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Title: Corrections for Measurements of Tritium in Subterranean Vapor using Silica Gel

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Abstract

Hazardous contaminants buried within vadose zones can accumulate in soil gas. The concentrations and spatial extent of these contaminants are measured to evaluate potential transport to ground water for public risk evaluation. Tritium is an important contaminant found in and monitored for in vadose zones across numerous sites within the United States nuclear weapons complex, including Los Alamos National Laboratory. The extraction, collection, and laboratory analysis of tritium from subterranean soil gas presents numerous technical challenges that have not been fully studied. Particularly, the lack of soil moisture in the soil gas in the vadose zone makes it difficult to obtain enough sample moisture (e.g., >5 g) to provide for the required sensitivity, and often, only small amounts of moisture can be collected. Further, although silica gel has high affinity for water vapor and is prebaked prior to sampling, there is still sufficient residual moisture in the prebaked gel to dilute the relatively small amount of sampled moisture; thereby, significantly lowering the "true" tritium concentration in the soil gas. This paper provides an evaluation of the magnitude of the bias from dilution, provides methods to correct past measurements by applying a correction factor (*CF*), and evaluates the uncertainty of the *CF* values. For this, ten-thousand Monte Carlo calculations were performed and distribution parameters of *CF* values were determined and evaluated. The mean and standard deviation of the distribution of *CF* values were 1.53 ± 0.36, and the minimum, median, and maximum values were 1.14, 1.43, and 5.27, respectively.

Keywords: tritium, soil gas monitoring, risk assessment, ground water.

Introduction

Background

Past operations within the nuclear weapons complex in the United States have resulted in environmental contamination at numerous locations, including Los Alamos National Laboratory (LANL) in New Mexico (NAP 1989). While the most highly contaminated sites have been remediated, LANL continues to perform environmental sampling to ensure public and environmental health and to demonstrate compliance with existing regulations (LANL 2007). One part of these efforts includes extraction of soil gas from subterranean monitoring wells (LANL 2009). These monitoring wells are used as access ports to sample bedrock and soil gas at different depths within the vadose zone where samples are taken for measurement of a variety of chemical and radiological contaminants, including tritium. Extraction and measurement of tritium in subterranean samples presents numerous technical challenges regarding the sampling, measuring, and interpretation of tritium concentration measurements in the soil gas.

Though tritium contamination in either the liquid or gas phase in the vadose zone does not generally represent a direct ingestion or inhalation dose pathway for humans or other biota, sampling of soil gas is performed for several important reasons. Firstly, contamination from most spills and buried waste initially enters the vadose zone, and detection of contamination in the soil gas or liquid is one of the first indicators of a breach of containment. Second, and important for risk assessment, the soil gas concentration data at different well depths is used to identify and establish temporal and spatial patterns in concentrations and to investigate plume transport. The major concern is to assess the potential for the plume to reach groundwater where the tritiated water would present a direct dose pathway to people through drinking water. Finally, the measurements can be also used to test and calibrate migration models for predicting the transport of contaminants to groundwater (Till and Grogan 2008).

Measurement Procedure and Calculations

A procedure (LANL 2009) was developed to ensure consistency in sampling soil gas in the vadose zone for tritium. The procedure generally follows the standard protocol for soil gas monitoring found in ASTM D5314-92 (ASTM 2006). The general sampling process includes using air pumps to purge sampling lines, extraction of the soil gas from the bed rock and transporting the sample to the surface where the soil gas is passed through about 135 g of prebaked silica gel contained within a sampling tube. The sampling continues until about 5 g (i.e., 5 mL) of soil gas moisture is collected. Thereafter, sampling, the tubes are immediately sealed and sent to an analytical laboratory where the collected moisture is driven off the silica gel by heating and then analyzed for tritium using liquid scintillation counting. Results are reported in Becquerels (*Bq*) per liter (*L*) and represent the concentration of tritium in the extracted vapor at a particular depth in the vadose zone. Eqn. 1 shows formula for the tritium concentration from the extracted vapor condensate:

$$C(Bq/L) = \frac{A}{V} = \frac{A}{M_E \div \rho_{water}} \quad \text{(Eqn. 1)}$$

where: A is the amount of radioactivity of tritium in the moisture (units of Bq), and

V is the volume of the liquid in the sample analyzed (unit of L),

M_E is the mass of the liquid extracted (unit of g), and

ρ is the density of water (unit of g cm^{-3}).

There are several potential sources of uncertainty in Eqn. 1. There is random error in the radioactivity measurements (A), the error of the measurements of mass of the sampled moisture (M_E) is a few percent, and the density of water (ρ) is considered to be a constant. However, the largest potential error is less obvious and is based on the assumption that the mass of the water extracted during laboratory analysis is solely from the vapor sampled, that is, we assume no bound water in the prebaked silica gel. This assumption has previously been shown to be wrong, even with prebaking.

Patton et al. (1997) found that silica gel baked in an oven at over $\geq 100^\circ$ C for extended time periods still contained substantial amounts of tightly bound water. The amount of residual moisture depends on the nature of the silica gel, but the amount is large enough to significantly affect results (Rosson et al. 2000, Guthrie et al. 2001) leading to underestimation of tritium releases to the environment (Simpkins and Hamby 1997). The error in the assumption occurs when the HTO in the sample undergoes isotopic exchange, or mixing, with the bound H_2O in the silica gel. This "dilution" reduces the tritium concentration in the extracted liquid, which is used to measure concentrations.

Correction, for residual moisture, to tritium concentration measurements is required. First, the mass of the liquid extracted from the silica gel (M_E) will be a combination of the sampled mass (M_S) and the residual moisture (M_R) in the silica gel, as shown in Eqn. 2.

$$M_E = M_s + M_R \qquad \text{(Eqn. 2)}$$

Ideally, M_E would equal M_S. However, if one makes the reasonable assumption that M_R contains a relatively small amount of tritium [background tritium concentrations in freshwater and water vapor are about 1 Bq L^{-1} (NCRP 1979, UNSCEAR 2000)], and that the tritium in the sample mixes thoroughly with the residual moisture, then Eqn. 3 shows how residual moisture dilutes the sample with "clean" water and results in a measured tritium concentration, C_M, that is biased low.

$$C_M(Bq/L) = \frac{A}{V} = \frac{A}{M_E \div \rho_{water}} = \frac{A}{(M_S + M_R) \div \rho_{water}} \qquad \text{(Eqn. 3)}$$

To correct for residual moisture in the sample, the mass of the residual water needs to be determined. The mathematical formulas to provide corrected concentrations, C_C, are shown in Eqns. 4 and 5.

$$C_C(Bq/L) = \frac{A}{(M_S + M_R) \div \rho} \times \frac{(M_S + M_R)}{M_S} \qquad \text{(Eqn. 4)}$$

$$C_C(Bq/L) = \frac{A}{(M_S + M_R) \div \rho} \times CF \qquad \text{(Eqn. 5)}$$

Here, CF is the correction factor that adjusts the measured tritium concentrations to account for residual moisture in the silica gel. The mass of the sampled water, M_S, is measured as the difference in masses of the cartridge containing the silica gel before and after sample collection. The mass of the residual moisture can be determined by knowing the fraction of residual moisture, by mass, in the prebaked silica gel prior to sampling.

$$M_R = M_{SilicaGel} \times F_{RM} \qquad \text{(Eqn. 6)}$$

F_{RM} is the fraction of the mass of the prebaked silica gel due to residual moisture. The correction factor, CF, then becomes:

$$CF = \frac{\left(M_{SilicaGel} \times F_{RM}\right) + M_S}{M_S}, \qquad \text{(Eqn. 7)}$$

which is substituted into Eqn. 5 to correct samples for the dilution due to residual moisture. $M_{SilicaGel}$ and M_S are measured in the laboratory per procedure, but measurement of the fractional mass of the moisture is needed for the correction.

Purpose of Study

Measurement techniques for sampling tritium in subterranean soil gas have not been thoroughly investigated, especially relative to sampling atmospheric air for tritium (Eberhart 1999). A specific concern was that dilution of samples with residual moisture in the prebaked silica gel can result in significant systematic biases in the tritium measurements. Other studies have shown that this correction can be significant and can vary with silica gel type, amount of moisture collected, and laboratory procedures (Eberhart 1999, Rosson et al. 2000), but this had not been investigated for subterranean soil gas measurement techniques. Correction of the tritium concentrations is particularly important for subterranean soil gas measurements because the soil gas is relatively dry and generally only small amounts of moisture are collected, which results in larger errors.

Sample specific data can be used to correct future measurements using Eqn. 7 on an individual basis; however, it was also important to assess the magnitude of correction factors for uncorrected historical data. In most of these cases, the required data to make these corrections were not collected. Therefore, the primary tasks of this study were to analyze the potential error, determine the correction factors (i.e., Eqn. 7), and investigate the uncertainty of the correction factors to be used for these tritium measurements. These corrections are required for more accurate measurement and analysis of tritium concentrations in subterranean soil gas and the assessment of the potential radiological hazards associated with the tritium.

METHODS

Determination of Residual Moisture (F_{RM}) in Silica Gel

A series of measurements (n = 18) were made of the residual moisture mass in silica gel that was used to collect soil gas vapor for tritium analysis. Soil gas measurements of tritium at LANL are made by two environmental contractors, and because each contractor uses a different silica gel, nine measurements were conducted on each gel type to allow assessment of intra- and inter-gel variability.

The following procedure was used for these measurements. First, silica gel from both contractors was prebaked separately at a temperature of 105° C for over two days, as required in the standardized procedures. The prebaked silica gel samples from both contractors were quickly separated into individual samples with masses of approximately 1, 2, 3, and 5 g. The prebaked masses (M_{before}) were recorded; then, samples were put in a furnace for complete denaturing. For denaturing, all samples were placed into a furnace at a temperature of 1000° C for 2 hours, and the final mass of the denatured gel (M_{final}) recorded. The residual/bound moisture fraction by mass was calculated as shown in equation 8.

$$F_{RM} = \frac{m_{before} - m_{final}}{m_{before}} \qquad \text{(Eqn. 8)}$$

Uncertainty Analysis for correction for residual moisture in silica gel

Analysis of the uncertainty of the correction factor, *CF*, was done using Monte Carlo simulation techniques (Till and Grogan 2008) using Crystal Ball software[3]. The Monte Carlo technique allows propagation of errors from each variable through the final calculations of *CF*. The distribution of each parameter in Eqn. 7 was determined based either on actual measurements or an assumed distribution in cases where empirical data was absent. The first parameter is the mass of the sample collected (M_S). Over 150 measurements of M_S collected from 2007 and 2008 field logbooks were analyzed and M_S ranged from about 2 to 46 g with a median of 15 g. Therefore, in the Monte Carlo simulations we assumed a triangular distribution with 2 g, 15 g, and 46 g as the

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[3] Oracle Software, 1515 Arapahoe St. Suite 1300, Denver, CO 80202

minimum, most likely, and maximum masses of collected samples, respectively. For the second parameter, the mass of the silica gel ($M_{SilicaGel}$), actual measurements have not been previously made so we assumed the typical amount of 135 g ± 13.5 g. This amount is based on the stated mass of silica gel in a cylinder, as written in the procedure (LANL 2006), with a 10% error. A normal distribution of fractional moisture content by mass (F_{RM}) was assumed and was based on the mean and standard deviations measurements made during the denaturing process. The values used for the distribution of F_{RM} were 6.4% ± 0.3% (further details are in the Results section). Ten-thousand Monte Carlo calculations were run and the final distribution for *CF* was determined from these results. As an additional test, the Monte Carlo generated distribution was compared to the summary statistics from 438 independent *CF* results that were calculated from actual vapor measurements made at several boreholes within LANL.

Results

The percent bound moisture for the silica gel used by the two environmental contractors was similar, with means and standard deviations of 6.5 ± 0.25% and 6.1 ± 0.14% (Table 1). The combined mean and standard deviation was 6.4 ± 0.3 %. There was no statistically significant difference between the two types of silica gels used by the contractors, so both sets of data were combined in the statistical analysis and all data are shown in Fig. 1, which shows the results in terms of water loss as a function of the initial mass of the silica gel. The regression slope was slightly over 6% residual moisture mass per gram of silica gel. For example, a sample canister with 100 g of silica gel would contain about 6 g of residual moisture in the canister. Given that sampling of vapor stops when about 5 g of vapor moisture is collected, the relative amount of residual moisture in the silica gel is enough to dilute the sample making correction important.

A typical correction factor (*CF*) can be estimated using Eqn. 7 assuming the initial mass of the silica gel was 135g, the fractional amount of moisture in the silica gel was 0.064, and the mass of the sampled vapor was 15 g. The correction factor becomes 1.57, as shown in Eqn. 9.

$$CF = \frac{(135g \times 0.064) + 15g}{15g} = 1.57 \qquad \text{(Eqn. 9)}$$

However, each individual variable in Eqn. 9 has an associated uncertainty. The overall uncertainty of the *CF* was determined through propagation of the individual uncertainties using Monte Carlo simulations from Crystal Ball, as described in the Methods section. The resulting distribution of values for *CF* is presented in Fig. 2. The mean and standard deviation of the distribution of *CF* values in Fig. 2 was 1.53 ± 0.36, and the minimum, median, and maximum values were 1.14, 1.43, and 5.27, respectively. Ninety-five percent of the *CF* values were less than about 2. The comparison distribution of *CF* values derived from an actual and independent set of measurements (n=438) showed a similar distribution to the Monte Carlo derived values with a mean and standard deviation of 1.66 ± 0.325. The minimum, median, and maximum *CF* values for the measurements were 1.17, 1.57, and 3.32, respectively. The *CF* value for the 25th percentile was 1.44 and was 1.82 for the 75th percentile.

Discussion and Conclusions

Correction factors for subterranean measurements of tritium in soil gas were determined. Application of these corrections would improve their accuracy and increase the inherent value of this data for future uses. The measurements of moisture in silica gel reported here resulted in a median correction factor of 1.43, and ranged from 1.14 to 5.27. These correction factors are similar to those found by Rosson et al. (2000) and Guthrie et al. (2001), though those studies did not fully assess the uncertainties in the correction factors, as was done here.

One of the main implications of the study is that the magnitude of the correction factor decreases non-linearly as the amount of moisture in the sample increases, as shown in Fig. 3. Further, the sensitivity (rate of change in CF with changes in sample mass) decreases with increased sample mass. Combined, this shows that larger samples need less correction and that the uncertainty would be less. Operationally, there is a balance that has to be struck during sampling because sampling in dry bedrock requires very long sampling times, which can be inconvenient and costly. Optimization of the sample times and mass is appropriate, and the relationship shown in Fig. 3 can help with decisions on required sampling times and masses. For example, Fig. 3 shows that the current limitation of having a minimum of a 5 g sample seems appropriate.

There are several important assumptions made that affect the correction factor, as described in this report. The first is that it is assumed that the tritium in the sampled HTO is fully mixed with the residual moisture in the silica gel. That is, the isotopic exchange is complete. Rosson et al. (2000) showed that this is a reasonable assumption though they found that amount of exchangeable water in the silica gel could be slightly higher (about 10%) than the mass of water content in the silica gel (determined through denaturing) possibly due to unaccounted alterations in hydroxyl groups or residual moisture during denaturing. A second assumption is that there is no isotopic difference in the concentrations of HTO and H_2O in the water evaporated during the processing of the sample in the laboratory. Rosson et al. (2000) showed that this is a reasonable assumption, especially for the higher temperatures used to drive the moisture off the silica gel, and the impact of the isotope effect for this process is only a few percent. The isotope effect for evaporation is much larger at lower temperatures (e.g., 10° C) and needs to be accounted for when calculating concentrations in soil water from subterranean soil gas measurements (Price 1958).

In summary, the impact of residual bound moisture on tritium measurements in soil vapor is sufficient to warrant correction. This paper provides a technique to calculate the distribution of correction factors (CFs) that can be used to correct historical data even in cases where needed information is missing. The calculations also show that the correction factor is largest for samples with the least amount of collected moisture and will approach one as more sample mass is collected, but the realistic amounts of moisture collected under normal sampling times require correction. Ultimately, this correction will provide more accurate data for measurement interpretation and risk assessment for public exposures.

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References

American Society for Testing and Materials (ASTM) (2006). Standard Guide for Soil Gas Monitoring in the Vadose Zone. ASTM D5314.

Eberhart, C.F. (1999). Using absolute humidity and radiochemical analyses of water vapor samples to correct underestimated atmospheric tritium concentrations. Los Alamos National Laboratory report LA-UR-99-1107.

Guthrie, E.B., Shen, N.C., & Bandong, B.B. (2001) Isotope exchange and fractionation corrections for extraction of tritiated water in silica gel by freeze-drying techniques. Lawrence Livermore National Laboratory Report UCRL-ID-148610.

Los Alamos National Laboratory (LANL). (2006). Sampling of ambient airborne tritium. LANL procedure ENV-MAQ-204, R13.

Los Alamos National Laboratory (LANL). (2007). Environmental Surveillance at Los Alamos during 2007. Los Alamos National Laboratory report LA-14385-ENV.

Los Alamos National Laboratory (LANL). (2009). Sampling for sub-atmospheric air. LANL Procedure EP-ERSS-SOP-5074.

National Academy Press (NAP). (1989). The nuclear weapons complex: Management for health, safety, and the environment. National Academy Press: Washington, D.C.

National Council on Radiation Protection (NCRP). (1979). Tritium in the environment. NCRP Report no. 62.

Okada, S., & Momoshima, N. (1993). Overview of tritium: characteristics, sources, and problems. Health Physics 65:595-609.

Patton, G.W., Cooper, A.T., & Tinker, M.R. (1997). Ambient air sampling for tritium-determination of breakthrough volumes and collection efficiencies for silica gel. Health Physics 72:397-407.

Price, A.H. (1958). Vapour pressure of tritiated water. Nature 181: 262.

Rosson, T., Jakiel, R., Klima, S., Kahn, B., & Fledderman, P. (2000). Correcting tritium concentrations in water vapor monitored with silica gel. Health Physics 78: 68-73.

Simpkins, A.A., Hamby, D.M. (1997). Predicted vs. measured tritium oxide concentrations at the Savannah River Site. Health Physics 72:179-185.

Till, J.E., & Grogan, H.A. (eds). (2008). Radiological risk assessment and environmental analysis. Oxford University Press: New York, New York.

United Nations Scientific Commission on the Effects of Atomic Radiation (UNSCEAR). (2000). Report of the United Nations Scientific Committee on the Effects of Atomic Radiation to the General Assembly.

Figure Captions

Figure 1. Decrease in water mass as a function of amount of silica gel in sample before denaturing in the high temperature oven.

Figure 2. Distribution of values for the correction factor.

Figure 3. Relationship between the correction factors, calculated using average values for residual moisture and mass of silica gel, and the mass of sampled moisture.

Table 1. Results of measurements made to determine the percent of residual, bound moisture in silica gel following prebaking. Results include samples from both LANL contractors.

Crucible	Mass of empty crucible (g)	Mass of crucible w/pre-denatured gel (g)	Net mass of gel (g)	Cruc. w/ denatured gel (g)	Mass of water loss (g)	Percent bound water
			Contractor 1			
1	49.3912	50.4388	1.0476	50.3682	0.0706	6.74
2	48.4071	49.4224	1.0153	49.3522	0.0702	6.91
3	52.2148	53.2605	1.0457	53.1904	0.0701	6.70
4	52.7999	55.8038	3.0039	55.6114	0.1924	6.41
5	51.6778	54.6539	2.9761	54.4636	0.1903	6.39
6	51.845	54.8281	2.9831	54.6384	0.1897	6.36
7	51.7259	56.7239	4.998	56.413	0.3109	6.22
8	49.3898	54.3796	4.9898	54.069	0.3106	6.22
9	48.4061	53.3839	4.9778	53.0701	0.3138	6.30
					AVERAGE	**6.47**
					STD	**0.25**
			Contractor 2			
1	52.2133	53.2349	1.0216	53.1747	0.0602	5.90
2	52.7987	53.7927	0.994	53.7314	0.0613	6.17
3	51.6764	52.6739	0.9975	52.6126	0.0613	6.15
4	51.8433	54.8441	3.0008	54.6586	0.1855	6.18
5	51.7246	54.7121	2.9875	54.5259	0.1862	6.23
6	49.3912	51.3687	1.9775	51.2461	0.1226	6.20
7	48.4074	53.3855	4.9781	53.0817	0.3038	6.10
8	52.2141	57.2201	5.006	56.921	0.2991	5.97
9	52.7997	57.7492	4.9495	57.4605	0.2887	5.83
					AVERAGE	**6.08**
					STD	**0.14**

Figure 1.

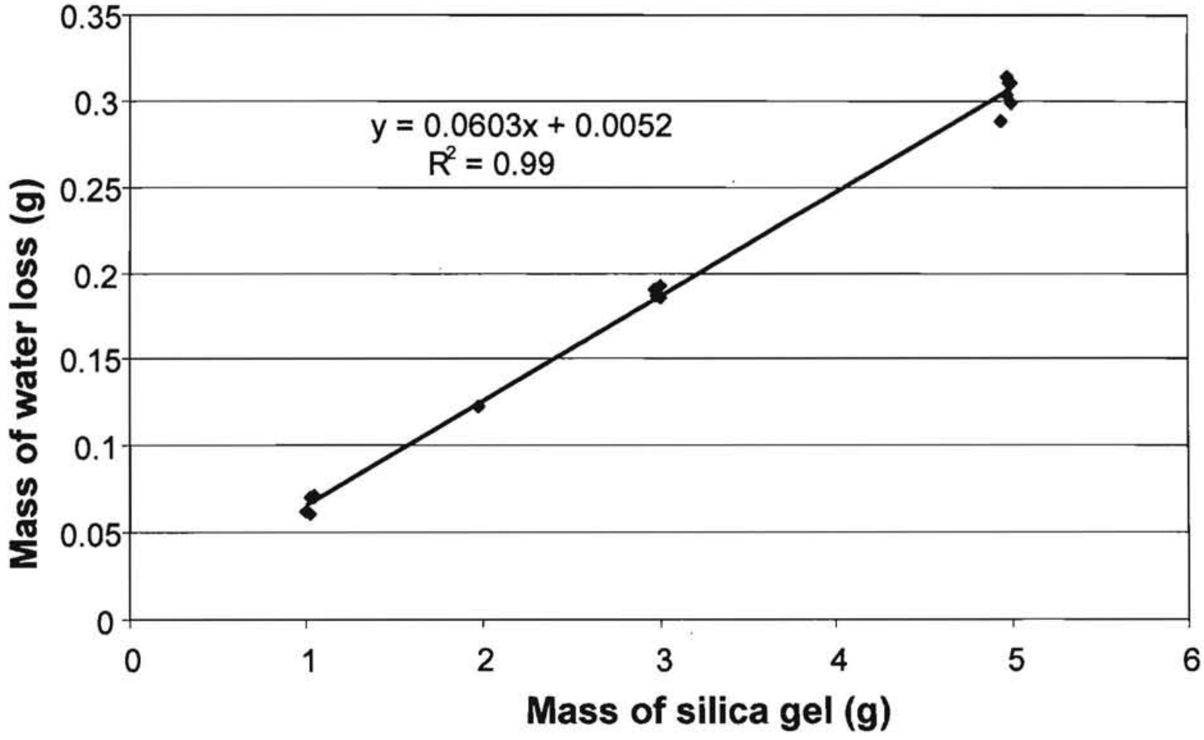
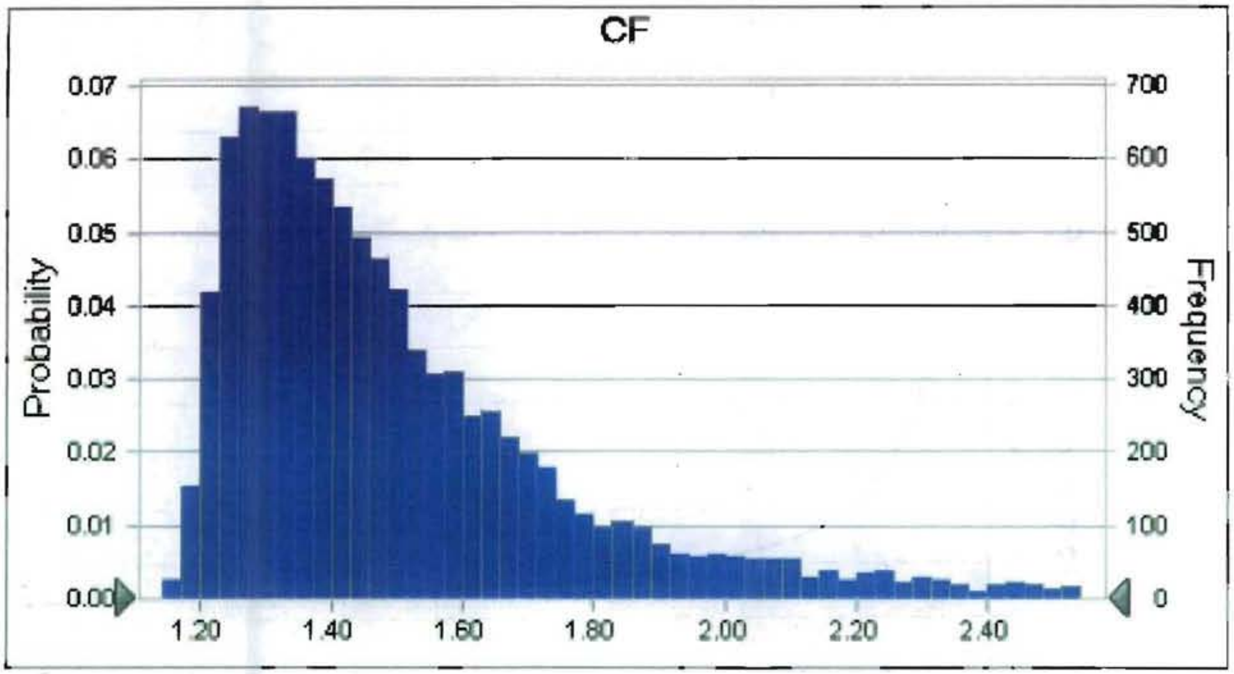
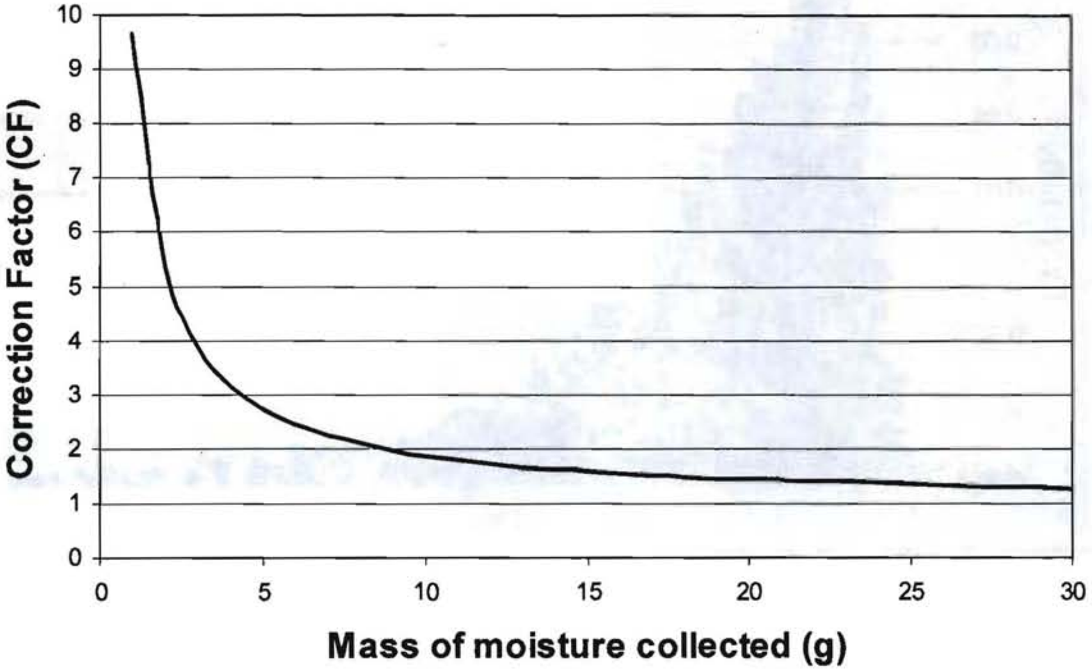

y = 0.0603x + 0.0052
R^2 = 0.99
Mass of water loss (g)
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
Mass of silica gel (g)
0
1
2
3
4
5
6

Figure 2.



CF
Probability
Frequency
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0.00
700
600
500
400
300
200
100
0
1.20
1.40
1.60
1.80
2.00
2.20
2.40

Figure 3.



Correction Factor (CF)
10
9
8
7
6
5
4
3
2
1
0
0
5
10
15
20
25
30
Mass of moisture collected (g)