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Abstract

The responses of the three photomultiplier tubes (PMTs) in a triple-to-double coincidence ratio (TDCR) liquid scintillation (LS) system are often not identical. Such asymmetries can have a significant influence on activity determinations. The problem is often solved by means of a minimization algorithm which can easily be applied when analytical methods are used for the efficiency calculation, as is usually done for pure beta emitters. However, for radionuclides with more complex decay schemes, the counting efficiencies are often calculated with stochastic methods and the computation of the required corrections becomes very challenging.

This paper presents a new numerical method to overcome the asymmetry problem for such complex decays. The new algorithm was tested with various radionuclides, and a more detailed study on ^{55}Fe is described. For the measurements, the asymmetry was varied by means of grey filter films which were placed in front of one of the photomultiplier tubes.

In the case of the pure electron-capture (EC) radionuclide ^{55}Fe, the asymmetry can also be taken into account with a very simple correction which is derived assuming monoenergetic emissions. This work is also of great importance for the planned extension of the International Reference System (SIR) at the BIPM which will be used for international comparisons in radionuclide metrology.

***Key words**:* TDCR; photomultiplier tube; asymmetry; complex decay schemes; international comparisons

1. Introduction

The triple-to-double coincidence ratio (TDCR) method is a very powerful tool and has been successfully applied to the activity standardization of a number of radionuclides (see, e.g., Broda et al., 2007). The method requires a dedicated liquid scintillation (LS) counter with three photomultiplier tubes (PMTs) from which triple and double coincidence counting rates are determined. In addition, the method comprises the computation of corresponding counting efficiencies $\varepsilon_T(\lambda)$ and $\varepsilon_D(\lambda)$ for triple and double coincidences as a function of a free parameter λ. The free parameter and, consequently, the required counting efficiencies are then determined using the following relation:

$$\frac{\varepsilon_T(\lambda)}{\varepsilon_D(\lambda)} = \frac{R_T}{R_D} \equiv TDCR\,, \qquad (1)$$

where R_T and R_D are the experimentally determined net counting rates for triple and double coincidences, respectively.

The above-mentioned approach is only valid if the free parameter λ is identical for all three photomultipliers. This is, however, often not the case. In most TDCR systems, the response of the PMTs is not identical, since, for example, the intrinsic quantum efficiencies are not identical either. The individual counting efficiencies of the three PMTs may also be different due to geometry effects related to the design of the optical chamber or the LS samples. This is referred to as a PMT asymmetry which may be very large in TDCR systems (see, e.g., Meyer and Simpson, 1990; Zimmerman et al., 2004). PMT asymmetries can have significant influence on activity determination – in particular when measuring radionuclides with low counting efficiencies such as ^{3}H or ^{55}Fe. Asymmetries can also become significant when the counting efficiency is voluntarily varied (as part of a primary calibration process) by means of PMT defocusing (Arenillas and Cassette, 2006).

In the following, the three PMTs in a TDCR system are referred to as A, B and C. For pure beta emitters, the PMT asymmetry can be taken into account by means of a numerical procedure assuming three independent free parameters λ_A, λ_B and λ_C. The method also requires determining the coincidence counting rates of any pair of PMTs, R_{AB}, R_{BC} and R_{AC}.

The three free parameters are then obtained from a multidimensional minimization algorithm which is used to minimize the loss function

$$\Delta = \left(\frac{\varepsilon_{\mathrm{T}}}{\varepsilon_{\mathrm{AB}}} - \frac{R_{\mathrm{T}}}{R_{\mathrm{AB}}} \right)^2 + \left(\frac{\varepsilon_{\mathrm{T}}}{\varepsilon_{\mathrm{BC}}} - \frac{R_{\mathrm{T}}}{R_{\mathrm{BC}}} \right)^2 + \left(\frac{\varepsilon_{\mathrm{T}}}{\varepsilon_{\mathrm{AC}}} - \frac{R_{\mathrm{T}}}{R_{\mathrm{AC}}} \right)^2, \quad (2)$$

where $\varepsilon_{\mathrm{T}} = \varepsilon_{\mathrm{T}}(\lambda_{\mathrm{A}}, \lambda_{\mathrm{B}}, \lambda_{\mathrm{C}})$, $\varepsilon_{\mathrm{AB}} = \varepsilon_{\mathrm{AB}}(\lambda_{\mathrm{A}}, \lambda_{\mathrm{B}})$, $\varepsilon_{\mathrm{BC}} = \varepsilon_{\mathrm{BC}}(\lambda_{\mathrm{B}}, \lambda_{\mathrm{C}})$ and $\varepsilon_{\mathrm{AC}} = \varepsilon_{\mathrm{AC}}(\lambda_{\mathrm{A}}, \lambda_{\mathrm{C}})$.

The minimization is often realized by means of a downhill simplex algorithm (Nelder and Mead, 1965; Press et al., 1992) and the PMT asymmetry problem was successfully solved in several laboratories when measuring beta emitters (see, e.g., Arenillas and Cassette, 2006; Broda et al., 2007; Zimmerman et al., 2010).

The minimization in Eq. 2 can be easily applied in the case of a pure beta emitter, since the required counting efficiencies are calculated with short computation times by means of an analytical model of the theoretical efficiencies. This just requires the computation of the ionization quenching function $Q(E)$, the beta spectrum $S(E)$ and some numerical integration procedures (see, Broda et al. (2007) and references therein). The triple counting efficiency is then given by

$$\varepsilon_{\mathrm{T}}(\lambda_{\mathrm{A}}, \lambda_{\mathrm{B}}, \lambda_{\mathrm{C}}) = \int_0^{E_{\max}} S(E) \left(1 - \exp\left(\frac{-E \cdot Q(E)}{3\lambda_{\mathrm{A}}}\right)\right)\left(1 - \exp\left(\frac{-E \cdot Q(E)}{3\lambda_{\mathrm{B}}}\right)\right)\left(1 - \exp\left(\frac{-E \cdot Q(E)}{3\lambda_{\mathrm{C}}}\right)\right) dE \,. \quad (3)$$

The above-mentioned approach cannot be applied to radionuclides with more complex decay schemes, e.g., for electron-capture (EC) decay or when beta emissions are coincident with gamma emissions or emissions of electrons from internal conversion. Such decays lead to more complex electron spectra and more than one electron per decay event may occur (including secondary electrons due to photon interaction in the sample). Hence, the efficiency computation becomes more complex, too, and the same holds for the required asymmetry correction. Razdolescu et al. (2008) applied a simplified KLM atomic rearrangement model to compute the ^{55}Fe efficiency. The quantum efficiencies of each individual PMT were determined applying a model for monoenergetic emissions and then used to compute the overall counting efficiency assuming that the ratios of quantum efficiencies correspond to the ratios of respective free parameters. (Note: the quantum efficiency ν_{X} as defined by Razdolescu et al. (2008) is inversely proportional to the free parameter as defined in this work, i.e. $\nu_{\mathrm{X}} \propto \lambda_{\mathrm{X}}^{-1}$ with $\mathrm{X} \in [\mathrm{A}, \mathrm{B}, \mathrm{C}]$.)

Although the approximation applied by Razdolescu et al. (2008) yields satisfactory results, a general solution of the PMT asymmetry problem is still missing. In the following, a new approach is discussed that can – in principle – be applied to any radionuclide.

2. Methodology of the new asymmetry correction – the stochastic approach

The new proposed methodology is based on the stochastic model that has been successfully applied in the past when asymmetries were low (see, e.g., Kossert et al., 2014, 2018). This approach requires the comprehensive computation of radioactive decay including beta transitions, gamma transitions and EC encompassing the atomic rearrangement that follows an internal conversion or EC processes. Again, it is to be noted that there are decay events for which more than one electron needs to be considered. If the number of electrons in the event number i is M_i and the energies of the individual electrons are E_{il}, the triple counting efficiency as a function of the free parameter λ (i.e. the symmetric case) is given by

$$\varepsilon_{\mathrm{T}}(\lambda) = \sum_{i=1}^{N} \left\{ 1 - \exp\left[\frac{-\sum_{l=1}^{M_i} E_{il} Q(E_{il})}{3\lambda} \right] \right\}^3 / N \quad , \tag{4}$$

with N being the number of decay events.

The counting efficiency for double coincidences can be computed in a similar manner. The free parameter is then determined after the efficiency computation using the experimental TDCR value (see Eq. 1).

This approach has been modified in the following way. As before, the stochastic method is used to calculate the electron energies E_{il} for all M_i electrons in a single decay event i. The results $E_{il}Q(E_{il})$ are stored in a file, in which one line represents a single decay event i. This calculation is done for a large number of decay events N (number of lines in the file).

The next step of the analysis is to determine the net counting rates for triple coincidences and the three double coincidence counting rates R_{AB}, R_{BC} and R_{AC}.

A numerical function *EffCalc()* is defined that computes $\varepsilon_{\mathrm{T}} = \varepsilon_{\mathrm{T}}(\lambda_{\mathrm{A}}, \lambda_{\mathrm{B}}, \lambda_{\mathrm{C}})$, $\varepsilon_{\mathrm{AB}} = \varepsilon_{\mathrm{AB}}(\lambda_{\mathrm{A}}, \lambda_{\mathrm{B}})$, $\varepsilon_{\mathrm{BC}} = \varepsilon_{\mathrm{BC}}(\lambda_{\mathrm{B}}, \lambda_{\mathrm{C}})$ and $\varepsilon_{\mathrm{AC}} = \varepsilon_{\mathrm{AC}}(\lambda_{\mathrm{A}}, \lambda_{\mathrm{C}})$ such as

$$\varepsilon_{\mathrm{T}}(\lambda_{\mathrm{A}},\lambda_{\mathrm{B}},\lambda_{\mathrm{C}}) =$$

$$\sum_{i=1}^{N}\left\{\left(1-\exp\left[\frac{-\sum_{l=1}^{M_i}E_{il}Q(E_{il})}{3\lambda_{\mathrm{A}}}\right]\right)\left(1-\exp\left[\frac{-\sum_{l=1}^{M_i}E_{il}Q(E_{il})}{3\lambda_{\mathrm{B}}}\right]\right)\left(1-\exp\left[\frac{-\sum_{l=1}^{M_i}E_{il}Q(E_{il})}{3\lambda_{\mathrm{C}}}\right]\right)\right\} / N \qquad (5)$$

and

$$\varepsilon_{\mathrm{XY}}(\lambda_{\mathrm{X}},\lambda_{\mathrm{Y}}) = \sum_{i=1}^{N}\left\{\left(1-\exp\left[\frac{-\sum_{l=1}^{M_i}E_{il}Q(E_{il})}{3\lambda_{\mathrm{X}}}\right]\right)\left(1-\exp\left[\frac{-\sum_{l=1}^{M_i}E_{il}Q(E_{il})}{3\lambda_{\mathrm{Y}}}\right]\right)\right\} / N \quad , \qquad (6)$$

with $\mathrm{X}\in[\mathrm{A},\mathrm{B},\mathrm{C}]$ and $\mathrm{Y}\in[\mathrm{A},\mathrm{B},\mathrm{C}]$ while $\mathrm{X}\neq\mathrm{Y}$. In addition, the function *EffCalc()* provides the loss function

$$\Delta = \left(\frac{\varepsilon_{\mathrm{T}}(\lambda_{\mathrm{A}},\lambda_{\mathrm{B}},\lambda_{\mathrm{C}})}{\varepsilon_{\mathrm{AB}}(\lambda_{\mathrm{A}},\lambda_{\mathrm{B}})}-\frac{R_{\mathrm{T}}}{R_{\mathrm{AB}}}\right)^2+\left(\frac{\varepsilon_{\mathrm{T}}(\lambda_{\mathrm{A}},\lambda_{\mathrm{B}},\lambda_{\mathrm{C}})}{\varepsilon_{\mathrm{BC}}(\lambda_{\mathrm{B}},\lambda_{\mathrm{C}})}-\frac{R_{\mathrm{T}}}{R_{\mathrm{BC}}}\right)^2+\left(\frac{\varepsilon_{\mathrm{T}}(\lambda_{\mathrm{A}},\lambda_{\mathrm{B}},\lambda_{\mathrm{C}})}{\varepsilon_{\mathrm{AC}}(\lambda_{\mathrm{A}},\lambda_{\mathrm{C}})}-\frac{R_{\mathrm{T}}}{R_{\mathrm{AC}}}\right)^2 \qquad (7)$$

– similar to that already introduced in Eq. 2 – which is then minimized. The function *EffCalc()* was realized in a custom-built C++ script using the functionality of ROOT, a software developed by CERN (Brun and Rademakers, 1997). It is to be noted that the procedure differs significantly from the procedure described in the Introduction, since two loops must be passed through: One loop over N events and the other loop over up to M_{i} electrons in one event. In this work, the number of events was selected to be $N = 2\cdot10^5$ to ensure low uncertainties due to the statistics in the computational procedures.

The ROOT package also provides the sophisticated minimization algorithms that were used. The numerical minimization then yields the three free parameters and, consequently, the required counting efficiencies. In this work, the minimizer routine “GSLMinimizer” (Moneta, 2006) was used with the option “kConjugatePR”. The step size of the individual free parameters was defined to be 0.002 and boundaries of the free parameters were defined to cover the expected range of the free parameters met in standard TDCR systems (from 0.6 to 40). Moreover, it is possible to set a tolerance (0.00002) which was chosen to reach values for Δ which are virtually 0 (e.g. 10^{-13}). With such a setting, the computation time for one minimization procedure is about 18 s when using a standard PC with a 2.8 GHz processor. In

addition, this setting did not lead to any erroneous local minimum when carrying out this study.

3. The monoenergetic approximation in the case of ^{55}Fe

When considering monoenergetic electron emissions with one electron per decay event, the counting efficiencies can be calculated from the experimental counting rates by

$$\varepsilon_{\mathrm{A}} = \frac{R_{\mathrm{T}}}{R_{\mathrm{BC}}}, \qquad \varepsilon_{\mathrm{B}} = \frac{R_{\mathrm{T}}}{R_{\mathrm{AC}}} \qquad \text{and} \qquad \varepsilon_{\mathrm{C}} = \frac{R_{\mathrm{T}}}{R_{\mathrm{AB}}}. \tag{8}$$

Combining these equations yields the triple counting efficiency

$$\varepsilon_{\mathrm{T}} = \varepsilon_{\mathrm{A}}\varepsilon_{\mathrm{B}}\varepsilon_{\mathrm{C}} = \frac{R_{\mathrm{T}}^3}{R_{\mathrm{AB}}R_{\mathrm{AC}}R_{\mathrm{BC}}} \tag{9}$$

and the double counting efficiency

$$\begin{aligned}\varepsilon_{\mathrm{D}} &= \varepsilon_{\mathrm{D,asym}} = \varepsilon_{\mathrm{A}} \cdot \varepsilon_{\mathrm{B}} + \varepsilon_{\mathrm{B}} \cdot \varepsilon_{\mathrm{C}} + \varepsilon_{\mathrm{A}} \cdot \varepsilon_{\mathrm{C}} - 2\varepsilon_{\mathrm{A}} \cdot \varepsilon_{\mathrm{B}} \cdot \varepsilon_{\mathrm{C}} \\ &= \frac{R_{\mathrm{T}}^2}{R_{\mathrm{BC}} \cdot R_{\mathrm{AC}}} + \frac{R_{\mathrm{T}}^2}{R_{\mathrm{AC}} \cdot R_{\mathrm{AB}}} + \frac{R_{\mathrm{T}}^2}{R_{\mathrm{BC}} \cdot R_{\mathrm{AB}}} - 2\frac{R_{\mathrm{T}}^3}{R_{\mathrm{AB}} \cdot R_{\mathrm{BC}} \cdot R_{\mathrm{AC}}} \cdot\end{aligned} \tag{10}$$

Hence, the activity A or a comparison indicator I_{comp} is given by

$$A = \frac{R_{\mathrm{T}}}{\varepsilon_{\mathrm{T}}} = \frac{R_{\mathrm{T}}}{\varepsilon_{\mathrm{A}}\varepsilon_{\mathrm{B}}\varepsilon_{\mathrm{C}}} = \frac{R_{\mathrm{AB}} \cdot R_{\mathrm{AC}} \cdot R_{\mathrm{BC}}}{R_{\mathrm{T}}^2} \equiv I_{\mathrm{comp}} \tag{11}$$

or

$$A = \frac{R_{\mathrm{D}}}{\varepsilon_{\mathrm{D}}} = R_{\mathrm{D}}\left(\frac{R_{\mathrm{T}}^2}{R_{\mathrm{BC}} \cdot R_{\mathrm{AC}}} + \frac{R_{\mathrm{T}}^2}{R_{\mathrm{AC}} \cdot R_{\mathrm{AB}}} + \frac{R_{\mathrm{T}}^2}{R_{\mathrm{BC}} \cdot R_{\mathrm{AB}}} - 2\frac{R_{\mathrm{T}}^3}{R_{\mathrm{AB}} \cdot R_{\mathrm{BC}} \cdot R_{\mathrm{AC}}}\right)^{-1}, \tag{12}$$

which means that the activity can be determined just from the net counting rates in various channels. Information about ionization quenching is not needed. Moreover, it is important to note that the calculation already accounts for a potential PMT asymmetry. Equation 11 defines a comparison indicator I_{comp} which will be discussed in Section 5.

Assuming that there is no PMT asymmetry, i.e. $R_{\mathrm{AB}} = R_{\mathrm{BC}} = R_{\mathrm{AC}} = R_{\mathrm{XY}}$, Eq. 10 yields

$$\varepsilon_{\mathrm{D,sym}} = 3\frac{R_{\mathrm{T}}^2}{R_{\mathrm{XY}}^2} - 2\frac{R_{\mathrm{T}}^3}{R_{\mathrm{XY}}^3}\,. \tag{13}$$

For this symmetric case, it can be shown that

$$\frac{R_{\mathrm{T}}}{R_{\mathrm{XY}}} = \frac{3\cdot TDCR}{1+2\cdot TDCR}\,. \tag{14}$$

Combining Eqs. 13 and 14 yields

$$\varepsilon_{\mathrm{D,sym}} = \frac{27\cdot TDCR^2}{\left(1+2\cdot TDCR\right)^3}\,, \tag{15}$$

which has been reported previously (see, e.g., Cassette, 2010; Bobin et al., 2012).

Using the ratio of the efficiencies from Eqs. 10 and 15, a new asymmetry correction can be defined by

$$k_{\mathrm{asym}} = \frac{\varepsilon_{\mathrm{D,asym}}}{\varepsilon_{\mathrm{D,sym}}} = \frac{\dfrac{R_{\mathrm{T}}^2}{R_{\mathrm{BC}}\cdot R_{\mathrm{AC}}} + \dfrac{R_{\mathrm{T}}^2}{R_{\mathrm{AC}}\cdot R_{\mathrm{AB}}} + \dfrac{R_{\mathrm{T}}^2}{R_{\mathrm{BC}}\cdot R_{\mathrm{AB}}} - 2\dfrac{R_{\mathrm{T}}^3}{R_{\mathrm{AB}}\cdot R_{\mathrm{BC}}\cdot R_{\mathrm{AC}}}}{\dfrac{27\cdot TDCR^2}{\left(1+2\cdot TDCR\right)^3}}\,. \tag{16}$$

This ratio is the core of a new approach, in which the analysis is first done without any asymmetry correction using only one common free parameter (Eq. 4). The results for the activity (or activity concentration) are then divided by k_{asym}.

4. TDCR measurements to test the algorithms

The measurements described here were carried out at LNHB using a compact portable TDCR counter similar to the system described by Mitev et al. (2017). The housing and the optical chamber were built using a 3D printer. The system comprises three Hamamastu R7600U-200 PMTs with an angle of 120° between any pair and a high voltage supply (900 V). The PMT signals are fed into a nanoTDCR module (labZY, 2020) which allows measurements with two different coincidence resolving times and two different dead-time settings simultaneously. The PMT thresholds were adjusted below the single electron peak for all three channels.

The LS samples were prepared using 20 mL polyethylene vials from PerkinElmer. For ^{55}Fe, about 10 mL of Ultima Gold™ AB was used before adding a weighed portion (about 104 mg) of an ^{55}Fe solution. A similar sample was prepared with ^{3}H but using Ultima Gold™ LLT. In both cases, comparable samples with non-radioactive components were prepared to measure the background counting rates, which were then subtracted.

The samples were measured in the portable TDCR system with and without grey filter films. The grey filter films were prepared with a laser printer with various neutral densities (NDs). In order to provoke an asymmetry, some foils were prepared to cover only one PMT (PMT A in most cases), while cylindrical foils were prepared to reduce the overall counting efficiency while keeping the symmetry more or less constant.

The analysis presented in this work is based on the experimental data gained when using a coincidence resolving time of 40 ns and an extendable dead time of 10 μs.

The ^{55}Fe measurement data were first analysed using the stochastic approach as described by Kossert (2020) based on an improved version of the MICELLE code (Grau Carles, 2007; Kossert and Grau Carles, 2010). In this analysis, a potential asymmetry was not taken into account. The corresponding MICELLE calculations were modified to compute $E_{il}Q(E_{il})$ for all M_i electrons in $N = 2 \cdot 10^5$ decay events which were stored in a file and then used to apply the asymmetry correction as described in Section 2.

In an alternative approach, the uncorrected results were corrected by the monoenergetic correction (k_{asym}) as described in Section 3. Hence, three different results can be obtained from each measurement:

- results without any asymmetry correction (Eq. 4),
- results with asymmetry correction applying the full model (Eqs. 5 to 7) and
- results with the monoenergetic asymmetry correction (Eqs. 4 and 16).

The results obtained when analysing ^{55}Fe are shown in Fig. 2 and, in the following discussion, we start with the data obtained at high efficiencies (right-hand side of the figure).

When measuring without any filter (first data points at the extreme-right of the abscissa), all results agree quite well, since there is only a low asymmetry. The results are, however, not exactly identical, since PMT A has a slightly higher intrinsic quantum efficiency than PMTs B and C.

When placing filter 1 in front of PMT A (second set of points from the right), the overall counting efficiency is reduced. The asymmetry is almost the same as without any filter, but now, the efficiency of PMT A is slightly lower. The mean value of the results obtained in

these two configurations when taking into account the asymmetry from the new stochastic approach is defined as the reference (blue horizontal line in Fig. 2).

When using another cylindrical grey filter (third set of points from the right), the efficiency is further reduced, but the asymmetry is still of minor importance. The situation changes when using the darker filter films 2 or 3 (points on the left-hand side). In this case, the asymmetry is pronounced and – if no asymmetry is taken into account – the results deviate from the reference by about 5.6 % and 11.6 %, respectively. This deviation diminishes considerably when the asymmetry is taken into account. Interestingly, the result obtained when using the simple monoenergetic approach is very similar to that when using the new and more complex asymmetry correction combined with the stochastic approach. The relative deviation between these two approaches was found to be lower than 0.04 % in all cases. A similar outcome was obtained when studying ^{53}Mn, which is also a pure EC radionuclide. It is to be emphasized that none of these EC radionuclides is really a monoenergetic emitter. For example, about 88 % of the ^{55}Fe decay events lead to K electron capture which means that much more energy is available compared to the remaining 12 % of the decays. Moreover, the atomic rearrangement is complex which leads to multiple combinations of electron and X-ray emissions.

The monoenergetic approach as presented here is actually based on the same assumptions that were made by Razdolescu et al. (2008) – although the formalism is different. Hence, it was to be anticipated that the monoenergetic approach presented here works just as well in the case of ^{55}Fe.

A closer look at Fig. 2 reveals a slight trend in the data. This trend cannot be attributed to the asymmetry corrections, since the results obtained with cylindrical filters also support this trend, and we conclude that the asymmetry corrections work very well. At the moment, the reason for the slight trend is not known. The same model gave consistent results over a wide efficiency range from about 40 % to 77 % for two TDCR systems at PTB (Kossert, 2020). Here, the counting efficiency was much lower for some of the measurements. Hence, the trend may be attributed to the model. This also includes a known dependence of the time distribution on the mean number of emitted photons and a related dependence on the coincidence resolving time (see, e.g., Bobin et al., 2012). This subject needs further investigation and is not discussed in further detail in this work.

The results for ^{3}H are shown in Fig. 3. Here, the efficiency was computed with an analytical method as described for PTB by Cassette et al. (2018, 2020). Again, the analysis was first

carried out without any asymmetry correction which may lead to deviations of about 12 % when using filter 3 in front of PMT A. Although the deviations are considerably reduced when applying the monoenergetic approach, this method does not lead to satisfactory results. This was, of course, expected as beta emitters are not at all monoenergetic. However, when applying the asymmetry correction as described in the Introduction of this article, all results agree very well.

5. Relevance for the proposed extension of the International Reference System for comparisons in radionuclide metrology

In radionuclide metrology, the mutual recognition of capabilities to measure activities is based on participation in international comparisons, in which a National Metrology Institute (NMI) or an institute designated for this task participates. A convenient way of making a comparison possible would be for participating NMIs to send an aliquot of a given radionuclide to an independent institution and subsequently report the corresponding activity. The independent institution could then measure the sample in an appropriate instrument and obtain an instrument reading. Assuming that the instrument reading is proportional to the activity and that this proportionality is constant during the comparison exercise, a comparison indicator could easily be defined. Consequently, it would be simple to compare the activity measurements of the different NMIs which have sent samples. Such an approach was successfully realized for photon-emitting radionuclides using ionization chambers and has been in use at the BIPM for more than 35 years (Rytz, 1983). The instrument reading is a (net) ionization current which is measured against the current of long-lived ^{226}Ra sources. This comparison mechanism is referred to as the International Reference System (SIR) and it would be advantageous to establish a similar system for pure beta emitters or radionuclides like ^{55}Fe, which only emit low-energy radiation and can therefore not be measured in an ionization chamber. New efforts were therefore undertaken to develop a similar method using LS counting instead (Coulon et al., 2020). This approach is called the extended SIR (ESIR). Establishing this methodology was found to be very challenging, since the counting efficiency may change from sample to sample. In addition, characteristics of the counter and/or LS cocktails may change over time – in particular when considering several decades. A new approach was proposed which is based on measurements in a custom-built TDCR counter, and comparison indicators were defined which aim to avoid the application of the full TDCR model. Applying the full model would comprise the consideration of decay data, ionization quenching and other model-related parameters. Some suitable comparison indicators were

found which compensate for possible changes of the counting efficiency very well, and comprehensive studies look promising (Coulon et al., 2020). The situation becomes, however, more complex when considering potential asymmetries which may also change over time. Here, the monoenergetic approach, as discussed in Section 3, is very helpful, since it allows the computation of the required correction at least for ^{55}Fe and similar pure EC radionuclides. The great advantage is that this correction only requires the experimentally determined net counting rates and no further model is required. In this regard, an additional consideration might be defining the apparent activity calculated using Eq. 11 as comparison indicator I_{comp} for ^{55}Fe. This was applied to the experimental data set of ^{55}Fe. The individual values $I_{\mathrm{comp},i}$ were used to calculate a mean $< I_{\mathrm{comp}} >$ and the residuals $(I_{\mathrm{comp},i} - < I_{\mathrm{comp}} >)/ < I_{\mathrm{comp}} >$. The residuals are shown in Fig. 4. The figure also shows residuals which were calculated in the same manner but using the determined activity concentration from the stochastic approach with the corresponding asymmetry correction as explained in Section 2. The residuals of these two approaches are comparable which indicates that I_{comp} is a suitable comparison indicator for ESIR in the case of ^{55}Fe. It should be kept in mind that the variation of both the counting efficiency and the asymmetry in this work can be considered as extreme and are much larger than expected when using well-defined reference conditions. In this sense, the variations applied in this study can be regarded as exaggerated.
Interestingly, both methods shown in Fig. 4. follow a similar trend which was already discussed in Section 2. This might be a further hint that this trend is not related to the efficiency computation but to an experimental effect.

A similar experiment with ^{55}Fe LS samples and partial grey filters was carried out at the BIPM with a TDCR counter as described by Coulon et al. (2020). The data were analysed in a different way applying a simple KLM atomic rearrangement model but also allowing for the PMT asymmetry. Here, it was also found that the asymmetry effects are well compensated for. When applying the indicator I_{comp}, the residuals were again found to be comparable with the residuals calculated from the full model, which confirms the findings as described above.

6. Discussion and outlook

In this article, it was demonstrated that PMT asymmetries in TDCR systems can be taken into account leading to excellent results. In the case of pure beta emitters, the required corrections had been developed in the past and were found to be reliable. Here, we presented a new

methodology which can also be applied to any other decay that can be computed by means of the stochastic model. In the case of EC nuclides, the results were found to be very good. For pure EC radionuclides with a low atomic number, the asymmetry can also be taken into account by means of a simplified approach referred to as the monoenergetic asymmetry correction.

The new asymmetry correction based on the stochastic model can certainly be improved and extended. It is desirable to reduce the computation time of the minimization procedure and some further developments related to this problem are planned. In addition, the methodology could be modified in such a way that the ionization quenching function $Q(E)$ is calculated directly before carrying out the minimization procedure. This just requires storing the electron energies E_{il} rather than the product $E_{il}Q(E_{il})$. With such a modification, more flexibility would be gained, since the ionization quenching model and/or the *kB* parameter could be changed without the need for additional MICELLE calculations. The drawback of such a methodology might, however, be a somewhat longer computation time, as $Q(E_{il})$ needs to be computed for each electron in all decay events.

The new stochastic approach with the asymmetry correction should also be tested for further radionuclides, e.g., when the function $\varepsilon_{\mathrm{D}}(TDCR)$ is ambiguous.

The study presented here is also relevant for the development of the ESIR for international comparisons in radionuclide metrology. A simple comparison indicator was found which requires neither any model nor any information on radionuclide data. This comparison indicator can be used for ^{55}Fe and is capable of compensating for efficiency changes as well as for variations of the PMT asymmetry.

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Figure captions:

Figure 1: Left: Photograph of the portable TDCR system with an LS vial and the nanoTDCR device. Right: Some of the grey filter films which were combined with the cap of the optical chamber to cover one PMT during the measurements.

Figure 2: Activity concentration as a function of the computed double counting efficiency for various measurements of an ^{55}Fe LS sample. A stochastic model was applied without any asymmetry correction and with two corrections as explained in Section 2 (green triangles) and Section 3 (blue diamonds). The uncertainty bars (often smaller than the symbol size) represent only a statistical uncertainty which was calculated as a standard deviation of the mean of several repetition measurements ($n \geq 4$).

Figure 3: Activity concentration as a function of the computed double counting efficiency for various measurements of a ^{3}H LS sample. An analytical model was applied without any asymmetry correction and with two corrections as explained in the Introduction (green triangles) and in Section 3 (blue diamonds). The uncertainty bars (sometimes smaller than the symbol size) represent only a statistical uncertainty which was calculated as a standard deviation of the mean of several repetition measurements ($n \geq 6$).

Figure 4: Residuals as a function of the computed double counting efficiency for various measurements of an ^{55}Fe LS sample. The full stochastic model was applied with the asymmetry correction as explained in Section 2 (green triangles). In addition, the comparison indicator from Eq. 11 was used. The uncertainty bars represent only a statistical uncertainty which was calculated as a standard deviation of the mean of several repetition measurements ($n \geq 4$).

Figures

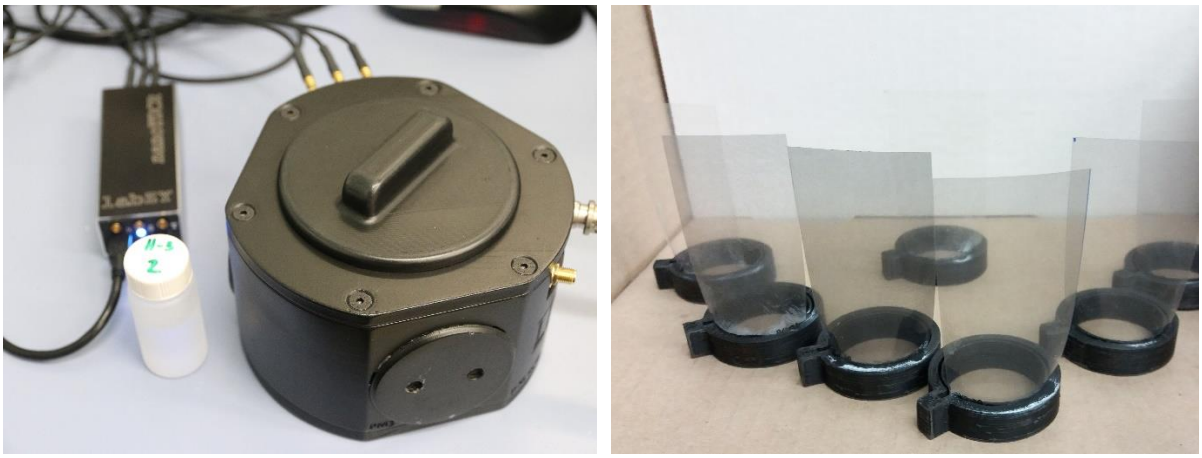

Figure 1

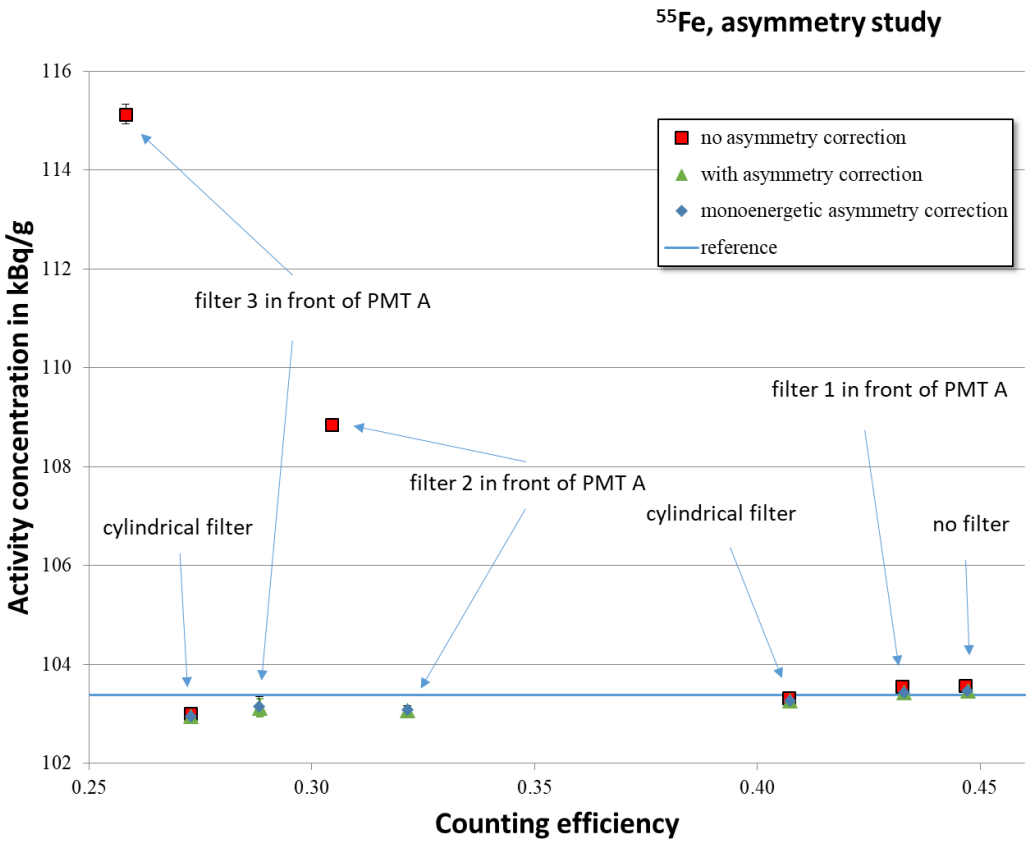

Figure 2

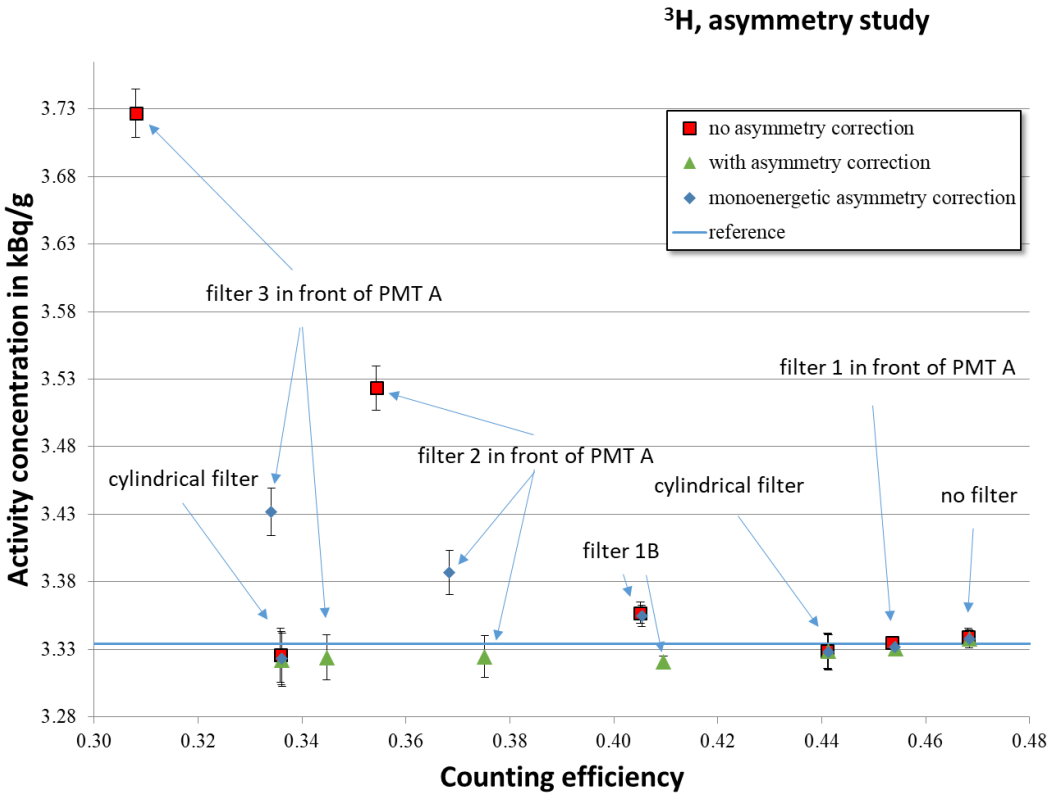

Figure 3

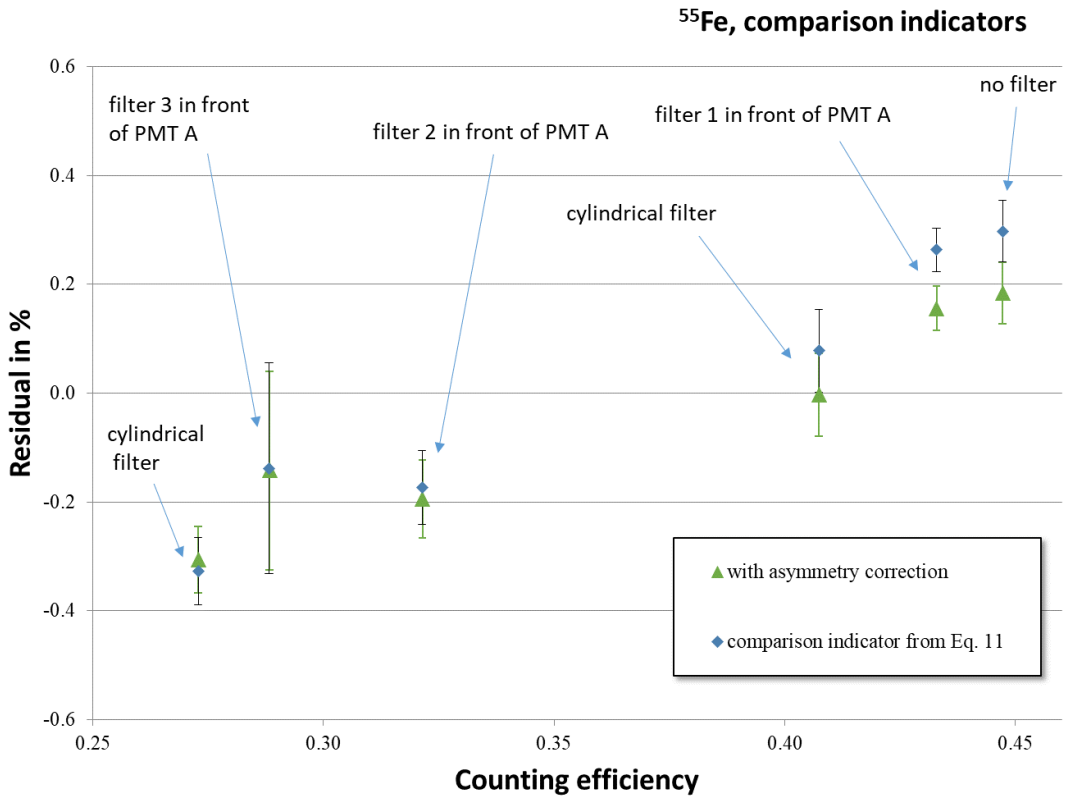

Figure 4