

## Article

# Enrichment of Low-Level Tritium in Groundwater via an Electrolysis Process for Liquid Scintillation Counting Applications

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**Abstract:** Tritium levels in the groundwater of arid regions are very low; in most cases, these low tritium levels cannot be detected using a conventional liquid scintillation counter (LSC). To measure the tritium activity concentration, low-level tritium in groundwater needs to be enriched by a known factor so that the scintillation counter can detect it. An electrolysis process with electrolytic cells was designed and fabricated in our laboratory following the International Atomic Energy Agency (IAEA) instructions. Nine spiked samples with a known quantity of tritium were enriched, and the tritium activity concentration was measured using the scintillation counter. The enriched water exhibits a comparable level of spiked samples, albeit with some degree of uncertainty. A correlation was drawn among the tritium activity, enrichment factor, and the required time for the electrolysis procedure. This study confirmed that an enrichment process of approximately ten- to fortyfold of the initial concentration of the tritium could be achieved using the electrolysis process with the fabricated electrolytic cells. The simple design and fabrication of the electrolysis process by controlling various parameters make it affordable to measure low-level tritium using a conventional LSC. Various statistical analyses confirmed the accuracy and precision of the data obtained by the electrolysis process. This enrichment technique would prove valuable in regions where tritium levels in groundwater are extremely low, making them challenging to detect using conventional liquid scintillation counter.

**Keywords:** electrolysis process; tritium enrichment; electrolytic cells; liquid scintillation counter; enrichment yield



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## 1. Introduction

In arid or semiarid regions, low rainfall and high evaporation rates result in a scarcity of water resources [1]. In rural areas, groundwater is the only water source for human consumption and agriculture. Natural tritium in groundwater can cause serious health effects [2–4]. However, the tritium concentration in groundwater is typically very low due to limited rainfall and slow recharge rates. The minimum detectable activity of a scintillation counter refers to the smallest amount of radiation that the counter can detect with a reasonable degree of accuracy. In most cases, conventional liquid scintillation counters are not sensitive enough to detect low-level tritium. Therefore, an enrichment process is necessary to measure the tritium activity concentration in groundwater samples [5]. Electrolytic enrichment of water is a process that involves using an electrolytic cell to increase the concentration of specific compounds such as tritium in water [6]. The electrolytic cell typically comprises two electrodes (an anode and a cathode) separated by an electrolyte solution. When an electric current is passed through the electrolytic cell, the water molecules dissociate into hydrogen ions (protons) and hydroxide ions ( $\text{OH}^-$ ). Depending on the electrolyte solution and the direction of the current, the concentration of the target compound can be enriched. Electrolytic enrichment can also increase the concentration of other ions or compounds in water, such as dissolved oxygen, hydrogen peroxide, or ozone.

These enriched solutions can be used in various applications, such as water treatment, disinfection, or industrial processes [7]. The enrichment process involves increasing the tritium concentration by a known factor through electrolysis. The severalfold enrichment of tritium in groundwater allows for estimating the level of tritium in groundwater and making informed decisions regarding water management and usage.

There are several methods of electrolytic enrichment, each with its advantages and disadvantages. For example, the alkaline electrolysis method uses an electrolyte solution, typically potassium hydroxide (KOH) or sodium hydroxide (NaOH) solution [8,9]. In proton exchange membranes (PEMs), electrolysis uses a solid polymer electrolyte membrane, which selectively conducts protons but not electrons, to separate the anode and cathode compartments [10]. PEM electrolysis can operate at lower temperatures and pressures than alkaline electrolysis, but it requires more expensive materials and can be less efficient. On the other hand, solid oxide electrolysis uses a solid oxide electrolyte [11], typically a ceramic material, to separate the anode and cathode compartments. Alkaline electrolysis is the most mature and widely used electrolytic enrichment method [12]. In alkaline electrolysis, an aqueous solution of potassium hydroxide or sodium hydroxide is used as the electrolyte, and the electrodes are made of nickel or steel. This method has many advantages due to its low operating temperature and pressure. However, alkaline electrolysis has some limitations, such as the production of a large amount of caustic waste and the need for frequent electrode replacement compared to other methods [13].

Many studies have been reported on the electrolysis process. For example, Plastino et al. [14] discuss a method for assessing tritium levels in water samples using electrolytic enrichment for liquid scintillation counting (LSC). The research entails optimizing the LSC system, conducting performance tests, and analyzing uncertainties. Feng et al. [15] examined a low-background liquid scintillation counting system that employed 0.1 L counting vials to enhance the measurement of airborne tritium in the environment. After a dark adaptation time exceeding 1440 min, the researchers discovered optimal counting could be achieved by mixing a 0.05 L water sample with a 0.05 L scintillation cocktail. The 0.1 L vial system displayed a minimum detectable activity (MDA) of  $0.18 \text{ Bq}\cdot\text{L}^{-1}$  during a continuous counting period of 3600 min, which was approximately 3.5 times lower than the MDA value of the 0.02 L vial system. The study suggests utilizing electrolytic enrichment for accurately determining samples with specific activity below  $0.4 \text{ Bq}\cdot\text{L}^{-1}$ . However, it also recommends using the 0.02 L vial system following the electrolysis enrichment process due to the cost and potential environmental impact associated with the available cocktail. Another report presented a new method for tritium enrichment in water using a solid-phase extraction (SPE) polyaniline film as an electrolysis electrode [16]. The SPE film selectively adsorbs tritiated water and allows nonradioactive water to pass through, resulting in efficient and selective tritium enrichment. The study suggests that SPE film electrodes offer a promising alternative to traditional electrolysis for tritium enrichment. Villa et al. [5] devised a technique that utilizes electrolytic tritium enrichment and a liquid scintillation counter to measure trace amounts of tritium in environmental water. The method underwent rigorous quality testing to ensure its accuracy. The researchers employed the method to analyze drinking water samples from Seville's public water supply and mineral waters from various springs in Spain to ascertain their sources. Recently, a highly sensitive technique was developed to detect low levels of tritium in seawater samples. This method involves electrolysis enrichment and ultralow-level liquid scintillation counting. By optimizing the measurement parameters, a detection limit of 0.45 Tritium Units (TU) for tritium was achieved using 0.7 L seawater samples. This method applies to most seawater samples, except for deep seawater. Zang et al. [17] employed this method to analyze tritium levels in the East China Sea. However, the above reports suggested that the electrolysis process increased the tritium concentration in water for detection by the conventional scintillation counter.

An enrichment process with 13 electrolytic cells was designed and fabricated in our laboratory by following the IAEA instructions. Nine samples with a known tritium

concentration were used in the enrichment process. A correlation between the enrichment factor with water volume and the corresponding time required for the electrolysis process was analyzed. Various statistical analyses were used to confirm the accuracy and validate the obtained data through electrolysis.

## 2. Materials and Methods

### 2.1. Samples

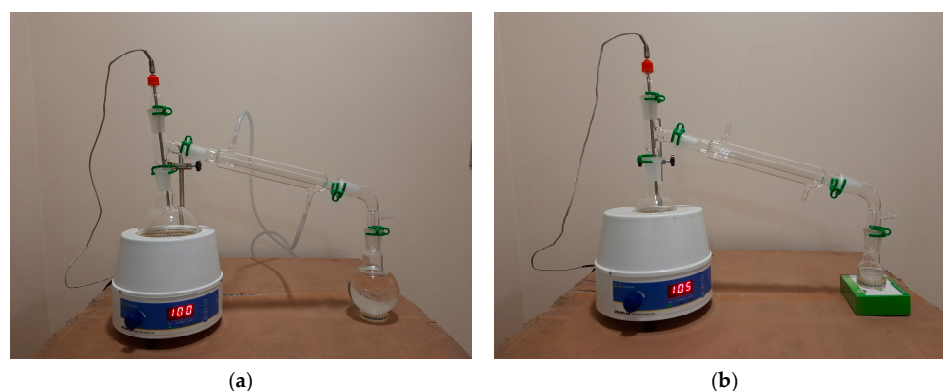
A series of tritium solutions were prepared by diluting the standard solution certified by Eckert & Zeigler, P.O: P700723 and source: 1676-44, with tritium-free water in a controlled manner. The resulting solutions were then analyzed to determine their activity concentration. Table 1 shows the specific activity concentration of the tritium for 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 ( $^3\text{H}$  and  $^{14}\text{C}$ ) 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 via dilution from the standard sample.

Sample ID	Spiked Activity ( $\text{Bq}\cdot\text{L}^{-1}$ )	$\pm$ Error ( $\text{Bq}\cdot\text{L}^{-1}$ )
Ref. [1]	1000	71
Ref. [2]	500	22
Ref. [3]	100	20
Ref. [4]	50	16
Ref. [5]	10.0	1.5
Ref. [6]	5.0	0.6
Ref. [7]	1.0	0.5
Ref. [8]	0.5	0.2
Ref. [9]	0.10	0.03

### 2.2. Primary Distillation

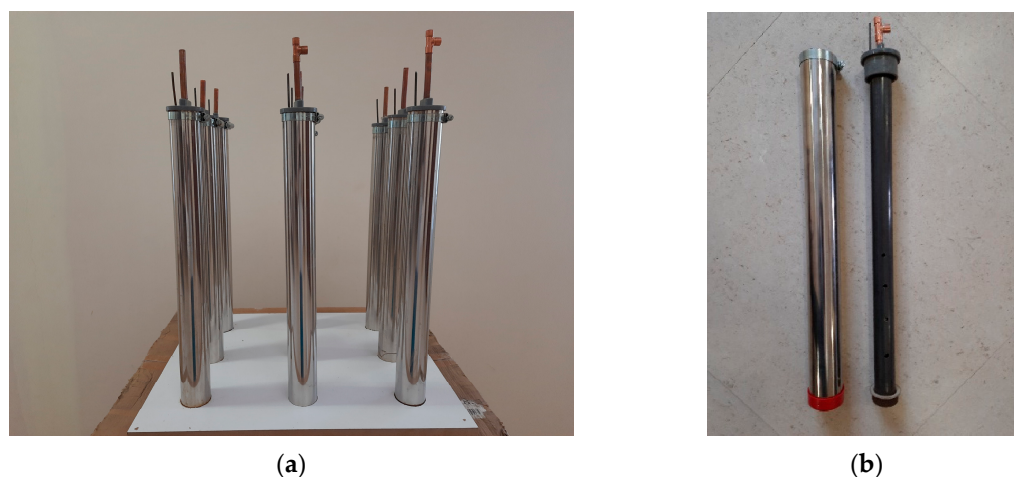
The primary distillation of groundwater involves heating water until it reaches boiling point, resulting in steam formation. This steam is then collected, allowed to cool, and condensed back into liquid form, leaving behind any impurities or contaminants that were in the water. A conventional apparatus was used, as shown in Figure 1a. The groundwater samples were distilled using a distillation process to remove all dissolved ions ( $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Ca}^{2+}$ ,  $\text{CO}_3^{2-}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ , etc.) and dissolved solids naturally present in groundwater. It was confirmed via a YSI 9500 photometer (Xylem brand, Ohio, USA) and Horiba LAQUAtwin (Kyoto, Japan) digital ion meters for  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{Ca}^{2+}$ ,  $\text{Na}^+$ , and  $\text{K}^+$ , that those various ions and salts were absent.



**Figure 1.** Photograph of the (a) primary distillation unit (up to 1 L) and (b) final distillation unit (up to 0.05 L).

### 2.3. Electrolytic Enrichment

A batch of 13 electrolysis cells were fabricated and developed in our laboratory. The electrolysis cells were designed to increase concentration of tritium in water samples to a detectable level via LSC. The design of the cells closely resembled the system used by the International Atomic Energy Agency (IAEA), which is commonly used for tritium enrichment [14,18]. The materials used for cell construction were 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. Mild steel, commonly used in constructing structures and equipment, is a form of carbon steel characterized by its low carbon content. Stainless steel, conversely, contains chromium, making it resistant to corrosion and staining. For this reason, stainless steel is an ideal material for electrolysis cells; otherwise, corrosion would be a significant issue after several electrolytic runs. The construction of the electrolysis cells involved careful consideration of various factors, such as the size of the cells, the spacing between the electrodes, and the materials used for the electrodes. These factors were optimized to ensure that the cells efficiently enriched the tritium level in the water samples. Figure 2 shows photographs of the electrolysis cells with their outer and inner parts.



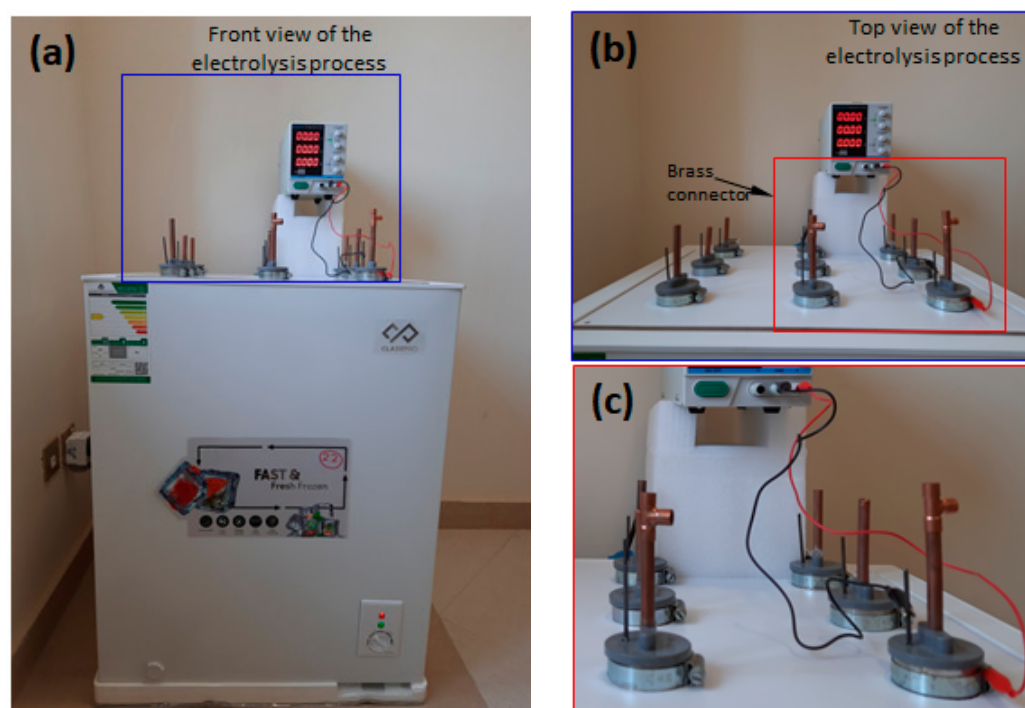
**Figure 2.** Photograph of (a) electrolysis cells and (b) the outer and inner parts of the cell, the outer part is made of stainless steel (left) and the inner part is mild steel (right).

In addition, several tests were carried out for the current passing through the cells and the corresponding time required for the electrolysis process to ensure that the tritium concentration could be increased to the desired level. A brass ring at the top of the anode tube (Figure 2b) was a mounting aid and an electrical connection. The cathode, on the other hand, was made of mild steel tubing. Before assembling the cell, the cathodes underwent special chemical treatment to enhance the cell's performance [1]. However, this treatment does not need to be repeated frequently, as a black surface layer typically develops over time, leading to a steady increase in the separation factor during the first 30 to 40 enrichment runs [7]. The electrolysis process was conducted at near-freezing temperatures to maximize the isotope discrimination. Throughout the process, tritiated water was clearly concentrated in the residual water present in the cell. This occurred due to the slightly higher binding energies between tritium and oxygen. Consequently, the tritium was enriched by an enrichment factor ranging from 10 to 40, with an uncertainty of  $\pm 2$ , depending on the initial and final volumes of water involved in the process. The electrolysis process is time-consuming and typically takes one to two weeks, depending on the initial water volume.

The water sample was weighed into the electrolytic cell (anode and cathode) for the electrolysis process, and later, 1 g sodium peroxide ( $\text{Na}_2\text{O}_2$ ) was added. Nine reference samples (spikes with known concentrations) were run to determine the exact enrichment

factor to control the electrolysis process. A so-called ES 400 electrolysis process was used, suitable for samples with a very low  $^3\text{H}$  content [19]. 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  $\text{H}_2$  and  $\text{O}_2$  (oxyhydrogen), which are discharged. Extra care was taken to release exhaust gases into the outdoor air. As a result, heavier  $^3\text{H}$  accumulates in the remaining water. Here, it should be mentioned that a tritium unit (TU) is the proportion of one tritium isotope per  $10^{18}$  H atoms. At 1 TU, a sample has an activity of  $0.118 \text{ Bq}\cdot\text{L}^{-1}$ . In our laboratory, nine cells can be simultaneously run for the electrolysis process. After electrolysis, the final volume of the water sample was always higher than 0.015 L to maintain a higher enrichment factor.

Multicell configurations comprising 10 to 15 cells are commonly used for simultaneous enrichment. To prevent evaporation, the temperature of the water sample in each cell must be cooled to a low temperature ranging from 0 to  $2^\circ\text{C}$ . Modern electrochemical enrichment systems typically integrate temperature control and electronic regulation mechanisms to facilitate electrolysis [14]. In this study, a constant temperature was maintained using an electrical refrigerator, as depicted in Figure 3. Next, each cell in the system must be evaluated for its isotopic separation performance. This was accomplished by introducing a known quantity of tritium water into the cell and measuring the "recovery of tritium." The recovery of tritium serves as an indicator of each cell's performance. Ideally, cells of similar quality should exhibit comparable performance. However, it is essential to note that significantly reduced tritium recovery was observed when the volume of the remaining water in a cell was less than 0.013 L. For this particular system, the minimum volume of the remaining water should exceed 0.013 L. Regular checks are conducted every six months to ensure the electrolytic enrichment system's ongoing performance. The tritium recovery in each cell is compared against a known standard, along with the final remaining water volume measurement. The enrichment factor (EF) is simply the tritium enrichment yield ( $\eta_{A,i}$ ) multiplied by the mass of the water added to each electrolytic cell before the electrolysis process ( $m_{v,i}$ ) and divided by the mass of the water remaining in the cell after the electrolysis process ( $m_{n,i}$ ) [14,20,21].



**Figure 3.** Photographs of the tritium enrichment apparatus; (a) electrolytic cells mounted inside the refrigerator at a constant temperature, (b) top view of the refrigerator, and (c) expanded image of cells.

#### 2.4. Neutralizing Alkalinity

It is essential to neutralize the alkalinity of the solution caused by the presence of electrolytes used for the electrolytic process. Nevertheless, the presence of salts derived from weak acids, such as borates, silicates, and phosphates, can also contribute to alkalinity. Certain organic acid salts can contribute to alkalinity in polluted water. Neutralization is achieved by adding an acidic substance to the solution, which then reacts with the alkaline substances to form a more neutral product. However, the acid and base reaction will result in water and salt formation. It is important to note that when adding acidic substances to neutralize alkalinity, the pH level of the solution should be carefully monitored to ensure that it does not become too acidic. A pH level of 7 is considered neutral, and it is essential to aim for this level when neutralizing an alkaline solution. A Horiba LAQUAtwin (HORIBA, Ltd., Kyoto, Japan) digital pH meter was used to control the alkalinity of the water samples.

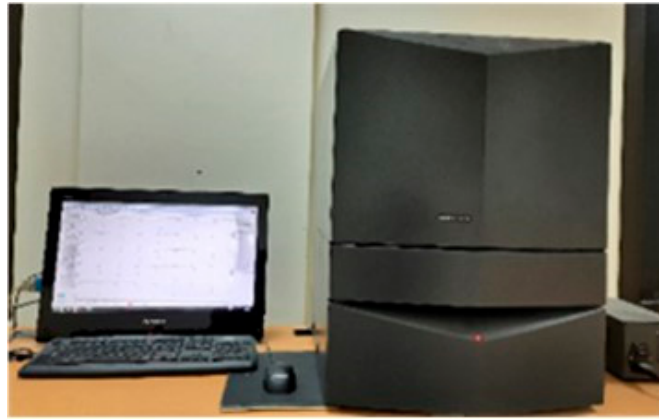
#### 2.5. Final Distillation

Once the electrolytic process is completed, confirming the absence of electrolytes in the solution is essential. Electrolytes are ions that carry an electric charge and can conduct electricity. If electrolytes are present in the solution, they can interfere with subsequent chemical reactions or processes during measurement with the scintillation counter. To remove the electrolytes, a final distillation was performed by heating it to its boiling point, and the resulting vapor was collected and condensed to produce water. After distillation, the water samples were tested again for the presence of any impurities using a YSI 9500 photometer and a Horiba digital meter. After confirming the absence of electrolytes, the water samples were transferred for the scintillation counting stages.

#### 2.6. Tritium Activity Measurement

Following the final distillation, a water sample of 0.01 L was combined with a scintillation cocktail of 0.01 L (Aqualight plus, Hidex, London, 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. The samples were stored in a cool and dark place and allowed to sit for at least four hours before measuring to prevent the luminescence effect.

Tritium analysis was performed using a liquid scintillation counter Hidex 300 SL (Figure 4). The analysis was based on the triple-to-double coincidence ratio (TDCR) method [22]. The liquid scintillation counter utilized in this study is equipped with three photomultiplier tubes, which enable the counting of the triple-to-double coincidence ratio. This feature provides an efficient approach for analyzing unknown samples [23–25]. 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 discussed earlier [26–28]. 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 4.** Liquid scintillation counter to measure tritium activity concentration (Hidex 300SL).

### 2.7. Mathematical Formulation

A standard source (provided by Hidex) was used for efficiency measurement, and measurement was carried out under the same conditions as the unknown samples. The efficiency of the tritium measurement can be calculated from the following equation:

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

Flashes are quantified using a liquid scintillation counter (Hidex 300 SL) 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 (zero-value samples) are also estimated to evaluate data with similar experimental conditions.

The tritium activity concentration during the counting time via LSC was calculated using the following equation:

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

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

- $c$  Activity concentration of tritium at the counting time ( $\text{Bq} \cdot \text{m}^{-3}$ );
- $f_A$  Correction factor for the decay;
- $\lambda$  Decay constant of tritium in  $\text{s}^{-1}$ ;
- $t_A$  Time between sampling and beginning of the measurement in s;
- $R_n$  Net count rate of the counting source in  $\text{s}^{-1}$ ;
- $\varepsilon$  Detection efficiency in  $\text{Bq}^{-1} \cdot \text{s}^{-1}$ ;
- $\rho$  Density of the water in  $\text{kg} \cdot \text{m}^{-3}$ ;
- $m_n$  Mass of solution remaining in the electrolysis cell after electrolysis, in g;
- $m_v$  Mass of the solution added to the electrolysis cell before electrolysis, in g;
- $m_M$  Mass of distillate in the scintillation vial, in g.

## 3. Results and Discussion

### 3.1. Tritium Enrichment Yield of the Electrolysis Cells

Since electrolysis cells are used more frequently, the tritium enrichment yield was checked regularly. The tritium enrichment yield is a metric that reflects the efficiency

of the electrolytic cells in retaining tritium during the enrichment process. For example, a yield of 1 indicates that 100% of the tritium has been retained, while a yield of more than 0.95 suggests that the electrolysis process has been performed adequately. For the tritium yield calculation, electrolytic enrichment was carried out for known concentrated tritiated water (standard sample provided by Hidex and reference samples prepared from the standard sample) by following the same experimental procedure mentioned in the experimental section. First, the tritium activity was measured using LSC before and after the enrichment procedure. Then, the tritium yield was calculated for each electrolytic cell using the following equation [16]:

$$\eta_{A,i} = \frac{a_{n,i} \cdot m_{n,i}}{a_{v,i} \cdot m_{v,i}} \quad (5)$$

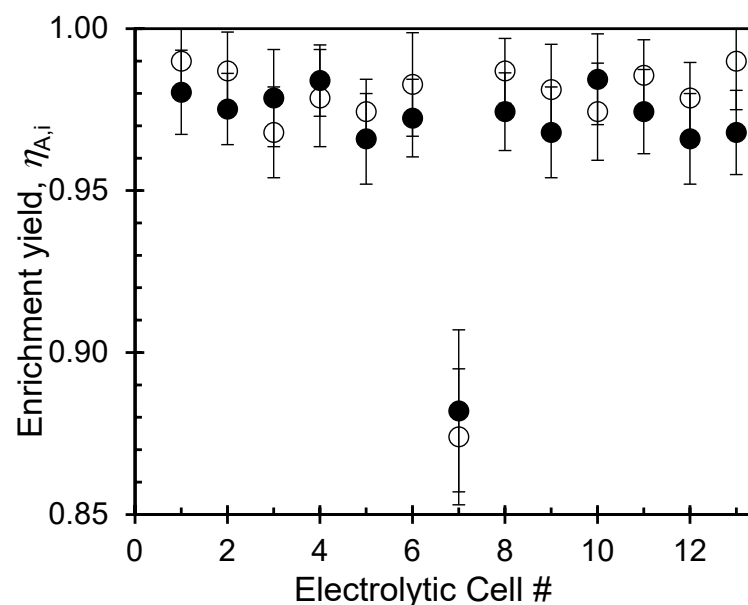
where

$\eta_{A,i}$  is the tritium enrichment yield of a specific electrolytic cell;

$a_{v,i}$  and  $a_{n,i}$  are the tritium activity before and after the electrolysis process;

$m_{v,i}$  and  $m_{n,i}$  are the mass of the water added and remaining in the electrolysis cell before and after the electrolysis process.

Figure 5 illustrates the tritium yield calculated for each cell in the experiment using Equation (5). The graph depicts a high level of tritium enrichment yield (more than 0.95) with minimal variability across the 13 cells, except for cell #7. The sudden decrease in performance observed in cell #7 could be attributed to an inadvertent reversal of the cell polarity, which occurred once by mistake during the experiment. For this reason, cell #7 was not used again for the electrolysis process.

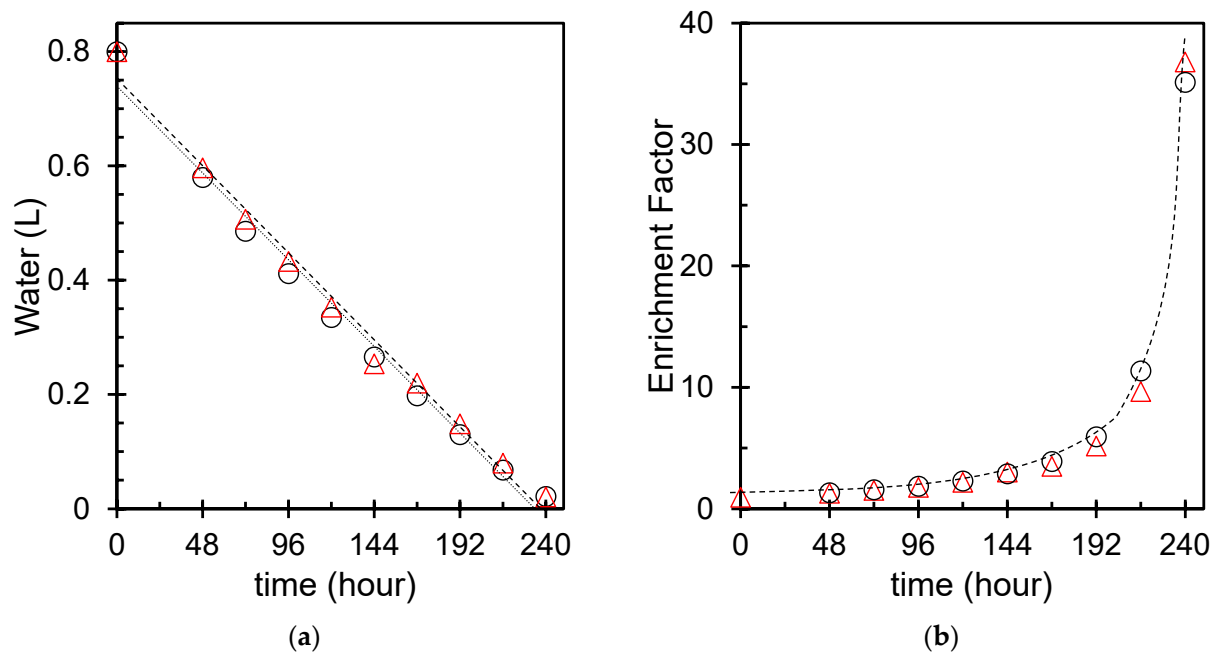


**Figure 5.** Tritium enrichment yield as determined in all 13 cells for standard sample 2 (500 Bq·L<sup>-1</sup>, solid circle) and standard sample 5 (10 Bq·L<sup>-1</sup>, open circle). Cell no. #7 shows a sudden low enrichment yield.

### 3.2. Time-Dependent Enrichment Factor

The volume of water used during the electrolysis process depends on the specific reaction occurring at the electrodes and the quantity of electrical current flowing through the electrolyte solution. During water electrolysis, the anode produces oxygen gas, while the cathode generates hydrogen gas, and the amount of hydrogen and oxygen produced is directly proportional to the electrical current passing through the solution [29]. The electrolysis process consumes water molecules, which reduces the water volume within

the electrolyte solution. As more electrical current flows through the solution, more water is used, and more gas is produced. The extent of change in the reduced water volume depends on the ratio of hydrogen to oxygen produced and the temperature and pressure conditions under which the reaction occurs. Figure 6 shows such a volume reduction with time for an applied voltage ranging from 2.2 to 2.7 volts across each cell. This voltage was sourced from a power supply with the current stabilized at a maximum of 10 amperes (A). Figure 6 shows that the volume of water decreases with electrolysis time.



**Figure 6.** Time dependent (a) water reduction and (b) enrichment factor during the electrolysis process for two typical samples 5 and 7 (black circles and red triangles).

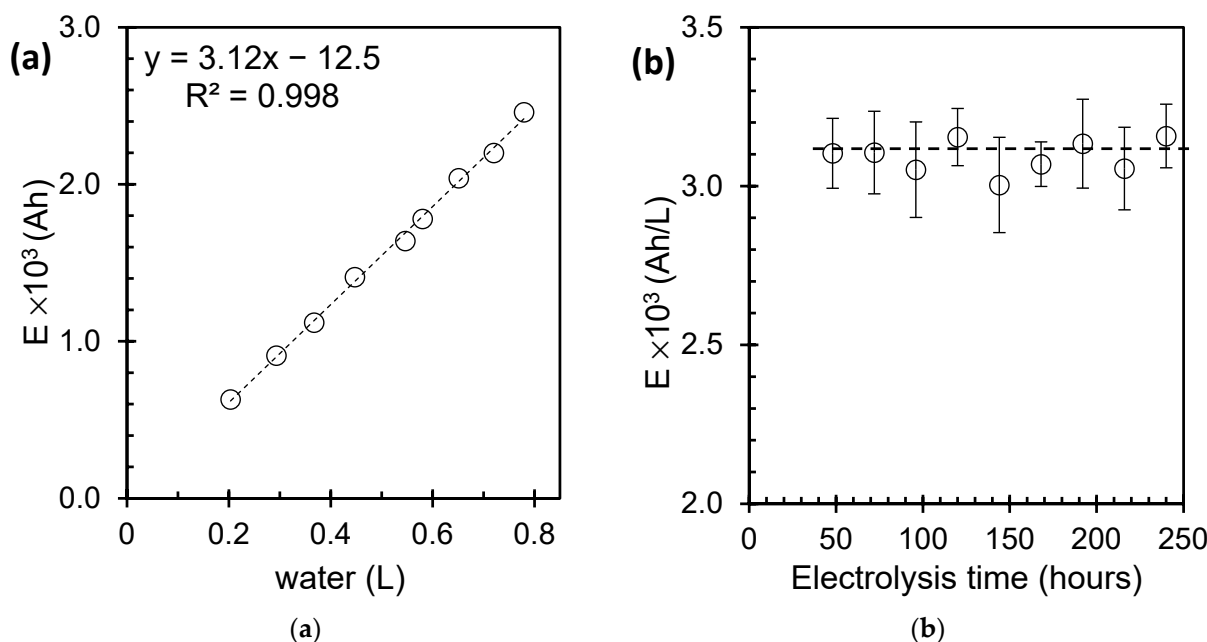
In addition to the current and electrolysis time, other factors, such as volume reduction, can also impact the tritium enrichment process. The volume reduction factor refers to the ratio of the initial volume of the solution to the final volume of the concentrated tritium product. This factor is important because it can impact 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. Finding the optimal volume reduction factor is important in the tritium enrichment procedure. The enrichment factor of each sample was calculated by the initial and final volume ratio multiplied by the tritium enrichment yield. For example, if 0.8 L of the water sample is reduced to 0.022 L at the end of the electrolysis process, and if the tritium enrichment yield is 96.66%, the enrichment factor will be 35.15.

### 3.3. Required Energy for the Electrolysis Process

The required energy for enrichment through the electrolysis process depends on the initial concentration and the desired enrichment level. The process involves applying an electric current to the tritiated water solution, causing the migration of hydrogen ions toward specific electrodes. The electrodes, typically made of nonreactive materials, do not interact with the electrolyte or the electrolysis products. The energy required in this electrolysis process is primarily utilized to overcome activation energy, provide the necessary electric potential, and compensate for energy losses caused by system inefficiencies such as electrolyte resistance, solution heating, and other factors. In the present study, each cell contained approximately 0.8 L of the water sample. To enhance the electrolysis process,

the cells were connected in a series configuration, meaning that the output of one cell was connected to the input of the next cell, creating a continuous pathway for the electric current. A voltage ranging from 2.2 to 2.7 volts was applied across each cell. This voltage was sourced from a power supply, which supplied the electrical energy for the electrolysis. Initially, the current stabilized at a maximum of 10 amperes (A), which means that a current of up to 10 A flowed through the electrolyte, facilitating the migration of ions. The high current aided in the efficiency of the electrolysis process.

The energy required for the electrolysis process was examined with regard to the volume of water used. Figure 7a illustrates a linear correlation, suggesting that a consistent amount of energy is needed for the electrolysis of each liter of water. This means that energy consumption remains relatively constant regardless of volume. In Figure 7b, the estimated energy consumption is approximately 3150 ampere-hours (Ah) for each liter of water. This measurement indicates the energy needed to carry out the electrolysis process for a given volume of water. The data presented in Figure 7 help us to understand the energy requirements and efficiency of the electrolysis process. This shows that as the volume of water needed for electrolysis increases, the overall energy consumption also increases proportionally.



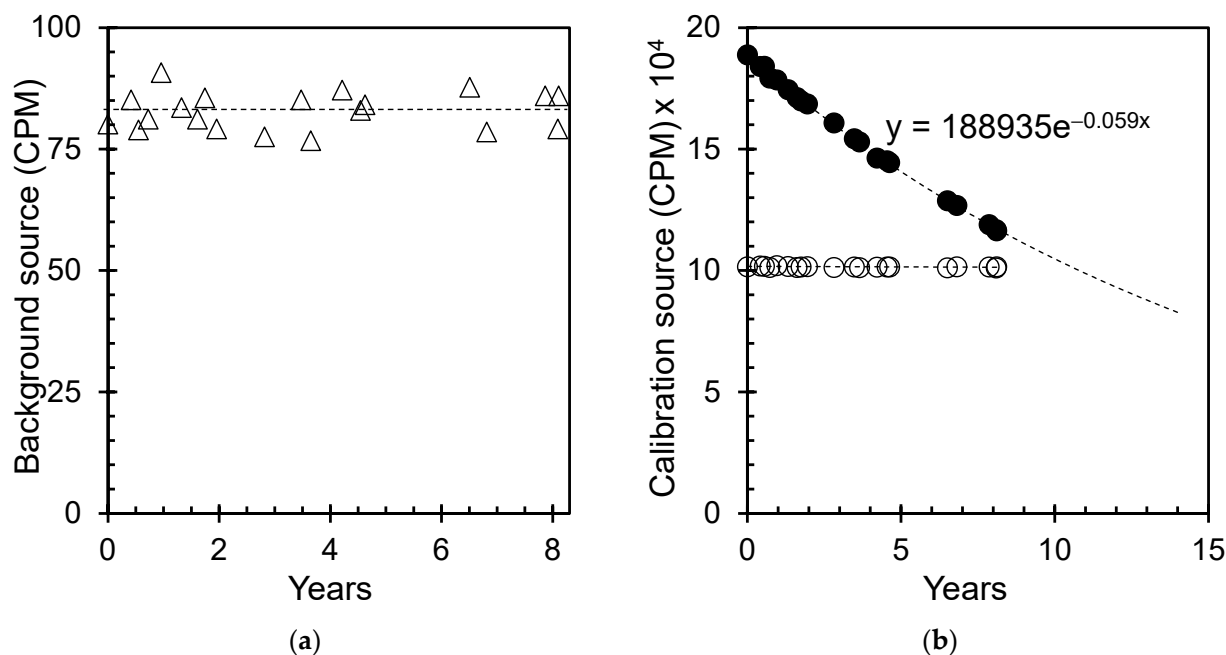
**Figure 7.** (a) Required energy for the electrolysis process as a function of water volume and (b) required energy per ml of water for different cells for typical sample 7.

### 3.4. Background Calibration for the Scintillation Counter

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 (<sup>14</sup>C) and tritium (<sup>3</sup>H) sources, as shown in Figure 8. Each sample was analyzed five times for 200 min. The activity-free water has demonstrated a consistent background reading over the past eight years, with minimal experimental error (Figure 8a). 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 <sup>14</sup>C source exhibited no significant changes, as expected due to its longer half-life of approximately 5715 ± 40 years [4].

In contrast, the standard tritium source (<sup>3</sup>H) 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 8b). By analyzing the gradual expo-

nential curve and decay equation, a rough estimation yielded a half-life of approximately 11.75 years for  $^3\text{H}$ , which is in close agreement with the published value of 12.3 years reported in the literature [30]. The stable background count and consistent  $^{14}\text{C}$  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.

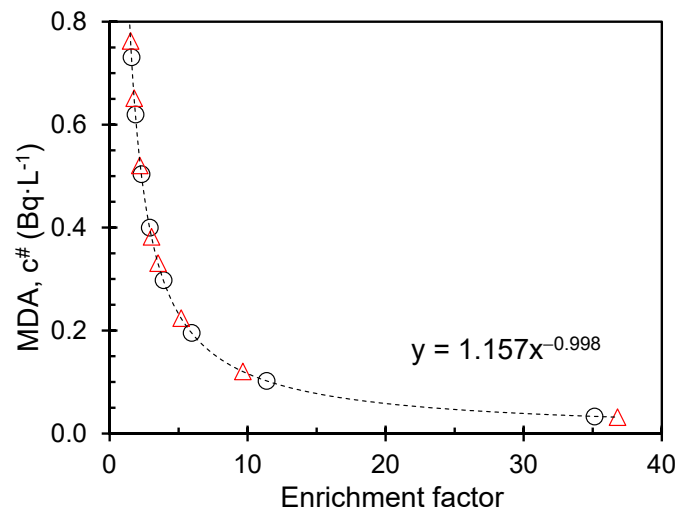


**Figure 8.** Eight-year record for the calibration source for the certified solution of (a) activity-free water for background levels, (b) a certified source of  $^{14}\text{C}$  indicated by open circles, and a certified source of  $^3\text{H}$  represented by solid circles. The flashes are measured in counts per minute (CPM). The dashed curve for  $^3\text{H}$  extends to visualize the exponential dependence with time.

### 3.5. Enrichment Factor and Minimum Detectable Activity

The minimum detectable activity (MDA) of a conventional liquid scintillation counter (LSC) is typically higher than the level of tritium present in the groundwater in most arid regions. An enrichment process by a known factor reduces the detection limit of the scintillation counter and enables accurate measurement of tritium levels in the sample.

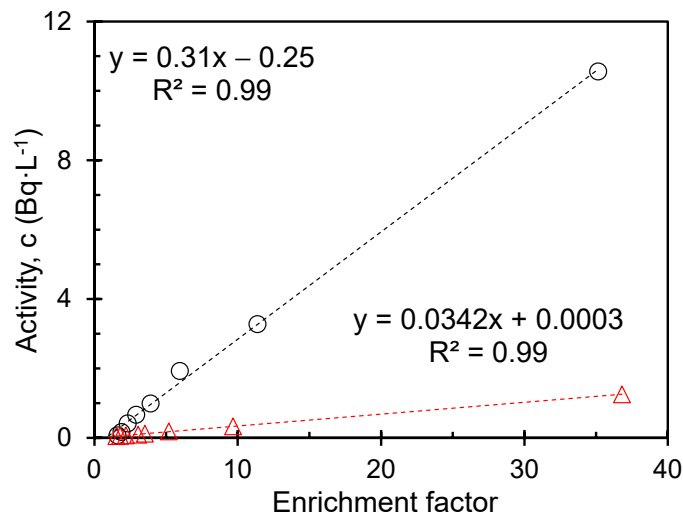
The relationship between the enrichment factor and the minimum detectable activity is essential because it helps determine the analytical performance of the method. MDA is the lowest concentration that can be reliably detected and quantified. As the minimum detectable activity (MDA) decreases, the method becomes more sensitive, allowing it to detect lower concentrations effectively. Figure 9 shows the minimum detectable activity as a function of the enrichment factor of the electrolysis process for two typical samples of 5 and 7 (black circles and red triangles). The figure shows a reverse relationship between the enrichment factor and the minimum detectable activity (MDA) in radioactivity measurements. The enrichment factor is defined as the ratio of the activity of the target in the enriched sample to the activity of the same in the original, unenriched sample. The target 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 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.



**Figure 9.** Minimum detectable activity, c#, as a function of enrichment factor of the electrolysis process for two typical samples 5 (black circles) and 7 (red triangles).

### 3.6. Enrichment Factor and Corresponding Activity

To understand the related activity of tritium, it is necessary to consider the enrichment factor, which quantifies the increase in the concentration of the tritium isotope. By applying the enrichment factor, one can calculate the corresponding activity of the enriched material. This calculation considers both the enrichment factor and the initial activity of the tritium. The activity of the enriched water is plotted against the enrichment factors shown in Figure 10. A linear correlation can be seen, inferring that the activity concentration of tritium increases with the enrichment of the water samples.



**Figure 10.** Tritium activity concentration, c, as a function of the enrichment factor of the electrolysis process for two typical samples 5 (black circles) and 7 (red triangles).

### 3.7. Data Validation

To evaluate the accuracy of the measurement system, the liquid scintillation counter (LSC) analyzed reference samples and compared the results. The specific activity of the reference sample was measured using LSC, and tabulated in Table 2. 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 [31]. 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 [31].

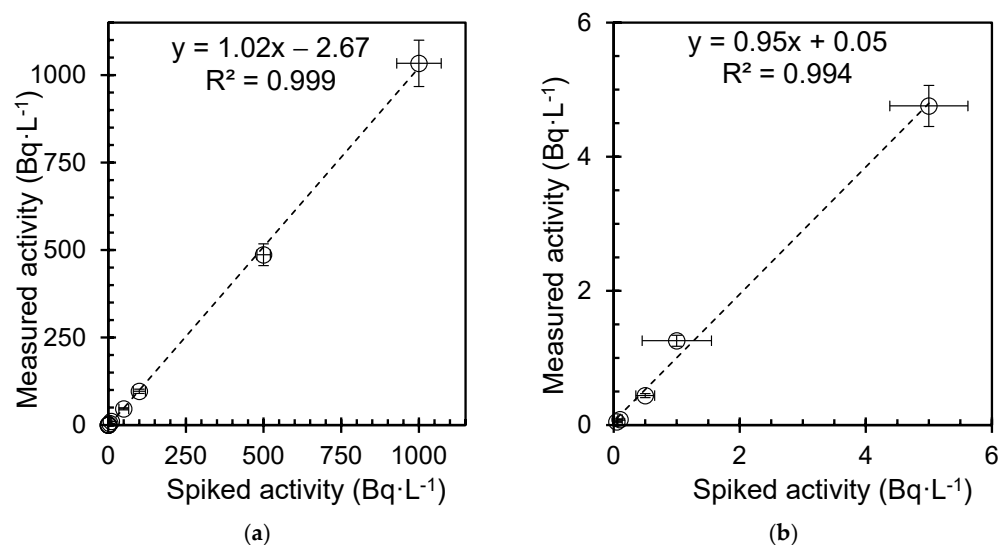
$$Z = \frac{A_s - A_m}{\sqrt{U_s^2 + U_m^2}} \tag{6}$$

where  $A_s$  represents the spiked tritium activity of the reference sample in  $\text{Bq}\cdot\text{L}^{-1}$ , while  $A_m$  represents the measured tritium activity in  $\text{Bq}\cdot\text{L}^{-1}$ .  $U_s$  and  $U_m$  correspond to 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  $-2$  and  $+2$ . From the table, it can be seen that the Z score values are between  $-0.3$  and  $0.5$ . A value between  $-0.3$  and  $0.5$  indicates that the measured values are within an acceptable range of the expected values, but there is still some variability or 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 using LSC.

Sample ID	Measured Activity ( $\text{Bq}\cdot\text{L}^{-1}$ ) $\pm$ Error ( $\text{Bq}\cdot\text{L}^{-1}$ )	Z
Ref. [1]	$1034 \pm 66$	$-0.35$
Ref. [2]	$487 \pm 31$	$0.35$
Ref. [3]	$96.7 \pm 6.2$	$0.16$
Ref. [4]	$46.6 \pm 3.0$	$0.21$
Ref. [5]	$10.57 \pm 0.68$	$-0.35$
Ref. [6]	$4.76 \pm 0.31$	$0.35$
Ref. [7]	$1.260 \pm 0.082$	$-0.46$
Ref. [8]	$0.44 \pm 0.03$	$0.39$
Ref. [9]	$0.08 \pm 0.01$	$0.50$

Another statistical comparison is made from the plot of spiked tritium activity and the measured tritium activity to confirm the accuracy and precision of the measurement data (Figure 11). Each data point represents one measurement, corresponding to values for the spiked and measured activities. 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 0.999 and 0.994 for high- and low-activity samples 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.



**Figure 11.** A comparison of spiked tritium activity concentration (known value) with measured tritium activity concentration using LSC and Equation 4; (a) high-activity samples and (b) low-activity samples.

#### 4. Conclusions

The present study aimed to develop a convenient and effective method to enrich tritium levels in groundwater for detection via a scintillation counter. An electrolysis process with 13 electrolytic cells was designed and fabricated according to the International Atomic Energy Agency (IAEA) instructions. The electrolysis method enriched nine standard samples of a known quantity of tritium, and an enrichment process of approximately ten- to fortyfold of the initial concentration could be achieved. The simple design and fabrication of the electrolysis process and the ability to control various parameters make it affordable to measure tritium levels using a conventional liquid scintillation counter. The spike samples confirmed and verified the data obtained from enriched tritium levels. The present study confirmed the effectiveness of the electrolysis method in enriching low-level tritium in groundwater, making it possible to detect tritium activity concentration using a conventional liquid scintillation counter.

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