

Interlaboratory comparison of the determination of ^{137}Cs and ^{90}Sr in water, food and soil: preparation and characterization of test materials

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Abstract Only reliable analytical results can serve as a basis of meaningful evaluation and protection of the environment against radioactive contaminants. So, laboratories dealing with the environmental radioactivity determinations should regularly demonstrate their ability to produce acceptable results. Since 2002, every two years organization of national interlaboratory comparisons (ILC) on the determination of different radionuclides in food and environmental samples is required by the Polish law. The aim of the paper is presentation how test materials applied in the Institute of Nuclear Chemistry and Technology (INCT, Warsaw, Poland) for the 2004 ILC on the determination of ^{137}Cs and ^{90}Sr in water, food and soil were prepared.

Key words ^{137}Cs • ^{90}Sr • determination • food • soil • water

Reliable measurements of radioisotope concentrations are of primary importance for the laboratories dealing with radioactivity determinations. Only reliable analytical results can serve as a basis of meaningful evaluation and protection of the environment against radioactive contaminants. Laboratories should demonstrate their ability to produce reliable results. This can be done by participation in the interlaboratory comparisons (ILC). It is also recommended by ISO/IEC 17025 standard [11]. Since 2002, every two years organization of national ILC on the determination of different radionuclides in food and environmental samples is required by the Polish law [1]. First, such ILC on the determination of cesium-137 and strontium-90 in water, food and soil has been organized by the National Atomic Energy Agency of Poland in 2004. Fourteen laboratories from different Polish research institutes and universities have participated in this experiment. The Institute of Nuclear Chemistry and Technology was a coordinator of the ILC.

The main goal of presented paper is to show the way of preparation of the test materials applied in the Institute of Nuclear Chemistry and Technology (INCT, Warsaw, Poland) for the 2004 ILC on the determination of ^{137}Cs and ^{90}Sr in water, food and soil. Detailed results of the ILC will be presented elsewhere under the auspices of the National Atomic Energy Agency of Poland.

Experimental: general

While analyses of ^{137}Cs in environmental samples produce difficulties only when the radioisotope content

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is present at a very low level – those of ^{90}Sr bring usually certain problems. Classical method of strontium analysis requires separation of the alkaline-earth cations (Ca^{2+} , Sr^{2+} , Ba^{2+} , Ra^{2+}) from other matrix elements through a carbonate precipitation. Calcium is eliminated through precipitation of strontium nitrate prior to barium and radium separation as the chromates. Then, ^{90}Y – the descender of ^{90}Sr is eliminated through a hydroxide precipitation. The purified ^{90}Sr is allowed to stand for growth of ^{90}Y . Noticeably, the traditional method is costly, time-consuming and hazardous. So, a great number of procedures have been elaborated, tested and published. For example, only in one journal – *Journal of the Radioanalytical and Nuclear Chemistry* in the period of 2000–2004 eleven different scientific groups have reported their own analytical methods [7–9, 12–19]. They are based mainly on the coprecipitation, ion exchange, solvent extraction or extraction chromatography.

Materials

Two types of water have been used: surface and potable water, taken from the public sources in Warsaw.

Wheat flour (confectionary type, grade 500) was supplied by Zakłady Przetwórstwa Zbożowego “Szymanów”, Sp. z o.o. (Teresin, Poland). Before treatment, it was homogenized by mixing for 5 h in a plastic drum placed in a mechanical homogenizer according to the procedures elaborated in the INCT [2–5].

Soil has been simulated using sand applied for glassware production. It was homogenized in the same way as wheat flour.

All the aforementioned materials were checked for the absence of ^{137}Cs (long-lasting γ -spectrometry) prior to their spiking with well defined amounts of certified radioactive standard solutions. Absence of ^{90}Sr has been checked by the LSC measurements. Details of both measurements will be presented in the next section.

^{137}Cs and ^{90}Sr radioisotopes were obtained as certified aqueous nitrate solutions from Amersham (Braunschweig; with the help of national representative – Biker Ltd, Warsaw).

All chemicals used were of analytical grade (Sigma-Aldrich, Poznań, Poland). Solvents (technical grade) were obtained from the Polish Chemicals SA (Gliwice).

In order to determine the moisture content, samples of the solid materials were dried to their constant mass at 105°C for 1 h or 70°C for 20 h, for soil or flour, respectively. For ^{137}Cs measurements, samples were placed in a 0.5 dm^3 Marinelli vessel and analyzed using a γ -ray spectrometer. Liquid samples were measured in the same way as prepared. The measuring time varied from 24 h to 7 days, depending on the radioactivity concentration. The detection limit was $0.01\text{ Bq}\cdot\text{kg}^{-1}$ at a 95% confidence level. Wheat flour samples for strontium-90 measurements were burned to ashes, dissolved in nitric acid and analyzed using LSC measurements (see, the next section).

Instrumentation

- Two gamma-ray spectrometers: (a) digital (DSPEC, ORTEC set) with a co-axial HPGe detector (ORTEC; resolution: 1.9 keV for the 1.33 MeV peak and the relative efficiency of 92.4%) and GAMMA VISION software; (b) with a co-axial HPGe detector (ORTEC; spectral resolution: 1.9 keV for the line of 1.33 MeV and the relative efficiency of 40%) with an ORTEC analogue line and a multichannel analyzer TUKAN (IEA, Świerk). In order to reduce the natural radiation background, the detectors have been placed in passive, 10 cm-thick lead shields,
- alpha-beta ray liquid scintillation counter TRICARB 2900 TR (Packard),
- ion chromatographic set DIONEX 2000isp,
- mechanical homogenizer (own construction of the INCT).

Experimental: details of sample preparation

Six samples of water and four solid samples containing both radioisotopes at concentration levels mentioned in Table 1 were prepared and distributed between the participants of the ILC.

Aqueous samples

Four aqueous solutions spiked with radioisotopes have been prepared in a total volume of 120 dm^3 , each.

Table 1. Radioactivity concentration levels of ^{90}Sr and ^{137}Cs in particular samples

Sample		^{90}Sr	^{137}Cs
Potable water	reference sample	natural background	natural background
	low activity sample	$0.02\text{ Bq}\cdot\text{dm}^{-3}$	$0.03\text{ Bq}\cdot\text{dm}^{-3}$
	high activity sample	$0.1\text{ Bq}\cdot\text{dm}^{-3}$	$0.1\text{ Bq}\cdot\text{dm}^{-3}$
Surface water	reference sample	natural background	natural background
	low activity sample	$0.1\text{ Bq}\cdot\text{dm}^{-3}$	$0.15\text{ Bq}\cdot\text{dm}^{-3}$
	high activity sample	$0.5\text{ Bq}\cdot\text{dm}^{-3}$	$0.5\text{ Bq}\cdot\text{dm}^{-3}$
Wheat flour	low activity sample	$0.1\text{ Bq}\cdot\text{dm}^{-3}$	$0.15\text{ Bq}\cdot\text{dm}^{-3}$
	high activity sample	$0.4\text{ Bq}\cdot\text{dm}^{-3}$	$0.4\text{ Bq}\cdot\text{dm}^{-3}$
Sand	low activity sample	–	$1\text{ kBq}\cdot\text{m}^{-2}$
	high activity sample	–	$5\text{ kBq}\cdot\text{m}^{-2}$

Concentrations of Na^+ , K^+ , Cs^+ , Mg^{2+} , Ca^{2+} , Sr^{2+} , Ba^{2+} , Cl^- , NO_3^- , SO_4^{2-} cations and anions were determined by means of ion-chromatography in all spiked solutions as well as in the natural waters. To avoid a possible loss of microamounts of the radioisotopes, e.g. by adsorption, non-active carriers of Cs^+ ($5 \text{ mg}\cdot\text{dm}^{-3}$) and Sr^{2+} ($1 \text{ mg}\cdot\text{dm}^{-3}$) were added as chlorides. pH value of all aqueous samples was maintained about 1 by the addition of an appropriate amount of concentrated nitric acid. Proper mixing of the components was assured by passing gaseous nitrogen through water placed in 200 dm^3 polyethylene (PE) containers for 15 min.

Solid samples

Two samples of wheat flour containing ^{137}Cs and ^{90}Sr and two of sand containing ^{137}Cs only were prepared by spiking the base materials with certified radioactive standard solutions.

Desired amounts of the radioisotope solutions were weighed out from the initial standards and dissolved in 500 cm^3 of acetone. $125 \text{ mg}\cdot\text{kg}^{-1}$ of cesium chloride and $100 \text{ mg}\cdot\text{kg}^{-1}$ of SrCl_2 were added in the course of flour spiking, while $2 \text{ mg}\cdot\text{kg}^{-1}$ of CsCl in the case of sand. Simultaneously, 10 kg portion of the base material has been poured with 4.5 dm^3 of acetone and homogenized by mixing for 5 h in a 50 dm^3 PE drum placed in the homogenizer. After completion of mixing, both components were combined and the material was homogenized for additional 5 h, transferred into PE plates and left for slow acetone evaporation (2–3 days). Dried materials were mixed manually several times per day. After final homogenization in the PE drums, the spiked material has been packed into the PP containers. Three randomly selected samples were analyzed for the ^{137}Cs content in order to check the homogeneity of the materials.

Experimental: analytical part

Analysis of content of cesium-137

450 cm^3 of aqueous solution or 250 g of solid material was placed in a Marinelli vessel and measured for the ^{137}Cs content using low background-level γ -ray spectrometry. Total 661.63 keV peak area (TPA) was applied for estimating the activity. The detector efficiency curve for the whole $60\text{--}1836 \text{ keV}$ range was checked using the AEA technology certified volumetric standards.

Radiocesium concentration has been calculated using the following formula:

$$A_u = \frac{R_u(E) \cdot f_d}{\varepsilon \cdot m}$$

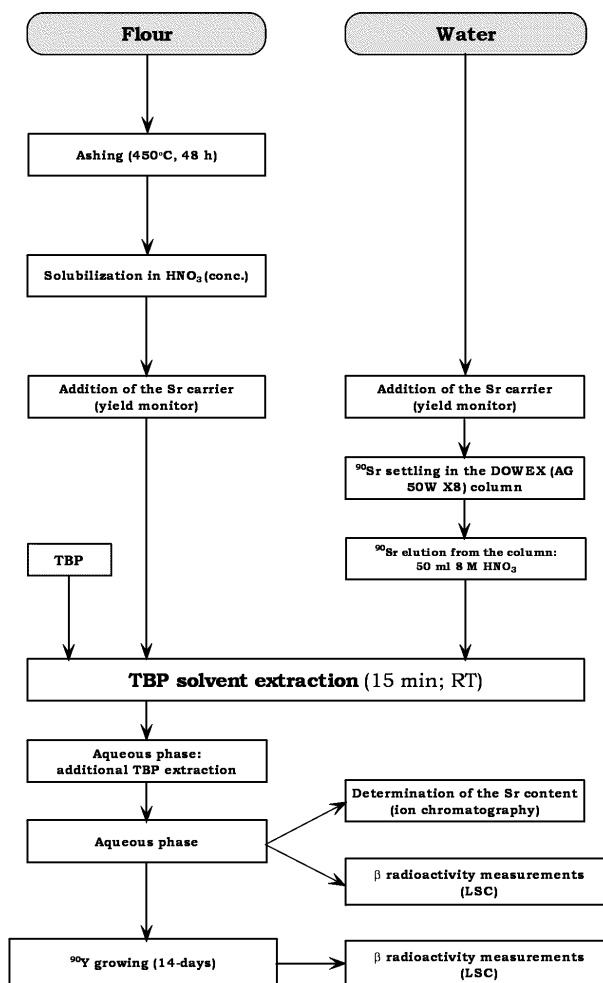
where A_u denotes the ^{137}Cs radioactivity (in $\text{Bq}\cdot\text{g}^{-1}$) corrected for its decay, R_u is the peak counting rate, ε is the detector efficiency for the ^{137}Cs spectral line ($E = 661.63 \text{ keV}$), m is the sample mass and f_d is a correction factor for the isotope decay during the measurement period.

Strontium-90 content analysis

Full course of the strontium-90 analysis is presented in Scheme 1. Supplementary details can be obtained from the authors on request.

Radioactivity measurements of the defined volumes of the TBP phase extract (usually: 5 cm^3) containing the ^{90}Y isotope were performed using the LSC method with the ULTIMA GOLD (Packard) or RIAFLUOR (NEN) scintillation cocktails. 96% efficiency of the detection has been achieved. Measurement times varied from 600 to 1200 min and the correction factor for the isotope decay during the measurement period was applied. Absolute ^{90}Sr content in the extract has been based on the comparison with the measurements of the certified standard treated using the same procedure. Radiochemical efficiency of ^{90}Y averages to $95\% \pm 3\%$.

Chemical and radiochemical efficiency of strontium determination (on the basis of non-radioactive carrier determination) was performed using the ion-chromatography method with an IonPac CS12A column, suppressor CSRS-11 and conductometric detection. 18 mM methanesulphonic acid eluent was applied. Detection limit for the strontium determination was $0.03 \text{ mg}\cdot\text{dm}^{-3}$. Yttrium content determinations were carried out using the IonPac CS3 column, post-column reaction system and spectrophotometric detection



Scheme 1. Scheme of strontium-90 analytical procedure.

Table 2. Assigned values of ^{90}Sr and ^{137}Cs in particular samples [$\text{Bq}\cdot\text{dm}^{-3}$]

Sample		^{90}Sr	^{137}Cs
Potable water	reference sample	below the detection limit	below the detection limit
	low activity sample	0.020 ± 0.002	0.031 ± 0.002
	high activity sample	0.102 ± 0.008	0.115 ± 0.008
Surface water	reference sample	below the detection limit	below the detection limit
	low activity sample	0.101 ± 0.007	0.157 ± 0.010
	high activity sample	0.501 ± 0.033	0.498 ± 0.033
Wheat flour	low activity sample	0.150 ± 0.005	0.285 ± 0.008
	high activity sample	0.479 ± 0.017	0.537 ± 0.019
Sand	low activity sample	–	6.15 ± 0.25
	high activity sample	–	31.60 ± 1.07

(wavelength: 520 nm). Gradient elution using 18 M Ω cm water and 0.4 M α -hydroxy isobutyric acid (pH 4) solution was performed. A mixture of 0.2 mM PAR + 1 M CH_3COOH + 3 M NH_4OH was applied as the complexing agent. Detection limit for yttrium determination appeared to be 0.01 $\text{mg}\cdot\text{dm}^{-3}$.

Results and conclusions

Bulk materials prepared as described above were used in the course of ILC. After dividing into individual samples, the latter were distributed to fourteen radiochemical laboratories for analysis. Because laboratories applied different measurement techniques, the analyzed samples differed in mass.

Homogeneity of test materials is of crucial importance for a comparability of the results and consequently for a successful assessment of laboratory performance. A consensus value is often used to determine the

assigned values. However, if the test materials used for the studies have traceable assigned values, then ILC provides an accuracy of results in the participating laboratories. The prepared test materials were spiked using certified radionuclide solutions traceable to SI. Target values of the ^{137}Cs and ^{90}Sr radioactivity concentration have been assigned considering the way the test materials were prepared. The uncertainties of the assigned values have been evaluated taking into account all possible sources of uncertainty using GUM [10] and EURACHEM Guides [6]. The assigned values are summarized in Table 2.

Figure 1 presents, as an example, comparison of the results reported by the participating laboratories with the assigned value. A plot of the normal curve with a maximum at the assigned value is obtained. So, it can be concluded that the procedures of assigning value and preparation of homogenous material are properly done.

The main conclusion drawn from the ILC'2004 is that the majority of the determinations remain in good

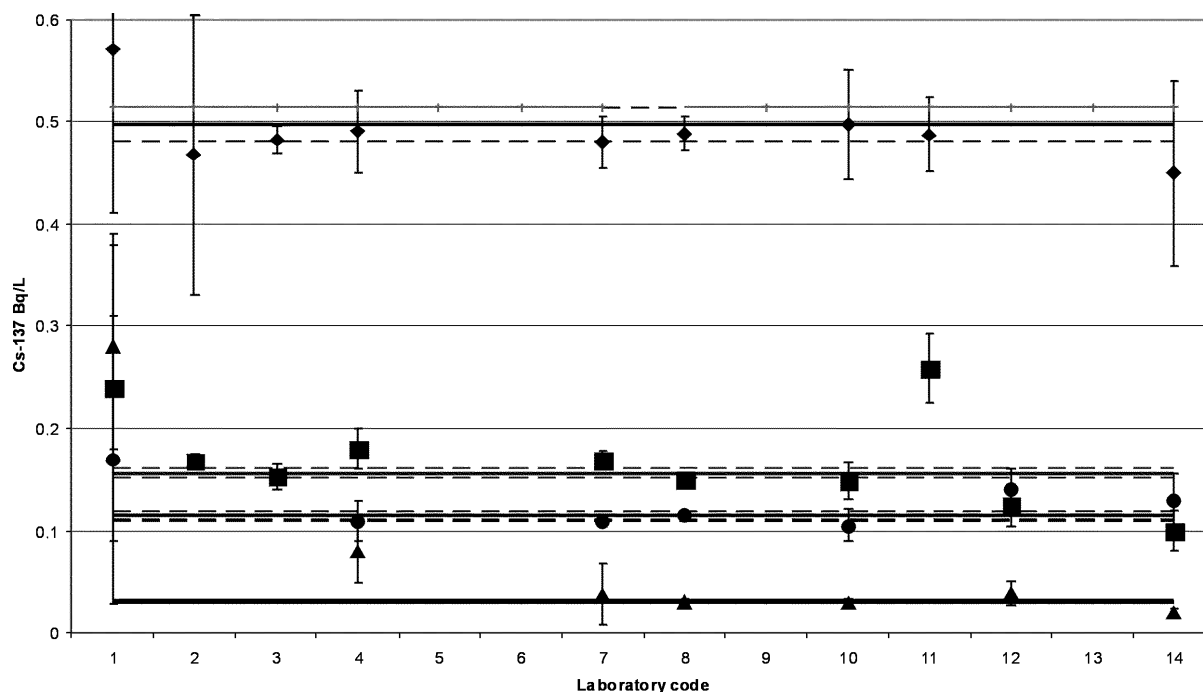


Fig. 1. An example presenting results obtained in the laboratories participating in the ILC'2004: determination of ^{137}Cs in water.

agreement with the assigned values and the results obtained by other laboratories. Such agreement means that the performance of laboratories is good and also that the samples are equivalent. As the analyzed samples were different in size and randomly chosen, it can be concluded that the bulk materials were homogeneous. Moreover, there were no losses of the radioisotopes added to the base materials. So, the presented way of preparation and characterization of the test materials allows the use of such materials for conducting proficiency tests on the determination of ^{137}Cs and ^{90}Sr .

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