

Measurement of Activity Concentration of Radionuclide Cs-137 in a Solution
COOMET PROJECT № 386/RU/06

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Abstract

A COOMET.RI(II)-K2.Cs-137 comparison of the measurement of a standardized solution of Cs-137 has enabled three national metrology institutes in the COOMET to demonstrate their traceability to the SI. The results of the comparison will be used to evaluate degrees of equivalence for these institutes through the measurements of the linking laboratory in the key comparison BIPM.RI(II)-K1.Cs-137.

Introduction

The objective of this project was to make the COOMET key comparison of national measurement standards of the activity concentration of a standardized solution of radionuclide Cs-137 traceable to the reference value of key comparison BIPM.RI(II)-K1.Cs-137. The comparison participants are those national measurement institutes (NMIs) of the COOMET that did not participate in the CIPM comparisons. The pilot laboratory and linking institute for the comparison COOMET.RI(II)-K2.Cs-137 to the BIPM.RI(II)-K1.Cs-137 is the D.I.Mendeleyev Institute for Metrology (VNIIM).

1. Participants in the COOMET.RI(II)-K2.Cs-137 comparison

Table 1 contains a list of the NMIs participating in the comparison and the names of the persons who carried out the measurements.

In accordance with the Technical Protocol of the comparison, the participants had to determine the activity concentration of Cs-137 in a solution. Moreover, the comparison participants had also to determine the activity concentration of any radionuclide impurities they identified in the solution.

Table 1. List of participants

NMI	Full name of NMIs	Country	Persons
BelGIM	Belarussian State Institute of Metrology	Belarus	Valeri Milevski Aliaksandr Ivaniukovich
CENTIS-DMR	Centro de Isótopos. Departamento de Metrología de Radionúclidos	Cuba	Pilar Oropesa Verdecia Yecenia Moreno León
SMU	Slovak Institute of Metrology	Slovakia	Anton Švec
VNIIM	D. I. Mendeleyev Institute for Metrology	Russia	Igor A. Kharitonov A.V. Zanevsky

2. Preparation of the solution

The Cs-137 radionuclide solution in 0.5 M nitric acid for the comparison was prepared by the V. G. Khlopin Radium Institute. Originally it was delivered by the “Mayak” enterprise in January 1973 with 0.8 % ^{134}Cs impurity as stated by the manufacturer (certificate No. 9/5037/23948 from 9.01.1973). Since 1973 it was stored in the Radium Institute in a sealed glass ampoule. In February 2007 the solution was centrifuged in order to purify it from colloid silicic acid, diluted with double distilled water and highly-pure HNO_3 , sealed into glass ampoules and transferred to the VNIIM accompanied with RI certificate No.6319 from 26.04.2007 indicating the upper-bound estimate of radioactive impurities as 0.2%.

The VNIIM remixed the solution received and dispensed 3.6 g aliquots into 6 NIST standard ampoules. The masses of the solution put into the ampoules were weighed by a pycnometric method using a Mettler AE240 balance. To avoid any possible errors, the ampoules after sealing were compared using a “Fidelis” ionization chamber being investigated in order to be introduced as a VNIIM reference standard.

Table 2 shows the results of weighing and its check-out by the ionization chamber. It is seen that all deviations of the mass/current ratio from the mean value are within 0.06% for ampoules with 3.6 g. Ampoule No. 2101/6 that was used by the VNIIM showed a 0.25% higher efficiency in the ionization chamber since it contained only 3.36 g of the solution. This ampoule was not flame-sealed because the solution was immediately used for the absolute measurements. Thus one can assume that the procedure of filling the ampoules was made correctly.

Table 2. Results of weighing and ionization chamber measurements

Ampoule No.	Addressee	Solution mass, g	Ionization current, pA	Mass/current, pA/g	Deviation, %
2101/1	SMU	3.61332	19.4894	5.39378	-0.051 %
2101/2	CENTIS-DMR	3.60856	19.4666	5.39458	-0.037 %
2101/3	reserve	3.61338	19.5047	5.39792	0.025 %
2101/4	BIPM	3.59342	19.3963	5.39774	0.022 %
2101/5	BelGIM	3.60914	19.4848	5.39874	0.041 %
Average				5.39655	0
Standard deviation				0.00222	0.041 %
2101/6	VNIIM	3.35953	18.17552	5.410144	0.252 %

Radionuclide impurities of the solution from ampoule No.2101/6 were checked with a HPGe γ -spectrometer and a scintillation β -spectrometer from the VNIIM reference standard. No γ -ray emitting impurities were identified in the γ -spectrum of a 25 kBq source at minimum detectable activity less than 0.5 Bq for such nuclides as ^{57}Co , ^{54}Mn , ^{60}Co , ^{152}Eu and ^{154}Eu . Thus, γ -ray emitting impurity content is less than 0.002 %. The β -spectrometer measurements in the energy range from 1400 to 2300 MeV show that $^{90}\text{Sr}+^{90}\text{Y}$ to ^{137}Cs ratio is less than 0.018%.

The VNIIM dispatched the ampoules to the participants in the COOMET.RI(II)-K2.Cs-137 comparison in accordance with the addressee from table 2. To provide the traceability of measurement results obtained by the NMIs participating in this COOMET comparison to the

reference value of the key comparison BIPM.RI(II)-K1.Cs-137, the VNIIM sent ampoule No. 2101/4 to the BIPM for a comparison within the International Reference System (SIR).

3. Results of measuring the Cs-137 activity concentration in the solution

In accordance with the Technical Protocol of the comparison, each of the comparison participants had to submit to the VNIIM a protocol of their measurement of the Cs-137 activity concentration in the solution with a complete uncertainty budget of the measurement result. The CENTIS-DMR Protocol of Measurements was sent to the VNIIM by Ms. Pilar Oropesa Verdecia on 10 December 2007 ("Cs-137 reportingform-CENTIS-DMR.pdf" 120 KB). The BelGIM Protocol of Measurement was submitted to the VNIIM by V. Milevski on 21 August 2007 ("BelGIM Cs-137 reporting form.doc" 151 KB) and the SMU Protocol – by A. Švec on 7 December 2007 ("Cs-137 reporting form SMU.doc" 80 KB).

Table 3 lists the Cs-137 standardization methods, as well as measurement results with uncertainty values for a coverage factor $k = 2$, given in accordance with the measurement protocols which were submitted. The detailed uncertainty budgets are given in Table 4.

Table 3. Methods used for measuring the Cs-137 activity concentration in the solution and the measurement results

NMI	Measurement method	Activity concentration * (kBq/g)	Uncertainty ($k = 2$)	
			Abs. (kBq/g)	Relative
BelGIM	UA-GH-GR-00-00-00	933.6	19.2	2.06 %
CENTIS-DMR	4P-LS-MX-CN-00-00	955	18	1.8 %
	UA-GH-GR-00-00-00	954	18	1.9 %
	4P-IC-GR-00-00-00	961	36	3.8 %
SMU	4P-IC-GR-00-00-00	953	20	2.2 %
VNIIM	4P-PC-BP-00-00-00	941.94	8.16	0.86 %

* reference date = 01.06.2007, 0:00 UTC

As it is seen from Table 3, two laboratories performed absolute measurements of the Cs-137 activity concentration in the solution: the VNIIM measured the activity concentration by the $4\pi\beta$ -counting method (4P-PC-BP-00-00-00), and the CENTIS-DMR by the CIEMAT-NIST liquid scintillator counting method (4P-LS-MX-CN-00-00). According to the current procedures, the indicated absolute methods were identified in the context of the COOMET.RI(II)-K2.Cs-137 comparison as the primary national standards of the VNIIM and CENTIS-DMR, respectively.

The CENTIS-DMR used an HPGe gamma spectrometer (UA-GH-GR-00-00-00) and an ionization chamber (4P-IC-GR-00-00-00) which had been calibrated with the standard ^{137}Cs point gamma sources certified by the National Metrology Institute of Hungary (MKEH) in 2000 and 2004. These measuring instruments, being part of the national measurement standard of Cuba, can be identified in this comparison as the secondary measurement standards traceable to the primary standard of the MKEH.

The SMU used an ionization chamber (4P-IC-GR-00-00-00) which had been calibrated at the PTB using their certified standards. Its efficiency curve was determined by the procedure described in [1]. For the Cs-137 comparison, the efficiency value calculated from the efficiency curve was used rather than the direct calibrated value (these two values differ slightly within their uncertainties). So the SMU ionization chamber can be identified in this comparison as a secondary measurement standard traceable to the PTB primary standard but not directly to their Cs-137 standard.

The BelGIM used an HPGe gamma spectrometer (UA-GH-GR-00-00-00) calibrated with standard solutions traceable to the VNIIM. The BelGIM gamma spectrometer was identified in this comparison as a secondary measurement standard traceable to the VNIIM primary measurement standard.

Table 4. Estimated relative values (%) of the standard uncertainty components identified by the participants for their measurement results

No.	Effect	BelGIM	CENTIS-DMR			SMU	VNIIM
			LS	Ge(HP)	IC		
1.	counting statistic	0.23	0.06	0.15	0.14	0.22	0.023
2.	weighing	0.065	0.04	0.01	0.008	$1.4 \cdot 10^{-5}$	0.06
3.	dilution		0.09				
4.	dead time		0.05	0.2	0.27*		0.29
5.	background		0.08		0.03	0.003	0.004
6.	counting time	0.014	0.005		0.08**		0.0001
7.	adsorption		0.45	0.45			
8.	impurities		0.3				0.0015
9.	decay-scheme parameters					0.26	0.25
10.	half life ($T_{1/2} = 1.5785 \times 10^5$ d; $u = 0.0024 \times 10^5$ d)	0.001	0.0032	0.009	0.0008	0.00035	0.04
11.	self absorption						0.16
12.	tracer		0.1				
13.	input parameters and statistical model		0.6				
14.	quenching		0.2				
15.	interpolation from calibration curve		0.1			1	
16.	calibration	1		0.75	1.7		
17.	other effects		0.25***	0.27****	0.8*****		0.1*****
combined uncertainty (1σ)		1.03	0.9	0.95	1.9	1.07	0.43

*linearity of the ionization chamber

**scale resolution of the ionization chamber equipment

***asymmetry of phototubes and limit effects

****self-absorption, counting time, measurement geometry

*****impurities, adsorption, sample geometry, long-term stability, measurement time

*****absorption in the backing film of a source

The comparison participants did not detect any radionuclide impurities in the solution. In particular, the ^{134}Cs activity was estimated as less than 0.2 % of the ^{137}Cs activity, for the comparison reference date, by CENTIS-DMR.

4. Results of SIR comparisons

As noted in the introduction to this report, the aim of the COOMET.RI(II)-K2.Cs-137 comparison consisted in providing traceability for the Cs-137 solution standardization results to the reference value of the BIPM.RI(II)-K1.Cs-137 key comparison. To enable this, the VNIIM as the linking NMI, performed a comparison in the SIR system by sending to the BIPM an aliquot of the same solution that had been dispatched to the participants of the COOMET.RI(II)-K2.Cs-137 comparison.

This result has been registered in the SIR. The result of the VNIIM agrees with the KCRV within the stated uncertainties. This enabled a robust link to be made between the COOMET.RI(II)-K2.Cs-137 comparison results and the results of the BIPM.RI(II)-K1.Cs-137 comparison.

5. Processing of the COOMET.RI(II)-K2.Cs-137 comparison results

In accordance with the CCRI(II)/05-01 Guidelines for key comparisons [2], each of the comparison participants has to submit to the pilot laboratory at least one result of measurements with an estimated uncertainty. In the present comparison, the CENTIS-DMR used three measurement methods in the comparison. Following item 9 of the CCRI(II) recommendations in [2], the Protocol of measurements that the CENTIS-DMR submitted to the VNIIM indicated the result of the liquid scintillation method, $A = 957$ kBq/g, with an estimated uncertainty $U = 1.8$ % for $k = 2$ as the CENTIS-DMR result for calculating the degrees of equivalence of the national standard of Cuba for the KCDB. Table 5 shows some characteristics of a sub-set of the measurement results where $d_i = (A_i - A) * 100 / A$, and E_n is a normalized error statistic (see Eqs.1 to 3).

Table 5. Some characteristics of a set of the results obtained in measuring the Cs-137 activity concentration in the solution

Institute	Method of measurement	A_i (kBq/g)*	$U_i (k = 2)$		d_i %	E_n
			kBq/g	%		
BelGIM	UA-GH-GR-00-00-00	933.6	19.2	2.06 %	-0.89 %	0.48
CENTIS-DMR	4P-LS-AP-00-00-00	955	18	1.8 %	+1.39 %	0.69
SMU	4P-IC-GR-00-00-00	953	20	2.2 %	+1.17 %	0.49
VNIIM	4P-PC-AP-NA-GR-CO	941.94	8.16	0.86 %		

* reference date = 0:00 UTC of June 1, 2007.

As noted above, the national measurement standard of Belarus is traceable to the national measurement standard of Russia, and due to this fact the measurement results of the BelGIM and VNIIM are correlated. If a weighted mean calculated without any allowance for the correlation of the BelGIM and VNIIM is taken as the comparison result, then the estimate of the comparison result will be biased and, consequently, incorrect.

On the other hand, it is seen from the table that the uncertainty of the VNIIM measurement result is considerably less than the uncertainty of the measurement results obtained by the other three comparison participants, and the VNIIM result will be the nearest approach to an estimate of the measurement result for any method of weighting.

In connection with this, as well as taking into account the fact that the VNIIM result will be used as the linking value of the COOMET.RI(II)-K2.Cs-137 and BIPM.RI(II)-K1.Cs-137

comparisons, the result of the activity concentration measurement presented by the VNIIM is taken as the COOMET comparison reference value.

Statistical consistency of the comparison data set was verified with a normal statistical test using the following formula:

$$E_n = \frac{|A_i - A|}{2\sqrt{u_i^2 + u^2 - 2\text{cov}(A_i, A)}} \quad (1)$$

For the BelGIM value, $\text{cov}(A_i, A) = u^2$, therefore formula (1) is transformed into:

$$E_n = \frac{|A_i - A|}{2\sqrt{u_i^2 - u^2}} \equiv \frac{|A_i - A|}{\sqrt{U_i^2 - U^2}} \quad (2)$$

For the other participants' value $\text{cov}(A_i, A) = 0$, therefore formula (1) is transformed into:

$$E_n = \frac{|A_i - A|}{2\sqrt{u_i^2 + u^2}} \equiv \frac{|A_i - A|}{\sqrt{U_i^2 + U^2}} \quad (3)$$

Where A_i is the result of a comparison participant, except for the VNIIM

A is the VNIIM result

u_i is the value of standard uncertainty of a participant measurement result, except for the VNIIM,

u is the standard uncertainty value of the VNIIM result,

U_i is the value of expanded uncertainty ($k = 2$) of a participant measurement result, except for the VNIIM, and

U is the expanded uncertainty value of the VNIIM result, as given in Table 5.

The values of E_n are also given in Table 5 and, as each is <1 , the data are deemed to be consistent.

6. Preliminary evaluation of the COOMET.RI(II)-K2.Cs-137 comparison results

For the convenience of comparison, the expanded uncertainty values and the values of deviation d_i from the VNIIM results are given in Table 5 in terms of relative units.

Table 5 shows that all the data of the comparison comply with a normal statistical test, and the deviations of the results d_i from the VNIIM value of activity concentration ($A = 941.94$ kBq/g, $u = 4.08$ kBq/g, $u/A = 0.43$ %) are all within 1.4 % (except the CENTIS-DMR ionization chamber measurement which was not used for equivalence and for which the standard deviation is 1.9%).

As an illustration, Figure 1 shows the results listed in Table 3 with their expanded uncertainties ($k = 2$). The horizontal line represents the weighted mean of the results of all the

$$\text{participants } \bar{A} = \frac{\sum \frac{A_i}{u_i^2}}{\sum \frac{1}{u_i^2}} = 944.01 \text{ kBq/g and its expanded uncertainty } U_{\bar{A}} = \frac{2}{\sqrt{\sum \frac{1}{u_i^2}}} = 6.31 \text{ kBq/g.}$$

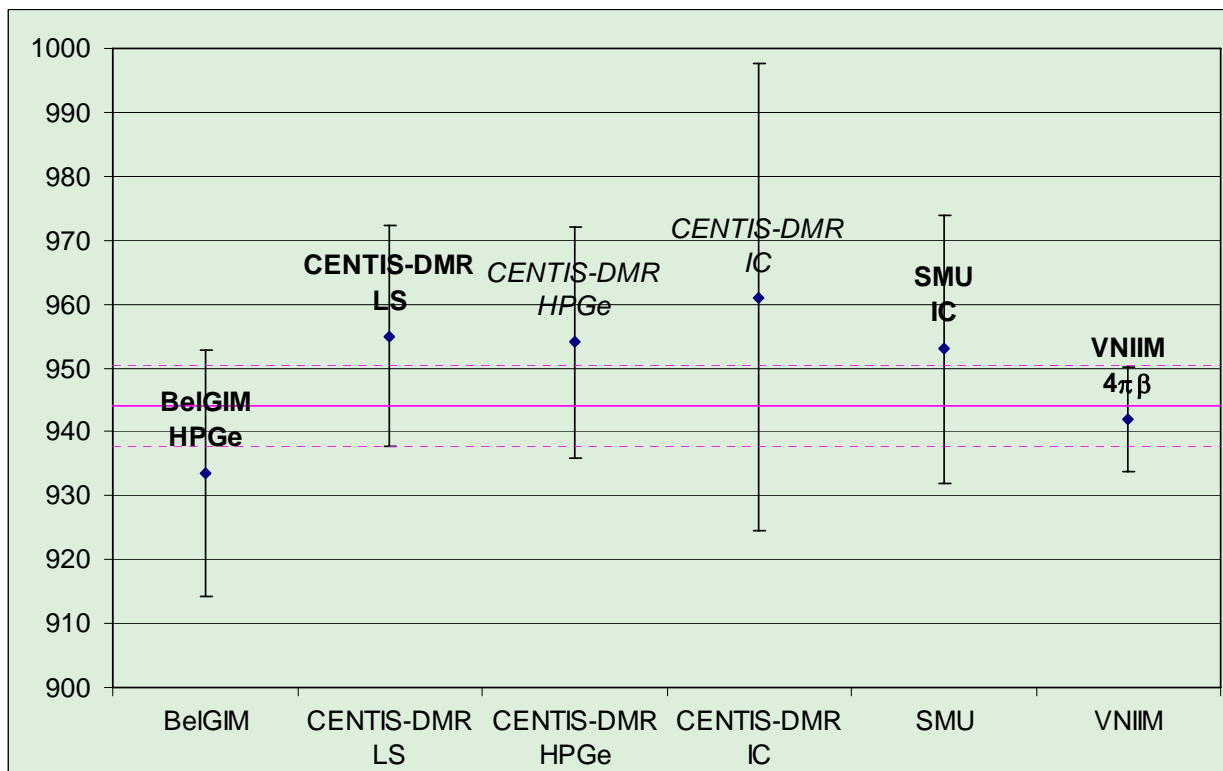


Fig. 1 Results of the COOMET.RI(II)-K2.Cs-137 comparison with expanded uncertainty bars ($k = 2$)

Conclusion

The results of three NMI participants in the COOMET.RI(II)-K2.Cs-137 comparison are consistent with each other and indicate agreement in the dissemination of activity measurements for solutions of ^{137}Cs .

In accordance with the Guidelines for CCRI(II) key comparisons [2], the results of the COOMET.RI(II)-K2.Cs-137 comparison, having been approved by the comparison participants, have been sent to the BIPM to establish a link of the results obtained with the key comparison reference value of the BIPM.RI(II)-K1.Cs-137 key comparisons. The degrees of equivalence for these participants will be published subsequently.

Acknowledgements

The VNIIM as the pilot laboratory thanks all the participants of this comparison, as well as the BIPM for the efforts in maintaining the SIR system.

References

- [1] Svec A., Schrader H., Fitting methods for constructing energy-dependent efficiency curves and their application to ionization chamber measurements 2002, *Applied Radiation and Isotopes* **56**, 1-2, 237-243.
- [2] CCRI(II), Guidelines for CCRI(II) key comparisons, 2005, [CCRI\(II\)/05-01](#).