Sofia University "St. Kliment Ohridski"



MASTERS THESIS

# Study on the applications of the Triple-to-Double Coincidences Ratio method

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#### Introduction

Liquid scintillation counting is a powerful method for measurement of activity of  $\alpha$ -,  $\beta$ - and electron capture (EC) emitting radionuclides and is widely used in laboratories around the world. It is well suited for activity measurements of low-energy  $\beta$ -emitters. To calculate the activity of the radionuclide, the detector must be callibrated with a standartized source with known activity and a low uncertainty. One way of producing such sources is by the use of the triple-to-double coincidence ratio (TDCR) method. It is based on the statistical properties of light emitted in a liquid scintillation cocktail and was developed for the absolute determination of activity of  $\alpha$ -,  $\beta$ - and EC-radionuclides ([1] and the references therein). This method is widely used in National Metrology Institutes (NMIs) for primary standartization [2]. A brief theoretical overview of the method and its practical aspects is presented in Part I of this thesis.

A novel detector system based on the TDCR method was recently developed at Sofia University referenced as TDCR-SU [3]. The TDCR-SU is equipped with a nanoTDCR device, a novel, state of the art, TDCR acquisition system. It is very compact and portable and can be used for in-situ measurements of very short half-life medical radionuclides.

The nanoTDCR was benchmarked against the well established MAC3 counting module by connecting it to the logical outputs of the constant fraction discriminator of the MAC3 and performing a simultanious measurement with the two modules on four different <sup>241</sup>Am sources. The difference between the counting rates reported by the two systems was less than 0.3%, which can be attributed to the different counting times of the two systems.

The performance of the TDCR-SU detector was quantified by comparison with the primary TDCR detector at the french primary metrology laboratory, Laboratoire National Henry Becquerel (LNHB). Both systems were in excellent agreement for measurements of <sup>3</sup>H and <sup>14</sup>C sources [3].

The objective of this thesis is to perform a series of studies with the already developed and benchmarked TDCR-SU detector and nanoTDCR device. The developement and functions of a web-based application for storage, filtering and exporting of nanoTDCR generated data are presented. A set of 3D printed mesh filters with different transparencies was produced. The performance of the designed filters was tested on the RCTD1 (the primary TDCR system at LNHB) and TDCR-SU systems. The set was used to perform a study on the efficiency variation technique and the optimal kB value for a <sup>3</sup>H sample was determined. The function of the nanoTDCR device to count in two coincidence windows simultaniously was explored and results from the measurements of a <sup>3</sup>H sample with 40 ns and 100 ns coincidence window are compared.

A study on the application of the TDCR method to measurements of tritiated water in liquid scintillators UltimaGold and UltimaGold LLT is presented. The optimal kB values for both liquid scintillation cocktails is determined using the efficiency variation technique and the specific activity of the tritiated water is obtained.

Experiments on the applicability of the TDCR model to measurements of <sup>222</sup>Rn and <sup>220</sup>Rn were performed with the TDCR-SU detector. The half-lifes of <sup>222</sup>Rn and <sup>212</sup>Pb were determined and the obtained results agree well with results from other authors.

## Part I: Theoretical background

#### CHAPTER 1

#### The Triple-to-Double Coincidence Ratio method

## 1.1 Liquid scintillators

Liquid scintillators are organic compounds that emit light after absorbing the kinetic energy of passing particles. A large category of practical organic scintillators consist of aromatic molecules, with alternating double bonds and  $\pi$ -electrons. The molecules are loosely bound to one another by Van der Waals forces and, due to that, the excitation energy can undergo substantial transfer. This is important for liquid scintillators that employ more than one species of molecules. In these systems a small amount of efficient scintillator is added to a bulk solvent, which absorbs most of the dissipated in the cocktail energy. Through interactions between the molecules, the excitation energy can find its way to one of the efficient scintillation molecules and cause light emission [4]. A third component is usually added as a wavelength shifter.

Only a fraction of the kinetic energy of a charged particle passing through the scintillator is converted to fluorescent energy. The bulk remaining energy is dissipated non-radiatively as heat or vibrational excitations. The fraction of the energy that is converted to light depends on the type of particle and its energy. In some cases the light output is constant with energy leading to a linear response of the scintillator. This is true for electrons with energies higher than 125 keV in organic crystals like anthracene or stilbene [4]. For heavy charged particles the light output is always less than that for electrons and is non-linear to much higher energies.

#### Ionization quenching

The higher the linear energy transfer of the particle is, the more ionization, with higher density of the scintillator excitation it produces. This leads to decreased efficiency of the scintillator, an effect known as "ionization quenching", which is similar in all types of organic scintillators. Due to it, the intensity of the light I, emitted by the scintillator, for an electron, a proton or an  $\alpha$ -particle is different and is approximately in the ratio 10:5:1 [5]. The intensity of the emitted light changes non-linearly with the energy, the stopping power and the type of particle. Birks [5] proposed a semi-empirical formula that describes the behaviour of the intensity I of the scintillation, known as Birks' law:

$$\frac{dI}{dx} = \frac{\eta_0 \frac{dE}{dx}}{1 + kB\frac{dE}{dx}},\tag{1.1}$$

where x is the range of the particle in the scintillator, dE/dx is the particle's stopping power,  $\eta_0$  is the absolute scintillation efficiency, which is the ratio of the sum of energies of all photons emitted during the scintillation event to the energy released in the cocktail. The specific density of the ionized and excited molecules along the trajectory of the particle is  $kB\frac{dE}{dx}$ , where kB is the ionization quenching parameter and is measured in units cm/MeV.

The fluorescence yield of the scintillator is given by

$$L(E) = \eta_0 \int_0^E \frac{dE}{1 + kB(dE/dx)} = \eta_0 EQ(E), \qquad (1.2)$$

where Q(E) is the ionization quenching function

$$Q(E) = \frac{1}{E} \int_0^E \frac{dE}{1 + kB(dE/dx)}.$$
 (1.3)

There are some problems which arise when calculating the ionization quenching function: the choice of an optimal value of the ionization quenching parameter kB, calculation of the values of the stopping power for energies under 1 keV and the lack of precise knowledge of the atomic composition and density of the used scintillator, which are necessary for the calculation of the stopping power dE/dx.

## **1.2** Liquid scintillation counting

Liquid scintillation counting (LSC) is the measurement of activity of a radioactive material dissolved in a liquid scintillator by counting the number of resulting light pulses. The liquid scintillator is usually contained in clear glass or polyethylene vial. These vials are then measured on purposefully designed detectors called liquid scintillation counters. Most detectors are equipped with an optical chamber, that houses the sample during measurement, and photomultiplier tubes, that register the scintillation events. The events are recorded for a certain time period and the counting rate of the sample is given as an output. The detection efficiency  $\varepsilon_{LSC}$  gives the relationship between the net (background corrected) counting rate  $n_0$  and the activity A, where

$$A = \frac{n_0}{\varepsilon_{LSC}}.$$

The detection efficiency  $\varepsilon_{LSC}$  must be known with high accuracy in order to calculate the activity of the source. It can be determined using a calibrated source with activity that is known with high accuracy. One way of producing such sources with is by the use of the TDCR method.

Liquid scintillation counting is a primary choice of a measurement technique for the measurement of low-energy  $\beta$ -emitters like <sup>3</sup>H , <sup>14</sup>C, <sup>55</sup>Fe , <sup>63</sup>Ni and others ( [6], [7], [8]). In the last five years the LSC technique was proposed for the measurement of activity of the radioactive noble gases <sup>85</sup>Kr, <sup>220</sup>Rn and <sup>222</sup>Rn absorbed in polymer materials ( [9], [10], [11], [12], [13]). Application of LSC spectrometry to <sup>222</sup>Rn absorbed in plastic scintillators has also been proposed ( [3], [14], [15], [16], [17]). The application of all these techniques requires adequate calibration of the LS spectrometer. It has been shown previously that this calibration can be performed using samples, cahracterised by primary activity measurements by the TDCR method ( [9], [18]).

# 1.3 Calculation of the detection efficiency for a TDCR detector

The detection efficiency for high-energy  $\beta$ -emitters and  $\alpha$ -emitters in liquid scintillation counting can be assumed to be 100% for all practical purposes [19]. This is not the case of low-energy  $\beta$ -emitters and some EC nuclides, where the detection efficiency is less than 100% and can vary with measurement conditions. In order to perform a precise absolute measurement of the activity of the source, the detection efficiency must be known with high accuracy. It can be calculated by the use of one particular model called the "free parameter" model, which is based on the statistical description of phenomena occurring in the LS counter and is described hereafter.

#### The free paremeter model

As a result of radioactive decay inside the liquid scintillation cocktail, an amount of energy E is released and the expected mean number of emitted photons can be expressed as [2]:

$$N = \frac{\eta_0 Q(E)E}{h\nu},\tag{1.4}$$

where  $h\nu$  is the mean photon energy and  $\eta_0$  is the absolute scintillation efficiency.

If we assume that the emitted photons are distributed according to the Poisson distribution with a mean value N, the number of photons reaching the photocathodes of the photomultiplier tubes (PMTs) n is also Poisson distributed [2]:

$$p(n,\bar{n}) = \frac{\bar{n}^n}{n!} e^{-\bar{n}},\tag{1.5}$$

$$\bar{n} = N\xi, \tag{1.6}$$

where  $\bar{n}$  is the mean number of photons,  $\xi$  is the geometrical detection efficiency of the PMT. The emission of n photons from the scintillator leads to the emission of mphotoelectrons from the photocathode, where m can be expressed by:

$$m = n\varepsilon_q \mu, \tag{1.7}$$

where  $\varepsilon_q$  is the quantum efficiency of the photomultiplier and  $\mu$  is the spectral matching factor between the flourescence spectrum of the scintillator and the absorbtion spectrum of the photocathode. The photoelectric process in the photocathode can be described by the binomial distribution [2]:

$$b(m; n, \varepsilon_q \mu) = \frac{n!}{m!(n-m)!} (\varepsilon_q \mu)^m (1 - \varepsilon_q \mu)^{n-m}, \qquad (1.8)$$

where  $b(m; n, \varepsilon_q \mu)$  is the probability that n incident photons on the photocathode lead to the emission of exactly m photoelectrons given that the quantum efficiency of the photomultiplier tube is  $\varepsilon_q \mu$ . We can express the probability for emission of at least one photoelectron from the probability of emission of exactly zero photoelectrons [2]:

$$p_e(n) = 1 - b(0; n, \varepsilon_q \mu) = 1 - (1 - \varepsilon_q \mu)^n,$$
 (1.9)

The mean number of photoelectrons  $\overline{m}$  produced by the emission of a particle with energy E in the cocktail can be calculated from equations (1.7), (1.6) and (1.4):

$$\bar{m} = N\varepsilon = \frac{L\xi\varepsilon_q\mu}{h\nu}Q(E)E, \qquad (1.10)$$

where  $\varepsilon$  is the total detection efficiency of the detector and is equal to the product of  $\xi$ ,  $\varepsilon_q$  and  $\mu$ .

In the case of a detector with R photomultipliers, the number of photons incident on each photomultiplier form a set  $\{n_i\}$  which fulfills the criteria  $n = n_1 + n_2 + \cdots + n_R$ . The probability for a given set  $\{n_i\}$  is given by the multinomial distribution [2]:

$$P_d = \frac{1}{R^n} \frac{n!}{n_1! n_2! \cdots n_R!}.$$
(1.11)

The probability for the formation of different types of pulses  $P_x$ , when there are n incident photons on the photomultipliers, can be computed using equation (1.9). For example, for two photomultipliers, A and B, working in coincidence, the probability for the formation of a coincident impulse  $P_x^{AB}$  with  $n_A$  photons reaching PMT A and  $n_B = n - n_A$  photons reaching PMT B is:

$$P_x^{AB} = p_e(n_A)p_e(n_B) = p_e(n_A)p_e(n-n_A) = (1 - (1 - \varepsilon_q \mu)^{n_A})(1 - (1 - \varepsilon_q \mu)^{n-n_A}) \quad (1.12)$$

Combining equation (1.11) with the probability of the formation of a pulse from a given type  $P_x$ , we get the probability of n photons creating a detectable pulse:

$$P_R(n) = P_d P_x = \frac{n!}{R^n} \sum_{n_1=0}^n \sum_{n_2=0}^{n-n_1} \cdots \sum_{n-n_1-\dots-n_{R-2}}^{n_R} \frac{P_x}{n_1! n_2! \cdots n_{R-1}! (n-n_1-\dots-n_{R-1})!}$$
(1.13)

Equation (1.5) gives the probability  $p(n, \bar{n})$  for n photons to reach the photocathodes of the PMTs of the detector when there are  $\bar{n}$  photons emitted from the cocktail. The detection efficiency for  $\bar{n}$  photons emitted form the cocktail is given by the expression [20]:

$$\varepsilon = P_E(\bar{n}) = \sum_{n=1}^{\infty} P(n,\bar{n}) P_R(n)$$
(1.14)

In the simplest case of one PMT, where  $P_x = p_e(n)$  and  $P_d = 1$ , we can express  $P_E$  as:

$$P_{E} = \sum_{n=0}^{\infty} p(n,\bar{n}) \left[ 1 - (1 - \varepsilon_{q}\mu)^{n} \right]$$
  
=  $1 - \sum_{n=0}^{\infty} \frac{\bar{n}^{n}}{n!} e^{-\bar{n}} (1 - \varepsilon_{q}\mu)^{n}$   
=  $1 - \left\{ \sum_{n=0}^{\infty} \frac{\left[\bar{n}(1 - \varepsilon_{q}\mu)\right]^{n} e^{-\bar{n}(1 - \varepsilon_{q}\mu)}}{n!} \right\} \frac{e^{-\bar{n}}}{e^{-\bar{n}(1 - \varepsilon_{q}\mu)}}$   
=  $1 - e^{-\bar{n}} e^{\bar{n}(1 - \varepsilon_{q}\mu)} = 1 - e^{-\bar{n}\varepsilon_{q}\mu} = 1 - e^{-\bar{m}}$  (1.15)

Thus, a cascade of three random processes abiding to: Poissonian distribution (1.5), binomial distribution (1.8) and multinomial distribution (1.11), can be resumed by only using Poissonian statistics for the mean number of photons emitted in the cocktail  $p(m, \bar{m})$  [2].

Let us examine the more complicated case of a detector with two photomultipliers, A and B, working in coincidence. In this case  $P_x$  is given by equation (1.12). Substituting in equation (1.11) we get the detection efficiency for a coincidence pulse with n incident photons on the photocathodes of the two PMTs:

$$P_R^{AB} = \frac{n!}{2^n} \sum_{n_A=0}^n \frac{(1-p_0^{n_A})(1-p_0^{n-n_A})}{n_A!(n-n_A)!},$$
(1.16)

where  $p_0 = 1 - \varepsilon_q \mu$  is the probability of emission of 0 phototelectrons if there is a photon incident on the photocathode. The detection probability P in the case of two PMTs in coincidence is given by:

$$P_{AB} = P_E = \sum_{n=1}^{\infty} \frac{p(n,\bar{n})}{2^n} \sum_{n_A=0}^n \binom{n}{n_A} (1-p_0^{n_A})(1-p_0^{n-n_A})$$
(1.17)

Developing the brackets in the second sum in (1.17) we get:

$$P_{AB} = \sum_{n=1}^{\infty} \frac{p(n,\bar{n})}{2^n} \sum_{n_A=0}^n \binom{n}{n_A} \left(1 - p_0^{n_A} - p_0^{n-n_A} + p_0^n\right)$$
(1.18)

For the calculation of the fininte sums we use the binomial formula:

$$(x+y)^{n} = \sum_{k=0}^{n} \binom{n}{k} x^{k} y^{n-k}$$
(1.19)

We can separate equation (1.18) into four sums for which we get [20]:

$$\sum_{n_A=0}^n \binom{n}{n_A} = 2^n \tag{1.20}$$

$$\sum_{n_A=0}^n \binom{n}{n_A} p_0^{n_A} 1^{n-n_A} = (1+p_0)^n = (2-\varepsilon_q \mu)^n = 2^n \left(1-\frac{\varepsilon_q \mu}{2}\right)^n \tag{1.21}$$

$$\sum_{n_A=0}^n \binom{n}{n_A} p_0^{n-n_A} 1^{n_A} = (1+p_0)^n = (2-\varepsilon_q \mu)^n = 2^n \left(1-\frac{\varepsilon_q \mu}{2}\right)^n \tag{1.22}$$

$$\sum_{n_A=0}^n \binom{n}{n_A} p_0^n = 2^n p_0^n = 2^n (1 - \varepsilon_q \mu)^n \tag{1.23}$$

If we substitute the calculated finite sums in the right hand member of equation (1.18) we can derrive the probability of counting  $P_{AB}$  for two PMTs in coincidence:

$$P_{AB} = \sum_{n=0}^{\infty} \frac{\bar{n}^{n}}{n!} e^{\bar{n}} \left\{ 1 - 2 \left( 1 - \frac{\varepsilon_{q}\mu}{2} \right)^{n} + (1 - \varepsilon_{q}\mu)^{n} \right\} =$$

$$= \sum_{n=0}^{\infty} \frac{\bar{n}^{n}}{n!} e^{-\bar{n}} - \sum_{n=0}^{\infty} 2 \frac{\bar{n}^{n}}{n!} e^{-\bar{n}} \left( 1 - \frac{\varepsilon_{q}\mu}{2} \right)^{n} + \sum_{n=0}^{\infty} \frac{\bar{n}^{n}}{n!} e^{-\bar{n}} (1 - \varepsilon_{q}\mu)^{n} =$$

$$= 1 - 2e^{-\bar{n}} e^{\bar{n}(1 - \varepsilon_{q}\mu/2)} \sum_{n=0}^{\infty} p(n, \bar{n}(1 - \varepsilon_{q}\mu/2)) + e^{-\bar{n}} e^{\bar{n}1 - \varepsilon_{q}\mu} \sum_{n=0}^{\infty} p(n, \bar{n}(1 - \varepsilon_{q}\mu)) =$$

$$= 1 - 2e^{-\bar{n} + \bar{n} \left(1 - \frac{\varepsilon_{q}\mu}{2}\right)} + e^{-\bar{n} + \bar{n}(1 - \varepsilon_{q}\mu)} = 1 - 2e^{-\bar{n}\varepsilon_{q}\mu/2} - e^{-\bar{n}\varepsilon_{q}\mu} =$$

$$= \left(1 - e^{-\frac{\bar{n}\varepsilon_{q}\mu}{2}}\right)^{2} = \left(1 - e^{-\frac{\bar{m}}{2}}\right)^{2}$$

$$(1.24)$$

Equations (1.24) and (1.15) can be derived by the assumption of pure Poisson process describing the statistics of photoelectrons without considering a binomial distribution [20]. The counting probability of various kinds of pulses, created by monoenergetic particles, are summarized in Table 1.1.

Using equations (1.15) and (1.24), the detection probability P of a LS counter with R identical PMTs becomes

$$P = 1 - e^{-\bar{m}/R},\tag{1.25}$$

where the mean number of photoelectrons created in all R PMTs is given by:

$$\bar{m} = \frac{EQ(E)}{\lambda}.$$
(1.26)

The free parameter  $\lambda$  in (1.26) is the average energy needed to create a photoelectron at the photocathode of the PMT:

$$\lambda = \frac{EQ(E)}{\bar{m}} = \frac{h\nu}{L\xi\varepsilon_q\mu}.$$
(1.27)

The probability of counting P is a function of the free parameter  $\lambda$  and the energy of the particle. To ensure the validity of the assumption that the detection probability follows a Poissonian distribution, the detector must be constructed in such a way that the detection probability of one photoelectron is not zero. To achieve this in practice, the position of the discriminator thresholds of each PMT must be just below the single-photoelectron peak.

**Table 1.1:** Detection probability for varoius kinds of pulses caused by monoenergetic particles in a detector with R photomultipliers with identical and non-identical response. The Poisson non-detection probability is  $p_0 = e^{-\bar{m}/R}$ . The signals are either from a single PMT (no coincidence), from two PMTs (with or without coincidence) or from three PMTs (no coincidence, double coincidence or triple coincidence)

R	Signal mode	Coincidence	Probability of counting $P(E, \lambda)$
			Identical PMTs, $p_A = p_B = p_C = p_0$
1	А	None	$1 - p_0$
2	А; В	None	$1 - p_0$
	AB	Double	$(1 - p_0)^2$
3	A; B; C	None	$1 - p_0$
	AB; BC; AC	Double	$(1 - p_0)^2$
	Т	Triple	$(1 - p_0)^3$
			Non-identical PMTs, $p_A \neq p_B \neq p_C$
1	А	None	$1 - p_A$
2	А; В	None	$(1 - p_A); (1 - p_B)$
	AB	Double	$(1-p_A)(1-p_B)$
3	A; B; C	None	$(1 - p_A); (1 - p_B); (1 - p_C)$
	AB; BC; AC	Double	$(1-p_A)(1-p_B); (1-p_A)(1-p_C); (1-p_B)(1-p_C)$
	AB + BC + AC	$\mathrm{D}_3^*$	$(1 - p_A)(1 - p_B) + (1 - p_A)(1 - p_C) +$
			$+(1-p_B)(1-p_C) - 2(1-p_A)(1-p_B)(1-p_C)$
	Т	Triple	$(1 - p_A)(1 - p_B)(1 - p_C)$

\* Logical sum of double coincidences

#### Counting efficiency

The counting efficiency of the LS counter  $\varepsilon$  is a function of the free parameter  $\lambda$  and depends on the type of disintegration of the radionuclide. In the case of pure  $\beta$ emitters  $\varepsilon$  is the product of the counting probability  $P(E, \lambda)$  of a given pulse (taken from table 1.1) and the normalized beta spectrum S(E), integrated over the entire decay energy range [2]:

$$\varepsilon(\lambda) = \int_0^{E_{max}} S(E) P(E, \lambda) dE, \qquad (1.28)$$

where  $E_{max}$  is the maximum  $\beta$  particle energy.

Electron-capture (EC) radionuclides decay along multiple paths and have more complex decay schemes. In the case of these radionuclides, the counting efficiency  $\varepsilon$  is calculated as the sum of products of intensities  $I(E_j)$  and the probability of counting  $P(E_j, \lambda)$  of a given type of signal (taken from Table 1.1) at certain energy  $E_j$ . The summation is performed over the entire discrete energy spectrum with k energies  $E_j$  [2]:

$$\varepsilon(\lambda) = \sum_{j=0}^{k} I(E_j) P(E_j, \lambda).$$
(1.29)

#### The triple-to-double coincidence ratio model

The TDCR method uses the described free parameter model for a system with three photomultipliers and thus requires a special 3-PMT counter. The system must allow the counting of double coincidence pulses (AB, BC and AC) and triple coincidence pulses (T). The logical sum of the double coincidences is defined as:

$$D = AB \lor BC \lor AC = AB + BC + AC - 2T, \tag{1.30}$$

where  $\lor$  is the logical *or* operator.

The theoretical counting efficiencies in a R = 3 PMT system can be calculated by substituting the appropriate counting probability  $P(E, \lambda)$  from Table 1.1 in (1.28) and are the following:

$$\varepsilon_2 = \int_0^{E_{max}} S(E) \left(1 - e^{-\bar{m}/3}\right)^2 dE, \qquad (1.31)$$

for two PMTs working in coincidence and

$$\varepsilon_T = \int_0^{E_{max}} S(E) \left(1 - e^{-\bar{m}/3}\right)^3 dE,$$
 (1.32)

for three PMTs working in coincidence. The logical sum of double coincidences is calculated as [2]:

$$\varepsilon_D = \int_0^{E_{max}} S(E) \left[ 3 \left( 1 - e^{-EQ(E)/3\lambda} \right)^2 - 2 \left( 1 - e^{-EQ(E)/3\lambda} \right)^3 \right] dE$$
(1.33)

The ratio of the triple coincidences counting efficiency to the logical sum of double coincidences counting efficiency is expressed as [2]:

$$\frac{\varepsilon_T}{\varepsilon_D} = \frac{\int_0^{E_{max}} S(E) \left(1 - e^{-EQ(E)/3\lambda}\right)^3 dE}{\int_0^{E_{max}} S(E) \left[3 \left(1 - e^{-EQ(E)/3\lambda}\right)^2 - 2 \left(1 - e^{-EQ(E)/3\lambda}\right)^3\right] dE},$$
(1.34)

where S(E) is the normalized spectrum of the energy transferred to the liquid scintillation cocktail, which includes  $\beta$ -particles, photoelectrons and Compton electrons, coming from X-ray and  $\gamma$ -ray interactions in the cocktail, and Auger and conversion electrons. Q(E) is the ionization quenching correction factor (1.3),  $E_{max}$  is the maximum  $\beta$ -particle energy and  $\lambda$  is the free parameter.

For a large number of detected events, the ratio of the triple coincidence counting rate to the logical sum of double coincidences counting rate T/D converges towards the ratio of counting efficiencies  $\varepsilon_T/\varepsilon_D$  [2]. The left-hand side of the expression for the ratio of the triple coincidences efficiency to the logical sum of double coincidences efficiency (1.34) can be obtained experimentally and the right-hand side can be calculated theoretically if S(E) is known and the value of kB in (1.3) is assumed.

Equation (1.34) is valid under the assumption of identical PMTs, but in a real counter this assumption is rarely true. In that case a set of three equations has to



**Figure 1.1:** Calculated counting efficiency for the logical sum of double coincidences as a function of the TDCR for some  $\beta$ - and EC-emitters (figure taken from [21]).

be solved [2]:

$$\frac{\varepsilon_{T}}{\varepsilon_{AB}} = \frac{\int_{0}^{E_{max}} S(E) \left(1 - e^{-EQ(E)/3\lambda_{A}}\right) \left(1 - e^{-EQ(E)/3\lambda_{B}}\right) \left(1 - e^{-EQ(E)/3\lambda_{C}}\right) dE}{\int_{0}^{E_{max}} S(E) \left(1 - e^{-EQ(E)/3\lambda_{A}}\right) \left(1 - e^{-EQ(E)/3\lambda_{B}}\right) dE},$$

$$\frac{\varepsilon_{T}}{\varepsilon_{BC}} = \frac{\int_{0}^{E_{max}} S(E) \left(1 - e^{-EQ(E)/3\lambda_{A}}\right) \left(1 - e^{-EQ(E)/3\lambda_{B}}\right) \left(1 - e^{-EQ(E)/3\lambda_{C}}\right) dE}{\int_{0}^{E_{max}} S(E) \left(1 - e^{-EQ(E)/3\lambda_{B}}\right) \left(1 - e^{-EQ(E)/3\lambda_{C}}\right) dE},$$

$$\frac{\varepsilon_{T}}{\varepsilon_{AC}} = \frac{\int_{0}^{E_{max}} S(E) \left(1 - e^{-EQ(E)/3\lambda_{A}}\right) \left(1 - e^{-EQ(E)/3\lambda_{B}}\right) \left(1 - e^{-EQ(E)/3\lambda_{C}}\right) dE}{\int_{0}^{E_{max}} S(E) \left(1 - e^{-EQ(E)/3\lambda_{A}}\right) \left(1 - e^{-EQ(E)/3\lambda_{C}}\right) dE},$$

$$(1.35)$$

where  $\lambda_A$ ,  $\lambda_B$  and  $\lambda_C$  are the free parameters of each PMT. Similar to the situation with identical PMTs, here the experimental ratios T/AB, T/BC and T/AC converge towards the theoretical counting efficiency rations  $\varepsilon_T/\varepsilon_{AB}$ ,  $\varepsilon_T/\varepsilon_{BC}$  and  $\varepsilon_T/\varepsilon_{AC}$  for



**Figure 1.2:** Influence of the kB parameter on the calculated activity using the TDCR model for <sup>3</sup>H

a large number of detected events. The values of the free paramters in equations (1.35) can be found using a Downhill Simplex algorithm [21], where the function to be minimized is the squared sum of differences between the theoretical and experimental ratios:

$$\Delta = \left(\frac{\varepsilon_T}{\varepsilon_{AB}} - \frac{T}{AB}\right)^2 + \left(\frac{\varepsilon_T}{\varepsilon_{BC}} - \frac{T}{BC}\right)^2 + \left(\frac{\varepsilon_T}{\varepsilon_{AC}} - \frac{T}{AC}\right)^2.$$
(1.36)

The minimization of the equation gives the values of the free parameters  $(\lambda_A, \lambda_B)$ and  $\lambda_C$  for a given kB value. The counting efficiency for a given coincidence type (double coincidence, triple coincidence, etc.) can be calculated using Table 1.1 and (1.28). The activity can be determined using the calculated counting efficiency and the counting rate for that coincidence type. As most information is contained in the logical sum of the double coincidences D, the activity A is expressed as:

$$A = \frac{D}{\varepsilon_D(kB, \lambda_A, \lambda_B, \lambda_C)},\tag{1.37}$$

Depending on the radionuclide, equation (1.36) can have 1 solution for pure  $\beta$ -emitters and 3 solutions for EC-emitters (see figure 1.1) [2]. In the case where the equation has three solutions, the counting efficiency must be varied experimentally to determine on which part of the curve the experimental TDCR lies.

Counting efficiencies calculated with the TDCR model are dependent on the choice of the kB parameter, which is the only adjustable parameter in the model.

For high energy  $\beta$ -emitters (over a few hundred keV), the influence of the chosen value of the kB parameter is negligible [2]. For radionuclides emitting low energy electrons (for example <sup>3</sup>H), the differences in the activities calculated with different kB values are significant. The dependance of the estimated activity of <sup>3</sup>H on the value of the kB parameter is illustrated on Figure 1.2.

Due to the specific requirements of the TDCR model, the use of specially designed LS counters, vials and multichannel analyzers is necessary.

## 1.4 Practical aspects of the TDCR model

There are some practical considerations which need to be taken for the proper application of the TDCR model. Special requirements exist for the liquid scintillation vials which need to be used as well as for the construction of the three PMT detector system.

#### Liquid scintillation vials

The main purpose of the liquid scintillation vials is to securely store the radioactive sample and cocktail and provide safe and stable handling. The most common types of vials used in liquid scintillation counting are plastic (polyethylene) vials and glass vials with low potassium content and a standard volume of 22 ml. The light output from plastic vials is higher than the one of clear glass vials due to their diffusive surface, which suppresses effects like total internal reflection and refraction [22]. The main drawback of plastic vials is the shorter long-term stability of the cocktail, which is caused mainly because it diffuses in the vial walls. There is no such effect in glass vials, but significant light trapping can occur due to the large difference in refractive indices between glass and air; this causes total internal reflection of some of the emitted light, which causes problems with the application of the TDCR model. It causes reduction of the total amount of light, emitted from the vial, thus reducing the detection efficiency, and it has a different probability of occurring depending on the location of the scintillation event inside the vial. The latter effect creates a dependency between the mean number of photons emitted from the vial and the location of the scintillation, which violates one of the primary assumptions of the TDCR model that the number of photons reaching the photocathodes of the PMTs follow a Poisson distribution with a mean value which is constant for the entire volume. A compromise can be achieved by using clear glass vials plastered with diffusive tape, or by creating diffusive glass vials by sandblasting or etching [19].

#### Liquid scintillation counters

The number of emitted photons in a liquid scintillation event is low in the case of low-energy  $\beta$ -emitters. This requires the use of very optimized optics and sensitive photomultipliers with high quantum efficiency of the photocathode. Quantum efficiency is defined as number of photoelectrons emitted from the photocathode divided by the number of incident photons and its range is from 20% to 40% [23]. As the TDCR model assumes non-zero detection probability for single photons, the PMTs must have good separation of the single electron peak from the noise peak for a proper adjustment of the analyzer's threshold. This requires the use of high-gain photodetectors with high peak-to-valley ratio on the single photon peak [24].

Considering that the signal from the phototubes is a few nanoseconds long, the electronics and signal processing unit of the detector must be able to process fast pulses. To reduce the effect of thermal noise in the PMTs, the analyzer of the detector must be able to detect coincident signal between the different PMTs. The usual duration of the coincident window (the maximum elapsed time between two pulses for which they are considered coincident) is between 40 - 200 ns.

When a photomultiplier tube is operated in a pulse detection mode, as in liquid scintillation counting, random pulses with small amplitudes following the signal output pulse may be observed. They are called afterpulses and often disturb the accurate counting of signals. There are two types of afterpulses: very short delay ones (several nanoseconds), caused by elastic scattering of electrons from the first dynode, and long delay ones, caused by positive ions created by the ionization of residual gases in the volume of the PMT [25]. The latter are following the signal after a delay in the order of microseconds, due to the slower movement of the heavier positive ions. To ensure the correct counting of scintillation pulses, the electronics of the LS detector must have a dead-time unit, which adds a dead-time period after each detected pulse to avoid false coincidences. The duration of the dead-time period is a few tens of microseconds. It is mandatory that the dead-time is from the extending type [2], that is whenever a pulse comes during a dead-time period, the period timer is set to zero and starts again. This ensures that every detected event will be preceded by an event free period. Precise knowledge of the dead-time is also important when measuring radionuclides with very short half-life daughter products in their decay chain (ex. <sup>214</sup>Po in the decay chain of <sup>222</sup>Rn with a half-life 160 µs). If the short lived product has half-life similar to the dead-time of the detector, a significant amount of the pulses, created by its decay, will be missed. By knowing the dead-time period with high precision, it is possible to make corrections when calculating the activity.

In order to implement the TDCR model, a specialized 3-PMT counter is needed. The three PMTs are positioned symmetrically around the vial at equal 120° angles. If the PMTs are identical, the simplified equations (1.32) and (1.33) can be used, but due to the high cost of matched PMTs, this is usually not the case. In non-identical PMT systems, the proper detection efficiency can be calculated using the system of equations (1.35).

A relationship exists between the coincident and non-coincident signals, which allows the formulation of two balance equations [6]:

$$A + B + C = T + D + S (1.38)$$

$$AB + BC + AC = 2T + D \tag{1.39}$$

To compute the equations, the detector must store information of the non-coincident signals (A, B, C), the logical sum of the non-coincident signals (S), the double coincidence signals (AB, BC, AC), the logical sum of the double coincidence signals (D) and the triple coincidence signals (T). Fulfillment of the balance equations on each acquisition run is a good indicator of the proper operation of the detector system [24].

#### Code for the implementation of the TDCR model

The determination of efficiency using the TDCR model requires the numerical integration of equations (1.3) and (1.35), the minimization of (1.36) and the computation of electron stopping powers. A specialized computer code has been developed to perform the calculations required by the TDCR method. The TDCR07c is an application devoted to the calculation of detection efficiencies and figure-of-merit of 3-photomultiplier tubes liquid scintillation counters for  $\beta$ -radionuclides [26]. The code, written by Philippe Cassette (LNHB), is used throughout this work to implement the TDCR method. The physical models used in the program are:

- Poisson statistics (1.15) for the light emission from the liquid scintillator
- Birks' law (1.1) for the non-linearity of the scintillator
- ICRU n°37 formula over 100 eV and linear extrapolation to zero under 100 eV for the stopping powers of the electrons in the LS cocktail

• Fermi model for the shape of the  $\beta$ -spectrum

The program uses the radionuclide atomic number and atomic mass, and the density and Z/A ratio of the LS cocktail as an input after which it presents various options for calculation to the user. One of the options (option 4) is to calculate the detection efficiencies from the three values of individual triple-to-double coincidence ratios (T/AB, T/BC, T/AC), when the asymmetry of the phototubes is not negligible. The program calculates the detection efficiencies of each 3 double coincidences  $(\varepsilon_{AB}, \varepsilon_{BC}, \varepsilon_{AC})$  and gives the relative quantum efficiencies of each PMT. A detailed explanation of the code can be found in [26].

#### Detection efficiency variation

The TDCR model provides means to calculate the detection efficiency of the detector system for given measurement conditions and for a given radionuclide. It is thus very useful to have a way of changing the conditions of the measurement in a way that changes the detection efficiency. If the application of the model is correct, the calculated activity of the measured sample should be independent of the variations in the detection efficiency. In a properly designed counter, the detection efficiency is always optimal, so the only way to vary the detection efficiency is to decrease it. There are several ways to decrease the detection efficiency of an LS counter: defocusing the photomultiplier tubes, decreasing the light output of the source by coaxial filters or by creating a set of quenched sources. There are indications that the three methods could be equivalent [19].

Detection efficiency variation is necessary in those situations where, as said previously, the detection efficiency versus the TDCR function has more than one solution. The only possibility in such a case is to vary the detection efficiency, to determine on which point on the curve the correct detection efficiency lies.

#### Determination of the kB parameter

The TDCR model has one external parameter, which is the ionization quenching parameter (kB) in the Birks' formula (1.3). The kB parameter characterizes the LS cocktail and, in the ideal case, it should be independent of the detection system. Due to the fact that it is the only variable parameter in the TDCR model, the choice of an optimal kB value starts to depend on the detection system parameters (geometry of the detector, vial type, cocktail volume, etc.). Measurements of the same sample



**Figure 1.3:** Calculated activity as a function of the TDCR at different kB values - high, optimal and low. A <sup>3</sup>H sample in a diffusive vial was used. The efficiency was varied using mesh filters with different density

in different conditions with different detection efficiencies give the possibility of determining the optimal kB value, for which the calculated activity of the sample does not depend on the measurement conditions. This is illustrated on Figure 1.3. In this example, the source that was measured is <sup>3</sup>H in a toluene based LS cocktail in a clear glass vial covered with diffusive tape. A set of 3D printed mesh filters with different density was used to reduce the detection efficiency. The activity was calculated using different values of the ionization quenching parameter kB. It is important to note that the optimal value for kB is chosen solely on the logic that the calculated activity of the source should be independent of the detection efficiency.

The choice of the kB parameter is very important for the correct calculation of the activity of low-energy emitters like <sup>3</sup>H (Figure 1.2). For the measurement of high-energy radionuclides, the influence of kB is less pronounced. This can be explained by the fact that the non-linearity of the light emission of the LS cocktail depends mainly on the non-linearity of the linear energy transfer of the electrons passing through the matter with energies less than 20 keV [19]. The light produced by higher energy  $\beta$ -emitters comes mainly from higher energy electrons, for which the linear energy transfer is constant.

#### Chapter 2

#### Design of the TDCR-SU detector system

A TDCR counter was recently developed in Sofia University's Faculty of Physics. The counter, hereafter called TDCR-SU, is an in-house built 3-PMT detector whose purpose is to preform primary measurements of activity of liquid scintillation samples by applying the triple-to-double coincidence ratio technique. The signals from the detector are analyzed by a specialized analyzer produced by the LabZY company, hereafter called nanoTDCR. A central database was designed specifically for processing and storing nanoTDCR output data.

The validity of the nanoTDCR device was tested by comparison of counting rates at the logical output of a MAC3 module. The performance of the TDCR-SU detector was validated by comparison with the French primary TDCR counter at Laboratoire National Henry Becquerel. The efficiency variation technique was also studied with the use of custom built 3D printed mesh filters and a <sup>3</sup>H LS sample.

## 2.1 The TDCR-SU counter

The design of the TDCR-SU counter was inspired from the design of the ENEA portable system [27]. The detector is equipped with three Hamamatsu R7600U-200 square photomultiplier tubes. They have small (30 mm x 30 mm) dimensions and a wide spectral response (300 nm - 600 nm) [23]. They work at a relatively low supply voltage (+850 V) and have a grounded cathode, which has lower dark noise [27]. The optical chamber of the TDCR-SU detector is made of Polytetrafluroethylene (PTFE, Teflon <sup>®</sup>), which is very reflective. The PMTs inside the optical chamber are positioned at a slight distance from the vial in a way that allows a full solid angle view of the vial. The optical chamber and PMTs are enclosed in a black Polyoxymetylene (POM) casing, which has a lid on the top that allows easy access

to the optical chamber, where the samples are inserted manually. The whole system, connected to the nanoTDCR analyzer and a portable computer, can be seen on Figure 2.1.



Figure 2.1: Snapshot of the TDCR-SU detector with LS vials for scale.

## 2.2 The nanoTDCR counting module

Due to the specific requirements of the TDCR method, a specialized counting module is needed. Currently the most widely used TDCR counting module worldwide is the MAC3, which is a standalone triple coincidence acquisition module conforming to the NIM standard. The coincidence window of the MAC3 is fixed and equal to 40 ns. The extendible dead-time base duration is configurable between 9 µs and 100 µs and is common to all three channels. Details on the operation and construction of the MAC3 can be found in [28].

Unlike most TDCR systems which use the MAC3 counting module, the TDCR-SU counter uses a nanoTDCR counting module developed by the labZY company [29]. The nanoTDCR is a standalone FPGA-based device dedicated to TDCR measurements. Similarly to the MAC3 it counts single events as well as coincidences between photomultipliers. The nanoTDCR has much additional functionality like software selectable coincidence window (from 8 ns to 190 ns) and dead-time base duration

(from 80 ns to 500 µs). It has the ability to count simultaneously using two independent coincidence windows and two independent dead-time base durations. Thus, one TDCR acquisition is equal to four measurements with a MAC3 and aditional spectrum acquisition. Unlike the other TDCR acquisition systems (including the MAC3), the nanoTDCR module has individual, extending type dead-time duration in each channel. In this regard it is very different from the other acquisition systems, which use a common dead-time for all channels More details on the operation of the nanoTDCR can be found in [3] and [30].

## 2.3 TDCR-SU and nanoTDCR performance evaluation

The evaluation of the performance of the TDCR-SU detector was first done by a comparison with the primary TDCR counter (RCTD1) at *Laboratoire National Henry Becquerel* (LNHB). The RCTD1 counter is a well-established TDCR counting system, which has been used since decades for absolute (primary) activity concentration measurements and standartization of radionuclides.

The operation of the nanoTDCR module was compared with the operation of the RCTD1's MAC3 module. The comparator thresholds of the TDCR-SU detector were adjusted using the nanoTDCR's MCA ability and the whole system was compared to RCTD1 by measurements of <sup>3</sup>H, <sup>14</sup>C, <sup>63</sup>Ni and <sup>241</sup>Am. These comparisons were done before the beginning of this thesis and they assert that the nanoTDCR is a fully functional TDCR counter.

#### Comparison between nanoTDCR and MAC3

The comparison between the nanoTDCR and the MAC3 modules was made using the RCTD1 detector. The PMTs of the primary TDCR counter were connected to the MAC3 module, which has logical output after the constant fraction discriminators. These output signals were used as input on the nanoTDCR module and a simultaneous measurement with the two modules was performed on four different <sup>241</sup>Am in UltimaGold sources with activities from 480 Bq to 4000 Bq. The results from the comparison are shown in Table 2.1 and the difference between the counting rates reported from the two systems is less than 0.3%, which can be attributed to the statistical variations of the different counting times of the two systems.

Source	Coinci	dences A	$B, s^{-1}$	Coincie	lences B	$C, s^{-1}$	Coincid	lences A	$C, s^{-1}$	Coincid	lences AI	$BC, s^{-1}$
	MAC3	nano TDCR	$\Delta, \%$	MAC3	nano TDCR	$\Delta, \%$	MAC3	nano TDCR	$\Delta, \%$	MAC3	nano TDCR	$\Delta, \%$
<sup>241</sup> Am-No1	490	490.5	-0.11	490	490.2	-0.04	490	490.2	-0.03	490	490.0	0.00
$^{241}\mathrm{Am}\text{-No2}$	1517	1519.7	-0.18	1516	1519.4	-0.22	1516	1519.3	-0.22	1516	1519.1	-0.21
$^{241}$ Am-No3	2557	2563	-0.23	2557	2562.6	-0.22	2557	2562.6	-0.22	2557	2562.3	-0.21
$^{241}$ Am-No4	4604	4599.7	0.09	4604	4599.4	0.1	4604	4598.8	0.11	4604	4599.1	0.11

**Table 2.1:** Comparison between the coincidence counting rates on nanoTDCR and MAC3, both measuring the same sources on RCDT1 simultaneously [3]

#### Adjustment of the thresholds of the TDCR-SU system

The proper operation of a TDCR system requires the adjustment of the thresholds of the discriminators of each PMT channel. If the discriminators are set too low, there will be high amount of false coincidences, due to the counting of noise and, if the discriminators are set too high, single photon events will be lost. The optimal discriminator threshold has to be in the valley between the single electron peak and the noise peak [19].

In order to find the optimal thresholds for the TDCR-SU system, nanoTDCR's MCA capabilities were used. The applied voltage on the PMTs was +850 V and the single electron spectrum was acquired without a source in the detector. The optimal thresholds were found to be 3.6 mV, 4.0 mV and 4.0 mV for PMTs A, B and C respectively. For more details see [3].

#### Comparison between the RCTD1 and TDCR-SU systems

After validating the proper operation of the nanoTDCR module, the same set of <sup>241</sup>Am sources were used to quantify the performance of the whole TDCR-SU detector. The sources were measured for 10 min counting time first on the RCTD1 detector and then on the TDCR-SU detector. The results from the comparison are shown on Table 2.2. The differences  $\Delta$  of the net (background corrected) counting rates  $n_0$  between the two detectors were calculated using

$$\Delta = \frac{n_0^{TDCR-SU}}{n_0^{RCDT1}} - 1$$

and are in all cases below 0.30 % and no systematic trend is observable, which indicates a linear response of the TDCR-SU detector in the range 480 - 4600 counts per second.

<sup>241</sup> Am Source	Logical s coincide	sum of net do nces $(D)$ , s <sup>-1</sup>	ouble	Net triple coincidences (T) , s <sup>-1</sup>			Ratio T/D		
	RCTD1	TDCR-SU	$\Delta,\%$	RCTD1	TDCR-SU	$\Delta, \%$	RCTD1	TDCR-SU	$\Delta, \%$
No 1	487	486.4	0.12	487	486.1	0.18	1.0000	0.9994	0.06
No 2	1513	1515.2	-0.15	1513	1514.1	-0.07	1.0000	0.9993	0.07
No 3	2553	2559.5	-0.25	2554	2557.6	-0.14	1.0004	0.9992	0.11
No 4	4600	4591.2	0.19	4601	4588.0	0.28	1.0002	0.9993	0.09

**Table 2.2:** Comparison between RCTD1 and TDCR-SU using a set of  $^{241}Am$  sources with increasing activity. The counting rates shown are the net counting rates, after the subtraction of background measurement [3]

The two detectors were also compared by measurements of three pure  $\beta^-$ -emitters, <sup>3</sup>H , <sup>14</sup>C and <sup>63</sup>Ni. The sources were measured on the RCDT1 and TDCR-SU detectors consecutively. The net counting rates were obtained after the subtraction of measurements of a blank sample. The activities of the sources were determined by applying the TDCR model for a detector with three non-identical PMTs. To preform the calculation, the TDCR07c program was used [26]. The same cocktail data and value for the kB parameter was used for the analysis of the results from the two detectors. The calculated activities are shown on Table 2.3. Both systems are in excellent agreement for the <sup>3</sup>H and <sup>14</sup>C sources. The discrepancy between the two detectors for the <sup>63</sup>Ni activity calculations is, most probably, due to low counting statistics or accidental illumination of the photodetectors before the measurement. Nevertheless, the calculated activities agree if expanded uncertainties (k = 2) are considered.

Source	Activity, Bq (RCTD1, LNHB)	Activity, (TDCR-SU)	$\Delta$ *, %
$^{3}\mathrm{H}$ , toluene-based LSC	1010.7 (2.1) [0.21%]	1010.9 (5.1) [0.50%]	-0.02%
$^{14}\mathrm{C},$ toluene-based LSC	1728.2~(2.4)~[0.14%]	1731.3~(4.7)~[0.27%]	-0.18%
<sup>63</sup> Ni, UltimaGold AB LSC	1325.9 (4.1) $[0.31\%]$	1313.9 (4.9) $[0.37\%]$	0.91%

**Table 2.3:** Comparison between RCTD1 and TDCR-SU activity measurements of  ${}^{3}H$ ,  ${}^{14}C$  and  ${}^{63}Ni$  [3]

Part II: Developments and results

#### Chapter 3

#### Creation of a web-application for data storage and analysis

Due to the large volume of the data that is produced in each measurement with the nanoTDCR, the development of an application with the ability to store and filter data was necessary. The nanoTDCR module collects data from live timers and counters for all coincident and non-coincident channels, A, B, C, AB, BC, AC, ABC, for two different extended dead times, EXT1 and EXT2, and two different coincidence windows, N and M. It stores data about the start time of each measurement, as well as some important detector parameters like the level of the discriminator thresholds and applied high voltage. This data is stored into a file after the end of each measurement. A typical output file from a measurement with 10 runs is 840 lines long.

In the scope of this thesis a web-based application was written in Python 3.6 using the Flask framework [31] to facilitate the analysis of the results from TDCR measurements. A web application was preferred over a local code because it can be used from any device, which has a web-browser and internet access. When the web-site of the application is accessed, the user is greeted with a login screen where he can enter his credentials. Only after valid username and password are entered, the user can access the application. The web-app is created in such a way that allows multiple accounts, each having access to his and only his data. This allows the use of the same application by many nanoTDCR systems without interference between users.

The application has a simple front-end interface (shown on Figure 3.1), where it allows the upload of multiple nanoTDCR files (with extension ".tdc" called tdc files hereafter) united under a common series name, which allows easier access later. The tdc files are uploaded to a server, which executes a routine that arranges all the data from the file into a MySQL database hosted on the server. The web-app has the ability to export data from the database, based on user selectable filters: series

a)			b)		
Upload	files		Export table		
Series	Series name Radon standartization		Series name	tritium	
	Series name is not used		Radionuclide	H-3	Ŧ
Upload files to database			Coincidence window N [ns]	100	Ŧ
Q Browse Select one or r	26 files sele	.tdc extension	Coincidence window M [ns]	Any	•
• Upload			Extended Dead Time 1 [us]	50	•
Series name fi	ield is required	41	Extended Dead Time 2 [us]	Any	•
			• Export		
			Number of entries to be exported:	10	

Figure 3.1: View of the index page of the web-app for nanoTDCR datafiles analysis. Multiple files can be uploaded under a common series name (a) and data can be exported into a coma separated values file (b).

name, as entered by the user, extended dead-time duration, coincidence window duration and radionuclide type. The exported data can be downloaded in the comma separated values format ("csv"), which can be easily manipulated by commonly used spreadsheet softwares (Microsoft Office Excel, LibreOffice Calc and others). The user is also provided with the ability to view and manipulate the database entries as well as the uploaded files.

The database has proved to be very useful repository for the TDCR measurement data. It allows safe and structured handling of nanoTDCR generated information with options for fast search, export and filtering of large quantities of data.

#### Chapter 4

## Study of the efficiency variation technique using 3D printed mesh filters

## 4.1 Design of the filters

In order to study the efficiency variation technique on the TDCR-SU detector, six 3D printed mesh filters were used. Five of them were printed using white PLA (Polylactic acid, a commonly used polymer for 3D printing) and the last one from black PLA. For easier printing, the filters were designed as a flat mesh. After printing the flat mesh, the whole detail is twisted into a cylindrical shape by overlapping the two outer slits, which are then glued together with glue. The cylindrical mesh has 15 slits, aiming conserve the triangular symmetry of the TDCR counter. The filters are 49 mm high, enough to enclose the whole vial. All filters have the same design and differ only in their opacity, which is determined by the width of the slits. The dimensions of the filters are summarized in Table 4.1. A snapshot of the completed filters is shown on Figure 4.1.

## 4.2 Evaluation of kB for a <sup>3</sup>H source

The filters were tested with a certified <sup>3</sup>H Wallac source and a background sample on the TDCR-SU detector. The source and background sample are contained in a flame sealed glass vial, which was covered with diffusive tape to reduce the effect of the total internal reflection on the boundary between glass and air (Figure 4.2).

The <sup>3</sup>H source is certified at 190600 dpm activity as of 1 April 1986. The activity of the source at the time of measurements, according to the source certificate, is 553.5(83) Bq and thus a 2 h counting time per measurement for the second experiment was chosen to ensure good counting statistics. To reduce the standard deviation



**Figure 4.1:** Photograph of the completed filters. From left to right - BF1, WF1, WF2, WF3, WF4 and WF5.

of the mean of the measured activity, 10 measurements of both  ${}^{3}\text{H}$  and background were made, first without a filter and then for each filter (white filters WF from 1 to 5 and BF1).

The nanoTDCR's feature for consecutive measurements was used to make all series of measurements. The thresholds of the comparators for PMTs A, B and C were set to 3.6 mV, 4.0 mV and 4.0 mV respectively. For all measurements the high voltage supplied to the phototubes was +850 V. The nanoTDCR has the ability to count simultaneously with two different extended dead times (EXT1 and EXT2) and two different coincidence windows (Window N and Window M). Each measurement with the nanoTDCR module is equal to four measurements – Window N and EXT1, Window M and EXT1, Window N and EXT2, Window M and EXT2. For all measurements Window N was set to 100 ns, Window M to 40 ns, EXT1 to 40 us and EXT2 to 100 us.



Figure 4.2: Source and background samples wraped in diffusive tape

## 4.3 Experimental results

The measured counting rates for extended dead-time EXT1 40 µs and EXT2 100 µs were the same, within the estimated uncertainties, but the counting rates for Window N 100 ns were higher than those for Window M 40 ns. All subsequent processing of the data was made once for Window N and once for Window M. The net coincidence counting rates for AB, BC, AC, T were calculated as:

$$n_i^0 = n_i - n_i^b, \quad i = AB, \ BC, \ AC, \ T,$$
(4.1)

where n is the counting rate of the sample,  $n^b$  is the counting rate of the background and  $n^0$  is the net coincidence counting rate. For each measurement a different background was subtracted to ensure that the different  $n_0^i$  estimates are independent and that the estimates of the uncertainties of the counting rates are uncorrelated.

The efficiency for the logical sum of the double coincidences was obtained for kB values from 0.007 cm/MeV to 0.018 cm/MeV with 0.0005 cm/MeV increments using the TDCR07c program for each measurement. The option for three non-identical PMTs was used. The mean and the standard deviation of the activity for each filter and each kB value were calculated. All calculated activities were corrected for the decay of <sup>3</sup>H (half-life – 12.312 years).

The calculated activity as a function of the TDCR was fitted with a linear function for every kB value from 0.009 cm/MeV to 0.018 cm/MeV. The optimal kB value is the one for which there is minimal or no dependence of the calculated activity on the detection efficiency. In the case of the Wallac <sup>3</sup>H source in a toluene-based cocktail the optimal kB value is 0.013 cm/MeV. The standard uncertainty of the kB parameter can be estimated if we assume that the real value is found in the interval from 0.012 cm/MeV to 0.014 cm/MeV with equal probability. The standard deviation  $\sigma$  of a uniform distribution in the interval from a to b is  $\sigma = (b-a)/\sqrt{12}$ , thus the uncertainty of the calculated activity of the sample, due to the uncertainty in the choice of ionization quenching parameter, is 0.28 %. The uncertainty due to variability in the background is less than 0.01% and the statistical uncertainty of the different measurements is 0.03%. The calculated activity of the Wallac <sup>3</sup>H sample, by means of the TDCR method, is 554.6(16) Bq with a combined relative uncertainty 0.3% at the time of the first measurement (16 Oct 2017). The certified activity of the source is 553.6(8.3) Bq. The two results are in excellent agreement and the difference in activities is less than 0.3%.

This experiment demonstrates the usability of the 3D printed mesh filters for efficiency variation in the TDCR method. The calculated activities for different



Figure 4.3: Activity as a function of the TDCR for kB values from 0.009 cm/MeV to 0.018 cm/Mev for the measurements with coincidence window 40 ns. The data points are shown with their expanded uncertainties (k = 2), which were calculated as the standard deviation of the 10 runs of each measurement. A good linearity is observed for TDCR in the range 0.3 to 0.5. The red line at kB = 0.013 cm/MeV shows the least slope.

detection efficiencies are in good agreement and the estimated kB value is consistent with values reported by other researchers. The calculated, by the TDCR method, activity of the Wallac <sup>3</sup>H source is in excellent agreement with that reported in the source certificate and the estimated combined relative uncertainty is 0.3%.

## 4.4 Measurements with mesh filters on RCTD1

In order to study the 3D printed mesh filters, they were measured at LNHB on the primary TDCR detector - RCTD1. The source that was measured was a tritiated water sample in UltimaGold liquid scintillation cocktail. A total of nine measurements were made, one with each filter. A measurement consists of 10 runs, 60 seconds each. Due to the short measurement durations, the statistical uncertianties are in



**Figure 4.4:** Activity as a function of the TDCR for kB values from 0.009 cm/MeV to 0.015 cm/Mev for the measurements of 3D printed mesh filters on LNHB's RCTD1 detector

the order of 0.2%.

The detection efficiency for tritiated water in UltimaGold cocktail is much lower than that for <sup>3</sup>H in toluene-based cocktail. In order to have a more complete set of data points for higher TDCRs, two more 3D printed mesh filters were prepared for the experiment (WFn1 and WFn2). The new filters are created in the same manner as the previous, but with wider slits.

The calculated activity of the sample as a function of the TDCR for kB values from 0.009 cm/MeV to 0.015 cm/MeV is shown on Figure 4.4. Good linearity can be observed for the filters above 0.32 TDCR. This indicates that the mesh filters can be used for efficiency variation as they give consistent results for measurements on the primary TDCR detector of LNHB - RCTD1.



**Figure 4.5:** Activity as a function of the TDCR for kB values 0.011 cm/MeV (blue), 0.013 cm/MeV (red) and 0.015 cm/MeV (green) and coincidence windows M 40 ns (hollow circles) and N 100 ns (filled circles). The data points are shown with their expanded uncertainties (k = 2), which were calculated as the standard deviation of the 10 runs of each measurement.

## 4.5 Coincidence window width

<sup>3</sup>H decays by the emission of a  $\beta^-$  particle with 18.564 keV maximum energy and 5.68 keV mean energy. In a typical LS cocktail around 1 keV of energy is needed to produce 1 photon, resulting in the emission of a Poisson distributed number of photons with an average of 5 to 6 photons per disintegration. Such low number of emitted photons leads to the possibility of significant time-spread in the signals from the PMT's, whose arrival times are distributed exponentially. If the coincidence window of the counter is too narrow some signals from low number of photon events could be missed. This is not the case for higher energy  $\beta$ -emitters and  $\alpha$ -emitters, which cause the emission of a large number of photons, for which it is much more probable that the coincidence events are more grouped together in time. Due to nanoTDCR's ability to count simultaneously with two different coincidence windows (Window N and Window M) it was interesting to evaluate the effect of the choice of coincidence window width on the calculated activity. The same data from the experiment on TDCR-SU for the evaluation of kB for a <sup>3</sup>H source was used, where the nanoTDCR was set to count with coincidence window N equal to 100 ns and coincidence window M equal to 40 ns. It is important to emphasize, that for the same measurement the nanoTDCR outputs the counting rates using two different coincidence window widths. In all measurements the counting rates for the 40 ns window were lower than those for 100 ns, which indicates a reduced detection efficiency at the narrower coincidence window. The detection efficiencies for each run were calculated in the same manner as for the previous experiment. The calculated activities as a function of TDCR are shown on Figure 4.5. The statistical uncertainties are estimated as the standard deviation of calculated activities for the 10 runs in each measurement.

The calculated activities at 40 ns coincidence window and at 100 ns coincidence window agree well within the estimated uncertainties, which indicates that the couning rates reported by the nanoTDCR give consistent results for both coincidence windows.

## 4.6 Filter characterisation

A good characteristic of a filter should be such that it provides means to make a priori estimation of the expected TDCR of a sample, measured with that filter. The transparency of a cylindrical mesh filter, which can be defined as the ratio of the area of the slits to the total area of the cylinder, is a poor parameter of the filter as it does not account for the reflectivity of the filter's material as well as effects like diffraction and transparency of the material itself. It is interesting then to find a characteristic parameter of a given filter that describes its light transmission properties and is independent of the measured source and used cocktail. One such characteristic could be the percent of light output R that is reduced by the filter. It can be calculated as:

$$R = \frac{\lambda_i \text{ with fitler } i}{\lambda_0 \text{ without filter}},\tag{4.2}$$

where  $\lambda_i$  and  $\lambda_0$  are figures of merit, defined as the number of photoelectrons created at the photocathode of the phototube per keV energy released in the cocktail (see Eq. (1.27) and the associated text). To determine the value of  $R_i$ , for each filter *i*, the figure of merit  $\lambda_i$  has to be determined from the TDCR model for measurement of a source with or without filter.

Measurements of the Wallac <sup>3</sup>H source described in section 4.2 were used to determine the R values of the 3D printed mesh filters. The figure of merit  $\lambda_0$ , without a filter, as well es the figures of merit  $\lambda_i$  for measurements with each filter i = (WF1, WF2, WF3, WF4, WF5) were calculated from the experimental T/AB, T/BC and T/AC ratios by using the TDCR07c code. The calculated values of the percent of light output that is reduced by the filter R were determined from (4.2) and are shown in Table 4.1.

Filter Name	PLA color	$\mathbf{Slits}$	$\begin{array}{c} {\rm Slit\ width,}\\ {\rm mm} \end{array}$	Transparency, $\%$	$\lambda_i, {f e}^-/{f keV}$	R
None	_	_	_	100	0.92	1.00
WF1	White	15	4.8	75	0.84	0.91
WF2	White	15	4.0	63	0.78	0.85
WF3	White	15	3.2	50	0.75	0.82
WF4	White	15	2.0	31	0.61	0.66
WF5	White	15	0.4	6	0.43	0.47
BF1	Black	15	4.8	75	0.50	0.54

**Table 4.1:** 3D printed mesh filter parameters. The transparency is calculated as the ratio of area of the slits to the total area of the cylinder.

After the filters were characterized using the reference sample and their  $R_i$  were found, a test sample was measured (<sup>3</sup>H in UltimaGold in diffusive vial) without a filter. The figure of merit of the test sample without a filter was calculated using the TDCR07c program and was found to be  $\lambda'_0 = 0.604 \text{ e}^-/\text{keV}$ . The experiment was performed to test if the already determined  $R_i$  values of the filters are independent of the source and cocktail which is measured and if they can be used to predict TDCR values that will be obtained when the filters are applied to the sample. The equation,

$$\lambda_i' = R_i \lambda_0',\tag{4.3}$$

was used to determine the expected figure of merit  $\lambda'_i$  for the test sample with filter *i*. The calculated figure of merit of each filter  $\lambda'_i$  is shown on Table 4.2. The predicted TDCR is calculated from  $\lambda'_i$  with the TDCR07c program, using the option to calculate TDCR and detection efficiency from figure of merit (TDCR predicted

column). After the expected TDCR values were determined the sample was measured with the mesh filters and the experimental TDCR value was recorded (TDCR measured column). The relative difference between the predicted and experimental TDCR values is shown in the last column.

**Table 4.2:** The figure of merit ( $\lambda'_0 = 0.604 \ e^-/keV$ ) shown in bold is for a <sup>3</sup>H sample that was measured without any filters. The expected figures of merit with each filter were calculated using the predetermined R values. The expected TDCR values were calculated using TDCR07c from the expected figures of merit and were compared to the experimentally measured ones.

Filter	R	$\lambda'_{\cdot}$ , e <sup>-</sup> /keV	TDCR	TDCR	Diff. %
			(predicted)	(measured)	
None	1.00	0.604	-	0.375	-
WF1	0.91	0.551	0.347	0.334	3.9
WF2	0.85	0.512	0.327	0.320	2.2
WF3	0.82	0.492	0.317	0.300	5.7
WF4	0.66	0.400	0.267	0.263	1.5
WF5	0.47	0.282	0.196	0.180	8.9

To test whether the R values of the filters are truly intrinsic to the filter, and do not depend on the geometry of the detector system, the same experiment was performed on the RCTD1 detector at LNHB. The same 3D printed mesh filters were used, whose R values are already known. A <sup>3</sup>H in UltimaGold sample in diffusive glass vial was measured without a filter on the RDCT1 detector and the calculated figure of merit of the sample is  $\lambda_{0,\text{RCTD1}} = 0.845 \text{ e}^-/\text{keV}$ . The expected figures of merit  $\lambda_{i,\text{RCDT1}}$  were calculated using this value and the already known  $R_i$  value for each filter i (Column  $\lambda_{i,\text{RCDT1}}$  of Table 4.3). The expected TDCR was calculated from the expected figures of merit using the TDCR07c code's option to calculate TDCR from given figure of merit (option 2). The results are shown on Table 4.3. The predicted TDCR values agree well with the measured TDCR values for filters WF1, WF2, WF3 and WF4. The discrepancy between the predicted and observed TDCR for WF5 could be due to the low amount of light in this case.

It seems that the R value, defined as the ratio of the figure of merit with filter to the figure of merit without a filter, is a good characteristic of a given filter, which is independent of the measured cocktail. A good agreement can be observed between the predicted TDCR values and the experimentally obtained TDCR values for the measurement of <sup>3</sup>H in UltimaGold samples on both the TDCR-SU detector at Sofia University and the RCTD1 detector at LNHB. The R value is a useful parameter of the filter, as it can be used to determine what TDCR value will be obtained when a measurement of a particular sample with that filter is done.

**Table 4.3:** The figure of merit  $(\lambda_{0,RCDT1} = 0.845 \text{ e}^-/\text{keV})$  shown in bold is for a <sup>3</sup>H sample that was measured without any filters on RCTD1. The expected figures of merit with each filters were calculated using the predetermined R values. The expected TDCR values were calculated using TDCR07c from the expected figures of merit and were compared to the experimentally measured ones.

Filter	R	$\lambda_{i, extbf{RCDT1}}, \  extbf{e}^-/ extbf{keV}$	TDCR (predicted)	TDCR (measured)	Diff, $\%$
None	1.00	0.845	-	0.471	-
WF1	0.91	0.772	0.448	0.438	2.2
WF2	0.85	0.716	0.426	0.423	0.7
WF3	0.82	0.689	0.415	0.402	3.1
WF4	0.66	0.560	0.356	0.367	-3.0
WF5	0.47	0.395	0.268	0.305	-12.0

#### Chapter 5

#### Application to LSC of tritiated water

The application of the TDCR method, using the TDCR-SU counter, to the measurement of tritiated water was studied. To perform the study two sets of tritiated water samples in two different LS cocktails were prepared. The efficiency variation technique was applied to two samples with different LS cocktails in order to determine the ionization quenching parameters of the two sets. The determined kB values were then used for the calculation of the specific activity of the samples.

## 5.1 Sample preparation

A total of ten liquid scintillation samples containing tritiated water and two background samples were prepared for measurement. The background samples (blanks) were produced in the same way as the tritiated water samples. They have the same water content, volume of the cocktail and vial type and the only difference is that they do not contain any activity. The samples containing <sup>3</sup>H are two sets of five samples, one <sup>3</sup>H in UltimaGold (UG for short) LS cocktail and the other <sup>3</sup>H in UltimaGold LLT (UGLLT for short) LS cocktail. All samples contain a known amount of tritiated water with the same specific activity. The masses of the droplets, summarized in Table 5.1, were measured on a sensitive balance with uncertainties in the order of 4 µg.

The vials used for the preparation of the sources are sandblasted glass vials. They have diffusive surface which ensures minimal total internal reflection on the boundary between glass and air. This is very important for the efficiency variation technique and for the proper application of the TDCR method.

## 5.2 Determination of the ionization quenching parameter

#### Measurements with 3D printed mesh filters

The two sets of samples are in two different LS cocktails which, supposedly, have two different ionization quenching coefficients kB. It is important then to apply the efficiency variation technique for the two cocktails in order to determine the corresponding optimal values for kB. One representative sample from both sets was chosen as the kB value determined for one cocktail should be applicable to the samples with the same cocktail, as long as the same geometry and vial type are used. The UG5 (<sup>3</sup>H in UltimaGold) and UGLLT2 (<sup>3</sup>H in UltimaGold LLT) samples were chosen due to their higher mass content of <sup>3</sup>H which would lead to higher activity of the sample and better counting statistics. To conduct the experiment the set of five 3D printed mesh filters, described in section 4.1, were used.

The sample and background were measured at least two times with each filter. A measurement consists of 11 runs, 3600 s each. The first run of each measurement is discarded, in order to remove noise from light excited fluorescence of the photocathodes of the PMTs.

The thresholds of the nanoTDCR were set to 3.6 mV, 4.0 mV and 4.0 mV for PMTs A, B and C respectively. The applied high-voltage was +850V and all results are shown for coincidence window 100 ns and dead-time base duration 60 µs.

Due to the lower light output from UG and UGLLT cocktails, compared to a toluene-based LS cocktail, only the first four more transparent mesh filters were used (WFn1, WFn2, WF1, WF2 and WF3).

#### Analysis and results

The results from the measurements were analyzed in the same manner as described in section 4.2. The net coincidence counting rates AB, BC, AC, T were calculated as:

$$n_i^0 = n_i - n_i^b, \quad i = AB, \ BC, \ AC, \ T,$$
 (5.1)

where n is the counting rate of the sample,  $n^b$  is the counting rate of the background and  $n^0$  is the net coincidence counting rate. For each measurement of <sup>3</sup>H a different background was subtracted to ensure that the different measurements are



**Figure 5.1:** Application of the efficiency variation technique to the UG5 sample. The points at  $TDCR \approx 0.3$  and below were omitted in the linear regression due to the observed non-linearity of the model calculations. The optimal kB value is found to be 0.013(2) cm/MeV.

independent and that the estimates of the uncertainties of the counting rates are uncorrelated. The efficiency for the logical sum of the double coincidences was obtained for kB values from 0.007 cm/MeV to 0.018 cm/MeV with 0.0005 cm/MeV increments using the TDCR07c program (described in section 1.4) for each measurement. The mean and standard deviation of the calculated specific activities were calculated for every filter and all kB values. The results from the UG sample are shown on Figure 5.1 and those from the UGLLT sample on Figure 5.2.

The results from the UG sample with WFn2 were omitted in the kB value determination because those measurements were done last and the it is suspected that the cocktail had become unstable. This was established after it was found that the TDCR changed in the course of the measurement. Measurements for all other filters do not show drift in the TDCR value.

A different ionization quenching parameter was observed for both LS cocktails. The optimal kB value for the UltimaGold cocktail is 0.013(2) cm/MeV and for the UltimaGold LLT cocktail is 0.0100(15) cm/MeV. These values were used for all subsequent calculations on the activity of the other samples.



**Figure 5.2:** Application of the efficiency variation technique to the UGLLT2 sample. The optimal kB value is found to be 0.0100(15) cm/MeV.

## 5.3 Determination of the specific activity

All UG and UGLLT samples were measured without filters on the TDCR-SU detector. All measurements consist of 11 runs of 3600 s each. The activity for each run in each measurement of each sample was calculated using the TDCR07c code using the measured T/AB, T/BC, T/AC ratios and the determined kB values. The uncertainty of the determined activity for each sample was calculated as the quadratic sum of the statistical uncertainty and the uncertainty coming from the choice of optimal kB value. The statistical uncertainty was calculated as the standard deviation of the calculated activities for each run in a measurement of a sample. The uncertainty coming from the choice of optimal kB was calculated by assuming that the real kBis found in the interval between  $kB_a = 0.015 \text{ cm/MeV}$  and  $kB_b = 0.011 \text{ cm/MeV}$ for the UltimaGold samples and between  $kB_a = 0.0115 \text{ cm/MeV}$  and  $kB_b = 0.0085$ cm/MeV for the UltimaGold LLT samples. The activity of the sample can be calculated for kB values at the endpoints of the interval  $[kB_a, kB_b]$ . Standard uncertainty of the activity can be calculated as  $\sigma_A = (A_a - A_b)/\sqrt{12}$  (the standard deviation of a uniform distribution), where  $A_a$  is the activity calculated for  $kB = kB_a$  and  $A_b$  is the activity calculated for  $kB = kB_b$ .

The average specific activities and the uncertainties of each sample are shown on Table (5.1). The calculated specific activity of sample UGLLT5 is an outlier, most probably due to some loss of activity in the preparation of the sample. The averaged specific activity for the UltimaGold LLT samples is 52.82(55) Bq/mg and for the UltimaGold samples is 53.26(44) Bq/mg. The uncertainties are estimated as the quadratic sum of the standard deviation of the activities of the samples and the uncertainty due to the choice of kB value. The estimated specific activities are comparable within the estimated uncertainties.

Sample name	Mass, mg	Activity, Bq	$\sigma_A, \operatorname{Bq}$ $(\operatorname{stat})^1$	$\sigma_A, \operatorname{Bq}$ (kB only) <sup>2</sup>	$\sigma_c$ , Bq $(\text{comb})^3$	Specific activity, Bq/mg
UGLLT1	7.955	416.52	0.26	2.84	2.86	52.36(36) [0.69%]
UGLLT2	13.54	718.76	0.36	4.88	4.90	53.08(36) [0.68%]
UGLLT3	7.850	417.96	0.31	2.85	2.87	53.24(36) [0.69%]
UGLLT4	7.508	394.88	0.29	2.67	2.69	52.59(36) [0.68%]
UGLLT5	7.346	380.48	0.25	2.58	2.60	51.79(35) [0.68%]
UG1	8.863	403.41	0.27	2.89	2.90	53.32(33) [0.61%]
UG2	7.594	471.11	0.35	3.38	3.40	53.28(45) [0.84%]
UG3	8.889	468.27	0.36	3.36	3.38	52.84(38) [0.72%]
UG4	7.492	399.62	0.35	2.85	2.87	53.50(38) [0.72%]
UG5	9.175	488.13	0.14	3.47	3.47	53.37(38) [0.71%]

 Table 5.1: Results from the measurements of all tritiated water samples.

<sup>1</sup> Statistical uncertainty of the activity calculated as the standard deviation of ten measurements.

 $^2$  Uncertainty coming from the choice of ionization quenching parameter.

 $^3$  Combined uncertainty taken as the quadratic sum of uncertainties.

#### Chapter 6

## Application to <sup>222</sup>Rn measurements

Radon is a radioactive noble gas without stable isotopes. Measurements and standartization of the activity of <sup>222</sup>Rn are of practical interest because it poses a risk to human health as it can be accumulated in people's homes and, when inhaled, it and its short lived progeny damage the lungs. <sup>222</sup>Rn is the second leading cause of lung cancer in the world [32], [33].

 $^{222}\mathrm{Rn}$  is produced by the decay of  $^{226}\mathrm{Ra}$  and in turn decays with a half-life of 3.8232(8) days through a decay chain containing two  $\alpha-\mathrm{emitters}$  ( $^{218}\mathrm{Po}$  and  $^{214}\mathrm{Po}$  and two  $\beta-\mathrm{emitters}$  ( $^{214}\mathrm{Bi}$  and  $^{214}\mathrm{Pb}$ ) to  $^{210}\mathrm{Pb}$  which has a much longer half-life (22.2 a). The decay chain of  $^{222}\mathrm{Rn}$  is shown on Figure (6.1). Due to the relatively long half-life of  $^{210}\mathrm{Pb}$ ,  $^{222}\mathrm{Rn}$  reaches equilibrium with its short lived progeny after a period of around 5 hours. The activity of  $^{210}\mathrm{Pb}$  is negligible during the first few days after the production of  $^{222}\mathrm{Rn}$ .

#### 6.1 Preparation of the sources

To perform a test on the TDCR measurements of the <sup>222</sup>Rn dissolved in a liquid scintillator, two sources of <sup>222</sup>Rn dissolved in a liquid scintillator UltimaGold LLT were made. Both sources are in clear high-performance glass vials (Perkin-Elmer), closed with plastic foil-line caps. The sources were prepared by first creating a 10 ml cocktail containing <sup>222</sup>Rn and then transferring 4 ml of the same cocktail into another glass vial. The first source was made by taking in 10 ml of air from a <sup>222</sup>Rn generator with a syringe and ejecting it slowly through an air filter and a pipette to the bottom of a vial, filled with 10 ml LS cocktail. The air filter was used to prevent <sup>222</sup>Rn daughter products from entering the cocktail. The two vials were then filled to the top with LS cocktail and were closed with foil-line caps to prevent Radon gas



Figure 6.1: The <sup>226</sup>Ra decay chain

from escaping. Both sources were measured on a RackBeta 1219 LS counter right after closing the vials. The first source (S1) showed around 500 cps and the second source (S2), around 20 cps. A background sample (Blank) was also prepared - 22 ml UltimaGold LLT in clear high-performance glass vial.

## 6.2 Standardization using the TDCR method

The measurement of the samples is done with the TDCR-SU detector with the nanoTDCR counting module. The nanoTDCR has the ability to count using two different dead times simultaniously and these dead times can be selected from 80 ns to 500 µs. Due to its very short half-life of 165 µs, the decay product of radon, <sup>214</sup>Po can decay during the dead-time of the detector [34]. This will result in a reduced detection efficiency for that radionuclide. The counting rate, calculated for the live time of the detector and taking into account the correction for decays of <sup>214</sup>Po during the effective dead-time of the detector, is [34]:

$$R = \varepsilon_{Rn222} S_{Rn222} A_{Rn222} + \varepsilon_{Po218} S_{Po218} A_{Po218} + \varepsilon_{Pb214} S_{Pb214} A_{Pb214} + \varepsilon_{Bi214} S_{Bi214} A_{Bi214} + \varepsilon_{Po214} S_{Po214} A_{Po214} e^{\lambda \tau_{eff}},$$
(6.1)

where  $\varepsilon$  are the detection efficiencies of the radionuclides which are, 100% for the  $\alpha$ -emitters and nearly 100% for the high-energy  $\beta$ -emitters, S are the corresponding

emission probabilities, which are practically 100% for all nuclides in the chain, and A are the activities of <sup>222</sup>Rn and its daughter products. If we take into account also the relations between the activity of <sup>222</sup>Rn and activities of its daughters after they reach secular equilibrium, which according to the Bateman equations are [15]:

$$\frac{A_{Po218}}{A_{Rn222}} = 1.000558; \quad \frac{A_{Pb214}}{A_{Rn222}} = 1.00547; \quad \frac{A_{Bi214}}{A_{Rn222}} = 1.00910; \quad \frac{A_{Po214}}{A_{Rn222}} = 1.00910$$
(6.2)

Equation (6.1) can be written as:

$$R = A_{Rn222} \left( 1.0091 \varepsilon_{Bi214} + 1.00545 \varepsilon_{Pb214} + 2.000558 + 1.0091 e^{\lambda \tau_{eff}} \right)$$
(6.3)

The efficiencies of the high-energy  $\beta$ -emitters,  $\varepsilon_{Po-214}$  and  $\varepsilon_{Bi-214}$ , can be calculated with the TDCR model using their respective energy spectra. The proper choice of kB value is insignificant because the detection efficiencies are very close to 100% and can be chosen in the middle of the range of possible kB values for the used cocktail. By far, of largest importance to the correct calculation of the activity of <sup>222</sup>Rn is the correction for <sup>214</sup>Po, decaying during the effective dead-time of the detector  $\tau_{eff}$ .

## 6.3 Experimental results

The two samples, S1 and S2, were measured with different high-voltages, applied to the PMTs, different extending dead-times and different coincidence windows. All measurements are summarized in Table 6.1. The nanoTDCR's feature for consecutive measurements was used to make all series of measurements. The thresholds of the comparators for PMTs A, B and C were set to 3.6 mV, 4.0 mV and 4.0 mV respectively for all measurements, as these thresholds were determined from previous experiments to be the optimal ones for high-voltage +850 V. The threshold settings influence only the detection of very low energy  $\beta$ -particles, which, in the case of <sup>222</sup>Rn and its progeny, are almost negligible, thus the same thresholds were used when the applied high-voltage was +650 V and +750 V. NanoTDCR's ability to count simultaneously with two different extended dead times and two different coincidence windows was used, thus each measurement with the nanoTDCR module is equal to four measurements – Window N and EXT1, Window M and EXT1, Window N and EXT2, Window M and EXT2. The used extended dead-times in each measurement are shown on Table 6.1. The coincidence window width has no effect on the measured activity and is not shown on the table. All measurements were done at least 5 h after closing the vial, when the secular equilibrium between  $^{222}$ Rn and its daughter products is reached.

#	Sample	Runs	Runtime, s	High voltage, V	Dead-time, µs	Activity <sup>**</sup> , Bq
1		10	300	650	40	195.85(17)
1	SI, Blank	10	300	650	100	196.25(19)
0 01		10	100	750	40	197.23(27)
Z	SI, Blank	10	100	750	100	197.33(28)
3		10	100	750	80	198.01(23)
	SI, Blank	, Blank 10	100	750	150	198.29(24)
		10	100	850	40	197.20(27)
4	S1, Blank	10	100	850	100	197.55(29)
~		10	100	750	40	11.68(8)
5	S2, Blank	10	100	750	100	11.71(8)
6	S1	24	1800	750	40	197.32(6)*
7	S1	22	3600	750	40	197.39(12)*

 Table 6.1: Measurement results from the TDCR-SU detector

\*the backgrounds used to determine the net counting rates were taken from measurement #2.

\*\*the  $^{222}$ Rn decay constant is assumed for the calculated activities and the reference date and time is 1/23/2018 9:00 UTC.

The net coincidence counting rates for AB, BC, AC, T were calculated as:

$$n_i^0 = n_i - n_i^b, \quad i = AB, \ BC, \ AC, \ T,$$
 (6.4)

where n is the counting rate of the sample,  $n^b$  is the counting rate of the background and  $n^0$  is the net coincidence counting rate. For each measurement of <sup>222</sup>Rn a different background was subtracted to ensure that the different measurements are independant and that the estimates of the uncertainties of the counting rates are uncorrelated. The efficiency for the logical sum of double coincidences was calculated using a program, written by Phillipe Cassette, which is based on the TDCR07c program (described in section 1.4). It applies the TDCR model for the two  $\beta$ -emitters in the <sup>222</sup>Rn chain and has added correction for the decay of <sup>214</sup>Po during the deadtime of the measurement. The program was used for every run with the following parameters:

Method	Sample	Activity*, Bq	$\sigma_A, \mathbf{Bq}$	$\sigma_A/{f A}\;,\%$	Comment
TDCR	S1	197.60	0.60	0.3%	3 measurements x 10 runs x 100 s
TDCR	S1	197.32	0.06	0.03%	1 measurement x 22 runs x 1800 s
TDCR	S2	11.693	0.082	0.71%	1 measurement x 10 runs

Table 6.2: Measurements of samples S1 and S2 with TDCR-SU

\*the  $^{222}$ Rn decay constant is assumed for the calculated activities and the reference date and time is 1/23/2018 9:00 UTC.

- **Dead-time base value in microseconds** the extended dead-time base duration is used to calculate the correction for decay of <sup>214</sup>Po during the dead time of the instrument.
- LS cocktail type the LS cocktail type is needed for the TDCR model in order to calculate the stopping power of the particles. This is important for the correction for the non-unitiy efficiency for the  $\beta$ -emitters in the decay chain of <sup>222</sup>Rn. The cocktail used in this experiment is UltimaGold LLT.
- Calculation type The program has several modes of operation, one of which is to calculate the *Detection efficiency and figure of merit from TDCR*. This option was used for all calculations.
- Quantum efficiency of the PMTs The quantum efficiencies that were used were calculated from measurements of <sup>3</sup>H at +850 V high voltage and are PMT A = 0.3032; PMT B = 0.3486; PMT C = 0.3482.

The program returns the detection efficiency for the logical sum of double coincidences, which is then used to calculate the activity of the sample. The mean and the standard deviation of the activity for each measurement with both extended deadtime base durations (EXT1 and EXT2) was calculated. The same calculation was performed on measurements with different coincidence windows. The calculated activities are independent of the used coincidence window duration (100 ns and 60 ns)



**Figure 6.2:** All measurements on the sample S1. The natural logarithm of the activity is presented on the ordinate. Linear regression was used and the slope of the function was determined.

within the estimated uncertainties. All activities are calculated at a reference time 1/23/2018 9:00 UTC using the half-life of  $^{222}$ Rn . For the longer measurements (1800 s and 3600 s per run) a correction for decay during measurement was also applied. The counting rate n at the start of the measurement is calculated as follows:

$$n = n_0 \frac{\lambda t}{1 - e^{\lambda t}},\tag{6.5}$$

where  $n_0$  is the measured counting rate, t is the measurement duration and  $\lambda$  is the decay constant of <sup>222</sup>Rn in  $s^{-1}$ . Source S1 was measured for a longer period of time to determine the half-life of the sample and to compare it to the half-life of <sup>222</sup>Rn . Two measurements were made: first 24 runs for 1800 s each for a total of 12 hours and second 22 runs for 3600 s, each for a total of 22 hours. The estimated half-life of the sample from the first set of runs was 3.74(3) days, which does not correspond to the half-life of <sup>222</sup>Rn , 3.8232(8) days [35]. The same sample S1 was then measured on the RackBeta detector for a period of 4 days. The analysis on the counting rates showed a half-life of 3.8265(77) days, which is comparable with the half-life of <sup>222</sup>Rn within the estimated uncertainties. The second measurement of S1 on the TDCR-SU system was made 5 days after the first one. The observed half-life from both measurements is 3.821(12) days, which is comparable to the half-life of  $^{222}$ Rn within the estimated uncertainties (Figure 2). All measurements from the follow-up experiment are shown on the figure below. To calculate the half-life, the natural logarithm of the calculated activities was used and, in all calculations, a weighted linear regression was used.

## 6.4 Cocktail instability

The TDCR is a good indicator of stability of the source in the liquid scintillation cocktail. If there is a change of the TDCR in the course of the measurements this could be linked to a physical or chemical effect happening inside the cocktail. Such instability is observed for measurements of <sup>220</sup>Rn in glass vials [36]. A plot of the TDCR for each measurement of <sup>222</sup>Rn at a given time is shown on Figure 6.3. A change in the TDCR can be seen between the first and second set of measurements. This indicates some instability in the cocktail that could be explained with the attachment of <sup>222</sup>Rn progeny to the walls of the glass vial. This increases the probability for total internal reflection and can decrease the triple coincidences counting rate, thus decreasing the TDCR. Further investigations are needed in order to determine the source of this instability and to find means to prevent it.



**Figure 6.3:** Drift of the TDCR between the first series of measurements and the second series of measurements

## 6.5 Conclusions from the experiments

TDCR counting of <sup>222</sup>Rn dissolved in UltimaGold LLT liquid scintillator with the TDCR–SU system are feasible. Measurements with high-voltage +750V and +850V give the same results within the estimated uncertainties (using same comparator thresholds) and those with high-voltage +650V underestimate the radon activity, probably due to decreased counting efficiency for <sup>214</sup>Pb and <sup>214</sup>Bi low-energy  $\beta$ -particles. The measurements with different extended dead times (40 µs and 100 µs) provide the same results within the estimated uncertainties and those with two different coincidence windows (40 ns and 100 ns) provide essentially the same results. Good agreement between the estimated <sup>222</sup>Rn half-life and that in the recommended data is observed. Instability of the TDCR is observed for <sup>212</sup>Rn dissolved in LS cocktail contained in a clear glass vial. Further experiments are needed to determine its cause.

#### CHAPTER 7

## Application to <sup>220</sup>Rn measurements

The radioactive isotope <sup>220</sup>Rn (Thoron) is an isotope of Radon. Measurements of Thoron are of practical interest because it is frequently present alongside <sup>222</sup>Rn and can interfere with the acurate <sup>222</sup>Rn activity determination. From the point of view of radioactivity metrology, measurements of <sup>220</sup>Rn provide a way to determine the half-life of <sup>212</sup>Pb.

Thoron is a short lived radionuclide with 55.6 s half-life and decays to  $^{216}$ Po with the emission of an  $\alpha$ -particle. The longest living nuclide in the decay chain of  $^{220}$ Rn is  $^{212}$ Pb, which has 10.64 h half-life and reaches secular equilibrium with its daughter nuclides after a about 10 periods of  $^{212}$ Bi or 10 h. The decay chain of  $^{220}$ Rn is shown on Figure 7.1.

The possibility to determine the <sup>212</sup>Pb activity and half-life by the use of TDCR counting and the stability of <sup>220</sup>Rn progeny dissolved in a LS cocktail is explored in this work.

Figure 7.1: <sup>220</sup>Rn decay chain



## 7.1 Half-life of <sup>212</sup>Pb and cocktail instability

For the following experiment a sample of <sup>220</sup>Rn in toluene-based liquid scintillation cocktail was prepared. A piece of 47 µm thick sheet of the polycarbonate Makrofol N was left in <sup>220</sup>Rn filled chamber for three days in order to absorb Thoron. The polycarbonate sheet was then placed in a Perkin Elmer high performance glass vial (clear, non-diffusive surface), which was then filled with 22 ml of toluene-based cocktail. The prepared source was left for about 10 h in order to reach secular equilibrium between the daughter products of Thoron. To determine the half-life of <sup>212</sup>Pb the prepared sample was measured on the TDCR-SU detector for a period of 58 hours in which 450 five minute measurements were made. The natural logarithm of the logical sum of double coincidences and triple coincidences as a function of elapsed, after the start of the measurements, time is shown on Figure 7.2.



**Figure 7.2:** Half-life of  ${}^{212}Pb$  estimated from the decrease in the net counting rate n of the logical sum of double coincidences (red) and the triple coincidences (black)

The half-life of <sup>212</sup>Pb, determined from the decrease of the logical sum of double coincidences, is 10.6321(56) days. The result is in good agreement with the half-life provided by LNHB's recommended data [35] and with recently published half-life

measurements [36].

The half-life of  $^{212}$ Pb, determined from the decrease of the triple coincidences, is 10.400(10) days which does not agree with the half-life of  $^{212}$ Pb. This discrepancy is caused by the instability of the TDCR, which exhibits a systematic decrease in the course of the measurements (shown on Fig. 7.3). The trend of decreasing TDCR indicates a decrease of the detection efficiency for  $^{220}$ Rn and its progeny. This could be caused by the attachment of decay products to the walls of the glass vial. Scintillations occurring near the walls of the clear glass vial have a larger probability for total internal reflection and thus lower probability for detection. This phenomenon affects the triple coincidences to a larger extent than the double coincidences, leading to a skewed estimate for the half-life of  $^{212}$ Pb, if the triple coincidences counting rate is considered.



**Figure 7.3:** Instability of the TDCR value in the course of the measurements

The half-life of <sup>212</sup>Pb, determined form the decrease of the logical sum of double coincidences counting rate, is in good agreement with other measurements found in the literature. The effect of decrease in the TDCR value in the course of the measurements was observed. It was also reported in [36]. It is still not fully understood and further experiments are needed in order to explain its occurrence.

#### Conclusion

In Part I of this thesis the theoretical principles of the TDCR method are briefly reviewed. A short overview of some important practical aspects is presented. The newly developed at Sofia University TDCR-SU detector is described. Comparisons with the primary TDCR counter at the french primary metrology laboratory LNHB are also reviewed.

A web-application for data storage and analysis was developed to facilitate handling, analysis and filtering of nanoTDCR data. The application has a simple frontend interface that allows the upload of multiple measurement files under a common series name which are arranged and stored in a MySQL database. The web-app has the ability to export data, based on user selectable filters, which can be downloaded in the comma separated values format, allowing easy manipulation by commonly used spreadsheet softwares.

A set of 3D printed mesh filters was developed in order to study and apply the efficiency variation technique for determination of Birks' ionization quenching parameter. The set was tested with a <sup>3</sup>H source in a glass vial covered by diffusive tape. The filters show good linear behaviour for TDCR values above 0.3 on both TDCR-SU and RCTD1 systems, which indicates that the mesh design does not violate the underlying assumptions of the TDCR method. An excellent agreement between the calculated activity of the source and its certificate was achieved. A combined relative uncertainty of 0.3% was achieved by the TDCR-SU measurements of the <sup>3</sup>H source.

The efficiency variation technique, using the 3D printed mesh filters, was used to determine the ionization quenching parameter of tritiated water in UltimaGold and UltimaGold LLT samples. The kB value for the UltimaGold cocktail was found to be 0.0013(2) cm/MeV and for the UltimaGold LLT 0.0100(15) cm/MeV. The estimated parameters were used to calculate the specific activity of tritiated water and a good agreement between the average specific activities calculated for both cocktails was observed.

A method for characterisation of the mesh filters is proposed and evaluated. It is found that the R-value, which gives the ratio of the figure of merit of the sample

with and without a filter, provides a good characteristic of the filters. It seems to be independent of the cocktail and the TDCR system used. This characteristic seems to be very convenient for the application of the efficiency variation technique in the TDCR method, as it allows to predict the expected TDCR ratios that will be measured with the different filters, given a measurement of a sample without a filter.

The application of the TDCR method to <sup>222</sup>Rn measurements was studied. The nanoTDCR's ability for counting simultaniously with two different dead-time base durations was used. The calculated <sup>222</sup>Rn activities for different dead-time base durations agree well within the estimated uncertainties. The half-life of <sup>222</sup>Rn was estimated by one-week measurements of the sample with higher activity and the result was 3.821(12) days which is in agreement with the reference half-life 3.8232(8) days [35].

The application of the TDCR method to <sup>220</sup>Rn measurements was studied. A Thoron in a clear glass vial source was measured on the TDCR-SU system. The halflife of <sup>210</sup>Pb estimated from the decrease in the logical sum of double coincidences counting rate is 10.6321(56) days, which is consistent with previous results stated in the literature. An instability in the TDCR with time was observed, but further experiments are needed to discover the source of the instability.

The TDCR-SU proves to be a very well performing miniature TDCR system. Future work on the detector will include the precise comparison of the different deadtime philosophies of the nanoTDCR and MAC3 as well as managing the instabilities of Radon measurements in glass vial.

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