General

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Tritium concentrations in pore gas monitoring
September 15, 2009

LA-UR 09-04059

- An internal procedure review has identified a systematic low bias in tritium pore gas measurements.
- The low bias is associated with bound water in the sample medium – silica gel
- The bias affects tritium concentrations measured in pore gas at TA-54, TA-50, and TA-21
- To account for bound water dilution, we have updated our procedures, training, and database.

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Properties of Silica Gel

- Silica gel contains water, bound to the molecules, at the start of sampling
- This bound water has essentially no tritium content
- So, when a pore vapor sample is pulled through the silica gel canister – and water vapor is absorbed onto the silica gel molecules - the tritiated sample water vapor is diluted by the "un-tritiated" bound water already present on the silica gel
- The sample water vapor distilled off the silica gel by the analytical lab, has a lower tritium concentration than the original sample

Accounting for Silica Gel Bound Water

- This bound water cannot be removed, prior to sampling, without heating the silica gel to a temperature that destroys the silica gel

- So, we must correct for the dilution by bound water – by determining the amount of bound water on the silica gel, prior to sampling.

- Then we can calculate a correction factor – to account for the dilution by silica gel bound water

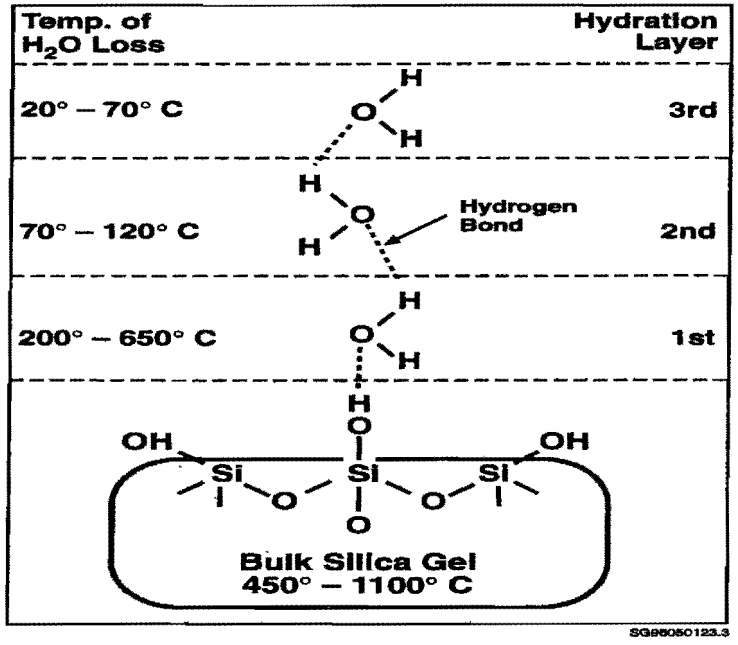

Fig. 2. Conceptual model of water sorption onto silica gel.

Calculating correction factors for bound water

- To correct for bound water dilution –
  - need to know how much bound water is on the silica gel prior to sampling, and
  - how much water is collected during sampling

- Determine the amount of water vapor collected during sampling.
  - This is done by measuring the pre and post sampling weights of the silica gel canister

- Determine the amount of bound water on the initial sample

  - Need the weight of the pre-sample silica gel. Typical value = 135 grams

  - Need the percent moisture for the silica gel. This is documented in the literature, in LANL experiments, and will be routinely evaluated for silica gel used in pore vapor measurements. Typical value for bound water = 6.4% of silica gel weight

  - Bound water = 135 g * 0.064 = 8.6 grams

Calculating the correction factor

- The correction factor is

$$\frac{\text{Amount of bound water on the silica gel + the amount of moisture collected}}{\text{amount of moisture collected}}$$

- The analytical laboratory sample tritium concentration is multiplied by the correction factor for bound water:

Example calculation of correction factor

– $\frac{(0.064*135) + \text{moisture collected}}{\text{moisture collected}}$ * (analytical lab concentration)

- $\frac{(8.6) + 10}{10}$ = 1.8 * (analytical lab concentration)

Does anyone else perform this correction?

- Established in Literature (see last slides)
  - Industry: silica gel is a common desiccant, so this property of silica gel has been studied and documented
  - DOE: SRNL, LLNL, LBNL, and PNNL have published silica gel experiments to support its use in monitoring
- DOE monitoring programs for ambient tritium use this correction
  - Lawrence Livermore National Laboratory
  - Lawrence Berkeley National Laboratory
  - Pacific Northwest National Laboratory
  - Savannah River National Laboratory
  - Los Alamos National Laboratory

References

- Scott, R. P. W.; Traiman, S. Solute-solvent interactions on the surface of silica gel. 111. Multilayer adsorption of water on the surface of silica gel. J. Chromatogr. 196:193-205; 1980.
  - Presents silica gel model for bound water – unless silica gel is heated to high temperatures (as in distillation), water remains bound.
- Rosson, et al; "Correcting Tritium Concentrations in Water Vapor Monitored with Silica Gel," Health Physics 78:68-73; 2002 (SRNL)
  - This SRNL publication documents 5-6% bound water in commercial silica gel samples, presents recommendations for correcting measured concentrations using field data.
- Guthrie, et al; "Isotope Exchange and Fractionation Corrections for Extraction of Tritiated Water in Silica Gel by Freeze-Drying Techniques," (LLNL, 2001)
  - Alternate technique for determining bound water. Freeze drying experiments show 5% bound water.
- Patton, et al; "Ambient air sampling for tritium – determination of breakthrough volumes and collection efficiencies for silica gel adsorbent," Health Physics. 72:397-407, 1997. (PNNL) bound water = 6.3%
  - PNNL experiments document silica gel bound water = 6.3%

References

- Eberhart; Experiments to estimate the amount of bound water in silica gel used in AIRNET monitoring. Personal Communication (LANL, 1999).
  - Spiked tritium samples evaporated onto silica gel. Recovery of tritium demonstrates bound water = 5% - 6%
- Whicker, Allen, Green; Experiments to estimate the amount of bound water in silica gel (LA-UR-09-03837, 2009)
  - LANL experiments on silica gel used in pore gas measurements = 6.4%
- General Engineering Laboratory, Charleston, SC, "Determination of Correction Factors to be used for Tritium Concentrations Measured on TEL-TALE® Indicating Silica Gel (Grade 48);" October 2004
  - Analytical laboratory study commissioned by LBL. Bound water estimated to be 5.1% - 5.8%
- Burns, D. and J. Kujawa, Paragon Analytics, Fort Collins, CO, "Determination of Effective Exchange Volumes of Water in Silica Gel Used for Tritium Analysis," October 2004
  - Analytical laboratory study commissioned by LBL. Bound water estimated to be 4.4% - 6.2%

Correcting pre-7/09 data

- Two methods possible
  - pre/post sample weights (50% of samples have this information in log books)
  - Analytical laboratory percent moisture (90% of samples have this information from the analytical laboratory data package)
  - We chose to use % moisture from the analytical lab, to have a more consistent correction method

- When % moisture not available, correct with a factor of 2 (Whicker, 2009)

% moisture data from analytical laboratory

- $$CF = \frac{\text{Bound Water moisture + sample moisture collected}}{\text{sample moisture collected}}$$

$$CF = \frac{135\text{ g} * 0.064 + \text{sample moisture collected}}{\text{sample moisture collected}}$$

135 g – Mass of silica gel, before sampling, or dry

$$CF = \frac{0.064 * M(dry) + MS}{MS}$$

$$CF = 0.064 * \%moisture + 1$$