

**BIPM comparison BIPM.RI(II)-K1.Eu-152 of**  
**activity measurements of the radionuclide  $^{152}\text{Eu}$  for the VNIIM (Russia), the LNE-**  
**LNHB (France) and the CNEA (Argentina), with linked results for the**  
**COOMET.RI(II)-K2.Eu-152 comparison**

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## **Abstract**

Three new participations in the BIPM.RI(II)-K1.Eu-152 comparison have been added to the previous results and this has produced a revised value for the key comparison reference value (KCRV), calculated using the power-moderated weighted mean. A link has been made to the COOMET.RI(II)-K2.Eu-152 comparison held in 2010 through the VNIIM who participated in both comparisons. Three National Metrology Institutes (NMIs) used the K1 or K2 comparisons to update their degree of equivalence. The degrees of equivalence between each equivalent activity measured in the International Reference System (SIR) and the KCRV have been calculated and the results are given in the form of a table for four NMIs in the BIPM.RI(II)-K1.Eu-152 comparison, three participants in the COOMET.RI(II)-K2.Eu-152 comparison and the 18 other participants in the previous CCRI(II)-K2.Eu-152 comparison. A graphical presentation is also given.

## **1. Introduction**

The SIR for activity measurements of  $\gamma$ -ray-emitting radionuclides was established in 1976. Each national metrology institute may request a standard ampoule from the BIPM that is then filled with 3.6 g of the radioactive solution, or a different standard ampoule for radioactive gases. 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 2012, the SIR has measured 966 ampoules to give 721 independent results for 67 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 standardizations. These comparisons are described as BIPM ongoing comparisons and the results form the basis of the BIPM key comparison database (KCDB) of the Comité International des Poids et Mesures Mutual Recognition Arrangement (CIPM MRA) [2]. The comparison described in this report is known as the BIPM.RI(II)-K1.Eu-152 key comparison and includes results published previously [3].

In addition, an international comparison was held in 2009 for this radionuclide, COOMET.RI(II)-K2.Eu-152 [4]. Four laboratories took part in this comparison including the VNIIM who participated in the SIR at the same time, enabling to link the COOMET.RI(II)-K2 comparison to the BIPM.RI(II)-K1 comparison. The SMU had previously participated in a CCRI(II) comparison and has updated their result through this COOMET (Euro-Asian Cooperation of National Metrology Institutions) comparison.

## 2. Participants

Ten NMIs have submitted 19 ampoules to the SIR for the comparison of  $^{152}\text{Eu}$  activity measurements since 1981. As the key comparison reference value has been re-evaluated for this comparison all the participants' details are given in Table 1a. In cases where 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 are used in the KCDB.

**Table 1a. Details of the participants in the BIPM.RI(II)-K1.Eu-152**

| Original acronym | NMI          | Full name  | Country       | Regional metrology organization | Date of measurement at the BIPM<br>YYYY-MM-DD |
|------------------|--------------|--|---------------|---------------------------------|---|
| –                | PTB          | Physikalisch-Technische Bundesanstalt  | Germany       | EURAMET                         | 1981-10-12<br>1989-04-12                      |
| NBS              | NIST         | National Institute of Standards and Technology   | United States | SIM                             | 1982-09-28<br>2001-11-27                      |
| LMRI<br>LPRI     | LNE-<br>LNHB | Laboratoire National de Métrologie et d'Essais -<br>Laboratoire National Henri Becquerel | France        | EURAMET                         | 1983-04-11<br>1994-04-19<br>2009-04-15        |

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Table 1a continued. Details of the participants in the BIPM.RI(II)-K1.Eu-152

| Original acronym | NMI       | Full name  | Country            | Regional metrology organization | Date of measurement at the BIPM        |
|------------------|-----------|--|--------------------|---------------------------------|--|
| OMH              | MKEH      | Magyar Kereskedelmi Engedélyezési Hivatal  | Hungary            | EURAMET                         | 1984-04-16<br>1992-09-22               |
| –                | VNIIM     | D.I. Mendeleev Institute for Metrology   | Russian Federation | COOMET                          | 1986-04-16<br>1998-12-09<br>2009-01-12 |
| UVVVR            | CMI-IIR   | Český Metrologický Institut/Czech Metrological Institute, Inspectorate for Ionizing Radiation        | Czech Republic     | EURAMET                         | 1986-06-24                             |
| –                | IRA       | Institut de Radiophysique Appliquée  | Switzerland        | EURAMET                         | 1993-05-19                             |
| –                | LNMRI/IRD | Laboratorio Nacional de Metrologia das Radiações Ionizantes/ Instituto de Radioproteção e Dosimetria | Brazil             | SIM                             | 1995-09-26<br>2000-11-08               |
| RC               | POLATOM   | National Centre for Nuclear Research, Radioisotope Centre  | Poland             | EURAMET                         | 1998-06-19                             |
| –                | CNEA      | Comisión Nacional de Energía Atómica   | Argentina          | SIM                             | 2011-10-12                             |

The BelGIM, CENTIS-DMR and SMU that took part in the COOMET international comparison, COOMET.RI(II)-K2.Eu-152 in 2009 and are also eligible for the KCDB are shown in Table 1b.

### 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.

**Table 1b. Details of the participants in the 2009 COOMET.RI(II)-K2.Eu-152 to be linked to BIPM.RI(II)-K1.Eu-152**

| <b>NMI</b> | <b>Full name</b>   | <b>Country</b> | <b>Regional metrology organization</b> |
|------------|--|----------------|--|
| BelGIM     | Belarussian State Institute of Metrology                           | Belarus        | COOMET                                 |
| CENTIS-DMR | Centro de Isótopos.<br>Departamento de Metrología de Radionúclidos | Cuba           | COOMET                                 |
| SMU        | Slovak Institute of Metrology                                      | Slovakia       | EURAMET                                |

A brief description of the standardization methods used by the laboratories, the activities submitted, the relative standard uncertainties ( $k = 1$ ) and the half-life used by the participants in the SIR are given in Table 2. The uncertainty budgets for the three new submissions are given in Appendix 1, previous uncertainty budgets are given in the earlier K1 report [3]. The uncertainty budgets for all the participants in the COOMET.RI(II)-K2.Eu-152 comparison were published in the final report [4]. The acronyms used for the measurement methods are given in Appendix 2.

The half-life used by the BIPM from 1981 to 1999 was 4869 (15) d [5] while the value currently in use is 4939.3 (3.7) days [6], that was decided for the CCRI(II)-K2.Eu-152 comparison in 1999. The current half-life value is in agreement with 4939 (6) d, the value recommended in the BIPM Monographie 5 [7]. The pre-1999 SIR data could be revised using the current half-life. However, the updated degrees of equivalence would not differ significantly as the SIR measurements were performed within a few months following the reference date.

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. The BIPM has developed a standard method for evaluating the activity of impurities using a calibrated Ge(Li) spectrometer [10]. The CCRI(II) agreed in 1999 [11] that this method should be followed according to the protocol described in [12] when an NMI makes such a request or when there appear to be discrepancies. No impurity measurements were carried out at the BIPM in this case.

**Table 2. Standardization methods of the participants for  $^{152}\text{Eu}$** 

| NMI      | Method used and acronym (see Appendix 2)  | Half-life             | Activity $A_i$ / kBq        | Reference date<br>YY-MM-DD | Relative standard uncert. $\times 100$ by method of evaluation |              |
|----------|---|-----------------------|-----------------------------|----------------------------|--|--------------|
|          |   |                       |                             |                            | A  | B            |
| PTB      | Pressurized IC<br>4P-IC-GR-00-00-00<br>calibrated by<br>$4\pi(\text{NaI}(\text{Tl}))\gamma$<br>4P-NA-GR-00-00-HE                      | –                     | 953                         | 81-01-01<br>0 h UT         | 0.08   | 0.71         |
|          |   | –                     | 1729                        | 89-01-01<br>0 h UT         | 0.04   | 0.21         |
| NIST     | $4\pi(\text{NaI}(\text{Tl}))\gamma$<br>4P-NA-GR-00-00-HE  | –                     | 1063                        | 82-08-27<br>18 h UT        | 0.01   | 0.34         |
|          | Pressurized IC *<br>4P-IC-GR-00-00-00   | 13.523<br>(10) a      | 164.6                       | 01-11-15<br>12 h UT        | 0.10   | 0.35         |
| LNE-LNHB | $4\pi(\text{NaI}(\text{Tl}))\gamma$<br>4P-NA-GR-00-00-HE  | 13.506<br>(30) a      | 3 822<br>3 822 <sup>†</sup> | 83-03-15<br>12 h UT        | 0.02   | 0.17         |
|          |   | 4933<br>(11) d<br>[8] | 5 004                       | 94-03-01<br>12 h UT        | 0.02   | 0.12         |
|          |   | 13.522<br>(16) a      | 8 717                       | 08-04-15<br>12 h UT        | 0.06   | 0.32         |
| MKEH     | $4\pi(\beta, x, e_x)\text{-}\gamma$<br>coincidence<br>4P-PP-MX-NA-GR-CO   | 13.33<br>(4) a<br>[9] | 3 625                       | 84-04-01<br>12 h UT        | 0.03   | 0.02         |
|          |   | [8]                   | 3 690                       | 92-10-01<br>12 h UT        | 0.04   | 0.25         |
| VNIIM    | $4\pi(x, e)\text{-}\gamma$ coinc.<br>4P-PC-MX-NA-GR-CO  | –                     | 3 080                       | 86-03-15<br>12 h UT        | 0.2  | 1.3          |
|          | $4\pi(\beta, e)\text{-}\gamma$ coinc.<br>4P-PC-MX-NA-GR-CO  | [8]                   | 2 696                       | 98-11-23<br>12 h UT        | 0.09   | 0.27         |
|          | $4\pi(\text{PC})\beta\text{-}\gamma$ coinc.<br>4P-PC-BP-NA-GR-CO<br>$4\pi(\text{NaI}(\text{Tl}))\gamma$<br>4P-NA-GR-00-00-HE          | 4939.3<br>d           | 2 544<br>2 570              | 08-07-01<br>0 h UT         | 0.49<br>0.25   | 0.09<br>0.32 |
| CMI-IIR  | $4\pi\beta\text{-}\gamma$ coincidence<br>4P-PC-BP-NA-GR-CO  | 4803 d                | 17 661                      | 86-06-02<br>12 h UT        | 0.07   | 0.40         |
| IRA      | Pressurized IC<br>4P-IC-GR-00-00-00<br>calibrated in 1993<br>by $4\pi(\beta, x, e)\text{-}\gamma$<br>coincidence<br>4P-PC-MX-NA-GR-CO | –                     | 2 181                       | 93-06-01<br>0 h UT         | 0.03   | 0.26         |

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Table 2 continued. Standardization methods of the participants for  $^{152}\text{Eu}$ 

| NMI        | Method used and acronym (see Appendix 2)   | Half-life   | Activity $A_i$ / kBq | Reference date<br>YY-MM-DD | Relative standard uncert. $\times 100$ by method of evaluation |      |
|------------|--|-------------|----------------------|----------------------------|--|------|
|            |  |             |                      |                            | A  | B    |
| LNMRI /IRD | Pressurized IC<br>4P-IC-GR-00-00-00  | –           | 393.7                | 95-06-26<br>0 h UT         | 0.2  | 1.1  |
|            | Pressurized IC<br>4P-IC-GR-00-00-00<br>calibrated in 2000<br>by $4\pi(\text{PPC})\beta\text{-}\gamma(\text{Ge})$<br>coincidence<br>4P-PP-BP-GH-GR-CO | [6]         | 415.7                | 00-09-15<br>12 h UT        | 0.7  | 0.9  |
| POLATOM    | $4\pi(\text{LS})\text{-}\gamma$ coinc.<br>and anti-coinc. [8]<br>4P-LS-BP-NA-GR-CO<br>4P-LS-BP-NA-GR-AC  | [6]         | 2 480                | 98-05-12<br>12 h UT        | 0.08   | 0.34 |
| CNEA       | 4P-PC-BP-NA-GR-CO  | 13.522<br>a | 183.5                | 10-07-05<br>0 h UT         | 0.47   | 0.25 |

† two ampoules submitted

\* calibrated in 1980 by  $4\pi(\text{NaI}(\text{Tl}))\gamma$  counting 4P-NA-GR-00-00-HE.Table 3. Details of the solution of  $^{152}\text{Eu}$  submitted

| NMI, Year                                | Chemical composition                             | Solvent conc. / ( $\text{mol dm}^{-3}$ ) | Carrier: conc. / ( $\mu\text{g g}^{-1}$ )         | Density / ( $\text{g cm}^{-3}$ ) | Relative activity of $^{154}\text{Eu}$ impurity† |
|--|--|--|---|----------------------------------|--|
| PTB, 1981<br>1989                        | Eu Chloride in HCl                               | 0.1                                      | Eu : 40   | 1.00                             | 0.34 (5) %                                       |
|  | $\text{EuCl}_3$ in HCl                           | 0.1                                      | $\text{EuCl}_3$ : 40                              | 1.00                             | 0.32 (6) %<br>$^{153}\text{Gd}$ : 0.27 (7) %     |
| NIST, 1982<br>2001                       | $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ in HCl | 1  | $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$<br>1100 | 1.016                            | 0.35 (4) %                                       |
|  | $\text{EuCl}_3$ in HCl                           | 1  | $\text{EuCl}_3$ : 500                             | 1.016 (1)                        | 0.19 (2) %                                       |
| LNE- LNHB,<br>1983<br>1994<br>2009       | $\text{EuCl}_3$ in HCl                           | 1  | $\text{EuCl}_3$ : 40                              | 1.027                            | 0.295 (30) %                                     |
|  | $\text{EuCl}_3$ in HCl                           | 1  | $\text{EuCl}_3$ : 70                              | 1.016                            | 0.42 (2) %<br>$^{153}\text{Gd}$ : 0.72 (3) %     |
|  | $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ in HCl | 1  | $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$<br>24.1 | 1.0159                           | 0.43 (3) %                                       |
| MKEH, 1984<br>1992                       | Eu in HCl  | 0.1                                      | Eu : 30   | –                                | 0.30 (6) %                                       |
|  | Eu in HCl  | 0.1                                      | Eu : 26   | –                                | 0.88 (9) %                                       |
| VNIIM, 1986<br>1998<br>2009 <sup>a</sup> | $\text{EuCl}_3$ in HCl                           | 0.1                                      | Eu : 10   | 1.001                            | 0.03 (1) %                                       |
|  | Eu in HCl  | 0.5                                      | Eu : 10   | 1.015                            | 0.05 (1) %                                       |
|  | Eu in $\text{HNO}_3$                             | 0.3                                      | –   | 1.009                            | 0.275 (8) %                                      |

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Table 3 continued. Details of the solution of  $^{152}\text{Eu}$  submitted

| NMI, Year                      | Chemical composition           | Solvent conc. / ( $\text{mol dm}^{-3}$ ) | Carrier: conc. / ( $\mu\text{g g}^{-1}$ ) | Density / ( $\text{g cm}^{-3}$ ) | Relative activity of $^{154}\text{Eu}$ impurity <sup>†</sup> |
|--------------------------------|--------------------------------|--|---|----------------------------------|--|
| CMI-IIR, 1986                  | $\text{EuCl}_3$ in HCl         | 0.08                                     | $\text{EuCl}_3 : 20$                      | –                                | 1.39 (5) %   |
| IRA, 1993                      | $\text{Eu}^{+++}$ in HCl       | 0.1                                      | $\text{Eu} : 90$                          | 1.000                            | 1.17 (1) %   |
| LNMRI/IRD, 1995<br>2000        | $\text{EuCl}_3$ in HCl         | 0.1                                      | $\text{EuCl}_3 : 100$                     | 1.016                            | < 1.10 (5) % *   |
|                                |                                |  | $\text{EuCl}_3 : 25$                      | 1.002                            | 0.63 (3) %   |
| POLATOM, 1998                  | $\text{EuCl}_3$ in HCl         | 1  | $\text{EuCl}_3 : 170$                     | 1.007                            | –  |
| CNEA, 2011                     | $\text{Eu}_2\text{O}_3$ in HCl | 0.1                                      | $\text{Eu}_2\text{O}_3 : 46$              | 1                                | –  |
| CCRI(II)-K2, 1999 <sup>b</sup> | Eu in HCl                      | 0.1                                      | –   | –                                | 0.67 (2) % <sup>††</sup>                                     |

<sup>†</sup> the ratio of the activity of the impurity to the activity of  $^{152}\text{Eu}$  at the reference date

<sup>††</sup> mean value of the measurements carried out by 14 participants of the CCRI(II) comparison.

\* this upper limit was used to correct the SIR measurement

<sup>a</sup> same solution as for the COOMET.RI(II)-K2.Eu-152 comparison

<sup>b</sup> solution used in the CCRI(II)-K2.Eu-152 comparison.

#### 4. Results

All the submissions to the SIR since its inception in 1976 are maintained in a database known as the "master-file". The SIR equivalent activity,  $A_{ei}$ , for each ampoule for the previous and new results is given in Table 4a. The date of measurement in the SIR is also given 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 submitted activities are compared with a given source of  $^{226}\text{Ra}$ , all the SIR results are normalized to the radium source number 5 [1].

The recent VNIIM, LNE-LNHB and CNEA results agree within standard uncertainty with their earlier result in the linked 1999 CCRI(II)-K2.Eu-152 comparison [3].

The most recent result of each NMI is normally eligible for the key comparison database (KCDB) of the CIPM MRA except for the LNMRI submission in 2000 that was identified as a pilot study.

An international comparison for this radionuclide, COOMET.RI(II)-K2.Eu-152 was held in 2009 [4] and the three laboratories from this comparison to be added to the matrix of degrees of equivalence are given in Table 1b.

The results  $(A/m)_i$  of the COOMET comparison have been linked to the BIPM.RI(II)-K1.Eu-152 comparison through the measurement in the SIR of one ampoule of the COOMET solution standardized by the VNIIM. The link is made using a normalization ratio deduced from the row indicated in Table 4a:

$$A_{ei} = (A/m)_i \times [A_{e\text{VNIIM}}/(A/m)_{\text{VNIIM}}] = (A/m)_i \times 21.422 \quad (\text{a})$$

The details of the links are given in Table 4b. The uncertainties for the COOMET comparison results linked to the SIR are comprised of the original uncertainties together with the uncertainty in the link,  $6 \times 10^{-4}$ , given by the relative standard uncertainty of the SIR measurement of the VNIIM ampoule.

**Table 4a. Results of SIR measurements of  $^{152}\text{Eu}$**

| NMI             | Mass of solution<br>$m_i$ / g | Activity submitted<br>$A_i$ / kBq | N° of Ra source used | SIR<br>$A_e$ / kBq | Relative uncert. from SIR | Combined uncert. $u_i$ / kBq |                  |
|-----------------|-------------------------------|-----------------------------------|----------------------|--------------------|---------------------------|------------------------------|------------------|
| PTB, 1981       | 3.551 29                      | 953                               | 3                    | 14 880             | $9 \times 10^{-4}$        | 110                          |                  |
|                 | 1989                          | 3.659 6                           | 1 729                | 3                  | 14 875                    | $9 \times 10^{-4}$           | 35               |
| NIST, 1982      | 3.609 95                      | 1 063                             | 3                    | 14 866             | $7 \times 10^{-4}$        | 52                           |                  |
|                 | 2001                          | 3.729 6 (2)                       | 164.6                | 1                  | 14 892                    | $11 \times 10^{-4}$          | 57               |
| LNE-LNHB, 1983  | 3.693 43                      | 3 822                             | 4                    | 14 979             | $6 \times 10^{-4}$        | 28                           |                  |
|                 | 3.693 42                      | 3 822                             |                      | 14 979             |                           | 28                           |                  |
|                 | 1994                          | 3.662 8                           | 5 004                | 4                  | 14 932                    | $6 \times 10^{-4}$           | 20               |
|                 | 2009                          | 3.617 0 (6)                       | 8 717                | 5                  | 14 932                    | $5 \times 10^{-4}$           | 50               |
| MKEH, 1984      | 3.603 2                       | 3 625                             | 4                    | 15 000             | $8 \times 10^{-4}$        | 38                           |                  |
|                 | 1992                          | 3.643 7                           | 3 690                | 4                  | 14 925                    | $11 \times 10^{-4}$          | 41               |
| VNIIM, 1986     | 3.589 72                      | 3 080                             | 4                    | 14 840             | $5 \times 10^{-4}$        | 190                          |                  |
|                 | 1998                          | 3.585 6 (1)                       | 2 696                | 4                  | 15 075                    | $5 \times 10^{-4}$           | 43               |
|                 | 2009                          | 3.6549 <sup>b</sup>               | 2 560 <sup>a,b</sup> | 3                  | 15 003 <sup>b</sup>       | $6 \times 10^{-4}$           | 50               |
| CMI-IIR, 1986   | 3.597 7                       | 17 661                            | 5                    | 15 013             | $7 \times 10^{-4}$        | 62                           |                  |
| IRA, 1993       | 3.578 9 (1)                   | 2 181                             | 3                    | 14 838             | $6 \times 10^{-4}$        | 40                           |                  |
| LNMRI/IRD, 1995 | 3.457 08                      | 393.7                             | 2                    | 15 210             | $9 \times 10^{-4}$        | 170                          |                  |
|                 | 2000                          | 3.421 23                          | 415.7                | 2                  | 14 740 <sup>c</sup>       | $10 \times 10^{-4}$          | 170 <sup>c</sup> |
| POLATOM, 1998   | 3.708 5                       | 2 480                             | 3                    | 14 770             | $6 \times 10^{-4}$        | 52                           |                  |
| CNEA, 2011      | 3.607 80                      | 183.5                             | 1                    | 14 770             | $14 \times 10^{-4}$       | 81                           |                  |

<sup>a</sup>  $A = 2560$  (8) kBq is the weighted mean result of the activity values obtained by different methods given in Table 2, taking into account correlations.

<sup>b</sup> result used to link the 2009 COOMET.RI(II)-K2.Eu-152 comparison.

<sup>c</sup> submitted as a pilot study; result not included in the KCRV nor the KCDB.

The SMU result in the COOMET comparison agrees within standard uncertainty with their earlier result in the linked 1999 CCRI(II)-K2.Eu-152 comparison [3].

**Table 4b. Results of the 2009 COOMET.RI(II) comparison of  $^{152}\text{Eu}$  and links to the SIR**

| NMI        | Measurement method and acronym (see Appendix 2 and [4]) | Activity* concentration measured $(A/m)_i$ / (kBq g <sup>-1</sup> ) | Standard uncert. $u_i$ / (kBq g <sup>-1</sup> ) | Equivalent SIR activity $A_{ei}$ / kBq | Combined standard uncert. $u_{ci}$ / kBq |
|------------|---|---|---|--|--|
| BelGIM     | UA-GH-GR-00-00-00                                       | 698   | 5   | 14 950                                 | 110                                      |
| CENTIS-DMR | UA-GH-GR-00-00-00                                       | 701.8   | 9.3   | 15 030                                 | 200                                      |
| SMU        | 4P-IC-GR-00-00-00                                       | 701.1   | 5.3   | 15 020                                 | 110                                      |
| VNIIM      | 4P-PC-BP-NA-GR-CO<br>4P-NA-GR-00-00-HE                  | 700.4   | 2.3   | see Table 4a                           |  |

\*referenced to 00:00 UTC 1 July 2008

#### 4.1 The key comparison reference value

In May 2013 the CCRI(II) decided to no longer calculate the key comparison reference value (KCRV) by using an unweighted mean but rather by using the power-moderated weighted mean [13]. This type of weighted mean is similar to a Mandel-Paule mean in that the NMIs' uncertainties may be increased until the reduced chi-squared value is one. In addition, it allows for a power smaller than two in the weighting factor. Therefore, all SIR key comparison results can be selected for the KCRV with the following provisions:

- only results for solutions standardized by primary techniques are accepted, with the exception of radioactive gas standards (for which results from transfer instrument measurements that are directly traceable to a primary measurement in the laboratory may be included);
- each NMI or other laboratory has only one result (normally the most recent result or the mean if more than one ampoule is submitted);
- possible outliers can be identified on a mathematical basis and excluded from the KCRV using the normalized error test with a test value of 2.5 and using the modified uncertainties;
- results can also be excluded for technical reasons.
- The CCRI(II) is always the final arbiter regarding excluding any data from the calculation of the KCRV.

The data set used for the evaluation of the KCRVs is known as the "KCRV file" and is a reduced data set from the SIR master-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 made only by the CCRI(II) during one of its biennial

meetings as for the case of  $^{152}\text{Eu}$  in May 2013, or by consensus through electronic means (e.g., email) as discussed at the CCRI(II) meeting in 2013.

In addition, following the advice of the CCRI(II) in May 2003, the results from the CCRI(II)-K2 comparison in 1999 linked to the SIR can be used for the KCRV with the additional restriction that the participant must have measured the  $^{154}\text{Eu}$  impurity of the solution (see [3, 14]).

Consequently, the KCRV for  $^{152}\text{Eu}$  has been calculated as 14 919 (35) kBq on the basis of the SIR results from the NIST(1982), VNIIM(2009), LNE-LNHB(2009) and the CNEA(2011) and of the CCRI(II)-K2 1999 comparison results from the BIPM (primary result only), CMI-IIR, IFIN-HH, IRA, IRMM, NMIJ, MKEH (former OMH), PTB, POLATOM (former RC), CIEMAT and the KRISS. The ENEA CCRI(II)-K2 1999 comparison result is not included as it is known to be biased [3]. This KCRV can be compared with the previous KCRV value of 14 942 (26) kBq published in 2004 [3] and the value of 14 923 (23) kBq obtained using the SIRIC efficiency curve of the SIR [15].

## 4.2 Degrees of equivalence

Every participant in a comparison is entitled to have one result included in the KCDB as long as the NMI is a signatory or designated institute listed in the CIPM MRA, and the result is valid (i.e., not older than 20 years). Normally, the most recent result is the one included. An NMI may withdraw its result only if all other participants agree.

The degree of equivalence of a given measurement standard is the degree to which this standard is consistent with the KCRV [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 result with the KCRV*

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

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

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

$$U_i = 2u(D_i). \quad (2)$$

When the result of the NMI  $i$  is included in the KCRV with a weight  $w_i$ , then

$$u^2(D_i) = (1-2w_i) u_i^2 + u^2(\text{KCRV}). \quad (3)$$

However, when the result of the NMI  $i$  is not included in the KCRV, then

$$u^2(D_i) = u_i^2 + u^2(\text{KCRV}). \quad (4)$$

#### 4.2.2 Comparison between pairs of NMI results

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

$$D_{ij} = D_i - D_j = A_{e_i} - A_{e_j} \quad (5)$$

and the expanded uncertainty ( $k = 2$ ) of this difference,  $U_{ij} = 2u(D_{ij})$ , where

$$u_{D_{ij}}^2 = u_i^2 + u_j^2 - 2u(A_{e_i}, A_{e_j}) \quad (6)$$

where any obvious correlations between the NMIs (such as a traceable calibration, or correlations normally coming from the SIR or from the linking factor in the case of linked comparison) are subtracted using the covariance  $u(A_{e_i}, A_{e_j})$  (see [16] for more detail). However, the CCRI decided in 2011 that these “pair-wise degrees of equivalence” no longer need to be published as long as the methodology is explained.

Table 5 shows the matrix of all the degrees of equivalence as they will appear in the KCDB. It should be noted that for consistency within the KCDB, a simplified level of nomenclature is used with  $A_{e_i}$  replaced by  $x_i$ . The introductory text is that agreed for the comparison. The graph of the 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. This graphical representation indicates in part the degree of equivalence between the NMIs but obviously does not take into account the correlations between the different NMIs. It should be noted that the final data in this paper, while correct at the time of publication, will become out-of-date as NMIs make new comparisons. The formal results under the CIPM MRA [2] are those available in the KCDB.

## Conclusion

The BIPM ongoing key comparison for  $^{152}\text{Eu}$ , BIPM.RI(II)-K1.Eu-152 currently comprises four results. These have been analysed with respect to the updated KCRV determined for this radionuclide. The results of the COOMET.RI(II)-K2.Eu-152 comparison held in 2009 have been linked to the BIPM comparison through the mutual participations of the VNIIM. This has enabled the table of degrees of equivalence to include further three results.

The results of sixteen other NMIs and two international laboratories that took part in the CCRI(II)-K2.Eu-152 comparison in 1999 were previously linked to the BIPM ongoing key comparison through the measurement of each of the comparison ampoules in the SIR prior to issue [3]. These linked results are included in the matrix of degrees of equivalence and shown on the graph.

The degrees of equivalence have been approved by the CCRI(II) and are published in the BIPM key comparison database. Further results may be added when other NMIs contribute  $^{152}\text{Eu}$  activity measurements to the ongoing K1 comparison or take part in other linked comparisons.

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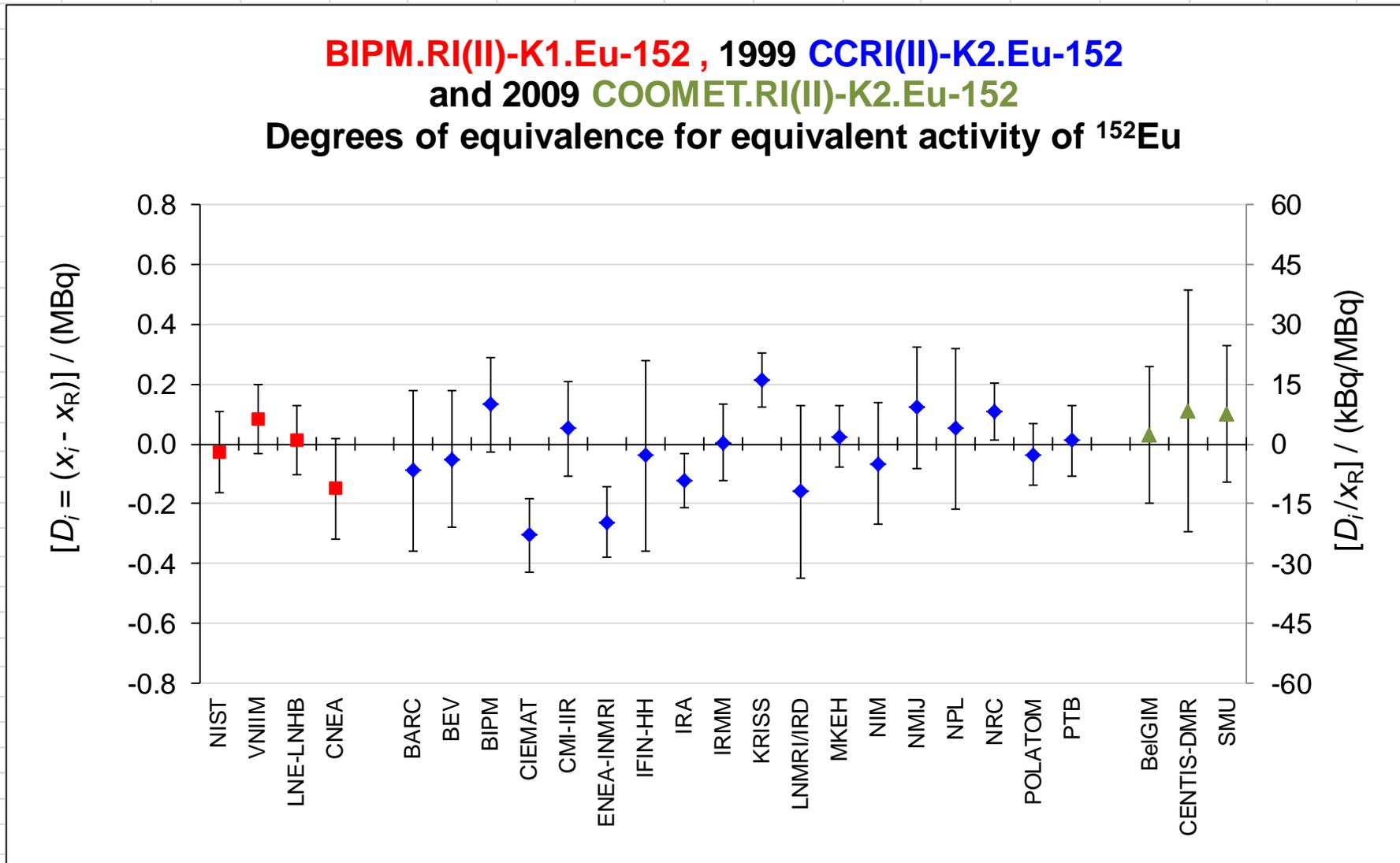
**Table 5. Table of degrees of equivalence and introductory text for <sup>152</sup>Eu**

|  |  |
|--|--|
| Key comparison BIPM.RI(II)-K1.Eu-152   |  |
| MEASURAND :  | Equivalent activity of <sup>152</sup> Eu |
| Key comparison reference value: the SIR reference value for this radionuclide is $x_R = 14\,919$ kBq with a standard uncertainty, $u_R = 35$ kBq (see Section 4.1 of the Final Report).<br>The value $x_i$ is 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 kBq, and $U_i = 2((1 - 2w_i)u_i^2 + u_R^2)^{1/2}$ when each laboratory has contributed to the calculation of $x_R$ .   |  |
| When required, 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 $U_{ij} \sim 2(u_i^2 + u_j^2)^{1/2}$ may be used in the following table.   |  |
| Linking CCRI(II)-K2.Eu-152 (1999) to BIPM.RI(II)-K1.Eu-152   |  |
| The value $x_i$ is the equivalent activity for laboratory $i$ participant in CCRI(II)-K2.Eu-152 having also been measured in the SIR (see Final report).   |  |
| The degree of equivalence of laboratory $i$ participant in CCRI(II)-K2.Eu-152 with respect to the key comparison 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 $U_i = 2((1 - 2w_i)u_i^2 + u_R^2)^{1/2}$ when the laboratory has contributed to the calculation of $x_R$ .   |  |
| When required, the degree of equivalence between two laboratories $i$ and $j$ , one participant in BIPM.RI(II)-K1.Eu-152 and one in CCRI(II)-K2.Eu-152, or both participant in CCRI(II)-K2.Eu-152, is given by a pair of terms: $D_{ij} = D_i - D_j$ and $U_{ij}$ , its expanded uncertainty ( $k = 2$ ), both expressed in MBq, where the approximation $U_{ij} \sim 2(u_i^2 + u_j^2)^{1/2}$ may be used.   |  |
| These statements make it possible to extend the BIPM.RI(II)-K1.Eu-152 matrices of equivalence to the other participants in CCRI(II)-K2.Eu-152.   |  |
| Linking COOMET.RI(II)-K2.Eu-152 (2010) to BIPM.RI(II)-K1.Eu-152  |  |
| The value $x_i$ is the equivalent activity for laboratory $i$ participant in COOMET.RI(II)-K2.Eu-152 having been normalized to the value of the VNIIM as the linking laboratory.   |  |
| The degree of equivalence of laboratory $i$ participant in COOMET.RI(II)-K2.Eu-152 with respect to the key comparison 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. The approximation $U_i = 2(u_i^2 + u_R^2)^{1/2}$ is used in the following table as none of the participants in COOMET.RI(II)-K2.Eu-152 contributed to the calculation of $x_R$ .   |  |
| When required, the degree of equivalence between two laboratories $i$ and $j$ , one participant in BIPM.RI(II)-K1.Eu-152 and one in COOMET.RI(II)-K2.Eu-152, or one participant in CCRI(II)-K2.Eu-152 and one in COOMET.RI(II)-K2.Eu-152, or both participant in COOMET.RI(II)-K2.Eu-152, is given by a pair of terms: $D_{ij} = D_i - D_j$ and $U_{ij}$ , its expanded uncertainty ( $k = 2$ ), approximated by $U_{ij} \sim 2(u_i^2 + u_j^2 - 2fu_iu_j)^{1/2}$ with $l$ being the linking laboratory when each laboratory is from the COOMET.RI(II)-K2 and $f$ is the correlation coefficient. |  |
| These statements make it possible to extend the BIPM.RI(II)-K1.Eu-152 matrices of equivalence to the other participants in COOMET.RI(II)-K2.Eu-152.  |  |

| Lab $i$ ↓  | $D_i$ | $U_i$ |
|------------|-------|-------|
|            | / MBq |       |
| NIST       | -0.03 | 0.13  |
| VNIIM      | 0.08  | 0.12  |
| LNE-LNHB   | 0.01  | 0.12  |
| CNEA       | -0.15 | 0.17  |
|            |       |       |
| BARC       | -0.09 | 0.27  |
| BEV        | -0.05 | 0.23  |
| BIPM       | 0.13  | 0.16  |
| CIEMAT     | -0.31 | 0.12  |
| CMI-IIR    | 0.05  | 0.16  |
| ENEA-INMRI | -0.26 | 0.12  |
| IFIN-HH    | -0.04 | 0.32  |
| IRA        | -0.12 | 0.09  |
| IRMM       | 0.00  | 0.13  |
| KRISS      | 0.21  | 0.09  |
| LNMRI/IRD  | -0.16 | 0.29  |
| MKEH       | 0.02  | 0.10  |
| NIM        | -0.07 | 0.20  |
| NMIJ       | 0.12  | 0.20  |
| NPL        | 0.05  | 0.27  |
| NRC        | 0.11  | 0.10  |
| POLATOM    | -0.04 | 0.10  |
| PTB        | 0.01  | 0.12  |
|            |       |       |
| BeIGIM     | 0.03  | 0.23  |
| CENTIS-DMR | 0.11  | 0.41  |
| SMU        | 0.10  | 0.23  |

Figure 1. Graph of degrees of equivalence with the KCRV for <sup>152</sup>Eu

(as it appears in Appendix B of the MRA)



N.B. The Right hand axis shows approximate values only

**Appendix 1. Uncertainty budgets for the activity of  $^{152}\text{Eu}$  submitted to the SIR**

VNIM 2009, 4P-NA-GR-00-00-HE

| Relative standard uncertainties                                 | $u_i \times 10^4$<br>evaluated by method |           |
|---|--|-----------|
|   | A  | B         |
| counting statistics   | 5  | –         |
| weighing  | 10                                       | 3         |
| dead time   | 17                                       | –         |
| counting time   | –  | 0.01      |
| impurities  | –  | 8         |
| background  | 1  | –         |
| half-life   | –  | 0.002     |
| interpolation from calibration curve                            | –  | 31        |
| extrapolation   | 14                                       | –         |
| <b>Quadratic summation</b>                                      | <b>25</b>                                | <b>32</b> |
| <b>Relative combined standard uncertainty, <math>u_c</math></b> | <b>41</b>                                |           |

VNIM 2009, 4P-PC-BP-NA-GR-CO

| Relative standard uncertainties                                 | $u_i \times 10^4$<br>evaluated by method |          |
|---|--|----------|
|   | A  | B        |
| counting statistics   | 6.3                                      | –        |
| weighing  | 10                                       | 3        |
| dead time   | –  | 2        |
| resolving time  | 2  | –        |
| counting time   | –  | 0.01     |
| impurities  | –  | 8        |
| background  | 13                                       | –        |
| half-life   | –  | 0.002    |
| extrapolation   | 46                                       | –        |
| <b>Quadratic summation</b>                                      | <b>49</b>                                | <b>9</b> |
| <b>Relative combined standard uncertainty, <math>u_c</math></b> | <b>50</b>                                |          |

LNE-LNHB 2009, 4P-NA-GR-00-00-HE

| <b>Relative standard uncertainties</b>                          | $u_i \times 10^4$<br>evaluated by method |           |
|---|--|-----------|
| <b>Contributions due to</b>                                     | <b>A</b>                                 | <b>B</b>  |
| counting statistics   | 3  | –         |
| weighing  | –  | 5         |
| dead time   | –  | 1         |
| impurities  | –  | 3         |
| background  | 5  | –         |
| half-life   | –  | 1         |
| efficiency calculation, including decay-scheme parameters       | –  | 10        |
| extrapolation of efficiency curve                               | –  | 30        |
| <b>Quadratic summation</b>                                      | <b>6</b>                                 | <b>32</b> |
| <b>Relative combined standard uncertainty, <math>u_c</math></b> | <b>33</b>                                |           |

CNEA 2011, 4P-PC-BP-NA-GR-CO

| <b>Relative standard uncertainties</b>                          | $u_i \times 10^4$<br>evaluated by method |           |
|---|--|-----------|
| <b>Contributions due to</b>                                     | <b>A</b>                                 | <b>B</b>  |
| counting statistics   | 46                                       | –         |
| weighing  | –  | 25        |
| dead time   | –  | 0.1       |
| resolving time  | –  | 0.1       |
| background  | $16 \times 10^{-5}$                      | –         |
| half-life   | –  | 0.012     |
| extrapolation of efficiency curve                               | 7.9                                      | –         |
| <b>Quadratic summation</b>                                      | <b>47</b>                                | <b>25</b> |
| <b>Relative combined standard uncertainty, <math>u_c</math></b> | <b>53</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      |
| alpha - particle              | AP      | selective sampling                                | SS      |
| mixture of various radiations | MX      | high efficiency                                   | HE      |
|                               |         |   |         |

| 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- $\gamma$ (Ge(HP))-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 |