BIPM comparison BIPM.RI(II)-K1.Cd-109 of activity measurements of the radionuclide ^{109}Cd and links for the 1986 international comparison CCRI(II)-K2.Cd-109

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Abstract

Since 1978, seven national metrology institutes (NMI), the BIPM and another laboratory have submitted twenty samples of known activity of ^{109}Cd to the International Reference System (SIR) for activity comparison at the Bureau International des Poids et Mesures. The activities ranged from about 2.5 MBq to 210 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 four NMIs and the BIPM. 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.Cd-109. The results of a CCRI international comparison, identifier CCRI(II)-K2.Cd-109 held in 1986 that have been approved for provisional equivalence for this radionuclide, have been linked to the SIR results. This has enabled three NMIs to update their results and a further eight NMIs and one international laboratory, the IRMM, to be linked to the SIR.

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) that was set up under the Mutual Recognition Arrangement (MRA) [2]. The comparison described in this report is known as the BIPM.RI(II)-K1.Cd-109 key comparison.

In addition, an international comparison was held in 1986 for this radionuclide, CCRI(II)-K2.Cd-109 [3] and this comparison has been given the status of having provisional equivalence in the KCDB. Although eighteen laboratories took part in this comparison, four of them have since submitted ampoules to the SIR. Three NMIs had previously submitted ampoules to the SIR and have updated their results and a further eight NMIs and one international laboratory are eligible to be linked to the BIPM key comparison through this CCRI(II) comparison, as listed in Table 1b.

2. Participants

Seven NMIs and another laboratory have submitted twenty ampoules for the comparison of ^{109}Cd activity measurements since 1978. The laboratory details are given in Table 1a. 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).

The eight NMIs and the international organization that took part in the CCRI(II) international comparison, CCRI(II)-K2.Cd-109 in 1986 and are also eligible for the KCDB are shown in Table 1b together with the three NMIs that used this comparison to update their results.

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 uncertainties 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. Consequently, an uncertainty budget is given for the IRA.

Table 1a. Details of the participants in the BIPM.RI(II)-K1.Cd-109

Original acronym	**NMI**	**Full name**	**Country**	**Regional metrology organization**	**Date of measurement at the BIPM** YYYY-MM-DD
NAC *	CSIR-NML	National Metrology Laboratory	South Africa	SADCMET	1978-04-18 1979-10-10 1981-03-24 1982-12-03
UVVVR	CMI-IIR	Český Metrologický Institut/Czech Metrological Institute, Inspectorate for Ionizing Radiation	Czech Republic	EUROMET	1978-09-01 1986-04-08
LMRI LPRI	BNM-LNHB	Bureau national de métrologie-Laboratoire national Henri Becquerel	France	EUROMET	1980-07-02 1998-01-23
–	NPL	National Physical Laboratory	United Kingdom	EUROMET	1980-10-09
AECL	–	Atomic Energy of Canada Ltd	Canada	SIM	1982-03-31
BIPM	–	Bureau International des Poids et Mesures	–	–	1986-03-24
–	PTB	Physikalisch-Technische Bundesanstalt	Germany	EUROMET	1994-11-24
ETL	NMIJ	National Metrology Institute of Japan	Japan	APMP	1996-04-05
–	IRA	Institut de Radiophysique Appliquée	Switzerland	EUROMET	2000-12-05

* another laboratory in the country

Table 1b. Details of the participants in the 1986 CCRI(II)-K2.Cd-109 to be linked to BIPM.RI(II)-K1.Cd-109

Original acronym	NMI	Full name	Country	Regional metrology organization
UVVVR	CMI-IIR	Český Metrologický Institut/Czech Metrological Institute, Inspectorate for Ionizing Radiation	Czech Republic	EUROMET
NAC*	CSIR-NML	National Metrology Laboratory	South Africa	SADCMET
–	IFIN	Institutul de Fizica si Inginerie Nucleara	Romania	EUROMET
(CBMN) IRMM	–	Institute for Reference Materials and Measurements	European Union	EUROMET
KSRI	KRISS	Korea Research Institute of Standards and Science	Republic of Korea	APMP
IPEN**	LNMRI	Laboratorio Nacional de Metrologia das Radiaçoes Ionizantes	Brazil	SIM
–	NIM	National Institute of Metrology	China	APMP
NBS	NIST	National Institute of Standards and Technology	United States	SIM
–	NPL	National Physical Laboratory	United Kingdom	EUROMET
–	OMH	Országos Mérésügyi Hivatal	Hungary	EUROMET
IEA	RC	Radioisotope Centre POLATOM	Poland	EUROMET
IMM	VNIIM	D.I. Mendeleyev Institute for Metrology	Russia	COOMET

* another laboratory in the country
** another laboratory in Brazil belonging to the National Nuclear Energy Comission (Comissão Nacional de Energia Nuclear - CNEN).

The half-life used by the BIPM is 464 (1) d [4]. The data could be revised using the half-life recommended by the IAEA [5], 462.6 (7) d. However, the degrees of equivalence would not differ significantly as the SIR measurements were performed within less than one year following the reference date. In the extreme case of eight months, for the AECL, the relative change in A_e is about 1×10^{-3}. In the 1986 CCRI(II)-K2.Cd-109 comparison a half life of 462.6 (4) days [6] was used.

Table 2. Standardization methods of the participants for ^{109}Cd

NMI	Method used and acronym (see Appendix 3)	Half-life	Activity / kBq	Reference date YY-MM-DD	Relative standard uncertainty × 100 by method of evaluation A	B
CSIR-NML	4π(LS)ce-x coincidence [7] 4P-LS-CE-NA-XR-CO	–	99 200 101 800	78-03-31 10 h UT	0.11	2.00
	4π(LS)ce-x coincidence [7] 4P-LS-CE-NA-XR-CO and 4π(LS)ce 4P-LS-CE-LS-CE-CO	–	176 400 187 900 and 176 800 188 400 *	79-09-28 13 h UT	0.13 0.10	1.80 2.00
	4π(LS)ce-x coincidence 4P-LS-CE-NA-XR-CO [8]	–	209 400 212 100	81-02-10 12h UT	0.10	1.82
			82 380 79 930	82-10-29 10 h UT	0.03	0.71
CMI-IIR	4π(NaI(Tl))x 4P-NA-XR-00-00-00	1.3 a	3 802	78-07-27 11 h UT	0.2	1.3
		453.5 d	17 670	86-03-19 12 h UT	0.07	0.93
BNM-LNHB	4π(PPC)ce 4P-PP-CE-00-00-00	–	2 716 2 712	80-02-19 0 h UT	0.03	0.14
	TDCR 4P-LS-MX-00-00-TD and 4π(PPC)ce 4P-PP-CE-00-00-00	–	6 916	97-10-01 12 h UT	0.99	
NPL	Pressurized IC [a] 4P-IC-GR-00-00-00	–	39 300	80-10-06 0 h UT	0.09	1.64
AECL	γ efficiency tracing using ^{109}Pd 4P-PC-BP-GL-GR-ET	462.3 (7) d	17 740	81-09-01 17 h UT	1.2	0.6
BIPM[b]	4π(PPC)ce 4P-PP-CE-00-00-00	462.6 (4) d	21 547 21 708	86-03-01 0 h UT	0.01	0.26
PTB	Pressurized IC [a] 4P-IC-GR-00-00-00	–	7 405	94-10-01 0 h UT	0.05	0.50
NMIJ	4π (PPC)ce 4P-PP-CE-00-00-00	–	13 903	96-03-01 12 h UT	0.19	0.40
IRA	Pressurized IC [c] 4P-IC-GR-00-00-00	462.9 (2.0) d	51 320	00-12-01 12 h UT	0.08	0.61

* results obtained using the second method although these have not been registered in the SIR

[a] calibrated by a primary method for the nuclide considered

[b] the two ampoules measured by the BIPM for the CCRI(II)-K2.Cd-109 and measured in the SIR are used to make the link for the CCRI(II) key comparison

[c] calibrated in 1986 against 4π(NaI(Tl))γ counting and 4π(LS)ce counting in the frame of the CCRI(II) comparison for this nuclide.

Details regarding the solution submitted are shown in Table 3, including any impurities, when present, as identified by the laboratories. Recently the BIPM has developed a standard method for evaluating the activity of impurities using a calibrated Ge(Li) spectrometer [9]. The CCRI(II) agreed in 1999 [10] that this method should be followed according to the protocol described in [11] when an NMI makes such a request or when there appear to be discrepancies.

Table 3. Details of the solution of ^{109}Cd submitted

NMI	Chemical composition	Solvent conc. / (mol dm^{-3})	Carrier: conc. /(μg g^{-1})	Density /(g cm^{-3})	Relative activity of any impurities†
CSIR-NML	CdCl in HCl	1	CdCl : 95	1.036	–
	$CdCl_2$ in HCl	1	$CdCl_2$: 100	1.036	–
			Cd^{++} : 610	1.037	–
			Cd^{++} : 300	1.037	–
CMI-IIR	$Cd(NO_3)_2$ in HCl	0.08	$Cd(NO_3)_2$: 50	–	< 0.1 %
	$CdCl_2$ in HCl	0.08	$CdCl_2$: 50	–	< 0.1 %
BNM-LNHB	$CdCl_2$ in HCl	1	$CdCl_2$: 25	1.016	^{110}Ag^{m} : 0.082 (2) % ^{60}Co : 0.0182 (5) % ^{65}Zn : 0.0142 (5) % ^{152}Eu : 0.0021 (1) % ^{134}Cs : 0.0004 (1) % ^{115}Cd^{m}: 0.03(1) %
			$CdCl_2$: 10	1.016	–
NPL	$CdCl_2$ in HCl	0.1	$CdCl_2$: 100	1.001	–
AECL	$CdCl_2$ in HCl	0.1	$CdCl_2$: 20	1.0	–
BIPM[a]	$CdCl_2$ in HCl	0.1	$CdCl_2$: 20	–	^{110}Ag^{m} : 3.6 (7) × 10^{-6} % ^{65}Zn : 1.4 (3) × 10^{-6} %
PTB	$CdCl_2$ in HCl	0.1	$CdCl_2$: 45	1.00	–
NMIJ	$CdCl_2$ in HCl	0.1	$CdCl_2$: 200	1.00	^{65}Zn: 0.0047 (5) %
IRA	$CdCl_2$ in HCl	0.1	$CdCl_2$: 20	1.000	negligible

[a] the solution used for the 1986 CCRI(II)-K2.Cd-109 comparison

† the ratio of the activity of the impurity to the activity of ^{109}Cd 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 ^{109}Cd arise from twenty ampoules and the SIR equivalent activity for each ampoule is given in Table 4a. 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 SIR corrections for impurities are negligible, except for the BNM-LNHB (1980) and the NMIJ solutions for which the correction reached 2.23 and 1.0123 respectively. Although the correction for BNM-LNHB (1980) is larger than a factor of two, the result is in good agreement with the other NMIs, showing the accuracy of the impurity correction applied. For the NMIJ solution, the impurity quoted in Table 3 has been confirmed by spectrometric measurements made at the BIPM, i.e. an activity ratio for ^{65}Zn/^{109}Cd of 0.0046 (7) %.

The measurement of the CMI-IIR (1978) ampoule was repeated at the BIPM one year later and produced a result lower than the first measurement by 2.5×10^{-2}. This change may have been caused by an unaccounted impurity that could also explain the low result compared to the other NMIs for the first measurement of this ampoule. Indeed an impurity level of only 3×10^{-5} of ^{60}Co would have the effect of increasing the first measurement result to about 8270 MBq and the second measurement of this ampoule would then agree with the first to within 3.6×10^{-3}. The subsequent submission in 1986 is also lower than the other values and may also have been contaminated. If the level of impurity had been about the same level as in 1978, the SIR result for 1986 would have been 8190 MBq instead of the 7913 MBq registered.

Measurements repeated at the BIPM for the CSIR-NML(1978) and the IRA(2000) after one and a half years and two years, respectively, produced comparison results higher by a factor of 1.006 and 1.009 respectively. This indicates that the half-life recommended by the IAEA [5] is more appropriate, particularly for measurements made a long time after the reference date, and that this value should be used in the future.

In principle, the chemical composition of the solutions could have an influence on the SIR measurements owing to the intense x-ray emission from ^{109}Cd. However, using the efficiency curve of the SIR [12], the contribution of the x-rays to the ionization current is estimated to be negligible. In consequence, the influence of the chemical composition on the SIR measurements can also probably be neglected in this case although a more detailed study could be performed.

No early submission has been withdrawn and no recent submission has been identified as a pilot study so the results of each NMI are eligible for Appendix B of the MRA. However, three of these results, for the CMI-IIR, CSIR-NML and the NPL have been superseded by the international comparison that was held in 1986. In addition, the AECL is not a designated laboratory of the NRC, Canada and so their results are not included in the KCDB.

The CCRI(II) comparison also enables the linking of another eight NMIs, the RC, IFIN, VNIIM, LNMRI, KRISS, NIST, NIM and OMH, and an international laboratory, the IRMM, to the SIR key comparison.

Table 4a. Results of SIR measurements of ^{109}Cd

NMI	Mass of solution / g	Activity submitted / kBq	N° of Ra source used	SIR A_e / MBq	Relative uncertainty from SIR	Total uncertainty $u_{c,i}$ / MBq
CSIR-NML	3.600 3.599 [a]	99 200 101 800	1	8161 8164	13×10^{-4}	160 160
	3.604 3.605 [b]	176 400 187 900 (and 176 800 188 400)	2	8217 8214 (and 8238 8236)	11×10^{-4}	150 150 (and 170 170)
	3.610 3.602 [c]	209 400 212 100	2	8186 8187	11×10^{-4}	150 150
	3.596 3.595 [d]	82 380 79 930	1	8166 8175 [#]	14×10^{-4}	59 59
CMI-IIR	3.596 50	3 802	1	7985	23×10^{-4}	110
	3.615 4	17 670	1	7913 [#]	25×10^{-4}	77
BNM-LNHB	3.685 56 3.679 70	2 716 2 712	1	8128 8110	240×10^{-4} *	200 200
	3.594 4	6 916	1	8187	42×10^{-4}	88
NPL	3.589 0	39 300	1	8128 [#]	16×10^{-4}	130
AECL	1.613 23 [e]	17 740	1	8112	28×10^{-4}	110
BIPM	3.605 6 3.632 5	21 547 21 708	1	8112 8114	16×10^{-4}	25 26
PTB	3.698 9	7 405	1	8153	37×10^{-4}	51
NMIJ	3.594 3	13 903	1	8157	23×10^{-4}	41
IRA	3.527 60 (10)	51 320	1	8065	14×10^{-4}	51

[#] values superseded by the international comparison in 1986
[a] mass of active solution before dilution : 0.545 58 g and 0.559 95 g respectively
[b] mass of active solution before dilution : 1.000 69 g and 1.065 82 g respectively
[c] mass of active solution before dilution : 1.009 83 g and 1.022 76 g respectively
[d] mass of active solution before dilution : 0.332 38 g and 0.322 50 g respectively
[e] mass of active solution before dilution
* the SIR uncertainty reflects the uncertainties of the impurity measurements quoted by the NMI.

The results of the international comparison CCRI(II)-K2.Cd-109 have been published [3]. The twelve laboratories to be added to the matrix of degrees of equivalence from this previous publication are those given in Table 1b. The results $(A/m)_i$ for these laboratories are linked to the SIR through the measurement in the SIR of the two ampoules standardized by 4π(PPC)ce measurements at the BIPM for the international comparison. The link is made using a ratio deduced from the BIPM line of Table 4a:

$$A_{ei} = (A/m)_i \times \tfrac{1}{2}\sum_{L=1}^{2}\left(A_{e,\mathrm{BIPM},L}/(A/m)_{\mathrm{BIPM},L}\right) = (A/m)_i \times 1.3576 \qquad \text{(a)}$$

The results of the links for the twelve laboratories are given in Table 4b. The uncertainties for the international comparison linked to the SIR are comprised of the original uncertainties together with the uncertainty in the link, 16×10^{-4}, given by the uncertainty of the SIR measurement of the BIPM ampoules of the CCRI(II)-K2.Cd-109 comparison.

Table 4b. Results of 1986 CCRI(II) measurements of ^{109}Cd linked to the SIR

NMI	Activity * concentration $(A/m)_i$ / (kBq g^{-1})	Relative standard uncertainty × 100	Linked SIR A_{ei} / MBq	$u(A_{ei})$ / MBq
CMI-IIR#	6055[a]	1.1	8220	91
CSIR-NML#	6033†	0.16	8190	18
IFIN	6440†	1.1	8743	96
IRMM	5972†	0.26	8108	25
KRISS	5994	0.32	8137	29
LNMRI	6000	0.22	8146	22
NIM	6030†	0.23	8186	23
NIST	5972†	0.55	8107	47
NPL#	5979	0.32	8117	29
OMH	5978	0.27	8116	25
RC	6014†	0.56	8165	47
VNIIM	5968	0.20	8102	21

* results from [3] with reference date 1986-03-01 at 00 h UT
# also measured in the SIR prior to this comparison
[a] result obtained using the 4π(NaI(Tl))x method which is presently in use at the CMI-IIR for the ^{109}Cd national reference (see text below)
† weighted mean of several methods.

The IRA (2000) SIR submission is based on the standardizations used for the international comparison and so may be compared with the IRA result in [3] through the link defined by equation (a). These two values agree within the combined SIR uncertainties. This indicates the robustness of the link between the CCRI(II) comparison and the SIR.

The results for the CSIR-NML and the NPL that are linked through the international comparison agree within one combined uncertainty with the original SIR equivalent activity values. The result for the CMI-IIR that is similarly linked through the international comparison agrees to within 3.7×10^{-3} with their 1986 SIR submission, if an impurity level as described earlier is presumed for their SIR submission.
As the CCRI comparison is more recent for these three NMIs, the earlier SIR results have been superseded by the values in Table 4b for the results presented in the KCDB. Details of the CSIR-NML measurement methods are given in [13].

The result for the CMI-IIR from the 1986 international comparison (8220 (90) MBq) is used for the degrees of equivalence in the KCDB although it does not represent exactly the measurements presently carried out in this NMI. An additional correction factor of 0.99 related to the x-ray emission probabilities is currently applied by the CMI-IIR to their 4π(NaI(Tl))x method. Using this correction would have produced an equivalent activity value of about 8140 (90) MBq that would then be in close agreement with the KCRV.

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 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 excluded from the KCRV, if necessary 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 ^{109}Cd has been identified as 8136 (14) MBq using the results in Table 4a from the NPL, AECL, CSIR-NML (1982), PTB, NMIJ, BNM-LNHB (1997), IRA, and the BIPM. The result of the CMI-IIR has not been included in the KCRV in view of the uncertainty over possible impurity levels.

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 1).

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

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

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

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

and any obvious correlations between the NMIs (such as a traceable calibration) are subtracted 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. The core of the matrix is based on five values from the SIR. The additional matrix cells show the twelve results from the 1986 international (CCRI(II)) comparison linked to those of the SIR: the three NMIs for which the SIR results have been superseded and the nine additional laboratories as given in Table 4b. 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, for example the uncertainty of the SIR measurement for the linked results.

Conclusion

The BIPM ongoing key comparison for ^{109}Cd, BIPM.RI(II)-K1.Cd-109 currently comprises five 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.

The results of eleven other NMIs and one international laboratory that took part in the CCRI(II)-K2.Cd-109 comparison in 1986 have been linked to the BIPM ongoing key comparison through two ampoules of the comparison measured in the SIR. These linked results are included in the matrix of degrees of equivalence approved by the CCRI(II).

Other results may be added as and when other NMIs contribute ^{109}Cd activity measurements to this comparison or take part in other linked comparisons.

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Table 5. Table of degrees of equivalence and introductory text for ^{109}Cd

Key comparison BIPM.RI(II)-K1.Cd-109

MEASURAND : **Equivalent activity of ^{109}Cd**

Key comparison reference value: the SIR reference value for this radionuclide is x_R = 8136 MBq
with a standard uncertainty, u_R = 14 MBq (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
$U_i = 2((1 - 2/n)u_i^2 + (1/n^2)\Sigma u_i^2)^{1/2}$ 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 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.

Linking CCRI(II)-K2.Cd-109 (1986) to BIPM.RI(II)-K1.Cd-109

The value x_i is the equivalent activity for laboratory *i* participant in CCRI(II)-K2.Cd-109
having been normalized to the value of the BIPM as the linking laboratory (see Final report)

The degree of equivalence of laboratory *i* participant in CCRI(II)-K2.Cd-109 with respect to the key comparison 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.
The approximation $U_i = 2(u_i^2 + u_R^2)^{1/2}$ is used in the following table.

The degree of equivalence between two laboratories *i* and *j*, one participant in BIPM.RI(II)-K1.Cd-109 and one in CCRI(II)-K2.Cd-109,
or both participant in CCRI(II)-K2.Cd-109, is given by a pair of terms: $D_{ij} = D_i - D_j$ and U_{ij}, its expanded uncertainty (k = 2),
both expressed in MBq, where the approximation $U_{ij} = 2(u_i^2 + u_j^2 - 2fu_l^2)^{1/2}$ is used with l being the linking laboratory
when both laboratories are linked, and f is the correlation coefficient.

These statements make it possible to extend the BIPM.RI(II)-K1.Cd-109 matrices of equivalence to the other participants in CCRI(II)-K2.Cd-109.

Table 5 continued. Degrees of equivalence for ^{109}Cd

Lab *j* ⟹

Lab *i* ⇓

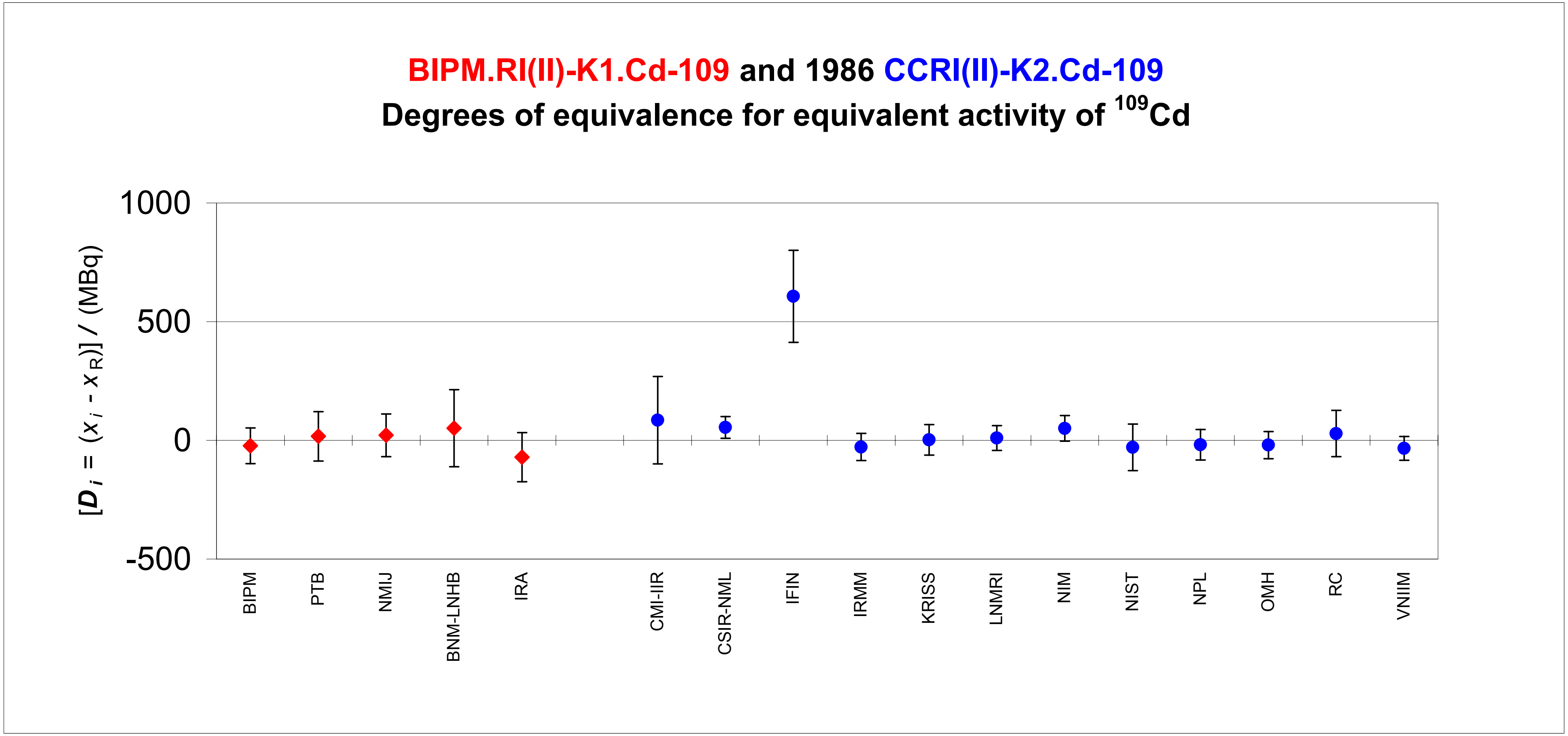
Lab *i*	D_i / MBq	U_i / MBq	BIPM D_{ij} / MBq	BIPM U_{ij} / MBq	PTB D_{ij} / MBq	PTB U_{ij} / MBq	NMIJ D_{ij} / MBq	NMIJ U_{ij} / MBq	BNM-LNHB D_{ij} / MBq	BNM-LNHB U_{ij} / MBq	IRA D_{ij} / MBq	IRA U_{ij} / MBq	CMI-IIR D_{ij} / MBq	CMI-IIR U_{ij} / MBq	CSIR-NML D_{ij} / MBq	CSIR-NML U_{ij} / MBq	IFIN D_{ij} / MBq	IFIN U_{ij} / MBq	IRMM D_{ij} / MBq	IRMM U_{ij} / MBq
BIPM	-23	75			-40	114	-44	97	-74	184	48	114	-107	186	-77	51	-630	195	5	62
PTB	17	104	40	114			-4	131	-34	203	88	144	-67	209	-37	108	-590	217	45	114
NMIJ	21	90	44	97	4	131			-30	194	92	131	-63	200	-33	90	-586	209	49	96
BNM-LNHB	51	162	74	184	34	203	30	194			122	203	-33	253	-3	180	-556	260	79	183
IRA	-71	104	-48	114	-88	144	-92	131	-122	203			-155	209	-125	108	-678	217	-43	114
CMI-IIR	85	184	107	186	67	209	63	200	33	253	155	209			30	182	-523	262	113	185
CSIR-NML	55	45	77	51	37	108	33	90	3	180	125	108	-30	182			-553	192	83	49
IFIN	607	194	630	195	590	217	586	209	556	260	678	217	523	262	553	192			635	195
IRMM	-28	57	-5	62	-45	114	-49	96	-79	183	43	114	-113	185	-83	49	-635	195		
KRISS	2	64	24	69	-16	117	-20	100	-50	185	72	117	-83	187	-53	58	-605	197	30	67
LNMRI	10	52	33	57	-7	111	-11	93	-41	181	81	111	-75	184	-45	43	-597	194	38	56
NIM	51	54	73	59	33	112	29	94	-1	182	121	112	-34	184	-4	45	-557	194	79	57
NIST	-29	98	-6	101	-46	139	-50	125	-80	200	42	139	-114	202	-84	94	-636	211	-1	100
NPL	-19	64	4	69	-36	117	-40	100	-70	185	52	117	-103	187	-73	58	-626	197	10	67
OMH	-20	57	3	62	-37	114	-41	96	-71	183	51	114	-105	185	-75	49	-627	195	8	60
RC	29	98	52	101	12	139	8	125	-22	200	100	139	-56	202	-26	94	-578	211	57	100
VNIIM	-34	50	-11	56	-51	110	-55	92	-85	181	37	110	-118	183	-88	41	-641	193	-5	54

Lab *j* ⟹

Lab *i* ⇓

Lab *i*	D_i / MBq	U_i / MBq	KRISS D_{ij} / MBq	KRISS U_{ij} / MBq	LNMRI D_{ij} / MBq	LNMRI U_{ij} / MBq	NIM D_{ij} / MBq	NIM U_{ij} / MBq	NIST D_{ij} / MBq	NIST U_{ij} / MBq	NPL D_{ij} / MBq	NPL U_{ij} / MBq	OMH D_{ij} / MBq	OMH U_{ij} / MBq	RC D_{ij} / MBq	RC U_{ij} / MBq	VNIIM D_{ij} / MBq	VNIIM U_{ij} / MBq
BIPM	-23	75	-24	69	-33	57	-73	59	6	101	-4	69	-3	62	-52	101	11	56
PTB	17	104	16	117	7	111	-33	112	46	139	36	117	37	114	-12	139	51	110
NMIJ	21	90	20	100	11	93	-29	94	50	125	40	100	41	96	-8	125	55	92
BNM-LNHB	51	162	50	185	41	181	1	182	80	200	70	185	71	183	22	200	85	181
IRA	-71	104	-72	117	-81	111	-121	112	-42	139	-52	117	-51	114	-100	139	-37	110
CMI-IIR	85	184	83	187	75	184	34	184	114	202	103	187	105	185	56	202	118	183
CSIR-NML	55	45	53	58	45	43	4	45	84	94	73	58	75	49	26	94	88	41
IFIN	607	194	605	197	597	194	557	194	636	211	626	197	627	195	578	211	641	193
IRMM	-28	57	-30	67	-38	56	-79	57	1	100	-10	67	-8	60	-57	100	5	54
KRISS	2	64			-8	63	-49	64	31	104	20	73	22	67	-27	104	35	61
LNMRI	10	52	8	63			-41	52	39	97	29	63	30	56	-19	97	43	48
NIM	51	54	49	64	41	52			80	98	69	64	71	57	22	98	84	50
NIST	-29	98	-31	104	-39	97	-80	98			-11	104	-9	100	-58	128	4	96
NPL	-19	64	-20	73	-29	63	-69	64	11	104			1	67	-48	104	15	61
OMH	-20	57	-22	67	-30	56	-71	57	9	100	-1	67			-49	100	14	54
RC	29	98	27	104	19	97	-22	98	58	128	48	104	49	100			62	96
VNIIM	-34	50	-35	61	-43	48	-84	50	-4	96	-15	61	-14	54	-62	96		

Figure 1. **Graph of degrees of equivalence with the KCRV for ^{109}Cd**
(as it appears in Appendix B of the MRA)



Appendix 1. Uncertainty budgets for the activity of ^{109}Cd submitted to the SIR

Uncertainty budget submitted by the IRA, in 2000.

(Reference of the measurement: M109Cd15A3_25102000)

Relative standard uncertainties	$u_i \times 10^4$ evaluated by method	
Contributions due to	**A**	**B**
Current of the first long lived reference source; ν = 14 *	6.5	–
Current of the second long lived reference source; ν = 19	6.3	–
Current of the ampoule of ^{109}Cd under measurement; ν = 14	4.7	–
Substitution factor of the reference source	–	5
Equivalent activity (calibration for ^{109}Cd)	–	52
Decay correction for the reference sources	–	2
Decay correction for ^{109}Cd	–	2.4
Gravimetric measurements	–	0.3
Background	–	0.7
Dimensions of the ampoule	–	30
Quadratic summation	**8.0**†	**60.3**
Total relative combined uncertainty u_c	**61**	

* number of degrees of freedom
† quadratic sum of 6.5 and 7.4 only

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 :

$x_i = A_{\mathrm{e}i}$ and $u_i = u_{A\mathrm{e}i}$ its uncertainty.

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

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

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

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

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 $\qquad (\mathrm{A}-4)$

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

Then the total combined uncertainty becomes

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

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

or, after recombination

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

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

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

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

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

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