BIPM comparison BIPM.RI(II)-K1.Yb-169 of activity measurements of the radionuclide ^{169}Yb and links for the 1997 regional comparison EUROMET.RI(II)-K2.Yb-169

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Abstract

Since 1978, six national metrology institutes (NMI) have submitted eleven samples of known activity of ^{169}Yb to the International Reference System (SIR) for activity comparison at the Bureau International des Poids et Mesures (BIPM), with comparison identifier BIPM.RI(II)-K1.Yb-169. The activities ranged from about 200 kBq to 46 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. A graphical presentation is also given. The results of a EUROMET regional comparison, comparison identifier EUROMET.RI(II)-K2.Yb-169, completed in 1997 for this radionuclide have been linked to the SIR results through those of the BNM-LNHB and the IRA. This has enabled five other NMIs and an international laboratory to have degrees of equivalence in the KCDB and two other NMIs to update their earlier results in the SIR.

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 form. For radioactive gases, a different standard ampoule is used. 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 2003, the SIR has measured 849 ampoules to give 615 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.Yb-169 key comparison.

In addition, a EUROMET comparison for this radionuclide, EUROMET.RI(II)-K2.Yb-169, was held in 1997 with the BNM-LNHB as the pilot laboratory (EUROMET Action No. 410). Although eleven laboratories took part in this comparison, only seven NMIs and an international laboratory, in addition to the BNM-LNHB and the IRA that are the linking laboratories, are eligible to be linked to the BIPM key comparison.

2. Participants

Six NMIs have submitted eleven ampoules for the comparison of ^{169}Yb 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.

Table 1a. Details of the participants in the BIPM.RI(II)-K1.Yb-169

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	1978-03-03 1980-09-22
–	OMH	Országos Mérésügyi Hivatal	Hungary	EUROMET	1981-12-04 1984-06-19
ASMW*	PTB	Physikalisch-Technische Bundesanstalt	Germany	EUROMET	1982-09-30 1983-07-12* 1984-10-23*
ÚVVVR	CMI-IIR	Český Metrologický Institut/Czech Metrological Institute, Inspectorate for Ionizing Radiation	Czech Republic	EUROMET	1984-02-09

continued overleaf.

Table 1a continued. Details of the participants in the BIPM.RI(II)-K1.Yb-169

Original acronym	**NMI**	**Full name**	**Country**	**Regional metrology organization**	**Date of measurement at the BIPM**
LPRI	BNM-LNHB	Bureau national de métrologie-Laboratoire national Henri Becquerel	France	EUROMET	1998-03-09
–	IRA	Institut de Radiophysique Appliquée	Switzerland	EUROMET	1998-04-03

* another laboratory in the country.

The nine NMIs and one other institute that took part in the EUROMET regional comparison, EUROMET.RI(II)-K2.Yb-169 in 1997 and are eligible for the KCDB are shown in Table 1b.

Table 1b. Details of the participants from the EUROMET.RI(II)-K2.Yb-169 comparison of 1997 that are eligible for the KCDB

NMI	**Full name**	**Country**
BNM-LNHB	Bureau national de métrologie-Laboratoire national Henri Becquerel	France
IFIN	Institutul de Fizica si Inginerie Nucleara	Romania
IRA	Institut de Radiophysique Appliquée	Switzerland
IRMM	Institute for Reference Materials and Measurements	European Union
LNMRI	Laboratorio Nacional de Metrologia das Radiaçoes Ionizantes	Brazil
NPL	National Physical Laboratory	U.K.
OMH	Országos Mérésügyi Hivatal	Hungary
PTB	Physikalisch-Technische Bundesanstalt	Germany
RC	Radioisotope Centre POLATOM	Poland
VNIIM	D.I. Mendeleyev Institute for Metrology	Russian Federation

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 2a. 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. As these results date prior to 1998, no uncertainty budgets have been provided.

Table 2a. Standardization methods of the participants for ^{169}Yb

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
NIST	Pressurized ionization chamber 4P-IC-GR-00-00-00 calibrated in 1977 by $4\pi(e,x)$-γ coinc. 4P-PP-MX-NA-GR-CO	–	4 191 4 075†	78-02-07 19 h UT	0.03	0.52
		32.02	5 890	80-08-26 17 h UT	0.01	0.87
OMH	$4\pi(e_X,x)$-γ coincidence 4P-PP-MX-NA-GR-CO	30.7 (3) [3]	7 062	81-10-01 12 h UT	0.03	0.72
		32.022 (8) [4]	14 272	84-06-30 12 h UT	0.02	0.25
PTB	4πPC-γ and 4πPPC-γ coinc. 4P-PC-MX-NA-GR-CO 4P-PP-MX-NA-GR-CO	–	46 410	82-10-01 0 h UT	0. 07	0.29
	4πPC-γ coinc. 4P-PC-MX-NA-GR-CO	–	24 550	83-06-03 12 h UT	0.10	0.90
	$4\pi(e_A,x)$-γ coinc. 4P-PC-MX-NA-GR-CO	–	36 660	84-09-27 12 h UT	0.14	1.20

continued overleaf.

Table 2a continued. Standardization methods of the participants for ^{169}Yb

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
CMI-IIR	4πPC-γ coinc. 4P-PC-MX-NA-GR-CO	32.02 (4)	19 360	84-01-30 11 h UT	0.19[††]	0.24[††]
BNM-LNHB	4πβ-γ coincidence and 4πγ counting 4P-PC-MX-NA-GR-CO 4P-NA-GR-00-00-HE	[4]	4 320.6	97-11-15 12 h UT	0.09	–
IRA	4πNaIγ and 4πPC(e,x)-γ coinc. 4P-NA-GR-00-00-HE 4P-PC-MX-NA-GR-CO	[4]	218.0	98-04-01 12 h UT	0.01	0.19

[†] two ampoules submitted

[††] original values were for an expanded uncertainty, $k = 3$.

The half-life used by the BIPM is 32.01 (2) days, the weighted mean of [5 to 7] which is in agreement with 32.018 (5) d the most recent evaluation published [8]. The SIR data could be revised using this new half-life. However, the updated degrees of equivalence would not differ significantly as most of the SIR measurements were performed within two months following the reference date. In the extreme case of four months, for the BNM-LNHB (1998) ampoule, the relative change in A_e would be about 6×10^{-4}. The half-life in reference [8] will be used in the future.

The standardization methods used in the EUROMET comparison by the ten participants are given in Table 2b.

Table 2b. Standardization methods for ^{169}Yb used by the EUROMET comparison participants

NMI	**Methods used and associated acronyms (see Appendix 3)**
BNM-LNHB	4πEC-γ coincidence 4P-PC-MX-NA-GR-CO 4πγ counting 4P-NA-GR-00-00-HE Gamma spectrometry UA-GH-GR-00-00
IFIN	4πEC-γ coincidence 4P-PC-MX-NA-GR-CO
IRA	4πEC-γ coincidence 4P-PC-MX-NA-GR-CO 4πγ counting 4P-NA-GR-00-00-HE
IRMM	4πγ counting 4P-NA-GR-00-00-HE 4πCsI(Tl) counting 4P-CS-MX-00-00-HE Liquid scintillation counting 4P-LS-MX-00-00-CN Gamma spectrometry UA-GH-GR-00-00
LNMRI	4πEC-γ coincidence 4P-PC-MX-NA-GR-CO

continued overleaf.

Table 2b continued. Standardization methods for ^{169}Yb used by the EUROMET comparison participants

NMI	Methods used and associated acronyms (see Appendix 3)
NPL	4πEC-γ coincidence 4P-PC-MX-NA-GR-CO
OMH	Ionization chamber and 4πEC-γ coincidence 4P-PP-MX-NA-GR-CO
PTB	4πEC-γ coincidence 4P-PC-MX-NA-GR-CO 4πγ counting 4P-NA-GR-00-00-HE
RC	4πEC-γ coincidence 4P-LS-MX-NA-GR-CO
VNIIM	4πEC-γ coincidence 4P-PC-MX-NA-GR-CO

Details regarding the solution submitted to the SIR 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 [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. Details of the solution issued for the EUROMET comparison are given in [12] and indicated in Table 3.

Table 3. Details of each solution of ^{169}Yb submitted

NMI	Chemical composition	Solvent conc. / (mol dm^{-3})	Carrier: conc. /(μg g^{-1})	Density /(g cm^{-3})	Relative activity of impurity[†]
NIST	$YbCl_3$ in HCl	0.1	Yb: 20	1.000 (2)	^{175}Yb: 1.9 (4) × 10^{-4} %
			Yb: 40	1.000 (2)	^{175}Yb : 0.57 (5) %
OMH	$YbCl_3$ in HCl	0.1	Yb: 25	–	< 5 × 10^{-3} %
					–
PTB	$YbCl_3$ in HCl	0.1	$YbCl_3$: 40	1.00	^{175}Yb : 0.014 (3) %
	$La(NO_3)_3$ in HNO_3	0.1	$La(NO_3)_3$: 20	1.001	< 0.1 %
	$YbCl_3$ in HCl	0.1	$YbCl_3$: 20	1.00	^{170}Tm : 3.95 (27) %
CMI-IIR	$YbCl_3$ + $LaCl_3$ in HCl	0.1	$YbCl_3$: 56 $LaCl_3$: 530	–	^{175}Yb < 0.08 % ^{177}Lu < 0.1 % ^{170}Tm : 1.9 %
BNM-LNHB*	$YbCl_3$ in HCl	0.5	$YbCl_3$: 11	–	–
IRA*	$YbCl_3$ in HCl	0.5	$YbCl_3$: 10	–	^{60}Co : 2.5 (5) × 10^{-3} %

[†] the ratio of the activity of the impurity to the activity of ^{169}Yb at the reference date

*diluted solution A used in the EUROMET action No. 410 [12].

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 ^{169}Yb arise from eleven 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 and are used in the KCDB and all references in this report.

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 smaller than 1.0005 in all cases.

The SIR measurement of the ASMW (1983) ampoule was repeated at the BIPM after two months and produced the same comparison result. Measurements repeated at the BIPM after periods of up to two and four months later for the PTB (1982) and the ASMW (1984) respectively produced results in agreement within the combined standard SIR uncertainty although a decreasing trend is observed. This may be linked to the ^{169}Yb half-life value used.

Measurements repeated at the BIPM after periods of up to three months later produced significantly decreasing results for the CMI-IIR. The drift measured could be explained by the presence of about 16 % of ^{170}Tm in the solution instead of the 1.9 % measured at the CMI-IIR using beta spectrometry. If a correction had been made for the higher impurity content, the SIR registered value would have increased by 2.2×10^{-3}. For their primary measurement, the CMI-IIR used two methods in parallel with different discrimination levels in the gamma channel (150 keV and 85 keV) that cancelled the effect of the Kx rays from ^{170}Tm in their measurement. However, the lower threshold, being close to the gamma ray energy from ^{170}Tm, may not have excluded this contribution from the measurement result using a NaI detector for the gamma channel.

In principle, the chemical composition of the solutions could have an influence on the SIR measurements owing to the intense x-ray emission from ^{169}Yb. However, using the efficiency curve of the SIR [13], the contribution of the x-rays to the ionization current is estimated to be only 15 %. In consequence, the influence of the chemical composition on the SIR measurements can probably be neglected in this case although a more detailed study could be performed.

One earlier result was withdrawn and does not appear here. No recent submission has been identified as a pilot study so the most recent result of each NMI is normally eligible for Appendix B of the MRA.

Other than the EUROMET exercise, no international or regional comparison for this radionuclide has been held to date so no other linking data are identified. As the CCRI has approved the EUROMET comparison for equivalence, the results of a further six laboratories can be linked to the SIR for degrees of equivalence and the PTB and the OMH are able to update their earlier SIR results.

The results of the international comparison EUROMET(II)-K2.Yb-169 held in 1997 have been published in detail, including uncertainty budgets [14], although anonymously. All the laboratories have agreed to be added to the matrix of degrees of equivalence from this previous publication and they are 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 ampoules standardized by the BNM-LNHB and the IRA. The link is made using an average ratio deduced from the results of the BNM-LNHB and the IRA:

$$A_{ei} = \left(A/m\right)_i \times \tfrac{1}{2}\sum_{L=1}^{2}\left(A_{e,\mathrm{NMI}(L)} \Big/ \left(A/m\right)_{\mathrm{NMI}(L)}\right) = \left(A/m\right)_i \times 6393 \qquad \text{(a)}$$

The values for A_e come from Table 4a and the values of A/m are the respective weighted means from Table 4b. The ratios calculated for the two linking laboratories differ by about 10^{-4}, showing the robustness of the link. Although the SIR result for the BNM-LNHB comes from only the coincidence method and the EUROMET result is the weighted mean from three different methods, this does not affect the linking value as the coincidence method in the EUROMET result outweighs the others.

Table 4a. Results of SIR measurements of ^{169}Yb

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
NIST	3.699 46 3.596 30	4 191 4 075	2	77 846 77 804[†]	11×10^{-4} 12×10^{-4}	420 420
	3.658 39	5 890	2	77 810	10×10^{-4}	680
OMH	3.608 6	7 062	2	75 490	14×10^{-4}	550
	3.603 0	14 272	2	76 650	10×10^{-4}	210
PTB	3.643 2	46 410	5	77 100	8×10^{-4}	240
	3.618 0 (1)	24 550	3	78 930	10×10^{-4}	720
	3.630 (2)	36 660	4	77 570[††]	9×10^{-4}	940
CMI-IIR	3.614 73	19 360	4	77 740	8×10^{-4}	250
BNM-LNHB	3.655 3	4 320.6	1	76 750[#]	21×10^{-4} [*]	170
IRA	3.504	218.0	1	78 500[#]	18×10^{-4}	210

[†] 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 [15]

[††] updated value to take into account the bremsstrahlung contribution in the ^{170}Tm correction

[*] mainly due to the decay correction

[#] results used to link the other participants in the EUROMET comparison to the SIR.

The linked results for the eight other 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, 1.4×10^{-3}, given by the combined uncertainty of the SIR measurements of the linking ampoules.

The two laboratories, the OMH and the PTB, with SIR results that are now superseded by the EUROMET results show agreement with their SIR earlier results at one and two standard uncertainties respectively.

Table 4b. Results of EUROMET measurements of ^{169}Yb

NMI	Code from [14]	Activity * concentration $(A/m)_i$ / (MBq g^{-1})	Relative standard uncertainty × 100	Linked SIR A_{ei} / kBq	Combined uncertainty u_c (A_{ei}) / kBq
BNM-LNHB	10	12.005$^{\$}$	0.07	76 750**	170
IFIN	5	11.989	0.92	76 650	710
IRA	6	12.278$^{\$}$	0.17	78 500**	210
IRMM	7	12.034$^{\$}$	0.24	76 940	210
NPL	4	12.026	0.42	76 890	340
LNMRI	8	12.106	0.98	77 400	770
OMH	9	12.041	0.12	76 980†	140
RC	2	11.977	0.60	76 570	470
PTB	1	12.001$^{\$}$	0.09	76 730†	130
VNIIM	3	12.020	0.31	76 850	260

* referenced to 15 November 1997, 12h UT

$^{\$}$ weighted mean as in [14] except for the IRMM result which uses all four reported values [16]

** values measured in the SIR (Table 4a)

† supersedes the earlier SIR result.

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.

Following this normal procedure gives a KCRV for ^{169}Yb of 77 400 (290) kBq using the results from the NIST (1978), OMH (1984), PTB (1982), ASMW (1984), IRA and the BNM-LNHB. However, the results of three NMIs are significantly different from the KCRV determined by the usual method and the linked results of the EUROMET comparison show a small negative bias.

Consequently, the CCRI(II) Key Comparison Working Group recommended that an evaluation of the KCRV for ^{169}Yb be determined by calculation using the SIR efficiency curve and recommended tabulated nuclear data. To ensure that such an evaluation is robust, a number of precautions were taken. First, a comparison of the calculated KCRV was made using data from the NDS [17] and then data from the BIPM *Monographie 5* [8]. The difference between the two values for the KCRV was 2.2×10^{-3} which is not significant because the uncertainties using the NDS and the BIPM Monographie 5 recommended data are 9×10^{-3} and 2.6×10^{-3} respectively.

Secondly, different efficiency curves were computed from which the KCRV for ^{169}Yb was calculated. Three evaluations were made, the first with a contribution from the ^{169}Yb results, the second without a contribution from the ^{169}Yb results, and the third using all the other KCRVs as currently published which of course does not include a value for ^{169}Yb. No difference in the KCRV was observed whether or not the ^{169}Yb results were included in the curve. This was expected because the fitted curve is insensitive to the ^{169}Yb data point as this has a large uncertainty and consequently little weight. The difference in the KCRV for ^{169}Yb calculated from the efficiency curves using the published KCRVs and that using the medians as for the previously published curve [13] is 2.6×10^{-3} which is again not significant.

The KCWG has accepted that the best evaluation of the KCRV for ^{169}Yb is the value calculated using the SIR efficiency curve based on the published KCRVs for all other radionuclides and the nuclear data published in BIPM *Monographie 5*. Consequently, the value of the KCRV for ^{169}Yb is 76 800 (200) 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

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

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

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

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

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

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. The additional matrix cells show the eight results from the 1997 EUROMET comparison linked to those of the SIR and 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 in Figure 1 where data points that predate 1983 are shown as black squares. 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 ^{169}Yb, BIPM.RI(II)-K1.Yb-169 currently comprises four 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 ^{169}Yb activity measurements to this comparison.

The results of seven other NMIs and the international laboratory that took part in the EUROMET.RI(II)-K2.Yb-169 comparison in 1997 have been linked to the BIPM ongoing key comparison through two linking laboratories whose results have been measured in the SIR. The linked results are included in the matrix of degrees of equivalence approved by the CCRI(II).

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Table 5. Introductory text for ^{169}Yb and table of degrees of equivalence

Key comparison BIPM.RI(II)-K1.Yb-169

MEASURAND : Equivalent activity of ^{169}Yb

Key comparison reference value: the SIR reference value x_R for this radionuclide is 76.8 MBq, with a standard uncertainty, u_R = 0.2 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 $U_i = 2(u_i^2 + u_R^2)^{1/2}$.

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.

Linking EUROMET.RI(II)-K2.Yb-169 (1997) to BIPM.RI(II)-K1.Yb-169

The value x_i is the equivalent activity for laboratory *i* participant in EUROMET.RI(II)-K2.Yb-169 having also been linked to the KCRV in the SIR (see Final Report).

The degree of equivalence of laboratory *i* participant in EUROMETRI(II)-K2.Yb-169 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 and $U_i = 2(u_i 2 + u_R 2)^{1/2}$

The degree of equivalence between two laboratories *i* and *j*, one participant in BIPM.RI(II)-K1.Yb-169 and one in EUROMET.RI(II)-K2.Yb-169, or both participant in EUROMET.RI(II)-K2.Yb-169, 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 $U_{ij} \sim 2(u_i^2 + u_j^2)^{1/2}$ is used, except where correlations due to the link are taken into account.

These statements make it possible to extend the BIPM.RI(II)-K1.Yb-169 matrices of equivalence to the other participants in EUROMET.RI(II)-K2.Yb-169.

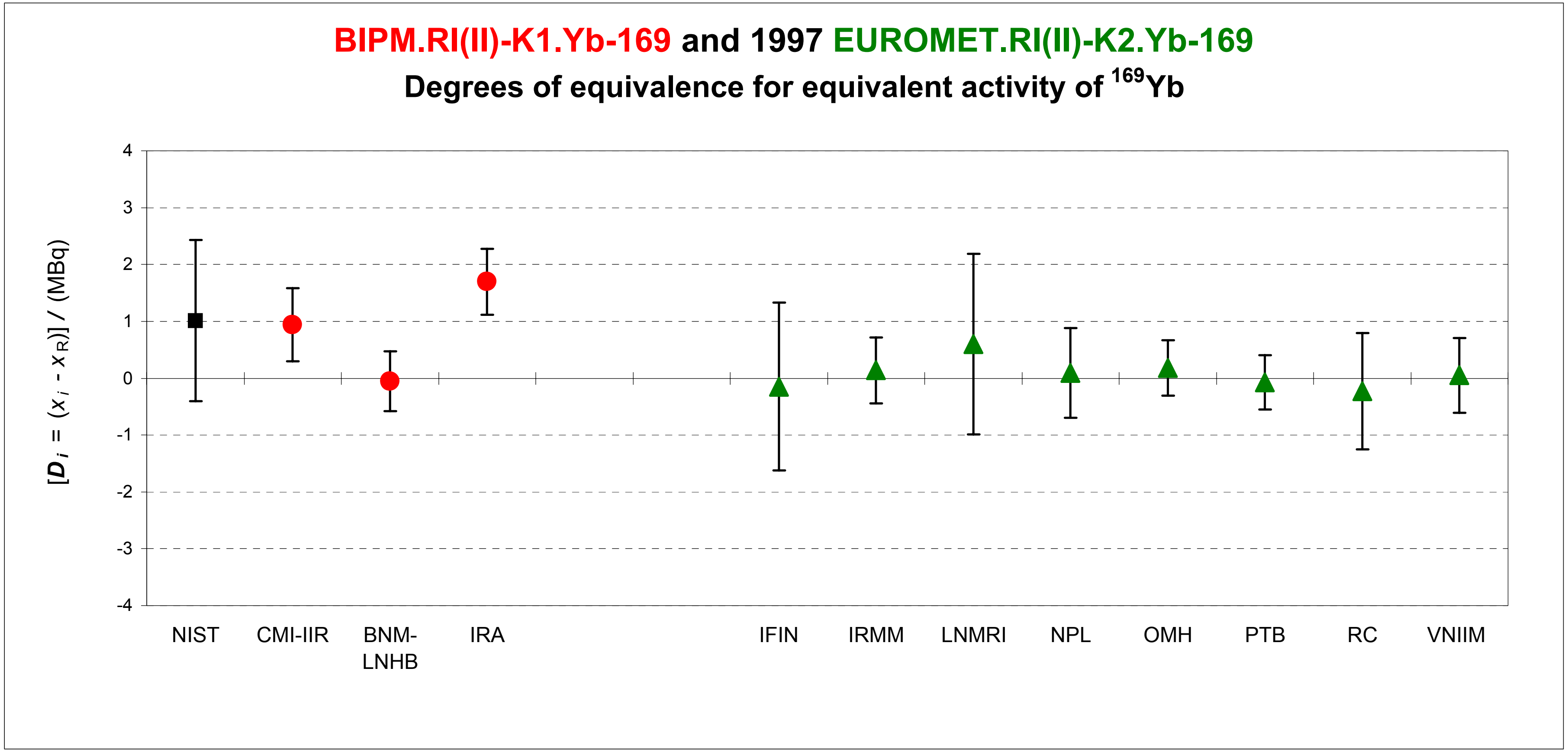
Table 5 continued. Degrees of equivalence

Lab *j* ⇨

Lab *i* ⇩			**NIST**		**CMI-IIR**		**BNM-LNHB**		**IRA**		**IFIN**		**IRMM**	
	D_i	U_i	D_{ij}	U_{ij}	D_{ij}	U_{ij}	D_{ij}	U_{ij}	D_{ij}	U_{ij}	D_{ij}	U_{ij}	D_{ij}	U_{ij}
	/ MBq		/ MBq		/ MBq		/ MBq		/ MBq		/ MBq		/ MBq	
NIST	**1.0**	1.4			**0.1**	1.4	**1.1**	1.4	**-0.7**	1.4	**1.2**	2.0	**0.9**	1.4
CMI-IIR	**0.9**	0.6	**-0.1**	1.4			**1.0**	0.6	**-0.8**	0.7	**1.1**	1.5	**0.8**	0.7
BNM-LNHB	**-0.1**	0.5	**-1.1**	1.4	**-1.0**	0.6			**-1.8**	0.5	**0.1**	1.4	**-0.2**	0.4
IRA	**1.7**	0.6	**0.7**	1.4	**0.8**	0.7	**1.8**	0.5			**1.9**	1.4	**1.6**	0.5
IFIN	**-0.2**	1.5	**-1.2**	2.0	**-1.1**	1.5	**-0.1**	1.4	**-1.9**	1.4			**-0.3**	1.4
IRMM	**0.1**	0.6	**-0.9**	1.4	**-0.8**	0.7	**0.2**	0.4	**-1.6**	0.5	**0.3**	1.4		
LNMRI	**0.6**	1.6	**-0.4**	2.1	**-0.3**	1.6	**0.7**	1.5	**-1.1**	1.6	**0.8**	2.1	**0.5**	1.6
NPL	**0.1**	0.8	**-0.9**	1.5	**-0.9**	0.8	**0.1**	0.7	**-1.6**	0.7	**0.2**	1.5	**-0.1**	0.7
OMH	**0.2**	0.5	**-0.8**	1.4	**-0.8**	0.6	**0.2**	0.3	**-1.5**	0.4	**0.3**	1.4	**0.0**	0.4
PTB	**-0.1**	0.5	**-1.1**	1.4	**-1.0**	0.6	**0.0**	0.3	**-1.8**	0.4	**0.1**	1.4	**-0.2**	0.4
RC	**-0.2**	1.0	**-1.2**	1.7	**-1.2**	1.1	**-0.2**	1.0	**-1.9**	1.0	**-0.1**	1.7	**-0.4**	1.0
VNIIM	**0.1**	0.7	**-1.0**	1.5	**-0.9**	0.7	**0.1**	0.5	**-1.7**	0.6	**0.2**	1.5	**-0.1**	0.6

Lab *i* ⇩			**LNMRI**		**NPL**		**OMH**		**PTB**		**RC**		**VNIIM**	
	D_i	U_i	D_{ij}	U_{ij}	D_{ij}	U_{ij}	D_{ij}	U_{ij}	D_{ij}	U_{ij}	D_{ij}	U_{ij}	D_{ij}	U_{ij}
	/ MBq		/ MBq		/ MBq		/ MBq		/ MBq		/ MBq		/ MBq	
NIST	**1.0**	1.4	**0.4**	2.1	**0.9**	1.5	**0.8**	1.4	**1.1**	1.4	**1.2**	1.7	**1.0**	1.5
CMI-IIR	**0.9**	0.6	**0.3**	1.6	**0.9**	0.8	**0.8**	0.6	**1.0**	0.6	**1.2**	1.1	**0.9**	0.7
BNM-LNHB	**-0.1**	0.5	**-0.7**	1.5	**-0.1**	0.7	**-0.2**	0.3	**0.0**	0.3	**0.2**	1.0	**-0.1**	0.5
IRA	**1.7**	0.6	**1.1**	1.6	**1.6**	0.7	**1.5**	0.4	**1.8**	0.4	**1.9**	1.0	**1.7**	0.6
IFIN	**-0.2**	1.5	**-0.8**	2.1	**-0.2**	1.5	**-0.3**	1.4	**-0.1**	1.4	**0.1**	1.7	**-0.2**	1.5
IRMM	**0.1**	0.6	**-0.5**	1.6	**0.1**	0.7	**0.0**	0.4	**0.2**	0.4	**0.4**	1.0	**0.1**	0.6
LNMRI	**0.6**	1.6			**0.5**	1.7	**0.4**	1.5	**0.7**	1.5	**0.8**	1.8	**0.6**	1.6
NPL	**0.1**	0.8	**-0.5**	1.7			**-0.1**	0.7	**0.2**	0.7	**0.3**	1.1	**0.0**	0.8
OMH	**0.2**	0.5	**-0.4**	1.5	**0.1**	0.7			**0.3**	0.2	**0.4**	0.9	**0.1**	0.5
PTB	**-0.1**	0.5	**-0.7**	1.5	**-0.2**	0.7	**-0.3**	0.2			**0.2**	0.9	**-0.1**	0.5
RC	**-0.2**	1.0	**-0.8**	1.8	**-0.3**	1.1	**-0.4**	0.9	**-0.2**	0.9			**-0.3**	1.0
VNIIM	**0.1**	0.7	**-0.6**	1.6	**0.0**	0.8	**-0.1**	0.5	**0.1**	0.5	**0.3**	1.0		

Figure 1. Graph of degrees of equivalence with the KCRV for ^{169}Yb
(as it appears in Appendix B of the MRA)



Appendix 1. Uncertainty budgets for the activity of ^{169}Yb submitted to the SIR

No uncertainty budgets have been submitted for the BIPM comparison.

The uncertainty budgets for the EUROMET comparison are given in [14]

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 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

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

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

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

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

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

Then the total combined uncertainty becomes

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

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

or, after recombination

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

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

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

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

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

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

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

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.

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

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

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

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

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

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
		high efficiency	HE
		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(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