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New Certified Reference Materials and Proficiency Test for Environmental Radioactivity Measurements

Abdulghani Shakhashiro[1], Paul Doherty[1], Jasmina Kožar Logar[2], Branko Vodenik[2], Leen Verheyen[3], Mark Taggart[4]

✉ admin@iarma.co.uk

[1]IARMA Limited, Naver House, Naver Road, Thurso, Highland, United Kingdom

[2]Institute Jožef Stefan, Jamova 39, 1000 Ljubljana, Slovenia

[3]Belgian Nuclear Research Centre – Institute for Environment, Health and Safety, Boeretang 200 – BE-2400 Mol, Belgium

[4]Environment Research Institute, Castle Street, Thurso, Caithness, United Kingdom

Abstract

A reliable determination of natural and anthropogenic radionuclides in environmental samples is necessary to comply with the radiation protection and environmental regulations.
This paper presents the results of the characterisation of massic activities of natural and anthropogenic radionuclides in soil and water matrices produced as test items to conduct the proficiency test ERAD-PT-2013. The Proficiency Test ERAD-PT-2013 was designed to investigate analytical performance in analysing both natural and anthropogenic radionuclides, to assist laboratories to identify analytical problems, and to improve the quality of measurement results. The proficiency test items, their spectral interferences and the activity concentration levels of the analytes were designed in a way to enable identification of potential analytical problems. Methodologies, data evaluation approach and evaluation of proficiency test results for each radionuclide are described and discussed.

Keywords: Proficiency test, Gamma-ray Spectrometry, Radiochemical Analysis, NORM in Soil.

Introduction

Measurement results influence important decisions in industry, environmental or food safety control.
Scientific measurements are a fundamental input to decisions made in many areas of economic, industrial and health activities. In particular, radiological measurements are used for evaluating the quality and conformity assessment of traded goods such as food/feed, ores, energy resources and chemical products.
The massic activity of radionuclides in soil and water is a critical factor in assessing the environment quality and the potential impact of possible pollutants. Water and soil are some of the main pathways for human exposure to radioactivity that may be present in the atmosphere due to natural processes; intentional (low-level) anthropogenic release; or as a consequence of nuclear or radiological incidents. The resulting environmental impact should be considered carefully to ensure safety and compliance with environmental regulations.
In all of these areas the quality of associated measurement results needs to be assured and demonstrated in order for them to be accepted as part of the decision making process. Measurement results must be accurate, reliable and comparable. This can only be realized by standardisation, harmonisation and assuring the quality of measurements. Otherwise, unreliable measurements could lead to inappropriate decisions, loss of resources and, in certain cases, to detrimental sequences.

Within this context, IARMA Limited (Naver House, Naver Road, Thurso, UK) produced a proficiency test set comprising of one soil test item (IARMA-001) and three water test items (IARMA-002, -003 and -004) containing natural and artificial radionuclides for environmental radioactivity measurements.

Materials and Methods

Preparation of the IARMA-001 soil material

The preparation of the IARMA-001 soil material was carried out according to the requirements of ISO Guides 30 series [1-5]. A careful study of all sources of uncertainty that may affect the validity of the certified values was undertaken.

The material was collected in a forestry area from the upper 2 cm layer of undisturbed soil. The bulk material was first air-dried in an oven, then milled and homogenised in one batch using a 300 litre rolling-drum homogeniser in a clean laboratory environment. The bulk material was then sieved using a vibro-separator to separate the fraction of particle size below 150 μm. The particle size distribution was measured using sieve analysis and it was observed that approximately 82 % of the particles were below 100 μm and that the most probable particle size was in the range 90 - 100 μm. The homogeneity of bulk material at all stages was checked prior to further processing or mixing.

Bottling of the material was performed under normal laboratory conditions; 400 secure HDPE bottles were filled with 200 g of material in one day taking all precautions to avoid segregation. The bottles were labelled and sterilized using gamma-ray irradiation with a total dose of 25 kGy using a ^{60}Co source. The characteristics and quality of the HDPE bottles assure resistance to the radiation dose used during the sterilization process especially for long-term storage. The 250 ml bottles were sealed to preserve the integrity of the reference material in the bottle.

Preparation of the IARMA-002, -003 and -004 water material

One batch of de-mineralised water was used to prepare the water material. The water was acidified and then analysed for the radionuclides of interest. It was found that the activity value of each measurand was below the detection limit of the analytical method, which is far below the spiked activity value. A portion of the blank water was spiked with an appropriate amount of a mixture of single radionuclide certified standard solutions traceable to the international standard of radioactivity through the Czech Metrological Institute. The spiked water was homogenised using a manual mixer in a 200 litre tank and then bottled into 250 ml portions in HDPE bottles. The total mass of the labelled bottle was recorded for further control of losses. Three test portions of 100 g were analysed by gamma-ray spectrometry. The relative standard deviation of each analyte was calculated and it was found that the relative standard deviations of all analytes were below the method repeatability relative standard deviation, demonstrating satisfactory homogeneity of the material. Table 1 lists the reference values and the associated relative combined standard uncertainties of the certified standard solutions used in preparation of the water test items.

Table 1

Characterisation of the IARMA-001 soil material

Four expert laboratories participated in the characterisation of the soil material to determine the property values of the material using well-validated and established analytical methods with an appropriate measurement uncertainty. The selection of expert laboratories was based on their demonstrated analytical performances through the application of a quality assurance system including method validation and well-established uncertainty budget and on good analytical performance in proficiency tests.

Each laboratory received three bottles of the IARMA-001 soil material along with a technical protocol and a reporting form. The expert laboratories were requested to perform three independent determinations of the massic activity of the studied radionuclides from each bottle using a validated

analytical method of high resolution gamma-ray spectrometry. In addition, the participating laboratories were asked to report the measurement result standard uncertainty along with the technical information about the analytical method, calibration procedure, measurement results metrological traceability and the applied quality control mechanism.

To determine the activity of radionuclides in the soil, gamma-ray spectrometers with different HPGe detectors were used by the expert laboratories. To avoid radon escape, the soil material was measured using a radon-tight sample container or active charcoal was added to the sample. The spectrum was collected after 30 days when the ^{226}Ra : ^{222}Rn equilibrium was reached. The shielding was made of 7 cm low background lead and 3 mm of copper. It is worth mentioning that efficiency transfer and summing corrections were carried out. The determination of the dry mass was carried out for each bottle by drying 3 g overnight at 80 °C.

Homogeneity of the IARMA-001 soil material

It is well known that the homogeneity study is vital to provide evidence that the variations associated with the property values of interest due to between-bottle heterogeneity are within the stated uncertainties and suitable for the intended use of the material. To assess the homogeneity of the IARMA-001 soil material, 10 bottles covering the whole bottling range were randomly selected and three test portions of approximately 25 g from each bottle were analysed for ^{40}K, ^{137}Cs, ^{208}Tl, ^{210}Pb, ^{212}Pb, ^{214}Pb, ^{214}Bi, ^{226}Ra, ^{228}Ac and ^{234}Th using a high resolution gamma-ray spectrometer equipped with broad energy detector. The analysis of samples for the homogeneity study was performed under repeatability conditions to minimize variations arising from the measurement technique and to detect and estimate the variations associated with the material heterogeneity.

In this work, the standard uncertainty associated with the between-bottle heterogeneity was calculated using the equation (1) as stated in ISO Guide 35 [5].

$$u_{\mathrm{bb}}^{*} = \sqrt{\frac{MS_{\mathrm{within}}}{n}} \sqrt[4]{\frac{2}{\nu_{MS_{\mathrm{within}}}}} \tag{1}$$

Where:

u_{bb}^{*}	Uncertainty originated from between-bottle heterogeneity.
MS_{within}	Within-bottle mean square from ANOVA calculation.
ν	Degree of freedom of mean square of within-bottle.
n	Number of measurements.

The results of the one way ANOVA calculation and applying the equation (1) for estimation of the uncertainty originating from between-bottle heterogeneity are reported in Table 2.

Table 2

Stability of the IARMA-001 soil material

The stability study provides information on the level of uncertainty associated with the material stability [5]. The short-term stability study is related to the definition of transport conditions in which the material will not suffer degradation. The long-term stability study is used to verify if the material may be stored at defined conditions such as room temperature, as temperature is a key factor in biological material degradation.

The isochronous design was adopted for the short-term stability study. Four sets, of three bottles each, of the IARMA-001 soil material were kept at -35 °C, 5 °C, 20 °C, and 60 °C for a period of 45 days. All bottles were analysed, under repeatability conditions to minimize the variability associated with the measurement, using the same method as for the homogeneity study mentioned above. Based on the results of the short-term stability study, no trend was detected as a result of the applied stress conditions and therefore it can be indicated that the shipment of IARMA-001 soil material at

temperatures between -30 $^{\circ}$C and 60 $^{\circ}$C does not cause any significant change to the reference values of the IARMA-001 soil material.

The uncertainty component associated with long-term stability u_{lts} during storage period at room temperature was evaluated by measuring one selected bottle (number 257) three times a year. Spectra were collected since October 2012. Nine measurement results of all studied radionuclides were evaluated and it was observed that the reproducibility standard deviation calculated from all measurement results is below the method reproducibility limit. In addition, no significant trend was detected. Following a conservative approach and based on the technical expertise of such a material and analytes and known information about the soil history, the u_{lts} was chosen as 1 % of the reference value, which guarantees the validity of the material for 5 years.

Assignment of the reference values of the IARMA-001 soil material

The reference values of all radionuclides of the IARMA-001 soil material were established on the basis of a consensus of all reported results (from the expert laboratories) estimated using the median as described in ISO 13528 [6], rounded off to the most significant number of the uncertainty. The arithmetic mean and Algorithm A mean as described in ISO/TS 20612 [7] were also calculated and compared with the median. No significant difference was observed between these location estimators, therefore, the reference value obtained using the median estimator was adopted.

According to the ISO Guide 35 [5] the combined uncertainty associated with the reference value consists of uncertainties related to the material characterisation u_{ch}, between-bottle homogeneity u_{bb} and long–term stability u_{lts}. These different uncertainty components were estimated and propagated to estimate the combined uncertainty of the reference value of studied elements u_{rm} as described in equation (2).

$$u_{rm}^2 = u_{ch}^2 + u_{bb}^2 + u_{lts}^2 \qquad (2)$$

The uncertainty component associated with the material characterization u_{ch} was estimated using the approach described in ISO 13528 [6]. In this approach, the uncertainty of characterization is estimated according to equation (3).

$$u_{ch} = \frac{S}{\sqrt{n}} \qquad (3)$$

where *S* is the standard deviation of all reported results in the characterization campaign and *n* is the number of reported results. Table 2 lists the reference values and associated uncertainties of the IARMA-001 soil material.

Assignment of the reference values of the IARMA-002, -003 and -004 water material

The final reference value for each radionuclide in the IARMA-002, -003 and -004 water, was calculated from the certified value listed in the certificate of the standard solution of each radionuclide used for spike, taking into account the successive gravimetric dilution steps, the mass of the spike and the amount of water spiked. The combined uncertainty of the reference values of the water material includes three major components of uncertainty associated with: the value of the certified standard solution as shown in Table 1; weighing for dilution (1.5 %); and stability (2.5 %).

Table 3 shows the certified massic activities and respective combined uncertainties of the radionuclides of interest in water IARMA-002, -003, and -004.

Table 3

To confirm the assigned reference values of the IARMA-002, -003 &-004 water material, three bottles from each were analysed at the Josef Stefan Institute Laboratory in Ljubljana, Slovenia.

Degree of equivalence of a measurement standard [6, 7] is the degree to which the value of a

measurement standard is consistent with its reference value. This is expressed quantitatively by the deviation from the reference value and the uncertainty of this deviation. The degree of equivalence between two measurement standards is expressed as the difference between their respective deviations from the reference value and the uncertainty of this difference.

The degree of equivalence between the assigned reference values of the water material and their actual measured values was calculated according to the approach of the Consultative Committee for Amount of Substance of BIPM [8, 9] using equations (4) and (5). For this purpose, the deviation from the reference value B is calculated according to equation (4) then the expanded uncertainty of both measured and reference values U_B is calculated with a coverage factor $k=2$ at a level of confidence of approximately 95 % as per equation (5).

$$B = |x_i - x_{ref}|$$ (4)

$$U_B = 2\sqrt{u_i^2 + u_{ref}^2}$$ (5)

Where:

x_i is the measured massic activity,
x_{ref} is the reference value of the massic activity of the material,
B is the deviation between the measured and the reference value,
u_i is the standard uncertainty of the measured activity,
u_{ref} is the standard uncertainty associated with the reference value,
U_B is the expanded uncertainty with a coverage factor $k=2$ at a level of confidence of approximately 95 %.

The values of the measured massic activity were found metrologically compatible with the reference values as stated in the standard source certificates at a level of confidence of approximately 95 %. The calculated Degree of Equivalence (D_e) using equation (6) found to be smaller than 2:

$$D_e = \frac{B}{U_B}$$ (6)

Results and Discussion

The proficiency test items were distributed in November 2013 to 18 laboratories in 16 countries. The deadline for receiving the results from the participants was set at 28 February 2014.

The participating laboratories were requested to analyse the soil test item IARMA-001 for: ^{40}K, ^{137}Cs, ^{208}Tl, ^{210}Pb, ^{212}Pb, ^{214}Pb, ^{214}Bi, ^{226}Ra, ^{228}Ac and ^{234}Th ; and the water test items IARMA-002, -003 and -004 for: ^{57}Co, ^{60}Co, ^{133}Ba, ^{134}Cs, ^{137}Cs, ^{152}Eu, ^{210}Pb and ^{241}Am.

The analytical results and associated uncertainties of the participating laboratories were compared with the reference values and uncertainties assigned to the materials, and a scoring system with predefined performance criteria was applied.

Bias assessment

The proficiency test scoring system applied by IARMA Limited evaluates not only the bias of the reported measurement result but also its uncertainty. In this scoring system, the reported results are evaluated against the acceptance criteria for bias and assigned the status "Acceptable", "Warning" or "Not Acceptable" accordingly [6, 7, 10, 11].

Bias, in this work, is considered as the deviation of the measured values (participants' reported results) from the reference value of the test material used in this proficiency test. Acceptance criteria for

reported results were designed based on the principle of fitness for purpose for environmental radioactivity applications, from what is considered practically reasonable, pragmatic, acceptable, and achievable for routine analyses of environmental samples.

According to the calculated relative bias B_{rel} using equation (7) expressed in percentage, the participant reported result (x_j) is sorted in one of three categories:

- Acceptable (A) if $|B_{rel}| \leq 20\ \%$,
- Acceptable with Warning (W) if $20\ \% < |B_{rel}| \leq 30\ \%$,
- Not Acceptable (N) if $|B_{rel}| > 30\ \%$.

$$B_{rel} = \frac{x_j - x_{ref}}{x_{ref}} \qquad (7)$$

The final score of the results is based only on the bias assessment as shown above. The measurement result uncertainty assessment is mainly to indicate whether the reported uncertainty needs a revision or re-assessment.

Underestimated uncertainty

U is calculated according to equation (9), which mainly depends on the uncertainty of participant reported result (u_j), and compared with the result bias $|B|$ calculated as per equation (4).
The participant reported result is assigned a "Pass" flag "P" for uncertainty if:

$$|B| \leq U \qquad (8)$$

where:

$$U = 2.58\sqrt{u_j^2 + u_{ref}^2} \qquad (9)$$

The coverage factor of 2.58 at a level of confidence of approximately 99 % was adopted to ensure that 99 % of the reported measurement results have a likelihood of occurring within the expanded uncertainty as calculated in equation (9).

Figure 1

Fig. 1 Demonstration of proficiency test evaluation approach – where the central line represents the analyte reference value and the two dashed horizontal lines above and below the central line denote the reference value ± its expanded uncertainty (k=2): the participants' results (a, b, c and d) are plotted with their expanded uncertainty (k=2)

To explain the uncertainty assessment approach, 4 cases are taken as shown in Figure 1. In case "a", the reported value will pass the bias criteria as its deviation from the reference value is less than 20 %. However, the reported measurement result uncertainty is too small, i.e. $|B| > U$, and gives a false impression about the accuracy / uncertainty of the result due to uncertainty underestimation. In this case, the reported result will pass the proficiency test criteria but the "N" flag for the uncertainty triggers a signal to the laboratory to revise the uncertainty budget without affecting the final score. If the result fails to pass both bias and uncertainty criteria then this is an indication of a gross or systematic error or even instability in the analytical system which requires a thorough investigation to find the root cause of the unacceptable result.

Overestimated uncertainty

To evaluate if the reported measurement result uncertainty is overestimated, an estimator P_r is calculated for each result, according to equation (10):

$$P_r = \sqrt{\left(\frac{u_{\text{ref}}}{x_{\text{ref}}}\right)^2 + \left(\frac{u_j}{x_j}\right)^2} \qquad (10)$$

The participant's result is assigned a "Pass" flag "P" for uncertainty according to equation (11) if:

$$P_r \leq P_a \qquad (11)$$

P_r mainly depends on the measurement result uncertainty reported by the participant. The Limit of Acceptable Precision P_a for each analyte is defined for the respective proficiency test in advance, including any adjustment due to the concentration or activity level of the analytes concerned and the complexity of the analytical problem. Participants' results are flagged as "Pass - P" for the claimed uncertainty when $P_r \leq P_a$. In this proficiency test, the P_a values used in the evaluation of all radionuclides are 15 % and 25 % for water and soil respectively.

Case "c" in Figure 1, shows an example of overestimation of the uncertainty. The result passes the bias criteria i.e. deviation from the reference value is smaller than 20 % and $|B| < U$. To assess if the uncertainty is overestimated, P_r is calculated (10) and compared with the maximum acceptable precision P_a (11). If $P_r > P_a$ then the reported uncertainty is flagged as overestimated without affecting the final score of the participant's result.

Performance evaluation results

An individual Performance Evaluation Report was provided to each participant three days after the deadline for reporting results, in order to provide a rapid feedback on the performance of the laboratory.

In total, 425 measurement results were reported from 15 laboratories in 12 countries.

The overall performance evaluation showed that 84 % of all reported results fulfilled the ERAD-PT-2013 criteria, 8 % were acceptable with warning and 8 % were not acceptable. Figure 2 shows the performance evaluation of the 15 participating laboratories.

Figure 2

Fig. 2 Summary performance evaluation of participant laboratories sorted by ascending order of the number of acceptable results where the white, grey and black colours of the columns denote "Acceptable", "Acceptable with Warning" and "Not Acceptable" results respectively, the 33 reported results comprise the 4 test items.

Natural and anthropogenic radionuclides in IARMA-001 soil material

The IARMA-001 soil material contains well-detectable ^{40}K and ^{137}Cs and the progenies of the natural thorium and uranium decay series.

In general, the participating laboratory performance was at a good level. An acceptable score was assigned to 81 % of all reported results for the soil test item IARMA-001. Only 7 % and 12 % were acceptable with warning and not acceptable respectively.

Lessons learned: ^{40}K

As shown on Figure 3, only one result for ^{40}K did not fulfill the proficiency test criterion. In this case it is suspected that the concerned laboratory does not have an appropriate CRM to validate results before reporting. It is suggested to review the efficiency calibration and method validation in this laboratory as it is observed that most of the results have a systematic negative bias. However, the results of six laboratories were slightly underestimated as shown in Figure 3.

Figure 3

Fig. 3 S-shape chart of reported results for ^{40}K in the soil test item IARMA-001

It was observed that the results of six laboratories were underestimated. The following points could suggest the root cause of such an effect:

- It is well known that the substantial presence of ^{40}K is in the detector background. Proper background correction is always necessary at regular intervals as the background might change. Proper and accurate correction for the spectral interference from the 1459.13 keV peak of ^{228}Ac should be validated to avoid a negative bias. In this case, the contribution of ^{228}Ac to this energy line of ^{40}K is 0.7 %. It is worth mentioning that an overestimation of the ^{40}K measurement result could also occur particularly when interference is not corrected for.
- If the sample density is higher than the calibration source, it shields the detector and in this case a relatively smaller background should be subtracted from the peak area.
- If the sample is not properly homogenized of before measurement.
- Moisture content inappropriately determined or corrected for.
- The correctness of the efficiency calibration should be validated using a reference material.

Lessons learned: ^{137}Cs

The reference value for ^{137}Cs in the IARMA-001 soil material is 52.0 Bq/kg. This massic activity is at least 30 times higher than a typical detection limit of a gamma spectrometer with a 30 % HPGe detector and a 100 cm^3 volume cylindrical sample holder. As expected, the participant laboratories demonstrated a high level of performance as 86 % of the reported results for ^{137}Cs fulfilled the proficiency test criterion. Only one result was not acceptable due to a systematic negative bias observed when examining the results from Laboratory15. The concerned laboratory should review the efficiency calibration procedure or use a single standard source for the calibration of each radionuclide, taking into consideration the density of the sample when low energy gamma-emitting radionuclides are determined. Three Laboratories reported underestimated measurement result uncertainty for ^{137}Cs as the observed bias of the reported results was not covered by the reported uncertainty. It is possible that certain sources of uncertainties were not included in the uncertainty budget such as the uncertainty of the dry mass correction and the uncertainty of the calibration source and/or the efficiency calibration.

Lessons learned: Progenies of the ^{238}U decay series

The ^{214}Pb, ^{214}Bi and ^{210}Pb radioisotopes were measured from the ^{238}U decay series. Most of the laboratories reported acceptable results for ^{210}Pb as shown in Figure 4. However, underestimated values for ^{214}Bi were observed as shown in Figure 5.

Figure 4

Fig. 4 S-shape chart of reported results for ^{210}Pb in the soil test item IARMA-001, for diagram details see Figure 3

Figure 5

Fig. 5 S-shape chart of reported results for ^{214}Bi in the soil test item IARMA-001, for diagram details see Figure 3

It is well known that the post-radon nuclides, ^{214}Bi and ^{214}Pb, are daughters of ^{222}Rn and have short half-lives, while ^{226}Ra is a long-lived radionuclide in the uranium/radium decay chain with a half-life of 1600 years. In this regard there are two challenges when these radionuclides are determined.

The first challenge is the variability of the concentration of radon in a counting room. This fact makes the background correction a more complicated task. The background correction should be estimated from background measurements taking into consideration different situations such as variation in the ventilation system, seasonal effects and working conditions. If possible, measures for reducing or stabilising the radon-daughter background such as continuous air refreshment / ventilation, use of old nitrogen as a vent purge gas and monitoring the radon concentration in the counting room are recommended.

The second challenge is the essential use of a ^{222}Rn gas-tight container to avoid its escape, otherwise, the values determined for ^{214}Pb, ^{214}Bi and ^{226}Ra can be underestimated due to the loss of ^{222}Rn. One of the important reasons for underestimating the activity of radon-daughters is due to the ^{222}Rn diffusion inside the sample container (particularly if it is not filled) and its accumulation at the top of the sample container. The period between filling the sample into a gas-tight container and starting the measurement is determined by the half-life of ^{222}Rn (3.8 days) and should be at least 23 days.

It is worth noting that sample containers are air tight but not necessarily radon tight as ^{222}Rn is a noble gas. It is recommended to use an aluminium container as a special radon-tight geometry with a cover sealed by a two component epoxy resin glue, to avoid any escape of radon gas from the sample. The reported results show that certain laboratories reported underestimated values for ^{214}Bi, ^{214}Pb and ^{226}Ra which most probably indicates a ^{222}Rn escape.

It should be mentioned that the external databases of nuclear data should be selected with the utmost care as the quality of the gamma-ray emission probability data for the natural radionuclides is not on the same level. Controlled and well-updated databases should be selected, such as Monographie BIPM-5 [12].

The user should also assure that the data which have been entered into the working libraries are treated as quality controlled documents with restricted access and must use the same database for the standard sources used in the efficiency/energy calibrations and for sample spectra evaluation. This recommendation aims at promoting of the use of controlled and updated nuclear databases.

Very often, the 63.28 keV-line is used for the determination of ^{234}Th. At this low energy, however, matrix variations between calibration and test sample can have considerable influence on the result due to different self-absorption and therefore it is necessary that they be taken into account. The 63.28 keV line is additionally interfered with by the 63.81 keV line of the ^{232}Th with an emission probability of 0.263 % . The use of the double line energies 92.37 keV and 92.79 keV of ^{234}Th with an emission probability of 4.81 % (2.42 % + 2.39 %) is not recommended to quantify ^{238}U.

In this proficiency test, the value of ^{234}Th is given as an information value due to the large uncertainty of gamma determination. Therefore, the reported results of ^{234}Th will not be formally evaluated.

Lessons learned: Progenies of the ^{232}Th decay series

The participating laboratories reported results for ^{208}Tl, ^{212}Pb and ^{228}Ac. Evaluation of the results

shows that 86 %, 93 %, and 100 % of the reported results were acceptable. This demonstrates good performance from this group of laboratories in comparison with world-wide proficiency testing scheme averages. For example, 40 % of the reported results of ^{208}Tl were not acceptable due to the use of invalid nuclear data libraries which contain the gamma emission probability modified with the branching ratio of ^{212}Bi into ^{212}Po by beta and ^{208}Tl by alpha decay with probability of 35.93 % [12, 13, 14]. This issue caused an overestimation of ^{208}Tl.

Lessons learned: Gamma emitting radionuclides in water test items IARMA-002, -003, and -004

The participant laboratories were asked to analyse 8 gamma-emitting radionuclides in the water test items namely: ^{57}Co, ^{60}Co, ^{133}Ba, ^{134}Cs, ^{137}Cs, ^{152}Eu, ^{210}Pb and ^{241}Am.

The design of the proficiency test items was aimed at checking the precision and trueness of the reported results and the True Coincidence Summing (TCS) effects, the appropriateness of its correction and the effect of spectral interferences. The different levels of the massic activities in the items might be of assistance in evaluation of the method linearity.

Table 4 presents the summary of the performance evaluation of the participating laboratories in the determination of radionuclides in the water test items.

Table 4

It can be noted that all of the reported results for ^{57}Co, ^{60}Co and ^{134}Cs fulfilled the proficiency test acceptance criteria, for , ^{137}Cs and ^{152}Eu only one not acceptable result was observed while, for ^{241}Am, two not acceptable results were scored.

The water test items contained four cascade decaying radionuclides, namely ^{60}Co, ^{133}Ba, ^{134}Cs and ^{152}Eu. From these isotopes the ^{60}Co has two consecutive transitions. The ^{60}Co has one clear cascade transition producing a simple TCS loss (summing-out) in close geometry. The ^{133}Ba and ^{134}Cs radionuclides have a more complex internal energy structure. The most probable cause for reporting low values of ^{133}Ba, ^{134}Cs and ^{152}Eu in the water test items is the lack of (or inadequate) coincidence summing corrections. This could explain why two laboratories obtained acceptable results with warning for underestimated values of ^{134}Cs which could be attributed to inappropriate TCS correction.

The most problematic radionuclide in the water test items was ^{210}Pb. The participant laboratories measured ^{210}Pb in the water test items at 46.52 keV using gamma-ray spectrometry.

From Table 4 it can be noticed that the level of analytical performance of ^{210}Pb is the lowest amongst the other radionuclides. The percentage of not acceptable results is 20 %.

The difficulties in the determination of ^{210}Pb were expected and could be attributed to the following main reasons:

- Extrapolation of the efficiency calibration curve to estimate the efficiency at 46.52 keV which could lead to a substantial error as the efficiency curve at this region has a significant slope;
- Inappropriate estimation of the absorption factor. At this low level of energy the absorption factor becomes a substantial source of variations;
- Absence of a rigid quality control and validation of the produced analytical results such as using duplicate analysis of samples and/or analysis of CRM or spiked samples;
- Inappropriate correction of the background

Conclusions

The proficiency test ERAD-PT-2013 was completed using environmental samples of different densities and containing natural and anthropogenic radionuclides. The test items contained radionuclides which require correction for true cascade summing effect.

The applied methodology for the preparation of the soil and water material used to organise ERAD-PT-2013, their composition, reference values and the associated uncertainties were appropriate to evaluate both the bias and uncertainty of the reported results and to assist in assuring the quality of

reported results, improve world-wide measurement results commutability, and to demonstrate the validity of gamma-ray spectrometry and radiochemical measurement results.

Most of the participant laboratories were able to report results which fulfil the proficiency test acceptance criteria. More efforts are yet needed to improve the quality of results for natural radionuclides of low energy gamma lines such as [210]Pb.

The full set of S-shape graphs for all studied measurands can be found in the Supplementary Material linked to this manuscript

Acknowledgements

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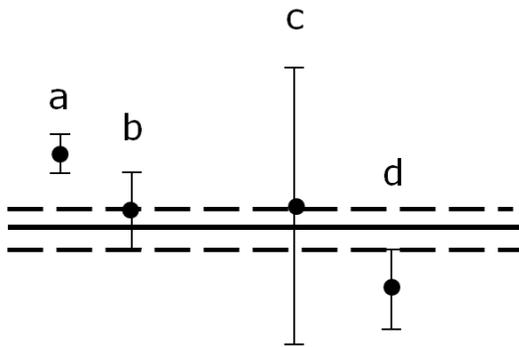
Fig. 1 Demonstration of proficiency test evaluation approach − where the central line represents the analyte reference value and the two dashed horizontal lines above and below the central line denote the reference value +/- its expanded uncertainty (k=2): the participants' results (a, b, c and d) are plotted with their expanded uncertainty (k=2)
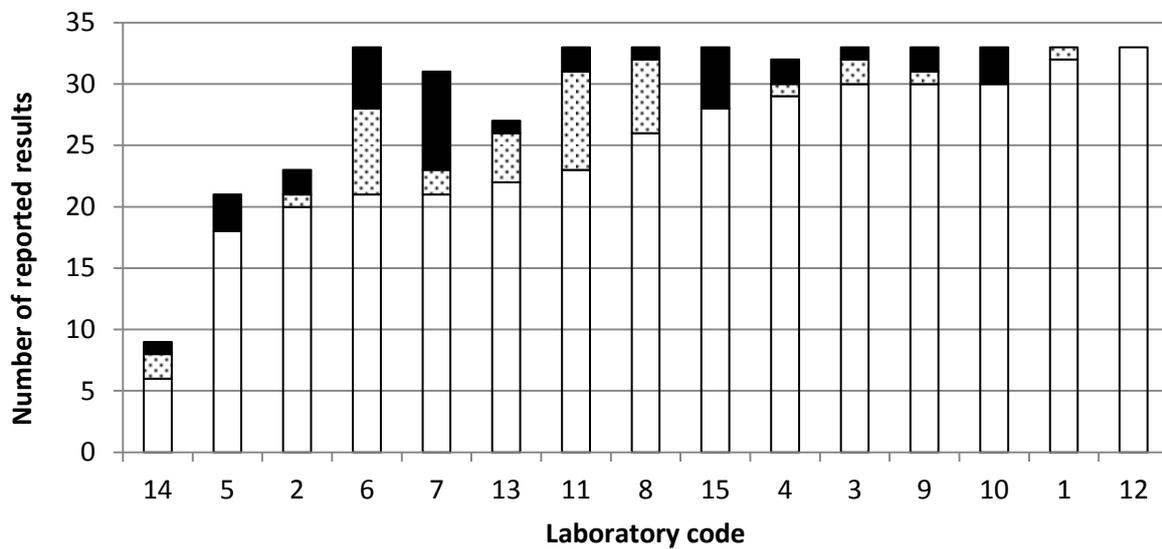

Fig. 2 Summary performance evaluation of participant laboratories sorted by ascending order of the number of acceptable results where the white, grey and black colors of the columns denote "Acceptable", "Acceptable with Warning" and "Not Acceptable" results respectively. The 33 reported results comprise the 4 test items.
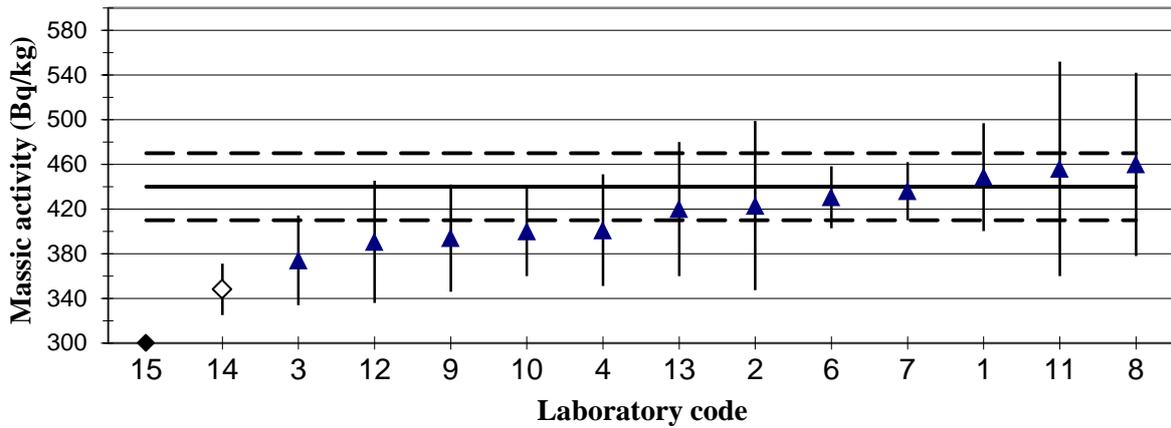
Fig. 3 S-shape chart of reported results for ^{40}K in the soil test item IARMA-001

In all S-shape Figures the central line represents the analyte reference value and the two dashed horizontal lines above and below the central line denote the reference value ± its expanded uncertainty (k=2). Participants' results are plotted with their expanded uncertainty (k=2).
The triangle shape symbol represents the participant result with acceptable performance, the open diamond is for acceptable with warning, and the filled diamond is for not acceptable performance.

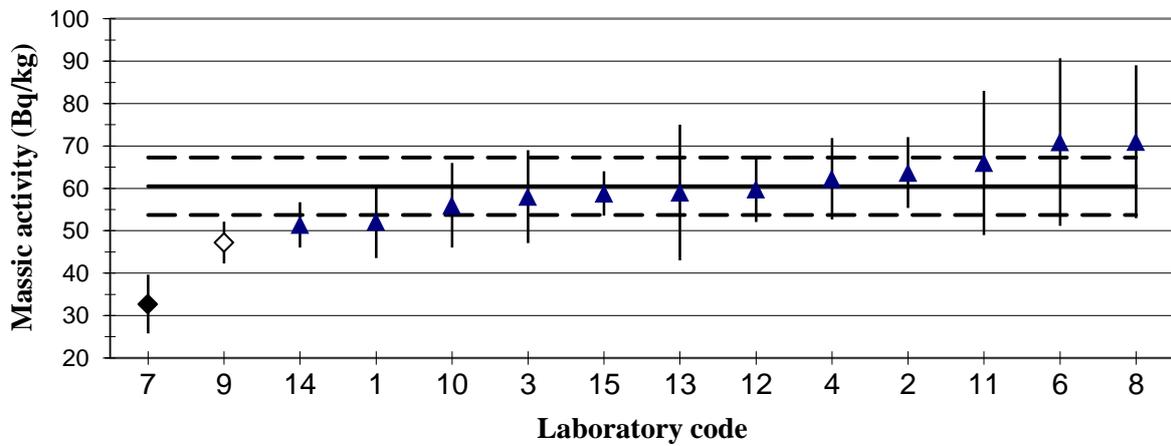**Fig. 4** S-shape chart of reported results for ^{210}Pb in the soil test item IARMA-001, for diagram details see Figure 3
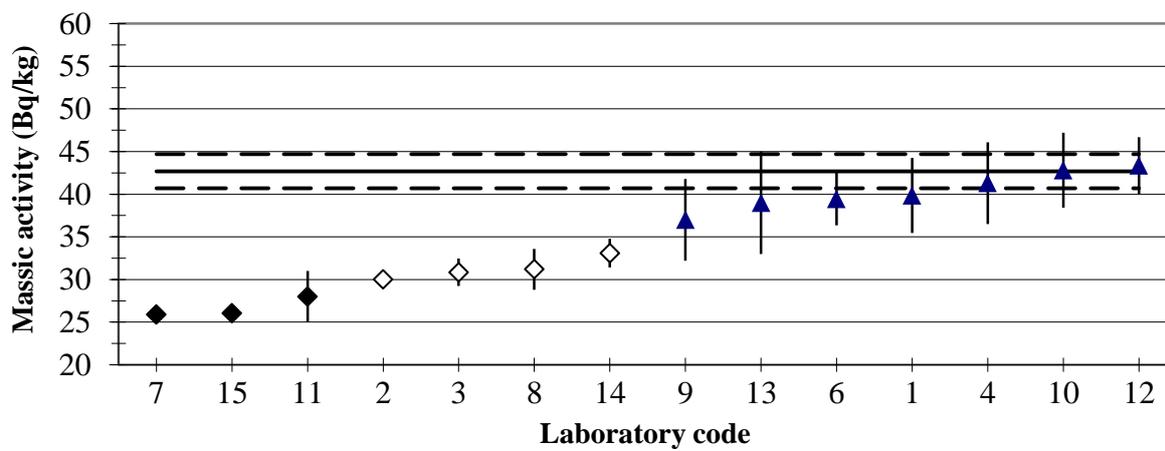
Fig. 5 S-shape chart of reported results for [214]Bi in the soil test item IARMA-001, for diagram details see Figure 3

Table1 Characteristics of the certified solutions of each radionuclide used in spiking of water material

Nuclide	Certificate number	Half-life time [days]	Massic activity [Bq/g]	Relative combined standard uncertainty [%]
^{57}Co	9031-OL- 570/13	271.26	59709.7	0.3
^{60}Co	9031-OL- 569/13	1925.4	73761.0	0.8
^{133}Ba	9031-OL- 571/13	3897	101299.8	0.4
^{134}Cs	9031-OL- 566/13	753	46651.6	0.3
^{137}Cs	9031-OL- 567/13	11019	103802.2	0.5
^{152}Eu	9031-OL- 572/13	4858	88208.1	0.5
^{210}Pb	9031-OL- 565/13	8108	32897.1	1.0
^{241}Am	9031-OL- 568/13	157800	112523.7	0.2

Reference date: 10-October-2013

Table 2 Reference values and associated uncertainties [Bq/kg] of the soil material

Radionuclide	u_{ch}	u_{bb}	u_{lts}	Massic activity[a]	Relative combined standard uncertainty[b] (%)
^{40}K	13.6	4.8	4.4	440	3.4
^{137}Cs	1.1	0.52	0.52	52.0	2.5
^{208}Tl	0.58	0.20	0.13	12.8	4.7
^{210}Pb	2.2	2.5	0.6	60.5	5.6
^{212}Pb	2.9	0.38	0.41	41.3	7.3
^{214}Pb	2.2	0.64	0.43	42.9	5.4
^{214}Bi	0.66	0.52	0.43	42.7	2.3
^{226}Ra	1.23	1.2	0.44	44.1	3.9
^{228}Ac	1.26	0.47	0.36	35.9	2.5
^{234}Th[c]	6.0	1.0	0.45	40.0	15.5

[a]Massic activities of daughter radionuclides are valid when secular equilibrium is maintained.
[b]Combined standard uncertainty (equation 2) expressed at 1 σ level and consists of the uncertainty associated with the characterisation of the soil u_{ch}, between-bottle homogeneity u_{bb} and long term stability u_{lts}.
[c]Information value only due to large uncertainty.

The reference date for decay correction is 01-November-2013.

Table 3 Reference massic activities and respective combined uncertainties of the radionuclides in water test items IARMA-002, -003, and -004

Radio-nuclide	IARMA-002		IARMA-003		IARMA-004	
	Massic Activity	Combined standard uncertainty[a]	Massic Activity	Combined standard uncertainty[a]	Massic Activity	Combined standard uncertainty[a]
	[Bq/kg]					
^{57}Co	3.08	0.10	6.83	0.22	16.54	0.52
^{60}Co	3.23	0.10	7.99	0.24	19.54	0.60
^{133}Ba	2.52	0.06	4.86	0.15	10.43	0.31
^{134}Cs	2.99	0.10	6.31	0.20	13.85	0.40
^{137}Cs	2.30	0.10	13.98	0.28	13.10	0.39
^{152}Eu	4.07	0.10	6.05	0.20	14.19	0.43
^{210}Pb	16.20	0.50	28.60	0.80	53.30	1.60
^{241}Am	2.70	0.10	7.10	0.20	16.24	0.49

[a]Combined uncertainty expressed at 1 σ level and consists of the uncertainties associated with the value of the certified standard used for spike, weighing for dilution and stability of the water.

Reference date: 01-November-2013

Table 4 Performance evaluation of water test items sorted by radionuclide

Radionuclide	Number of Acceptable results	Number of Acceptable results with warning	Number of Not Acceptable results	Total of reported results
^{57}Co	22	4	0	36
^{60}Co	28	0	0	28
^{133}Ba	24	1	1	26
^{134}Cs	23	5	0	28
^{137}Cs	39	2	1	42
^{152}Eu	21	3	1	25
^{210}Pb	27	5	8	40
^{241}Am	24	1	2	27