounded off to the most significant figure.

6.2. STATISTICAL EVALUATION

The principles and applications of the statistical programme used for the evaluation of data have been described in a previous report [4]. Calculations are based on the assumption of non-parametric distribution of data to which distribution-free statistics are applicable. The "less than" values are segregated from the results and the remaining values are checked for the presence of outliers using a box and whisker plot test. Outliers are identified in the tables with an asterisk. Median values are calculated from all results passing the test. These values are considered to be the most reliable estimates of the true values. Confidence intervals were taken from a non-parametric sample population. They represent a two-sided interval representing 95% confidence limits.

Massic activities for 14 radionuclides were reported and results are shown in Table 2, Appendix I with the number of reporting laboratories for each radionuclide. The number of reported "less than" values are shown in parentheses. The results for the most frequently measured radionuclides can be found in Tables 3 to 8, Appendix I and Figures 3 to 9, Appendix II, while the less frequently measured radionuclides are presented in Table 9, Appendix I. The recommended values and information values obtained after statistical treatment are presented in Table 10, Appendix I.

Following the International Union of Pure and Applied Chemistry (IUPAC) [6] and the International Organization for Standardization (ISO) [7] recommendations for assessment of laboratory performance, the Z-score methodology was used for the evaluation of the intercomparison results. The performance of a laboratory was considered to be acceptable if the difference between the robust mean of the laboratory and the assigned value is less than or equal to two. The analysis is regarded as being out of control when |Z| > 3.

6.3. EXPLANATION OF TABLES

6.3.1. Laboratory code

Each laboratory was assigned an individual code number to ensure anonymity.

6.3.2. Method code

The analytical techniques employed by participants are specified with following codes:

Alpha spectrometry

Code Method A Treatment, evaporation/precipitation, ion exchange, electro-deposition follow by alpha spectrometry.

Beta counting

Code	Method
B0	Low level GM counter
B1	LSC (Liquid Scintillation Counter)
B2	Precipitation (oxalate, hydroxide), scavenging, beta counting of Y oxalate follow by
	beta counting (low level proportional gas counter)

Gamma spectrometry

Code	Method
G	High resolution Ge spectrometry

Mass spectrometry

Code	Method
ICPMS	Treatment, ion exchange, electro-deposition, leaching, ICP-MS (Inductively Coupled
	Plasma Mass Spectrometry).

6.3.3. Number of results

The number of determinations corresponds to the number of individual results from which the laboratory mean was calculated. When no mention was made in a participant's report as to the number of measurements made, it was assumed to be one.

6.3.4. Massic activity

The activity corresponds to the arithmetical or weighted mean computed from all the individual results obtained from the participants with the corresponding standard deviation or weighted uncertainty.

6.4. EXPLANATION OF FIGURES

The figures (Figs 3 to 9, Appendix II) present the data with the corresponding standard deviation or weighted uncertainty in order of ascending massic activity. Also shown are:

- (i) the distribution medians (full lines) and corresponding confidence intervals (dashed horizontal lines),
- (ii) the limits for accepted laboratory means (vertical lines).

The performance of laboratories in terms of accuracy was expressed by Z-scores, which were calculated for each radionuclide. Figures 10 to 16 in Appendix III present the Z-scores for accepted values only. The distributions of Z-scores are symmetric which indicates that the overall performance of the laboratories was satisfactory.

6.5. CRITERIA FOR RECOMMENDATION

Median values and confidence intervals (95% significance level) were calculated as estimations of true massic activities. The median values of the data within the confidence interval were considered as the **recommended values** when:

- 1. At least 5 laboratory means were available, calculated from at least 3 different laboratories.
- 2. The relative uncertainty of the median did not exceed \pm 5% for activities higher than 100 Bq kg⁻¹, \pm 10% for activities from 1-100 Bq kg⁻¹ and \pm 20% for activities lower than 1 Bq kg⁻¹.

An activity value was classified as an **information value** when it satisfies condition 1, but not condition 2.

7. RESULTS AND DISCUSSION

7.1. ANTHROPOGENIC RADIONUCLIDES

Results of the analysis of ³H, ⁹⁰Sr, ¹³⁷Cs, ²³⁸Pu, ²³⁹⁺²⁴⁰Pu, and ²⁴¹Am reported by participants are presented in Table 3, Tables 5 to 8, Appendix I, Figure 3 and Figures 5 to 9, Appendix II.

7.1.1.³H

Data were reported from seven laboratories (Table 3, Appendix I, Fig. 3, Appendix II). The data showed good homogeneity and all data passed the outlier test. The Z-score (Fig. 10, Appendix III) is below 1.7, showing good performance. The median, given as the information value, is 37 Bq kg⁻¹ (95% confidence interval is 33-41 Bq kg⁻¹).

7.1.2. ⁹⁰Sr

Data were reported from seven laboratories (Table 5, Appendix I, Fig. 5, Appendix II). All the data passed the outlier test and showed good homogeneity. Z-score values are below 1.6, showing good performance by the laboratories (Fig. 12, Appendix III). The median, given as the information value, is 107 mBq kg⁻¹ (95% confidence interval is 89–115 mBq kg⁻¹).

7.1.3.¹³⁷Cs

Data were reported from 11 laboratories (Table 6, Appendix I, Fig. 6, Appendix II). The laboratories mainly used direct gamma spectrometry for ¹³⁷Cs analysis. The data is homogenous within two standard deviations of the distribution mean. Z-score values are below 1.7, showing good performance by the laboratories (Fig. 13, Appendix III). The median, given as the recommended value, is 0.36 Bq kg⁻¹ (95% confidence interval is 0.34–0.37 Bq kg⁻¹).

7.1.4.²³⁸Pu

Six data sets were reported (Table 7, Appendix I, Fig. 7, Appendix II), one of them reported a value as LLD (Lower Limit of Detection). Five results did pass the outlier test and showed good homogeneity, within two standard deviations of the distribution mean. Z-score values are below 1.5, showing good performance by the laboratories (Fig. 14, Appendix III). The median, given as the recommended value, is 3.1 mBq kg⁻¹ (95% confidence interval is 2.9–3.3 mBq kg⁻¹).

7.1.5.²³⁹⁺²⁴⁰Pu

Six data sets were reported (Table 7, Appendix I, Fig. 8, Appendix II), one of them reported a value as LLD. The majority of participants used a conventional method based on sample treatment, ion-exchange separation followed by electrodeposition and alpha spectrometry. The data is homogeneous within two standard deviations of the distribution mean. Z-score values are below 2, showing good performance by the laboratories (Fig. 15, Appendix III). The median, given as the recommended value, is 14 mBq kg⁻¹ (95% confidence interval is 12–15 mBq kg⁻¹).

7.1.6.²⁴¹Am

Data from 5 laboratories were reported (Table 8, Appendix I, Fig. 9, Appendix II). All the data passed the outlier test and they all fall less than 2 standard deviations from the distribution mean. Z-score values are below 1.2 (Fig. 16, Appendix III). The median, given as the recommended value, is 20.1 mBq kg⁻¹ (95% confidence interval is 19.0–20.2 mBq kg⁻¹).

7.2. NATURAL RADIONUCLIDES

⁴⁰K

Data were reported from 11 laboratories (Table 4, Appendix I, Fig. 4, Appendix II). All results passed the outlier test. The data showed good homogeneity. Results are between two standard deviations from the distribution mean. Z-score values are below 2.0, showing good performance by the laboratories (Fig. 11, Appendix III). The median, given as the recommended value, is 11.4 Bq kg^{-1} (95% confidence interval is $10.7-11.7 \text{ Bq kg}^{-1}$).

7.3. LESS FREQUENTLY REPORTED RADIONUCLIDES

The results for the less frequently reported radionuclides are listed in Table 9, Appendix I.

7.3.1. ⁹⁹Tc

Three results were reported, ranging from 159 to 250 mBq kg⁻¹.

7.3.2.²³⁴U, ²³⁵U and ²³⁸U

Four laboratories reported results for 234 U and 238 U, three of them reported for 235 U. Data were rather homogeneous and ranged from 40 to 46 mBq kg⁻¹ for 234 U, and from 35 to 45 mBq kg⁻¹ for 238 U. The three values for 235 U are (1.4 ± 0.5), (1.8 ± 0.2) and (54 ± 7) mBq kg⁻¹.

7.3.3.²³⁷Np

One laboratory analysed this radionuclide by using ICPMS ($7 \pm 3 \text{ mBq kg}^{-1}$).

7.3.4. ²³⁹Pu and ²⁴⁰Pu

One laboratory analysed ²³⁹Pu and ²⁴⁰Pu by ICPMS. The ²³⁹Pu and ²⁴⁰Pu massic activities reported were (10 ± 2) mBq kg⁻¹ and (8 ± 2) mBq kg⁻¹, respectively. The derived ²³⁹⁺²⁴⁰Pu concentration is 18 ± 2 mBq kg⁻¹, higher than the value determined by the same laboratory by alpha spectrometry $(15 \pm 3 \text{ mBq kg}^{-1})$.

8. FINDINGS AND CONCLUSIONS

In this interlaboratory comparison, 12 laboratories reported concentrations of natural and anthropogenic radionuclides in a sea water sample from the Irish Sea (IAEA-443). The median concentrations for the sets of individual data – after rejection of outliers – were chosen as the most reliable estimates of the true values and are reported as recommended and information values.

A summary of the recommended and information values with confidence intervals for the most frequently reported anthropogenic and natural radionuclides can be found in the summary table below as well as in Table 10, Appendix I.

Radionuclide	<u>Median</u>	$\frac{\text{Confidence interval}}{(\alpha = 0.05)}$
Recommended value		
⁴⁰ K	11.4	10.7–11.7
¹³⁷ Cs	0.36	0.34-0.37
²³⁸ Pu ²³⁹⁺²⁴⁰ Pu	0.0031	0.0029-0.0033
²⁴¹ Am	0.014 0.0201	0.012–0.015 0.0190–0.0202
Information value		
³ H	37	33–41
⁹⁰ Sr	0.107	0.089-0.115

SUMMARY TABLE: RECOMMENDED AND INFORMATION VALUES FOR THE IAEA-443 REFERENCE MATERIAL (Reference date: 1 January 2007, unit: Bq kg⁻¹)

Appendix I

DATA REPORT - TABLES

Sample	¹³⁷ Cs	⁴⁰ K	⁹⁰ Sr	²³⁸ Pu	²³⁹⁺²⁴⁰ Pu
1	0.97	0.88	0.95	0.89	0.90
2	1.00	1.00	1.02	0.89	0.90
3	1.00	1.00	1.02	1.01	1.03
4	1.01	1.02	1100	1.02	1.05
5	1.02	1.09		1.12	1.06
Minimum	0.97	0.88	0.95	0.89	0.90
Maximum	1.02	1.09	1.03	1.12	1.06
Mean	1.00	1.00	1.00	1.00	1.00
Median	1.01	1.01	1.02	1.01	1.03
Std. Dev.	0.02	0.07	0.04	0.08	0.07
Coef. Var. (%)	2	7	4	8	7

TABLE 1. HOMOGENEITY TESTS ^(*) FOR RADIONUCLIDES IN IAEA-443

(*) Normalized activity = x/X (individual/mean value): initially expressed in this manner to ensure confidentiality of results.

Radionuclide	Number of results	Radionuclide	Number of results
³ H ⁴⁰ K ⁹⁰ Sr ⁹⁹ Tc ¹³⁷ Cs ²³⁴ U ²³⁵ U	14 28 17 6 27 9 9(1)	²³⁸ U ²³⁷ Np ²³⁸ Pu ²³⁹ Pu ²⁴⁰ Pu ²³⁹⁺²⁴⁰ Pu ²⁴¹ Am	9 6 18 (1) 4 4 18 (1) 16
		Gross alpha	1

TABLE 2. RADIONUCLIDES REPORTED FOR IAEA-443

(*) "Less than" values are shown in parenthesis.

Lab Code	Method Code	No. of Results	Weight (g)	³ H [#]
2	B2	3	500	32.91 ± 0.02
4	B2	2	8	41 ± 5
5	B1	1	10	38 ± 3
6	B1	2	250	34.9 ± 1.3
10	B2	1	10.2	36.9 ± 3.7
11a	B2	3	8.047	38.0 ± 1.2
11b	B2	2	8.025	37.4 ± 1.3
Number of Median	reported lab. mea accepted lab. mea interval ($\alpha = 0.0$	ans		7 7 37 33–41

TABLE 3. RESULTS FOR ³H IN IAEA-443(Reference date: 1 January 2007, unit: Bq kg⁻¹)

Uncertainties at 2σ

TABLE 4. RESULTS FOR ⁴⁰K IN IAEA-443(Reference date: 1 January 2007, unit: Bq kg⁻¹)

Lab Code	Method code	No. of Results	Weight (kg)	⁴⁰ K [#]
1	G	1	0.3	9 ± 3
2	G	3	0.06; 1	12 ± 3
3	G	6	1	11.7 ± 1.2
4	G	2	2.4	11.5 ± 0.9
5	G	1	1.75	11.4 ± 0.6
6	G	3	0.5	11 ± 2
7	G	2	1	11.0 ± 1.6
9	G	5	2	10.7 ± 0.9
10	G	1	3.069	11.5 ± 0.8
11	G	3	1	10.9 ± 0.7
12	G	3	0.27	12.6 ± 2.2
Number of	reported lab. mea		11	
	accepted lab. mea	11		
Median	•			11.4
Confidence	interval ($\alpha = 0.0$	5)		10.7-11.7

Uncertainties at 2σ .

* Result rejected by the test for outliers.

Lab Code	Method Code	No. of Results	Weight (kg)	⁹⁰ Sr [#]
2	B1	2	1	0.089 ± 0.008
3	B0	6	0.5	0.11 ± 0.02
4	B1	3	1	0.10 ± 0.03
6	B2	2	0.2	0.09 \pm 0.02
9	B1	3	2	0.11 ± 0.03
10	B1	1	3.115	0.107 ± 0.016
11	B1	2	0.7	0.115 ± 0.012
	reported lab. mea			7
	accepted lab. me	ans		7
Iedian				0.107
onfidence	e interval ($\alpha = 0.0$	5)		0.089-0.115

TABLE 5. RESULTS FOR 90 Sr IN IAEA-443(Reference date: 1 January 2007, unit: Bq kg⁻¹)

Uncertainties at 2σ .

TABLE 6. RESULTS FOR ¹³⁷Cs IN IAEA-443(Reference date: 1 January 2007, unit: Bq kg⁻¹)

ab Code	Method code	No. of Results	Weight (kg)	¹³⁷ Cs [#]
1	G	1	0.3	0.32 ± 0.14
2	G	3	0.06; 1	0.39 ± 0.08
3	G	6	0.5 -1	0.37 \pm 0.04
4	G	2	2.4	0.36 \pm 0.03
5	G	1	1.75	0.34 ± 0.03
6	G	3	0.5	0.35 ± 0.08
7	G	2	1	0.34 \pm 0.07
9	G	5	2	0.36 \pm 0.06
10	G	1	3.069	0.37 \pm 0.03
11	G	3	0.7-1	0.38 ± 0.03
12	G	3	0.27	0.32 ± 0.09
Number of	reported lab. mea	ins		11
	accepted lab. mea		11	
Median				0.36
Confidence	interval ($\alpha = 0.0$	5)		0.34-0.37

Uncertainties at 2σ .

* Result rejected by the test for outliers.

ab.	Method Code	No. of results	Weight (kg)	²³⁸ Pu [#]	$^{239+240}Pu^{\#}$
3	А	6	0.5	0.0033 ± 0.0007	0.015 ± 0.003
4	Α	2	0.997; 1	$0.0031 \ \pm \ 0.0008$	0.014 ± 0.003
6	Α	1	0.2	<0.01	< 0.01
9	А	5	2	$0.0031 \ \pm \ 0.0006$	0.014 ± 0.001
10	Α	1	0.5	$0.0029\ \pm\ 0.0006$	$0.012 \ \pm \ 0.002$
11	А	2	0.994; 1.017	0.0030 ± 0.0001	$0.014 \hspace{.1in} \pm \hspace{.1in} 0.001$
umber	r of reported l	ab. means		5	5
Number of accepted lab. means				5	5
Median				0.0031	0.014
Confidence interval ($\alpha = 0.05$)				0.0029-0.0033	0.012-0.015

TABLE 7. RESULTS FOR ²³⁸Pu AND ²³⁹⁺²⁴⁰Pu IN IAEA-443 (Reference date: 1 January 2007; unit: Bq kg⁻¹)

Uncertainties at 2σ .

TABLE 8. RESULTS FOR 241 Am IN IAEA-443(Reference date: 1 January 2007, unit: Bq kg⁻¹)

0.02 ± 0.004
0.020 ± 0.004
0.020 ± 0.004
0.020 ± 0.003
$0.019 \hspace{0.2cm} \pm \hspace{0.2cm} 0.002$

Uncertainties at 2σ .

TABLE 9. RESULTS FOR THE LESS FREQUENTLY MEASURED RADIONUCLIDES REPORTED IN IAEA-443

Isotope	Lab. code	Method Code	No. of results	Weight (kg)	Activity (Bq kg ⁻¹)
⁹⁹ Tc	3	В0	2	0.5	0.20 ± 0.04
-	6	B1	2	0.2	0.25 \pm 0.04
-	8	B2	2	0.745; 0.754	0.159 ± 0.003
²³⁴ U	4	А	4	0.997-1.0	0.040 ± 0.006
-	6	А	1	0.2	0.045 ± 0.011
-	7	А	2	1.034	0.045 ± 0.001
-	10	А	1	0.5	0.046 ± 0.007
²³⁵ U	4	А	4	0.997-1.0	0.0014 ± 0.0005
-	6	А	1	0.2	0.0018 ± 0.0002
-	7	А	2	1.034	$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$
²³⁸ U	4	А	4	0.997-1.0	0.035 ± 0.006
-	6	А	1	0.2	0.045 ± 0.011
-	7	А	2	1.034	0.039 ± 0.001
-	10	А	1	0.5	0.040 ± 0.007
²³⁷ Np	3	ICPMS	4	0.01	0.007 ± 0.003
²³⁹ Pu	3	ICPMS	4	0.01	$0.010 \hspace{0.2cm} \pm \hspace{0.2cm} 0.002$
²⁴⁰ Pu	3	ICPMS	4	0.01	0.008 ± 0.002

(Reference date: 1 January 2007, unit: Bq kg⁻¹)

TABLE 10 SUMMARY OF RECOMMENDED AND INFORMATION VALUES FOR IAEA-443 (Reference date: 1 January 2007, unit: Bq kg⁻¹)

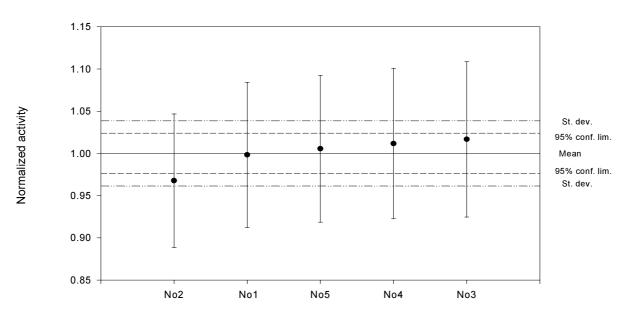
Radionuclide	Median	Confidence interval	Expanded uncertainty	Number of
		$(\alpha = 0.05)$	(%) (k=2)	results*
	Recommended value			
⁴⁰ K	11.4	10.7 - 11.7	8.8	11
¹³⁷ Cs	036	0.34 - 0.37	10.3	11
²³⁸ Pu	00031	0.0029 - 0.0033	12.9	5
²³⁹⁺²⁴⁰ Pu	0014	0.012 - 0.015	19.7	5
²⁴¹ Am	00201	0.0190 - 0.0202	6.0	5
	Information value			
³ H	37	33 - 41	22	7
⁹⁰ Sr	0107	0.089 - 0.115	24.5	7

* Number of accepted laboratory means which were used to calculate the recommended values and the confidence intervals.

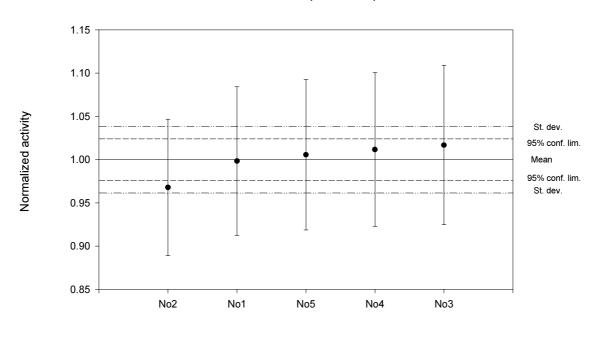
Appendix II

DATA EVALUATION – FIGURES



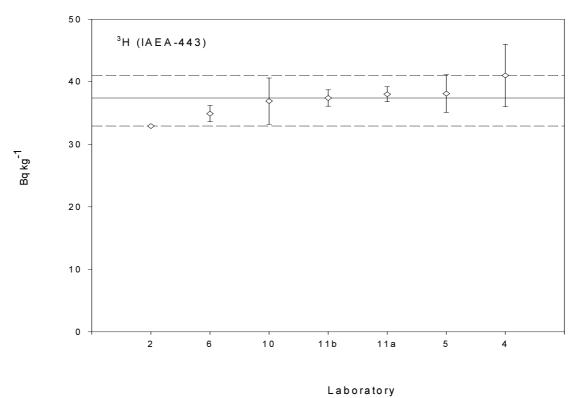


Sample number *FIG.1. Homogeneity test for* ¹³⁷*Cs in IAEA-443.*



²³⁹⁺²⁴⁰Pu (IAEA-443)

Sample number FIG.2. Homogeneity test for ²³⁹⁺²⁴⁰Pu in IAEA-443.



Laborator

FIG. 3. Data evaluation for ^{3}H .

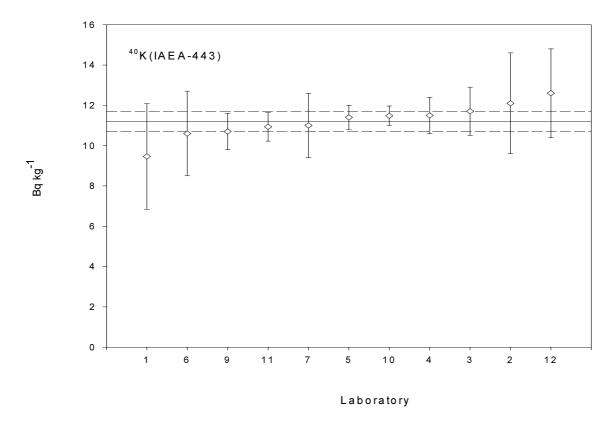


FIG. 4. Data evaluation for 40 *K.*

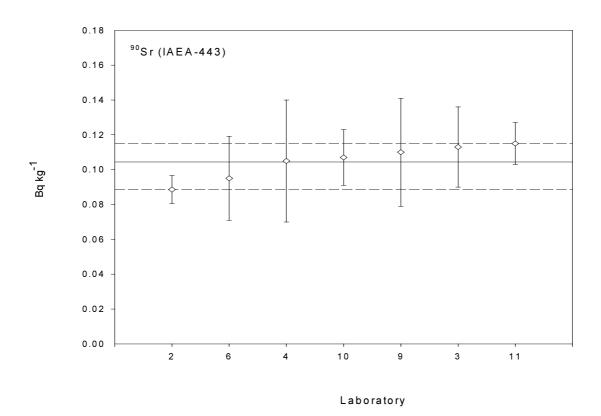


FIG.5. Data evaluation for ⁹⁰Sr.

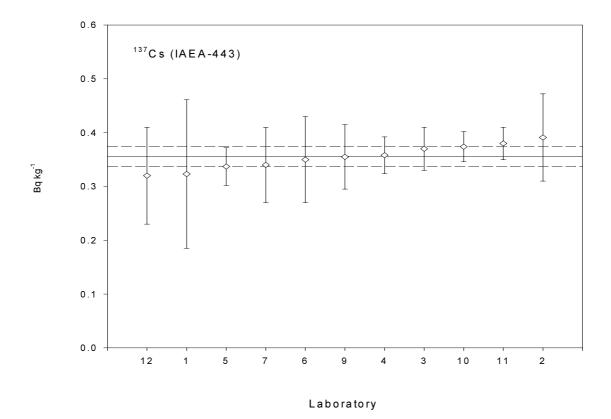


FIG. 6. Data evaluation for ^{137}Cs .

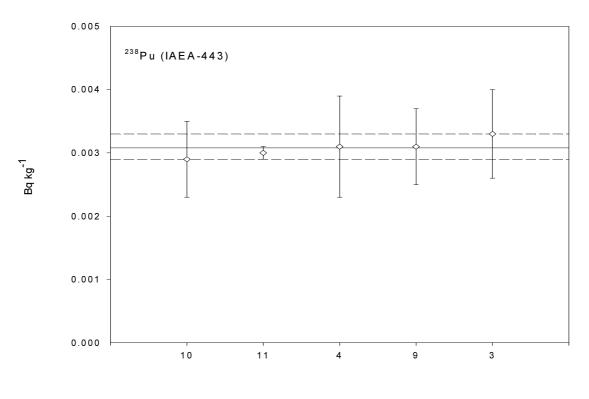
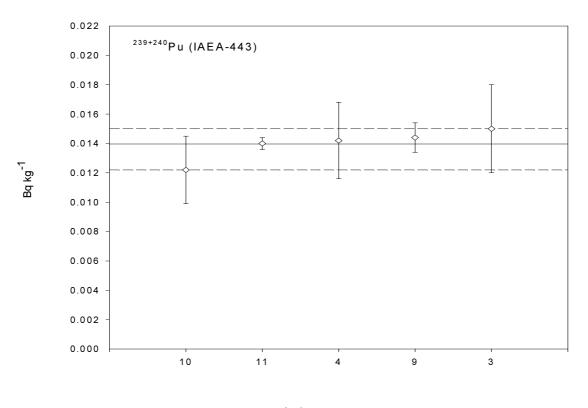




FIG. 7. Data evaluation for ²³⁸Pu.



Laboratory

FIG. 8. Data evaluation for ²³⁹⁺²⁴⁰Pu.

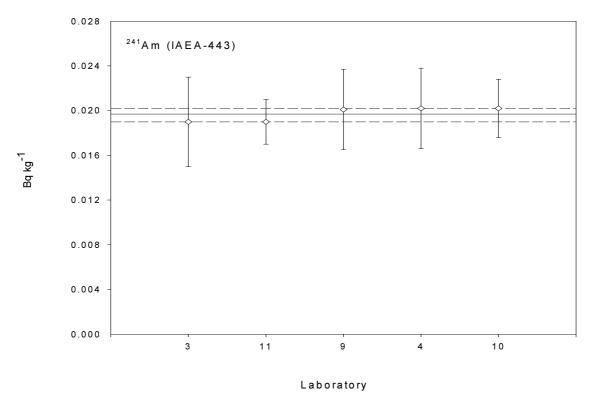


FIG. 9. Data evaluation for ^{241}Am .

Appendix III

Z-SCORES – FIGURES

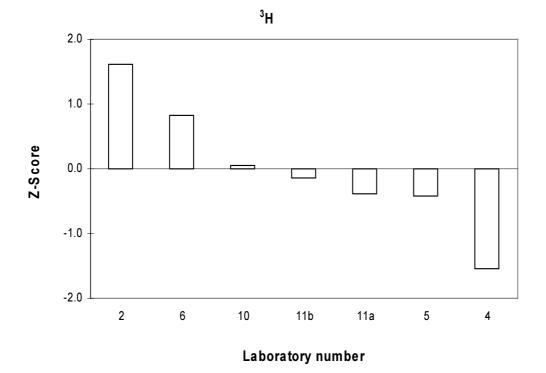
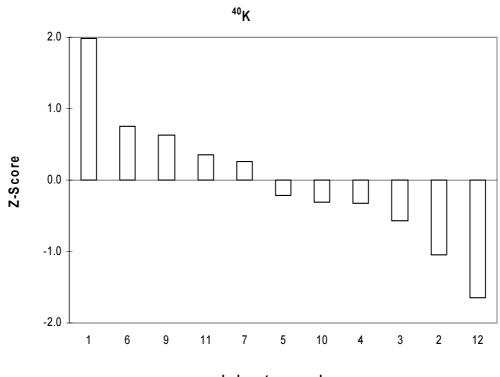


FIG.10. Z-score values for ${}^{3}H$.



Laboratory number

FIG.11. Z-score values for 40 *K.*

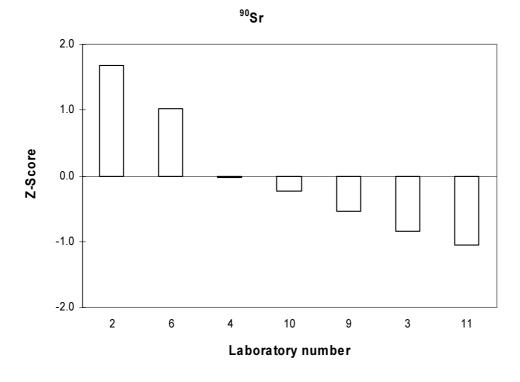


FIG.12. Z-score values of ⁹⁰Sr.

¹³⁷Cs

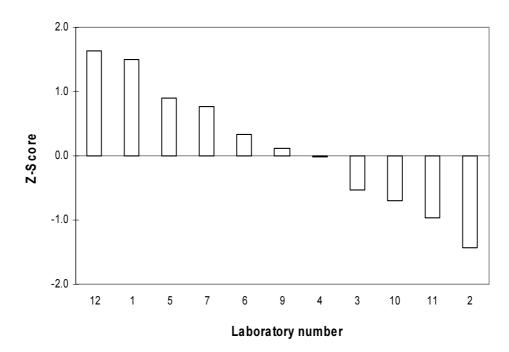
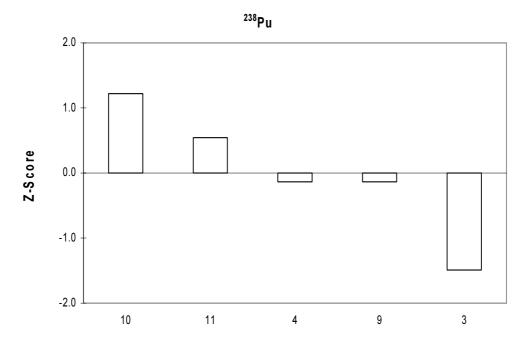
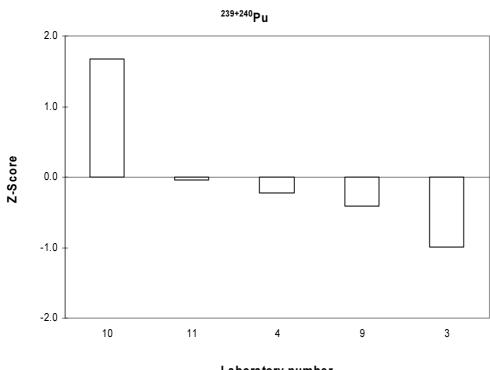


FIG.13. Z-score values of ^{137}Cs .



Laboratory number

FIG.14. Z-score values of ²³⁸Pu.



Laboratory number

FIG.15. Z-score values of ²³⁹⁺²⁴⁰Pu.

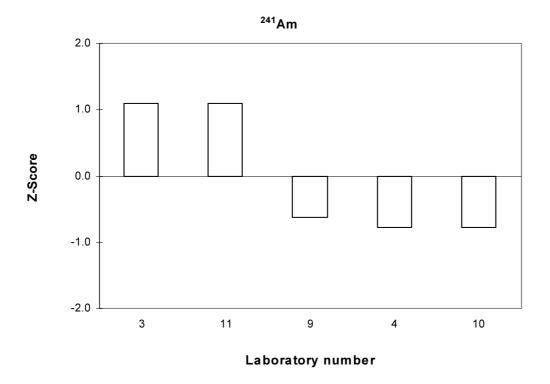


FIG. 16. Z-score values of ^{241}Am .

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REFERENCES

- [1] POVINEC, P.P., PHAM, M.K. IAEA reference materials for quality assurance of marine radioactivity measurements. J. Radioanal. Nucl. Chem. **248 (1)** (2001) 211-216.
- [2] SANCHEZ-CABEZA, J.-A., PHAM, M.K, POVINEC P.P., IAEA programme on the quality of marine radioactivity data, J. Environ. Rad. **99** (2008) 1680-1686.
- [3] POVINEC, P.P., PHAM, M.K., BALLESTRA, S. "Report on the intercomparison run IAEA-381: radionuclides in Irish sea water", IAEA/AL/118, IAEA/MEL/66, IAEA, Monaco (1999) 43p.
- [4] POVINEC, P.P., et al., Certified reference material for radionuclides in seawater IAEA-381 (Irish Sea Water). J. Radioanal. Nucl. Chem. **251 (3)** (2002) 369-374.
- [5] International Standard Organization (ISO), Guide 35 "Certification of reference materials General and statistical principles", ISO, Geneva (2006).
- [6] THOMPSON, M., WOOD, R., The international harmonized protocol for the proficiency testing of analytical chemistry laboratories, (IUPAC Technical Report), J. Pure Appl. Chem. 78 1 (2006) 145-196.
- [7] International Standard Organization (ISO), Guide 43 "Proficiency testing and interlaboratory comparisons", ISO/IEC, Geneva (1997).

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