PAMSGRAM

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*The **PAMSGRAM** is a FAXED notice for State and Local air pollution control agencies which highlights issues meriting attention by PAMS monitoring staff.*

The Variation of the Relative Humidity of Air Released from Canisters after Ambient Sampling

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Dalton's Law of partial pressures and the hypothesis that water vapor equilibrium above a canister surface is identical to that established above liquid water can be used to predict the variation of the percent relative humidity (%RH) of air released from canisters used in ambient air sampling, typically 6L canisters pressurized with 18L of air. During sampling, water vapor partial pressure increases as air enters the canister. When (and if) the water vapor partial pressure exceeds its saturation vapor pressure, the rate of water vapor condensation on the canister walls equals its sampling rate into the canister. Under constant temperature conditions, the %RH of air subsequently released from the canister can be calculated. This development shows that the air released from the canister is less humid than the original sample, following the relationship, $\%RH = 100\% (6L/V_s)$ for $V_s > V_r$ where V_s is the residual air volume and V_r is the residual air volume at which water is predicted to be completely removed (using the assumptions) from the canister wall. Also, for $V_s < V_r$, the %RH is constant and equal to its value at V_r. V_r is shown to depend on the %RH of the ambient air sample. Experimental values are shown to agree reasonably well with predictions. However, experimental values were systematically lower than predicted especially when ambient air with mid-range %RH was sampled. This difference appears to be related to the loss of water vapor by condensation of the sampling apparatus upstream of the canister. Adsorption of water vapor on the canister walls may affect the shape of the V_s versus %RH near the residual volume V_r as well and this may be different for different canisters due to wall surface conditions.

NOTE: The results of mathematical prediction of the %RH of air released from a canister are summarized below and graphical information is provided to allow predictions to be made for a variety of situations.

Three ranges of %RH of the ambient air that is initially sampled into the canister are conveniently treated:

! 0%RH ≤ original ambient %RH ≤ 33.3%RH

No condensation occurs and (neglecting any adsorbed water vapor) the relative humidity of air released from the canister should be constant at its original ambient air value although in practice some water vapor will be adsorbed on the canister wall.

! 33.3%RH < original ambient %RH < 70%RH

1. Locate the ambient sample %RH on the abscissa (the value of 60%RH was chosen in Figure 1 as an example) and the point of intersection of this value with the curve A.

2. Identify the value of canister volume on the ordinate scale corresponding to the point of intersection (8L in the example). This value is the volume V_r at which all condensed water vapor on the canister walls has been evaporated during the process of releasing the sample air from the canister.

3. Use V_r to locate a point of intersection on curve B. This point $V_r = V_s$ divides the curve B into two sections, (1) $V_s \leq V_r$ and (2) $V_s \geq V_r$.

NOTE: In general (for any ambient %RH), as the sample is released from the canister (at any stage having a volume V_s remaining in the canister), the curve B indicates the %RH (on the abscissa scale) of the released sample air over the range 18L $\leq V_s \leq V_r$

4. For the example, for $V_s \leq$ 8L, since all condensed water in the canister will have been evaporated, the mixture of water vapor and air will be constant and the %RH of the remaining sample air will be released at its value at V_s = 8L. In the example this value is 74%RH.

5. For $V_s \geq V_r$, the abscissa value corresponding to V_s indicates the predicted %RH value of released air. In the example, this applies for any sample volume between 18L and 8L.

6. Figure 2 shows the modification of Figure 1 to predict the %RH of released sample air for the example (when the %RH of the ambient air sample was 60%). To do this locate the ordinate value corresponding to the volume V_s remaining in the canister [between 18L (30 psig) and 6L (0 psig)] and read the abscissa value of %RH for the point of intersection of V_s and the curve.

- 70%RH $\leq$ original ambient %RH $\leq$ 100%RH

Refer to Figure 1 and note from curve A that $V_r \leq$ 6L which is equivalent to stating that some condensed water is always on the canister wall for 18L $\leq V_s \leq$ 6L. The %RH of released air is determined by using curve B in Figure 1. to find the value of %RH corresponding to the entire range of values of $V_s \geq$ 6L.

RESULTS OF EXPERIMENTAL DETERMINATION OF THE %RH OF SAMPLE AIR RELEASED FROM PRESSURIZED CANISTERS

Figures 3 and 4 show the %RH of air released from canisters initially pressurized to 18L when 34%, 61% and 90%RH (23 ± 1°C) ambient air samples were made available to a sampling manifold. The predicted values are shown for comparison. The curves in Figure 4 correspond to a 61%RH value for ambient air and involve both water vapor condensation and then total evaporation of available water vapor from the canister wall as the sample air is released. Two experimental examples (Can 1 and Can 2) are shown. The two differ as the sample volume remaining approaches V_r. The Can 2 values show the general features of the predicted characteristic. However, the experimental value of constant %RH for $V_s \leq V_r$ occurs at a higher value (58%RH) than predicted (76%), probably due to the condensation of water vapor on the inlet lines during sampling. Can 1 shows a monitonically increasing value of %RH as residual canister volume decreases. Recent experimental work indicates that different canisters exhibit different behaviors near V_r. Additional experimental work is being carried out to investigate whether these differences may be related to the condition of the interior surface of the canister.

Adjustments must be made to the predicted values when ambient conditions of temperature change appreciably between sampling and release of air. Obviously, more or less water is condensed in the canister when the ambient temperature at which the canister is held becomes lower or higher than the temperature at which the sample was taken. Consideration should also be given to the mass of water in the canister since the condensation of water in the canister for the same %RH but different temperatures may lead to droplets with various surface to volume ratios. Another factor that could make a difference in the response profile of %RH versus canister pressure is the manner in which water is introduced into the canister. Water added to synthetic samples for humidification by using a certain number of µL probably has a different surface distribution in the canister than humidified samples introduced directly from the ambient air.

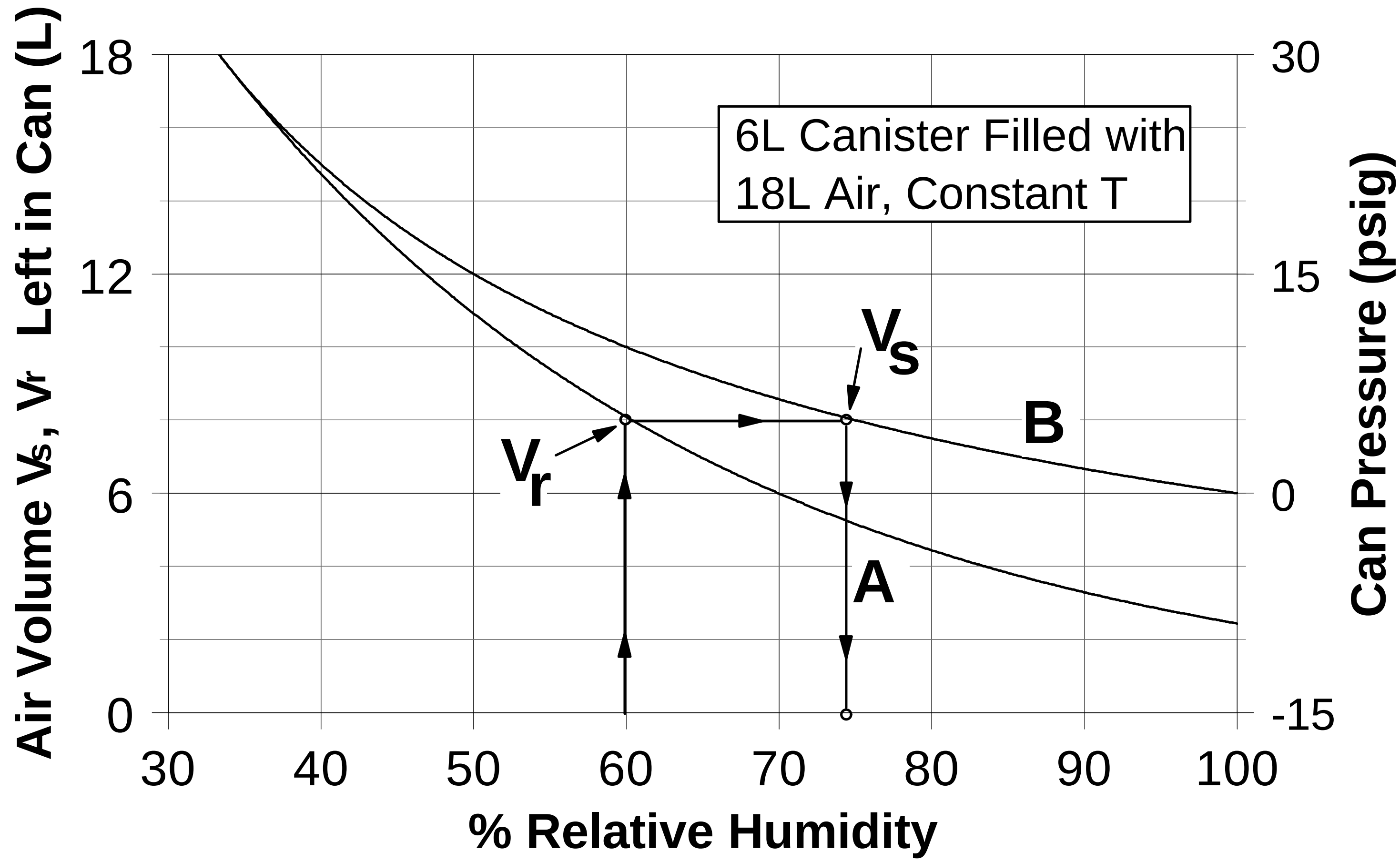

Figure 1. **A** - Original %RH of the sample air vs the remaining sample volume, V_r, in the canister when all condensed water is evaporated; **B** - residual sample volume, V_s, vs %RH of air released from canister.

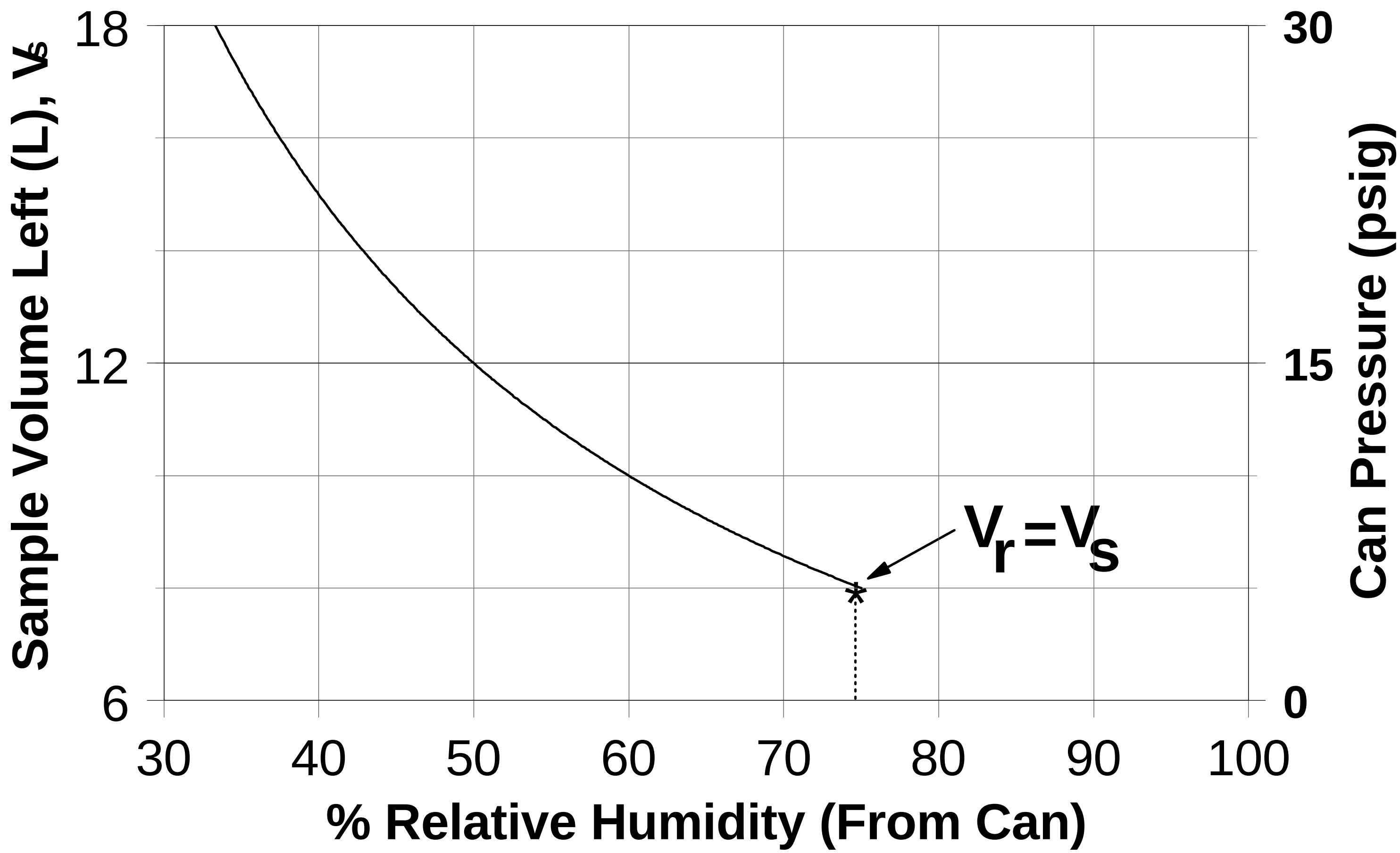

Figure 2. Residual sample volume, V_s, vs %RH of air released from canister

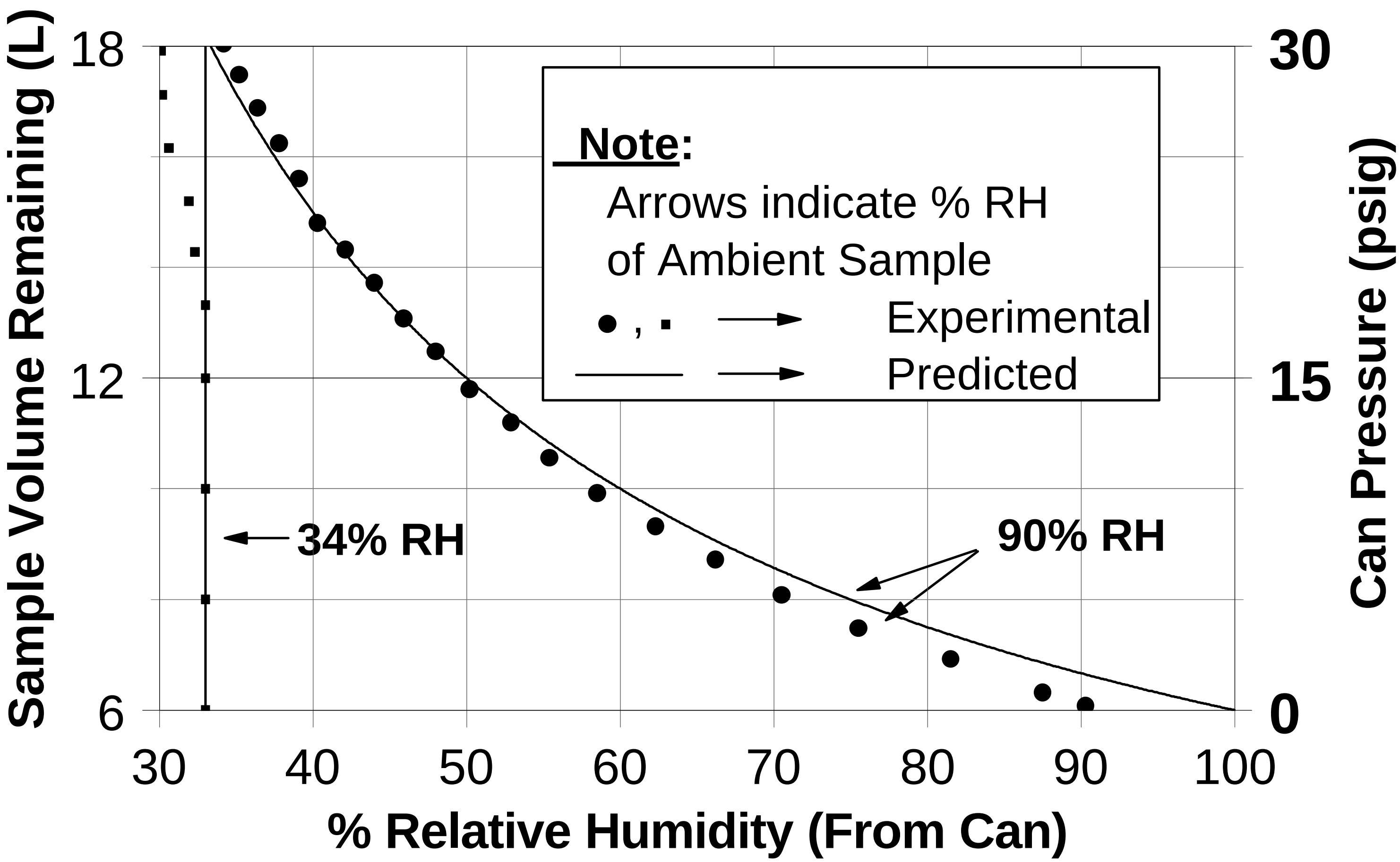

Figure 3. Comparison of predicted and experimental %RH values of released air vs volume of sample remaining in canister; 34% RH and 90% RH ambient air samples.

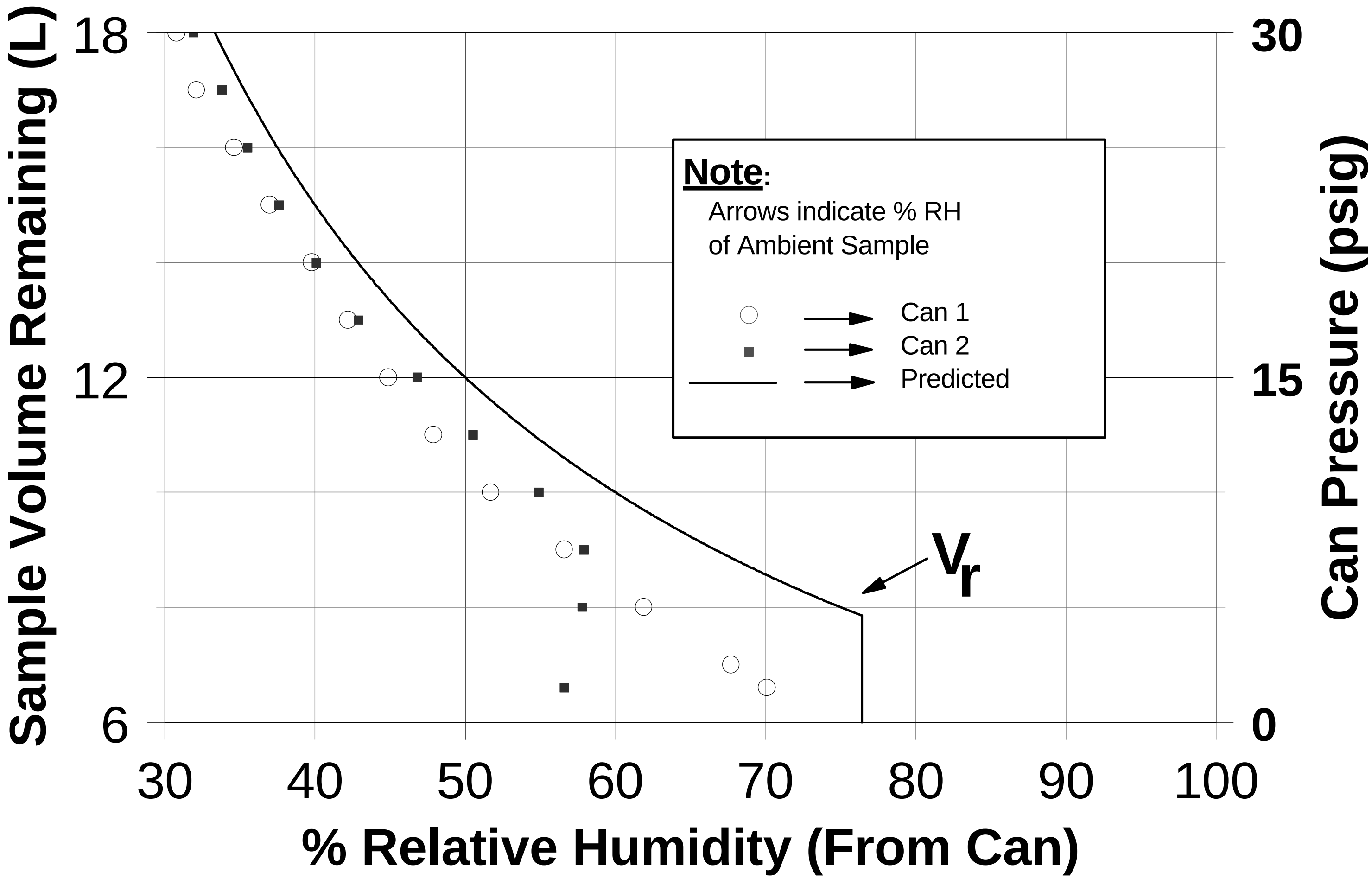

Figure 4. Comparison of predicted and experimental %RH values of released air vs volume of sample remaining in canister; 61% RH ambient air sample.