Update of the comparison BIPM.RI(II)-K1.Co-56 of activity measurements of the radionuclide ^{56}Co to include the result of the CMI-IIR

C. Michotte, S. Courte, G. Ratel, J. Sochorová[1]

BIPM, [1]CMI-IIR (Czech Republic)

Abstract

In 2006, the Český Metrologický Institut/Czech Metrological Institute - Inspectorate for Ionizing Radiation (CMI-IIR) submitted an ampoule of known activity of ^{56}Co to the International Reference System (SIR) for activity comparison at the Bureau International des Poids et Mesures. The activity was about 6.7 MBq. The degrees of equivalence between each of the four national metrology institute results now measured in the SIR and the re-evaluated key comparison reference value (KCRV) have been calculated and the results are given in the form of a matrix. A graphical presentation is also given. The comparison identifier is BIPM.RI(II)-K1.Co-56.

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, the SIR has measured over 931 ampoules to give 686 independent results for 64 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 CIPM Mutual Recognition Arrangement (CIPM MRA) [2]. The comparison described in this report is known as the BIPM.RI(II)-K1.Co-56 key comparison and the earlier results have been published in [3].

2. Participants

Four NMIs have now submitted seven ampoules for the comparison of ^{56}Co activity measurements since 1980, the most recent being that of the CMI-IIR in 2006. The laboratory details are given in Table 1. In cases where the laboratory has changed its name since the original submission, both the earlier and the current acronyms are given, as it is the latter that are used in the KCDB.

Table 1. Details of the participants in the BIPM.RI(II)-K1.Co-56

Original acronym	NMI	Full name	Country	Regional metrology organization	Date of measurement at the BIPM
LMRI LPRI BNM-LNHB	LNE-LNHB	Laboratoire national de métrologie et essais -Laboratoire national Henri Becquerel	France	EURAMET	1980-02-04 1998-03-10 and 1998-05-07
–	NPL	National Physical Laboratory	United Kingdom	EURAMET	1991-04-05
–	PTB	Physikalisch-Technische Bundesanstalt	Germany	EURAMET	1995-12-12
–	CMI-IIR	Český Metrologický Institut - Inspectorate for Ionizing Radiation	Czech Republic	EURAMET	2006-04-05

3. NMI standardization methods

Each NMI that submits ampoules to the SIR has measured the activity either by a primary standardization method or by using a secondary method, for example a calibrated ionization chamber. In the latter case, the traceability of the calibration needs to be clearly identified to ensure that any correlations are taken into account.

A brief description of the standardization methods for each laboratory, the activities submitted and the relative standard uncertainties (k = 1) are given in Table 2. The uncertainty budget of the CMI-IIR is given in Appendix 1.

The newly evaluated half-life used by the BIPM is 77.236 (26) days [4] and all the previous results have been re-evaluated to take this updated half-life into account. The previous half-life used was 77.31 (19) days [5].

Table 2. Standardization methods of the participants for ^{56}Co

NMI	Method used	Half-life / d	Activity / kBq	Reference date YYYY-MM-DD	Relative standard uncertainty × 100	
					Type A	Type B
LNE-LNHB	4πx-γ coincidence 4P-PP-MX-NA-GR-CO	77.31 (19) [5]	3082.4# 3078.2	1979-12-06	0.035	0.082
	4πβ-γ coincidence 4P-PP-MX-NA-GR-CO and 4πγ well-type counting 4P-NA-GR-00-00-HE		4831# 4876	1997-12-25 12h UT	0.15	–
NPL	High pressure ionization chamber* 4P-IC-GR-00-00-00	–	95.64	1991-03-15 12h UT	0.03	0.60
PTB	High pressure ionization chamber** 4P-IC-GR-00-00-00	–	8730	1995-11-01	0.04	0.41
CMI-IIR	4πβ(PC)-γ 4P-PC-BP-NA-GR-CO	77.236 (26) d [4]	6708	2006-03-30 10 h UT	0.10	0.54

* calibrated by absolute standardization for the nuclide considered

** calibrated by means of 4πβ(PPC)-γ coincidence (4P-PP-BP-NA-GR-CO) and 4π (NaI)-γ-counting (4P-NA-GR-00-00-HE)

two ampoules submitted

Details regarding the solution submitted are shown in Table 3, including any impurities, when present, as identified by the laboratories. When given, the standard uncertainties on the evaluations are shown. 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. The CMI-IIR ampoule has been measured with the BIPM Ge(Li) spectrometer (see section 4).

Table 3. Details of the solution of ^{56}Co submitted

NMI	Chemical composition	Solvent conc. / (mol dm^{-3})	Carrier: conc. /(μg g^{-1})	Density /(g cm^{-3})	Relative activity of impurity†
LNE-LNHB 1980	$CoCl_2$ in HCl	0.1	$CoCl_2$: 5	0.999	^{57}Co: 1.15 (0.05) % ^{58}Co: 0.53 (0.02) %
1998		1	$CoCl_2$: 50	1.016	^{57}Co: 0.921 (0.006) % ^{58}Co: 0.42 (0.01) % ^{60}Co: 0.030 (0.002) %
NPL 1991	$CoCl_2$ in HCl	0.1	$CoCl_2$: 20	1	^{57}Co: 26.0 (0.8) % ^{58}Co: 0.39 (0.01) %
PTB 1995	$CoCl_2$ in HCl	0.1	$CoCl_2$: 50	1.00	^{57}Co: 1.10 (0.02) % ^{58}Co: 0.50 (0.01) %
CMI-IIR 2006	$CoCl_2$ in HCl	0.1	$CoCl_2$: 20	1	^{57}Co: 1.2 (0.05) % ^{58}Co: 0.65 (0.007) %

† the ratio of the activity of the impurity to the activity of ^{56}Co 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 activity measurements for ^{56}Co arise from seven 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 reproduced in Tables 3 and 4. 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].

Repeat measurements made at the BIPM after periods of up to more than one year later produced comparison results for the LNE-LNHB (1998) showing a significant increasing trend. Following the advice of the CCRI(II), measurements were made at the BIPM concerning the impurities noted by the LNE-LNHB in 1998. Slightly different impurity values were determined although in agreement within the expanded uncertainty. However, this does not reduce the trend cited above.

The SIR measurement of the CMI-IIR ampoule was repeated after a period of five months producing a comparison result in agreement within the combined standard uncertainty. The use of the impurity ratios measured at the BIPM would not change the CMI-IIR results significantly.

No submission has been identified as a pilot study so the most recent result of each NMI is eligible for Appendix B of the CIPM MRA.

No international or regional comparison for this radionuclide has been held to date so no linking data are identified.

Table 4. Results of SIR measurements of ^{56}Co

NMI	Mass of solution /g	Activity submitted/ kBq	N° of Ra source used	SIR A_e /kBq	Relative uncertainty from SIR	Total standard uncertainty u_i / kBq
LNE-LNHB 1980	3.625 07 3.620 13	3082.4 3078.2	4	5009 5008	5×10^{-4}	5 5
1998	3.654 2 3.688 4	4831 4876	4	5094 † 5093	5×10^{-4} 6×10^{-4}	8 8
NPL 1991	3.595 30	95.64	2	5076	9×10^{-4}	31
PTB 1995	3.609 98	8730	5	5063	4×10^{-4}	21
CMI-IIR 2006	3.610 24	6708	5	5029	4×10^{-4}	28

† the mean of the two A_e values is used with an averaged uncertainty, as attributed to an individual entry [9]

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:
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, 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 more recent or the mean if more than one ampoule is submitted at the same time);

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 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 only made by the CCRI(II), normally during one of its biennial meetings.

Consequently, the KCRV for ^{56}Co has been re-evaluated from 5080 (10) kBq [3] to 5066 (14) using the results from the NPL, PTB, LNE-LNHB(1998) and the CMI-IIR. It is interesting to note that the updated KCRV value is closer to the value of 5057 (23) kBq obtained using the SIRIC [10] efficiency curves of the SIR.

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 CIPM 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

$$D_i = A_{ei} - \mathrm{KCRV} \tag{1}$$

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

$$U_i = 2u_{D_i}, \tag{2}$$

taking correlations into account as appropriate [11].

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

$$u_{D_{ij}}^{\;2} = u_i^{\;2} + u_j^{\;2} - 2u(A_{e,i}, A_{e,j}) \qquad (4)$$

where any obvious correlations between the NMIs (such as a traceable calibration) are subtracted using the covariance $u(A_{ei}, A_{ej})$, 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 appear in Appendix B of the KCDB. It should be noted that for consistency within the KCDB, a simplified level of nomenclature is used with A_{ei} replaced by x_i. The introductory text is that agreed for the comparison. The graph of the first column of results in Table 5, corresponding to the degrees of equivalence with respect to the KCRV (identified as x_R in the KCDB), is shown in Figure 1. This 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 correlations into account.

Conclusion

The BIPM ongoing key comparison for ^{56}Co, BIPM.RI(II)-K1.Co-56 currently comprises four results. These have been analysed with respect to the re-evaluated 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 ^{56}Co activity measurements to this comparison.

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Table 5. Table of degrees of equivalence and introductory text for ^{56}Co

Key comparison BIPM.RI(II)-K1.Co-56

MEASURAND : **Equivalent activity of ^{56}Co**

Key comparison reference value: the SIR reference value for this radionuclide is x_R = 5066 kBq,
with a standard uncertainty u_R = 14 kBq.
x_R is computed as the mean of the participants' results.

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 kBq, with n the number of laboratories,
$U_i = 2((1-2/n)u_i^2 + (1/n^2)\Sigma u_i^2)^{1/2}$.

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 kBq.

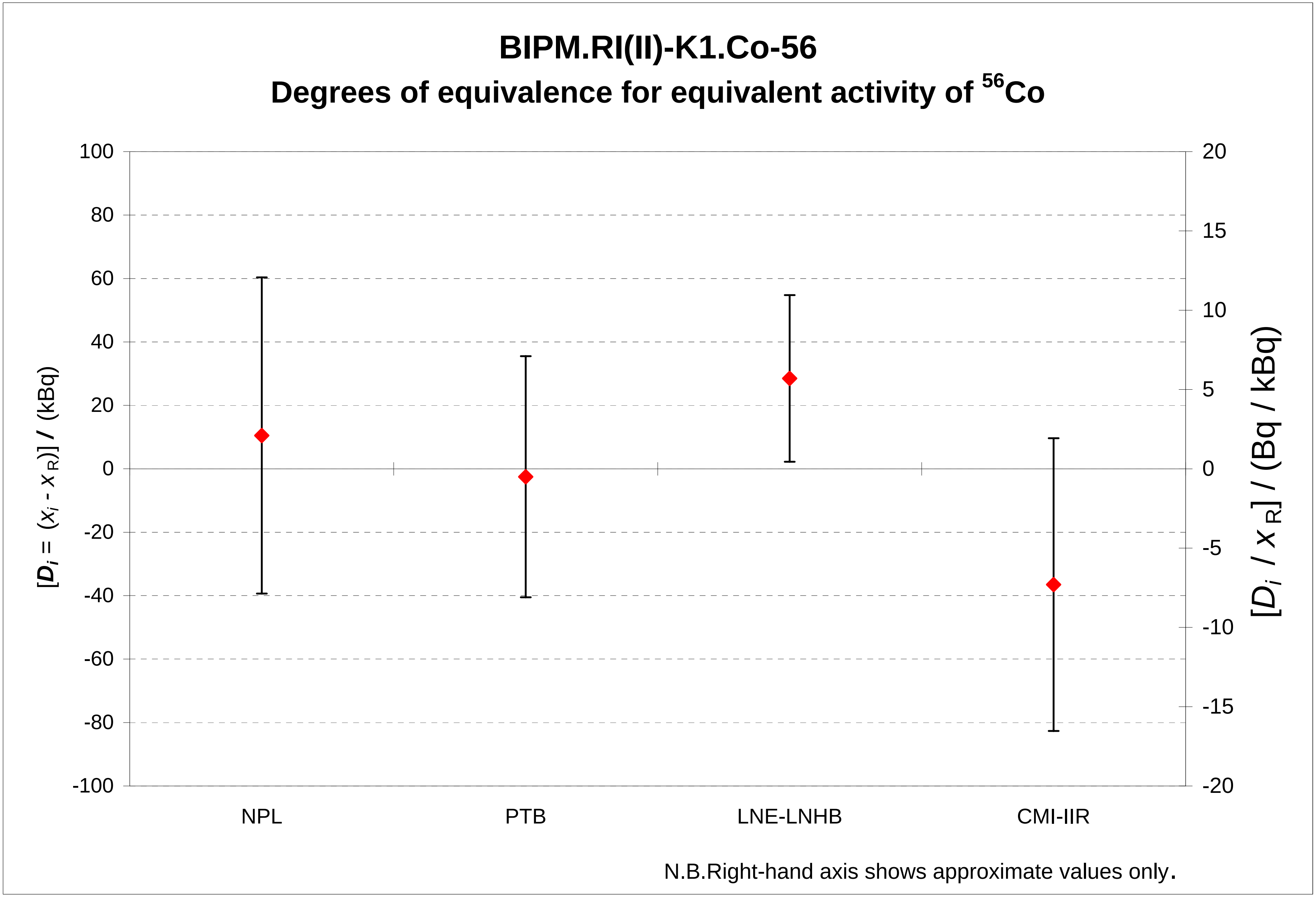
The approximation $U_{ij} \sim 2(u_i^2 + u_j^2)^{1/2}$ is used in the following table.

Lab *j* ⟹

Lab *i* ⇓

	D_i / kBq	U_i / kBq	NPL D_{ij} / kBq	NPL U_{ij} / kBq	PTB D_{ij} / kBq	PTB U_{ij} / kBq	LNE-LNHB D_{ij} / kBq	LNE-LNHB U_{ij} / kBq	CMI-IIR D_{ij} / kBq	CMI-IIR U_{ij} / kBq
NPL	11	50			**13**	75	**-18**	64	**47**	84
PTB	-3	38	**-13**	75			**-31**	45	**34**	70
LNE-LNHB	29	26	**18**	64	**31**	45			**65**	58
CMI-IIR	-37	46	**-47**	84	**-34**	70	**-65**	58		

Figure 1 Graph of the degrees of equivalence for the radionuclide Co-56



Appendix 1 - Uncertainty budget of the CMI-IIR for ^{56}Co

Uncertainty evaluation of the CMI-IIR activity measurement

Relative standard uncertainties	$u_{rel.} \times 10^4$	
Contributions due to	**Type A evaluation**	**Type B evaluation**
Counting statistics	10	–
Weighing	–	5
Dead time	–	4
Pile-up	–	1
Counting time	–	1
Background	–	15
Half life	–	1
Adsorption	–	5
Impurities	–	10
Extrapolation of efficiency curve	–	50
Quadratic summation	**10**	**54**
Total relative combined uncertainty u_c	**55**	

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
photons + electrons	PE	selective sampling	SS
alpha - particle	AP	high efficiency	HE
mixture of various radiations	MX	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(Ge(HP))-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