Metrologia **52** (2015) *Tech. Suppl.* 06012

Update of the BIPM comparison BIPM.RI(II)-K1.Bi-207 of activity measurements of the radionuclide ^{207}Bi to include the 2010 result of the LNE-LNHB (France)

C. Michotte, G. Ratel, S. Courte, C. Bobin[1] and M. Moune[1]
BIPM and [1]Laboratoire national de métrologie et d'essais -Laboratoire national Henri Becquerel (LNE-LNHB), France

Abstract

In 2010, the Laboratoire national de métrologie et d'essais - Laboratoire national Henri Becquerel (LNE-LNHB) submitted one sample of known activity of ^{207}Bi to the International Reference System (SIR) for activity comparison at the Bureau International des Poids et Mesures (BIPM), with comparison identifier BIPM.RI(II)-K1.Bi-207. The value of the activity submitted was about 180 kBq. There is now one result in the BIPM.RI(II)-K1.Bi-207 comparison. The key comparison reference value (KCRV) has been evaluated for the first time using the LNE-LNHB result and a PTB result dating 1982. The degree of equivalence between the LNE-LNHB equivalent activity measured in the SIR and the KCRV has been calculated and is reported.

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 with 3.6 g of the radioactive solution. For radioactive gases, a different standard ampoule is used. Each 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, A_e, are all given in [1].

From its inception until 31 December 2008, the SIR has measured 914 ampoules to give 670 independent results for 63 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 standardizations. These comparisons are described as BIPM ongoing comparisons and the results form the basis of the BIPM key comparison database (KCDB) of the Comité International des Poids et Mesures Mutual Recognition Arrangement (CIPM MRA) [2]. The comparison described in this report is known as the BIPM.RI(II)-K1.Bi-207 key comparison and includes results published previously [3].

2. Participants

In addition to the ampoule submitted by the LNE-LNHB in 2010, the PTB and the VNIIM have submitted ampoules for inclusion in this comparison. The laboratory details are given in Table 1, with the earlier submissions being taken from [3]. The dates of measurement in the SIR given in Table 1 are used in the KCDB and all references in this report.

Table 1. Details of the participants in the BIPM.RI(II)-K1.Bi-207

NMI	Full name	Country	Regional metrology organization	Date of measurement at the BIPM YYYY-MM-DD
PTB	Physikalisch-Technische Bundesanstalt	Germany	EURAMET	1982-06-03
VNIIM	D.I. Mendeleyev Institute for Metrology	Russian Federation	COOMET	1991-07-02
LNE-LNHB	Laboratoire national de métrologie et d'essais - Laboratoire national Henri Becquerel	France	EURAMET	2010- 03-30

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 appropriate correlations are taken into account.

A brief description of the standardization methods used by the laboratories, the activities submitted, the relative standard uncertainties ($k = 1$) and the half-life used by the participants are given in Table 2. The uncertainty budgets for the new LNE-LNHB submission is given in Appendix 1 attached to this report. The list of acronyms used to summarize the methods is given in Appendix 2.

The half-life presently used by the BIPM is 12 020(510) d from the BIPM Monographie-5 [4] and all the SIR results have been updated accordingly. This half-life value agrees within uncertainty with the other values used previously [3].

Table 2. Standardization methods of the participants for ^{207}Bi

NMI	Method used and acronym (see Appendix 2)	Half-life / a	Activity A_i / kBq	Reference date YYYY-MM-DD	Relative standard uncertainty / 10^{-2} by method of evaluation A	B
PTB	4πγ(NaI) and 4P-NA-PH-00-00-HE	-	480.7	1982-01-01 0 h UTC	0.84	
	calibrated Ge(Li) UA-GL-PH-00-00-00		482.5		0.80	
VNIIM	Calibrated Ge(Li)† UA-GL-PH-00-00-00	-	1212	1991-05-24 12 h UTC	0.20	1.74
LNE-LNHB	4πγ(NaI) 4P-NA-PH-00-00-HE	32.9(14) [4]	178.9	2008-12-15 12 h UT	0.27	0.39

† traceable through primary realizations made at the VNIIM of ^{133}Ba, ^{134}Cs and ^{152}Eu activities.

Details regarding the solutions submitted are shown in Table 3, including any impurities, when present, as identified by the laboratories. When given, the standard uncertainties on the evaluations are shown. The BIPM standard method for evaluating the activity of impurities using a calibrated Ge(Li) spectrometer is described in [5]. The CCRI(II) agreed in 1999 [6] that this method should be followed according to the protocol described in [7] when an NMI makes such a request or when there appear to be discrepancies. However, no such impurity measurement has needed to be carried out at the BIPM in the present case.

Table 3. Details of each solution of ^{207}Bi submitted

NMI / SIR year	Chemical composition	Solvent conc. / (mol dm^{-3})	Carrier: conc. /(μg g^{-1})	Density /(g cm^{-3})	Relative activity of any impurity†
PTB	$BiCl_3$ in HCl	1.0	$BiCl_3$: 45	1.005	–
VNIIM	$BiCl_3$ in HCl	1.0	$BiCl_3$: 50	1.01	–
LNE-LNHB	$BiCl_3$ in HCl	1.0	$BiCl_3$: 50	1.016	–

† the ratio of the activity of the impurity to the activity of ^{207}Bi 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 "master-file". The recent submission has added one ampoule for the activity measurements for ^{207}Bi giving rise to three ampoules in total. The SIR equivalent activity, A_{ei}, for each ampoule for the previous and new results is given in Table 4 for each NMI, *i*. 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 submitted activities are compared with a given source of ^{226}Ra, all the SIR results are normalized to the radium source number 5 [1].

No recent submission has been identified as a pilot study so the most recent result of each NMI is normally eligible for Appendix B of the MRA.

No international or regional comparison for this radionuclide has been held to date so no linking data are identified.

Table 4. Results of SIR measurements of ^{207}Bi

NMI / SIR year	Mass of solution m_i / g	Activity submitted A_i / kBq	N° of Ra source used	SIR $A_{e,i}$ / kBq	Relative uncertainty from SIR	Combined standard uncertainty u_i / kBq
PTB 1982	3.7182	480.7 482.5	3	10 834† 10 874*	8×10^{-4}	91† 87*
VNIIM 1991	3.5226	1212	3	10 400	5×10^{-4}	180
LNE-LNHB 2010	3.6550(6)	178.9	1	10 889	18×10^{-4} **	55

† result based on a primary measurement method, to be used for the KCRV
* The result to be registered in the KCDB is based on the unweighted mean of the two activity measurement results obtained at the PTB (i.e. 129.5(10) kBq g^{-1}), giving an equivalent activity of 10 852(88) kBq
** The uncertainty contribution of the decay correction is 12×10^{-4}

4.1 The key comparison reference value

In May 2013 the CCRI(II) decided to no longer calculate the key comparison reference value (KCRV) by using an unweighted mean but rather by using the power-moderated weighted mean [8]. This type of weighted mean is similar to a Mandel-Paule mean in that the NMIs' uncertainties may be increased until the reduced chi-squared value is one. In addition, it allows for a power smaller than two in the weighting factor. Therefore, all SIR key comparison results can be selected for the KCRV with the following provisions:

a) only results for solutions standardized by primary techniques are accepted, with the exception of radioactive gas standards (for which results from transfer instrument measurements that are directly traceable to a primary measurement in the laboratory may be included);
b) each NMI or other laboratory has only one result (normally the most recent result or the mean if more than one ampoule is submitted);
c) possible outliers can be identified on a mathematical basis and excluded from the KCRV using the normalized error test with a test value of 2.5 and using the modified uncertainties;

d) results can also be excluded for technical reasons.
e) The CCRI(II) is always the final arbiter regarding excluding any data from the calculation of the KCRV.

The data set used for the evaluation of the KCRVs is known as the “KCRV file” and is a reduced data set from the SIR master-file. 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 made only by the CCRI(II) during one of its biennial meetings as for the case of ^{207}Bi in June 2011, or by consensus through electronic means (e.g., email) as discussed at the CCRI(II) meeting in 2013.

As mentioned above, the rules to calculate a KCRV have been recently modified. Consequently, the KCRV agreed in 2011 for ^{207}Bi has been re-calculated as 10 865(48) kBq on the basis of the SIR results from the PTB and the LNE-LNHB. This can be compared with the value of 10 920(37) kBq obtained using the SIRIC efficiency curve of the SIR [9] and the 2003 DDEP evaluation of the nuclear data.

4.2 Degrees of equivalence

Every participant in a comparison is entitled to have one result included in the KCDB as long as the NMI is a signatory or designated institute listed in the CIPM MRA, and the result is valid (i.e., not older than 20 years). Normally, the most recent result is the one included. An NMI may withdraw its result only if all other participants agree.

The degree of equivalence of a given measurement standard is the degree to which this standard is consistent with the KCRV [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 result with the KCRV*

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

$$D_i = A_{\mathrm{e}\,i} - \mathrm{KCRV} \qquad (1)$$

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

$$U_i = 2u(D_i)\,. \qquad (2)$$

When the result of the NMI i is included in the KCRV with a weight w_i, then

$$u^2(D_i) = (1\text{-}2w_i)\, u_i^2 + u^2(\mathrm{KCRV})\,. \qquad (3)$$

However, when the result of the NMI i is not included in the KCRV, then

$$u^2(D_i) = u_i^2 + u^2(\mathrm{KCRV}). \qquad (4)$$

4.2.2 *Comparison between pairs of NMI results*

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

$$D_{ij} = D_i - D_j = A_{\mathrm{e}\,i} - A_{\mathrm{e}\,j} \qquad (5)$$

and the expanded uncertainty (k = 2) of this difference, $U_{ij} = 2u(D_{ij})$, where

$$u_{D_{ij}}{}^2 = u_i{}^2 + u_j{}^2 - 2u(A_{\mathrm{e}i}, A_{\mathrm{e}j}) \qquad (6)$$

where any obvious correlations between the NMIs (such as a traceable calibration, or correlations normally coming from the SIR or from the linking factor in the case of linked comparison) are subtracted using the covariance $u(A_{\mathrm{e}i}, A_{\mathrm{e}j})$ (see [10] for more detail). However, the CCRI decided in 2011 that these “pair-wise degrees of equivalence” no longer need to be published as long as the methodology is explained.

Table 5 shows the matrix of all the degrees of equivalence as they will appear in the KCDB. It should be noted that for consistency within the KCDB, a simplified level of nomenclature is used with $A_{\mathrm{e}i}$ replaced by x_i. The introductory text is that agreed for the comparison. The graph of the 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 graphical representation indicates in part the degree of equivalence between the NMIs but obviously does not take into account the correlations between the different NMIs. It should be noted that the final data in this paper, while correct at the time of publication, will become out-of-date as NMIs make new comparisons. The formal results under the CIPM MRA [2] are those available in the KCDB.

Conclusion

The BIPM ongoing key comparison for ^{207}Bi, BIPM.RI(II)-K1.Bi-207 currently comprises one result.

The KCRV has been determined for this radionuclide for the first time, using the present LNE-LNHB result and an earlier result from the PTB. The results have been analysed with respect to the KCRV, providing degrees of equivalence for the LNE-LNHB. The degrees of equivalence have been approved by the CCRI(II) and are published in the BIPM key comparison database. Other results may be added when other NMIs contribute ^{207}Bi activity measurements to this comparison or take part in other linked comparisons.

Acknowledgements

The authors would like to thank the NMIs for their participation in this comparison, and Dr J.M. Los Arcos of the BIPM for editorial assistance.

References

[1] Ratel G., The Système International de Référence and its application in key comparisons, *Metrologia*, 2007, **44**(4), S7-S16

[2] CIPM MRA: *Mutual recognition of national measurement standards and of calibration and measurement certificates issued by national metrology institutes*, International Committee for Weights and Measures, 1999, 45 pp. http://www.bipm.org/en/cipm-mra/.

[3] Ratel G. and Michotte C., BIPM comparison BIPM.RI(II)-K1.Bi-207 of activity measurements of the radionuclide Bi-207, *Metrologia*, 2002, **39** Tech. Suppl., 06004.

[4] Bé M.-M., Chisté V., Dulieu C., Mougeot X., Browne E., Chechev V., Kuzmenko N., Kondev F., Luca A., Galán M., Arinc A., Huang X., 2004, Table of radionuclides, *Monographie BIPM-5*,Vol. 5.

[5] Michotte C., Efficiency calibration of the Ge(Li) detector of the BIPM for SIR-type ampoules, 1999, *Rapport BIPM*-1999/03, 15 pp.

[6] *Comité Consultatif pour les Étalons de Mesures des Rayonnements Ionisants* 16th meeting (1999), 2001, CCRI(II) 81-82.

[7] Michotte C., Protocol on the use of the calibrated spectrometer of the BIPM for the measurement of impurities in ampoules submitted to the SIR, 2001, *CCRI(II)/01-01*, 2pp.

[8] Pommé S., Determination of a reference value, associated standard uncertainty and degrees of equivalence for CCRI(II) key comparison data, European Commission, Joint Research Centre, Institute for Reference Materials and Measurements, 2012, Report EUR 25355 EN. Errata notice published in the CCRI(II) working document, 2013, CCRI(II)/13-18.

[9] Cox M.G., Michotte C., Pearce A.K., Measurement modelling of the International Reference System (SIR) for gamma-emitting radionuclides, Monographie BIPM-7, 2007, 48 pp.

[10] Michotte C. and Ratel G., Correlations taken into account in the KCDB, CCRI(II) working document, 2003, CCRI(II)/03-29.

Table 5. Introductory text for ^{207}Bi and table of degrees of equivalence

Key comparison BIPM.RI(II)-K1.Bi-207

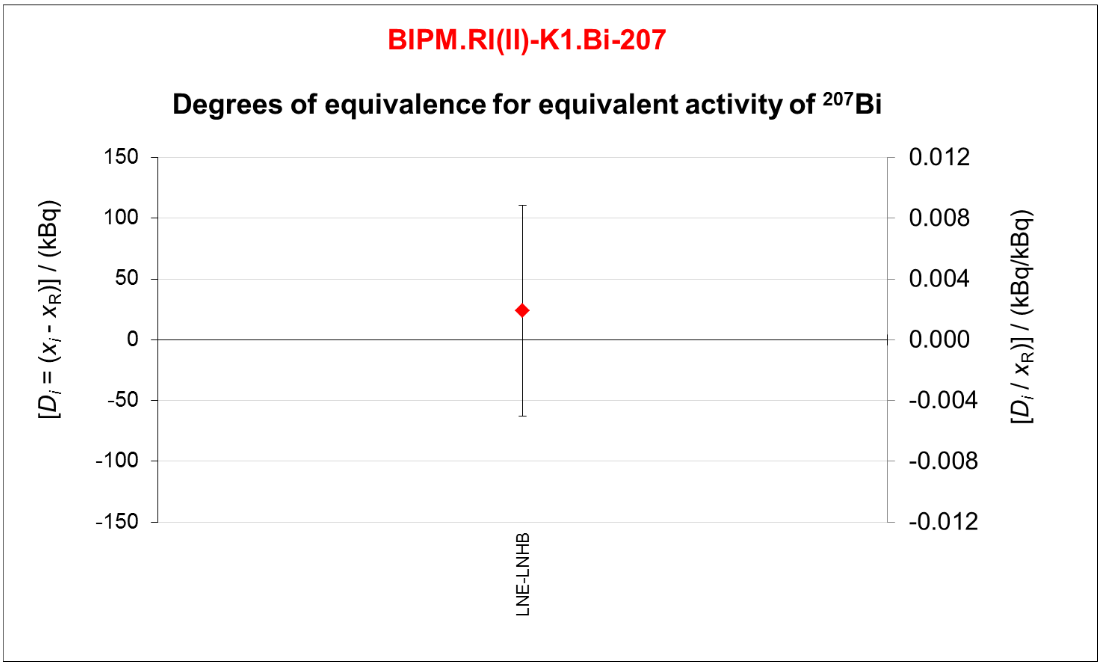
MEASURAND : Equivalent activity of ^{207}Bi

Key comparison reference value: the SIR reference value for this radionuclide is x_R = 10 865 kBq with a standard uncertainty, u_R = 48 kBq (see Section 4.1 of the Final Report).
The value x_i is 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 kBq, and
$U_i = 2((1 - 2w_i)u_i^2 + u_R^2)^{1/2}$ when each laboratory has contributed to the calculation of x_R, w_i being the weight of laboratory *i* in the KCRV.

Lab *i*	D_i	U_i
	/ kBq	
LNE-LNHB	24	87

Figure 1. Graph of degrees of equivalence with the KCRV for ^{207}Bi
(as it appears in Appendix B of the MRA**)**



Appendix 1. Uncertainty budgets for the activity of ^{207}Bi submitted to the SIR

LNE-LNHB

Relative standard uncertainties	$u_i \times 10^4$ evaluated by method	
Contributions due to	**A**	**B**
counting statistics	15	–
weighing	–	10
live-time technique	–	1
background	10	–
efficiency calculation	–	35
half-life	–	15
extrapolation	20	–
Quadratic summation	**27**	**39**
Relative combined standard uncertainty, u_c	**48**	

Appendix 2. Acronyms used to identify different measurement methods

Each acronym has six components, geometry-detector (1)-radiation (1)-detector (2)-radiation (2)-mode. When a component is unknown, ?? is used and when it is not applicable 00 is used.

Geometry	**acronym**	**Detector**	**acronym**
4π	4P	proportional counter	PC
defined solid angle	SA	press. prop counter	PP
2π	2P	liquid scintillation counting	LS
undefined solid angle	UA	NaI(Tl)	NA
		Ge(HP)	GH
		Ge(Li)	GL
		Si(Li)	SL
		CsI(Tl)	CS
		ionization chamber	IC
		grid ionization chamber	GC
		bolometer	BO
		calorimeter	CA
		PIPS detector	PS
Radiation	**acronym**	**Mode**	**acronym**
positron	PO	efficiency tracing	ET
beta particle	BP	internal gas counting	IG
Auger electron	AE	CIEMAT/NIST	CN
conversion electron	CE	sum counting	SC
mixed electrons	ME	coincidence	CO
bremsstrahlung	BS	anti-coincidence	AC
gamma rays	GR	coincidence counting with efficiency tracing	CT
X - rays	XR	anti-coincidence counting with efficiency tracing	AT
photons (x + γ)	PH	triple-to-double coincidence ratio counting	TD
alpha - particle	AP	selective sampling	SS
mixture of various radiation	MX	high efficiency	HE

Examples

method	acronym
4π(PC)β–γ-coincidence counting	4P-PC-BP-NA-GR-CO
4π(PPC)β–γ-coincidence counting eff. trac.	4P-PP-MX-NA-GR-CT
defined solid angle α-particle counting with a PIPS detector	SA-PS-AP-00-00-00
4π(PPC)AX-γ(GeHP)-anticoincidence counting	4P-PP-MX-GH-GR-AC
4π CsI-β,AX,γ counting	4P-CS-MX-00-00-HE
calibrated IC	4P-IC-GR-00-00-00
internal gas counting	4P-PC-BP-00-00-IG