Romanian Reports in Physics, Vol. 63, Supplement, P. 1195–1204, 2011

Dedicated to Professor Marin Ivaşcu's 80th Anniversary

RESULTS OF PROFICIENCY TESTS ON THE MEASUREMENT OF VOLUME RADIOACTIVE SOURCES FROM THE MIXTURE: ^{134}Cs and ^{137}Cs*

MARIA SAHAGIA*, ANDREI ANTOHE, AURELIAN LUCA, CONSTANTIN IVAN

*"Horia Hulubei" National Institute for Physics and Nuclear Engineering, IFIN-HH, P.O.Box MG-6, RO-077125 Bucharest-Magurele, Romania
E-mail: msahagia@nipne.ro; msahagia@yahoo.com

Received July 28, 2011

Abstract. The Radionuclide Metrology Laboratory (RML) from IFIN-HH organized proficiency tests regarding the measurement of the radioactive content of the food products, water equivalent, with the involved laboratories. RML prepared 14 solid volume sources, of cylindrical shape, containing a mixture of Cs-134 and Cs-137 radionuclides, uniformly distributed in a water equivalent matrix. 13 participants from the National Sanitary Veterinary and Food Safety Authority (ANSVSA), each of them measuring a different source, and 7 accredited laboratories from IFIN-HH, which measured a single source in a round robin test, took part in exercise. The results obtained in these exercises, as well as the improvements since two similar previous tests, are presented.

Key words: proficiency test, food products, mixture of Cs-134 and Cs-137 radionuclides.

1. INTRODUCTION

The Radionuclide Metrology Laboratory (RML) is accredited by RENAR for calibration in the field of radioactivity measurement, and for testing in the measuremnt of low level radioactivity; it assures the metrological traceability chain, from the international level, up to the end users. An important number of the Romanian analysis laboratories measure the environment and food chain radioactive content. A special attention is paid to the radionuclides ^{134}Cs and ^{137}Cs. They are both beta - gamma-ray emitters and usually are measured by the gamma-ray spectrometry method. In order to improve the sensitivity of the method, relatively large volume samples are measured. RML prepares solid volume standards, of cylindrical shape,

* Paper accepted for presentation at the conference "PTconf" The Third International Proficiency Testing Conference, September 2011, Iaşi, Romania.

with source dimensions: inner diameter 73 mm, height (37 ± 5) mm, in plastic containers, with wall thickness 0.5 mm, outer diameter 78 mm, usually known as the SARPAGAN geometry. The radioactive content is uniformly distributed in three types of matrices: water equivalent, soil and zeolite [1, 2]. The sources with water equivalent matrix, consisting from a polyacrylamide-water gel, prepared according to the procedure described in [1], are used for the measurement of liquids, and water equivalent solids. These sources are IFIN-HH qualified, authorized for radiological safety and internationally recognised, as mononuclide sources, with published Calibration and Measurement Capability (CMCs) files [3, 4]. IFIN-HH, RML participated at many international comparisons and PT exercises on the measurement of the volume activity sources, to verify the quality of its own standards, and to check the methods for the preparation of solid samples and the application of the gamma-ray spectrometry method [5]. RML organized in the past national comparisons of radioactive sources [6, 7]. This paper describes a recent exercise, on the measurement of water equivalent volume standard sources, from a mixture of ^{134}Cs and ^{137}Cs, and compares its results with those obtained in previous exercises.

2. ORGANIZATION OF THE PROFICIENCY TESTS

Among the most frequent users of radioactive volume standard sources, are the specialist laboratories belonging to the National Sanitary Veterinary and Food Safety Authority (ANSVSA), involved in the evaluation of the foodstuff radioactivity content. The laboratories are provided with systems based on the use of the gamma-ray spectrometry method, with high resolution, HPGe, or low resolution, NaI(Tl) detectors and spectrometry analysers. RML is the traditional provider of volume standard sources, mainly from the radionuclides ^{134}Cs and ^{137}Cs.

2.1. PRELIMINARY STEPS OF THE TESTS (COMPARISONS)

The Proficiency Test (PT), as a comparison exercise, started at the formal request of ANSVSA. The prescriptions of the Work Procedure (WP) Code AC-PL-LMR-07, “Organization of interlaboratory comparisons on the activity measurement of radioactive solutions and solid sources” were followed. The formal invitation was addressed to the participants, according to the form: AC-PL-LMR-07-01, which established: the type of samples to be distributed with their main characteristics, the primary documents, type of reported results and a precise schedule of work. RML laboratory decided then to extend the proficiency test for the IFIN-HH gamma-ray spectrometry laboratories, in order to help them to evaluate their performances and to demonstrate their participation in such exercises on the requirement of accreditation bodies.

2.2. PREPARATION AND DISTRIBUTION OF SAMPLES

The subject of the comparison consisted from a set of standard volume radioactive sources, considered as blind samples, of cylindrical geometry, type SARPAGAN, containing a mixture of the radionuclides ^{134}Cs and ^{137}Cs, with the total nominal activity of 1000 Bq, uniformly distributed in a water equivalent solid matrix.

2.2.1. Preparation, testing and calibration of sources, activity and its uncertainty

A mixture solution, from ^{134}Cs and ^{137}Cs, with the component radioactive concentrations of: ^{134}Cs – (1 140 ± 25) Bq g^{-1} and ^{137}Cs – (1 238 ± 26) Bq g^{-1}, was prepared by gravimetrical dilution, from standard solutions. A number of 14 sources were prepared, by gravimetrical dispensing of precisely determined solution masses, with the analytical balance, in each SARPAGAN container. The WP code AC-PL-LMR-10 and relevant work instructions were followed. The individual activities of sources, for each radionuclide, were calculated as the product of radioactive concentration and source mass. Then the sources were conditioned as liquid water equivalent and polymerized at the IFIN-HH Irradiator IRASM. Supplementary tests were performed: the vertical uniformity of radionuclide distribution and the variation of the ratio - counting rate *versus* activity, N_γ/A. The uniformity was better than 2% and the standard deviation of N_γ/A was 0.2%. The activity uncertainty was calculated by combining the uncertainty of solution concentration with weighting and was established as $u_c = 2.2\%$, $k = 1$, for both radionuclides.

2.2.2. Distribution of sources

The distribution was done in accordance with the prescriptions of the form AC-PL-LMR-07-01. The activity of sources was under the limit of CNCAN exemption for transport and use; they were accompanied by the technical form, AC-PL-LMR-07-02, and the reporting form, code AC-PL-LMR-07-03. 13 sources went to the participants from the ANSVSA network and the 14-th one was used by the IFIN-HH gamma-spectrometry laboratories, RENAR accredited and/or CNCAN notified for testing.

2.3. MEASUREMENT OF SAMPLES BY PARTICIPANTS AND REPORTING OF RESULTS

The measurement reports, code AC-PL-LMR-07-03, contained two types of measurement informations, relevant for the judgement of results and for establishing a possible connection between them and the measurement conditions:

(i) the used equipment and its calibration state, calibrating laboratory, used standards and date of the last calibration; (ii) conditions of measurement, processing of data and applied corrections, if relevant. RML recommended to use the decay data published in the Monographie BIPM-5 [8], mandatory for the metrology activity.

2.3.1. Participants from the ANSVSA network. Equipment and measurement conditions

The gamma-ray spectrometers contained both high energy resolution-HPGe and low resolution – NaI(Tl) detectors. The calibration of the equipment was perfomed by: National Institute of Metrology, Bucharest; two IFIN-HH collectives; Institute of Public Health, Cluj; MECRO SYSTEM srl., Bucharest. It is of recent date. Mononuclide ^{134}Cs and ^{137}Cs standard sources, in SARPAGAN recipients, provided by IFIN-HH, RML, were used for calibration.

The laboratories follow common procedures of measurement, processing of data and reporting, consisting from: the sample is placed at zero distance from the detector window and measurement is done in established energy intervals, centred on the full absorpion peaks: 604.69 keV and 795.84 keV for ^{134}Cs; 661.66 keV for ^{137}Cs. This was a simplifying factor in calibration and in processing of data: there was in these cases a simple relative measurement. In the case of ^{137}Cs, when using Na(Tl) detectors, the main problem is the influence of overlapping of ^{134}Cs radiations on its gamma-ray energy. The ratio signal: background was very variable, depending on the shielding, efficiency and used energy interval, but it is large, due to the relatively high activity of sources.

2.3.2. Participants from IFIN-HH. Equipment and measurement conditions

Only high resolution HPGe detectors were used. The calibration of the equipment was performed by: IFIN-HH, RML and CMRID, MECRO SYSTEM srl and own calibration. The participant laboratories usually perform all kind of measurements for a large variety of radionuclides and types of samples. Volume ^{134}Cs and ^{137}Cs and point ^{60}Co,^{133}Ba, ^{137}Cs, ^{152}Eu and ^{241}Am sources, provided by IFIN-HH, RML and IAEA standard solution, were used in calibration. Various distances source-detector were used. For this reason, the main problem was to calculate the coincidence summation for ^{134}Cs and the corrections due to the source shape and dimensions, source matrix and those due to the distance source - detector, by several softwares. No overlapping of photopeaks occured, due to the use of high resolution HPGe detectors. Various softwares were implemented, including corrections for the above influences.

3. PROFICIENCY TESTS RESULTS

3.1. REPORTED RESULTS AND REMARKS REGARDING THEIR ACCEPTANCE

The results are presented in Table 1 for ANSVSA network and Table 2 for IFIN-HH laboratories. The following data are presented: conventionally true activity (reference activity certified by RML) A_{CA}, [Bq]; reported activity A_R and uncertainty, calculated according the formula recommended by RML; difference: $U = \frac{A_R - A_{CA}}{A_{CA}}\,[\%]$; $E_n = \frac{U}{k\sqrt{u_{c1}^2 + u_{c2}^2}}$ $(k = 2)$. The combined uncertainty of A_{CA} is $u_{c1} = 2.2\%$ $(k = 1)$ for both radionuclides. Acceptance condition: $E_n \le 1$, Y/N (passed or not).

Table 1

ANSVSA network results

^{134}Cs on 01.11.2010					^{137}Cs on 01.11.2010				
A_{CA}	$A_R \pm u_{c2\%}$	U [%]	E_n	Y/N	A_{CA}	$A_R \pm u_{c2}$ [%]	U [%]	E_n	Y/N
545	545±3%	- 0.1	0.01	Y	592	581± 3%	-1.8	0.24	Y
546	544±6%	- 0.4	0.03	Y	593	522±7%	- 12	0.72	Y*
544	492± 2%	- 9.6	1.5	N**	591	615±3%	+4.2	0.57	Y
547	390±14%	- 29	1.0	Y*	594	715±14%	+20	0.71	Y*
545	484±26%	- 11	0.21	Y*	591	593±26%	+0.3	0.01	Y
568	578±11%	+ 1.6	0.07	Y	617	547±14%	-11	0.39	Y
542	520±5%	-4.0	0.37	Y	588	571±4%	-3.0	0.33	Y
551	542±8%	-1.5	0.10	Y	598	570±8%	- 4.8	0.28	Y
547	527±7%	-3.7	0.48	Y	594	582±8%	-2.2	0.14	Y
567	546± 7%	-3.7	0.27	Y	616	622±4%	+1.0	0.11	Y
543	584±15%	+7.7	0.25	Y	589	615±16%	+4.4	0.14	Y
545	578± 7%	+ 6.1	0.40	Y	591	617±7%	+4.3	0.29	Y
546	618±11%	+13	0.58	Y*	593	622±12%	+4.9	0.20	Y

Notes and comments on Table 1. Y* means: the results are not satisfactory enough, but the test was passed, because large uncertainties were reported. N** means: the analyst measured correctly the source, both radionuclides, but underestimated the uncertainty.

The results reflect the measurement conditions and the skill of the analyst, as follows. The fourth analyst reported different results from the others and a further analysis is necessary, although he passed the E_n and z-score tests for both nuclides, due to the high value of the standard deviation of the comparison. The fifth analyst reported much larger uncertainties than the others; these values allowed for passing the acceptance test; the z score is also passed. A further analysis of the results quality will depend on the agreement of their reported uncertainties with the regulation requirements.

Table 2

IFIN-HH laboratories' results.
Source code SEG 8-586, with the conventionally true activity: ^{134}Cs - A_{CA}= 546.3 Bq and ^{137}Cs - A_{CA} = 593.3 Bq and uncertainty u_{c1} = 2.2% for both radionuclides, was measured by 7 participants from IFIN-HH

^{134}Cs on 01.11.2010					^{137}Cs on 01.11.2010				
P	$A_R \pm u_{c2,\%}$	U [%]	E_n	Y/N	P	$A_R \pm u_{c2,\%}$	U [%]	E_n	Y/N
1	542±2.6%	-0.79	0.12	Y	1	579±2.6%	- 2.4	0.36	Y
2	544±3.4%	-0.42	0.05	Y	2	589±2.8%	-0.72	0.10	Y
3	449±2.4%	-18	2.8	N	3	598±1.7%	+0.71	0.13	Y
4	463±7%	-15	1.0	Y *	4	609 ± 7%	+ 2.6	0.18	Y
5	525 ± 11%	-3.9	0.18	Y	5	544 ± 11%	- 8.3	0.38	Y
6	556±5%	+1.7	0.16	Y	6	573±5.5%	-3.5	0.30	Y
7	540± 5%	- 1.2	0.12	Y	7	589±4.5%	-0.71	0.07	Y

Comments on Table 2. Although various standards and measurement geometries were used, the results are in good agreement, except participants 3 and 4, ^{134}Cs measurement; both of them passed the z-score test, due to the high standard deviation of the comparison, but their results are not satisfactory enough.

3.2. STATISTICAL ANALYSIS OF RESULTS

The values of the ratio $R = A_R/A_{CA}$, with their uncertainties, were calculated by dividing the corresponding columns in Tables 1 and 2 and combining the uncertainties. Some distribution parameters were calculated, such as follows.

3.2.1. ANSVSA network

Only the arithmetic mean, with the consideration of all participants is presented, as this one was an evaluation test. For ^{134}Cs, $(R)_{mean}$ = 0.974, with a standard deviation (considered as the fitness-for-purpose – ISO 13528:2005), S_{n-1} = 0.103. From a total of 13 results, 84% are within the interval $(R)_{mean} \pm S_{n-1,}$ and 92% are within $(R)_{mean} \pm 2 S_{n-1}$, reflecting an approximately normal distribution. The mean is (-2.6)% biased from the ideal value: R =1.00. For ^{137}Cs, $(R)_{mean}$ =1.003 and S_{n-1} = 0.082. 77% and 92% of results are within $(R)_{mean} \pm S_{n-1}$, respectively $(R)_{mean} \pm 2S_{n-1}$; an almost normal distribution, with $(R)_{mean}$ only 0.3% over R =1.00, was obtained. In the case of ^{134}Cs, coincidence summation corrections were not necessary. In the case of ^{137}Cs, due to the mixture with ^{134}Cs, when using NaI(Tl) detectors, the overlapping corrections were necessary.

3.2.2. IFIN-HH participants

A deeper analysis was done, including the calculation of the arithmetic and weighted means, as well as the median values, and applying the Chauvenet criterium, such as presented in Table 3 [9]. Three estimators were calculated: Arithmetic mean (A), Weighted mean (W), Median value (M)

Table 3

The summarising estimators for IFIN-HH comparison

	$R = A_R/A_{CA}$, ^{134}Cs	$R = A_R/A_{CA}$, ^{137}Cs
A	a) 7 results: (0.946±0.077) b) results 3 rejected: (0.967± 0.071) c) results 3 and 4 rejected: (0.991±0.024)	a) 7 results: (0.982±0.034) b) result 5 rejected: (0.993±0.024)
W	a) 7 results: (0.924± 0.040) b) results 3 rejected: (0.980 ±0.053) c) results 3 and 4 rejected: (0.994±0.056)	a) 7 results: (0.991±0.042) b) results 5 rejected: (0.993±0.042)
M	a) 7 results: (0.988±0.049) b) results 3 and 4 rejected: (0.994±0.056)	a) 7 results: (0.993±0.042) b) result 5 rejected: (0.993±0.042)

Discussion of Table 3

(i) Arithmetic means. ^{134}Cs, all 7 results: 71% results are within $(R)_{\text{mean}} \pm S_{\text{n-1}}$ and 100% within $(R)_{\text{mean}} \pm 2S_{\text{n-1}}$. $(R)_{\text{mean}}$ is (–5.4)% biased from R = 1.00, a value superior to the expanded uncertainty of the standard source, $2u_{c1}$ = 4.4%; even this fact suggests that results 3 and 4 are influenced by systematic errors, in our oppinion due to the noncorrected coincidence summation. Applying the Chauvenet criterium for rejection of results 3 and 4, the arithmetic mean is only 0.9% under the ideal R = 1.00. The set of remaining 5 values is robust. For ^{137}Cs, all 7 results, 71% and 100% of results are respectively within the two confidence intervals, suggesting almost a normal distribution. $(R)_{\text{mean}}$ is (–1.8)% biased from R = 1.00, a value smaller than $2u_{c1}$, what suggests that the distribution is centred on it. The Chauvenet criterium eliminates result 5, the new mean being only 0.7% under R = 1.00, and the result is robust.

(ii) Weighted means. For ^{134}Cs, 7 results, $(R)_{\text{mean}}$ drops to a (–7.6)% bias from normal, due the high influence of the 3-rd laboratory's result, with an underestimated uncertainty; the result 5 had not an important influence, as uncertainty was estimated correctly. After the application of the Chauvenet criterium, the result became only (–0.6)% biased. For ^{137}Cs, 7 results, the (–0.9)% bias is due to the small influence of result 5, with a realistic uncertainty evaluation. After rejecting the result 5, the bias lowers to (–0.7)%.

(iii) Medians. They were influenced by the rejected results, but not by their uncertainties.

The general conclusion is that, after the rejection of two ^{134}Cs and one ^{137}Cs result, the three different calculations of the mean value are equivalent; they agree with the ideal, R = 1.00, within their standard uncertainty, providing robust results.

3.2.3. Final reports

Two reports, for the two groups of participant laboratories, were drawn up, in agreement with the form AC-PL-LMR-07-04, summarizing all the data and conclusions; they were first sent as electronic files to the participants, for formulating observations and improvements. The final, approved versions, were sent with the calibration certificates of the samples, certifying the true conventional activities.

4. CONCLUSIONS FROM THE COMPARISONS OF ^{134}Cs AND ^{137}Cs VOLUME SOURCES

4.1. RECENT PTs (COMPARISONS)

Two different groups of participants took part in a similar comparison. The ANSVSA network took the advantage of using the same kind of standards as the comparison sample, mononuclide volume ^{134}Cs and ^{137}Cs, and following a standardized method of measurement, while IFIN-HH laboratories used a large variety of standards and sample geometries, as well as various methods of measurement. For ^{134}Cs, a coincidence summation correction was necessary in IFIN-HH, while the overlap influence for some ANSVSA laboratories was necessary for ^{137}Cs. The highly skilled personnel from both groups obtained good results. The means of the results, expressed in terms of difference between $(R = A_R/A_{CA})_{mean}$ and the ideal value, R = 1.00 were similar, with a significant smaller spread in the case of IFIN-HH.

4.2. PROGRESS FROM PREVIOUS NATIONAL COMPARISONS ORGANIZED BY RML

A similar comparison, involving mononuclide ^{134}Cs and ^{137}Cs SARPAGAN sources, was organized in 1992 and one for ^{152}Eu in 1993. The results were published in references [6, 7]. These comparisons included laboratories located all over Romania, and belonging to a large variety of specializations. The standards were different as radionuclide, shape, matrix and provider. The equipment contained both high resolution HPGe or Ge(Li) and low resolution NaI(Tl) detectors. 13 laboratories measured ^{134}Cs and 23 measured ^{137}Cs. The exercise was simpler due to higher activities and mononuclide sources. The results were very similar to those reported in [10], for a similar exercise organized by the NPL-UK. Regarding the ^{152}Eu comparison, a multigamma-ray emitter, most of the 15 participants applied coincidence summation corrections. As compared with the present results, one may notice that the progress is due to the standardization of the method and to the use of radioactive standards similar to the measured samples in the case of ANSVSA network; in IFIN-HH one notices the exclusive use of high resolution detectors and the extension of applied corrections: coincidence summation, geometry and matrix type. Some high quality softwares, such as the GESPECOR or ETNA [11, 12] programs were introduced in practice.

5. CONCLUSIONS

Two rounds of comparisons, regarding volume sources, containing a radionuclide mixture were organized, for two entities: ANSVSA network and IFIN-HH gamma-ray spectrometry laboratories.

The E_n acceptance test was adopted for the evaluation of individual results; the number of unaccepted results was not significant.

The final results, expressed in term of bias from the conventionally true activity certified by IFIN-HH, RML were satisfactory, emphasizing an improvement since the last exercises; they were similar for the two participant entities.

Acknowledgements. Many thanks are due to Mrs. Cristina Sulea from IISPV Bucharest, to the participants in the tests from ANSVSA network and from IFIN-HH: Aurelian Luca, Beatris Neacsu, Romeo Calin, Ileana Radulescu, Laurentiu Done, Ana Pantelica, Daniela Gurau; a special acknowledgement is addressed to Dr. Corneliu Ponta and Daniel Negut from IFIN-HH, IRASM Department, for their generous help in the preparation of sources.

REFERENCES

1. M. Sahagia M, E.L. Grigorescu, *Water equivalent standard sources*, Nucl. Instr. and Meth., **A312**, 236–239 (1992).
2. M. Sahagia M, A.C. Razdolescu, A. Luca, R. Macrin, *Volume standard sources in soil matrix*, Rom. J. Phys., **42**, 659–663 (1997).
3. G. Ratel, C. Michotte, J. Leena, A. Iglicki, M. Sahagia, Y. Hino, *Update of the BIPM comparison BIPM.RI(II)-K1.Cs-134 to include the result of the BARC (India),CNEA (Argentina), IFIN-HH (Romania) and the link for the regional comparison APMP.RI(II)-K2.Cs-134 to include the VNIIM and the INER*, Metrologia, **44**, Techn. Suppl. 06004 (2007).
4. *** http://kcdb.bipm.org/AppendixC/default.asp?reset=18met=RI
5. A. Luca, A.C.Wätjen, E.L. Grigorescu, M. Sahagia, C. Ivan, *Conclusions from the participation at proficiency tests for gamma-ray spectrometry measurements*, Rom. J. Phys., **55**, 724–732 (2010).
6. M. Sahagia, E.L. Grigorescu, C. Popescu, A.C. Razdolescu, *National comparison on environmental sample activity measurements*, Nucl. Instr. and Meth., **A339**, 38–42 (1994).
7. M. Sahagia, A.C. Razdolescu, *National comparison of the volumic Eu-152 standard sources*, Rom. J. Phys., **39**, 743–748 (1994).

8. M-M. Bé, V. Chisté, C. Dulieu, X. Mougeot, E. Browne, V. Chechev, N. Kuzmenko, F. Kondev, A. Luca, M. Galán, A. Arinc, X. Huang, *Monographie BIPM-5: Table of Radionuclides*, Vols. 1-6, 2004–2011, Bureau International des Poids et Mesures, Pavillon de Breteuil, F-92310 Sèvres, France.
9. S.I. Kafala, T.D. MacMahon, P.W. Gray, *Treatment of discrepant data. Testing of evaluation methods*, Nuclear Instr. And Meth., **A339**, 151–157 (1994).
10. S.M. Jerome, *NPL Report RSA(Ext)*, National Physical Laboratory, UK, 5 February 1990.
11. O. Sima, D. Arnold, *Transfer of the efficiency calibration of Gamma-ray detectors using the GESPECOR software*, Appl. Radiat. Isot., **56**, 71–75 (2002).
12. M.C. Lepy, M-M. Bé, F. Piton, *ETNA (Efficiency Transfer for Nuclide Activity Measurements)*, Note Technique LNHB/01/09/A, 2001, Laboratoire National Henri Becquerel (LNHB), France.