Activity measurements of the radionuclide ^{99}Tc^{m} for the PTB, Germany in the ongoing comparison BIPM.RI(II)-K1.Tc-99m

G. Ratel, C. Michotte, K. Kossert§ and H. Janßen§
BIPM and §PTB

Abstract

In 2005, the Physikalisch-Technische Bundesanstalt (PTB), Germany, submitted an ampoule with about 79 MBq activity of ^{99}Tc^{m} to the International Reference System (SIR) for activity comparison at the Bureau International des Poids et Mesures (BIPM), to update their value in the key comparison database for the BIPM.RI(II)-K1.Tc-99m comparison. A graphical presentation is also given of the results for all six NMI participants.

1. Introduction

The SIR for activity measurements of γ-ray-emitting radionuclides was established in 1976. Each 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].

Since 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) of the Mutual Recognition Arrangement (MRA) [2]. The comparison described in this report is known as the BIPM.RI(II)-K1.Tc-99m key comparison and was first described in [3] with an update in [4].

2. Participants

Details of the PTB submissions over the years are given in Table 1. The details of the other five participants are in [4].

Table 1. Details of the PTB participation in the BIPM.RI(II)-K1.Tc-99m

NMI	Full name	Country	Regional metrology organization	Date of measurement at the BIPM
PTB	Physikalisch-Technische Bundesanstalt	Germany	EUROMET	1983-10-25 10 h 54 UT 1985-07-04 09 h 40 UT 2005-11-16 09 h 24 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 method for the laboratory, the activity submitted and the relative standard uncertainties (k = 1) are given in Table 2. The uncertainty budget of the PTB is given in Appendix 1 and for the earlier submissions in [3] and [4]. The list of acronyms used to summarize the methods is given in Appendix 2.

The half-life used by the BIPM is 6.0067 (10) hours [5]. The half-life given in Table 2 is the value (with its uncertainty) as used by the participant.

Details regarding the solution submitted are shown in Table 3, including any impurities, when present, as identified by the laboratory. When given, the standard uncertainties on the evaluations are shown. The BIPM has a standard method for evaluating the activity of impurities in SIR ampoules 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 impurities were detected in this latest submission.

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 ^{99}Tc^{m} arise from ten ampoules including the ampoule submitted for this comparison. The SIR equivalent activity for each PTB ampoule, A_{ei}, 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.

Table 2. Standardization methods of the PTB for $^{99}Tc^m$

NMI	Method used and acronym (see Appendix 2)	Half-life / d	Activity A_i / kBq	Reference date YY-MM-DD	Relative standard uncertainty × 100 by method of evaluation A	B
PTB	4πPC-γ , 4πPPC- γ 4P-PC-BP-NA-GR-CO 4P-PP-BP-NA-GR-CO 4π(NaI)γ 4P-NA-GR-00-00-00	–	5 200	83-10-25 11 h UTC	0.07	0.50
	Pressurized ionization chamber calibrated as above in 1983 4P-IC-GR-00-00-00	–	30 430	85-07-03 23 h UTC	0.05	0.48
	Pressurized ionization chamber calibrated in Nov. 2005 by 4πPCce-x coinc. and 4πPPCce-photon coinc. 4P-PC-CE-NA-XR-CO 4P-PP-CE-NA-MX-CO	0.25028 (4)	79 440	05-11-16 11 h UTC	0.07	0.41

Table 3. Details of the PTB solutions of $^{99}Tc^m$ submitted

NMI	Chemical composition	Solvent conc. / (mol dm^{-3})	Carrier: conc. /(µg g^{-1})	Density /(g cm^{-3})	Relative activity of impurity†
PTB	NaCl in HCl	0.5	NaCl: 90	1.008	–
					^{99}Mo : 4 (1) × 10^{-3} % ^{103}Ru : 2.0 (5) × 10^{-4} %
	NaCl in water	–	NaCl: 9000	1.0046	–

† the ratio of the activity of the impurity to the activity of $^{99}Tc^m$ at the reference date.

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 as shown in Table 4, all the SIR results are normalized to the radium source number 5 [1].

The SIR measurements were repeated at the BIPM for up to 2 days later, producing comparison results in agreement within the combined SIR uncertainty. These measurements confirm the validity of the half-life value used and the absence of impurity in the solution.

Table 4. The PTB results of SIR measurements of $^{99}Tc^m$

NMI	Mass of solution m_i / g	Activity submitted A_i / kBq	N° of Ra source used	SIR A_e / kBq	Relative uncertainty from SIR	Combined uncertainty $u_{c,i}$ / kBq
PTB	3.682 6	5 200	2	153 240	12×10^{-4}	790
	3.619 24	30 430	3	153 430	9×10^{-4}	750
	3.6382 (9)	79 440	5	152 710	8×10^{-4}	640

The three PTB results which cover a period of more than 20 years are consistent within the uncertainties.

The recent submission has not been identified as a pilot study, so it is 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.

4.1 The key comparison reference value

In the previous update report [4], the KCRV for $^{99}Tc^m$ has been identified as 153 140 (330) kBq using the results from the PTB (1983), IRA (1984), LNE-LNHB (1998) and the NPL.

Normally, modifications to the KCRV are only made by the CCRI(II) 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

$$D_i = A_{ei} - \mathrm{KCRV} \qquad (1)$$

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

$$U_i = 2u_{D_i}, \qquad (2)$$

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

$$D_{ij} = D_i - D_j = A_{ei} - A_{ej} \qquad (3)$$

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

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

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. This 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 $^{99}Tc^{m}$, BIPM.RI(II)-K1.Tc-99m currently comprises six results, the latest from the PTB being in agreement with their previous results and with the KCRV within one standard uncertainty. All six NMI results have been analysed with respect to the KCRV 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 other NMIs contribute $^{99}Tc^{m}$ activity measurements to this comparison.

Acknowledgements

The authors would like to thank Drs R. Klein, O. Ott and H. Schrader for the measurements at PTB, Mr Sammy Courte of the BIPM for his measurements in the SIR and Dr P.J. Allisy-Roberts of the BIPM for editorial assistance.

References

[1] Ratel G. The international reference system for activity measurements of γ-emitting radionuclides (SIR), 2006, *BIPM Monograph XX*, (in preparation).

[2] 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/pdf/mra.pdf.

[3] Ratel G., Michotte C., 2004, BIPM comparison BIPM.RI(II)-K1.Tc-99m of activity measurements of the radionuclide $^{99}Tc^{m}$, *Metrologia*, 41, *Tech. Suppl.*, 06005

[4] Ratel G., Michotte C., Johansson L., 2005, Update of the BIPM.RI(II)-K1.Tc-99m comparison of activity measurements for the radionuclide $^{99}Tc^{m}$ to include the NPL, *Metrologia* **42,** 06015.

[5] 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, volume 1.

[6] Michotte C., 1999, Efficiency calibration of the Ge(Li) detector of the BIPM for SIR-type ampoules, *Rapport BIPM*-1999/03, 15 pp.

[7] *Comité Consultatif pour les Étalons de Mesures des Rayonnements Ionisants* 16th meeting (1999), 2001, CCRI(II) 81-82.

[8] Michotte C., 2001, Protocol on the use of the calibrated spectrometer of the BIPM for the measurement of impurities in ampoules submitted to the SIR, *CCRI(II)/01-01*, 2pp.

[9] Ratel G., 2005, Evaluation of the uncertainty of the degree of equivalence, *Metrologia* **42**, 140-144.

Table 5. Table of degrees of equivalence and introductory text for $^{99}Tc^m$

Key comparison BIPM.RI(II)-K1.Tc-99m

MEASURAND : **Equivalent activity of $^{99}Tc^m$**

Key comparison reference value: the SIR reference value for this radionuclide is x_R = 153.1 MBq, with a standard uncertainty u_R = 0.3 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 reference value (see Final Report).

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.

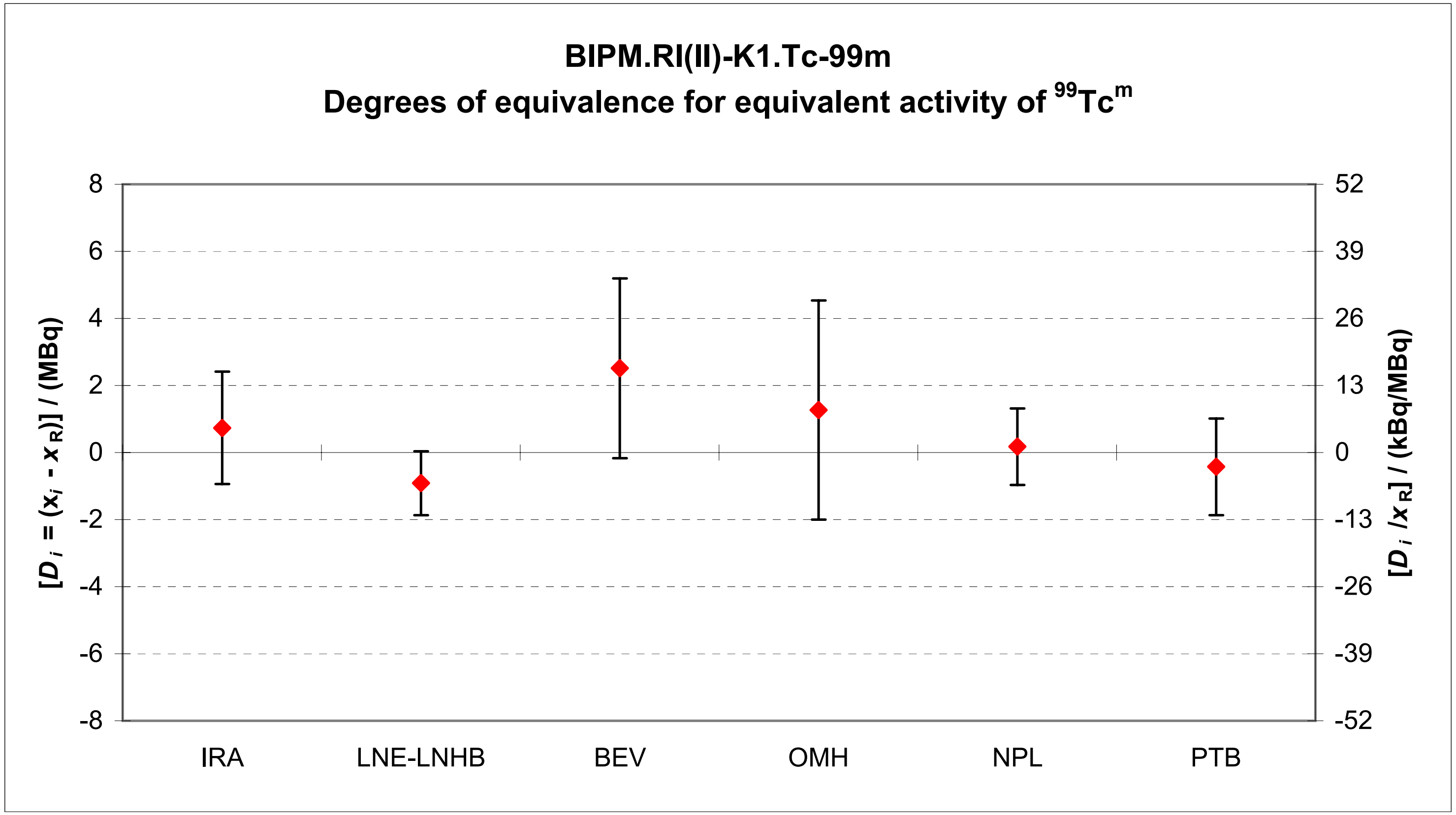
Lab j ⇒

Lab i ⇓

Lab i	D_i / MBq	U_i / MBq	IRA D_{ij} / MBq	IRA U_{ij} / MBq	LNE-LNHB D_{ij} / MBq	LNE-LNHB U_{ij} / MBq	BEV D_{ij} / MBq	BEV U_{ij} / MBq	OMH D_{ij} / MBq	OMH U_{ij} / MBq	NPL D_{ij} / MBq	NPL U_{ij} / MBq	PTB D_{ij} / MBq	PTB U_{ij} / MBq
IRA	**0.7**	1.7			**1.7**	1.8	**-1.8**	3.0	**-0.5**	3.6	**0.6**	2.0	**1.2**	2.0
LNE-LNHB	**-0.9**	1.0	**-1.7**	1.8			**-3.4**	2.8	**-2.2**	3.3	**-1.1**	1.6	**-0.5**	1.6
BEV	**2.5**	2.7	**1.8**	3.0	**3.4**	2.8			**1.3**	4.1	**2.3**	2.3	**2.9**	2.9
OMH	**1.3**	3.3	**0.5**	3.6	**2.2**	3.3	**-1.3**	4.1			**1.1**	3.5	**1.7**	3.4
NPL	**0.2**	1.1	**-0.6**	2.0	**1.1**	1.6	**-2.3**	2.3	**-1.1**	3.5			**0.6**	1.8
PTB	**-0.4**	1.4	**-1.2**	2.0	**0.5**	1.6	**-2.9**	2.9	**-1.7**	3.4	**-0.6**	1.8		

Figure Graph of degrees of equivalence with the KCRV for $^{99}Tc^{m}$

(as it appears in Appendix B of the MRA)



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

Appendix 1. Uncertainty budget for the activity of $^{99}Tc^{m}$ submitted by the PTB

Relative standard uncertainties	$u_i \times 10^4$ evaluated by method	
Contributions due to	**A**	**B**
statistics (current measurement of BIPM-type ampoule)	6	–
linearity of current measurement	–	5
Ra reference source current	2.5	–
background	–	< 1
calibration factor for $^{99}Tc^{m}$	–	40
geometry correction	–	5
half-life	–	3
weighing	–	2.5
adsorption	–	< 0.1
radionuclide impurities	–	< 0.1
Quadratic summation	**6.5**	**40.8**
Relative combined standard uncertainty, u_c	**41**	

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