

**Activity measurements of the radionuclide  $^{153}\text{Sm}$**   
**for the ANSTO, Australia in the ongoing comparison BIPM.RI(II)-K1.Sm-153**

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### **Abstract**

In 2004, the Australian Nuclear Science and Technology Organisation (ANSTO) submitted two samples of known activity of  $^{153}\text{Sm}$  to the International Reference System (SIR). The value of the activity submitted was about 920 MBq. This key comparison result has been added to the matrix of degrees of equivalence in the key comparison database that now contains five results, identifier BIPM.RI(II)-K1.Sm-153.

## **1. Introduction**

The SIR for activity measurements of  $\gamma$ -ray-emitting radionuclides was established in 1976. Each national metrology institute (NMI) may request a standard ampoule from the BIPM that is then filled (3.6 g) with the radionuclide in liquid (or gaseous) form. 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  $^{226}\text{Ra}$  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 2004, the SIR has measured 872 ampoules to give 634 independent results for 62 different radionuclides. The SIR makes it possible for national laboratories to check the reliability of their activity measurements at any time. This is achieved by the determination of the equivalent activity of the radionuclide and by comparison of the result with the key comparison reference value determined from the results of primary realizations. These comparisons are described as BIPM ongoing comparisons and the results form the basis of the BIPM key comparison database (KCDB) that was set up under the CIPM Mutual Recognition Arrangement (MRA) [2]. The comparison described in this report is known as the BIPM.RI(II)-K1.Sm-153 key comparison.

## **2. Participants**

In addition to the ANSTO, four NMIs have submitted ampoules for the comparison of  $^{153}\text{Sm}$  activity measurements since 1998. The ANSTO details are given in Table 1 and the details of the other participants are given in [3].

**Table 1. Details of the ANSTO participation in the comparison BIPM.RI(II)-K1.Sm-153**

NMI	Full name	Country	Regional metrology organization	Date of measurement at the BIPM
ANSTO	Australian Nuclear Science and Technology Organisation	Australia	APMP	2004-09-22

### 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 the laboratory, the activities submitted and the relative standard uncertainties ( $k = 1$ ) are given in Table 2. The uncertainty budget is given in Appendix 1. The acronyms used for the measurement methods are given in Appendix 2.

**Table 2. Standardization methods of the ANSTO for  $^{153}\text{Sm}$** 

NMI	Method used and acronym (see Appendix 2)	Half-life / d	Activity / kBq	Reference date YY-MM-DD	Relative standard uncertainty $\times 100$ by method of evaluation	
					A	B
ANSTO	Pressurized ionization chamber calibrated by $4\pi\beta\text{-}\gamma$ coincidence meas. in June 2003 4P-??-BP-NA-GR-CO	1.928 49 (11) [4]	915 900 907 600*	04-09-07 12 h UTC	0.03	0.94

\* two ampoules submitted

The half-life used by the BIPM is 46.284 (4) hours [5] which is in very good agreement with the more recent evaluation by the same author published in [4].

Details regarding the solution submitted are shown in Table 3, including any impurities, when present, as identified by the laboratory. Recently the BIPM has developed a standard method for evaluating the activity of impurities using a calibrated Ge(Li) spectrometer [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.

For this submission, the measurement of the ampoule at the BIPM was delayed by a week due to transport/logistics problems so that the contribution of the impurities to the ionization current became important. A 5 % discrepancy in the SIR result when compared with the KCRV was observed and this motivated a  $\gamma$ -spectrometry measurement at the BIPM. The resulting relative activities of  $^{152}\text{Eu}$ ,  $^{154}\text{Eu}$  and  $^{155}\text{Eu}$  are in agreement with the ANSTO values within one or two combined standard uncertainties. In addition, a  $^{156}\text{Eu}$  impurity was measured at the BIPM, as given in Table 3. The consequences on the ANSTO SIR results are discussed in section 4.

**Table 3. Details of the solution of  $^{153}\text{Sm}$  submitted**

NMI	Chemical composition	Solvent conc. / (mol dm <sup>-3</sup> )	Carrier: conc. / (μg g <sup>-1</sup> )	Density / (g cm <sup>-3</sup> )	Relative activity of any impurity <sup>†</sup>
ANSTO	Sm in HCl	0.1	Sm: 720	1.04	$^{152}\text{Eu}^m$ : $1.20 (9) \times 10^{-2} \% \#$ $^{152}\text{Eu}$ : $1.43 (10) \times 10^{-3} \%$ $^{154}\text{Eu}$ : $7.8 (7) \times 10^{-4} \%$ $^{155}\text{Eu}$ : $2.3 (3) \times 10^{-4} \%$ $^{156}\text{Eu}$ : $1.16 (14) \times 10^{-3} \% *$

<sup>†</sup> the ratio of the activity of the impurity to the activity of  $^{153}\text{Sm}$  at the reference date

<sup>#</sup> negligible influence on the SIR measurement

\* measured at the BIPM

#### 4. Results

All the submissions to the SIR since its inception in 1976 are maintained in a database known as the "mother-file". The previous activity measurements for  $^{153}\text{Sm}$  arise from seven ampoules and the SIR equivalent activity,  $A_{ei}$ , for each ampoule is given in [3] for each NMI,  $i$ . The SIR equivalent activities for the ANSTO ampoule are given in Table 4. The date of measurement in the SIR is given in Table 1 and is used in the KCDB and all references in this report. The relative standard uncertainty arising from the measurements in the SIR is 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  $^{226}\text{Ra}$ , all the SIR results are normalized to the radium source number 5 [1].

The ionization chamber measurement by the ANSTO at the reference date was insensitive to the europium impurities as the ionization current was then dominated by the  $^{153}\text{Sm}$  activity. Unfortunately, at the time of the SIR measurement almost 15 days later, the correction for impurities is 1.187 and becomes 1.234 when the  $^{156}\text{Eu}$  impurity detected at the BIPM is also taken into account. The final result corrected for all impurities in Table 4 is in agreement with the KCRV within the combined standard uncertainty.

Measurements repeated at the BIPM one day later produced comparison results in agreement within less than  $2 \times 10^{-3}$ .

**Table 4. Results of SIR measurements of  $^{153}\text{Sm}$  for the ANSTO**

NMI	Mass of solution / g	Activity submitted/ kBq	N° of Ra source used	SIR $A_e$ / MBq	Relative uncertainty from SIR	Total uncertainty $u_{c,i}$ / MBq
ANSTO	3.6353	915 900	1	565.6	$1.1 \times 10^{-2}$ *	8.0
	3.6024	907 600		565.3 †#		8.1

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

# corrected for ANSTO impurities and the  $^{156}\text{Eu}$  impurity measured at the BIPM

\* due to the combination of a long delay between the reference date and the SIR measurement, and the uncertainties of the activity of the impurities.

#### 4.1 The key comparison reference value

The key comparison reference value for  $^{153}\text{Sm}$  is 573 700 (1 200) kBq as given in [3]. Although the KCRV may be modified whenever an NMI participates, such modifications are only made by the CCRI(II), normally during one of its biennial meetings. However, due to the uncertainty coming from the large impurity correction of the ANSTO SIR measurement, it is not recommended to include this result in the KCRV.

#### 4.2 Degrees of equivalence

Every NMI that has submitted ampoules to the SIR is entitled to have one result included in Appendix B of the KCDB as long as the NMI is a signatory or designated institute listed in the MRA. Normally, the most recent result is the one included. Any NMI may withdraw its result only if all the participants agree.

The degree of equivalence of a given measurement standard is the degree to which this standard is consistent with the key comparison reference value [2]. The degree of equivalence is expressed quantitatively in terms of the deviation from the key comparison reference value and the expanded uncertainty of this deviation ( $k = 2$ ). The degree of equivalence between any pair of national measurement standards is expressed in terms of their difference and the expanded uncertainty of this difference and is independent of the choice of key comparison reference value.

##### 4.2.1 *Comparison of a given NMI with the KCRV*

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

$$D_i = A_{e_i} - \text{KCRV} \quad (1)$$

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

$$U_i = 2u_{D_i}, \quad (2)$$

taking correlations into account as appropriate [8].

#### 4.2.2 Comparison of any two NMIs with each other

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

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

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

$$u_{D_{ij}}^2 = u_i^2 + u_j^2 - 2u(A_{ei}, A_{ej}) \quad (4)$$

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 will 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. The graphical representation indicates in part the degree of equivalence between the NMIs but does not take into account the correlations between the different NMIs. However, the matrix of degrees of equivalence shown in yellow in Table 5 does take the known correlations into account.

### Conclusion

The result for the ANSTO in this ongoing comparison agrees with the KCRV within the combined standard uncertainties.

The BIPM ongoing key comparison for  $^{153}\text{Sm}$ , BIPM.RI(II)-K1.Sm-153 currently comprises five results. These have been analysed with respect to the KCRV determined for this radionuclide, and with respect to each other. The matrix of degrees of equivalence has been approved by the CCRI(II) and is published in the BIPM key comparison database.

Other results may be added as and when NMIs contribute  $^{153}\text{Sm}$  activity measurements to this comparison or take part in linked comparisons.

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**Table 5. Table of degrees of equivalence and introductory text for <sup>153</sup>Sm**  
**Key comparison BIPM.RI(II)-K1.Sm-153**

**MEASURAND :** Equivalent activity of <sup>153</sup>Sm

**Key comparison reference value:** the SIR reference value  $x_R$  for this radionuclide is 573.7 MBq, with a standard uncertainty,  $u_R = 1.2$  MBq (see Section 4.1 of the Final Report). the value  $x_i$  is taken as the equivalent activity for laboratory  $i$ .

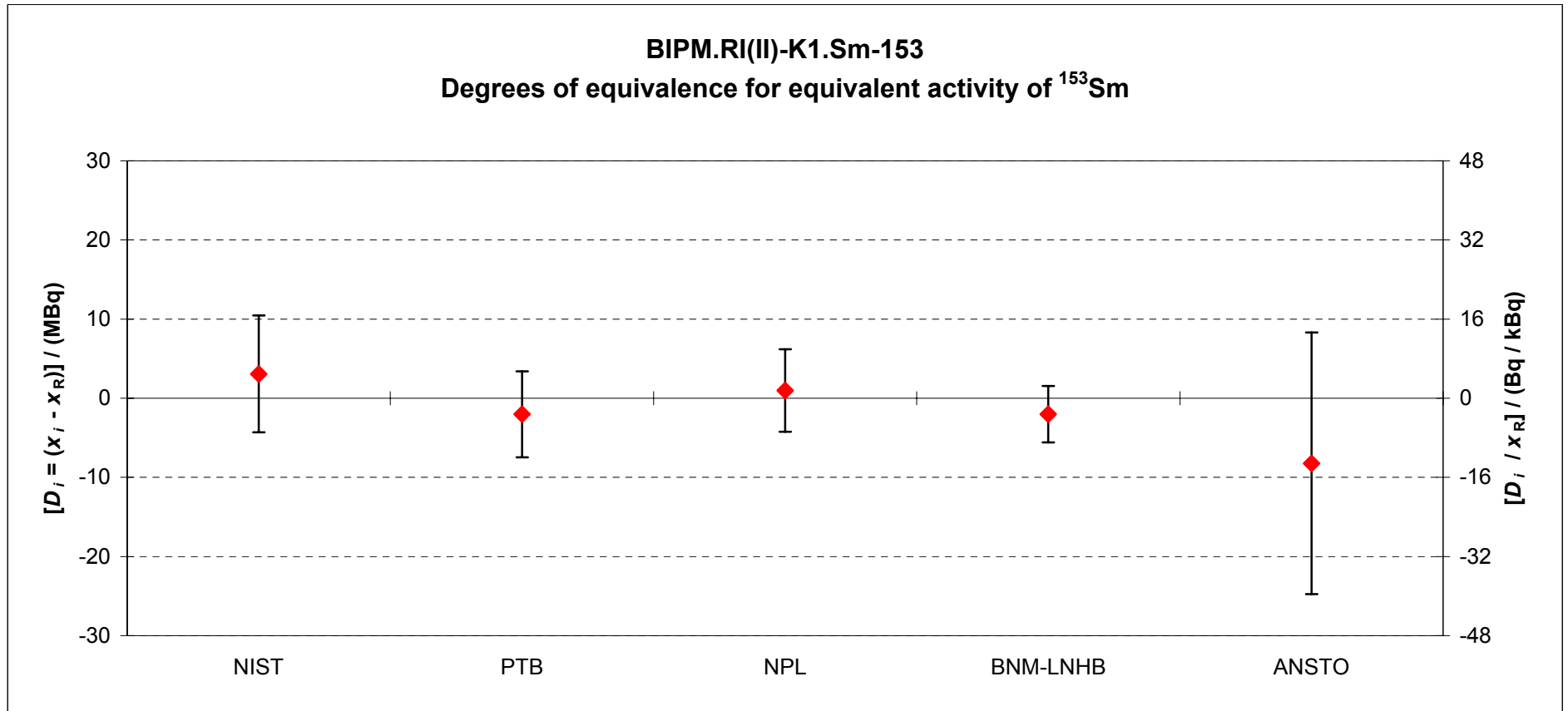
The degree of equivalence of each laboratory with respect to the reference value is given by a pair of terms:  $D_i = (x_i - x_R)$  and  $U_i$ , its expanded uncertainty ( $k = 2$ ), both expressed in MBq, and  $U_i = 2((1 - 2/n)u_i^2 + (1/n^2)\sum u_i^2)^{1/2}$  when each laboratory has contributed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

The degree of equivalence between two laboratories is given by a pair of numbers:  $D_{ij} = D_i - D_j = (x_i - x_j)$  and  $U_{ij}$ , its expanded uncertainty ( $k = 2$ ), both expressed in MBq. The approximation  $U_{ij}^2 \sim 2^2(u_i^2 + u_j^2)$  is used in the following table.

Lab  $j$   $\longrightarrow$

Lab $i$ $\downarrow$	$D_i$ $U_i$		NIST		PTB		NPL		BNM-LNHB		ANSTO	
	/ MBq		$D_{ij}$	$U_{ij}$	$D_{ij}$	$U_{ij}$	$D_{ij}$	$U_{ij}$	$D_{ij}$	$U_{ij}$	$D_{ij}$	$U_{ij}$
NIST	3.1	7.4			5.1	11.3	2.1	11.0	5.1	9.7	11.3	18.7
PTB	-2.0	5.4	-5.1	11.3			-3.0	8.5	0.0	6.6	6.2	17.3
NPL	1.0	5.2	-2.1	11.0	3.0	8.5			3.0	6.2	9.2	17.2
BNM-LNHB	-2.0	3.6	-5.1	9.7	0.0	6.6	-3.0	6.2			6.2	16.3
ANSTO	-8.2	16.5	-11.3	18.7	-6.2	17.3	-9.2	17.2	-6.2	16.3		

**Figure 1.** Graph of degrees of equivalence with the KCRV for  $^{153}\text{Sm}$   
(as it appears in Appendix B of the MRA)



**Appendix 1. Uncertainty budgets for the activity of  $^{153}\text{Sm}$  submitted to the SIR****Uncertainty budget for the ANSTO measurement (2004)**

Relative standard uncertainties	$u_i \times 10^4$ evaluated by method	
	A	B
Contributions due to		
Current measurement	3.1	–
Radium stability correction	–	20.0
$^{153}\text{Sm}$ calibration factor	–	92.0
Weighing	–	0.2
Background current	0.0	–
$^{153}\text{Sm}$ decay correction	–	2.0
$^{152}\text{Eu}^m$ impurity correction	–	1.1
$^{152}\text{Eu}$ impurity correction	–	0.2
$^{154}\text{Eu}$ impurity correction	–	0.1
$^{155}\text{Eu}$ impurity correction	–	0.0
<b>Quadratic summation</b>	<b>3.1</b>	<b>94.1</b>
<b>Relative combined standard uncertainty, <math>u_c</math></b>	<b>94.2</b>	

## 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
$4\pi$	4P	proportional counter	PC
defined solid angle	SA	press. prop counter	PP
$2\pi$	2P	liquid scintillation counting	LS
undefined solid angle	UA	Nal(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 ( $x + \gamma$ )	PH	triple-to-double coincidence ratio counting	TD
photons + electrons	PE	selective sampling	SS
alpha - particle	AP	high efficiency	HE
mixture of various radiation	MX	digital coincidence counting	DC

Examples	method	acronym
$4\pi$ (PC) $\beta$ - $\gamma$ -coincidence counting		4P-PC-BP-NA-GR-CO
$4\pi$ (PPC) $\beta$ - $\gamma$ -coincidence counting eff. trac.		4P-PP-MX-NA-GR-CT
defined solid angle $\alpha$ -particle counting with a PIPS detector		SA-PS-AP-00-00-00
$4\pi$ (PPC)AX- $\gamma$ (GeHP)-anticoincidence counting		4P-PP-MX-GH-GR-AC
$4\pi$ CsI- $\beta$ ,AX, $\gamma$ counting		4P-CS-MX-00-00-HE
calibrated IC		4P-IC-GR-00-00-00
internal gas counting		4P-PC-BP-00-00-IG