Update of the BIPM.RI(II)-K1.Rn-222 comparison of activity measurements for the radionuclide ^{222}Rn to include the PTB

G. Ratel, C. Michotte, K. Kossert[§], H. Janßen[§],
BIPM, [§]PTB, Germany

Abstract

In 2005, the Physikalisch-Technische Bundesanstalt (PTB), Germany submitted a sample of known activity of ^{222}Rn to the International Reference System (SIR). The value of the activity submitted was about 1.1 MBq. This key comparison result joins that of Switzerland in the key comparison database that now contains two results, identifier BIPM.RI(II)-K1.Rn-222. Consequently, the KCRV and the degrees of equivalence have been evaluated.

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 form or a different standard ampoule for radioactive gases. 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 2005, the SIR has measured 891 ampoules to give 651 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 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.Rn-222 key comparison.

2. Participants

In addition to the present submission, one other NMI has submitted 2 ampoules for the comparison of ^{222}Rn activity measurements since 2001 [3]. The details of both participants are given in Table 1.

Table 1. Details of the participation in the BIPM.RI(II)-K1.Rn-222 comparison

NMI	**Full name**	**Country**	**Regional metrology organization**	**Date of measurement at the BIPM** **YYYY-MM-DD**
IRA	Institut de Radiophysique Appliquée	Switzerland	EUROMET	2001-03-09 12 h 38 UT 2003-01-27 14 h 44 UT
PTB	Physikalisch-Technische Bundesanstalt	Germany	EUROMET	2005-05-26 9 h 07 UT

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 budgets are given in Appendix 1. The acronyms used for the measurement methods are given in Appendix 2.

Table 2. Standardization method of the participants for ^{222}Rn

NMI	Method used and acronym (Appendix 2)	Half-life / d	Activity / kBq	Reference date YY-MM-DD	Relative standard uncertainty × 100 by method of evaluation	
					A	B
IRA	4π NaI(Tl) γ counting 4P-NA-GR-00-00-00	3.8235 (4)	12.62	01-03-06 08 h 36 UT	0.4	
	Pressurized ionization chamber calibrated in November 2002 by defined solid angle counting and SA-PS-AP-00-00-00	3.8230 (4)	367.1	03-01-22 12 h 00 UT	0.04	0.30
	4π NaI(Tl) γ counting 4P-NA-GR-00-00-00		368.2		0.04	0.48
PTB	NaI(Tl) detector calibrated in October 2004 by defined solid angle counting [4] SA-PS-AP-00-00-00	3.8235 (3)	1067.	05-05-23 0 h 00 UT	0.10	0.91

The half-lives given in Table 2 are the values (with their uncertainty) as used by the participants. The half-life used by the BIPM is 3.8235 (3) days [5]. The date of measurement in the SIR is given in Table 1 and is used in the KCDB and all references in this report.

Details regarding the gas samples submitted are shown in Table 3. In view of the production mode of ^{222}Rn (diffusion from ^{226}Ra), no radioactive impurity is expected in the samples.

Table 3. Details of the solution of ^{222}Rn submitted

NMI	Chemical composition	Amount / mol	Volume of ampoule / cm^3	Gas pressure in the ampoule at 20.5 °C / Pa
IRA	^{222}Rn gas and air	–	–	–
		^{222}Rn : 2.96×10^{-13}	5.16	^{222}Rn : 1.40×10^{-4} air : ~ 15
PTB	^{222}Rn gas and air	^{222}Rn : 8.45×10^{-13}	~ 5	^{222}Rn : 3.8×10^{-4} air : 10

4. Results

All the submissions to the SIR since its inception in 1976 are maintained in a database known as the "mother-file". The activity measurements for ^{222}Rn arises from three ampoules and the SIR equivalent activity for each ampoule, A_{ei}, is given in Table 4 for the NMI, i. The assumption is made that the ^{222}Rn decay chain (^{218}Po / ^{214}Pb / ^{214}Bi / ^{214}Po / ^{210}Pb) is in equilibrium with the parent at the SIR measurement date. 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 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 IRA ampoules submitted in 2001 and 2003 were re-measured in the SIR, for up to 5 days and 2 days respectively after the first measurement and the results agreed within two combined uncertainties in each case. The results of 2001 and 2003 agree within one standard uncertainty.

The SIR measurements of the PTB ampoule were repeated at the BIPM for up to 8 days, producing comparison results in agreement within the standard SIR uncertainty. These measurements confirm the validity of the half-life value used.

Although the IRA submission in 2001 was submitted as a pilot study, the 2003 result is eligible for Appendix B of the MRA.

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

Table 4. Results of SIR measurements of ^{222}Rn

NMI	Activity submitted/ kBq	N° of Ra source used	SIR A_{ei} /kBq	Relative uncertainty from the SIR	Total standard uncertainty u_i / kBq
IRA	12.62	1	10 072#	43×10^{-4}	59
	367.1 368.2	1	10 013* 10 043	17×10^{-4}	35* 52
PTB	1067.	3	9 908	7×10^{-4}	92

value differing from the previously published report, due to a one hour time difference identified in the BIPM measurement
* value to be used for the equivalence (see [3]).

4.1 The key comparison reference value

The key comparison reference value is derived from the unweighted mean of all the results submitted to the SIR with the following provisions:

a) only primary standardized solutions 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 more recent or the mean if more than one ampoule is submitted at the same time);
c) any outliers are identified using a reduced chi-squared test and, if necessary, excluded from the KCRV using the normalized error test with a test value of four;
d) exclusions must be approved by the CCRI(II).

The reduced data set used for the evaluation of the KCRVs is known as the KCRV file and is the reduced data set from the SIR mother-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 only made by the CCRI(II), normally during one of its biennial meetings.

Both the IRA (2003) and PTB values are eligible to be included in a KCRV for ^{222}Rn. Now that there are two candidates for a KCRV and that the IRA (2003) and PTB results agree within the standard uncertainties, the CCRI(II) has recommended the evaluation of the KCRV. Consequently, the KCRV for ^{222}Rn, derived from the unweighted mean of the IRA (2003) and the PTB results, is 9961 (53) kBq.

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 [6].

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

$$D_{ij} = D_i - D_j = A_{e\,i} - A_{e\,j} \tag{3}$$

and the expanded uncertainty of this difference U_{ij}

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

where any obvious correlations between the NMIs (such as a traceable calibration) are subtracted using the covariance $u(A_{\mathrm{e}i}, A_{\mathrm{e}j})$, 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. This 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 BIPM ongoing key comparison for ^{222}Rn, BIPM.RI(II)-K1.Rn-222 currently comprises two results, from the IRA and the PTB. The KCRV and the degrees of equivalence between the participants have been calculated for publication in the BIPM key comparison database.

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References

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Table 5. Table of degrees of equivalence and introductory text for ^{222}Rn

Key comparison BIPM.RI(II)-K1.Rn-222

MEASURAND : Equivalent activity of ^{222}Rn

**Key comparison reference value: the SIR reference value for this radionuclide is x_R = 9.96 MBq,
with a standard uncertainty u_R = 0.05 MBq.
x_R is computed as the mean of the results obtained by primary methods.**

**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, with n the number of laboratories,
$U_i = 2[(1 - 2/n)u_i^2 + (1/n^2)\Sigma u_i^2]^{1/2}$ when each laboratory has contributed to the computation of x_R.**

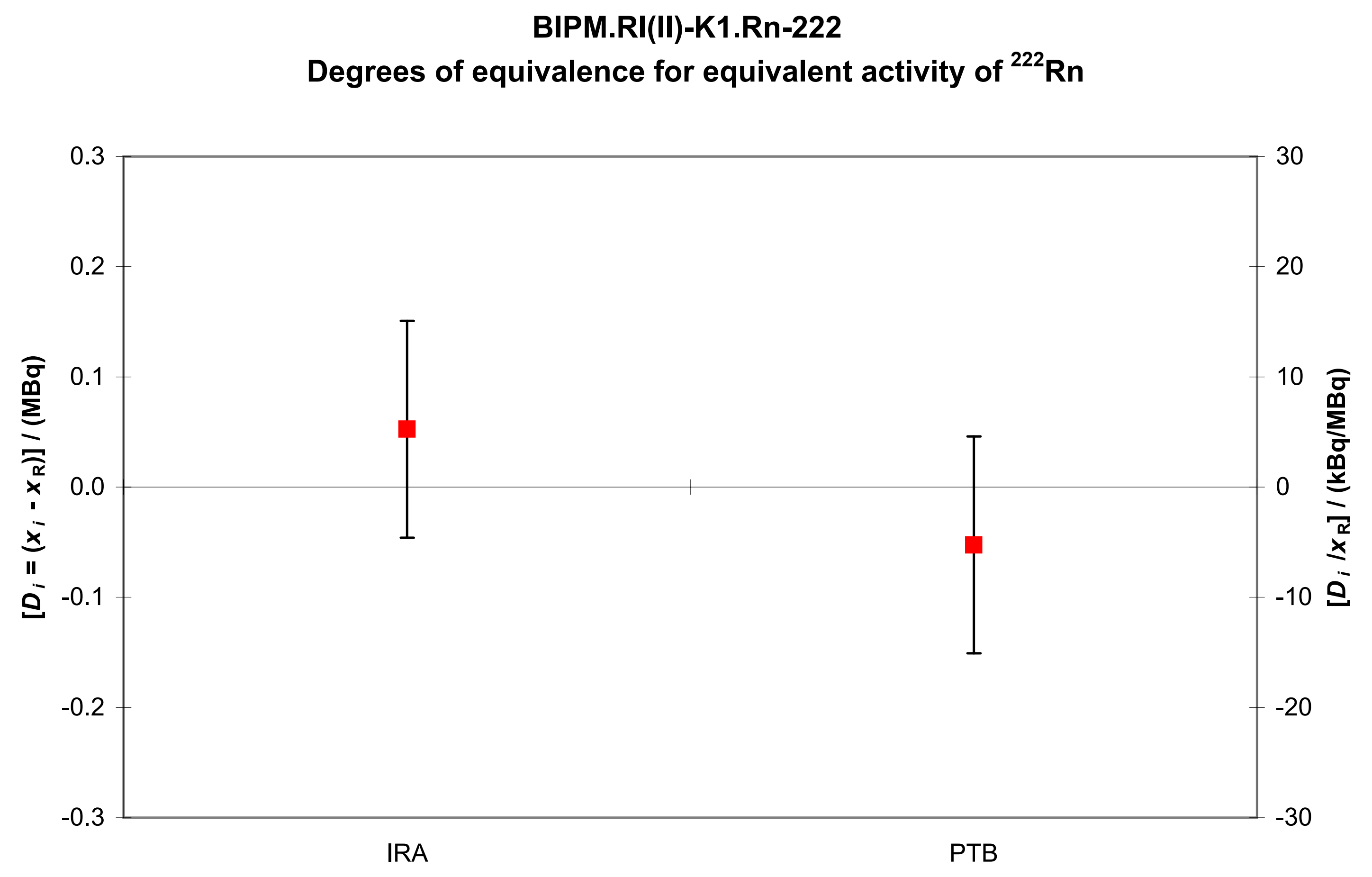
**The degree of equivalence between two laboratories is given by a pair of terms:
$D_{ij} = D_i - D_j = (x_i - x_j)$ and U_{ij}, its expanded uncertainty (k = 2), both expressed in MBq.
The approximation $U_{ij} \sim 2(u_i^2 + u_j^2)^{1/2}$ is used in the following table.**

Lab *j* ⇨

Lab *i* ⇩

			IRA		PTB	
	D_i	U_i	D_{ij}	U_{ij}	D_{ij}	U_{ij}
	/ MBq		/ MBq		/ MBq	
IRA	**0.05**	0.10			**0.11**	0.20
PTB	**-0.05**	0.10	**-0.11**	0.20		

Figure 1 Graph of the degrees of equivalence with the KCRV



N.B. The right-hand axis gives approximate relative values only

Appendix 1. Uncertainty budgets for the activity of ^{222}Rn submitted to the SIR

Uncertainty budget for the IRA measurement (2003)

Relative standard uncertainties	$u_i \times 10^4$ evaluated by method	
Contributions due to	**A**	**B**
current of reference source	1.8	–
current of ^{222}Rn	3.7	–
reference source substitution factor	–	4.5
reference source decay correction	–	2.4
^{222}Rn decay correction	–	0.02
calibration factor of ionization chamber using		
4π NaI γ counting	–	48
or using defined solid angle alpha counting	–	or 30
Quadratic summation	**4.1**	**48.3 or 30.4**
Relative combined standard uncertainty, u_c	**48 or 31**	

Uncertainty budget for the PTB measurement (2005)

Relative standard uncertainties	$u_i \times 10^4$ evaluated by method	
Contributions due to	**A**	**B**
Statistics (^{222}Rn count rate before and after transfer to BIPM-type ampoule)	8	–
^{226}Ra reference source count rate	< 5	–
Calibration factor for ^{222}Rn	–	90
Geometry correction	–	10
Dead time correction	–	10
Background	–	< 5
Half life	–	< 0.5
Quadratic summation	**9.5**	**91.3**
Relative combined standard uncertainty, u_c	**92**	

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