Activity measurements of the radionuclide ^{111}In for the PTB, Germany in the ongoing comparison BIPM.RI(II)-K1.In-111

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Abstract

In 2005, the Physikalisch-Technische Bundesanstalt (PTB) submitted a sample of known activity of ^{111}In to the International Reference System (SIR). The value of the activity submitted was about 28 MBq. This key comparison result is the first result for Germany in the matrix of degrees of equivalence in the key comparison database that now contains six results, identifier BIPM.RI(II)-K1.In-111.

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, A_e, are all given in [1].

From its inception until 31 December 2004, the SIR has measured 872 ampoules to give 634 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 CIPM Mutual Recognition Arrangement (MRA) [2]. The comparison described in this report is known as the BIPM.RI(II)-K1.In-111 key comparison.

2. Participants

In addition to the present solution from the PTB, five other NMIs and two other laboratories have submitted eleven ampoules for the comparison of ^{111}In activity measurements since 1977. The PTB details are given in Table 1 and the details of the other participants are given in [3].

Table 1. Details of the PTB participation in the comparison BIPM.RI(II)-K1.In-111

NMI	Full name	Country	Regional metrology organization	Date of measurement at the BIPM YYYY-MM-DD
PTB	Physikalisch-Technische Bundesanstalt	Germany	EUROMET	2005-04-25

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 methods for the laboratory, the activities submitted and the relative standard uncertainties ($k = 1$) are given in Table 2. The uncertainty budget is given in Appendix 1. The acronyms used for the measurement methods are given in Appendix 2.

The half-life used by the BIPM is 2.804 9 (1) days [4], which is very close to the value recommended by the IAEA, 2.804 7 (5) d [5] as used by the PTB.

Details regarding the solution submitted are shown in Table 3, including any impurities, when present, as identified by the laboratory. The BIPM has a standard method for evaluating the activity of impurities using a calibrated Ge(Li) spectrometer [6]. The CCRI(II) agreed in 1999 [7] that this method should be followed according to the protocol described in [8] when an NMI makes such a request or when there appear to be discrepancies. No impurity measurement was carried out in this case.

Table 2. Standardization methods of the PTB for ^{111}In

NMI	Method used and acronym (see Appendix 2)	Half-life / d	Activity / kBq	Reference date YY-MM-DD	Relative standard uncertainty × 100 by method of evaluation	
					A	B
PTB	Pressurized ionization chamber calibrated in April/May 2005 by 4πPPCe$_c$-γ coinc. 4P-PP-MX-NA-GR-CO	2.804 7 (5)	28 090	05-04-25 0 h UTC	0.06	0.51

Table 3. Details of the solution of ^{111}In submitted

NMI	Chemical composition	Solvent conc. / (mol dm^{-3})	Carrier: conc. /(μg g^{-1})	Density /(g cm^{-3})	Relative activity of any impurity†
PTB	$In(NO_3)_2 \cdot 5\ H_2O$ in HCl	0.1	$In(NO_3)_2 \cdot 5\ H_2O$: 65	1.00	^{114}In^m : 1.58 (4) × 10^{-3}

† the ratio of the activity of the impurity to the activity of ^{111}In 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 ^{111}In arise from eleven ampoules and the SIR equivalent activity, A_{ei}, for each ampoule is given in [3] for each NMI, i. The SIR equivalent activity for the new PTB ampoule is given in Table 4. The date of measurement in the SIR is given in Table 1 and is used in the KCDB and all references in this report. The relative standard uncertainty arising from the measurements in the SIR is 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 SIR correction for the ^{114}In^m impurity has a negligible influence on the final result.

Table 4. Results of SIR measurements of ^{111}In for the PTB

NMI	Mass of solution / g	Activity submitted/ kBq	N° of Ra source used	SIR A_e / kBq	Relative uncertainty from SIR	Total uncertainty $u_{c,i}$ / kBq
PTB	3.6094 (9)	28 090	5	43 530	7 × 10^{-4}	230

4.1 The key comparison reference value

The KCRV for ^{111}In has been identified as 43 000 (120) kBq as given in [3]. Although the KCRV may be modified whenever an NMI participates, such modifications follow approved criteria [3] and 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

$$D_i = A_{ei} - \mathrm{KCRV} \tag{1}$$

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

$$U_i = 2u_{D_i}\,, \tag{2}$$

taking correlations into account as appropriate [9].

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

$$D_{ij} = D_i - D_j = A_{ei} - A_{ej} \tag{3}$$

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

$$u_{D_{ij}}^{\ 2} = u_i^{\ 2} + u_j^{\ 2} - 2u(A_{e,i}, A_{e,j}) \tag{4}$$

where any obvious correlations between the NMIs (such as a traceable calibration) are subtracted using the covariance $u(A_{ei}, A_{ej})$, 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. Consequently, the uncertainties in the table of degrees of equivalence cannot be generated from the column in the table that gives the uncertainty of each participant with respect to the KCRV. 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 will appear in Appendix B of the KCDB. 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 where the black squares indicate results obtained prior to 1985. The graphical 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 result for the PTB in this ongoing comparison agrees with the KCRV at the level of two standard uncertainties.

The BIPM ongoing key comparison for ^{111}In, BIPM.RI(II)-K1.In-111 currently comprises six results. 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 NMIs contribute ^{111}In activity measurements to this comparison or take part in linked comparisons.

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Table 5. Table of degrees of equivalence and introductory text for ^{111}In

Key comparison BIPM.RI(II)-K1.In-111

MEASURAND : **Equivalent activity of ^{111}In**

<u>Key comparison reference value:</u> the SIR reference value x_R for this radionuclide is 43.00 MBq, with a standard uncertainty of 0.12 MBq (see Section 4.1 of the Report), 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
$U_i = 2((1 - 2/n)u_i^2 + (1/n^2)\Sigma u_i^2)^{1/2}$ when each laboratory has contributed to the calculation of x_R,
with n the number of laboratories.

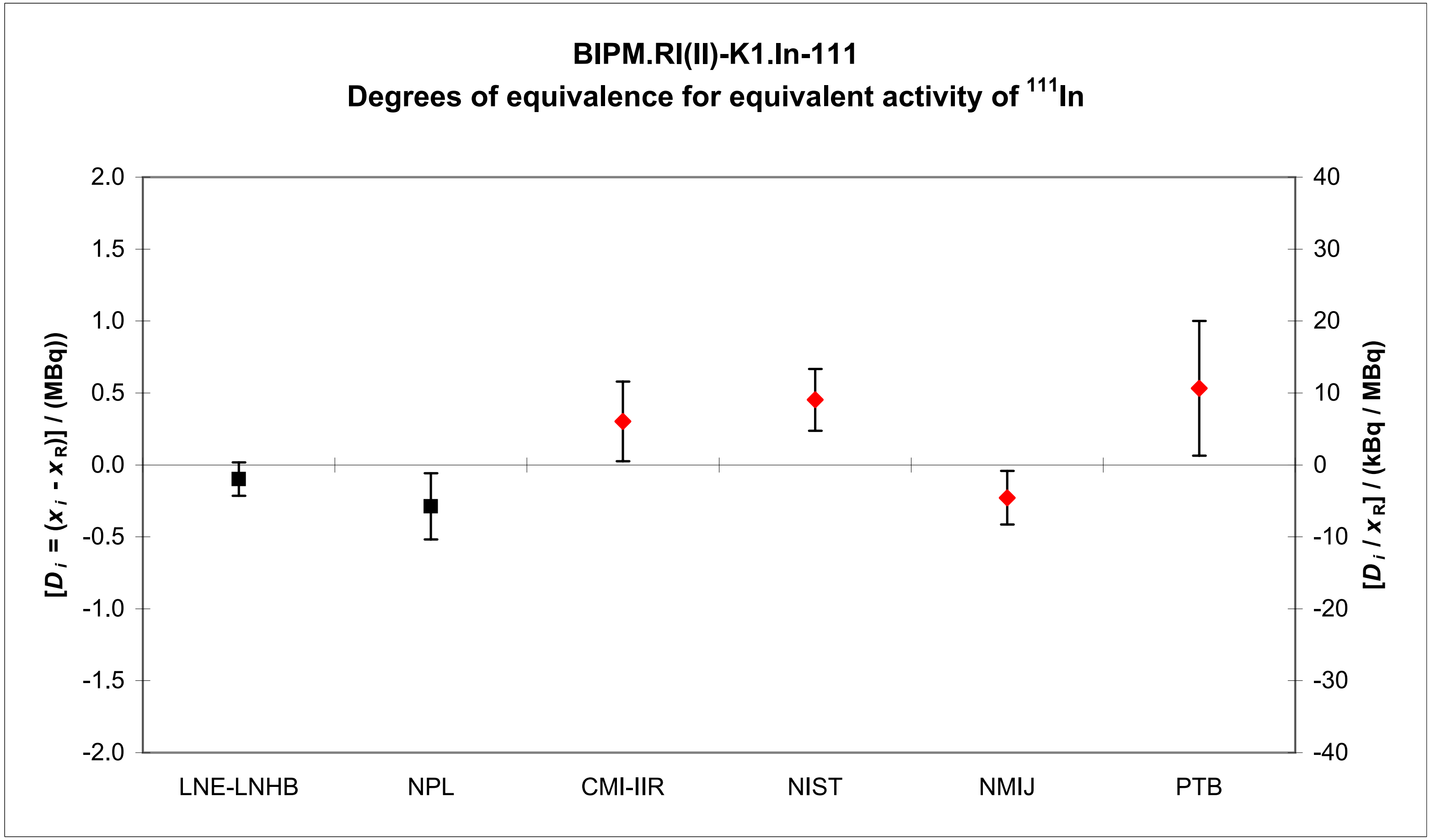
The degree of equivalence between two laboratories is given by a pair of numbers:
$D_{ij} = D_i - D_j = (x_i - x_j)$ and U_{ij}, its expanded uncertainty (k = 2), both expressed in MBq.
The approximation $U_{ij} \sim 2(u_i^2 + u_j^2)^{1/2}$ is used in the following table.

Lab *j* ⇨

Lab *i* ⇩

Lab *i*	D_i / MBq	U_i / MBq	LNE-LNHB D_{ij} / MBq	LNE-LNHB U_{ij} / MBq	NPL D_{ij} / MBq	NPL U_{ij} / MBq	CMI-IIR D_{ij} / MBq	CMI-IIR U_{ij} / MBq	NIST D_{ij} / MBq	NIST U_{ij} / MBq	NMIJ D_{ij} / MBq	NMIJ U_{ij} / MBq	PTB D_{ij} / MBq	PTB U_{ij} / MBq
LNE-LNHB	**-0.10**	0.12			**0.19**	0.28	**-0.40**	0.33	**-0.55**	0.26	**0.13**	0.22	**-0.63**	0.47
NPL	**-0.29**	0.23	**-0.19**	0.28			**-0.59**	0.41	**-0.74**	0.35	**-0.06**	0.33	**-0.82**	0.53
CMI-IIR	**0.30**	0.28	**0.40**	0.33	**0.59**	0.41			**-0.15**	0.40	**0.53**	0.38	**-0.23**	0.56
NIST	**0.45**	0.22	**0.55**	0.26	**0.74**	0.35	**0.15**	0.40			**0.68**	0.31	**-0.08**	0.52
NMIJ	**-0.23**	0.19	**-0.13**	0.22	**0.06**	0.33	**-0.53**	0.38	**-0.68**	0.31			**-0.76**	0.50
PTB	**0.53**	0.47	**0.63**	0.47	**0.82**	0.53	**0.23**	0.56	**0.08**	0.52	**0.76**	0.50		

Figure 1. Graph of degrees of equivalence with the KCRV for ^{111}In
(as it appears in Appendix B of the MRA)



N.B. Right-hand axis shows approximate values only

Appendix 1. Uncertainty budget for the activity of ^{111}In submitted to the SIR

Uncertainty budget for the PTB measurement (2005)

Relative standard uncertainties	$u_i \times 10^4$ evaluated by method	
Contributions due to	**A**	**B**
Ionization current statistics (^{111}In)	5	–
Linearity of current measurement	–	5
Radium reference source current	2.5	–
Calibration factor	–	50
Geometry correction	–	5
Weighing	–	2.4
Adsorption	–	< 0.1
Impurities	–	1
Background	–	< 1
Decay correction	–	6.6
Quadratic summation	**5.6**	**51.0**
Relative combined standard uncertainty, u_c	**51**	

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
photons + electrons	PE	selective sampling	SS
alpha - particle	AP	high efficiency	HE
mixture of various radiations	MX	digital coincidence counting	DC

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(Ge(HP))-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