

Correlations for High Humidity Corrections of Rate Coefficients for Adsorption of Organic Vapors and Gases on Activated Carbons in Air-Purifying Respirator Cartridges

Gerry O. Wood,*

Los Alamos National Laboratory, Industrial Hygiene and Safety Group,
MS K486, Los Alamos, NM 87545, *gerry@lanl.gov*

Peter Lodewyckx,

Royal Military Academy, Department of Chemistry, 30 Avenue Renaissance,
1000 Brussels, Belgium

Abstract

Estimations of service lives of organic vapor air-purifying respirator cartridges (and other packed beds of activated carbon granules) require estimations of adsorption rate coefficients. Previous work has shown that these are affected by both preadsorbed water and by water vapor in the airstream. This paper presents further correlations that allow rate coefficients at humid conditions to be estimated from those measured or calculated at dry conditions.

Introduction

Methods of estimating service lives for organic vapor (OV) respirator cartridges are in much demand for setting change-out schedules. High humidity is a use condition that is often encountered and needs to be taken into account in such methods (models or equations).

Service lives of organic vapor (OV) air-purifying respirator cartridges depend on the rates of adsorption of OVs from flowing air, as well as on the capacities of the activated carbon contents for the OVs. These dependencies are described by the Reaction Kinetic form of the Wheeler-Jonas equation (Wood and Moyer, 1989):

$$t_b = \frac{W_e W}{C_o Q} - \frac{W_e \rho_B}{k_v C_o} \ln \left(\frac{C_o - C}{C} \right), \quad (1)$$

where t_b (min) is the breakthrough time, C_o (g/cm^3) is the challenge vapor concentration, C is the breakthrough concentration, W_e (g/g carbon) is the gravimetric capacity, W (g) is the weight of carbon, Q (cm^3/min) is the volumetric air flow rate, k_v is the adsorption rate coefficient, and ρ_B (g/cm^3) is the packed density of the granular carbon bed.

Both adsorption rates and capacities (and, therefore, breakthrough times) can be reduced by the presence of water in the air or on the carbon (Lodewyckx and Vansant, 2000 and 1999). The objective of the work reported here was to further explore the effects of water on OV adsorption rate coefficients.

Background

Lodewyckx and Vansant (2000) investigated the influence of humidity on the overall mass transfer coefficient (adsorption rate coefficient). Experimental breakthrough times for 0.1% and 1% breakthrough fractions were used to calculate rate coefficients for various carbons, chemical vapors, and combinations of prehumidification and airstream relative humidities (RHs). A 2x2 matrix solution of Eq. (1) gives:

$$k_v = \frac{\rho_B Q}{W} \left[\frac{t_{1\%} \ln(999) - t_{0.1\%} \ln(99)}{t_{1\%} - t_{0.1\%}} \right] \quad (2)$$

Their resulting correlation for rate coefficients in the presence of humidity was:

$$k_v' = k_v \left[1 - \left(\frac{A_{tot}}{TPV} \right) \right] \quad (3)$$

where k_v is for dry conditions, A_{tot} is the total pore volume (cm^3/g) occupied by water in the absence of organic vapor, and TPV is the total pore volume (cm^3/g) of the activated carbon. The A_{tot} is a dynamic function of time, temperature, flow velocity, bed depth, water initially present, and water displaced by organic vapors.

Nelson and Correia (1979) summarized their work with others at the Lawrence Livermore National Laboratory in the 1970s. They measured 618 vapor breakthrough curves for 121 chemicals and three types of activated carbons in commercial respirator cartridges. Test conditions, results, analyses, and conclusions from these were reported in a series of papers cited in this summary. Other variables included vapor concentration, airflow rate, number of cartridges (1 or 2) in parallel, preconditioning RH (0 – 90%), and test RH (0 – 90%). The original analysis of this data resulted in a table of correction factors to be applied to service lives to take into account these RH conditions. However, these correction factors were only averages of those obtained for several different chemicals and cartridges and valid only at 1000 ppm. The separate effects of RHs on rate and capacity were lumped together.

Data Analysis

Lodewyckx and Vansant (2000) tabulated experimental rate coefficients for six chemical/carbon combinations and matrices of prehumidified vs. airstream relative humidities. We have used these and an additional four unpublished tables for the work reported here. The four are for 1,1,1-trichloroethane, n-butanol, cyclohexane, and 1,2-dichloroethane on BPL-HA carbon. Prehumidified and airstream RHs for these included 0, 50, 70, and 80% RH. Unpublished 0.1% (of $5 \text{ g}/\text{m}^3$ challenge vapor concentration) breakthrough times $t_{0.1\%}$ were also tabulated for nine of these matrices and used for this report. The exception is that the data for the low micropore, high macropore C Granular carbon was not used.

We examined these matrices of rate coefficients and breakthrough times at different prehumidified and airstream RHs and found no consistent trend among the rate coefficients at dry conditions, defined as where both RHs $\leq 50\%$. Therefore, we averaged them and used the averages as the reference $k_v(\text{Dry})$ and $t_{0.1\%}(\text{Dry})$ values. We then calculated ratios of k_v/ϕ and $t_{0.1\%}/\phi$ at higher prehumidified and/or airstream RHs to these dry reference values.

Nelson (1988) has provided us with the original full experimental breakthrough curve data, test conditions, interpolations of 1% and 10% breakthrough times, and calculated curve geometric centroids (stoichiometric times and fractions) for the 618 curves. Theoretically, the stoichiometric times t_{sto} correspond to the first term of Equation 1. With Nelson's data and using Equation 1 we have calculated 1% breakthrough adsorption rate coefficients $k_{v,1\%}$ for each breakthrough curve by:

$$k_{v1\%} = \frac{\rho_B Q}{W} \left[\frac{t_{sto} \ln(99)}{t_{sto} - t_{1\%}} \right] \quad (4)$$

As with the Lodewyckx/Vansant data, matrices of rate coefficients and breakthrough times at different prehumidified RHs and airstream RHs were set up. Those at dry ($\leq 50\%$ RH) conditions were averaged and used as the references for ratios $k_{v1\%}\phi/k_{v1\%}(\text{Dry})$ and $t_{1\%}\phi/t_{1\%}(\text{Dry})$ at higher prehumidified and/or airstream RHs.

Results

When we plotted ratios of rate coefficients, $k_v\phi/k_v(\text{Dry})$, against ratios of breakthrough times, $t_b\phi/t_b(\text{Dry})$, we obtained linear correlations with positive intercepts.

The following figure (*Figure 1*) is an example of this for carbon tetrachloride on R1 Extra carbon (Lodewyckx/Vansant data).

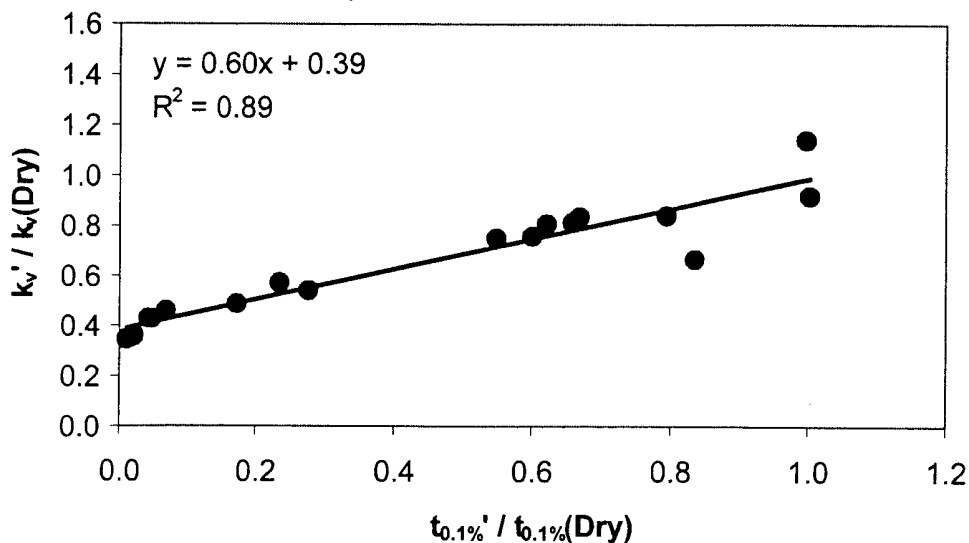


Figure 1. Plot of wet/dry ratios of adsorption rate coefficients vs. wet/dry ratios of 0.1% breakthrough times for carbon tetrachloride on R1 Extra carbon (Lodewyckx and Vansant, 2000).

The next figure (*Figure 2*) shows such results from all nine Lodewyckx/Vansant chemical/carbon combinations at 5 g/m^3 concentrations.

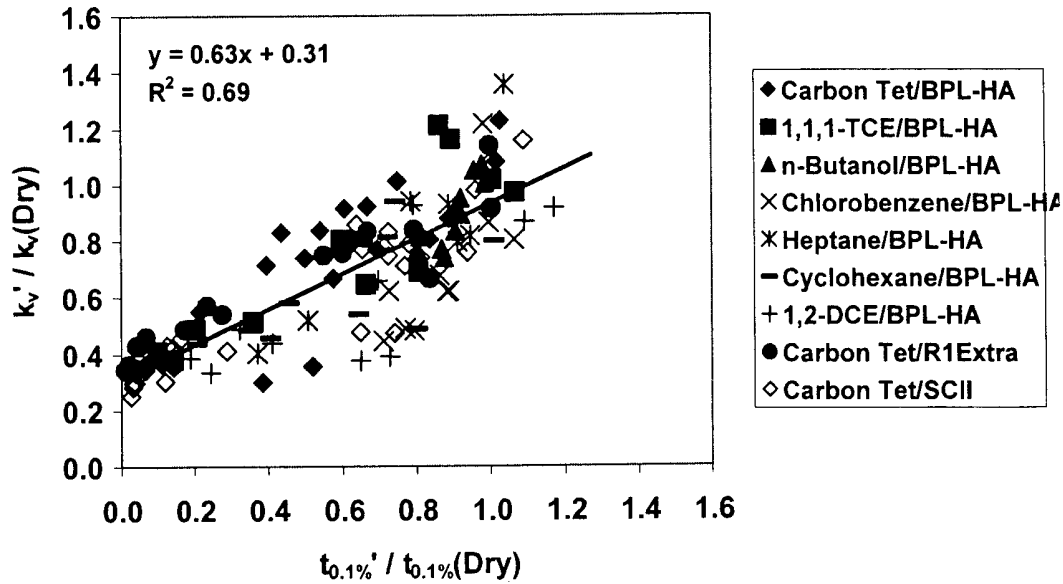


Figure 2. Plot of adsorption rate coefficient ratios vs. 0.1% breakthrough time ratios for nine chemical/carbon combinations from Lodewyckx and Vansant (2000).

The next figure (Figure 3) shows the plot of these ratios for seven Nelson et al. chemical/carbon combinations at 1000-ppm vapor.

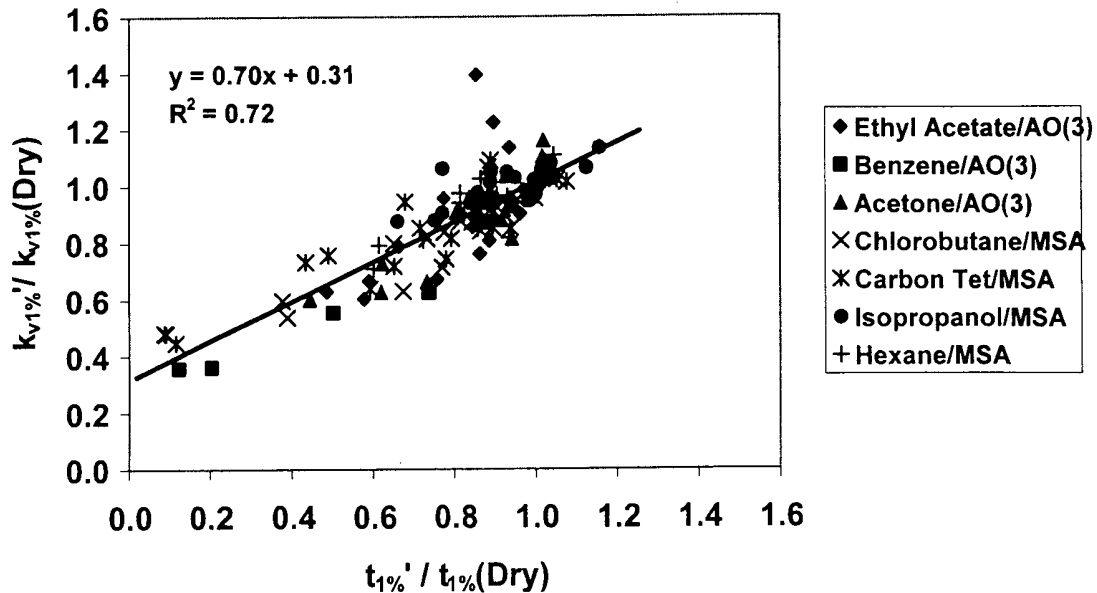


Figure 3. Plot of adsorption rate coefficient ratios vs. 1% breakthrough time ratios for seven chemical/cartridge combinations from Nelson (1988).

The next figure (Figure 4) shows the same for vapor concentrations from 100 – 2000 ppm, 50% prehumidified

RH, 80% airstream RH, and four organic vapors on two types of cartridges [benzene/MSA, methyl acetate/MSA, methyl chloroform/MSA, and acetone/AO(3)].

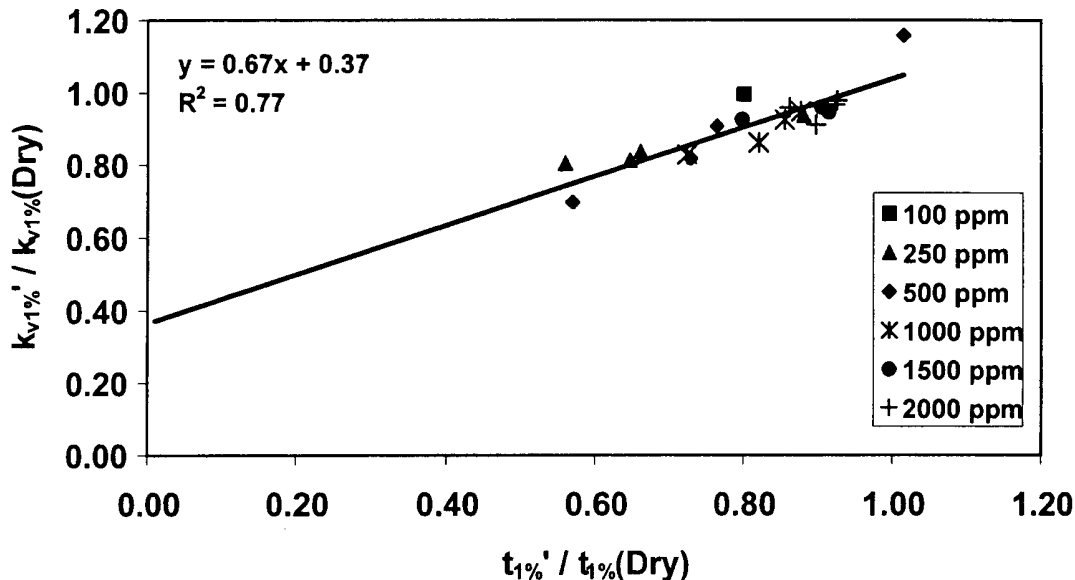


Figure 4. Ratio plots for a range of vapor concentrations for four vapor/cartridge combinations at 50% prehumidified RH and 80% airstream RH.

Minimum least squares best-fit lines and equations are shown on the graphs. The R^2 values also shown are squares of the Pearson product moment correlation coefficient.

Discussion and Conclusions

The Nelson et al. ratios at 1000 ppm and the Lodewyckx/Vansant ratios at 5 g/m^3 are plotted together in Figure 5. The standard least squares fit of the 248 data points gives an intercept of 0.30 and a slope of 0.68. However, since breakthrough time $t_b \phi @ t_b(\text{Dry})$ as capacity $W_e \phi @ W_e(\text{Dry})$ and rate coefficient $k_v \phi @ k_v(\text{Dry})$, this plot must go through the point (1,1) and the slope and intercept must total 1.00. The number of degrees of freedom for best-fit and error analyses can be reduced from two to one by requiring that Slope = 1 - Intercept.

Another observation from Figure 5 is that the scatter around the best-fit line increases with increasing ratios. An examination of residuals showed that relative rate coefficient ratio residuals (those divided by the corresponding calculated rate coefficient ratios) were more constant than residuals themselves. Using the above relationship between Intercept and Slope, we found the best-fit line (Intercept = 0.33 and Slope = 0.67), which minimized the sum of the squares of relative residuals.

We also calculated a relative standard deviation of 0.163 or 16.3% of a best-fit line value. This corresponds to 95% confidence limits of $\pm 32\%$, shown in Figure 5.

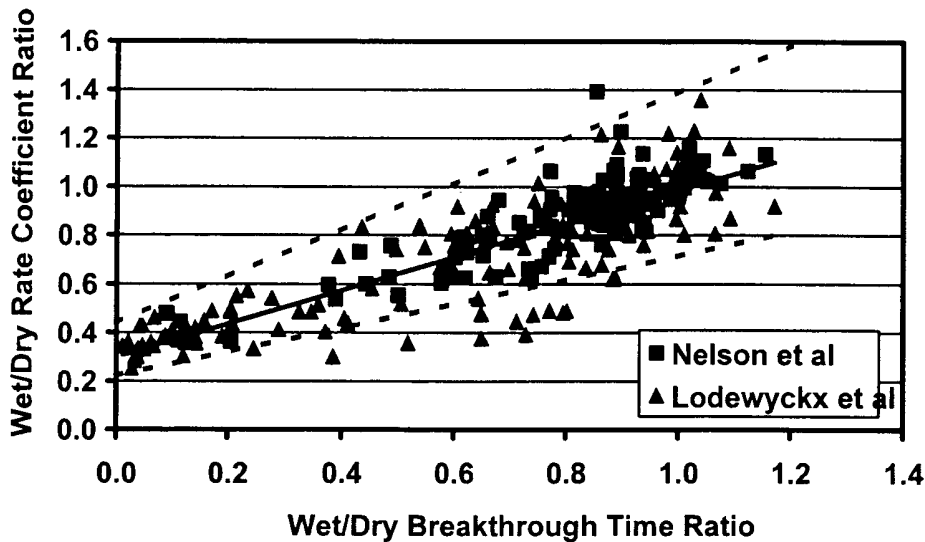


Figure 5. Plot of adsorption rate coefficient ratios vs. breakthrough time ratios for two extensive data sets with a total of 248 data points. Dashed lines represent 95% confidence limits.

Summary

In summary,

$$k_v' = k_v(\text{Dry}) \left[0.33 + 0.67 \left(\frac{t_b'}{t_b(\text{Dry})} \right) \right] \quad (5)$$

This relationship is consistent with data at both 0.1% and 1% breakthrough fractions. It is apparently independent of organic vapor concentration (Figure 4). The uncertainty in $k_v\phi$ is $\pm 32\%$ from the correlation plus the uncertainty contributed by $k_v(\text{Dry})$. How much these contribute to the uncertainty in the calculation of breakthrough time (cartridge service life) depends on the relative magnitudes and uncertainties of the two terms in Equation (1).

We must note that since t_b is itself a function of k_v (Equation 1), Equation 5 can only be solved by an iteration process. However, this is easily done by using a computer.

By combining Equations 3 and 5,

$$t_b' = t_b(\text{Dry}) \left[1 - \left(\frac{A_{\text{tot}}}{0.67\text{TPV}} \right) \right] \quad (6)$$

From this we see that as A_{tot} , the pore volume filled with water, approaches 67% of the total pore volume (TPV), the breakthrough time $t_b\phi$ approaches zero. This is a combined effect of the loss of micropore volume (adsorption space) and slower kinetics due to replacement/steric hindrance in the whole pore system.

References

- Lodewyckx, P. and E.F. Vansant. (2000) The influence of humidity on the overall mass transfer coefficient of the Wheeler-Jonas Equation. *Am. Ind. Hyg. Assoc. J.* 61:461-468.
- Lodewyckx, P. and E.F. Vansant. (1999) Influence of humidity on adsorption capacity from the Wheeler-Jonas Model for prediction of breakthrough times of water immiscible organic vapors on activated carbon beds. *Am. Ind. Hyg. Assoc. J.* 60:612-617.
- Nelson, G.O. and A.N. Correia. (1976) Respirator cartridge efficiency studies: VIII. Summary and conclusions. *Am. Ind. Hyg. Assoc. J.* 37:514-525.
- Nelson, G.O. (1988) Private communication. Miller-Nelson Research, Inc., Monterey, CA.
- Wood, G.O. and E.S. Moyer. (1989) A review of the Wheeler Equation and comparisons of its applications to organic vapor respirator cartridge breakthrough data. *Am. Ind. Hyg. Assoc. J.* 50:400-407.

