BIPM comparison BIPM.RI(II)-K1.Mn-54 of activity measurements of the radionuclide ^{54}Mn

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Abstract

Since 1976, twelve national metrology institutes (NMI), the BIPM, an international laboratory and one other laboratory have submitted thirty-five samples of known activity of ^{54}Mn to the International Reference System (SIR) for activity comparison at the Bureau International des Poids et Mesures. The activities ranged from about 300 kBq to 41 MBq. The degrees of equivalence between each equivalent activity measured in the SIR and the key comparison reference value (KCRV) have been calculated and the results are given in the form of a matrix for twelve laboratories. A graphical presentation is also given. The results of this comparison have been approved by Section II of the Consultative Committee for Ionizing Radiation (CCRI(II)), comparison identifier BIPM.RI(II)-K1.Mn-54.

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 (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 are all given in [1].

Since its inception and until 31 December 2002, the SIR has measured 835 ampoules to give 606 independent results for 62 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.Mn-54 key comparison.

2. Participants

Twelve NMIs, the BIPM, an international laboratory and one other laboratory have submitted thirty-five ampoules for the comparison of ^{54}Mn activity measurements since 1976. The laboratory details are given in Table 1. In cases where the laboratory has changed its name since the original submission, both the earlier and the current acronyms are given, as it is the latter that are used in the KCDB. The AECL was an invited participant in various SIR comparisons, as in the early years, J.G.V. Taylor of the AECL was a personal member of the predecessor to the CCRI(II).

Table 1. Details of the participants in the BIPM.RI(II)-K1.Mn-54

Original acronym	NMI	Full name	Country	Regional metrology organization	Date of measurement at the BIPM
BIPM	–	Bureau International des Poids et Mesures	–	–	1976-07-23 1976-12-01
ASMW*	PTB	Physikalisch-Technische Bundesanstalt	Germany	EUROMET	1976-09-01 1977-06-14 1979-03-02
ETL	NMIJ	National Metrology Institute of Japan	Japan	APMP	1976-11-22 1993-11-25
–	NPL	National Physical Laboratory	United Kingdom	EUROMET	1976-12-29
UVVVR	CMI-IIR	Český Metrologický Institut/Czech Metrological Institute, Inspectorate for Ionizing Radiation	Czech Republic	EUROMET	1977-02-24 1978-08-31 1979-09-07
–	OMH	Országos Mérésügyi Hivatal	Hungary	EUROMET	1977-03-10 1982-11-02 1998-10-28
AAEC	ANSTO	Australian Nuclear Science and Technology Organisation	Australia	APMP	1977-03-15
IAEA	–	International Atomic Energy Agency	–	–	1979-02-13

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Table 1 continued. Details of the participants in the BIPM.RI(II)-K1.Mn-54

Original acronym	NMI	Full name	Country	Regional metrology organization	Date of measurement at the BIPM
NBS	NIST	National Institute of Standards and Technology	United States	SIM	1979-07-06 2002-06-19
AECL	–	Atomic Energy of Canada Ltd	Canada	–	1980-11-27 1983-07-07
LMRI LPRI	BNM-LNHB	Bureau national de métrologie-Laboratoire national Henri Becquerel	France	EUROMET	1983-06-03 1992-12-18 1999-10-19
IER	IRA	Institut de Radiophysique Appliquée	Switzerland	EUROMET	1989-04-28
–	LNMRI	Laboratorio Nacional de Metrologia das Radiaçoes Ionizantes	Brazil	SIM	2000-11-07
–	BEV	Bundesamt für Eich- und Vermessungswesen	Austria	EUROMET	2001-09-27
–	BARC	Bhabha Atomic Research Centre	India	APMP	2002-05-16

* another laboratory in the country

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 each laboratory, the activities submitted and the relative standard uncertainties ($k = 1$) are given in Table 2. The list of acronyms used to summarize the methods is given in Appendix 3. 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. Consequently, the BNM-LNHB, LNMRI, BEV, BARC and the NIST have provided uncertainty budgets.

Table 2. Standardization methods of the participants for ^{54}Mn

NMI	Method used and acronym (see Appendix 3)	Half-life / d	Activity A_i / kBq	Reference date YY-MM-DD	Relative standard uncertainty × 100 by method of evaluation	
					A	B
BIPM	4π(PC)-γ coinc. 4P-PC-MX-NA-GR-CO	312.2 (3)	3 517.9	75-06-04 0 h UT	0.01	0.14
			3 244.1	77-01-01 0 h UT	0.11	0.21
PTB	4π(e_A,x)-γ coinc. 4P-PC-MX-NA-GR-CO	–	1 718.3 1 715.9 †	76-06-09 12 h UT	0.06	0.10
	4π(PC)-γ coinc. 4P-PC-MX-NA-GR-CO and 4π(PPC)-γ coincidence 4P-PP-MX-NA-GR-CO	–	4 431.9 4 431.4 †	77-05-01 0 h UT	0.03	0.11
	Pressurized IC 4P-IC-GR-00-00-00 calibrated in 1977 by the primary methods above	–	6 689	79-03-01 0 h UT	0.01	0.20
NMIJ	4πx-γ coincidence 4P-PC-XR-NA-GR-CO	–	2 569.3 2 561.0 †	76-11-01 12 h UT	0.03	0.35
	4π(e,x)–γ coinc. 4P-PC-MX-NA-GR-CO	–	1 057	93-11-01 0 h UT	0.4	0.5
NPL	Pressurized IC * 4P-IC-GR-00-00-00	–	691.3 668.4 †	76-12-20 0 h UT	0.03	0.96
CMI-IIR	4πx-γ coincidence 4P-PP-XR-NA-GR-CO	312.2	40 370	77-01-18 11 h UT	0.07	0.35 **
			3 601	78-07-26 11 h UT	0.10	0.37
			3 112	79-07-17 10 h UT	0.10	0.37
OMH	4π(e,x)–γ coinc. 4P-PP-MX-NA-GR-CO	312.3 (3) [3]	2 013.7 2 014.7 †	77-03-01 12 h UT	0.15	0.32
			3 782	82-11-01 12 h UT	0.02	0.27
	4π(PPC)-γ coinc. 4P-PP-MX-NA-GR-CO	[4]	3 314	98-10-27 0 h UT	0.03	0.33

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Table 2 continued. Standardization methods of the participants for ^{54}Mn

NMI	Method used and acronym (see Appendix 3)	Half-life / d	Activity A_i / kBq	Reference date YY-MM-DD	Relative standard uncertainty × 100 by method of evaluation	
					A	B
ANSTO	4π(e,x)–γ coinc. 4P-PC-MX-NA-GR-CO	–	1 387.7	77-03-01 0 h UT	0.08	0.41
IAEA/ CMI-IIR	4π(e,x)–γ coinc. 4P-PC-MX-NA-GR-CO	312.2	3 515	78-07-26 11 h UT	0.10	0.37
NIST	4π(e,x)–γ coinc. 4P-PP-MX-NA-GR-CO and 4π(e,x)–γ anti-coincidence 4P-PP-MX-NA-GR-AC	312.07 (5)	2 218.4	79-04-30 17 h UT	0.06	0.28
	Pressurized IC 4P-IC-GR-00-00-00 calibrated in 1979 by the primary methods above.	312.12 (6)	1 474.0	02-06-01 17 h UT	0.06	0.25
AECL	4π(PC)-γ coinc. 4P-PC-MX-NA-GR-CO	312.21 (10)	16 579 17 336 †	80-08-15 17 h UT	0.03	0.35
			2 262.9 2 254.6 †	83-06-01 5 h UT	0.05	0.33
BNM-LNHB	4π(PPC)-γ coinc. 4P-PP-XR-NA-GR-CO	–	2 881 2 923 †	83-05-27 12 h UT	0.10	0.09
	4π(PPC)x-γ coinc. 4P-PP-XR-NA-GR-CO	–	448.00	92-11-19 12 h UT	0.15	0.06
	4π(e,x)–γ coinc. 4P-PP-MX-NA-GR-CO	312.16 (5)	2 119	99-06-14 12 h UT	0.10	0.24
IRA	4πPC(e,x)–γ coinc. 4P-PC-MX-NA-GR-CO and 4πγ(NaI(Tl)) 4P-NA-GR-00-00-00	–	2 037	89-04-01 0 h UT	0.01	0.12
LNMRI	Pressurized IC 4P-IC-GR-00-00-00 calib. by 4πβ-γ coinc. in 2000 4P-PP-MX-NA-GR-CO	312.2 (2)	318.1	00-09-15 12 h UT	0.4	0.6

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Table 2 continued. Standardization methods of the participants for ^{54}Mn

NMI	Method used and acronym (see Appendix 3)	Half-life / d	Activity A_i / kBq	Reference date YY-MM-DD	Relative standard uncertainty × 100 by method of evaluation	
					A	B
BEV	Pressurized IC traceable to NPL 4P-IC-GR-00-00-00	312.15	532.9	01-09-01 0 h UT	0.07	0.68
BARC	4π(e,x)–γ coinc. 4P-PC-MX-NA-GR-CO	312.2	1 089	02-02-06 6 h 30 UT	0.68	0.13

† two ampoules submitted
* calibrated by a primary measurement of the same radionuclide
** maximum likely error (99 % level) of 1.3×10^{-2}

The half-life used by the BIPM is 312.2 (3) days and this is in good agreement with the value of 312.3 (4) days recommended by the IAEA [4] that will be used in the future.

Details regarding the solution 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. Recently the BIPM has developed a standard method for evaluating the activity of impurities using a calibrated Ge(Li) spectrometer [5]. The CCRI(II) agreed in 1999 [6] that this method should be followed according to the protocol described in [7] when an NMI makes such a request or when there appear to be discrepancies.

Table 3. Details of the solution of ^{54}Mn submitted

NMI	Chemical composition	Solvent conc. / (mol dm^{-3})	Carrier: conc. /(μg g^{-1})	Density /(g cm^{-3})	Relative activity of impurity†
BIPM	$MnCl_2$ in HCl	0.1	$MnCl_2$: 5	0.999	< 0.1 %
	Mn in HCl	0.1	–	–	–
PTB	$MnCl_2$ in HCl	0.1	$MnCl_2$: 20	–	–
			$MnCl_2$: 15	–	^{65}Zn : 0.05 (1) % ^{55}Fe : < 0.08 %
			$MnCl_2$: 20	1.00	^{51}Cr : 1.2 (1) % ^{65}Zn : 0.02 (1) % ^{55}Fe : < 0.1 %
NMIJ	$MnCl_2$ in HCl	0.1	$MnCl_2$: 50	–	–
				1.00	^{55}Fe : 0.3 (1) %

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Table 3. Details of the solution of ^{54}Mn submitted

NMI	Chemical composition	Solvent conc. / (mol dm^{-3})	Carrier: conc. /(μg g^{-1})	Density /(g cm^{-3})	Relative activity of impurity†
NPL	$MnCl_2$ in HCl	0.1	$MnCl_2$: 100	–	^{65}Zn : 0.06 %
CMI-IIR	$MnCl_2$ in HCl	0.01	$MnCl_2$: 20	–	<0.1 %
	$MnSO_4$ in HCl	0.08	$MnSO_4$: 50	–	^{51}Cr : 0.2 (2) %
				–	< 0.01 %
OMH	Mn in HCl	0.1	Mn : 25	–	–
	$MnCl_2$ in HCl	0.1	$MnCl_2$: 25	–	^{60}Co : 0.07 (2) % ^{65}Zn : 0.08 (2) %
					^{60}Co : 0.009 (1) %
ANSTO	$MnCl_2$ in HCl	0.1	–	–	< 0.2 %
IAEA/ CMI-IIR	$MnSO_4$ in HCl	0.08	$MnSO_4$: 50	–	^{51}Cr : 0.2 (2) %
NIST	$MnCl_2$ in HCl	1	$MnCl_2$: 64	1.016 (2)	–
		0.4	$MnCl_2$: 80	1.006 (1)	–
AECL	$MnCl_2$ in HCl	0.3	Mn^{++} : 10	1.0	< 0.2 %
		0.1	$MnCl_2$: 8	1.00	< 0.2 %
BNM-LNHB	$MnCl_2$ in HCl	0.1	$MnCl_2$: 10	0.999	^{46}Sc : 0.032 (3) %
			$MnCl_2$: 5	1.00	^{57}Co : 0.0023 (5) %
	Mn^{++} in HCl	0.1	Mn^{++}: 10	1.001	^{154}Eu : 0.008 (1) %
IRA	$MnCl_2$ in HCl	0.1	$MnCl_2$: 10	1.000	^{51}Cr < 0.008 % ^{59}Fe < 0.002 %
LNMRI	$MnCl_2$ in HCl	0.1	$MnCl_2$: 30	0.9996	–
BEV	$MnCl_2$ in HCl	0.1	$MnCl_2$: 30	1.0	^{65}Zn : 9 (1) × 10^{-5} % ^{134}Cs : 0.0011 (1) %
BARC	Mn in HCl	0.1	–	1.0	–

† the ratio of the activity of the impurity to the activity of ^{54}Mn 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 "mother-file". The activity measurements for ^{54}Mn arise from thirty-five ampoules and the SIR equivalent activity for each ampoule, A_{ei}, is given in Table 4 for each NMI, *i*. The dates of measurement in the SIR are given in Table 1.

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 correction for impurities is generally very small with a maximum of 1.0024 for OMH (1982). The measurement of the BNM-LNHB ampoule submitted in 1983 was repeated at the BIPM after a period of four months and produced a comparison result in agreement within the combined SIR uncertainty. This measurement confirms the validity of the evaluation of the ^{46}Sc impurity correction.

Three earlier results were withdrawn and are not included here. Normally, the most recent result of each NMIs is eligible for Appendix B of the MRA. However, the LNMRI (2000) submission was identified as a pilot study, the IAEA no longer undertakes the metrology of activity and the AECL is not a designated laboratory of the NRC, Canada, therefore none of these results is included in the KCDB.

No international or regional comparison for this radionuclide has been held to date, although a CCRI(II) comparison is being planned so at the moment no linking data are identified.

Table 4. Results of SIR measurements of ^{54}Mn

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
BIPM	3.741 67	3517.9	3	19 231	10×10^{-4}	33
	3.741 78 *	3244.1	3	19 258	7×10^{-4}	46
PTB	3.602 4 (5) 3.597 3 (5)	1718.3 1715.9	3	19 263 19 248†	8×10^{-4} 7×10^{-4}	28 28
	3.660 9 (1) 3.660 5 (1)	4431.9 4431.4	4	19 217 19 217	5×10^{-4}	23
	3.625 6	6689	4	19 209 ††	5×10^{-4}	39
NMIJ	3.644 94 3.633 16	2569.3 2561.0	3	19 271 19 275	5×10^{-4}	69 69
	3.610 50	1057	3	19 230	7×10^{-4}	130

continued overleaf

Table 4 continued. Results of SIR measurements of ^{54}Mn

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
NPL	3.690 8	691.3	2	19 179	9×10^{-4}	190
	3.568 7	668.4		19 153†	8×10^{-4}	190
CMI-IIR	1.129 84**	40 370	5	19 048	4×10^{-4}	68
	3.603 03	3601	3	19 331	6×10^{-4}	74
	3.470 22	3112	3	19 222	6×10^{-4}	72
OMH	3.601 6	2013.7	3	19 232	5×10^{-4}	69
	3.603 4	2014.7		19 244	6×10^{-4}	69
	3.602 2	3782	4	19 145	7×10^{-4}	54
	3.612 6	3314	3	19 212	5×10^{-4}	64
ANSTO	3.596 5	1387.7	3	19 221	4×10^{-4}	81
IAEA	3.576 85	3515	3	19 334	7×10^{-4}	75
NIST	3.661 90	2218.4	3	19 219	6×10^{-4}	56
	3.629 8 (2)	1474.0	3	19 268	6×10^{-4}	51
AECL	0.973 89‡	1657.9	3	19 260	6×10^{-4}	68
	1.018 36‡	1733.6		19 270		68
	0.145 047‡	2262.9	3	19 268	6×10^{-4}	64
	0.144 518‡	2254.6		19 260†	5×10^{-4}	64
BNM-LNHB	3.562 4	2881	4	19 173	5×10^{-4}	27
	3.615 3	2923		19 175		28
	3.609 7	448.0	2	19 125	7×10^{-4}	34
	3.574 29	2119	3	19 308	7×10^{-4}	51
IRA	3.594 5	2037	3	19 229	6×10^{-4}	25
LNMRI	3.467 14	318.1	1	***	15×10^{-4}	***
BEV	3.596 0	532.9	2	19 060	10×10^{-4}	130
BARC	3.637 6	1089	3	19 470	8×10^{-4}	140

* mass before dilution : 0.627 74 g
** mass after transfer at the BIPM to an NBS-type ampoule
*** pilot study
† the mean of the two A_e values shown for the same measurement date is used with an averaged uncertainty, as attributed to an individual entry [8]
†† change in the registered SIR result because of a correction of the SIR time difference
‡ mass before dilution.

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, or ionization chamber measurements that are directly traceable to a primary measurement in the laboratory;
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) 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.

Consequently, the KCRV for ^{54}Mn has been identified as 19 252 (20) kBq using the results from the ASMW, BIPM (1976), NPL, ANSTO, PTB (1977), NIST (1979), CMI-IIR (1979), AECL (1983), IRA, NMIJ (1993), OMH (1998), BNM-LNHB (1999) and the BARC.

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

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

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 (see Appendix 2).

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} where

$$u_{D\,ij}{}^2 = u_i{}^2 + u_j{}^2 - \sum_k \left(f_k u_{\mathrm{corr},k}\right)_i^2 - \sum_k \left(f_k u_{\mathrm{corr},k}\right)_j^2 \tag{4}$$

and any obvious correlations in the standard uncertainties for a given component, $u_{\mathrm{corr},k,}$, between the NMIs (such as a traceable calibration) are subtracted using an appropriate correlation coefficient, f_k, 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 ^{54}Mn, BIPM.RI(II)-K1.Mn-54 currently comprises twelve results. These have been analysed with respect to the KCRV determined 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 ^{54}Mn activity measurements to this comparison either through the SIR, or by participating in a CCRI(II) comparison.

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Table 5. Table of degrees of equivalence and introductory text for ^{54}Mn

Key comparison BIPM.RI(II)-K1.Mn-54

MEASURAND : Equivalent activity of ^{54}Mn

Key comparison reference value: the SIR reference value x_R for this radionuclide is 19.25 MBq, with a standard uncertainty, u_R = 0.02 MBq (see Section 4.1 of the Final Report). the value x_i is taken as 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 $U_i = 2((1 - 2/n)u_i^2 + (1/n^2)\Sigma u_i^2)^{1/2}$ when each laboratory has contributed to the calculation of x_R, with n the number of laboratories.

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

Lab *j* ⟹

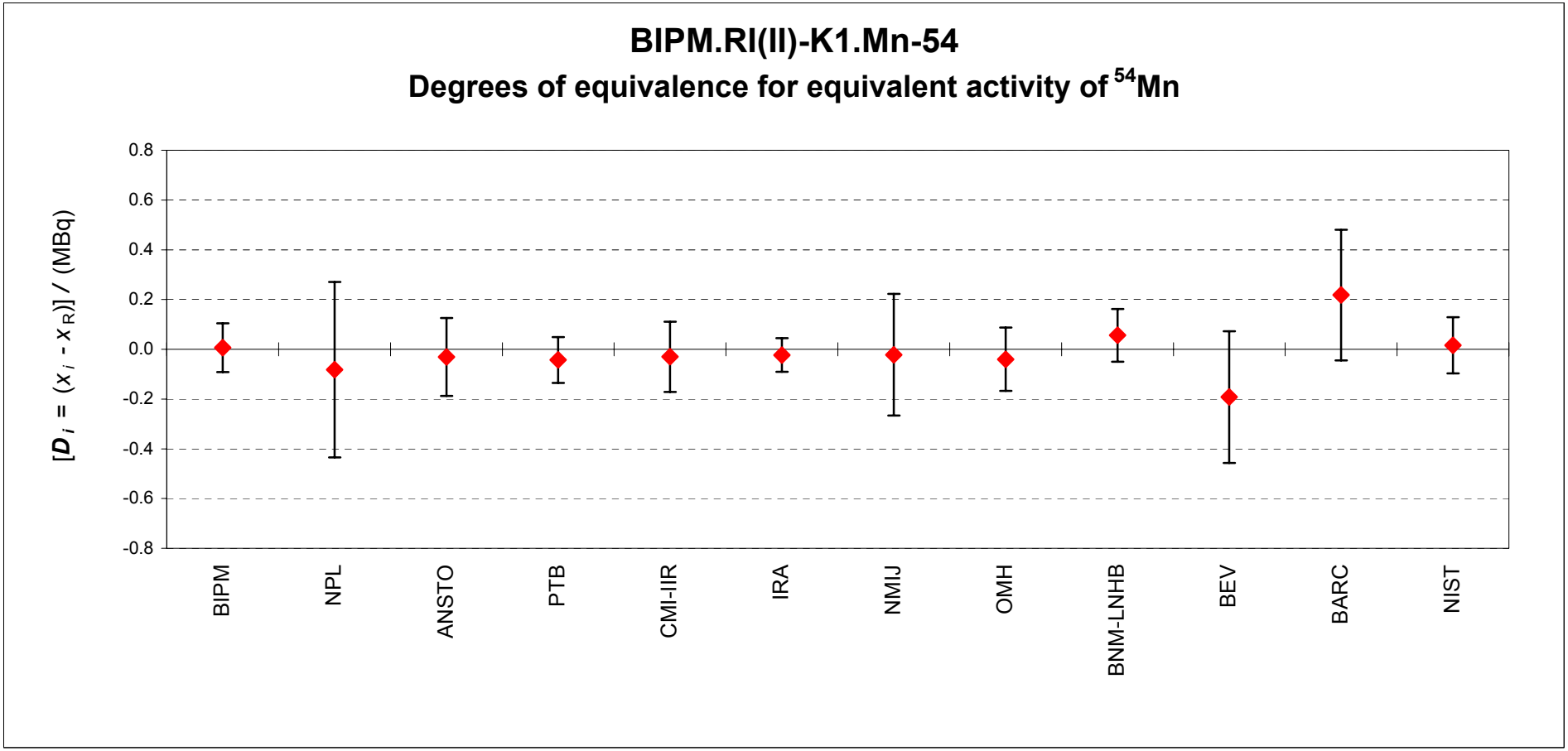
Lab *i* ⇩

Lab *i*	D_i / MBq	U_i / MBq	BIPM D_{ij} / MBq	BIPM U_{ij} / MBq	NPL D_{ij} / MBq	NPL U_{ij} / MBq	ANSTO D_{ij} / MBq	ANSTO U_{ij} / MBq	PTB D_{ij} / MBq	PTB U_{ij} / MBq	CMI-IIR D_{ij} / MBq	CMI-IIR U_{ij} / MBq	IRA D_{ij} / MBq	IRA U_{ij} / MBq
BIPM	**0.01**	0.10			**0.09**	0.39	**0.04**	0.19	**0.05**	0.12	**0.04**	0.17	**0.03**	0.10
NPL	**-0.08**	0.35	**-0.09**	0.39			**-0.05**	0.41	**-0.04**	0.39	**-0.05**	0.41	**-0.06**	0.38
ANSTO	**-0.03**	0.16	**-0.04**	0.19	**0.05**	0.41			**0.01**	0.18	**0.00**	0.22	**-0.01**	0.17
PTB	**-0.04**	0.09	**-0.05**	0.12	**0.04**	0.39	**-0.01**	0.18			**-0.01**	0.16	**-0.02**	0.09
CMI-IIR	**-0.03**	0.14	**-0.04**	0.17	**0.05**	0.41	**0.00**	0.22	**0.01**	0.16			**-0.01**	0.15
IRA	**-0.02**	0.07	**-0.03**	0.10	**0.06**	0.38	**0.01**	0.17	**0.02**	0.09	**0.01**	0.15		
NMIJ	**-0.02**	0.24	**-0.03**	0.28	**0.06**	0.46	**0.01**	0.31	**0.02**	0.27	**0.01**	0.30	**0.00**	0.26
OMH	**-0.04**	0.13	**-0.05**	0.16	**0.04**	0.40	**-0.01**	0.21	**0.00**	0.15	**-0.01**	0.19	**-0.02**	0.14
BNM-LNHB	**0.06**	0.11	**0.05**	0.14	**0.14**	0.39	**0.09**	0.19	**0.10**	0.13	**0.09**	0.18	**0.08**	0.11
BEV	**-0.19**	0.26	**-0.20**	0.28	**-0.11**	0.28	**-0.16**	0.31	**-0.15**	0.27	**-0.16**	0.30	**-0.17**	0.26
BARC	**0.22**	0.26	**0.21**	0.29	**0.30**	0.47	**0.25**	0.32	**0.26**	0.29	**0.25**	0.31	**0.24**	0.28
NIST	**0.02**	0.11	**0.01**	0.14	**0.10**	0.39	**0.05**	0.19	**0.06**	0.13	**0.05**	0.18	**0.04**	0.11

Lab *i* ⇩

Lab *i*	D_i / MBq	U_i / MBq	NMIJ D_{ij} / MBq	NMIJ U_{ij} / MBq	OMH D_{ij} / MBq	OMH U_{ij} / MBq	BNM-LNHB D_{ij} / MBq	BNM-LNHB U_{ij} / MBq	BEV D_{ij} / MBq	BEV U_{ij} / MBq	BARC D_{ij} / MBq	BARC U_{ij} / MBq	NIST D_{ij} / MBq	NIST U_{ij} / MBq
BIPM	**0.01**	0.10	**0.03**	0.28	**0.05**	0.16	**-0.05**	0.14	**0.20**	0.28	**-0.21**	0.29	**-0.01**	0.14
NPL	**-0.08**	0.35	**-0.06**	0.46	**-0.04**	0.40	**-0.14**	0.39	**0.11**	0.28	**-0.30**	0.47	**-0.10**	0.39
ANSTO	**-0.03**	0.16	**-0.01**	0.31	**0.01**	0.21	**-0.09**	0.19	**0.16**	0.31	**-0.25**	0.32	**-0.05**	0.19
PTB	**-0.04**	0.09	**-0.02**	0.27	**0.00**	0.15	**-0.10**	0.13	**0.15**	0.27	**-0.26**	0.29	**-0.06**	0.13
CMI-IIR	**-0.03**	0.14	**-0.01**	0.30	**0.01**	0.19	**-0.09**	0.18	**0.16**	0.30	**-0.25**	0.31	**-0.05**	0.18
IRA	**-0.02**	0.07	**0.00**	0.26	**0.02**	0.14	**-0.08**	0.11	**0.17**	0.26	**-0.24**	0.28	**-0.04**	0.11
NMIJ	**-0.02**	0.24			**0.02**	0.29	**-0.08**	0.28	**0.17**	0.37	**-0.24**	0.38	**-0.04**	0.28
OMH	**-0.04**	0.13	**-0.02**	0.29			**-0.10**	0.16	**0.15**	0.29	**-0.26**	0.31	**-0.06**	0.16
BNM-LNHB	**0.06**	0.11	**0.08**	0.28	**0.10**	0.16			**0.25**	0.28	**-0.16**	0.30	**0.04**	0.14
BEV	**-0.19**	0.26	**-0.17**	0.37	**-0.15**	0.29	**-0.25**	0.28			**-0.41**	0.38	**-0.21**	0.28
BARC	**0.22**	0.26	**0.24**	0.38	**0.26**	0.31	**0.16**	0.30	**0.41**	0.38			**0.20**	0.30
NIST	**0.02**	0.11	**0.04**	0.28	**0.06**	0.16	**-0.04**	0.14	**0.21**	0.28	**-0.20**	0.30		

Figure 1. Graph of degrees of equivalence with the KCRV for ^{54}Mn
(as it appears in Appendix B of the MRA)



Appendix 1. Uncertainty budgets for the activity of ^{54}Mn submitted to the SIR

The BNM-LNHB, LNMRI, BEV, BARC and the NIST have submitted detailed uncertainty budgets as follows:

BNM-LNHB uncertainty budget (1999)

Relative standard uncertainties	$u_i \times 10^4$ evaluated by method	
Contributions due to	**A**	**B**
extrapolation	10	–
weighing*	–	–
dead time	–	<1
coincidence resolving time	–	–
background	–	<1
timing	–	<1
half-life	–	<1
delay mismatch	–	–
gamma sensitivity of beta counter	–	24
radionuclide impurities	–	<1
jitter	–	<1
Quadratic summation	**10**	**24**
Relative combined standard uncertainty, u_c	**26**	

* included in extrapolation.

LNMRI uncertainty budget (2000)

Relative standard uncertainties	$u_i \times 10^4$ evaluated by method	
Contributions due to	**A**	**B**
counting statistics	40	–
weighing	–	10
dead time	–	30
background	–	2
timing	–	5
half-life	–	1
adsorption	–	9
extrapolation	–	50
Quadratic summation	**40**	**60**
Relative combined standard uncertainty, u_c	**72**	

BEV uncertainty budget (2001)

Relative standard uncertainties	$u_i \times 10^4$ evaluated by method	
Contributions due to	**A**	**B**
counting statistics	7	–
weighing	–	5
background	–	57
impurities	–	10
half-life	–	3
calibration factor	–	33
current measurement	–	10
Quadratic summation	**7**	**68**
Relative combined standard uncertainty u_c	**69**	

BARC uncertainty budget (2002)

Relative standard uncertainties	$u_i \times 10^4$ evaluated by method	
Contributions due to	**A**	**B**
counting statistics	66	–
weighing	–	2.6
dead time	–	4.5
coincidence resolving time	–	12
background (essentially gamma channel)	–	1
timing	–	1
half-life	–	3.2
extrapolation (variation by source self absorption)	17	–
Quadratic summation	**68**	**14**
Relative combined standard uncertainty, u_c	**69**	

NIST uncertainty budget (2002)

Relative standard uncertainties	$u_i \times 10^4$ evaluated by method	
Contributions due to	**A**	**B**
PIC A* net response per gram of BIPM-02-54, measured relative to RRS10	1	–
PIC A net response for RRS10 measured relative to RRS20	5	–
PIC A net response per Bq of ^{54}Mn in solution, measured relative to RRS20	3	–
activity used to calibrate PIC A net response per Bq of ^{54}Mn in solution	–	21
PIC A charge collection	–	5
gravimetric measurements	–	5
live time	–	5
half-life of ^{54}Mn	0.02	–
half-life of ^{226}Ra	0.4	
source positioning	–	5
photon emitting impurities	–	10
Quadratic summation	**5.9**	**25**
Relative combined standard uncertainty u_c	**26**	

* PIC A, pressurized ionization chamber A

Appendix 2. Evaluation of the uncertainty of the degree of equivalence

Table 5 indicates for each laboratory the degree of equivalence D_i with its associated uncertainty U_i. This appendix presents the procedure used to evaluate these uncertainties.

The degree of equivalence of one laboratory is defined as the difference between the individual value of the equivalent activity A_{ei} for an NMI i and a suitable reference value which has been evaluated by the KCDB Working Group and the expanded uncertainty of this difference. Currently, the reference value, KCRV, for a given radionuclide is calculated as the arithmetic mean value of the SIR experimental entries for this radionuclide. Briefly at least four situations can occur depending on the consistency of the experimental SIR data sets :

1. All data are consistent and contribute to the reference value; this is the general case;

2. The value obtained by a laboratory that no longer exists, is used as long as it fits the usual quality criteria; it is taken into account when evaluating the reference value but does not appear in the matrices of results;

3. A value, that has been identified for example as an outlier, is not taken into account for the evaluation of the reference value but, nevertheless, the corresponding laboratory appears in the matrices of results.

The situation where a laboratory that no longer exists but contributes to the reference value and where an outlier has been identified in the data set can occur. This is a combination of both situation 2) and situation 3). The results, deduced from these two preceding cases, are also presented here, case 4.

In the following, the expression of the uncertainty for these four cases is considered on the assumption that the uncertainties of the different equivalent activities A_{ei} are not correlated. For the sake of coherence with the definition of the variables used in the text, the following notation is used :

$x_i = A_{ei}$ and $u_i = u_{Aei}$ its uncertainty.

Case 1. All *n* laboratories contribute to the reference value, and appear in Table 5. In this case obviously we have

$$x_{ref} = \bar{x} = \frac{\sum_{j=1}^{n} x_j}{n} \qquad (A-1)$$

$$D_i = x_i - x_{ref} \qquad (A-2)$$

$$D_i = x_i - \frac{\sum_{j=1}^{n} x_j}{n} = x_i\left(1 - \frac{1}{n}\right) - \frac{\sum_{j \neq i}^{n} x_j}{n} \qquad (A-3)$$

At this stage the uncertainty of D_i has to be calculated. Applying the method of Gauß for the propagation of the uncertainties it is necessary to calculate the partial derivatives of D_i with respect to the x_i.

So $\frac{\partial D_i}{\partial x_i} = \left(1 - \frac{1}{n}\right)$, and $\qquad (A-4)$

$$\frac{\partial D_i}{\partial x_j} = -\frac{1}{n}, (j \neq i). \qquad (A-5)$$

Then the total combined uncertainty becomes

$$u_{c_i}^2 = \left(\frac{\partial D_i}{\partial x_i}\right)^2 u_i^2 + \sum_{j \neq i}\left(\frac{\partial D_i}{\partial x_j}\right)^2 u_j^2 \qquad (A-6)$$

$$= \left(1 - \frac{1}{n}\right)^2 u_i^2 + \frac{1}{n^2}\sum_{j \neq i} u_j^2 \qquad (A-7)$$

or, after recombination

$$= \left(1 - \frac{2}{n}\right) u_i^2 + \frac{1}{n^2}\sum_{j=1}^{n} u_j^2. \qquad (A-8)$$

When a coverage factor of 2 is used (A-8) becomes

$$U_i^2 = 2^2\left[\left(1 - \frac{2}{n}\right) u_i^2 + \frac{1}{n^2}\sum_{j=1}^{n} u_j^2\right]. \qquad (A-9)$$

Case 2. A laboratory was used to evaluate the reference value but does not appear in Table 5.

Let us assign the subscript *n* to the additional laboratory that contributes to the reference value. The uncertainty of this laboratory will appear only in the second part of equation (A-9). Accordingly, equation (A-9) becomes

$$U_i^2 = 2^2\left[\left(1-\frac{2}{n}\right)u_i^2+\frac{1}{n^2}\left(\sum_{j=1}^{n}u_j^2\right)\right], \text{for } i=1,n-1. \qquad (A-10)$$

Case 3. The reference value was evaluated with all reported values except one.

For the sake of simplicity let us assign the subscript $n + 1$ to the ineligible laboratory so that the subscript for the other laboratories will run from 1 to n. Under this assumption the treatment of the ineligible laboratory will be slightly different and two formulae are deduced.

The ineligible laboratory does not contribute to the reference value, so the term $(1 – 2/n)$ in (A-9) reduces to 1 and the uncertainty is simply given by

$$U_{n+1}^2 = 2^2\left[u_{n+1}^2+\frac{1}{n^2}\sum_{j=1}^{n}u_j^2\right]. \qquad (A-11)$$

In the evaluation of the uncertainty related to the n other laboratories the contribution from laboratory $n + 1$ disappears totally and the uncertainty remains given by the expression (A-10) without restriction over the subscript range i. e.

$$U_i^2 = 2^2\left[\left(1-\frac{2}{n}\right)u_i^2+\frac{1}{n^2}\sum_{j=1}^{n}u_j^2\right]. \qquad (A-12)$$

Case 4. A laboratory that no longer exists contributes to the reference value and an outlier has been identified for another laboratory.

Let us assign the subscript n to the defunct existing laboratory so that the expression for the mean (A-1) remains applicable. In addition the outlier will be labelled by $n + 1$. For the $(n – 1)$ first laboratories which contribute to the mean value and appear in Table 5 the uncertainty of D_i is given by

$$U_i^2 = 2^2\left[\left(1-\frac{2}{n}\right)u_i^2+\frac{1}{n^2}\sum_{j=1}^{n}u_j^2\right], \text{for } i=1,n-1. \qquad (A-13)$$

For the laboratory $n + 1$ that is ineligible for the KCRV, its coefficient $(1 – 2/n)$ in (A-13) reduces to 1 and the expression of the uncertainty in Table 5 becomes

$$U_{n+1}^2 = 2^2\left[u_{n+1}^2+\frac{1}{n^2}\sum_{j=1}^{n}u_j^2\right], \qquad (A-14)$$

similar to (A-11).

Appendix 3. 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	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
bremsstrahlung	BS	coincidence	CO
gamma ray	GR	anti-coincidence	AC
X - rays	XR	coincidence counting with efficiency tracing	CT
alpha - particle	AP	anti-coincidence counting with efficiency tracing	AT
mixture of various radiation e.g. X and gamma	MX	triple-to-double coincidence ratio counting	TD
		selective sampling	SS

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(GeHP)-anticoincidence counting	4P-PP-MX-GH-GR-AC
4π CsI-β,AX,γ counting	4P-CS-MX-00-00-00
calibrated IC	4P-IC-GR-00-00-00
internal gas counting	4P-PC-BP-00-00-IG