

Activity measurements of the radionuclide ^{67}Ga for the CIEMAT
in the BIPM comparison BIPM.RI(II)-K1.Ga-67

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Abstract

The Centro de Investigaciones Energéticas, Medioambientales y Tecnológicas (CIEMAT, Spain) has submitted a sample of known activity of ^{67}Ga to the International Reference System (SIR) recently for activity comparison at the Bureau International des Poids et Mesures. The value of the activity submitted was about 8 MBq. The degrees of equivalence between each equivalent activity measured to date in the SIR and the key comparison reference value (KCRV) have been calculated and the results are given in the form of a matrix for eight NMIs including the CIEMAT. A graphical presentation is also given. The results of this comparison have been approved by Section II of the Consultative Committee for Ionizing Radiation (CCRI(II)), comparison identifier BIPM.RI(II)-K1.Ga-67.

1. Introduction

The SIR for activity measurements of γ -ray-emitting radionuclides was established in 1976. Each national metrology institute (NMI) may request a standard ampoule from the BIPM that is then filled (3.6 g) with the radionuclide in liquid (or gaseous) form. The NMI completes a submission form that details the standardization method used to determine the absolute activity of the radionuclide and the full uncertainty budget for the evaluation. The ampoules are sent to the BIPM where they are compared with standard sources of ^{226}Ra using pressurized ionization chambers. Details of the SIR method, experimental set-up and the determination of the equivalent activity are all given in [1].

From its inception until 31 December 2002, the SIR has measured 835 ampoules to give 606 independent results for 62 different radionuclides. The SIR makes it possible for national laboratories to check the reliability of their activity measurements at any time. This is achieved by the determination of the equivalent activity of the radionuclide and by comparison of the result with the key comparison reference value determined from the results of primary realizations. These comparisons are described as BIPM ongoing comparisons and the results form the basis of the BIPM key comparison database (KCDB) that was set up under the Mutual Recognition Arrangement (MRA) [2]. The comparison described in this report is part of the BIPM.RI(II)-K1.Ga-67 key comparison and the results are displayed in the KCDB.

2. Participants

In addition to the CIEMAT, seven other NMIs and one other laboratory have submitted twelve ampoules for the comparison of ^{67}Ga activity measurements since 1978. The date of the CIEMAT submission is given in Table 1 and those of the other submissions are given in [3].

Table 1. Details of the CIEMAT participation in the BIPM.RI(II)-K1.Ga-67

NMI	Full name	Country	Regional metrology organization	Date of measurement at the BIPM
CIEMAT	Centro de Investigaciones Energéticas, Medioambientales y Tecnológicas	Spain	EUROMET	2003-03-19

3. NMI standardization methods

Each NMI that submits ampoules to the SIR has measured the activity either by a primary standardization method or by using a secondary method, for example a calibrated ionization chamber. In the latter case, the traceability of the calibration needs to be clearly identified to ensure that any correlations are taken into account.

A brief description of the standardization method for the laboratory, the activity submitted and the relative standard uncertainties ($k = 1$) are given in Table 2. The uncertainty budget is given in Appendix 1.

Table 2. Standardization method of the CIEMAT for ^{67}Ga

Method used and acronym [3]	Half-life / d	Activity A_i / kBq	Reference date YYYY-MM-DD	Relative standard uncertainty $\times 100$ by method of evaluation	
				A	B
$4\pi\beta(\text{PPC})-\gamma$ coincidence 4P-PP-AE-NA-GR-CO	3.259 (10)	7916	2003-03-12 10 h UT	0.70	0.52

Details regarding the solution submitted are shown in Table 3, including any impurities and their uncertainties as identified by the laboratory. The BIPM has developed a standard method for evaluating the activity of impurities using a

calibrated Ge(Li) spectrometer [4]. The CCRI(II) agreed in 1999 [5] that this method should be followed according to the protocol described in [6] when an NMI makes such a request or when there appear to be discrepancies. No supplementary measurements were made for this latest result.

Table 3. Details of the solution of ^{67}Ga submitted

Chemical composition	Solvent conc. / (mol dm^{-3})	Carrier: conc. / ($\mu\text{g g}^{-1}$)	Density / (g cm^{-3})	Relative activity of impurity [†]
$\text{C}_6\text{H}_5\text{Na}_3\text{O}_7$ in HCl	0.1	$\text{C}_6\text{H}_5\text{Na}_3\text{O}_7$: 230	1	–

[†] the ratio of the activity of the impurity to the activity of ^{67}Ga at the reference date.

4. Results

All the submissions to the SIR since its inception in 1976 are maintained in a database known as the "mother-file". The previous activity measurements for ^{67}Ga arise from twelve ampoules and the SIR equivalent activity, A_{ei} , for each ampoule is given in [3] for each NMI, i . The activity measurement for the CIEMAT is given in Table 4. The relative standard uncertainties arising from the measurements in the SIR are also shown. This uncertainty is additional to that declared by the NMI for the activity measurement shown in Table 2. Although activities submitted are compared with a given source of ^{226}Ra , all the SIR results are normalized to the radium source number 5 [1].

The half-life used by the BIPM is 78.26 (7) hours [7] which is in good agreement with the recently published evaluation of 78.22 (2) hours [8]. The date of measurement in the SIR is given in Table 1.

Measurements made up to 5 days later agree with the first result within the SIR uncertainties and this indicates that any impurity content is indeed negligible.

Table 4. Results of SIR measurements of ^{67}Ga for the CIEMAT

Mass of solution m_i / g	Activity submitted A_i / kBq	N° of Ra source used	SIR A_e / kBq	Relative uncertainty from SIR	Combined uncertainty $u_{c,i}$ / kBq
3.663	7 916	1	117 940	19×10^{-4}	1 050

4.1 The key comparison reference value

The key comparison reference value for ^{67}Ga has been identified as 116 040 (520) kBq as given in [3]. Although the KCRV may be modified when other NMIs participate, on the advice of the Key Comparison Working Group of the

CCRI(II), such modifications are only made by the CCRI(II), normally during one of its biennial meetings.

4.2 Degrees of equivalence

Every NMI that has submitted ampoules to the SIR is entitled to have one result included in Appendix B of the KCDB as long as the NMI is a signatory or designated institute listed in the MRA. Normally, the most recent result is the one included. Any NMI may withdraw its result only if all the participants agree.

The degree of equivalence of a given measurement standard is the degree to which this standard is consistent with the key comparison reference value [2]. The degree of equivalence is expressed quantitatively in terms of the deviation from the key comparison reference value and the expanded uncertainty of this deviation ($k = 2$). The degree of equivalence between any pair of national measurement standards is expressed in terms of their difference and the expanded uncertainty of this difference and is independent of the choice of key comparison reference value.

4.2.1 *Comparison of a given NMI with the KCRV*

The degree of equivalence of a particular NMI, i , with the key comparison reference value is expressed as the difference between the results

$$D_i = A_{e_i} - \text{KCRV} \quad (1)$$

and the expanded uncertainty ($k = 2$) of this difference, U_i , known as the equivalence uncertainty, hence

$$U_i = 2u_{D_i}, \quad (2)$$

taking correlations into account as appropriate.

4.2.2 *Comparison of any two NMIs with each other*

The degree of equivalence, D_{ij} , between any pair of NMIs, i and j , is expressed as the difference in their results

$$D_{ij} = D_i - D_j = A_{e_i} - A_{e_j} \quad (3)$$

and the expanded uncertainty of this difference U_{ij} where

$$u_{D_{ij}}^2 = u_i^2 + u_j^2 - \sum_k (f_k u_{\text{corr},k})_i^2 - \sum_k (f_k u_{\text{corr},k})_j^2 \quad (4)$$

and any obvious correlations in the standard uncertainties for a given component, $u_{\text{corr},k}$, between the NMIs (such as a traceable calibration) are subtracted using an appropriate correlation coefficient, f_k , as are normally those correlations coming from the SIR.

The uncertainties of the differences between the values assigned by individual NMIs and the key comparison reference value (KCRV) are not necessarily the same uncertainties that enter into the calculation of the uncertainties in the degrees of equivalence between a pair of participants. However, the effects of correlations have

been treated in a simplified way as the degree of confidence in the uncertainties themselves does not warrant a more rigorous approach.

Table 5 shows the matrix of all the degrees of equivalence as they appear in Appendix B of the KCDB with the CIEMAT result added. It should be noted that for consistency within the KCDB, a simplified level of nomenclature is used with A_{ei} replaced by x_i . The introductory text is that agreed for the comparison. The graph of the first column of results in Table 5, corresponding to the degrees of equivalence with respect to the KCRV (identified as x_R in the KCDB), is shown in Figure 1. This representation indicates in part the degree of equivalence between the NMIs but does not take into account the correlations between the different NMIs. However, the matrix of degrees of equivalence shown in yellow in Table 5 does take the known correlations into account.

Conclusion

The BIPM ongoing key comparison for ^{67}Ga , BIPM.RI(II)-K1.Ga-67 now comprises eight results, including the 2003 result for the CIEMAT. These have been analysed with respect to the KCRV determined for this radionuclide, and with respect to each other. The matrix of degrees of equivalence has been approved by the CCRI(II) and is published in the BIPM key comparison database. Other results may be added as and when other NMIs contribute ^{67}Ga activity measurements to this comparison.

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References

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Table 5. Table of degrees of equivalence and introductory text for ⁶⁷Ga
Key comparison BIPM.RI(II)-K1.Ga-67

MEASURAND : Equivalent activity of ⁶⁷Ga

Key comparison reference value: the SIR reference value x_R for this radionuclide is 116.04 MBq, with a standard uncertainty of 0.52 MBq (see *Metrologia*, 2003, 40, *Technical Supplement*, 06014), the value x_i is taken as the equivalent activity for laboratory i .

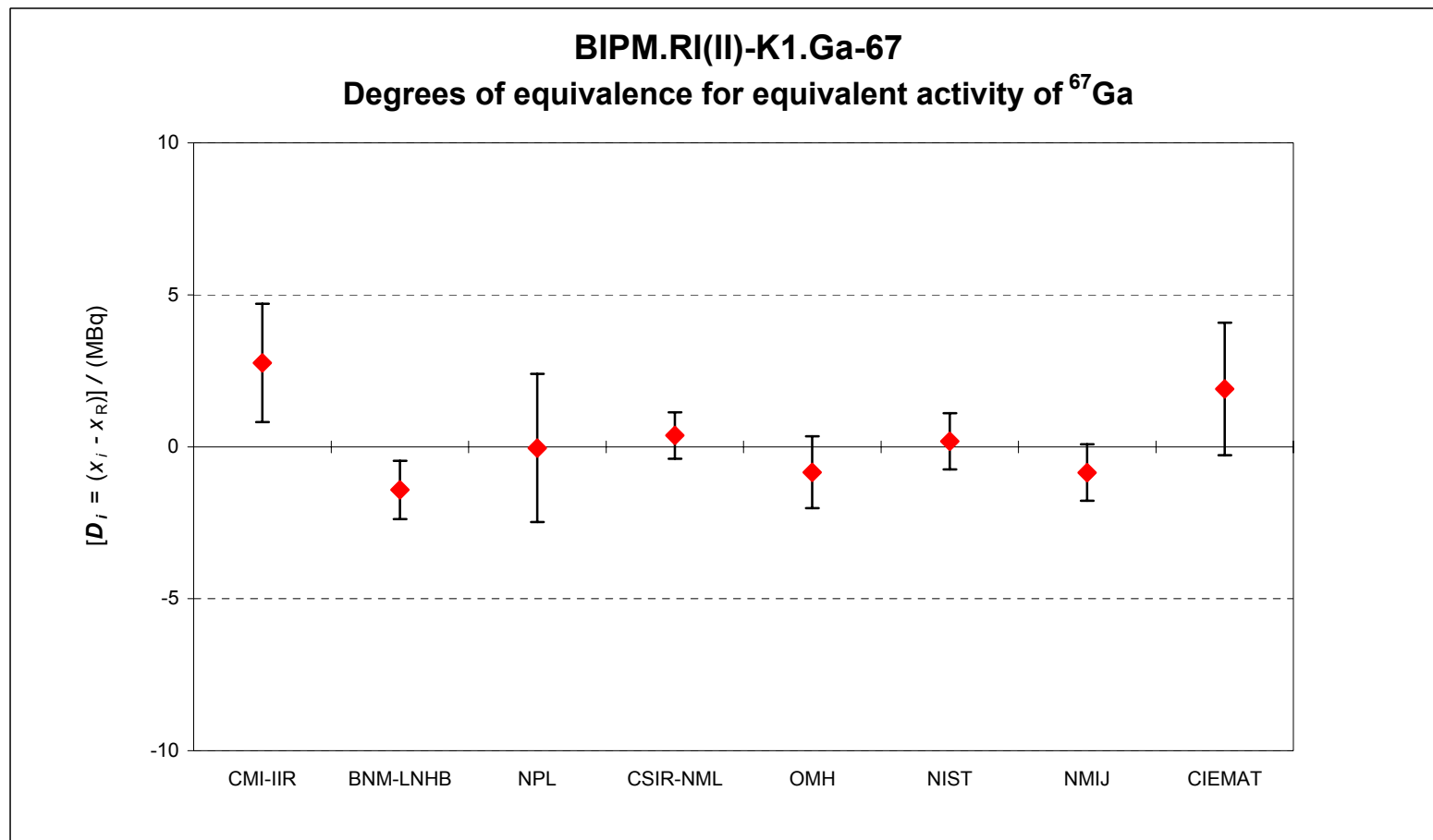
The degree of equivalence of each laboratory with respect to the reference value is given by a pair of terms: $D_i = (x_i - x_R)$ and U_i , its expanded uncertainty ($k = 2$), both expressed in MBq, and $U_i = 2((1 - 2/n)u_i^2 + (1/n^2)\sum u_i^2)^{1/2}$ when each laboratory has contributed to the calculation of x_R , with n the number of laboratories.

The degree of equivalence between two laboratories is given by a pair of numbers: $D_{ij} = D_i - D_j = (x_i - x_j)$ and U_{ij} , its expanded uncertainty ($k = 2$), both expressed in MBq. The approximation $U_{ij}^2 \sim 2^2(u_i^2 + u_j^2)$ is used in the following table.

Lab i ↓		Lab j →									
		CMI-IIR		BNM-LNHB		NPL		CSIR-NML		OMH	
		D_i	U_i	D_{ij}	U_{ij}	D_{ij}	U_{ij}	D_{ij}	U_{ij}	D_{ij}	U_{ij}
		/ MBq		/ MBq		/ MBq		/ MBq		/ MBq	
CMI-IIR		2.8	1.9								
BNM-LNHB		-1.4	1.0	4.2	2.4			2.4	2.3	3.6	2.5
NPL		0.0	2.4	-4.2	2.4	1.4	2.9	-1.4	2.9	-0.6	1.5
CSIR-NML		0.4	0.8	-2.8	3.6			-0.4	2.9	0.8	3.1
OMH		-0.8	1.2	-2.4	2.3	1.8	1.1	0.4	2.9	1.2	1.4
NIST		0.2	0.9	-3.6	2.5	0.6	1.5	-0.8	3.1	-1.2	1.4
NMIJ		-0.9	0.9	-2.6	2.3	1.6	1.2	0.2	2.9	-0.2	0.9
CIEMAT		1.9	2.2	-3.6	2.4	0.6	1.2	-0.8	2.9	-1.2	1.0
				-0.9	3.0	3.3	2.3	1.9	3.5	1.5	2.2
										2.7	2.4

Lab i ↓		Lab j →					
		NIST		NMIJ		CIEMAT	
		D_{ij}	U_{ij}	D_{ij}	U_{ij}	D_{ij}	U_{ij}
		/ MBq		/ MBq		/ MBq	
CMI-IIR		2.6	2.3	3.6	2.4	0.9	3.0
BNM-LNHB		-1.6	1.2	-0.6	1.2	-3.3	2.3
NPL		-0.2	2.9	0.8	2.9	-1.9	3.5
CSIR-NML		0.2	0.9	1.2	1.0	-1.5	2.2
OMH		-1.0	1.4	0.0	1.5	-2.7	2.4
NIST				1.0	1.1	-1.7	2.2
NMIJ		-1.0	1.1			-2.8	2.3
CIEMAT		1.7	2.2	2.8	2.3		

Figure 1. Graph of degrees of equivalence with the KCRV for ^{67}Ga
(as it appears in Appendix B of the MRA)



Appendix 1. Uncertainty budget for the activity of ^{67}Ga submitted to the SIR**CIEMAT ampoule BIPM-301**

Relative standard uncertainties	$u_i \times 10^4$	
	evaluated by method	
Contributions due to	A	B
counting	27	–
weighing of source	–	10
dead-time	–	45
coincidence resolving time	–	22
Gandy effect	–	1
background	19	–
half life (3.259 (10) d)	–	10
extrapolation of efficiency curve	62	–
Quadratic summation	70	52
Total relative combined uncertainty u_c	87	