Update of the BIPM comparison BIPM.RI(II)-K1.Ra-223 of activity measurements of the radionuclide ^{223}Ra to include the 2021 result of the POLATOM (Poland)

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Abstract Since 2014, 4 laboratories have submitted 4 samples of ^{223}Ra 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.Ra-223. Recently, the POLATOM (Poland) participated in the comparison and the key comparison reference value (KCRV) has been updated. 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 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 2021, the SIR has been used to measure 1033 ampoules to give 788 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.Ra-223 key comparison. The results of earlier participations in this key comparison were published previously [3].

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.Ra-223.

NMI or laboratory	**Previous acronyms or other institutes**	**Full name**	**Country**	**RMO**	**Date of SIR measurement** yyyy-mm-dd
LNE-LNHB	LMRI, LPRI, BNM-LNHB	Laboratoire National de métrologie et d´Essais -Laboratoire National Henri Becquerel	France	EURAMET	2018-03-15
NPL	-	National Physical Laboratory	United Kingdom	EURAMET	2014-06-04
POLATOM	IBJ, RC	National Centre for Nuclear Research Radioisotope Centre POLATOM	Poland	EURAMET	2021-09-10
PTB	-	Physikalisch-Technische Bundesanstalt	Germany	EURAMET	2014-07-08

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 by the BIPM is 11.43(3) days as published in BIPM Monographie 5 vol. 6 [4].

Table 2: Standardization methods of the participants for ^{223}Ra.

NMI or laboratory	**Method used and the acronym**	**Activity A_i/kBq**	**Relative standard uncertainty /10^{-2}**		**Reference date**	**Half-life /d**
			A	**B**	**yyyy-mm-dd**	
LNE-LNHB	TDCR (4P-LS-BP-00-00-TD)	1239.1	0.01	0.19	2018-03-15 12:00 UT	
NPL	4πLS-γ coincidence (4P-LS-MX-GH-GR-CO)	1193.2	0.1	0.26	2014-05-08 12:00 UT	
POLATOM	TDCR (4P-LS-MX-00-00-TD)	919.9	0.06	0.364	2021-09-10 12:00 UT	11.43(3) [4]
PTB	CIEMAT/NIST (4P-LS-MX-00-00-CN) TDCR (4P-LS-MX-00-00-TD [5])	4149.0[a]	0.04	0.22[b]	2014-07-01 00:00 UT	11.43(3)

[a] The final result is the weighted mean of the results of the two methods.
[b] The relative combined uncertainty (0.23 %) of the TDCR result is adopted for the final result. This is larger than the internal and external relative uncertainties of the weigthed mean

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 ^{223}Ra 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[c]**
LNE-LNHB 2018	Barium in HCl with NaCl	HCl: 1 NaCl: 0.054	Ba: 22	1.016	None detected
NPL 2014	^{223}Ra in HCl[a]	1	-	1.02	None detected
POLATOM 2021	$RaCl_2$ in HCl, NaCl and sodium citrate[d]	HCl: 0.005 NaCl: 0.11 sodium citrate:0.03	$RaCl_2$	1	None detected[b]

... Continuation of Table 3.

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**[c]
PTB 2014	$^{223}RaCl_2$, NaCl, sodium citrate dihydrate, calcium chloride dihydrate in HCl[e]	unknown but low concentration	unknown but low concentration	approx. 1.000	^{227}Ac: < 0.03 %

[a] ^{223}Ra in equilibrium with progeny

[b] Radioactive solution was measured on gamma spectrometer using HPGe detector. No impurities were detected in the solution.

[c] The ratio of the activity of the impurity to the activity of ^{223}Ra at the reference date

[d] Xofigo®(radium Ra-223 dichloride) injection was used. Chemical composition was taken from drug prescribing information.

[e] Chemical composition for the ampoule submitted to the SIR was taken from manufacturer's information. For absolute activity determination a dilution step was required using a carrier solution with a carrier concentration of 0.5% $BaCl_2 \cdot 2H_2O$ in 1 mol/L HCl(aq.). The dilution step was confirmed by liquid scintillation measurements when the activity was lower after about 2-3 weeks.

4. Results

All the submissions to the SIR since its inception in 1976 are maintained in a dedicated database [6]. The latest submission has added 1 ampoule for the activity measurements for ^{223}Ra giving rise to 4 ampoules in total.

The SIR equivalent activity, A_{ei}, 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.

Table 4: Results of SIR measurement of ^{223}Ra.

NMI or laboratory / SIR year	m_i /**g**	A_i /**kBq**	^{226}**Ra source**	$A_{\mathbf{e}i}$ /**kBq**	**Relative uncert. from SIR /10^{-4}**	$u_{\mathbf{c}i}$ /**kBq**	$A_{\mathbf{e}i}$ **for KCRV /kBq**
LNE-LNHB 2018	3.674 7	1239.1	2	54 400	11	120	54 400(120)
NPL 2014	3.623 95	1193.2	1	54 740	46[a]	300	54 740(300)
POLATOM 2021	3.637 40(30)	919.9	2	55 055	10	210	55 060(210)
PTB 2014	3.629 9	4149.0	2	54 590	16[a]	150	54 590(150)

[a] uncertainty dominated by the contribution from the decay correction

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 [7] 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 [7], 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) 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 may only use 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 an updated KCRV for ^{223}Ra in 2021 of **54 670(140) kBq** with the power α =1.25 that has been calculated using the previously published results, selected as shown in Table 4, for the NPL (2014), PTB (2014), LNE-LNHB (2018), and the present POLATOM (2021) result. This can be compared with the previous KCRV value of 54 530(96) published in 2021 [3].

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

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

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

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

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

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

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

$$D_{ij} = D_i - D_j = A_{ei} - A_{ej} \tag{5}$$

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

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

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 [8] 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 B1 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 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 ^{223}Ra, BIPM.RI(II)-K1.Ra-223, currently comprises 4 results. The KCRV has been recalculated to include the result from the POLATOM (Poland). The results have been analyzed with respect to the updated KCRV, providing degrees of equivalence for 4 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 ^{223}Ra activity measurements to this comparison or take part in other linked comparisons.

6. References

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Appendix A. Introductory text for ^{223}Ra degrees of equivalence

Key comparison BIPM.RI(II)-K1.Ra-223

MEASURAND: Equivalent activity of ^{223}Ra

Key comparison reference value: the SIR reference value x_{R} for this radionuclide is 54 670 kBq , with a standard uncertainty, u_{R} equal to 140 kBq (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.Ra-223

Table B1: The table of degrees of equivalence for BIPM.RI(II)-K1.Ra-223

NMI i	D_i /**MBq**	U_i /**MBq**
NPL	0.07	0.56
PTB	-0.08	0.35
LNE-LNHB	-0.27	0.32
POLATOM	0.39	0.42

Appendix C. Graph of degrees of equivalence with the KCRV for ^{223}Ra (as it appears in Appendix B of the MRA)

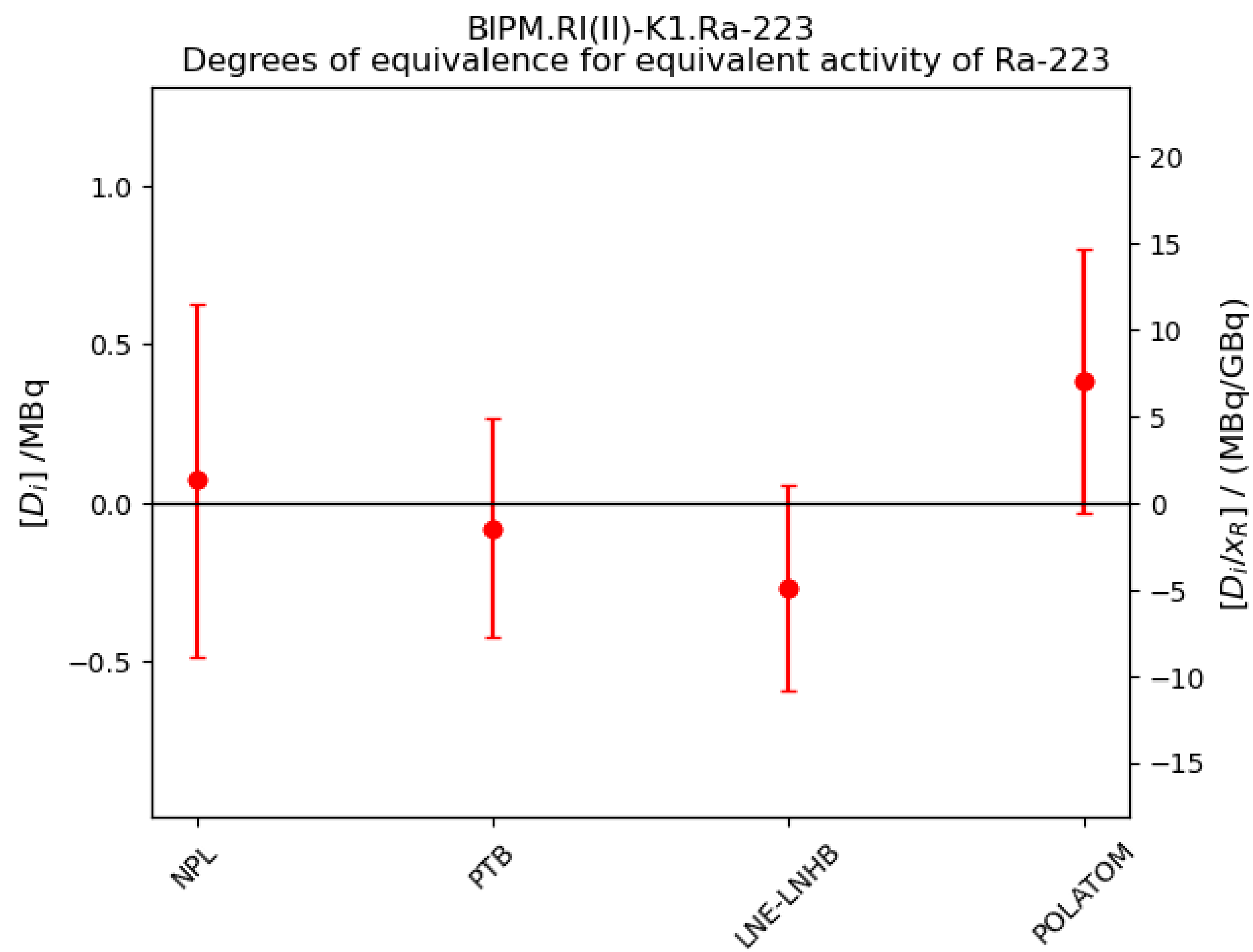

Figure C1. Degrees of equivalence for equivalent activity of ^{223}Ra.

Appendix D. Uncertainty budgets for the activity of ^{223}Ra submitted to the SIR

The POLATOM has submitted a detailed uncertainty budget as follows:

SIR/SIRTI reporting form - radioactive solution page 3a
BIPM.RI(II)-K1

Measurement method	TDCR method	
ACRONYM	4P-LS-MX-00-00-TD	**Comments:**
Activity concentration at reference date / kBq g^{-1}	252.9000	
Relative standard uncertainty / 10^{-2}	0.37	
Date of measurement at the NMI (YYYY-MM-DD)	2021-09-10	The TDCR system

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	0.060	A	Counting statisctics and background in %
Background			
Weighing	0.033	B	in %
Dilution			
Dead time	0.001	B	in %
Resolving time	0.001	B	in %
Pile-up, afterpulse			
Adsorption	0.040	B	in %
Impurities	negligible	B	in %
Decay correction	negligible		
Decay data			
Extra-/Inter-polation of efficiency curve	0.200	B	in %
Quenching, kB value			
Tracer			
Reproducibility			
Method	0.300	B	in %
Combined standard uncertainty	**0.369**		

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	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
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