Update of the BIPM comparison BIPM.RI(II)-K1.Ba-133 of activity measurements of the radionuclide ^{133}Ba to include the 2009 result of the IRA (Switzerland) and the 2012 results of the LNE-LNHB (France) and BEV (Austria)

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Abstract

Since 2009, 3 national metrology institutes (NMI) have submitted 3 samples of known activity of ^{133}Ba 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.Ba-133, to update their earlier result dating more than 15 years ago. The values of the activity submitted were between about 2 MBq and 3 MBq. There are now nine results in the BIPM.RI(II)-K1.Ba-133 comparison. 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 table. A graphical presentation is also given.

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 with 3.6 g of the radioactive solution. For radioactive gases, a different standard ampoule is used. Each NMI completes a submission form that details the standardization method used to determine the absolute activity of the radionuclide and the full uncertainty budget for the evaluation. The ampoules are sent to the BIPM where they are compared with standard sources of ^{226}Ra using pressurized ionization chambers. Details of the SIR method, experimental set-up and the determination of the equivalent activity, A_e, are all given in [1].

From its inception until 31 December 2013, the SIR has measured 973 ampoules to give 728 independent results for 67 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 standardizations. These comparisons are described as BIPM ongoing comparisons and the results form the basis of the BIPM key comparison database (KCDB) of the Comité International des Poids et Mesures Mutual Recognition Arrangement (CIPM MRA) [2]. The comparison described in this report is known as the BIPM.RI(II)-K1.Ba-133 key comparison. The results of earlier participations in this key comparison were published previously [3, 4].

2. Recent participants

The IRA, LNE-LNHB and BEV have submitted ampoules for inclusion in this comparison, which replace their earlier SIR submissions. The laboratory details are given in Table 1, with the earlier submissions being taken from [4]. 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 dates of measurement in the SIR given in Table 1 are used in the KCDB and all references in this report.

Table 1. Details of the participants in the BIPM.RI(II)-K1.Ba-133

Original acronym	**NMI**	**Full name**	**Country**	**Regional metrology organization**	**Date of measurement at the BIPM** YYYY-MM-DD
LMRI	LNE-LNHB	Laboratoire national de métrologie et d'essai -Laboratoire national Henri Becquerel	France	EURAMET	1979-11-07 2012-03-07
–	BEV	Bundesamt für Eich- und Vermessungswesen	Austria	EURAMET	1998-06-25 2012-06-12
	IRA	Institut de Radiophysique Appliquée	Switzerland	EURAMET	2009-04-15

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 appropriate correlations are taken into account.

A brief description of the standardization methods used by the laboratories, the activities submitted, the relative standard uncertainties (k = 1) and the half-life used by the participants are given in Table 2. The SIR uncertainty budgets are given in Appendix 1 attached to this report. The list of acronyms used to summarize the methods is given in Appendix 2.

The half-life used by the BIPM is 3835(37) d [5].

Table 2. Standardization methods of the participants for ^{133}Ba

NMI	Method used and acronym (see Appendix 2)	Half-life / d	Activity A_i / kBq	Reference date YYYY-MM-DD	Relative standard uncertainty / 10^{-2} by method of evaluation A	B
LNE-LNHB	4π(NaI(Tl))γ 4P-NA-GR-00-00-HE	3835(37)	4083 4067[†]	1979-04-11 0 h UTC	0.01	0.14
		3850(2)	2983	2011-10-01 12 h UTC	0.13	0.42
BEV	Pressurized IC[a]	3848	767	1998-06-01 0 h UTC	0.28	0.66
		3849.65	2698	2011-11-01	0.02	0.67
IRA	Pressurized IC 4P-IC-GR-00-00-00 calibrated in 1984 by 4π(PC)β-γ coincidence 4P-PC-BP-NA-GR-CO	3850(2)	2178	2008-09-01 0 h UTC	0.02	0.20

[†] two ampoules submitted
[a] calibrated by the NPL.

Details regarding the solutions 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. The BIPM standard method for evaluating the activity of impurities using a calibrated Ge(Li) spectrometer is described in [6]. The CCRI(II) agreed in 1999 [7] that this method should be followed according to the protocol described in [8] when an NMI makes such a request or when there appear to be discrepancies. However, no such impurity measurement has needed to be carried out at the BIPM for the three latest ^{133}Ba submissions.

Table 3. Details of each solution of ^{133}Ba submitted

NMI / SIR year	Chemical composition	Solvent conc. / (mol dm^{-3})	Carrier: conc. /(µg g^{-1})	Density /(g cm^{-3})	Relative activity of any impurity†
LNE-LNHB 1979	$BaCl_2$ in HCl	1	$BaCl_2$: 15	1.02	< 10^{-4} %
2012	$BaCl_2$•$2H_2O$ in HCl	1	[Ba] = 22[a] or 73[b]	1.016	–
BEV 1998	$BaCl_2$ in HCl	0.1	$BaCl_2$: 30	1.0	–
2012	$BaCl_2$ in HCl	0.1	$BaCl_2$: 30	1.0	^{134}Cs: 4.36(15) × 10^{-5}
IRA 2009	$BaCl_2$ in HCl	1	$BaCl_2$: 60	1.0163	^{134}Cs: 1.033(9) × 10^{-3} ^{137}Cs: 3.168(47) × 10^{-4}

† the ratio of the activity of the impurity to the activity of ^{133}Ba, at the reference date
[a] from the solution provider
[b] measured by ICP-AES; probable release of Ba from the glassware

4. Results

All the submissions to the SIR since its inception in 1976 are maintained in a database known as the "master-file". The recent submissions have added three ampoules for the activity measurements for ^{133}Ba giving rise to 41 ampoules in total. The SIR equivalent activity, A_{ei}, for each ampoule is given in Table 4 for each NMI, *i*. 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 submitted activities are compared with a given source of ^{226}Ra, all the SIR results are normalized to the radium source number 5 [1].

The three new results from IRA, LNE-LNHB and BEV agree within standard uncertainty with their earlier SIR result or linked result from the 1984 CCRI(II)-K2.Ba-133 comparison [3].

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.

The APMP.RI(II)-K2.Ba-133 comparison has been held in 2006. The results of seven participants were linked to the BIPM.RI(II)-K1.Ba-133 comparison through the measurement in the SIR of one ampoule of the APMP comparison, as explained in [9].

Table 4. Results of SIR measurements of ^{133}Ba

NMI / SIR year	Mass of solution m_i / g	Activity submitted A_i / kBq	N° of Ra source used	SIR $A_{e,i}$ / kBq	Relative uncertainty from SIR	Combined uncertainty $u_{c,i}$ / kBq
LNE-LNHB 1979	3.688 61 3.673 46	4083 4067	3	43 926 43 930	9×10^{-4}	72 72
2012	3.770 9	2983	3	43 880	8×10^{-4}	190
BEV 1998	3.633	767	1	43 670	13×10^{-4}	320
2012	3.591 10	2698	3	44 060	9×10^{-4}	300
IRA 2009	3.650 81(9)	2178	2	43 920	12×10^{-4}	100

4.1 The key comparison reference value

In May 2013 the CCRI(II) decided to no longer calculate the key comparison reference value (KCRV) by using an unweighted mean but rather by using the power-moderated weighted mean [10]. This type of weighted mean is similar to a Mandel-Paule mean in that the NMIs' uncertainties may be increased until the reduced chi-squared value is one. In addition, it allows for a power smaller than two in the weighting factor. Therefore, all SIR key comparison results can be selected for the KCRV with the following provisions:

a) only results for solutions standardized by primary techniques are accepted, with the exception of radioactive gas standards (for which results from transfer instrument measurements that are directly traceable to a primary measurement in the laboratory may be included);
b) each NMI or other laboratory has only one result (normally the most recent result or the mean if more than one ampoule is submitted);
c) possible outliers can be identified on a mathematical basis and excluded from the KCRV using the normalized error test with a test value of 2.5 and using the modified uncertainties;
d) results can also be excluded for technical reasons.
e) The CCRI(II) is always the final arbiter regarding excluding any data from the calculation of the KCRV.

The data set used for the evaluation of the KCRVs is known as the "KCRV file" and is a reduced data set from the SIR master-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 made only by the CCRI(II) during one of its biennial meetings as for the case of ^{133}Ba in May 2013, or by consensus through electronic means (e.g., email) as discussed at the CCRI(II) meeting in 2013.

The recent IRA and BEV results are based on IC measurements and are thus not eligible for the KCRV. Consequently, using the LNE-LNHB recent result produces an updated KCRV for ^{133}Ba of 43.906(55) MBq that has been calculated by using the previously published results [4] from the PTB(1978), ANSTO, ASMW(1978), AECL, CMI-IIR(1980), NPL, BIPM, VNIIM, KRISS, LNMRI, MKEH(1996), CNEA, NIST(1998), IFIN-HH, NMIJ(2006) and the LNE-LNHB (2012). This can be compared with the previous KCRV value of 43.932(67) MBq published in 2007 [4] and the value of 44.04(13) MBq obtained using the SIRIC efficiency curve of the SIR [11].

4.2 Degrees of equivalence

Every participant in a comparison is entitled to have one result included in the KCDB as long as the NMI is a signatory or designated institute listed in the CIPM MRA, and the result is valid (i.e., not older than 20 years). Normally, the most recent result is the one included. An NMI may withdraw its result only if all other participants agree.

The degree of equivalence of a given measurement standard is the degree to which this standard is consistent with the KCRV [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 result with the KCRV*

The degree of equivalence of the result of a particular NMI, i, with the key comparison reference value is expressed as the difference D_i between the values

$$D_i = A_{\mathrm{e}\,i} - \mathrm{KCRV} \qquad (1)$$

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

$$U_i = 2u(D_i)\,. \qquad (2)$$

When the result of the NMI i is included in the KCRV with a weight w_i, then

$$u^2(D_i) = (1\text{-}2w_i)\, u_i^2 + u^2(\mathrm{KCRV})\,. \qquad (3)$$

However, when the result of the NMI i is not included in the KCRV, then

$$u^2(D_i) = u_i^2 + u^2(\mathrm{KCRV}). \qquad (4)$$

4.2.2 *Comparison between pairs of NMI results*

The degree of equivalence between the results of any pair of NMIs, i and j, is expressed as the difference D_{ij} in the values

$$D_{ij} = D_i - D_j = A_{\mathrm{e}\,i} - A_{\mathrm{e}\,j} \qquad (5)$$

and the expanded uncertainty (k = 2) of this difference, $U_{ij} = 2u(D_{ij})$, where

$$u_{D_{ij}}^{\ 2} = u_i^{\ 2} + u_j^{\ 2} - 2u(A_{\mathrm{e},i}, A_{\mathrm{e},j}) \qquad (6)$$

where any obvious correlations between the NMIs (such as a traceable calibration, or correlations normally coming from the SIR or from the linking factor in the case of linked comparison) are subtracted using the covariance $u(A_{\mathrm{e}i}, A_{\mathrm{e}j})$ (see [12] for more detail). However, the CCRI decided in 2011 that these “pair-wise degrees of equivalence” no longer need to be published as long as the methodology is explained.

Table 5 shows the matrix of all the degrees of equivalence as they will appear in 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 results in Table 5, corresponding to the degrees of equivalence with respect to the KCRV (identified as x_{R} in the KCDB), is shown in Figure 1. This graphical representation indicates in part the degree of equivalence between the NMIs but obviously does not take into account the correlations between the different NMIs.

The results of six NMIs who participated in the 1984 CCRI(II)-K2.Ba-133 comparison were withdrawn from the KCDB.

It should be noted that the final data in this paper, while correct at the time of publication, will become out-of-date as NMIs make new comparisons. The formal results under the CIPM MRA [2] are those available in the KCDB.

Conclusion

The BIPM ongoing key comparison for ^{133}Ba, BIPM.RI(II)-K1.Ba-133 currently comprises nine results, including the three new results that replace earlier results in the KCDB.

The SIR results, together with the previously published APMP.RI(II)-K2.Ba-133 results, have been analysed with respect to the updated KCRV determined for this radionuclide, providing degrees of equivalence for sixteen national metrology institutes. The degrees of equivalence have been approved by the CCRI(II) and are published in the BIPM key comparison database. Other results may be added when other NMIs contribute ^{133}Ba activity measurements to this comparison or take part in other linked comparisons.

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Table 5. Introductory text for ^{133}Ba and table of degrees of equivalence

Key comparison BIPM.RI(II)-K1.Ba-133

MEASURAND : **Equivalent activity of ^{133}Ba**

Key comparison reference value: the SIR reference value for this radionuclide is x_R = 43 906 kBq
with a standard uncertainty, u_R = 55 kBq (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
$U_i = 2((1 - 2w_i)u_i^2 + u_R^2)^{1/2}$ when each laboratory has contributed to the calculation of x_R with a weight w_i.

When required, 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 $U_{ij} \sim 2(u_i^2 + u_j^2)^{1/2}$ may be used.

Linking APMP.RI(II)-K2.Ba-133 (2006) to BIPM.RI(II)-K1.Ba-133

The value x_i is the equivalent activity for laboratory *i* participant in APMP.RI(II)-K2.Ba-133
having been normalized through the NMIJ as linking laboratory (see Section 5 of the Final report).

The degree of equivalence of laboratory *i* participant in APMP.RI(II)-K2.Ba-133 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.

Table 5 continued

When required, the degree of equivalence between two laboratories *i* and *j*, one participant in BIPM.RI(II)-K1.Ba-133 and one in APMP.RI(II)-K2.Ba-133, or both participant in APMP.RI(II)-K2.Ba-133, 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.

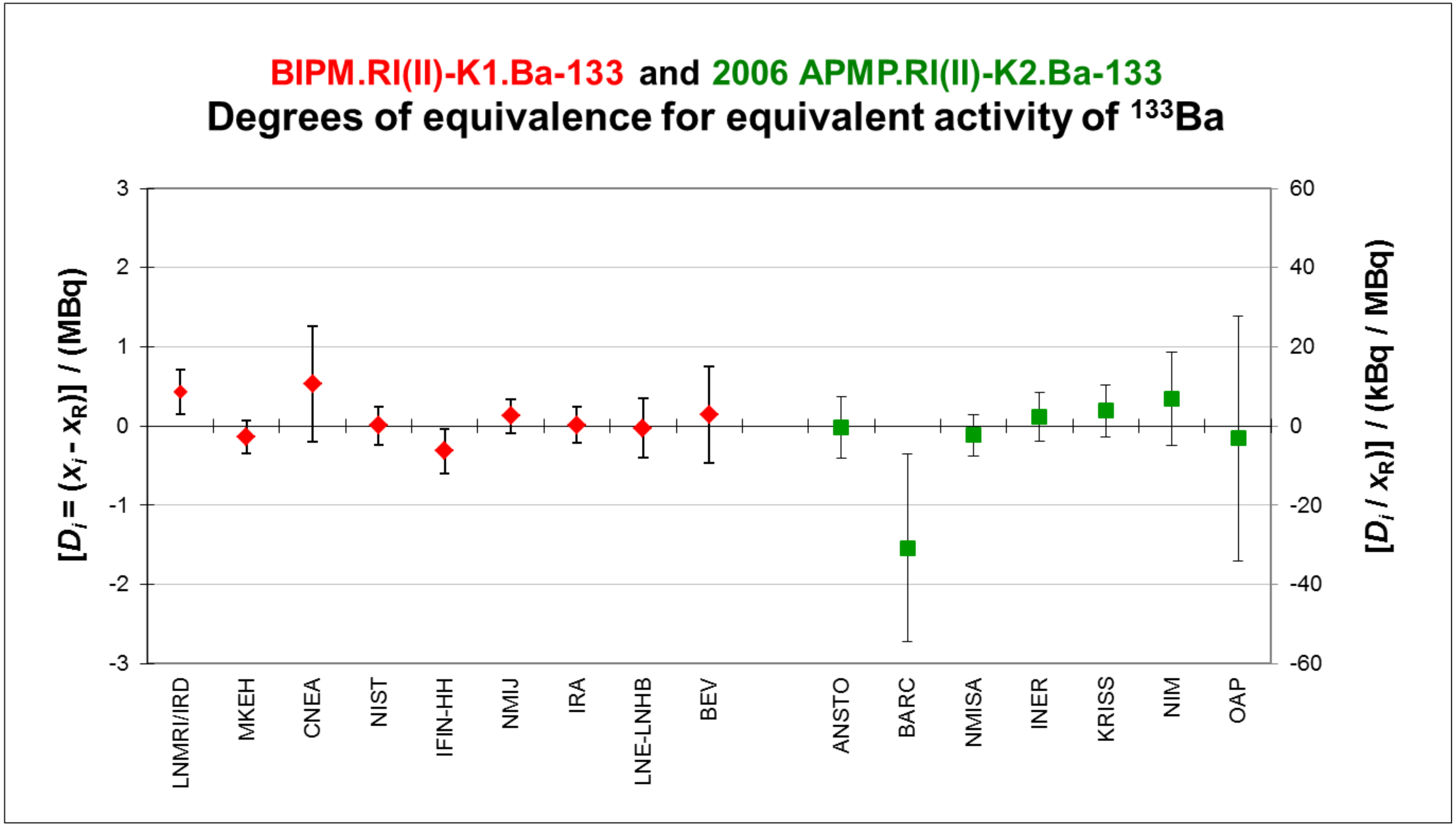
These statements make it possible to extend the BIPM.RI(II)-K1.Ba-133 matrices of equivalence to the other participants in APMP.RI(II)-K2.Ba-133.

Lab *i*	D_i / MBq	U_i / MBq
LNMRI	**0.43**	0.28
MKEH	**-0.13**	0.21
CNEA	**0.53**	0.73
NIST	**0.00**	0.25
IFIN-HH	**-0.32**	0.28
NMIJ	**0.12**	0.21
IRA	**0.01**	0.23
LNE-LNHB	**-0.03**	0.38
BEV	**0.15**	0.61

ANSTO	**-0.02**	0.38
BARC	**-1.54**	1.19
NMISA	**-0.12**	0.25
INER	**0.11**	0.30
KRISS	**0.19**	0.32
NIM	**0.34**	0.59
OAP	**-0.16**	1.54

Figure 1. Graph of degrees of equivalence with the KCRV for ^{133}Ba

(as it appears in Appendix B of the MRA)



N.B. The Right hand axis shows approximate values only

Appendix 1. Uncertainty budgets for the activity of ^{133}Ba submitted to the SIR

IRA(2009) – IC measurement

Relative standard uncertainties	$u_i \times 10^4$ evaluated by method		Comment
Contributions due to	**A**	**B**	
current of the reference source	1.9	–	$\nu = 20^{\dagger}$
current of the ^{133}Ba ampoule	1.0	–	$\nu = 20^{\dagger}$
background	–	0.08	from the difference in background current before and after measurements
reference source decay correction	–	2.8	
^{133}Ba decay correction	–	0.17	
reference source substitution factor*	–	7	
solution mass	–	0.23	
equivalent activity (^{133}Ba calib.)	–	19	
Quadratic summation	**2.2**	**20.4**	
Relative combined standard uncertainty, u_c	**21**		

† number of degrees of freedom
* The substitution factor is the multiplicative correction factor of the given reference source current to obtain the main reference source current

LNE-LNHB(2012) – 4π gamma counting

Relative standard uncertainties	$u_i \times 10^4$ evaluated by method		Comment
Contributions due to	**A**	**B**	
counting statistics	8	–	standard deviation of the mean of 9 sources measured
weighing	–	10	gravimetric measurements using pycnometer method
dead time	–	1	live-time technique
background	10	–	from counting statistics
decay correction	–	–	negligible
detection efficiency	–	40	Monte-Carlo Geant4 code
zero-energy extrapolation	–	5	conservative calculation
Quadratic summation	**12.8**	**41.5**	
Relative combined standard uncertainty, u_c	**43**		

BEV(2012) – IC measurement

Relative standard uncertainty contributions due to	$u_i \times 10^4$	evaluation method	Relative sensitivity factors	Comment
counting statistics	2.1	A	1.00	
weighing	0.56	B	-1.00	
background	–	–	–	included into *
impurities	0.037	B	-4.35 $\times 10^{-5}$	
^{133}Ba decay correction	0.019	B	3.28 $\times 10^{-3}$	
calibration factor	67	B	-1.00	
current measurement *	2.9	B	1.00	
ionization chamber	2.9	B	1.00	
filling height	2.9	B	1.00	
Relative combined standard uncertainty, u_c	**67**			

Appendix 2. Acronyms used to identify different measurement methods

Each acronym has six components, geometry-detector (1)-radiation (1)-detector (2)-radiation (2)-mode. When a component is unknown, ?? is used and when it is not applicable 00 is used.

Geometry	acronym	Detector	acronym
4π	4P	proportional counter	PC
defined solid angle	SA	press. prop counter	PP
2π	2P	liquid scintillation counting	LS
undefined solid angle	UA	NaI(Tl)	NA
		Ge(HP)	GH
		Ge(Li)	GL
		Si(Li)	SL
		CsI(Tl)	CS
		ionization chamber	IC
		grid ionization chamber	GC
		bolometer	BO
		calorimeter	CA
		PIPS detector	PS
Radiation	**acronym**	**Mode**	**acronym**
positron	PO	efficiency tracing	ET
beta particle	BP	internal gas counting	IG
Auger electron	AE	CIEMAT/NIST	CN
conversion electron	CE	sum counting	SC
mixed electrons	ME	coincidence	CO
bremsstrahlung	BS	anti-coincidence	AC
gamma rays	GR	coincidence counting with efficiency tracing	CT
X - rays	XR	anti-coincidence counting with efficiency tracing	AT
photons (x + γ)	PH	triple-to-double coincidence ratio counting	TD
alpha - particle	AP	selective sampling	SS
mixture of various radiation	MX	high efficiency	HE

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-HE
calibrated IC	4P-IC-GR-00-00-00
internal gas counting	4P-PC-BP-00-00-IG