Standardization of $^{59}$Fe by efficiency extrapolation $4\pi\beta-\gamma$ anticoincidence method

C J da Silva¹, P A L da Cruz¹, A Iwahara¹, J S Loureiro¹, A. Ruzzarin² and L Tauhata¹

¹Laboratório Nacional de Metrologia das Radiações Ionizantes/Instituto de Radioproteção e Dosimetria/Comissão Nacional de Energia Nuclear (LNMRI/IRD/CNEN), Av. Salvador Allende, s/no – Barra da Tijuca, Rio de Janeiro, Brazil, CEP 22783-127
²Programa de Engenharia Nuclear/Coordenação de Programas de Pós-Graduação em Engenharia/Universidade Federal do Rio de Janeiro (PEN/COPPE/UFRJ)-Rua Moniz de Aragão, 360, Bloco 1, Ilha do Fundão – Cidade Universitária, Rio de Janeiro, Brazil, CEP 21941-594

E-mail: iawahara@ird.gov.br

Abstract. A solution of $^{59}$Fe was standardized in the frame of a Bureau International des Poids et Mesures (BIPM) international key-comparison piloted by Asian Pacific Metrology Program (APMP) regional metrology organization. The method used was the live-timed $4\pi\beta-\gamma$ anticoincidence counting with extended dead-time with efficiency extrapolation method. The confirmation of these results was performed by conventional $4\pi\beta-\gamma$ coincidence counting with efficiency extrapolation and CIEMAT/NIST liquid scintillation counting methods. The value of the evaluated anticoincidence measurement was used to calibrate the LNMRI second standard ionization chambers for providing $^{59}$Fe solutions to nuclear medicine canters in the procedures of anaemia diagnosis. Besides this value was adopted as the comparison value of LNMRI and sent to APMP organization. The half-life of $^{59}$Fe was determined following the decay of one ampoule sample with $^{59}$Fe solution in an ionization chamber (Centronic model IG12).

1. Introduction

The radionuclide $^{59}$Fe decays by beta emission mainly to the excited levels of 1099 and 1291 keV of $^{59}$Co followed by the emission of two major gamma rays with energy of 1099.3 and 1291.6 keV, respectively. It is a radionuclide used in nuclear medicine for detection of problems of bone joints and allows the diagnosis of anaemia. The method used at LNMRI for the activity standardization of $^{59}$Fe solution was the live-timed $4\pi\beta-\gamma$ anticoincidence counting with extended dead-time with efficiency extrapolation technique. The confirmation of this result was checked by conventional $4\pi\beta-\gamma$ coincidence counting with extrapolation technique and CIEMAT/NIST liquid scintillation counting methods whose results agreed with the anticoincidence result within the respective uncertainties (coverage factor $k=2$). The result of anticoincidence measurements was used to calibrate the LNMRI...
secondary standard ionization chambers for providing $^{59}$Fe solutions to nuclear medicine centers in the procedures of anaemia diagnosis. The half-life of $^{59}$Fe was determined following the decay of ampoule sample with $^{59}$Fe solution in an ionization chamber during 20 days of measurements giving result consistent with those found in literature.

2. Methodology

2.1 $4\pi\beta-\gamma$(NaI) anticoincidence counting method

The anticoincidence method was originally developed by Bryant [1] and improved by de Carlos and Granados [2] that incorporated the concept of shared dead time for beta and gamma channels. Due to dead-time correction difficulties, Baerg et al. [3] developed an anticoincidence system based on extendable dead-times and the lived-time technique. Using the same concept, the live-time $4\pi\beta$(LS)-$\gamma$(NaI(Tl)) anticoincidence system and extendable dead-time operating at LNMRI, is based on specialized modules (MTR2, MI1, MI2 and MI3) developed for the dead-time and counting implementation in the different channels [4,5,6]. Basically the anticoincidence counting method consists in obtaining an experimental extrapolation curve, that links the activity of the source $N_0$ to the beta ($N_\beta$), gamma ($N_{\gamma}^W$) and coincidence count rates $N_c$ given by equation (1). Because coincidences are measured indirectly, $N_c$ is calculated as $N_{\gamma}^W - iN_{\gamma}^W$ in equation (1) where $N_{\gamma}^W$ is the count rate for a given gamma window and the $iN_{\gamma}^W$ is the gamma count rate for uncorrelated events. In this case it is not necessary the use of a coincidence unit by eliminating the uncertainties introduced by the inevitable accidental counts inherent to that unit. Using an extrapolation technique in equation (1), $N_{Ap}$ tends to $N_0$, the activity, when beta efficiency given by ratio $N_{\beta}/N_{\gamma}$ tends to 1. The variation of beta efficiency in this work was carried out by electronic discrimination using a single channel analyzer module in beta counting channel.

$$N_{Ap} = \frac{N_{\beta}N_{\gamma}^W}{N_{\gamma}^W - iN_{\gamma}^W}$$

(1)

The detector for beta events consists of a scintillation cell coupled to two photomultipliers placed at an angle of 180 degrees relative to each other. The counting cell of the liquid scintillation counter is made of polyethylene painted inside with TiO in order to reflect light. A scintillation crystal of NaI(Tl) for gamma counting is coupled to the scintillation cell forming the anticoincidence detection set-up.

2.2 $4\pi\beta(PC,LS)-\gamma$(NaI) coincidence counting method

The coincidence method was precursor to the anticoincidence method, but basically the operation of them is quite similar. The fundamental difference is that the coincidence method is based on the actual beta-gamma coincidence count whereas in the anticoincidence method the coincidence count is obtained through uncorrelated beta-gamma events. In the same way it consists in obtaining an experimental extrapolation curve, that links the activity of the source $N_0$ to the count rates of beta, gamma and coincidence $N_\beta$, $N_{\gamma}$ and $N_c$, respectively, given by equation (2) where the ratio $N_{\beta}/N_{\gamma}$ represents a measure of the detection efficiency in the beta-channel.

$$N_0 = \frac{N_{\beta}N_{\gamma}}{N_c} \cdot \left[1 + C\left(\frac{1 - N_c/N_{\gamma}}{N_c/N_{\gamma}}\right)^{-1}\right]^{-1}$$

(2)
The extrapolation technique is applied by varying the detection efficiency preferably in the region of high values of \( N_c/N_{\gamma} \). The parameter \( C \) represents the slope of expression (2) and it depends on the radionuclide decay scheme. Using a linear fitting, the source activity \( N_0 \) is obtained from the extrapolation of expression (2) when the ratio \( N_c/N_{\gamma} \) tends to unity. Two detectors configurations set-ups have been used in the measurement of \(^{59}\)Fe. The first one consisted of a gas flow \( 4\pi \) proportional counter (PC) coupled to a 10.2 cm ×10.2 cm crystal of NaI(Tl) and to a coaxial HPGe. The counting gas of the \( 4\pi \) counter is a mixture of 90% argon and 10% methane operating at 0.1 MPa pressure. The second set-up consists of the same scintillation cell described in 2.1 and coupled to the same NaI(Tl) scintillation crystal of first set-up. Both set-ups are coupled to the same electronic chain comprising the coincidence system used in this work. Beta particles originating from \(^{59}\)Fe are counted in the beta channel and the gamma rays of 1099 keV and 1291 keV are counted in the gamma channel for different gamma energy windows. The gamma window condition in the PC-NaI set-up counting was done around the 1099 and 1291 keV. For PC-HPGe the gamma window was set around 1291 keV photopeak and for LS-NaI counting was around the two photopeaks simultaneously. The range of beta efficiency variation in PC counting was 0.90 to 0.65 using inactive carriers of FeCl\(_3\) at various concentrations in source preparation. For liquid scintillation counting the efficiency variation, from 0.91 to 0.76, was carried out using electronic discrimination. The experimental results of the coincidence measurements were fitted using nonlinear regression Levenberg-Marquardt algorithm [7]. The final result reported was adopted as the weight mean of four results.

2.3 CIEMAT/NIST counting method

The CIEMAT/NIST method is based on statistical Free Parameter model of the scintillation photons distribution and their detection probabilities in counting systems consisting in two photomultipliers at 180° from each other [8]. An efficiency versus extinction curve is obtained from a set of \(^3\)H standard samples in order to characterize the experimental condition. This experimental curve is compared with the theoretical curve of Free Parameter versus \(^3\)H efficiency. Thus, a new Free Parameter versus Extinction curve is obtained [9]. Measurements of the radionuclide samples to be standardized are performed on the commercial equipment and the quench values obtained are interpolated in the Free Parameter Curve versus \(^3\)H standard extinction curve. The value of the Free Parameter obtained is interpolated in the theoretical curve of Free Parameter versus radionuclide efficiency to find its activity (Bq).

The computational codes for theoretical calculation of the detection efficiency curve CIEMAT/NIST method depending on the Free Parameter and take into account the quenching from the Birks equation, the radionuclide decay schemes, the particles and photon and particle interactions in the scintillation cocktail and system measurement evaluated by use Monte Carlo simulation codes ([10,11]).

Figure 1 shows the representation of this process of semi-empirical standardization. The CIEMAT / NIST method, despite its dependence on the \(^3\)H standard for the characterization of the experimental condition, has excellent application for the standardization of beta emitters, with great accuracy and minimized uncertainty. However, its application to the standardization of radionuclides that decay by electron capture and by internal conversion of electrons is of high complexity, since in these cases the theoretical curve of Free Parameter versus Efficiency offers more than one possibility of efficiency values.
3. Results and discussion

3.1 Anticoincidence measurements

Twenty liquid scintillation sources were prepared from commercial scintillation cocktails manufactured by PerkinElmer, Inc. (USA): ten from the brand OPTIPHASE Hisafe3 and 10 from Ultima Gold. The samples were prepared using 15 mL of cocktail scintillation plus 20 to 30 mg of $^{59}$Fe solution contained in a glass vial with low potassium content. The beta particles are detected in the liquid scintillator and the pulses from the two coupled photomultipliers are processed in the corresponding electronic chain. For counting in the gamma channel an energy window encompassing the peaks of 1099.2 and 1291.6 keV was fitted. The beta efficiency variation, in order to obtain the extrapolation curve, was made by electronic discrimination using pulse height analyzer module in the beta channel and ranged from 0.80 to 0.95. The statistical Grubbs’ test [12] was used to detect outliers in the data set of 20 results. The results of three of them were discarded for the final calculation of the activity because they presented inconsistent values. The final activity value adopted was the weighted mean of 17 results giving 468.73±1.59 kBq/g at reference date of June 1st, 2014, 00:00 UTC. The uncertainty refers to ~68% level of confidence (k=1).

Relative uncertainty components for activity concentration by anticoincidence counting method are presented in Table 1.

### Table 1. Relative uncertainty components for activity concentration by anticoincidence counting method.

| Uncertainty components, in % of the activity concentration due to | Type | Standard relative uncertainty (%) |
|---------------------------------------------------------------|------|-----------------------------------|
| Extrapolation of efficiency curves                            | A    | 0.17                              |
| Weighing                                                      | B    | 0.05                              |
| Counting statistics                                           | A    | 0.25                              |
| Lived-time                                                    | B    | 0.01                              |
| Background                                                    | B    | 0.15                              |
| Half-life                                                     | B    | 0.021                             |
| Timing                                                       | B    | 0.010                             |
| Combined relative uncertainty                                 |      | 0.34                              |
| Expanded relative uncertainty (k=2)                           |      | 0.68                              |

Figure 1. CIEMAT/NIST model: Diagram of standardization.
3.2 Coincidence measurements

Ten sources were prepared by dropping known masses of $^{59}$Fe onto VYNS film previously gold coated on both sides. The solution masses ranged from 16 mg to 30 mg. For liquid scintillation counting five samples were prepared using 15 mL commercial OPTIPHASE HISAFE3 cocktail contained in a glass vial with low potassium content. The masses of $^{59}$Fe added to each cocktail ranged from 20 to 30 mg. The gamma window condition in the PC-Nal set-up counting was done around the 1099 and 1291 keV. For PC-HPGe the gamma window was set around 1291 keV photopeak and for LS-Nal counting was around the two photopeaks simultaneously. The range of beta efficiency variation in PC counting was 0.90 to 0.65 using inactive carriers of FeCl$_3$ at various concentrations in source preparation. For liquid scintillation counting the efficiency variation, from 0.91 to 0.76, was carried out using electronic discrimination. The experimental results of the coincidence measurements were fitted using nonlinear regression Levenberg-Marquardt algorithm [7]. The final result reported was adopted as the weight mean of four results. Table 2 presents the activity results with respective standard uncertainties of the fitting procedures and the final result determined as the weighted mean of these results. The uncertainty budget is presented in Table 3.

Table 2. Results of the activity concentration by coincidence counting. The uncertainties refer to extrapolation procedure component of efficiency curves for each gamma window counting condition.

| Method used                  | Activity (kBq/g) | Standard uncertainty (kBq/g) | Relative standard uncertainty (%) |
|------------------------------|-----------------|------------------------------|----------------------------------|
| PC-Nal(Tl) (Gamma window: 1099 keV) | 475.14          | 2.88                         | 0.60                             |
| PC-Nal(Tl) (Gamma window: 1291 keV) | 471.42          | 2.80                         | 0.59                             |
| LS-Nal(Tl) (Gamma window: 1099+1291 keV) | 473.12 | 1.94                         | 0.41                             |
| PC-HPGe (Gamma window: 1291 keV) | 475.51          | 3.39                         | 0.70                             |
| Laboratory final result (weighted mean) | 473.99 | 0.89                         | 0.19                             |

Table 3. Relative uncertainty components for activity concentration by coincidence counting method.

| Uncertainty components, in % of the activity concentration due to | Type | Standard relative uncertainty (%) |
|------------------------------------------------------------------|------|----------------------------------|
| Extrapolation of efficiency curves                               | A    | 0.19                             |
| Weighing                                                         | B    | 0.050                            |
| Dead-time                                                        | B    | 0.0061                           |
| Resolving time                                                   | B    | 0.016                            |
| Gandy effect                                                     | B    | 0.068                            |
| Background                                                       | B    | 0.48                             |
| Background                                                       | B    | 0.024                            |
| Counting statistics                                              | A    | 0.18                             |
| Combined relative uncertainty                                    |      | 0.51                             |
| Expanded relative uncertainty (k=2)                              |      | 1.0                              |
The weighted mean was adopted as the final activity of coincidence measurements given 473.99 kBq/g with evaluated standard uncertainty of ±2.37 kBq/g at reference date. The consistency of the activity results was analyzed based on the use of Birge ratio criterion [13] where the ratio between external and internal uncertainties should be close to 1 or less. The Birge ratio calculated was 0.770 suggesting that the results are consistent.

3.3 CIEMAT/NIST measurements

The theoretical calculations of the $^{59}$Fe detection efficiency were performed by computational code CN2003 [11]. A set of eight standard tracer tritium ($^3$H) samples in 10 mL of cocktail OPTIPHASE Hisafe3 for the commercial Wallac 1414 Liquid Scintillation Counter characterizing in terms of the quenching parameter by the introduction of the chemical quenching agent in increasing degree. The measurements of eight $^{59}$Fe samples also in OPTIPHASE Hisafe 3 were performed under the same conditions to the tracer. In this condition the Free Parameter is common to the both radionuclides ones, allowing the correlation between their experimental and theoretical efficiencies, according the fig. 1. The final result of activity, adopted as the weighted mean of 8 results gave 469.33±1.80 kBq/g at reference date. The uncertainty refers to standard uncertainty (k=1). Relative uncertainty components for activity concentration by CIEMAT/NIST counting method are depicted in Table 4.

| Component                              | Type | Relative standard uncertainty (%) |
|----------------------------------------|------|-----------------------------------|
| $^3$H activity                          | B    | 0.052                             |
| $^3$H weighing                          | B    | 0.0020                            |
| $^3$H Quenching (SQPE)                 | A    | 0.088                             |
| $^3$H statistic counts                  | A    | 0.0081                            |
| Nuclear and Atomic data                | B    | 0.10                              |
| Photomultiplier assmetry               | B    | 0.23                              |
| kB value                               | B    | 0.10                              |
| $^{59}$Fe weighing                      | B    | 0.0011                            |
| $^{59}$Fe Quenching (SQPE)             | A    | 0.023                             |
| $^{59}$Fe statistic counts             | A    | 0.0070                            |
| $^{59}$Fe source activities            | A    | 0.27                              |
| Combined relative uncertainty          |      | 0.40                              |
| Expanded relative uncertainty (k=2)    |      | 0.79                              |

3.4 Calibration factors and half-life

The estimation of the half-life was performed by measuring the decay of $^{59}$Fe for a period of 25 days in the ionization chamber. No gamma impurity was detected using calibrated HPGe spectrometer. The logarithm of the ion charge, which is the proportional to activity, measured in the ionization chamber as a function of the measurement time is a linear function and presented as $\ln(A) = -\lambda \Delta t + a$, where A is the ion charge, $\Delta t$ is the time interval from the first measurements and $\lambda$ is the decay constant of $^{59}$Fe. Least square method using Levenberg-Marquardt algorithm [7] was performed to determine these parameters. The value of half-life determined is $(44.547 \pm 0.035)$ days which is 0.12% larger than the suggested half-life in this comparison $(44.495 \pm 0.008)$ days. The components of uncertainties evaluated come from the fitted $\lambda$ value (0.0014%), chamber stability checked by $^{226}$Ra sample measurements during the period (0.05%) and average charge measurements (0.06%) giving a total of 0.078%. The consistency of the results obtained by the three methods is shown in Figure 2.
Figure 2. Results of activities determined by the three methods. The uncertainty bars refer to coverage factor $k=2$.

4. Conclusions

A $^{59}$Fe solution was standardized by the live-timed $4\pi\beta-\gamma$ anticoincidence with extended dead-time method. The validation of this result was carried out by two other methods: coincidence and CIEMAT/NIST. The results were equivalent within the uncertainties evaluated at 95% confidence level. The results of the coincidence method, using samples prepared in thin VYNS films and liquid scintillation cocktails showed statistically equivalent results. The value of the anticoincidence method was adopted as the reference activity in LNMRI because it presented the lowest uncertainty. The calibration factors for three IG11 model ionization chambers were determined increasing the number of calibrated radionuclides available for users of nuclear medicine. The half-life was determined which was statistically consistent at 95% level of confidence with the suggested value of comparison.

References

[1] Bryant J 1967 IAEA Symposium on Standardization of Radionuclides SM-79/211
[2] de Carlos J E and Granados C E 1973, Nucl. Instr. and Meth. 112 209
[3] Baerg A P, Munzenmayer K and Bowes, G C 1976 Metrologia 12 77
[4] Bouchard J 2000 Appl. Radiat. Isot. 52 441
[5] Bouchard J 2002 Appl. Radiat. Isot. 56 269
[6] da Silva C J, Iwahara A, Poledna R, Bernardes E M O, de Prinizio M A R, Delgado J U and Lopes R T 2008 Appl. Radiat. Isot. 66 886
[7] da Silva W C P 2011 LAB Fit Curve Fitting Software. Federal University of Campina Grande, Brazil
[8] da Cruz P A L, da Silva C J, Iwahara A, Loureiro J S., de Oliveira A E., Tauhata L and Lopes R T 2016 IOP Publishing, Journal of Physics. Conference Series 733 012099
[9] Malonda A G, Coursey B M 1987 Appl. Radiat. Isot. 39 165
[10] OECD/NEA, 2008. Penelope: A Code System for Monte Carlo Simulation of Electron and Photon Transport. Nuclear Agency Energy/Organization for Economic Co-operation and Development
[11] Gunther E 2003 Program CN2003: A program to calculate the LC efficiency of a nuclide vs. efficiency the tracer H-3 (CIEMAT/NIST). PTB/Germany
[12] Grubbs F E 1950 Annals of Mathematical Statistics 21(1) 27
[13] Birge R T 1932 Phys. Rev. 40 207