Protocol for BIPM.RI(II)-K5 comparisons

Protocol for the continuous comparison of activity measurements using the extension of SIR (ESIR)

Pilot laboratory: Bureau International des Poids et Mesures (BIPM)

Contents

1. Objective of the comparison

The International Reference System (SIR) provides international comparisons of radioactivity standardization capabilities with the KCDB reference: BIPM.RI(II)-K1. The system is based on re-entrant ionization chambers and a specific approach to provide robust comparison values since 1976 (Ratel, 2007; Rytz, 1978). The SIR addresses a number of gamma-ray emitting radionuclides. It has been completed by a linked transportable instrument, the SIRTI (Michotte et al., 2013), to evaluate degrees of equivalence for short-lived radionuclides (BIPM.RI(II)-K4 comparison) especially for laboratories far from the BIPM which is located in Sèvres (France).

An extension of the SIR (the ESIR) was developed to complete the BIPM's centralized services in radionuclide metrology for radionuclides not covered by the SIR and the SIRTI. After two decades of study (Coulon et al., 2020, 2021, 2022), the ESIR is operational and at the June 2023 meeting of the section II of the Consultative Committee for Ionizing Radiation (CCRI(II)), it was decided to launch the new comparison BIPM.RI(II)-K5 based on the ESIR in 2024.

This document provides the protocol to carry out this comparison.

2. Participants

Participants can be any NMI or designated institute of a CIPM MRA Member State. The pilot laboratory is the BIPM. Laboratories wishing to participate should contact Romain Coulon (romain.coulon@bipm.org). The shipping instructions are the same as for BIPM.RI(II)-K1 comparison. The procedure BIPM/RI-SIR-T20 is therefore applicable, with the exception of paragraphs 5, 6.2 and 8.2.

3. Radionuclides

It has been decided to start the BIPM.RI(II)-K5 comparison with the following 13 radionuclides, which are not known to pose major technical difficulties (simple decay scheme, suitable half-life, availability with low amount of potential radioactive impurities and availability in suitable chemical form to obtain stable liquid scintillation samples) with the TDCR standardization technique implemented in the ESIR:

- **^{3}H, 14C, ^{35}S, ^{36}Cl, ^{45}Ca, ^{55}Fe, ^{63}Ni, ^{89}Sr, ^{90}Sr, ^{147}Pm, ^{99}Tc, ^{241}Am, ^{241}Pu.**

4. Standard solutions

At first, the participants must ensure that their solution is sufficiently chemically stable to be quantitatively sampled by the BIPM.

Second, the participants must respect the following restrictions on the submitted solutions.

In the present phase, the ESIR does not allow corrections for impurities. Laboratories must therefore ensure that their solutions are as pure as possible with a relative impact on the detection efficiency below 10^{-4} in TDCR measurement.

The ampoule used for the BIPM.RI(II)-K5 comparison does not necessarily have to be of the SIR-type. Any type of glass ampoule is suitable. The ampoule must be flame-sealed and pre-treated with a suitable carrier solution. Also, the sealing must not be let at least 3 cm above the bottleneck.

As a guideline, parameters of solutions that might be eligible for BIPM.RI(II)-K5 comparisons are listed below. The solutions should be transparent, clear and colourless. If participants would like to send a solution that differs from requirements in the Table 1, please ask the BIPM. This case could be discussed within the KCWG(II).

Table 1. Specification of standard solutions to be used in BIPM.RI(II)-K5 comparisons.

Radionuclide	Mass of solution /g	Mass activity /(kBq/g)	Max activity /(kBq)	Solvent conc. /(mol/L)	Carrier molecule /(g/l)
^{3}H	1 – 2	100 – 400	800	Only HTO	No organic
^{14}C	1 – 2	50 – 200	400	NaOH: 1 (!) Acetic acid, sodium salt, [1,2-^{14}C] ($C_2H_3NaO_2$)	Benzoic acid (!) No carrier Glycose in water
^{35}S	1 – 2	50 – 200	400	HCl: 0.1 (!)	H_2SO_4 (!)
^{36}Cl	1 - 2	50 - 200	400	H_2O	NaCl:0.2(*)
^{45}Ca	1 – 2	50 – 200	400	HCl:1 (!) HCl: 1 (*)	$CaCl_2$: 0.01 (!) $CaCl_2$: 0.04 (*)

^{55}Fe	1 – 2	100 – 400	800	HCl: 1 (*) HCl: 0.1	$FeCl_2$ $FeCl_3.H_2O$: 0.01 (*) $FeCl_3$ 0.058 (or 0.097 $FeCl_3 \cdot 6H_2O$)
^{63}Ni	1 – 2	50 – 200	400	HCl: 0.1 (!!) HCl: 1 (*) HCl: 0.1	$NiCl_2$: 0.10 (!!) $NiCl_2$: 0.08 (*) $NiCl_2$: 0.065 (or $NiCl_2$ $6H_2O$: 0.12)
^{89}Sr	1 – 2	50 – 200	400	HCl: 1 (*) HCl: 0.1	$SrCl_2.6H_2O$: 0.09 (*) $SrCl_2$.: 0.03 (or $SrCl_2.6H_2O$: 0.05)
^{90}Sr	1 – 2	25 – 100	200	HCl: 1 (*)	$SrCl_2$ + YCl_3: 0.05 + 0.05 (!!) $SrCl_2$ + YCl_3: 0.03 + 0.03 (or $SrCl_2 \cdot 6H_2O$: 0.05 and $YCl_3 \cdot 6H_2O$: 0.046)
^{147}Pm	1 – 2	50 – 200	400	HCl: 0.1 (!) HCl: 1 (*) HCl: 0.5	No carrier
^{99}Tc	1 – 2	50 – 200	400	0.9 % NaCl (!!) HCl: 3 (*) For $NH_4{}^{99}TcO_4$: $NH_{3(aq.)}$: 0.1	No carrier
^{241}Am	1 – 2	50 – 200	200	HNO_3: 0.1 HCl: 1 (!!) HCl: 0.1 (*)	$La(NO_3)_3$ 0.035 (or 0.047 $La(NO_3)_3 \cdot 6H_2O$) $EuCl_3$: 0.020 (!!) $EuCl_3$: 0.001 (*)
^{241}Pu	1 – 2	50 – 200	400	HNO_3: 3 (!!) HNO_3: 2	No carrier

(*) from NIST handbook NCRP 58

(!) from (Larry Lucas) ref IPL

($) from (Larry Lucas) ref SRM

In the RI-SIR-F-05 reporting form, the participants are invited to provide information

- on impurity studies which comprise
  - a brief description of measurement methods used to search for radioactive impurities (in comment)
  - when relevant, information on activity ratio or detection limit
- on the LS source
  - The LS cocktail
  - The type of vials
- on the model (when CIEMAT/NIST or TDCR)
  - the parameters of the beta spectrum with reference
  - the code used with parameters

4.1. Special case of the ^{14}C solution

In the case of ^{14}C solutions, carbonate compounds cannot be accepted for ESIR submissions.

1.1. Special case of the ^{36}Cl solution

In the case of ^{36}Cl, it is recommended to use a beta spectrum close to experimentally obtained ones:

- $C(W) = 1 - 1.326W + 0.6328W^2$ derived by (Kossert et al., 2010), from data measured by (Rotzinger et al., 2008).
- To update with LNHB result ICRM 2025.

1.2. Special case of the ^{89}Sr solution

In the case of ^{89}Sr, ^{85}Sr impurities could be included. A gamma spectroscopy has to be carried out by participant to estimate the concentration of ^{85}Sr in the solution ensuring that the relative impact on the detection efficiency is below 10^{-4}.

1.3. Special case of the ^{90}Sr/^{90}Y solution

In the case of ^{90}Sr/^{90}Y, to avoid adsorption of ^{90}Sr to the glass, a concentration of 1 mol/L HCl is required.

1.4. Special case of the ^{241}Am solution

It is possible for this radionuclide to carry out simultaneously BIPM.RI(II)-K5 and BIPM.RI(II)-K1 comparisons. If possible, the laboratory is invited to submit 3.6 g of standard solution contained in an SIR-type ampoule with an activity greater than 11 MBq plus a diluted fraction of this solution in a second ampoule (not necessarily of the SIR-type) with an activity below 200 kBq.

2. Realization

2.1. Liquid scintillation sources

Since an ampoule is received at the BIPM, at least 4 liquid scintillation (LS) sources are prepared plus one blank vial prepared the same way. The LS sources contain:

- 15 mL of Ultima Gold cocktail or 15 mL of ProSafe+,
- An aliquot of the solution with a mass m_i comprised between 50 mg and 200 mg with
  - A targeted double coincidence count rate between 5×10^3 s^{-1} and 2×10^4 s^{-1},
  - A minimum number of drops = 5,
- Completed by a mass of distilled water equal to (1 g - m_i) (Example: If 150 mg of the radioactive solution shall be added 850 mg of distilled water are to be used).

One of the two calibrated BIPM balances are used: Mettler Toledo XPE26C or Mettler Toledo XPR36DR. A buoyancy correction is applied. The stability of the mass measurement is evaluated by reproducibility tests performed before each preparation.

The LS sample preparation follows the sequence below.

- 15 mL of Ultima Gold or ProSafe+ is put into the vials
- 1 mL (minus the targeted mass of aliquots) of distilled water is added to the vials
- The vials are closed, shake
- The weighted aliquots of the radioactive solution is added to the vials
- The vials are closed and shake

The blank vial will be prepared using 15 mL of Ultima Gold plus 1 mL distilled water (without weighing).

In the specific cases of ^{241}Am and ^{241}Pu, 0.02 g of the complexing agent HDEHP is added to the source.

The vials are glass vials covered with diffusive tapering tape.

2.2. TDCR measurement

These LS sources with a blank source are measured by the BIPM TDCR system within 5 days after their preparation. The Yantel nano TDCR system is used with the following parameters:

- Measurement duration = 720 s
- Number of repetitions = 10 times
- Extended dead time = 10 µs (also 50 µs for information)
- Coincidence resolving time = 50 ns (also 100 ns for information)

The TDCR system will measure the following counting rates which are live-time based:

- The logic sum of the double coincidence count rate: $R_{\mathrm{D}i}$,
- The triple coincidence count rate: $R_{\mathrm{T}i}$,
- The double coincidence count rate between the channel A and the channel B: $R_{\mathrm{AB}i}$,
- The double coincidence count rate between the channel B and the channel C: $R_{\mathrm{BC}i}$,
- The double coincidence count rate between the channel A and the channel C: $R_{\mathrm{AC}i}$,
- The count rate of the channel A: $R_{\mathrm{A}i}$,
- The count rate of the channel B: $R_{\mathrm{B}i}$,
- The count rate of the channel C: $R_{\mathrm{C}i}$.

These count rates are corrected from the accidental coincidences.

For at least one of the 4 sources, the measurements are repeated with 5 grey filters with neutral density of 0.1, 0.2, 0.3, 0.4, 0.5.

3. Calculation

The comparison indicator is calculated as follows

$$I_i = \frac{R_{\mathrm{D}i} Q_i}{m_i \varepsilon_{\mathrm{D}i} \left(\frac{R_{\mathrm{T}i}}{R_{\mathrm{AB}i}}, \frac{R_{\mathrm{T}i}}{R_{\mathrm{BC}i}}, \frac{R_{\mathrm{T}i}}{R_{\mathrm{AC}i}}, k_{\mathrm{B}} \right)}$$

where

- Q_i is the decay correction factor,
- $\varepsilon_{\mathrm{D}i}$ is the double count rate efficiency evaluated by a TDCR model parametrized by a Birks constant k_{B}.

The value of k_{B} is evaluated by an “efficiency variation” procedure using grey filters at the first use of a given radionuclide in an ESIR comparison.

The ratio between the activity A_i evaluated by the participant and the comparison indicator is

$$\kappa_i = \frac{A_i}{I_i}.$$

The KCRV is calculated using the PMM (Pommé & Keightley, 2015),

$$KCRV = \mathrm{PMM}(\kappa_i)$$

and the degree of equivalence is:

$$D = \frac{\kappa_i}{KCRV} - 1.$$

Any outlier, possibly revealed by the PMM, is first discussed with the participant allowing to correct typing errors. If need, results could be discussed at CCRI(II)/KCWG(II) meetings to decide whether or not they could be included in the KCRV.

4. Uncertainty budget of the ESIR

The uncertainty budget contains several components detailed in the Table 2.

The impact of the background correction is small. The background count rate is indeed about 2 s^{-1} whereas the expected count rates for LS sources are between 5×10^3 s^{-1} and 2×10^4 s^{-1}.

Counting statistics are expected to be the most impacting factor. A type A evaluation will be carried out on the 10 repeated measurements.

The decay correction depends on the evaluated nuclear data. By default, the most recent BIPM monography-5 will be used by the BIPM and the corresponding half-lives used for the analysis will be stated in the report.

The influence of the weighing should be small with a solution mass greater than 50 mg, while ensuring an accuracy of the mass measurements in the µg range. An uncertainty is evaluated based on the repeatability test of the pycnometer mass measurement, completed by consistency tests (χ^2 test and Chauvenet test) applied to the results obtained from the four LS sources.

The TDCR model used is fixed for a given radionuclide with fixed Birks constant, energy spectrum, stopping power, etc. However, its capability to make reproducible to reference value for a range of encountered solutions and cocktails is evaluated with the systematic efficiency changing procedure imposing a photon reduction up to 68 % (neutral density of 0.5, see 2.2). The dark uncertainty that makes to measurement dataset consistent with regards to the Chi-squared test is evaluated (e.g. DerSimonian Lair procedure (DerSimonian & Laird, 1986)). the highest value encountered is considered in the uncertainty budget.

Finally, the consistency of the comparison indicator I_i is continuously re-evaluated by periodic control using ^{3}H and ^{14}C toluene-based LS sources. The long-term reproducibility is continuously evaluated (type B) by estimating a possible dark uncertainty that could appear due to possible long term random fluctuations (e.g. DerSimonian Lair procedure (DerSimonian & Laird, 1986)). Having observed consistent results for 3 years, the impact of the latter component is expected to remain small.

The yearly test with a pure solution of a long-lived radionuclide is also carried out.

The ESIR aims to achieve a relative standard uncertainty of less than 6×10^{-4} in order to not affect significantly the degrees of equivalence.

Table 2. Typical uncertainty budget of the ESIR measurement based on the Co-60 pilot study. It will depend on the radionuclide.

Component	Type of evaluation	Target relative standard uncertainty
Background correction	A	$< 2 \times 10^{-5}$
Counting statistics	A	$< 5 \times 10^{-4}$
Decay correction	B	$< 1 \times 10^{-4}$
Weighing	B	$< 1 \times 10^{-4}$
Long term reproducibility	B	$< 1 \times 10^{-4}$
TDCR model	B	$< 2 \times 10^{-4}$
Combined		$\mathbf{< 6 \times 10^{-4}}$

5. Reporting

The analysis is performed once the activity value A_i, together with an uncertainty budget, has been obtained from the NMI using the Excel reporting form BIPM/RI-SIR-F-05. The acronyms for describing the measurement methods are also listed in the reporting form. If the participant submits several results corresponding to different standardization methods, a single value and uncertainty (e.g. one of the results or a weighted mean of some or all results) representing its national reference should also be provided, as this will be used to calculate the degrees of equivalence for the KCDB. The production of drafts A and B follows the usual process for CCRI comparison reports.

The participants could also participate as pilot study. In this case the degree of equivalence will not be reported to the KCDB.

References

Coulon, R., Broda, R., Cassette, P., Courte, S., Dupire, A., Jerome, S., Judge, S., Kossert, K., Liu, H., Michotte, C., & Nonis, M. (2022). The new international reference system for pure α- and pure β-emitting radionuclides and some electron capture decaying radionuclides by liquid scintillation counting. *Journal of Radioanalytical and Nuclear Chemistry*, *331*(8), 3221–3230. https://doi.org/10.1007/s10967-022-08337-7

Coulon, R., Broda, R., Cassette, P., Courte, S., Jerome, S., Judge, S., Kossert, K., Liu, H., Michotte, C., & Nonis, M. (2020). The international reference system for pure β-particle emitting radionuclides: an investigation of the reproducibility of the results. *Metrologia*, *57*(3), 035009. https://doi.org/10.1088/1681-7575/ab7e7b

Coulon, R., Judge, S., Liu, H., & Michotte, C. (2021). The international reference system for pure beta-particle emitting radionuclides: an evaluation of the measurement uncertainties. *Metrologia*, *58*(2), 025007. https://doi.org/10.1088/1681-7575/abe355

DerSimonian, R., & Laird, N. (1986). Meta-analysis in clinical trials. *Controlled Clinical Trials*, *7*(3), 177–188. https://doi.org/10.1016/0197-2456(86)90046-2

Kossert, K., Grau Carles, A., & Nähle, O. J. (2010). Cerenkov Counting an Liquid Scintillation Counting of <sup>36<\sup>Cl. In P. Cassette (Ed.), *International Conference on Advances in Liquid Scintillation Spectrometry (LSC 2010)*.

Michotte, C., Nonis, M., Bobin, C., Altzizoglou, T., & Sibbens, G. (2013). *The SIRTI: a new tool developed at the BIPM for comparing activity measurements of short-lived radionuclides world-wide*. www.bipm.org/utils/common/pdf/rapportBIPM/RapportBIPM-2013-02.pdf

Pommé, S., & Keightley, J. (2015). Determination of a reference value and its uncertainty through a power-moderated mean. *Metrologia*, *52*(3), S200–S212. https://doi.org/10.1088/0026-1394/52/3/S200

Ratel, G. (2007). The Système International de Référence and its application in key comparisons. *Metrologia*, *44*(4). https://doi.org/10.1088/0026-1394/44/4/S02

Rotzinger, H., Linck, M., Burck, A., Rodrigues, M., Loidl, M., Leblanc, E., Fleischmann, L., Fleischmann, A., & Enss, C. (2008). Beta Spectrometry with Magnetic Calorimeters. *Journal of Low Temperature Physics*, *151*(3–4), 1087–1093. https://doi.org/10.1007/s10909-008-9787-5

Rytz, A. (1978). International coherence of activity measurements. *Environment International*, *1*(1–2), 15–18. https://doi.org/10.1016/S0160-4120(78)80071-3