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ESTIMATING SERVICE LIVES OF ORGANIC VAPOR CARTRIDGES

Gerry O. Wood

Los Alamos National Laboratory, University of California, Industrial
Hygiene and Safety Group, MS K-486, Los Alamos, NM 87545

Procedures were developed for estimating service lives of air-purifying organic vapor respirator cartridges, including methods for untested compounds and use conditions (concentration, temperature, and airflow rate). Correlations of adsorption capacities and adsorption-rate coefficients based on equilibrium and breakthrough curve data were reviewed. These correlations were combined using the Reaction Kinetic (modified Wheeler) equation to estimate breakthrough times. The proposed estimation procedure showed 95% confidence intervals of up to ± 50% when no breakthrough data were assumed. It is shown how even limited breakthrough curve data for one vapor/carbon combination can be used to substantially improve accuracy of the estimation. Only dry conditions (below 50% relative humidity) have been considered so far.

“Will Brand X organic vapor cartridge work for vapor Y and for how long?” In the workplace many industrial hygienists face the option of using air-purifying respirators to protect workers from gases and vapors of harmful compounds. While this question seems simple, the answer to it is quite complex.

Air-purifying respirators and their associated organic vapor cartridges come in various designs and sizes. There are hundreds of thousands of organic compounds known, many of which are volatile enough and toxic enough to pose an inhalation hazard. The work practices and environmental conditions under which these compounds are used also can vary widely.

What is needed is a way of incorporating all these variables into a model that will provide an immediate answer to this question without the delays and expenses of laboratory testing. Microcomputer technology should be useful in implementing this. The model must be founded on both experimental data and theoretical considerations.

While some experimental breakthrough time (service life), breakthrough curve, and adsorption-capacity data have been reported, they are only for limited sets of environmental conditions and numbers of compounds. For example, the extensive studies of Gary Nelson et al.(1-4) at Lawrence Livermore National Laboratory in the 1970s included only 121 gases and vapors. At the Los Alamos National Laboratory, breakthrough curves for 27 hydrocarbons and fluorocarbons have been measured and analyzed.(5) Cartridge manufacturers and other researchers have also developed data; however, these often are not readily available or are in varying formats.

This paper presents one step in a program to provide a useful model for service-life prediction, even for compounds and use situations for which no data are available.

BACKGROUND

The following information is required as input for estimating organic vapor respirator cartridge service lives.

(1) Activated carbon bed design, including type of carbon, carbon weight, packed bed volume, and micropore volume. This can be obtained from the manufacturer or by independent cartridge analysis.
(2) Environmental conditions in the workplace, such as temperature, relative humidity, vapor types, and concentrations. These can be measured or estimated for each situation.
(3) Use conditions, such as average breathing rate due to work load, and cartridge use protocol. These can be estimated or controlled.
(4) Adsorption capacity of the carbon for the vapor. This is determined by vapor properties, carbon properties, environmental conditions, and use conditions.
(5) Adsorption rate of the vapor on the carbon as air passes through the cartridge. This is determined by breathing rate and the nature of the vapor and carbon.

A number of equations have been proposed to describe the increase of vapor effluent from a cartridge with time (breakthrough curve) as air contaminated with gas or vapor at a selected concentration is passed through the cartridge at a selected airflow rate.(6) The Reaction Kinetic (RK) equation, solidly based on the elementary principles of Conservation of Mass and first order kinetics, was selected from among these as the model to use.(7) The modified Wheeler equation(6) and an equation developed by Yoon and Nelson(8) have the same mathematical form as the RK equation,(7) which can be expressed as:

$$t_b = \left(\frac{W_e W}{C_o Q}\right) - \left(\frac{W_e \rho_\beta}{k_v C_o}\right) \ln\left[\frac{C_o - C_x}{C_x}\right] \qquad \textbf{(1)}$$

where

t_b = breakthrough time (min)
C_x = exit concentration (g/cm^3)
C_o = inlet concentration (g/cm^3)
Q = volumetric flow rate (cm^3/min)
W = weight of carbon adsorbent (g)
ρ_β = bulk density of the packed bed (g/cm^3)
W_e = equilibrium adsorption capacity (g/g carbon)
k_v = adsorption rate coefficient (min^{-1}).

The first term on the right side of Equation 1 is the stoichiometric time, t_{sto}. It can be obtained for any shape of breakthrough curve as the centroid of the curve defined mathematically by the integral:

$$t_{sto} = \int_0^{\infty} (1 - C_x / C_o) dt = W_e W / C_o Q. \qquad \textbf{(2)}$$

It is proportional to the equilibrium adsorption capacity, which is attained either with very fast adsorption (k_v very large) or at very long times (C_x/C_o approaching unity). For symmetrical breakthrough curves, such as those described by the RK equation (and its equivalents), the breakthrough percent corresponding to t_{sto} is 50%; however, for unsymmetrical curves it may be higher or lower.

A number of equations have been proposed to describe the capacity of an adsorbent as a function of gas or vapor concentration.(9) The Dubinin/Radushkevich (D/R) adsorption isotherm equation has a parameter (the affinity coefficient, β) that correlates the adsorption isotherms of different compounds.(10) Because of this and other reasons discussed elsewhere,(9) the D/R equation was selected for capacity estimates:

$$W_o = W_o d_L \exp[-(K R^2 T^2/\beta^2)(\ln\{\rho/\rho_{sat}\})^2] \qquad \textbf{(3)}$$

where

W_o = carbon micropore volume (cm^3/g)
d_L = liquid density of adsorbate (g/cm^3)
T = absolute temperature (°K)
ρ = partial pressure corresponding to concentration C_x
ρ_{sat} = saturation vapor pressure at temperature T
R = ideal gas constant
K = carbon structural constant, and
β = affinity (similarity) coefficient

Absorption Capacities

In previous work(11) a database of 1350 adsorption capacities for dry commercial activated carbons (equilibrated at 50% relative humidity or less) was fit to the D/R equation. The carbon structural constant, K, and affinity coefficient, β, in Equation 3 were replaced by an empirical coefficient, b′, and a function of molar polarization P_e, to give:

$$W_e = W_o d_L \exp[-b' W_o P_e^{-1.8} R^2 T^2 (\ln\{\rho/\rho_{sat}\})^2] \qquad \textbf{(4)}$$

for

$$b' = 3.56 \times 10^{-5} mol^2 cal^{-2} cm_o^2 (cm_L^3/mol)^{1.8} \qquad \textbf{(5)}$$

Capacities for "special" activated carbons, organic acids, organic bases, gases, and solids were excluded from the databases(11) until their special properties could be considered. These were not in the 1350 data used.

Molar polarization can be calculated from liquid density, d_L, molecular weight, M_w, and refractive index, n_D, values extensively tabulated in handbooks:

$$P_e = \left(\frac{n_D^2 - 1}{n_D^2 + 2}\right) \frac{M_w}{d_L}. \qquad \textbf{(6)}$$

Alternately, P_e can be estimated quite well from only additive parameters based on molecular structure.(12)

The standard deviation of the model residuals (differences between model predictions and data) for capacities was 0.029 g/g carbon.(11)

Adsorption Rates

Also in previous work,(5) reciprocal rate coefficients were calculated from 1% and 10% breakthrough times and stoichiometric times for 685 breakthrough curves. Again, only data for experiments at or below 50% relative humidity were considered. The logarithm of the following equation was fit to the data:

$$1/k_{vb} = ((1/v_L) + 0.027)(I + S_b/P_e) \qquad \textbf{(7)}$$

with the results:

$I = 0.000825$ min − (cm/sec)
$S_{1\%} = 0.036$ min − (cm/sec) − (cm^3/mole)
$S_{10\%} = 0.050$ min − (cm/sec) − (cm^3/mole)

The subscript b in Equation 7 and those of S represent the percent breakthrough (1% or 10%) selected for calculations; the v_L is the linear airflow velocity (cm/sec). The I, $S_{1\%}$, and $S_{10\%}$ are empirical coefficients from fitting the data to this model. For interpolation to other breakthrough percents:

$$S_b = 0.063 - 0.0058 \ln[(C_o - C_x)/C_x] \qquad \textbf{(8)}$$

The combined relative standard deviation of model residuals in $1/k_{vb}$ is 25%.(5)

BREAKTHROUGH CAPACITIES AND TIMES

The global correlations for adsorption capacities (Equations 4 and 5) and rate coefficients (Equations 7 and 8) have now been combined with Equation 1 to estimate breakthrough times and capacities. A subset(3) of the extensive Livermore data(1–4) was used to test this procedure. Average bed weights (56.1 or 62.2 g) and densities (0.375 or 0.389 g/cm^3) for the two types of cartridges were used, instead of those measured for each compound tested. Molar polarizations, vapor pressures, and liquid densities were obtained from Reference 3 or from data in Reference 12. Reported micropore volumes of 0.729 and 0.676 cm^3/g were used.(4) Other input conditions were 22 °C, 1 atm, 53.3 L/min airflow, corresponding linear velocities, and 1000 ppm concentration.

Since liquid densities are required for capacity calculations by Equation 4, 5-ethylidene-2-norborene, a solid at ambient conditions, was excluded from this comparison. Due to association with or dissolution in water preadsorbed on the carbon, the 12 amines in this data set also were excluded from the comparison. The calculated capacity value for methyl iodide was also a significant outlier (× 2) for some unknown reason.

Adsorption capacities calculated by Equation 4 can be compared with those reported in Table I of Reference 3 as "Wt. solvent adsorbed per wt of carbon, $t_{100\%}$." Calculated capacities for 107 compounds averaged 96% of experimental ones. This ranged from 3% for methyl chloride (the capacity model does not apply for gases)(11) to 123% for allyl acetate. The standard deviation and relative standard deviation of the model residuals (differences between calculated and actual values) were estimated using sample residuals (differences between calculated and experimental values) by the usual equations.(13) The standard deviation and relative standard deviation of capacities were estimated to be 0.044 g/g and 16%, respectively. Corresponding values for t_{s10} were 12 min and 17%. The distributions are assumed to be normal, so that the average of the model residuals is assumed to be zero.

Figure 1 shows comparisons of calculated and experimental 1% and 10% breakthrough times for the 107 compounds of this data subset. Overall standard deviations of breakthrough time residuals were 15 min and 12 min (relative standard deviations of 24% and 18%), respectively. Therefore, the 95% confidence intervals for the estimation procedure can be taken as about 50% and 40%, respectively. These uncertainties are in the range of variability of commercial organic vapor cartridges.(14)

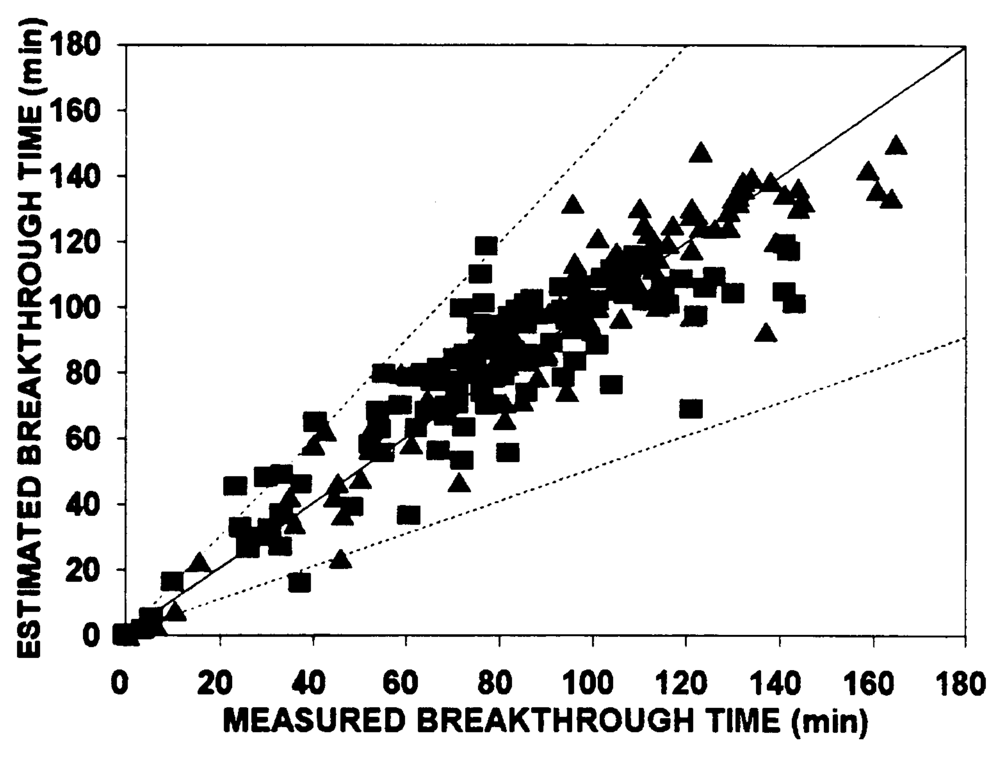

FIGURE 1. Comparison of breakthrough times estimated by the procedures in this paper with experimental values from data in Reference 3. Squares = 1% breakthrough; triangles = 10% breakthrough; solid line = equivalency; dashed lines = ± 50%.

When individual measured bed weights and densities, rather than average ones, were used in the breakthrough time calculations, the overall relative standard deviations were unchanged.

EXAMPLE OF ESTIMATING BREAKTHROUGH TIME

The cartridge Type 3 of Reference 4 is assumed with characteristics given in Table I of that paper (except that the 80 cm^3 carbon volume should be for one cartridge,(3) not for a pair, as incorrectly stated in the table footnote). A hexane challenge concentration of 500 ppm (0.38 torr at 1 atm) in 50% relative humidity air at 22 °C flowing through a pair of cartridges at a total of 53.3 L/min also is assumed. What is an estimate of the 50 ppm (10%) breakthrough time?

First, the equilibrium capacity is estimated by Equations 4 and 5:

$$W_e = (0.454)(0.6603)\exp[-(3.56 \times 10^{-5})(0.454)(29.877)^{-1.8}(1.987)^2(295)^2(\ln\{0.38/121\})^2] = 0.199 \text{ g/g},$$

where the liquid density of hexane is 0.6603 g/cm^3, the molar polarization is 29.877 cm^3/mole, and the saturation vapor pressure is 121 torr.

Second, the linear flow velocity for a bed cross-section of 39.6 cm^2 and two parallel cartridges is calculated:

$$v_L = \frac{(53.3)\left(1000\,\text{cm}^3/\text{L}\right)}{(39.6)(2)(60\,\text{s}/\text{min})} = 11.22\,\text{cm}/\text{s}.$$

Third, the reciprocal adsorption rate coefficient is estimated by Equations 7 and 8:

$$\begin{aligned} 1/k_{v10\%} &= [(1/11.22) + 0.027][0.000825 + (0.050/29.877)] \\ &= 2.9 \text{ x } 10^{-4}\text{ min} = 1/(3447\text{ min}^{-1}). \end{aligned}$$

Fourth, the total carbon bed weight is calculated to be W = (80)(2)(0.441) = 70.6 g and the vapor concentration in gravimetric units is $C_o = (500 \times 10^{-6})(86.16)/(24.217) = 0.00178$ g/L, where 86.16 g/mol is the molecular weight and 24.217 L/mol is the molar volume at 22 °C.

Finally, the 10% breakthrough time is estimated from Equation 1:

$$\begin{aligned} t_{b10\%} &= \frac{(0.199)(70.6)}{(0.00178)(53.3)} - \frac{(0.199)(0.441)}{(3447)\left(1.78\times10^{-6}\right)}\ln\{9\} \\ &= 117\,\text{min}. \end{aligned}$$

DISCUSSION

This sample breakthrough time estimate compares favorably (−18%) with the experimental value of 143 min in Table IV of Reference 4. However, the key word in this process is "estimate." Data from various sources have been combined using some simplifying assumptions and empirical correlations of parameters in theoretical relationships. The rate coefficient correlation has been obtained using data from only two sources, and its generality has yet to be established. Therefore, such estimates will never be as accurate as experimental data. However, in the absence of such data they can provide useful guidelines (within ± 50%) in making decisions on the applicability of organic vapor air-purifying respirators and the advisability of cartridge testing.

Estimates can be improved by knowing more about the carbon bed/vapor system. For example, having data from one entire breakthrough curve allows one to:

(1) Obtain t_{sto} by curve fitting or integration, as in Equation 2; calculate W_e at the experimental C_o by equating the first term of Equation 1 with t_{sto}; calculate W_o, the micropore volume, from W_e using Equations 4–6; and then estimate W_e for another concentration, vapor, and/or temperature by Equations 4–6;

(2) Obtain k_{vb} at two breakthrough percents, b, using $(W_eW/C_oQ) = t_{sto}$ and measured breakthrough time t_b in Equation 1; calculate S_b values from Equation 7, assuming I = 0.000825 min − cm/sec; express S_b as a function of C_x/C_o as in Equation 8; and then estimate k_v for another breakthrough percent, vapor, and/or flow velocity by Equation 7; and

(3) Combine estimates of W_o and k_v to calculate breakthrough time for another vapor, concentration, temperature, breakthrough time, and/or flow rate by Equation 1.

Having data from two or more breakthrough curves allows one to calculate b′, as well as W_o, from Equation 4; to calculate I, as well as S_b values, from Equation 7; and to check the effect of flow velocity on k_v, if flow rates differ by at least a factor of 4.

The estimation process given above incorporates vapor concentration, airflow rate, and temperature parameters. Relative humidity and mixed-vapor effects have yet to be included. The calculations shown can easily be performed on a microcomputer, or even a handheld calculator.

The data set of 107 experiments used to test the proposed estimation procedure was only a small part of the databases used to develop the correlation parameters. It was 8% of the capacity database and 16% of the rate database. Ideally, an independent data set would have been used; however, that would have required consciously omitting this data set from the correlations, with potential bias. Agreements with data presented above and in Figure 1 must be considered in light of the test data set being a subset of the correlation databases.

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