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E.B. Guthrie, N.C. Shen, B.B. Bandong

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ISOTOPE EXCHANGE AND FRACTIONATION CORRECTIONS FOR EXTRACTION OF TRITIATED WATER IN SILICA GEL BY FREEZE-DRYING TECHNIQUES

Everett B. Guthrie, Nancy C. Shen and Bryan B. Bandong
Environmental Monitoring Radiological Laboratory
Analytical and Nuclear Chemistry Division
Lawrence Livermore National Laboratory
P.O. Box 808, L-232, Livermore, CA 94551

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ABSTRACT

A concentration correction curve was established for measuring the activity concentration of airborne tritiated water collected with dried silica gel and extracted by the LLNL Environmental Monitoring Radiological Laboratory freeze-dry technique. A tracer study using standard tritiated water with silica gel showed that the concentration of tritium in the extracted water is lower than that in the adsorbed water by a fraction proportional to the amount of adsorbed water. The observed decrease in tritium concentration in the extracted water can be accounted for by dilution due to isotopic exchange with both non-tritiated water and hydroxyl groups within the silica gel matrix. For the range of 8 – 35% adsorbed water, which is typical of samples collected in LLNL monitoring stations, the derived exchangeable water in the silica gel material under investigation was (5.12 ± 0.08) %. The contribution of the H_2O/HTO vapor pressure effect using published empirical data in the literature was also considered in calculating the degree of isotopic exchange.

INTRODUCTION

Airborne tritium in environmental atmospheric samples at Lawrence Livermore National Laboratory is monitored by collection of tritiated water (HTO) on silica gel (SiG) columns. Tracer studies have indicated that tritium concentrations measured in water desorbed from the SiG by techniques such as direct distillation or azeotropic distillation are consistently lower than in the original tracer solution [Patton and Cooper, 1997; Rosson et al., 2000]. Sources of the discrepancy include isotopic exchange and isotopic fractionation (vapor pressure

isotope effect) in reducing the tritium concentration of HTO adsorbed on and then desorbed from the silica gel. The present study investigates the degree of these effects using the Environmental Monitoring Radiological Laboratory (EMRL) freeze-dry method.

Non-tritiated water (H_2O) and hydroxyl groups (OH) contained in the silica gel will isotopically exchange with tritium in the adsorbed tritiated water [Rosson et al., 1998]. These chemically bound moieties are retained in the silica gel even when drying at 100 ^{o}C. Manufacturers of SiG have reported a maximum weight loss between 100 and 950 ^{o}C (the temperature when SiG chemically decomposes) of about 5.5 – 6.5%, depending on the type and grade of the gel. The water and hydroxyl groups retained in the silica gel after drying, and prior to field sampling application, is herein referred to as *exchangeable water*. The percent exchangeable water in SiG is experimentally determined in the present report.

The isotope vapor pressure effect for HTO relative to H_2O in silica gel adsorption experiments results in successively greater enrichment for HTO in the condensed phase until vaporization is taken to completion. The isotope separation factor α is defined as the mole fraction of HTO to H_2O in the condensed phase; i.e. liquid phase or adsorbed in silica gel, relative to the same mole fraction in the vapor (gas) phase. Baumgartner and Kim [1990] compiled published values of α, confirmed the values with their own measurements and developed a semi-empirical curve of α versus temperature that shows a decrease of α with increasing temperature. For the current investigation, α values will not be measured experimentally but will be derived from the semi-empirical function developed by Baumgartner and Kim.

TREATMENT OF ISOTOPIC EXCHANGE AND FRACTIONATION

If exchange of tritiated water with H_2O and OH groups in the silica gel is complete, then we can express the following material balance for tritium:

amount of tritium in adsorbed water = amount of tritium in desorbed water

This can be expressed mathematically as follows:

$$CW = C'(W + X) \tag{1}$$

Where C = initial concentration of ^{3}H in adsorbed water, e.g. in pCi/L
C' = ^{3}H concentration of desorbed water (which has been diluted with exchangeable water); e.g. in pCi/L
X = fraction of exchangeable water in SiG before adsorption
W = fraction of adsorbed water in SiG
= wet weight of SiG − dry weight of SiG
dry weight of SiG

Thus the fraction of exchangeable water can be calculated by rearranging Eqn 1:

$$X = W\left[\frac{C}{C'} - 1\right] \tag{2}$$

In the preparation of tracer solutions for the present study, the tritium concentrations C and C' must be corrected for isotope fractionation effects. For the "spiked" silica gel standard, the tritium tracer solution concentration C adsorbed in the silica gel is lower by a factor f_1 than the concentration measured in the standard solution C_m:

$$f_1 = \frac{C}{C_m} \tag{3}$$

C_m is the initial concentration of the standard tritium solution.

For the present investigation, the spiked SiG standards were prepared by adding known weights of SiG to specified amounts of frozen standard solutions of known tritium concentration. The standard solution was frozen prior to addition of the SiG to prevent the loss of solution via vaporization that would otherwise occur in the highly exothermic reaction between SiG and water at room temperature. In this manner, the preparation of the spiked SiG occurs in a controlled process and complete equilibration is attained. The other procedure for preparing the spiked

SiG standard is by bubbling a known amount of tritium solution of known activity through a dry SiG column, and the process taken to completion by bubbling the standard solution to dryness. In either case of preparation methods of the spiked SiG standard, $f_1 = 1.0$, and thus $C = C_m$.

For the extraction of the adsorbed water from the SiG during the freeze-drying stage, the tritium concentration in the water vapor distilled from the SiG, C'_m, will be lower than the tritium concentration adsorbed on the silica gel, C', by a correction factor f_2:

$$f_2 = \frac{C'_m}{C'} \tag{4}$$

where C'_m is the tritium concentration measured in the distillate.

The value of f_2 can be derived from the following semi-empirical function developed by Baumgartner and Kim [1990]:

$$ln\ f_2 = \frac{37813.2}{T^2} - \frac{136.571}{T} + 0.124096 \tag{5}$$

where T = absolute temperature; i.e. in $^\circ$K.

In the present experiment during the freeze-drying stage, the silica gel was heated to 100 $^\circ$C (373 $^\circ$K). At this temperature, Equation (5) gives $f_2 = 0.97$.

In terms of f_1, f_2, C_m and C'_m, Equation (1) may be written in the form:

$$\left(\frac{1}{W}\right)X + 1 = \frac{f_1 f_2 C_m}{C'_m} \tag{6}$$

Note that in Equation (6), a plot of 1/W versus the factor on the right-hand side of the equation would give a linear curve with a slope = X and an ordinate intercept = *1*. Thus, this method provides for an empirical method of obtaining the percent exchangeable water, X, for a given type and grade of silica gel by performing

measurements at different percent water loading of adsorbed tritium standard solution in silica gel.

PROCEDURE

Triplicate runs at each %-adsorbed water loading were conducted covering a range of %-adsorbed water from 8 – 33 %. This range was selected since it encompasses the range typically obtained with actual field samples. Spiked SiG standards were prepared by adding known weights of dried SiG to known amounts of frozen tritium standard solution as discussed in the preceding section. Prior to addition of the standard tritium solution, SiG samples were vacuum-dried in an oven at 110 $^{\circ}$C for 24 hours. Tritium concentrations were determined by liquid scintillation analysis counting the samples for a period of time to meet a preset 2-sigma counting error of 2% at the 95 % confidence level.

Freeze drying was carried for at least 3 days. As had been mentioned above, the SiG samples were heated to 100 $^{\circ}$C in a heating mantle during the freeze-drying stage. Seven-and-half (7.5) mL aliquots of the distillate were collected and counted in a liquid scintillation analyzer.

RESULTS

Measurements of tritiated water tracer adsorbed on the silica gel are presented in Table I. Using the data of Table I, the plot of Equation (6) is provided in Figure 1. The derived value for the percent exchangeable water (%), X, is 5.12 ± 0.08. By comparison, other values reported in the literature are:

Present Study (freeze-dry)..5.12 ± 0.08
Rosson et al, 1998 (azeotropic distillation) ....5.9 ± 0.7
Rosson et al, 2000 (direct distillation).................................6.3 ± 0.5
Fox, 1998 (azeotropic distillation) ....5.3 ± 0.2
Hudson, 2001 (He Mass Spectrometry................................5.8
               single measurement only)

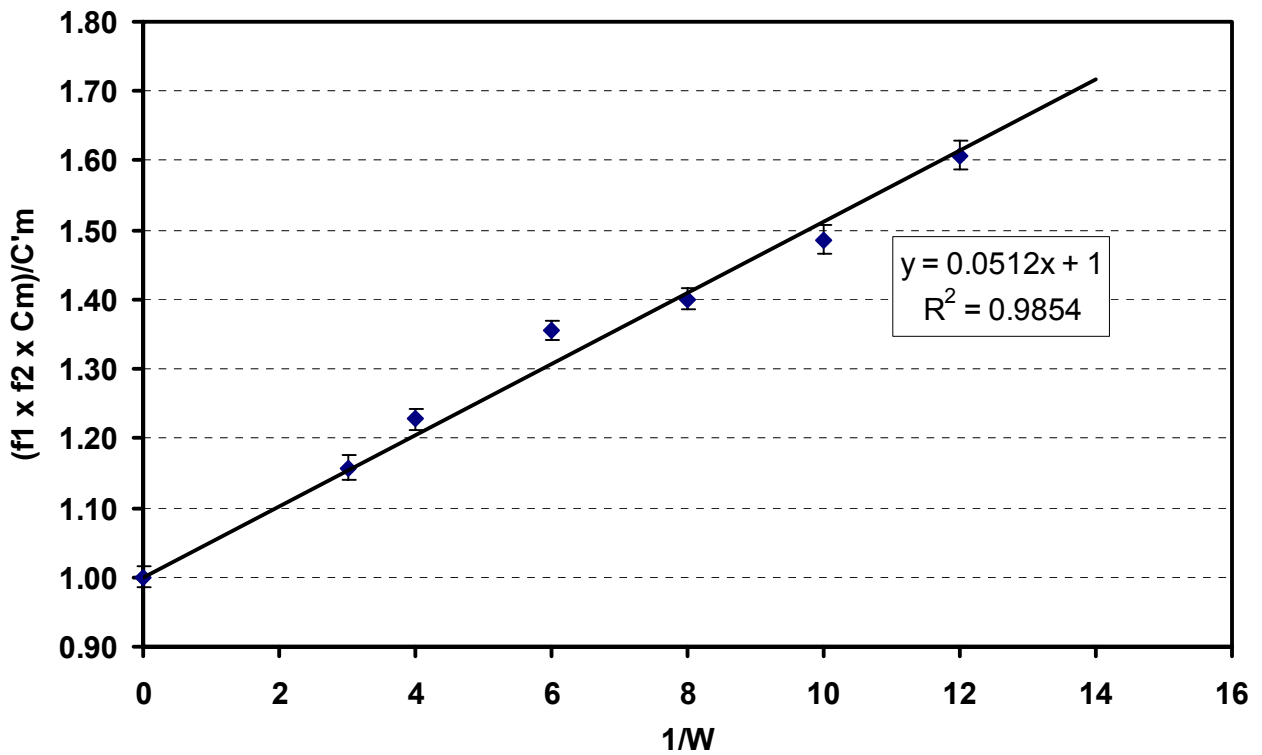Relatively good agreement can be seen among the reported values.

Figure 1. Derivation of the % exchangeable water, *X*, using the technique of Equation (6).

Table I. Measurements of tritiated water tracer solution adsorbed on silica gel columns and extracted by freeze-dry method.

Tracer Solution Activity (C_m):						
				Measured Activity, pCi/L	2σ Error, pCi/L	
			Replicate 1	40500	635	
			Replicate 2	40000	631	
			Replicate 3	41000	641	
			Average +/- Std.Dev.	*40500*	*500*	
wt. Tracer solution, grams	wt. Dry Si Gel, grams	% Adsorbed water *(W)*	Run Replicate Number	recovered water activity, pCi/L *(C'_m)*	recovered water 2σ Error, pCi/L	% tritium recovered *(C'_m/C_m)*
50	150	33.33	Replicate 1	33440	578	
			Replicate 2	34195	584	
			Replicate 3	34113	582	
			Average +/- Std.Dev.	*33916*	*414*	83.7
50	200	25.00	Replicate 1	32269	569	
			Replicate 2	31971	563	
			Replicate 3	31700	564	
			Average +/- Std.Dev.	*31980*	*284*	79.0
50	300	16.67	Replicate 1	29100	544	
			Replicate 2	28800	536	
			Replicate 3	29000	538	
			Average +/- Std.Dev.	*28967*	*153*	71.5
50	400	12.50	Replicate 1	28100	529	
			Replicate 2	27800	528	
			Replicate 3	28200	532	
			Average +/- Std.Dev.	*28033*	*208*	69.2
50	500	10.00	Replicate 1	26300	515	
			Replicate 2	26900	520	
			Replicate 3	26100	512	
			Average +/- Std.Dev.	*26433*	*416*	65.3
50	600	8.33	Replicate 1	24200	497	
			Replicate 2	24200	492	
			Replicate 3	24900	499	
			Average +/- Std.Dev.	*24433*	*404*	60.3
Derived % Exchangeable Water in Silica Gel						**5.12 +/- 0.08**

CORRECTING EMRL DATA FOR ISOTOPIC EXCHANGE AND FRACTIONATION USING THE ABOVE DATA

Equation (1) can be rewritten as follows:

$$\frac{C}{C'} = \frac{X + W}{W} \tag{7}$$

or expressing C and C' in terms of measurable values,

$$\frac{C}{C'_m} = \frac{1}{f_2} \left[\frac{X + W}{W} \right] \tag{8}$$

and substituting for X and f_2,

$$C = 1.0309 (C'_m) \left[\frac{0.0512 + W}{W} \right] \tag{9}$$

Equation (9) can be used to correct the measured concentration C'_m given the fraction of adsorbed water W. This function is depicted graphically in Figure 2.

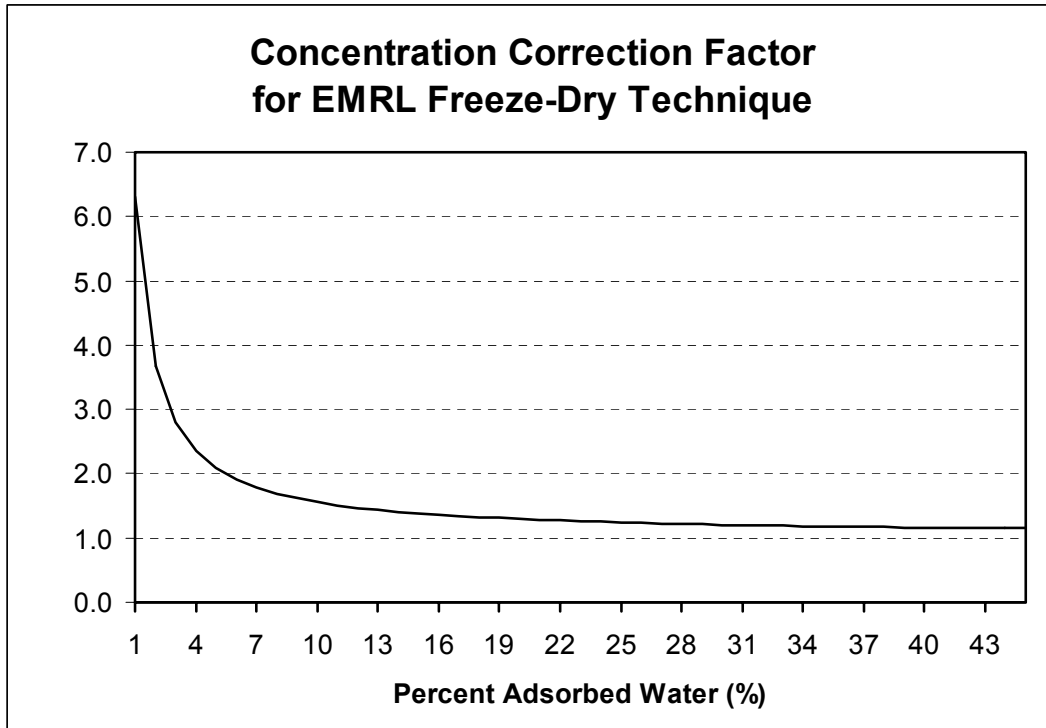**Concentration Correction Factor for EMRL Freeze-Dry Technique**

Figure 2. Concentration correction factor for HTO collected in SiG and measured by EMRL freeze-dry method.

As demonstration of the application of Equation (9), Table II exhibits correction factor for selected water loading (% adsorbed water). For example, for a 10% adsorbed water, the correction factor is 1.559. Thus to obtain the true tritium concentration in the adsorbed water (and hence the true airborne concentration collected in the silica gel), the measured tritium activity C'_m in the distillate from the freeze-drying process is multiplied by 1.559; i.e. $C = 1.559 \times C'_m$. This means that a correction of 55.9% needs to be applied to the measured tritium actvity.

Table II. Airborne tritium activity correction factors as a function of the percent adsorbed water in the silica gel.

% Adsorbed Water	Correction Factor ($C/C'm$)
1	6.309
5	2.087
10	1.559
15	1.383
20	1.295
25	1.242
30	1.207
35	1.182
40	1.163
45	1.148
50	1.136

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