PNNL- 26196

Pacific Northwest
NATIONAL LABORATORY

Proudly Operated by **Battelle** Since 1965

Soil Gas Sample Handling: Evaluation of Water Removal and Sample Ganging

October 2016

Bradley G Fritz
David G Abrecht
James C Hayes
Donald P Mendoza

U.S. DEPARTMENT OF
ENERGY

Prepared for the U.S. Department of Energy
under Contract **DE-AC05-76RL01830**

PACIFIC NORTHWEST NATIONAL LABORATORY
operated by
BATTELLE
for the
UNITED STATES DEPARTMENT OF ENERGY
under Contract DE-AC05-76RL01830

Printed in the United States of America

Available to DOE and DOE contractors from the
Office of Scientific and Technical Information,
P.O. Box 62, Oak Ridge, TN 37831-0062;
ph: (865) 576-8401
fax: (865) 576-5728
email: reports@adonis.osti.gov

Available to the public from the National Technical Information Service
5301 Shawnee Rd., Alexandria, VA 22312
ph: (800) 553-NTIS (6847)
email: orders@ntis.gov <http://www.ntis.gov/about/form.aspx>
Online ordering: http://www.ntis.gov

This document was printed on recycled paper.
(8/2010)

PNNL- 26196

Soil Gas Sample Handling: Evaluation of Water Removal and Sample Ganging

Bradley G Fritz
David G Abrecht
James C Hayes
Donald P Mendoza

October 2016

Prepared for
the U.S. Department of Energy
under Contract DE-AC05-76RL01830

Pacific Northwest National Laboratory
Richland, Washington 99352

Contents

Figures

Tables

1.0 Introduction

Soil gas sampling is currently conducted as part of an On-Site Inspection (OSI), done in support of the Comprehensive Nuclear-Test-Ban Treaty (CTBT). Soil gas samples are collected and analyzed for radioxenon and Ar-37 to detect signatures of an underground nuclear test. Some issues that can impact sampling and analysis of these samples are excess moisture in the soil gas that can interfere with the soil gas collection equipment and sample processing time. Here we discuss three potential improvements to the current sampling protocol; a desiccant for water removal, use of molecular sieve to remove CO_2 from the sample during collection, and a ganging manifold to allow composite analysis of multiple samples.

2.0 Water Removal

When collecting soil gas samples, it is necessary to remove excess water vapor to prevent condensation within the sampler. Condensation in sample lines can damage instrumentation, plug flow, adsorb water soluble analytes of interest, and impact gas purification processes. Often, soil gas samples are nearly saturated, meaning that even a slight decrease in sample gas temperature below the sub-surface soil temperature can result in condensation. There are several proven methodologies for preventing condensation from occurring in gas streams. These methods include heating the system to prevent condensation of water in the gas collection lines, active removal of water using a water condenser and passive removal of water.

For evaluation of potential water mitigation methodologies, several conservative assumptions were made about the condition of the sample. It was assumed that the sample would be completely saturated (relative humidity = 100%) at 20° C. At this relative humidity (RH) and temperature, the absolute humidity is 17.5 g H_2O/m^3. It is also assumed that sample line temperatures could reach as low as 0° C, that the gas sample volume would be up to 2 m^3, and that flow rates could be as high as 10 L/min. Based on these assumptions, a condensation prevention approach would have to maintain RH <100% at 0° C. This could be done by either maintaining the entire system temperature at 20° C, or by decreasing the absolute humidity to less than 4.9 g H_2O/m^3. Further, a removal approach must remove at least 0.13 g H_2O/min, and be capable of removing a total of 25 g of water.

Several potential condensation prevention methods were considered; heating the system to prevent condensation, use of a chiller to condense (i.e. remove) water vapor, removal of water vapor with a Nafion® dryer, or adsorption of water vapor with desiccant. Of these options, passive removal of water vapor with desiccant was chosen as the best option. Heating of the system would require additional power; the remote field locations make this an unwanted design hurdle. Further, condensation could still occur in the sample storage container or the analyzer, both of which are not desirable. Active removal with a chiller or Nafion® dryer were both viable options, but would require additional power and hardware which would increase the size and complexity of the sampling system. Therefore, passive removal of water vapor with a desiccant was deemed the best choice to prevent condensation within the soil gas sampling system.

A variety of desiccants were initially considered. The criterion for selection includes the minimum removal rate and capacity requirements described above (0.13 g H_2O/min, 25 g H_2O/sample). In addition to capacity and sorption rate, price, availability, disposal, regeneration, and competition with analytes of interest were secondary considerations in the desiccant selection process. Potential desiccants were evaluated against these criteria (Table 1), and silica gel was identified as the best option for water removal from soil gas sampling streams. It is cheaper, easier to regenerate, and has a higher capacity than other desiccants. Additionally, research indicates that silica gel will reduce the humidity of the sample stream quicker than molecular sieve in the temperatures and humidity ranges that are expected. At high humidity and low temperature, silica gel has a higher capacity for moisture (Figure 1). If the goal were to remove most or all of the moisture from the sample stream, then molecular sieve would be a better choice. Similarly, if elevated temperatures were a concern, then molecular sieve would be a better choice than silica gel; however, if the air temperature is greater than the soil temperature, then condensation will not occur and a decrease in silica gel efficiency will not impact sampler performance.

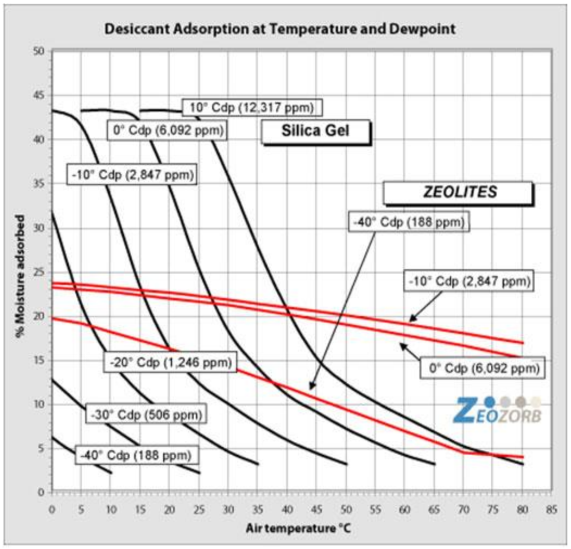
Silica gel can also be regenerated for reuse. While the low cost of silica gel makes one time use followed by disposal a viable option, reuse may be desirable for remote sampling locations where shipment of supplies is difficult. Additionally, if the use of indicating silica gel was preferable, then disposal could become more costly, making regeneration an attractive option. The regeneration of silica gel can be done using an oven or a microwave to bake the water off. The approach recommended for a field application would be an inline process, using an airline heater (A39TH, Walker Filtration, Erie PA) to blow hot air though the sampler desiccant housing. The heater could be set to the desired temperature, and a pump of compressed air cylinder used to force the hot air through the desiccant bed. This approach would require minimal handling of the silica gel outside of the housing and would be straightforward to implement.

Table 1. Comparison criteria for three desiccant options considered.

Sorbent	Capacity (g H_2O/ 100 g sorbent)	Price ($/lb)	Unregulated disposal	Regeneration	Sorption of noble gases
Molecular-sieve (zeolite)	20-30	30	Yes*	Yes- 200 to 350°C	Yes- some types
Calcium sulfate (drierite)	10-14	10	Yes*	Yes- 210°C	No information
Silica Gel	30-40	7	Yes*	Yes- 120°C	Possibly

*The cobalt based indicator used on many indicating desiccants required regulated disposal of the desiccant. Using a non-indicating version removes the regulated disposal requirement.

**Others desiccants considered but not meeting most criteria- clay, activated alumina, calcium chloride, calcium oxide



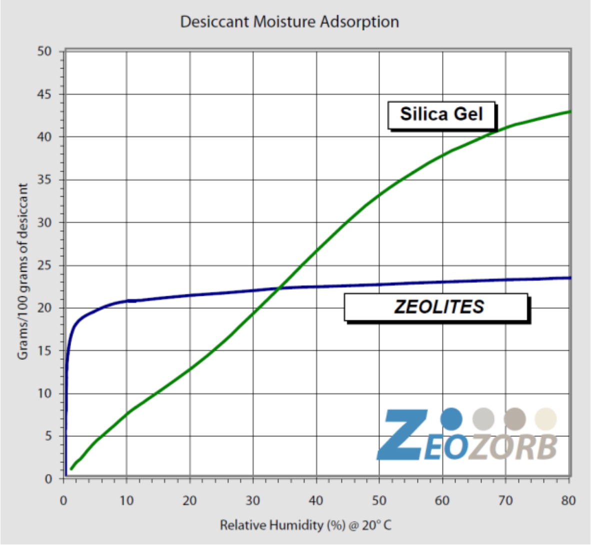


Figure 1. Moisture capacity of silica gel and molecular sieve (zeolite) as a function of temperature and RH (graphs from Drytechnic.com[1,2])

Field testing with the silica gel sorbent used approximately 1 kg of new, granular non-indicating silica gel. This fresh silica gel was used for five consecutive 0.5 m^3 samples (2.5 m^3 total). At the end of the last sample, the sample stream had a relative humidity less than 10% after passing through the silica gel cartridge (Figure 3B). This demonstrates that silica gel has sufficient capacity to prevent condensation within the sampler during collection of a 2 m^3 sample.

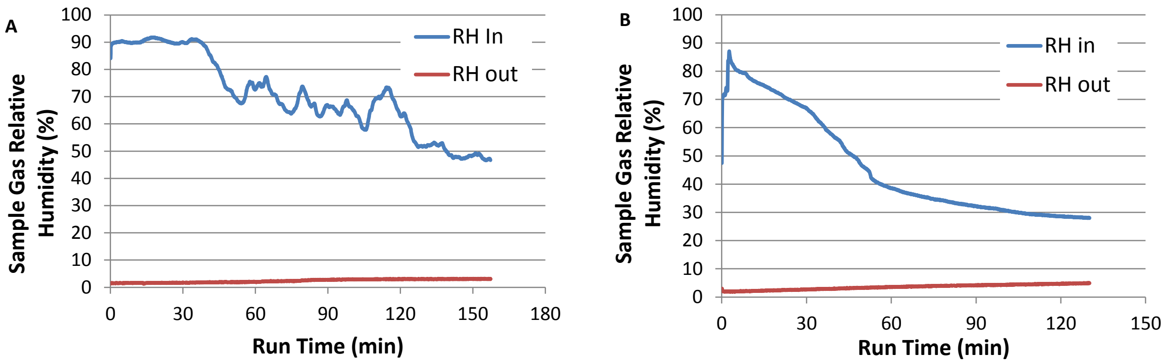


Figure 2. Relative humidity of the incoming and outgoing sample air for the first (A) and fifth (B) samples using 1 kg of new silica gel desiccant

3.0 Removal of CO2

In addition to moisture removal, removal of excess carbon dioxide (CO_2) would be desirable for a field sampling system. Removal of CO_2 can be (and currently is) done in the laboratory prior to analysis. However, partial removal in the field would be useful, and could reduce the energy required during sample processing. To that end, several CO_2 sorbents were investigated. Various forms of soda lime have long been used for CO_2 removal in breathing apparatus. Similarly, certain size classes of molecular sieve have long been known to remove CO_2 from gas streams. While soda lime is a viable option for CO_2 removal, several properties make it less desirable to use than molecular sieve. Soda lime cannot be regenerated and must be disposed of as hazardous waste. Also, the chemical reaction of CO_2 and soda lime is exothermic; given the high concentrations of CO_2 present in soil gas at some locations, the excess heat generated could

---

[1] http://www.drytechinc.com/pdf/The-misconceptions-of-Silica-Gel-FINAL-1.pdf accessed 11-8-16
[2] www.Drytechinc.com/docs/SilicaGel-vs-ZEOLITES-Desiccant-Moisture-Adsorption-Rates.pdf accessed 11-8-16

be problematic. A 3% CO_2 concentration could result in up to 0.5° C/min of temperature increase. Therefore, a molecular sieve option for removal of CO_2 was identified for testing. Since CO_2 is used as an indicator of soil gas sample integrity, the removal of CO_2 would occur downstream of the sampler. In other words, using molecular sieve at the sampler inlet to remove CO_2 and water concurrently is not desirable.

Molecular sieve comes in several sizes; the size refers to the pore opening size. Molecules small enough to get into the interior pore space get trapped. Therefore, different sizes of molecular sieve will trap some compounds while allowing others to pass. In this manner CO_2 could be selectively removed from the sample stream.

A test was conducted to evaluate the effectiveness of molecular sieve to remove CO_2. A standard gas mixture of 5% CO_2 in air was passed through a packed bed of molecular sieve, and the CO_2 concentration in the outlet stream measured. When the gas standard was passed through a 13X molecular sieve (13X 4x8 bead, Delta Adsorbents, Roselle, IL) CO_2 concentration was reduced below ambient air concentrations (0.04%). However, when passed through a 3A molecular sieve, the decrease in measured concentration was less that the resolution of the instrument. In other words, the 3A molecular sieve did not remove any CO_2 at the flow rate tested (4 L/min). In one published study, size 13X molecular sieve was found to have the highest CO_2 capacity of all the zeolites tested (Choi et al 2009). Size 3A molecular sieves were not evaluated in that study. Based on these results, a 13X molecular sieve would be recommended for CO_2 removal during sample collection.

4.0 Uptake Measurements

One concern with any desiccant or CO_2 sorbent is the potential to adsorb analytes of interest (noble gases). Some published research is available on the sorption of noble gases by molecular sieves and silica gel (Lloyd and McNees 1961). This research indicates that molecular sieve (size 5A) has the highest capacity for xenon, with 13X about half of the 5A size (Figure 3). Silica gel appears to have a capacity between five and 20 times lower than molecular sieve (13X) for xenon. Additionally, the presence of water was observed to decrease the capacity of both silica gel and mol-sieve for xenon (Lloyd and McNees 1961). While this provides a strong indication that silica gel and molecular sieve (13X) will not remove noble gas from the sample stream, a laboratory test was conducted to verify this.

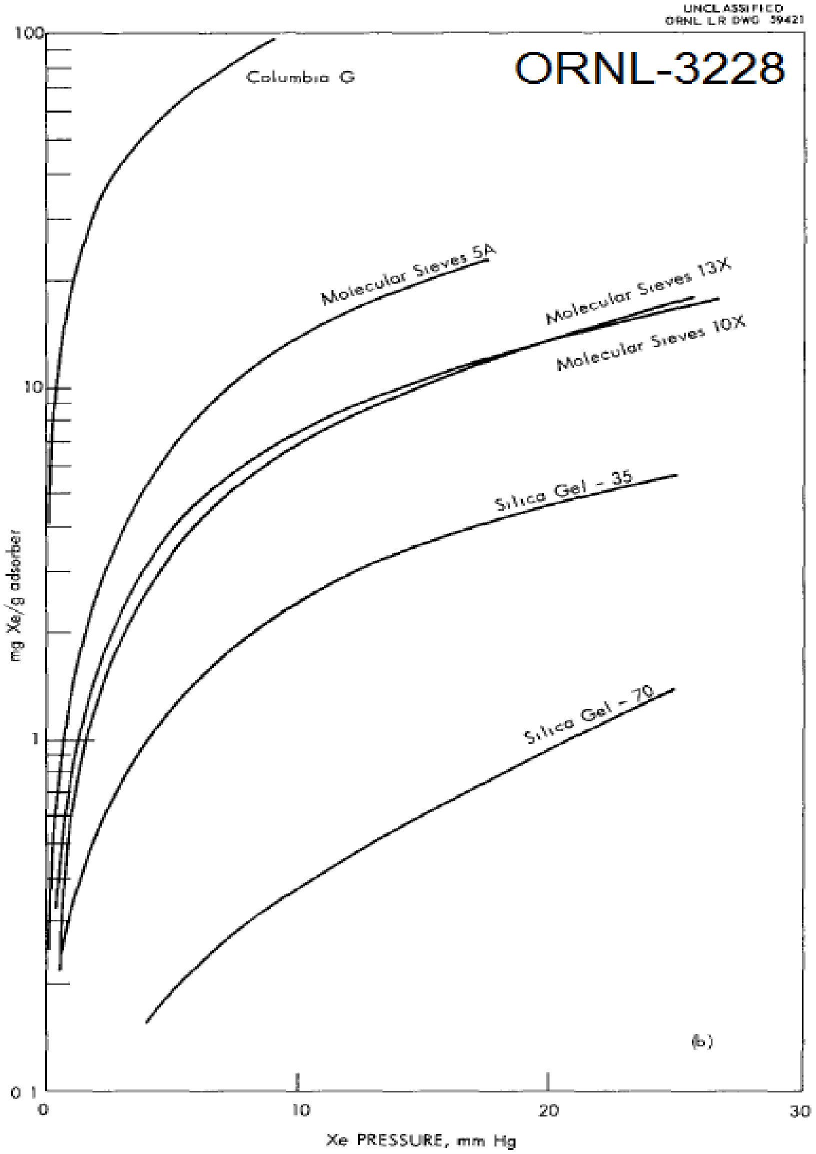


Figure 3. Adsorption of xenon by various materials at 2°C (From Lloyd and McNees 1961)

4.1 Methods

Gas adsorption isotherms were measured for molecular sieves (13X 4X8B, Delta Adsorbents) and silica gel (Type A) to assess the noble gas uptake in the presence of humidity. Measurements were performed using an IGA-200 gravimetric sorption analyzer equipped with dual vapor generators and a residual gas analyzer on the outlet (Hiden Isochema) in dynamic mode. Flowing gas was continuously passed over the sample at 1000 mbar and the indicated sample temperature. This gas flow consisted of a mixture of three input gas streams varied in appropriate ratios to obtain the humidity and analyte concentration (Ar, Xe): a saturated nitrogen (N_2) stream, a dry stream consisting of the supply concentration of the analyte (10% v/v Xe in N_2, Oxarc Inc., 30% v/v Ar in N_2, Mesa Specialty Gas), and a dry N_2 stream for balance. Laboratory nitrogen was generated from the vapor of local liquid nitrogen supply. The sample was maintained at the same temperature as the vapor generator bath for each measurement to minimize the chance for condensation in the instrument.

During the measurements, the mass of the sample was recorded using the internal balances of the instrument to obtain kinetic traces and to develop the isotherm. Although the IGA-200 has automated algorithms for identifying equilibrium based on standard IUPAC isotherm definitions, the isotherm type for these materials was not known *a priori* and the equilibrium point was thus assessed manually. Buoyancy corrections to the mass due to the changes in gas density with changes in composition were included in the mass calculation using material densities obtained from Archimedes' method but were found to contribute less than 0.5 μg deviation to the "depleted" mass (i.e., the mass of the sample without analyte) throughout all tested gas compositions, which was found to be a negligible contribution to the results.

Samples were exposed to gas streams with varying compositions up to 0.7% for Xe and up to 2.1% for Ar in streams of 30%, 60%, and 80% relative humidity at 20°C and 10°C to assess the uptake of noble gas in the material in the presence of humidity within the Henry's law regime. Noble gas concentration was increased steadily during the measurements. During the initial tests with xenon, the samples were also exposed to a second round of decreasing concentration after the initial adsorption to assess hysteresis effects. No hysteresis was found, and this process was not followed for argon.

Mass spectroscopy using a residual gas analyzer (RGA) attachment of the IGA-200 instrument was used to identify gaseous species being desorbed from the sample after exposure to the highest concentrations of noble gas. Gas was sampled through a heated capillary from the continuously flowing outlet stream. This measurement was performed only for select conditions for xenon, since it required an additional independent adsorption and desorption after the test for hysteresis was performed. However, because this test was dropped for argon, mass spectroscopy was performed on all argon samples. Masses 40 and 131 were used for argon and xenon, respectively, and were compared to mass 44 representing the CO_2 impurity in the nitrogen stream to obtain a ratio.

4.2 Results and discussion

In all measurements, the materials were found to lose mass as the noble gas concentration increased, regardless of the gas or material identity (Ar vs. Xe or molecular sieve vs. silica gel), the temperature, or the humidity (Figure 4). The kinetics of the change were found to be very sensitive to humidity for silica gel, particularly for 30% humidity where the measurements became intractable because of slow kinetics, whereas for molecular sieves the kinetics appeared to be independent of the humidity.

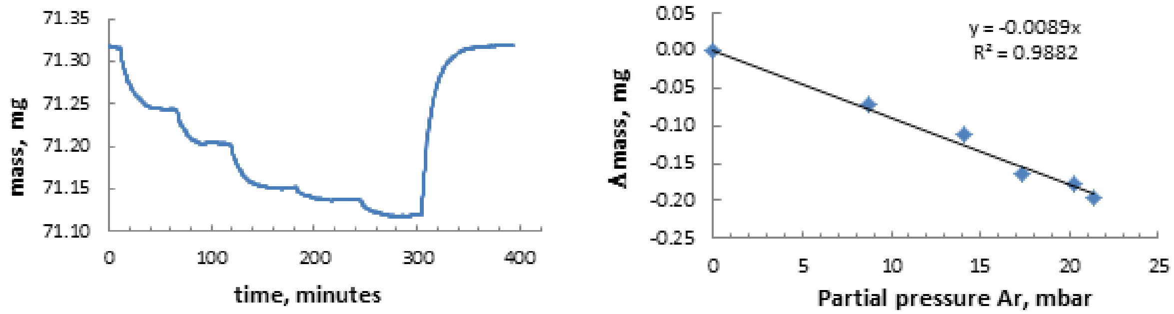


Figure 4. Kinetic trace of the mass change of the molecular sieves exposed to sequentially increasing argon concentrations (Left). The resulting isotherm, constructed from the endpoints of each step shown in the kinetic trace, representing the equilibration point (Right).

Mass spectroscopy, in all measured cases, showed that the noble gas concentration in the outlet stream (or held up in the capillary) decreases at a much faster rate than the mass recovers in the solid after the return to a wet, pure nitrogen stream. An example of this behavior is shown in Figure 5. This decoupling of the rates suggests that the change in mass is only due to changes in water adsorption in the sorbents due to the composition of the gas rather than adsorption of the noble gas or displacement of the water at the surface by noble gas.

For each of the isotherms measured, linear regression of the data points gave R^2 values of 0.95 or better, indicating that the measured were maintained within the Henry's law regime. As previously mentioned, Henry's law constants were negative for all measurements, indicating a loss of mass with increasing noble gas concentration (Figure 6). For molecular sieves, the Henry's law constant decreases consistently with increasing humidity, although the effect is far more pronounced with argon. For silica gel, xenon shows a flat or slightly increasing Henry's law trend with increased humidity while argon shows the reverse trend with a similar magnitude. The effects of temperature between 10°C and 20°C were minor and trends were not easily extracted from this small difference.

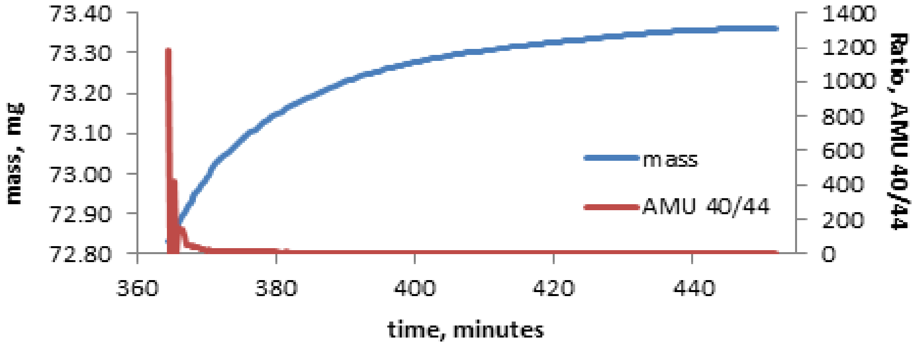


Figure 5. Mass spectroscopy measurements of the AMU 40/44 ratio for the test shown in Figure 4. The concentration of argon measured by the ratio of atomic weights equilibrates much faster than the mass, which was typical for all of the samples measured.

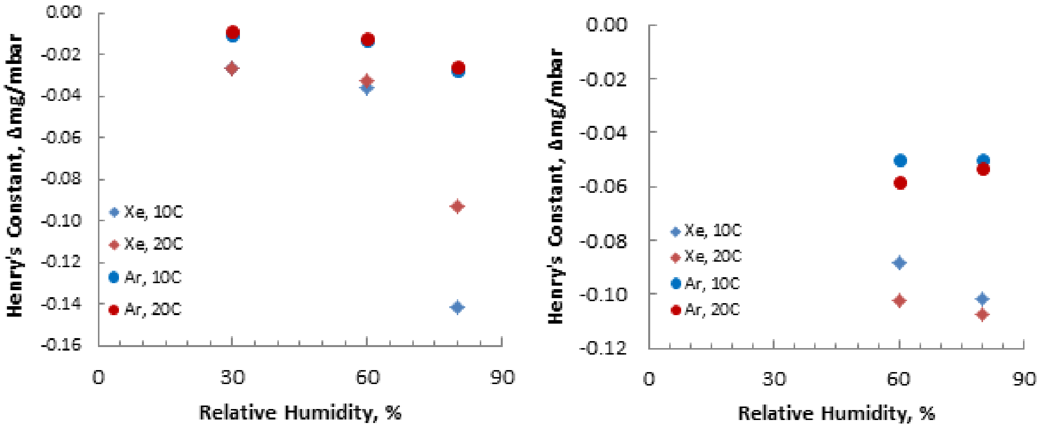


Figure 6. Henry's law constants calculated for molecular sieves (Left) and silica gel (right).

5.0 Sample Ganging

In practice, the soil gas samples collected for treaty verification are of interest if the concentration is elevated above background levels. Processing a large quantity of samples in a relatively short time requires either a high throughput system or a way to gang samples to quickly identify a region of interest. One way to reduce the analytical demand is to combine samples together and analyze as a composite sample. This is known as sample ganging. For example, parts of eight samples could be combined to make a single sample; if the concentration of this composite sample were at the background concentration, then all eight samples could be considered to be background, and no further analysis would be necessary. If the sample concentration were elevated, portions of some of the samples could be combined to identify the sample with an elevated concentration. Considering that most samples collected in a treaty verification field effort will be at or near background concentrations, sample ganging can significantly reduce the time and money necessary for sample analysis.

It is assumed that all soil gas samples will be contained in a pressurized gas cylinder. Therefore, a simple sample manifold system is necessary for sample ganging. Prior to design of a ganging manifold, a purging calculation was done. This was to determine if sample line purging was necessary to prevent cross-contamination. For the calculation purposes, it was assumed that a 1 meter long 0.39 cm ID tube was filled with contaminated sample from the previous run, at a concentration of 1000 mBq/m^3. If this 11.7 cm^3 volume were then combined with 2m^3 of sample at the background concentration (3 Bq/m^3). The measured background of this sample impacted by cross-contamination is then 9 Bq/m^3 (Figure 3). This worst case example resulting in a three-fold increase in concentration is sufficient to include consideration of a purging step in the design of a ganging manifold.

Conceptually, the design of a sample ganging manifold is straightforward. Each of the 8 cylinders will be connected to a diffusion resistant pressure regulator to prevent back-diffusion of high concentration gas into a low concentration sample. Each regulator will be connected to the primary manifold line through a three-way valve to allow sample isolation and local purging. The primary manifold line will connect to the analyzer, with another 3-way valve in-line to allow for purging of the entire system (Figure 7 & 8). This design requires manual operation, which minimizes the hardware necessary and eliminates the need for any software or electronics or power. This reduces the weight and size of the ganging manifold, allowing it to be easily disassembled, packaged in a case, and shipped to field sites.

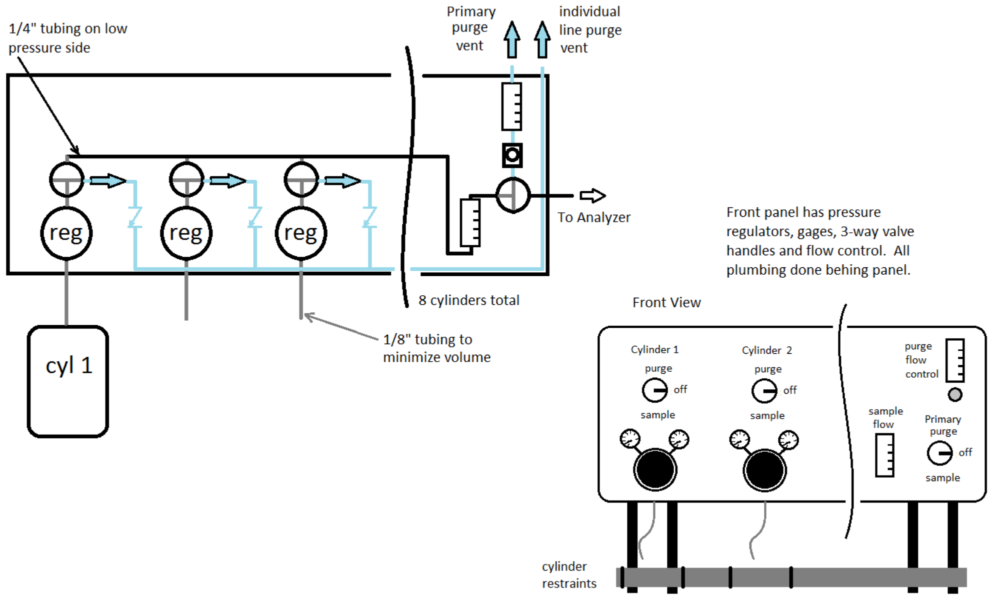


Figure 7. Conceptual sketch of sample ganging manifold.

Figure 8. Preliminary design of sample ganging manifold

6.0 Conclusions

This study measured the effects of humidity and temperature on the uptake of noble gases on silica gel and molecular sieves in the Henry's law regime. It was found that increased noble gas concentrations up to 0.7% xenon and 2.1% argon at all humidity's measured resulted in a *decreased* total mass of the materials being measured, and kinetic mass spectroscopy studies of the outlet stream showed that the noble gas concentration equilibrated much faster than the mass of the sample, suggesting that the mass change is due to a change in water on the surface rather than adsorption of nobles. We therefore conclude that xenon and argon are not adsorbed in significant quantities by these materials at these concentrations in the presence of water.

As expected, the change in uptake of water on the surface is dependent on the relative humidity, but is also strongly dependent on whether argon or xenon was used. This result suggests the choice of carrier gas in assessing the uptake of moisture on molecular sieves and on silica gel is important to the overall results.

7.0 References

Choi, S, JH Drese, CW Jones. 2009. Adsorbent Materials for Carbon Dioxide Capture from Large Anthropogenic Point Sources. ChemSusChem, 2: 796–854.

Lloyd, MH and RA McNees. 1961. Adsorption of Krypton and Xenon by various materials. ORNL-3228, Oak Ridge National Laboratory, Oak Ridge TN.

Pacific Northwest
NATIONAL LABORATORY

U.S. DEPARTMENT OF
ENERGY

Proudly Operated by **Battelle** *Since 1965*

902 Battelle Boulevard
P.O. Box 999
Richland, WA 99352
1-888-375-PNNL (7665)

www.pnnl.gov