Romanian Reports in Physics **71**, 209 (2019)

TRITIUM STANDARDIZATION BY THE LSC-TDCR METHOD AND PARTICIPATION AT INTERNATIONAL COMPARISONS

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Received February 21, 2018

Abstract. This paper presents the results obtained in the standardization of ^{3}H, by using the LSC-TDCR method at IFIN-HH. The improvements regarding preparation and measurement of samples, processing and analysis of experimental data finalized by reporting the results (activity or activity concentration of a solution and its associated combined standard uncertainty) are described. The method and basic results of a bilateral (Horia Hulubei National Institute for R&D in Physics and Nuclear Engineering (IFIN-HH), Romania with the Laboratoire National d'Essais – Commissariat à l'Energie Atomique et Energies Alternatives, Laboratoire National Henri Becquerel (LNE-CEA, LIST, LNHB), France) and two ^{3}H international comparisons, involving our laboratory, are presented: (i) CCRI(II)-K2.H-3, 2009, key comparison and (ii) the supplementary comparison CCRI(II)-S12.H-3, 2016. The TDCR06b software was used in case (i) and the improved TDCR07c in case (ii). The recommendations from the recent papers related to the preparation of samples, measurement and processing of the primary data, with special attention paid to the influence of kB parameter and to the involved statistical model, were applied carefully.

Key words: ^{3}H, supplementary comparison, LSC-TDCR method.

1. INTRODUCTION

The IFIN-HH system for the standardization of radionuclides by liquid scintillation – triple to double coincidence ratio (LSC-TDCR) method was installed with the assistance of the LNE-LNHB and was used in international comparisons by participating at the CCRI(II)-K2.Sr-89 [1] and CCRI(II)-K2.Tl-204 key comparisons and in a bilateral comparison with LNE-LNHB on the measurement of tritiated water [2]. In the most recent comparison exercise, the value of activity concentration certified by the LNHB and that measured at IFIN-HH were in a very good agreement. Differences of 0.12% up to 0.19% were obtained using three types of scintillators: ultima-gold, home-made cocktail and InstaGel, which were considered as method for type A evaluation of uncertainties. The calculation software applied was RDSPECTR, written at LNHB. The interesting findings were: (a) different values of the quenching parameter, kB = 0.012; 0.007; 0.009 cm $(\text{MeV})^{-1}$ had to be used in calculation for the three scintillators, measured in the same system; (b) in the case of ultima-gold scintillator, the difference in activity was of 2.3% when using the values kB = 0.012 and 0.009 cm $(\text{MeV})^{-1}$. Optical grey filters were used to vary the efficiency, within the interval 0.33–0.44. The authors concluded that some additional uncertainty components should be taken into account for future measurements: photomultipliers asymmetry, kB and $\mathrm{d}E/\mathrm{d}x$ values, and suspected deviations from the Poisson statistics.

2. MEASUREMENTS AND RESULTS OBTAINED WITHIN THE CCRI(II)-K2.H-3 COMPARISON, 2009

The CCRI(II)-K2.H-3, 2009, key comparison had as pilot laboratory the LNE-LNHB, who prepared and distributed the solution of tritiated water. The measurements performed at IFIN-HH were made using two LSC-TDCR counters: the classical photomultipliers (PMs) based one, and the new miniaturized counter, based on the use of six channel photomultipliers (CPMs) [3, 4]. The data were processed using the TDCR06B software, written by Ph. Cassette [5], which hadn't yet taken into account the asymmetry of the PMs.

The results obtained with the PM system were reported in the comparison [4]. The scintillator used was ultima gold LLT, and a value of kB = 0.011 cm $(\text{MeV})^{-1}$ was chosen, using the same optical grey filter procedure for efficiency variation and choosing the minimum slope of activity *versus* efficiency curve [4]. The relative uncertainties were evaluated by the two methods: the type A evaluation resulted in a component: u_A = 0.63%; the type B evaluation took into account the difference in activity calculation by using successive kB values, as:

$$u_{kB} = \frac{(A_{kB_{11}} - A_{kB_{10}}) + (A_{kB_{12}} - A_{kB_{11}})}{2A_{kB_{11}}}\ [\%] \tag{1}$$

In relation (1), u_{kB} is the uncertainty due to the choice of the kB = 0.011 cm $(\text{MeV})^{-1}$; A_{kB10}, A_{kB11}, A_{kB12} are activities calculated using the following values of kB = 0.010; 0.011; 0.012 cm $(\text{MeV})^{-1}$. In our case u_{kB} = 0.6%; the remaining components, weighing, background etc. were less than 0.1%.

The results of the entire comparison are presented in the preliminary Draft B report on this comparison [6]. The conclusion is that some additional uncertainties should be considered, as: (a) the choice of a u_{kB} = 0.7%, instead of the used u_{kB} = 0.6%, is in agreement with the previous assumption that each 0.001 cm (MeV)$^{-1}$ difference of *kB* induces an approximate difference of 0.7% in activity calculation [2], and (b) supplementary components as: PM's asymmetry; in this case the double coincidence counting rates (AB, BC, AC) varied between 4% and 7% at IFIN-HH, while at LNHB it was from 15% up to 18%; input parameters and statistical model. For example, in the 6 CPMs system measurement it was necessary to choose a *kB* = 0.019 cm (MeV)$^{-1}$, a value significantly different from that corresponding to the classical LS-TDCR system, where *kB* = 0.011 cm (MeV)$^{-1}$. This value was chosen to correspond to the smallest difference of activity as compared with the PM system. TDCR value was obtained for *kB* = 0.019 cm (MeV)$^{-1}$, and consequently it was used in the calculation of efficiencies, as the efficiencies were much smaller. The activity values obtained with the 6 CPMs and the classical TDCR systems agreed to within the specified uncertainties, with an activity difference of only 0.4% achieved at a counting efficiency of ε_D = 0.17 for the 6 CPMs system. We suspect that the difference between the two *kB* values necessary to be used in the two systems could be due to the influence of the phototube mismatch. This result is also in agreement with those reported in [3] for two similar systems compared at LNHB. These results raise some questions about the proper value of *kB* and model of calculation.

3. PARTICIPATION WITHIN THE CCRI(II)-S12.H-3 SUPPLEMENTARY COMPARISON, 2016

A supplementary comparison, consisting of the calculation of the activity and standard uncertainty of a tritium source measured using the LSC-TDCR method, was organized within the Key Comparison Working Group (KCWG) of the Consultative Committee for Ionizing Radiation (CCRI(II)) of the International Committee for Weights and Measures (CIPM). A diffusive vial with tritiated water was prepared and measured at LNE-LNHB using the TDCR system, in the conditions stipulated in the Protocol of comparison. The detection efficiency was varied using two procedures: application of grey filters and defocusing of the photomultipliers focusing electrodes. Two sets of experimental data acquisition files, as spreadsheets, were received in our laboratory, to be used for the calculation of the activity and for the estimation of its associated uncertainty.

3.1. CALCULATION OF ACTIVITY

We considered that both sets of experimental data are equally consistent and independent of each other and, consequently, they were processed in a similar manner. In order to correctly calculate the activity we have used the most appropriate software, the proper ionization quenching treatment and we have studied the influence of the statistical model.

3.1.1. Software to be used

As one can see from the measurement data, the three photomultipliers are nonsymmetrical in efficiency, the difference between them being of 8%. The improved software TDCR07c, which takes into account this difference, was used for the calculation of the LS efficiency: http://www.nucleide.org/ICRM_LSCWG/icrmsoftware.htm. The considered decay data were obtained from [7]. The calculation was based on a number of 1000 channels of the analyzed spectrum.

3.1.2. Calculation of the ionization quenching and the choice of the kB value

The Birks formula was used in the calculation. The stopping power formula was a combination of the ICRU 37 formula for energies above 100 eV and a linear extrapolation to zero for energies lower than 100 eV [7, 8]. The calculations used kB values from 0.007 cm $(\text{MeV})^{-1}$ to 0.015 cm $(\text{MeV})^{-1}$, for both sets of experimental data. For the two methods of variation of the TDCR ratio, the relationship existing between activity A and TDCR=T/D were determined using all the above kB values. D and T are the net counting rates of logical sum of the double and triple coincidences (corrected for background counting rate). The minimum curve slope, in both methods, corresponds to kB = 0.010 cm $(\text{MeV})^{-1}$. The efficiencies ε_D (logical sum of double coincidences) and ε_T (logical sum of triple coincidences) were calculated in both situations for the maximum T/D value, as follows: no filter applied and respectively 800 V focalization voltage, using the kB = 0.010 cm $(\text{MeV})^{-1}$, using TDCR07c software, and by fulfilling the following condition:

$$\frac{\varepsilon_T}{\varepsilon_D} = \text{TDCR} = \frac{T}{D}. \qquad (2)$$

The activity was calculated according to the following relation:

$$A = \frac{D}{\varepsilon_D}. \qquad (3)$$

Two sets of quantities were obtained.

– No optical grey filter: ε_D = 0.5517; T/D = 0.5003; A_filter = 11472 Bq;

– 800V focalization: ε_D = 0.5535; T/D = 0.5020; A_focus =11469 Bq.

The final result, activity on the reference time, was calculated as the arithmetic mean of the two individual activity values: A_{mean} = 11470.5 Bq. The two individual activities, A_{filter} and A_{focus}, differ with only ± 1.5 Bq (0.013%) from their mean value.

3.2. CALCULATION OF UNCERTAINTIES

The prescriptions of the JCGM 100:2008, GUM 1995 [10] with minor corrections, were followed. At the same time, the indications from [11] were used in calculations. The uncertainty components, evaluated by type A and type B methods, were combined according to the GUM rule.

3.2.1. The counting statistic uncertainty, due to the counting of D and T and calculation of efficiency εD

The law of uncertainties propagation over the formula (3) was applied. The relative uncertainty (%) resulted as:

$$(u_{\text{A}} / \text{A})^2 = (u_{\text{D}} / \text{D})^2 + (u_{\varepsilon\text{D}} / \varepsilon_{\text{D}})^2 \tag{4}$$

u_{D} was calculated from the standard uncertainty of a measurement, as presented in the spreadsheet file, and the number of measurements, 10. The standard deviations of *D* individual values*,* of 0.24% and respectively 0.12%, were divided by $\sqrt{10}$, in order to obtain the standard deviation of the mean *D.*

Calculation of $u_{\varepsilon\text{D}}$: It was calculated from the uncertainty of *T/D,* using the efficiency *vs T/D* variation relations and by applying the law of uncertainty propagation; these relations were calculated from the experimental data, applying a criterion of least squares fitting (ORIGIN software). Linear plots were considered as satisfactory, according to the high values of the correlation factors, in both experimental procedures (applying filters and defocusing).

– efficiency variation with filters:

$$\varepsilon_D = (0.0246 \pm 0.0107) + (1.157 \pm 0.031)\ T / D$$

$$R = 0.99928 \text{ correlation factor}$$

– efficiency variation with defocus:

$$\begin{gathered} \varepsilon_D = (0.0641 \pm 0.0092) + (0.975 \pm 0.018)\ T / D \\ R = 0.99946 \text{ correlation factor} \end{gathered} \tag{5}$$

The uncertainties of ε_D were calculated according to relations (5), using uncertainty propagation law, from the uncertainties of *T/D*, as:

$$u_{\varepsilon D} = 1.157\, u_{T/D} \text{ for filter variation;} \quad u_{\varepsilon D} = 0.975\, u_{T/D} \text{ for defocus.} \tag{6}$$

Calculations of $u_{T/D}$ were done from the uncertainties of *T* and *D* from experimental data, taking into account their correlations, relation (7):

$$[u_{T/D}/(T/D)]^2 = u_T^2/T^2 + u_D^2/D^2 - 2u^2(T,D)/(T\cdot D) \tag{7}$$

Relations (6) and (7) provide the following values:
– for no filter measurement, $\varepsilon_D = 0.5517$:

$u_{T/D} = 0.00032$; $u_{\varepsilon D} = 0.000371$ and $u_{\varepsilon D}/\varepsilon_D = 0.000672 = 0.0672\%$

– for no defocus measurement, $\varepsilon_D = 0.5535$:

$u_{T/D} = 0.000257$; $u_{\varepsilon D} = 0.000251$ and $u_{\varepsilon D}/\varepsilon_D = 0.000453 = 0.0453\%$

From the previous relations, by applying relation (4), results:

– no filter:

$$\frac{u_A}{A} = \sqrt{(0.0024/3.162)^2 + 0.000672^2} = 0.00101 = 0.101\%$$

– no defocus (800 V focalization):

$$\frac{u_A}{A} = \sqrt{(0.0012/3.162)^2 + 0.000453^2} = 0.00059 = 0.059\%. \tag{8}$$

3.2.2. Other uncertainties, evaluated by type B method

Two types of components were considered: (i) specific for each method: dead time correction, background counting rates, pile-up, quenching parameters; (ii) common components: input parameters, statistical model, and decay scheme parameters.

The specific uncertainties were calculated also from the propagation of uncertainties, as presented in Table 1, A and B evaluations of the specific uncertainties of the activity in % for (i), and their mode of calculation.

Table 1

Method specific uncertainties

Component	Grey filter, *u,%*	Defocus *u,%*	Mode of calculation
Counting statistics	0.103	0.059	– Point 3.2.1.
Dead time	0.006	0.006	– relation (22) from [11] with $\tau = 5$ ns
Background	0.0037	0.0089	– ratio of counting rate, blank/sample, multiplied by the background rate uncertainty and quadratic summation of the two background counting rates: blank rate *D* and blank rate *T*
Pile-up	0.0253	0.0254	– product of counting rate, *D*, s^{-1}, and coincidence resolving time, 40 ns
Quenching parameters	0.676 *	0.672 *	– relative difference from value $kB = 0.012$ cm $(\text{MeV})^{-1}$ and used value, $kB = 0.010$ cm $(\text{MeV})^{-1}$, divided by $\sqrt{3}$, relation (25) from [11]
Combined uncertainty	0.684	0.675	– square root of quadratic sum of all uncertainty components

*) These values are in agreement with $u_{\text{kB}} = 0.64\%$ reported in [12]

The combined standard uncertainty of the mean activity of the two methods is (9):

$$u_{A\text{ mean absolute}} = \frac{1}{2}\sqrt{u^2_{A\text{ filter absolute}} + u^2_{A\text{ defocus absolute}}} = \\ = \frac{1}{2}\sqrt{(11472 \cdot 0.00684)^2 + (11469 \cdot 0.00675)^2} = 54.8\text{ Bq}. \tag{9}$$

Or expressed in its relative form: $u_{rel} = 54.8 / 11471 = 0.478\%$.

3.2.3. Common uncertainties evaluated by type B methods and final result

The supplementary common uncertainties (ii) are:

– The input parameters and statistical model. As it is known, all TDCR computing software are based on the Poisson distribution of the counted photons. In Fig. 6 from [11] there are presented by comparison activities calculated with Poisson distribution and a new proposed, [13], Polya statistics. These statistics are aimed to avoid the problems of total reflection in non-diffusive vials. Using these data, an uncertainty of $u_{\mathrm{model}} = 0.34\%$ was calculated as half of the difference of the values resulted from Poisson and Polya, $L = 0.05$ statistics, calculated by Broda [13] the closest from the Poisson statistics on the figure. The two curves (Activity *vs.* TDCR) were extrapolated linearly from TDCR ≈ 0.38 up to TDCR = 0.5, as is our case, using the graphs presented in this reference, indicated as Fig. 6.

The uncertainty in maximum beta spectrum energy resulted in an uncertainty of $u_{\mathrm{spectra}} = 0.0054\%$.

These two common components were quadratically added to the uncertainty from relation (9), and the final combined standard uncertainty is:

$$u_c = \sqrt{0.478^2 + 0.34^2 + 0.0054^2} = 0.587\% .$$

The IFIN-HH final result, reported within the comparison, on the reference time, was:

$$A = (11.471 \pm 0.068)\ \mathrm{kBq} \quad (k = 1).$$

The result of the comparison CCRI(II)-S12.H-3, calculated as the power moderate weighted mean (PMM) of the results reported by the 17 participating primary laboratories, such as presented in the paper [14] and considered as Comparison Reference Value (CRV) is:

$$A_{Comparison} = \mathrm{CRV} = (11.495 \pm 0.019)\ \mathrm{kBq} \quad (k = 1).$$

4. COMPARATIVE RESULTS IN ACTIVITY MEASUREMENT AND IN EVALUATION OF UNCERTAINTIES

An analysis of activity measurement, expressed by the comparison of uncertainty budgets as reported in each comparison with the differences from the comparison reference values (CRVs), Δ[%], and their expanded uncertainties U[%] is presented in Table 2.

Table 2

Reported uncertainties and relative differences from the comparison reference values

Type of reported uncertainty	Relative uncertainty,% Bilateral comparison with LNE-LNHB, (software RDSPECTR 2004)	Relative uncertainty,% CCRI(II)-K2.H-3, (software TDCR06B 2009)	Relative uncertainty,% CCRI(II)-S12.H-3 mean values of the two methods: grey filters and defocus (software TDCR07c 2016)
Counting statistics	0.14	0.63	0.081
Weighing	0.1	0.1	–
Dead time	–	–	0.006
Background	0.1	0.08	0.0063
Pile-up	–	–	0.0254
Quenching parameters (*kB* value)	0.74	0.60	0.674
Statistical model	–	–	0.34
Beta spectrum	–	–	0.0054
Combined uncertainty	0.80	0.88	0.587
Relative difference from CRV, Δ,%, and its expanded uncertainty, *U*,%, *k* = 2	Δ = – 1.5 *U* = 1.89	Δ = 1.77 *U* = 2.05	Δ = – 0.21 *U* = 1.17

From the data presented in Table 2 one may summarize:

– The uncertainty and difference from CRV are much lower in the comparison CCRI(II)-S12.H-3 as compared with the previous ones, due to the fact that in this last case the uncertainties due to the samples' preparation (weighing, liquid scintillator and vial type) and to the liquid scintillator counter, with its characteristics and adjusted parameters [14], do not occur.

– Except the uncertainty due to the statistical model and beta spectrum, introduced in the CCRI(II)-S12.H-3 comparison, the same types of uncertainties were evaluated during all comparisons.

– The statistical uncertainty was higher in the CCRI(II)-K2.H-3 comparison, due to the small number of prepared sources, having an important contribution in the uncertainty budget.

– The uncertainty due to the adjustment of the quenching parameter *kB* has a determinant contribution in the budget. Its value, u_{kB} = 0.674%, in CCRI(II)-S12.H-3 comparison, carefully determined, proves that a value of 0.7% is more realistic than a 0.6% one.

– In all cases, the differences Δ[%], from the CRVs are lower than their expanded uncertainties, *U*[%], which demonstrated that our results are equivalent with the other international primary standards for tritium.

5. CONCLUSIONS

A series of three comparisons, one bilateral and two international, regarding the standardization of tritiated water were presented. Their common and different points were analyzed (types of the involved uncertainties and the differences of IFIN-HH reported results from the comparison reference values).

The aspects regarding the influence of the used computing software, of the ionization quench parameter (*kB*), of the statistical model, and of the other parameters on the final result were discussed in this work.

The most recent comparison, CCRI(II)-S12.H-3, consisting of the analysis of the same set of experimental data by all the participants, involved a detailed study, according to the comparison Protocol, of all influencing models and parameters, and of all sources of uncertainties. The recommendations presented in paper [11] were found to be very important in uncertainties' calculations, for both type A and type B methods.

Acknowledgements. This work was supported by a grant provided by the Romanian National Authority for Scientific Research, Program Nucleu PN 16 42 02 04.

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