Update of the BIPM comparison BIPM.RI(II)-K1.Tb-161 of activity measurements of the radionuclide ^{161}Tb to include the 2022 result of the NPL (United Kingdom)

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Abstract Since 2019, 2 laboratories have submitted 2 samples of ^{161}Tb 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.Tb-161. Recently, the NPL (United Kingdom) participated in the comparison and the key comparison reference value (KCRV) has been evaluated for the first time. The degrees of equivalence between each equivalent activity measured in the SIR and the updated KCRV have been calculated and the results are given in the form of a table. A graphical representation is also given.

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 2022, the SIR has been used to measure 1045 ampoules to give 799 independent results for 72 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 continuous 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.Tb-161 key comparison. The results of earlier participations in this key comparison were published previously [3].

Successful participation in this comparison by a laboratory may provide evidential support for Calibration and Measurement Capability (CMC) claims for ^{161}Tb measured using the laboratory's method(s) used in the comparison or methods calibrated by those used for the comparison. This comparison may also be used to support CMC claims for those radionuclides measured in the laboratory using the same method and having a degree of difficulty at or below that of the radionuclide measured in this comparison as indicated in the current Measurement Methods Matrix (MMM) [4]

2. Participants

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.Tb-161.

NMI or laboratory	**Previous acronyms or other institutes**	**Full name**	**Country**	**Regional Metrology Organization (RMO)**	**Date of SIR measurement** yyyy-mm-dd
IRA	IER	Institut de Radiophysique	Switzerland	EURAMET	2019-08-29
NPL	-	National Physical Laboratory	United Kingdom	EURAMET	2022-03-17

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 and the half-life used by the participants are given in Table 2. The uncertainty budget for the new submission is given in Appendix D attached to this report; previous uncertainty budgets are given in the earlier K1 report [3]. The list of acronyms used to summarize the methods is given in Appendix E.

The half-life used previously by the BIPM was 6.953(2) days [5] and this was changed to the more recent evaluation of 6.962 5(26) days [6]. All the results in Table 4 have been updated accordingly.

Table 2: Standardization methods of the participants for ^{161}Tb.

NMI or laboratory	**Method used and the acronym**	**Activity** A_i**/MBq**	**Relative standard uncertainty /10^{-2}**		**Reference date**	**Half-life /d**
			A	**B**	**yyyy-mm-dd**	
IRA	4π (PS) β-γ coincidence (4P-PS-BP-CB-GR-CO) 4π (LS) β-γ coincidence (4P-LS-BP-CB-GR-CO)	61 970[a]	0.16	0.56	2019-08-22 12:00 UT	6.955(2)
NPL	4π(LS)β-γ digital coincidence counting (4P-LS-BP-GH-GR-CO)	54 612	0.023	0.185	2022-03-14 12:00 UT	6.9571(36) (NPL evaluation using [5], [8], [9])
	CIEMAT/NIST efficiency tracing (4P-LS-BP-00-00-CN)	54 486 [b]	0.032	0.261		

[a] The activity is the mean of 25 efficiency extrapolated activities obtained with two coincidence techniques, 8 sources, from 2 dilutions, and 3 γ settings. The degrees of freedom of the twenty five efficiency extrapolations range from 40 to 77 [7].

[b] The final result of 54 572(87) kBq obtained by the two methods has been calculated as a weighted mean at lowest level before application of dilution factors and inclusion of dilution uncertainty.

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.

Table 3: Details of each solution of ^{161}Tb submitted.

NMI or laboratory / SIR year	**Chemical composition**	**Solvent conc.** /(mol dm^{-3})	**Carrier conc.** /(µg g^{-1})	**Density** /(g cm^{-3})	**Relative activity of any impurity**[a]
IRA 2019	Tb^{3+} in HCl	0.1	25	1.000(6)	^{160}Tb: 4.44(22)x10^{-3} %
NPL 2022	Gd^{3+} in HCl	0.1	25	1	^{160}Tb: 3.95(10)x10^{-3} %

[a] The ratio of the activity of the impurity to the activity of ^{161}Tb at the reference date

4. Results

All the submissions to the SIR since its inception in 1976 are maintained in a dedicated database based on CSV formatted files controlled by the Git version control system [10]. Machine-readable versions of this report (XML and JSON documents) are attached to this document [11]. The latest submission has added 1 ampoule for the activity measurements for ^{161}Tb giving rise to 2 ampoules in total.

The SIR equivalent activity, $A_{\mathrm{e}i}$, for each ampoule received from each NMI, i, including both previous and new results, 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 ($u(A_i)$) 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]. Table 4 also shows the comparison results selected for the KCRV as explained in section 4.1.

The impurity correction of the SIR measurements amounts to 1.01 and 1.006 for the IRA and NPL, respectively. Measurements repeated at the BIPM after periods of up to 2 weeks later produced results in agreement within two combined standard uncertainty for the NPL (2022).

Table 4: Results of SIR measurement of ^{161}Tb.

NMI or laboratory / SIR year	Mass m_i /g	A_i /**MBq**	^{226}**Ra source**	$A_{\mathrm{e}i}$ /**MBq**	**Relative uncert. from SIR** /$\mathbf{10^{-4}}$	$u_{\mathbf{c}i}$ /**MBq**	$A_{\mathbf{e}i}$ **for KCRV** /**MBq**
IRA 2019	3.642 43(21)	61 970	1	1710	17	10	1710(10)
NPL 2022	3.609 27	54 612	2	1702.4	12	3.8	1701.6(34)[a]
		54 486		1698.5		4.9	-

[a] The result was obtained using an average between methods.

4.1. The key comparison reference value

In May 2013, the CCRI(II) decided to calculate the key comparison reference value (KCRV) by using the power-moderated weighted mean [12] rather than an unweighted mean, as had been the policy. 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 α smaller than two in the weighting factor. As proposed in [12], α is taken as $2 - 3/N$ where N is the number of results selected for the KCRV. Therefore, all SIR key comparison results can be selected for the KCRV with the following provisions:

(a) results for solutions standardized by only 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 may use only one result (normally the most recent result or the mean if more than one ampoule is submitted);

(c) results more than 20 years old are included in the calculation of the KCRV but are not included in data shown in the KCDB or in the plots in this report, as they have expired;

(d) 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;

(e) results can also be excluded for technical reasons; and

(f) the CCRI(II) is always the final arbiter regarding excluding any data from the calculation of the KCRV.

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, or by consensus through electronic means (e.g., email) as discussed at the CCRI(II) meeting in 2013.

Consequently, using the recent result produces a first KCRV for ^{161}Tb in 2022 of **1704.7(41) MBq** with the power α =0.5 that has been calculated using the previously published result, selected as shown in Table 4, for the IRA (2019), and the present NPL (2022) result.

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). No recent submission has been identified as a pilot study so the most recent result of each NMI is normally eligible for inclusion on the KCDB platform of the CIPM MRA [2]. 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

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

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

$$U_i = 2u(D_i) \tag{2}$$

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

$$u^2(D_i) = (1 - 2w_i)u_i^2 + u^2(\mathrm{KCRV}) \tag{3}$$

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

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

The introductory text in Appendix A is the one agreed by the CCRI(II) for all the K1 comparisons.

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

$$D_{ij} = D_i - D_j = A_{\mathrm{e}i} - A_{\mathrm{e}j} \tag{5}$$

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

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

where any obvious correlations between the NMIs (such as a traceable calibration, 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 [13] 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.

Appendix B 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 C1. 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.

5. Conclusion

The BIPM continuous key comparison for ^{161}Tb, BIPM.RI(II)-K1.Tb-161, currently comprises 2 results. The KCRV has been evaluated for the first time including the 2019 IRA result and the latest result from the NPL (United Kingdom). The results have been analyzed with respect to the KCRV, providing degrees of equivalence for 2 national metrology institutes. 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 ^{161}Tb activity measurements to this comparison or take part in other linked comparisons.

6. References

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Appendix A. Introductory text for ^{161}Tb degrees of equivalence

Key comparison BIPM.RI(II)-K1.Tb-161

MEASURAND: Equivalent activity of ^{161}Tb

Key comparison reference value: the SIR reference value x_{R} for this radionuclide is 1704.7 MBq , with a standard uncertainty, u_{R} equal to 4.1 MBq (see Section 4.1 of the Final Report). The value x_i is taken as the equivalent activity for a laboratory i.

The degree of equivalence of each laboratory with respect to the reference value is given by a pair of terms: $D_i = (x_i - x_{\mathrm{R}})$ and U_i, its expanded uncertainty ($k = 2$), both expressed in MBq, and $U_i = 2((1 - 2w_i)u_i^2 + u_{\mathrm{R}}^2)^{1/2}$, where w_i is the weight of laboratory i contributing to the calculation of x_{R}.

Appendix B. Table of degrees of equivalence for BIPM.RI(II)-K1.Tb-161

Table B1: The table of degrees of equivalence for BIPM.RI(II)-K1.Tb-161

NMI i	D_i /**MBq**	U_i /**MBq**
IRA	5	13
NPL	-3.1	7.4

Appendix C. Graph of degrees of equivalence with the KCRV for ^{161}Tb (as it appears in Appendix B of the MRA)

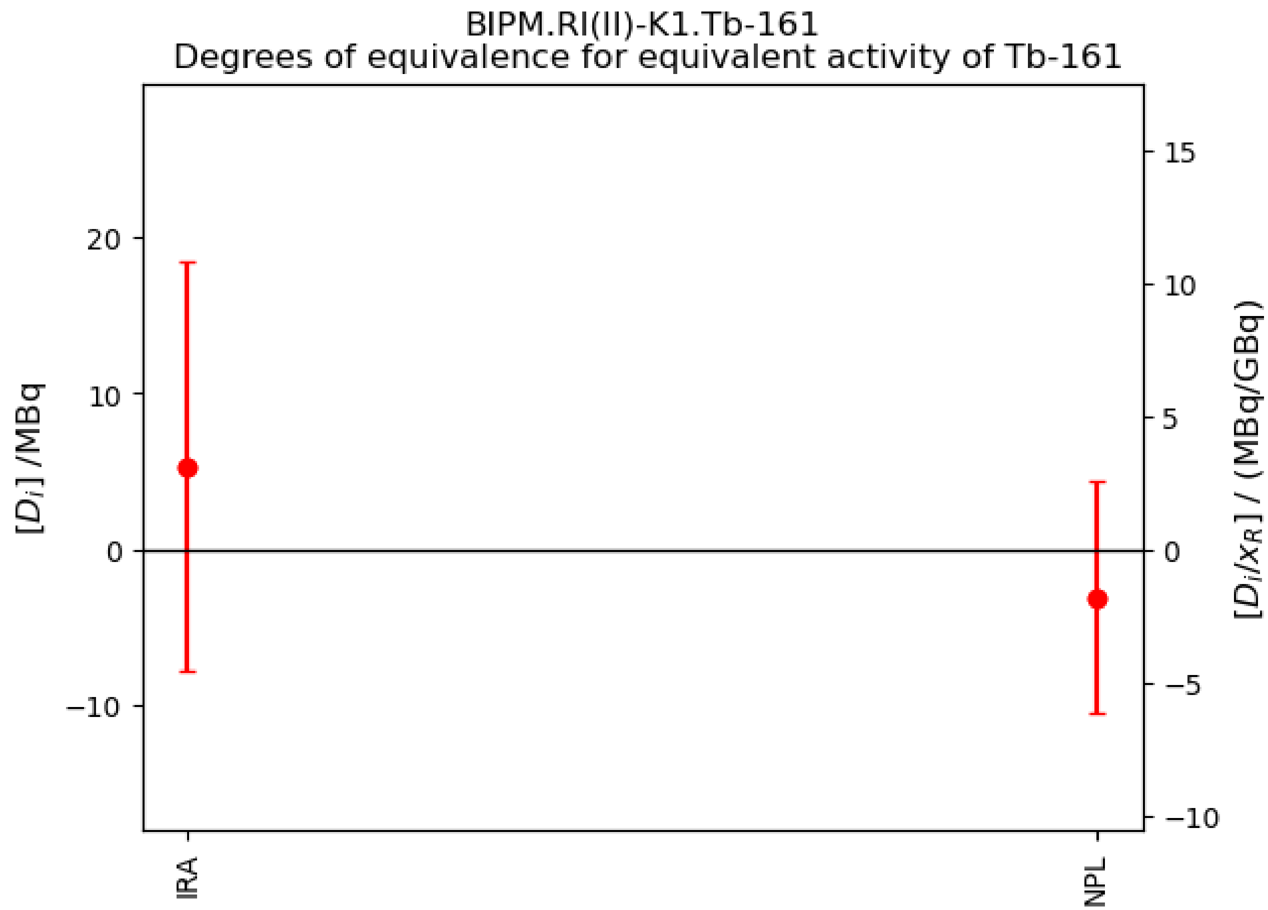

Figure C1. Degrees of equivalence for equivalent activity of ^{161}Tb.

Appendix D. Uncertainty budgets for the activity of ^{161}Tb submitted to the SIR

Uncertainty budget from NPL (method 1)

SIR/SIRTI reporting form - radioactive solution page 3a

BIPM.RI(II)-K1 or BIPM.RI(II)-K4

Measurement method	4pi(LS)-gamma digital coincidence counting	
ACRONYM	4P-LS-GH-BP-CO	**Comments:**
Activity concentration at reference date / kBq g^{-1}	15131	Date of measurements was 2022-03-14 to 2022-03-15. Used Goldstar Quanta Scintillation Cocktail
Relative standard uncertainty / 10^{-2}	0.19	
Date of measurement at the NMI (YYYY-MM-DD)	2022-03-14	

For relative methods:

Primary methods or standards used for calibration	
Date of calibration	
Date of primary measurement	

Uncertainty budget

Uncertainty component	**Relative uncertainty / 10^{-2}**	**Evaluation type (A or B)**	**Comment**
Counting statistics	0.023	A	
Background	0.003	A	
Weighing	0.02	B	
Dilution	0.076	B	
Dead time (LS)	0.032	B	
Dead time (HPGe)	0.0015	B	
Resolving time	0.045	B	
Pulse-pile up (LS)	0.015	B	
Pulse-pile up (HPGe)	0.005	B	
Decay correction	0.006	B	
Impurities	0.004	B	
Extra-/Inter-polation of efficiency curve	0.067	B	
Gamma gate selection	0.1	B	
Accidental coincidences	0.01	B	
Reproducibility	0.1	B	
Combined standard uncertainty	**0.19**		

Uncertainty budget from the NPL (method 2)

SIR/SIRTI reporting form - radioactive solution

BIPM.RI(II)-K1 or BIPM.RI(II)-K4

Measurement method	CIEMAT/NIST Efficiency Tracing	
ACRONYM	4P-LS-BP-CN	**Comments:**
Activity concentration at reference date / kBq g^{-1}	15096	Used Goldstar Quanta Scintillation Cocktail
Relative standard uncertainty / 10^{-2}	0.26	
Date of measurement at the NMI (YYYY-MM-DD)	2022-03-18	

For relative methods:

Primary methods or standards used for calibration	
Date of calibration	
Date of primary measurement	

Uncertainty budget

Uncertainty component	Relative uncertainty / 10^{-2}	Evaluation type (A or B)	Comment
Counting statistics	0.032	A	
Background	0.0006	A	
Sample Weighing	0.015	B	
Tracer weighing	0.0001	B	
Dead time	0.087	B	
Selection of kB value	0.009	B	
Dilution	0.076	B	
Cocktail	0.1	B	
Sample Decay correction	0.021	B	
Tracer Decay correction	0.0008	B	
Trace curve fitting	0.0033	A	
tracer activity per unit mass	0.01	B	
Nuclear Data	0.21	B	
Combined standard uncertainty	0.26		

Appendix E. 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**
4 π	4P	proportional counter	PC
defined solid angle	SA	press. Prop. Counter	PP
2 π	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
		Cerenkov detector	CD
		calorimeter	CA
		solid plastic scintillator	SP
		PIPS detector	PS
		CeBr3	CB

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	anticoincidence	AC
gamma rays	GR	coincidence counting with efficiency tracing	CT
x-rays	XR	anticoincidence counting with efficiency tracing	AT
photons $(x + \gamma)$	PH	triple-to-double coincidence ratio counting	TD
photons + electrons	PE	selective sampling	SS
alpha particle	AP	high efficiency	HE
mixture of various radiation	MX	digital coincidence counting	DC

Examples of methods	**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
4πCsI-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