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The Système International de Référence and its application in key comparisons

Guy Ratel

Bureau International des Poids et Mesures, Pavillon de Breteuil, F-92312 Sèvres Cedex, France

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Abstract

The paper begins with the reasons which led to the installation of the Système International de Référence (SIR) more than 30 years ago, describes its main features and presents briefly the way it works. Then more detail is given on the treatment of impurities and on the determination of the efficiency curve. The improvements, which have been made recently to update the SIR and make it more efficient, are also discussed. A brief survey of the status of the present SIR is then given before focusing on the new developments which are in progress to enlarge the scope of the SIR towards measurements of radiopharmaceuticals with short half-lives and of α - and β -particle emitters.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The Système International de Référence (SIR) was designed and established in 1976 to serve as a basis for extending the capabilities for international comparisons run by the Bureau International des Poids et Mesures (BIPM) in the area of activity measurement. Indeed, before its installation the only means available to check the consistency and to ensure the quality of measurements concerning radionuclides that were carried out in various laboratories relied on the systematic and regular organization of international comparisons.

These international comparisons required a careful preparation of a large amount of master solution from which more or less equal aliquots were taken and dispensed into flame-sealed glass ampoules. The preparation and the sending of these ampoules has always been a heavy task which has become even heavier with the increasing complexity and number of administrative procedures for importing and exporting samples. Depending on how difficult it was to measure the radionuclide chosen for the comparison, a preparatory or trial comparison was often organized first. The consequence of this was a significant extension of the time necessary to complete a comparison. Furthermore the results were not totally free of correlation because each laboratory measured a solution with the same chemical composition, although this may remove potential systematic effects related to source preparation. Notwithstanding these drawbacks these

international comparisons provide a valuable instantaneous snapshot of the capabilities of the laboratories in ascertaining the activity of a particular radionuclide and continue to deliver interesting information. They can also be used to test the relevance of different methods in the accurate determination of radionuclide activity or to compare the methods directly. However, the early requirement for a quick and precise comparison of different standardizations carried out in the various laboratories was used by the Comité Consultatif pour les Etalons de Mesure des Rayonnements Ionisants (CCEMRI), the predecessor of the Comité Consultatif pour les Rayonnements Ionisants (CCRI), to encourage the BIPM to set up a reliable, stable and precise system that was as simple as possible and which could fulfil the expectations and requirements of the radionuclide metrology community.

This paper describes the experimental arrangement of the SIR and the way it works. It summarizes the present status of the system and gives some significant figures which illustrate its importance for activity metrology. The crucial role played by the SIR since the coming into effect of the Comité International des Poids et Mesures Mutual Recognition Arrangement (CIPM MRA) in 1999 [1] is also explained. The limitations of the SIR inherent in the choices which prevailed at the time it was established are indicated in the later paragraphs, which also describe the current projects to address these limitations and thus extend the scope and the universality of the SIR.

2. Description of the Système International de Référence (SIR)

It is not the intention here to make an exhaustive description of the SIR. Several papers have already dealt with this subject and the interested reader can refer to them, in particular to those of Rytz [2, 3] written at the time of the installation of the SIR and which contain a more complete description of the experimental set-up. Additionally a general presentation of activity measurements with ionization chambers is available in [4].

Among the four main criteria, which were required to set up the SIR as mentioned in the introduction, the simplicity of operation as well as the reliability of the measurements strongly directed the choice of instrumentation towards the use of a well-type ionizing chamber as the key device. Further requirements such as the use of flame-sealed ampoules, directly filled with an aliquot of the radioactive solution by the participating laboratory so that no particular handling at the BIPM was necessary, contributed strongly to making the SIR efficient and simple to use. This latter characteristic also contributes to the speed with which the measurements can be made at the BIPM.

However, this idealized picture does not reflect entirely the real situation as the choice of a commercial ionization chamber with appropriate specifications for measuring the ampoules had to be a compromise concerning the type of radioactive processes which were to be detected. Consequently, since its conception, the SIR is only suitable for measuring γ emitting radionuclides as the metal walls of the chamber are too thick to enable a precise and reproducible detection of β particles or indeed any detection of α -particles.

As for all other activities of the BIPM, the SIR was established to provide a service to the designated national laboratories from countries which have signed the Convention du Mètre. Since the CIPM MRA was established in 1999, the SIR has been designated as the method by which national metrology institutes (NMIs) may compare their results for activity measurements of γ -emitting radionuclides. As a consequence of the requirement for all such measurements to be supported by a Quality System (QS), the BIPM also implemented a Quality System in 2006 for the operation of the SIR. The BIPM QS follows the guidance in ISO 17025 [5], and is peer-reviewed biennially by scientific experts from the NMIs. Annual internal audits ensure that the QS is properly maintained.

2.1. Participation in the SIR

Whenever a radionuclide metrology laboratory standardizes a solution of a particular radionuclide that decays by emission of γ -rays and wishes to compare their results with those obtained previously by other national laboratories, the easiest way to do this is to submit an ampoule of the same solution to the SIR. The laboratory is required to fill one or more glass ampoules (as supplied by the BIPM) of a well-characterized type filled with aliquots of 3.6 g taken from the standardized solution. The ampoules are flame-sealed and subsequently sent to the BIPM. A reporting form indicating the important characteristics of the radioactive solution, such as its chemical composition, its density, the deposited mass, the value of the

activity of the solution at the specified reference date with its uncertainty, the method used for the standardization, the full uncertainty budget and last but not least the amount of impurities present in the solution, needs to be available for the subsequent analysis in the SIR. As the SIR is, since the signing of the CIPM MRA, not only used to compare the measurement capabilities of national laboratories but is also the accepted tool to evaluate reference values and degrees of equivalence between laboratories, each participant needs to indicate in advance on their reporting form the intended purpose of the submission: whether it is to be used for an equivalence determination or whether it is solely a tentative or pilot measurement to check a newly implemented device or method or even to test a newly developed measurement method.

2.2. Operation of the SIR

The SIR is based on the use of two commercial re-entrant ionization chambers filled with nitrogen at 2.0 MPa. The chambers are housed within a shielded lead castle constructed with 5 cm thick lead bricks. They are coupled to an electronic device suitable for measuring currents as low as some hundreds of femtoamperes with relatively high precision (typically some parts in 10^4). Since the installation of the SIR and until recently, one of the chambers was used only for check purposes, the more sensitive one being used for the NMI measurements. Both chambers are operated with a negative polarization voltage of 500 V.

The SIR measurements are based on the principle of the Townsend balance with stepwise compensation and consist of measuring precisely the time t necessary to charge a capacitor of capacitance C , the value of which is surveyed regularly, to a well-known constant voltage U a number of times n chosen in advance. In short, from the knowledge of these different parameters, the ionization current produced by a radioactive source, placed in the ionization chamber, and for convenience labelled here with the index i , taking into account the leakage current I_f ('f' for the French word 'fuite' meaning leakage) which is measured separately, can then be evaluated simply as

$$I_i - I_f = \frac{CnU}{t} - I_f. \quad (2.1)$$

As the original intention of the SIR was to set up a system to deliver activity results quickly, it was designed not to rely on absolute activity determinations being made at the BIPM for every submission, which would have been too time consuming as well as being a drain on resources. Relative measurements seemed a more convenient way to achieve the proposed goal, provided that a sufficiently stable reference was used to enable the comparison. In fact this role was allocated to five radium sources having regard to the quite long half-life of this radionuclide $T_{1/2} = 1600$ a, $u = 7$ a [6], and so comparisons in the SIR were reduced to comparisons between two similar ionization currents, one produced in the chamber by the NMI-submitted ampoule and the other induced by one of the five radium sources with an expression identical to (2.1). Consequently, the important feature of the SIR is the use of the five ^{226}Ra reference sources. These are made of radium sulphate sealed in double-walled platinum-iridium

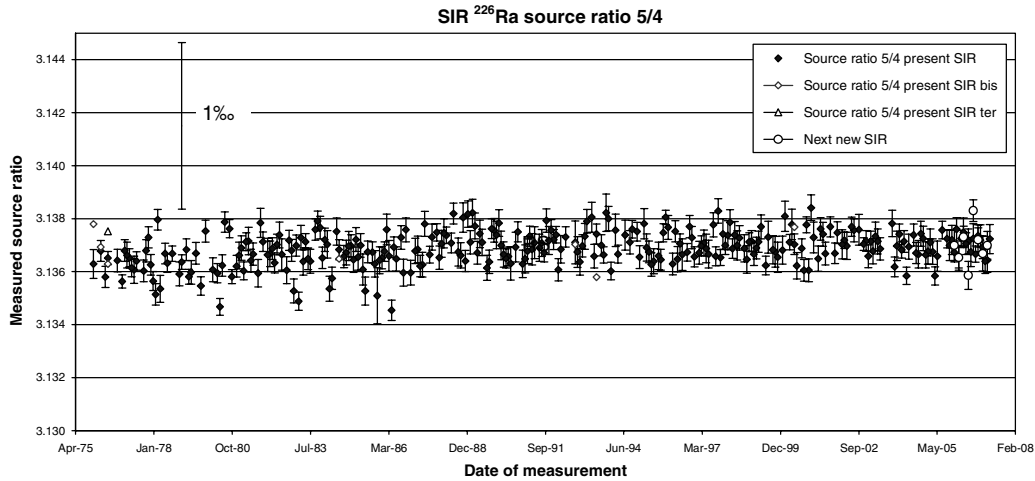


Figure 1. Ratio of the measurements of the reference radium sources numbers 5 and 4 since April 1975 with an indication of the 10^{-3} level of uncertainty. These represent monthly measurements although some additional measurements have been made. They correspond to the labels bis and ter of the legend.

cylinders of identical geometrical sizes [2]. The ratio between the activities of two successive Ra sources is about three, so that the total dynamic range in activity covered by the SIR sources is roughly 81 times, for a total activity of the five sources amounting to 16.4 MBq. To reduce experimental systematic effects, the same conditions are used for the samples and for the radium source to be measured. This is achieved by choosing the radium source that gives the most similar ionization current.

Recalling that the current collected in an ionization chamber is proportional to the activity of the sample placed in it and provided that the activity of the submitted radionuclide is known, it is appropriate to define a so-called equivalent activity of a radionuclide as that activity which will produce in the ionization chamber a current equal to that produced by the radium source of the highest activity. A similar concept was also introduced by Dryák and Dvořák [7]. Clearly, taking into account the decay of both the NMI sample, labelled *s*, and the radium source, labelled Ra in the following, between their respective dates of reference, t_r and t_o , and the date of measurement t_m common to the sample and to the radium source, and following [3], the equivalent activity can be expressed as

$$\frac{A_e e^{-\lambda_{Ra}(t_m - t_o)}}{A_s e^{-\lambda_s(t_m - t_r)}} = \frac{F_j (I_{Ra} - I_f)}{(I_s - I_f)} \quad (2.2)$$

In equation (2.2), an ad hoc normalizing coefficient, F_j , with $j = 1$ to 4, has been introduced to transform the measured current, obtained with the source of radium used to match the current of the sample, into the current which would have been produced by the highest-activity radium source. The parameter λ_s is the decay constant of the sample and is defined as

$$\lambda_s = \frac{\ln(2)}{(T_{1/2})_s} \quad (2.3)$$

A similar expression is also valid for the radium source where the label is changed to Ra.

Using this method, the SIR measurements reduce to the precise determination of ionization currents.

In order to fulfil the requirements of long-term stability for the system, the stability of the sources and that of the ionization chambers have to be checked regularly. Indeed, in parallel with the measurements of the samples sent by the laboratories, measurements are carried out each month to monitor the ratios of the currents produced by the different sources $r_j = I_{j+1}/I_j$, with $j = 1$ to 4, so that the ratio $r_{5,j}$ between the currents due to the source of the highest activity and to any of the other four sources is concurrently and easily determined as $F_j = r_{5,j=1,\dots,4} = \prod_{l=j}^4 r_l$. At the same time the two ionization chambers are checked using the second most active source. These periodic measurements, which have been carried out over a period of more than thirty years, demonstrate that the source ratios are stable within some parts in 10^4 , these figures increasing slightly as the activity of the considered source decreases. Both chambers exhibit a stability of the same order of magnitude. These results contribute to giving confidence in the perennial character of the SIR as illustrated in figure 1.

To ensure the continuity of the SIR without a break, the electronics are regularly maintained with internal calibrations as part of the QS. In addition a completely new version of the SIR electronics has been designed, developed and constructed and this is halfway through a two-year test to ensure its compatibility with the requirements for a consistent and stable measuring system. The 'new' SIR is also capable of providing absolute current measurements which will be recorded to enable an eventual transfer of the earlier measurement results to characterize a new SIR ionization chamber should this become necessary. In this way the continuity of the SIR is assured.

2.3. Corrections for impurities

Nowadays, most of the radionuclides of relevance to industrial or medical and also to metrological applications do not exist as such in nature but are mainly produced artificially in reactors and particle accelerators. To obtain the final product in a usable form some complex chemical treatments are necessary to dissolve the raw material and to prepare a stabilized solution. As a consequence it is unusual to obtain a solution with a pure content of the required radionuclide component and it is

common that the sample sent to the BIPM also contains some radionuclide impurities. It is a major task for the laboratories to identify and quantify the various impurities that may be present in the sample. However, a precise value of the impurity content is necessary for the correct analysis in the SIR.

Normally the BIPM uses the values communicated by the laboratory to correct the SIR measurements accordingly to ensure robust equivalent activity results. When impurities are reported, or when the SIR results show a discrepancy with previously registered results, several SIR measurements are carried out over a period of time depending closely on the half-life of the radionuclide under investigation. A steady change, either an increase or decrease in the evaluated equivalent activity, is a significant indicator of the presence of unaccounted for impurity. At this stage measurements are also made with the BIPM Ge(Li) spectrometer to compare the NMI assessment or to provide an independent impurity value. A detailed description of the calibration of the BIPM Ge(Li) is available in [8] and the procedure followed at the BIPM, as approved by the CCRI, for measuring impurities in the solutions submitted to the SIR by the NMIs is given in [9]. In [10], the discrepancies between the BIPM and the NMI impurity determinations for various radionuclides, which may result in dramatic changes in the resulting robustness of the results, are indicated as well as improvements which can be achieved for short-lived radionuclides when the actual impurity content is taken into account correctly.

Equation (2.2) applies for any kind of radionuclide emitting γ -rays that is able to produce an ionization current in the SIR chamber. This is similarly valid for any impurity. For reasons that are easily understood the inverse of equation (2.2) will now be considered. If some impurities, n , are present in the solution, each of them labelled in the following by the index i , each will contribute to the overall response of the chamber with an additional current given by

$$\frac{A_i e^{-\lambda_i(t_m-t_r)}}{A_{ei} e^{-\lambda_{Ra}(t_m-t_0)}} = \frac{I_i}{F_j(I_{Ra} - I_f)}. \quad (2.4)$$

As the denominator $F_j(I_{Ra} - I_f)$ is identical for each contribution, the additional current is merely a function of the ratio between the activity of the impurity and its equivalent activity corrected, as usual, for the decay of both the impurity and the radium source. In the general case, with several impurities present in the solution the correction term (2.4) becomes

$$\sum_{i=1}^n \frac{A_i e^{-\lambda_i(t_m-t_r)}}{A_{ei} e^{-\lambda_{Ra}(t_m-t_0)}} = \frac{\sum_{i=1}^n I_i}{F_j(I_{Ra} - I_f)}. \quad (2.5)$$

Since the total current I_{tot} collected in the chamber is the sum of all the contributions that are due to the main radionuclide (designated rad), and the impurities, equation (2.2) takes the expression

$$\begin{aligned} \frac{A_{rad} e^{-\lambda_{rad}(t_m-t_r)}}{A_{erad} e^{-\lambda_{Ra}(t_m-t_0)}} + \sum_{i=1}^n \frac{A_i e^{-\lambda_i(t_m-t_r)}}{A_{ei} e^{-\lambda_{Ra}(t_m-t_0)}} \\ = \frac{(I_{rad} + \sum_{i=1}^n I_i - I_f)}{F_j(I_{Ra} - I_f)} = \frac{(I_s - I_f)}{F_j(I_{Ra} - I_f)}. \end{aligned} \quad (2.6)$$

Considering that the purpose of the measurements is to determine the equivalent activity of the main radionuclide,

expression (2.6) should be slightly reformulated to factor this in the first term, so that this expression becomes

$$\begin{aligned} \frac{A_{rad} e^{-\lambda_{rad}(t_m-t_r)}}{A_{erad} e^{-\lambda_{Ra}(t_m-t_0)}} \left(1 + \sum_{i=1}^n \frac{A_i}{A_{rad}} \frac{A_{erad}}{A_{ei}} e^{-(\lambda_i - \lambda_{rad})(t_m-t_r)} \right) \\ = \frac{(I_s - I_f)}{F_j(I_{Ra} - I_f)}, \end{aligned} \quad (2.7)$$

from which the equivalent activity of the main radionuclide is easily deduced:

$$\begin{aligned} A_{erad} = A_{rad} \frac{e^{-\lambda_{rad}(t_m-t_r)} F_j(I_{Ra} - I_f)}{e^{-\lambda_{Ra}(t_m-t_0)} (I_s - I_f)} \\ \times \left(1 + \sum_{i=1}^n \frac{A_i}{A_{rad}} \frac{A_{erad}}{A_{ei}} e^{-(\lambda_i - \lambda_{rad})(t_m-t_r)} \right). \end{aligned} \quad (2.8)$$

The above expression for the corrected equivalent activity leads to some important comments. First the knowledge of the equivalent activity of the impurities is a prerequisite for a correct evaluation of the impurity correction. This can be difficult if the radionuclides reported as impurities by the NMI have not already been measured in the SIR. In the following paragraph, the method currently used to overcome this principal difficulty will be outlined. The second point is that the absolute value of the activity of the impurity or at least the ratio of activity of impurity to activity of main radionuclide at the reference date $R_i = \frac{A_i}{A_{rad}}$ should also be stated as accurately as possible by the NMI or otherwise can be determined at the BIPM. Michotte, in [10], has already stressed that, depending on the difference in sensitivity of the chamber for the two radionuclides, the main radionuclide and its impurity, which is indicated by the value of the ratio of their equivalent activity $\frac{A_{erad}}{A_{ei}}$, the contribution of the impurity can be magnified and that impurities, even those for which the ratio R_i defined above is as small as some part in 10^4 , may have a non-negligible impact on the final SIR result. The influence on the final results of the values of the half-lives of the different components of the radioactive solution has also been discussed in [10].

2.4. Efficiency curve of the SIR

After some years and with the measurements of an appreciably large number of ampoules, the SIR became a repository of many reliable results. The absolute standardizations of the solutions submitted to the SIR, which were carried out by the NMIs with the utmost care, were a guarantee of the quality of the registered data. Consequently, it seemed judicious to exploit this substantial amount of information to determine the efficiency of the ionization chamber used as a function of the energy. Each photon crossing the active volume of an ionization chamber will create charges inducing a current which is then detected with the appropriate electronic devices. When the radionuclide to be measured decays by the emission of several γ -rays of different energies, each of these will contribute to the total current. The sum of all these independent contributions will give rise to the final total ionization current. Normally, the chamber will respond differently to the various excitations caused by these photons, and with each radionuclide having a particular signature in energy represented by its individual decay-scheme, the

detection efficiency can be defined for each radionuclide. So, for a given radionuclide characterized by various energy levels of energy E_i and emission probability p_i the detection efficiency can be written as

$$\varepsilon_{\text{rad}} = \sum_{i=1}^n p_i(E_i)\varepsilon_i(E_i), \quad (2.9)$$

where the photon efficiency $\varepsilon_i(E_i)$ is normally any smooth function depending on the energy of the measured γ -line. In the first step the assumption was made by Rytz [3] that the efficiency could be separated into a part linearly dependent on the energy from which the actual efficiency could deviate by a small amount $\delta(E_i)$, following an idea of Schrader and Weiß [11]. Thus it was equivalent to state

$$\varepsilon_i(E_i) = KE_i + \delta(E_i), \quad (2.10)$$

Hence the expression (2.9) becomes

$$\varepsilon_{\text{rad}} = \sum_{i=1}^n p_i(E_i) (KE_i + \delta(E_i)) = K \sum_{i=1}^n E_i p_i(E_i) \times \left(1 + \frac{\delta(E_i)}{KE_i}\right), \quad (2.11)$$

or

$$\varepsilon_{\text{rad}} = K \sum_{i=1}^n E_i p_i(E_i) f_i, \quad (2.12)$$

with

$$f_i = 1 + \frac{\delta(E_i)}{KE_i}. \quad (2.13)$$

It is now possible to reformulate the expression (2.2) in a more convenient way. After a slight transformation it becomes

$$(I_s - I_f)e^{\lambda_s(t_m - t_r)} = A_s F_j (I_{\text{Ra}} - I_f) e^{\lambda_{\text{Ra}}(t_m - t_0)} \frac{1}{A_e} = A_s K' \frac{1}{A_e}. \quad (2.14)$$

Thus an important characteristic of the equivalent activity appears. Since the current produced in the chamber by a reference source of radium, when corrected for its decay, should not vary over time, the quantity $F_j(I_{\text{Ra}} - I_f)e^{\lambda_{\text{Ra}}(t_m - t_0)}$ does the same and can be shortened to a constant K' . As a consequence, the current produced in the chamber by the specific radionuclide then clearly appears to be proportional to the activity of the nuclide, so that the multiplicative factor can be regarded as the efficiency of the chamber. This implies that the inverse of the equivalent activity is proportional to the chamber efficiency and that, in consequence, expressions (2.12) and (2.14) can be put together. Hence the efficiency can be written as

$$\varepsilon_{\text{rad}} = K \sum_{i=1}^n E_i p_i(E_i) f_i = K' \frac{1}{A_e}. \quad (2.15)$$

The constants K and K' have been judiciously chosen [3] so that, when the equivalent activity is expressed in kBq, the energies can be expressed in MeV, a natural unit in nuclear physics. With this choice (2.15) becomes its final expression as used in the SIR

$$\sum_{i=1}^n E_i p_i(E_i) f_i = \frac{10^5}{6} \frac{1}{A_e}. \quad (2.16)$$

Hence the efficiency curve defined by the expression (2.16) is a function of the energy and was first experimentally established in a region where the curve is nearly linear, using mono-energetic radionuclides such as ^{54}Mn ($E = 834.838$ keV, $u = 0.005$ keV), and ^{60}Co which has two lines of relatively close energy ($E_1 = 1173.240$ keV, $u = 0.003$ keV and $E_2 = 1332.508$ keV, $u = 0.004$ keV) but with similar emission probabilities (99.85%, $u = 0.03\%$ and 99.9988%, $u = 0.0002\%$, respectively) so that the mean energy with a fictitious emission probability equal to the sum of the individual emission probabilities can be used. At the time when some factors f_i were approximately known for the SIR chamber, it was possible to draw a provisional curve and to extend the region of validity of the curve by selecting one particular f_ℓ factor corresponding to the energy level ℓ exhibiting the largest emission probability for a given radionuclide in equation (2.16) as follows:

$$f_\ell = \frac{\frac{10^5}{6} \frac{1}{A_e} - \sum_{i=1, i \neq \ell}^n E_i p_i(E_i) f_i}{E_\ell p_\ell(E_\ell)} \quad (2.17)$$

and re-iterating the entire process.

With the help of new radionuclides with more complex decay schemes submitted by the NMIs over the years, the curve has been extended towards the higher energy region with ^{24}Na (maximum energy $E = 2754.177$ keV, $u = 0.011$ keV) and towards lower ones with ^{153}Gd ($E = 97.431$ 03 keV, $u = 0.000$ 17 keV). The coefficients f_i have also been established more reliably. Radionuclides with even lower energies have been measured tentatively, such as for instance ^{125}I ($E_\gamma = 35.4919$ keV, $u = 0.0005$ keV [12]), but at these energies the results are not reliable as the influence of factors such as the ampoule wall thickness is significant. The establishment of the SIR efficiency curve has been a long-term iterative process which necessitates at each step a re-evaluation of the factors and hence of the entire curve. After some time, attempts were made to model the efficiency curve by means of analytical functions, in particular using polynomials of the third order in $\ln(E)$ in the range of 50 keV to 200 keV and of the fourth order above 200 keV [10]. This was very useful to obtain f_i factors by interpolation for γ -energies or radionuclides which had not yet been measured in the SIR chambers. This is relevant in accounting for impurities more precisely and consequently in obtaining more robust values for the equivalent activity.

A further correction was considered which may, under certain conditions, have a non-negligible influence. Indeed, although the chambers are too thick to enable the direct and precise measurement of beta-emitters, they contribute through their induced bremsstrahlung to produce a small current, and this must be taken into account to eliminate an otherwise systematic bias of the results. To account for the effects of the β particles, (2.17) has to be slightly modified according to [10] and therefore becomes

$$f_\ell = \frac{\frac{10^5}{6} \frac{1}{A_e} - \sum_{i=1, i \neq \ell}^n E_i p_i(E_i) f_i - \sum_j \varepsilon_\beta(\bar{E}_{\beta,j}) p_{\beta,j}}{E_\ell p_\ell(E_\ell)}, \quad (2.18)$$

where $\bar{E}_{\beta,j}$ represents the mean energy of the j β -spectrum. Further details are given in [8].

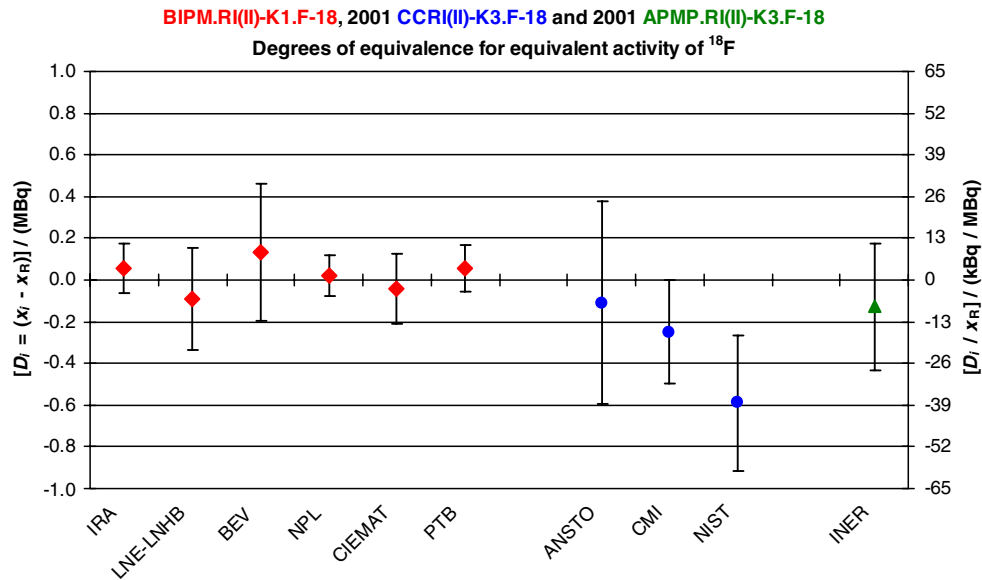


Figure 2. Results of the ^{18}F measurement in the SIR. The values represented by diamonds (comparison BIPM.RI(II).K1.F-18) have been obtained by direct SIR measurements of ampoules submitted by the laboratories. The values represented by circles (comparison CCRI(II)-K3.F-18) and by a triangle (comparison APMP.RI(II)-K3.F-18) have been linked to the SIR through the NPL.

A major improvement for modelling the SIR efficiency curve was achieved recently by Michotte *et al* [13]. This uses exponentials of polynomials adjusted to the experimental SIR data by non-linear least squares minimization. The model takes into account all impurity corrections and the β -spectrum shapes. The nuclear characteristics of the relevant radionuclides are entered in an auxiliary file that is used as input by the FORTRAN program so that the efficiency curve can be recalculated easily when it is required, for instance, at each time a major change in one of the nuclear parameters has been identified. A further advantage of this new method is that the program allows correlations between nuclear data and also between experimental entries to be taken into account. Last but not least it evaluates the uncertainties on the individual f_i parameters at the same time, which are necessary to evaluate the equivalent activity of impurities not yet measured in the SIR. Furthermore, this procedure is sensitive enough to help discriminate between different sets of competitive nuclear parameters, or to reveal some inconsistencies in the experimental data which require further investigation.

2.5. Reporting results

The SIR radionuclide activity comparisons are BIPM ongoing comparisons and so each laboratory result is analysed and registered in the master file of SIR data. If the result is as expected, the participating laboratory is informed directly, otherwise the procedures of the CIPM MRA are invoked. Once the laboratory has commented on their result, a joint report is produced to include the degrees of equivalence of the result with the Key Comparison Reference Value (KCRV) and with the other participants in the same radionuclide comparison. Once this report has been approved by the participant and the CCRI, it is submitted for publication and the results are submitted to the key comparison database of the CIPM MRA.

Any SIR result that has been submitted for a radionuclide solution that has been standardized by the NMI using a primary

method is eligible to be included in the KCRV, as long as the recommendations of the CCRI are followed. Any changes to the KCRV have to be approved by the CCRI section II.

3. Status of the present SIR

The SIR is a striking example of the close and constant collaboration between the BIPM and the NMIs. Indeed the SIR provides a service to the national laboratories but could not achieve its defined goal without the active participation of the NMIs in submitting their carefully standardized samples. About twenty-five laboratories are contributors to the SIR, about ten of which are annual contributors. For instance in 2006, the BIPM received 31 ampoules from 13 laboratories allowing 17 new results to be entered in the SIR master-file for 12 different radionuclides, i.e. ^{18}F , ^{57}Co , ^{60}Co , ^{67}Ga , $^{99}\text{Tc}^m$ (2 results), $^{110}\text{Ag}^m$, ^{111}In , ^{131}I (2 results), ^{133}Ba , ^{134}Cs (3 results), ^{201}Tl (2 results) and ^{222}Rn . The results for ^{237}Np , which will constitute a new entry, are under analysis.

To process radionuclides with short half-lives, such as ^{18}F ($T_{1/2} = 1.8290$ h; $u = 0.0005$ h), $^{99}\text{Tc}^m$ ($T_{1/2} = 6.0067$ h; $u = 0.0010$ h), ^{131}I ($T_{1/2} = 8.021$ d; $u = 0.001$ d) the SIR software has been altered to enable account to be taken precisely of the decay of the samples during the measurements. To illustrate this point the results of the ^{18}F measurements are shown in the first part of figure 2. Detailed descriptions of the characteristics of the solutions sent to the BIPM and of the measurements carried out in the SIR for this radionuclide are given in [14, 15]. Due to the very short half-life of this radionuclide, which is important in medical imaging, only laboratories close to the BIPM could submit samples to the SIR. The other participants in figure 2 participated through the use of a secondary transfer method. Consequently, precise measurements, however, could only be achieved by a rapid delivery to the BIPM of the samples with high enough activities and a good synchronization of the measurements at the BIPM

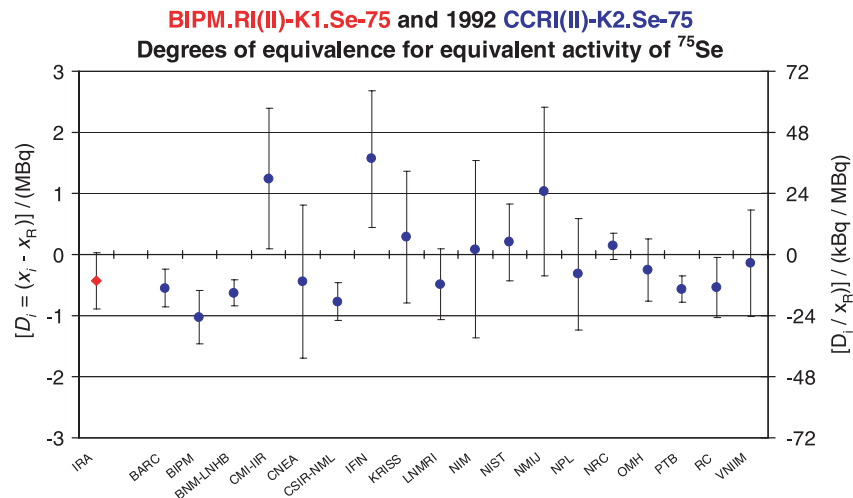


Figure 3. Results of the CCRI(II) comparison of a solution of ^{75}Se (circles) linked to the SIR results (diamond). (The acronyms for the CSIR-NML and the OMH have recently been changed to NMISA and MKEH, respectively.)

and the distributing laboratory to reduce the uncertainties induced by the rapid decay of the radionuclide. This process is not possible for distant laboratories, which, unfortunately, for the moment remain excluded from direct comparisons of these radionuclides. However, a new procedure is in development as outlined in section 4.1, to overcome this limitation and which can be easily followed by distant laboratories to enable them to link into the SIR.

In 1999, after the signing of the CIPM MRA [1], a new policy was introduced conferring on the SIR a key role in comparisons carried out in the frame of the CCRI. Since then the SIR has been used to evaluate the KCRV and the degree of equivalence between national laboratories. It is now a requirement that the participants send a detailed uncertainty budget with their measurement result, which enables the BIPM to evaluate potential correlations occurring when the KCRV and the degree of equivalence are being calculated. Furthermore the laboratories have to indicate if the submissions are to be used to obtain a degree of equivalence or simply to test a new measurement method. In the latter case the results can be withdrawn by the participant during a one-month period, and are entered in the master file with a special index if they are accepted but cannot be evaluated for degrees of equivalence.

Another important role played by the SIR is illustrated by figure 3. In parallel to the SIR, the CCRI(II) regularly organizes international comparisons of radionuclides that are of particular interest. As the SIR has been selected as the tool for evaluating the KCRV and degrees of equivalence, the results of these comparisons also have to be linked to the SIR results, where this is possible. Normally this is done by measuring some specially prepared ampoules, filled with 3.6 g of the same solution that has been distributed to the participants, in the SIR ionization chamber, the mean value of the CCRI(II) comparison being used to evaluate the link. This procedure has been extended to include results of comparisons organized in the regional metrology organizations (RMOs) providing that the comparison has been declared beforehand to the CCRI(II) and accepted. However, only NMIs or designated laboratories in countries associated with the Conférence Générale des Poids et Mesures (CGPM) are

eligible for inclusion in the CIPM MRA key comparison database. For ^{75}Se , all the ampoules distributed to the participants were measured in the SIR chamber prior to distribution [16] so that the link was easy to establish as shown in figure 3 [17]. In this case, all the results obtained by primary standard laboratories using primary measurement methods qualified as contributions to the determination of the KCRV.

From time to time the various compilations of nuclear data are improved and the SIR has also to be receptive to these revisited evaluations. Now that nuclear data are being published by the CCRI in the BIPM Monograph 5 series [18], these data are being used for the SIR and consequently any improvements should be reflected in the SIR evaluations. This is the case for the emission probabilities as was reported in section 2.4 but it also concerns the half-life values of the radionuclides, which have a direct influence on the SIR results. In consequence, when any change in a half-life value is detected, particularly when the half-life is short, a new re-evaluation of all SIR entries for the corresponding radionuclide has to be undertaken. Although the results for several radionuclides have been re-evaluated, a prime example is for ^{131}I for which the half-life changed from ($T_{1/2} = 8.02$ d; $u = 0.01$ d) to ($T_{1/2} = 8.021$ d; $u = 0.001$ d) and all the data were recalculated. However, sometimes, when the new final results demonstrate significant changes, a new evaluation of the KCRV, and consequently of the degrees of equivalence of the laboratories, is also required. The validation of the new results requires approval by the CCRI(II).

Radioactive gas samples can also be submitted to the BIPM using special gas ampoules specifically designed by the NIST for this purpose. This has extended the scope of the SIR for instance, to ^{133}Xe and particularly to ^{222}Rn , the measurement of which is important for environmental surveys. In the same frame, a comparison of samples of ^{85}Kr , organized under the auspices of the CCRI(II), which will be linked to the SIR once it is finished, will be underway in the near future.

For completeness it should be mentioned that some further studies, which will continue to improve the validity of the SIR measurements, have been started. These regard the determination of the dependence of the response of the

chamber as a function of the variation of the mass of solution as delivered in the ampoules and its variation as a function of the density of the solution. This will enable the results to be corrected more precisely for these conditions. As far as measurements of gas ampoules are concerned, the influence of the gas pressure on the reproducibility of the results is also being investigated.

4. Current projects for the extension of the scope of the SIR

4.1. Implementation of a travelling well-type NaI(Tl) detector for measuring short-lived γ -ray emitters

As mentioned earlier, successful measurements of radionuclides emitting γ -rays with short half-lives have been made but these have been restricted to laboratories located relatively close to the BIPM. The CCRI(II), being well aware of the constant increase of the use of these kinds of radionuclides for diagnosis or therapy in developed countries and of the necessity for all such countries to compare their own standardizations of these radionuclides with those obtained in European countries close to the BIPM, decided to set up the Transfer Instrument Working Group (TIWG) in 2003 to study the possibility of extending the scope of the SIR. After considerable discussion it was decided that the BIPM could only achieve this goal by using a transfer instrument which would circulate between the comparison participants. Obviously this device should also be linked to the original SIR so that measurements carried out with this new TI system can be compared with those obtained in the traditional way. The TIWG proposed at the following CCRI(II) meeting that a 76 mm by 76 mm NaI(Tl) detector equipped with a 2 cm diameter well be used and that all the events above a given low threshold be counted. A source composed of a mixture of $^{93}\text{Nb}^m$ ($T_{1/2} = 16.12$ a; $u = 0.15$ a) and ^{94}Nb ($T_{1/2} = 20\,300$ a; $u = 16$ a [19]) produced by the IRMM was foreseen to fulfil two aims: the x-ray emission at 17 keV of $^{93}\text{Nb}^m$ should serve to set the counting threshold and the ^{94}Nb would check the long-term stability of the system. In this case ^{94}Nb will have a similar role to that played by the radium sources for the traditional SIR as the measurement of a short-lived radioactive sample will be made relative to a measurement of the long-lived ^{94}Nb source. Furthermore an equivalent activity is to be defined in the same terms as for the traditional SIR system. The TI system has been assembled at the BIPM and preliminary experiments are underway. A solution of high activity of $^{99}\text{Tc}^m$ prepared at the LNE-LNHB ($T_{1/2} = 6.0067$ h; $u = 0.0010$ h) has been measured in the SIR chamber and later in the transfer instrument after having waited several half-lives to ensure that the activity of the sample was sufficiently reduced to avoid distortions due to dead-time effects. The consecutive measurements in the SIR and in the transfer instrument of the sample enable the linking factor, defined as the ratio between the equivalent activity in the SIR and the equivalent activity in the transfer instrument, to be evaluated. Comparisons of $^{99}\text{Tc}^m$ will be scheduled first with the LNE-LNHB and the NPL. If these first measurements are consistent with their SIR measurements, the comparisons will then be extended to more distant laboratories, in particular the NIST. Further details on the test procedures and the

preliminary measurements were presented to the CCRI(II) in 2007 [20].

4.2. Extension to β emitters

Undeniably the SIR is a valuable tool that is much appreciated by the national laboratories, which can rely on it to obtain a rapid and precise comparison of their data. However, the major drawback, which was identified at an early stage by the CCRI(II), is that the present SIR can only measure γ -ray emitting radionuclides. If β -particles play a role, it is only through corrections for the bremsstrahlung they induce in the chambers. To resolve this limitation, the CCRI(II) decided some years ago to study the possibility of extending the SIR to β -particles through a working group, the Extended SIR Working Group (ESIR WG). Early on the ESIR working group proposed to use a liquid-scintillation spectrometer instead of an ionization chamber for this extension of the SIR with the benefit that at the same time α -particle emitters could also be included in that the energy transfer between the particle and the environment takes place in the scintillator.

To check the validity of using liquid scintillation to extend the SIR, several international comparisons of different suitable radionuclides have been organized by the CCRI(II), in which the BIPM was an active participant. From these various exercises some expertise has been collected, which can be summarized as follows. Pure β -emitters such as ^{14}C ($E_{\text{max}} = 156.468$ keV, $u = 0.004$ keV [12]), ^{90}Sr ($E_{\text{max}} = 545.9$ keV; $u = 1.4$ keV), ^{89}Sr ($E_{\text{max}} = 1495.1$ keV, $u = 2.2$ keV) and ^{90}Y ($E_{\text{max}} = 2279.8$ keV, $u = 1.7$ keV) with relatively high to high maximum energy, as well as α -emitters like ^{238}Pu or ^{241}Am , are comparatively easy to standardize and should not present a major difficulty to be included in the SIR. Whereas for ^{204}Tl , a β -emitter with a small electron-capture branch (with a branching ratio of 2.92%, $u = 0.13\%$ [12]), the measurements may be sensitive to the chemical stability of the solution and great care has to be taken in the preparation of the sample with an appropriate carrier concentration to maintain the stability of the solution. For this nuclide, however, high concentrations do not appear to affect results obtained by liquid-scintillation counting as was demonstrated in a recent international comparison of solutions of this nuclide [21]. Another aim of the working group is to extend the SIR to other types of decay such as pure electron capture as for ^{55}Fe and ^{165}Er , which are not yet covered by the present SIR, or photon emission of low energy (E lower than 50 keV) for which the response of the original chamber is unreliable as indicated by a comparison of ^{125}I . For these radionuclides the CIEMAT-NIST model to be applied to obtain the equivalent activity of the solution is not yet sufficiently validated. Furthermore the preparation by the BIPM of samples for counting would not be appropriate for the extension of the SIR as this requires fast and precise measurements.

Several commercial liquid scintillators with good characteristics are available and could be used for the purpose of extending the SIR. However, their reproducible production cannot be guaranteed and this may produce discrepant results which would be unacceptable for the SIR. Well aware of these particular problems coupled to the chemical or the physical nature of the radionuclide to be measured, the ESIR WG

plans to establish a recipe for preparing the samples for each radionuclide in a normalized way to avoid the risks of unstable preparation as occurred for ^{204}Tl . The validation of the composition of the prepared scintillator requires the study of its stability under normal storage conditions; this is crucial to enable checks of the samples at a later stage. Therefore the participants of the working group were asked to develop suitable scintillators which should at least be stable over a period of six months. The CIEMAT presented results obtained with a scintillator, named XAN6040, based on 60% of xylene and 40% of naphthalene, which showed a remarkable stability for a batch of 20 different nuclides. The decision was taken to send aliquots of the CIEMAT scintillator to various laboratories so that they could prepare their own samples and test the stability of the scintillator after air travel for different radionuclides. The results were disappointing as the same quality of stability was not obtained in any other laboratory. This resulted in a decision that the scintillator had to be prepared at the place of use, i.e. at the BIPM, and consequently that the radioactive samples should be sent to the BIPM as they are in the traditional SIR and the necessary preparation work carried out at the BIPM. To fulfil this goal, a rigorous study of the procedures used at the CIEMAT to prepare the scintillator was made and similar methods were adopted at the BIPM. To avoid any discrepancies due to the use of different chemicals, the same raw material was ordered at the BIPM. Preparation and checks of the scintillator are underway.

However, during the meeting of the ESIR WG in April 2007, the CIEMAT, the PTB and the LNE-LNHB each proposed different methods and procedures to be set up for extending the SIR. The method of the PTB, which has already been presented at a conference [22], and that of the CIEMAT [23] exhibit strong similarities. The method proposed by the LNE-LNHB [24], based on the use of a liquid-scintillation counter coupled to a Compton spectrometer, where a virtual reference source is internally created within the liquid-scintillation cocktail to be measured by means of the Compton effect, is original and looks very promising but may be more difficult to implement for routine measurements. To monitor the possibilities, ^3H ($T_{1/2} = 12.312\text{ a}$; $u = 0.1\text{ a}$ and $E_{\text{max}} = 18.591\text{ keV}$; $u = 0.001\text{ keV}$) has been suggested, as its efficiency as a tracer in the CIEMAT/NIST method has been demonstrated many times. However, its relatively short half-life could be regarded as a drawback and the possibility of other radionuclides such as ^{14}C or ^{63}Ni should be investigated. As ^{14}C requires particular care to avoid the loss of activity through the formation of carbon dioxide gas, ^{63}Ni could be a more serious candidate. As far as the actual method to be used for the extension of the SIR to β -emitters, no final decision has yet been made by the CCRI(II).

5. Conclusion

In this paper, an overview of the International Reference System (SIR) has been presented since its foundation up to the present, together with the reasons for its establishment. The developments over the 31 years of existence of the SIR have been designed to respond to the needs of the NMIs and to fulfil the increasing demand of the metrological community for precise and accurate results.

The decision to use the SIR as the cornerstone for evaluating and the degrees of equivalence between laboratories has emphasized its importance for radionuclide activity measurements but on the other hand has required improvements to the efficiency of the SIR procedures and to the data analysis to increase the robustness of the results. The particular care which is now brought to the treatment of potential impurities in the radioactive solutions is one such illustration of these improvements and the production of a β -response curve to take bremsstrahlung contributions into account is another.

The present operation of the SIR is limited to γ -emitters but steps are being taken to enable the measurement of other decay modes. To overcome the inherent problems with long-distant transport of short-lived radionuclides, a transfer system is being set up so that NMIs distant from the BIPM will no longer be disadvantaged. These two examples demonstrate the vitality of the SIR in seeking new solutions, and its reactivity to provide the metrological community with appropriate comparison tools, such as the extension of the SIR to β -emitters and the use of a travelling transfer well-type NaI(Tl) detector for measuring short-lived nuclides. This clearly shows that the SIR, although in its 31st year of existence, has not attained the age of senility but that of maturity in which it aims to remain an essential instrument for comparing solutions of radionuclides at the highest level of accuracy by responding appropriately to the needs of the NMIs.

Acknowledgments

In the first place the author would like to dedicate this paper to the memory of Dr A Rytz, the founder of the SIR. Without his original impetus and the constant support of the former CCEMRI(II), now the CCRI(II), this work would not have been possible. Indeed the SIR is a team project and the author's sincere thanks are extended to the whole team. Since Dr C Michotte joined the team in 1997, she has much ameliorated the measurements, particularly with the improvements in accounting for impurities and the precise determination of the efficiency curve of the ionization chambers. Mr C Colas, who performed all the measurements with care since the beginning until his recent retirement, and his successor, Mr S Courte, have maintained the system and ensured that it is a valuable tool for the NMIs, while Mr M Nonis has kept the electronics in order and improved the experimental setup. The author would like to express his gratitude to all the contributors to the SIR, who have provided interesting and well-standardized solutions over the last 30 years as without their help and their constant support the SIR would not have reached its present level of completeness. Last but not least, the author would like to signify his profound gratitude to Dr P Allisy-Roberts for her constant support for the SIR and also her constructive comments on this paper.

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