

SAMPLING FOR TRITIATED WATER VAPOUR

by

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ABSTRACT

Collection of tritiated water vapour $(\text{HTO})_v$ from air by bubbling the air through non-tritiated water and subsequent measurement of the accumulated activity by liquid scintillation counting is often used as a simple method of monitoring for $(\text{HTO})_v$ in air.

Expressions for the collection efficiency of a model collecting device of this kind are derived here in terms of the initial mass of water in the collector, the total air flow, the humidity in the air entering and leaving the collector, the intrinsic efficiency of the collector and the ratio of the relative isotopic concentration $[T/H]$ in the vapour phase to that in the liquid phase at the effective operating temperature of the device.

Predictions from the model are compared to the measured efficiencies of collectors with and without fritted glass air dispersers, for water masses from 50 g to 200 g, air volumes 0.1 to 20 m³, air flow rates up to 160 cm³/s and water temperatures in the range 5°C–35°C. Intrinsic efficiencies greater than 95% and agreement between predictions and results to within a few percent is demonstrated for a practicable range of the variables.

Introduction

A simple method of collecting a sample of tritiated water vapour $(\text{HTO})_v$ from air is to bubble the air through water as shown in figure 1. This is, of course, a particular application of the general laboratory technique of gas washing. The comparative collection efficiencies of various kinds of gas washing bottles were investigated experimentally many years ago⁽¹⁾.

The method has been widely applied for tritium monitoring since the collected activity may be easily measured in a liquid scintillation counter⁽²⁾. Collection efficiencies observed in particular sampling systems have been reported^(3–5). In the last reference a theoretical expression ignored the sampling conditions and was of very limited applicability.

Here, the influence of relevant variables upon the collection efficiency is investigated theoretically. The experimental determinations of some of the parameters are reported and the experimentally observed dependence of the collection efficiency on some of the parameters is compared to the theoretical predictions.

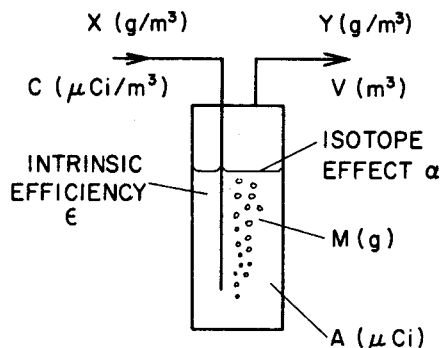
Theory

Suppose that in the model bubbler shown in figure 2, air containing water (H_2O) at X g/m³ and $(\text{HTO})_v$ at C $\mu\text{Ci}/\text{m}^3$ is being bubbled through water. Let ϵ be the fraction of the air from which the ingoing tritiated water is removed and assume that this fraction is saturated by water vapour from the bubbler. Suppose that the saturated vapour density at the bubbler water/air



Figure 1: Laboratory and field bubbler: Nominal volume is 250 cm³.

Figure 2: Model bubbler.



interface is $Y \text{ g/m}^3$ and that the ratio of specific activity of HTO in the vapour phase to that in the liquid phase at the water/air interface under the particular dynamic conditions is α , the isotope effect coefficient.

Let the mass of water in the bubbler be $M \text{ g}$ and the activity of the tritium in it, $A \text{ } \mu\text{Ci}$.

The rate of change of mass of water in the bubbler with air volume $V \text{ m}^3$ passed through is given by

$$\frac{dM}{dV} = \epsilon (X - Y) \quad (\text{i})$$

and, assuming that the activity is uniformly distributed in the bubbler water, the rate of change of activity in the bubbler with air volume is given by

$$\frac{dA}{dV} = \epsilon \left(C - \frac{\alpha A Y}{M} \right) \quad (\text{ii})$$

Equation (i) may be integrated directly to give

$$M = M_0 - \epsilon (Y - X)V \quad (\text{iii})$$

where M_0 is the initial mass of water in the bubbler.

Assuming that α is independent of V and M , if $X \neq Y$ the solution for A can be shown to be

$$A = \frac{MC}{(Y-X)W} \left[1 - \left(\frac{M}{M_0} \right)^W \right] + A_0 \left(\frac{M}{M_0} \right)^{W+1} \quad (\text{iv})$$

where A_0 is the activity initially in the bubbler.

$$W = \left(\frac{\alpha Y}{Y - X} \right) - 1$$

If $X = Y$ then

$$A = \frac{M_0 C}{\alpha X} \left[1 - \exp \left(-\frac{\epsilon \alpha X V}{M_0} \right) \right] + A_0 \exp \left(-\frac{\epsilon \alpha X V}{M_0} \right) \quad (\text{v})$$

In the trivial case of $Y = 0$,

$$A = \epsilon C V + A_0 \quad (\text{vi})$$

while in the special limiting case of $X = 0$ and $\alpha = 1$,

$$A = A_0 - \frac{CM}{Y} \ln \left(\frac{M}{M_0} \right) \quad (\text{vii})$$

The fraction of the sampled activity that is retained in the bubbler is the number of practical interest. This is the overall collection efficiency (E) and when, as is usually the case, $A_0 = 0$,

$$E = A/CV. \quad (\text{viii})$$

Figures 3–5 illustrate how variations in X , Y , ϵ and α affect the variation of collection efficiency with air volume sampled. For convenience the inefficiency $(1-E)$ is shown, expressed as a percentage. The initial mass of water M_O is 100g in all these figures. However, since the variables X , Y and M_O could have been combined as (X/M_O) and (Y/M_O) in the model, the curves shown can be interpreted for other values of M_O by normalising the values of X and Y to the new M_O ; i.e. by multiplying by $(M_O/100)$.

When the mass of water introduced into the bubbler and the mass of water lost from the bubblers are both small compared to the mass of water in the bubbler, the efficiency may be approximated by the expression

$$E = \epsilon - \frac{\epsilon^2 \alpha Y V}{2M_O} \quad (\text{ix})$$

When $W = 1$, (i.e., $X/Y = 1-(\alpha/2)$), $(1-E)$, calculated from equations (iv) and (viii), is linearly dependent upon volume V and is identical to the value calculated from equation (ix). A convenient set of conditions that produce a value of unity for W ($X = 10\text{g/m}^3$, $Y = 20\text{g/m}^3$, $\alpha = 1$) is repeated on figures 3–5. Hence in figure 3, the linear relation ($X = 10$) is also the approximation for all values of X as given by equation (ix). In figure 4, $W = 1$ for the three cases where $\alpha = 1$ so that equation (ix) predicts $(1-E)$ identical to the value from equations (iv) and (viii). In the other case ($\alpha \neq 1$) and in figure 5, linear approximations from equation (ix) are shown by the dashed lines.

Note from figures 3–5 that the inefficiency is most sensitive to the values of Y/M_O and ϵ for the ranges of variables shown. Clearly, equation (ix) is adequate for predicting bubbler performance over a wide range of sampling conditions and values of ϵ . Determination of values of ϵ , α and the effects of the sampling conditions upon the overall collection efficiency of a particular bubbler are considered separately in the following sections.

Intrinsic efficiency (ϵ) of a bubbler

In general, ϵ will depend upon the extent of the dispersion of the two phases and their time of interaction, the air flow rate and the temperature. A high value for ϵ is desirable, from the point of view of overall collection efficiency.

Values of ϵ are difficult to predict *ab initio*. However the measured value of E is the lower limit of ϵ which might be expected to be the dominant limiting parameter determining E when

$$\frac{\alpha Y V}{2M_O} < 1 - \epsilon \text{ and } \ll 1 \quad (\text{x})$$

The intrinsic efficiency, ϵ , may be estimated therefore from the measured E without the estimate's being very dependent upon the α and Y which are difficult to measure accurately.

To determine experimentally when ϵ decreases below, say, 0.98, the sampling conditions should be chosen so that $\alpha Y V < .04 M_O$. For the conditions $M_O > 50 \text{ g}$, $\alpha = 1$ and $Y = 20 \text{ g/m}^3$, V should therefore be less than 0.1 m^3 . Figure 6 shows the method used to measure ϵ for various kinds of bubblers, masses of water, temperatures and air flow rates. In these experiments input humidity X was 3 g/m^3 and the ambient air temperature was $\sim 23^\circ\text{C}$.

Figures 7 and 8 summarize the results of the measurements. The efficiencies predicted from the sampling conditions, using equation (ix), with Y (taken from psychrometric tables) corresponding to the temperature of the bulk of the bubbler water and values for α and ϵ of unity are also shown. Because this represents a lower limit to the efficiency that could be attributed to the sampling conditions, where the experimental points drop below this curve, the intrinsic

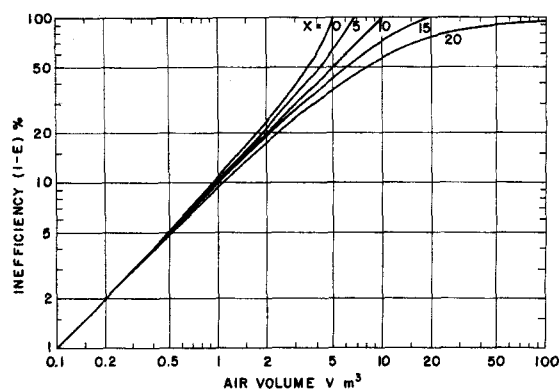


Figure 3: Calculated variations of collection inefficiencies with air volume for different values of sample humidity. Fixed parameters are $Y = 20 \text{ g/m}^3$, $M = 100\text{g}$, $\alpha = 1$, $\epsilon = 1$. Values of sample humidity ($X \text{ g/m}^3$) are given on the appropriate curves.

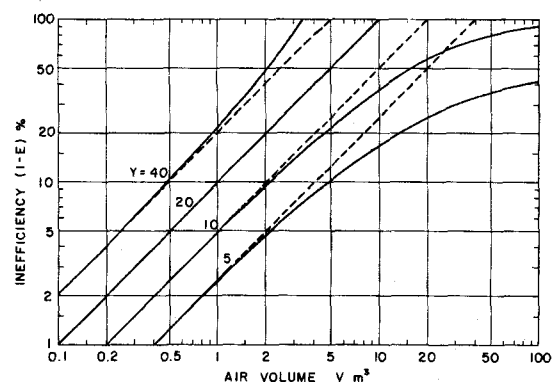


Figure 5: Calculated variations of collection efficiencies with air volume for different values of effluent air humidity. Fixed parameters are $X = 10 \text{ g/m}^3$, $M = 100\text{g}$, $\alpha = 1$, $\epsilon = 1$. Values of effluent air humidity ($Y \text{ g/m}^3$) are given on the appropriate curves. The solid lines are calculated from equations (iv), (v) or (vii) with (viii). The linear dashed extensions are from the approximate equation (ix).

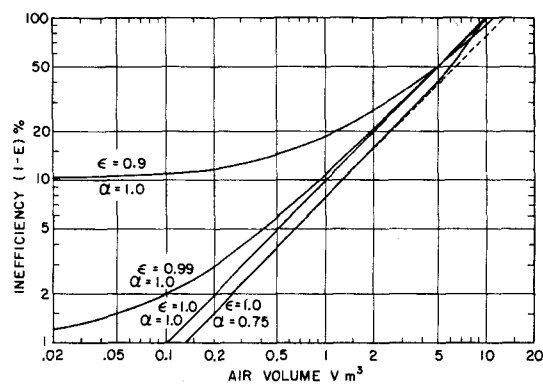


Figure 4: Calculated variations of collection efficiencies with air volume for different values of intrinsic efficiency ϵ and isotope effect coefficient α . Fixed parameters are $X = 10 \text{ g/m}^3$, $Y = 20 \text{ g/m}^3$, $M = 100\text{g}$. Values of the intrinsic efficiency ϵ and isotope effect coefficient α are given on the appropriate curves. The dashed linear extension when $\alpha \neq 1$ is calculated from equation (ix).

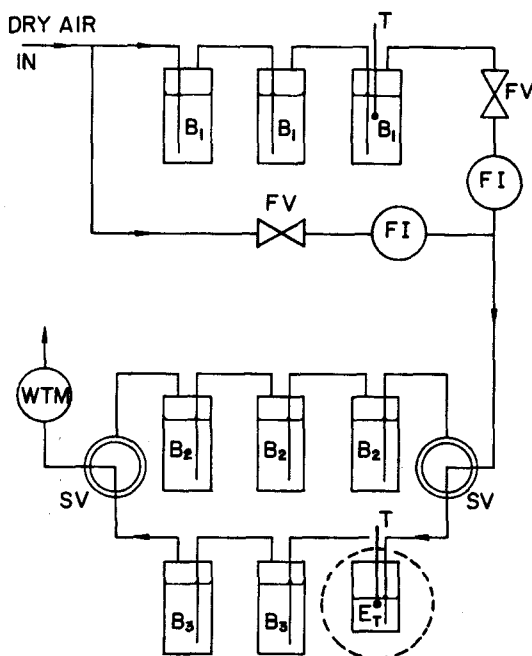


Figure 6: Outline of experimental arrangement for measuring properties of various bubblers. Tritiated water vapour was introduced into an air stream by passage through a series of bubblers (B_1) filled with tritiated water then diluted with dry air to give the requisite relative humidity. A metered flow was passed firstly, through the bubbler (E_t) under test and secondly, through a series of bubblers (B_3) to collect the activity escaping from the test bubbler. A measured volume of 0.096 m^3 was used throughout. The valves (FV) and rotameters (FI) were used for setting up the flow rates and for maintaining steady conditions. The wet-test meter (WTM) was used to measure the total volume of air passed by the test bubbler. During set up of the flows and after completion of a particular sample, the tritiated flow was diverted by valves (SV) through the second series of bubblers (B_2). The water temperature (T) in the last tritiated source bubbler and the test bubbler were measured during each sample. The activity in the test bubbler and the activities in the series of bubblers collecting the escaped activity were determined by diluting the water in each bubbler to a known volume and measuring the activity in an aliquot with a liquid scintillation counter. The experimental efficiency was then $A/(A + \sum B_3)$. Sufficient members of the B_3 series were included in the measurement to ensure that the activity not accounted for was less than 1% of the total lost. Generally, 2 were sufficient.

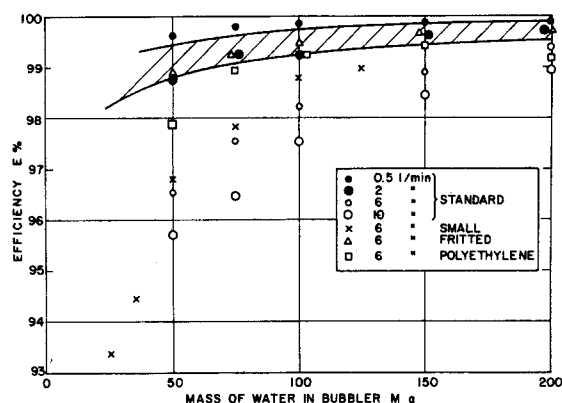


Figure 7: Measured efficiencies with different quantities of sampling water for various bubblers at a fixed air flow rate and for one bubbler at various flow rates. The band defined by the hatched area is the range of minimum efficiencies calculated from equation (ix) for all conditions used assuming an intrinsic efficiency $\epsilon = 1$. The standard bubbler is the one illustrated in figure 1. 'Small' refers to a similar one of volume 125 cm³. 'Fritted' refers to the standard type with a fritted stone air disperser. The polyethylene bubbler was similar in size to the standard with a coarse frit.

efficiency was the limiting parameter. This occurs with the smaller water masses and at the higher flow rates with the standard bubbler as might be expected. Nevertheless, even with only 25g of water ϵ was greater than 0.93. In all cases with 200g of water as collector, the intrinsic efficiency was greater than 0.99. With the fritted bubblers which more finely dispersed the air in the water a reduction in ϵ with decreasing M_0 was not observed at the flow rate used. Indeed, the total efficiency was better than predicted from the sampling conditions alone. In this case and at the lowest flow rate in the standard bubbler, agitation and mixing of the water in the bubbler was noticeably less than in the other cases. The effective temperature of the water at the air/water interfaces may therefore have been lower than that of the bulk of the water, resulting in a lower effective value for Y , and accounting, in part, for the high collection efficiency observed.

Clearly, the intrinsic efficiencies of even simple bubblers are high enough and are sufficiently independent of mass of water and flow rate for most practical purposes when used with air flow rates below 10 l/min and water masses above 50g in these types of bubbler.

Isotope effect coefficient (α)

The specific activity of (HTO)_v is known to be less than that of the water phase with which it is in equilibrium. The coefficient ranges from 0.86 at 0°C through 0.91 at 20°C to 0.94 at 50°C^(6,7). However equilibrium conditions are not necessarily attained in a bubbler; the high efficiencies observed above (figure 7) are not completely explained by α 's having equilibrium values. Appropriate values of α can be estimated for particular conditions from the initial rate of change of efficiency (E) with air volume (V) since, from equation ix,

$$\alpha = -\left(\frac{dE}{dV}\right) \frac{2M_0}{\epsilon^2 Y} \quad (xi)$$

This is demonstrated in the next section.

Variation of collection efficiency with sampled air volume

Figure 9 shows the results of two experiments in which the efficiencies of two bubblers were measured for various sampled air volumes under different conditions using the apparatus outlined in

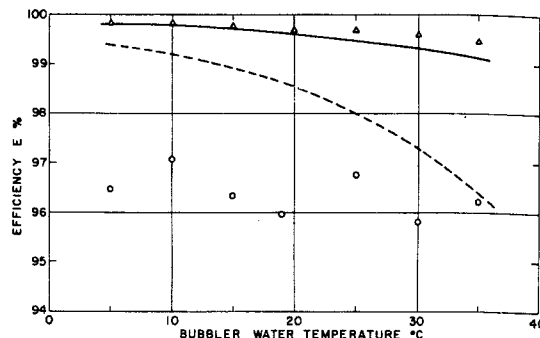


Figure 8: Measured efficiencies of bubblers at various water temperatures.

△ – Bubbler with fritted glass disperser and $M_0 = 200g$.

○ – Laboratory bubbler as in figure 1 with $M_0 = 50g$.

The solid and dashed curves are the lower limits to the respective efficiencies calculated assuming that $\epsilon = 1$ and α is the equilibrium value for the measured temperature.

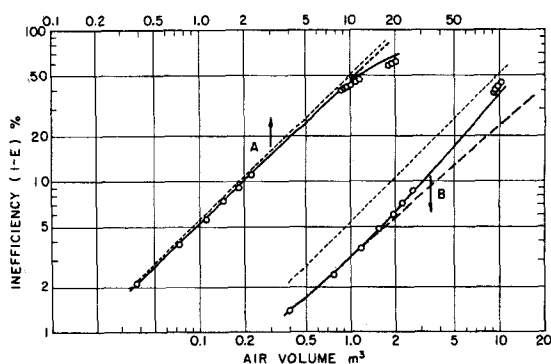


Figure 9: Measured inefficiencies of bubblers with $M = 200\text{g}$, sampling at 6 l/min for various total air volumes. Series A = $X \sim 18\text{ g/m}^3$, $Y \sim 23\text{ g/m}^3$. Series B = $X \sim 3.4\text{ g/m}^3$, $Y \sim 15\text{ g/m}^3$.

Solid lines are calculated variations using values for α determined from the initial values of (dE/dV) . For series A, $\alpha = 0.85$, for series B, $\alpha = 0.71$. Dashed lines are calculated from equation (ix) using the same conditions. The dotted lines are calculated using the ambient temperature (23°C) to determine Y and equilibrium α in equation (ix).

figure 6 with the samples B3 being replaced periodically. The appropriate values of α were determined using equation (xi) from the initial slopes established by the experimental points. The curves for the complete experiment were calculated from equation (iv) and are drawn in figure 9. Note that linear approximations also on figure 9, using the ambient temperatures from which to estimate Y and the equilibrium values of α predict the efficiencies to within a few percent anyway. Of practical note here is that although carried out under similar ambient conditions, the evaporative self cooling of the series B with the drier input air results in a reduced loss rate and higher collection efficiency than in the A series. The actual bubbler bulk water temperature was about 3°C below the laboratory air temperature.

Conclusion

The most important parameters determining the overall collection efficiency for $(\text{HTO})_v$ of a bubbler are the intrinsic efficiency and the humidity of the effluent air. Deviation of the former from unity may be disregarded for a practicable range of air flow rates, temperatures and bubbler types. The dependence of the efficiency upon the humidity lost in the effluent air may be linearly related to the total air flow with a precision adequate for most monitoring purposes.

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