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**Evaluation of an Ambient Air  
Sampling System for Tritium  
(as Tritiated Water Vapor) Using  
Silica Gel Adsorbent Columns**

**G. W. Patton  
A. T. Cooper  
M. R. Tinker**

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**August 1995**

**Prepared for the U.S. Department of Energy  
under Contract DE-AC06-76RLO 1830**

**Pacific Northwest Laboratory  
Operated for the U.S. Department of Energy  
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## Summary

Ambient air samples for tritium analysis (as the tritiated water vapor [HTO] content of atmospheric moisture) are collected for the Hanford Site Surface Environmental Surveillance Project (SESP) using the solid adsorbent silica gel. The silica gel has a moisture sensitive indicator which allows for visual observation of moisture movement through a column. Despite using an established method, some silica gel columns showed a complete change in the color indicator for summertime samples suggesting that breakthrough had occurred; thus a series of tests was conducted on the sampling system in an environmental chamber.

The purpose of this study was to determine the maximum practical sampling volume and overall collection efficiency for water vapor collected on silica gel columns. Another purpose was to demonstrate the use of an impinger-based system to load water vapor onto silica gel columns to provide realistic analytical spikes and blanks for the Hanford Site SESP. Breakthrough volumes ( $V_b$ ) were measured and the chromatographic efficiency (expressed as the number of theoretical plates [N]) was calculated for a range of environmental conditions. Tests involved visual observations of the change in the silica gel's color indicator as a moist air stream was drawn through the column, measurement of the amount of a tritium tracer retained and then recovered from the silica gel, and gravimetric analysis for silica gel columns exposed in the environmental chamber.

For all tests, flows were 1 to 1.5 L/min with the relative humidity at approximately 30%. Visual observations and gravimetric tests were conducted from 20°C to 50°C. Tracer tritium recovery tests were conducted at 20°C and 40°C. The basic test apparatus was an air pump connected to a primary silica gel column (18-cm x 5.9-cm diameter) with flow rates measured and controlled with a rotameter. For the tracer tritium tests, an impinger was installed upstream of the primary column and a backup silica gel column was added to prevent loss of tritium to the test chamber environment. Samples were prepared for analysis by vacuum-distillation and counted by liquid scintillation. The visual observations yielded relative breakthrough volumes (air volume/adsorbent depth [ $\text{m}^3/\text{cm}$ ]) of 0.36 for 20°C, 0.20 for 30°C, 0.15 for 40°C, and 0.077 for 50°C. Average tritium tracer recoveries at 20°C were 71% with no observed breakthrough. Mean tritium tracer recoveries at 40°C dropped from 75% for volumes  $\leq 3.0 \text{ m}^3$ , to 0% for a volume of  $5.0 \text{ m}^3$ .

Moisture loading and frontal chromatographic profiles were measured for water vapor migrating through the silica gel columns. Moisture indicating silica gel was packed into a 5-segment column, using metal screens to divide the segments. Moist air was drawn through the column until the third segment showed a partial color change of the indicator. The columns were disassembled and each segment was weighed and the moisture content was calculated. Moisture loadings (g  $\text{H}_2\text{O}/\text{g}$  silica gel) ranged from 0.063 to 0.16 for the first and second segments, 0.027 to 0.047 for the third segments (transition zone), and 0 to 0.011 for the fourth and fifth segments. Frontal chromatographic profiles were produced by expressing the moisture loading of each segment as a percentage of the first segment. The chromatographic efficiency of the silica gel columns was determined by graphical evaluation of the chromatographic profiles. The number of theoretical plates per adsorbent depth ranging from 1.7 N/cm at 20°C to 0.60 N/cm at 50°C. The number of theoretical plates decreased with increasing temperature, indicating a greater chromatographic efficiency at lower temperatures.

Established chromatographic theory (Senum 1981<sup>(a)</sup>; You and Bidleman 1984<sup>(b)</sup>) was used to estimate the overall collection efficiency of the silica gel columns as a function of the ratio of the sampling volume to breakthrough volume and the chromatographic efficiency. Using the SESP sampling volume of 9.5 m<sup>3</sup> and a 54-cm column, the overall collection efficiency was 99.9% at 20°C, 95% at 30°C, and <80% at 40°C. The mean summer temperature at the Hanford Site is 25°C, thus the system is adequate for most ambient air sampling. However, maximum temperatures can approach 40°C, with temperatures inside the sampling hatches near 50°C for short time periods. Thus, it was necessary to reduce the air volumes collected for summertime samples to allow for a higher probability that a quantitative sample could be obtained.

- 
- (a) Senum, G. L. 1981. "Theoretical Collection Efficiencies of Adsorbent Samplers." *Environ. Sci. Technol.* 15:1073-1075.
- (b) You, F., and T. F. Bidleman. 1984. "Influence of Volatility on the Collection of Polycyclic Aromatic Hydrocarbon Vapors with Polyurethane Foam." *Environ. Sci. Technol.* 18:330-333.

## Acknowledgments

The authors thank the following people who contributed to the production of this report: K. L. Price for technical review, ETB Communications Support Team for text processing, L. G. Wattenburger and K. A. Corcoran for graphics (Boeing Computer Services, Richland), M. K. DeSmet for editing and report production, R. A. Gregg for assistance with the environmental test chamber, T. L. Van Arsdale for preparation of the initial silica gel columns, E. A. Lepel for preparation of the tritium standard, and B. M. Gillespie for coordinating activities between PNL and IT Corporation, Richland, Washington. The assistance of IT Corporation in preparing silica gel columns is appreciated.





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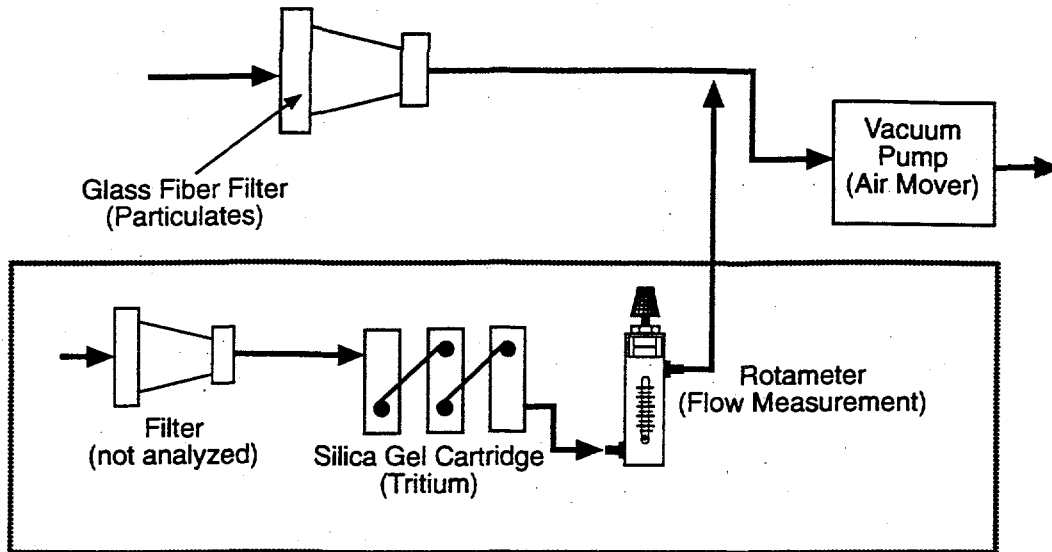
# 1.0 Introduction

Tritium is a contaminant of concern for environmental monitoring at nuclear facilities because it is an important byproduct of nuclear reactors. Tritium is a key ingredient for fusion-based nuclear weapons, is used in commercial applications (e.g., luminescent devices), and is an important tracer for chemical and biological studies. Small amounts of tritium are also naturally produced by interactions of cosmic-rays with the atmosphere (Eisenbud 1987). Tritium has a 12.3 yr half-life and is a low energy beta emitter (0.018 MeV). The two primary forms of tritium that are reported for Hanford Site airborne effluents are tritium gas ( $^3\text{H}^1\text{H}$  or  $^3\text{H}_2$  [HT]) and tritiated water vapor ( $^3\text{H}^3\text{H}^{16}\text{O}$  [HTO]), with HTO having a higher potential for human radiological dose compared to HT (Till and Meyer 1983; Dirkes et al. 1994). Upon release, HTO equilibrates with ambient water vapor and moves through the environment as a mixture.

Ambient air concentrations of HTO are too low for practical measurement using real-time devices, therefore adsorbents must be used to collect atmospheric moisture which is analyzed for HTO content (Budnitz 1974). Both solid and liquid adsorbents can be used to collect water vapor from ambient air. Compared to liquid adsorbent sampling systems (bubblers or impingers), solid adsorbent air sampling systems are generally more rugged (e.g., no glass to break or evaporation problems), allow for higher air sampling rates, and generally allow for lower limits of detection. However, solid adsorbents function as frontal gas chromatographic systems and the breakthrough volume ( $V_b$ ) and chromatographic efficiency of the adsorbent, number of theoretical plates (N), must be determined to evaluate the overall collection efficiency of the system (Bidleman 1985). Air samples collected beyond the breakthrough volume or with low efficiency beds may not retain a quantitative amount of the analyte.

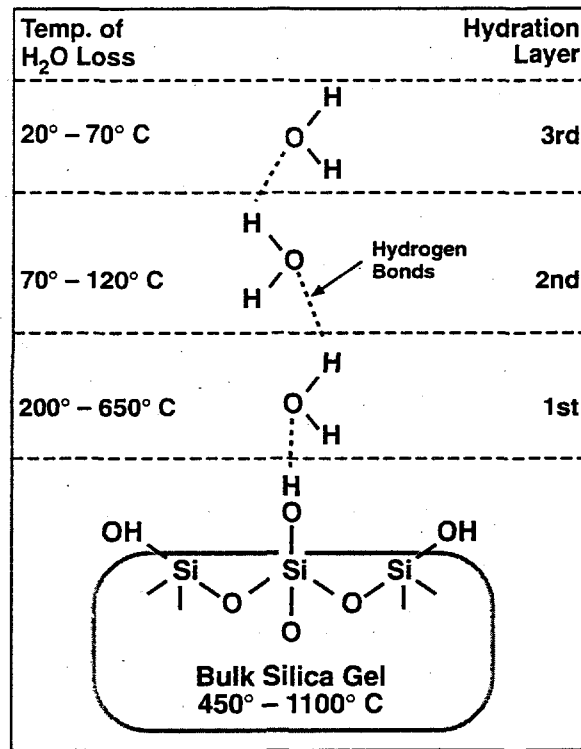
The Hanford Site Surface Environmental Surveillance Project (SESP) collects ambient air samples for tritium analysis (as HTO) using solid adsorbent silica gel (Dirkes et al. 1994). Air samples are collected using silica gel packed into three clear-plastic gas-drying columns (5.9-cm diameter x 18-cm length each) connected in a series (Figure 1.1). Air is passed through the columns at roughly 0.24 L/min for 4 weeks with a typical sample volume of 9.5 m<sup>3</sup>. The silica gel has a moisture-sensitive indicator ( $\text{CoCl}_2$ ) on its surface (Lodge 1989a) which allows for visual observation of the extent of moisture penetration (breakthrough) into the columns. Ambient air concentrations measured at the Hanford Site are typically less than 2 pCi/m<sup>3</sup> for downwind perimeter samples, with the U.S. Department of Energy (DOE) derived concentration guide set at 100,000 pCi/m<sup>3</sup> (Patton and Cooper 1993; Dirkes et al. 1994). The derived concentration guide is the concentration of a specific radionuclide in air that could be continuously inhaled at average annual rates and not exceed an effective dose equivalent of 100 mrem/yr.

The adsorption of water vapor onto silica gel was investigated by Scott and Trainman (1980) and a conceptual model based upon their study is shown in Figure 1.2. Water adsorbs to bulk silica gel in a number of distinct layers (hydration layers). The initial hydration layer is attached by hydrogen bonding to siloxol (Si-OH) groups on the surface of the bulk silica gel. This hydration layer is tightly held but can be removed by heating above 200°C with moisture loss complete at 650°C. A second hydration layer can form and attach to the first layer by hydrogen bonding and can be removed by heating 70°C to 120°C. A third hydration layer can attach through hydrogen bonding and can be removed by heating 20°C to 70°C.



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Figure 1.1. Hanford Site Ambient Air Sampling System for Tritium



S9507010.5

Figure 1.2. Conceptual Model of Water Sorption onto Silica Gel

Silica gel used for air sampling for the Hanford SESP is baked at 220°C prior to use, thus sampling columns are installed with the first hydration layer essentially intact. As sampling begins, water vapor loads into the second hydration layer and this material should not migrate through the column under field conditions. As sampling continues, water vapor begins to load into the third hydration layer and this material may be subject to migration through the column at ambient temperatures. The frontal chromatographic movement of water through the silica gel column should be directly proportional to the vapor pressure of water at ambient temperature. As the second hydration layer fills, the sampling system becomes analogous to a gas chromatography column where the second water layer serves as the liquid phase, the ambient air stream is the mobile phase, and the water vapor analyte partitions between the mobile and the liquid phase.

Despite using an established sample collection method for silica gel columns (Lodge 1989b), breakthrough was suspected for some samples collected during the summertime because the moisture indicator had changed color for the entire column length. Based on these observations, a series of tests was conducted under controlled conditions using the silica gel columns in an environmental test chamber with temperature and relative humidity similar to Hanford Site ambient conditions. The tests involved visual observation of vapor penetration (breakthrough volumes), tritium tracer recovery studies using a tritiated moisture source, and gravimetric analysis of silica gel columns exposed in the environmental chamber. The purpose of this study was to determine the maximum practical sampling volume and overall collection efficiency for water vapor collected on a silica gel column. Another purpose was to demonstrate the use of an impinger-based system to load water vapor onto silica gel columns to provide realistic analytical spikes and blanks for the Hanford Site SESP.

## 2.0 Experimental

Silica gel columns for the initial observation tests were prepared using 6/16 mesh (J. T. Baker, Phillipsburg, New Jersey) indicating silica gel. The silica gel was baked overnight at 220°C to remove any residual moisture prior to loading into the sample columns. Sample columns for all studies were commercially available gas drying jars made from 4-mm thick acrylic plastic (W. A. Hammond Drierite Company, Xenia, Ohio). For some initial visual observation tests (30°C and 40°C), 5% (by weight) of moisture-indicating Drierite (CaSO<sub>4</sub>) was uniformly mixed with the silica gel columns to allow for easier observation of the change in the moisture indicator (blue to pink for Drierite versus blue to light blue for silica gel).

Silica gel columns used for the tritium tracer recovery tests and the analytical blank tests were prepared by IT Corporation, Richland, Washington, using 6/16 mesh (J. T. Baker, Phillipsburg, New Jersey) silica gel. The silica gel was baked overnight at 220°C prior to loading into sampling columns. The tritium tracer solution was prepared using a tritium standard from the U.S. Environmental Protection Agency (EPA) Environmental Monitoring System Laboratory, Las Vegas, Nevada, and the tritium activity was calculated to be  $95.3 \pm 4.1$  pCi/mL on March 1, 1994. Deep well water with no measurable tritium activity was used to prepare the tritium tracer and was also used for the analytical blank determinations.

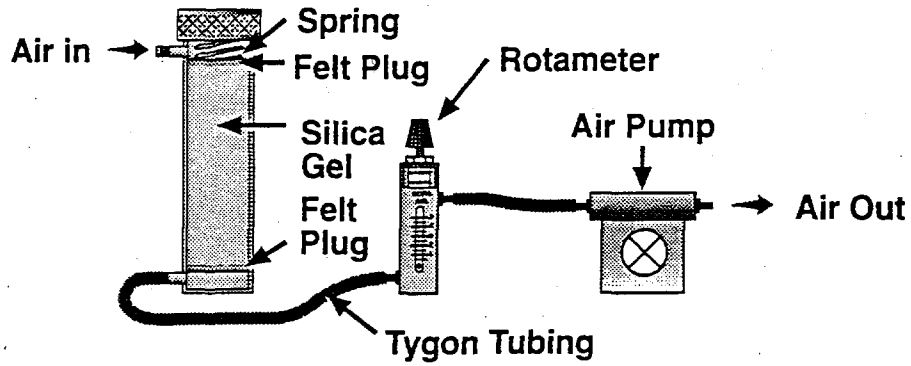
Tests were conducted in a Tenney Engineering Model WI-TR walk-in environmental test chamber equipped with a Versa-Tenn II control system. Thermocouples and a Vaisala hygrometer located in the air stream inlet were used to control chamber conditions. Inside the chamber, a Vaisala Model HMI 32 hygrometer and a Fluke Model 80T-150U temperature probe were used to monitor test conditions. Chamber conditions were continuously recorded on a chart recorder.

The silica gel columns were assembled and tested in three configurations as shown in Figure 2.1. A Thomas Industries, Inc., Model 107CA14 low-volume air pump was used for all tests. Air flows were measured and controlled using 14 to 140 L/h rotameters (Dwyer Instruments, Inc., Michigan City, Indiana).

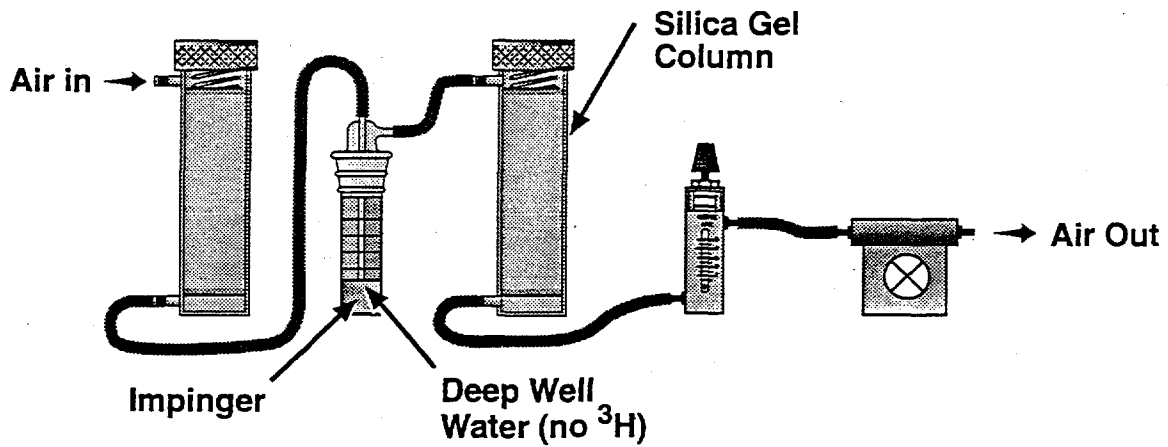
### 2.1 Visual Observations

Visual observation tests were conducted by placing silica gel columns into the test chamber and pulling known volumes of air through the columns (Figure 2.1a). Tests were conducted at 20°C, 30°C, 40°C, and 50°C with the relative humidity at roughly 30%. By measuring the distance the indicating silica gel had changed color as a function of the air volume, it was possible to calculate the breakthrough volume at each temperature. The tests were conducted using single silica gel columns and faster flow rates of 1 to 1.5 L/min (as opposed to the 3-column series and slower flow rate [0.24 L/min] used in the field) to permit a reasonable time period for the experiments, with the test results linearly extrapolated to field sampling conditions. For one set of samples at 40°C, a second silica gel column was added behind the primary column and moisture penetration was monitored through both columns.

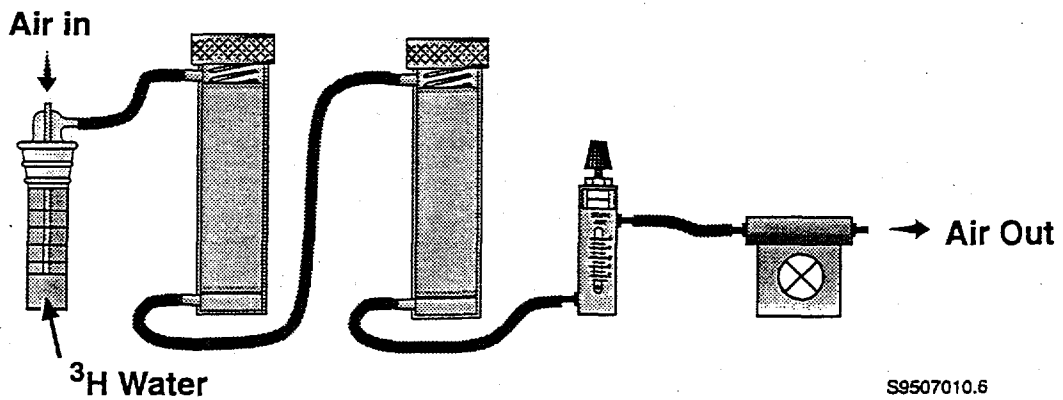
a.) Visual Observations (no spiked tritium)



b.) Analytical Blanks



c.) Tritium Recovery Studies



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Figure 2.1. Silica Gel Column Testing Apparatus



## 2.2 Tritium Recoveries

### 2.2.1 Analytical Blanks

Analytical blanks were prepared by evaporating either 58, 85, or 118 mL of tritium-free deep well water onto three separate silica gel assemblies prepared for field collection by IT Corporation. The deep well water was placed into an impinger with the test apparatus as shown in Figure 2.1b. These tests were conducted at ambient temperatures (approximately 20°C). Moisture (i.e., background tritium) was removed from the air stream using 1 or 2 columns of Drierite upstream of the impinger. Air pumps and flow measurement and control were as in Section 2.0. Total water recovery ranged from 61 to 124 mL with an average recovery of  $98\% \pm 12\%$ . All blank results were below a nominal detection limit of  $<4.9 \pm 15$  pCi/sample and no blank corrections were made to the analytical results for the tritium tracer studies (Section 2.2.3).

### 2.2.2 Calibration of Tritium Tracer Solution

A 2-mL aliquote of the tritium tracer solution was diluted to 100 mL (final concentration of 1.91 pCi/mL) with tritium-free water and was sent to the analytical laboratory to verify the concentration. The laboratory result was  $1.95 \pm 0.12$  pCi/mL (102% recovery) and no corrections were used for the analytical results from the recovery studies.

### 2.2.3 Analytical Recoveries for Tritium Tracer Tests

Silica gel columns were evaluated at 20°C and 40°C at air volumes from 2.6 to 5.1 m<sup>3</sup>. Flow rates ranged from 1.0 to 1.5 L/min. The relative humidity was maintained at roughly 30%. The silica gel columns were assembled and used as shown in Figure 2.1c. Basically, the apparatus is an air pump connected in series to the following: impinger (containing the tritium tracer solution), primary silica gel column, followed by a backup column (Drierite or silica gel) to trap any tritium that may have broken through the primary column. Air flows were measured with rotameters as in Section 2.0.

0.95 to 0.99 mL of a 95 pCi/mL tritiated water standard was measured and added to the impinger at the beginning of each test. The impinger was wrapped with heating tape and maintained at a slightly higher temperature than the test chamber to facilitate evaporation and allow for a narrow band of analyte to be loaded onto the test column. The heating tape was left on throughout the test. For the last set of 40°C samples, the second column was filled with silica gel and both columns were analyzed to allow for a better estimate of the overall mass balance of the test solution. At the end of each test the silica gel columns were capped and delivered to IT Corporation for analysis using vacuum distillation to remove the moisture followed by liquid scintillation counting. Table 2.1 gives the number of columns exposed at each temperature as well as other test parameters. A background silica gel column (no tritium was spiked onto the column) was placed inside the test chamber during most test runs and a representative air volume was collected to allow for background correction of the analytical results.

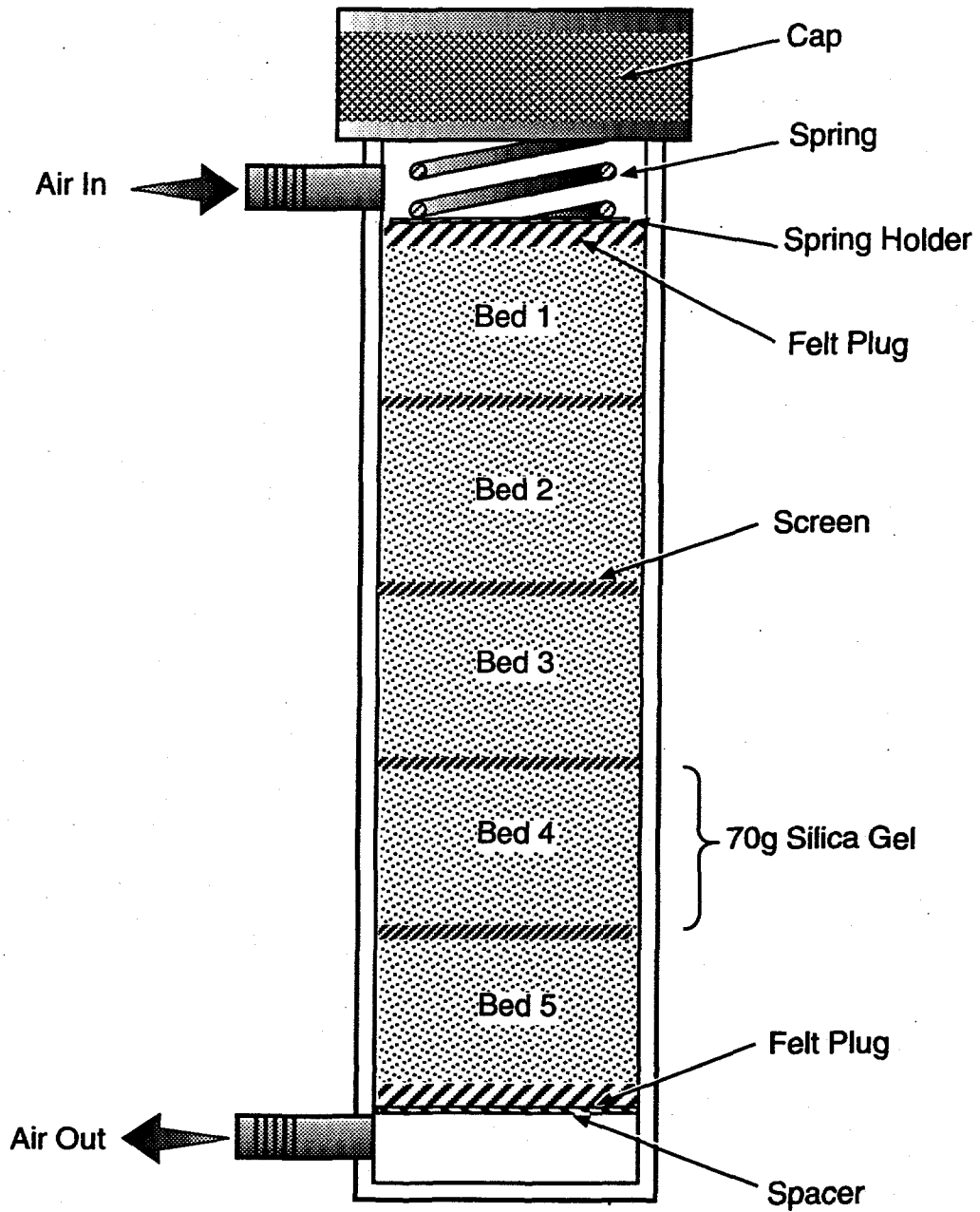
**Table 2.1. Test Parameters for Silica Gel Evaluations**

| Temperature | Test # | Relative Humidity | # Columns Visual Test | <sup>3</sup> H Spike | # Background Columns | # Gravimetric Columns |
|-------------|--------|-------------------|-----------------------|----------------------|----------------------|-----------------------|
| 50°C        | 1      | 19% - 46%         | 1                     | no                   | 0                    | 0                     |
| 30°C        | 2      | 28% - 32%         | 1                     | no                   | 0                    | 0                     |
| 40°C        | 3      | 12% - 16%         | 1                     | no                   | 0                    | 0                     |
| 20°C        | 4      | 27% - 31%         | 3                     | yes                  | 1                    | 0                     |
| 20°C        | 5      | 25% - 31%         | 3                     | yes                  | 1                    | 0                     |
| 20°C        | 6      | 30% - 38%         | 3                     | yes                  | 0                    | 1                     |
| 40°C        | 7      | 23% - 35%         | 3                     | yes                  | 1                    | 0                     |
| 40°C        | 8      | 32% - 37%         | 3 <sup>(a)</sup>      | yes                  | 1                    | 0                     |
| 30°C        | 9      | 26% - 27%         | 3                     | no                   | 0                    | 2                     |
| 40°C        | 10     | 29% - 30%         | 0                     | no                   | 0                    | 2                     |
| 50°C        | 11     | 30% - 33%         | 0                     | no                   | 0                    | 2                     |

(a) Front and back silica gel columns, both were analyzed for tritium content.

### 2.3 Gravimetric Analysis of Silica Gel Columns

Silica gel (prepared as in Section 2.0) was packed into a column in 5 sections as shown in Figure 2.2. The silica gel was separated into distinct segments by using metal screens. Each segment contained between 58 to 70 g of silica gel. (The first segment of the 20°C test contained only 34 g of silica gel.) The segmented columns were exposed by drawing air through the columns at constant temperature and 30% relative humidity until the first and second segments showed a complete color change in the indicator, the third bed had changed color for only the initial portion, and the fourth and fifth bed showed no observable color change. The silica gel column was disassembled and each segment was placed into airtight screw-cap jars. The silica gel from each segment was weighed and then baked in a 220°C oven until a constant weight was reached.



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Figure 2.2. Segmented Silica Gel Column Used for Gravimetric Tests

## 3.0 Results and Discussion

### 3.1 Visual Observations and Breakthrough Volumes

A total of 21 silica gel columns for visual tests were exposed in the environmental test chamber under varying temperature and humidity conditions (Table 2.1). A summary of visual observation results as both relative and absolute breakthrough volumes is given in Table 3.1. Figure 3.1 shows the linear movement of the moisture fronts through the silica gel columns.

Relative breakthrough volume is defined for this report as the maximum ratio of the sample volume to adsorbent bed depth with no visually observed breakthrough (air volume/bed depth [ $\text{m}^3/\text{cm}$ ]) and is equal to the slopes of the lines shown in Figure 3.1. Absolute breakthrough volume for a given column length is calculated by multiplying the relative breakthrough volume by the actual adsorbent depth. The initial test results were for single silica gel columns exposed at each temperature which yielded relative breakthrough volumes of  $0.13 \text{ m}^3/\text{cm}$  for  $30^\circ\text{C}$  and  $0.077 \text{ m}^3/\text{cm}$  for  $50^\circ\text{C}$ , both at roughly 30% relative humidity. The initial test at  $40^\circ\text{C}$  had a relative breakthrough volume of  $0.16 \text{ m}^3/\text{cm}$ , however the test chamber could only generate 13% relative humidity. Additional tests were conducted that involved replicate samples and the visual observations associated with these tests yielded relative breakthrough volumes of  $0.36 \text{ m}^3/\text{cm}$  for  $20^\circ\text{C}$  (number of samples [n] = 9),  $0.20 \text{ m}^3/\text{cm}$  for  $30^\circ\text{C}$  (n = 3), and  $0.15 \text{ m}^3/\text{cm}$  for  $40^\circ\text{C}$  (n = 6), all at 30% relative humidity. The

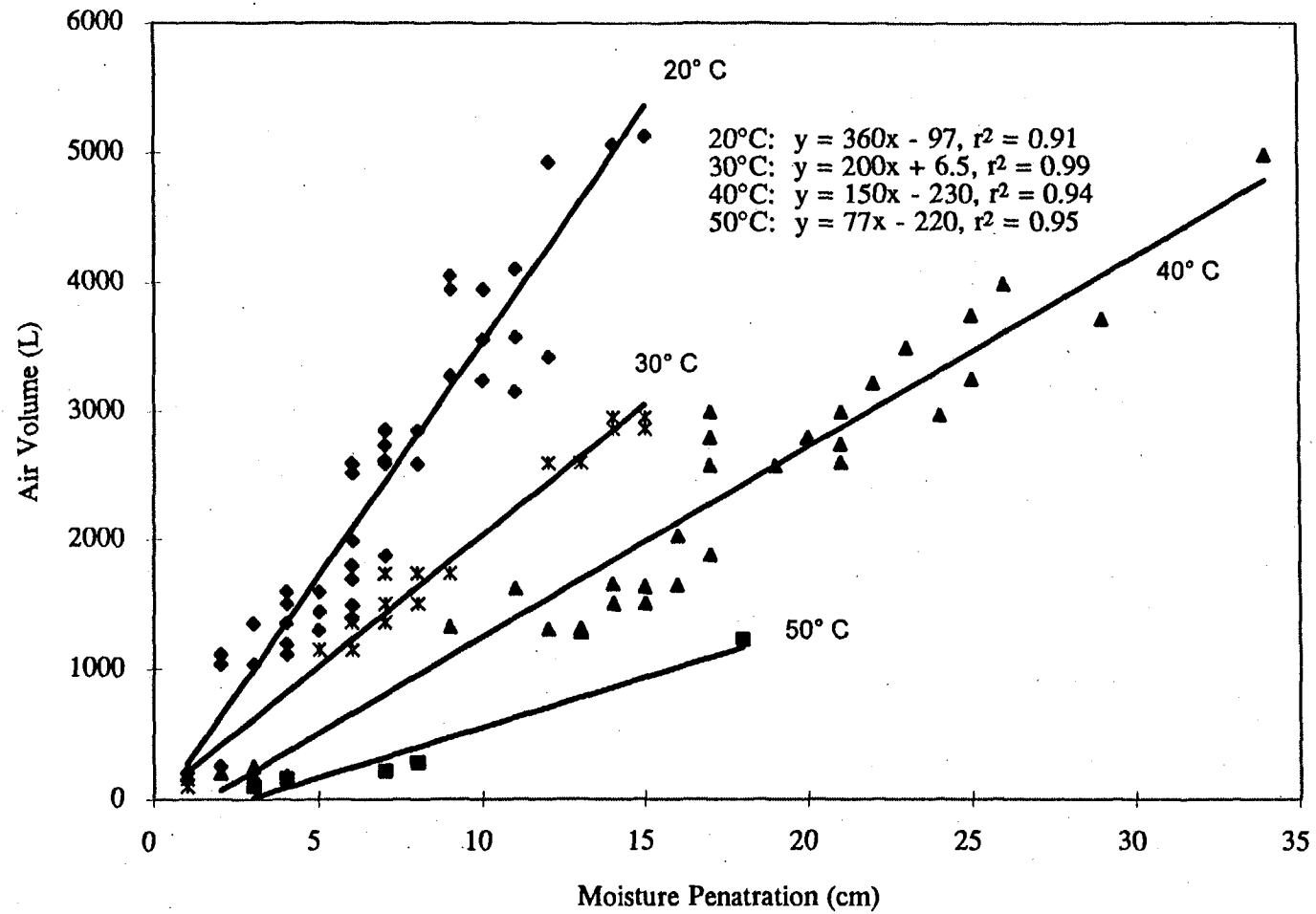
**Table 3.1.** Visual Observation Results: Breakthrough Volumes (Relative and Absolute) and Sampling Volume to Breakthrough Volume Ratios

| Temperature | # of Columns | Relative Humidity | Breakthrough Volumes                                      |   | $V_s/V_b^{(c)}$ |
|-------------|--------------|-------------------|---|---|-----------------|
|             |              |                   | ( $\text{m}^3/\text{cm}$ ) Relative Volume <sup>(a)</sup> | ( $\text{m}^3$ ) Absolute Volume <sup>(b)</sup> |                 |
| 20°C        | 9            | 25% - 38%         | 0.36  | 19  | 0.50            |
| 30°C        | 1            | 28% - 32%         | 0.13  | 7.0   | 1.4             |
| 30°C        | 3            | 26% - 27%         | 0.20  | 11  | 0.86            |
| 40°C        | 6            | 23% - 37%         | 0.15  | 8.1   | 1.2             |
| 40°C        | 1            | 12% - 16%         | 0.16  | 8.6   | 1.1             |
| 50°C        | 1            | 19% - 46%         | 0.077   | 4.2   | 2.3             |

(a) Maximum ratio of sample volume to adsorbent depth ( $\text{m}^3/\text{cm}$ ), calculated as the slope of the least squares line from a plot of air volume versus moisture penetration (as implied from the change in color of the indicating silica gel).

(b) Breakthrough volume for a 54-cm column (relative breakthrough volume multiplied by the column length).

(c) Sampling volume ( $9.5 \text{ m}^3$ ) to breakthrough volume ratio for 54-cm column as used by Hanford Site SESP.



**Figure 3.1.** Visual Observations of Moisture Penetration for 20°C to 50°C. The slope of the line at each temperature provides the relative breakthrough volume ( $m^3/cm$ ).

relative breakthrough volumes for the replicate samples were calculated by combining the data for each temperature and generating a least squares line through the data, with the slope equal to the relative breakthrough volume. Figure 3.2 shows a linear relationship between the relative breakthrough volume and temperature, with relative breakthrough volumes inversely proportional to temperature.

The typical field sampling volume for the Hanford Site ambient air samples for tritium is 9.5 m<sup>3</sup>. Thus the ratio of the field sampling volumes to the experimental breakthrough volumes (V<sub>s</sub>/V<sub>b</sub>) ranged from 0.50 at 20°C to 2.3 at 50°C for the visual tests. A ratio of 0.50 indicates that only half of the silica gel in the column was needed to equal the breakthrough volume, thus the current system would be well below the breakthrough volume at 20°C. At 30°C, the V<sub>s</sub>/V<sub>b</sub> ratio of 0.86 is close to unity, that is, the sampling volume is almost identical to the breakthrough volume. The V<sub>s</sub>/V<sub>b</sub> ratio is above 1 for the 40°C and 50°C evaluations, indicating that the field samples collected under these temperature conditions would exceed the breakthrough volumes. Average summertime temperature at the Hanford Site is around 25°C, and the current system should be below the breakthrough volume for most sampling periods. However, summertime high temperatures can easily approach an ambient temperature of 40°C and maximum temperature inside the sampling hutch could approach 50°C for short time periods. Fairly rapid moisture movement can occur during the high temperature periods with the migration rate being 4.7 times faster at 50°C compared to 20°C. The overall collection efficiency of the silica columns are discussed in Section 3.4.

The tests at 40°C with relative humidities of 13% (n = 1) and 30% (n = 6) yielded some limited information on the effect of humidity on breakthrough volumes at 40°C. The test at 13% relative humidity had a slightly higher relative breakthrough volume of 0.16 m<sup>3</sup>/cm compared to an average breakthrough volume of 0.15 m<sup>3</sup>/cm for 30% relative humidity, but this difference was probably not beyond the range of experimental error. Hanford Site average relative humidities range from 30% to 85%, and additional studies are needed to better estimate the effects of relative humidity on tritium breakthrough.

### 3.2 Analytical Recoveries for Tritium Tracer Tests

The recovery results for the tritium tracer test are given in Table 3.2. Percent recovery was calculated as follows:

$$\% \text{ recovery} = \frac{(\text{pCi recovered} - \text{BCF})}{\text{pCi spiked}} \times 100$$

where BCF (background correction factor) = pCi background  $\times \frac{\text{sample m}^3}{\text{background m}^3}$ .

No breakthrough was observed visually for the 20°C test and the average recovery of the tritium tracer was 70.5% ± 6.4% (n = 8) (Figure 3.3). There was a linear relationship between the total amount of water recovered from the column and the overall tritium recovery, with higher HTO recoveries for samples with larger water volumes recovered (Figure 3.4). The tritium tracer solution accounted for only 1 mL of water out of total water recoveries that ranged from 17 to 32 mL, with the

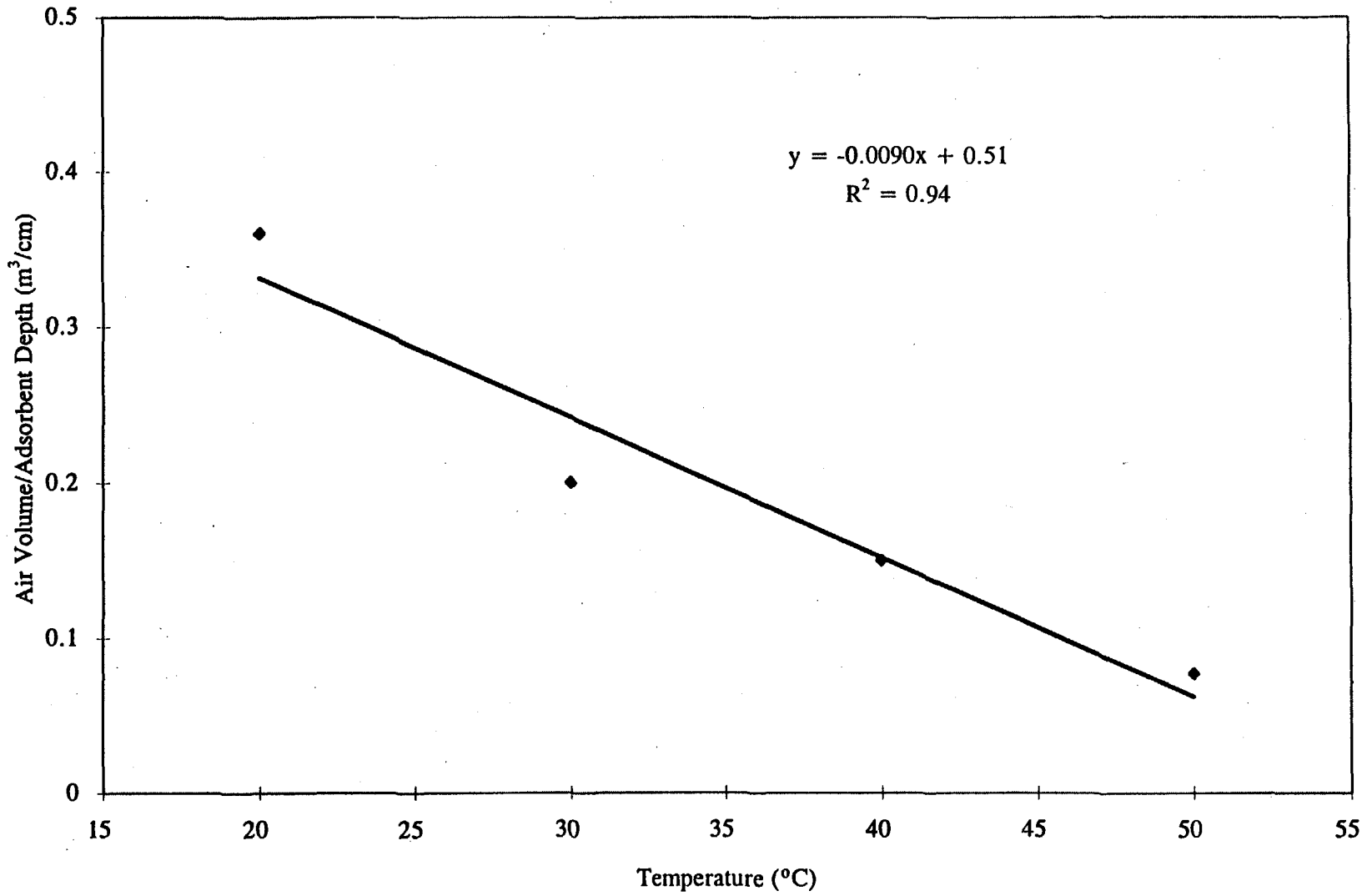


Figure 3.2. Relative Breakthrough Volume Versus Temperature

**Table 3.2. Tritium Tracer Recovery Results**

| Temperature   | Relative Humidity | Percent Recovery (Air Volume [m <sup>3</sup> ]) |                               |                              |
|---|-------------------|---|-------------------------------|------------------------------|
|   |                   |   |                               |                              |
| 20°C  | 30%               | 60 <sup>(a)</sup><br>(2.7) <sup>(c)</sup>       | ns <sup>(b)</sup><br>(ns)     | 80<br>(5.1)                  |
| 20°C  | 30%               | 66<br>(2.6)                                     | 72<br>(3.9)                   | 74<br>(4.9)                  |
| 20°C  | 30%               | 66<br>(2.6)                                     | 76<br>(4.0)                   | 70<br>(5.1)                  |
| 40°C  | 30%               | 88<br>(2.8)                                     | 54<br>(4.0)                   | 0 <sup>(d)</sup><br>(5.0)    |
| 40°C  | 30%               | Front Back <sup>(e)</sup><br>65 0.0<br>(2.7)    | Front Back<br>73 0.0<br>(3.0) | Front Back<br>42 18<br>(3.7) |
| <p>(a) Percent recovery.<br/>                     (b) ns = no sample.<br/>                     (c) Air volume collected.<br/>                     (d) Result was not different from background sample.<br/>                     (e) Both front and back silica gel columns were analyzed.</p> |                   |   |                               |                              |

balance of the moisture coming from the test chamber atmosphere. The typical amount of moisture collected for field samples is around 100 mL, thus there should be no recovery problem from insufficient moisture for field samples since HTO recovery was above 80% for the sample with greater than 30 mL of total water recovery. However, for sampling systems using small air volumes or sampling a low humidity environment, the results may need corrections for samples with low total water recoveries.

Average analytical recoveries for the 40°C test (Figure 3.3) were 75% ± 11% (n = 3) for air volumes ≤ 3 m<sup>3</sup>, 48% ± 8.5% (n = 2) for air volumes > 3 m<sup>3</sup> and < 5 m<sup>3</sup>, and 0% (n = 1) for an air volume of 5.0 m<sup>3</sup>. One of the tests at 40°C used a second silica gel cartridge placed downstream of the primary column to collect moisture that penetrated the primary column. No tritium was measured in the second silica gel column for air volumes of 2.7 m<sup>3</sup> and 3.0 m<sup>3</sup>; however, at 3.7 m<sup>3</sup>, 30% of the recovered tritium was found in the second column.

The impinger-based water vapor loading system that was used to generate the analytical blanks (Section 2.2.1) and tritium tracer columns (Section 2.2.3) functioned well for these tests and could be used to provide representative quality control samples for evaluating ambient air sampling systems.



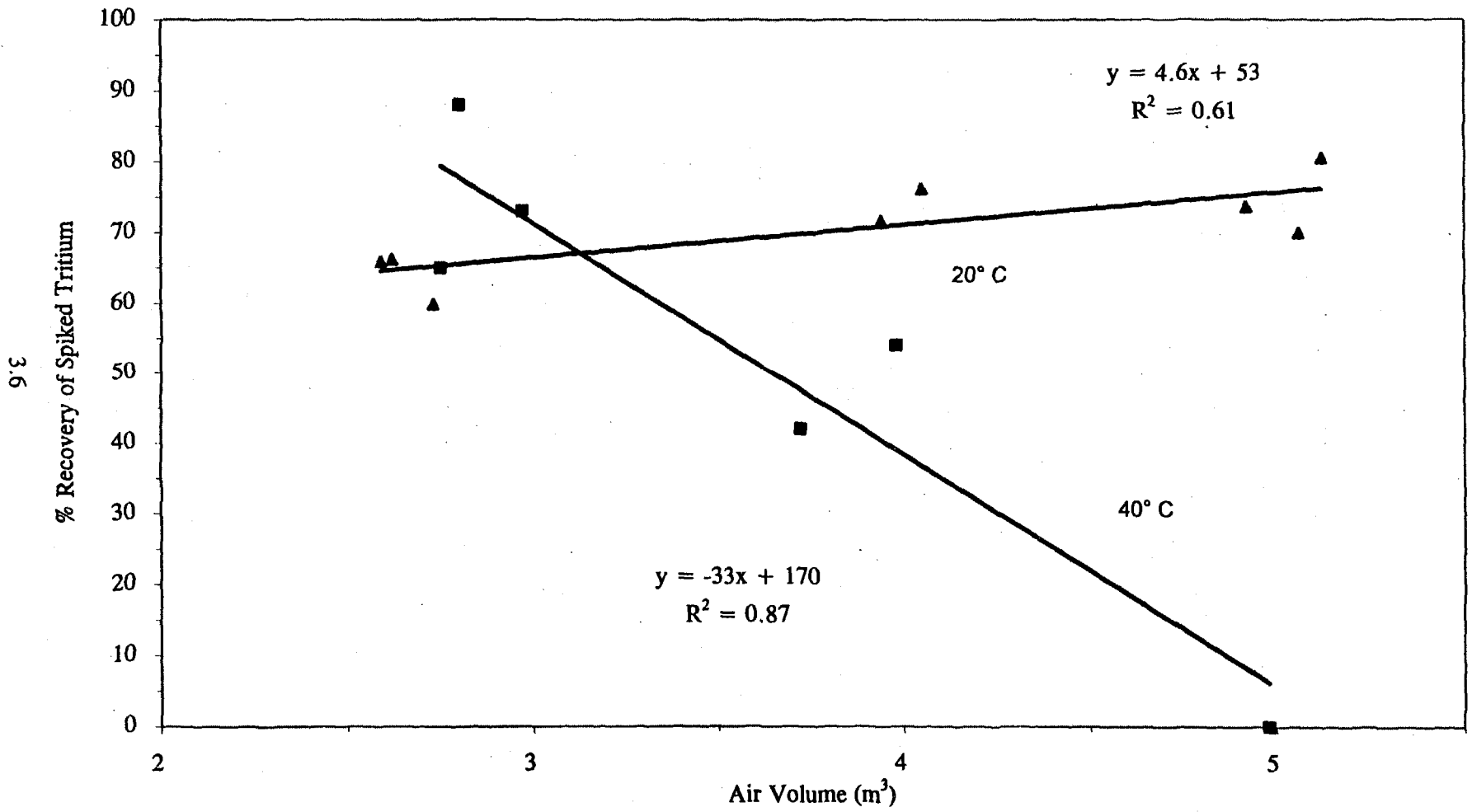


Figure 3.3. Tritium Recovery Versus Air Volume at 20°C and 40°C

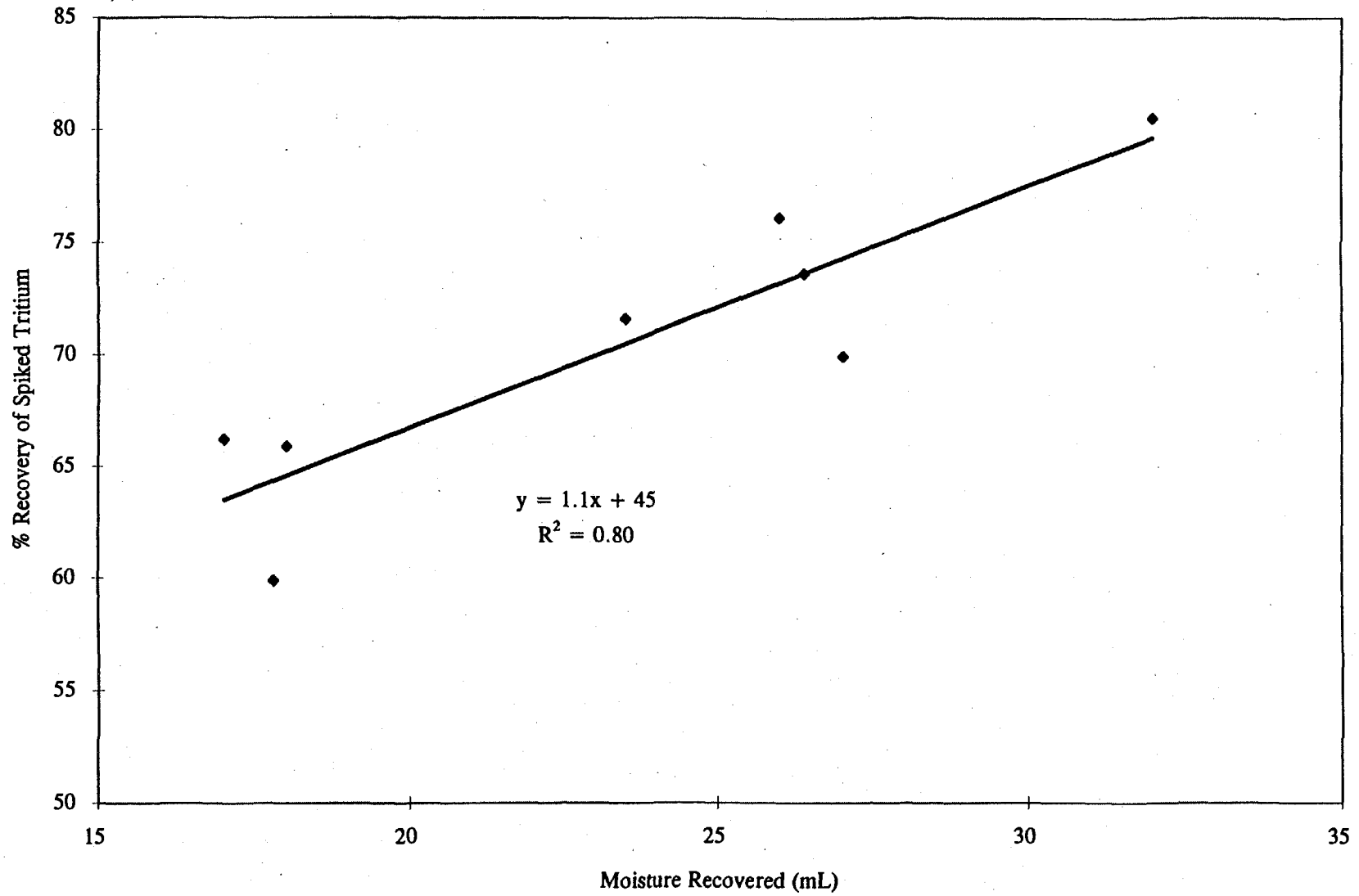


Figure 3.4. Effect of Total Moisture Recovery on Tritium Recovery

### 3.3 Gravimetric Analysis

The gravimetric results from segmented silica gel columns (Figure 2.2) exposed at 20°C to 50°C and 30% relative humidity are given in Table 3.3. For all tests, the moisture sensitive indicator had completely changed color for the first and second segments with moisture loadings (g H<sub>2</sub>O/g silica gel) ranging from 0.16 to 0.063, which was less than the equilibrium loading capacity (0.2 g H<sub>2</sub>O/g silica gel) of the adsorbent (Dean 1992). The third segment (transition zone) showed color change for only the leading portion with no color change observed for the trailing portion with moisture loading ranging from 0.027 to 0.047. The fourth and fifth bed segments showed no color change and moisture loading ranged from 0 to 0.011. The indicator appears to be an efficient marker of moisture movement through the columns because of the 8 to 15 fold difference in moisture loading between the second (complete color change) and fourth bed segments (no color change), with only 4 cm of silica gel composing the third segment (transition zone).

Frontal chromatographic profiles were produced for water vapor collected on the segmented silica gel columns by expressing the amount of water found in each segment as a percentage of the amount found in the first bed. This frontal movement of moisture through the silica gel columns is shown in Figure 3.5. The chromatographic efficiency, expressed as the number of theoretical plates (N), for the silica gel columns can be calculated by a graphic method shown in Figure 3.6 (You and Bidleman 1984). The parameters N, P<sub>50</sub>, N/P<sub>50</sub> ratio, and the calculated total N for the SESP air sampling system are given in Table 3.4. P<sub>50</sub> is the bed depth where the moisture content is 50% of the first bed segment. The ratio of N/P<sub>50</sub> gives the number of theoretical plates per bed depth and allows for the calculation of N for any given bed length. Both N and N/P<sub>50</sub> values decreased with increasing temperature, indicating greater chromatographic efficiency at lower temperatures. At 20°C, the silica gel column had 14 theoretical plates with a N/P<sub>50</sub> ratio of 1.7 N/cm. The number of plates dropped to 6.4 (N/P<sub>50</sub> = 0.67 N/cm) for the 30°C evaluation. There was only a small decrease in the number of plates and N/P<sub>50</sub> ratios for the 30°C, 40°C, and 50°C evaluations with N of 6.4, 5.8, and 5.0, and N/P<sub>50</sub> of 0.67, 0.65, and 0.60, respectively.

### 3.4 Overall Collection Efficiency

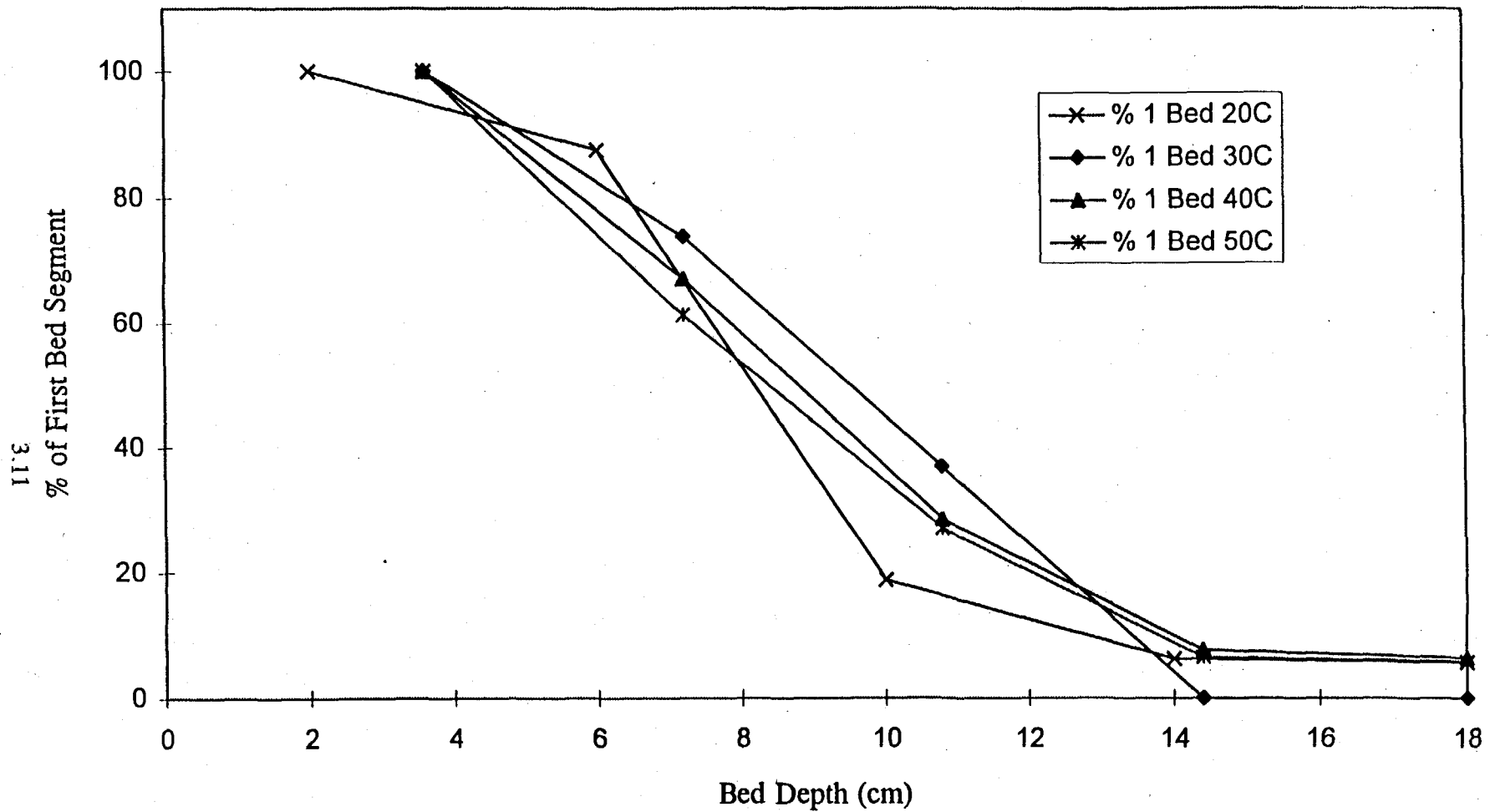
Senum (1981) evaluated the effect of breakthrough volume and chromatographic efficiency (N) on the overall collection efficiency for solid phase adsorbent sampling systems and produced a chart showing overall collection efficiency isopleths as a function of N and the sampling volume/retention volume ratio (V<sub>r</sub>/V<sub>r</sub>). Senum's chart is used as the template for Figure 3.7, except that the elution chromatography term (V<sub>r</sub>, retention volume) has been replaced with the frontal chromatography term (V<sub>b</sub>, breakthrough volume). The terms V<sub>b</sub> and V<sub>r</sub> for an adsorbent bed are equivalent when V<sub>b</sub> is defined as the midpoint of the chromatographic front as shown in Figure 3.6 (Reilley et al. 1962; You and Bidleman 1984). As seen in Figure 3.7, for a given N, the overall collection efficiency decreases as the sampling volume approaches the breakthrough volume (i.e., overall collection efficiency is inversely proportional to the V<sub>r</sub>/V<sub>b</sub> ratio). For a given V<sub>r</sub>/V<sub>b</sub> ratio, the overall collection efficiency is directly proportional to the chromatographic efficiency (i.e., overall collection efficiency increases with an increasing number of theoretical plates [N]).

**Table 3.3. Gravimetric Test Results for Moisture-Exposed Silica Gel Columns**

| Column <sup>(a)</sup><br>Segment   | Silica Gel<br>(g) | Indicator <sup>(b)</sup><br>Change | Weight Loss<br>After Heating (g) | g H <sub>2</sub> O per<br>g Silica Gel |
|------------------------------------|-------------------|------------------------------------|----------------------------------|--|
| <b>20°C, Test #6<sup>(c)</sup></b> |                   |                                    |                                  |  |
| #1                                 | 34                | 100%                               | 5.3                              | 0.16                                   |
| #2                                 | 70                | 100%                               | 9.4                              | 0.13                                   |
| #3                                 | 70                | 50%                                | 2.0                              | 0.029                                  |
| #4                                 | 70                | 0%                                 | 0.6                              | 0.0086                                 |
| #5                                 | 70                | 0%                                 | 0.5                              | 0.0071                                 |
| <b>30°C, Test #9</b>               |                   |                                    |                                  |  |
| #1                                 | 63                | 100%                               | 8.0                              | 0.13                                   |
| #2                                 | 64                | 100%                               | 6.0                              | 0.094                                  |
| #3                                 | 64                | 50%                                | 3.0                              | 0.047                                  |
| #4                                 | 64                | 0%                                 | 0.0                              | 0.0                                    |
| #5                                 | 64                | 0%                                 | 0.0                              | 0.0                                    |
| <b>30°C, Test #9</b>               |                   |                                    |                                  |  |
| #1                                 | 62                | 100%                               | 7.0                              | 0.11                                   |
| #2                                 | 63                | 100%                               | 6.0                              | 0.095                                  |
| #3                                 | 63                | 50%                                | 2.0                              | 0.032                                  |
| #4                                 | 63                | 0%                                 | 0.0                              | 0.0                                    |
| #5                                 | 63                | 0%                                 | 0.0                              | 0.0                                    |
| <b>40°C, Test #10</b>              |                   |                                    |                                  |  |
| #1                                 | 58                | 100%                               | 6.7                              | 0.12                                   |
| #2                                 | 62                | 100%                               | 4.9                              | 0.079                                  |
| #3                                 | 62                | 50%                                | 2.1                              | 0.034                                  |
| #4                                 | 63                | 0%                                 | 0.40                             | 0.0063                                 |
| #5                                 | 62                | 0%                                 | 0.30                             | 0.0049                                 |
| <b>40°C, Test #10</b>              |                   |                                    |                                  |  |
| #1                                 | 63                | 100%                               | 7.2                              | 0.11                                   |
| #2                                 | 63                | 100%                               | 4.7                              | 0.075                                  |
| #3                                 | 63                | 50%                                | 2.0                              | 0.032                                  |
| #4                                 | 63                | 0%                                 | 0.70                             | 0.011                                  |
| #5                                 | 63                | 0%                                 | 0.60                             | 0.0095                                 |

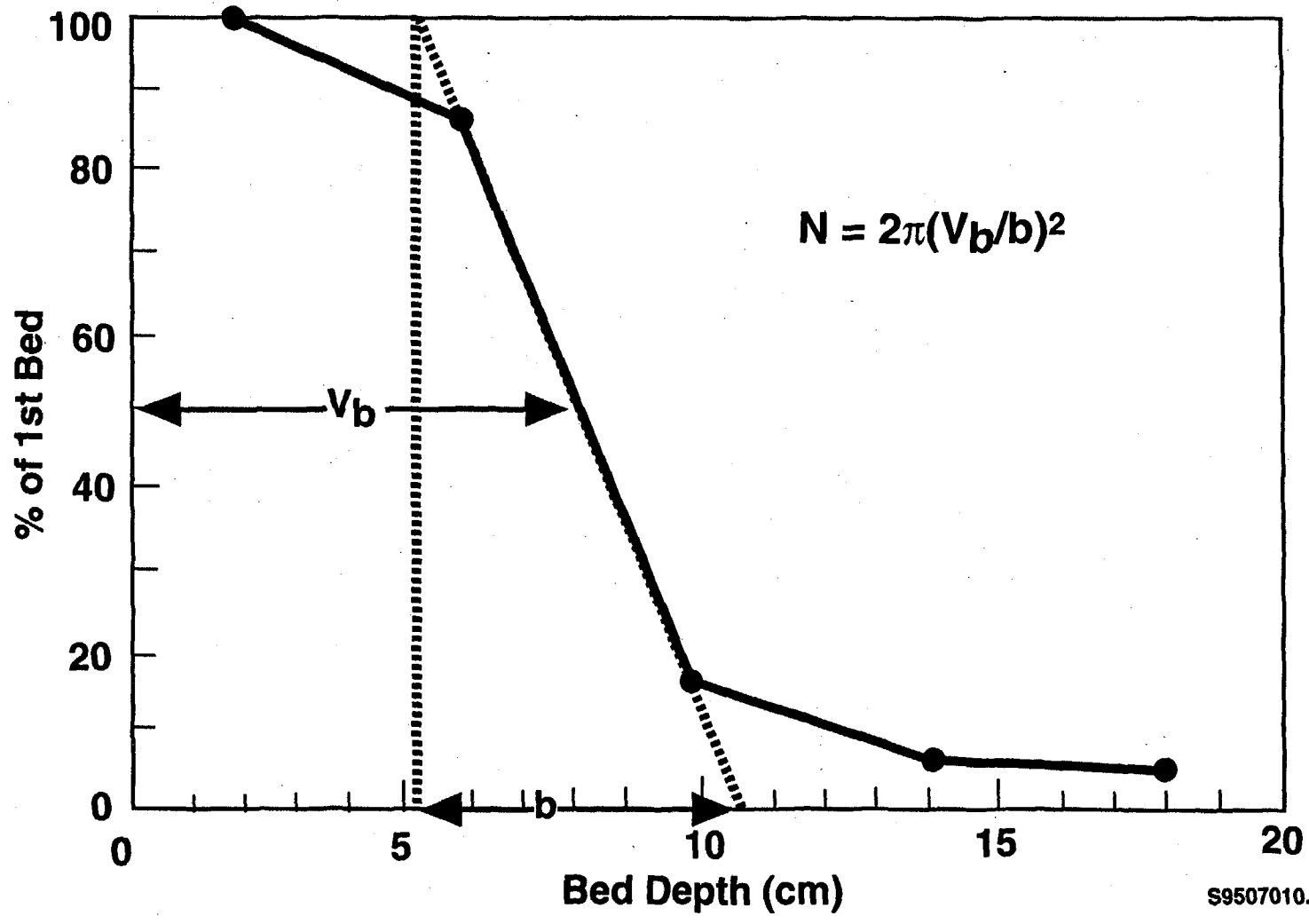
**Table 3.3. (contd)**

| Column <sup>(a)</sup><br>Segment   | Silica Gel<br>(g) | Indicator <sup>(b)</sup><br>Change | Weight Loss<br>After Heating (g) | g H <sub>2</sub> O per<br>g Silica Gel |
|--|-------------------|------------------------------------|----------------------------------|--|
| <b>50°C, Test #11<sup>(c)</sup></b>  |                   |                                    |                                  |  |
| #1   | 59                | 100%                               | 6.3                              | 0.11                                   |
| #2   | 63                | 100%                               | 4.3                              | 0.068                                  |
| #3   | 65                | 50%                                | 2.0                              | 0.031                                  |
| #4   | 62                | 0%                                 | 0.50                             | 0.0081                                 |
| #5   | 63                | 0%                                 | 0.40                             | 0.0063                                 |
| <b>50°C, Test #11</b>  |                   |                                    |                                  |  |
| #1   | 64                | 100%                               | 6.8                              | 0.11                                   |
| #2   | 67                | 100%                               | 4.2                              | 0.063                                  |
| #3   | 63                | 50%                                | 1.7                              | 0.027                                  |
| #4   | 68                | 0%                                 | 0.40                             | 0.0059                                 |
| #5   | 67                | 0%                                 | 0.40                             | 0.0060                                 |
| <p>(a) Segment #1 was the head of the column (i.e., the first segment exposed).</p> <p>(b) 100% represents a complete change of color for the moisture indicator, 50% represents a change of color for the first half of the silica gel segment, and 0% represents no observable color change.</p> <p>(c) Test numbers from Table 2.1.</p> |                   |                                    |                                  |  |



**Figure 3.5.** Frontal Movement of Water Vapor Through Silica Gel Columns. The 20°C test is for one sample, the tests at 30°C, 40°C, and 50°C are the average of two samples (Table 3.3).

3.12



S9507010.2

Figure 3.6. Graphical Calculation of the Number of Theoretical Plates

**Table 3.4. Theoretical Plate Measurements for Water Vapor on Silica Gel Columns**

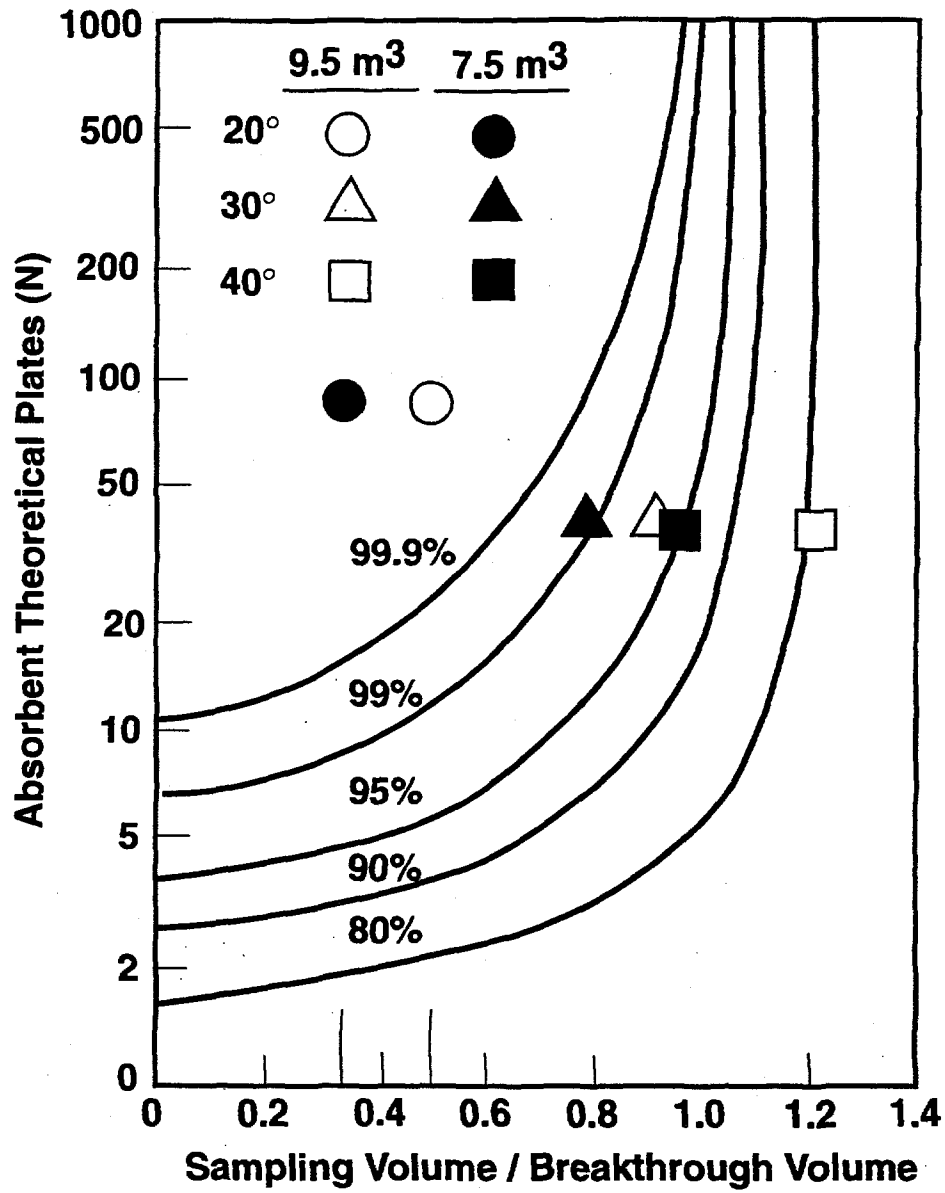
| Temperature         | N <sup>(a)</sup> | (cm) <sup>(b)</sup><br>P <sub>50</sub> | (N/cm)<br>N/P <sub>50</sub> | SESP Air Sampler<br>N <sup>(c)</sup> |
|---------------------|------------------|--|-----------------------------|--------------------------------------|
| 20°C                | 14               | 8.2                                    | 1.7                         | 92                                   |
| 30°C <sup>(d)</sup> | 6.4              | 9.6                                    | 0.67                        | 36                                   |
| 40°C <sup>(d)</sup> | 5.8              | 8.9                                    | 0.65                        | 35                                   |
| 50°C <sup>(d)</sup> | 5.0              | 8.4                                    | 0.60                        | 32                                   |

(a) Number of theoretical plates (18-cm column).  
 (b) Bed depth where the moisture content is 50% of the first bed segment.  
 (c) Number of theoretical plates (54-cm column).  
 (d) Average of two tests (Table 3.3).

The  $V_s/V_b$  and N results from this study are shown in Figure 3.7 for 20°C, 30°C, and 40°C, using the 9.5 m<sup>3</sup> SESP ambient sampling volume and a comparison sampling volume of 7.5 m<sup>3</sup>. At 20°C, the overall collection efficiency is above 99.9% for both the 7.5 m<sup>3</sup> and 9.5 m<sup>3</sup> sample volumes. The overall collection efficiency for 30°C was above 95% for 9.5 m<sup>3</sup> and above 99% for 7.5 m<sup>3</sup>. At 40°C, the overall collection efficiency was below 80% at 9.5 m<sup>3</sup> and near 95% for 7.5 m<sup>3</sup>. The  $V_s/V_b$  ratio at 50°C was 2.3 which was beyond the scale of Figure 3.7 and water vapor would not be quantitatively retained on the column. Table 3.5 gives the maximum practical sampling volumes for a 54-cm silica gel column for overall collection efficiencies ranging from 99.9% to 80%. At 95%, overall collection efficiency the maximum practical sampling volume ranges from 19 m<sup>3</sup> at 20°C to 3.8 m<sup>3</sup> at 50°C. Values above the dashed line in Table 3.5 represent the region of practical sample collection for the SESP sampling volume of 9.5 m<sup>3</sup>.

In order to allow for a higher probability that a quantitative sample could be collected by the Hanford Site SESP, it was necessary to reduce the air volumes for summertime samples to 7.5 m<sup>3</sup>, which would allow for 95% collection efficiency with a constant 40°C temperature. This reduction in the air volume collected should not impact the limit of detection because only an aliquot (typically 5 mL out of approximately 100 mL) of the total moisture collected by the silica gel is used for analysis.





S9507010.1

Figure 3.7. Overall Collection Efficiency Relationship Between  $V_s/V_b$  Ratio, N, and Overall Collection Efficiency. The isopleth lines show overall collection efficiency. (Adapted with permission from G. I. Senum, *Environ. Sci. & Technol.* 15:1074. Copyright [1981] American Chemical Society.)

**Table 3.5. Maximum Practical  $V_s/V_b$  Ratios and Sampling Volumes for Water Vapor Collected on a 54-cm Silica Gel Column**

| Temperature | Maximum Practical $V_s/V_b$<br>(Maximum Sampling Volume $m^3$ ) |                     |                     |                     |                     |
|-------------|---|---------------------|---------------------|---------------------|---------------------|
|             | 99.9% CE <sup>(a)</sup>   | 99% CE              | 95% CE              | 90% CE              | 80% CE              |
| 20°C        | <b>0.8</b><br>(15)  | <b>0.9</b><br>(17)  | <b>1.0</b><br>(19)  | <b>1.1</b><br>(21)  | <b>1.2</b><br>(23)  |
| 30°C        | 0.6<br>(6.6)  | <b>0.8</b><br>(8.8) | <b>0.9</b><br>(9.9) | <b>1.0</b><br>(11)  | <b>1.2</b><br>(13)  |
| 40°C        | 0.6<br>(4.9)  | 0.8<br>(6.5)        | 0.9<br>(7.3)        | <b>1.0</b><br>(8.1) | <b>1.2</b><br>(9.7) |
| 50°C        | 0.6<br>(2.5)  | 0.7<br>(2.9)        | 0.9<br>(3.8)        | 1.0<br>(4.2)        | 1.2<br>(5.0)        |

Note: Values above the bold line represent practical sample collection for the SESP sampling volume of 9.5  $m^3$ .  
(a) CE = Overall collection efficiency (30% relative humidity).

## 4.0 Conclusion

Ambient air samples for tritium analysis (as the HTO content of atmospheric moisture) are collected for the Hanford Site SESP using moisture indicating silica gel. Some silica gel columns showed a complete change in the moisture indicator for summertime samples suggesting that breakthrough (moisture penetration) had occurred. The purpose of this study was to determine the maximum practical sampling volume and overall collection efficiency for water vapor collected on silica gel columns and to demonstrate the use of an impinger-based system to load water vapor onto silica gel columns to provide realistic analytical spikes and blanks for quality control samples.

Breakthrough volumes ( $V_b$ ) were measured and the chromatographic efficiency (expressed as the number of theoretical plate numbers [N]) was calculated for a range of environmental conditions. Tests involved visual observations of the change in the silica gel indicator as a moist air stream was drawn through the column, measurement of the amount of a tritium tracer and a tritium-free tracer retained and then recovered from the silica gel, and gravimetric analysis for exposed silica gel columns.

The visual observations yielded relative breakthrough volumes (air volume/adsorbent depth [ $\text{m}^3/\text{cm}$ ]) of 0.36 for 20°C, 0.20 for 30°C, 0.15 for 40°C, and 0.077 for 50°C; all at 30% relative humidity. The actual breakthrough volume for a given bed depth can be calculated by multiplying the relative breakthrough volume by the bed depth.

Average tritium tracer recoveries at 20°C were 71% and at 40°C were 75% for volumes  $\leq 3.0 \text{ m}^3$  (no breakthrough was observed for these samples). The overall recovery of tritium-free water (analytical blank) from the silica gel columns was 98%  $\pm$  12%, with all results for tritium below the detection limit. Thus, the impinger-based water vapor loading system functioned well and could be used to produce representative quality control samples for evaluating air sampling systems.

Frontal chromatographic profiles were measured for water vapor migrating through the silica gel columns, using metal screens to divide the column into five segments. Moist air was drawn through the column until half of the column showed a change in the indicator. The columns were disassembled and each segment was weighed and the moisture content was calculated. Frontal chromatographic profiles were produced by expressing the moisture loading of each segment as a percentage of the first segment and the chromatographic efficiency was determined by graphical evaluation. The number of theoretical plates per adsorbent depth ranged from 1.7 N/cm at 20°C to 0.60 N/cm at 50°C. The number of theoretical plates decreased with increasing temperature, indicating a greater chromatographic efficiency at lower temperatures. The total number of theoretical plates for a given bed depth is calculated by multiplying the N/cm value (above) by the bed depth.

Gas chromatographic theory was used to calculate the overall collection efficiency of the silica gel columns as a function of the ratio of the sampling volume to breakthrough volume ( $V_s/V_b$ ) and the total number of theoretical plates in the column (N). Using the SESP sampling volume of 9.5  $\text{m}^3$  and a 54-cm column, the overall collection efficiency was 99.9% at 20°C, 95% at 30°C, and <80% at 40°C.

The mean summer temperature at the Hanford Site is 25°C, thus the SESP system is adequate for most ambient air sampling. However, maximum temperatures can approach 40°C, with temperatures inside the sampling hatches near 50°C for short time periods. Thus, it was necessary to reduce the air volumes collected for summertime samples to allow for a higher probability that a quantitative sample could be obtained.

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