# Results of the EURAMET.RI(II)- S7.Sm-151 Supplementary Comparison (EURAMET Project 1292)

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## Abstract

An international comparison of the activity standardisation of the relatively long-lived gamma-ray emitter $^{151}$Sm has been recently completed. A total of six laboratories measured a solution prepared by CEA/LNHB and CEA/LANIE. Aliquots of the master solution were standardized in terms of activity per mass unit by participant laboratories using 2 different techniques. The results of the comparison can be used as the basis for establishing equivalence among the laboratories.
The activity measurements of this comparison are part of the joint research project "Metrology for Radioactive Waste Management" of the European Metrology Research Programme (EMRP). One aim of this project is a new determination of the $^{151}$Sm half-life.

## 1. Introduction

Samarium-151 is a relatively long-lived nuclide produced by fission during the irradiation of uranium fuel rods in nuclear reactors. It decays by two β disintegrations to $^{151}$Eu. The most intense transition (~ 99 %) reaches the $^{151}$Eu ground state with a maximum energy of 76.3 keV, the second one (~ 1 %) populates the $^{151}$Eu first exited level with a maximum energy of 54.8 keV. Both transitions are first forbidden.

The currently recommended half-life value of $^{151}$Sm is 90 (6) a, derived from only three experimental values. Therefore, $^{151}$Sm is one of the three nuclides selected with the objective of improving the half-life in the framework of a coordinated research project (ENV09 2013) of the European Metrology Research Programme.

The half-life, $T_{1/2}$, can be determined by the relationship between the activity $A$ and the number $N$ of radioactive atoms in a solution:

$$T_{1/2} = \frac{\ln 2 \cdot N}{A}$$

where $A$ is the activity and $N$ is the number of $^{151}$Sm nuclei.

Therefore, the determination of the half-life requires the measurement of the activity and of the number of $^{151}$Sm atoms, per gram of the same solution, at the same time of reference

To date, for this nuclide, no previous comparison of activity concentration was conducted in the frame of EURAMET or of the CCRI(II). Hence, in order to increase the reliability of the activity measurements carried out in this exercise, the participants of the ENV09 project proposed the organisation of an international comparison. It was registered as a EURAMET.RI(II)- S7.Sm-151 Supplementary Comparison, (EURAMET Project 1292).

## 2. Participants

Six laboratories participated in the activity measurements: LNE-LNHB (pilot laboratory), CMI, IRMM, POLATOM, PTB and SMÚ.

Table 1 presents the list of participating laboratories and contact persons as well as the date of submission of their results to LNE-LNHB.

**Table 1- List of participants and date of submission of their final results to the Pilot Laboratory**

| **Participant** | | **Contact Person** | **Date of submission of final results to LNE-LNHB** |
|---|---|---|---|
| LNE- LNHB | Laboratoire National d'Essai – Laboratoire National Henri Becquerel | Carole Fréchou | 11/06/2014[a] |
| ČMI | Czech Metrology Institute | Jana Sochorová | 20/07/2014 |
| IRMM | Institute for Reference Materials and Measurements | Stefaan Pommé | 03/07/2014 |
| POLATOM | National Centre for Nuclear Research Radioisotope Centre | Tomasz Dziel | 26/06/2014 |
| PTB | Physikalisch-Technische Bundesanstalt | Karsten Kossert | 12/06/2014 |
| SMÚ | Slovenský Metrologický Ústav | Matej Krivošík | 22/07/2014 |

[a] LNE-LNHB submitted their results on 11 June 2014 to José María Los Arcos at the BIPM, who kindly acted as repository, prior to the submission of the results from the other laboratories to LNE-LNHB.

## 3. Protocol

A technical protocol to be followed for the comparison was agreed between partners; it included an EXCEL file to be completed and recommendations of necessary nuclear data from the NUCLEIDE database.

A decay scheme and full data tables were sent to the participants, including the histogram of the beta spectra calculated as allowed transitions by X. Mougeot (2014). In June 2014 a measurement of these beta spectra was carried out at LNHB and the validity of an allowed shape was confirmed. This information was sent to the participants.

As already mentioned, the recommended half-life value for starting this exercise was taken as 90 (6) a. The measurement of the mass concentration being planned between May and June, the participants were asked to carry out their activity measurements between April and June, in order to minimize the uncertainty of the decay correction.

The reference data was established as 1$^{st}$ April 2014, 0:00 UTC.

## 4. Preparation of the $^{151}$Sm solution

Within the framework of a research programme on transmutation of long-lived radionuclides undertaken by the French Atomic Energy Commission, targets of highly enriched actinides and fission products were irradiated in the fast neutron reactor Phénix. These experiments named PROFIL-R and M are described in (Isnard *et al.*, 2013). As a part of these experiments, 5.8 mg of samarium oxide powder enriched in $^{149}$Sm (95.1 %) were irradiated.

After irradiation, the container was opened in a hot cell to remove all the powder. The opening aimed at ensuring a total extraction of the powder and at avoiding any presence of the steel container (Ferlay *et al.*, 2010). After irradiation around 400 µg of $^{151}$Sm had been produced by the nuclear reactions. This irradiated powder was dissolved in a hot cell facility in 14 M $HNO_3$ in a closed Teflon container (Savillex, USA) at a temperature around 100 °C. Finally, the radioactive solution was supplied to the Isotopic and Elementary Nuclear Analysis Laboratory (CEA-LANIE) to carry out determinations of isotope ratios and concentration for samarium, europium and gadolinium.

To perform these analyses, it was necessary to separate the europium from the samarium and gadolinium in order to prevent isobaric interference. This chemical purification was performed at CEA-LANIE in July 2011 by High Performance Liquid Chromatography (HPLC) using 2-hydroxy-2-methylbutyric acid (HMB) (Bourgeois *et al.* 2011). The purified fractions were removed off line and analysed by TIMS and/or ICPMS MC. After these measurements, a 5-mL solution containing about 1.2 µg of $^{151}$Sm in 20 µg of total Sm in 3 mol/L $HNO_3$ was available for the ENV09 project.

In February 2014, this solution was slowly heated to dryness and sent to LNE-LNHB for the purpose of this comparison. The residue was then dissolved using 5 mol/L HCl and diluted with de-ionized water to reach 1 mol/L HCl. During this step, a suitable amount of carrier was added in order to have a 100 fold excess (in mole fraction) of stable lanthanide compared to $^{151}$Sm knowing that the initial amount of stable samarium only represents a 15 fold excess. For mass

spectrometry measurements it was necessary to keep the isotopic composition of samarium unchanged. Thus the carrier element chosen was holmium, another lanthanide with a very similar chemical behavior and heavier than samarium, in order to avoid interferences in the mass spectrum. To reach the 100 fold excess in stable lanthanide, 114 µg of holmium ($HoCl_3$, 6 $H_2O$) were added during this dissolution step. The solution was shaken and then weighed portions were put into 5-mL standard LNHB ampoules (LMRI-type), pretreated with the holmium carrier solution (10 µg/g Ho in 1 mol/L HCl), which were then flame-sealed. These steps were all performed on March 4$^{th}$ 2014.

Table 2 contains information about the distribution scheme. Around 1 g of solution was sent to each laboratory for radioactivity measurements and 2 g to the mass spectrometry measurement laboratory. For the latter, the amount was sent in 2 ampoules in order to enable additional tests on the final solution.

**Table 2 - List of material distributed to participants. The date of shipment was March 2014.**

| **Participant** | | **Mass of solution with buoyancy correction taken into account /g** | **Approximate activity of $^{151}$Sm distributed** | **Vial number** |
|---|---|---|---|---|
| LNE- LNHB | Laboratoire National d'Essai – Laboratoire National Henri Becquerel | 1.3408 (6) | ~ 130 kBq/g | Sm151-LNHB |
| ČMI | Czech Metrology Institute | 1.0318 (6) | 70 - 80 kBq/g | Sm151-CMI |
| IRMM | Institute for Reference Materials and Measurements | 1.0291 (6) | 70 - 80 kBq/g | Sm151-IRMM |
| POLATOM | National Centre for Nuclear Research Radioisotope Centre | 1.0246 (6) | 70 - 80 kBq/g | Sm151-POLATOM |
| PTB | Physikalisch-Technische Bundesanstalt | 1.0370 (6) | 70 - 80 kBq/g | Sm151-PTB |
| SMÚ | Slovenský Metrologický Ústav | 1.0225 (6) | 70 - 80 kBq/g | Sm151-SMU |

## 5. Adsorption tests

Several participants included a minor component for adsorption into their uncertainty budget.

At POLATOM, after removing the $^{151}$Sm solution the original ampoule was rinsed twice using 5 mL of distilled water and filled with Ultima Gold scintillator. The water was

transferred into 2 vials with Ultima Gold scintillator and left for measurement in the LS counter Tri-Carb 2910 TR.

At PTB, the original ampoule was rinsed with 1 mL water. The water was used to prepare an LS sample. In total three such rinsings were carried out and the sum of activities determined by LSC was about 152 Bq. After that, the empty ampoule was filled with Ultima Gold sealed with an adhesive tape and placed in a sample holder (adapter). The measurement yielded an activity of 162 (81) Bq. Since the first rinsings were done rather quickly, it is not clear whether the effect is really adsorption (or due to the slow dissolving of the dry salt). Thus, no correction was applied, but an uncertainty component was added to take this effect into account.

At IRMM, the original ampoule was rinsed twice with 1 mL 2M HCl and once with 1 mL of water. Both the ampoule body and top were placed in an LSC vial, filled with LS cocktail and counted. The activity measured was less than 0.01 % of the total activity contained in the ampoule and could be due to both adsorbed activity and active solution left over after the rinsing. This amount was not taken into account in the activity calculations, but only included in the uncertainty budget.

## 6. Radioactive impurities

The radioactive material was prepared by irradiating a $Sm_2O_3$ powder in the Phénix reactor at Marcoule (France). After a first purification in 2011, the solution was analysed at LNE-LNHB by gamma spectrometry for potential impurities. The relative activities of $^{154}$Eu and $^{155}$Eu, compared to those of samarium, were found to be 0.038 % and 0.017 %, respectively. Three years after, the impurities were checked again, and they were found to be 0.033 % ($^{154}$Eu) and 0.011 % ($^{155}$Eu).

In addition, the participants in this comparison were asked to check the solution for radioactive impurities after preparation of the ampoules. Gamma spectrometry measurements were conducted and small amounts of $^{154}$Eu and $^{155}$Eu, about $10^{-4}$ relative to $^{151}$Sm, were indeed found. These amounts of impurities were estimated as being negligible for the purpose of the comparison. However, all participants included a small additional component in their uncertainty budgets to take this effect into account.

## 7. Weighing and dilutions

All participants measured the original solution without dilution. The balances used as well as their traceability data are presented in Table 3. The pycnometer method, i.e. weighing of a polyethylene micro-pipette carrying the solution, prior to and after drop deposition for sample preparation, was adopted for all source preparations.

**Table 3 - Information on weighing procedures and balances.**

| | LNE-LNHB | IRMM | ČMI | PTB | POLATOM | SMÚ |
|---|---|---|---|---|---|---|
| Balance | Mettler MT5 | Mettler Toledo AX26 | ME 365-OCE | Mettler XP 26 | Mettler MT5 | Mettler Toledo AG204 |
| Calibration date | November 2012 | November 2012 | October 2013 | November 25th, 2013 | October 2013 | July 2014 |
| Traceability to SI | Use of 8 calibrated mass standards | Use of calibrated weights (class E2) - Calibration on 6-May-2014 | Calibrated by accredited laboratory | Traceable to the national German mass standard: DKD calibration certificate | Central Office of Measures in Poland | Traceable to the national Slovak mass standard |
| Temperature control | Yes | Yes | Yes | Yes | Yes | Yes |
| Humidity control | Yes | Yes | Yes | Yes | Yes | Yes |
| Buoyancy correction (and standard uncertainty) | 1.001077 (0.000015) | 1.001039 (0.000015) | 1.001050 (0.000015) | 1.001004 (0.000012) | 1.0011 (0.0001) | not applied |
| Weighing procedure | Pycnometer method | Pycnometer method | Pycnometer method | Pycnometer method | Pycnometer method | Pycnometer method |

## 8. Measurement methods

All the participants made use of Liquid Scintillation Counting (LSC) for the activity determination. Two of them applied the CIEMAT/NIST efficiency tracing method and the TDCR method (PTB, IRMM), and five the TDCR method only (LNE-LNHB, POLATOM, CMI, SMU, PTB).

In the following, details on the various methods and individual results are presented. The stated uncertainties are standard uncertainties ($k = 1$).

### *8.1 Liquid scintillation counting – CIEMAT/NIST method*

For the CIEMAT/NIST efficiency tracing method commercial counters with two photomultiplier tubes (PMT) were used. Tritium activity standards were employed in all laboratories; PTB used its own $^{3}$H standards (HTO), and IRMM used its own tritiated water standard. Both participants used Ultima Gold as the scintillation cocktail, with IRMM also using Instagel Plus. To stabilize the cocktail, at PTB 0.96 mL of water was added for the glass vial samples and 0.46 mL for the PE-vials. At IRMM part of the counting samples were prepared using 15 mL of Ultima Gold and 1 mL of deionised water and another part of the samples were prepared using 15 mL of InstaGel Plus.

Experimental details are summarized in Table 4.

**Table 4 - Experimental setups in the measurement of $^{151}$Sm by the CIEMAT/NIST method.**

| | **IRMM (1)** | **IRMM (2)** | | **PTB (1)** | **PTB (2)** |
|---|---|---|---|---|---|
| Counter | Packard TRI-CARB 3100 TR/AB | Wallac 1220 Quantulus | | Wallac 1414-003 Guardian | Tricarb 2800 TR |
| Age | 22 a (upgraded in 1999) | 13 a | | 18 a | 8 a |
| Quench parameter | *tSIE* | *SQP*(*E*) | | *SQP*(*E* ) | *tSIE* |
| Nuclide used for determination of quench parameter | $^{133}$Ba | $^{152}$Eu | | $^{152}$Eu | $^{133}$Ba |
| Efficiency obtained with an unquenched standard of $^{3}$H | 63.5 % (in 15mL Toluene) | 51 % (in 15mL Ultima Gold) | | 51 % | ~55 % |
| Options used (e.g. low-level counting) | None | Guard detector in anticoincidence | | Guard disconnected | None |
| Type of phototubes | Hamamatsu R331-08 | ET 9956 | | Not indicated | Hamamatsu R331-08 |
| Operating temperature | 12 °C | 14 °C | | 20 °C | 20 °C |
| Coincidence resolving time | 20 ns | 20 ns | | 25 ns | 25 ns |
| Maximum $^{151}$Sm achieved efficiency | 81.9 % | 82.4 % | | 73.4 % | 77.4 % |
| Quenching agent | $CH_3NO_2$ | $CH_3NO_2$ | | $CH_3NO_2$ (with pseudocumene) | $CH_3NO_2$ (with pseudocumene) |
| Scintillation cocktail | Ultima Gold Instagel Plus | Ultima Gold Instagel Plus | | Ultima Gold | Ultima Gold |
| Computer code used to calculate efficiency | MICELLE 2 CN2005 | MICELLE 2 CN2005 | | PTB codes + MICELLE 2 | PTB codes + MICELLE 2 |

### *8.2 Liquid scintillation counting – TDCR method*

The TDCR method was applied at PTB, IRMM, POLATOM, ČMI, SMÚ and LNE-LNHB. All institutes used their custom-built counter systems with 3 PMTs, except SMÚ, where a commercial counter was used. Ultima Gold was selected as scintillation cocktail by PTB, POLATOM, ČMI, SMÚ and IRMM (who also used Instagel Plus). LNE-LNHB preferred Hionic Fluor. All participants used glass vials. PTB also prepared some samples with PE vials and LNHB used diffusive glass. As for CIEMAT/NIST measurements, IRMM and PTB added from 0.5 mL to 1 mL of water to some samples. Experimental details are summarized in Table 5.

**Table 5 - Experimental setups in the measurement of $^{151}$Sm by the TDCR method**

| | **IRMM**[#] | **PTB (1)** | **PTB (2)** | **LNE-LNHB** | **POLATOM** | **ČMI** | **SMÚ** |
|---|---|---|---|---|---|---|---|
| Type of counter | Custom-built at IRMM | Custom-built at PTB | Custom-built at PTB | Custom-built at LNHB | TDCR Custom-built at POLATOM | Custom-built at CMI | Hidex 300SL |
| Age | 5 a | 5 a | 2 a | 15 a | | 4 a | 4 a |
| Efficiency obtained with an unquenched standard of $^{3}$H | | ~60 % | ~60 % | ~50 % | 41 % | 55 % | ~ 60 % |
| Type of phototubes | Burle/RCA 8850 | Hamamatsu R331-05 | Hamamatsu R331-05 | Burle 8850 | RCA 8850 | Burle 8850 | Electron Tubes type 9102KA |
| Operating temperature | Room temp. (~ 22 °C) | 20 °C | 20 °C | 22 °C | 22 °C | 22 °C | 20 °C |
| Coincidence resolving time | 50 ns | 40 ns | 40 ns | 40 ns | 40 ns | 45 ns | 35 ns |
| Maximum $^{151}$Sm achieved efficiency | 77.4 % | 88 % | 86 % | 84 % | 77.6 % | 82 % | 86.4 % |
| Quenching agent | $CH_3NO_2$ | $CH_3NO_2$ (with pseudocumene) | $CH_3NO_2$ (with pseudocumene) | Grey filters | none | none | $CH_3NO_2$ |
| Scintillation cocktail | Ultima Gold Instagel Plus | Ultima Gold | Ultima Gold | Hionic Fluor | Ultima Gold | Ultima Gold | Ultima Gold |
| Computer code used to calculate efficiency | MICELLE 2 and CN2005 | PTB codes + MICELLE 2 | PTB codes + MICELLE 2 | LNHB + PENELOPE | TDCRB-03 | TRIDA-B (based on SPEBETA) | MICELLE 2 |

[#]IRMM used the same sources for CIEMAT/NIST and TDCR methods

## 9. Results and uncertainties

### *9.1 Results and uncertainties obtained by all methods*

The detection efficiency was calculated by using various programs.

PTB used the MICELLE 2 program with $kB$ = 0.0075 cm·MeV$^{-1}$ for both methods (Kossert et al., 2014).

IRMM also used the MICELLE 2 program with $kB$ = 0.0075 cm·MeV$^{-1}$ to derive its TDCR result, and both MICELLE 2 and CN2005 with $kB$= 0.0075 cm·MeV$^{-1}$ and $kB$ = 0.0110 cm·MeV$^{-1}$ for the CIEMAT/NIST result.

SMÚ used the MICELLE 2 program with a $kB$ value from 0.0075 cm·MeV$^{-1}$ to 0.015 cm·MeV$^{-1}$.

POLATOM used the TDCRB-03 program with $kB$ = 0.011 cm·MeV$^{-1}$.

ČMI applied the program TRIBA-B which is based on SPEBETA (Cassette, 1992) with $kB$ = 0.012 cm·MeV$^{-1}$.

At LNE-LNHB the detection efficiency was calculated with the TDCR model using two different beta spectra: one is the spectrum corresponding to an allowed transition and one is the spectrum given by LNE-LNHB and corresponding to an allowed transition taking into account atomic effects (electron screening and exchange effect). The result reported is the arithmetic mean of the two detection efficiency values, and the standard deviation associated with this calculation was calculated by assuming that these two calculations have the same likelihood and that the results have a uniform distribution between these two extreme. This approach was motivated by the fact that no experimental shape or form factor is available for this radionuclide. The optimum $kB$ value was obtained by varying the detection efficiency using grey filters.

For the calculation of secondary electrons as a result of photon interaction, most participants stated the use of cross sections from the XCOM data base (Berger et al., 2010).

The participants were also asked to provide details on their uncertainty evaluation. Tables 6 and 7 show the full uncertainty budgets for the LS methods.

The activity concentration determined by all individual methods is listed in Table 8. Figure 4 shows the same data.

**Table 6 - Uncertainty budget for the CIEMAT/NIST method as reported by the PTB and the IRMM. Values are expressed as relative standard uncertainties.**

| | PTB | | | IRMM | | |
|---|---|---|---|---|---|---|
| **Contribution due to** | ***u*(*a*)/*a* in %** | **Type (A/B)** | **Comment** | ***u*(*a*)/*a* in %** | **Type (A/B)** | **Comment** |
| Counting statistics | 0.16 | A | | 0.005 | A | (For a single measurement of one source = 0.1 %) |
| Weighing | 0.06 | B | | 0.14 | A | |
| Background | 0.03 | A | | 0.003 | A | Valid for a single measurement of one source |
| Dead time | 0.1 | B | | 0.1 | B | Estimation. Automatic correction by counter |
| Resolving time | - | | | | | |
| Decay data | 0.5 | B | Mainly beta spectrum | 0.3 | B | $^{151}$Sm decay data from DDEP and simulation using CN2005 |
| Quenching | 0.05 | B | Quenching indicator SQP(E) and tSIE | 0.2 | A | Due to the uncertainty of the quench parameter as obtained from the instruments |
| Tracer | 0.32 | B | | 0.2 | A | For a standard uncertainty of 0.72 % for the IRMM 3H reference solution |
| Extrapolation of efficiency curve | - | | | 0.05 | B | |
| Half-life | <0.01 | B | | $8.3\ 10^{-3}$ | B | |
| Impurities | 0.1 | B | | 0.05 | B | Eu-154, Eu-155 |
| Adsorption | 0.19 | B | | 0.01 | A | |
| PMT asymmetry | 0.07 | B | | - | | |
| Counting time | 0.01 | B | | - | | |
| Ionization quenching and *kB* | 0.3 | B | | 0.08 | B | From the CN2005 calculations |
| Sample stability | - | | | 0.1 | A | Samples in InstaGel behaved better than those in Ultima Gold + 1 mL water |
| LS spectrometer dependence | - | | | 0.03 | A | Negligible difference between the two instruments used |
| LS cocktail stability dependence | - | | | | | |
| Calculation code dependence | - | | | 0.1 | B | MICELLE2 gives about 0.1 % lower efficiencies compared to CN2005 |
| Mass dependence | - | | | 0.1 | A | Results from samples in Ultima Gold + 1 mL water showed a mass dependence |
| **Combined relative standard uncertainty** | **0.74** | | | **0.49** | | |
| *Combined relative type B uncertainty* | *0.71* | | | *0.33* | | |

**Table 7 - Uncertainty budget for the TDCR method as reported by IRMM, LNE-LNHB, PTB, POLATOM, ČMI and SMÚ. Values are expressed as relative standard uncertainties.**

| | **IRMM** | | **LNE-LNHB** | | **PTB** | |
|---|---|---|---|---|---|---|
| **Contribution due to** | ***u*(*a*)/*a* in % (Type A/B)** | **Comment** | ***u*(*a*)/*a* in % (Type A/B)** | **Comment** | ***u*(*a*)/*a* in % (Type A/B)** | **Comment** |
| Counting statistics | 0.03 (A) | For a single measurement of one source = 0.25 % | 0.14 (A) | Including variability between sources | 0.06 (A) | Standard deviation of the mean |
| Weighing | 0.14 | | 0.1 (B) | | 0.06 (B) | |
| Background | 0.003 (A) | | 0.01 (A) | | 0.03 (A) | |
| Dead time | 0.1 (B) | Estimation. Non-extending live time | <0.01 (B) | Uncertainty of the live-time clock | 0.03 (B) | |
| Resolving time | - | | | Included in dead-time | - | |
| Pile-up | - | | 0.02 (B) | Probability of occurrence of 2 disintegrations during the resolving time | - | |
| Decay data | 0.3 (B) | $^{151}$Sm decay data from DDEP and simulation using CN2005 | 0.3 (B) | | 0.5 (B) | Mainly beta spectra |
| Half-life | $1.1\ 10^{-2}$ (B) | | <0.01 (B) | | <0.01 (B) | |
| Extrapolation of efficiency curve | | | | | - | |
| Impurities | 0.05 (B) | $^{154}$Eu, $^{155}$Eu | 0.06 (B) | Gamma-ray spectrometry | 0.1 (B) | |
| Adsorption | 0.01 (A) | | | No adsorption observed | 0.19 (B) | |
| PMT asymmetry | 0.15 (A) | | | Taken into account in the calculation | 0.05 (B) | |
| Counting time | | | | | 0.01 (B) | |
| Ionization quenching and *kB* | 0.3 (B) | | 0.4 (B) | *kB* factor, best value obtained by varying the detection using grey filters | 0.39 (B) | |
| Sample stability | 0.05 (A) | | | | - | |
| Shape factor dependence | | | | | - | |
| TDCR value | | | | | 0.17 (B) | And fitting procedure |
| **Combined relative standard uncertainty** | **0.50** | | **0.53** | | **0.70** | |
| *Combined relative type B uncertainty* | *0.44* | | *0.51* | | *0.70* | |

**Table 7 (Cont.) - Uncertainty budget for the TDCR method as reported by IRMM, LNE-LNHB, PTB, POLATOM, ČMI and SMÚ. Values are expressed as relative standard uncertainties.**

| | **POLATOM** | | **ČMI** | | **SMÚ** | |
|---|---|---|---|---|---|---|
| **Contribution due to** | ***u*(*a*)/*a* in % (Type A/B)** | **Comment** | ***u*(*a*)/*a* in % (Type A/B)** | **Comment** | ***u*(*a*)/*a* in % (Type A/B)** | **Comment** |
| Counting statistics | 0.15 (A) | SD from series of different sources measurements | 0.1 (A) | | 0.2 (A) | |
| Weighing | 0.05 (B) | | 0.01 (B) | | 0.2 (B) | |
| Background | | | 0.01 (B) | | 0.1 (A) | |
| Dead time | | | 0.01 (B) | | 0.1 (B) | |
| Resolving time | | | 0.01 (B) | | 0.1 (B) | |
| Pile-up | | | | | NA | |
| Decay data | 0.2 (B) | Calculations for different variants of simplified decay scheme | 0.3 (B) | | 0.1 (B) | |
| Half-life | 0.002 (B) | | 0.01 (B) | | 0.1 (B) | |
| Extrapolation of efficiency curve | 0.2 (B) | | 0.7 (B) | | | |
| Impurities | 0.1 (B) | | 0.15 (B) | | 0.1 (B) | Gamma-ray spectrometry $^{154}$Eu, $^{155}$Eu |
| Adsorption | 0.01 (B) | | 0.1 (B) | | 0.2 (B) | |
| PMT asymmetry | | | 0.05 (B) | | | |
| Counting time | | | | | | |
| Ionization quenching and *kB* | 0.4 (B) | Calculations for different kB values | 0.8 (B) | | 0.2 (A) | Calculations for different *kB* values |
| Sample stability | | | | | | |
| Shape factor dependence | | | | | | |
| TDCR value | | | | | | |
| Other | 0.3 (B) | Value connected with system stability | | | | |
| **Combined relative standard uncertainty** | **0.6** | | **1.12** | | **0.47** | |
| *Combined relative type B uncertainty* | *0.59* | | *0.80* | | *0.41* | |

**Table 8 - Individual results for the activity concentration. The uncertainties are standard uncertainties (*k* = 1).**

| Participant | *a* in kBq g$^{-1}$ | *u* in kBq g$^{-1}$ | Measurement method | Involved Staff |
|---|---|---|---|---|
| PTB | 79.41 | 0.59 | 4P-LS-MX-00-00-CN | Karsten Kossert |
| PTB | 79.04 | 0.56 | 4P-LS-MX-00-00-TD | Karsten Kossert and Ole Nähle |
| LNE- LNHB | 77.87 | 0.41 | 4P-BP-LS-00-00-TD | Philippe Cassette and Isabelle Tartès |
| IRMM | 78.5 | 0.4 | 4P-LS-MX-00-00-CN | Timotheos Altzitzoglou and Andrej Rozkov |
| IRMM | 78.86 | 0.40 | 4P-LS-MX-00-00-TD | Timotheos Altzitzoglou |
| POLATOM | 79.51 | 0.48 | 4P-BP-LS-00-00-TD | Tomasz Dziel |
| ČMI | 77.9 | 0.93 | 4P-BP-LS-00-00-TD | Jana Sochorová and Pavel Auerbach |
| SMÚ | 80.25 | 0.38 | 4P-BP-LS-00-00-TD | Matej Krivošík and Jarmila Ometáková |

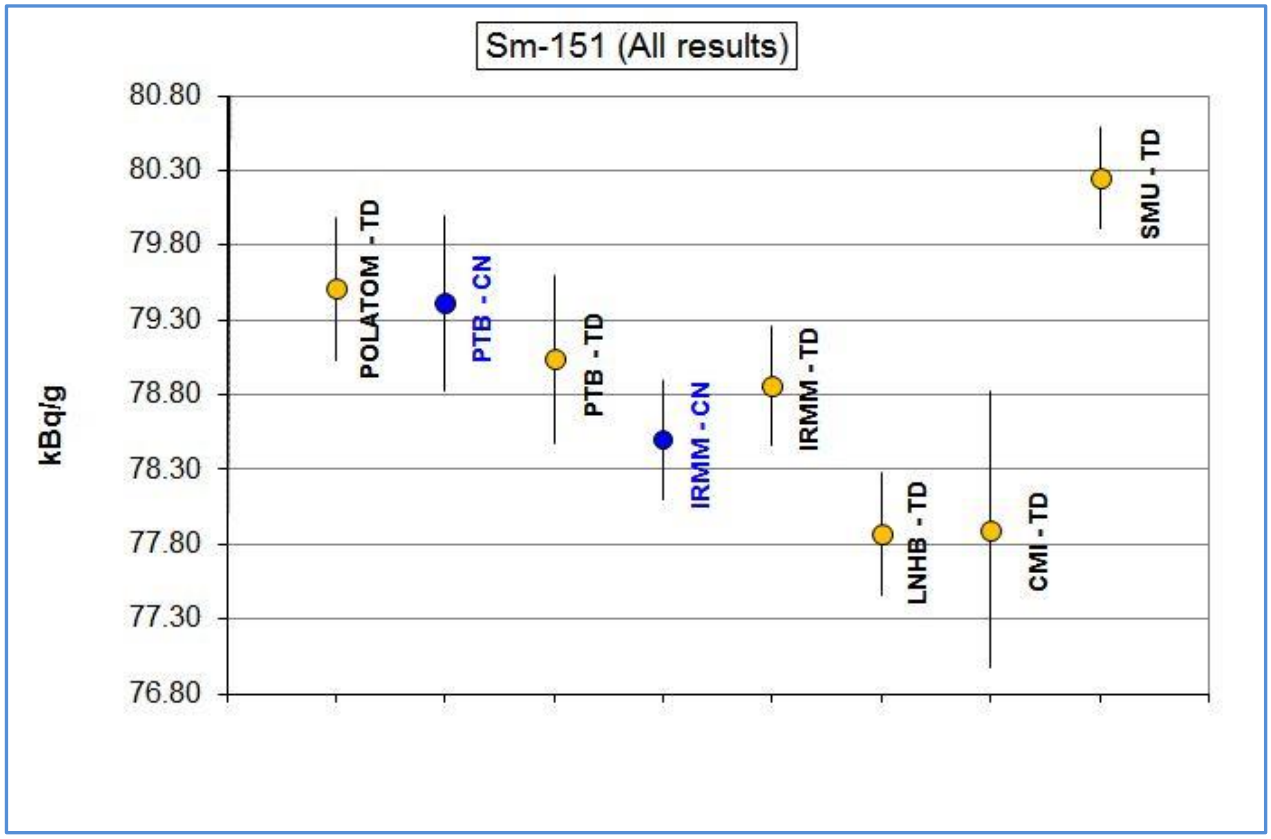


**Figure 1. Activity concentration of the same $^{151}$Sm solution determined by all individual methods**

## *9.2 Final Results*

The final results for the activity concentration adopted by each participant are listed in Table 9 and plotted in Figure 2.

**Table 9. Final results for the activity concentration *a*, as reported by the participants. The stated uncertainties *u* are combined standard uncertainties (*k* = 1).**

| Participant | *a* in kBq g$^{-1}$ | *u* in kBq g$^{-1}$ | Measurement methods | Comments |
|---|---|---|---|---|
| ČMI | 77.9 | 0.93 | 4P-BP-LS-00-00-TD | |
| IRMM | 78.7 | 0.4 | 4P-LS-MX-00-00-CN<br>4P-LS-MX-00-00-TD | The final result is calculated as the mean value of the results obtained by the LSC CN and the LSC TDCR methods. The uncertainty obtained with a single method is kept as more realistic, due to correlations between both methods through common components (i.e. modelling, decay parameters, sources used).<br>The same sources (a subset in case of TDCR) were used for the two methods, as well as the same efficiency calculation codes. It is worth noticing that TDCR gave 0.45% higher activity concentration results as compared to the C/N method. |
| LNE- LNHB | 77.87 | 0.41 | 4P-LS-BP-00-00-TD | |
| POLATOM | 79.51 | 0.48 | 4P-LS-BP-00-00-TD | |
| PTB | 79.22 | 0.41 | 4P-LS-MX-00-00-CN<br>4P-LS-MX-00-00-TD | The final result was calculated as the weighted mean of the results of the CIEMAT/NIST method and the TDCR method. The uncertainty corresponds to the internal uncertainty of the weighted mean (which is larger than the external uncertainty). |
| SMÚ | 80.25 | 0.38 | 4P-BP-LS-00-00-TD | |

The six final results are not all in agreement within the uncertainty limits, each of the POLATOM, PTB, LNHB and ČMI values agrees with two or three others, only the IRMM value agrees with four other results, whilst the SMÚ result is in agreement with the POLATOM result only.

Consequently, the set of data is not consistent with a reduced $\chi^2$ of 4.4, but no result was found to be an outlier. The arithmetic mean is 78.91 kBq $g^{-1}$, and the weighted mean is 79.08 kBq $g^{-1}$, with an external uncertainty of 0.38 kBq $g^{-1}$. The LWEIGHT program (*Limitation of Relative Statistical Weight Method,* Bé 2015) recommends a modified weighted mean with an expanded uncertainty of 0.8 kBq $g^{-1}$ to cover the most precise value.

Omitting the SMU value, the set of five results is then consistent with a reduced $\chi^2$ of 2.3, the weighted mean is 78.73 kBq $g^{-1}$ with an external uncertainty of 0.31 kBq $g^{-1}$.

Finally, the power-moderated mean of all six values is 79.0 kBq $g^{-1}$, with a relative uncertainty of 0.48 %, i.e. an associated uncertainty of 0.4 kBq $g^{-1}$.

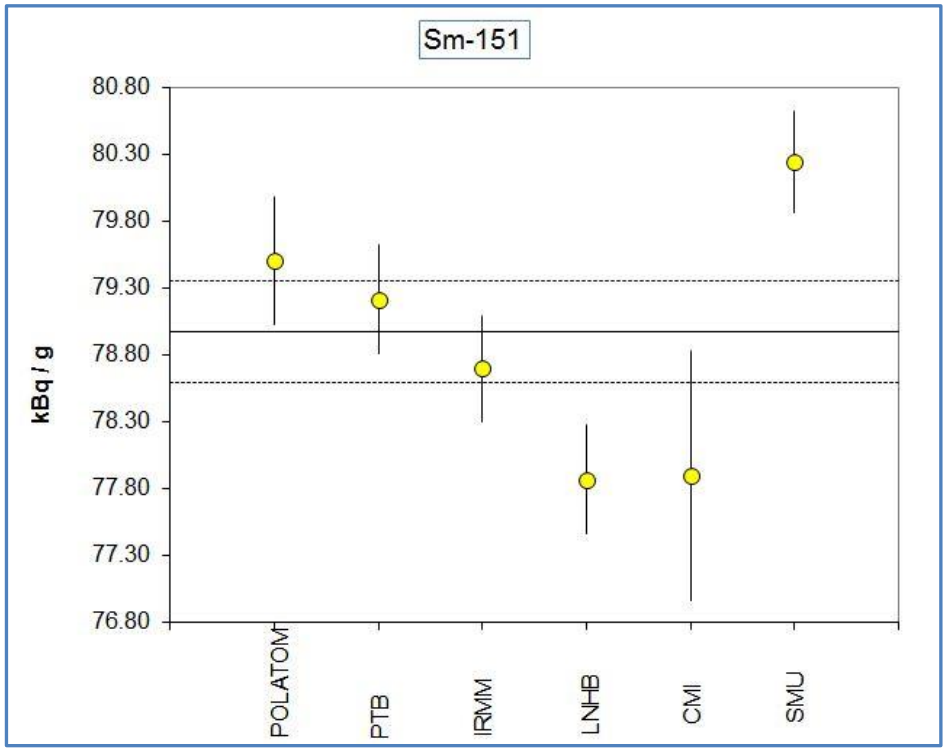


**Figure 2 - Final laboratory results for the activity concentration of aliquots of the same $^{151}$Sm solution. Uncertainty bars are given with a coverage factor *k* = 1. The horizontal line corresponds to the value of the power-moderated mean of all six results (Pommé, 2012).**

## 10 Comparison reference value and degrees of equivalence

The degree of equivalence (DoE) of a given measurement standard is the degree to which this standard is consistent with the key comparison reference value (KCRV) and is expressed quantitatively in terms of the deviation from the key comparison reference value and the expanded uncertainty of this deviation ($k$ = 2).

However, only CCRI(II) or BIPM key comparisons can define the KCRV values and RMO key comparisons must establish the link to the KCRV and compute the DoE. Supplementary comparisons (as the present one) can compute the DoE with respect to the comparison reference value (CRV), although it is not mandatory (CIPM 2014).

### *10.1 The comparison reference value (CRV)*

The proposed comparison reference value of the present EURAMET.RI(II)-S7.Sm-151 Supplementary Comparison has been defined as the power-moderated mean (PMM) of the six final laboratory results. Consequently, the CRV is 79.0 (4) kBq $g^{-1}$ using the final laboratory results in Table 9. The stated uncertainty corresponds to the standard uncertainty of the PMM.

### *10.2 Degrees of equivalence*

The degree of equivalence of a particular NMI or DI, *i*, with the CRV is expressed as the difference $D_i$ of the activity concentration result $a_i$ given in Table 9 with respect to the CRV

$$D_i = a_i - \text{CRV}$$

and the expanded uncertainty ($k$ = 2) of this difference, $U_i$, known as the equivalence uncertainty, also taking into account the correlation between the PMM and each data included in the mean (Pommé, 2012), hence:

$$U_i = 2u_{D_i} .$$

Table 10 shows the table of the degrees of equivalence with the CRV. The degrees of equivalence are also illustrated in Figure 3.

**Table 10 - Degrees of equivalence with the proposed CRV.**

| Laboratory | $D_i$ in kBq/g | $U_i$ in kBq/g |
|---|---|---|
| POLATOM | 0.53 | 1.09 |
| PTB | 0.24 | 1.00 |
| IRMM | -0.28 | 0.99 |
| LNHB | -1.11 | 1.00 |
| ČMI | -1.08 | 1.81 |
| SMÚ | 1.27 | 0.97 |

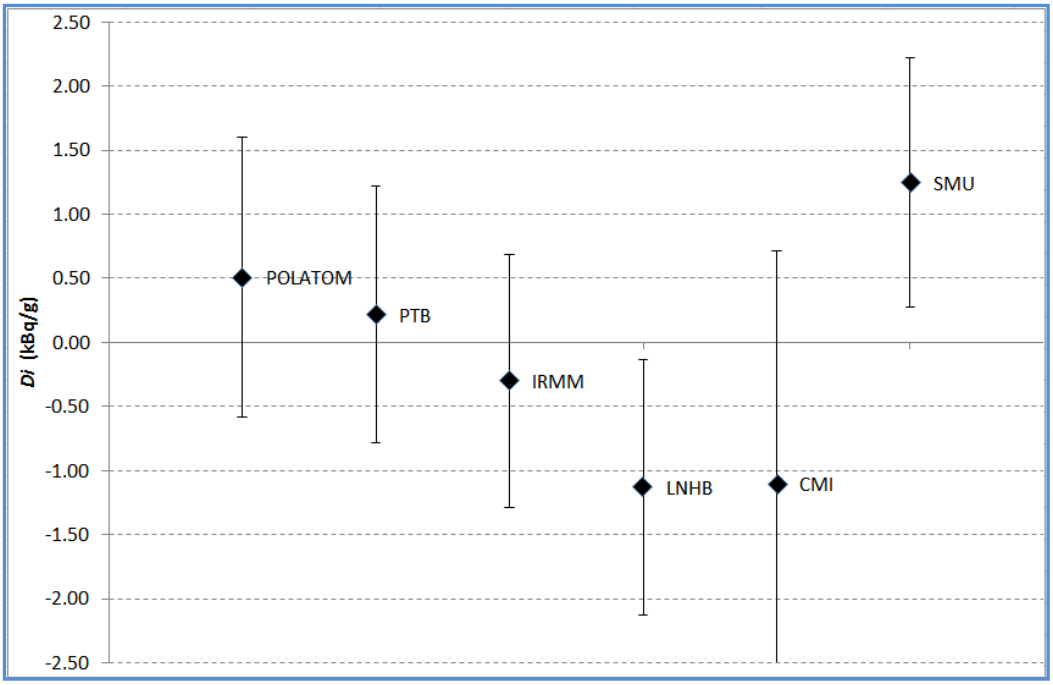


**Figure 3: The degrees of equivalence for each participant with the proposed CRV (*k* = 2).**

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