

Preparation of tritiated water vapour using bubbling method

Rui Meng, Mingyan Sun

Institute of nuclear. Rocket Force University of Engineering, Xi'an, 710025, China

Abstract

The tritiated water vapour with known theoretical concentration can be prepared by bubbling method. For saturation factor S and isotope fractionation factor F , the main parameters affecting the concentration of tritiated water vapour produced by bubbler, this paper conducted bubbling experiments under different conditions based on the developed bubbler, and determined the range of the flow rate at $S=1$. The quantitative relationship between isotope fractionation factor F and temperature was obtained. Finally, by theoretical calculations, a simplified formula for the tritiated water concentration ignoring the volume of the blown-in gas was obtained, and a model for the saturated tritiated water concentration with the temperature as the independent variable was developed by combining the above experimental findings.

Keywords

Bubbling; Tritiated water vapour ; Saturation factor ; Isotope fractionation factor.

1. Introduction

According to the principle of tritiated water vapour preparation by bubbling and the calculation formula [1], it is assumed that the bubbler is filled with $V_{H_2O}^0$ (mL) of tritium water with a concentration of $C_{H_2O}^0$ (Bq/mL); the saturation factor of the bubbler is S ; the isotope fractionation factor is F ; and the saturated water content in unit volume of air is γ_t (g/L). The instantaneous concentration of tritiated water in the bubbler is C_{H_2O} (Bq/mL) when V_{gas} (L) of dry gas is blown in, and the concentration of tritiated water vapour blown out is C_{gas} (Bq/L), as follows:

$$C_{gas} = FS\gamma_t C_{H_2O}^0 \left(1 - \frac{V_{gas} S \gamma_t}{V_{H_2O}^0}\right)^{(F-1)} \quad (1)$$

By analyzing the parameters in formula (1), we can see that $C_{H_2O}^0$, V_{gas} and $V_{H_2O}^0$ can be accurately measured, and γ_t (10^{-3} g/L) is the saturated water content of the air at different temperatures, which can be calculated by consulting the humidity table or the formula below [2]:

$$\gamma_t = 4.85 \times 10^{\frac{6.9t}{230+t}} \quad (2)$$

The above parameters are constant and can be given directly by calculation if the external environment is determined, so the effects of F and S are mainly considered.

2. Saturation factor and isotope fractionation factor

For saturation factor, we usually want the bubbler to produce saturated tritiated water vapour, i.e. $S=1$, to ensure the stability of the bubbling microprocess and thus minimize the effect of saturation factor on the concentration calculation. In the case of a given structure of the bubbler, the saturation factor is mainly related to the size of the bubble flow rate. For the isotope fractionation factor, the size of F is stable at $S=1$ and when other bubbling conditions remain

unchanged, which can be measured experimentally. Its magnitude is mainly related to the bubbling temperature [3].

2.1. Saturation factor S

The saturation factor S is the degree of exchange between the gas phase and the liquid phase during the bubbling process, and its magnitude is the ratio of the actual mass of water lost during the bubbling process and the mass of water that should be taken away by the air. The mass of water that should be taken away by the air drummed into the bubbler can be calculated theoretically by the volume of air drummed into the bubbler V_{g_t} and the saturated water content γ_t at the corresponding temperature.

The actual water loss before and after the bubbling experiment can be measured by the weight difference method, and the saturation factor S can be calculated by the following formula [4]:

$$S = \frac{m_1 - m_2}{V_{g_t} \gamma_t} \quad (3)$$

Where, m_1 denotes the mass of the bubbler before bubbling, in unit g; m_2 denotes the mass of the bubbler at the end of bubbling, in unit g; V_{g_t} denotes the volume of dry gas entering the bubbler, in unit L; γ_t denotes the saturated water content per unit volume, in unit g/L.

2.2. Isotope fractionation factor F

The size of isotope fractionation factor F is the ratio of tritium activity per unit mass in the gas phase to the liquid phase during the bubbling process (specific activity), expressed as

$$F = \left(\frac{HTO}{H_2O} \right)_{gas} / \left(\frac{HTO}{H_2O} \right)_{H_2O}. F \text{ is an important parameter involved in the calculation of tritiated}$$

water vapour concentration from bubbling and needs to be determined accurately.

Based on the derivation of the equation for the preparation of tritiated water by bubbling, Zhao Yamin proposed the condensation and liquid scintillation method [5]. The tritiated water vapour from the bubble was collected by condensation in the experimental setup, and the specific activity of the sample was determined using a liquid scintillator after sample preparation. F can be measured by formula 4:

$$F = \frac{C_{\text{Condensate}}}{C_{H_2O}^0} \quad (4)$$

Where, $C_{\text{Condensate}}$ denotes the measured specific activity of condensed tritiated water, in unit Bq/g; $C_{H_2O}^0$ denotes the known initial specific activity of tritiated water, in unit Bq/g.

3. Experimental study

3.1. Saturation factor measurement using weight difference method

The weight difference method was used to measure the saturation factor of the bubbler, which should minimize the error in measuring S . The following requirements should be met [6]: (1) the air blown into the bubbler must be pure and free of water; (2) the preparation must ensure that the temperature does not change; and (3) the air flow rate can be adjusted. The experimental setup includes the tritiated water generator built using bubbler: temperature-controlled bubbler, flow controller (adjustable bubble flow rate, displaying the volume of air under standard conditions), temperature and pressure sensors (measuring the temperature and pressure of the bubbler, used to correct the volume of air drummed into the bubbler), pump, desiccator; electronic balance (accuracy of 0.01g); gas piping. The experiment temporarily used

drinking water instead of tritium water in the bubbler. The maximum flow rate of the pump is 10 L/min. The bubbler device was developed and processed in advance, and was selected as a cylindrical bubbler with a radius of 1.5cm at the bottom, where A1 and A2 were the inlet and outlet ports respectively, and the maximum liquid volume was more than 100mL, as shown in Figure 1.

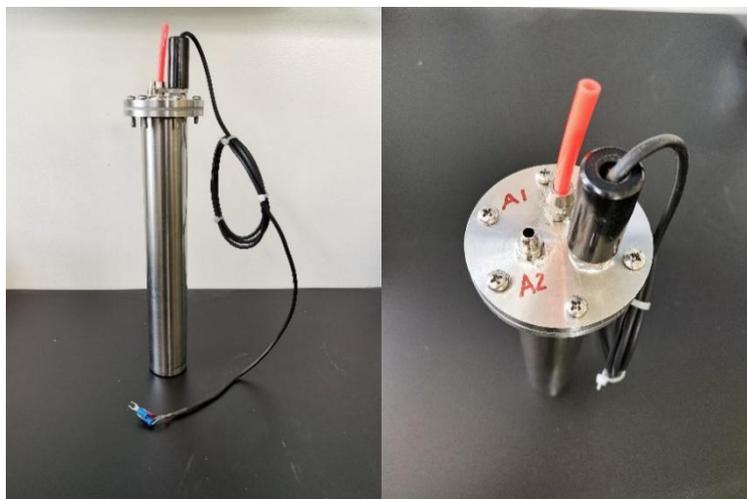


Figure 1. Physical diagram of bubbler

The experimental steps include:

- (1) The bubbler temperature was controlled at 15°C, and the mass of the bubbler was measured at 480.55g with an electronic balance after filling 65mL of water. The bubbler flow rate was adjusted to 1L/min by the flow controller, and the pump was turned on for bubbling. After stabilization, the bubbler temperature P_1, T_1 ;
- (2) After 100 min of bubbling, the bubbling was stopped and the cumulative flow rate value was recorded. The total volume of air actually blown into the bubbler (L) was calculated after correction for temperature and pressure:

$$V_{\text{gas}} = \frac{p_0 V_0 T_1}{p_1 T_0} \tag{5}$$

Where, P_1 is the measured pressure inside the bubbler, in unit kPa; T_1 is the measured temperature inside the bubbler, in unit K; P_0 is the gas pressure at the standard condition as 101.325 Kpa; T_0 is the temperature at the standard condition at 273.15 K; V_0 is the measured total volume of air in the bubbler, in unit L.

- (3) The actual water loss $m_1 - m_2$ (g) of the bubbler was measured using an electronic balance. The saturation water content γ_i at 15°C can be determined as 12.83×10^{-3} (g/L) by formula 2. By substituting it into formula 3, the size of saturation factor can be calculated;
- (4) The above steps were repeated by varying the bubble flow rate in the range of 1L/min to 10L/min.

The experimental data were compiled and presented in Table 1. According to the experimental results, for the developed bubbler, under the condition that the bubbling flow rate is less than 5L/min, it can be considered that $S=1$, and the output is considered as saturated tritiated water vapour.

Table 1 Experimental measurement results of saturation factor at different flow rates

Bubbling flow rate/(L·min-1)	Mass of tritium water before bubbling /g	Mass of tritium water after bubbling /g	Actual mass of water loss/g	Theoretical mass of water loss /g	Saturation factor

1	480.55	479.28	1.27	1.283	0.99
3	479.28	475.47	3.82	3.849	0.99
5	475.47	469.11	6.36	6.415	0.99
7	469.11	460.40	8.71	8.981	0.97
9	460.40	449.55	10.85	11.547	0.94

3.2. Experimental measurement of isotope fractionation factor

Based on the above tritiated water generator, an experimental device for isotope fractionation factor measurement was built with a sampling device and a low background liquid scintillator, as shown in Figure 2.

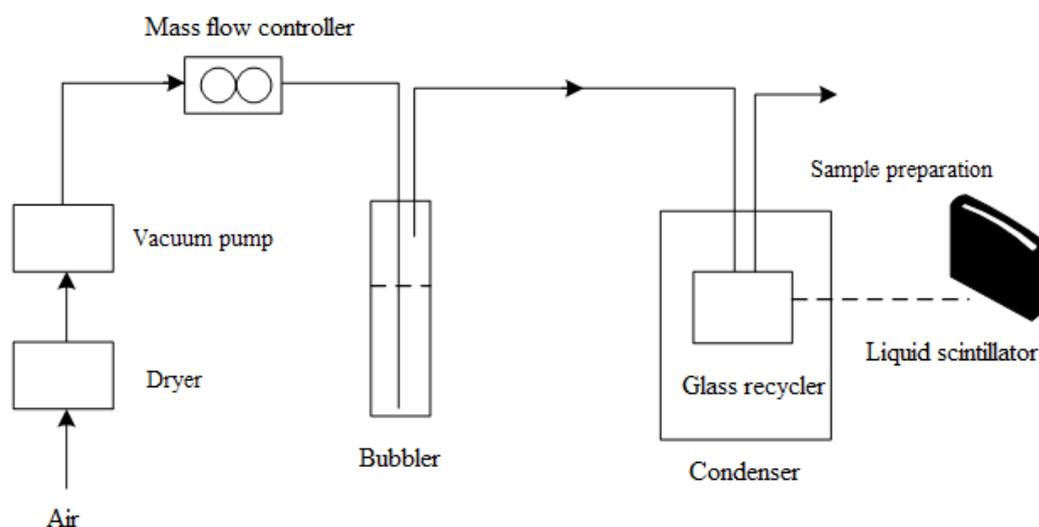


Figure 2 Experimental device for isotope fractionation factor measurement

The experimental apparatus includes, tritiated water generator: bubbler, flow controller (to adjust the bubbling flow rate), temperature, pressure sensor, pump, dryer, standard tritiated water (initial concentration of 1×10^5 Bq/g); tritiated water basic sampling system (recovery efficiency up to 99 %): glass recycler, liquid nitrogen condenser, condensed tritiated water collection bottles; low background liquid scintillator.

The experimental steps include:

- (1) The bubbler was filled with 100 mL of standard tritium water at an initial concentration of 1×10^5 Bq/g, and the bubbler flow rate was adjusted to 5 L/min by the flow controller. based on the previous simulation and experimental results, the bubbler was at a condition of $S = 1$.
- (2) A thermostatic cold trap was regulated, and the glass recycler was placed in a liquid nitrogen condenser for the recovery of tritiated water. The bubbler was set to a certain temperature and then started bubbling;
- (3) After accumulating 100 L of gas flow, the bubbling was stopped, and the tritiated water collected by condensation was sampled and weighed by an electronic balance. The unit mass activity value $C_{\text{Condensate}}$ (Bq/g) of the condensed tritiated water was obtained by using the liquid scintillator to measure the constant activity size. The isotope fractionation factor F was obtained according to formula 4:
- (4) All other conditions were kept constant, and the above procedure was repeated by changing the bubbler temperature;
- (5) The above procedure was repeated by fixing a certain temperature and changing only the bubble flow rate;

The experimental measurements of F at different temperatures are shown in Table 2.

Table 2 Experimental measurement results of isotope fractionation factor at different temperatures

No.	Temperature (°C)	Mass of condensed tritium sample (g)	Total sample activity (Bq)	Initial tritium water concentration (Bq/g)	Isotope fractionation factor F
1	5	2.03	1.44×10^5	1×10^5	0.71
2	9	2.03	1.54×10^5	1×10^5	0.76
3	13	1.99	1.57×10^5	1×10^5	0.79
4	17	2.08	1.66×10^5	1×10^5	0.80
5	21	2.01	1.69×10^5	1×10^5	0.84
6	25	2.16	1.84×10^5	1×10^5	0.85
7	29	2.05	1.78×10^5	1×10^5	0.87

Because the F value increases approximately linearly at different temperatures, it can be considered as a function of temperature, and the data are fitted to obtain the F value as a function of temperature t as in Figure 3, and the relationship is:

$$F = 0.0063t + 0.6951 \tag{6}$$

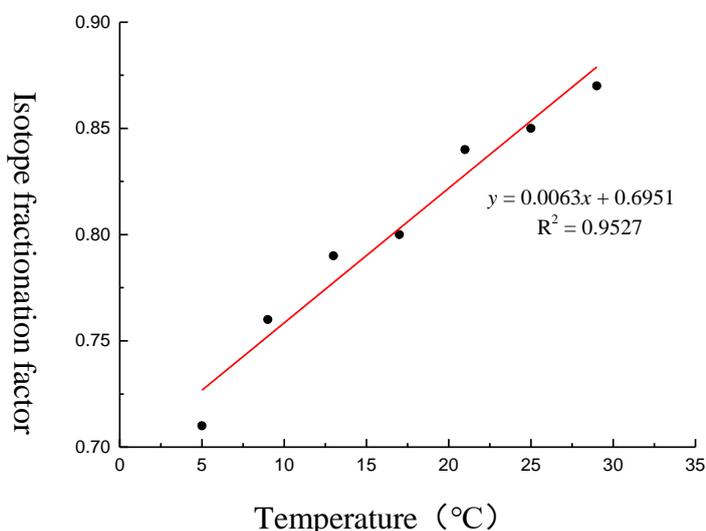


Figure 3 Linear fit of F values at different temperatures

4. Conclusion

Based on the above experimental study, the following conclusions were drawn:

- (1) For the developed and processed bubbler, in the flow rate range less than 5L/min, $S=1$ can be considered as true.
- (2) Based on this bubbler, when tritiated water is prepared using the bubbling method, the value of the isotope fractionation factor F can be accurately determined beforehand by the temperature magnitude.

(3) When the bubbling temperature and the initial concentration of tritiated water in the bubbler are known, the theoretical value of the tritiated water concentration generated at the bubbler outlet can be calculated. According to the basic formula 1 of tritiated water vapour concentration calculation by bubbling method, the unit of tritiated water concentration C_{gas} is converted into international unit Bq/m³, which can be deformed to:

$$C_{gas} = FS\gamma_t C_{H_2O}^0 \left(1 - 10^{-3} \frac{V_{gas} S \gamma_t}{V_{H_2O}^0} \right)^{(F-1)} \tag{6}$$

Where, the unit of saturated water content γ_t becomes mg/L, which can be calculated by formula 2, and the units of the remaining parameters are the same as those in formula 1. In the actual bubbling process, $10^{-3} V_{gas} S \gamma_t / V_{H_2O}^0$ is far less than 1. According to the Taylor series expansion formula [7], the exponential part can be expanded by series and take the first two terms, i.e:

$$C_{gas} = FS\gamma_t C_{H_2O}^0 \left[1 + 10^{-3} (1-F) V_{gas} S \gamma_t / V_{H_2O}^0 \right] \tag{7}$$

Where, $10^{-3} (1-F) V_{gas} S \gamma_t / V_{H_2O}^0$ denotes the correction term for the isotope coefficient F , which is usually close to 1 and V_{gas} can be neglected when it is small. The equation can be further simplified as:

$$C_{gas} = FS\gamma_t C_{H_2O}^0 \tag{8}$$

When $S=1$, and the initial concentration $C_{H_2O}^0$ of tritiated water is known, the theoretical calculation model of tritiated water concentration with temperature as the independent variable can be obtained by combining formulas 2, 6 and 8. Assuming that $C_{H_2O}^0$ is 1×10^5 Bq/mL and 1×10^6 Bq/mL, the variation of the theoretical values of tritiated water concentration generated by the variable temperature method in the range of 1°C to 20°C is shown in Figure 4.

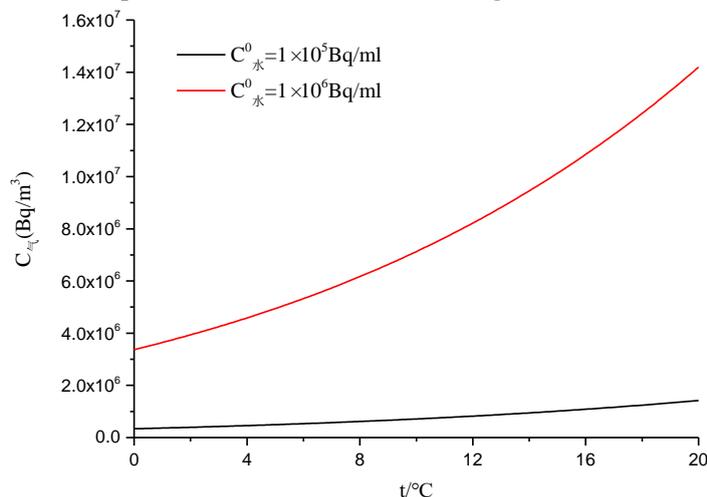


Figure 4 Theoretical values of tritiated water concentration at different temperatures for two initial tritium water concentrations

References

- [1] Osborne R V , Snyder W S . Sampling for tritiated water vapor[J]. 1974.
- [2] Zhang X Y, et al. Handbook of Practical Chemistry[M]. National Defense Industry Press, 1986.
- [3] Hong Y X. The Determination of Isotope Fractionation Coefficient of Tritium Gas Generator System [J]. Science & Technology Vision, 2015(23): 247-247.

- [4] Wang J S. Study of screening and measurement techniques for tritium in air[D]. China Academy of Engineering Physics, 2014.
- [5] Yang H Y. Theory of tritiated water vapour sampling by bubbling method and derivation of its quantitative formula[J]. Radiation Protection Bulletin, 1984, 000(006):24-27.
- [6] Cheng Y, Li X Y, Hong Y X, et al. Determination of Saturated Coefficient of Tritiated water vapour Generator System[J]. Atomic Energy Science and Technology, 2008, 42(003): 262-265.
- [7] Liu D M. A New Approach for Taylor Expansion of Analytic Function [J]. Journal of Changchun Normal University, 2016(4):4-7.