



# A Comparison of Desiccant Materials used for Monitoring Atmospheric Tritium Concentrations in a Semi-Arid Climate

Luke R. Paulus, Health Physicist  
Douglas W. Walker, Health Physicist  
State of Idaho, INEEL Oversight Program

KC Thompson, Health Physicist  
Bechtel BWXT Idaho, LLC



#### Idaho Falls Office

900 N. Skyline Dr. Ste C  
Idaho Falls, ID 83402  
Ph. (208) 528-2600  
Fax: (208) 528-2605

#### Boise Office

1410 N. Hilton  
Boise, ID 83706  
Ph. (208) 373-0498  
Fax: (208) 373-0429

#### World Wide Web

<http://www.oversight.state.id.us>  
Toll Free: 1-800-232-4635

This report was funded by a grant from the U. S. Department of Energy, Grant No. DE-FG07-001D-13952

# Table of Contents

<b>Abstract</b> .....	<b>1</b>
<b>Introduction</b> .....	<b>1</b>
<b>Methods and Materials</b> .....	<b>2</b>
<b>Results and Discussion</b> .....	<b>6</b>
<i>Moisture Collection</i> .....	6
<i>Tritium Concentrations in Atmospheric Moisture</i> .....	9
<i>Atmospheric Tritium Concentrations</i> .....	11
<b>Conclusion</b> .....	<b>12</b>
<b>References</b> .....	<b>14</b>
<b>Appendix A – Volume Measurement Calibration</b> .....	<b>15</b>
<b>Appendix B – Field Data</b> .....	<b>17</b>

# Table of Figures

Figure 1. Routine air and radiation monitoring stations operated by INEEL OP as part of the Environmental Surveillance Program.....	1
Figure 2. The flow charts show the sampling protocol used for collecting atmospheric moisture using two separate columns.....	3
Figure 3. Photographs of air sampler used to collect atmospheric moisture using two separate desiccant columns with two separate dry gas meters, flow controllers, and flow meters. ....	4
Figure 4. Map shows the Idaho National Engineering and Environmental Laboratory (INEEL).....	5
Figure 5. Collection/Retention efficiency with respect to NOAA-ARL absolute humidity measurements is shown as a function of average temperature during sampling period. ....	8
Figure 6. Average absolute humidity measurements (g H <sub>2</sub> O per kg of air) made by NOAA-ARL during the sampling period and the corresponding absolute humidity measurements determined using molecular sieve and silica gel desiccants are shown as a function of average temperature during sampling period.....	9
Figure 7. Direct comparison between tritium concentrations measured in distillate collected using silica gel with respect to the tritium concentrations measured in distillate collected using molecular sieve.. ....	10

Figure 8. Comparison of concentrations of airborne tritium measured using silica gel with respect to airborne tritium measurements made using molecular sieve..... 11

Figure 9. All of the average absolute humidity measurements (g H<sub>2</sub>O per kg of air) made by NOAA-ARL during the sampling period and the corresponding absolute humidity measurements determined using molecular sieve and silica gel desiccants are shown as a function of average temperature during sampling period..... 13

Figure A-10. Comparison of calibrated volume measurements using both dry gas meters used during this study. .... 15

Figure A-11. Calibration Results comparing volumes of air sampled using the calibrated dry gas meters to a "known" volume derived from a calibrated flow meter. The "known" volume was derived from the sampling time multiplied by the volumetric flow rate. .... 16

## Table of Tables

**Table 1.** Mixing ratios calculated using molecular sieve, silica gel, and determined by NOAA – ARL at CFA tower. Mixing ratios are given in units of grams H<sub>2</sub>O per kilogram of air. .... 7

**Table 2.** Retention efficiencies determined with respect to NOAA-ARL mixing ratios for molecular sieve and silica gel adsorbents. .... 8

**Table 3.** Tritium concentrations (in Bq L<sup>-1</sup>) in atmospheric moisture samples collected by INEEL OP and submitted to ISU EML for liquid scintillation counting. .... 10

**Table A -1.** Dry Gas Meter Calibration Data..... 15

**Table B-1.** Field Data used during this study. .... 17

**Table B-2.** Weather Data..... 18

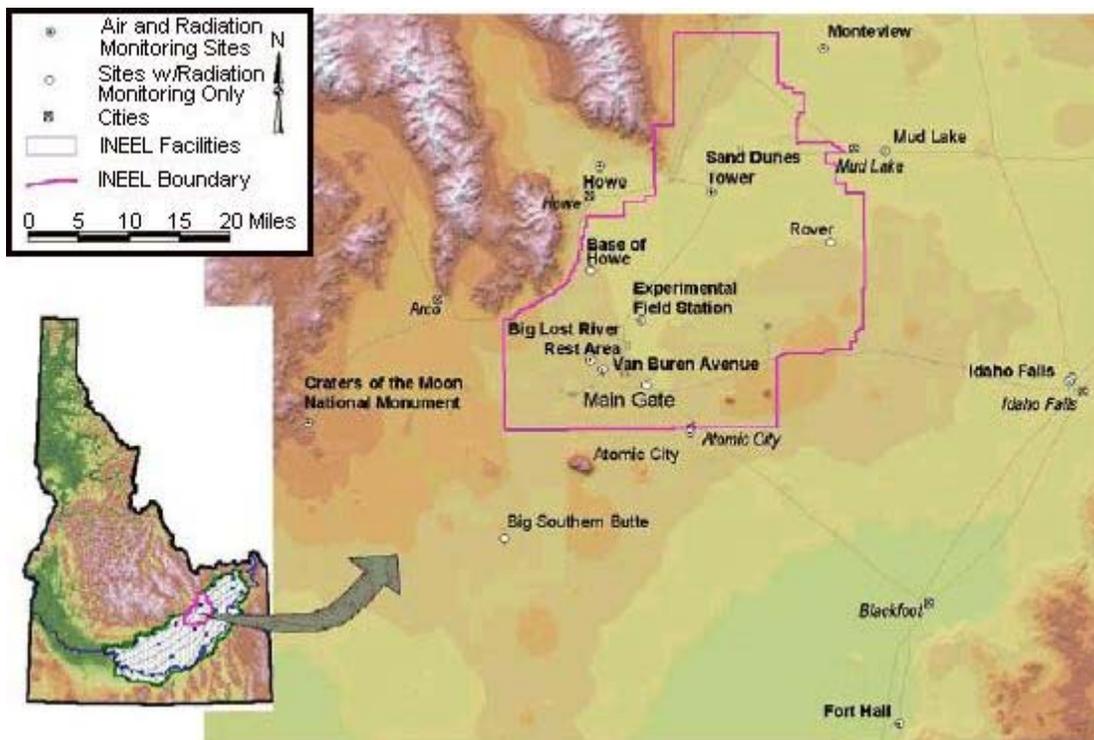
## **Abstract**

Atmospheric tritium monitoring involves the collection of tritiated water vapor by collecting atmospheric moisture from air that is drawn through a bed of desiccant material. This study is a comparison between molecular sieve and silica gel adsorbent media used for atmospheric moisture sampling conducted in the semi-arid climate of the Idaho National Engineering and Environmental Laboratory. Water vapor was collected simultaneously using two columns containing different desiccant materials (one column containing molecular sieve and the other containing silica gel). Data collected during air sampling periods were compared with meteorological data collected and atmospheric moisture collection efficiencies were determined. Breakthrough of atmospheric moisture past the desiccant material was suspected with both media at elevated temperatures indicating that smaller sample volumes, lower volumetric flow rates, or longer adsorbent columns should be used during summer when ambient temperatures are elevated.

# Introduction

A common methodology for monitoring atmospheric tritium involves the collection of tritium oxide or tritiated water vapor ( $\text{HTO}_{(g)}$ ) by collecting atmospheric moisture from air pumped through a column of desiccant material at a measured flow rate. The column of desiccant material is weighed prior to deployment and then again at the conclusion of deployment to determine the total amount of water collected. By heating the desiccant, the adsorbed water is driven off (desorbed) and the vapor is condensed and collected as distillate. Tritium concentrations in the distillate are measured using liquid scintillation counting (LSC) techniques.

The state of Idaho operates an independent environmental surveillance program as part of the Idaho National Engineering and Environmental Laboratory Oversight Program (INEEL OP). The INEEL OP was established in 1990 to objectively report to the citizens of Idaho the impacts of the Department of Energy's activities at the Idaho National Engineering and Environmental Laboratory (INEEL) on public health and the environment. Environmental Surveillance Reports are published by INEEL OP on a quarterly and annual basis. As part of this surveillance program, INEEL OP operates a network of samplers designed to collect atmospheric moisture on and around the INEEL to monitor atmospheric tritium concentrations.



**Figure 1.** Routine air and radiation monitoring stations operated by INEEL OP as part of the Environmental Surveillance Program.

Questions arose regarding the most “appropriate” method to measure airborne tritium concentrations at environmental levels considering the climate at the INEEL. Historically, INEEL OP has used molecular sieve beads as the adsorbent to collect atmospheric moisture, whereas the contractor programs conducting atmospheric moisture sampling for the Department of Energy Idaho Operations Office (DOE-ID) have used silica gel. Previous studies have indicated that water vapor will migrate through a bed of silica gel if dry air is passed through a previously hydrated bed (Straight 1978 and Eberhart 1999). Other studies involving silica gel as a water vapor trap conducted at Pacific Northwest Laboratory (PNL) and Los Alamos National Laboratory (LANL) indicated that the elevated temperatures affect moisture collection efficiency (Patton et al 1997 and Eberhart, 1999). Experiments involving molecular sieve also have demonstrated breakthrough or loss of adsorbed moisture at low humidity, but only after most of the desiccant bed was saturated (Singh et al. 1984). Elevated temperatures observed in the sampler housing corresponded to a reduction in collection efficiency indicating that sampling rates may require adjustment to maintain adequate moisture collection efficiency. In some instances, refrigeration has been used to maintain constant temperatures in sampler housings.

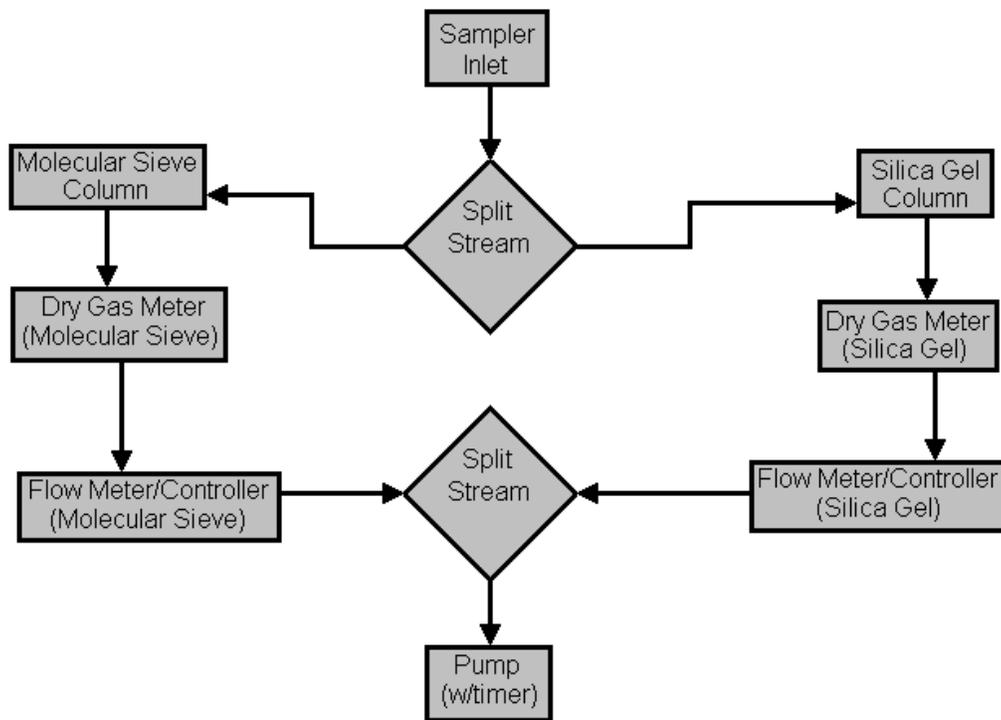
Climate conditions at the INEEL are consistent with its altitude above sea level, latitude, and inter-mountain setting. The region is semi-arid. The air is relatively dry lending itself to intense solar heating of air near the ground’s surface during daylight hours and radiational cooling at night. Temperature extremes range from  $-40^{\circ}\text{C}$  in winter months to  $38^{\circ}\text{C}$  in summer months (Clawson et al., 1989). Temperatures measured in housing used for atmospheric moisture sampling have been observed as high as  $50^{\circ}\text{C}$ .

Another concern regarding the use of desiccant materials for tritiated water vapor collection is possible isotopic separation during the removal of moisture from the desiccant material when heated. Studies conducted using silica gel have shown decreases in tritium concentrations after the desorption process with respect to known adsorbed moisture tritium concentrations (Rosson et al. 2000). A study conducted by Ontario Hydro suggests that the behavior of  $\text{H}_2\text{O}$  for 4A molecular sieve is representative of the isotopic species HTO and  $\text{D}_2\text{O}$  (Singh et al 1984).

## **Methods and Materials**

INEEL OP routinely monitors airborne tritium by pumping air through a column of molecular sieve to trap moisture from the air. The collected moisture is then removed from the desiccant trap and subsequently analyzed for tritium by mixing a suitable volume of condensed vapor with liquid scintillation cocktail and counting using standard liquid scintillation counting (LSC) techniques. The total volume of air sampled and the mass of moisture collected (assuming 100% collection efficiency) must be calculated to convert the concentration in the collected moisture to the tritium concentration in air. The total volume of air can be determined either by multiplying the average volumetric flow rate by the sampling time or the volume is measured directly using a dry gas meter. This study compared two desiccant materials for airborne tritium monitoring by simultaneously collecting atmospheric moisture through a bed of molecular sieve

and a bed of silica gel. Efforts were made to follow sampling protocols similar to those used during routine atmospheric tritium monitoring. A flow chart indicating the flow of air through the atmospheric moisture sampler used during this study is shown in **Figure 2**.



**Figure 2.** The flow charts show the sampling protocol used for collecting atmospheric moisture using two separate columns.

Efforts were taken to minimize elevation of the temperature of the desiccant materials during the sampling period. The vacuum pump was placed on the exterior of the louvered sampler housing to minimize the heating of the desiccant during the sampling period. A louvered housing was used to allow air to pass through the sampler housing to keep the temperatures inside the housing as close to ambient temperatures as possible.

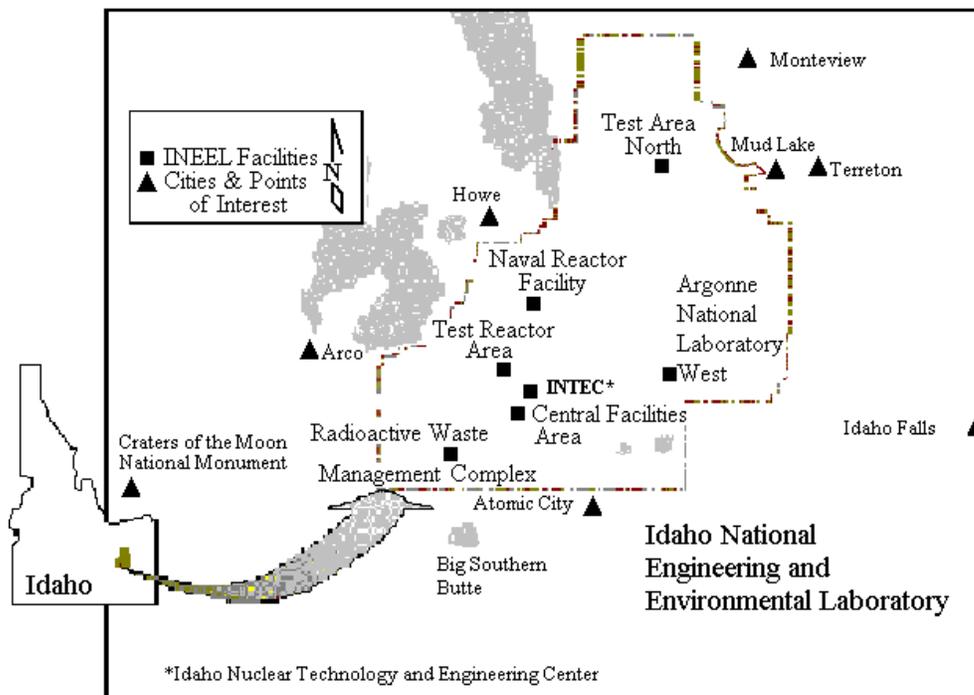
To compare the effectiveness of molecular sieve adsorbents and silica gel adsorbents for collecting atmospheric moisture, air was sampled at the rate of  $1.9 \pm 0.2 \text{ L min}^{-1}$  ( $4.0 \pm 0.5 \text{ SCFH}$ ) through two plastic columns operated in parallel (**Figure 3**). The plastic columns containing the adsorbents are cylinders with a diameter of 6.5-cm and 35-cm long. One column contained ten-percent (by mass) 6-16 mesh indicating silica gel mixed with 6-12 mesh non-indicating silica gel. The other column contained ten-percent (by mass) ADCOA 4-8 mesh, 4A indicating molecular sieve mixed with Davison 4-8 mesh, 4A non-indicating molecular sieve. Each column was loaded with  $500 \pm 50 \text{ g}$  of adsorbent. The columns were weighed to the nearest  $\pm 0.1\text{-g}$  prior to deployment. The outlet for each column was connected to a  $0.1$  to  $2.4\text{-L min}^{-1}$  ( $0.2$  to  $5.0 \text{ SCFH}$ ) volumetric flow meter with flow control valve and a calibrated

Equimeter R-275 dry gas meter for measuring sample volume (**Appendix A**). A single pump was used to ensure consistent sample volumes would be collected despite occasional power loss at the sampling location. Elapsed sampling times were determined using a timer that measured the time that electrical power was supplied to the pump.



**Figure 3.** Photographs of air sampler used to collect atmospheric moisture using two separate desiccant columns with two separate dry gas meters, flow controllers, and flow meters. Inset 1 shows the two distinct columns containing silica gel (on left) and molecular sieve (on right). Inset 2 shows the two separate flow meters and flow controllers used along with the timer in the background.

The air sampler was placed next to a meteorological tower at the INEEL Central Facilities Area (CFA). This tower is centrally located on the INEEL near the southern boundary (**Figure 4**). This tower is part of a pre-existing meteorological monitoring network maintained by the National Oceanic and Atmospheric Administration - Air Research Laboratory (NOAA - ARL) to collect, store, and report meteorological data including temperature, wind speed, barometric pressure, and relative humidity (NOAA ARL 2001). Average meteorological data for the deployment period were used for this study and average values for absolute humidity were calculated from temperature, barometric pressure, and relative humidity data. The sampling location was chosen due to its proximity to a low-level atmospheric tritium source. Tritium has been detected in elevated quantities in ground water collected from wells at CFA. This ground water has been used for irrigation of the grounds at CFA.



**Figure 4.** Map shows the Idaho National Engineering and Environmental Laboratory (INEEL). Desiccant study was performed near the Central Facilities Area located in the south-central portion of the INEEL.

Paired atmospheric moisture samples were collected February 2000 through March 2001 using both molecular sieve and silica gel desiccants. Columns were weighed empty and containing fresh desiccant adsorbent to the nearest  $\pm 0.1$ -g prior to deployment. These columns were exchanged when visual inspection of one or the other column at the sampling location indicated approximately 80% moisture saturation. After collection, columns were weighed to the nearest  $\pm 0.1$ -g and then the adsorbents were removed from the columns and heated to approximately 300 °C to recover adsorbed moisture. Adsorbents were heated until approximately 50-mL of moisture was recovered, typically 50 to 60 percent of the available sample mass. Condensed moisture was submitted to the Idaho State University Environmental Monitoring Laboratory (ISU EML) for tritium analysis using LSC techniques (ISU EML 1995). Results of these analyses were reported as the tritium concentration in moisture collected from the atmosphere.

Airborne tritium concentrations were determined by multiplying the concentration of tritium in the moisture ( $\text{Bq mL}^{-1}$ ) by the concentration of moisture in the atmosphere ( $\text{g m}^{-3}$ ). Atmospheric moisture concentrations were determined by dividing the net mass gained by each column by the volume of air pumped through the column. Atmospheric moisture concentrations were compared with absolute humidity average mixing ratios ( $\text{g H}_2\text{O kg}^{-1}$  dry air) corresponding to sampling period as calculated by NOAA-ARL. Relative collection efficiencies for both silica gel and molecular sieve were also determined with respect to NOAA mixing ratios.

# Results and Discussion

## Moisture Collection

Accurate determination of airborne tritium concentrations is dependent upon accurate measurement of moisture concentration. Mixing ratios were determined using molecular sieve and silica gel by dividing the total mass of moisture collected (i.e., the net column mass gain) by the mass of air sampled. Air mass was calculated from the volume of air sample and correcting for ambient temperature and pressure (**Appendix B**). Average mixing ratios were calculated by NOAA-ARL using data collected at the CFA meteorological tower. These results are shown in **Table 1**.

Since the NOAA-ARL mixing ratio corresponds to the available moisture, retention efficiencies for both molecular sieve and silica gel adsorbents were determined. Retention efficiency was determined by dividing the total moisture collected by the moisture available. This can also be calculated by dividing the measured mixing ratio by the NOAA-ARL mixing ratio. Retention efficiencies are shown in **Table 2**. Some of the columns experienced breakthrough. That is, after most of the adsorbent was saturated with moisture, a fraction of moisture passed on through the adsorbent. The collection efficiency values calculated for these samples are questionable since sampling continued after the desiccant bed was no longer adsorbing additional moisture. The molecular sieve adsorbent showed a distinct edge to which moisture saturation occurred by visual inspection during the sampling period. During hot, dry periods the silica gel showed a diffuse edge to which moisture saturation had occurred.

Additional meteorological data were collected and averaged with each sampling period. These included average temperature, average barometric pressure, mean wind speed, and total precipitation (**Appendix B**). Collection efficiency values and calculated mixing ratios were compared with these measurements. Collection efficiency and mixing ratios were compared with average temperature for samples that did not show evidence of sample breakthrough (see **Figure 5** and **Figure 6**, respectively). The adsorbent media demonstrated similar collection efficiency and mixing ratios when the sampling volume was less than the breakthrough volume.

**Table 1.** Mixing ratios calculated using molecular sieve, silica gel, and determined by NOAA – ARL at CFA tower. Mixing ratios are given in units of grams H<sub>2</sub>O per kilogram of air.

Start Date	Stop Date	Molecular Sieve Air Volume (m <sup>3</sup> ) Sampled	Silica Gel Air Volume (m <sup>3</sup> ) Sampled	Mean Relative Humidity	NOAA-ARL	Molecular Sieve	Silica Gel
7 February 2000	5 April 2000	44.1	44.1	74.8%	3.5 ± 0.3	0.5 ± 0.1 <sup>a</sup>	0.5 ± 0.1 <sup>a</sup>
5 April 2000	4 May 2000	36.2	37.8	52.6%	4.2 ± 0.3	2.6 ± 0.3 <sup>b</sup>	2.5 ± 0.3 <sup>b</sup>
4 May 2000	25 May 2000	21.1	21.2	55.0%	5.1 ± 0.4	4.0 ± 0.4	3.9 ± 0.4
25 May 2000	16 June 2000	22.2	21.8	39.1%	4.8 ± 0.4	3.7 ± 0.4	3.1 ± 0.3 <sup>b</sup>
16 June 2000	10 July 2000	23.3	24.1	31.1%	4.7 ± 0.4	3.4 ± 0.3	2.5 ± 0.3 <sup>b</sup>
10 July 2000	3 August 2000	22.5	22.9	30.0%	5.3 ± 0.4	4.0 ± 0.4	2.1 ± 0.2 <sup>b</sup>
3 August 2000	5 September 2000	30.8	31.6	33.5%	5.1 ± 0.4	3.1 ± 0.3 <sup>b</sup>	2.4 ± 0.2 <sup>b</sup>
5 September 2000	28 September 2000	25.0	25.4	39.2%	4.0 ± 0.3	3.2 ± 0.3	2.8 ± 0.3 <sup>b</sup>
28 September 2000	23 October 2000	28.7	29.8	55.2%	4.2 ± 0.3	3.2 ± 0.3	3.2 ± 0.3
23 October 2000	16 November 2000	29.5	29.5	80.3%	3.5 ± 0.3	3.0 ± 0.3	2.8 ± 0.3
16 November 2000	29 December 2000	57.3	57.3	88.5%	2.3 ± 0.2	1.8 ± 0.2	1.9 ± 0.2
29 December 2000	1 February 2001	47.4	48.2	86.9%	1.8 ± 0.1	2.4 ± 0.2 <sup>a</sup>	1.5 ± 0.2 <sup>a</sup>
1 February 2001	1 March 2001	41.2	41.5	88.3%	2.3 ± 0.2	2.0 ± 0.2	1.9 ± 0.2
1 March 2001	22 March 2001	30.4	30.2	79.5%	3.6 ± 0.3	2.9 ± 0.3	2.8 ± 0.3
Average:		32.8	33.2	59.6%	3.9	2.8	2.4

<sup>a</sup> Data points considered "outliers" and were not used in **Figure 5**.

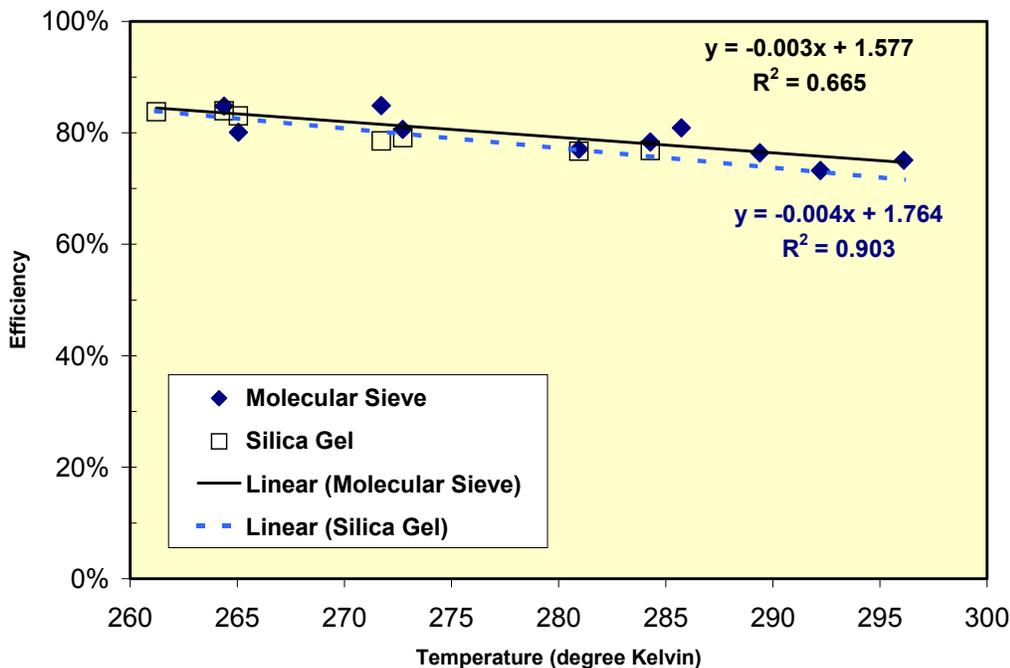
<sup>b</sup> Sampling volume exceeded the breakthrough volume and not plotted in **Figure 5**.

**Table 2.** Retention efficiencies determined with respect to NOAA-ARL mixing ratios for molecular sieve and silica gel adsorbents.

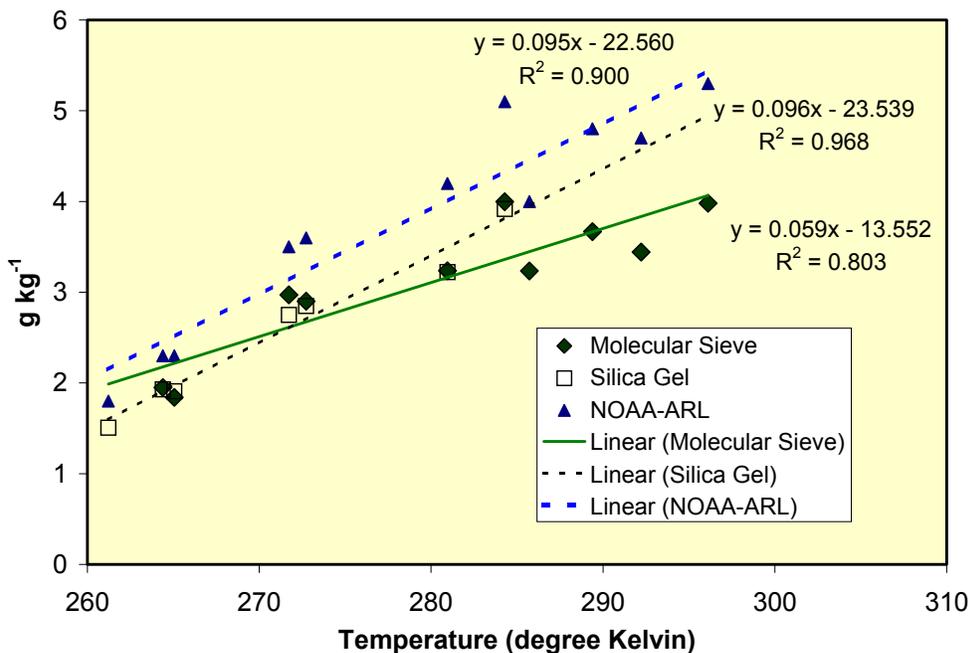
Start Date	Stop Date	Molecular Sieve	Silica Gel
7 February 2000	5 April 2000	13.8% <sup>a</sup>	13.2% <sup>a</sup>
5 April 2000	4 May 2000	61.7% <sup>b</sup>	58.8% <sup>b</sup>
4 May 2000	25 May 2000	78.4%	76.8%
25 May 2000	16 June 2000	76.4%	65.0% <sup>b</sup>
16 June 2000	10 July 2000	73.2%	52.4% <sup>b</sup>
10 July 2000	3 August 2000	75.1%	39.6% <sup>b</sup>
3 August 2000	5 September 2000	61.2% <sup>b</sup>	47.7% <sup>b</sup>
5 September 2000	28 September 2000	80.9%	69.2% <sup>b</sup>
28 September 2000	23 October 2000	77.1%	76.7%
23 October 2000	16 November 2000	84.9%	78.5%
16 November 2000	29 December 2000	80.1%	83.1%
29 December 2000	1 February 2001	131.2% <sup>a</sup>	83.8% <sup>a</sup>
1 February 2001	1 March 2001	84.8%	84.0%
1 March 2001	22 March 2001	80.6%	79.1%
Average:		75.7%	64.9%

<sup>a</sup> Values considered "outliers" and were not plotted in **Figure 4**.

<sup>b</sup> Sampling volume exceeded the breakthrough volume and not plotted in **Figure 4**.



**Figure 5.** Collection/Retention efficiency with respect to NOAA-ARL absolute humidity measurements is shown as a function of average temperature during sampling period. Collection/Retention efficiency was not calculated for atmospheric moisture samples collected using molecular sieve or silica gel when sample breakthrough was suspected.



**Figure 6.** Average absolute humidity measurements ( $\text{g H}_2\text{O}$  per  $\text{kg}$  of air) made by NOAA-ARL during the sampling period and the corresponding absolute humidity measurements determined using molecular sieve and silica gel desiccants are shown as a function of average temperature during sampling period. Absolute humidity values determined using molecular sieve and silica gel are not shown for samples suspected of breakthrough.

## Tritium Concentrations in Atmospheric Moisture

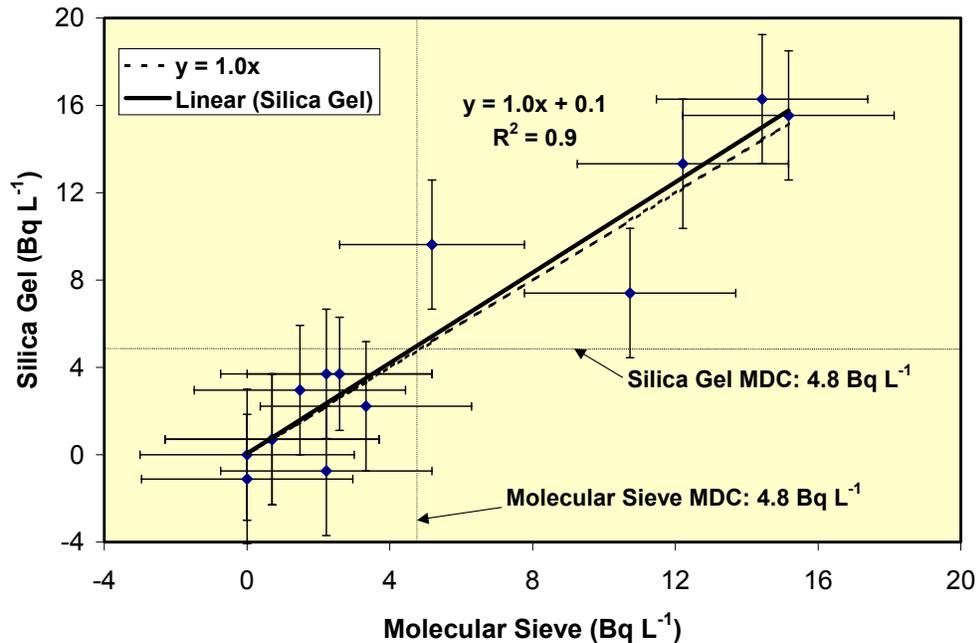
Desiccant materials used for this study were heated until approximately 50-mL of distillate was recovered. The subsequent distillate was analyzed via LSC techniques (ISU EML 1995). LSC analysis results were compared to a tritium standard that was traceable to the National Institute of Standards and Testing (NIST) and tritium concentrations in the distillate were determined. Tritium concentrations measured in the distillate are found in **Table 3**. The *a priori* laboratory Minimum Detectable Concentration (MDC) varied between  $4.1$  and  $4.8 \text{ Bq L}^{-1}$  ( $0.11$  to  $0.13 \text{ nCi L}^{-1}$ ) during the course of this study.

Water vapor collected with molecular sieve and silica gel showed similar tritium concentrations. All of the atmospheric moisture samples collected over the same time periods at this location had tritium concentrations that agreed within 3-sigma counting uncertainty. This agreement is shown in **Figure 7**. Linear regression analysis indicated a slope of 1.0 with a good correlation coefficient ( $R^2 = 0.9$ ). The majority of samples collected had tritium concentrations less than the MDC ( $4.8 \text{ Bq L}^{-1}$  or  $0.13 \text{ nCi L}^{-1}$ ). Several samples collected during summer months had elevated tritium concentrations likely due to the local irrigation using ground water with elevated tritium.

**Table 3.** Tritium concentrations (in Bq L<sup>-1</sup>) in atmospheric moisture samples collected by INEEL OP and submitted to ISU EML for liquid scintillation counting.

Start Date	Stop Date	Molecular Sieve	Silica Gel	MDA
7 February 2000	5 April 2000	2.6 ± 2.6 <sup>a</sup>	3.7 ± 2.6	4.4
5 April 2000	4 May 2000	3.3 ± 3.0	2.2 ± 3.0	4.8
4 May 2000	25 May 2000	2.2 ± 3.0	3.7 ± 3.0	4.8
25 May 2000	16 June 2000	5.2 ± 2.6	9.6 ± 3.0	4.1
16 June 2000	10 July 2000	10.7 ± 3.0	7.4 ± 3.0	4.8
10 July 2000	3 August 2000	14.4 ± 3.0	16.3 ± 3.0	4.4
3 August 2000	5 September 2000	15.2 ± 3.0	15.5 ± 3.0	4.4
5 September 2000	28 September 2000	12.2 ± 3.0	13.3 ± 3.0	4.4
28 September 2000	23 October 2000	1.5 ± 3.0	3.0 ± 3.0	4.8
23 October 2000	16 November 2000	0.0 ± 3.0	-1.1 ± 3.0	4.8
16 November 2000	29 December 2000	2.2 ± 3.0	-0.7 ± 3.0	4.8
29 December 2000	1 February 2001	0.7 ± 3.0	0.7 ± 3.0	4.8
1 February 2001	1 March 2001	0.7 ± 3.0	0.7 ± 3.0	4.8
1 March 2001	22 March 2001	0.0 ± 3.0	0.0 ± 3.0	4.8

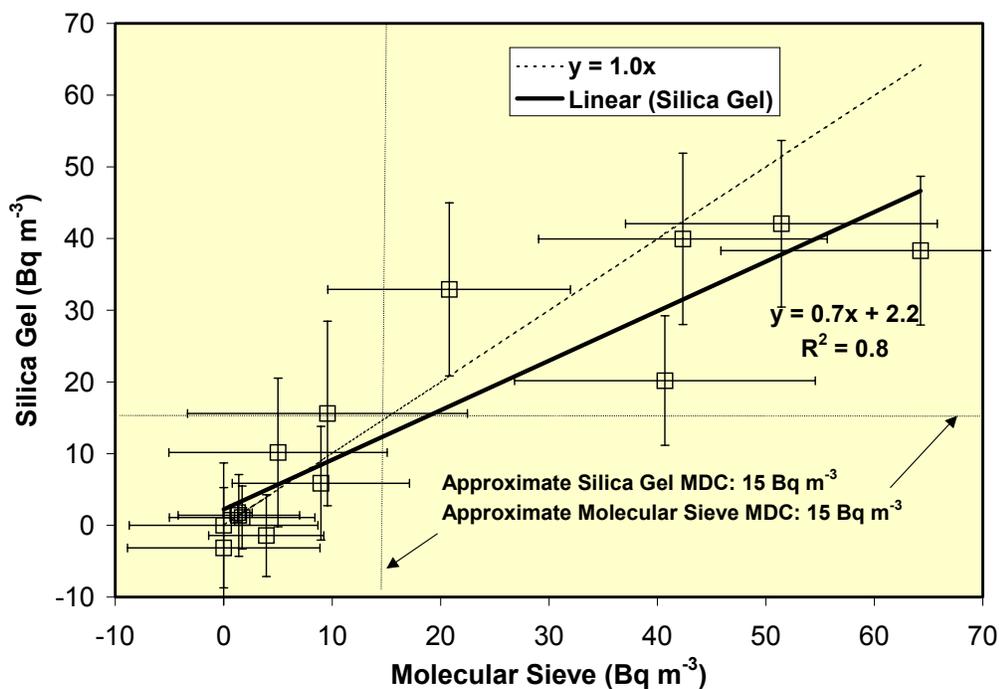
<sup>a</sup> 2-sigma counting uncertainty



**Figure 7.** Direct comparison between tritium concentrations measured in distillate collected using silica gel with respect to the tritium concentrations measured in distillate collected using molecular sieve. Dashed line represents an ideal comparison between the desiccants, the solid line represents the actual trend line comparing the two measurements, and the error bars represent 2-sigma counting uncertainty in the tritium measurement. The Minimum Detectable Concentration (MDC) was 4.8 Bq L<sup>-1</sup> (0.13 nCi L<sup>-1</sup>) for either adsorbent.

## Atmospheric Tritium Concentrations

Airborne tritium concentrations were determined using the tritium concentration in distillate, volume of air sampled, and quantity of moisture collected. Atmospheric tritium concentrations were determined assuming no efficiency correction (i.e., all of the moisture that passed through the desiccant column was adsorbed to the desiccant) and that airborne tritium is found entirely in the form of tritiated water vapor ( $\text{HTO}_{(g)}$ ). Measurement uncertainty including volume measurement and quantity of moisture collected were propagated into the overall atmospheric tritium concentration measurement uncertainty. All of the atmospheric tritium concentrations calculated over the same time periods agreed within 3-standard deviations for both the molecular sieve and silica gel desiccant materials. This relationship is evident in **Figure 8**. Calculated atmospheric tritium concentrations ranged between  $-3.1$  to  $64.2 \text{ Bq m}^{-3}$  ( $-0.08$  to  $1.74 \text{ pCi m}^{-3}$ ) with MDC values ranging from  $2.1$  to  $20.7 \text{ Bq m}^{-3}$  ( $0.06$  to  $0.56 \text{ pCi m}^{-3}$ ). Linear regression analysis indicated relatively good agreement between molecular sieve and silica gel with a slope of  $0.7$  and that correlated relatively well ( $R^2 = 0.8$ ).



**Figure 8.** Comparison of concentrations of airborne tritium measured using silica gel with respect to airborne tritium measurements made using molecular sieve. The typical Minimum Detectable Concentration (MDC) for either adsorbent was  $15 \text{ Bq m}^{-3}$ . No moisture collection efficiency correction was applied to either measurement. The dashed line represents ideal comparison and the solid line represents the best-fit trend line.

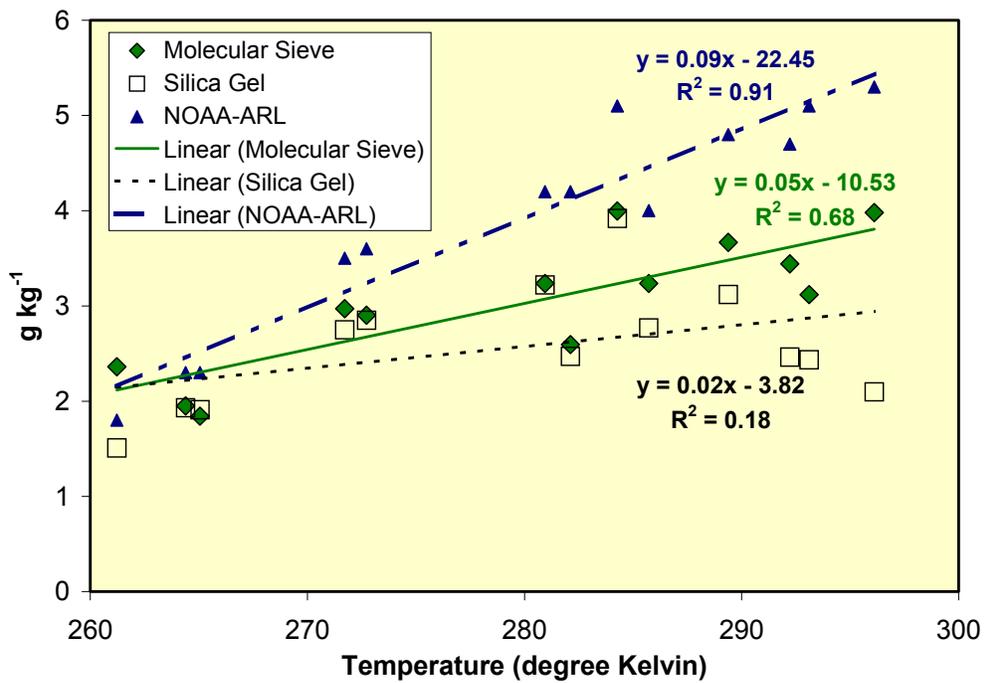
## Conclusion

As observed in previous studies, the atmospheric moisture collection efficiency for silica gel and molecular sieve decreases as the ambient temperatures increase. When the ambient temperatures increase, the likelihood that there is some loss of moisture or sample breakthrough increases. As shown with other studies (Straight 1978, Eberhart 1999, Patton et al. 1997, Singh et al. 1984), a fraction of the moisture adsorbed to the desiccant materials was driven off by relatively warm and dry air. This is evident in an apparent decrease in atmospheric moisture collection efficiencies observed using both the molecular sieve and the silica gel at higher temperatures. Breakthrough was more evident with the silica gel at temperatures greater than 285 K as shown by the smaller mixing ratios observed using the silica gel data at elevated ambient temperatures. This was also observed with visual inspection of the desiccant beds during the sampling period. Visual inspection of the moisture-indicating desiccant during the sampling period, the molecular sieve showed a distinct edge to which moisture saturation had occurred. On the other hand, during hot, dry periods the silica gel showed a diffuse edge to which saturation had occurred.

Average atmospheric tritium concentrations were derived from the quantity of moisture collected, assuming that all of the tritium collected remains adsorbed on the desiccant. From the data given in **Table 2** and in **Figure 9**, either the volumetric flow rates need to be reduced (i.e., reduce sample volume) over the same sampling period duration or use a longer adsorbent column at elevated ambient temperatures for the silica gel when ambient temperatures exceed 285 K. Additionally, a secondary desiccant column filled with a moisture indicating adsorbent should be placed directly in line behind either the molecular sieve or silica gel columns to indicate the occurrence of sample breakthrough.

There were no significant differences in tritium concentrations measured in distillate collected from either molecular sieve or silica gel. Tritium concentrations in moisture collected using molecular sieve and silica gel were within  $\pm 3$ -standard deviations (counting uncertainty). These measurements were based upon LSC analysis from an aliquot of the 50-mL distillate sample submitted to ISU EML.

No effort was made to change sampling protocols routinely used by INEEL OP for monitoring atmospheric tritium concentrations. The only difference involved was the use of different desiccant materials. Tritium concentrations observed using either desiccant showed little difference at environmental concentrations. Atmospheric concentrations were underestimated when the sampling volume exceeded the breakthrough volume. This was more noticeable with the silica gel at elevated ambient temperatures.



**Figure 9.** All of the average absolute humidity measurements (g H<sub>2</sub>O per kg of air) made by NOAA-ARL during the sampling period and the corresponding absolute humidity measurements determined using molecular sieve and silica gel desiccants are shown as a function of average temperature during sampling period. This plot differs from Figure 6 by showing all of the absolute humidity values determined using molecular sieve and silica gel, including samples suspected of breakthrough.

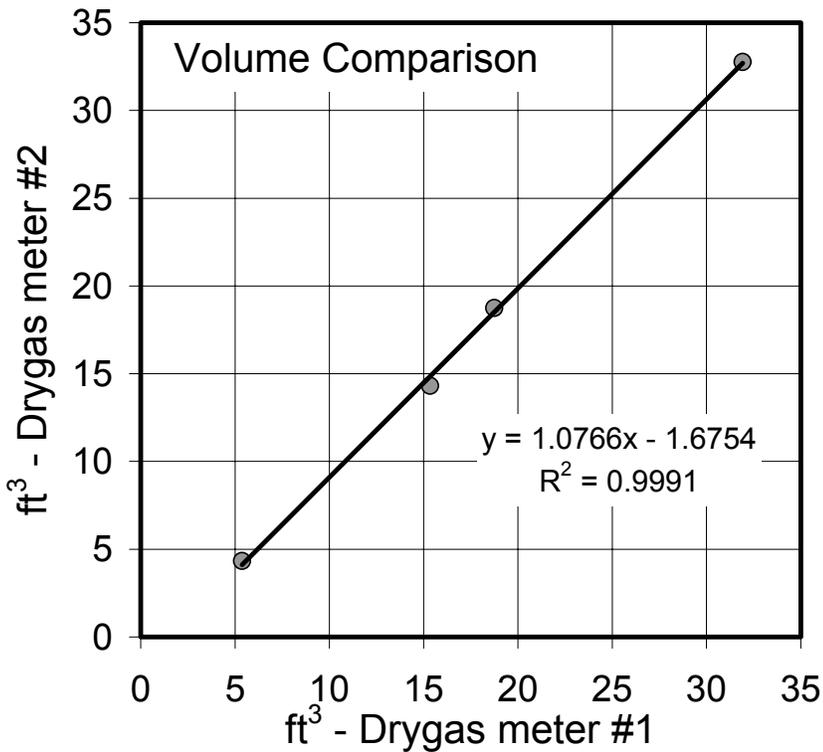
## References

- Straight RJ. *HT-HTO Sampling at the Nevada Test Site*. In: Behaviour of Tritium in the Environment. Proceedings of the International Symposium on the behaviour of tritium in the environment held in San Francisco, 16 – 20 October 1978: International Atomic Energy Agency, Vienna, 1979.
- Clawson KL, Start GE, Ricks NR. *Climatology of the Idaho National Engineering Laboratory*, 2<sup>nd</sup> Edition. Idaho Falls, ID: U.S. Department of Commerce National Oceanic and Atmospheric Administration Environmental Research Laboratories Air Resource Laboratory; DOE/ID-12118), 1989.
- Eberhart CF. *Using Absolute Humidity and Radiochemical Analyses of Water Vapor Samples to Correct Underestimated Atmospheric Tritium Concentrations*. Los Alamos: LA-UR-99-1107; submitted to the 92<sup>nd</sup> Annual Meeting of the Air & Waste Management Association in St. Louis, MO, 1999.
- Patton GW, Cooper AT, Tinker MR, “Ambient Air Sampling for Tritium ---Determination of breakthrough volumes and collection efficiencies for silica gel adsorbent.” *Health Physics* 72: 397 – 407, 1997.
- Rosson R, Jakiel R, Klima S, Kahn B, Fledderman P. “Correcting tritium concentrations in water vapor monitored with silica gel.” *Health Physics* 78: 68 – 73: 2000.
- Singh VP, Ruthven DM. *Adsorption of Moisture on Molecular Sieve Adsorbents at Low Humidity*. Toronto: Ontario Hydro; F84026; 1984.
- National Oceanic and Atmospheric Administration Air Resources Laboratory (NOAA ARL) Field Research Division. Tabular Display of Weather --- Mesonet Data. Available at <http://www.noaa.inel.gov/metdata/>. Accessed 26 March 2001.
- Idaho State University Environmental Monitoring Laboratory (ISU EML). *Operation and calibration of the Beckman LS7500 and Wallac 1415 liquid scintillation counters*. Pocatello, ID: Procedure Number EML-95-07 Revision 2; 1995.

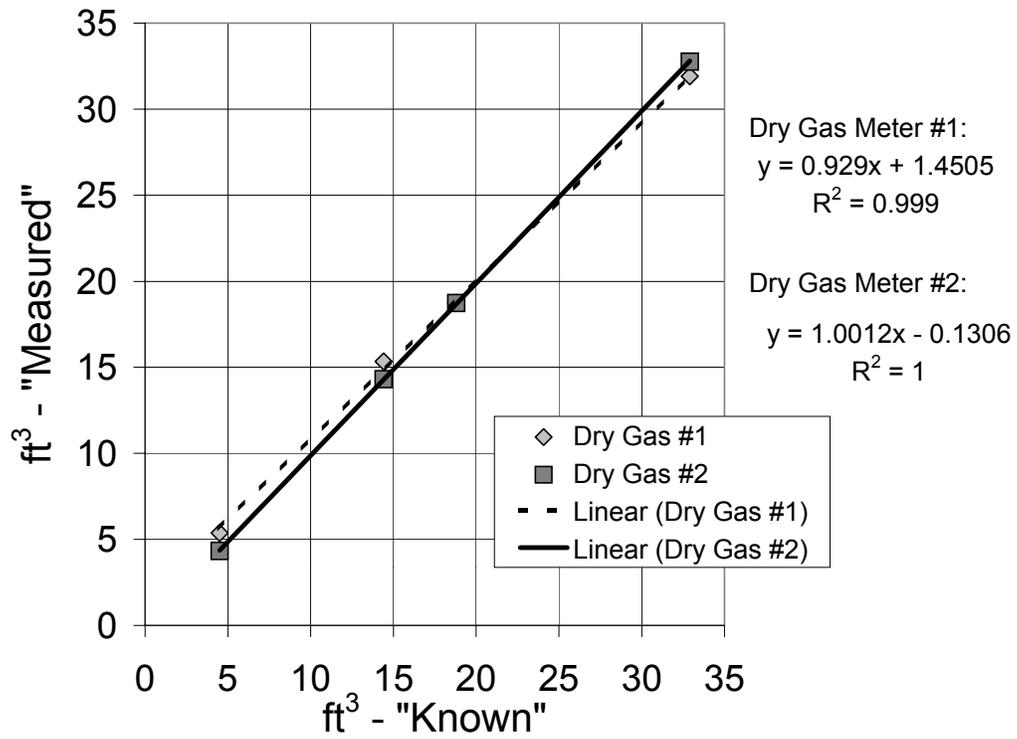
# Appendix A – Volume Measurement Calibration

**Table A -1.** Dry Gas Meter Calibration Data

Dry Gas #1 Serial #: 5825028						
Dry Gas #2 Serial #: 5825029						
Hour	Dry Gas#1 Reading	Dry Gas#2 Reading	Flow Rate (SCFH)	Net Volume Dry Gas#1 (ft <sup>3</sup> )	Net Volume Dry Gas#2 (ft <sup>3</sup> )	Derived Net Volume from flow rate (ft <sup>3</sup> )
0.0	15.56	-0.5	1.0	-	-	-
4.5	20.94	3.83	1.0	5.38	4.33	4.5
23.3	39.69	22.58	1.0	18.75	18.75	18.8
56.2	71.61	55.35	1.0	31.92	32.77	32.9
70.6	86.95	69.66	1.0	15.34	14.31	14.4



**Figure A-10.** Comparison of calibrated volume measurements using both dry gas meters used during this study.



**Figure A-11.** Calibration Results comparing volumes of air sampled using the calibrated dry gas meters to a "known" volume derived from a calibrated flow meter. The "known" volume was derived from the sampling time multiplied by the volumetric flow rate.

## Appendix B – Field Data

**Table B-1.** Field Data used during this study.

Sample ID	Start Date	Stop Date	Material	Empty Column Mass	Column Mass (start)	Column Mass (stop)	Hour Start	Hour Stop	Flow Rate (scfh)	Dry Gas Meter Start	Dry Gas Meter Stop	Volume of Air Sampled (m <sup>3</sup> )
OP001TTR01	2/7/00 11:57	4/5/00 14:50	Sieve	872.0	1372.1	1395.1	70.6	1464.2	1.0	87.0	30.3	44.1
OP001TTR02	2/7/00 11:57	4/5/00 14:50	Gel	861.7	1361.8	1383.9	70.6	1464.2	1.0	70.7	30.6	44.1
OP002TTR01	4/5/00 14:50	5/4/00 14:28	Sieve	908.6	1409.2	1510.8	1464.2	2159.8	4.0	30.3	1178.7	36.2
OP002TTR02	4/5/00 14:50	5/4/00 14:28	Gel	907.7	1408.3	1509.3	1464.2	2159.8	4.0	30.6	1192.8	37.8
OP002TTR03	5/4/00 14:31	5/25/00 13:44	Sieve	872.3	1372.5	1463.5	2159.8	2663.1	4.0	1178.7	1821.1	21.1
OP002TTR04	5/4/00 14:31	5/25/00 13:44	Gel	860.7	1360.6	1450.3	2159.8	2663.1	4.0	1192.8	1840.3	21.2
OP002TTR05	5/25/00 13:44	6/16/00 12:28	Sieve	908.4	1409.3	1497.3	2663.1	3189.7	4.0	1821.1	2488.6	22.2
OP002TTR06	5/25/00 13:44	6/16/00 12:28	Gel	908.2	1408.0	1481.7	2663.1	3189.7	4.0	1840.3	2496.5	21.8
OP002TTR07	6/16/00 12:30	7/10/00 14:40	Sieve	860.6	1360.7	1447.4	3189.7	3767.8	4.0	2488.6	3184.7	23.3
OP002TTR08	6/16/00 12:30	7/10/00 14:40	Gel	872.3	1372.3	1436.5	3189.7	3767.8	4.0	2496.5	3213.2	24.1
OP003TTR01	7/10/00 14:41	8/3/00 13:11	Sieve	908.2	1409.1	1506.4	3767.8	4341.3	4.0	3184.7	3849.9	22.5
OP003TTR02	7/10/00 14:41	8/3/00 13:11	Gel	908.2	1408.9	1461.1	3767.8	4341.3	4.0	3213.2	3888.5	22.9
OP003TTR03	8/3/00 13:14	9/5/00 12:17	Sieve	863.0	1363.8	1467.9	4341.3	5108.6	4.0	3849.9	4784.6	30.8
OP003TTR04	8/3/00 13:14	9/5/00 12:17	Gel	870.8	1370.8	1454.3	4341.3	5108.6	4.0	3888.5	4827.6	31.6
OP003TTR05	9/5/00 12:22	9/28/00 9:28	Sieve	908.6	1437.3	1525.2	5108.6	5658.3	4.0	4784.7	5556.4	25.0
OP003TTR06	9/5/00 12:22	9/28/00 9:28	Gel	908.2	1408.8	1485.1	5108.6	5658.3	4.0	4827.6	5602.1	25.4
OP004TTR01	9/28/00 9:28	10/23/00 13:47	Sieve	862.0	1363.3	1464.1	5654.3	6260.8	4.0	5556.4	6463.0	28.7
OP004TTR02	9/28/00 9:28	10/23/00 13:47	Gel	872.9	1372.8	1476.9	5654.3	6260.8	4.0	5602.1	6525.6	29.8
OP004TTR03	10/23/00 13:47	11/16/00 14:20	Sieve	909.0	1409.9	1504.5	6260.8	6839.3	4.0	6463.0	7422.8	29.5
OP004TTR04	10/23/00 13:47	11/16/00 14:20	Gel	908.9	1409.5	1497.2	6260.8	6839.3	4.0	6525.7	7468.2	29.5
OP004TTR05	11/16/00 14:20	12/29/00 10:38	Sieve	861.7	1363.8	1478.6	6839.3	7867.6	4.0	7422.8	9396.7	57.3
OP004TTR06	11/16/00 14:20	12/29/00 10:38	Gel	872.8	1373.5	1492.6	6839.3	7867.6	4.0	7468.2	9352.5	57.3
OP011TTR01	12/29/00 10:40	2/1/01 13:14	Sieve	908.7	1372.9	1494.6	7867.6	8686.1	4.0	9396.7	11044.0	47.4
OP011TTR02	12/29/00 10:40	2/1/01 13:14	Gel	909.4	1412.2	1491.3	7867.6	8686.1	4.0	9352.5	10961.3	48.2
OP011TTR03	2/1/01 13:18	3/1/01 11:17	Sieve	682	1362.7	1449.5	8686.1	9355.8	4.0	1044.1	2443.2	41.2
OP011TTR04	2/1/01 13:18	3/1/01 11:17	Gel	872.9	1374.4	1461	8686.1	9355.8	4.0	961.3	2321.2	41.5
OP011TTR05	3/1/01 11:20	3/22/01 14:10	Sieve	909.5	1410.1	1505.4	9355.8	9862.7	4.0	2443.2	3430.8	30.4
OP011TTR06	3/1/01 11:20	3/22/01 14:10	Gel	908.9	1409.4	1502.5	9355.8	9862.7	4.0	2321.2	3283.0	30.2

**Table B-2. Weather Data**

<b>Start Date</b>	<b>Stop Date</b>	<b>Mean Wind Speed (mph)</b>	<b>Total Precipitation (inches)</b>	<b>Mean Temperature (°F)</b>	<b>Mean Temperature (°C)</b>	<b>Mean Barometric Pressure (in-Hg)</b>	<b>Mean Relative Percent Humidity</b>	<b>Mixing Ratio (g H<sub>2</sub>O/kg Air)</b>
2/7/00 11:57	4/5/00 14:50	9.4	1.43	33.2	0.7	25.008	74.8%	3.5
4/5/00 14:50	5/4/00 14:28	10.6	0.53	48.4	9.1	25.019	52.6%	4.2
5/4/00 14:31	5/25/00 13:44	11.9	1.10	52.3	11.3	24.971	55.0%	5.1
5/25/00 13:44	6/16/00 12:28	13.6	0.12	61.5	16.4	24.998	39.1%	4.8
6/16/00 12:30	7/10/00 14:40	12	0.23	66.6	19.2	25.021	31.1%	4.7
7/10/00 14:41	8/3/00 13:11	9.7	0.27	73.6	23.1	25.113	30.0%	5.3
8/3/00 13:14	9/5/00 12:17	11	0.32	68.2	20.1	25.068	33.5%	5.1
9/5/00 12:22	9/28/00 9:28	10.4	0.02	54.9	12.7	25.085	39.2%	4.0
9/28/00 9:28	10/23/00 13:47	9.8	0.49	46.3	7.9	25.076	55.2%	4.2
10/23/00 13:47	11/16/00 14:20	7.4	0.61	29.7	-1.3	24.993	80.3%	3.5
11/16/00 14:20	12/29/00 10:38	6.7	0.23	17.7	-7.9	25.171	88.5%	2.3
12/29/00 10:40	2/1/01 13:14	5.2	0.36	10.8	-11.8	25.162	86.9%	1.8
2/1/01 13:18	3/1/01 11:17	6.4	0.65	16.5	-8.6	25.006	88.3%	2.3
3/1/01 11:20	3/22/01 14:10	8.8	0.18	31.5	-0.3	25.022	79.5%	3.6