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Measurement of tritium concentration in heavy water by azeotropic distillation

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HIGHLIGHTS

- Measurement of tritium concentration in heavy water by azeotropic distillation for the first time in Iran.
- Comparison of the results with the NRC.
- Examining the changes in tritium concentration with increasing degree of enrichment of heavy water.
- Drowning regression line for tritium concentration in heavy water purity.

ABSTRACT

In this work, the concentration of tritium in D₂O of various degrees of purity was measured. Samples were taken from the Arak heavy water plant and tritium concentrations were determined using a liquid scintillation detector (LSC) based on tritium decay. In the present work, instead of simple distillation, is used the azeotropic distillation method. Absorption and fluorescence spectra were recorded using a Shimadzu UV-2100 spectrometer and an LS50B fluorescence spectrometer. The tritium concentration in the samples varied from 1.75 ± 0.80 to 6.16 ± 1.01 Bq.L⁻¹ in D₂O enrichment from 0.35% to 77.50%. The correlation coefficient between tritium concentration and D₂O purity in heavy water was obtained as $R^2 = 0.853$. Deviation for 99.8% D₂O enriched in heavy water. This was observed from a straight line, leading to a drop in R^2 . The results of this measurement showed that the tritium concentration did not exceed the value set by the Nuclear Regulatory Commission (NRC).

KEYWORDS

Tritium
Liquid Scintillation Detector
Heavy Water
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1 Introduction

Tritium is a radioactive isotope of hydrogen with a half-life of 12.32 years. Tritium was discovered in 1934 by physicist Ernest Rutherford M.L. Oliphant and Paul Hartek, who bombarded deuterium with energetic deuterons according to the D(d,p)T reaction. Willard Frank Libby and Aristide V. Gross showed that tritium in natural waters was probably formed due to the reaction of cosmic rays with atmospheric nitrogen (Lucas and Unterweger, 2000). Tritium can also be produced by the nuclear reaction of ⁶Li(n,T)α bombarded with neutrons from nuclear reactors. The mass difference between tritium with ordinary hydrogen sometimes causes significant differences in the chemical properties of its compounds (Chemistry, 2023). Therefore, tritium is used less often than deuterium as an isotopic marker in chemical reactions (Britannica, 2020). If the mix of deuterium and tritium is placed at

high temperatures and high pressure, nuclear fusion will occur. The beta decay of tritium to He-3 can be easily detected or caused some other compound to fluorescence. Therefore, tritium is used as a radioactive marker in biological research in the form of tritiated water (HTO or T₂O) (IAEA, 2023). It is also produced as a byproduct of a heavy water reactor where neutrons are absorbed by deuterons or triplet fission of U-235 in a fuel pellet (Fireman et al., 1961; Nir et al., 1966). Because it emits very low energy radiation and leaves the body relatively quickly, for a given amount of activity ingested, tritium is one of the least dangerous radionuclides (Thompson et al., 1954; Glasstone and Sesonske, 1981). Since tritium is always in water, it passes directly with water into soft tissues and organs. The dose absorbed by these tissues is generally uniform and depends on the type of tissue (Carsten, 1979; Dyadin et al., 1979). The tritium concen-

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tration is sometimes given in “tritium units” as TU, which means 1 tritium per 10^{18} hydrogen atoms, or 7.17 decays per minute per kg of water, or 0.118 Bq.L^{-1} (Thompson et al., 1954). Therefore, it is important to know that tritium activity in drinking water should not exceed 100 Bq.L^{-1} (Thompson et al., 1954). The β decay of tritium produces He-3 which has a high thermal neutron capture cross-section of 5500 barns (Phillips et al., 1980). For this reason, it is very important to determine the concentration of tritium in heavy water which is used as a coolant and neutron moderator in heavy water reactors. During heavy water production and heavy water reactor operation, the concentration of tritium, which is a toxic substance, increases. The amount of tritium released in air and water depends on the type of reactor. In pressurized water reactors (PWRs), most of the tritium released into the environment is produced by the interaction of neutrons with boron and lithium. Boron is added to the primary cooling water to control the nuclear fission reaction in the fuel, and lithium is added to control corrosion. This problem does not exist for boiling water reactors (BWR) because in these reactors boron or lithium is not added to the primary water (Glasstone and Sesonske, 1981). Tritium is also produced in greater amounts in PWR and BWR fuel rods as a result of triple fission. PWR cooling water is continuously removed from the reactor for chemical treatment, volume control, and radioactivity reduction, and then most of this water is returned to the reactor vessel. Some fission products may enter the water, which is removed by passing the water through ion exchange resins. However, tritium water is not affected by this process because tritium water is chemically identical to normal water (Carsten, 1979; Dyadin et al., 1979). Part of the cooling water does not return to the reactor tank and is placed in storage tanks. After further purification and dilution, it is periodically released into the environment to bring the tritium concentration to the virtual level set by the US Nuclear Regulatory Commission (NRC) for the nuclear industry. Water contaminated with tritium can break down chromosomes and cause genetic abnormalities. Also, drinking this type of water increases the risk of cancer (NRC, 2023; Peterson Jr and Baker, 1985; Council et al., 2006; Makhijani, 2008). The study aimed to determine tritium concentration in Iranian heavy water products and to study its change in the production process. Before this work, there was no information about its H-3 contamination level.

2 Materials and methods

Seven samples of heavy water with different of D_2O concentrations in H_2O : 0.35%, 13.5%, 35.20%, 56.16%, 58.20%, 77.50%, and 99.80% were prepared from the Arak Heavy Water Plant. Samples were prepared in the laboratory with special conditions. Heavy water was mixed with demineralized light water and the concentration of heavy water was determined using infrared methods to control the process. 250 mL of each sample was filtered through Whatman paper. 0.5 g of sodium hydroxide (NaOH) was added to 100 mL of filtered samples to eliminate metal and

radionuclide interference and to prevent H_2 gas from escaping from the samples. In addition, 0.1 g potassium permanganate (KMnO_4) was added for oxidizing trace organics in sample aliquots to eliminate quenching interferences. After mixing thoroughly, 10 mL cyclohexane solvent was added to create azeotrope in the water sample. Then distilled at 75°C . The distillation apparatus is shown in Fig. 1. A sample of distilled water was transferred to an azeotropic vessel. 10 mL of the lower layer (water phase) was collected and cooled to room temperature. 10 mL aliquot was transferred to a clean scintillation counting vial, then 10 mL of Ultima Gold scintillation cocktail was added thereto and the prepared vial was shaken well for 15 minutes. To maximize the efficiency of radio luminescence from β decay source, samples have been held at 4°C for one hour. The same procedure was done for blank and standard samples. The blank sample with very low tritium content was prepared from the deepest well water sources. A Perkin Elmer Model LS50B luminescence spectrophotometer was used to measure the fluorescence spectrum, and a Shimadzu double beam absorbance photo spectrometer, model UV-2100, was used to measure the absorbance spectrum to confirm the complete removal of organic and inorganic impurities causing luminescence quenching in the samples. The final count was recorded by two LSC detectors. Two Malisa Star Counter Measurement model ST003-2 is located inside a lead housing and worked in the coincidence system. All chemicals and reagents used in this study were analytical-grade reagents. Deionized water was used to prepare all the solutions and the glass containers were washed with this kind of water. All chemicals such as potassium permanganate, sodium hydroxide, acetone, methanol, cyclohexane, and sulfuric acid were prepared by Merck Company. The Ultima Gold cocktail brand (based on ethoxylated alkylphenol, a naphthalene solvent that has a very low vapor pressure and a high flash point) is manufactured by the Perkin Elmer Company. To ensure the disappearance of organic and inorganic impurities in the quenching samples, all heavy distilled water samples were collected in an azeotropic vessel and their spectrum was recorded with a Shimadzu UV-2100 absorption spectrometer in the wavelength range of 190 to 1100 nm.

3 Analytical and Numerical Calculations

The tritium activity of the samples (Act) for each sample was determined using Eq. (1) (ASTM, 1978; EMSL, 1980):

$$Act = \frac{R_a - R_b}{eff \times F \times V \times e^{-\lambda t}} \quad (1)$$

where R_a , R_b , eff , F , V , λ , and t are the gross count (s^{-1}), background count (s^{-1}), detection efficiency, recovery factor, sample volume (mL), tritium decay constant (day^{-1}) and decay time between sampling and counting in days respectively. The measurement result is subject to uncertainty due to the counting statistics (counting uncertainty). The component of the combined standard uncertainty of the measurement of the tritium concentration in the sample $U_{cc}(Act)$, was calculated using Eq. (2) (ASTM,

1978):

$$U_{cc}(Act) = \frac{\sqrt{\frac{R_a}{t_a} + \frac{R_b}{t_b}}}{eff \times F \times V \times e^{-\lambda t}} \quad (2)$$

where t_b and t_a are sample and background counting times in seconds, respectively. Equations (3) and (4) were used to calculate eff and its uncertainty U_{eff} (EMSL, 1980).

$$eff = \frac{R_{DWTS} + R_b}{A_{DWTS}} \quad (3)$$

$$U_{eff} = \sqrt{\frac{R_{DWTS} + R_b}{Act_{DWTS}^2} + eff^2 \left(\frac{U_{DWTS}}{Act_{DWTS}}\right)^2} \quad (4)$$

where eff , Act_{DWTS} , R_b , R_{DWTS} , U_{DWTS} , t_{DWTS} , and t_b are efficiency, reference tritium activity in distilled water (Bq), background aliquot counting rate (s^{-1}), the uncertainty of reference material activity (Bq), counting time of reference tritium material in distilled water (seconds), the counting time of the background sample (ASTM, 1978; EMSL, 1980). The values of efficiency and uncertainty of detector efficiency are 2.107 and 0.003 respectively (ASTM, 1978). The recovery correction factor, F , can be obtained from Eq. (5) (Hilmen, 2000).

$$F = \frac{R_{DWTS} - R_b}{eff \times Act_{RWTS}} \quad (5)$$

where Act_{RWTS} is the activity of undistilled raw water of the tritium standard (Bq) (Council et al., 2006). In this recovery work, the correction factor is 0.986. The minimum detectable activity (MDA) is typically used to distinguish the measurement from the background. MDA was assessed using Eq. (6) (Hilmen, 2000).

$$MDA = \frac{2.71 + 3.29 \sqrt{R_b \times t_a \left(1 + \frac{t_a}{t_b}\right)}}{eff \times t_a \times F \times V \times e^{-\lambda t}} \quad (6)$$

where R_a , t_a , and t_b are background count rate (s^{-1}), counting time of sample (s), and counting time of background (s), respectively.

4 Figure of Merit

The tritium beta decay particle is counted with a window setting where the Figure of Merit (FOM) is at its maximum, and FOM indicates the signal-to-noise ratio according to Eq. (7). In this work, a FOM of 3.29 seconds was obtained (EMSL, 1980; Moghissi et al., 1973; Sodd and Scholz, 1969).

$$FOM = \frac{eff^2}{R_b} \quad (7)$$

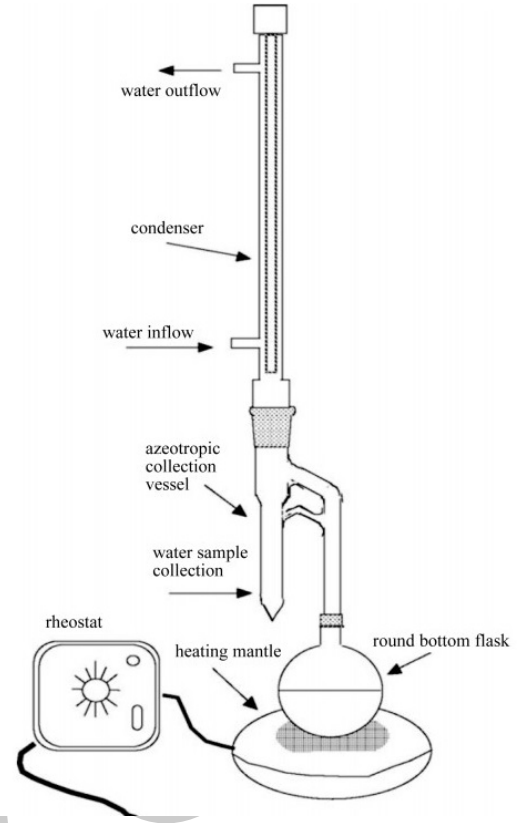


Figure 1: Schematic diagram of the distillation apparatus.

5 Results and Discussion

The result of the absorption spectrum of a sample with a concentration of 99.80% heavy water in light distilled water is shown in Fig. 2, which shows that the absorption is close to zero, therefore the cleaning is excellent and the cations and anions have been completely removed in the prepared samples. Then, the fluorescence spectrum was recorded in the 300 to 800 nm range using a Perkin Elmer LS50B spectrometer, in which the 350 nm peak was observed. The luminescence results in a sample with a heavy water concentration of 99.80% are shown in Fig. 3. The luminescence after distillation and purification is close to zero, therefore azeotropic distillation is devoid of any substance interfering with tritium analysis. The result of the calculation of activity and MDA are listed in Table 1 and Table 2, respectively. Figure 4 shows the linear regression trend Tritium concentration in heavy water enrichment samples. The data indicate that the concentration of tritium in heavy water samples correlates with D_2O enrichment in light water.

The concentration of tritium in the final production of heavy water enriched with 99.8% D_2O was 5.26 ± 0.90 $Bq.L^{-1}$, which shows that with D_2O enrichment, it increased from 14.86 TU for natural water to 52.18 TU for 77.50% purity of D_2O . The maximum level of tritium contamination in drinking water given by the National Interim Drinking Water Regulations (NIPDWR) is 20,000 $pCi.L^{-1}$ (Rand et al., 1976). 1 TU equals 3.23 $pCi.L^{-1}$, therefore the concentration of tritium activity measured in these samples is lower than the National Interim Primary

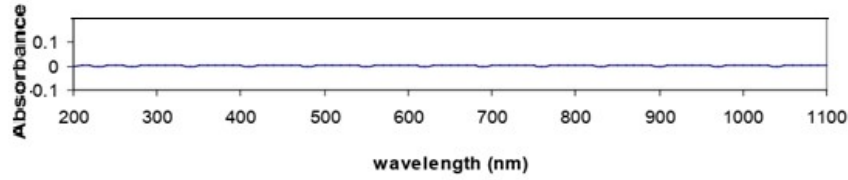


Figure 2: Absorbance spectrum of 99.8% heavy water enrichment sample.

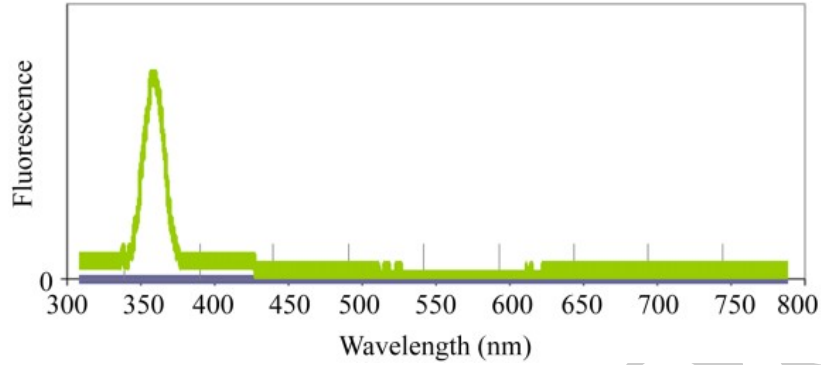


Figure 3: Fluorescence spectrum of 99.8% heavy water enrichment sample.

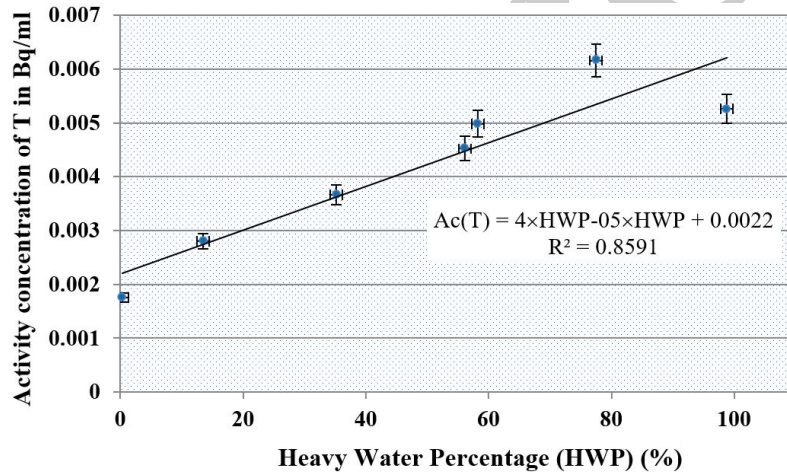


Figure 4: The graph of tritium activity concentration versus the heavy water percentage (HWP) with a fitting factor of $R^2 = 0.852$.

Table 1: Results of measurement of Tritium concentration in heavy water.

Heavy water enrichment (%)	Act (Bq.L ⁻¹)	U _{cc} (Act) (Bq.L ⁻¹)	TU	U _{cc} (TU)
Tritium standard water (DWS)	1661.15	2.50	14077.55	21.18
0.35	1.75	0.80	14.86	6.78
13.50	2.80	0.90	23.81	7.63
35.20	3.66	0.90	30.99	7.63
56.16	4.52	0.90	38.32	7.63
58.20	4.98	0.90	42.18	7.63
77.50	6.16	1.00	1.00	8.47
98.80	5.26	0.90	44.59	7.63

Drinking Water Regulations(NIPDWR). Thus, based on the values set by the Nuclear Regulatory Commission (NRC) and NIPDWR of the European Union, the obtained results do not indicate any environmental or biolog-

ical hazards. Heavy water reactors should be responsible for the concentration of primary tritium and its changes during the operation of the reactor as a poison.

Table 2: Calculated values of minimum detectable activity concentration.

Heavy water enrichment (%)	MDA (Bq.L ⁻¹)
Tritium standard water (DWS)	12.2
0.35	1.4
13.50	2.1
35.20	2.9
56.16	2.9
58.20	2.9
77.50	3.2
98.80	2.9

6 Conclusions

In this work, tritium concentration was measured by the azeotropic distillation method. The results showed that the amount of tritium increased with the increase in the concentration of heavy water, but a slight abnormality was observed when the concentration increased from 77.5% to 99.8%. In general, the increase of tritium followed a linear pattern with a fitting coefficient of $R^2 = 0.852$.

Conflict of Interest

The authors declare no potential conflict of interest regarding the publication of this work.

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