Abstract

In 1978, the National Bureau of Standards (NBS, now the National Institute of Standards and Technology, NIST) (USA), submitted a sample of known activity of $^{203}$Pb to the international reference system (SIR) for activity comparison at the BIPM. The value of the activity submitted was about 220 MBq. The result of this comparison has been approved by Section II of the Consultative Committee for Ionizing Radiation (CCRI(II)).

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 until 31 December 2002, the SIR has measured 835 ampoules to give 606 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 Mutual Recognition Arrangement (MRA) [2]. The comparison described in this report is known as the BIPM.RI(II)-K1.Pb-203 key comparison.

2. Participants

The NIST is the only participant to date for the comparison of $^{203}$Pb activity measurements and one ampoule was submitted in 1978. The laboratory details are given in Table 1. As the laboratory has changed its name since the original
submission, both the earlier and the current acronyms are given, as it is the latter that is used in the KCDB.

Table 1. Details of the participants in the BIPM.RI(II)-K1.Pb-203

<table>
<thead>
<tr>
<th>Original acronym</th>
<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>NBS</td>
<td>NIST</td>
<td>National Institute of Standards and Technology</td>
<td>United States</td>
<td>SIM</td>
<td>1978-11-20 12 h 20 UT</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 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 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 budget was provided in this case.

Table 2. Standardization method of the participant for \(^{203}\text{Pb}\)

<table>
<thead>
<tr>
<th>NMI</th>
<th>Method used and code (see Appendix)</th>
<th>Half-life / d</th>
<th>Activity / kBq</th>
<th>Reference date</th>
<th>Relative standard uncertainty (\times 100) by method of evaluation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>A</td>
</tr>
</tbody>
</table>
| NIST | Pressurized IC 4P-IC-GR-00-00-00 calibrated in 1978 by 4π(e,x)-γ coincidence 4P-PP-MX-NA-GR-CO | 2.163 (5)     | 218 600        | 78-11-16 23 h 30 UT | 0.01 0.58

Details regarding the solution submitted are shown in Table 3, including any impurities, when present, as identified by the laboratory. 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 [3]. The CCRI(II) agreed in 1999 [4] that this method should be
followed according to the protocol described in [5] when an NMI makes such a request or when there appear to be discrepancies.

### Table 3. Details of the solution of $^{203}\text{Pb}$ submitted

<table>
<thead>
<tr>
<th>NMI</th>
<th>Chemical composition</th>
<th>Solvent conc. (mol dm$^{-3}$)</th>
<th>Carrier conc. (µg g$^{-1}$)</th>
<th>Density (g cm$^{-3}$)</th>
<th>Relative activity of impurity$^{\dagger\dagger}$</th>
</tr>
</thead>
</table>
| NIST | Pb in HCl | 0.5 | Pb : 100 | 1.007 (2)* | $^{200}\text{Tl}$: 3.3 (3) $\times$ 10$^{-3}$ %  
$^{201}\text{Tl}$: 2.0 (5) $\times$ 10$^{-1}$ %  
$^{201}\text{Pb}$: 5.0 (3) $\times$ 10$^{-2}$ %$^{\dagger\dagger}$ |

* density at 24.4 °C
$^{\dagger}$ the ratio of the activity of the impurity to the activity of $^{203}\text{Pb}$ at the reference date
$^{\dagger\dagger}$ decayed to $^{201}\text{Tl}$ at the time of the SIR measurement.

### 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 measurement for $^{203}\text{Pb}$ arises from one ampoule and the SIR equivalent activity for each ampoule, $A_{ei}$, is given in Table 4 for the NMI, $i$. 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 $^{226}\text{Ra}$, all the SIR results are normalized to the radium source number 5 [1].

The half-life used by the BIPM was that provided by the NIST of 2.163 (5) days, which is in agreement with the more recent evaluation of 2.1614 (4) d [6]. However, the original value for the equivalent activity has been modified to take the new half-life value into account. The date of measurement in the SIR is given in Table 1.

The ampoule was measured four times in the SIR, up to 14 days after the first measurement, each measurement giving the same result. These measurements confirm the validity of the half-life value used and the evaluation of the impurity corrections ($2.0 \times 10^{-3}$ for the last measurement of the series).

It is interesting to note that the NIST result is in agreement within the uncertainties with the value of 56 410 (170) kBq deduced from the efficiency curve of the SIR [7] and the nuclear data from [6].

As this submission has not been identified as a pilot study, the result of the NIST is eligible for Appendix B of the MRA. However, as only one NMI has submitted an activity for this comparison, a key comparison reference value cannot be computed and consequently no degrees of equivalence can be derived. Nevertheless, details of how this will be done once another NMI submits a sample are given in the next section of this report for completeness.
Table 4. Results of SIR measurements of $^{203}$Pb

<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 $A_{ei}$/kBq</th>
<th>Relative uncertainty from the SIR $u_i$/kBq</th>
<th>Total standard uncertainty $u_i$/ kBq</th>
</tr>
</thead>
<tbody>
<tr>
<td>NIST</td>
<td>3.631 91</td>
<td>218 600</td>
<td>5</td>
<td>56 630</td>
<td>$9 \times 10^{-4}$</td>
<td>330</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 or other laboratory 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, if necessary, excluded from the KCRV 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.

Although the NIST value is eligible to be included in a KCRV for $^{203}$Pb, this cannot be computed until another NMI fulfils the criteria described.

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.

However, as no KCRV can be determined at present for this radionuclide, no degrees of equivalence can be expressed.
Conclusion

The BIPM ongoing key comparison for $^{203}$Pb, BIPM.RI(II)-K1.Pb-203 currently comprises one result from the NIST. Consequently, no KCRV can be determined for this radionuclide, nor can degrees of equivalence be calculated for publication in the BIPM key comparison database. Once another NMI contributes $^{203}$Pb activity measurements to this comparison, the KCRV and degrees of equivalence will be determined and the approval of the CCRI(II) sought prior to publication.

Acknowledgements

The authors would like to thank the NMIs for their participation in this comparison, 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, and Dr P.J. Allisy-Roberts of the BIPM for editorial assistance.

References


## Appendix  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.

<table>
<thead>
<tr>
<th>Geometry acronym</th>
<th>Detector acronym</th>
<th>Mode acronym</th>
<th>Mode acronym</th>
</tr>
</thead>
<tbody>
<tr>
<td>$4\pi$</td>
<td>proportional counter</td>
<td>PC</td>
<td></td>
</tr>
<tr>
<td>defined solid angle</td>
<td>press. prop counter</td>
<td>PP</td>
<td></td>
</tr>
<tr>
<td>$2\pi$</td>
<td>liquid scintillation counting</td>
<td>LS</td>
<td></td>
</tr>
<tr>
<td>undefined solid angle</td>
<td>NaI(Tl)</td>
<td>NA</td>
<td></td>
</tr>
<tr>
<td>Ge(HP)</td>
<td>GH</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ge-Li</td>
<td>GL</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Si-Li</td>
<td>SL</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CsI</td>
<td>CS</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ionization chamber</td>
<td>IC</td>
<td></td>
<td></td>
</tr>
<tr>
<td>grid ionization chamber</td>
<td>GC</td>
<td></td>
<td></td>
</tr>
<tr>
<td>bolometer</td>
<td>BO</td>
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<td></td>
</tr>
<tr>
<td>calorimeter</td>
<td>CA</td>
<td></td>
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<td>PIPS detector</td>
<td>PS</td>
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<tr>
<td>Radiation acronym</td>
<td>Mode acronym</td>
<td>Mode acronym</td>
<td>Mode acronym</td>
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<tr>
<td>positron</td>
<td>PO</td>
<td>efficiency tracing</td>
<td>ET</td>
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<tr>
<td>beta particle</td>
<td>BP</td>
<td>internal gas counting</td>
<td>IG</td>
</tr>
<tr>
<td>Auger electron</td>
<td>AE</td>
<td>CIEMAT/NIST</td>
<td>CN</td>
</tr>
<tr>
<td>conversion electron</td>
<td>CE</td>
<td>sum counting</td>
<td>SC</td>
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<tr>
<td>bremsstrahlung</td>
<td>BS</td>
<td>coincidence</td>
<td>CO</td>
</tr>
<tr>
<td>gamma ray</td>
<td>GR</td>
<td>anti-coincidence</td>
<td>AC</td>
</tr>
<tr>
<td>X - rays</td>
<td>XR</td>
<td>coincidence counting with efficiency tracing</td>
<td>CT</td>
</tr>
<tr>
<td>alpha - particle</td>
<td>AP</td>
<td>anti-coincidence counting with efficiency tracing</td>
<td>AT</td>
</tr>
<tr>
<td>mixture of various radiation e.g. X and gamma</td>
<td>MX</td>
<td>triple-to-double coincidence ratio counting</td>
<td>TD</td>
</tr>
<tr>
<td></td>
<td></td>
<td>selective sampling</td>
<td>SS</td>
</tr>
</tbody>
</table>

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