Metrologia, 2013, **50**, *Tech. Suppl.*, 06012

Measurement of activity concentration of radionuclide Eu-152 in a solution COOMET PROJECT № 423/RU/08

I.A.Kharitonov[1)], A.V.Zanevsky[1)], V.Milevski[2)], A.Ivaniukovich[2)], P. Oropesa Verdecia[3)], Y.Moreno León[3)] and A.Švec[4)]

[1)]VNIIM, [2)]BelGIM, [3)]CENTIS-DMR, [4)]SMU

Abstract

The COOMET.RI(II)-K2.Eu-152 comparison of measurements of a standardized solution of Eu-152 has enabled the demonstration of the traceability to the SI of the national measurement standards of three national metrology institutes of the COOMET countries. The comparison results will be used to evaluate the degrees of equivalence for these institutes through the measurements of the linking laboratory in the BIPM.RI(II)-K1.Eu-152 key comparison.

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 Eu-152 in order to enable the traceability of measurement results to the reference value of key comparison BIPM.RI(II)-K1.Eu-152. The comparison participants are those national measurement institutes (NMIs) of the COOMET which have not participated in the CIPM comparisons. The pilot laboratory and linking institute for the comparison COOMET.RI(II)-K2.Eu-152 to the BIPM.RI(II)-K1.Eu-152 is the D.I.Mendeleyev Institute for Metrology (VNIIM).

1. Participants of the COOMET.RI(II)-K2.Eu-152 comparison

Table 1 contains the 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 Eu-152 in a solution by the methods available to them. Moreover, the comparison participants had also to determine the activity concentration of radionuclide impurities in the solution.

Table 1. List of participants

NMI	Full name of NMIs	Country	Persons
BelGIM	Belarussian State Institute of Metrology	Belarus	Aliaksandr Ivaniukovich Valeriy Milevski
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 Kharitonov Andrew .Zanevsky

2. Preparation of the solution

The Eu-152 radionuclide solution in 4 M nitric acid for the comparison was prepared by the State Scientific Center Research Institute of Atomic Reactors (Dimitrovgrad, Russia). The solution contained less than 0.15% ^{154}Eu impurity, as stated by the manufacturer (certificate No. 936 dated 11.12.2006).

The VNIIM remixed the solution that was received and dispensed 3.6 g aliquots into seven NIST standard ampoules. The mass of solution put into each ampoule was weighed by a pycnometric method using a Mettler AE240 balance. To avoid any possible errors, the sealed ampoules were compared with the help of a “Fidelis” ionization chamber that is being characterized as a future VNIIM reference standard.

Table 2 shows the results of weighing and checking with the ionization chamber. As shown, all deviations of the mass/current ratio from the mean value are within 0.35% for all the ampoules. Thus, one can assume that the procedure of filling the ampoules was made correctly.

Table 2. Results of weighing and checking the aliquots

Ampoule No.	Addressee	Solution mass / g	Ionization current /pA	Current/mass /(pA/g)	Deviation
2101/1	BelGIM	3.6584	28.45952	7.788594	-0.19 %
2101/2	CENTIS-DMR	3.6567	28.5071	7.805245	+0.02 %
2101/3	SMU	3.6619	28.64049	7.83062	+0.35 %
2101/4	reserve	3.6464	28.48748	7.821932	+0.24 %
2101/5	BIPM	3.6549	28.45988	7.796159	-0.10 %
2101/6	reserve	3.6511	28.36964	7.779539	-0.31 %
2101/7	VNIIM	3.6526	28.46687	7.802991	-0.01 %
Average				7.803583	0
Standard deviation				0.017929	0.23 %

Radionuclide impurities in the solution from the source ampoule were checked with a HPGe γ-spectrometer from the VNIIM reference standard. The 1274.5 keV γ-rays of ^{154}Eu impurity were identified in the γ-spectrum. The γ-spectrometer measurements show that the ^{154}Eu to ^{152}Eu ratio is 0.275 % with the standard uncertainty u_c = 0.008 % at the reference date. No other impurities were observed.

The VNIIM dispatched the ampoules to the participants of the COOMET.RI(II)-K2.Eu-152 comparison in accordance with addresses 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.Eu-152, the VNIIM sent ampoule №2101/5 to the International Bureau of Weights and Measures (BIPM) for a comparison within the International Reference System (SIR).

3. Results of measuring the Eu-152 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 Eu-152 activity concentration in the solution, including a complete uncertainty budget for the measurement result. The CENTIS-DMR Protocol of Measurements was sent to the VNIIM by Ms. Pilar Oropesa Verdecia on 26 February 2010 ("Eu-152 reporting form.pdf" 123 KB). The BelGIM Protocol of Measurement was submitted to the VNIIM by A.Ivaniukovich on 10 March 2010 ("BelGIM Eu-152 reporting form.doc" 190 KB) and the SMU Protocol – by A.Švec on 4 February 2010 ("Eu-152 report SMU.doc" 74 KB).

Table 3 lists the Eu-152 standardization methods, as well as measurement results with the uncertainty values for a coverage factor $k = 2$, given in accordance with the measurement protocols that were submitted. The detailed uncertainty budgets are given in Table 4.

Table 3. Methods used for measuring the Eu-152 activity concentration in the solution and the measurement results of each participant

NMI	Measurement method	Activity concentration* (kBq/g)	Uncertainty (k = 2)	
			(kBq/g)	Relative
BelGIM	UA-GH-GR-00-00-00	698	10	1.4%
CENTIS-DMR	UA-GH-GR-00-00-00	701.8	18.6	2.6%
	4P-IC-GR-00-00-00	709	28	4.0%
SMU	4P-IC-GR-00-00-00	701.1	10.6	1.5%
VNIIM	4P-NA-GR-00-00-HE	703.067	5.71	0.812%
	4P-PC-BP-NA-GR-CO	696.069	6.97	1.002%

* reference date = 01.07.2008, 0:00 UTC

As it is seen from the above Table 3, only one laboratory performed absolute measurements of the Eu-152 activity concentration in the solution: the VNIIM measured the activity concentration by both the $4\pi\gamma$-counting method (4P-NA-GR-00-00-HE) and the $4\pi\beta$-γ-coincidence counting method (4P-PC-BP-NA-GR-CO). According to the present procedures, the indicated absolute methods were identified in the context of the COOMET.RI(II)-K2.Eu-152 comparison as the primary national standards of the VNIIM.

The CENTIS-DMR used an HPGe gamma spectrometer (UA-GH-GR-00-00-00) and an ionization chamber (4P-IC-GR-00-00-00) that had been calibrated with the standard ^{152}Eu point gamma sources certified by the National Metrology Institute of Hungary (MKEH) in 2000 and 2004. The ionization chamber measured 3.2 ml of the ^{152}Eu solution transferred into a 10 R glass ampoule. 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 ^{152}Eu primary standard of the MKEH**.**

The SMU used an ionization chamber (4P-IC-GR-00-00-00) that had been calibrated at the PTB using their certified standards for about 20 radionuclides including ^{152}Eu. Firstly, the calibration coefficients obtained were used to construct the calibration curve [1] and then the resulting calculated calibration coefficients were applied. The solution was measured directly in the original ampoule, no weighing was performed and the mass value indicated by the distributing laboratory was used. The SMU ionization chamber can be identified in this comparison as a secondary measurement standard traceable to the PTB primary standard.

The BelGIM used an HPGe gamma spectrometer (UA-GH-GR-00-00-00) calibrated with the Co-57 standard sources traceable to the Czech Metrology Institute (CMI), taking into account the difference between 121.48 keV and 122.06 keV γ-ray counting efficiencies and cascade summing effect. The BelGIM gamma spectrometer was identified in this comparison as a secondary measurement standard traceable to the ^{57}Co primary measurement standard of the CMI.

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

№	Effect	BelGIM	CENTIS-DMR		SMU	VNIIM	
			Ge(HP)	IC		4πγ	4πβ-γ
1.	counting statistic	0.11	0.38	0.6	0.17	0.05	0.063
2.	weighing	0.08	0.05	0.3	0.001	0.104	0.104
3.	dilution						
4.	dead time	0.065	0.1	0.27*		0.17	0.02
5.	background			0.03	0.02	0.01	0.13
6.	counting time			0.14**		0.0001	0.0001
7.	resolving time						0.02
8.	adsorption						
9.	impurities					0.08	0.08
10.	decay-scheme parameters	0.47			0.29		
11.	half life ($T_{1/2} = 1.5785 \times 10^5$ d; $u = 0.0024 \times 10^5$ d)	0.1	0.0003	0.0003	0.02	0.00002	0.00002
12.	self absorption				0.01		
13.	tracer						
14.	extrapolation					0.14	0.46
15.	input parameters and statistical model						
16.	quenching						
17.	interpolation from calibration curve	0.1			0.67	0.31	
18.	calibration	0.3	1.15	1.7			
19.	other effects	0.36*** 0.05****	0.5*****	0.8******			
combined uncertainty (1σ)		0.7	1.3	2.0	0.75	0.406	0.501

*linearity of the ionization chamber
**scale resolution of the ionization chamber equipment
***true coincidence correction
****counting efficiency
***** adsorption, self-absorption, counting time, measurement geometry
******impurities, adsorption, sample geometry, long-term stability, measurement time

All of the comparison participants used gamma-ray spectrometry to detect radionuclide impurities in the solution. For the comparison reference date, the ^{154}Eu to ^{152}Eu activity ratio was estimated by the CENTIS-DMR as 0.0074 ± 0.0006, by the SMU as 0.0025 ± 0.0008, by the VNIIM

($k = 1$) as 0.0027 5 ± 0.0000 8 while the BelGIM detected no impurities. No other impurities were identified by the participants.

4. Results of SIR comparisons

As noted in the introduction to this report, the aim of the COOMET.RI(II)-K2.Eu-152 comparison is to provide traceability of the Eu-152 solution standardization results to the reference value of the BIPM.RI(II)-K1.Eu-152 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.Eu-152 comparison.

This result has been registered in the SIR. The result of the VNIIM (Table 5) agrees with the KCRV within the stated uncertainties. This will enable a robust link to be made between the COOMET.RI(II)-K2.Eu-152 comparison results and the results of the BIPM.RI(II)-K1.Eu-152 comparison.

5. Processing of the COOMET.RI(II)-K2.Eu-152 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 comparison being considered, the CENTIS-DMR used two measurement methods. Following item 9 of the CCRI(II) recommendations in [2], in the Protocol of measurements that the CENTIS-DMR submitted to the VNIIM, the result obtained with the calibrated HPGe gamma spectrometer method, 701.8 kBq/g with an estimated uncertainty $U = 2.6\%$ for $k = 2$, was indicated as the CENTIS-DMR result to be used in calculating the degree of equivalence of the national standard of Cuba for the KCDB. The VNIIM result to determine the equivalence is the weighted mean of the results of both methods, $A = 700.363$ kBq/g with an estimated uncertainty $U = 0.656\%$ for $k = 2$, where the uncertainty components due to mass, impurities and half life are common for both methods, and hence are not included in the statistical weights and added after averaging.

Table 5 shows some characteristics of a subset of the measurement results where:

$d_i = (A_i - A)*100/A$, and

E_n is the normalized error statistic (see Eqs.1, 2).

Table 5. Some characteristics of a set of the results obtained in measuring the Eu-152 activity concentration in the solution

Institute	Method of measurement	A_i (kBq/g)*	U_i ($k = 2$) kBq/g	U_i ($k = 2$) %	d_i %	E_n
BelGIM	UA-GH-GR-00-00-00	698	10	1.4%	-0.34%	0.219
CENTIS-DMR	UA-GH-GR-00-00-00	701.8	18.6	2.6%	+0.21%	0.075
SMU	4P-IC-GR-00-00-00	701.1	10.6	1.5%	+0.11%	0.301
VNIIM	weighted mean of 4P-NA-GR-00-00-HE and 4P-PC-BP-NA-GR-CO	700.363	4.594	0.656%		

* reference date = 0:00 UTC of June 1, 2008.

As noted above, only the VNIIM used its own national primary standard for applying absolute measurement methods. All the other participants used their secondary standards traceable to the national measurement standards of other CIPM MRA signatories: Czech Republic, Hungary and Germany.

On the other hand, it is seen from the table that the uncertainty of the VNIIM measurement result is considerably less than that 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.Eu-152 and BIPM.RI(II)-K1.Eu-152 comparisons, the result of the activity concentration measurement presented by the VNIIM is taken as the COOMET key comparison reference value.

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

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

where $\mathrm{cov}(A_i, A) = 0$, therefore formula (1) is transformed into:

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

where:

A_i is the measurement 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 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.Eu-152 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 = 700.363 kBq/g, u = 4.594 kBq/g, u/A = 0.656%) are all within 0.4%.

As an illustration, Figure 1 shows the results listed in Table 3 with their uncertainties ($k = 1$). The horizontal line represents the weighted mean of the results of all the participants $\overline{A} = \frac{\sum \frac{A_i}{u_i^2}}{\sum \frac{1}{u_i^2}}$ = 700.17 kBq/g and its standard uncertainty $u_{\overline{A}} = \frac{1}{\sqrt{\sum \frac{1}{u_i^2}}}$ = 1.89 kBq/g.

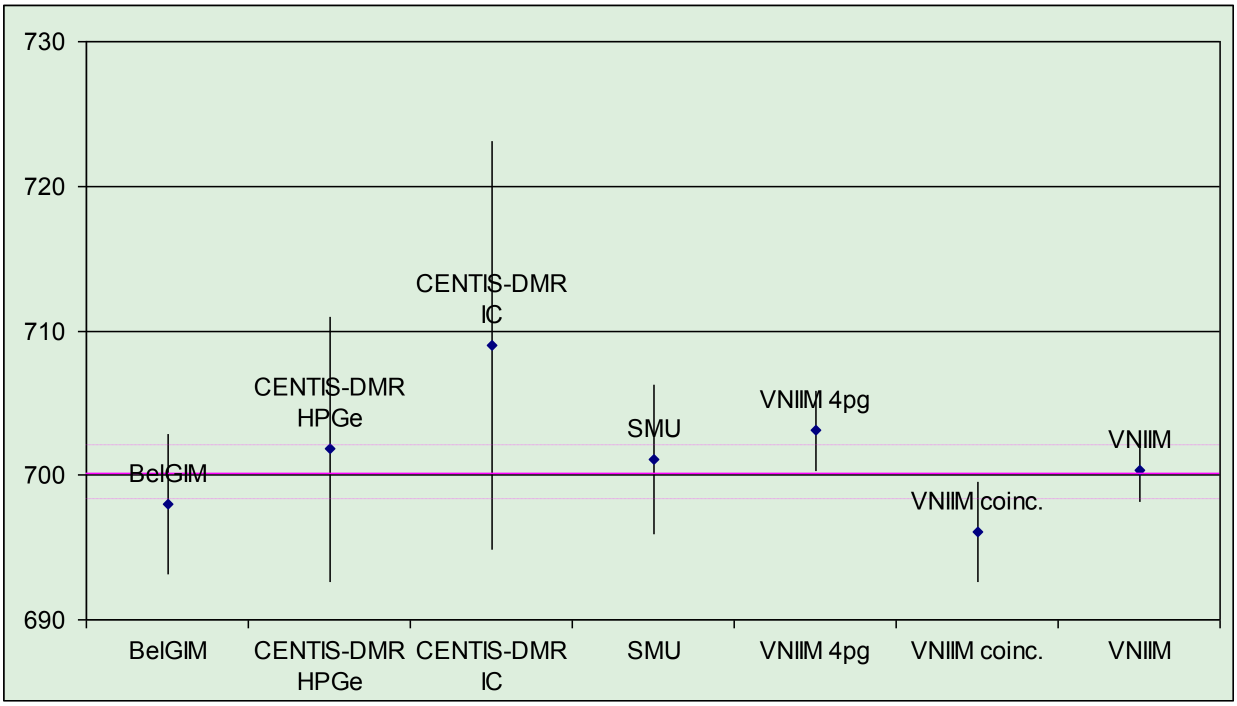

Fig. 1 Results of the COOMET.RI(II)-K2.Eu-152 comparison with standard uncertainty bars (k = 1)

Conclusion

The results of four NMI participants in the COOMET.RI(II)-K2.Eu-152 comparison are consistent with each other and indicate agreement in the dissemination of activity measurements for solutions of ^{152}Eu.

In accordance with the Guidelines for CCRI(II) key comparisons [2], the results of the COOMET.RI(II)-K2.Eu-152 comparison, having been approved by the comparison participants, have been sent to the BIPM to establish a link of the results obtained with the reference value of the BIPM.RI(II)-K1.Eu-152 key comparisons. The degrees of equivalence for these participants will be published subsequently.

Acknowledgements

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

References

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[2] CCRI(II) (2005) Guidelines for CCRI(II) key comparisons, CCRI(II)/05-01