Update of the BIPM comparison BIPM.RI(II)-K1.Am-241 of activity measurements of the radionuclide ^{241}Am to include the 2009 results of the POLATOM (Poland), MKEH (Hungary) and the 2011 results of the LNE-LNHB (France)

C. Michotte*, G. Ratel* and S. Courte*, T. Dziel#, A. Listkowska#,
I. Csete§, K. Rózsa§, L. Szücs§, A. Zsinka§, C. Fréchou**, C. Bobin**, S. Pierre**

*BIPM, #POLATOM, §MKEH, **LNE-LNHB

Abstract

Since 2009, 3 national metrology institutes (NMI) have submitted 3 samples of known activity of ^{241}Am 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.Am-241. The values of the activity submitted were between about 3 MBq and 38 MBq. These 3 results replace their earlier results obtained in the linked CCRI(II)-K2.Am-241 in 2003. There are now five results in the BIPM.RI(II)-K1.Am-241 comparison, 16 results remaining from the CCRI(II)-K2.Am-241 comparison and 2 results in the COOMET.RI(II)-K2.Am-241 comparison. The degrees of equivalence between each equivalent activity measured in the SIR and the KCRV dating 2007 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 2016, the SIR has measured 998 ampoules to give 753 independent results for 68 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 CIPM Mutual Recognition Arrangement (CIPM MRA) [2]. The comparison described in this report is known as the BIPM.RI(II)-K1.Am-241 key comparison. The results of earlier participations in this key comparison were published previously [3, 4].

2. Last participants

The ampoules submitted by the POLATOM and the MKEH in 2009 and by the LNE-LNHB in 2011 replace their earlier participation in the CCRI(II)-K2.Am-241 comparison. One other laboratory participated but ultimately was allowed to withdraw its result because the activity of the solution received by the BIPM was much too small. The laboratory details are given in Table 1, with the earlier submissions from the same laboratories 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 date of measurement in the SIR is also given in Table 1 and is used in the KCDB and all references in this report.

Table 1. Details of the participants in the BIPM.RI(II)-K1.Am-241

Original acronym	**NMI**	**Full name**	**Country**	**Regional metrology organization**	**Date of measurement at the BIPM**
OMH	MKEH[1]	Magyar Kereskedelmi Engedéyezési Hivatal/Hungarian Trade Licensing Office	Hungary	EUROMET	1977-03-14 1979-12-13 2009-02-25
–	POLATOM	Institute of Atomic Energy, Radioisotope Centre POLATOM	Poland	EURAMET	2009-01-28
–	LNE-LNHB	Laboratoire national de métrologie et d'essais - Laboratoire national Henri Becquerel	France	EURAMET	2011-05-05

[1] Now called BKFH

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 to date is 158 150 (730) d [5] which is in agreement with 158 004 (219) d, the evaluated value published in the Monographie 5 [6] and with that recommended by the IAEA, 157 850 (240) d [7] used in the CCRI(II) and the COOMET comparisons. Nevertheless, in view of the long half-life of ^{241}Am, the SIR results and uncertainties do not depend on which of these the half-life values is used in the calculation.

Table 2. Standardization methods of the participants for ^{241}Am

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
MKEH	4πα–γ coincidence 4P-PC-AP-NA-GR-CO	158 100 (700)	8 116 8 111	1977-03-01 12 h UT	0.14	0.30
		157 860 (180)	14 831	1979-10-01 12 h UT	0.04	0.11
		158 004 (219) [6]	37 639	2009-03-01 0 h UT	0.05	0.17
POLATOM	4π(LS)–γ coinc. and anticoinc. 4P-LS-AP-NA-GR-CO 4P-LS-AP-NA-GR-AC	158 004 (219) [6]	16 316	2009-01-01 11h UT	0.21	0.53
LNE-LNHB	4πα(PC)–γ anticoinc. 4P-PC-AP-NA-GR-AC	158 004 (219) [6]	3 389.5	2011-04-01 12h UT	0.05	0.14
	Defined solid angle counting SA-PS-AP-00-00-00		3 390		0.3	0.2

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 [8]. The CCRI(II) agreed in 1999 [9] that this method should be followed according to the protocol described in [10] when an NMI makes such a request or when there appear to be discrepancies. No impurity was detected in the MKEH (2009) solution using the HPGe detector of the BIPM. No such impurity measurement was carried out at the BIPM for the POLATOM(2009) and LNE-LNHB(2011) ^{241}Am solutions.

Table 3. Details of each solution of ^{241}Am 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†
MKEH 1977	^{241}Am + Eu in HNO_3	3	Eu : 20	1.098	–
1979			Eu : 25	1.098	–
2009	^{241}Am in HNO_3	1	–	1.03	–
POLATOM 2009	^{241}Am + $LaCl_3$ in HCl	1	$LaCl_3$: 88.3	1.016	< 0.1 %
LNE-LNHB 2011	^{241}Am + $Eu(NO_3)_3 \cdot 5H_2O$ in HNO_3	1	Eu: 10	1.032	^{244}Cm: $5.00(25) \times 10^{-3}$ %

† the ratio of the activity of the impurity to the activity of ^{241}Am, 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 "master-file". The last submissions have added three ampoules for the activity measurements for ^{241}Am giving rise to 16 ampoules in total. The SIR equivalent activity, A_{ei}, for each ampoule from MKEH, POLATOM and LNE-LNHB 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 correction factor for density ρ applied to all the ^{241}Am results is based on a study of A. Rytz in 1978 (see [3]) and is evaluated as $[1 - 4\times10^{-3}(\rho - 1)/0.1]$.

Table 4. Results of SIR measurements of ^{241}Am

NMI / SIR year	Mass of solution m_i / g	Activity submitted A_i / kBq	N° of Ra source used	SIR $A_{e,i}$ / kBq Original value	SIR $A_{e,i}$ / kBq Corrected for density	Relative uncertainty from SIR	Combined uncertainty $u_{c,i}$ / MBq
MKEH 1977	3.604 0 3.601 7	8 116 8 111	1	2069.4 2070.4	2061.1 2062.1	17×10^{-4} 17×10^{-4}	7.8
1979	3.603 2	14 831	1	2053.8	2045.6	17×10^{-4}	4.2
2009	3.6167	37 639	2	2040.4	2038.0	11×10^{-4}	4.3
POLATOM 2009	3.431 39	16 316	1	2061.1	2059.8	13×10^{-4}	12
LNE-LNHB 2011	3.787 1	3 389.5 3 390	1	2045.3 2045.3	2042.7# 2042.7	24×10^{-4}##	5.8# 8.8

result selected by the LNE-LNHB to be used for the KCRV and the degrees of equivalence
uncertainty increased to take account of the uncertainty of the SIR background current

Measurements repeated at the BIPM after periods of up to seven year later for the MKEH (2009) produced comparison results in agreement within two combined standard uncertainties. Measurements repeated at the BIPM after periods of up to four days later for the LNE-LNHB produced comparison results in agreement within standard uncertainty.

The results of POLATOM agrees within standard uncertainty with its earlier result from the linked CCRI(II)-K2.Am-241 comparison.

The results of the MKEH (2009) and the LNE-LNHB do not agree with their earlier result from the linked CCRI(II)-K2.Am-241 comparison. In the case of LNE-LNHB, it should be noted that the influence of the ^{244}Cm impurity present in the 2011 solution is negligible. In addition, the activity of the solution sent to the BIPM is less than the recommended limit for the SIR (11 MBq) and the subsequent ionization current produced in the ionization chamber is only about 0.6 pA. Consequently the uncertainty of the SIR measurement was increased to take account of the uncertainty of the SIR background current, which is usually considered as negligible.

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 links of the earlier CCRI(II)-K2.Am-241 and COOMET.RI(II)-K2.Am-241 comparisons were published in a previous report [4].

4.1 The key comparison reference value

Although the KCRV may be modified when other NMIs participate, on the advice of the Key Comparison Working Group (KCWG) of the CCRI(II), such modifications are made only by the CCRI(II) during one of its biennial meetings as for the case of ^{241}Am in May 2007, or by consensus through electronic means (e.g., email) as discussed at the CCRI(II) meeting in 2013.

In the present case, because of the unexpected spread in the SIR results, the KCWG is investigating the issue and proposed to postpone the update of the KCRV for ^{241}Am. Consequently the KCRV of 2055.8(2.8) MBq, as previously published in [4], is used.

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

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

taking correlations into account as appropriate [12].

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

$$u_{D_{ij}}{}^2 = u_i{}^2 + u_j{}^2 - 2u(A_{ei}, A_{ej}) \quad (6)$$

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 $u(A_{ei}, A_{ej})$ (see [11] 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. 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 ^{241}Am, BIPM.RI(II)-K1.Am-241 currently comprises five results, including the three new results that replace one earlier result in the KCDB.

The results have been analysed with respect to the KCRV determined for this radionuclide in 2007, providing degrees of equivalence for the five national metrology institutes, and for the remaining 18 NMIs or international laboratory through the linked CCRI(II)-K2.Am-241 and COOMET.RI(II)-K2.Am-241 comparisons in 2003 and 2006, respectively. 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 ^{241}Am activity measurements to this comparison or take part in other linked comparisons.

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Table 5. Introductory text for ^{241}Am and table of degrees of equivalence

Key comparison BIPM.RI(II)-K1.Am-241

MEASURAND : **Equivalent activity of ^{241}Am**

Key comparison reference value: the SIR reference value x_R for this radionuclide is 2055.8 MBq, with a standard uncertainty, u_R = 2.8 MBq (see section 4.1 of the Report).

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.

Linking CCRI(II)-K2.Am-241 to BIPM.RI(II)-K1.Am-241

The value x_i is the equivalent activity for laboratory i participant in CCRI(II)-K2.Am-241 having been normalized using the SIR measurement of the NPL undiluted solution of the CCRI(II)-K2 comparison.

The degree of equivalence of laboratory i participant in CCRI(II)-K2. 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 as none of these laboratories contributed to the KCRV.

Linking COOMET.RI(II)-K2.Am-241 to BIPM.RI(II)-K1.Am-241

The value x_i is the equivalent activity for laboratory i participant in COOMET.RI(II)-K2.Am-241 having been normalized using the SIR measurement of the VNIIM solution of the COOMET.RI(II)-K2 comparison.

The degree of equivalence of laboratory *i* participant in COOMET.RI(II)-K2. 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 $U_i = 2(u_i^2 + u_{\mathrm{R}}^2)^{1/2}$ is used in the following table as these laboratories did not contribute to the KCRV.

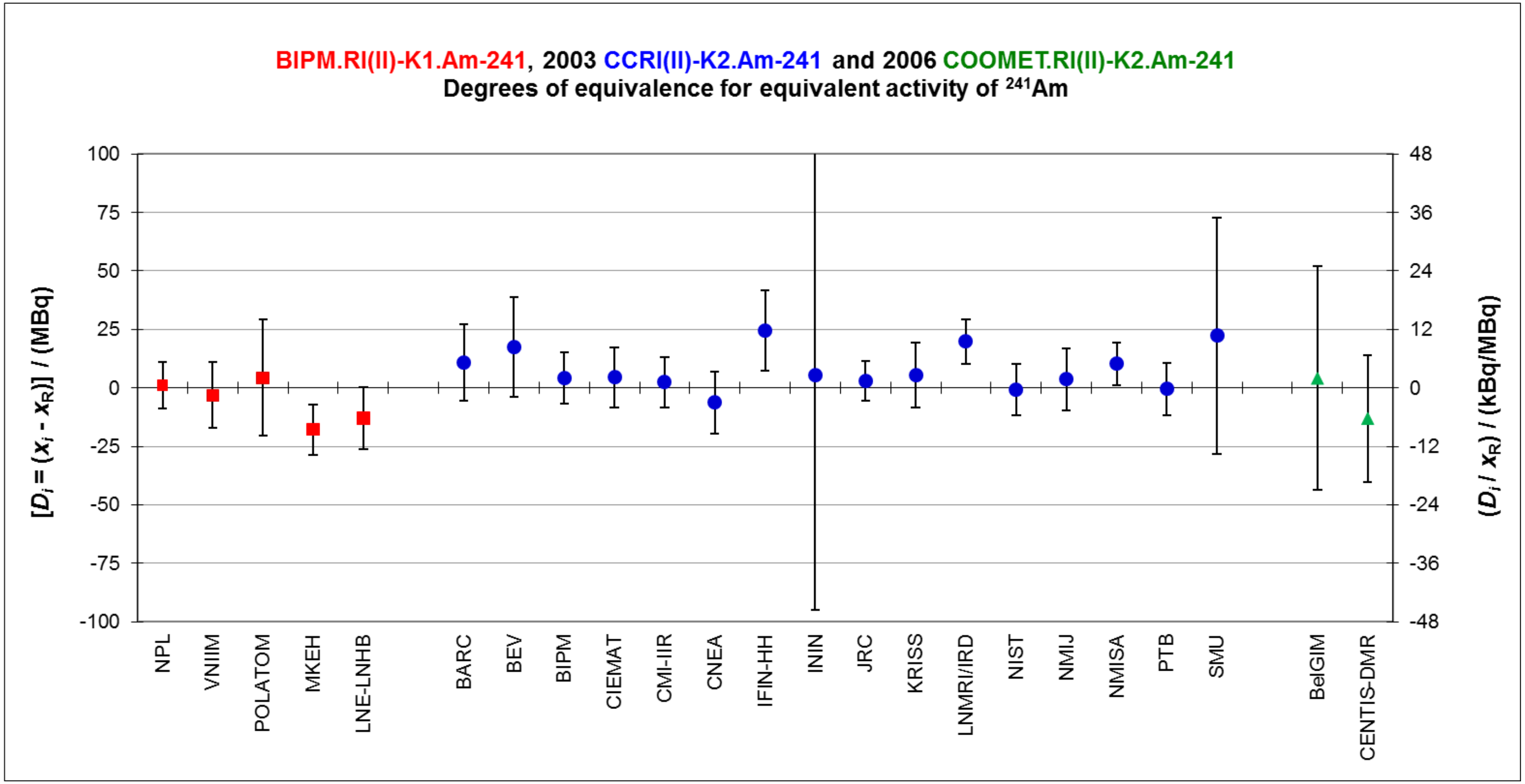
These statements make it possible to extend the BIPM.RI(II)-K1.Am-241 matrices of equivalence to all participants in the CCRI(II)-K2.Am-241 and the COOMET.RI(II)-K2.Am-241 comparisons.

Table 5. Continued

Lab *i* ⇩

	D_i	U_i
	/ MBq	
NPL	**1**	10
VNIIM	**-3**	14
POLATOM	**4**	25
MKEH	**-18**	11
LNE-LNHB	**-13**	13
BARC	**11**	16
BEV	**17**	21
BIPM	**4**	11
CIEMAT	**5**	13
CMI-IIR	**2**	11
CNEA	**-6**	13
IFIN-HH	**24**	17
ININ	**5**	101
JRC	**3**	9
KRISS	**5**	14
LNMRI/IRD	**20**	10
NIST	**-1**	11
NMIJ	**4**	13
NMISA	**10**	9
PTB	**-1**	11
SMU	**22**	51
BelGIM	**4**	48
CENTIS-DMR	**-13**	27

Figure 1. **Graph of degrees of equivalence with the KCRV for ^{241}Am**
(as it appears in Appendix B of the MRA**)**



N.B. The right hand scale is indicative only.

Appendix 1. Uncertainty budgets for the activity of ^{241}Am submitted to the SIR

POLATOM

Relative standard uncertainties	$u_{rel,i} \times 10^4$ evaluated by method	
Contributions due to	**A**	**B**
counting statistics	21	-
weighing	-	16
dead time	-	1
counting time	-	1
anticoincidence gate	-	1
half-life	-	1
extrapolation	-	50
Quadratic summation	**21**	**53**
Relative combined standard uncertainty, u_c	**57**	

MKEH (2009)

Relative standard uncertainties	$u_{rel,i} \times 10^4$ evaluated by method	
Contributions due to	**A**	**B**
counting statistics	4.6	-
weighing	-	5
dead time	-	0.5
resolving time	-	3
delay mismatch	-	5
background	-	< 0.1
counting time	-	0.5
half-life	-	< 0.5
extrapolation	-	15
adsorption	-	< 2
impurities	-	< 0.1
Quadratic summation	**4.6**	**17**
Relative combined standard uncertainty, u_c	**18**	

LNE-LNHB (2011) – anticoincidence method

Relative standard uncertainties	$u_{rel,i} \times 10^4$ evaluated by method	
Contributions due to	**A**	**B**
counting statistics	-	10
weighing	-	10
dead time (live-time technique)	-	1
background	5	-
half-life	-	1
Quadratic summation	**5**	**14**
Relative combined standard uncertainty, u_c	**15**	

LNE-LNHB (2011) – defined solid angle counting

Relative standard uncertainties	$u_{rel,i} \times 10^4$ evaluated by method	
Contributions due to	**A**	**B**
counting statistics (including background)	30	-
weighing	-	10
counting time	-	5
geometry factor and retrodiffusion	-	14
half-life	-	negl.
extrapolation of efficiency curve	-	2
Quadratic summation	**30**	**18**
Relative combined standard uncertainty, u_c	**35**	

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
		Cerenkov light detector	CD
		calorimeter	CA
		solid plastic scintillator	SP
		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