TDCR and CIEMAT/NIST Liquid Scintillation Methods applied to the Radionuclide Metrology

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Abstract: In this work are presented TDCR and CIEMAT/NIST methods of liquid scintillation implemented in National Institutes of Metrology for activity standardization of radionuclides which decay by beta emission and electron capture. The computer codes to calculate the detection efficiency take into account: decay schemes, beta decay theory, quenching parameter evaluation, Poisson statistic model and Monte Carlo simulation for photon and particle interactions in the detection system. Measurements were performed for ^{3}H, ^{14}C, ^{99}Tc pure beta emitters in a large energy range, and $^{68}Ge/^{68}Ga$ which decay by electron capture and positron emission, with uncertainties smaller than 1% (k = 1).

Keywords: Liquid scintillation; TDCR; CIEMAT/NIST; beta emitters; radionuclide standardization.

1. INTRODUCTION

Although known for a long time, the use of liquid scintillation technique for the radionuclide standardization was only possible from the cooperation between the laboratories of the international metrology network to find theoretical and technological solutions that enable its implementation. Thus, the cooperation between National Institute Standards and Technology (NIST/USA) and the Centro de Investigaciones Energéticas, Medioambientales y Tecnológicas (CIEMAT/Spain) resulted in the development of semi-empirical CIEMAT/NIST method [1].

The cooperation between the Laboratoire National Henri Becquerel/France and Radioisotope Center/Poland (LNHB/RC) was important step towards the rise TDCR (Triple-to Double Coincidence Ratio Method) method for absolute radionuclide standardization [2]. The development of computational codes for the detection efficiency calculation [3] and MAC3 unit (Module d'acquisition de coincidences triples) that uses the extended dead-time technique [4] represented the final step to TDCR method implementation. Due the consistency in the measurements and minimized uncertainty levels obtained, the CIEMAT/NIST and TDCR methods were adopted by the Bureau International des Poids et Mesures (BIPM) as references for the radionuclide standardization.

In the present work, these methods were used to perform measurements of beta emitters, ^{3}H and ^{14}C, as well as ^{99}Tc from the key-comparison organized by the BIPM with participation of the national laboratories of the international radionuclide metrology network [5]. Another important step in this work was the application of TDCR method to standardize $^{68}Ga/^{68}Ga$, nuclides that decay by electron capture and positron emission, which was performed in cooperation with the LNHB/France. The last two nuclides are important because of their increasing use in nuclear medicine [6].

1.1 Liquid Scintillation Counting

The TDCR and CIEMAT/NIST methods are based on statistical Free Parameter model [7] of the scintillation photons distribution and their detection probabilities in counting systems consisting of three or two photomultipliers, respectively.

The liquid scintillation process occurs when a radionuclide solution is dissolved in cocktail of the scintillator substances and the kinetic energy of the particles is transferred to the molecules of the medium, with the consequent light emission. The light photons are captured in the photomultiplier photocathode producing electrons which are multiplied by dynodes with the generation of electronic signal of enough amplitude to be processed in the electronic chain.

G. F. KNOLL [8] describes the main process of scintillation light: the fluorescence arising from the transition between of energy levels from the structure of organic molecules of the scintillator substances with aromatic structure which present alternating double bonds and π electrons with the light emission on the order of nanoseconds. BIRKS [9] studied the mechanism of particles interaction with the chemical medium of the scintillator organic substances. In this, the charged particles emitted in scintillator liquid interact with the molecules of the medium, lose kinetic energy and some molecules experiment transformations, such as ionization, free radical formation, excitement or rupture in neutral or ionized fragments.

The quenching from ionization process is produced by excited molecules of the solvent and manifests itself in those parts of the liquid where local excited molecules concentration is high.

The Eq. 1 presents the Birks's expression for the evaluating quenching from light generated by particles and photons interaction with cocktail molecules that it takes into account the correction due loss light photons intensity as a result of the ionization caused by radiation in its trajectory in chemical medium.

$$m(E) = \int_0^E \frac{A\,dE}{1 + kB\,dE/dx} \qquad (1)$$

Where, m(E) is the average number photoelectrons; A is the a characteristic parameter of the scintillation cocktail; kB is the a semi-empirical parameter and; dE/dx is the stopping power coefficient.

The Free Parameter (λ) is the average energy required to produce a photoelectron on photocathode. Thus, if the photons emissions follow the Poisson statistical law, the photomultiplier tube detection efficiency can be determined by the introduction of the Free Parameter concept and the detection efficiency for the probability of zero photoelectrons generation when m value is expected is given by Eq. 2 and 3.

The detection efficiency for beta emitters takes into account the energy spectrum S(E) obtained by application of the of Fermi theory according to Eq. 4.

$$P(x/m) = \frac{m^x e^{-m}}{x!} \qquad (2)$$

$$\varepsilon = 1 - P(0) = 1 - \frac{(\nu m)^0 e^{-m}}{0!} = 1 - e^{-\nu m} \qquad (3)$$

$$\varepsilon = \int_0^E S(E)(1 - e^{-\nu m})dE \qquad (4)$$

The computational codes for theoretical calculation of the detection efficiency curve in TDCR and CIEMAT/NIST methods 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].

1.2 CIEMAT/NIST method

This measurement system consists of two photomultipliers placed in coincidence at 180° to each other. The detection efficiency is given by,

$$\varepsilon = \left(1 - e^{-\frac{\nu m}{2}}\right)^2 \qquad (5)$$

The CIEMAT/NIST method uses a set of standard tracer tritium (^3H) samples for the commercial scintillator characterizing in terms of the quenching parameter by the introduction of the chemical quenching agent in increasing degree. The measurements of the radionuclide samples are performed under the same conditions to the tracer, and the Free Parameter is common to the both radionuclides ones, allowing the correlation between their experimental and theoretical efficiencies, according to figure 1.

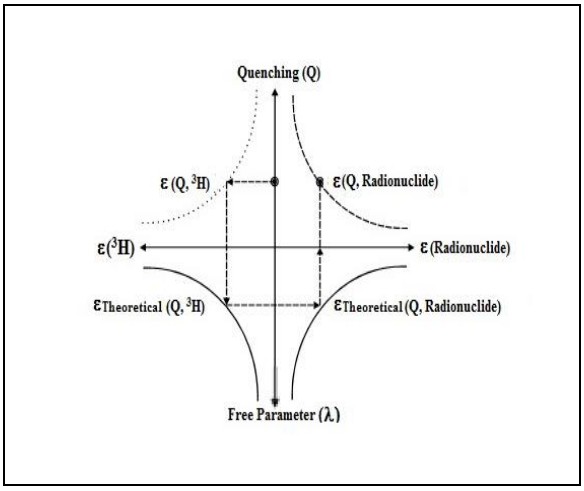

Figure 1 CIEMAT/NIST model for the radionuclide standardization.

1.3 TDCR method

The measurement system comprises three photomultiplier tubes placed in coincidence at 120° to each other. The figure 2 shows the TDCR systems.

The Eq. 6, 7, 8 and 9 are used to calculation of the photomultiplier detection efficiency, detection efficiency for the logical sum of the three double coincidences, efficiency ratio between the triple to double coincidences and TDCR for beta emitters.

The TDCR method is applied to the absolute standardization of radionuclide solutions by interpolating of the ratio between the triple and double coincidences counts obtained experimentally to the theoretical efficiency versus TDCR as a function of Free Parameter.

The counting efficiency variation can be performed by three different ways: photomultiplier defocusing, use of the filters of increasing optical density around sample glass vials and the addition of chemical quenching agent in the liquid scintillation cocktail.

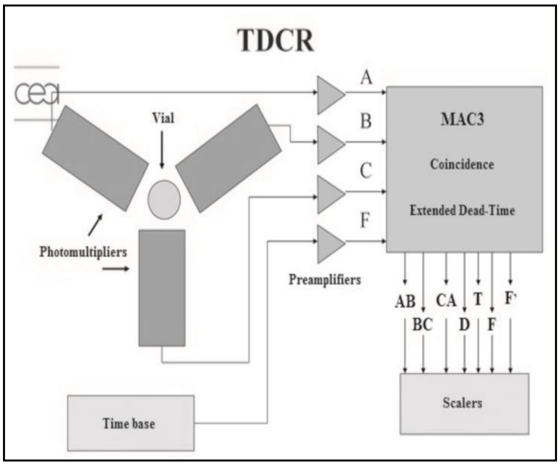

Figure 2. TDCR measurement system.

$$\varepsilon = 1 - e^{-\frac{\nu m}{3}} \qquad (6)$$

$$\varepsilon_D = 3\left(1 - e^{-\frac{\nu m}{3}}\right)^2 - 2\left(1 - e^{-\frac{\nu m}{3}}\right)^3 \qquad (7)$$

$$TDCR = \frac{\varepsilon_T}{\varepsilon_D} = \frac{\left(1-e^{-\frac{\eta}{3}}\right)^3}{3\left(1-e^{-\frac{\eta}{3}}\right)^2 - 2\left(1-e^{-\frac{\eta}{3}}\right)^3} \qquad (8)$$

Where,

$$\eta = \frac{\nu}{3}\int_0^E \frac{A\,dE}{1 + kB\,dE/dx} \qquad (9)$$

$$TDCR = \frac{\int_0^{E_{max}} S(E)\left(1-e^{\frac{-\nu m}{3}}\right)^3 dE}{\int_0^{E_{max}} S(E)\left(3\left(1-e^{\frac{-\nu m}{3}}\right)^2 - 2\left(1-e^{\frac{-\nu m}{3}}\right)^3\right) dE} \qquad (10)$$

1.4 Scintillation cocktails

At present, the commercial scintillation cocktails have chemical composition that allows the radioactive solutions dissolution in water, constituting a homogeneous solution. The most common are composed of a DIN solvent (diisopropyl naphthalene), a fluorescent solute such as 2,5 Dipheniloxazole substance and a surfactant.

2. EXPERIMENTAL PROCEDURE

The measurements of ^{3}H and ^{14}C solutions were performed by TDCR and CIEMAT/NIST methods in the scintillation cocktails Hisafe3 and Ultima Gold. The ^{99}Tc solution from the international key-comparison organized by the BIPM was measured by TDCR, Coincidence 4πβ(PC)–γ(NaI) and Anticoincidence 4π β(LS)–γ(NaI) systems of the LNMRI/Brazil. The $^{68}Ge/^{68}Ga$ solution was submitted to the comparison between LNMRI/Brazil and LNHB/France to measure by TDCR systems.

The radionuclide solutions used in the experimental standardization and comparisons were: ^{3}H (IPL 958-62-4) in water; ^{14}C (LMRI) in glucose and water; ^{99}Tc – NPL/UK DA-11337, in NH_4OH 0.1 M and; $^{68}Ge/^{68}Ga$ (Eckert & Ziegler Analytics) in HCl 0.1 N. The standardization ^{99}Tc solution by Coincidence and Anticoincidence methods was performed using the tracer standard ^{60}Co.

2.1 Computational codes for liquid scintillation methods

The theoretical calculations of the radionuclide detection efficiency were performed by computational codes CN2003 (11) to CIEMAT/NIST and TDCR07c [12] to TDCR. The TDCR07c code was modified to suit the specificities $^{68}Ge/^{68}Ga$ decay scheme [13].

2.3 Coincidence system

The 4πβ(PC)-γ(NaI) coincidence system consists of a gas flow 4π proportional counter coupled to a crystal of NaI(Tl) and the sources are prepared by dropping known masses of onto VYNS film previously gold coated on both sides.

2.2 Anticoincidence system

The 4πβ(LS)-γ(NaI) anticoincidence system with extended dead time is based on specialized modules developed to implement 4πβ–γ coincidence counting without the use of a resolving time.

The coincidence rate is obtained indirectly by subtracting the no correlatedγ-rate from the total γ-rate.

3. RESULTS

In the CIEMAT/NIST method the theoretical radionuclide efficiency was evaluated for the value of the kB parameter of the Birks' expression of 0.0075 cm.MeV^{-1}.

In the TDCR method the kB parameter was fixed from the sample measurements by use of filters of increasing optical density around sample glass vials, and the choice was made for the kB that produced the slightest variation and lower slope of linear fit curve: ^{3}H (kB = 0.013 cm.MeV^{-1}), ^{14}C (kB = 0.008 cm.MeV^{-1}), ^{99}Tc (KB = 0.008 cm.MeV^{-1}) and $^{68}Ge/^{68}Ga$ (KB = 0.010 cm.MeV^{-1}).

The assessment took into account the uncertainty components from the atomic and nuclear parameters and the experimental procedure, evaluated according to BIPM [14].

3.1 ^{3}H solution standardization

The table 2 and figure 3 show that the results obtained for the standardization of ^{3}H solution in Hisafe3 and Ultima Gold cocktails performed by TDCR method are consistent from each other within a standard uncertainty.

3.2 ^{14}C solution standardization

The table 3 and figure 4 show that the results of the ^{14}C standardization performed by TDCR and CIEMAT/NIST methods were consistent from each other for the two cocktails used within a standard uncertainty.

Table 2. Uncertainty budget (k = 1) of the ^{3}H solution standardization by TDCR method.

	Type	Hisafe3 (%)	Ultima Gold (%)
Weighing	B	0.05	0.05
Statistic counts	A	0.57	0.58
Source activities	A	0.36	0.66
kB value (grey filters)	A	0.28	0.20
Nuclear and atomic data	B	< 0,01	< 0,01
Combined uncertainty (k = 1)		0.73	0.90

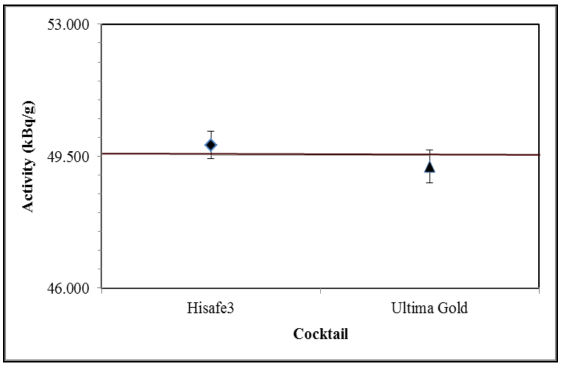

Figure 3. Results of the ^{3}H solution standardization by TDCR method (k = 1).

3.2 ^{14}C solution standardization

The table 3 and figure 4 show that the results of the ^{14}C standardization performed by TDCR and CIEMAT/NIST methods were consistent from each other for the two cocktails used within a standard uncertainty.

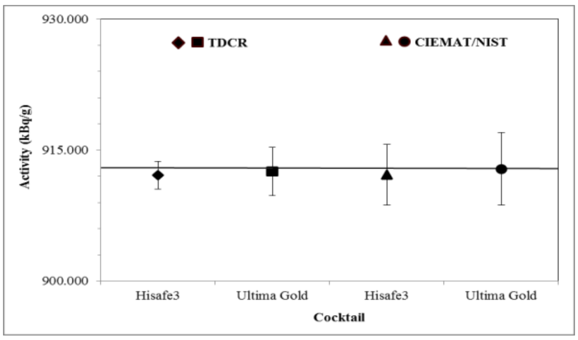

Figure 4. Results of the ^{14}C solution standardization by TDCR and CIEMAT/NIST methods (k = 1).

Table 3. Uncertainty budget (k = 1) of the ^{14}C solution standardization by TDCR method.

Component	Type	Hisafe3 (%)	Ultima Gold (%)
^{3}H activity	B	0.03	0.03
^{3}H weighing	B	< 0,01	< 0,01
^{3}H Quenching (SQPE)	A	0.03	0.04
^{3}H statistic counts	A	0.03	0.03
Nuclear and Atomic data	B	0.07	0.07
Photomulplier asimetry	B	0.25	0.25
kB value	B	0.23	0.23
^{14}C weighing	B	0.06	0.05
^{14}C Quenching (SQPE)	A	0.04	0.03
^{14}C statistic counts	A	0.07	0.08
^{14}C source activities	A	0.10	0.27
Combined uncertainty (k = 1)		0.38	0.45

3.3 ^{99}Tc solution standardization

The standardization of ^{99}Tc-IPL/UK solution, from key-comparison organized by the BIPM in 2012 was held on TDCR using Hisafe3 cocktail. The results were compared to the obtained by Coincidence 4π β(PC) – γ(NaI) and Anticoincidence 4π β(LS) – γ(NaI) systems, using ^{60}Co tracer.

3.4 ^{68}Ge/^{68}Ga solution standardization

The comparison held between LNMRI/Brazil and LNHB/France of the ^{68}Ge/^{68}Ga solution by TDCR method was performed using the same computer code TDCR07c modified to suit the specificities of the decay scheme. The results obtained by both laboratories shown in table 5 and figure 6 were consistent each other within a standard uncertainty (k = 1).

The table 4 and figure 5 shows that the results obtained for the three methods were consistent form each other within standard uncertainty (k = 1).

The use of the TDCR method in the standardization of ^{99}Tc solution from BIPM key-comparison presented result comparable to the obtained by Coincidence and Anticoincidence $4\pi\beta-\gamma$ absolute methods (k = 1).

Table 4. Uncertainty budget (k = 1) of the ^{99}Tc solution standardization by TDCR, Coincidence and Anticoincidence methods.

Component	Type	Method		
		TDCR (%)	Anticoincidence (%)	Coincidence (%)
Statistic counts	A	0.21	Included in fitting	Included in fitting
Fitting curve	A		0.38	0.53
Weighing	B	0.05	0.05	0.05
Background	A	< 0.001	0.29	0.2
Live time technique	B	0.01	0.01	
Decay (half-time)	B	< 0,001	< 0,001	< 0,001
Dead time	B			0.04
Resolving time	B			0.04
Gandy effect	B			0.08
^{60}Co activity	B		0.22	0.22
kB value	A	0.05		
Shape form	A	0.21		0.08
Source activities	B	0.08		
Uncertainty (k = 1)		0.32	0.53	0.62

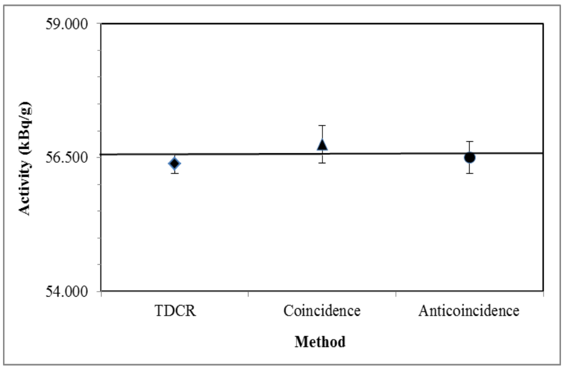

Figure 5. Results of the ^{99}Tc solution standardization by TDCR, Coincidence and Anticoincidence methods (k = 1).

4. CONCLUSIONS

The results obtained by TDCR and CIEMAT/NIST methods based on Free Parameter model were consistent at each other for the standardization of pure beta emitters as ^{3}H and ^{14}C either for Hisafe3 and Ultima Gold cocktails within a standard uncertainty, as shown in table 2 and figure 3 for ^{3}H, and Table 3 and Fig 4 for ^{14}C. The standardization of the others radionuclides were performed only in Hisafe3.

The good performance obtained in the comparison between LNMRI/Brazil and LNHB/France for the ^{68}Ge/^{68}Ga solution standardization by TDCR, presented in table 5 and figure 6 (k = 1), showed that this method can be applied to the standardization of radionuclides that present complex decay scheme.

In the BIPM key-comparison for ^{68}Ge/^{68}Ga to be performed since 2014, the TDCR method will be compared with the other absolute methods to evaluate its measurement consistency.

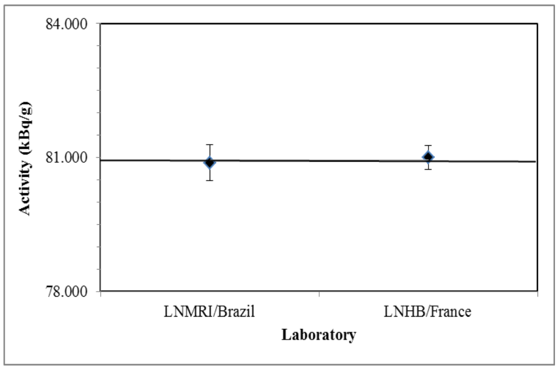

Figure 6. Results of the ^{68}Ge/^{68}Ga solution standardization by TDCR method in the LNMRI/Brazil and LNHB/France radionuclide metrology laboratories (k = 1).

Table 5. Uncertainty budget (k = 1) of the ^{68}Ge/^{68}Ga solution standardization by TDCR method of the LNMRI/Brazil and LNHB/France.

Component	Type	LNMRI (%)	LNHB (%)
Weighing	B	0.05	0.05
Statistic counts	A	0.26	0.11
Source activities	A	0.31	0.11
kB value (grey filters)	A	0.06	0.06
Nuclear and atomic data	B	0.28	0.28
Combined uncertainty (k = 1)		0.50	0.33

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