



Measurement of the tritium concentration in the fractionated distillate from environmental water samples



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ABSTRACT

Standard procedures for the measurement of tritium in water samples often require distillation of an appropriate sample aliquot. This distillation process may result in a fractionation of tritiated water and regular light water due to the vapor pressure isotope effect, introducing either a bias or an additional contribution to the total tritium measurement uncertainty. The current study investigates the relative change in vapor pressure isotope effect in the course of the distillation process, distinguishing it from and extending previously published measurements. The separation factor as a quantitative measure of the vapor pressure isotope effect is found to assume values of 1.04 ± 0.036 , 1.05 ± 0.026 , and 1.07 ± 0.038 , depending on the vigor of the boiling process during distillation of the sample. A lower heat setting in the experimental setup, and therefore a less vigorous boiling process, results in a larger value for the separation factor. For a tritium measurement in water samples where the first 5 mL are discarded, the tritium concentration could be underestimated by 4–7%.

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1. Introduction

Standard practices for beta counting measurements include the use of gas-filled detectors, such as proportional or Geiger-Mueller counters, or various types of scintillation counters (ASTM, 2011). For many applications, in particular for water samples containing low-energy beta emitters, liquid scintillation counting may display distinct advantages over other current measurement practices. The use of liquid scintillation counting for beta measurements can avoid or minimize such sources of measurement bias as self-absorption in a sample matrix, backscattering from source support or detector materials, or the effects of variable detection efficiencies over the ranges of beta energies in the samples. The counting efficiency for radionuclides with maximum beta energies ≥ 200 keV is expected to be essentially 100% in liquid scintillation counting. For beta energies < 200 keV, appropriate calibration procedures provide an accurate measure of the detection system counting efficiency (ASTM, 2011).

Tritium is a low-energy beta emitter with a maximum beta energy of 18.6 keV (Johnson and Birky, 2012). The necessary

instrument calibration is usually accomplished using a radioactive standard to calibrate the physical signal efficiency in the one or two photomultiplier tubes and for quench effects in the sample (ASTM, 2011). Novel liquid scintillation instruments, however, can also employ an absolute activity measurement method based on a triple to double coincidence ratio (TDCR) method, using three phototubes instead, and obviating the necessity for a radioactive standard in the instrument (Cassette and Bouchard, 2003). The physical and statistical model used to calculate the detection efficiency in a TDCR instrument has been described previously (Broda et al., 1988; Grau Malonda and Coursey, 1988). A commercially available instrument employing the TDCR methodology has been used in the course of this investigation.

To minimize quench effects and to reduce dissolved salts and interfering radionuclides, standard procedures for the measurement of tritium in water samples usually involve the distillation of an appropriate sample aliquot in the sample preparation (USDOE, 1997; ASTM, 2008), assuming that environmental organic contaminants which could enrich the distillate with quenching agent are negligible. However, the vapor pressure isotope effect (VPIE) during the distillation process may result in a tritium gradient in the accumulating distillate, introducing an additional contribution to the total uncertainty budget for the tritium measurement. This uncertainty contribution can be reduced if the same fraction of the distillate is collected and measured for the calibration standard

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solution as for every sample. A bias resulting from the VPIE can be quantified and corrected. This study was designed to evaluate the bias correction factor for a water sample aliquot prepared and measured according to a specific measurement protocol (Savannah River Nuclear Solutions, 2010). The experimental results allowed for a quantification of the VPIE as functions of cumulative mass of the distillate, the amount of water distilled from the sample, and the heat settings for the distillation process.

Vapor pressure effects have been studied both theoretically (Topley and Eyring, 1934; Bigeleisen, 1961; Jones, 1968) and experimentally (Van Hook, 1968; Baumgaertner and Kim, 1990; Cappa et al., 2003; Luz et al., 2009; Kim and Lee, 2011). Lighter isotopes of an element generally have a higher vapor pressure than heavier isotopes. For water, molecules containing ^2H , ^3H , or ^{18}O are therefore expected to exhibit slightly higher boiling points and evaporate at a slower rate than $^1\text{H}_2^{16}\text{O}$. Experimentally, this has been confirmed for low temperatures; however, some heavy isotopes exhibit lower vapor pressures than their lighter isotopes at high temperatures (Bigeleisen, 1961; Van Hook, 1968). In water, this inversion is observed for temperatures ≥ 450 K. At the temperatures attained during the distillation process, inversion is not expected to be observable, such that the liquid remaining in the sample container will become isotopically heavier as the distillation progresses. This increase in the concentration of the heavier isotopes in the remaining liquid will result in an increase of the tritium activity concentration in the distillate with the duration of the distillation process.

An approximate measure for the VPIE is provided by the separation factor, α , for the equilibrium vaporization of an HTO/ H_2O mixture. The VPIE is defined as:

$$\text{VPIE} = \frac{P_{\text{HHO}}}{P_{\text{HTO}}} \approx \alpha, \quad (1)$$

where P_{HHO} and P_{HTO} are the vapor pressures for the pure isotopic substances H_2O and HTO, respectively. When HTO is present only in trace amounts, α can be approximated as (Baumgaertner and Kim, 1990):

$$\alpha \approx \frac{(A_{\text{T}})_{\text{c}}}{(A_{\text{T}})_{\text{g}}}, \quad (2)$$

where $(A_{\text{T}})_{\text{c}}$ and $(A_{\text{T}})_{\text{g}}$ are the tritium activity concentrations in the condensed and the gaseous phases, respectively. In this study, $(A_{\text{T}})_{\text{c}}$ is the activity concentration of the diluted standard solution in the boiling flask, and $(A_{\text{T}})_{\text{g}}$ is the activity concentration in the distillate.

The experimental setup used and the fact that the current study allowed for an investigation of the relative change in VPIE in the course of the distillation process distinguish it from and extend previously published measurements (Van Hook, 1968; Baumgaertner and Kim, 1990; Cappa et al., 2003; Luz et al., 2009; Kim and Lee, 2011).

2. Methods and materials

This study was conducted using a set of diluted standard solutions obtained from a National Institute of Standards and Technology (NIST) traceable master solution (Eckert & Ziegler Analytics, 1380 Seaboard Industrial Boulevard NW, Atlanta, GA 30318). The master solution was delivered in a sealed Flame Reagent Bottle and contained $9308 \text{ Bq} \pm 20\%$ tritium in $500.28 \text{ g H}_2\text{O}$ at the reference date. The diluted standard solutions were prepared by successive mass measurements using two scales, a model A-160 and a model XL400D (FisherScientific, 300 Industry Drive, Pittsburgh, PA 15275). The model A-160 scale is used for

mass measurements $< 50 \text{ g}$; the model XL400D has a range from 50 g to 400 g . The more sensitive mass measurements were performed with the model A-160 which had a calibration uncertainty of $< 2 \times 10^{-6}$ and a measurement uncertainty of $< 0.3\%$, as determined by repeated measurements of the same filled and sealed vial.

Eight diluted standard solutions were prepared for distillation. The nominal activity concentrations for the diluted standard solutions were adjusted such that they would provide twice to ten times the count rates observed in the blank samples. The nominal tritium activity concentrations in Distillation Sequences 1 through 8 are shown in Table 1.

The distillations were performed using the experimental setup schematically depicted in Fig. 1. Approximately 300 mL of the diluted standard solution were weighed into a 1000-mL boiling flask, boiled, and evaporated. The distillate was collected in 29-mL glass vials. All the vials were weighed before and after they were filled in the distillation process, in order to determine the total distillate recovery with respect to the total mass of the diluted standard solution in the 1000-mL boiling flask. The distillate recovery for each distillation provides a measure of the distillate loss or concentration by evaporation and escape from the distillation apparatus and for condensate on glass surfaces in the apparatus which could not be collected in the 29-mL vials. The mass recovery in the individual distillation sequences was $\geq 98\%$. Independent checks on the total activity recovery yielded recovery results that mirrored the mass recovery within $< 1.0\%$, except for Distillation Sequences 6 to 8 where the activity recovery appears to be $1\text{--}2\%$ lower than the mass recovery. While routine instrument quality control includes periodic measurements of the background and of a well-defined standard sample, the evaluation of the distillate recovery, both with respect to mass and to activity, provides the most important internal quality assurance check in this study.

The boiling flask was heated using an electrical heater (Electromante, Electrothermal, Electrothermal House, Unit 12A, Purdeys Way, Purdeys Industrial Estate, Rochford, Essex, SS4 1ND, England) with variable heat settings; the heat setting indicators range from 1 to 10 for the lowest to the highest heat setting, respectively. These heat settings are not directly correlated with specific boiling or heating plate temperatures, but indicate a more rapid approach to the boiling point and a more vigorous boil the higher the setting. To investigate the VPIE at different boiling intensities, Distillation Sequences 1 through 8 were conducted at different heat settings. For heat settings below setting indicator 8, boiling could not be observed in the boiling flask, such that no significant amount of distillate could be collected. Distillation Sequences 1 and 2 were boiled at the highest heat setting. Distillation Sequences 3, 4, and 5 only used heat setting indicator 10 until the first distillate drops were collected in the 29-mL vial, then the heat setting indicator was reduced to 8. For Distillation Sequences 6, 7, and 8, heat setting indicator 8 was used for the duration of the distillation process. From the amount of time it took to evaporate and distill the various sample aliquots at the different heat settings it is possible to estimate the average power input to the system. The highest heat setting corresponds to an average power input of

Table 1
Nominal tritium activity concentrations in the diluted standard solutions.

Distillation sequence	Nominal tritium activity concentration [Bq/g]
2	0.16
1,3,4	0.16
5	0.16
6,7,8	0.67

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