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

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Abstract: This work presents 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 used 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 pure emitters³³H,¹⁴C,⁹⁹Tc and for⁶⁸Ge/⁶⁸Ga which decay by electron capture and positron emission, with uncertainties smaller than 1% (k = 1).

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.

The present work uses these methods to perform measurements of beta emitters,³³H and¹⁴C, as well as⁹⁹Tc 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 $^{68}$Ge/$^{68}$Ga nuclides in secular equilibrium, which decay by electron capture and positron emission, 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 counting systems consisting of three or two photomultipliers based on statistical Free Parameter model [7] of the scintillation photons distribution and their detection probabilities.

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 captured in the photomultiplier photocathode produces 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 in 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, excitation or rupture in neutral or ionized fragments.

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

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

$$m(E) = \int_0^E \frac{A \, dE}{1 + k_B \frac{dE}{dx}}$$  \hspace{1cm} (1)

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

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

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

$$P(x/m) = \frac{m^x e^{-m}}{x!}$$  \hspace{1cm} (2)

$$\varepsilon = 1 - P(0) = 1 - \frac{(vm)^0 e^{-m}}{0!} = 1 - e^{-vm}$$  \hspace{1cm} (3)

$$\varepsilon = \int_0^E S(E)(1 - e^{-vm}) \, dE$$  \hspace{1cm} (4)
The computational codes for theoretical calculation of the detection efficiency 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 primary method
This counting system consists of two photomultipliers placed in coincidence at 180° to each other. 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 figure 1 shows the correlation between Free Parameter, quenching and efficiencies for standard tracer and radionuclide in analysis by CIEMAT/NIST method.

The equation 5 gives the detection efficiency for two photomultipliers obtained from Poisson model.

$$\varepsilon = \left(1 - e^{-\frac{vm}{2}}\right)^2$$  \hspace{1cm} (5)

1.3 TDCR method for absolute standardization
The counting system comprises three photomultiplier tubes placed in coincidence at 120° to each other. The figure 2 shows the TDCR systems. The equation 6, 7, 8 and 9 calculate 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 ratio for beta emitters.

Figure 1. CIEMAT/NIST model for the radionuclide standardization.

Figure 2. TDCR measurement system.
\[ \varepsilon = 1 - e^{-\frac{vm}{3}} \]  
\[ \varepsilon_D = 3 \left(1 - e^{-\frac{vm}{3}}\right)^2 - 2 \left(1 - e^{-\frac{vm}{3}}\right)^3 \]  
\[ TDCR = \frac{\varepsilon_T}{\varepsilon_D} = \frac{(1 - e^{-\frac{n}{3}})^3}{3 \left(1 - e^{-\frac{n}{3}}\right)^2 - 2 \left(1 - e^{-\frac{n}{3}}\right)^3} \]

Where,
\[ \eta = \sqrt[3]{\frac{1}{2} \int_0^E A \, dE} \left(1 + kB \, dE/dx \right) \]

Then,
\[ TDCR = \frac{\int_0^{E_{max}} S(E) \left(1 - e^{-\frac{vm}{3}}\right)^3 \, dE}{\int_0^{E_{max}} S(E) \left(3 \left(1 - e^{-\frac{vm}{3}}\right)^2 - 2 \left(1 - e^{-\frac{vm}{3}}\right)^3\right) \, dE} \]

The absolute standardization of radionuclide solutions combines the 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 is performed by either, photomultiplier defocusing or use of the filters of increasing optical density around sample glass vials or the addition of chemical quenching agent in the liquid scintillation cocktail.

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. The table 1 presents the density and the stoichiometric composition of the main scintillation cocktails provided by the commercial Perkin Elmer Company.

**Table 1.** Stoichiometric composition of liquid scintillators by PerkinElmer Company.

| Chemical Element | C    | H    | N    | O    | P    | S    | Na   | Density (g/cm³) | Z/A  | WM    |
|------------------|------|------|------|------|------|------|------|----------------|------|-------|
| HiSafe3          | 19.17| 28.12| 0.02 | 2.88 | 0.06 | 0.00 | 0.00 | 0.99           | 0.5458| 306.70|
| Ultima Gold      | 16.81| 24.54| 0.04 | 1.52 | 0.11 | 0.02 | 0.02 | 0.98           | 0.5459| 255.76|
| Ultima Gold XR   | 18.11| 29.80| 0.04 | 2.83 | 0.11 | 0.03 | 0.03 | 0.99           | 0.5476| 297.98|
| Ultima Gold AB   | 18.67| 28.49| 0.01 | 2.53 | 0.01 | 0.00 | 0.00 | 0.98           | 0.5485| 293.47|
| Ultima Gold LLT  | 18.57| 28.43| 0.01 | 2.56 | 0.01 | 0.00 | 0.00 | 0.98           | 0.5486| 292.68|
| Insta-Gel Plus   | 18.53| 30.93| 0.01 | 3.90 | 0.00 | 0.00 | 0.00 | 0.95           | 0.549 | 315.71|
| Hionic-Fluor     | 10.83| 18.77| 0.08 | 1.97 | 0.18 | 0.04 | 0.04 | 0.95           | 0.5449| 188.87|

2. Experimental Procedure

\(^3\)H and \(^{14}\)C solutions were measured by TDCR and CIEMAT/NIST methods in the scintillation cocktails HiSafe3 and Ultima Gold.

The \(^{99m}\)Tc solution from the international key-comparison organized by the BIPM was measured by TDCR, Coincidence \(4\pi\beta(\text{PC})-\gamma(\text{NaI})\) and Anticoincidence \(4\pi\beta(\text{LS})-\gamma(\text{NaI})\) counting systems.
The $^{68}\text{Ge}/^{68}\text{Ga}$ solution was submitted to the comparison between LNMRI/Brazil and LNHB/France to measurements in TDCR counting system.

The radionuclide solutions used in the experimental standardization were $^3\text{H}$ (IPL 958-62-4) in water; $^{14}\text{C}$ (LMRI) in glucose and water; $^{99}\text{Tc}$ – NPL/UK DA-11337, in NH$_4$OH 0.1 M and; $^{68}\text{Ge}/^{68}\text{Ga}$ (Eckert & Ziegler Analytics) in HCl 0.1 N. The standardization $^{99}\text{Tc}$ solution by Coincidence and Anticoincidence counting systems used the tracer standard $^{60}\text{Co}$.

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. Some changes were introduced in the TDCR07c code to suit $^{68}\text{Ge}/^{68}\text{Ga}$ decay scheme [13].

2.2 Coincidence counting system
The 4$\pi$β-(PC)-\(\gamma\)(NaI) Coincidence counting system consists of a gas flow 4$\pi$ proportional counter coupled to a crystal of NaI(Tl). The sources are prepared by dropping known masses of onto VYNS film previously gold coated on both sides.

2.3 Anticoincidence counting system
The 4$\pi$β-(LS)-\(\gamma\)(NaI) Anticoincidence counting system with extended dead time is based on specialized modules developed to implement 4$\pi$β–\(\gamma\) coincidence counting without the use of a resolving time. The coincidence rate is obtained indirectly by subtracting the no correlated\(\gamma\)-rate from the total \(\gamma\)-rate.

3. Results
The theoretical radionuclide efficiencies by CIEMAT/NIST method was calculated using kB parameter value of 0.0075 cm.MeV$^{-1}$, according to Birks’ expression. The kB parameter for TDCR method was obtained from the sample measurements by use of filters of increasing optical density around sample glass vials. The choice of the optimum kB was made for the value that produced the slightest variation and lower slope of linear fit curve: $^3\text{H}$ (kB = 0.013 cm.MeV$^{-1}$), $^{14}\text{C}$ (kB = 0.008 cm.MeV$^{-1}$), $^{99}\text{Tc}$ (KB = 0.008 cm.MeV$^{-1}$) and $^{68}\text{Ge}/^{68}\text{Ga}$ (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 $^3\text{H}$ solution standardization
The table 2 and figure 3 show that the results obtained for the standardization of $^3\text{H}$ solution in HiSafe3 and Ultima Gold cocktails performed by TDCR method are consistent from each other, within a standard uncertainty.

| Table 2. Uncertainty budget (k = 1) of the $^3\text{H}$ 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 figure 4 and table 3 show that the results of the $^{14}$C standardization by TDCR and CIEMAT/NIST methods were consistent from each other for the two cocktails, 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            |
| Photomulpplier 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 figure 5 and table 4 show the results obtained to the standardization of $^{99}$Tc-IPL/UK solution, from key-comparison organized by the BIPM in 2012, measured by TDCR and using HiSafe3 cocktail. The results were compared to the obtained by Coincidence $4\pi \beta(\text{PC}) - \gamma(\text{NaI})$ and Anticoincidence $4\pi \beta(\text{LS}) - \gamma(\text{NaI})$ counting systems, using $^{60}$Co tracer.

![Figure 5](image)

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

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

| Component               | Type | 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     |                      |                 |
| Combine uncertainty (k = 1) | 0.32 | 0.53 | 0.62 |

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

The comparison between LNMRI/Brazil and LNHB/France of the $^{68}$Ge/$^{68}$Ga solution by TDCR method was performed using the same computer code TDCR07c. The results obtained by both laboratories shown in figure 6 and table 5 were consistent each other, within a standard uncertainty.
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     |

4. Conclusion
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 for HiSafe3 and Ultima Gold cocktails, within a standard uncertainty. The standardization of the others radionuclides were performed only in HiSafe3.

The standardization of $^{99}$Tc-IPL/UK solution, from key-comparison organized by the BIPM in 2012 was performed by TDCR and using HiSafe3 cocktail. This result was compared with those obtained by Coincidence and Anticoincidence counting systems and were consistent each other, within a standard uncertainty.

The good performance obtained by comparison between LNMRI/Brazil and LNHB/France for the $^{68}$Ge/$^{68}$Ga solution standardization performed by TDCR show that this method can be applied to the standardization of radionuclides that present complex decay scheme. In the end of BIPM key-comparison, for $^{68}$Ge/$^{68}$Ga in progress will be evaluated the consistency of the results obtained by TDCR counting system compared to the others absolute methods.

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