

BIPM comparison BIPM.RI(II)-K1.Th-228 of activity measurements of the radionuclide ^{228}Th

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Abstract

Since 1986, two national metrology institutes (NMI) have submitted two samples of known activity of ^{228}Th 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.Th-228. The values of the activity submitted were about 300 kBq and 2 MBq. A key comparison reference value (KCRV) has been evaluated for the first time for ^{228}Th . There is only one result remaining in the BIPM.RI(II)-K1.Th-228 comparison, the 1986 NIST result being outdated. The degrees of equivalence between each equivalent activity measured in the SIR and the KCRV have been calculated and the results are given in the form of a table. A graphical presentation 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 2015, 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.Th-228 key comparison.

2. Participants

The NIST in 1986 and the PTB in 2010 each submitted one ampoule for inclusion in this comparison. 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.Th-228

NMI	Former acronym	Full name	Country	Regional metrology organization	Date of measurement at the BIPM YYYY-MM-DD
NIST	NBS	National Institute of Standards and Technology	United States	SIM	1986-07-24
PTB		Physikalisch-Technische Bundesanstalt	Germany	EURAMET	2010-04-07

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. Full uncertainty budgets have been requested as part of the comparison protocol only since 1998. When submitted by the NMIs, the uncertainty budgets are 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 used by the BIPM is 698.56(33) days [3].

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 [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. However, no such impurity measurement has needed to be carried out at the BIPM for ^{228}Th .

Table 2. Standardization methods of the participants for ^{228}Th

NMI	Method used and acronym (see Appendix 2)	Half-life / d	Activity A_i / kBq	Reference date YYYY-MM-DD	Relative standard uncertainty / 10^{-2} by method of evaluation	
					A	B
NIST	$4\pi(\alpha+\beta)$ liquid scintillation counting 4P-LS-MX-00-00-HE	698.7(7)	324.9	1986-07-01	0.30	0.48
PTB	CIEMAT/NIST 4P-LS-MX-00-00-CN and TDCR [7] 4P-LS-MX-00-00-TD	698.2(6)	1943.0	2010-04-01	0.06 [§]	0.31 [§]

[§] from TDCR method only (values were rounded up)

Table 3. Details of each solution of ^{228}Th submitted

NMI / SIR year	Chemical composition	Solvent conc. / (mol dm^{-3})	Carrier: conc. / ($\mu\text{g g}^{-1}$)	Density / (g cm^{-3})	Relative activity of any impurity [†]
NIST 1986	^{228}Th in HNO_3	2	—	1.065	< 0.01 %
PTB 2010	^{228}Th in HNO_3	2	—	1.065	—

[†] the ratio of the activity of the impurity to the activity of ^{228}Th 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 present submissions give rise to two ampoules for the activity measurements for ^{228}Th . 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].

The assumption is made that the daughter radionuclides were in equilibrium with the parent at the reference dates.

The measurement at the BIPM for the PTB was repeated after a period of two months later and produced a comparison result in agreement within standard uncertainty.

The question was raised on whether the chemical composition of the solutions could have an influence on the SIR measurement results, in particular because of the high acid concentration of the solutions submitted and owing to the intense β -particle and x-ray emissions from ^{228}Th and daughters. Using the efficiency curve of the SIR obtained with the software SIRIC [9], the relative contribution of the β -particles to the ionization current is estimated to only 2.6 parts in 1000 while the relative contribution of the x-rays to current is about 1.5 parts in 100. However, in the case of ^{241}Am for which the main contribution to the IC current is from the 59 keV γ -ray (i.e. a lower energy than the ^{228}Th x-rays), the solution density effect is known to be about 4 parts in 1000 for a density of 1.1 g cm^{-3} . In consequence, the density effect is expected to be negligible (less than 6 parts in 10^5) for ^{228}Th . In addition, the PTB ampoule was measured in the second IC of the SIR, whose geometry slightly differs from the first one, giving a significantly different response for low-energy photon emitters. In the case of ^{228}Th , the results of the measurements made in both IC agree within two standard uncertainties. Finally, the mean of the NIST and PTB results is very close to the SIRIC value of 12 974(25) kBq. All these arguments seem to indicate that the chemical effect is not significant in the present case.

The 1.5 % discrepancy between the NIST and PTB results cannot be related to the potential chemical effects mentioned above because both NMIs submitted solutions with the same chemical composition. Both the PTB and NIST ampoules contained about 3.85 g of solution which is slightly outside the usual range for the SIR (3.4 g – 3.8 g). However, the mass effect on the SIR is also expected to be negligible for such a high-energy γ -ray emitter like ^{228}Th (and daughters).

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 ^{228}Th

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
NIST 1986	3.847 69	324.9	2	12 875	9×10^{-4}	73
PTB 2010	3.859 03	1943.0	3	13 063	5×10^{-4}	42

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; and
- 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 ^{228}Th in March 2015, or by consensus through electronic means (e.g., email) as discussed at the CCRI(II) meeting in 2013.

Consequently, the first KCRV for ^{228}Th has been calculated as 12 971(94) kBq on the basis of the SIR results from the NIST and the PTB.

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

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

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

$$U_i = 2u(D_i). \quad (2)$$

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

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

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

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

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

$$D_{ij} = D_i - D_j = A_{ei} - A_{ej} \quad (5)$$

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

$$u_{D_{ij}}^2 = u_i^2 + u_j^2 - 2u(A_{ei}, A_{ej}) \quad (6)$$

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 $u(A_{ei}, A_{ej})$ (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_{ei} 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 ^{228}Th , BIPM.RI(II)-K1.Th-228 currently comprises one result, from the PTB.

This result has been analysed with respect to the first KCRV determined for this radionuclide, based on the NIST and the PTB results, providing a degree of equivalence for the PTB. 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 ^{228}Th activity measurements to this comparison or take part in other linked comparisons.

Acknowledgements

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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] Bé M.-M., Chisté V., Dulieu C., Browne E., Chechev V., Kuzmenko N., Helmer R., Nichols A., Schönfeld E., Dersch R., 2004, Table of radionuclides, *Monographie BIPM-5*, Vol. 2.
- [4] Michotte C., Efficiency calibration of the Ge(Li) detector of the BIPM for SIR-type ampoules, 1999, *Rapport BIPM-1999/03*, 15 pp.
- [5] *Comité Consultatif pour les Étalons de Mesures des Rayonnements Ionisants 16th meeting (1999)*, 2001, *CCRI(II)* 81-82.
- [6] 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.
- [7] Kossert K. and Nähle, O., Activity determination of ^{228}Th by means of liquid scintillation counting. LSC2010, Advances in Liquid Scintillation Spectrometry: Proceedings of the 2010 International Conference on Liquid Scintillation Spectrometry, Paris, France, 6-10 September 2010, edited by Philippe Cassette, in Radiocarbon, the University of Arizona, Tucson, Arizona, USA, ISBN 978-0-9638314-7-7, 151-160.
- [8] Pommé S, Keightley, J., Determination of a reference value and its uncertainty through a power-moderated mean, *Metrologia*, 52, 2015, S200-S212.
- [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 ^{228}Th and table of degrees of equivalence

Key comparison BIPM.RI(II)-K1.Th-228

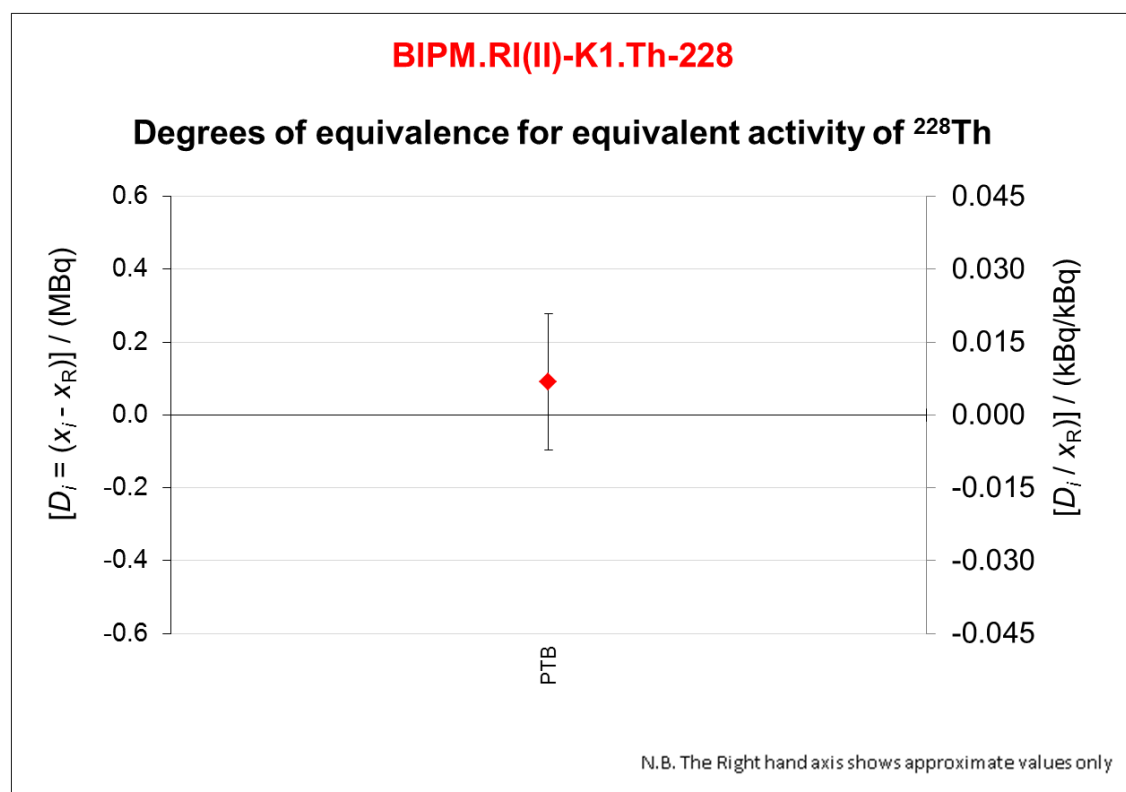
MEASURAND : Equivalent activity of ^{228}Th

Key comparison reference value: the SIR reference value for this radionuclide is $x_R = 12\,971\text{ kBq}$ with a standard uncertainty, $u_R = 94\text{ kBq}$ (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 MBq, 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 .

Lab i	D_i U_i	
	/ MBq	
PTB	0.09	0.19

Figure 1. Graph of degrees of equivalence with the KCRV for ^{228}Th (as it appears in Appendix B of the MRA)

Appendix 1. Uncertainty budgets for the activity of ^{228}Th submitted to the SIR

The PTB is the only NMI to have submitted a detailed uncertainty budget as follows:

TDCR method

Relative standard uncertainties	Comment	$u_i \times 10^4$ evaluated by method	
		A	B
Contributions due to			
counting statistics	No impurity detected	2	–
weighing		–	8
dilution (weighing)		–	8
dead time		–	3
background		5	–
counting time		–	1
adsorption		–	5
radionuclide impurities		–	5
half-life		–	1
TDCR value		–	< 1
input parameters and statistical model	Incl. decay scheme parameters	–	20
ionization quenching and kB (model)		–	2
LS counting efficiency for α particles		–	15
PMT asymmetry		–	1
potential Rn-220 loss		–	10
Quadratic summation		5	30
Relative combined standard uncertainty, u_c		31	

CIEMAT/NIST method

Relative standard uncertainties	Comment	$u_i \times 10^4$ evaluated by method	
Contributions due to		A	B
counting statistics		3	—
weighing		—	8
dilution (weighing)		—	8
dead time		—	10
background		5	—
counting time		—	1
adsorption		—	5
radionuclide impurities	No impurity detected	—	5
half-life		—	1
tracer	Incl. interpolation from calibration curve	—	< 1
input parameters and statistical model	Incl. decay scheme parameters	—	20
ionization quenching and kB (model)		—	2
quenching (indicator)		—	1
LS counting efficiency for α particles		—	15
PMT asymmetry		—	2
potential Rn-220 loss		—	10
Quadratic summation		6	32
Relative combined standard uncertainty, u_c		33	

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 ($x + \gamma$)	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
$4\pi(\text{PC})\beta\text{-}\gamma$ -coincidence counting	4P-PC-BP-NA-GR-CO
$4\pi(\text{PPC})\beta\text{-}\gamma$ -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
$4\pi(\text{PPC})\text{AX-}\gamma(\text{GeHP})$ -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