

A review of the TAEA proficiency test on natural and anthropogenic radionuclides activities in black tea

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Abstract

A proficiency test amongst 15 Turkish laboratories with participation of 5 non-Turkish laboratories was organized to determine the ¹³⁷Cs, ⁴⁰K and ⁹⁰Sr massic activities in black tea powder samples. The bulk material, consisting of tea produced in 2014, was mixed with contaminated tea that was withdrawn from the market after the Chernobyl accident. Nineteen laboratories reported 41 results. The evaluation of the results was based on the accuracy and precision criteria adopted by the IAEA Proficiency Testing Group and resulted in 49% acceptable results, 19% acceptable with warning and 32% were found to be not acceptable.

Keywords: radioactivity in tea powder, radioactivity proficiency test, environmental gamma ray spectrometry, ²²⁶Ra, ⁴⁰K, ⁹⁰Sr measurements

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1. Introduction

^{137}Cs and ^{90}Sr are two of the main indicative radionuclides in nuclear emergency cases and for environmental radioactivity monitoring due to their high abundance as fission products and relatively long half-lives. These radionuclides also pose significant health risks after a nuclear incident due to both external radiation exposure (gamma rays emitted by ^{137}Cs) and internal exposure. Tea leaves, widely consumed in Turkey and in the world, accumulate ^{137}Cs and ^{90}Sr in large amounts. During and after a nuclear fall-out event, ^{137}Cs and ^{90}Sr that are deposited on the ground enter the soil and are assimilated by the plants. These fission products may also be taken up directly by the deposits on the leaves. Because of the dynamics of cesium and strontium and physical characteristics of tea plant, ^{137}Cs and ^{90}Sr are retained in tea leaves for long times (Gökmen et al., 1995).

To efficiently handle the aftermath of nuclear power reactor incidents like Chernobyl and Fukushima and other radiological emergency situations it is important that there are efficient networks of laboratories that perform radioactivity measurements. As contributors to such a network, the university and institute laboratories in Turkey rely on proficiency tests (PTs) to demonstrate the reliability of their analyses. It is desirable for Turkish laboratories to participate more often in PTs, but radioactivity measurement PTs organized by institutes in other countries often limit the number of participants due to limited supply of reference materials. Furthermore, importation/exportation procedures may hamper distribution of samples. The Turkish Atomic Energy Authority (TAEA), being the European Association of Metrology Institutes (EURAMET) designated institute for ionizing radiation metrology in Turkey, is dedicated to organizing PTs on a regular basis to enable Turkey's national laboratories to check their analysis methods and help them in their accreditation processes.

This paper describes the second PT organized by SNTRC (Sarayköy Nuclear Research and Training Center) of TAEA in the radioactivity field. It concerned the determination of massic activities (Bq/kg, dry mass) of ^{137}Cs , ^{40}K and ^{90}Sr in black tea leaves. A total of 65 test samples were prepared, and 20 of them were distributed in November 2015 to 20 laboratories in 5 countries (15 laboratories from Turkey). The results of this PT are presented in this work and general recommendations for laboratories to perform better analyses are provided.

2. Materials and methods

2.1. Collection and pretreatment of the material

Black tea plants and processed black tea leaves produced in the Eastern Black Sea region of Turkey were exposed to radioactive contamination after the Chernobyl nuclear power plant accident. All contaminated processed tea was withdrawn from the market and stored in proper conditions or buried in soil at controlled sites by TAEA in 1986 and 1987. In this PT, the test material was prepared by using 8 kg of this contaminated black tea and mixing it with about 20 kg uncontaminated black tea produced in 2014. The bulk material was subjected to mixing and coarse sieving. The sieved material was oven-dried at 105 °C for about 48 hours until the humidity of the material was less than 2 %, and was then milled with a ring pulverizer and mixed in an industrial mixer for three consecutive days. The mixer was turned off at 2 hour periods so that dust was allowed to settle and any stuck material was scraped from the walls of the mixer for a more thorough mixing. The mixed material was then sieved again to have a mesh size < 0.25 mm and finally remixed. Sixty-five plastic containers were filled with 300 g material in a single day to avoid segregation and sterilized with about 10 kGy ^{60}Co radiation at the on-site sterilization plant to prevent microbial growth.

2.2. Homogeneity and activity determination of the PT material

The homogeneity of ^{137}Cs and ^{40}K was tested by analyzing 10 randomly selected plastic bottles, each having about 300 g sample, by taking three independent sub-sample amounts of 25 g from each bottle and using gamma-ray spectrometry to test the in-bottle and between-bottle homogeneity of the tea powder material; target values of specific activities were determined for each radionuclide. The gamma-ray spectrometric system consisted of an n-type coaxial high purity germanium (HPGe) detector with 50 % relative efficiency. The detector was installed in a 10 cm thick lead shield. Canberra digital electronics and Genie 2000 software were used (Canberra Industries, 2009).

The analysis results were subjected to the Grubbs outlier test (Grubbs, 1969), normal distribution, modality test and ANOVA test (ISO 35, 2006). There was no reason to exclude any data according to the outlier test. The results were normally distributed which allowed using Gaussian distribution parameters when calculating the uncertainties due to inhomogeneity. Multimodality might be an indicator of inhomogeneity and should be checked during PTs and reference material preparation. All results had single modality which ensured that there was no accumulation of results at two or more values. A one-way ANOVA approach was considered to evaluate the in-bottle and between-bottle inhomogeneity (ISO 35, 2006). The uncertainty due to inhomogeneity was determined as 0.8% for ^{137}Cs and ^{40}K . This uncertainty value was also treated for ^{90}Sr inhomogeneity. The outcome of the homogeneity test showed that uncertainties due to heterogeneity were within acceptable limits and the material could be considered sufficiently homogeneous for the tested radionuclides for the range of mass used.

The reference activities of ^{137}Cs and ^{40}K were determined by TAEA, PTB (Physikalisch-Technische Bundesanstalt) and The European Commission's Joint Reserahc Centre (JRC-Geel) by using gamma-ray spectrometry with HPGe-detectors and for the reference date 1 November

2015 (which is the reference data used throughout this paper). TAEA did a direct comparison of peak areas, corrected for density and composition, with the reference material, clover sample IAEA-156. The activities of ^{137}Cs and ^{40}K were determined to be 1690 ± 33 Bq/kg and 540 ± 14 Bq/kg, respectively, at a coverage factor $k=2$ at the TAEA laboratory. JRC-Geel measured the tea sample at two distances on two detectors and calculated a mean value of 1705 ± 26 Bq/kg and 533 ± 16 Bq/kg for ^{137}Cs and ^{40}K , respectively, at a coverage factor $k=2$. At JRC-Geel, an efficiency curve determined using a liquid multinuclide reference source from National Physical Laboratory (NPL) was used. The efficiency transfer was performed with Monte Carlo calculations using EGSnrc. PTB measured three tea samples by use of two calibrated detectors of different construction and calculated the weighted mean value of 1712 ± 27 Bq/kg and 542 ± 9 Bq/kg for ^{137}Cs and ^{40}K , respectively, at a coverage factor $k=2$. At PTB the detectors were calibrated by use of activity standards from primary standardization of PTB, and the Monte Carlo code GESPECOR was used for the geometry transfer and the density correction to correct for differences between the calibration source and the tea samples. The final reference activity values were calculated as the power-moderated mean (Pommé and Keightley, 2015) of the TAEA, PTB and JRC-Geel results and amounted to 1703 ± 32 Bq/kg and 539 ± 14 Bq/kg for ^{137}Cs and ^{40}K , respectively, at a coverage factor $k=2$.

The activity of ^{90}Sr was measured by using liquid scintillation efficiency tracing (CIEMAT/NIST) method (Garcia-Toraño et al., 1991) at TAEA laboratories. The applied method was based on the digestion of the sample (ashing using microwave furnace and dissolving by acid procedure), the separation of Sr by Sr-resin extraction chromatography and the subsequent measurement of the activity using a Wallac 1220 Quantulus ultralow-level liquid scintillation spectrometer. For the instrument efficiency calibration, the CIEMAT/NIST ^3H efficiency tracing

method was used with ^3H standard. The activity of ^{90}Sr was determined to be 155 ± 16 Bq/kg at a coverage factor $k=2$ (this value was also confirmed by JRC-Geel).

The dry weight of the sample material was taken into account in the calculation of the activities by considering the moisture content in the sample material. Reference activity and the combined standard uncertainties are given in Table 1. While the reference activity values in Table 1 for ^{137}Cs and ^{40}K are the power-moderated mean of the TAEA, PTB and JRC-GEEL results, the reference activity value for ^{90}Sr is only the TAEA's result.

The uncertainties for the reference values of ^{137}Cs and ^{40}K measured at TAEA laboratories were calculated by the following equation:

$$U_{TV} = k\sqrt{u_{sm}^2 + u_{rmm}^2 + u_{arm}^2 + u_h^2 + u_{sts}^2 + u_{lts}^2}$$

Here U_{TV} is the expanded uncertainty of the target value, k is the coverage factor, u_{sm} is the sample material counting uncertainty considering background counting, u_{rmm} is the standard reference material counting uncertainty considering background counting, u_{arm} is the uncertainty of the activity of the standard reference material, u_h is the uncertainty due to heterogeneity and u_{sts} and u_{lts} are the uncertainties due to short- and long-term instability of the material. u_{sts} and u_{lts} were assumed to be negligible in the characterization study since no degradation of the sample is expected in the short- or long-term. The relative uncertainty component due to inhomogeneity, u_h , were determined as 0.8 % for all radionuclides in the test sample. All contributions to the uncertainty budget of the measurements at TAEA laboratories are presented in Table 2. Uncertainties due to weighing, dead time correction, counting time determination and half-life were calculated as well but since these have negligible contributions to the final uncertainty, they were omitted in the uncertainty budget. For the TAEA measurements, the contributions of full energy peak efficiencies, gamma-ray emission probabilities and true coincidence summing

correction factors were also neglected because these parameters were cancelled out in the method of direct comparison of peak areas with the standard reference materials.

2.3. Performance evaluation and scoring

There are several performance evaluation and scoring systems to analyze PT data. However, results of different systems may have different meanings and are not always comparable (Shakhashiro and Mabit, 2009). In this PT study, the IAEA criteria in IAEA/AQ/18 (IAEA, 2010) are used for the performance evaluation of the participating laboratories. The reported results were evaluated against the predefined criteria for accuracy and precision and the status was assigned as “accepted” or “not accepted” accordingly (Shakhashiro and Mabit, 2009; IAEA, 2010).

2.3.1. Relative bias

Relative bias of a reported result is a criterion in performance evaluation and scoring. The relative bias (RB) between the analyst’s value ($value_{analyst}$) and the reference value ($value_{ref}$) was calculated as the following:

$$relative\ bias = \frac{value_{analyst} - value_{ref}}{value_{ref}} \times 100\%$$

Relative bias was also calculated as complementary information and additional parameter for the performance evaluation of the participating laboratories. The scores of a reported result for both trueness, precision and, if necessary, relative bias, are combined for the final evaluation of the result. If a result obtains “acceptable” status for both trueness and precision criteria, it is assigned “acceptable” for the final score. If a result obtains “not acceptable” status for both

trueness and precision criteria, it is assigned “not acceptable” for the final score. In cases where a result obtained a “not acceptable” status in terms of either the trueness or precision criteria, a further evaluation containing the relative bias of the reported result was needed. In this case the relative bias (RB) was compared with a bias limit value called *maximum acceptable bias* (MAB). Similar to the LAP value, the MAB value was also defined for each radionuclide in the sample by considering the activity concentration of the radionuclide in the sample and the complexity of the analysis and was set as 15% for ^{137}Cs and ^{40}K , and 20% for ^{90}Sr . If $\text{RB} \leq \text{MAB}$, the final score was assigned “warning” or “acceptable with warning”. If $\text{RB} > \text{MAB}$, the final score was assigned “not acceptable”.

2.3.2. The U-score

The U-score is calculated to determine whether a laboratory’s result is acceptable or not from the point of accuracy. A particular advantage of the U-score is that the uncertainties of the reported results are also taken into account. The combined standard uncertainties are considered in the U-score calculation (ISO 17043, 2010).

The U-score was calculated by using the following formula:

$$U_{score} = \frac{|value_{ref} - value_{analyst}|}{\sqrt{unc_{ref}^2 + unc_{analyst}^2}}$$

The calculated U-score was compared with the critical value in the t-statistics table to determine if the analyst’s value (reported value) differs significantly from the reference value at a given level of probability. The laboratory performance was evaluated as acceptable if the U-score was < 2.58 for a level of probability at 99 %.

2.3.3. The Precision score

A precision related constant, P, was calculated to determine if a laboratory result was acceptable or not from the point of precision. The P value was calculated by using the following formula:

$$P = \sqrt{\left(\frac{unc_{ref}}{value_{ref}}\right)^2 + \left(\frac{unc_{analyst}}{value_{analyst}}\right)^2} \times 100\%$$

To compare with the P value, a limit value for precision (Limit of Acceptable Precision or LAP) is needed. LAP is defined for each radionuclide in the sample by considering the activity concentration of the radionuclide in the sample and the complexity of the analysis (IAEA, 2010).

For this PT, the LAP value was set as 15% for ^{137}Cs and ^{40}K , and 20% for ^{90}Sr . The P value of a reported result for ^{137}Cs and ^{40}K should be < 0.15 to pass the test. For ^{90}Sr it should be < 0.20 to pass the test and be assigned as “acceptable” for “precision”.

3. Results and discussion

A total of 20 laboratories in 5 different countries (15 of which from Turkey) registered for the test. Nineteen of these laboratories reported their results. Four laboratories out of 19 reported results for all of ^{137}Cs , ^{40}K and ^{90}Sr . Fourteen laboratories out of 19 reported results for ^{137}Cs and ^{40}K . One laboratory out of 19 reported result for only ^{90}Sr . Thus, in total, 41 results were submitted.

The percentage of acceptable and not acceptable scores for each radionuclide is presented in Fig. 1. It is seen that laboratory performances for ^{137}Cs and ^{40}K measurements are close to each

other. The reported results for ^{90}Sr are satisfactory and all five of them are acceptable. Considering the 41 submitted results from all 19 laboratories for the three radionuclides, the percentages of acceptable results, unacceptable results and warnings are 49 %, 32 % and 19 %, respectively.

The S-shape charts and the statistical performance evaluation tables sorted by radionuclide are presented in Figure 2. Figure 3 shows the ^{137}Cs and ^{40}K results for each laboratory in the same plot, which is convenient to obtain an understanding of the performance of the participants.

It can be seen in Fig. 3 that the results reported by the laboratories coded 11, 14, 20, 22, 36 and 46, which are shown in ovals, should be particularly examined. The laboratories coded 20 and 46 reported extremely low results for ^{137}Cs . The reported result for ^{40}K of laboratory coded 20 is also extremely low while that for laboratory coded 46 is very high. While the case of laboratory coded 20 could be attributed to an inappropriate efficiency calibration, the case of laboratory coded 46 cannot be explained by an inappropriate efficiency calibration alone; there may also have been an ambient background subtraction problem for ^{40}K . A review of the calibration material matrix and calibration calculations were recommended to laboratory coded 20.

Laboratories coded 11, 14 and 22 reported relatively high results for both ^{137}Cs and ^{40}K , which could be attributed to an inappropriate efficiency calibration. A review of the calibration procedures and the application of the proper corrections, if necessary, were recommended.

Laboratory coded 36 reported a relatively low result for ^{137}Cs but a very high result for ^{40}K , suggesting a background correction problem in the calculation of ^{40}K activity. A review of the background correction procedure was recommended. By considering the reference standard

materials they used and the corrections they reported, the self-absorption correction should have been taken into account in the calculations.

4. Summary and Conclusions

This proficiency test helped to estimate the performance of participating laboratories on determining the activities of natural and anthropogenic radionuclides in tea powder. Nineteen participating laboratories reported 41 results. Fourteen of the participants reported results for only ^{137}Cs and ^{40}K , four of the participants reported results for all three radionuclides and one participant laboratory reported result for only ^{90}Sr .

The evaluation results showed that 32% of the reported results were in the “not acceptable” range. All of the “not acceptable” results were reported by the national laboratories.

This PT demonstrated problems in the technical capacity of numerous laboratories, especially in Turkey, in analyzing ^{90}Sr . Laboratories capable of measuring ^{90}Sr and/or reporting reliable and valid results were significantly fewer than those for ^{137}Cs and ^{40}K . Seeing that 100% of the five reported ^{90}Sr results were acceptable and that the ^{137}Cs and ^{40}K results of the same laboratories (except No. 8 which did not submit gamma-ray spectrometry results) were acceptable, one can possibly assume a correlation between resources (available equipment) and quality of results.

The PT shows the need for further improvements in measuring procedures for the determination of natural and anthropogenic radionuclides and the need for capacity building of such procedures in some of Turkey’s national laboratories. A workshop on assessment of the PT results and on providing a short training to the national participant laboratories is recommended to enhance the comparability and reliability of their radioactivity measurements.

Several factors such as detector type, detector calibration, background correction, sample characteristics and sample preparation can affect the accuracy and precision of the measurements of the radionuclides. This shows that gamma-ray spectrometry analysis is not a simple task and it requires specific equipment, proper procedures, and experienced staff. It was recommended to the participants to control their detector calibrations regularly with reference materials or materials with known activity. Regular record keeping of backgrounds are also important to check background stability, which is very important in measurement of environmental samples. A complete estimation of the uncertainty budget, and taking into consideration all sources of uncertainties, would prevent underestimating or overestimating the reported uncertainty.

In the general assessment, this proficiency test provided a chance for TAEA as well as for the participants to notice the critical points for future tests. While evaluating the results, it was noted that having more data about the sample preparation and measurement processes of the participating laboratories could help us to assess the reasons of the unsatisfactory or failed results.

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Figure captions:

Fig.1. The percentage of the results of each radionuclide having acceptable, not acceptable and warning scores.

Fig.2. Reported results for activity values of ^{137}Cs , ^{40}K and ^{90}Sr with their expanded uncertainties for $k = 2$.

Fig.3. Reported activity values of ^{137}Cs and ^{40}K given in the same laboratory order for a complete and easy comparison.

Table captions:

Table 1: Target values with combined standard uncertainties of the radionuclides in the test sample

Table 2: Contributions to the uncertainty budget in the calculation of the activity values of ^{137}Cs , ^{40}K and ^{90}Sr measured at TAEA laboratories.

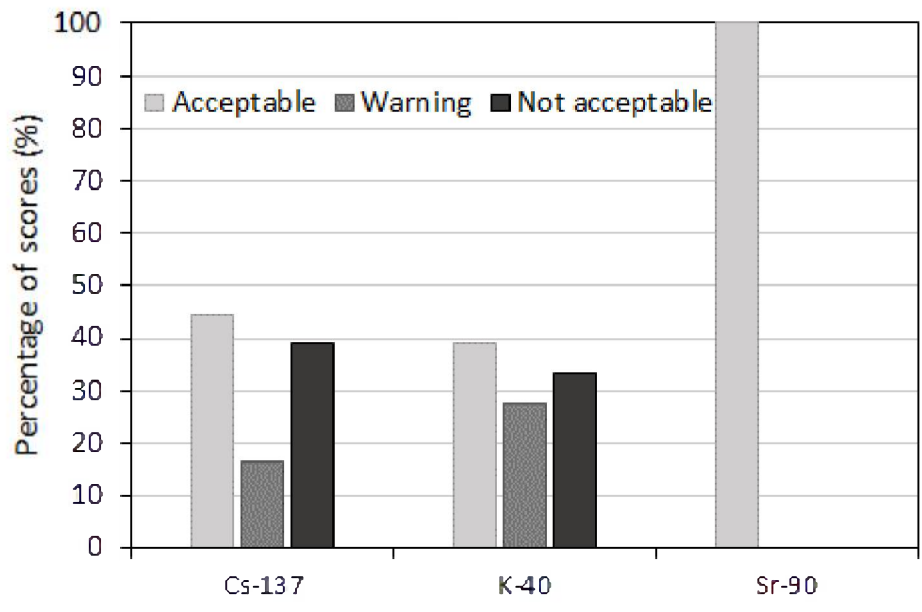


Fig.1

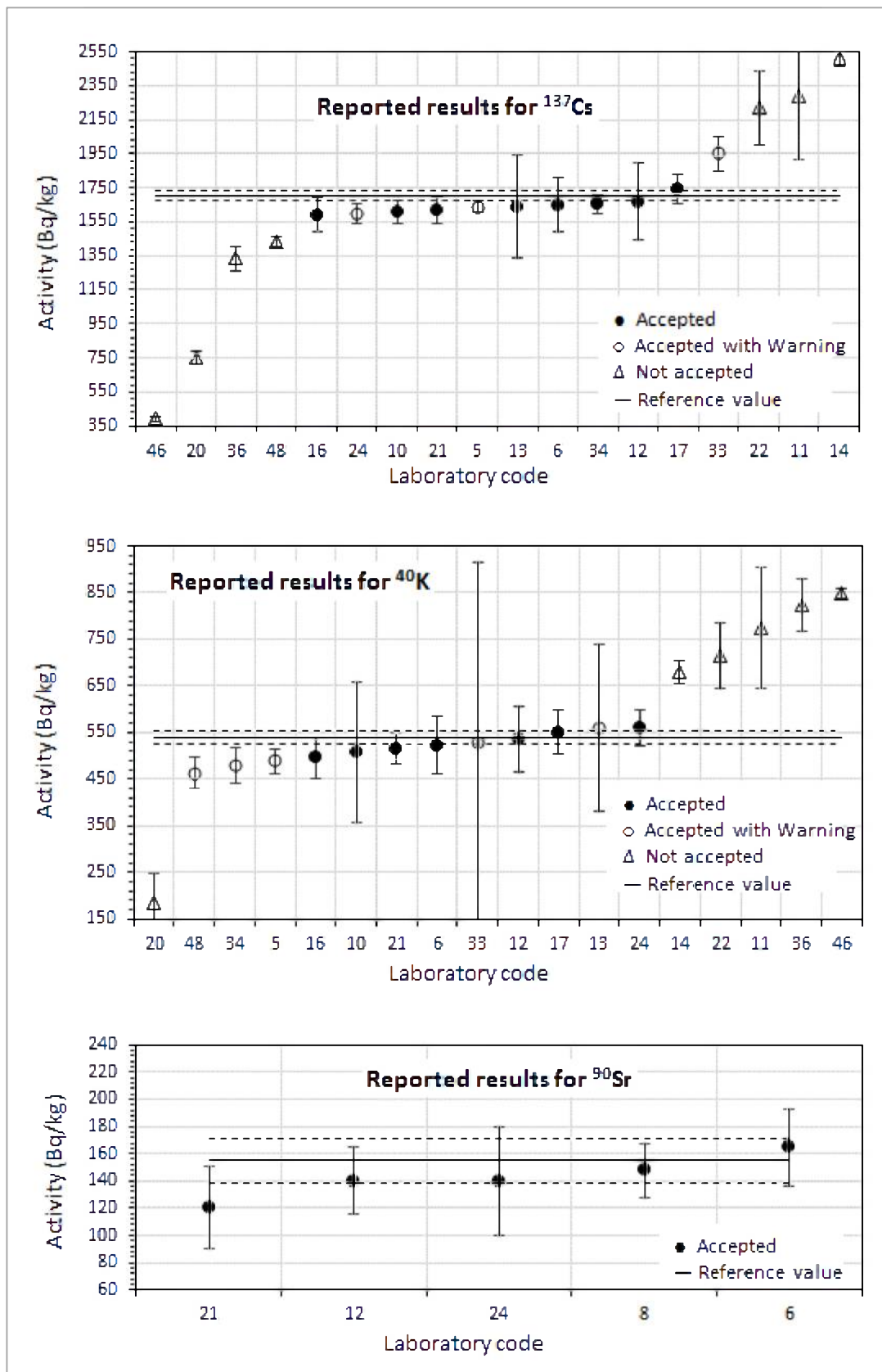


Fig.2

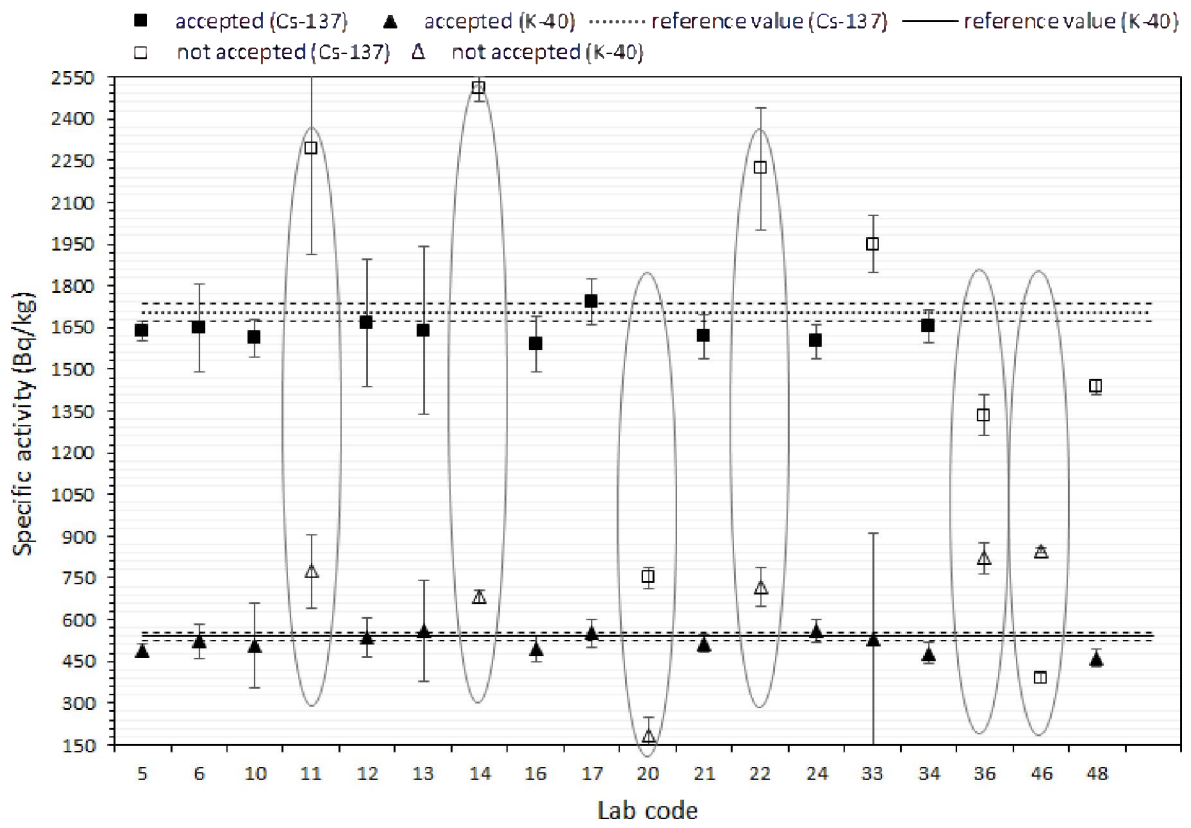


Fig.3

Table 1: Target values with combined standard uncertainties of the radionuclides in the test sample

Nuclide	Activity (Bq/kg)	Uncertainty (Bq/kg)
Cs-137	1703	16
K-40	539	7
Sr-90	155	8

For all measurements the reference date is 01 November 2015, the combined standard uncertainty is expressed at 1σ level.

Table 2: Contributions to the uncertainty budget in the calculation of the assigned activity values of ^{137}Cs , ^{40}K and ^{90}Sr

Uncertainty component	u (%) (k=1)		
	^{137}Cs	^{40}K	^{90}Sr
Sample and background counting statistics	0.20	1.50	1.24
Standard reference material and background counting statistics	0.20	1.40	-
Activity of the reference material	1.80	1.50	-
Heterogeneity of the sample material	0.80	0.80	0.80
Sample mass*	0.10	0.10	0.10
Half-life*	<0.01	<0.01	-
Dead time correction*	0.01	0.01	-
Tracer	-	-	0.20
Efficiency	-	-	0.43
Chemical recovery	-	-	4.92
Decay correction	-	-	0.02

Combined standard uncertainty	1.99	2.66	5.16
Expanded uncertainty (k=2)	3.98	5.32	10.32

*negligible contributions in the combined standard uncertainty calculation