

STANDARDIZATION OF TRITIUM BY CIEMAT/NIST METHOD WITH LIQUID SCINTILLATION COUNTING IN TURKEY AND UNCERTAINTY BUDGET

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TÜRKİYE'DE TRİTYUMUN SIVI SİNTİLASYON SAYIM SİSTEMİNDE CIEMAT / NIST YÖNTEMİYLE STANDARDİZASYONU VE BELİRSİZLİK BÜTÇESİ

Abstract:

Radioactivity measurements used in many applications and disciplines must be accurate and reliable. Quality control parameters, instrument calibrations, and accuracy of the applied radiochemical methods are performed using traceable radioactive standards and reference materials. The liquid scintillation counting (LSC) system is highly preferred to standardize radionuclides in radionuclide metrology. It has quick and easy sample preparation steps that allow standardization of short-lived radionuclides. Besides, the counting efficiency of the detector in the LSC system can be calculated either by the direct measurement method such as TDCR or by using a tracer technique such as the CIEMAT/NIST method. For these reasons, the number of radionuclides standardized by the LSC method has increased over time. In this study, tritium standard solutions prepared from high activity tritium reference solution were counted by using the LSC system. Activity concentration values and their uncertainties were calculated using the CIEMAT/NIST method.

Özet:

Birçok uygulama ve disiplin alanında kullanılan radyoaktivite ölçümlerinin doğru ve güvenilir olması çok önemlidir. Kalite kontrol, cihaz kalibrasyonu ve geliştirilen radyokimyasal metotların doğruluğu radyoaktif standartlar ve referans malzemeler kullanılarak yapılmaktadır. Radyonüklit metrolojisinde sıvı sintilasyon sayım (SSS) sistemi, özellikle kısa ömürlü radyonüklitlerin standardizasyonuna olanak sağlayan hızlı ve kolay numune hazırlama adımlarına sahip olması nedeniyle sıklıkla tercih edilmektedir. SSS cihazındaki dedektörün sayım verimi TDCR gibi doğrudan ölçüm yöntemiyle veya CIEMAT/NIST yöntemi gibi bir izleyici tekniği kullanılarak hesaplanabilir. Bu nedenlerden dolayı SSS yöntemiyle standardizasyonu yapılan radyonüklitlerin sayısı her geçen gün artmaktadır. Bu çalışmada hazırlanan trityum standart çözeltileri SSS sisteminde sayılmış ve CIEMAT/NIST yöntemi kullanılarak belirsizlik değerleriyle birlikte aktivite konsantrasyonları hesaplanmıştır.

Keywords: H-3, LSC, CIEMAT/NIST, standardization, uncertainty.

Anahtar Kelimeler: H-3, sıvı sintilasyon sayımı, CIEMAT/NIST, standardizasyon, belirsizlik.

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1. Introduction

The reference material is a stable and sufficiently homogeneous material used to test the quality of products and check their traceability. Since the homogeneity, stability, and the concentration value of the reference materials is determined and guaranteed in the proficiency test exam, it is highly safe to use by laboratories. Everyday, thousands of laboratories around the world perform many analyses with different methods in different matrices and provided analysis results to their customers. The common goal of these laboratories is to present the fastest research with the most reliable results. Quality controls are no longer necessary all over the world and have become a necessity.

Radioactive measurements are used in many fields such as nuclear decay and reactions, environmental monitoring, quality control of radiopharmaceuticals, nuclear energy and weapon industry, radioecological and geochemical studies. Accurate measurement of radioactivity is crucial in these applications and disciplines. (Colle, 2009, pg. 1). The availability of radionuclidic standards is essential to calibrate the instruments and determine the chemical yield of the methods. So, radioactive standards must be traceable to national and international measurement compliance.

In Turkey, alpha-, gamma-, and beta-emitting radioactive standards are prepared by using different methods in Radionuclide Metrology Laboratories of the Radiation Metrology Group of Nuclear Energy Research Institute (NUKEN), Turkish Energy, Nuclear and Mineral Research Authority (TENMAK). Turkey is a member of the European Commission Association of National Metrology Institutes (EC EUARMAT), and NUKEN-TENMAK is the designated institute in ionizing radiation metrology. One of NUKEN's responsibilities is to produce radioactive standard sources and reference materials needed by our country and to carry out the necessary research and development activities.

Tritium (^3H) is produced in the upper atmosphere by interacting cosmic rays with atmospheric gases. Releasing by nuclear reactors, uranium fuel reprocessing plants, and medical wastes are of the other tritium source. Although tritium has relatively low radiotoxicity, it is necessary to monitor the activity concentrations in the environment to follow the circulation in the atmosphere.

From this point of view, we prepared and standardized tritium standard solution by using high activity tritium reference solution, $[^3\text{H}]\text{H}_2\text{O}$. Using LSC, tritium activity concentration was successfully standardized with the CIEMAT/NIST (C/N) efficiency tracing method. The CIEMAT/NIST is a powerful activity standardization method, especially for betas or positron-emitting and electron capture radionuclides such as ^{129}I , ^{151}Sm , and $^{166\text{m}}\text{Ho}$. (Altitzoglou & Rozkov, 2016). LSC is the most suitable measurement technique which is used to determine the low energetic β -emitter radionuclides like ^3H , ^{14}C , ^{35}Si , ^{63}Ni , etc. since sixty years and high energetic β -emitters (^{32}P , ^{89}Sr etc.), electron capture nuclides (^{55}Fe) and α -emitters (^{226}Ra) in recent years. All processes emitting light photons both directly and indirectly are detected in the LSC system to measure the activity of radionuclides.

Both radiochemical and analytical measurement results become meaningful and reliable if they are given with measurement uncertainty. Reporting the analysis results together with the uncertainty value is an essential requirement according to the ISO/IEC 17025 quality system. Procedures for the determination of measurement uncertainty are explained in detail in the relevant section of the document (Anonymous, 2017). This work presents the results of activity standardization of tritium standard solution using C/N method within the uncertainty limits.

2. Materials and Method

2.1. Materials

Tritium (^3H) ($35.10 \pm 0.80 \text{ kBq.g}^{-1}$ and reference date: 01 January 2013) certified reference solutions were purchased from Physikalisch-Technische Bundesanstalt (PTB-6.11-2005-1665). 20 mL Teflon coated low diffusion polyethylene vials (Perkin Elmer) and Ultima Gold (UG) scintillation cocktail (Perkin Elmer), deionized water supplied from our laboratory were used. All reagents and chemicals (nitromethane as quenching agent) were analytical reagent grade and used as purchased without further purification.

2.1. Source preparation

The original ^3H certified reference solution has very high activity concentration to produce radioactive standard solution. Therefore, quantitative dilutions have to be made for an acceptable activity concentration. First, a certain amount of the ^3H certified reference solution was added in a calibrated volumetric flask using the pycnometer method (Sibbens & Altitzoglou, 2007; Wyllie, 1989) and completed with distilled water to get an activity concentration of $800.50 \pm 10.40 \text{ Bq.g}^{-1}$ ($k=1$). Thus, the main stock ^3H standard solution was prepared. Then, approximately 1 g of solution was taken from this solution using the pycnometer by gravimetrically and put in a standard glass ampoule. The mouth of the ampoule was sealed with the heat of gas flame according to the literature (Sibbens & Altitzoglou, 2007; Wyllie, 1989). The other nine ampoules were prepared as described above. Thus, ten radioactive ^3H solutions in sealed standard glass ampoules were ready for standardization. All dilutions were performed using calibrated balance, checking for zero readings and a test weight before and after each weighing process.

Two ampoules were selected to standardize a radioactive ^3H solution using a quench calibration curve with a liquid scintillation counting system. The selected ampoules were opened, respectively. Different amounts of the radioactive ^3H solution were transferred to 15 mL of the Ultima Gold liquid scintillation cocktail mixed with 1 mL of deionized water in each vial. Thus, five vials at different activity concentrations were prepared from each ampoule. A vial containing only a scintillation cocktail was prepared for the background measurement. A total of 11 vials were shaken and left to dark adapt in the LSC instrument at a temperature between 12 and 14 °C. These vials were visually colorless and homogeneous (Figure 1).

2.2 Preparation of quench set

One of the main problems encountered in liquid scintillation spectrometry measurement is that the measurement results are lower than expected due to "quenching," caused by the color or chemical properties of the sample or scintillator mixtures. As a result, the counting efficiency decreases. Therefore, the quench set containing tritium standard with known activity and a varying amount of nitromethane as a quenching agent was prepared and measured by using LSC. The quench curve was plotted to find the counting efficiency correctly (Nazife, 2020).

In this study, the quench set was prepared by "15 mL UG plus 1 mL deionized water" cocktail mix, ^3H standard reference solution and nitromethane. The required amounts of ^3H standard reference were added to 9 vials containing the cocktail, respectively. One vial

contained only a cocktail solution for the background measurement. Some of the vials were quenched with nitromethane ranged from 20 to 120 μL . The prepared quench set was counted ten times with the LSC to check the sample stability.

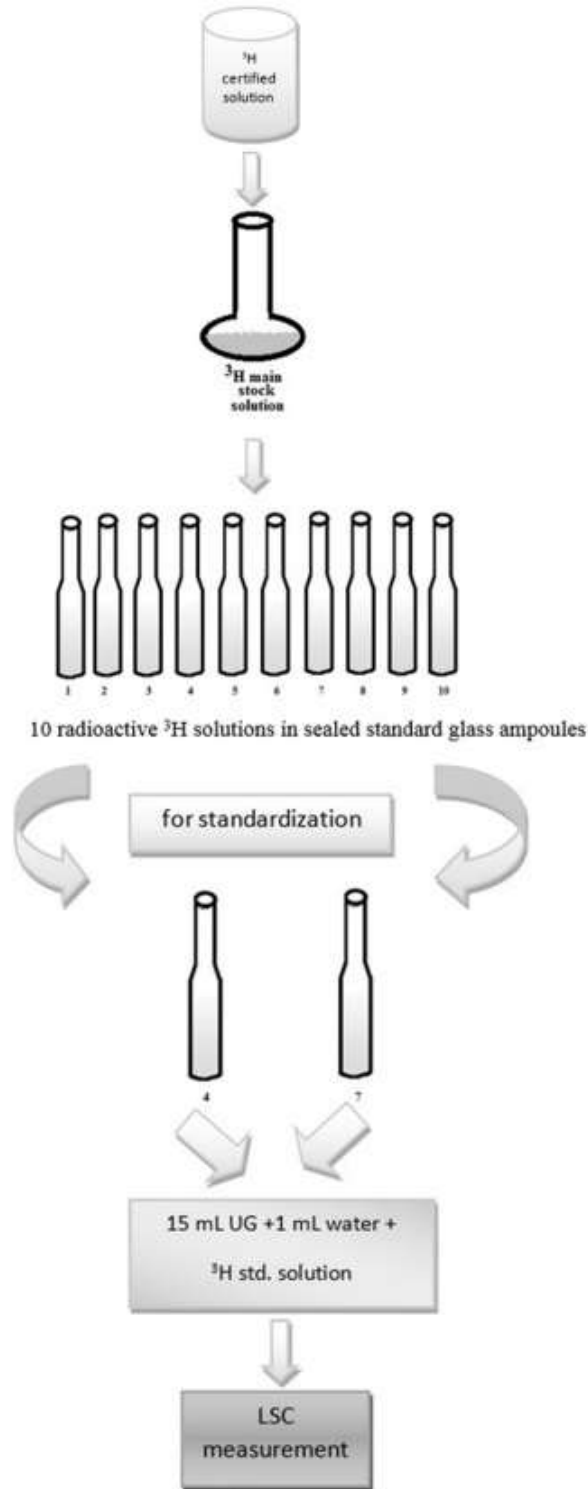


Figure 1. Scheme of source preparation steps from original ^3H certified reference solution to a radioactive ^3H ampoule solution.

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The Quench curve of tritium, efficiency (%) versus quench parameter [SQP(ϵ)], was plotted and fitted to a polynomial equation. Here, the quenched parameter, SQP(ϵ) values, were obtained from the registry file, and the efficiency value was calculated using Eq. (1) and Eq.(2) for each measurement. The net count rate in cps was obtained by using Easy View program utilizing a result of measurement. The activity of each sample was calculated from the sample mass and the activity concentration of the tritium standard solution.

$$Efficiency = \epsilon = \frac{cpm}{dpm} = \frac{Count\ rate}{Activity} \quad (1)$$

$$Activity = Activity_0 * Mass \quad (2)$$

2.3. Source measurement

Activity measurements were performed by using Perkin Elmer 1220 Quantulus ultra low-level liquid scintillation counter (Turku, Finland) with an external standard of ^{152}Eu . The quench level was quantified with Spectral Quench Parameter of External standard, SQP(ϵ).

Analytical results were determined by using WinQ programme. The counting windows were set to channels 50-350 in the beta spectrum. Spectra were analyzed using Easy View Spectrum Analysis Software.

All sample vials that contain tritium and blank vial were remeasured during 6-8 weeks. The count rate of each vial was corrected for the background by subtracting the count rate of the blank for dead time and decay.

3. Results and Discussion

The objective of the study is to prepare ^3H radioactive solutions in sealed standard glass ampoules and standardize these solutions by using LSC. Prepared standard ^3H ampoule solutions in this study should be used in the calibration of radioactivity measuring instruments and monitoring of radiochemical procedures. For this purpose, main stock ^3H standard solution was prepared from the original ^3H certified reference solution. This main stock solution with an acceptable activity concentration was added to each ampoule with a pycnometer. Then the mouths of these ampoules were tightly sealed with heat to prevent the escape of the evaporated liquid from the solution surface during storage. Ten ampoules with almost similar activities were prepared. The activities of these standard ^3H ampoules, which ranged approximately from 738 to 798 Bq, were given in Table 1.

Table 1. Prepared standard ^3H ampoules ($U_{activity} \% = 1.30$, $k = 1$)

Ampoule Code	Mass (g)	^3H value (Bq)
A1	0.9974	798.42 ± 10.38
A2	0.9960	797.30 ± 10.36
A3	0.9967	797.86 ± 10.37
A4	0.9892	791.85 ± 10.29
A5	0.9908	793.14 ± 10.31
A6	0.9865	789.69 ± 10.27

A7	0.9864	789.61 ± 10.26
A8	0.9868	789.93 ± 10.27
A9	0.9831	789.97 ± 10.23
A10	0.9217	737.82 ± 9.59

Combined uncertainty due to preparation of standard ³H ampoule solution was calculated as 1.30 % (Eq. 3, Eq. 4, and Table 2). The significant contribution of the uncertainty components comes from the uncertainty of the certified ³H standard solution. The uncertainty contribution from half-life time, weight, and used calibrated volumetric flask were much lower than that of certified ³H standard solution.

$$Activity_{H-3, ampoule}(Bq) = \frac{A_0 * e^{\left(\frac{-0.693}{T_{1/2}} * t\right)} * w_1}{V} * w_2 \quad (3)$$

where;

A₀ : the activity of tritium certified reference solution in Bq g⁻¹,

T_{1/2} : the half-life of tritium

t : difference time between reference time of certified ³H standard solution and experimental time

V : volume of stock solution, ml

w₁ : mass of added ³H certified reference solution, g

w₂ : mass of added main stock ³H solution, g

$$\left(\frac{U_{activity}}{Activity}\right)^2 = \left(\frac{U_{std}}{std}\right)^2 + \left(\frac{U_{decay factor}}{decay factor}\right)^2 + \left(\frac{U_{mass}}{mass}\right)^2 + \left(\frac{U_{flask}}{volume of flask}\right)^2 + \dots \quad (4)$$

Table 2. Uncertainty budget of the prepared main stock ³H standard solution (k = 1)

Uncertainty components	Relative uncertainty (%) on the activity concentration for main stock ³ H standard solution
Activity from certified ³ H standard solution	
Sample	1.29
Weighing	0.03
Decay correction	0.026
The volume of the calibrated flask	0.11
Combined uncertainty (quadratic sum) (%)	1.30

Two of the ten ampoules were randomly selected for standardization, and these selected ampoules were carefully opened. The required amount of the solution was added to each vial. Five vials were prepared from each ampoule. A total of ten ampoules were prepared, which was the same media as the quench set. All measurements were performed by using LSC with 5–350

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window channels, 30 min counting time, and three replicates. One month later, these vials were remeasured for three days, and then it was repeated twice, once a week. Finally, these measurements were repeated two months later during four days.

After measurements, the activity value of each vial was calculated from Eq. 5. The net count rate in cps and the quenched parameter, [SQP (ϵ)] values were obtained from the registry file using Easy View program. The counting efficiency of ^3H was calculated by using the following polynomial equation [Eq. 6] obtained from Quench curve (Figure 2).

$$Activity_{H-3,vial}(Bq) = \frac{Net\ count\ rate\ (cps)}{Efficiency_{H-3}} \quad (5)$$

$$\epsilon_{H-3} = 1.16 \times 10^{-1} - 4.88 \times 10^{-2} * [SQP(\epsilon)] + 6.67 \times 10^{-5} * [SQP(\epsilon)]^2 - 2.92 \times 10^{-8} * [SQP(\epsilon)]^3 \quad (6)$$

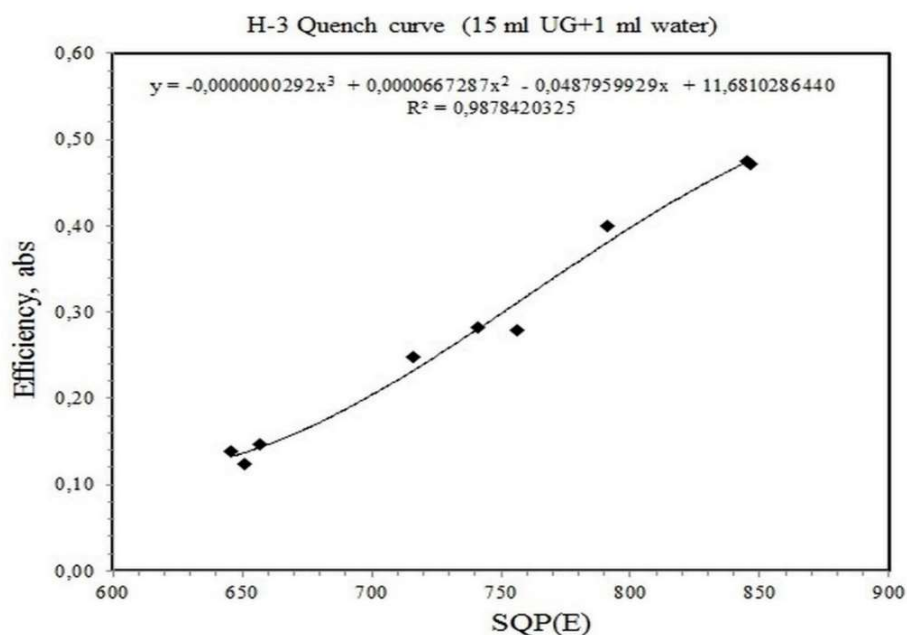


Figure 2. The Quench curve of tritium for 15 mL Ultima Gold + 1 mL deionized water

Measured mean activity concentration value of ten vials were calculated by using Eq. 5 (Table 3). Relative error percentage and relative standard deviation percentage were also given in Table 3. As it can be seen from the table, the percentage deviations (relative error) of the measured values concerning the added values were within the range from -0,26 % to -4,22 %. It is clear from the table that the determined activity concentration values were in good agreement with the added ones. The experimental relative standard deviation for all activity values that were obtained ranged from 0,82 % to 1,86 % within the acceptable values (<10%) reported by Aslan et al., 2015. All vials were measured 24 times at different times within two months under the same condition. As seen from Figure 3, these results showed that all source stabilities were satisfactory (Figure 2).

Then, the activity value for each ampoule was recalculated by using these vial measurement results. The measured mean activities for ampoule 4 and 7 were 803.15 Bq and 800.46 Bq, respectively. Relative error values were within acceptable limits (Table 4).

Table 3. Activity and uncertainty values of ^3H determined in the vials ($k = 1$)

Sample code	Added ^3H activity, Bq	Measured ^3H activity, Bq	Relative Error, %	Relative Standard Deviation, %
S4-1	56.22 ± 0.76	57.95 ± 1.54	3.13	1.19
S4_2	54.83 ± 0.74	$55.37 \pm 1,48$	1.02	1.84
S4_3	49.79 ± 0.67	$50.19 \pm 1,34$	-0.91	1.42
S4_4	69.00 ± 0.94	$71.04 \pm 1,88$	-2.93	1.27
S4_5	20.17 ± 0.27	$19.22 \pm 0,56$	-0.26	1.41
S7_1	48.01 ± 0.64	$48.53 \pm 1,29$	1.09	0.82
S7_2	48.56 ± 0.67	$50.09 \pm 1,34$	-3.15	2.14
S7_3	43.11 ± 0.60	$44.71 \pm 1,20$	-3.71	1.71
S7_4	44.22 ± 0.61	$46.08 \pm 1,23$	-4.22	1.86
S7_5	47.14 ± 0.63	$47.94 \pm 1,28$	-1.69	0.95

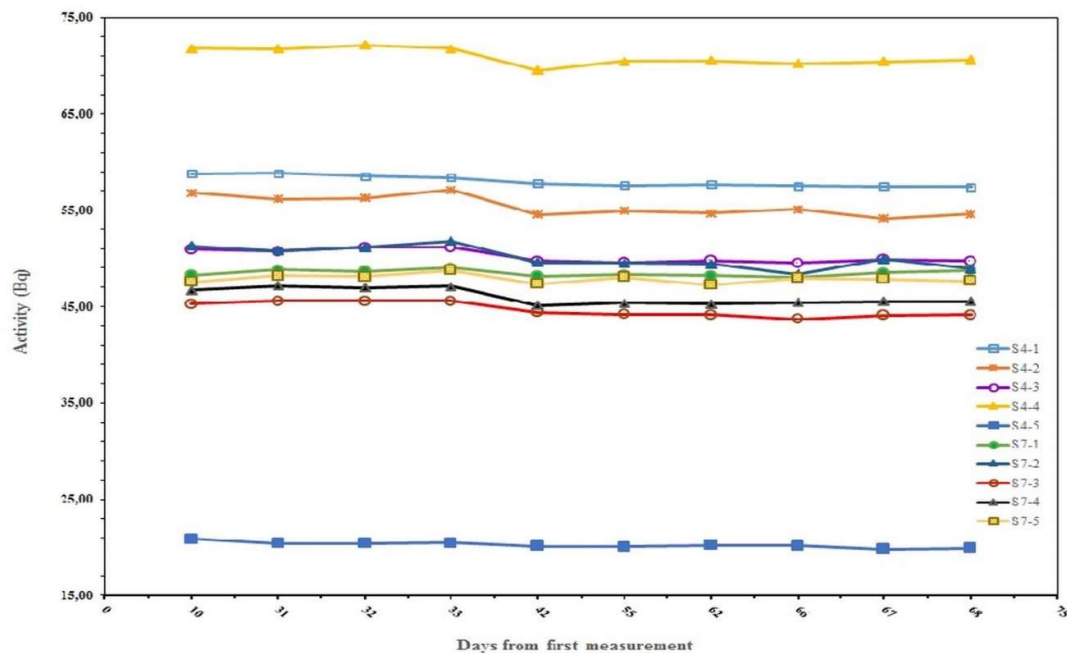


Figure 3. Variation of measured activity over a time period of 68 days for ^3H in each vial. The activity value is the mean value of each vial.

Table 4. Activities of ^3H in prepared ampoules ($k = 1$)

Ampoule code	Added ^3H , Bq	Measured ^3H , Bq	Relative Error, %
A4	791.85 ± 10.29	803.15 ± 21.44	-1.43
A7	789.61 ± 10.26	800.46 ± 21.37	-1.37

The typical uncertainty budget for a single measurement of ^3H activity concentrations in a vial at the 1σ level ($k = 1$) is presented in Table 5. Initially, all uncertainty components and their contributions to the measurement results from beginning to end of the procedures were identified to prepare the uncertainty budget table. Uncertainties arising from counting statistics, including background, weighing, counting efficiency, decay correction and quenching were considered. Uncertainties for weighing and reference solution received from supplier's data in the certificate were used, and uncertainties due to counting statistic, instrument, and quenching parameters were calculated from instrument data such as count rates and SQP(ϵ) %. Finally, the individual uncertainties were combined to give an overall uncertainty.

In this study, the uncertainty due to ^3H quench curve preparation was first calculated as 2,26 %. Then, this uncertainty was used in the uncertainty calculation of activity measurement in a vial. The main uncertainty contributions on the ^3H activity concentration mainly were due to the quench curve preparation and the used certified ^3H standard solution.

Table 5. Uncertainty budget of ^3H activity concentration for S4_1 sample ($k = 1$)

Uncertainty component	The relative uncertainty of the individual parameters, (%)	Relative uncertainty (%) on the activity concentration
counting statistic (including background)	0.46	0.46
quench curve	2.26	2.24
SQP(ϵ)	0.15	0.41
repeatability	1.19	0.24
activity from certified ^3H standard	1.14	1.30
weight	0.12	
decay correction	0.026	
Combined uncertainty (%), (quadratic sum)		2.67

4. Conclusion

The standard ^3H ampoules were prepared with the pycnometer method and standardized using a quench curve with a liquid scintillation counting system. These standard ^3H ampoules are offered to users for the calibration of radioactivity measuring instruments and for the monitoring of radiochemical procedures.

The variety and need for radioactive analyzes in our country will increase as the nuclear power plant becomes operational in the following years. We will continue to prepare different beta radioactive standard solutions according to the demands of a liquid scintillation working group in the radionuclide metrology laboratory in Turkey.

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