Technical Implementation of the Correction Factor Calculation for Tritium in Pore-Gas Data, Revision 1

by

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Background

Tritium concentration in pore gas is usually measured by adsorbing moisture from the air sample onto the silica gel, distilling and collecting the water from silica gel, and measuring the tritium concentration in the collected water.

Such a procedure, although the best available, carries inherent error resulting from the residual water that is always present on the "dry" silica gel. In effect, this residual water dilutes tritium in the water that has been distilled from the silica gel, thus lowering the results of the measurement.

To account for this dilution, tritium concentration results reported by the analytical laboratory have been recalculated using the correction factor from the equation below (from Whicker et al., 2009):

$$CF = \frac{M_{drysilicagel} \bullet R_{residual} + M_{sample}}{M_{sample}} \qquad \text{Equation 1}$$

Where:

$M_{drysilicagel}$	is the weight of "dry" silica gel before sample moisture adsorption
$R_{residual}$	is the fraction of residual moisture on the "dry" silica gel (typically R=0.064 [Whicker et al., 2009, see the discussion of temperature below]); and
M_{sample}	is the weight of the moisture recovered from silica gel or adsorbed on silica gel (obtained from raw analytical data or calculated from field data using the mass of the sample cartridge before and after sample collection).

Equation 1 can be modified to use the percent moisture value measured by the analytical laboratory. Percent moisture, as used by the laboratory, is defined as

$$p_{\%} = \frac{M_{sample}}{(M_{drysilicagel} + M_{sample})} \bullet 100\%$$

Where:

$M_{drysislcage}+M_{sample}$ represent the weight of the wet silica gel

In fraction form, it is

$$p = \frac{M_{sample}}{(M_{drysilicagel} + M_{sample})}$$

By inverting this equation and dividing the right side by M_{sample}, one will derive

$$\frac{1}{p} = \frac{M_{drysilicagel}}{M_{sample}} + 1 \text{ and from here } \frac{M_{drysilicagel}}{M_{sample}} = \frac{1}{p} - 1$$

By modifying Equation 1, one will derive

$$CF = \frac{M_{drysilicagel}}{M_{sample}} \bullet R_{\mathrm{Re}\,sidual} + 1$$

Using expression for $M_{drysisilicagel}/M_{sample}$, one will derive the final Equation 2:

$$CF = (\frac{1}{p} - 1) \bullet R_{residual} + 1 \qquad \text{Equation 2}$$

Technical/Experimental Constrains on Using Equations 1 and 2

Two factors used in Equations 1 and/or 2 are crucial for the proper computation of the correction factor: (1) fraction of residual moisture on the "dry" silica gel ($R_{residual}$) and (2) percent moisture on the wet silica gel (p or $p_{\%}$). Both depend on how the silica gel is treated before or after sample collection.

The fraction of residual moisture on the "dry" silica gel was experimentally investigated by Whicker et al. (2009). A residual moisture of $R_{residual} = 0.064$ was determined for the "standard" gel preparation temperatures of 110°C and 1000°C to determine hard-bound residual moisture. Both field preparation of the silica gel before sampling and (analytical) laboratory determination of the percent moisture should use a temperature close to 110°C for sample preparation. Based on verbal confirmation from both field contractors and analytical laboratory (ARS), this has been the case for tritium samples analyzed.

Percent moisture on the wet silica gel is determined from the weight of the "wet" silica gel (silica gel with sample adsorbed) and the amount of water recovered during the drying/distillation process. The primary reason for distillation is to recover liquid water for tritium measurement by liquid scintillation. Hypothetically, there are two possibilities when distillation can be stopped: (1) when enough volume of sample is collected for scintillation measurements (5 mL for the analytical laboratory used), and (2) when all loosely bound moisture is removed (see above discussion of temperatures). If case 1 routinely occurred, the percent moisture information would not accurately reflect the moisture in the sample. Analysis of the raw analytical data indicates usually 10 to 25 mL of water is collected and confirmation from the contract laboratory ensures that case 2 always occurs.

Implementation

Depending on availability of the data, several different paths may be chosen by Los Alamos National Laboratory (LANL) to calculate the correction factor. The preferred choice for all tritium data collected before July 2009 was method 1 if percent moisture data were available. For historical data where percent moisture data are not available, method 5 is used. For future data, method 3 will be used. Bound water measurements will be done routinely and entered into the calculations.

1. **Percent moisture from the analytical laboratory is available in the database.**

   For gas samples measured for tritium, ER Database (ERDB) reports percent moisture defined by equation: $\%p=(M_{sample}/M_{wet\ silicagel})*100\%$. To calculate the correction factor, users should apply Equation 2. Note that the database lists moisture content as a percentage; the value needs to be changed from percent to a fraction.

   Example:

Old std result	210
Old std minimum detectable activity (MDA)	150
Old std uncertainty	120
% Moisture	12 => *as a fraction 12/100=0.12*

   Correction Factor: CF = (1/0.12-1)*0.064+1=1.469

2. **Weights of sample cartridge (with adsorbed sample), empty cartridge, and recovered moisture are available <u>from hard copy analytical laboratory.</u>**

   The weight of "wet" silica (silica with moisture adsorbed on the silica) is calculated by subtracting weight of the empty cartridge from weight of the "full" cartridge." Next, the weight of the dry silica ($M_{drysilicagel}$) is calculated by subtracting weight of the recovered moisture (M_{sample}) from the weight of the wet silica. The correction factor is calculated using Equation 1. Apply the CF to the standard result, standard uncertainty and standard MDA.

   Example:

Weight of cylinder with gel	611 g
Weight of empty cylinder	455 g

Calculated weight of "wet" gel *611 – 455=156 g (weight of wet gel may be listed in the raw data)*
Amount of liquid collected 6.8233 g (or mL)
Calculated weight of "dry" gel *156 – 6.8233= 149.1767 (weight of wet gel may be listed in the raw data)*
Correction factor: CF = [(149.1767)*0.064+6.8233]/6.8233 = 2.399

Old std result	210
Old std MDA	150
Old std uncertainty	120
New std result	210*2.399=503.8
New std MDA	150*2.399=359.9
New std uncertainty	120*2.399=287.9

3. Weights of sample cartridge with and without adsorbed sample, empty cartridge (or weight of the dry silica gel inside the cartridge) are available from the field data.

Correctly recorded field data should allow direct use of method 1.

Example:

Weight of dry gel ($M_{drysilicagel}$) 140 g
(Note: weight of the dry gel can be calculated as a difference between weight of cylinder with gel before sampling – weight of empty cylinder)
Weight of cylinder with gel before sampling 611 g
Weight of cylinder with gel after sampling 621 g
Calculated weight of collected sample M_{sample} *= 621 – 611=10 g*
Bound water is measured as 0.064 for current silica gel batches.
Correction factor: CF = [140*0.064+10]/10 = 1.896

Old std result	210
Old std MDA	150
Old std uncertainty	120
New std result	210*1.896=398.2
New std MDA	150*1.896=284.4
New std uncertainty	120*1.896=227.5

4. Weights of sample cartridge with and without adsorbed sample are available from the field data (but no weight of empty cartridge).

In this case one has to assume the weight of the "dry" silica gel ($M_{drysilicagel}$) equals 135 g. The remainder of the calculation follows that in method 3 above.

5. **When field silica gel weight/percent moisture data are unavailable, assume CF = 2.**

   A correction factor of 2 was determined using a Monte Carlo analysis of 2 yr of weight/percent moisture data (Whicker et al., 2009).

Justification of the Implementation Priorities

Two major factors need to be considered when choosing implementation of the correction factor computation: the trustworthiness of the data and the availability of the necessary data.

For past tritium measurements, there was no formal requirement to collect silica field weights. Therefore, silica gel field weights are only available for approximately 50% of samples collected before July 2009. In addition, without a formal requirement, there were no quality assurance checks implemented for silica gel field weights. In contrast, the percent moisture data for past tritium measurements were collected by certified analytical laboratories required to follow good analytical laboratory practices. The percent moisture data were available for 90% of the tritium measurements collected before July 2009. Based on this comparison, the percent moisture data available provide a more defensible method to correct pre–July 2009 tritium measurements.

For post–July 2009 tritium pore-vapor measurements, silica gel weights will be used to determine the correction factor, following Equaltion 1. The silica gel weights provide a more direct measurement to the correction factor as the initial weight of the silica gel and the amount of sample moisture are both measured.

Reference

Whicker, J.J., J.M. Dewart, S.P. Allen, W.F. Eisele, M.C. McNaughton, and A.A. Green, June 17, 2009. "Corrections for Measurement of Tritium in Subterranean Vapor Using Silica Gel," Los Alamos National Laboratory document LA-UR-09-03837, Los Alamos, New Mexico. (Whicker et al., 2009)