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CCRI(II) activity comparison of ^{241}Pu CCRI(II)-K2.Pu-241

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Abstract

In 2010, seven laboratories took part in the CCRI(II) key comparison of activity concentration measurements of ^{241}Pu, CCRI(II)-K2.Pu-241, using seven different methods. The spread of all results except one is 4×10^{-2} in relative terms. The results based on the CIEMAT/NIST efficiency tracing method are shown to be dependent on the beta spectrum shape selected and further work is proposed.

The KCRV has been determined as the arithmetic mean of six independent results based on four different methods. The results of the comparison have been analysed with respect to the KCRV. The degrees of equivalence with the KCRV have been approved by the CCRI(II) and are published in the BIPM key comparison database.

1. Introduction

The organization of an activity comparison of ^{241}Pu was decided by the Consultative Committee for Ionizing Radiation (CCRI(II)) at its 20th meeting in 2009. The radionuclide ^{241}Pu is a fissile isotope which is almost a pure beta emitter decaying to ^{241}Am. Consequently the standardization of ^{241}Pu should be preceded by a chemical separation. One method of standardization is to measure ^{241}Pu as a pure beta emitter and subtract the small in-growth of ^{241}Am as an impurity. A second method is to measure the ^{241}Am in-growth and deduce the activity of the mother ^{241}Pu from the fit of the in-growth curve. The participants were recommended to use the ^{241}Pu decay data from the Decay Data Evaluation Project [1]

The National Physical Laboratory (NPL) in the UK was the pilot laboratory for this comparison exercise. Before distribution of the samples to participating laboratories, a chemical separation of americium from the ^{241}Pu solution was performed on the 19 October 2009 in order to purify the solution from the in-growing ^{241}Am daughter (see also section 3). After the separation, a solution of ^{241}Pu in 2M HNO_3 was prepared at an activity concentration level of approximately 100 kBq g^{-1} for distribution to the participants. The 5 ml ampoules were filled with 3 g of the solution using a pycnometer method and weighing. Impurities present in the solution were determined by alpha spectrometry and mass spectrometry. A ^{241}Pu half life of 5234 d; u = 15 d from the *Monographie* BIPM-5 [1] was recommended to the participants. The PTB used their own ^{241}Pu half-life value (5240 d; u = 40 d) but this choice had a negligible effect on the comparison result.

The ampoules were distributed to the participants in November 2009 and the dead-line for submission of results was originally planned as 31 May 2010. As some of the participants were experiencing difficulties with the standardization, the dead-line was later changed to 30 September 2010. The reference date was fixed as 1 February 2010, 12 h UTC. All activity values in this report are given at the reference date unless stated otherwise.

All the participants reported their results to the BIPM directly using the new Excel reporting forms. A Visual Basic Application called *KCsoft* developed at the BIPM enables the information given in the forms to be read and produces Excel tables automatically. These tables are then copied into the appropriate format to produce the tables included in this report.

2. Participants and measurement methods

The list of participants and their final result for the comparison is given in Table 1. All the participants except the IAEA and the LNE-LNHB used more than one method. The NIST, NMISA and the NPL used several methods to check consistency but used a single measurement method for their official comparison result.

Four laboratories used the CIEMAT/NIST efficiency tracing method (CNET) and five laboratories used the triple-to-double-coincidence-ratio (TDCR) method. Three laboratories used the ^{241}Am in-growth method based, respectively, on α spectrometry (IAEA), 4πα(LS)-γ(NaI) live-timed anticoincidence counting (NIST) or γ-ray spectrometry (NPL). The initial content of ^{241}Am in the ^{241}Pu solution is of course crucial for this method and this is discussed in section 4. Some of the methods are described in more detail hereafter.

Isotope dilution alpha spectrometry with a ^{242}Pu tracer (IAEA)

> An aliquot of the ^{241}Pu solution was diluted without addition of tracer. Another aliquot of the ^{241}Pu solution was diluted and spiked with a ^{242}Pu tracer (NIST SRM4334F; the purity of this tracer was checked by alpha spectrometry and its alpha activity by liquid scintillation (LS) counting). The Pu was separated from Am by extraction chromatography, using TEVA resin - aliphatic quaternary amine, in both solutions, and then alpha-spectrometry sources were prepared by micro-co-precipitation of Pu with NdF_3. The alpha spectra were collected with Passivated Ion Implanted Planar Silicon PIPS detectors immediately following the separation; the alpha-emitting Pu isotope ratios and the purity of the sources were checked. Then the sources were repeatedly measured for six months to determine the activity concentration of the in-growing ^{241}Am. The ^{241}Pu activity concentration was calculated from the ^{241}Am results.

Liquid Scintillation (LS) comparative measurements of matched sources (NIST)

> The method consists of comparative LS measurements of matched sources of the CCRI(II)-K2 solution against a NIST well-characterized master solution, identified as A1, that has been followed by in-growth measurements at NIST for more than 30 years. The NIST A1 solution was re-standardized in May 2010 by 4πα(LS)-γ(NaI) live-timed anticoincidence counting of the ^{241}Am in-growth and then linked to the CCRI(II)-K2 solution by preparing composition-matched cocktails and counting them in three different LS counters. The matched LS comparisons resulted in a total of 75 NPL/A1 activity ratios (5 sources of each, measured 3 times on 5 occasions in 3 different counters) that were normally distributed.

Combination of mass spectrometry and α spectrometry measurements (NPL)

> The ^{241}Pu activity was determined from mass spectrometric measurements of the ^{241}Pu solution combined with α spectrometry measurements. The activity of ^{239}Pu and ^{240}Pu,

present as impurities in the ^{241}Pu solution, was first determined by alpha spectrometry with a PIPS detector using efficiency tracing with ^{236}Pu (see Figure 4). Secondly, the $^{239+240}$Pu activity result was combined with the mass spectrometric analysis (mass spectrometry ratio $^{239+240}$Pu/^{241}Pu) to deduce the ^{241}Pu activity.

Table 1 – List of participants and comparison results

Participant		Contact person	*A* / kBq g^{-1}	*u* / kBq g^{-1}	Measurement methods	Staff involved
IAEA	IAEA NAEL Chemistry Unit Seibersdorf	Gyula Kis-Benedek	90.73	0.52	Isotope dilution alpha spectrometry and ^{241}Am in-growth	Gyula Kis-Benedek
IRMM	EC-JRC Institute for Reference Materials and Measurements	Timos Altzitzoglou	93.90 [#]	0.75 [##]	4P-LS-MX-00-00-CN 4P-LS-MX-00-00-TD	T. Altzitzoglou
LNE-LNHB	Laboratoire National d’Essai – Laboratoire National Henri Becquerel	Carole Fréchou	90.2	1.5	4P-LS-MX-00-00-TD	P. Cassette
NIST	National Institute of Standards and Technology	Lizbeth Laureano-Perez	92.22	0.40	LS measurements (UA-LS-MX-00-00-00) traceable to 4πα(LS)-γ(NaI) Live-Timed Anticoincidence measurements CNET [$] TDCR [$] ^{241}Am in-growth by LTAC [$]	R. Colle, L. Laureano-Perez Ryan Fitzgerald
NMISA	National Metrology Institute of South Africa	Freda van Wyngaardt	85.8	1.1	TDCR 4P-LS-BP-00-00-TD CIEMAT/NIST [$] 4P-LS-BP-00-00-CN	W.M. van Wyngaardt, M.J. van Staden, J. Lubbe and B.R.S. Simpson W.M. van Wyngaardt, B.R.S. Simpson, J. Lubbe and M.J. van Staden
NPL	National Physical Laboratory	Lena Johansson	92.37	0.39	^{241}Am and ^{237}U in-growth by γ-ray spectrometry UA-GH-GR-00-00-00 Mass spectrometry with alpha spectrometry [$]	Andy Stroak, Lena Johansson Chris Gilligan, Lena Johansson
PTB	Physikalisch-Technische Bundesanstalt	Karsten Kossert	91.8 [#§]	0.9	4P-LS-MX-00-00-CN 4P-LS-MX-00-00-TD	Karsten Kossert Karsten Kossert, Ole Nähle

[#] Weighted mean result.

[##] Uncertainty of the TDCR method which is more representative than the uncertainty of the mean

[$] Additional measurements carried out for confirmation but not used for the comparison result

[§] Use of the PTB ^{241}Pu half-life (5240 d; u = 40 d) instead of [1] but negligible effect on the comparison result

3. Uncertainty evaluations

Table 2 presents all the reported uncertainty budgets. For each method, most of the uncertainty components evaluated by the participants are similar. Using the ^{241}Am in-growth method, the IAEA and the NPL reported uncertainties that are among the smallest of the comparison.

The standardization methods based on liquid scintillation show the largest uncertainty. Among the participants using the CNET and TDCR methods the IRMM reported results with the smallest uncertainty. A relative standard uncertainty of 10^{-3} was reported by the IRMM in relation to observed instabilities with some cocktails (see section 7). The PTB reported a large relative uncertainty of 2.4×10^{-2} for the ionization quenching (kB value) in the TDCR measurement. The LNE-LNHB and NMISA reported a dominant uncertainty contribution related to the beta spectrum shape. There is incoherence between the NMISA and the PTB concerning the influence of the beta shape factor on uncertainty for the CNET and the TDCR methods: for the NMISA the influence of this shape factor is lower for the TDCR than for the CNET and the contrary is reported by the PTB. Finally, the NMISA reported after the comparison that an additional uncertainty due to quench-matching between the ^{3}H tracer and the ^{241}Pu sources ought to have been included (see section 10).

For the CNET method, all the participants used a tritium tracer standardized by themselves with a relative standard uncertainty between 0.7 % and 1 % (see Table 6). For the IRMM and the PTB the subsequent uncertainty values on the ^{241}Pu activity concentration have about the same values, i.e. the sensitivity coefficient is close to 1 (see Table 2). In fact, the tritium uncertainty is the dominant component of the uncertainty budget for these two laboratories. Similarly for the IAEA, the ^{242}Pu tracer uncertainty shows a sensitivity coefficient close to one and also corresponds to the largest component in their uncertainty budget.

LSC CIEMAT/NIST	**IRMM**				**NMISA**				**PTB**			
Quantity *Q*	Rel. *u*(*Q*) / 10^{-2}	Type	Rel. *u*(*A*) / 10^{-2}	Comment	Rel. *u*(*Q*) / 10^{-2}	Type	Rel. *u*(*A*) / 10^{-2}	Comment	Rel. *u*(*Q*) / 10^{-2}	Type	Rel. *u*(*A*) / 10^{-2}	Comment
Counting statistics	0.11	A	0.12		0.29	A	0.25	Statistical analysis of 12 values		A	0.04	
Weighing	0.15	A	0.15		0.05	B	0.05	*u*(Mass) = 0.02 mg		B	0.05	
Background	7	A	0.035		2.4	A	0.009	Background square root statistics applied		A	0.03	
Dead time	0.1	A	0.1		10	B	0.05	$u(\tau_D)$ = 0.1 µs		B	0.1	
Resolving time												
Pile-up												
Decay data	0.42	B	0.42	From CN2005 (E. Günther, PTB - Aug.2005)	22	B	1.66	Uncertainty in evaluated decay scheme parameters – mainly due to average energy of the beta spectrum		B	0.4	
Quenching	0.045		0.045	*kB* value	11.1 *	B	0.62	Effect on the figure-of-merit value (extracted from the tracer) due to uncertainty in *kB*		B B	0.1 0.1	 *kB* value
Tracer	0.7	B	0.7	Incl. the unc. of the eff. extr. curve	embodied in *					B	0.96	
Extrapolation of efficiency curve	0.3	B	0.3	Incl. unc. of the quench parameter								
Calibration factor												
Half-life	0.3	B	0.01		0.29	B	0.008			B	0.01	
Impurities	10	A	0.015	Although not involved in the analysis	30	B	0.03	Am-241		B	0.05	
Adsorption	10	A	0.015		59	B	0.2	Adsorption to the source glass vials		B	0.05	
					58	B	0.021	Adsorption to the ampoule				
Measuring time					0.001	B	0.001	Calibration of timer		B	0.01	
After-pulse					8.5	B	0.014	Rel. *u*(*Q*) is average of after-pulse corrections				
Asymmetry										B	0.05	
Sample stability	0.1	A	0.1									
Figure-of-merit value					0.34 *	A	0.002	Statistical analysis of 9 values due to different vial efficiencies				
Combined uncertainty			**0.90**				**1.8**				**1.0**	

TDCR method	**IRMM**				**LNE-LNHB**				**NIST**			
Quantity *Q*	Rel. $u(Q)$ / 10^{-2}	Type	Rel. $u(A)$ / 10^{-2}	Comment	Rel. $u(Q)$ / 10^{-2}	Type	Rel. $u(A)$ / 10^{-2}	Comment	Rel. $u(Q)$ / 10^{-2}	Type	Rel. $u(A)$ / 10^{-2}	Comment
Counting statistics	0.3	A	0.3	Std deviation of the mean		A	0.2	Experimental standard deviation		A A	0.21 0.24	Count repeatability Single source reproducibility (11 efficiency points)
Weighing	0.15	A	0.15			A & B	0.15	Including variability between sources		B	0.05	
Background	0.25	A	0.25			A	0.02		1.5	A	1×10^{-5}	Std deviation of 4 background meas. at 11 efficiency points
Dead time	0.2	A	0.2			B	0.01	Pulse width of the live-time clock				
Resolving time						B	0.4	Correlation between channels				
Pile-up						B	0.1					
Decay data	0.25	B	0.25	Endpoint energy, beta shape factor		B	1.30	Beta spectrum shape	0.96 20	A B	0.07 0.65	Beta endpoint energy Beta shape factor
Quenching	0.01	A	0.5	*kB* value		B	0.8	*kB* factor	8.3	B	0.86	$kB = 0.012$ cm·MeV^{-1}; $u = 0.001$cm·MeV^{-1}
Tracer												
Extrapolation of efficiency curve												
Calibration factor												
Half-life	0.3	B	0.01			B	0.003		0.28 various	A A	0.006 0.000 1	 impurities
Impurities	10	A	0.2			B	0.03	From std uncertainty of alpha activity	various	A	0.16	
Adsorption	10	A	0.015									
Measuring time												
Reproducibility						A	0.7	Experimental std deviation of the activity using grey filters				
After-pulse												
Asymmetry	0.25	A	0.25									
Sample stability	0.1	A	0.1									
TDCR model									33	B	0.61	Energy conversion factor in the Polya-based TDCR model ($L = 0.03$; $u = 0.01$)
TDCR value/Fit												
Combined uncertainty			**0.80**				**1.7**				**1.3**	

TDCR method	NMISA				PTB			
Quantity *Q*	Rel. $u(Q)$ / 10^{-2}	Type	Rel. $u(A)$ / 10^{-2}	Comment	Rel. $u(Q)$ / 10^{-2}	Type	Rel. $u(A)$ / 10^{-2}	Comment
Counting statistics	0.35	A	0.065	Statistical analysis of 29 values		A	0. 1	
Weighing	0.05	B	0.05	u(Mass) = 0.02 mg		B	0.05	
Background	5	A	0.1	Background square root statistics applied		A	0.05	
Dead time	10	B	0.05	$u(\tau_D) = 0.1$ µs		B	0.03	
Resolving time								
Pile-up								
Decay data	22	B	1.1	Uncertainty in evaluated decay scheme parameters – mainly due to average energy of the beta spectrum		B	1.2	
Quenching	11.1	B	0.45	$u(kB) = 0.001$ g (cm^2 MeV)$^{-1}$		B	2.4	Ionization quenching, *kB* value
Tracer								
Extrapolation of efficiency curve								
Calibration factor								
Half-life	0.29	B	0.005			B	0.01	
Impurities	11.8	B	0.03	Am-241		B	0.05	
Adsorption	58	B	0.02	Source vial		B	0.05	
	58	B	0.021	Ampoule				
Measuring time	0.001	B	0.001	Calibration of timer		B	0.01	
Reproducibility								
After-pulse	63	B	0.5	Rel. $u(Q)$ is average of after-pulse corrections				
Asymmetry						B	0.01	
Sample stability								
TDCR model								
TDCR value/Fit						B	0.06	
Combined uncertainty			**1.3**				**2.7**	

	IAEA				**NPL**				**NPL**			
	Isotope dilution alpha spectrometry and **Am-241 in-growth**				**Am-241 and U-237 in-growth** by γ-ray spectrometry				**Mass spectrometry with alpha spectrometry**			
Quantity *Q*	Rel. $u(Q)$ / 10^{-2}	Type	Rel. $u(A)$ / 10^{-2}	Comment	Rel. $u(Q)$ / 10^{-2}	Type	Rel. $u(A)$ / 10^{-2}	Comment	Rel. $u(Q)$ / 10^{-2}	Type	Rel. $u(A)$ / 10^{-2}	Comment
Counting statistics	0.15	A	0.18	Pu-242			0.21				0.32	
	0.17	A	0.027	Pu(239,240,241)								
	0.13	A	0.18	Pu-238+Am-241								
	1.5	A	0.013	Tail								
Weighing	0.000 8	A	0.030				0.000 1	10 mL solution			0.08	
Background	24	A	0.000 3	background (Pu-242)			0.005				1×10^{-5}	
	24	A	6×10^{-5}	background (Pu(239,240,241))								
	23	A	0.000 3	background (Pu-238+Am-241)								
	26	A	0.000 2	background (tail)								
Dead time												
Resolving time												
Pile-up												
Decay data	0.28	B	0.000 2	alpha emission ratio								
Quenching												
Tracer	0.37	B	0.42	Pu-242							0.36	
Extrapolation of efficiency curve												
Calibration factor							0.25	Like for like measurement with standardised Am-241 source				
Half-life	0.29	B	0.002 9	Pu-241			0.008	Uncertainty in in-growth function over one year			0.008	
	0.14	B	0.16	Am-241								
Impurities	1.0	A	0.22	Pu 238/(239+240) ratio			0.09	U-237 also present			0.1	Decay products of Pu-236
	2.5	A	0.10	Pu 242/239+240 ratio								
Adsorption	0.001 6	A	0.001 8									
Measuring time												
Reproducibility											0.6	
Curve fitting							0.25	Fitting of in-growth curve			0.05	Alpha peak fitting
Mass spectrometry											0.32	
Combined uncertainty			**0.57**				**0.42**				**0.84**	

	NIST **Liquid Scintillation comparative measurements**				**NIST** **Live-Timed Anticoincidence** measurement of the NIST reference solution A1			
Quantity *Q*	Rel. $u(Q)$ / 10^{-2}	Type	Rel. $u(A)$ / 10^{-2}	Comment	Rel. $u(Q)$ / 10^{-2}	Type	Rel. $u(A)$ / 10^{-2}	Comment
Counting statistics		A	0.17 *	Precision for $\nu = 75$ (normal). Incl. LS counters dependencies		A	0.08	Standard deviation of the distribution for 5 values using 5 sources and 2 blanks
Weighing		B	0.05 + 0.05	Dilution and LS sources		B	0.05	
Background		A	embodied in *					
Dead time		B	0.06	Live-time determination		B	0.1	
Resolving time								
Pile-up								
Decay data								
Quenching								
Tracer								
Extrapolation of efficiency curve						B	0.18	
Calibration factor		B	0.38	Uncertainty for Live-Timed Anticoincidence determination of Pu-241				
Half-life	0.28	B	0.004		0.28	B	0.28	Pu-241 (NIST A1 solution)
							0.13	Am-241
Impurities								
Adsorption								
Measuring time								
Reproducibility								
Combined uncertainty			**0.43**				**0.38**	

4. Impurities

The impurities (activity ratios) reported by the participants are detailed in Table 3 and many discrepancies can be noted. Consequently, uncertainties in Table 3 often seem to be underestimated. However, the IAEA alpha-spectrometry measurements and the NPL mass spectrometry measurement agree with each other except for ^{242}Pu.

The ^{241}Am content of the solution as measured by the participants is of course fundamental for the ^{241}Am in-growth method. The IRMM, NMISA and the PTB concluded from their measurements that the measured amount of ^{241}Am was close to that expected from in-growth assuming ^{241}Pu was separated from americium at the end of October 2009. This is a correct conclusion, as indeed the separation was performed on the 19 October 2009. The results from alpha-spectrometry measurements, conducted by the pilot laboratory, on the solution immediately after the separation reveal an activity ratio of 6 (3) × 10^{-5} of ^{241}Am to ^{241}Pu. The uncertainty is high in this case due to the presence also of ^{238}Pu, which has a similar α-peak energy to ^{241}Am. The IAEA repeated the purification of the solution and separated Pu from Am by extraction chromatography using TEVA resin (aliphatic quaternary amine). The NIST reported an ^{241}Am content, at the reference date, significantly higher than the other participants.

The relative standard uncertainty reported for the ^{241}Pu activity concentration due to impurities ranges from 0.015 × 10^{-2} (for IRMM/CNET) to 0.2 × 10^{-2} (for IRMM/TDCR and IAEA). The IRMM explained that there is a difference in the data treatment for the CNET and TDCR methods and hence the difference in the uncertainty contributions.

5. Preliminary measurements

The preliminary measurements reported in Table 4 were carried out at reception of the ampoule and when opening the ampoule for making sources. The checks for adsorption on the walls were all carried out by liquid scintillation and the results had a negligible effect on the final ^{241}Pu activity concentration.

6. Weighing and dilutions

The information reported by the participants is summarized in Table 5. Most participants used the pycnometer method for weighing and most participants did not dilute the solution. The buoyancy corrections reported are all around one part in a thousand.

Participant	IAEA		IRMM		LNE-LNHB		LNE-LNHB	
Detector for impurity measurement	Alpha-spectrometry system		2 planar HPGe detectors (45% rel. eff. and 500 mm^2) [a]		LS counter Wallac 1414		Alpha silicon spectrometer	
Activity ratio and standard uncertainty at reference date								
^{241}Am	[b]		4.7×10^{-4} [c]	4×10^{-5}			6.00×10^{-4}	7×10^{-6}
^{238}Pu	1.278×10^{-4}	1.1×10^{-6}						
^{239}Pu	5.281×10^{-4}	4.4×10^{-6}						
^{240}Pu							6.0×10^{-4}	1×10^{-5}
^{242}Pu	2.404×10^{-5}	2.9×10^{-6}					3.0×10^{-5}	2×10^{-6}
^{244}Pu								
Gross alpha					1.20×10^{-3}	3×10^{-5}		
^{237}U								
Correction applied on comparison result?			**CNET**	**TDCR**	yes		no	
			no	yes				
Correction factor				0.995 (2) typ.				
Comment			The contribution of the ^{241}Am spectrum to the ^{241}Pu spectrum is negligible.		The alpha impurities activity was subtracted from raw counts prior to treatment with the TDCR model. The alpha impurity correction cannot be resumed in a single correction factor as the correction process is not linear.		The purpose of this measurement is to identify the alpha impurities in order to check that the ^{241}Am content is compatible with the date of purification of the solution.	

Continued overleaf

Table 3 – Impurities reported by the participants

Participant	**NIST**	**NIST**	**NMISA**	**NPL**	**PTB**
Detector for impurity measurement	HPGe (n-type/coaxial/Be/ 54 cm³)	Silicon surface-barrier alpha detector	NaI(Tl) γ-ray detector	TIMS [d]	HPGe (n-type/coaxial/Be/127 cm³)
Activity ratio and standard uncertainty at reference date					
^{241}Am		2.71×10^{-3} 2.1×10^{-4}	4.1×10^{-4} [c] 3×10^{-5}		4.90×10^{-4} [c] 0.02×10^{-4}
^{238}Pu		4.61×10^{-4} 4.3×10^{-5}		$1.257\,13 \times 10^{-4}$ 9.3×10^{-8}	
^{239}Pu		1.28×10^{-3} 8×10^{-5}		$3.539\,6 \times 10^{-5}$ 1.6×10^{-8}	
^{240}Pu				$4.882\,6 \times 10^{-4}$ 5.2×10^{-7}	
^{242}Pu		$< 1.3 \times 10^{-4}$		$5.136\,9 \times 10^{-6}$ 4.1×10^{-9}	
^{244}Pu				9.63×10^{-9} 1.1×10^{-10}	
Gross alpha					1.10×10^{-3} [e] 0.06×10^{-3}
^{237}U					2.44×10^{-5} 0.06×10^{-5}
Correction applied on comparison result?		yes	yes	yes	yes
Correction factor		Depends on sample size [g]			Different values
Comment	None detected [f]		[h]	[i]	

[a] Measurement of point sources by γ-ray spectrometry and measurement of LS sources by LSC. The results from both methods and all detectors agree with each other very well.

[b] Am/Pu isotopes have been separated by chromatography.

[c] Measured amount of ^{241}Am close to that expected from in-growth assuming ^{241}Pu was separated at the end of October 2009.

[d] Mass spectrometry performed by TIMS at the IRMM.

[e] Determined by analysis of LSC spectra.

[f] Detection limits at 11 June 2010, in terms of massic photonic emission rates, are:
< 0.53 s^{-1} g^{-1} for 20 keV $< E <$ 75 keV ; < 0.40 s^{-1} g^{-1} for 80 keV $< E <$ 330 keV ; < 0.53 s^{-1} g^{-1} for 340 keV $< E <$ 1880 keV.

[g] Corrections for ^{238}Pu due to the ^{241}Am in-growth during Pu counting depend on Pu-241 solution sample size and recoveries. Corrections for ^{242}Pu due to the fact that ^{242}Pu and ^{241}Pu α particles (branching ratio = 0.002 45 %) have the same energy (4.9 MeV) are related to the ^{241}Pu sample size.

[h] The double-coincidence count rates (and triples when TDCR method was used) were corrected for the counts due to ^{241}Am (assuming 100 % efficiency) before the data analysis was undertaken.

[i] When using a HPGe γ-ray spectrometer (to measure the ^{241}Am and ^{237}U in-growth), the contaminants are excluded.

Table 4 – Preliminary measurements reported by the participants

	IAEA	**IRMM**	**NIST**	**NMISA**	**PTB**
Ampoule number	A09894	A09888 //BC2821	A09891	A 09892	A09893
Activity concentration before opening	84 kBq g^{-1}			0.003 0 pA (approximates to 0.013 4 MBq of Am-241)	
Detector	HPGe			Ionization chamber	
Total mass of solution / g	3.024			3.137 89	
Residual activity at ref. date (LSC) / Bq	164	12		112 (on 30 March 2010)	
***u* / Bq**	5	1.2		23	
Correction factor applied	1.000 603	1		1	
u	0.000 016	0.000 015		0.000 21	

7. Preparation of ^{241}Pu and tracer sources

No description of the solid ^{241}Pu sources made by the IAEA and NPL has been reported. The IAEA also produced ^{241}Pu sources spiked with a NIST ^{242}Pu SRM. The NPL produced solid sources from the ^{241}Pu solution, spiked with a ^{236}Pu tracer which had previously been standardized by primary methods at the NPL.

Table 6 summarizes the reported information about the cocktails prepared by the participants who used a method based on liquid scintillation. All participants used Ultima Gold or Ultima Gold AB scintillators except NMISA who used Quicksafe A. In addition, the LNE-LNHB used Hionic fluor and the NIST used a cocktail based on Xylene. Only the IRMM and PTB used a quenching agent (nitromethane) and added water to the cocktails. The NMISA added HDEHP (bis(2-ethylhexyl)phosphoric acid). The IRMM observed instabilities with some cocktails while those with water added appeared to be stable (see footnote of Table 6).

For the CNET method, all the participants used a tritium tracer standardized by themselves with a standard uncertainty between 0.7 % and 1 %.

Table 5 – Weighing and dilutions

Participant	**IAEA**	**IRMM**	**LNE-LNHB**	**NIST**
Action on the solution before use		Ampoule shaking - ampoule opening - transfer of the solution to the pycnometer		
Diluent				3.4 M HNO_3
Dilution factor		1	1	2.42 306.904 4
Number of sources		16	15	
Type of source		liquid	liquid	
Mass of source		20 to 84 mg	17 to 29 mg	
Balance	Mettler Toledo AX 205/M	Mettler Toledo AX26	Mettler MT5 n°L62910	Mettler Toledo M5
Calibration date	2009 October	07 Sept. 2010	19 Nov. 2009	14 July 2010
Traceability to SI	The balance was calibrated with the internal weights, and checked with external calibration weights before use	Via standard set of weights, traceable to the IRMM standard kilogram, directly traceable to the BIPM	Standard weights	Calibrated process traceable to NIST
Temperature control	yes	yes	yes	yes
Humidity control	no	yes	yes	no
Buoyancy correction and std uncertainty (typ.)		1.001 055 0.000 002	1.00096	1.001 0.0002
Weighing procedure	The vessels were kept in the weighing room for several hours before use. For each weight three readings were taken and the averages were used for calculations. The solutions were directly transferred to the vessels and weighted after closing the cap of the vessel.	Pycnometer method for gravimetric dispensing of aliquots	Pycnometer method	Mass differences from dispensing with plastic pycnometer

Table 5 – Weighing and dilutions

Participant	**NMISA** (TDCR)	**NPL**	**PTB**
Action on the solution before use	3.12954 g of the solution received was transferred to a 5 ml flask.		The ampoule was centrifuged.
Diluent			
Dilution factor	1	1	1
Number of ^{241}Pu sources	4		6
Type of source	liquid		liquid
Mass of source	54 to 84 mg		50 mg
Balance	Mettler M3	Mettler	Mettler Toledo XP26 and XP205
Calibration date	22 Feb 2010	30 April 2010	13 Nov. 2009
Traceability to SI	Mass pieces calibrated by the Mass lab. of the NMISA on 18 July 2006	UKAS	Traceable to the national German mass standard: DKD calibration certificate
Temperature control	yes	yes	yes
Humidity control	yes	yes	yes
Buoyancy correction and std uncertainty (typ.)	1.001 067 0.000 010	1.001 00 0.000 01	1.000 959 0.000 011
Weighing procedure	Mass differences from dispensing with plastic pycnometer	The solution was transferred to a 10 ml ampoule by the pycnometer method	Mass differences from dispensing with plastic pycnometer

Table 6 – Cocktails prepared for the measurements by liquid scintillation and model used

Participant	**IRMM** CNET	**IRMM** TDCR	**LNE-LNHB** TDCR	**NIST** LS comp. meas.	**NMISA** TDCR	**NMISA** CNET	**PTB** TDCR and CNET
Scintillator	Ultima Gold, UGAB and UGAB+UGF *	Ultima Gold *	Ultima Gold, UGAB, Hionic Fluor	UGAB and PCS **	Quicksafe A	Quicksafe A	Ultima Gold
Additive	Water (1mL) in some UG samples	Water (1mL)	None	None	8.3 mL/L HDEHP	8.3 mL/L HDEHP	0.95 mL water
Quenching agent	CH_3NO_2	CH_3NO_2	None	None	None	None	CH_3NO_2 (diluted with pseudocumene)
Vial	Packard High-Performance glass	Packard High-Performance glass	20 mL low-K glass vials	Glass, 20 mL	Polyethylene	Custom-made flat-faced glass vials	20 mL glass with low potassium content
Volume / cm^3	15 or 16	16	10	typically 10	12	12	16
Tracer and its origin and	tritiated water IRMM	N/A	N/A	N/A	N/A	tritiated water NMISA	tritiated water PTB
relative std uncertainty	7×10^{-3}					7.1×10^{-3}	10×10^{-3}
Code	CN2005 (E. Günther, PTB) - Aug. 2005	TDCRB-02p (R. Broda et al., April 2002)	TDCR07c	N/A	Local program suite based on EFFY 2	Local program suite based on EFFY 2	PTB codes
***kB* value**	0.0075 cm MeV^{-1}	0.016 cm MeV^{-1}	0.009-0.011 cm MeV^{-1} #		0.009 $g(cm^2 MeV)^{-1}$	0.009 $g(cm^2 MeV)^{-1}$	0.0075 cm MeV^{-1}
Quenching correction formula	Birks formula	Birks formula	Birks + ICRU37 with linear extrapolation to 0 below 100 eV		Locally developed program IONQUEN: Q(E) from Birks formula; SP > 0.4 keV from Bethe formula; SP < 0.4 keV from Gibson *Monographie* BIPM-3 (1980) SP = $k/\sqrt{E}$; Ionization potentials from ICRU37.		Birks formula

* The exercise (source preparation-measurements-analysis) was repeated for a second time from which the results are reported here. The first time, sources in UGAB, UGABF were not very stable and sources in UG gave results approx. 1.3 % lower. However, the samples in UG + 1 mL H_2O were stable and the results the same as in the second round. The sources in UG were not stable the second time as well and gave results about 20 % lower than the other sources. All other sources were stable during the measurement period. Sources in UGAB gave results approx. 0.3% lower than the 93.9 kBq/g obtained from samples in UG + 1mL H_2O and sources in UGABF approx. 0.7 % lower.

** Phase Combining Systems from Amersham Biosciences: Xylene (isomer mixture) 60 % to 70 %.

[#] The determination of the *kB* parameter was made by successive measurement of a source with various coaxial grey filters (0 to 70 % optical density range). The optimal *kB* is the one for which the curve of the activity versus filter density has the minimal slope.

8. Liquid scintillation counters

The information reported by the participants is summarized in Table 7. Most LS counters are about 10 years old but some are much older. Some points of interest are given hereafter.

- The NMISA did not measure the quench parameter as is usually the case for the users of commercial LS counters but aimed to prepare the tracer sources to be chemically similar to the Pu-241 sources, so as to achieve direct matching of the quench states. Subsequent measurements showed that this was not achieved at the desired accuracy.
- The NMISA used both a long resolving time (470 ns) and a short non-extending dead time (1 μs). However they applied a correction for satellite pulses that nevertheless remains lower than 1 % (see Table 2). The other participants reported dead-time values ranging from 5 μs to 50 μs.
- The NMISA counter has a low efficiency because it is more than 30 years old.

9. Semiconductor detectors

The IAEA and the NPL used semi-conductor detectors to measure the α particles or γ rays emitted by the ^{241}Pu daughter ^{241}Am (see Table 8) and α-emitting impurities such as ^{239}Pu and ^{240}Pu. An important characteristic of these measurements is the very low count rate of a few counts per second. A typical alpha spectrum of the ^{241}Pu solution (spiked with ^{236}Pu), measured at the NPL, is shown in Figure 1. In this case, a ^{236}Pu tracer was used to determine the detection efficiency (see section 7). Due to the relatively low count rate, the source was positioned close to the detector covering a solid angle of almost 2π.

Participant	**IRMM**			**LNE-LNHB**
LS counter	Packard TRI-CARB 3100 TR/AB	Wallac 1220 Quantulus	IRMM-TDCR	TDCR LS counter n°1
brought into service in	May 1992 - Upgraded Feb. 1999	mars-2001	2009	
Quench parameter	tSIE	SQP(E)		TDCR
measured using	^{133}Ba	^{152}Eu		
Efficiency for unquenched ^{3}H	50 % – 53 %	50 % – 53 %		50 %
Number and type of PMT	2 Hamamatsu R331-08	2 PMTs 9956	3 Burle/RCA 8850	3 Burle 8850
Operating temperature / °C	12	14	Room temp. (24 - 26 %)	20
Resolving time / ns	20	20	20	40
Tracer	^{3}H	^{3}H		
Efficiency variation method	chemical quenching	chemical quenching	defocusing	grey filters and defocusing
Discrimination level				valley before SER
Max ^{241}Pu efficiency	48.4 %	48 %	42 %	48 %
Dead-time correction method			live time	live-time
Dead time τ and std uncertainty / µs			5	50
Type of dead time			non-extending	extending
Count rate (typ.) / s^{-1}	700 - 3500	700 - 3500	700 - 3500 half of that for doubles	1000
Typical time for one measurement / s	600	600	2400	500 to 3600
TDCR value (typ.)			0.43	0.2 to 0.5
Background rate / s^{-1}	0.56	0.2	5.5 for doubles	9
Number of sources measured	16	16	8	15

Participant	**NIST**						
LS counter	NIST TDCR spectrometer		Beckman LS 6500		Packard Tri-carb A2500TR		Wallac 1414 Winspectral
brought into service in							
Quench parameter			Horrocks number		transformed Spectral Index of the External Standard (proprietary)		SQPE (proprietary)
measured using					^{133}Ba		^{152}Eu
Efficiency for unquenched ^{3}H							
Number and type of PMT	3 Burle 8850 with ORTEC base				Hamamatsu R331-08		
Operating temperature / °C	20		ambient		ambient		ambient
Resolving time / ns	50				coincidence resolving time : 18 ns pulse resolving time : 12 μs		
Tracer							
Efficiency variation method	PMT focusing voltage						
Discrimination level			about 1 keV		about 1 keV		about 1 keV
Max ^{241}Pu efficiency	30 % (doubles)						
Dead-time correction method	live time (MAC3 electronics)		live time		live time		live time
Dead time τ, std uncertainty / μs	50						
and measurement method	oscilloscope		gated oscillator		gated oscillator		gated oscillator
Type of dead time	extending						
Count rate (typ.)	200 doubles						
Typical time for one measurement	1200						
TDCR value (typ.)	0.34						
Background rate	6.4						
Number of sources measured	1						

Participant	**NMISA**		**PTB**				
LS counter	NMISA TDCR counter [#]		Wallac 1414-003 Guardian*		Tricarb 2800 TR		PTB TDCR counter
brought into service in	before 1981		1996		2006		2008
Quench parameter			SQP(E)		tSIE		
measured using			^{152}Eu		^{133}Ba		
Efficiency for unquenched ^{3}H	~ 22 % (double coinc.)		~ 50 %		~ 55 %		~ 60 %
Number and type of PMT	3 high gain PMTs 8850		2		2 Hamamatsu R331-08		3 Hamamatsu R331-05
Operating temperature / °C	18		20		20		20
Resolving time / ns	470		25		25		40
Tracer	None for TDCR		^{3}H		^{3}H		
Efficiency variation method	None		chemical quenching		chemical quenching		chemical quenching
Discrimination level	approx. 2 keV						below SEP
Max ^{241}Pu efficiency	21% (doubles)		34.4%		40.6%		57.2%
Dead-time correction method							live time
Dead time τ, std uncertainty / μs	1.0 0.1						30 0.02
and measurement method	Two-detector, two-source method						
Type of dead time	non extending						extending
Count rate (typ.)	2000		1700		2000		2700
Typical time for one measurement	300		900		900		300
TDCR value (typ.)	0.63						0.60
Background rate	1.5		1		1		7
Number of sources measured	4		6		6		6

[#] equipment also used for the CNET method

*guard disconnected

Table 8 – Semiconductor detectors

Participant	**IAEA** Isotope dilution alpha spectrometry and ^{241}Am in-growth	**NPL** Mass spectrometry with α spectrometry	**NPL** ^{241}Am and ^{237}U in-growth by γ-ray spectrometry
Semiconductor type	PIPS Planar	PIPS Planar	HPGe Coaxial
Solid angle / sr		< 2π	
Diameter / mm		20	80
Active area / mm^2	450		
Discrimination level			59.9 keV
Live-time clock	yes	yes	
Pulser technique	yes		yes
Count rate (typ.) / s^{-1}	1	2	2
Background rate / s^{-1}	1.9261E-05		
Typical time for one measurement	180 000	87 000	87 000
Number of sources measured	3	1	1

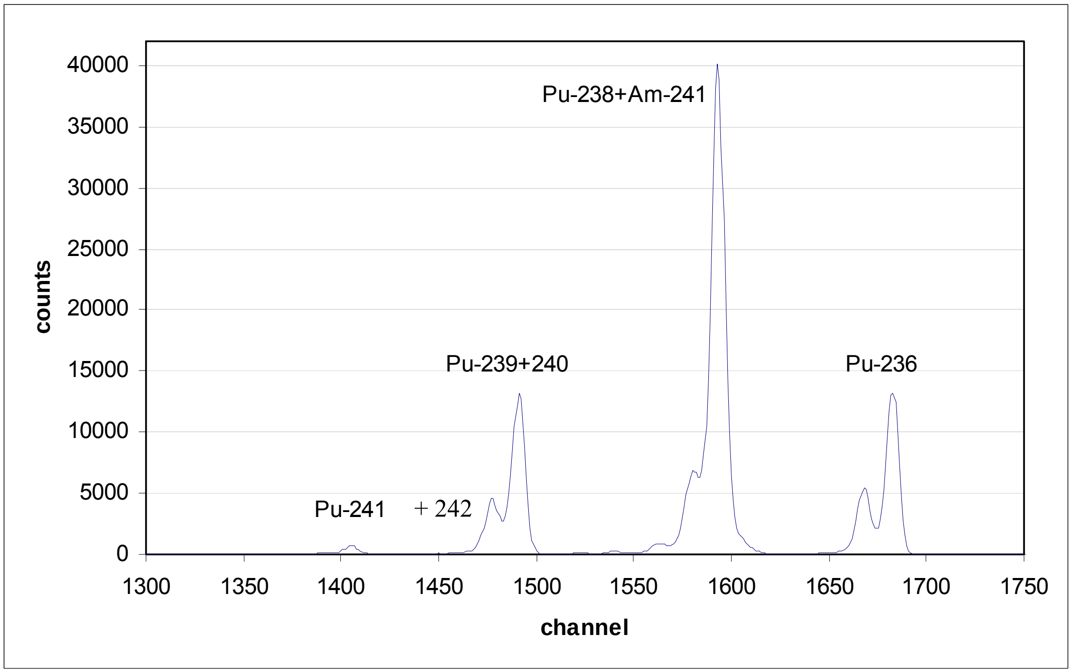


Figure 1 – Alpha spectrum measured at the NPL using a PIPS detector.

10. Discussion of the comparison results

Table 9 and Figure 2 present the comparison results by method. The participants who used more than one measurement method reported results that are self-consistent within one or two standard uncertainties. The PTB explained that the mean CNET and TDCR result that they reported is robust because on one hand the CNET result depends on the activity of the ^{3}H tracer but on the other hand it is less sensitive to the *kB* value than the TDCR result.

The results of the four participants who used the CNET method agree within one standard uncertainty, except for the NMISA (see below). The results of the five participants who used the triple-to-double-coincidence-ratio (TDCR) method agree within two standard uncertainties, except for the NMISA (see below). The results of the three participants who used the ^{241}Am in-growth method based, respectively, on α spectrometry (IAEA), $4\pi\alpha$(LS)-γ(NaI) live-timed anticoincidence counting (NIST) or γ-ray spectrometry (NPL) agree within two standard uncertainties.

For the IRMM and the PTB the tritium uncertainty is the dominant component of the uncertainty budget (due to a sensitivity coefficient close to 1) and this means that the ^{241}Pu activity measured by the CIEMAT/NIST method is highly correlated to the tritium activity. Indeed, the IRMM CNET result in this comparison is 2 % higher than the PTB CNET result and this corresponds to the tritium 2009 comparison where the IRMM obtained results about 2.5 % higher than the PTB. Similarly for the IAEA, the ^{242}Pu tracer uncertainty is also the dominant component and consequently the ^{241}Pu activity measured by this laboratory is highly correlated to the NIST ^{242}Pu SRM activity.

Table 9 also shows that the NMISA and the IAEA are the only participants who reported an adsorption correction factor (for the LS vial walls and the ampoule walls respectively) deduced from LS measurements.

Importance of the beta spectrum shape

In addition to the official results given in the Tables and Figures cited above, the NMISA reported higher results obtained with other beta spectrum shapes than the one given in Table 10 (see Figure 3). The NMISA favoured the beta shape factor of the type $1.0 + K(q^2 + p^2)$ from Grau Malonda [7] because the single parameter K could be easily adjusted to match the currently recommended beta spectrum average energy of 5.8 keV [1] for $K = 10.8$. With this beta shape factor the NMISA obtained consistent results when using both the CNET and the TDCR methods. When the shape parameter $K = -1.27$ is applied, the resulting beta spectrum shape is identical to the shape proposed by Cassette,

$$S(W) = 1 - 1.2\,W + 1.4/W - 0.1W^2 \text{ [10]},$$

based on three coefficients and related to a recent measurement of the beta spectrum [6]. However the extracted average energy of 5.16 keV is much lower than the recommended value of 5.8 keV. It is important to note that selecting $K = -1.27$ brings the NMISA result into line with the other participants. Thus the NMISA concluded that their systematically low official results are entirely due to the choice of the shape constant and not to any other measurement discrepancy.

The beta spectrum shapes used by the participants are plotted in Figure 4. If not directly provided by the laboratory, these were calculated using the program SPEBETA from LNE-

LNHB [9] on the basis of the information given in Table 10. All the spectra were re-normalized to the same area for comparison purposes. It is of interest to note that the allowed and Cassette [10] shapes used by the NMISA as a test are both similar to all the other shapes used by the other participants. On the contrary, the shape retained by the NMISA for their official result looks quite different. It is not clear why the NMISA found discrepancies between the TDCR and the CNET methods using the allowed or the Cassette beta shapes while the other participants found agreement within uncertainty (see Figure 2). The NMISA reported after the comparison that subsequent measurements showed that the ^{3}H tracer standards prepared for the CIEMAT/NIST method did not match their Pu-241 sources as well as previously believed.

After the comparison, further data analysis has been carried out at the IRMM using the EFFY5 program (while they used CN2005 for the comparison result) for the CNET efficiency calculations. Different activity concentration values were obtained from the IRMM CNET measurement data when changing the beta spectrum shape in the EFFY5 program. The results are summarized in Figure 5 where a linear dependence of the ^{241}Pu activity concentration is observed as a function of the beta spectrum average energy (slope equal to -15.3 (7) kBq g^{-1} keV^{-1}). When plotting the comparison results based on the CNET method as a function of the beta spectrum average energy, the same linear dependence is observed with a slope equal to -14.4 (2.0) kBq g^{-1} keV^{-1} (Figure 6). It can be concluded that the large spread of comparison results observed for the CNET method seems to come mainly from differences in the beta spectrum shape used by the participants.

Participant	**Method**	***A* / kBq g^{-1}**	***u* / kBq g^{-1}**	**Mean date of meas.**	**Correction factor**	**Value**	**Uncertainty**
IRMM	LSC **CIEMAT/NIST** method [a] using the program created by E. Günther of PTB (ver.2005 - Aug.2005)	93.8	0.84	18-Sep-2010	Decay	1.03 typ.	0.000 1
					Impurities	1	0.001 5
					Adsorption in the ampoule	1	1.5×10^{-4}
					Dead time	1 [b]	0.001
					Background	0.999 5 to 0.999 9	3.5×10^{-4}
					Decay during measurement	1.000 000 46	
NIST	**CIEMAT/NIST** efficiency tracing [$]	94.0	1.8				
NMISA	**CIEMAT/NIST** method [$]	85.6 [e]	1.5	17-Aug-2010	Decay	1.026 50 (mean factor)	0.000 08
					Impurities (in-growth of ^{241}Am)	0.13 %	0.03 %
					Adsorption in the ampoule	0 %	0.021 %
					Adsorption in the vials	0.34 %	0.20 %
					Dead time	0.16 % to 0.25 %	0.05 %
					Background	0.24 % to 0.36 %	0.009 %
					Satellite pulses	0.165 %	0.014 %
PTB	LSC **CIEMAT/NIST**	91.9	1.0	Dec-2009			

Continued overleaf

Participant	Method	A / kBq g^{-1}	u / kBq g^{-1}	Mean date of meas.	Correction	Value	Uncertainty
IRMM	LSC **TDCR** method using the program TDCRB-02p by R. Broda et al. (April 2002) transported to RealBasic.	93.9	0.75	18-Sep-2010	Decay	1.03 typ.	0.000 1
					Impurities	0.995 typ.	0.002
					Adsorption in the ampoule	1	1.5×10^{-4}
					Dead time	1	0.002
					Background	0.99 to 0.995	2.5×10^{-3}
					Decay during measurement	1.000 000 46	
LNE-LNHB	LSC **TDCR** method [d]	90.2	1.5	Feb-2010	Decay	0.9913	2.5×10^{-5}
					Impurities	*	
NIST	**TDCR** [$] [2,3]	94.5	1.2		Decay	~ 2 kBq	0.01 % (rel.)
					Impurities	*	0.16 % (rel.)
					Shape factor	3.20 %	20 % (rel.)
NMISA	**TDCR** efficiency calculation technique [4,5]	85.8 [e]	1.1	31-May-2010	Decay	1.015 95 (mean factor)	0.000 05
					Impurities (in-growth of ^{241}Am)	0.095 %	0.03 %
					Adsorption in the ampoule	0 %	0.02 %
					Dead time	0.2 % to 0.3 %	0.05 %
					Background	0.22 %	0.10 %
					Satellite pulses	0.80 %	0.50 %
		91.6 [$, c]	1.1 [$, c]	31-May-2010			
PTB	**TDCR**	91.1	2.5	02-Dec-2009			

Continued overleaf

Participant	Method	*A* / kBq g^{-1}	*u* / kBq g^{-1}	Mean date of meas.	Correction factor	Value	Uncertainty
IAEA	Isotope dilution alpha spectrometry and **Am-241 in-growth** [g]	90.73	0.52		Adsorption in the ampoule	1.000 603	0.000 016
NIST	**Am-241 in-growth** by 4πα(LS)-γ(NaI) Live-Timed Anticoincidence meas. [$]	92.7	1.4		Impurities		
NPL	**Am-241 and U-237 in-growth** by γ-ray spectrometry [f]	92.37	0.39				
NIST	Liquid Scintillation comparative measurements [g] (traceable to 4πα(LS)-γ(NaI) Live-Timed Anticoincidence meas.)	92.22	0.40	2-May-2010			
NPL	Mass spectrometry with alpha spectrometry [$,g]	92.49	0.78				

[$] Not used for the comparison result

* The alpha impurities counting rate is subtracted from raw counts prior to treatment with the TDCR model. The alpha impurity correction cannot be resumed in a single correction factor as the correction process is not linear.

[a] All sources were measured with both a Packard Tri-Carb and a Wallac Quantulus LSC giving the same results well within the stated uncertainty. The result reported here is the weighted mean of the results of 9 samples in UG + 1 mL H_2O and 4 samples in UGAB (See also Table 8). No mass dependence of the activity concentration was observed.

[b] Correction applied automatically by the LS counter.

[c] Result when using a beta shape factor [$S(W) = 1 - 1.2W + 1.4/W - 0.1W^2$] derived by P. Cassette [10], based on the latest measurement of the beta spectrum [6].

[d] Alpha activity was first measured using a Wallac 1414 LS counter. Assuming a detection efficiency of one for α particles in double and triple coincidences, the triple and double background counting rates are subtracted from the alpha counting rate in order to get the TDCR value used for the calculation of detection efficiency. Efficiency variation in the TDCR method is achieved using coaxial grey filter around the sources.

[e] Result when using the beta shape factor as given in Table 4. This beta shape gives the beta spectrum average energy in agreement with [1].

[f] Measurement of Am-241 and U-237 in-growth from mother nuclide Pu-241 by frequent γ-ray spectrometry using a HPGe detector over a time period of one year. By fitting the experimental values to the theoretical in-growth function an activity of Pu-241 could be determined for the date of chemical separation (21 Oct 2009). This value was decay corrected to the reference date (1 Feb 2010).

[g] See text.

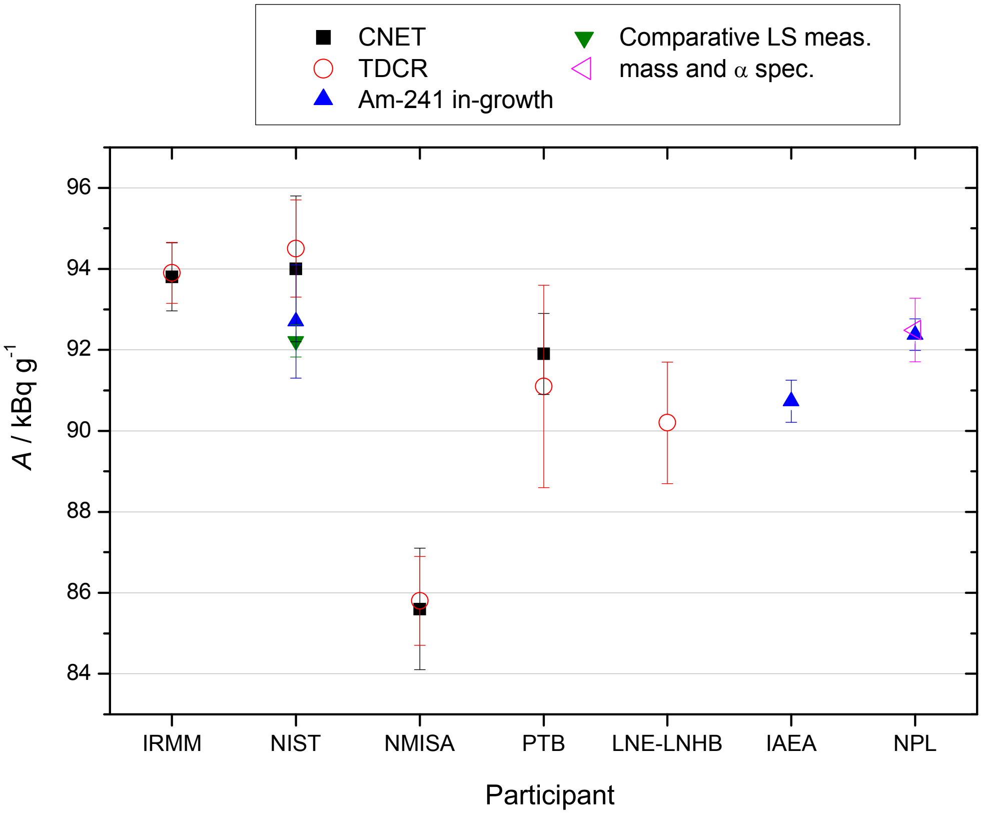


Figure 2 – Comparison results by measurement method.

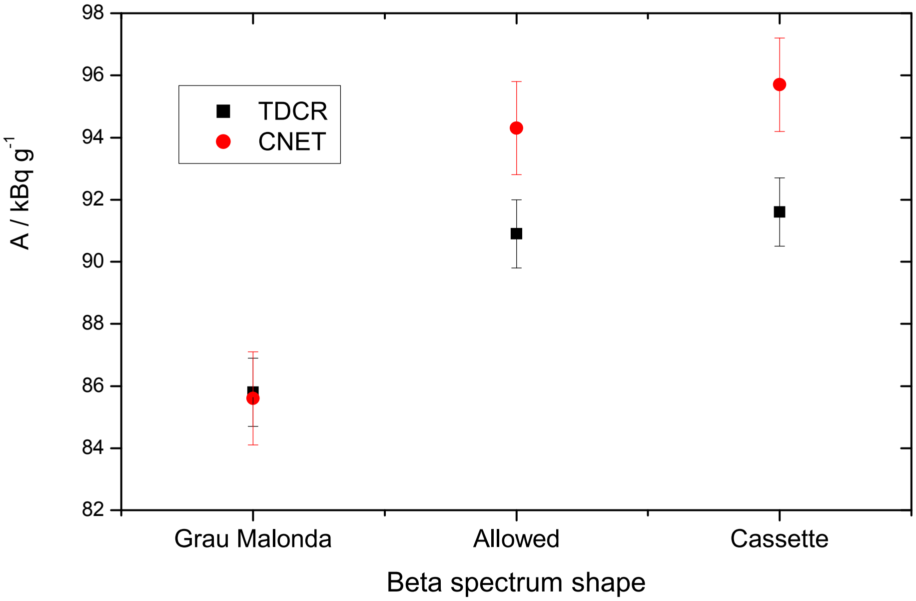


Figure 3 – NMISA results using different beta spectrum shapes: $1.0 + 10.8(q^2 + p^2)$ from [7]; the allowed shape; a shape factor from P. Cassette [10]

Table 10 – Nuclear data used by the participants

	^{236}Pu, p_α	**^{239}Pu, p_α**	**^{240}Pu, p_α**	**^{241}Pu, p_β**	**^{241}Am, E_γ and p_γ**	**^{241}Pu, p_α**	**^{237}U, E_γ and p_γ**	**Reference**	**Beta spectrum end-point and average energy and shape factor**
IAEA								DDEP (2006-2009)	
IRMM								*Monographie* BIPM-5	20.8 keV ; 5.2 keV 1st forbidden 1 (spectrum calculated with an allowed shape)
LNE-LNHB								DDEP (2006-2009)	20.8 (2) keV ; 5.0 keV 1st forbidden Experimental spectrum (modified from [6] to comply with an end-point energy of 20.8 keV)
NMISA				1				*Monographie* BIPM-5	20.8 (2) keV ; 5.8 keV 1st order forbidden non unique $1.0 + K(q^2 + p^2)$ [7] with K = 10.8 adjusted to get an average energy in agreement with [1]
NPL (α spec.)	0.999 (5)	0.879 3 (10)	0.999 0 (20)						
NPL (γ spec.)				0.999 975 6	59.9 keV 0.359 2 (17)	0.000 024 4	59.9 keV 0.341 (9)		
PTB								DDEP [a]	21.6 keV ; 5.3 keV 1st forbidden non unique $1-1.9582 \cdot W+0.96078 \cdot W^2$ [8]

[a] except for the ^{241}Pu half-life (see text page 1)

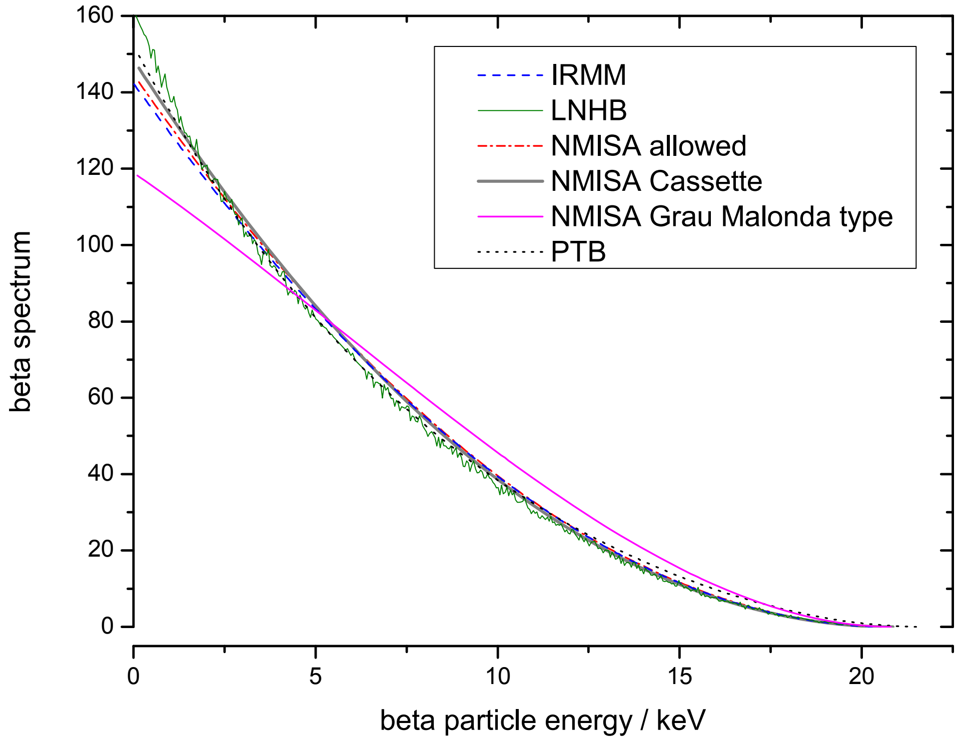


Figure 4 – Normalized beta spectrum shapes used by the participants (see text).

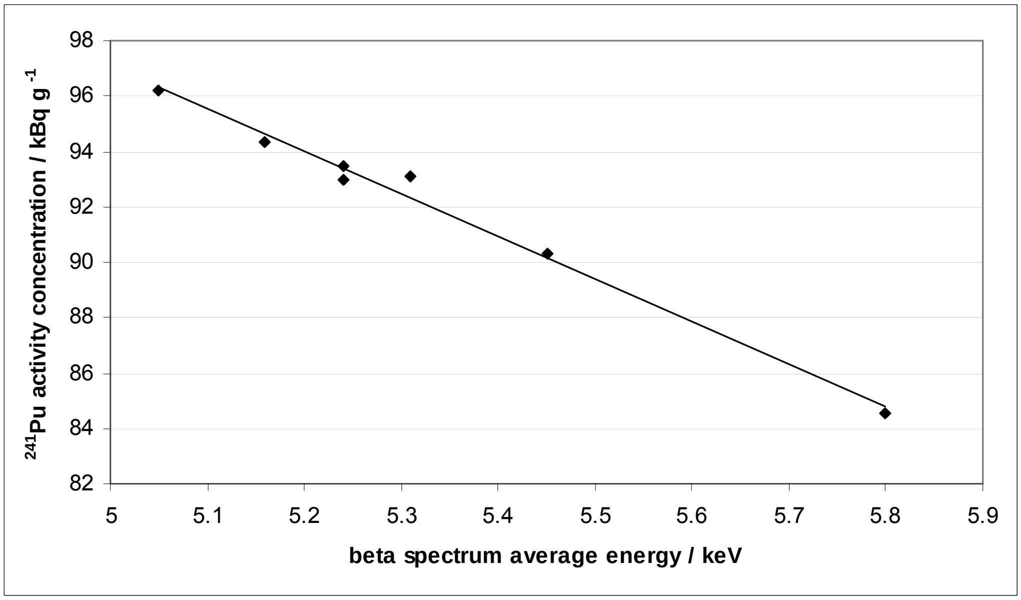


Figure 5 – Influence of the ^{241}Pu beta spectrum shape on the ^{241}Pu activity concentration obtained by the CNET method, as evaluated by the IRMM (see text).

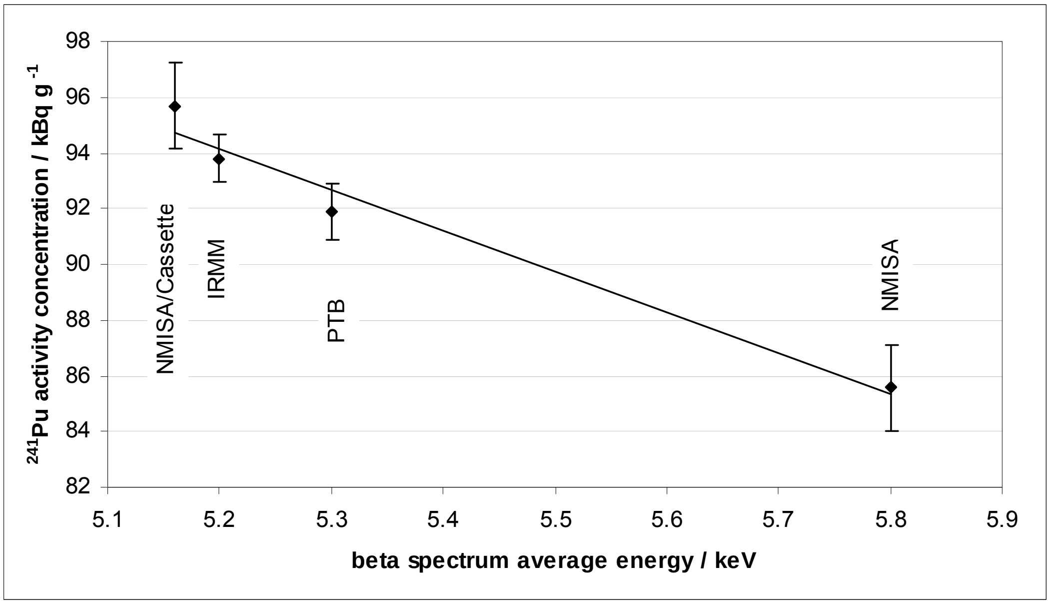


Figure 6 – Results of the comparison using the CNET method plotted as a function of the beta spectrum average energy.

11. Key comparison reference value and degrees of equivalence

Every participant in the comparison is entitled to have one result included in the key comparison database (KCDB) as long as the laboratory is a signatory or designated institute listed in the CIPM MRA [11]. Normally, the most recent result is the one included. Any participant 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. 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.

11.1 The key comparison reference value

The key comparison reference value (KCRV) of the present CCRI(II)-K2.Pu-241 key comparison has been defined as the arithmetic mean of a selection of the comparison results as discussed by the Key Comparison Working Group (KCWG) and approved by the CCRI(II). The strong dependence of some of the comparison results on a tracer activity (such as the CNET method or the isotope dilution alpha spectrometry method) has been mentioned in section 10. However, the KCWG proposed to include these results as long as the tracer was standardized by the participant using a primary method. Consequently, only the IAEA result based on the isotope dilution alpha spectrometry method with a tracer from the NIST has not been included in the KCRV.

The KCWG proposed to include the NPL in-growth measurement result in the KCRV because the HPGe γ-ray spectrometer used was calibrated at the NPL with their primary standards. The NIST result which is based on relative measurements to a NIST well-characterized and primary master solution is also included in the KCRV. Finally, the TDCR results from the NMISA using the Cassette beta spectrum shape, 91.6 (11) kBq g^{-1}, (see Table 9) is included in the KCRV while the NMISA official result in Table 1 is used for the calculation of their degree of equivalence.

Consequently, the KCRV is 92.0 (5) kBq g^{-1} using the results in Table 1 from IRMM, LNE-LNHB, NIST, NPL, PTB, and the NMISA/Cassette result given above and has been agreed by the CCRI(II).

11.2 The degrees of equivalence

The degree of equivalence D_i of a particular NMI, i, with the KCRV is expressed as the difference of the activity concentration result A_i given in Table 1 with respect to the KCRV

$$D_i = A_i - \mathrm{KCRV}$$

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

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

taking correlations into account as appropriate [12].

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

$$D_{ij} = D_i - D_j = A_i - A_j$$

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

$$u_{Dij}{}^2 = u_i{}^2 + u_j{}^2 - 2u(A_i, A_j)$$

where any obvious correlations between the NMIs (such as a traceable calibration) are subtracted using the covariance $u(A_i, A_j)$ (see [13] for more detail).

The uncertainties of the differences between the values assigned by individual NMIs and the 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 and care should be taken when making such calculations.

Table 11 shows the table of the degrees of equivalence with the KCRV as they appear in the KCDB. It should be noted that for consistency within the KCDB, a simplified level of nomenclature is used with A_i replaced by x_i. The introductory text is that agreed for the comparison. The graph of the results in Table 11, corresponding to the degrees of equivalence with respect to the KCRV (identified as x_R in the KCDB), is shown in Figure 7. The 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.

Table 11. Table of degrees of equivalence and introductory text for ^{241}Pu

Key comparison CCRI(II)-K2.Pu-241

MEASURAND : **Activity concentration of ^{241}Pu**

Key comparison reference value: the reference value for this radionuclide is x_R = 92.0 kBq g^{-1}, with a standard uncertainty u_R = 0.5 kBq g^{-1}.
x_R is computed as the arithmetic mean of a selection of the participants' results.

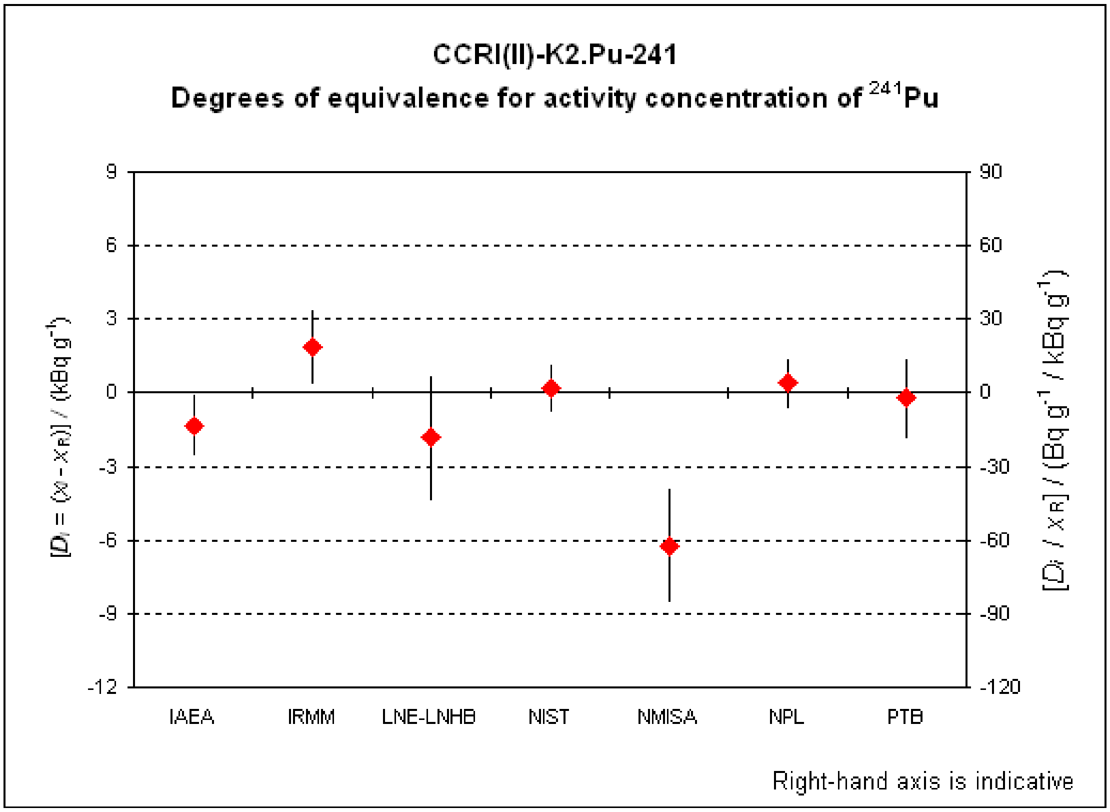
The degree of equivalence of each laboratory with respect to the reference value is given by a pair of terms: $D_i = (x_i - x_R)$ and U_i, its expanded uncertainty (k = 2), both expressed in kBq g^{-1}, $U_i = 2((1-2/n)u_i^2 + (1/n^2)\Sigma u_i^2)^{1/2}$ when the laboratory has contributed to the calculation of x_R, with n the number of laboratories.

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 kBq g^{-1}.

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

Lab *i* ⇩	D_i	U_i
	/ kBq g^{-1}	
IAEA	-1.3	1.3
IRMM	1.9	1.5
LNE-LNHB	-1.8	2.6
NIST	0.2	1.0
NMISA	-6.2	2.3
NPL	0.4	1.0
PTB	-0.2	1.7

Figure 7. Graph of degrees of equivalence with the KCRV for ^{241}Pu



Conclusion

Seven laboratories took part in the CCRI(II) key comparison of activity concentration measurements of ^{241}Pu, CCRI(II)-K2.Pu-241, using seven different methods. The spread of all results except one is 4×10^{-2} in relative terms. The results based on the CIEMAT/NIST efficiency tracing method are shown to be dependent on the beta spectrum shape selected. A recent measurement of the ^{241}Pu beta spectrum shape with a cryogenic detector [6] should play a role in future decay data evaluation for this nuclide and consequently improve the accuracy of future ^{241}Pu standardizations using liquid scintillation.

The KCRV has been determined as the arithmetic mean of six independent results based on four different methods. The results of the comparison have been analysed with respect to the KCRV. The degrees of equivalence with the KCRV have been approved by the CCRI(II) and are published in the BIPM key comparison database.

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 are those available in the KCDB.

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