# A Review of the Wheeler Equation and Comparison of Its Applications to Organic Vapor Respirator Cartridge Breakthrough Data

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This project was undertaken to study the effect of dry airflow rate and bed weight on organic vapor respirator cartridge breakthrough curves for a single vapor (acetone) and challenge concentration (1060 ppm average). Dried cartridges from a single manufactured lot were used. The data were analyzed using three applications of the Wheeler equation, including (1) varying bed weight, (2) varying residence time, and (3) fitting the breakthrough curve. These approaches are discussed and equations given. Values for the adsorption capacity  $(W_e)$  and the rate coefficient  $(k_v)$  are presented and compared. Based on these comparisons, limitations of the Wheeler equation are discussed and guidelines given concerning its use.

## Introduction and Background

For respirator sorbent cartridges, the equilibrium sorbent capacity, although an important parameter, is less important than the sorbent bed breakthrough time for characterizing predictive performance. Numerous equations have been proposed for predicting sorbent bed breakthrough times. In 1920, Bohart and Adams<sup>(1)</sup> derived an equation for treating the breakthrough behavior of chlorine through charcôal. Mecklenburg<sup>(2,3)</sup> proposed his equation in the late 1920s in his study of gas mask filtration. Later, during World War II, Klotz<sup>(4)</sup> presented a modification of the Mecklenburg equation. Others who have proposed predictive equations include Danby et al., <sup>(5)</sup> Sillén, <sup>(6)</sup> Wheeler and Robell, <sup>(7)</sup> Van Dongen and Stamperius, <sup>(8)</sup> Nelson and Correia, <sup>(9)</sup> and Grubner (statistical moments).

Of these, a modification of the Wheeler equation is probably the most widely used. The Wheeler equation, originally derived for catalysis with bed poisoning, assumes that the rate-controlling removal process is first order and irreversible. It was initially derived from a continuity equation of mass balance between the gas entering an adsorption bed and the sum of the gas adsorbed by the bed and the gas penetrating through the bed. Jonas and coworkers, using a modification of the Wheeler equation for adsorption (Equation 1), have shown that the "adsorption capacity" and "rate coefficient" in a packed charcoal bed can be derived from the linear relationship between gas breakthrough time and sorbent weight. The modified Wheeler equation is

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

where

 $t_b$  = breakthrough time (min)  $C_x$  = exit concentration (g/cm<sup>3</sup>)  $C_o = inlet concentration (g/cm^3)$ 

Q = volumetric flow rate (cm<sup>3</sup>/ min)

W = weight of adsorbent (g)

 $\rho_{\beta}$  = bulk density of the packed bed (g/cm<sup>3</sup>)

 $W_e$  = adsorption capacity (g/g)

 $k_v = rate coefficient (min^{-1}).$ 

The values for  $C_o$ , W, and Q are established by the experimental test conditions, as is the temperature, which remains constant. The value of  $\rho_B$ , which is dependent on the fill weight, granular size, shape of the adsorbent, and fill volume, can be determined experimentally and is part of the manufacturer's production criteria.  $C_x$  is a time-dependent variable whose value of interest (ratio of  $C_{x/}$   $C_o$ ) may be preselected.

Rehrmann and Jonas<sup>(15)</sup> did a study on the dependence of gas adsorption rates on carbon granule size and linear flow rate. They showed, in accordance with adsorption kinetic theory, that although the adsorption capacity of the charcoal was invariant, the vapor breakthrough time for the bed varied. This was caused by the effect of the linear velocity, granule size, and granule shape on the rate coefficient  $(k_v)$ . If these parameters and temperature are fixed, however, then the rate coefficient also becomes fixed.

Thus, if one conducts experiments using charcoal beds of different weights (W) and determines the breakthrough times ( $t_b$ ) for a selected penetration fraction,  $C_x$ ,  $C_o$ , values for  $W_o$  and  $k_v$  can be calculated from Equation 1. Rewriting Equation 1 yields the following form:

$$t_b = \left(\frac{W_e W}{C_o Q}\right) - \left(\frac{W_e \rho_\beta}{k_v C_o}\right) \ln \left(C_o / C_x\right)$$
 (2)

If one plots the breakthrough time  $(t_b)$  as a function of the bed weight (W), the theory predicts that a straight line

results, where the slope and intercept allow calculation of the adsorption capacity and rate coefficient. The slope is equal to  $W_{\bullet}/C_{\circ}Q$ , and the y-axis intercept is equal to

$$\left(\frac{-W_e\rho_\beta}{k_vC_o}\right)\ln\left(\frac{C_o}{C_x}\right)$$
.

The x-axis intercept,  $W_c$  (critical bed weight), is equal to  $\rho_\beta$  Q ln  $(C_o/C_x)/k_v$ . By knowing the slope, a value for  $W_e$  (adsorption capacity) can be determined. Inserting  $W_e$  into the y-axis intercept relationship, one can calculate the rate coefficient  $k_v$ . Also,  $k_v$  could be calculated from the x-axis intercept value.

Further, it has been demonstrated that the modified Wheeler equation which Jonas and Rehrmann used to characterize small sorbent columns (1 to 2.5 g) at low volumetric flow rates (285 cm³/min) and small cross-sectional areas (0.833 to 4.23 cm²) holds for commercially available respirator cartridges when tested at a high flow rate (64 L/min). Organic vapor (OV) cartridges stacked to resemble a packed column of varying bed length and sorbent weight gave results with an acetone challenge vapor which were reproducible and showed good correlation ( $R^2 > .99$ ) when evaluated with the modified Wheeler equation. Values obtained for  $W_e$  and  $k_v$  suggested that significant differences were obtained when the experimental test conditions were changed.

Yoon and Nelson<sup>(19,20)</sup> have presented a gas adsorption kinetic model which basically is a further modification of the modified Wheeler equation and is similar in form to the Danby equation.<sup>(5)</sup> When the Yoon and Nelson equation is compared with the Wheeler equation, the major difference lies in the logarithmic concentration ratio term. Yoon and Nelson's model includes a correction term for reversibility of adsorption of the contaminant adsorbed. Thus, the  $\ln{(C_o/C_x)}$  Wheeler term becomes  $\ln{(C_o-C_x)/C_x}$ . This  $-C_x$  term becomes more important as the breakthrough percentage increases.

This correction accounts for the deviation between the experimental data and the Wheeler model at higher breakthrough concentrations. At breakthrough concentrations below 10%, however, this correction term is not significant ( $\leq 5\%$  error). The lower range (0-10% breakthrough) is the portion of the curve which is the most important for practical purposes. The form of the Yoon and Nelson equation is

$$t_b = \left(\frac{W_e}{C_o Q}\right) W - \left(\frac{\rho_\beta W_e}{k_\nu C_o}\right) \ln \left(\frac{C_o - C_x}{C_x}\right)$$
 (3)

which can be written as follows:

$$\ln\left(\frac{C_o - C_x}{C_x}\right) = -\left(\frac{k_v C_o}{W_e \rho_\beta}\right) t_b + \left(\frac{k_v W}{Q \rho_\beta}\right)$$
(4)

Thus, if one plots  $\ln{(C_o - C_x)}/C_x$  versus  $t_b$ , the model predicts that the slope will equal  $-k_vC_o/W_e\rho_\beta$  and the intercept will equal  $k_vW/Q\rho_\beta$ . This is the way that Yoon and Nelson<sup>(19)</sup> fitted large portions of Gary Nelson's breakthrough curves. This application of the Wheeler equation was first proposed by Jonas et al. (21) It differs from the other two approaches by

using data over a range of breakthrough concentrations and assuming  $W_e$  and  $k_\nu$  constant over this range.

Ackley<sup>(22)</sup> has proposed a residence time model for describing respirator sorbent beds. The longer the bed residence time, the greater the probability of reaction or adsorption. The relationship between breakthrough time and bed residence time fixes the model parameters and allows one to correlate data and predict bed performance. The residence time  $(\tau)$  is equal to the bed depth divided by the superficial velocity  $V_f$  (cm/sec) and thus can be expressed in terms of the volume of the sorbent  $V_1$  (cm<sup>3</sup>) and the airflow rate, Qair (L/min), as follows:

$$\tau (\text{sec}) = .06 \left( \frac{V_1}{\text{Qair}} \right)$$
 (5)

The volume of the sorbent is equal to the sorbent weight divided by the bed density. Thus,

$$\tau (\text{sec}) = \frac{W}{Q\rho_{\beta}} (.06)$$
 (6)

and residence time can be varied by changing bed size (W) and/or flow velocity (Q). The  $\tau$  term can be substituted in Equation 3 to give the following:

$$t_b = \left(\frac{W_e \rho_\beta}{C_o}\right) \left[\left(\frac{\tau}{.06}\right) - \left(\frac{1}{k_v}\right) \ln \frac{(C_o - C_x)}{C_x}\right]$$
 (7)

If one plots  $t_b$  versus  $\tau$ , the equation predicts a straight line with the slope equal to  $W_e \rho_B / .06 C_o$  and the intercept equal to  $-W_e \rho_B / C_o k_v \ln (C_o - C_x) / C_x$ .

In summary, three ways of applying the same modified Wheeler equation have been proposed: (1) varying sorbent bed weight, (2) varying penetration fraction, and (3) varying bed residence time. Each approach should yield the same values of  $W_{\bullet}$  and  $k_{v}$  from slopes and intercepts of straight line plots of experimental data. This paper will examine whether these different approaches produce the same results.

### **Experimental Materials and Methods**

The laboratory test system is as described by Moyer. (18) Dry air was used for all experiments and the cartridges (lot 42-2-85, cross-sectional area  $\approx 71~\text{cm}^2$ , Pulmosan, Flushing, N.Y.) were dried in a vacuum oven at  $100^{\circ}$  C for at least 24 hr before testing. Miran® 1A general purpose infrared gas analyzers (The Foxboro Co., Foxboro, Mass.) were used for continuous monitoring of the upstream and downstream vapor concentration. The analytical wavelength employed was  $8.2~\mu\text{m}$  for acetone. The acetone challenge was established by feeding solvent (syringe pump or Laboratory Data Control [Riviera Beach, Fla.] Minipump® Model 396) to the airstream at a predetermined rate.

The dried airstream containing the challenge vapor was pulled through the cartridge cell housing which contained four cartridges in series, as previously described. The spacer units allowed for the selecting of cartridges in series to resemble a packed column of varying bed length and sorbent weight as well as for the consecutive sampling of the gas

TABLE I
Acetone Breakthrough Times, Calculated Curves, and Experimental Conditions

Number of	Average Vapor Concentration	Average Air- Flow Rate	Total Charcoal	Bed Density	Docidono	40. 5	Breakthrough Curve Fit Parameters		
Cartridges 1	(ppm)	(L/min)	Weight (g)	(g/cm³)	Residence Time (sec)	1% Breakthrough Time (min)	W, (g/g)	k <sub>v</sub> (min <sup>-1</sup> )	R
2	1100	83.0	65. <b>8</b>	0.411	0.116	24	0.102	10 260	0.97
3	1100 1100	83.0	131.0	0.409	0.231	57	0.102		0.97
4	1100	83.0	192.7	0.481	0.347	89	0.108	12 630	0.96
1	1090	83.0	255.1	0.399	0.463	121	0.111	8910	0.990
2	1095	83.0	63.3	0.396	0.116	23	0.102	10 980	0.960
3	1090	83.0	126.1	0.394	0.231	57	0.111	10 510	0.967
4	1085	83.0	192.1	0.400	0.341	92	0.114	9740	0.988
1	1050	83.0	254.6	0.398	0.463	127	0.114	9900	0.975
2	1060	63.9	65.4	0.409	0.150	36	0.110	9140	0.963
3	1055	63.9	130.2	0.407	0.300	83	0.113	10 080	0.967
4	1045	63.9	192.4	0.401	0.451	127	0.114	10 210	0.970
1	10.70	63.9	257.6	0.403	0.601	173	0.113	9010	0.978
2	1080	63.9	62.1	0.388	0.150	33	0.112	8490	0.980
3	1080	63.9	128.5	0.402	0.300	82	0.118	8450	0.986
4	1080	63.9	194.1	0.404	0.451	128	0.115	9010	0.981
1	1020	63.9	257.7	0.403	0.601	173	9117	8920	0.983
2	1020	40.0	66.0	0.413	0.240	55 O.O98	0.080	7130	0.940
3	1025	40.0	132.4	0.414	0.480	125	0.100	7610	0.955
4	1030	40.0	194.4	0.405	0.720	193	0.103	7040	0.958
1	1090	40.0	259.9	0.405	0.960	26 <b>6</b>	0.105	6670	0.965
2	1070	40.8 40.8	65.8	0.411	0.235	57	0.112	6900	0.984
3	1075	40.8 40.8	131.0	0.409	0.471	124	0.112	6680	0.981
4	1080		192.7	0.401	0.70 <b>6</b>	192	0.113	6380	0.987
1	1050	40.8	255.1	0.399	0.941	261	0.115	6580	0.983
2	1035	32.4	66.5	0.416	0.296	69	0.100	6200	0.980
3	1035	32.4	130.4	0.408	0.593	151	0.101	6110	0.980
4	1030	32.4	192.1	0.400	0.880	233	0.103	5820	0.985
1	1030	32.4	256.7	0.401	1.185	320	0.103	5860	0.976
2	1015	31.9	62.5	0.391	0.301	73	0.106	7450	0.950
3	1010	31.9	126.1	0.394	0.602	159	0.104	8060	0.917
4	1010	31.9	190.2	0.396	0.903	245	0.104	6810	0.940
1		31.9	252.6	0.395	1.204	337	0.107	6340	0.950
2	1070	94.6	64.6	0.404	0.101	22	0.106	12 585	0.941
3	1070	94.6	127.5	0.398	0.203	52	0.110	15 350	0.896
	1060	94.6	189.7	0.395	0.304	82	0.111	16 620	0.929
4	1055	94.6	252.4	0.394	0.406	112	0.114	10 000	0.987
1	1060	94.3	61.9	0.397	0.102	20	0.102	10 660	0.964
2	1050	94.3	127.5	0.398	0.204	50	0.105	13 760	0.943
3	1045	94.3	190.6	0.397	3.05	79	0.106	12 130	
4	1045	94.3	254.6	0.398	0.407			13 640	0.980
1	1060	110.3	64.5	0.403	0.087			13 370	0.923
2	1055	110.3	133.2	0.416	0.174				0.939
3	1045	110.3	181.6	0.378	0.261			12 960 13 310	0.976
4	1045	110.3	266.0	0.416	0.348			13 310 10 780	0.980
1	1040	114.8	65.1	0.407	0.084			10 780	0.981
2	1040	114.8	130.1	0.407				11 230	0.976
3	1045	114.8	195.2	0.407	0.167			12 310	0.975
4	1045	114.8	260.6	0.407	0.251 0.334			14 720 13 680	0.959

downstream of each cartridge with an infrared (IR) closed-loop system configuration. After penetration of one cartridge reached approximately 20%, the downstream sampling line was switched to downstream of the next cartridge in the stack. Throughout the entire run, the challenge concentration ( $C_0$ ) was monitored continuously. Thus, four breakthrough curves ( $C_x$  versus time) could be obtained during a single experimental run.

The data collection was done automatically by means of a Tektronix Digital Processing Oscilloscope (DPO) (Tektronix, Portland, Oreg.) which was interfaced with a Digital PDP 11 computer ([32K word memory] Equipment Corp., Concorde, Mass.).

The system first was calibrated by introducing known concentrations of the component into a calibrated IR loop. The absorbance was monitored by the DPO as a function of concentration. The system then was ready to run. After zeroing the system, the minimum and maximum absorbance values and sampling intervals were entered. The cartridges were weighed and placed in the cell holder. The cell holder was connected to the downstream vacuum source and the flow rate through the system adjusted to the desired value between 32 and 115 L/min by means of a standard dry test meter. When final adjustments were completed, the inlet gas stream containing the acetone challenge was placed on-line and the computer monitoring system activated.

After all the cartridges had shown breakthrough (0.2% to 20%), the cell holder was removed and disassembled, and final weights were determined for the individual cartridges. Next, each individual cartridge was dismantled and the sorbent removed in order to obtain the weight of the empty cartridge case. From this weight the amount of sorbent present in each cartridge and the amount of sorbate adsorbed was calculated.

The data were entered into the computer, which calculated the upstream and penetration vapor concentrations and printed out a copy of the breakthrough curve (ppm ersus time) and upstream concentration (ppm versus time). These data then were stored on a disk for future data analysis. Also, from the fill volume of the cartridge and the orbent weight, a value for  $\rho_{\beta}$ , the bulk density of the packed ped (g/cm<sup>3</sup>), could be determined.

The number of points obtained in the 48 breakthrough curves measured, and even the breakthrough curves themselves, are too extensive to be given in this paper. Breakthrough times for the selected 1% breakthrough fraction were obtained from graphical interpolation of breakthrough curves plotted as  $C_x$  versus time and from average challenge concentrations,  $C_0$ .

These data were analyzed by Equation 3 and the three applications of it discussed in the Introduction. A standard y = a + bx linear least squares regression curve fit was used. This assumes significant experimental error only in the dependent y variable. Therefore, in the bed weight and residence time variation applications, the breakthrough time was the y variable. For the breakthrough fraction variation approach, the less certain  $\ln[(C_0 - C_x)/C_x]$  for selected times

was taken as the y variable. Regression coefficients (R) also were calculated as a measure of the linearity of the data fits.

#### Results and Discussion

Table I summarizes the experimental conditions, 1% breakthrough times, and total breakthrough curve fit parameters ( $W_e$ ,  $k_v$ , and R) for each of the 48 measurements. Duplicate experiments were in very good agreement. Average upstream challenge concentrations during each canister breakthrough are given in Table I. These, in turn, were averaged for the calculations using the bed weight variation and bed residence time variation approaches. The largest variation of  $C_o$  at a single flow rate was 40 ppm (4%) at 32 L/min. The range for the entire 48 experiments was 1020-1100 ppm (8%). An average cartridge volume of  $160 \, \mathrm{cm}^3$  was used for calculations.

Individual values from this table are plotted in Figure 1 as 1% breakthrough time versus total bed weight for four of the six flow rates. For clarity, the other two are not shown. As the Wheeler equation predicts, such plots are straight lines with slopes  $(W_e/C_oQ)$  that decrease with increasing airflow rate. Table II includes the slopes and intercepts of these plots at each flow rate and the parameters calculated from them by this application of the Wheeler equation.

In Figure 2, individual 1% breakthrough times are plotted against bed residence times for all 48 measurements at six airflow rates. This gives a very good linear correlation (R = 0.9985) yielding from Equation 7,  $W_e = 0.106 \ g/g$  and  $k_v = 11 \ 400 \ min^{-1}$ . When these data are broken into individual airflow rate subsets (Table III), however, distinct values of  $k_v$  are obtained, increasing with increasing airflow. The capacity parameter,  $W_e$ , is not a function of velocity.

Figure 3 shows the semilog plots predicted by Equation 4 to be linear. There appears to be some curvature to these plots, particularly below 1% penetration. Good correlations (R > 0.91), however, were obtained for all breakthrough curves, allowing calculation of the capacity and kinetic parameters listed in Table I. These are averaged for the airflow rate subsets in Table IV. Again,  $k_v$  increases significantly with airflow rate, while  $W_e$  is essentially constant.

When the adsorption capacity values,  $W_e$ , are compared (Table V), it can be seen that there is excellent agreement among the three methods. No significant effect was observed because of airflow rate, bed weight, or selected penetration fraction or range. The maximum between 64 and 83 L/min is not considered significant. The overall average  $W_e$  values were 0.112, 0.111, and 0.108 g/g for the bed weight, residence time, and breakthrough fraction variation methods, respectively.

The kinetic parameter, k<sub>v</sub>, however, differed with the various methods and was influenced by flow rate and selected penetration fraction. For example, at 32 L/min airflow, k<sub>v</sub> values of 4730, 5050, and 6580 min<sup>-1</sup> were obtained by the bed weight and residence time method (for 1% breakthrough) and by the breakthrough fraction method, respectively. At the highest flow rate used (113 L/min), the k<sub>v</sub> values were 9460, 8730, and 12 780 min<sup>-1</sup>, respectively. If one uses a 10% breakthrough percentage rather than 1%, the bed

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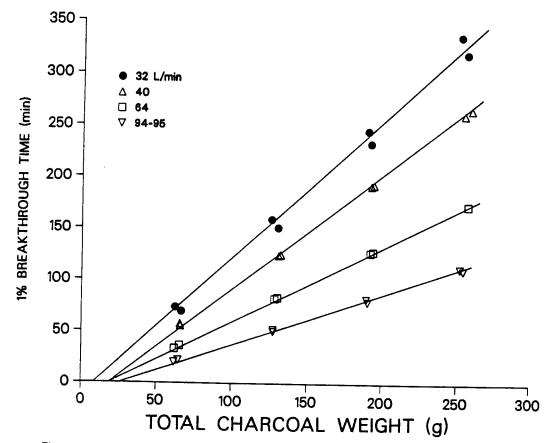


Figure 1—The 1% acetone breakthrough time versus total cartridge bed weight plots at four average airflow rates.

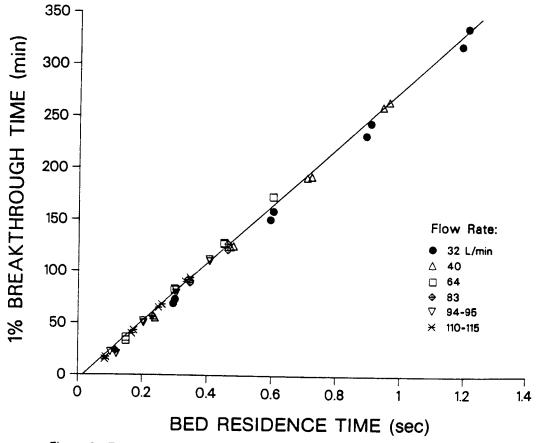


Figure 2—The 1% acetone breakthrough versus bed residence time for all airflow rates.

TABLE II

Modified Wheeler Equation Parameters Calculated by the Bed Weight

Variation Approach at Six Airflow Rates and 1% Breakthrough

Average Airflow Rate (L/min)	Average Challenge Conc. (ppm)	Linear Regression Fit Parameters			A	Adsorption	Rate	Critical
		Slope (min/g)	Intercept (min)	R	Average Bed Density (g/cm³)	Capacity W. (g/g)	Coefficient k <sub>v</sub> (min <sup>-1</sup> )	Bed Weight W <sub>c</sub> (g)
32.2	10 <b>30</b>	1.348	-16.830	0.997	0.400	0.100		
40.4	1050	1.085	-16.798	1.000		0.106	4730	12.5
63.9	1060	0.714		_	0.407	0.110	4880	15.5
83.0			-10.618	1.000	0.402	0.116	7940	14.9
	1100	0.527	-10.848	0.999	0.401	0.115	7440	=
94.5	1060	0.475	-9.430	0.999	0.396	0.113		20.6
112.6	1050	0.387	-8.569	0.996		_	8670	19.8
			5.503	0.390	0.405	0.109	9460	22.2

weight and residence time methods give  $k_{\nu}$  values of 3620 and 3870 min<sup>-1</sup> for 32 L/min. This observed effect of selected penetration fraction on calculated  $k_{\nu}$  suggests that the curve-fitting approach is less valid than the other two. The curvatures of the plots in Figure 3 also suggest this.

For the combined data (48 breakthrough curve measurements) employing the bed residence time method (Figure 2), the lowest value of  $W_{\rm e}(0.106~{\rm g/g})$  and the highest value of  $k_{\rm v}$  (11 400 min<sup>-1</sup>) were obtained. The combined  $k_{\rm v}$  was higher than any of the constant velocity residence time  $k_{\rm v}$ 's because of the enhanced influence of velocity when the data are handled this way.

#### Conclusions

The modified Wheeler equation is a simple model relating penetration fraction to breakthrough time with two adjustable parameters, We and kv. As noted, consistent values of the capacity parameter, We, were obtained by the three independent methods. This is what would be expected and is especially true for cases where the capacity term is dominant.

The rate parameter,  $k_v$ , however, is quite dependent on the method of data analysis, selected breakthrough fraction, selected functionality of the logarithmic term, and flow rate. One of the most interesting results was that the  $k_v$  values calculated by all three methods were approximately propor-

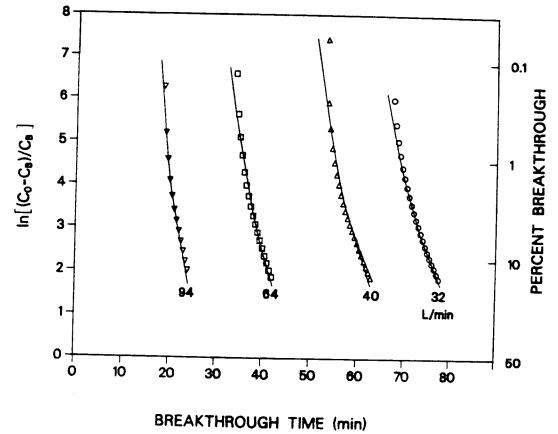


Figure 3—Semilog plots of acetone breakthrough curves for one cartridge at four airflow rates.

TABLE III

Modified Wheeler Equation Parameters Calculated by the Residence Time Variation Approach at Six Airflow Rates and 1% Breakthrough

Average Airflow		ar Regressi Parameter:	Adsorption Capacity	Rate Coefficient		
Rate (L/min)	Slope (min/g)	Intercept (min)	R	W. (g/g)	k <sub>v</sub> (min <sup>-1</sup> )	
32.2	287	-15.66	0.999	0.106	5050	
40.4	291	-13.52	1.000	0.108	5920	
63.9	307	-10.75	1.000	0.116	7860	
83.0	28 <del>9</del>	-10.15	0.999	0.113	7860	
94.5	296	-9.31	0.999	0.113	8770	
112.6	298	-9.41	1.000	0.110	8730	

TABLE IV
Modified Wheeler Equation Parameters
Calculated by the Breakthrough Curve
Fitting Approach at Six Airflow Rates

Average Airflow	Capacit	y, W <b>.</b> (g/g)	Rate Coefficient, k <sub>v</sub> (min <sup>-1</sup> )		
Rate (L/min)	Average	% Rel. Std. Dev.^	Average	% Rei. Std. Dev. <sup>A</sup>	
32.2	0.092	32.9	6580	12.2	
40.4	0.107	6.1	6870	5.6	
63. <del>9</del>	0.114	2.2	9160	7.2	
83.0	0.109	4.3	10 410	10.4	
94.5	0.108	3.4	13 090	17.1	
112.6	0.107	11.3	12 780	10.2	

<sup>&</sup>lt;sup>A</sup>n = 8

tional to the square root of the airflow rate. Similar airflow velocity dependences have been reported by others and generally are attributed to the effect of velocity on the diffusional and convectional transfer of molecules to the carbon surface from the flowing air. The implication of this dependence on airflow velocity is that breakthrough data at significantly different airflow rates should be examined carefully

before combining them to calculate a single  $W_e$  and  $k_v$  using the Wheeler equation. When the data were combined for all 48 experiments using the residence time variation approach, a significantly larger  $k_v$  resulted (Table V).

Thus, the modified Wheeler equation does not characterize the system completely and has limitations. Until the influences on k<sub>v</sub> are defined, this parameter will continue to be an empirical one with little physical significance and of limited use of extrapolating to other situations and conditions. In the meantime, the modified Wheeler equation can be used, but the following guidelines should be adhered to.

- 1. Bed weight variation for constant flow rate (or residence time variation for nearly constant flow rate) is the method of choice for data taking and analysis. In the case of canisters or cartridges, this can be accomplished by stacking two or more in series in the test flow system.
- 2. Data should be reported as slope, intercept, standard deviation, and linear correlation for breakthrough time versus bed weight (or residence time). Alternately, non-linear data fitting can be done.
- Calculated values of W<sub>e</sub> and k<sub>v</sub> must be accompanied by descriptions of the equations and parameters used to calculate them. This will allow recalculation by another model, if desired.
- 4. Breakthrough times should be measured at more than one breakthrough fraction, preferably differing by a factor of 10 and encompassing the range of interest in practical applications. For industrial organic vapor respirator applications, 1% and 10% are suggested.
- 5. In addition to bed weight variation, the effects of flow rate, challenge concentration, relative humidity, and temperature for each system should be examined by varying each of these in a systematic manner. This will allow application of the results to real situations, which usually differ from the laboratory test conditions.

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TABLE V

Comparison of Modified Wheeler Parameters Obtained by Three Approaches

Average Airflow Rate (L/min)	Adso	rption Capacit	y, W. (g/g)	Adsorption Rate Coefficient, k <sub>v</sub> (min 1)			
	Bed Weight Variation	Residence Time Variation	Breakthrough Curve Fitting	Bed Weight Variation	Residence Time Variation	Breakthrough Curve Fitting	
32.2	0.106	0.106	0.092	4730	5050	6580	
40.4	0.110	0.108	0.107	4880	5920	6870	
63.9	0.116	0.116	0.114	7940	7860	9160	
83.0	0.115	0.113	0.109	7440	7860	10 410	
94.5	0.113	0.113	0.108	8670	8770	13 090	
112.5	0.109	0.110	0.107	9460	8730	12 780	
Combined		0.106			11 400		
Averaged	0.112	0.111	0.108				

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# Third Supplement to NIOSH Manual of Analytical Methods, **Third Edition**

The third supplement to the NIOSH Manual of Analytical Methods, 3rd ed. is now in press and is expected to be mailed to subscribers in August/September 1989 by the U.S. Government Printing Office, Washington, D.C. (telephone [202] 783-3238). The supplement includes 35 methods involving 64 compounds (including 7 compounds for screening tests) and will be available in loose-leaf format. Improved sampling and analytical methods for MDA, total isocyanates, and bulk asbestos will be included in the supplement. Important changes to existing analytical methods include revisions to the methods for fibers, asbestos, mercury, silica, and formaldehyde.

Of particular importance is the fact that new methods or the revisions in the supplement are based on the new OSHA regulatory standards whenever applicable.

A transmittal notice advising the withdrawal or replacements and indexes of the existing NIOSH methods will be included with the supplement.

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