

**Contract No. and Disclaimer:**

**This manuscript has been authored by Savannah River Nuclear Solutions, LLC under Contract No. DE-AC09-08SR22470 with the U.S. Department of Energy. The United States Government retains and the publisher, by accepting this article for publication, acknowledges that the United States Government retains a non-exclusive, paid-up, irrevocable, worldwide license to publish or reproduce the published form of this work, or allow others to do so, for United States Government purposes.**

# Vapor Pressure Isotope Effects in the Measurement of Environmental Tritium Samples

R. Atkinson, T. Eddy, W. Kuhne, T. Jannik, A. Brandl

## 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 magnitude of the vapor pressure isotope effect is characterized as functions of the amount of water distilled from the sample aliquot and the heat settings for the distillation process. The tritium concentration in the distillate is higher than the tritium concentration in the sample early in the distillation process, it then sharply decreases due to the vapor pressure isotope effect and becomes lower than the tritium concentration in the sample, until the high tritium concentration retained in the boiling flask is evaporated at the end of the process. At that time, the tritium concentration in the distillate again overestimates the sample tritium concentration. The vapor pressure isotope effect is more pronounced the slower the evaporation and distillation process is conducted; a lower heat setting during the evaporation of the sample results in a larger bias in the tritium measurement. The experimental setup used and the fact that the current study allowed for an investigation of the relative change in vapor pressure isotope effect in the course of the distillation process distinguish it from and extend previously published measurements. The separation factor as a quantitative measure of the vapor pressure isotope effect is found to assume values of  $1.034 \pm 0.033$ ,  $1.052 \pm 0.025$ , and  $1.066 \pm 0.037$ , 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, this implies that the tritium concentration could be underestimated by 3 – 6%.

## 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  $\geq 200$  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 (DOE 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 will 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 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 (SRS 2010). The VPIE was investigated 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  $^2\text{H}$ ,  $^3\text{H}$ , or  $^{18}\text{O}$  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  $\geq 450$  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,  $\alpha$ , for the equilibrium vaporization of a HTO / H<sub>2</sub>O mixture. The VPIE is defined as:

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

where  $P_{\text{HHO}}$  and  $P_{\text{HTO}}$  are the vapor pressures for the pure isotopic substances H<sub>2</sub>O and HTO, respectively. When HTO is present only in trace amounts,  $\alpha$  can be approximated as (Baumgaertner and Kim 1990):

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

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

## 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 Bq  $\pm$  20% tritium in 500.28

g H<sub>2</sub>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 measurement < 50 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 Figure 1. Approximately 300 mL of the diluted standard solution were boiled and evaporated in the 1000-mL boiling flask. 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 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 – 2% lower than the mass recovery.

The boiling flask was heated using an electrical heater (Electromantle, 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 on 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 approximately 100 W, while the reduced heat setting at indicator setting 8 has an average power input of approximately 50 W. For the heat settings used during Distillation Sequences 3, 4, and 5, the average power input is estimated to amount to approximately 60 W.

The 300-mL diluted standard solutions were distilled into thirteen to fourteen batches of approximately 25 mL each. These batches were analyzed individually, providing a sequence of tritium activity concentration data as a function of the total amount of distillate obtained from evaporation of the diluted standard solution.

Aliquots of 10 mL were extracted from the 25-mL batches and transferred into 20-mL polyethylene vials (PerkinElmer, 940 Winter Street, Waltham, MA 02451). After the samples were weighed, approximately 12 mL of Ultima Gold LLT liquid scintillation cocktail (PerkinElmer Life & Analytical Sciences B.V., Rigaweg 22, 9723TH Groningen, Netherlands) were added to the vial. The vials were dark adapted by storing them in a cool and dark location for 10 h to

reduce the effects of chemoluminescence on the measurement result. The samples were counted for 9000 s, which reduced the average counting uncertainty to  $< 1\%$ .

The tritium measurements were performed using a LabLogic 300SL Liquid Scintillation Counter with TDCR Technology (Hidex, Mustionkatu 2, FIN-20750 Turku, Finland). The user interface software is provided by MikroWin™ (Mikrotek Laborsysteme GmbH, Olper Strasse 35, D-51491 Overath, Germany). Instrument output was transferred to a vendor-provided PC-application spreadsheet with macros where the raw data could be analyzed and a graphic routine provided for convenient data visualization.

Standard sample preparation processes require the discard of the first 10 mL of distillate and use of the next 50 mL for analysis (ASTM 2008). The importance of only discarding the first 10-mL fraction is emphasized; in any case, the same fraction for samples and standards alike needs to be discarded. The scientific reasoning for this discard was investigated in terms of the VPIE and the resulting tritium activity concentration gradient. To this end, the first 5 mL of distillate in every distillation sequence were collected and analyzed separately. The subsequent distillate fractions were analyzed in their 25-mL increments. Initial analysis of the first 5-mL and the subsequent 25-mL samples showed effects which could not be explained by the current understanding of the VPIE. To investigate these effects, the 25-mL sample collected immediately after the first 5-mL sample was split into an additional 5-mL and a subsequent 20-mL fractions in Distillation Sequences 6, 7, and 8.

## Results and Discussion

The results of the distillation sequences are grouped into three sets according to the use of different heat settings during the distillation process. The separation factor,  $\alpha$ , is shown as a function of the total mass of the distillate in Figures 2 - 4. The data in these figures generally exhibit similar behavior. The activity concentration in the first 5-mL sample overestimates the

nominal activity concentration in the diluted standard solution, resulting in values for  $\alpha < 1.0$ . For subsequent sample batches, the activity concentration is lower than the nominal activity concentration in the diluted standard solution and  $\alpha > 1.0$ . After reaching a minimum, the activity concentration in the distillate slowly increases towards completion of the distillation process. The separation factor exhibits a broad maximum over several 25-mL batches and then decreases slowly, again reaching values  $< 1.0$  in the last distillate batches.

Values of the separation factor  $> 1.0$  in the earlier sample batches can be understood qualitatively through the VPIE. HTO being isotopically heavier than H<sub>2</sub>O has a lower vapor pressure at temperatures around the boiling point of water, such that it is preferentially retained in the condensed phase in the boiling flask. As a result, the HTO is isotopically depleted in the vapor phase and in the distillate compared to the isotopic mixture in the initial diluted standard solution. As the liquid remaining in the boiling flask concentrates HTO, the activity concentration in the vapor eventually increases (Kim and Baumgaertner 1997), reducing  $\alpha$  until  $\alpha < 1.0$  in the last batches in the distillation process.

The VPIE has been calculated and measured for various evaporation conditions; the natural logarithm of the VPIE is expected to follow a power law expansion as a function of temperature (Jones 1968; Van Hook 1968; Baumgaertner and Kim 1990):

$$\ln \text{VPIE} = \ln \frac{P_{HHO}}{P_{HTO}} = \frac{A}{T^2} + \frac{B}{T} + C \approx \ln(\alpha), \quad (3)$$

where  $A$ ,  $B$ , and  $C$  are constants and  $T$  is the absolute temperature. For temperatures ranging from  $-43^\circ\text{C}$  to  $+127^\circ\text{C}$ ,  $\alpha$  decreases monotonously with values of 1.17 at  $0^\circ\text{C}$ , 1.10 at  $20^\circ\text{C}$ , and 1.03 at  $100^\circ\text{C}$  (Baumgaertner and Kim 1990; Rosson et al. 1998). The broad maximum for  $\alpha$  in the distillation data, prior to the increase in the tritium activity concentration in the vapor, provides a measure for the separation factor at  $100^\circ\text{C}$ . Assuming the data for the first 25-mL sample to be representative for this broad maximum, the average values for  $\alpha$  at  $100^\circ\text{C}$  as determined in this study are  $1.034 \pm 0.033$ ,  $1.052 \pm 0.025$ , and  $1.066 \pm 0.037$  for distillation at the

highest heat setting, initial heating at the highest heat setting and eventual heat setting reduction, and distillation at a reduced heat setting, respectively. The values of  $\alpha$  as estimated from the individual distillations by calculation of the activity concentration ratio in the initial diluted standard solution and in the first 25-mL sample of the distillate are shown in Tables 2 - 4.

The uncertainty budgets for the data displayed in Figures 2 - 4 and in Tables 2 - 4 include the propagated contributions from the counting uncertainties in the distillate and a suitable blank sample, the uncertainty in the distillate mass measurement, and uncertainties due to the instrumental response, such as the uncertainty on the counting efficiency and the uncertainty due to the environmental conditions in the laboratory. As the measurement of  $\alpha$  is a relative measurement between the  $^3\text{H}$  activity in the dilute standard and in the distillate, the uncertainties on the absolute values of the standard and the dilute standard activities can be neglected for these uncertainty budgets.

These results are consistent with the measurements of  $\alpha$  reported previously. However, there appears to be an increase in  $\alpha$  with decreasing vigor of the boiling process. This effect, in part, could be attributed to reduced mixing of the bulk and surface volumes of the dilute standard solution at a lower heat setting, since the standard solution was not agitated by other means during the distillation process. At lower internal mixing rates, evaporation is expected to cool the surface layer of the liquid in the boiling flask (Cappa et al. 2003; Kim and Lee 2011), increasing  $\alpha$  according to its functional dependence on temperature (Baumgaertner and Kim 1990). The absolute magnitude of this increase in  $\alpha$ , however, is slightly larger than expected from comparison with previous theoretical and experimental studies which report separation factor values of 1.04, 1.04 – 1.05, and 1.06 – 1.07 for temperatures of 80°C, 70°C, and 50°C, respectively. While the separation factor obtained at the highest heat setting is most consistent with the previously established values at 100°C, the results obtained at initial heating at the highest heat setting and eventual heat reduction and at the reduced heat setting seem to correspond more closely to temperatures of 70°C and 50°C, respectively.

Previous studies have shown that surface cooling effects can be large, even  $> 25^{\circ}\text{C}$  (Ward and Stanga 2001), when evaporation rates are fast and the induced temperature gradient between the surface and the bulk liquid only persists within the first few millimeters of the liquid surface. As the temperatures in the bulk and surface volumes of the dilute standard solution were not measured in the course of the distillation process and the time for complete evaporation of the liquid in the boiling flask increased at least two-fold at the lower heat setting, it is conceivable that the surface temperatures were actually well below the boiling point of the HTO/H<sub>2</sub>O mixture for distillation at the lower heat setting. In that case, the observed trend for the values for  $\alpha$  would correspond more closely in magnitude with expectations.

Operational experience requires discard of a specified first fraction of the distillate (ASTM 2008) in order to reduce materials that could interfere in the liquid scintillation counting process. Such interfering materials might mimic a high tritium activity concentration in the first fraction, thereby resulting in an unexpectedly low determination of  $\alpha$  in that fraction. The measured tritium activity concentrations in the analyzed samples show such behavior. However, preparation of the dilute standard solution only used de-ionized water and standard solution. The observed effect in the first 5-mL fraction of distillate cannot be fully explained by interference. The magnitude of the increase in tritium activity concentration in those samples is a function of the heat settings used during the distillation process. The higher heat settings resulted in a higher tritium activity concentration, or conversely in a lower value for  $\alpha$ . A higher boiling point for HTO with respect to H<sub>2</sub>O could result in earlier condensation of the heavier isotopic composition, artificially enhancing the tritium concentration in the first small fraction of distillate.

Distillation Sequences 6 - 8 were used to further investigate the observed effect resulting in a depression of  $\alpha$  in the first 5-mL fraction of the distillate. The following 25-mL fraction was collected in two separate vials, one holding an additional 5-mL sample, the other one containing the remaining 20 mL. The results of the measurements of these fractions are shown in Table 5.

The tritium activity concentration in the first and second 5-mL samples does not follow a clear uniform pattern in these three distillation sequences. In Distillation Sequences 7 and 8, the tritium activity concentration still increases for the second 5-mL fraction. At  $\alpha(20 \text{ mL})$ , however, the broad maximum for  $\alpha$  has been reached. Small variations in the discard volume of the first fraction might induce an additional uncertainty contribution to the measurement of the tritium activity concentration in water samples. The first non-discarded fraction will underestimate the true tritium activity concentration in the sample due to the VPIE. Experimental results do not need to account for the VPIE if the measured fraction is the same for the standard used to calibrate the liquid scintillation counter and the water samples to be analyzed. If an absolute calibration routine, i.e., TDCR, is used for the liquid scintillation counter, the measurement results will have to be corrected for the bias introduced by the VPIE. For the dilute standard solutions using only de-ionized water as carrier material, this bias is reduced in most samples when the first 5-mL fraction is combined with the subsequent 25 mL, as shown in Table 6. However, the value for  $\alpha(\text{comb.})$  is then no longer representative of the broad maximum for  $\alpha$  observed in Figures 2 - 4.

Controlled environmental conditions, such as accurate measurements of the boiling temperature and controlled atmospheric pressure during the distillation process, might allow for a more accurate determination of the initial distillate volume at which the high initial activity concentration in the distillate is compensated by the VPIE. The initial discard could be optimized to ensure consistency in routine sample analyses.

Depending on the specific laboratory reporting requirements, the additional uncertainty contribution due to the combination of the first two distillate fractions might be deemed acceptable. This could reduce the laboratory work load and waste and would avoid individual and measurement variability from the uncertainty on the individual sample discard volume.

## Conclusions

Standard procedures for the analysis of tritium in water samples account for operational experience with the measurement of the tritium activity concentration using liquid scintillation counting. Distillation of an appropriate sample aliquot minimizes quench effects and reduces dissolved salts and interfering radionuclides. However, the VPIE results in a fractionation of the isotopic composition between the vapor phase, which is collected as the distillate, and the condensed phase remaining in the boiling flask. At the boiling point of the HTO/H<sub>2</sub>O mixture, the lighter isotopic composition of water (<sup>1</sup>H<sub>2</sub>O) is expected to exhibit larger vapor pressure, accumulating the heavier HTO in the liquid remaining in the boiling flask. The tritium activity concentration will be underestimated early in the distillation process, but will be overestimated towards the end of the process. This is reflected in the separation factor,  $\alpha$  which is expected to be  $> 1$  earlier and subsequently to decrease until it is  $< 1$  for fractions collected late in the distillation process.

The separation factor has been estimated from the broad maximum observed when the ratio of the tritium concentrations in a dilute standard solution to the tritium concentration of the distillate is plotted as a function of the amount of water distilled. Depending on the vigor of the boil, or the heat settings used in the distillation process,  $\alpha$  was estimated as  $1.034 \pm 0.033$ ,  $1.052 \pm 0.025$ , and  $1.066 \pm 0.037$ , increasing with decreasing heat input. These values are consistent with the results from previous studies, although the statistical power of the current results is limited.

Standard tritium measurement procedures require the discard of an initial fraction of the distillate to reduce interfering materials in the liquid scintillation counting process. The initial fractions containing the first 5 mL of the collected distillate showed a marked increase in the tritium activity concentration. Since only de-ionized water and standard solution were used in the preparation of the dilute standard solution, this increase does not appear to be fully explained

by the possible presence of interfering material. Additional, non-radiometric analyses might help to exclude contaminants more definitively.

If a middle fraction of the distillate is chosen for subsequent liquid scintillation counting, the VPIE will generally result in an underestimate of the tritium activity concentration in the original water sample. In counting systems and sample preparation procedures where the calibration standard and the water samples to be analyzed are drawn from the same distillate fraction, the results will be accurate without additional correction. However, when absolute calibration methods are used for instrument calibration, such as the TDCR method, the measurements incur a bias of the magnitude of  $\alpha$  for which a multiplicative correction is warranted.

In the case of pure HTO/H<sub>2</sub>O mixtures, the magnitude of the bias could be reduced by combining the first 5-mL and the subsequent 25-mL fractions. However, the resulting sample will no longer be representative for the VPIE, or  $\alpha$ , in the process, and the magnitude of the bias incurred will be difficult to quantify. However, the additional uncertainty contribution incurred by combining these two initial fractions is expected to be of the order of a few per cent only and would most likely not increase the total measurement uncertainty substantially.

### Acknowledgements

This manuscript has been co-authored by Savannah River Nuclear Solutions, LLC under Contract No. DE-AC09-08SR22470 with the U.S. Department of Energy. The United States Government retains and the publisher, by accepting this article for publication, acknowledges that the United States Government retains a non-exclusive, paid-up, irrevocable, worldwide license to publish or reproduce the published form of this work, or allow others to do so, for United States Government purposes. The work presented in this manuscript was prepared through the Savannah River National Laboratory's National Center for Radioecology (NCoRE). Neither the U.S. Government or its employees, nor any of its contractors,

subcontractors or their employees, makes any express or implied: 1. warranty or assumes any legal liability for the accuracy, completeness, or for the use or results of such use of any information, product, or process disclosed; or 2. representation that such use or results of such use would not infringe privately owned rights; or 3. endorsement or recommendation of any specifically identified commercial product, process, or service. The opinions, findings, conclusions or recommendations expressed herein are those of the authors and do not necessarily represent the views of the Department of Energy, Savannah River National Laboratory or the key partners and member organizations of NCoRE.

## References

- ASTM International. Standard test method for tritium in drinking water. West Conshohocken, PA: ASTM D4107-08; 2008.
- ASTM International. Standard practices for the measurement of radioactivity. West Conshohocken, PA: ASTM D3648-04R11; 2011.
- Baumgaertner F, Kim M-A. Isotope effects in the equilibrium and non-equilibrium vaporization of tritiated water and ice. *Appl. Radiat. Isot.* 41(4): 395-399; 1990.
- Bigeleisen J. Statistical mechanics of isotope effects on the thermodynamic properties of condensed systems. *J. Chem. Phys.* 34: 1485-1493; 1961.
- Broda R, Pochwalski K, Radoszewski T. Calculation of liquid-scintillation detector efficiency. *Appl. Radiat. Isot.* 39(2): 159-164; 1988.
- Cappa C D, Hendricks M B, DePaolo D J, Cohen R C. Isotopic fractionation of water during evaporation. *J. Geophys. Res.* 108(D16): 4525; 2003.

- Cassette P, Bouchard J. The design of a liquid scintillation counter based on the triple to double coincidence ratio method. *Nuclear Instruments and Methods in Physics Research A* 505: 72-75; 2003.
- Grau Malonda A, Coursey B M. Calculation of beta-particle counting efficiency for liquid-scintillation systems with three phototubes. *Appl. Radiat. Isot.* 39(12): 1191-1196; 1988.
- Johnson T E, Birky B K. *Health physics and radiological health*. 4<sup>th</sup> ed. Baltimore, MD: Lippincott Williams & Wilkins; 2012.
- Jones W M. Vapor pressures of tritium oxide and deuterium oxide. Interpretation of the isotope effects. *J. Chem. Phys.* 48: 207-214; 1968.
- Kim K, Lee X. Isotopic enrichment of liquid water during evaporation from water surfaces. *Journal of Hydrology* 399: 364-375; 2011.
- Kim M A, Baumgaertner F. Tritium fractionation in anomalous water bound to environmental samples. *J. Environ. Radioactivity* 36(2-3): 111-127; 1997.
- Luz B, Barkan E, Yam R, Shemesh A. Fractionation of oxygen and hydrogen isotopes in evaporating water. *Geochimica et Cosmochimica Acta* 73: 6697-6703; 2009.
- Rosson R, Jakiel R, Kahn B. Isotopic exchange and vapor pressure isotope effect in tritium oxide adsorption on silica gel. *J. Phys. Chem. B* 102: 10342-10346; 1998.
- Savannah River Nuclear Solutions LLC. Determination of tritium (HTO) in water. Aiken, SC: SRS Technical Reference: Procedure L3.23-10026; 2010.
- Topley B, Eyring H. The separation of the hydrogen isotopes by electrolysis. Part I. *J. Chem. Phys.* 2: 217-230; 1934.
- U.S. Department of Energy. EML procedures manual, 28<sup>th</sup> ed. Oak Ridge, TN: EML Publications: HASL-300; 1997.

Van Hook W A. Vapor pressures of the isotopic waters and ices. J. Phys. Chem. 78(4): 1234-1244; 1968.

Ward C A, Stanga D. Interfacial conditions during evaporation or condensation of water. Phys. Rev. E 64(5): 051509; 2001.

Figure 1: Schematic of the experimental setup for distillation of the diluted standard solutions.

Figure 2: Separation factor as a function of cumulative distillate mass for Distillation Sequences 1 and 2, using the highest heat setting for the duration of the distillation process.

Figure 3: Separation factor as a function of cumulative distillate mass for Distillation Sequences 3, 4, and 5, using the highest heat setting until the first drops of distillate were collected and using a reduced heat setting thereafter.

Figure 4: Separation factor as a function of cumulative distillate mass for Distillation Sequences 6, 7, and 8, using a reduced heat setting for the duration of the distillation process.

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

Table 2: The separation factor,  $\alpha$ , as estimated from the first 25-mL sample for heating at the highest heat setting for the duration of the distillation process

Distillation Sequence	$A_{T_c}$ [Bq/g]	$A_{T_g}$ [Bq/g]	$\alpha$
1	0.179	0.169	1.057
2	0.158	0.156	1.011
Average			1.034
Standard Deviation			0.033

Table 3: The separation factor,  $\alpha$ , as estimated from the first 25-mL sample for heating at the highest heat setting until the first drops of distillate are collected and subsequent heating at a lower heat setting

Distillation Sequence	$A_{T_c}$ [Bq/g]	$A_{T_g}$ [Bq/g]	$\alpha$
3	0.165	0.155	1.067
4	0.161	0.151	1.065
5	0.176	0.172	1.023
Average			1.052
Standard Deviation			0.025

Table 4: The separation factor,  $\alpha$ , as estimated from the first 25-mL sample for heating at a reduced heat setting for the duration of the distillation process

Distillation Sequence	$A_{T_c}$ [Bq/g]	$A_{T_g}$ [Bq/g]	$\alpha$
6	0.746	0.674	1.107
7	0.710	0.673	1.056
8	0.703	0.679	1.035
Average			1.066
Standard Deviation			0.037

Table 5: The separation factor,  $\alpha$ , as estimated from the first 5-mL, the second 5-mL, and the subsequent 20-mL fractions for Distillation Sequences 10 - 12

Distillation Sequence	$\alpha$ (first 5 mL)	$\alpha$ (second 5 mL)	$\alpha$ (20 mL)
6	1.015	1.067	1.127
7	1.023	0.970	1.104
8	0.996	0.990	1.049

Table 6: Bias reduction by combination of the first 5-mL and the subsequent 25-mL fractions

Distillation Sequence	$\alpha(5 \text{ mL})$	$\alpha(25 \text{ mL})$	$\alpha(comb.)$
1	0.785	1.057	0.946
2	0.816	1.011	0.933
3	0.826	1.067	0.972
4	0.873	1.065	0.989
5	0.904	1.023	0.976
6	1.015	1.107	1.080
7	1.023	1.056	1.048
8	0.996	1.035	1.019







