

Article

An Advanced Optimization Method to Minimize the Detection Limit of Liquid Scintillation Counter to Measure Low-Level Tritium Activity in Groundwater

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Simple Summary: In regions with arid climates, the tritium concentration in groundwater is often extremely low, making it difficult to detect using conventional liquid scintillation counters (LSCs) due to their higher minimum detectable activity (MDA). This study aims to address this issue by exploring various methods that can effectively lower the detectable activity of tritium. One approach is to enrich the tritium activity concentration by increasing it ten- to fortyfold compared to the initial concentration. Other strategies include minimizing background radiation by using low-background materials for sample containers, improving the measurement efficiency of the scintillation counter, extending the counting time, and shielding the sample from environmental radiation using the shutter option in LSC. Additionally, reducing interfering contaminants in the sample can lower the uncertainty associated with tritium concentration measurement in water samples. These efforts are crucial for accurately detecting and monitoring low-level tritium in water, ensuring public health and safety.

Abstract: In arid regions, the tritium concentration in groundwater is typically very low and often falls below the minimum detectable activity (MDA) of the conventional liquid scintillation counter (LSC). Therefore, to measure the tritium activity concentration, it is necessary to lower the detection limit so that the scintillation counter can detect it. In the present study, several methods are discussed which are effective at lowering the detectable activity of tritium. One of these methods is to enrich the tritium activity concentration by ten- to fortyfold of the initial concentration of the tritium. Twelve spiked samples with known amounts of tritium, five with high concentrations and seven with low concentrations, were enriched by the electrolysis process. The results indicated that enriching the tritium levels in groundwater lowers the MDA value. Other methods are minimizing background radiation using low-background materials for sample containers, increasing the measurement efficiency of the scintillation counter and counting time, and shielding the sample from environmental radiation using the shutter option in LSC. Moreover, reducing the number of interfering contaminants in the sample can lower the uncertainty in measuring the tritium concentration in the water sample, which is beneficial for detecting low-level tritium in water to ensure public health and safety.

Keywords: minimum detectable activity; decision threshold; counting time effect; liquid scintillation counter; tritium enrichment; efficiency; optimization conditions



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1. Introduction

Conventional liquid scintillation counters (LSCs) are extensively employed in radiation measurement [1]. Nonetheless, they may not always be capable of detecting low-level radiation effectively [2,3]. This limitation is especially relevant in the case of tritium, a naturally occurring radioactive isotope of hydrogen in the environment, including groundwater, which emits low-energy beta particles [4]. However, the detection limit of conventional LSCs is sufficiently low to permit accurate measurement of tritium levels in groundwater

samples [3]. The minimum detectable activity (MDA) is a significant factor in environmental radioactivity measurements, as it represents the lowest amount of radioactivity that can be detected and measured with certainty as tritium. The sensitivity of the scintillation counter is indicated by a low MDA value, which can detect even low levels of tritium. Therefore, it is a critical parameter for LSC to evaluate environmental samples such as soil, water, air, and food containing radioactive isotopes [5–7].

In contrast, a high MDA value means that the analytical method is less sensitive and may miss low levels of radioactivity. The MDA value evaluates the analytical method's precision and reliability and determines whether the sample's radioactivity level exceeds the regulatory limits. If the measured radioactivity level is lower than the MDA, the sample is considered to be below the analytical method's detection limit, and the result is reported as "less than MDA" [8]. If the measured radioactivity level exceeds the MDA, the sample's radioactivity level can be determined. Many studies have been reported in which the minimum detectable activity for the scintillation counter is optimized. For example, Feng et al. [5] examined a low-background liquid scintillation counting system that employed 100 mL counting vials to enhance the measurement of airborne tritium in the environment. After a dark adaptation time exceeding 1440 min, the researchers discovered that optimal counting could be achieved by mixing a 50 mL water sample with a 50 mL scintillation cocktail. The 100 mL vial system displayed a minimum detectable activity (MDA) of 1.5 TU during a continuous counting period of 3600 min, which was approximately 3.5 times lower than the MDA value of the 20 mL vial system. The study suggests utilizing electrolytic enrichment for accurately determining samples with specific activity below 4 TU. Here it is important to note that one tritium unit (1 TU) is equal to 0.118 Bq/kg. However, it also recommends using the 20 mL vial system following the electrolysis enrichment process due to the cost and potential environmental impact associated with the available cocktail. A new method for determining the MDA in low-level tritium based on the Feldman–Cousins unified approach was suggested by Lee et al. [8]. The method efficiently integrates the construction of confidence intervals with the determination of the decision threshold and minimum detectable activity (MDA). The suggested method provides more accurate and efficient results for MDA determination in low-level measurements. A separate study examined the influences on sensitivity and the determination of MDA for measuring plutonium isotopes. This was achieved by varying the counting time of the sample [9]. Lequang et al. reported reducing the MDA for environmental radioactivity using gamma-ray spectrometry by improving the ability to reduce background radiation [10]. They devised a shielding setup consisting of 5 cm of lead and 2 mm of copper, resulting in the minimum detectable activity (MDA) for ^{40}K , ^{232}Th , and ^{238}U being 2.60 to 4.24 times lower than previous configurations. An approach utilizing electrolytic enrichment and ultralow background liquid scintillation counting was developed to measure tritium levels in seawater. Testing on 84 seawater samples showed that 92% were above the detection limit, with activities ranging from 0.8 TU to 12 TU by Lin et al. [11]. Zang et al. [12] employed optimized measurement parameters to achieve a detection limit of 0.45 TU for tritium when analyzing 700 mL seawater samples. This method was successfully applied to determine tritium levels in the East China Sea. However, most of the above reports were conducted theoretically following computer simulation for isotopes other than tritium by modifying the instrument detector and need to prove optimization conditions experimentally to minimize the MDA for conventional liquid scintillation counter.

Therefore, optimum conditions were identified and applied to minimize the detectable activity for tritium activity measurement. Certified standard samples with known tritium activity were used, and an enrichment process was employed. A correlation was drawn between the MDA and the enrichment factor, counting efficiency, counting time, sample-to-scintillation cocktail ratios, shielding with shutter, and background radiation. Furthermore, various statistical analyses were applied to confirm the accuracy and precision of the obtained data for MDA.

2. Materials and Methods

2.1. Samples

A series of tritium solutions were prepared by diluting the standard solution certified by Eckert & Zeigler (Berlin, Germany), P. O: P700723 and source: 1676-44, with tritium-free water in a controlled manner. The resulting solutions were then analyzed to determine their activity concentration. Table 1 shows the specific activity concentration of the tritium for the prepared samples. The prepared samples with known activity concentrations allow tritium calibration and validation, ensuring that the measured values align with the expected values within the minimal uncertainties. In addition, two standard samples (^3H and ^{14}C) with a very high activity concentration and another background sample with a very low tritium concentration, known as a dead water sample from Hidex UK, were also used without further purification and modifications.

Table 1. Estimated tritium activity concentration for reference samples prepared by dilution from a standard sample.

| Sample ID | Spiked Activity (TU) | \pm Error (TU) |
|-----------|----------------------|------------------|
| Sample 1 | 8500 | 604.4 |
| Sample 2 | 4250 | 182.7 |
| Sample 3 | 850 | 166.2 |
| Sample 4 | 425 | 133.4 |
| Sample 5 | 85 | 12.29 |
| Sample 6 | 43 | 5.254 |
| Sample 7 | 8.50 | 4.661 |
| Sample 8 | 4.25 | 1.271 |
| Sample 9 | 0.85 | 0.297 |
| Sample 10 | 0.45 | 0.085 |
| Sample 11 | 0.15 | 0.127 |
| Sample 12 | 0.08 | 0.085 |

2.2. Electrolytic Enrichment

The electrolysis process involves four steps. First, primary distillation involves heating water until it reaches boiling, forming steam. This steam is then collected, allowed to cool, and condensed back into liquid form, leaving behind the impurities or contaminants in the water. Second, our laboratory fabricated and developed 13 electrolysis cells to increase the tritium concentration in water samples using liquid scintillation counters. The electrolysis cells were designed to increase the concentration of tritium in the water samples to a detectable level by LSC. The materials used for cell construction are mild steel and stainless steel, commonly used in electrolysis cells. Mild and stainless steel were chosen due to their chemical and physical properties, making them suitable for electrodes in electrolysis cells. The water sample was weighed into the electrolytic cell (anode and cathode) for the electrolysis process, and later, 1 g sodium peroxide (Na_2O_2) was added. A so-called ES 400 electrolysis process was used, suitable for samples with a very low ^3H content. The cells were connected in series, and a 2.2–3.2 V voltage was applied across the cells. The current was stabilized at a maximum of 10 A and reduced in the electrolysis run's final stage. During electrolysis, the "light" water decomposes primarily into H_2 and O_2 (oxyhydrogen), which are discharged. Extra care was taken for exhaust gases into the outdoor air. Throughout the process, tritiated water was explicitly concentrated in the residual water present in the cell. This occurred due to the slightly higher binding energies between tritium and oxygen. The electrolysis process was conducted at near-freezing temperatures of $-5\text{ }^\circ\text{C}$, resulting in tritium enrichment by a factor of $(10\text{--}40) \pm 2$. The process takes one to two weeks, depending on the water volume. In the absence of tritium loss, the enrichment factor (EF) can be calculated by multiplying the tritium enrichment yield ($\eta_{A,i}$) with the mass of water filled into each electrolytic cell prior to the electrolysis process ($m_{v,i}$) and then dividing it by the mass of water remaining in the cell after the electrolysis process

($m_{n,i}$) [13–15]. The third step is related to the neutralization of the alkalinity of the solution caused by the presence of electrolytes used for the electrolytic process. Neutralization was performed by adding an acidic substance to the solution, which reacted with the alkaline substances to form a more neutral product by introducing carbon dioxide gas to the alkaline water. A Horiba LAQUAtwin (Japan) digital pH meter was used to control the alkalinity of the water samples. In the fourth step, after confirming the absence of electrolytes in the solution, a final distillation was performed by heating it to its boiling point, and the resulting vapor was collected and condensed. After final distillation, the water samples were tested using a YSI 9500 photometer and a Horiba digital meter for any contaminants (for example, Cl^- , SO_4^{2-} , Ca^{2+} , CO_3^{2-} , Mg^{2+} , Na^+ , K^+ , etc., and dissolved solids) present in the sample, and the samples were transferred for the scintillation counting process.

2.3. Tritium Activity Measurement

Following the final distillation, a water sample of 10 mL was combined with a scintillation cocktail of 10 mL (Aqualight plus, Hidex, UK) to convert the energy emitted during tritium decay into light flashes. The Hidex AquaLight plus scintillation cocktail is a high-safety and general-purpose solution designed for counting aqueous and nonaqueous samples, including alpha beta separation and general beta counting, with optimal performance for low-level tritium counting, high sample capacity, ultralow background, and high efficiency at low temperatures [16,17]. The specimens were kept in a cool and dim environment and allowed to sit for at least four hours before measuring to prevent the luminescence effect.

Tritium analysis was performed using a Hidex 300 SL liquid scintillation counter, as depicted in Figure 1. The analysis was conducted based on the triple-to-double coincidence ratio (TDCR) method. The equipment with three photomultiplier tubes enables the measurement of the triple-to-double coincidence ratio, offering an effective approach for analyzing tritium concentration for unknown samples [18–20]. Each sample was analyzed five times for 200 min in a controlled environment, free from temperature fluctuations and direct sunlight. Monthly calibration with a standard source was used to monitor the device's performance, and background radiation levels were kept under constant review using a shield in the Mikrowin parameter option for super low-level measurement. The details of the calculation procedures have been published previously [21,22]. In addition, to prevent static electricity effects, the Hidex 300 SL has a mechanism to discharge static electricity from the sample before measurement, which increases the sample processing time by 1–2 s.

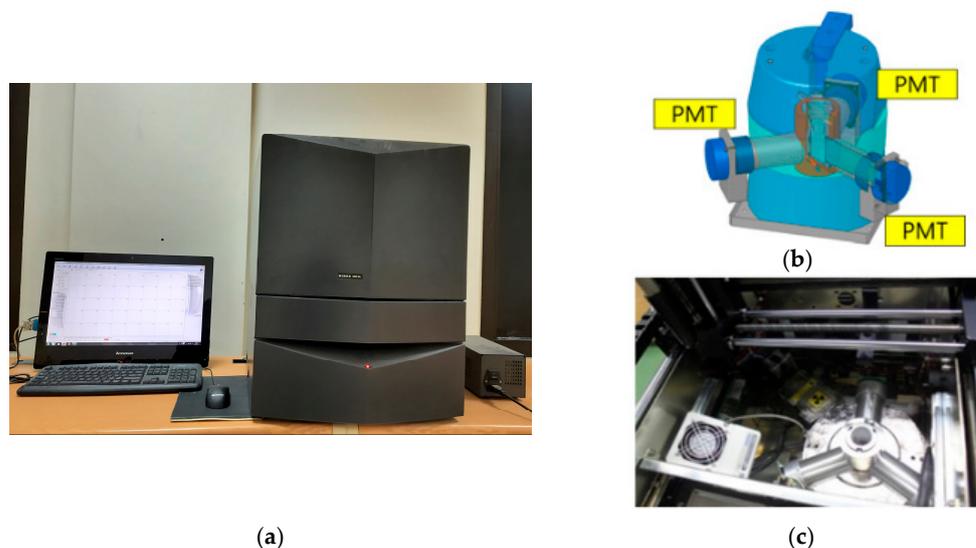


Figure 1. (a) Front view of the scintillation counter (Hidex 300SL), (b) illustration of the photomultiplier tubes, and (c) photograph of the photomultiplier tubes.

2.4. Mathematical Formulation

A standard source (provided by Hidex) was used for efficiency measurement under the same conditions as the unknown samples. As a result, the efficiency of the measurement can be estimated using the following equation.

$$\varepsilon = \frac{R_n}{c \cdot m_M} \quad (1)$$

Flashes are captured by the scintillation detector in counts per minute (CPM). Each sample was measured five times for 200 min. The average of the five runs was then determined. Standards and blanks (background samples) are also estimated to evaluate the data with similar experimental conditions.

The tritium activity concentration during the counting time by LSC was calculated using the following equation [23–25]:

$$c = \frac{R_n}{\varepsilon \cdot m_M} \quad (2)$$

If the decay correction factor and enrichment steps are included, then the equation can be rewritten as

$$c = \frac{m_n \cdot \rho \cdot f_A \cdot R_n}{\varepsilon \cdot \eta_{A,i} \cdot m_v \cdot m_M} \quad (3)$$

$$c = \frac{m_n \cdot \rho \cdot e^{\lambda \cdot t_A} \cdot R_n}{\varepsilon \cdot \eta_{A,i} \cdot m_v \cdot m_M} \quad (4)$$

where

c , the activity concentration of tritium at the counting time (Bq/m³);

f_A , the correction factor for the decay;

λ , decay constant of tritium in s⁻¹;

t_A , the time between sampling and the beginning of the measurement in s;

R_n , net count rate of the counting source in s⁻¹;

ε , detection efficiency in Bq⁻¹·s⁻¹;

ρ , the density of the water in kg·m⁻³;

m_n , the mass of solution remaining in the electrolysis cell after electrolysis, in g;

m_v , the mass of the solution filled into the electrolysis cell before electrolysis, in g;

m_M , mass of distillate in the scintillation vial, in g.

The mass conversion was made using the water volume as 1 m³ = 1000 kg.

2.5. Data Validation

Statistical analysis is essential in the validation process of analytical methods because it serves multiple important purposes. Initially, through statistical methods, one can evaluate the dependability, accuracy, and consistency of the technique, thus verifying the authenticity of the outcomes [26]. Then, one can quantify the method's precision through standard deviation, decision threshold, and statistical error studies. Most of the calculations using equations (for example, activity concentration, MDA, decision threshold, etc.) and statistical analysis (for example, standard deviation, uncertainty, Z-score, R² value) were performed using MATLAB and Microsoft Excel (2016).

3. Results and Discussion

3.1. Enrichment of Tritium Concentration

The detection limit of conventional liquid scintillation counters (LSCs) is typically higher than the level of tritium present in the groundwater in most arid regions. Hence, an enrichment process increases the tritium concentration in the sample by a known factor, thereby reducing the detection limit of the scintillation counter and enabling accurate measurement of tritium levels in the sample. Through the electrolysis process, the sample

is processed through an electrolytic cell to increase the tritium concentration. As more electrical current flows through the solution, more water is used, and more gas is produced.

In addition to current, other factors, such as volume reduction with electrolysis time, can impact the tritium enrichment process, as shown in Figure 2a. The volume reduction factor refers to the ratio of the initial volume of the solution to the final volume of the concentrated tritium product. This factor is essential due to its impact on the overall efficiency of the enrichment process. For example, if the volume reduction factor is too low, the process may require multiple rounds of electrolysis to achieve the desired level of tritium concentration, which can be time consuming and costly. On the other hand, if the volume reduction factor is too high, it can lead to tritium losses or other unwanted effects. Therefore, finding the optimal volume reduction factor is important in the tritium enrichment procedure. The enrichment factor of the sample is calculated by the initial and final volume ratio multiplied by the tritium enrichment yield. For example, if an 800 g water sample is enriched, 22 g remains at the end of the electrolysis process, the tritium enrichment yield is 96.66%, and the enrichment factor will be 35.15.

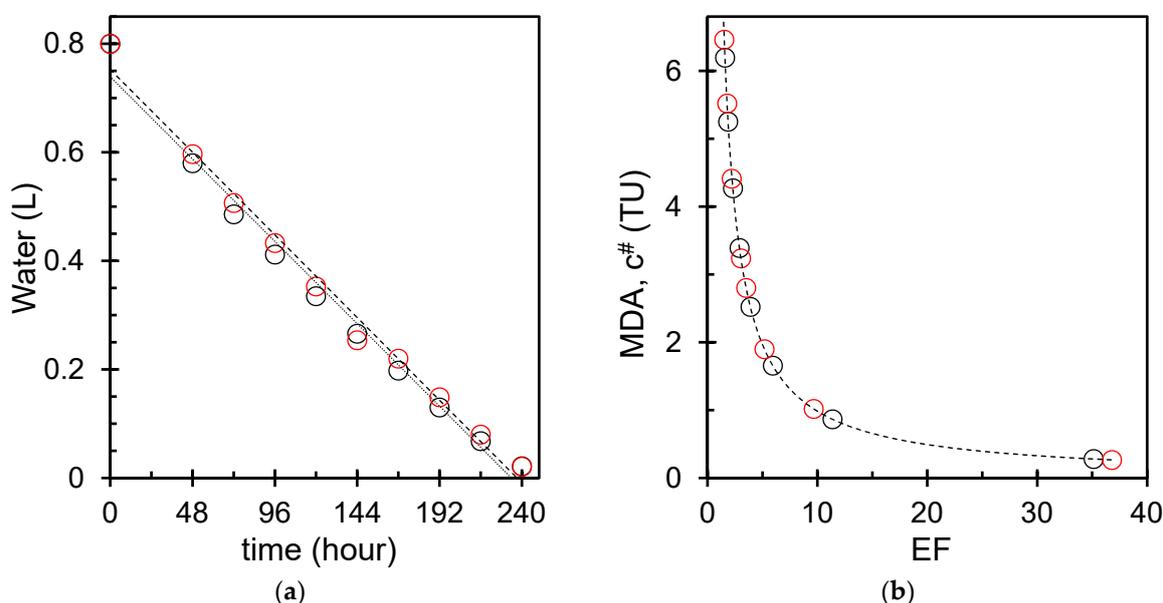


Figure 2. (a) Time-dependent water reduction and (b) minimum detectable activity, $c^\#$, as a function of enrichment factor by electrolysis process for two typical samples 5 and 7 (black and red circles).

The relationship between the enrichment factor and the minimum detectable activity is essential because it helps determine the analytical performance of the method. MDA refers to the minimum detectable concentration of the analyte that can be accurately detected and measured. The lower the MDA, the more sensitive the method is, which means it can detect lower analyte concentrations. Figure 2b shows the minimum detectable activity as a function of the enrichment factor by the electrolysis process for two typical samples of 5 and 7 (black and red circles). The results show an inverse correlation between the enrichment factor and the minimum detectable activity (MDA) in radioactivity measurements. The enrichment factor represents the ratio of the analyte's activity in the enriched sample to its activity in the original unenriched sample. The target analyte is concentrated by enriching the sample, increasing the signal-to-noise ratio, and improving the analytical method's sensitivity. As a result, MDA is reduced, meaning that lower target analyte levels can be reliably detected and quantified. In other words, as the enrichment factor increases, the MDA decreases. Therefore, by increasing the enrichment factor, MDA can be reduced, making it easier to detect and quantify low concentrations of the analyte.

3.2. Counting Efficiency and Background Radiation

The scintillation counter's efficiency might depend on the background radiation counted by the detector. Background radiation can obscure the radiation emitted by the sample, making it challenging to detect low-level radiation. Increasing the efficiency of a detection system refers to improving its ability to detect and measure radioactivity by maximizing the number of radiation events detected and minimizing the number of missed events. This can be achieved by optimizing the detection system's design and configuration, including the detector's type and size, the electronics, and the data acquisition system. Additionally, calibration of the detection system with standard sources and quality control procedures can help ensure accurate and precise measurements. By increasing the efficiency of the detection system, the MDA value can be reduced, which allows for the detection of lower levels of radioactivity with greater accuracy and sensitivity.

Regular monitoring of device performance is crucial in estimating tritium concentration using a scintillation counter. To achieve this, the liquid scintillation counter (LSC) performance was periodically assessed using standard sources. Calibration was carried out using a trusted source of certified activity-free water and carbon-14 (^{14}C) and tritium (^3H) sources, as shown in Figure 3. The activity-free water demonstrated a consistent background reading over the past eight years, with minimal experimental error (Figure 3a). This indicates that there is always a minimal level of radiation in the activity-free solution and its surrounding environment. On the other hand, the count per minute (CPM) for the standard ^{14}C source exhibited no significant changes, as expected due to its longer half-life of approximately 5715 ± 40 years [27].

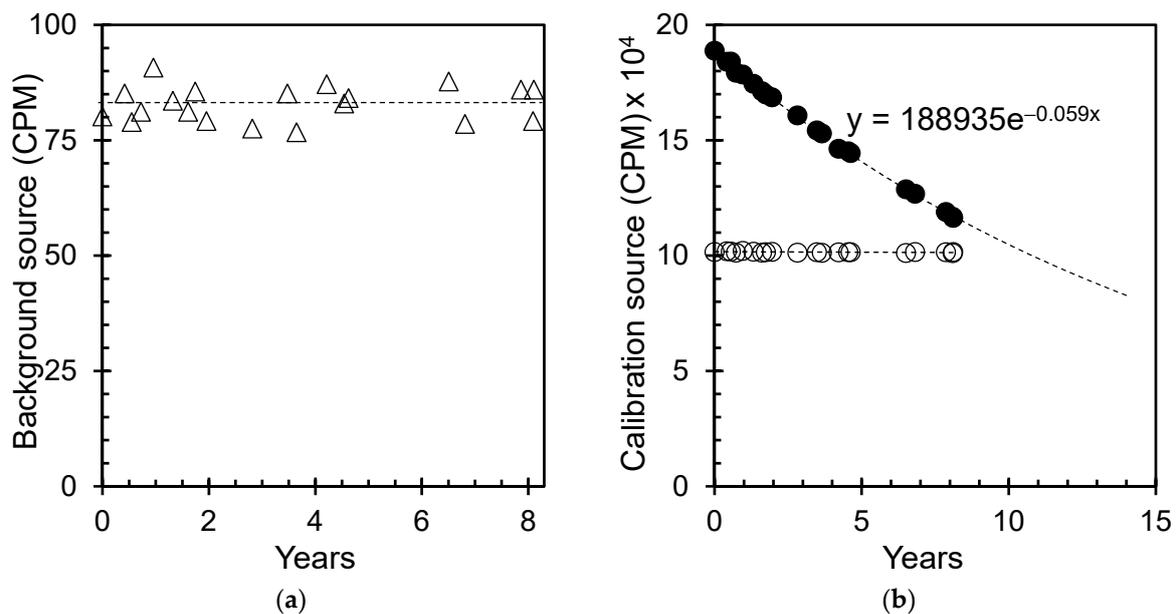


Figure 3. Eight-year record for the calibration source for the certified solution of (a) activity-free water for background levels, (b) a certified source of ^{14}C indicated by open circles, and a certified source of ^3H represented by solid circles. The flashes are measured in counts per minute (CPM). The dashed curve for ^3H extends to visualize the exponential dependence with time.

In contrast, the standard tritium source (^3H) displayed an exponential decline in the count over the last eight years since the device was initialized. The count reached approximately 0.6162 times the initial count (Figure 3b). By analyzing the gradual exponential curve and decay equation, a rough estimation yielded a half-life of approximately 11.75 years for ^3H , which is in close agreement with the published value of 12.3 years reported in the literature [28]. The stable background count and consistent ^{14}C count over time indicate the excellent performance of the liquid scintillation device. It is worth noting

that the background effect can be disregarded if the measured value is approximately 1000 times greater than the background count [29].

3.3. Counting Time-Dependent Decision Threshold, Detection Limit, and Standard Uncertainty

The decision threshold of a liquid scintillation counter corresponds to the minimum detectable activity of the device, signifying the lowest attainable level of radioactivity that can be identified with a specific level of confidence. Adjusting decision thresholds based on counting time is crucial in various fields, including environmental monitoring and medical imaging [30]. It is especially vital when dealing with low-level contaminants or radiation and detecting low-dose exposures. The counting time-dependent decision threshold involves modifying a measurement technique's minimum detectable activity or decision threshold in response to changes in the measurement duration or counting time. As the measurement duration increases, the signal-to-noise ratio improves, thus enhancing the sensitivity of the measurement technique and enabling it to detect lower levels of the analyte [31]. For this, adjustments to the MDA or decision threshold can be made, representing the lowest level of the analyte that is considered significant and distinguishable from the background noise. Once the MDA is established, it can be utilized as a criterion for deciding whether a sample contains a notable level of radioactivity above the background. If the radioactivity level of a sample falls below the MDA, it is indistinguishable from the background and considered undetectable. The detection time of the counter evaluates the decision threshold and the minimum detectable activity. Equations (5) and (6) were utilized to calculate the decision threshold and minimum detection limit [24–26].

$$c^* = k_{1-\alpha} \times \varphi \times \sqrt{\left[R_o \times \left(\frac{1}{t_{total}} + \frac{1}{t_o} \right) \right]} \quad (5)$$

$$c^\# = c^* \times k_{1-\beta} \times \sqrt{\left(c^{\#2} \cdot u_{rel}^2(\varphi) \right) + \varphi^2 \cdot \left(\frac{c^\#}{t_{total} \cdot \varphi} + \frac{R_o}{t_{total}} + \frac{R_o}{t_o} \right)} \quad (6)$$

where

c^* , decision threshold in $\text{Bq} \cdot \text{m}^{-3}$;

$c^\#$, detection limit in $\text{Bq} \cdot \text{m}^{-3}$;

$k_{1-\alpha}$, quantile of the normal distribution for $\alpha = 0.0014$;

$k_{1-\beta}$, quantile of the normal distribution for $\beta = 0.05$.

After the implementation of the auxiliary quantities ψ and θ , the detection limit $c^\#$ can be calculated using the following equation:

$$c^\# = \frac{c^* \cdot \psi}{\theta} \cdot \left[1 + \sqrt{1 - \frac{\theta}{\psi^2} \cdot \left(1 - \frac{k_{1-\beta}^2}{k_{1-\alpha}^2} \right)} \right] \quad (7)$$

where

$$\theta = 1 - k_{1-\beta}^2 \cdot u_{rel}^2(\varphi) \quad (8)$$

$$\psi = 1 + \frac{k_{1-\beta}^2}{2 \cdot c^*} \cdot \varphi \cdot \frac{1}{t_{total}} \quad (9)$$

Liquid scintillation counting requires a certain amount of time to achieve statistical confidence, and the scintillation counter's detection limit influences this duration. The detection limit specifies the smallest quantity of radioactivity the counter can detect while maintaining a certain confidence level. The counting time needed to attain the desired level of statistical confidence relies on several variables, including the detection limit of the counter, the sample size, the activity of the sample, and the level of statistical confidence sought. Therefore, it is essential to consider the counter's detection limit and adjust the counting time accordingly to achieve the desired level of statistical confidence when using a

liquid scintillation counter such as the Hidex 300 SL. Figure 4 shows the decision threshold as a function of counting time. The illustration demonstrates that the counting time significantly influences the decision threshold. A higher counting time lowers the decision threshold. A similar trend for the detection limit with counting time was also observed (Figure 5). The tritium level is usually very low for water, and the counting time must be long enough for a low detection limit. In this study, the range of tritium activity was predicted to be very low and, for some samples, impossible to detect. Hence, we selected a counting time of 200 min with five repetitions for the samples, for which the detection limit was approximately 0.236 TU. Our results align with the previous work by Feng et al. [5], where the MDA value was reduced from 6 TU to 1.525 TU with a continuous counting time of 3600 min. Therefore, they suggested enriching the water sample to lower the MDA value by a few orders of magnitude.

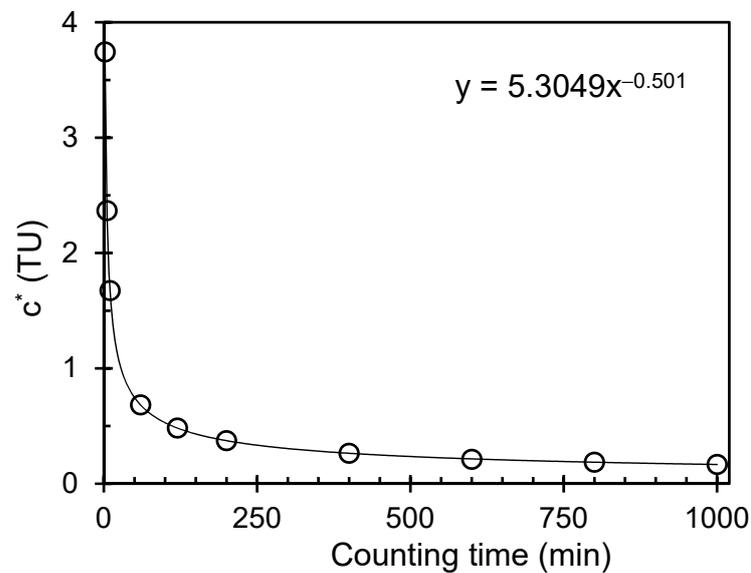


Figure 4. Counting time-dependent decision threshold, c^* (TU), for a standard sample 7, calculated using Equation (5).

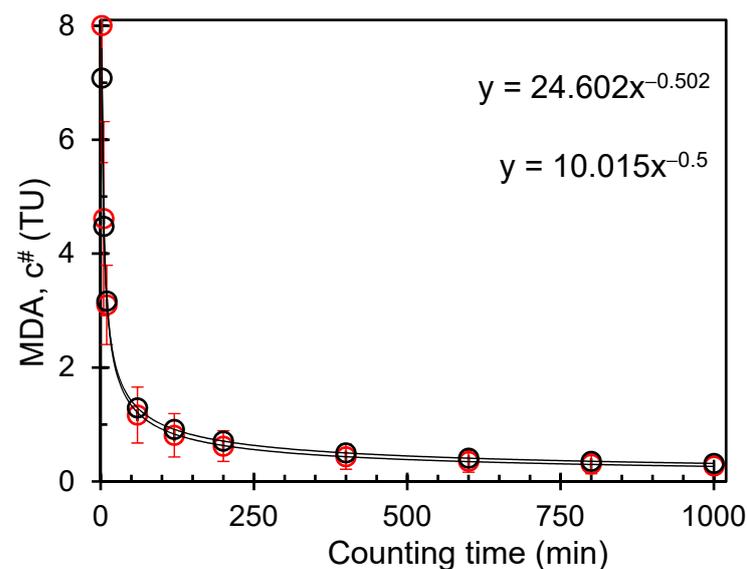


Figure 5. Counting time-dependent minimum detection limit using MikroWin software (red circle) and Equation (7) (black circle) for a standard sample 7.

To calculate the standard uncertainty of activity concentration $u(c)$, Equation (10) is used. In the absence of electrolysis, the relative standard uncertainties linked to the tritium yield and the masses before and after electrolysis are eliminated. This is because the tritium yield is considered constant, and any errors in mass measurement would offset each other while determining the difference between the two masses. As a result, the standard uncertainty of activity concentration in such instances is determined only by counting statistics and liquid scintillation counter efficiency uncertainties [23–25].

$$u(c) = c \cdot \sqrt{\frac{1}{(R_g - R_o)^2} \cdot \left(\frac{R_g}{T_{tot}} + \frac{R_o}{T_o} \right) + u_{rel}^2(\varphi)} \quad (10)$$

with

$$u_{rel}^2(\varphi) = u_{rel}^2(f_A) + u_{rel}^2(m_n) + u_{rel}^2(m_v) + u_{rel}^2(m_M) + u_{rel}^2(\varepsilon) + u_{rel}^2(\eta_{Ai}) + u_{rel}^2(\rho) \quad (11)$$

where

t_o , the sum of the duration of the single background measurements to j in s; $u_{rel}(f_A)$, relative standard uncertainty of the correction factor for the decay; $u_{rel}(\eta_{A,i})$, relative standard uncertainty of the tritium yield of electrolysis cell i ; $u_{rel}(m_n)$, relative standard uncertainty of the mass of solution remaining in the cell after electrolysis; $u_{rel}(m_v)$, relative standard uncertainty of the mass of the solution filled into the electrolysis cell before electrolysis; $u_{rel}(m_M)$, relative standard uncertainty of the mass of distillate in the scintillation vial; $u_{rel}(\rho)$, relative standard uncertainty of the density of water; and $u_{rel}(\varepsilon)$, relative standard uncertainty of the detection efficiency.

The estimated standard uncertainty calculated using Equation (10) against counting time is plotted in Figure 6a. The variation shows a power law; the standard uncertainty decreases with counting time. When the counting statistics contribute significantly to the overall uncertainty, extending the counting time can help minimize the uncertainty. The reason might be that a longer counting time provides more data points, which can improve the statistical precision of the measurement. In addition, by increasing the sample volume, the effects of random error can be reduced, leading to a decrease in the standard uncertainty.

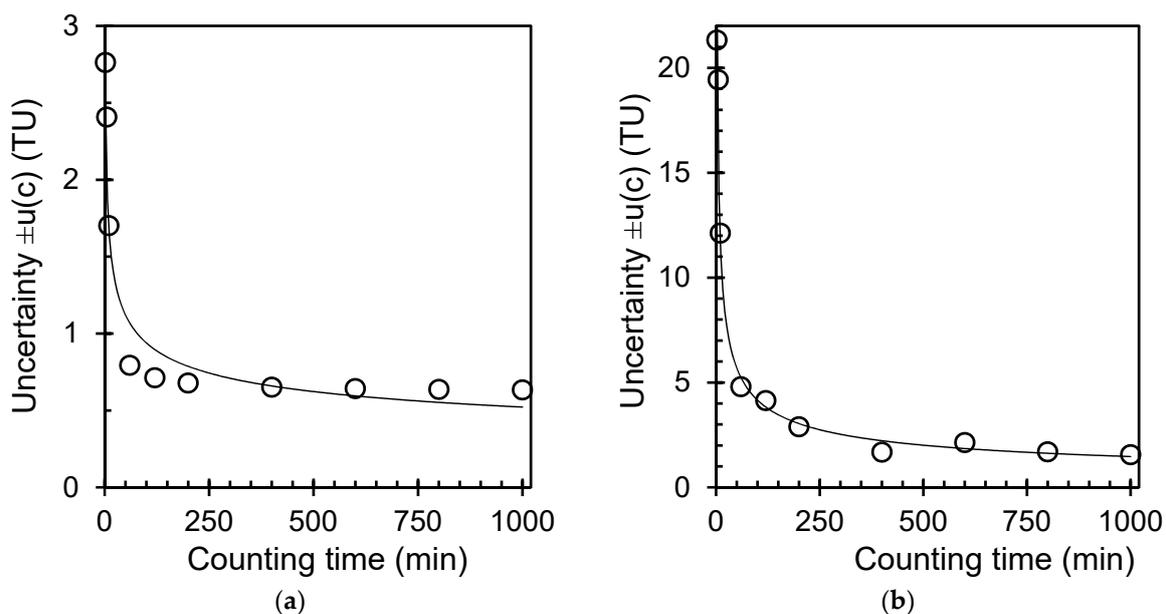


Figure 6. Counting time-dependent measurement error, $\pm u(c)$ (TU) using (a) Equation (10) and (b) MikroWin software for sample 5.

For time-dependent measurement error (one sigma), MikroWin software from Hidex was used. “One sigma error” refers to the degree of variability or dispersion in a set of data, which is quantified by the standard deviation. This statistical measure is represented by the Greek letter “sigma” (σ), and it reflects how far the data points deviate from the mean or central value [32]. The one sigma error conveys a given measurement’s precision level in measuring accuracy. It also reflects our confidence level in the reported value, with a lower one-sigma error indicating higher precision and confidence in the measurement result (Figure 6b). The higher the counting time is, the lower the uncertainty. Counting times of more than seven hours have almost similar errors.

To verify the accuracy of the measurement system, the tritium concentration was measured for the prepared samples by LSC and compared to assess the accuracy of the measurement system. To assess the quality of the analytical procedures, the Z score value was computed using the ISO13528 guidelines established by the International Organization for Standardization in 2015 [9]. The Z score value is a statistical tool utilized to determine the degree of variation between the actual and anticipated values. The calculation involves factoring in the number of measurements taken, the standard deviation of the measurements, and the difference between the measured and anticipated values. The resulting Z score value is then compared against a predetermined set of standards to determine the quality of the analytical procedures [9].

$$Z = \frac{A_s - A_m}{\sqrt{U_s^2 + U_m^2}} \dots\dots\dots (12)$$

where A_s is the spiked tritium activity of the reference sample (TU) and A_m is the measured tritium activity of the reference sample (TU). U_s and U_m are the spiked and measurement uncertainties of the reference sample, with a confidence level of 95% and a coefficient of 2 ($k = 2$). The resulting Z score value must fall between -1 and 1 for quality. The specific activity of the reference sample with a Z score is listed in Table 2. The table shows that the Z score values are between -0.3 and 0.5 , indicating that the measured values are within an acceptable range of the expected values with uncertainty in the measurements. Nevertheless, the measured values are within an acceptable range of the expected values, indicating that the measurement system is accurate and precise.

Table 2. Tritium activity concentration of reference samples measured by Hidex 300 SL.

| Sample ID | Measured Activity, C (TU) | \pm Error (TU) | Z |
|-----------|---------------------------|------------------|----------|
| Sample 1 | 8760 | 560.9 | -0.315 |
| Sample 2 | 4124 | 264.1 | 0.392 |
| Sample 3 | 820 | 52.42 | 0.175 |
| Sample 4 | 395 | 25.29 | 0.222 |
| Sample 5 | 89.5 | 5.740 | -0.333 |
| Sample 6 | 40.3 | 2.590 | 0.372 |
| Sample 7 | 10.7 | 0.694 | -0.458 |
| Sample 8 | 3.73 | 0.253 | 0.401 |
| Sample 9 | 0.69 | 0.081 | 0.508 |
| Sample 10 | 0.42 | 0.061 | 0.278 |
| Sample 11 | <MDA | | |
| Sample 12 | <MDA | | |

Another statistical comparison is made from the plot to confirm the accuracy and precision of the measurement data. For this, the spiked tritium activity values are plotted on the x -axis, and the measured tritium activity values are plotted on the y -axis, as shown in Figure 7. The known value of the tritium activity concentration in a sample and the measured activity concentration of tritium in the same sample were compared. Each data point represents one measurement, corresponding to values for the spiked and measured

activities. The line of best fit is added to the plot to show the relationship between the two variables.

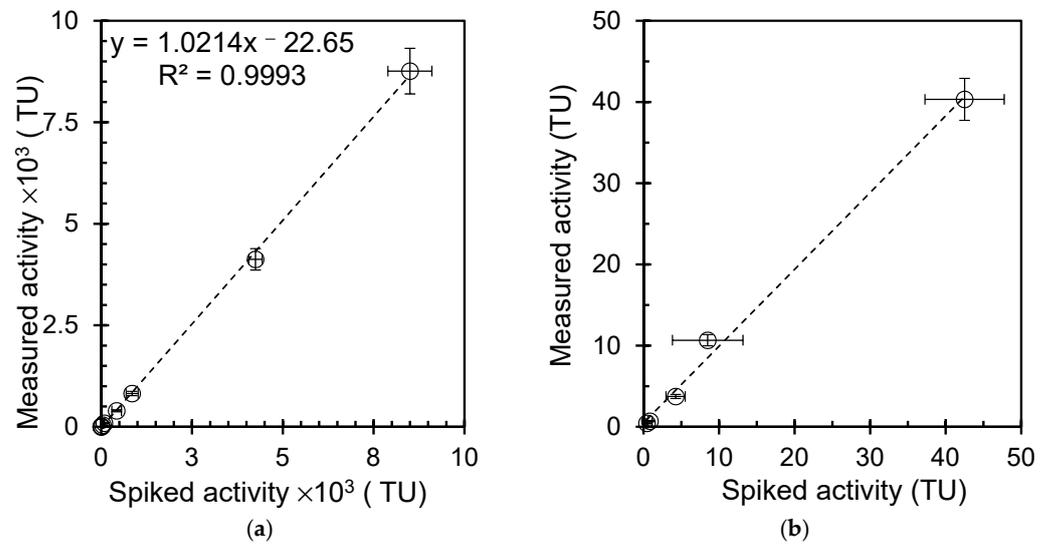


Figure 7. A comparison of spiked tritium activity concentration (known value) with measured tritium activity concentration; (a) high activity samples and (b) low activity samples.

The plot in the figure shows a linear relationship between the two variables, and the data points closely follow the line of best fit. An R^2 value of 0.9993 is very high and suggests a robust linear correlation between the plotted variables. The results also suggest that the measured data are precise and accurate compared to the spike activity data, with little or no variability in the data points.

MikroWin is a software program provided by Hidex that is often used for data analysis of liquid scintillation counters. MikroWin can calculate the MDA by inputting the necessary parameters and running the appropriate analysis for the sample. This can be used to optimize the liquid scintillation counting procedures and improve the quality and reliability of their results. The variation in the MDA can depend on several factors, including the background radiation levels and the counting time used for the measurement. The estimated MDA value using MikroWin software by Hidex and the calculated MDA value using Equation (7) for a sample are shown in Figure 8. The plot shows a linear dependence with a very high R^2 (0.9962) value, again suggesting a robust linear correlation between the two methods. The results suggest that both methods' minimum activity concentration data are precise and accurate.

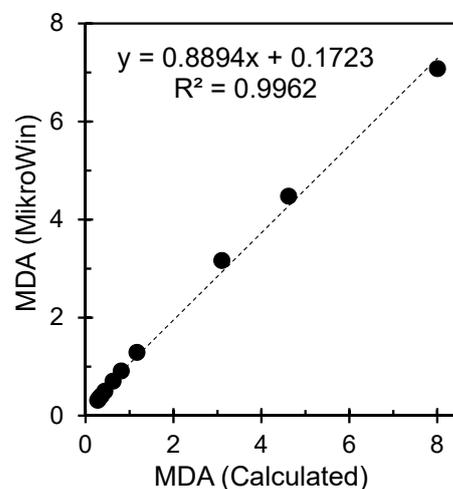


Figure 8. Variation of minimum detectable activity using MikroWin software and Equation (7).

3.4. Effect of the Volume Ratio of Water Sample with Scintillation Cocktail

The scintillation cocktail contains fluorescent compounds and organic solvents, aiding in converting energy from radioactive decay into detectable light flash through a photomultiplier tube. The efficiency of scintillation counting and the overall sensitivity of measurements can be influenced by the volume ratio of the water sample to the scintillation cocktail. Figure 9 shows such efficiency with water-to-scintillation cocktail volume ratios. The results show that the efficiency depends on the volume ratio with a maximum of approximately 10:10. The results can be explained by the way that when the water sample volume is excessive compared to the scintillation cocktail, excess water (sample) can provide more radioactive particles but also more water (quenching), thus reducing the light yield that, the net effect, resulted in less efficiency.

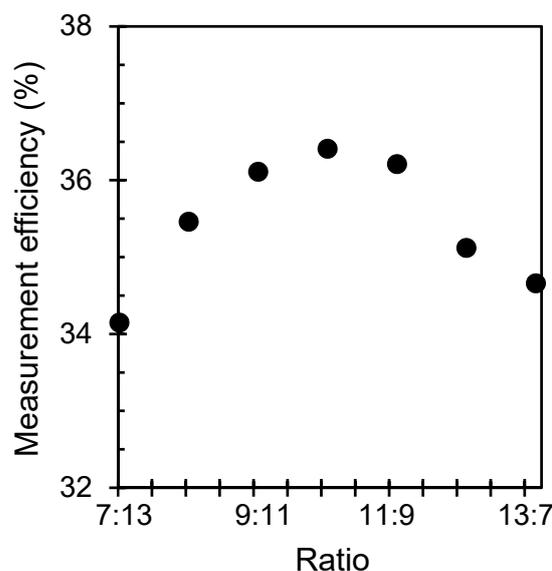


Figure 9. Variation in the measurement efficiency of tritium by LSC as a function of the volume ratio of water sample with scintillation cocktail (Hidex AquaLight plus).

Conversely, when the scintillation cocktail is excessive, there is a higher light yield from the cocktail, but a lower water sample (radioactive particles) introduced; the net effect is then also less efficiency. Hence, applying an optimum volume ratio (in our study, 10:10) is crucial based on the measurement's specific requirements and the sample's characteristics. The optimal ratio might also depend on other factors, such as sample activity, the type of scintillation cocktail, and the desired sensitivity of the measurement.

Interfering contaminants in a sample can abruptly and precisely detect and calculate the tritium activity concentration. These substances can be other radioactive isotopes, chemical compounds, or physical particles with similar characteristics or producing comparable signals to the target radiation. Therefore, the presence of these contaminants can affect the accuracy and sensitivity of the analytical method, resulting in inaccurate results. For a precise calculation, sample preparation and storage should be performed in an isolated environment to mitigate the impact of interfering contaminants. Moreover, to improve the accuracy and precision of the tritium activity measurements, shielding the sample from background radiation can be done using physical barriers or materials that block or absorb unwanted radiation. Background radiation may come from natural sources or electronic equipment. Some shielding materials, for example, lead, concrete, and other materials, can attenuate radiation. In this case, the shutter option in LSC should be turned on, and a unique sample holder with radiation protection should be used to store samples. Additionally, low-background counting techniques and instruments, such as underground or shielded counting laboratories, can be utilized to minimize the impact of background

radiation. Reducing background radiation improves the signal-to-noise ratio, which can also help lower the MDA and improve the accuracy of the radioactivity measurements.

4. Conclusions

The present study aims to find an optimization method to minimize the detectable activity of conventional scintillation counters to estimate the low-level tritium activity concentration in groundwater. Several methods have been proposed to lower the detection limit. First, enriching water samples ten- to fortyfold of the initial concentration of the tritium by the electrolysis process can significantly lower the MDA by an order of magnitude. Second, the background radiation in the environment should be reduced as much as possible. By reducing the background radiation in the sample, the signal-to-noise ratio can be improved, increasing the accuracy and precision of the tritium activity measurements. Third, the counting time required for the LSC detection system to measure the tritium activity should be sufficient to improve the sensitivity of the detection system and reduce the minimum detectable activity. Fourth, shielding the samples from background radiation using lead or other radiation-absorbing materials, which can be used as physical barriers to block or absorb unexpected background radiation. Moreover, the ratio between the water sample and the scintillation cocktail (10:10) shows maximum counting efficiency. Finally, the shutter option in LSC should be turned on, and a unique sample holder with radiation protection should be used to store samples to lower the MDA value, as it enables accurate detection to quantify low radioactivity levels, essential for ensuring public health and safety.

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