Electrolytic Process for Concentrating Trace Tritium in Water for Tritium Activity Measurement by Liquid Scintillation Counter

Al Mamun

Department of Physics, College of Science, University of Hafr Al Batin, Al Jamiah, Hafr Al Batin 39524, Saudi Arabia
Email: almamun@uhb.edu.sa

Received: 2 June 2023; Revised: 28 August 2023; Accepted: 1 September 2023

Abstract: In arid regions, the water contains very low levels of tritium, which cannot be detected by conventional liquid scintillation counters (LSC). For the evaluation of the tritium activity concentration, it is crucial to enrich the low-level tritium of groundwater with a known factor. To address this, we developed an electrolysis process with specially designed electrolytic cells following the guidelines of the International Atomic Energy Association (IAEA). The electrolysis process enriched nine spiked samples with known quantities of tritium, and the tritium activity concentration was measured by a scintillation counter. The enriched water showed comparable activity levels to the spiked samples. In addition, the enrichment factor and tritium activity are correlated. Our study demonstrated that the electrolysis process with fabricated electrolytic cells could achieve an enrichment factor of approximately ten to forty times the initial tritium concentration. The simple design and fabrication of the electrolysis process and its ability to control various parameters make it cost-effective for measuring low-level tritium using a conventional LSC.

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

1. Introduction

In arid or semiarid regions, the scarcity of water resources is exacerbated by low rainfall and high evaporation rates. Groundwater is the primary water source for human consumption and agriculture in rural areas. However, natural tritium present in groundwater can pose significant health risks. Unfortunately, the tritium concentration in groundwater is typically very low, and the conventional LSC has less sensitivity to detect such low levels of tritium. Consequently, an enrichment process is essential to accurately measure the tritium activity concentration in groundwater samples. Electrolytic enrichment of water involves utilizing an electrolytic cell to enhance the tritium concentration in water. The cell consists of two electrodes, an anode and a cathode, separated by an electrolyte solution. When an electric current passes through the cell, the water molecules dissociate into hydrogen ions (H+) and hydroxide ions (OH-). Depending on the electrolyte solution and the direction of the current, the concentration of the target compound can be increased. Electrolytic enrichment can also raise the concentration of other ions or compounds in water, such as dissolved oxygen, hydrogen peroxide, or ozone. Therefore, before the enrichment process, water distillation must be performed.

There are various electrolytic enrichment methods, each with its advantages and drawbacks. Proton exchange membranes (PEMs) employ a solid polymer electrolyte membrane to separate the anode and cathode compartments,
offering lower operating temperatures and pressures than alkaline electrolysis but requiring more expensive materials and potentially less efficiency. On the other hand, solid oxide electrolysis uses a solid oxide electrolyte, typically a ceramic material, to separate the compartments. Alkaline electrolysis is the most established and widely used electrolytic enrichment method. It employs an aqueous solution of potassium hydroxide or sodium hydroxide as the electrolyte with nickel or steel electrodes. This method benefits from operating at low temperatures and pressures. However, the alkaline electrolysis process generates substantial caustic waste and frequent electrode replacement compared to other methods.

Numerous studies have investigated the electrolysis process for various applications. Villa et al. developed a technique involving electrolytic tritium enrichment and liquid scintillation counting for measuring trace amounts of tritium in environmental water. The method underwent rigorous quality testing and was applied to analyze water samples from Seville’s public supply and various springs in Spain. Plastino et al. focused on assessing tritium levels in water samples using electrolytic enrichment for liquid scintillation counting (LSC). They optimized the LSC system performance tests and analyzed uncertainties. Feng et al. explored a low-background LSC system using 100 mL counting vials to enhance airborne tritium measurement. Their studies revealed the optimal counting procedure involving a 50 mL water sample mixed with a 50 mL scintillation cocktail in a 100 mL vial system, which exhibited a lower minimum detectable activity (MDA) than a 20 mL vial system. Another study proposed a novel method for tritium enrichment in water using a solid-phase extraction (SPE) polyaniline film as an electrolysis electrode. The SPE film demonstrated efficient and selective tritium enrichment, offering an alternative to traditional electrolysis. Recently, a susceptible method was developed using electrolysis enrichment and ultralow-level LSC to detect low levels of tritium in seawater samples. In our previous study, we estimated the radon level in groundwater and aimed to measure the tritium activity in groundwater. Therefore, an enrichment process with 13 electrolytic cells was designed and fabricated following IAEA instructions in our laboratory. Nine samples with known tritium concentrations were used to correlate the enrichment factor and corresponding tritium activity concentration.

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: P 700,723 and source: 1,676-44, with tritium-free water in a controlled manner. The resulting solutions were then enriched and analyzed to determine their activity concentration. Table 1 shows the 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.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Spiked activity (Bq/L)</th>
<th>± Error (Bq/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ref 1</td>
<td>1,000</td>
<td>71.32</td>
</tr>
<tr>
<td>Ref 2</td>
<td>500</td>
<td>21.56</td>
</tr>
<tr>
<td>Ref 3</td>
<td>100</td>
<td>19.61</td>
</tr>
<tr>
<td>Ref 4</td>
<td>50</td>
<td>15.74</td>
</tr>
<tr>
<td>Ref 5</td>
<td>10</td>
<td>1.45</td>
</tr>
<tr>
<td>Ref 6</td>
<td>5</td>
<td>0.62</td>
</tr>
<tr>
<td>Ref 7</td>
<td>1</td>
<td>0.55</td>
</tr>
<tr>
<td>Ref 8</td>
<td>0.5</td>
<td>0.15</td>
</tr>
<tr>
<td>Ref 9</td>
<td>0.1</td>
<td>0.035</td>
</tr>
</tbody>
</table>

Table 1. Estimated tritium activity concentration for reference samples prepared by dilution from standard samples
The following diagram was used for the electrolysis process to enrich the tritium activity concentration in groundwater (Figure 1).

![Diagram of electrolysis process](image)

**Figure 1.** Schematic diagram of the electrolysis process to enrich the tritium activity concentration in groundwater

### 2.2 Primary distillation

The primary distillation of groundwater involves heating water until it reaches the 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 in the water. Traditional glassware with a heating mantle was used to remove all dissolved ions (Cl\(^-\), SO\(_4^{2-}\), Ca\(^{2+}\), CO\(_3^{2-}\), Mg\(^{2+}\), Na\(^+\) and K\(^+\)) and dissolved solids naturally present in groundwater. It is confirmed by a YSI 9,500 photometer (Xylem brand, USA) and Horiba LAQUAtwin (Japan) digital ion meters for SO\(_4^{2-}\), NO\(_3^-\), Ca\(^{2+}\), Na\(^+\), and K\(^+\) that those various ions and salts are absent. Therefore, these ions are neither influenced by the electrolysis process nor corrode the electrodes during the electrolysis process.

### 2.3 Electrolytic enrichment

A batch of 13 electrolysis cells was fabricated and developed in our laboratory. The electrolysis cells were designed to increase the concentration of tritium in the water samples to a detectable level by LSC. The design of the cells resembled the system used by the International Atomic Energy Agency (IAEA), which is commonly used for tritium enrichment.\(^{12,19}\) 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. 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 2a-b shows photographs of electrolysis cells with their outer and inner parts.

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 used as a mounting aid and for an electrical connection. The cathode, on the other hand, is made of mild steel. Before assembling the cell, the cathodes undergo special chemical treatment to enhance the cell’s performance, as described by Zutshi and Sas-Hubicky.\(^{20}\) 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. The electrolysis process was conducted at near-freezing temperatures to maximize isotope discrimination (Figure 2c). Throughout the process, tritiated water was explicitly concentrated in the residual water present in the cell due to the slightly higher binding energies between tritium and oxygen. Consequently, the tritium is enriched by an enrichment factor ranging from 10 to 40, with an uncertainty of ± 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 (Na$_2$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, which is suitable for samples with a very low $^3$H content.\textsuperscript{21} 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 final stage of the electrolysis run. During electrolysis, the “light” water decomposes primarily into H$_2$ and O$_2$ (oxyhydrogen). Extra care was taken for exhaust gases into the outdoor air. As a result, heavier $^3$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 Bq/L. 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 15 mL to maintain a higher enrichment yield.

Multicell configurations comprising 10 to 15 cells are commonly used for simultaneous enrichment. To prevent evaporation, the water sample in each cell must be cooled to a low temperature ranging from 0 to 2 °C. Modern electrochemical enrichment systems typically integrate temperature control and electronic regulatory mechanisms to facilitate electrolysis.\textsuperscript{15} This study maintained a constant temperature using an electrical refrigerator, as depicted in Figure 2. Next, each cell in the system was 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 13 mL. Hence, for this particular system, the minimum volume of the remaining water should exceed 13 mL. Regular checks were conducted every six months to ensure the electrolytic enrichment system’s ongoing performance. Finally, the tritium recovery in each cell is compared against a known standard, along with the final remaining water volume. The enrichment factor (EF) is simply the tritium enrichment yield ($\eta$, i) multiplied by the mass of the water filled into each electrolytic cell before the electrolysis process ($m_w$, i) and divided by the mass of the water remaining in the cell after the electrolysis process ($m_w$, i).\textsuperscript{12,22,23}
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. Neutralization is achieved by adding an acidic substance to the solution, which then reacts with the alkaline substances to form a neutral product. However, the acid and base reaction will result in water and salt formation. Therefore, it is essential 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. For example, 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 (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 by scintillation counter. Therefore, 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.

3. Results and discussion

3.1 Enrichment yield of the electrolysis cells

The tritium enrichment yield measures the efficiency of the electrolytic cells in retaining tritium during the enrichment process. A yield of 1 signifies a complete retention of 100% tritium, while a yield exceeding 0.966 indicates a satisfactory performance of the electrolysis process. To calculate the tritium yield, electrolytic enrichment was performed on known concentrated tritiated water, including a standard sample provided by Hidex and reference samples prepared from the standard sample. The experimental procedure mentioned in the previous section was followed. Initially, the tritium activity was measured using LSC before and after enrichment. Subsequently, the tritium yield for each electrolytic cell was determined using the following equation (14):

\[
EF = \eta_{\text{r},i} \times \frac{m_{\text{r},ij}}{m_{\text{r},ij}}
\]

(1)

where

\( \eta_{\text{r},i} \): tritium enrichment yield of a specific electrolytic cell;
\( a_{\text{r},i} \) and \( a_{\text{r},o} \): tritium activity before and after the electrolysis process;
\( m_{\text{r},i} \) and \( m_{\text{r},o} \): mass of the water filled and remaining in the electrolysis cell before and after the electrolysis process, respectively.

Figure 3 presents the tritium yield computed for each cell in the experiment using Equation 2. The graph shows a consistently high tritium enrichment yield (above 0.95) with minimal variation among the 13 cells, except for cell number 7. The notable decline in performance observed in cell #7 can be attributed to an accidental polarity reversal that occurred once during the experiment. Consequently, cell #7 was excluded from further use in the electrolysis process.
3.2 Enrichment factor

The water volume in the electrolysis process is influenced by the specific reactions at the electrodes and the magnitude of the electrical current passing through the electrolyte solution. The quantity of hydrogen and oxygen formation is directly proportional to the amount of electrical current flowing through the solution. Therefore, more water is utilized when a higher electrical current is applied, resulting in increased gas production. The extent of the reduction in water volume depends on factors such as the ratio of hydrogen to oxygen generated and the temperature and pressure conditions during the reaction. Figure 4 demonstrates a decrease in water volume as the electrolysis time progresses.

In addition to the current and electrolysis time, the volume reduction factor plays a significant role in the tritium
enrichment process. This factor represents the ratio between the initial volume of the solution and the final volume of the concentrated tritium product. If the volume reduction factor is too low, multiple rounds of electrolysis may be required to achieve the desired tritium concentration, resulting in increased time and costs. Conversely, if the volume reduction factor is too high, it can lead to tritium losses or undesired effects. Hence, determining the optimal volume reduction factor is essential in the tritium enrichment procedure. For instance, if 800 mL of the water sample is reduced to 22 mL at the end of the electrolysis process and the tritium enrichment yield is 96.66%, the enrichment factor would be 35.15.

3.3 Energy for the electrolysis process

The energy required for tritium enrichment in the electrolysis process depends on the initial concentration and the desired enrichment fold. This process involves the application of an electric current to the tritiated water solution, causing the movement of hydrogen ions toward specific electrodes. These electrodes, typically made of inert materials, do not interact with the electrolyte or the electrolysis products. The energy utilized in this electrolysis process is primarily used to overcome activation energy, provide the necessary electric potential, and compensate for energy losses resulting from system inefficiencies such as electrolyte resistance, solution heating, and other factors. In the present study, each cell contained approximately 800 mL of water sample. To enhance the electrolysis process, the cells were connected in a series configuration, where 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 obtained from a power supply, which provided the electrical energy required for electrolysis. Initially, the current reached a maximum of 10 amperes (A), meaning that a current of up to 10 A flowed through the electrolyte, facilitating the migration of ions. The high current contributed to the efficiency of the electrolysis process.

The energy required for the electrolysis process was examined concerning the volume of water used in the cells. Figure 5a illustrates a linear correlation, suggesting that a certain amount of energy is needed for the electrolysis of each mL of water. This means that energy consumption remains relatively the same regardless of volume. The estimated energy consumption was approximately 11,340 coulomb or 3.15 ampere-hours (Ah) for each amount of water (Figure 5b). The data presented in Figure 5 help to understand the energy requirements and efficiency of the electrolysis process. This shows that as the volume of water is needed for electrolysis, the overall energy consumption increases.

Figure 5. (a) Required energy (in coulomb, C) for the electrolysis process as a function of water volume and (b) required energy per ml of water for different cells for typical samples
proportionally.

3.4 Minimum detectable activity and enrichment factor

The conventional LSC often has a higher minimum detectable activity (MDA) than the tritium levels found in groundwater, particularly in arid regions. To address this limitation, an enrichment process is employed. A lower MDA indicates greater sensitivity, enabling the detection of lower concentrations of the analyte. Figure 6 displays the MDA as a function of the enrichment factor achieved through electrolysis for two typical samples denoted as 5 and 7 (represented by black and red circles). The figure demonstrates an inverse relationship between the radioactivity measurement enrichment factor and MDA. Through enrichment, the target analyte becomes concentrated through enrichment which increases the signal-to-noise ratio and enhances the sensitivity of tritium analysis. As a result, MDA decreases, enabling the reliable detection and quantification of lower concentrations of the target analyte. In simpler terms, as the enrichment factor increases, the MDA decreases. The initial MDA of the LSC was 1.52 Bq/L without any enrichment of the water. The MDA value can be minimized to 0.032 Bq/L with an enrichment factor of 36.8. The enrichment factor can reach 38 while an EF greater than 30 will show significant uncertainty. Therefore, increasing the enrichment factor lowers MDA, facilitating the detection and quantification of analyte concentrations that are otherwise challenging to identify.

![Figure 6](image)

**Figure 6.** Minimum detectable activity as a function of enrichment factor by the electrolysis process for two typical samples 5 (black circles) and 7 (red circles)

3.5 Enrichment factor and corresponding activity

To comprehend the relationship between tritium activity and enrichment, it is important to evaluate the enrichment factor, which quantifies the increase in tritium concentration. The enrichment factor is typically expressed as the ratio of the tritium concentration in the water sample after enrichment to the total tritium concentration before electrolysis. By utilizing the enrichment factor, one can calculate the activity of the enriched material, taking into account both the enrichment factor and the initial tritium activity. Figure 7 illustrates the plot of tritium activity against the corresponding enrichment factors. The graph exhibits a linear correlation, indicating that the activity concentration of tritium increases with the enrichment of water samples.

When determining the tritium activity of the enriched water, it is crucial to consider additional factors that can influence the activity beyond the enrichment factor and initial activity. These factors encompass radioactive decay, decay chains, and the specific half-lives of the isotopes. Therefore, it is vital to accurately incorporate decay equations and decay constants associated with specific isotopes to ascertain the corresponding activity at any given time.
The tritium activity measured by a conventional LSC is plotted against the enrichment factor, as shown in Figure 7. Each data point represents one measurement, corresponding to enrichment and related activity values. The plot in the figure shows a linear relationship with an $R^2$ value of 0.998, and suggests a robust linear correlation between the enrichment factor and the corresponding tritium activity. The results also suggest that the measured data are precise and accurate and can be used where conventional LSCs face challenges due to their higher detection limits.

4. Conclusions

This study aims to develop a convenient and efficient technique for enriching tritium levels in groundwater to enable detection using a scintillation counter. An electrolysis process was devised and constructed with 13 electrolytic cells. The enrichment process successfully increased the tritium concentration in nine standard samples by approximately ten to forty-fold. The straightforward design and controllable parameters of the electrolysis method make it cost-effective for measuring tritium levels with a conventional LSC. The accuracy of the obtained data was confirmed through the analysis of reference samples. This enrichment technique is precious in regions with very low tritium levels in groundwater, where conventional LSC faces challenges due to its higher detection limits. Further research interest lies in using tritium activity to estimate the groundwater age in arid regions.

Conflict of interests

The author declares no competing financial interest.

References


