

Proficiency testing schemes on determination of radioactivity in food and environmental samples organized by the NAEA, Poland

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Abstract. This paper presents the approach of conducting proficiency tests (PT) on the determination of radionuclides in food and environmental samples adopted by the Institute of Nuclear Chemistry and Technology (INCT), Warsaw, Poland and the results of the provided PTs. The PTs have been organized by the National Atomic Energy Agency (NAEA), Poland, since 2004. The activity of the following radionuclides: ^{241}Am , ^{137}Cs , ^3H , ^{239}Pu , ^{226}Ra and ^{90}Sr were determined. The test materials: water, milk powder, wheat flour and soil, were prepared by spiking blank materials with standard solution of the radionuclide of interest. The activity concentrations were calculated and associated uncertainties were evaluated before sending the test materials to the laboratories. The results provided by the participants were statistically evaluated by means of z and $zeta$ scores as well as using the International Atomic Energy Agency (IAEA) criteria for trueness and precision. Observed trends and some benefits for the participants have been presented.

Key words: proficiency tests • radioactivity • man-made radioisotopes

Introduction

Participation in the interlaboratory comparisons (ILC) and PT schemes is an important tool to assess the laboratory competence. It allows also improving the quality of laboratory routine work and comparing its results with those of other laboratories. It can be also used to verify reliability of the data produced by a laboratory and provide confidence in measurement results to the users of laboratory services. The INCT has been involved in conducting PTs on the determination of selected man-made radionuclides since 2004. The PTs were conducted on the request of the NAEA what is required by the Polish law [1]. The aim of these PTs was to demonstrate the performance of the radiochemical laboratories which create the radiation monitoring network in Poland. Eleven leading laboratories involved in the radioactive contamination measurements in Poland participated in PTs. The PTs were provided in accordance with ISO/IEC Guide 43-1:1997 [3] and the IUPAC harmonized protocol [11].

The activity concentration of the following radionuclides: ^{241}Am , ^{137}Cs , ^3H , ^{239}Pu , ^{226}Ra and ^{90}Sr were determined in water, milk powder, wheat flour and soil. The test materials were prepared by spiking blank materials with standard solution of the radionuclide of interest. The activity concentrations were calculated by formulation from the quantities used. Associated uncertainties were evaluated from the standard uncertainties of the

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standard solution activity concentration and uncertainties associated with the mode of preparation of test material such as dilution, weighing etc. The procedure adopted for the test material preparation and assignment of activity concentration values with associated uncertainties is described in the paper. The results of the PTs, observed trends in laboratory performance and benefits for the laboratories participating in PTs were evaluated and presented as well.

Experimental

Materials and methods

Potable water, taken from the public sources in Warsaw, commercially available wheat flour and milk powder were used as raw materials. Soil has been simulated using sand applied for glassware production. Sand was chosen because of lack of man-made radionuclides in it. Prior to spiking with radioisotopes, all mentioned above materials were checked for the content of radionuclides to be determined. Solid materials were sieved by appropriate sieves and homogenized by mixing.

Test materials were prepared by spiking a given mass of the appropriate raw material with a known amount of the certified standard solution of the radionuclide of interest supplied by Amersham (^{241}Am , ^{137}Cs , ^{239}Pu , ^{226}Ra and ^{90}Sr) and POLATOM (^3H). All certified solutions contained appropriate nonactive carriers.

In the case of water samples, an appropriate amount of standard solutions were weighed and added to raw water in a polyethylene (PE) container. In the case of ^{241}Am , ^{137}Cs , ^{239}Pu , ^{226}Ra and ^{90}Sr relevant non-radioactive carriers (appropriate salts, mainly nitrates or chlorides) were added (about 10^{-5} M) in order to avoid a possible loss of microamounts of radioisotopes. An appropriate amount of concentrated HNO_3 was added to a water sample to set pH at a value equal to about 1. A spiked water sample was mixed by passing gaseous N_2 and distributed into bottles made of polyethylene terephthalate (PET) of 1.5 or 5 dm³. Concentrations of Na^+ , K^+ , Cs^+ , Mg^{2+} , Ca^{2+} , Sr^{2+} , Ba^{2+} , Cl^- , NO_3^- , SO_4^{2-} as well as transition metals were determined by ion chromatography in all water samples before confectioning into appropriate bottles.

Water containing ^3H was prepared by adding a weighed amount of the tritium standard solution into the weighed amount of distilled water. The obtained water was mixed carefully prior to the distribution into the PET bottles of 1.5 or 5 dm³.

Solid samples were prepared by adding appropriate weighed amount of standard solutions of ^{241}Am , ^{137}Cs , ^{226}Ra or ^{90}Sr to 0.5 dm³ of acetone together with relevant carriers and 100 cm³ of 0.1 M HNO_3 . Next, a spike

acetone solution was added to the raw test material of known mass while mixing. The obtained slurry was kept open and allowed to dry with occasionally (every 1 or 2 h) manual mixing. Finally, the dried material was transferred into a PE drum and homogenized by mixing in a special homogenizer for 8 h. Then, the homogeneity was tested by measuring the activity concentration of the radionuclide in question in six sub-samples taken from different parts of the drum.

The procedure of plutonium spiking was different. Appropriate portions of a raw material of milk powder, wheat flour and sand were weighed into small polypropylene (PP) bottles. Then, an appropriate amount of standard solution of ^{239}Pu was added by weight into each portion separately. The samples were sent to the participants in unhomogenized form. Therefore, the participants were asked to analyze the whole mass of the sample.

The procedures for moisture content determination were established on the basis of water desorption curves determined at various temperatures. The following procedures were recommended:

- Sand – drying a ca. 5 g sub-sample of sand for 1 h at 105°C.
- Wheat flour – drying a ca. 1 g sub-sample of flour for 20 h at 70°C.
- Milk powder – drying a ca. 1 g sub-sample of milk powder for 26 h at 80°C.

Assigned values and associated uncertainties

Before spiking, the samples of raw materials were analyzed in order to determine the content of radioisotopes in question. It was found that in all cases the activity concentration of radionuclides to be determined was below detection limits of the measurement methods used by us. Values of detection limits were at least 2–3 times lower than the activity concentration of radionuclides present in the spiked test materials. As an example, the results for ^{137}Cs and ^{90}Sr are shown in Table 1.

Assigned values of activity concentration of the radionuclides were determined from formulation [4, 5, 11]. The certified activity concentration of each radionuclide provided by the producers, mass of the standard solutions applied for spiking, the dilution steps and mass of material to be spiked were taken into account. Expanded combined standard uncertainty U ($k = 2$) was evaluated in accordance with GUM (Guide to the Expression of Uncertainty in Measurement, ISO recommendations) [3]. The following sources of uncertainty were taken into account: uncertainty of the certified standard solution activity provided in the certificates, weighing of the standard solutions and raw materials, and uncertainty associated with the determination of

Table 1. Comparison of ^{137}Cs and ^{90}Sr activity concentration in raw and spiked test materials

Material	Radionuclide			
	^{137}Cs		^{90}Sr	
	Raw material	Spiked material	Raw material	Spiked material
Water	$\leq 0.015\text{ Bq}\cdot\text{dm}^{-3}$	$0.073 \pm 0.007\text{ Bq}\cdot\text{dm}^{-3}$	$\leq 0.010\text{ Bq}\cdot\text{dm}^{-3}$	$0.076 \pm 0.005\text{ Bq}\cdot\text{dm}^{-3}$
Wheat flour	$\leq 0.1\text{ Bq}\cdot\text{kg}^{-1}$	$0.184 \pm 0.007\text{ Bq}\cdot\text{kg}^{-1}$	$\leq 0.1\text{ Bq}\cdot\text{kg}^{-1}$	$2.30 \pm 0.02\text{ Bq}\cdot\text{kg}^{-1}$
Sand	$\leq 0.1\text{ Bq}\cdot\text{kg}^{-1}$	$1.55 \pm 0.08\text{ Bq}\cdot\text{kg}^{-1}$		

Table 2. Values of standard deviation for proficiency assessment $\hat{\sigma}$ (Bq·dm⁻³ for water, Bq·kg⁻¹ d.m. for sand, milk powder and wheat flour)

Material	Radioisotope	$X_{\text{ref}} \pm U (k = 2)$	$X_{\text{lab}} \pm t_{0.95}S$	$\hat{\sigma}$
Potable water	¹³⁷ Cs	0.073 ± 0.007	0.077 ± 0.013	0.015
	⁹⁰ Sr	0.076 ± 0.005	0.068 ± 0.019	0.015
	²⁴¹ Am	2.008 ± 0.198	1.938 ± 0.216	0.10
	²²⁶ Ra	0.997 ± 0.015	1.011 ± 0.160	0.068
	³ H	20.7 ± 0.6	21.66 ± 2.58	0.93
Milk powder	¹³⁷ Cs	0.436 ± 0.039	0.436 ± 0.064	0.070
	⁹⁰ Sr	0.056 ± 0.030	0.067 ± 0.050	0.050
	²⁴¹ Am	1.918 ± 0.045	2.103 ± 0.346	0.125
Wheat flour	¹³⁷ Cs	0.184 ± 0.007	0.178 ± 0.076	0.031
	⁹⁰ Sr	2.30 ± 0.02	2.33 ± 0.43	0.35
Sand	¹³⁷ Cs	1.55 ± 0.08	1.57 ± 0.39	0.17

moisture content. The results of analysis were referred to the dry mass of tested materials.

Performance evaluation

Individual laboratory performance has been expressed in terms of z and $zeta$ scores, according to the equations [4, 5, 11]:

$$(1) \quad z = \frac{(x_{\text{lab}} - x_{\text{ref}})}{\hat{\sigma}}$$

$$(2) \quad zeta = \frac{x_{\text{lab}} - x_{\text{ref}}}{\sqrt{u_{\text{ref}}^2 + u_{\text{lab}}^2}}$$

where x_{lab} and x_{ref} are the results reported by a participant and assigned value, respectively; u_{ref} and u_{lab} – standard uncertainty of assigned values and reported by the participant, respectively and $\hat{\sigma}$ is the standard deviation for proficiency assessment. The last parameter – $\hat{\sigma}$ – was calculated as standard deviation of reproducibility. The arithmetic mean of all laboratory means was calculated after rejection of outliers. HISTO (Statistical Analysis, Histograms and Outlier Rejection for Intercomparison Data) software provided by the IAEA was applied [9] for calculations. The examples of calculated values of $\hat{\sigma}$ are shown in Table 2.

In the case of ²³⁹Pu determination in water, milk powder and soil, the number of results provided by the participating laboratories was too small to perform a proper statistical evaluation. Then, the values of standard deviation for proficiency assessment were established arbitrary by the PT provider according to the IAEA [2, 7]. Examples are shown in Table 3.

The results obtained by the participants were also evaluated according to the criteria for trueness and

Table 3. Values of standard deviation for proficiency assessment $\hat{\sigma}$ for the determination of ²³⁹Pu (Bq·dm⁻³ for water, Bq·kg⁻¹ d.m. for sand, milk powder and wheat flour)

Material	$X_{\text{ref}} \pm U (k = 2)$	$\hat{\sigma}$
Drinking water	1.78 ± 0.048	0.30
Milk powder	1.82 ± 0.20	0.35
Sand	0.28 ± 0.03	0.06

precision proposed by the IAEA [2, 7, 8, 10]. The criteria are as follows:

1. Result passes trueness criterion, if:

$$(3) \quad |x_{\text{ref}} - x_{\text{lab}}| \leq 2.58\sqrt{u_{\text{ref}}^2 + u_{\text{lab}}^2}$$

2. Result passes precision criterion if:

$$(4) \quad \sqrt{\left(\frac{u_{\text{ref}}}{x_{\text{ref}}}\right)^2 + \left(\frac{u_{\text{lab}}}{x_{\text{lab}}}\right)^2} \cdot 100\% \leq \hat{\sigma} [\%]$$

Value of $\hat{\sigma}$ is the same as used in calculation of z -score value or it is a maximum value of uncertainty which can be accepted.

Results and discussion

Test materials prepared as described above were used in the course of PTs. Till now five PTs have been conducted (one PT yearly). 12 to 15 laboratories (from the total number of 17: 11 from the radioactivity monitoring network and 6 from outside the network) participated in each PT. Test materials, radionuclides and levels of their activity concentration were proposed by the NAEA on the basis of typical routine analyzes carried out by Polish laboratories and demanded by the Polish law [1, 6]. Before sending the test samples to the PT participants, the values of the activity concentrations were assigned. Assignment of property values was based on formulation. The metrological traceability was established by using the certified standard solutions traceable to the SI units. Uncertainties of property values assigned by formulation are, as a rule, lower than those evaluated by other methods [6]. Therefore, the PT materials could be used to assess precision as well as accuracy of the results provided by the participants.

Amounts of test samples sent to the PT participants were customized for the participating laboratory requirements. Samples of test materials were homogenized except solid samples containing ²³⁹Pu which were spiked individually for each laboratory without homogenization. Those samples are provided with individually assigned values traceable to the SI unit. Samples of water were homogeneous from their nature, as there were real solu-

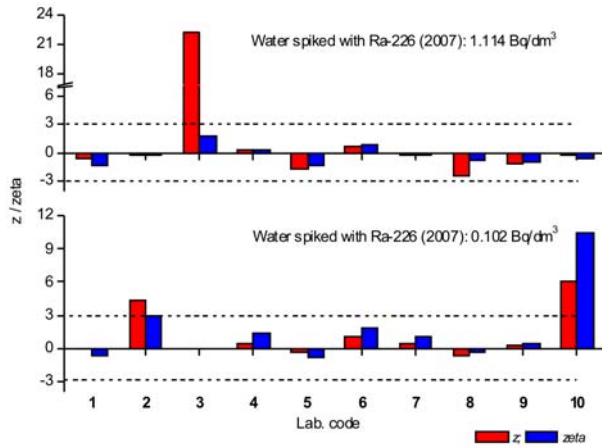


Fig. 1. *z* and *zeta* scoring of the results of ²²⁶Ra measurement in water in PT organized in 2007.

tions. Homogeneity of solid materials spiked with ²⁴¹Am, ¹³⁷Cs or ⁹⁰Sr was tested taking samples of a size being the smallest one analyzed by the participants. Fisher's test was applied to assess if there are not statistically significant differences between uncertainty of the applied measurement method and the observed measurement variations. In the case of all test materials spiked with ²⁴¹Am, ¹³⁷Cs or ⁹⁰Sr no evidence of inhomogeneity was found. The uncertainty associated with the inhomogeneity was estimated to be insignificant comparing with that arising from the measurement step. It resulted from the very low presence of radioactivity in test materials. However, such radioactivity level was closed to the routine activity measurement of the real samples [6]. From the NAEA point of view, it is important to obtain a realistic evaluation of the trueness of measurements under routine conditions and an estimation of the comparability of results from the different radioactivity monitoring laboratories. The performance of participating laboratories was then evaluated by means of *z* and *zeta* scores as it is recommended by ISO Guides and IUPAC Harmonized Protocol [4, 5, 11]. On the other hand, the radiochemical laboratories participate, as a rule, in the ILC/PT conducted by the IAEA and are used to the evaluation approach used by the IAEA. It is known that the IAEA approach is more rigorous than the *z*-scoring one [10]. Therefore, the results provided by the laboratories were also evaluated using the criteria for the trueness and precision applied by the

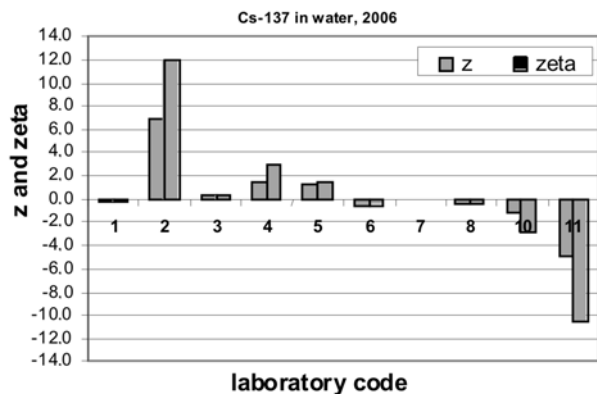


Fig. 2. *z* and *zeta* scoring for ¹³⁷Cs determination in water (PT organized in 2006).

IAEA [10]. It can help the laboratories to compare their performance during participation in the PTs organized both by the IAEA and the NAEA.

An example of a performance evaluation can be seen in Figs. 1 and 2.

Monitoring of laboratory performance over the time is one of the objectives of the participation in the PT. In order to ascertain long-lasting trends, the scoring of laboratory results from the PTs organized in 2004–2008 has been compared. Some examples of water analysis results of individual laboratories obtained in few PTs have been shown in Fig. 3.

It can be seen that the high experienced laboratories specialized in radioactivity measurement in water reveal results of very good accuracy ($|z| \leq 2$). It can be noticed also (see Figs. 1 and 2) that the laboratories have problems with the procedures of uncertainty estimation. However, the improvement of uncertainty evaluation

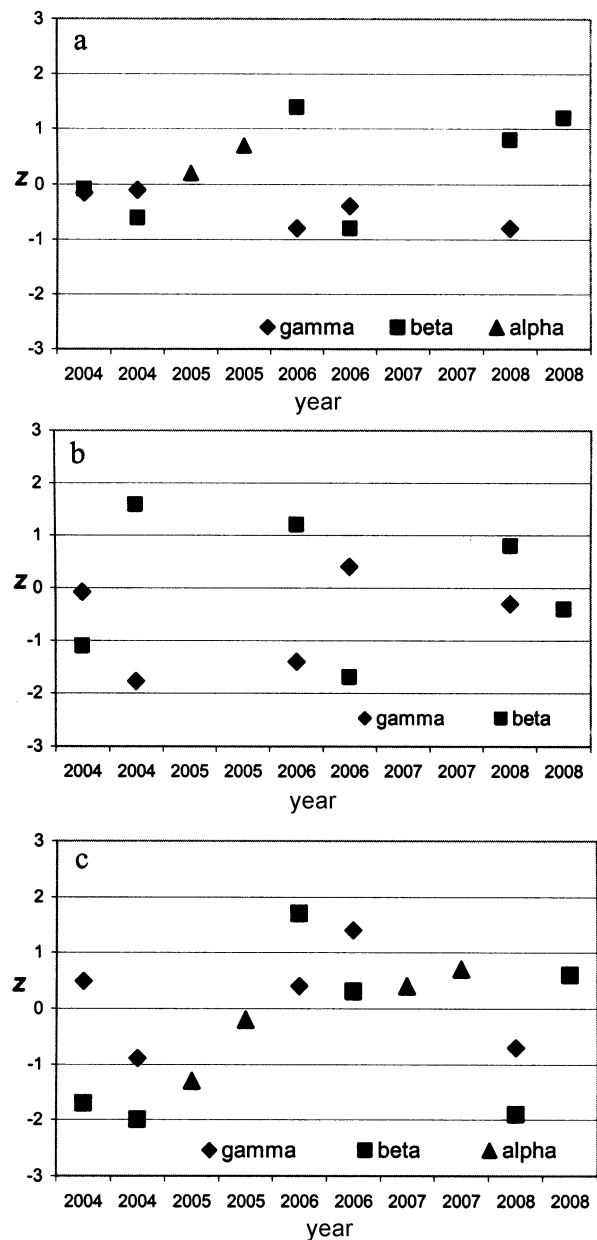


Fig. 3. Performance of three laboratories: a – Laboratory 1; b – Laboratory 2; c – Laboratory 3 during the PT in the years 2004–2008.

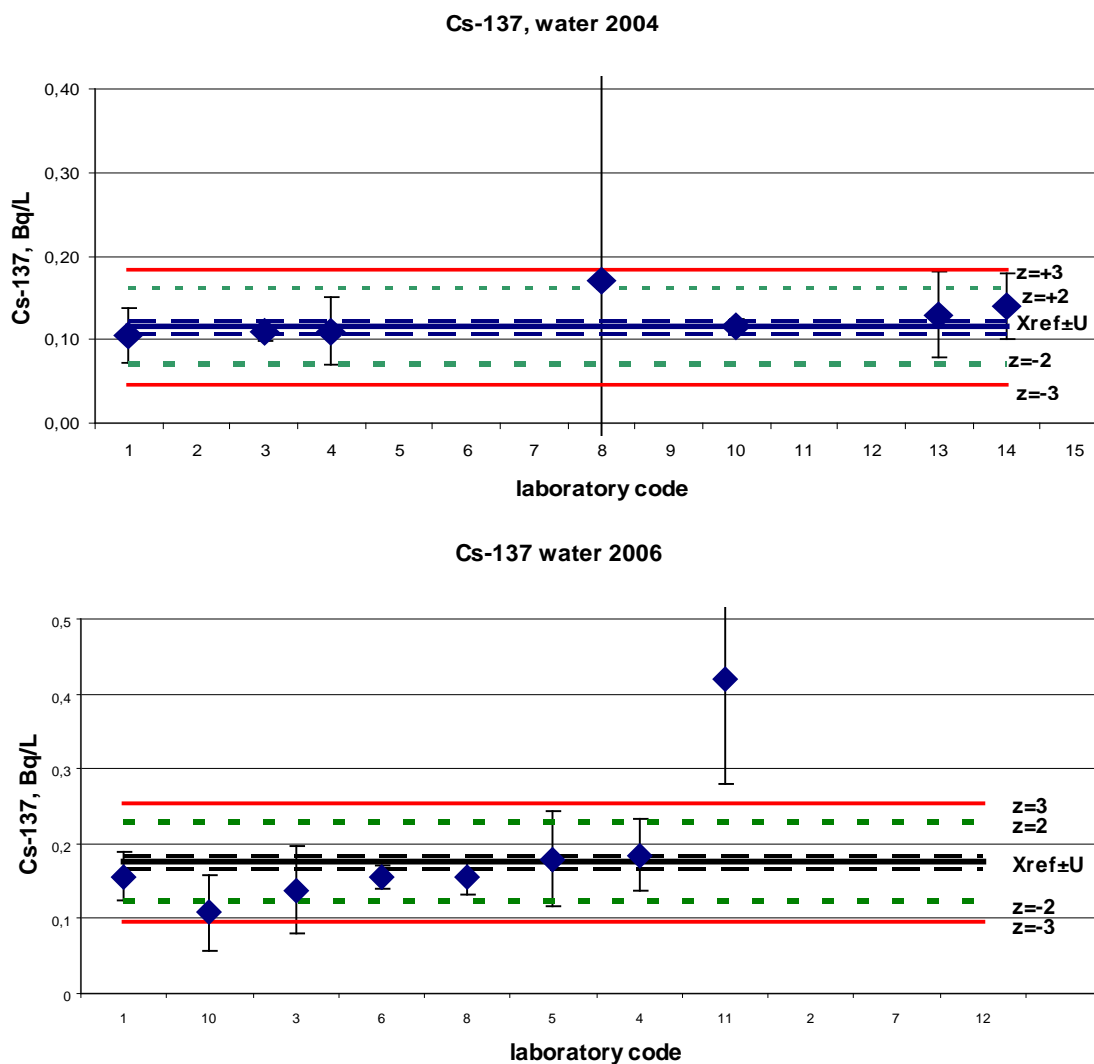


Fig. 4. Results of the determination of radioactivity concentration of ^{137}Cs in water in 2004 and 2006.

procedure has been observed in some cases, as can be seen from Fig. 4 (laboratory no. 8). All provided results are satisfactory ($|z| \leq 3$) except for laboratory 11 in 2006, which started determination of ^{137}Cs in 2006.

Conclusions

National PTs provide the participating laboratories with the test materials of matrix composition and radioactivity levels close to routinely analyzed samples. Participation in such PTs could provide the users of laboratories' services, e.g. the NAEA and also the society, in confidence to the results produced by the laboratories and could give the laboratories more confidence to their skill and procedures applied. All leading laboratories from the radioactivity monitoring network, participating in the PTs organized by the NAEA are high-experienced in the determination of radioactivity in environmental and food samples. The results provided by these laboratories, as a rule, fit for purpose. During a few recent years, the improvement in the analytical procedures applied, and laboratory performance can be observed in the case of some PT participants.

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