BIPM comparison BIPM.RI(II)-K1.Bi-207
of activity measurements of the radionuclide Bi-207

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Abstract
Since 1982, two national metrology institutes (NMIs) have contributed two results of known activity of $^{207}$Bi to the International Reference System (SIR) for activity comparison at the Bureau International des Poids et Mesures. The activities ranged from about 500 kBq to 1.2 MBq. The degrees of equivalence between the two NMIs determined from the equivalent activity measured in the SIR have been calculated and the results are given in the form of a matrix. The results of this comparison have been approved by Section II of the Consultative Committee for Ionizing Radiation (CCRI(II)), comparison identifier BIPM.RI(II)-K1.Bi-207.

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 $^{226}$Ra using pressurized ionization chambers. Details of the SIR method, experimental set-up and the determination of the equivalent activity are all given in [1].

Since its inception, the SIR has measured over 818 ampoules to give 590 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 where this is possible, being 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 Mutual Recognition Arrangement (MRA) [2]. The comparison described in this report is known as the BIPM.RI(II)-K1.Bi-207 key comparison.
2. Participants

Two NMIs have submitted ampoules for the comparison of $^{207}$Bi activity measurements since 1982. The laboratory details are given in Table 1.

Table 1. Details of the participants in the BIPM.RI(II)-K1.Bi-207

<table>
<thead>
<tr>
<th>NMI</th>
<th>Full name</th>
<th>Country</th>
<th>Regional metrology organization</th>
<th>Date of measurement at the BIPM</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTB</td>
<td>Physikalisch-Technische Bundesanstalt</td>
<td>Germany</td>
<td>EUROMET</td>
<td>1982-06-03</td>
</tr>
<tr>
<td>VNIIM</td>
<td>D.I. Mendeleyev Institute for Metrology</td>
<td>Russian Federation</td>
<td>COOMET</td>
<td>1991-07-02</td>
</tr>
</tbody>
</table>

3. NMI standardization methods

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

A brief description of the standardization methods for each laboratory, the activities submitted and the relative standard uncertainties ($k = 1$) are given in Table 2. Full uncertainty budgets have been requested as part of the comparison protocol only since 1998. Consequently, no uncertainty budgets were provided in these two cases.

The half-life used by the BIPM is 11 600 (700) days [3]. This is a change, following the advice of the CCRI(II), from 12 200 (300) days that had been used at the time to the original measurements.

Table 2. Standardization methods of the participants for $^{207}$Bi

<table>
<thead>
<tr>
<th>NMI</th>
<th>Method used</th>
<th>Half-life / d</th>
<th>Activity / kBq</th>
<th>Reference date</th>
<th>Relative standard uncertainty $\times 100$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTB</td>
<td>$4\pi\gamma$(NaI) + calibrated Ge(Li)</td>
<td>-</td>
<td>482</td>
<td>82-01-01</td>
<td>0.23</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.77</td>
</tr>
<tr>
<td>VNIIM</td>
<td>Calibrated Ge(Li)$^1$</td>
<td>-</td>
<td>1212</td>
<td>91-05-24*</td>
<td>0.20</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.74</td>
</tr>
</tbody>
</table>

$^1$ traceable through primary realizations made at the VNIIM of $^{133}$Ba, $^{134}$Cs and $^{152}$Eu activities.
* referenced at 12:00 UTC.
Details regarding the solution submitted are shown in Table 3, including any impurities, when present, as identified by the laboratories. When given, the standard uncertainties on the evaluations are shown. Recently the BIPM has developed a standard method for evaluating the activity of impurities using a calibrated Ge(Li) spectrometer [4]. The CCRI(II) agreed in 1999 [5] that this method should be followed according to the protocol described in [6] when an NMI makes such a request or when there appear to be discrepancies.

### Table 3. Details of the solution of $^{207}$Bi submitted

<table>
<thead>
<tr>
<th>NMI</th>
<th>Chemical composition</th>
<th>Solvent conc. / (mol dm$^{-3}$)</th>
<th>Carrier: conc. /($\mu$g g$^{-1}$)</th>
<th>Density /($g$ cm$^{-3}$)</th>
<th>Impurity (Relative activity at reference date)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTB BiCl$_3$ in HCl</td>
<td>1.0</td>
<td>BiCl$_3$: 45</td>
<td>1.005</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td>VNIIM BiCl$_3$ in HCl</td>
<td>1.0</td>
<td>BiCl$_3$: 50</td>
<td>1.01</td>
<td>–</td>
<td></td>
</tr>
</tbody>
</table>

### 4. Results

All the submissions to the SIR since its inception in 1976 are maintained in a database known as the "mother-file". The activity measurements for $^{207}$Bi arise from two ampoules and the SIR equivalent activity for each ampoule $A_{ei}$, is given in Table 4 for each NMI, $i$. The dates of measurement in the SIR are given in Table 1. The relative standard uncertainties arising from the measurements in the SIR are also shown. This uncertainty is additional to that declared by the NMI for the activity measurement shown in Table 2. Although activities submitted are compared with a given source of $^{226}$Ra, all the SIR results are normalized to the radium source number 5 [1].

The dates of measurement in the SIR are given in Table 1. The results take into account the new value for the half-life that has been used.

Neither NMI indicated any impurities present. No impurity measurements were made at the BIPM.

An earlier submission was withdrawn and is not included here. Consequently, the results in Table 4 of each NMI are eligible for Appendix B of the MRA.

No international or regional comparison for this radionuclide has been held to date so no linking data are identified.
Table 4. Results of SIR measurements of $^{207}$Bi

<table>
<thead>
<tr>
<th>NMI</th>
<th>Mass of solution /g</th>
<th>Activity submitted/ kBq</th>
<th>N° of Ra source used</th>
<th>SIR $A_e$/kBq</th>
<th>Relative uncertainty from SIR</th>
<th>Total standard uncertainty $t_i$/ kBq</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTB</td>
<td>3.7182</td>
<td>482</td>
<td>3</td>
<td>10 848</td>
<td>$8.9 \times 10^{-4}$</td>
<td>88</td>
</tr>
<tr>
<td>VNIIM</td>
<td>3.5226</td>
<td>1212</td>
<td>3</td>
<td>10 400</td>
<td>$5.5 \times 10^{-4}$</td>
<td>183</td>
</tr>
</tbody>
</table>

4.1 The key comparison reference value

The key comparison reference value is derived from the unweighted mean of all the results submitted to the SIR with the following provisions:

a) only primary standardized solutions are accepted, or ionization chamber measurements that are directly traceable to a primary measurement in the laboratory;

b) each NMI has only one result (normally the most recent result or the mean if more than one ampoule is submitted);

c) any outliers are identified using a reduced chi-squared test and excluded from the KCRV, if necessary using the normalized error test with a test value of four;

d) exclusions must be approved by the CCRI(II).

The reduced data set used for the evaluation of the KCRVs is known as the KCRV file and is the reduced data set from the SIR mother-file. Although the KCRV may be modified when other NMIs participate, on the advice of the Key Comparison Working Group of the CCRI(II), such modifications are only made by the CCRI(II), normally during one of its biennial meetings.

A key comparison reference value is normally based on at least two primary realizations. In this case, as there is only one NMI that has made a primary realization, no KCRV can be determined. As soon as another NMI submits an ampoule with a primary realization for $^{207}$Bi, a KCRV will be determined and for this reason, the following explanations are included.

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

\[
D_i = A_{ei} - \text{KCRV}
\]

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

\[
U_i = 2u_{i},
\]

taking correlations into account as appropriate.

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

\[
D_{ij} = D_i - D_j = A_{ei} - A_{ej}
\]

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

\[
u_{D_{ij}}^2 = u_i^2 + u_j^2 - \sum_k (f_ku_{k,corr})_i^2 - \sum_k (f_ku_{k,corr})_j^2
\]

and any obvious correlations in the standard uncertainties for a given component, \( u_{corr,k} \), between the NMIs (such as a traceable calibration) are subtracted using an appropriate correlation coefficient, \( f_k \), as are normally those correlations coming from the SIR.

As the half-life of \(^{207}\text{Bi}\) is long, the uncertainty in this value is an insignificant component so can be neglected in the correlations.

Although the relative uncertainty due to the same Ra source being used can be taken as completely correlated, the uncertainties attributed to the SIR are insignificant when compared to the NMI uncertainties in this comparison and consequently the results are taken to be uncorrelated.

Table 5 shows the matrix of the degrees of equivalence between the two NMIs as they will appear in Appendix B of the KCDB. The introductory text is that agreed for the comparison. 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.

**Conclusion**

The BIPM ongoing key comparison for \(^{207}\text{Bi}\), BIPM.RI(II)-K1.Bi-207 currently comprises two results. These have been analysed with respect to each other. The matrix of degrees of equivalence has been approved by the CCRI(II) and will be
published in the BIPM key comparison database. Other results may be added as and when other NMIs contribute $^{207}$Bi activity measurements to this comparison. Indeed, NMIs are encouraged to submit ampoules of this radionuclide to enable the determination of a KCRV.

**Acknowledgements**

The authors would like to thank the NMIs for their participation in this comparison and Mr Christian Colas of the BIPM for his dedicated work in maintaining the SIR since its inception and for the thousands of measurements he has made over the years.

**References**


Table 5. Table of degrees of equivalence and introductory text for $^{207}$Bi

Key comparison BIPM.RI(II)-K1.Bi-207

**MEASURAND:** Equivalent activity of $^{207}$Bi

Key comparison reference value: there is no SIR reference value for this radionuclide at the moment, the value $x_i$ is taken as the equivalent activity for laboratory $i$.

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

<table>
<thead>
<tr>
<th>Lab $i$</th>
<th>Lab $j$</th>
<th>$D_{ij}$</th>
<th>$U_{ij}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTB</td>
<td>VNIIM</td>
<td>-0.45</td>
<td>0.41</td>
</tr>
<tr>
<td>VNIIM</td>
<td>PTB</td>
<td>0.45</td>
<td>0.41</td>
</tr>
</tbody>
</table>