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16. Abstracts

The initial stages of the development of an improved certification program for organic vapor cartridges and canisters are described, which will ensure that cartridges and canisters provide adequate protection against the organic gases and vapors for which they are certified, and provide information to the user on the proper use and limitation of the device. Significant results of a literature review pertaining to adsorption are presented, together with a summary of laboratory tests conducted under the same project, a proposed test method for organic vapor respirator sorbents and recommendations for further research required to complete the development of an improved test method for organic vapor respirator sorbents.

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Support Division and the National Aeronautics and Space Administration (NASA) under interagency agreement NIOSH-IA-75-32 between NASA and the National Institute for Occupational Safety and Health (NIOSH). Mr. David L. Smith was the Project Officer for the Control Technology Research Branch, Division of Physical Sciences and Engineering, NIOSH. Mr. Dennis M. Smoot was the Principal Investigator for Bendix Launch Support Division, and Mr. Thomas A. Schehl was the Project Officer for NASA.

The purpose of this project was to begin development of a test method to be used in the certification of organic vapor respirator cartridges and canisters. This report and the recommendations contained herein will form the basis for continuing research to complete development of the improved test method.

Specific technical comments on this report are invited from interested individuals. These comments should be addressed in writing to the NIOSH Project Officer.

and L. The current bench test for organic vapor respirator sorbents requires successful performance against various atmospheres of carbon tetrachloride. It has previously been shown that the CCl_4 bench tests, as currently used by NIOSH, are not sufficiently indicative of the performance of respirator sorbents against the wide variety of organic vapors against which a NIOSH-approved respirator might ultimately be used.

The purpose of this project was to begin development of an improved bench test method for organic vapor respirator sorbents. The literature pertaining to adsorption capacity and dynamic breakthrough behavior of sorbents was reviewed. Based upon this review, a tentative approval scheme was proposed to NIOSH. This scheme was evaluated using adsorption data generated on this project.

This report presents significant results of a literature review of adsorption, a summary of laboratory tests conducted under this project, a proposed test method for organic vapor respirator sorbents and recommendations for further research required to complete development of an improved test method for organic vapor respirator sorbents.

using cartridges as received), and 32 liters/minute (four tests using cartridges equilibrated in humid air). Service life is defined as the length of time required to reach 5 ppm breakthrough; a service life of at least 50 minutes is required for approval. Successful performance by a cartridge against these tests results in its approval for all organic vapors.

Nelson and Harder [1] have published the results of a study conducted at the Lawrence Livermore Laboratory on the performance of commercially available organic vapor respirator cartridges against 121 different organic vapors and gases. Fifty-one of these gases and vapors produced shorter service lives than carbon tetrachloride. This includes vinyl chloride, a proven carcinogen, which gave a service life of 3.8 minutes. In a similar study carried out by Freedman et al [2] at the Bureau of Mines, approved cartridges were tested against 1000 ppm each of 29 organic vapors and gases. Sixteen of these gases had service lives shorter than the 50 minutes required in 30 CFR 11.

Many toxic gases and vapors do not have detectable odors at their threshold limit value (TLV). Since respirator cartridges currently do not have built-in service life indicators, workers could be exposed to dangerous concentrations of toxic vapors while wearing approved respirators.

For these reasons, NIOSH and NASA jointly contracted with the Bendix Launch Support Division to begin development of an improved certification program for organic vapor cartridges and canisters.

1.2 Purpose of the Study

The objective of this study is to begin development of an improved certification program for organic vapor cartridges and canisters which will:

1. Ensure that approved cartridges and canisters provide adequate protection against the organic gases and vapors for which they are certified.

2. Provide information to the user on the proper use and limitations of the device.

adsorbed; concentration; and flowrate through the bed. Because of all the variables involved, a particular carbon will have a specific adsorption capacity for each different compound; this adsorption capacity is a function of concentration.

When a stream of gas containing an adsorbable impurity is flowed through an adsorbent bed, most of the impurity is at first removed. However, as the charcoal approaches saturation capacity, more and more of the impurity passes through the bed without being adsorbed. Eventually, when saturation occurs, the effluent concentration equals the input concentration. The S-shaped plot of effluent concentration versus time is called the breakthrough curve. The quantity, or extent, of breakthrough is often referred to in terms of a certain percentage of the input concentration; thus if the input concentration is 100 ppm, 10 percent breakthrough occurs when the effluent concentration is 10 ppm. Service life of an adsorbent bed is defined in terms of the time required to reach a specified effluent concentration. Service life of an adsorbent bed is determined by the identity of the substance being removed, by its concentration, flowrate, the temperature, and other variables; service life is decreased by increasing the flowrate; by increasing the input concentration; and by increasing the temperature or humidity. In general, service life is less for small, low-boiling compounds than for other compounds.

Thus, a major problem in formulating a respirator cartridge certification program is the determination of the service life of a respirator cartridge without having to test each type of cartridge against each possible toxic organic vapor. The literature was searched to find the best methods for predicting service life and adsorption capacity.

which has been successful for this purpose is the use of various forms of the Polanyi potential theory. As used by Robell et al [3], the log of the amount absorbed, is plotted against the adsorption potential, A:

$$A = \frac{T}{V_m} \log (p_s/p)$$

where A = adsorption potential
T = temperature (°K)
V_m = molar volume at normal boiling point (cc/mole)
p_s = saturation vapor pressure (torr)
p = partial pressure (torr)

The potential plot gives a smooth line which is relatively straight at higher values of A, but which curves at values of A below about 10. Robell and coworkers found variations as great as 30 percent but recommended the use of the potential plot as the best correlation available. However, the curvature of the line makes calculation difficult, necessitating the use of graphs rather than straightforward calculations.

Dubinin [4] and coworkers discovered an empirical modification of the Polanyi potential theory which does give a straight line in many cases. This correlation is generally recognized as the best currently available for prediction of adsorption capacity in microporous solids. The Dubinin equation is written as follows:

$$w_s = \rho W_o \exp \left[- \frac{BT^2}{\beta^2} \left[\log(p_s/p) \right]^2 \right]$$

where w_s = adsorption capacity (grams solvent/gram adsorbent)
ρ = solvent density (g/cc)
W_o = maximum adsorption space (cc)
B = microporosity constant
T = temperature (°K)
β = affinity coefficient
p_s = saturation vapor pressure of the solvent at temperature T (torr)
p = equilibrium partial pressure of the solvent (torr)

tionships. Among the factors that may be used as affinity coefficients are molar volumes, electronic polarizations, and molecular parachors. Table 1 compares these methods.

TABLE 1

COMPARISON OF AFFINITY COEFFICIENTS

	$\beta(\exp)^1$	$\beta(P_e)^2$	$\beta(V_m)^3$	$\beta(\Omega)^4$
carbon tetrachloride	1.00	1.00	1.00	1.00
benzene	0.92	0.98	0.92	0.94
chloroform	0.87	0.79	0.83	0.83
ethyl acetate	0.85	0.83	1.01	0.98
methanol	0.34	0.31	0.42	0.40
tetrachloroethane	1.31	1.14	1.09	1.17

1. Experimental coefficients were taken from an article by Reucroft et al [5].

2. Electronic polarizations were calculated from the Lorenz-Lorentz equation:

$$P_e = \frac{n^2-1}{n^2+2}\,\frac{M}{\rho} ,$$

where n = refractive index, M = molecular weight, and ρ = density.

3. Molar volumes were calculated from molecular weights and densities at 20° C.

4. Molecular parachors were calculated from the equation:

$$\Omega = \frac{\gamma^{1/4} M}{\rho} ,$$

where γ = surface tension.

β	B	W_o	r	$S_{y \cdot x}$
Experimental	1.00×10^{-6}	0.60	0.9964	0.0599
P_e	0.82×10^{-6}	0.57	0.9952	0.0675
V_m	1.60×10^{-6}	0.73	0.9982	0.0459
Ω	1.43×10^{-6}	0.69	0.9989	0.0344

As can be seen from the correlation coefficients (r) and the standard errors of estimate of y from x ($S_{y \cdot x}$), the affinity coefficients calculated from molecular parachors give the best results for the six sample compounds selected. Unfortunately, surface tension data are not available for all compounds, so affinity coefficients for many compounds must be calculated from molar volumes. The most convenient source of affinity coefficients is molar volume ratios calculated from densities at 20° C. However, Robell [6] maintains that molar volumes at the normal boiling point should be used. There is little experimental data available on molar volumes at the boiling point, so Robell used approximation methods to determine these.

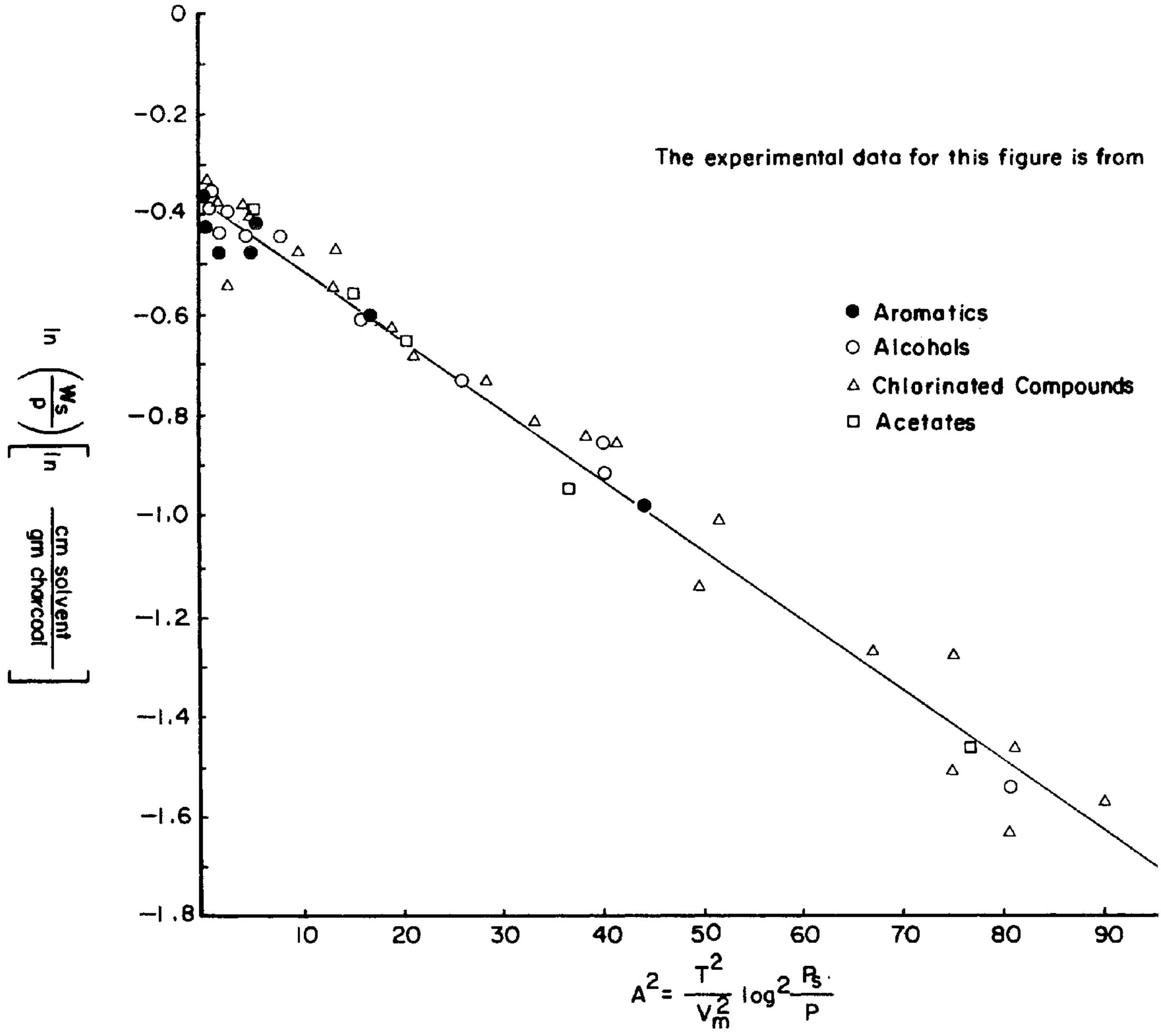
Jonas [5] recommends that affinity coefficients be calculated from electronic polarizations, using a reference compound from each of three groups: nonpolar, weakly polar, and strongly polar. This method has not as yet been tested with Nelson's data.

Nelson's data for type I cartridges was used to calculate regression lines, using molar volumes (59 points) and electronic polarizations (56 points), with the results shown in Table 3 (the molar volume data is plotted in Figure 1):

TABLE 3

DUBININ EQUATION RESULTS FOR NELSON'S TYPE I
CARTRIDGES USING TWO TYPES OF AFFINITY COEFFICIENTS

	B	W_o	r
V_m	1.62×10^{-6}	0.67	0.9898
P_e	0.9×10^{-6}	0.62	0.9851



The experimental data for this figure is from

Fig I. POTENTIAL PLOT FOR TYPE I CARTRIDGES

3.2.1 Bohart-Adams Equation

In a classical paper published in 1920, Bohart and Adams [7] treat the breakthrough behavior of chlorine through charcoal. They derived an equation for the breakthrough curve which may be written as follows:

$$\frac{c}{c_0} = \frac{a}{a_0} \exp[k(c_0 t - a_0 x/v)]$$

where c = breakthrough concentration
c_0 = input concentration
a = residual adsorption capacity
a_0 = initial adsorption capacity
k = adsorption rate constant
x = bed depth
v = flow rate of contaminant
t = breakthrough time

Because of the mathematical form of this equation and because of the difficulty in evaluating the variable a, this equation has not been tested during this study.

3.2.2 Mecklenburg Equation

If we assume that, at breakthrough time, the penetration of gas through the bed has been negligible, then it follows that:

weight of gas supplied = weight of gas adsorbed

The weight of gas supplied is equal to the flowrate L times the concentration c_0 times the duration of flow, t_b,$(t_b L c_0)$.

If we assume that adsorption is instantaneous and local to the extent of complete saturation, then there is a length h of the total column length z in which no adsorption has occurred. Therefore, all adsorption has occurred in z-h of the column. The weight of gas adsorbed equals the adsorption capacity N_0 times the volume of adsorbent $A(z-h)$.

A = cross-sectional area of the bed (cm^2)
L = volumetric flow rate (cm^3/min)
c_o = input concentration (g/cc)
z = bed depth (cm)
h = "dead layer" depth (cm)

This is the Mecklenburg equation, propounded by Mecklenburg in two articles on gas mask filtration in 1925 [8] and 1930 [9]. The "dead layer" depth h is assumed to be equal to the critical bed depth I; the critical bed depth is that value below which breakthrough would be instantaneous. The major difference between the various forms of the Mecklenburg equation is in the expression used to calculate I.

3.2.3 Klotz Equation

During World War II, a large amount of research on charcoal adsorption and breakthrough behavior was performed under the auspices of the National Defense Research Council. One of the results of this work is the so-called Klotz [10] equation, a variation of the Mecklenburg equation. As it is currently used, this equation is as follows:

$$t_b = \frac{w_s \rho_c A}{Q C_o} \left[z - \frac{1}{a_c \rho_c} \left(\frac{dG}{\eta} \right)^{0.41} \left(\frac{\eta}{\rho_a D} \right)^{0.67} \ln(C_o/C_b) \right]$$

where w_s = adsorption capacity (gram of solvent/gram of charcoal)
ρ_c = charcoal density (g/cc)
A = cross-sectional area of bed (cm^2)
Q = volumetric flow rate (liters/min)
z = bed depth (cm)
d = diameter of adsorbent particle (cm)
G = mass flow rate (g/cm^2-sec)
η = viscosity of air-vapor mixture (g/cm-sec)
a_c = specific surface area (cm^2/g)
ρ_a = density of air-vapor mixture (g/cc)
D = diffusion coefficient of the vapor (cm^2/sec)
C_b = breakthrough concentration (g/liter)
C_o = input concentration (g/liter)
t_b = breakthrough time (min)

above, I_t is expressed as a function of the Reynolds number, dG/η, the Schmidt number, $\eta/\rho_a D$, and the log of the input/effluent concentration ratio. The specific function used is due to Gamson [11] et al. The derivation of this equation for I_t assumes the ratio C_o/C_b is large; it should be used only for breakthrough less than 20 percent. The equation was derived for turbulent flow, but it appears to hold for laminar flow through charcoal.

The Klotz equation gives fairly accurate breakthrough times for some types of compounds. However, small, low-boiling compounds such as methanol, ethanol, propanol, methyl chloride, vinyl chloride, and ethyl chloride break through much quicker than is predicted by the equation. Table 4 compares experimental and calculated 1 percent breakthrough times. The experimental values of w_s from Nelson's [1] Type I cartridges were used in the calculations.

3.2.4 Danby Equation

The following breakthrough equation was published by Danby et al [12] in 1946:

$$t = \frac{1}{kc_o}\left[\ln[\exp(kN_o\lambda/L)-1] - \ln(c_o/c - 1)\right]$$

where k = adsorption rate constant (cc/g-min)
N_o = adsorption capacity (cc/g)
λ = bed depth (cm)
L = linear flow rate (cm/min)
c_o = input concentration (g/cc)
c = effluent concentration at time t (g/cc)
t = breakthrough time (min)

This equation has not been evaluated in this study because the mathematical form of the equation makes determination of the constants k and N_o difficult.

mesitylene	105	93.8	-10.7
p-cymene	92.9	87.8	-5.5
methanol	3.2	12.1	+278
ethanol	45.3	76.9	+69.8
2-propanol	81.8	109	+33.3
allyl alcohol	105	130	+23.8
propanol	111	133	+19.8
sec-butanol	121	122	+0.8
butanol	141	142	+0.7
2-pentanol	111	118	+6.3
3-methyl-1-butanol	121	120	-0.8
4-methyl-2-pentanol	96.1	105	+9.3
pentanol	130	126	-3.1
2-ethyl-1-butanol	101	113	+11.9
methyl chloride	0.7	3.3	+371
vinyl chloride	6.6	12.7	+92.4
ethyl chloride	10.7	15.4	+43.9
2-chloropropane	35.9	43.4	+20.9
allyl chloride	44.6	52.7	+18.2
1-chloropropane	34.8	51.0	+46.6
2-chloro-2-methylpropane	52.3	60.8	+16.3
1-chlorobutane	88.1	85.3	-3.2
2-chloro-2-methylbutane	79.3	82.3	+3.8
1-chloropentane	96.6	94.8	-1.9
chlorocyclopentane	106	108	+1.9
chlorobenzene	131	124	-5.3
1-chlorohexane	95.8	96.9	+1.1
o-chlorotoluene	122	117	-4.1
1-chloroheptane	101	91.1	-9.8
3-chloromethylheptane	80.5	80.4	-0.1
dichloromethane	15.8	24.9	+57.6
t-1,2-dichloroethylene	50.3	56.5	+12.3
1,1-dichloroethane	40.1	68.2	+70.1
c-1,2-dichloroethylene	42.6	62.9	+47.7
1,2-dichloroethane	79.7	95.0	+19.2
1,2-dichloropropane	90.3	99.8	+10.5
1,3-dichloropropene	110	111	+0.9
1,4-dichlorobutane	129	119	-7.8
o-dichlorobenzene	132	123	-6.8
chloroform	52.4	71.5	+36.5
methyl chloroform	58.9	80.8	+37.2
trichloroethylene	83.0	97.9	+18.0

1,1,2,2-tetrachloroethane	131	128	-2.3
pentachloroethane	117	112	-4.3
methyl acetate	46.5	60.1	+29.2
vinyl acetate	81.1	92.4	+13.9
ethyl acetate	84.7	81.6	-3.7
isopropyl acetate	85.6	103	+20.3
propyl acetate	99.0	101	+2.0
allyl acetate	95.6	104	+8.8
sec-butyl acetate	101	91.9	-9.0
butyl acetate	96.9	102	+5.3
isopentyl acetate	88.3	88.3	0.0
1,3-dimethylbutyl acetate	76.0	79.5	+4.6
pentyl acetate	87.3	93.3	+6.9
hexyl acetate	85.3	89.0	+4.3

Average deviation = +4.0 minutes.

The experimental data for this table is from Reference [1].

where t = breakthrough time (min)
B = adsorption capacity (g/cc)
c_o = input concentration (g/cc)
v_o = flow rate (cc/min)
V = volume of adsorbent (cc)
c = effluent concentration (g/cc)
k = adsorption rate constant (min)

If the volume terms in this equation are converted to weight terms, the equation is identical (except for reciprocal rate constants) to the modified Wheeler equation discussed below.

3.2.6 Modified Wheeler Equation

Jonas and coworkers [**5**,14 through 18] have used the following breakthrough equation, a modification of an equation derived by Wheeler [19]:

$$t_b = \frac{w_s}{C_oQ}\left[W - \frac{\rho Q}{k}\ln(C_o/C_b)\right]$$

where t_b = breakthrough time (min)
w_s = adsorption capacity (g/g)
C_o = input concentration (g/liter)
Q = volumetric flow rate (liters/min)
W = weight of charcoal (g)
ρ = density of charcoal (g/cc)
k = adsorption rate constant (min^{-1})
C_b = breakthrough concentration (g/cc)

In the Klotz variation of the Mecklenburg equation discussed previously (paragraph 3.2.3), diffusion is treated as the rate-controlling mechanism in contaminant removal. The derivation of the Wheeler equation assumes that the adsorption itself is rate-controlling, and that, at the beginning, the number of available adsorption sites is very much larger than the number of molecules being adsorbed. Regardless of the validity of the assumptions, the constant, k, becomes an overall mass transfer and adsorption rate

d_p = diameter of adsorbent particle (cm)
A = cross-sectional area of adsorbent bed (cm^2)
k = adsorption rate constant (min^{-1})
Q = flow rate (cc/min)

Using Nelson's [1] experimental data for Type I cartridges, the above equation gives a value of 6191 min^{-1} for k. Table 5 compares experimental 1 percent breakthrough times with those calculated from the Wheeler equation, using this value of k. Average densities and carbon weights were used in the calculations. Also shown in Table 5 are calculated times using the experimental constant for carbon tetrachloride (5688 min^{-1}). The times calculated using the maximum k deviate from the experimental more than those calculated from the Klotz equation (Table 4). Those calculated using the carbon tetrachloride constant are about the same as the Klotz times. Table 6 compares rates constants for different vapors. These constants were calculated from the Wheeler equation using Nelson's [1] experimental data. As can be readily seen from the table, these constants vary widely from the maximum value of k given above.

3.2.7. van Dongen Equation

Another equation similar to the two preceding was recently derived by van Dongen [20]:

$$t_b = E_g E_p H \left[\frac{L}{v} - \frac{d_p}{6E_g k} \ln(c_o/c) \right]$$

where t_b = breakthrough time (sec)
E_g = porosity parameter of charcoal bed
E_p = porosity parameter of charcoal pellets
H = adsorption capacity parameter
L = bed depth (cm)
v = real velocity of gas in bed (cm/sec)
k = adsorption rate constant (cm^4/g-sec)
c_o = input concentration (g/cc)
c = breakthrough concentration (g/cc)
d_p = diameter of carbon pellets (cm)

ethylbenzene	105	118	+12.4	112	+6.7
m-xylene	116	111	-4.3	105	-9.5
cumene	103	98.0	-4.9	93.1	-9.6
mesitylene	105	103	-1.9	98.0	-1.9
p-cymene	92.9	97.1	+4.5	92.3	-0.6
methanol	3.2	12.3	+284	11.7	+266
ethanol	45.3	79.7	+75.9	75.7	+67.1
2-propanol	81.8	114	+39.4	109	+33.3
allyl alcohol	105	136	+29.5	129	+22.9
propanol	111	140	+26.1	133	+19.8
sec-butanol	121	130	+7.4	123	+1.7
butanol	141	151	+7.1	144	+2.1
2-pentanol	111	128	+15.3	122	+9.9
3-methyl-1-butanol	121	130	+7.4	124	+2.5
4-methyl-2-pentanol	96.1	116	+20.7	110	+14.5
pentanol	130	137	+5.4	130	0.0
2-ethyl-1-butanol	101	125	+23.8	118	+16.8
methyl chloride	0.7	3.5	+400	3.3	+371
vinyl chloride	6.6	13.3	+102	12.6	+90.9
ethyl chloride	10.7	16.3	+52.3	15.5	+44.9
2-chloropropane	35.9	46.5	+29.5	44.2	+23.1
allyl chloride	44.6	55.6	+24.7	52.8	+18.4
1-chloropropane	34.8	54.6	+56.9	51.9	+49.1
2-chloro-2-methylpropane	52.3	66.0	+26.2	62.7	+19.9
1-chlorobutane	88.1	92.5	+5.0	87.9	-0.2
2-chloro-2-methylbutane	79.3	90.3	+13.9	85.8	+8.2
1-chloropentane	96.6	104	+7.7	98.6	+2.1
chlorocyclopentane	106	118	+11.3	112	+5.7
chlorobenzene	131	134	+2.3	127	-3.1
1-chlorohexane	95.8	107	+11.7	102	+6.5
o-chlorotoluene	122	128	+4.9	122	0.0
1-chloroheptane	101	102	+1.0	96.6	-4.4
3-chloromethylheptane	80.5	90.5	+12.4	86.0	+6.8
dichloromethane	15.8	26.1	+65.2	24.8	+57.0
t-1,2-dichloroethylene	50.3	60.6	+20.5	57.5	+14.3
1,1-dichloroethane	40.1	72.3	+80.3	68.7	+71.3
c-1,2-dichloroethylene	42.6	67.3	+58.0	64.0	+50.2
1,2-dichloroethane	79.7	101	+26.7	95.8	+20.2
1,2-dichloropropane	90.3	107	+18.5	102	+13.0
1,3-dichloropropene	110	119	+8.2	113	+2.7
1,4-dichlorobutane	129	130	+0.8	124	-3.9
o-dichlorobenzene	132	136	+3.0	129	-2.3
chloroform	52.4	76.1	+45.2	72.2	+37.8
methyl chloroform	58.9	87.0	+47.7	82.6	+40.2
trichloroethylene	83.0	104	+25.3	99.1	+19.4

1,1,2,2-tetrachloroethane	131	140	+6.9	133	+1.5
pentachloroethane	117	122	+4.3	116	-0.9
methyl acetate	46.5	63.3	+36.1	60.1	+29.2
vinyl acetate	81.1	99.5	+22.7	94.5	+22.7
ethyl acetate	84.7	87.1	+2.8	82.8	-2.2
isopropyl acetate	85.6	111	+29.7	105	+22.7
propyl acetate	99.0	109	+10.1	103	+4.0
allyl acetate	95.6	113	+18.2	108	+13.0
sec-butyl acetate	101	101	0.0	96.2	-4.8
butyl acetate	96.9	112	+15.6	107	+10.4
isopentyl acetate	88.3	98.3	+11.3	93.4	+11.3
1,3-dimethylbutyl acetate	76.0	89.2	+17.4	84.8	+11.6
pentyl acetate	87.3	104	+19.1	98.5	+12.8
hexyl acetate	85.3	99.9	+17.1	94.9	+17.1
		average deviation= +12.0 min		average deviation= +7.1 min	

The experimental data for this table is from Reference [1].

m-xylene	0.536	4.41	0.4034	59.7	116	5607
cumene	0.538	5.00	0.4110	60.0	103	5618
mesitylene	0.565	4.99	0.4048	59.5	105	4932
p-cymene	0.594	5.57	0.3845	56.9	92.9	4508
methanol	0.018	1.33	0.3743	55.4	3.2	1073
ethanol	0.168	1.92	0.3801	55.5	45.3	1672
2-propanol	0.314	2.50	0.3841	55.7	81.8	2246
allyl alcohol	0.362	2.42	0.3821	55.4	105	2607
propanol	0.384	2.50	0.3868	55.7	111	2763
sec-butanol	0.438	3.08	0.3882	55.9	121	4516
butanol	0.512	3.08	0.3881	55.5	141	4628
2-pentanol	0.517	3.67	0.3857	56.7	111	3220
pentanol	0.552	3.67	0.3716	55.0	130	5106
3-methyl-1-butanol	0.525	3.67	0.3741	55.0	121	4630
4-methyl-2-pentanol	0.545	4.28	0.3764	55.7	96.1	2985
2-ethyl-1-butanol	0.582	4.25	0.3713	55.7	101	2780
methyl chloride	0.008	2.10	0.3764	55.7	0.7	1006
vinyl chloride	0.038	2.60	0.3789	55.7	6.6	1470
ethyl chloride	0.048	2.68	0.3791	56.1	10.7	1918
2-chloropropane	0.167	3.27	0.3838	56.8	35.9	2436
allyl chloride	0.194	3.18	0.3936	55.5	44.6	2922
1-chloropropane	0.196	3.27	0.3822	55.8	34.8	1887
2-chloro-2-methylpropane	0.279	3.85	0.3878	57.0	52.3	2568
1-chlorobutane	0.391	3.85	0.3848	55.8	88.1	4938
2-chloro-2-methylbutane	0.439	4.43	0.3851	57.0	79.3	3294
1-chloropentane	0.505	4.43	0.3864	56.8	96.6	4076
chlorocyclopentane	0.562	4.35	0.3808	55.6	106	3937
chlorobenzene	0.688	4.68	0.3822	55.8	131	5649
1-chlorohexane	0.591	5.02	0.3720	55.8	95.8	3674
o-chlorotoluene	0.741	5.26	0.3801	55.5	122	4994
1-chloroheptane	0.625	5.60	0.3700	55.5	101	6250
3-chloromethylheptane	0.614	6.18	0.3764	55.7	80.5	3691
dichloromethane	0.101	3.53	0.3847	55.4	15.8	1818
t-1,2-dichloroethylene	0.268	4.03	0.3841	55.7	50.3	3064
1,1-dichloroethane	0.327	4.12	0.3881	55.5	40.1	1667
cis-1,2-dichloroethylene	0.298	4.03	0.3840	55.3	42.6	1916
1,2-dichloroethane	0.456	4.12	0.3840	55.3	79.7	2786
1,2-dichloropropane	0.554	4.70	0.3848	55.8	90.3	3155
1,3-dichloropropene	0.606	4.62	0.3857	56.7	110	3944
1,4-dichlorobutane	0.755	5.28	0.3808	55.6	129	6218
o-dichlorobenzene	0.911	6.11	0.3925	57.3	132	4763
chloroform	0.415	4.97	0.3861	55.6	52.4	2139
methyl chloroform	0.530	5.55	0.3903	56.2	58.9	2054

1,2,3-trichloropropane	0.915	6.13	0.3823	56.2	132	[illegible]
carbon tetrachloride	0.677	6.40	0.3847	55.4	90.0	4697
perchloroethylene	1.01	6.90	0.3815	55.7	129	5365
1,1,2,2-tetrachloroethane	1.07	6.98	0.3788	55.3	131	4767
pentachloroethane	1.13	8.41	0.3869	56.1	117	4901
methyl acetate	0.214	3.08	0.3808	55.6	46.5	2345
vinyl acetate	0.391	3.58	0.3757	55.6	81.1	2878
ethyl acetate	0.350	3.66	0.4179	60.6	84.7	3830
isopropyl acetate	0.507	4.16	0.3938	57.1	85.6	2457
propyl acetate	0.507	4.25	0.3855	55.9	99.0	4055
allyl acetate	0.517	4.16	0.3791	56.1	95.6	3081
sec-butyl acetate	0.537	4.83	0.3855	55.9	101	6325
butyl acetate	0.595	4.83	0.3716	55.0	96.9	3488
isopentyl acetate	0.584	5.41	0.3770	55.8	88.3	3792
1,3-dimethylbutyl acetate	0.588	6.00	0.3745	55.8	76.0	3177
pentyl acetate	0.616	5.41	0.3764	55.7	87.3	3114
hexyl acetate	0.658	6.00	0.3750	55.5	85.3	3277

Average k = 3599

Standard Deviation = 1356

The experimental data for this table is from Reference [1].

$$t_{10} = \frac{7.6 \times 10^5 W_c W_s}{MQ\sqrt{C}}$$

and $W_s = a + bt$

where W_c = weight of carbon (g)
W_s = weight of solvent adsorbed (g)
M = molecular weight
t_{10} = 10 percent breakthrough time (min)
Q = flow rate (liters/min)
C = concentration (ppm)
t = normal boiling point (°C)
a,b = coefficients determined by solvent type (See Table 7, taken from [21])

TABLE 7

COEFFICIENTS FOR NELSON'S EQUATION [21]

Solvent Class	a	b
Acetates	-0.050	0.0038
Alcohols	-0.46	0.0071
Alkanes	0.095	0.0022
Alkyl benzenes	0.12	0.0024
Amines	0.037	0.0033
Ketones	0.034	0.0029
Monochlorides	0.032	0.0033
Dichlorides	-0.092	0.0048
Trichlorides	-0.080	0.0058
Tetrachlorides	0.19	0.0049

When the adsorption of a substance from a moving gas stream is treated in rigorous mathematical detail, a system of partial differential equations results which is insoluble by ordinary analytical techniques. However, in some cases, the solution may be described by a series of statistical moments.

The first statistical moment indicates the location of the centroid of the area under the curve; it is the mean on the time axis. The second statistical moment expresses the variance of the probability density curve; the square root of the variance standard deviation, which defines the deviation of individual points of the curve from the mean. The third statistical moment is the specific asymmetry of the curve. The fourth is the "specific excess"; it furnishes information about the flattening of the distribution curve in comparison to the normal Gaussian curve.

The chromatographic curve can be generated from its moments by a series such as the Gram-Charlier series. Theoretically, the frontal (breakthrough) chromatogram can be generated from an elution (pulse) chromatogram by means of statistical moments. However, the mathematics of this treatment is too complex to solve unless many simplifications of the various adsorption mechanisms are made. Work on the statistical moments theory of gas-solid chromatography is still going on and there are differences of opinion as to its utility for prediction of breakthrough curves.

In a paper published in 1968, Grubner [22] states that the statistical moments theory of gas-solid chromatography "may also have significance for interpreting the frontal, or the so-called breakthrough, curves in the chromatography of gases and liquids. On the other hand, it must be pointed out that experimental verification and utilization of this theory have overcome only the first steps and that the conclusions so far drawn may be of limited validity."

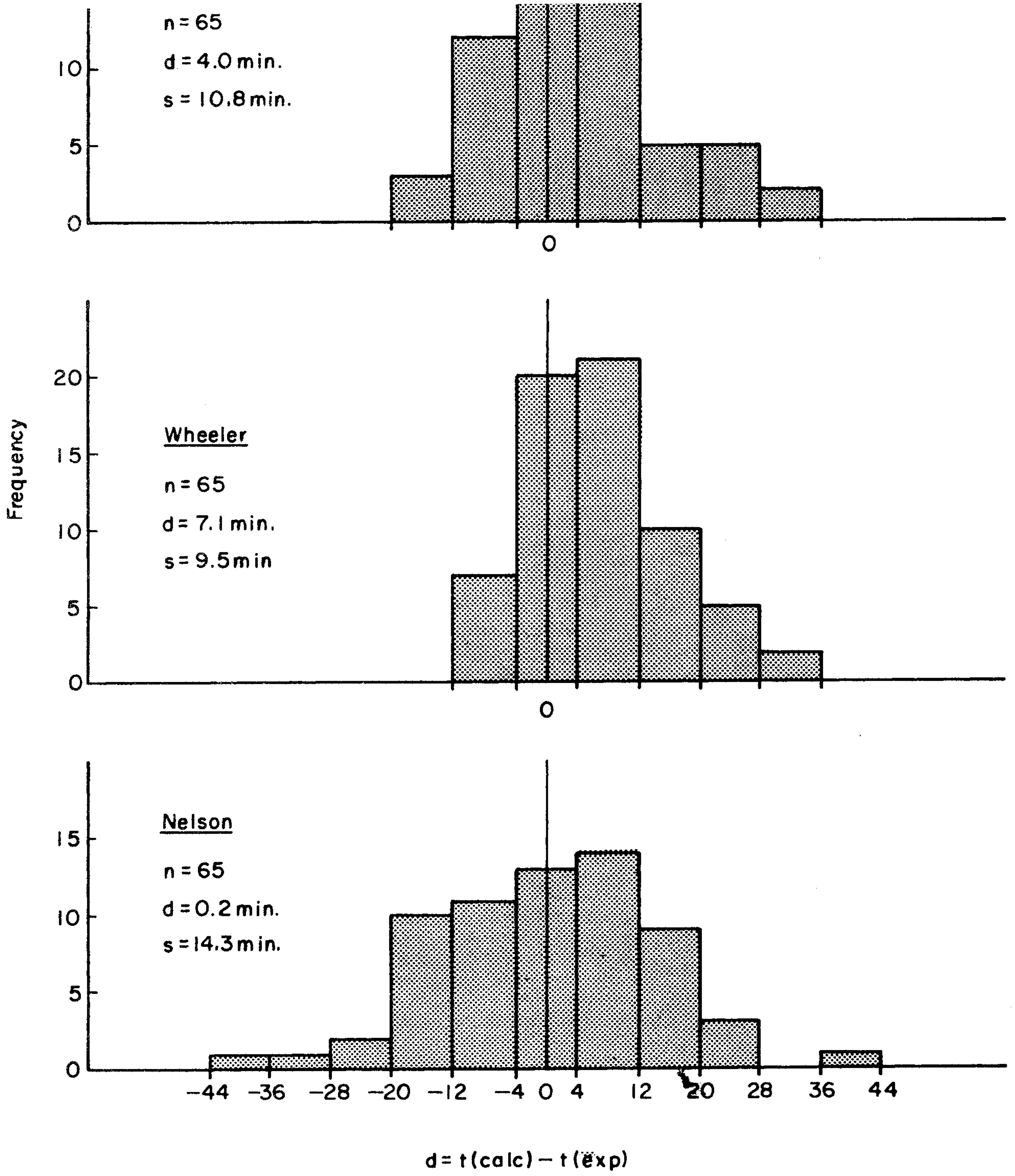
In a 1974 report, van Dongen and Stamperius [20] state that although the statistical moments theory is "quite valuable with respect to the improvement of the adsorption efficiency, it provides no direct insight in the shape of the breakthrough curve."

ethylbenzene	105	107	+1.9
m-xylene	116	108	-6.9
cumene	103	102	-1.0
mesitylene	105	109	+3.8
p-cymene	92.9	103	+10.9
methanol	3.2	-0.5	-116
ethanol	45.3	53.2	+17.4
2-propanol	81.8	52.4	-35.9
allyl alcohol	105	99.8	-5.0
propanol	111	96.7	-12.9
sec-butanol	121	84.3	-30.3
butanol	141	128	-9.2
2-pentanol	111	112	+0.9
3-methyl-1-butanol	121	136	+12.4
4-methyl-2-pentanol	96.1	118	+22.8
pentanol	130	149	+14.6
2-ethyl-1-butanol	101	144	+42.6
methyl chloride	0.7	-24.0	-3530
vinyl chloride	6.6	-5.6	-185
ethyl chloride	10.7	28.5	+166
2-chloropropane	35.9	47.8	+33.1
allyl chloride	44.6	59.2	+32.7
1-chloropropane	34.8	60.0	+72.4
2-chloro-2-methylpropane	52.3	54.7	+4.6
1-chlorobutane	88.1	78.8	-10.6
2-chloro-2-methylbutane	79.3	74.8	-5.7
1-chloropentane	96.6	92.6	-4.1
chlorocyclopentane	106	98.1	-7.5
chlorobenzene	131	105	-19.8
1-chlorohexane	95.8	100	+4.4
o-chlorotoluene	122	112	-8.2
1-chloroheptane	101	105	+4.0
3-chloromethylheptane	80.5	102	+26.7
dichloromethane	15.8	30.1	+90.5
t-1,2-dichloroethylene	50.3	37.4	-25.6
1,1-dichloroethane	40.1	45.9	+14.5
c-1,2-dichloroethylene	42.6	51.0	+19.7
1,2-dichloroethane	79.7	79.1	-0.8
1,2-dichloropropane	90.3	83.1	-8.0
1,3-dichloropropene	110	97.4	-11.5
1,4-dichlorobutane	129	137	+6.2
o-dichlorobenzene	132	133	+0.8
chloroform	52.4	58.4	+11.5
methyl chloroform	58.9	66.3	+12.6
trichloroethylene	83.0	81.3	-2.0

1,1,2,2-tetrachloroethane	131	137	+4.6
pentachloroethane	117	123	+5.1
methyl acetate	46.5	57.4	+23.4
vinyl acetate	81.1	66.4	-18.1
ethyl acetate	84.7	64.5	-23.8
isopropyl acetate	85.6	70.1	-18.1
propyl acetate	99.0	83.1	-16.1
allyl acetate	95.6	86.9	-9.1
sec-butyl acetate	101	81.5	-19.3
butyl acetate	96.9	93.6	-3.4
isopentyl acetate	88.3	94.9	+7.5
1,3-dimethylbutyl acetate	76.0	88.8	+16.8
pentyl acetate	87.3	100	+14.5
hexyl acetate	85.3	104	+21.9

Average deviation = +0.2 min.

The experimental data for this table is from Reference [1].


n = 65
d = 4.0 min.
s = 10.8 min.
10
5
0
0
Wheeler
n = 65
d = 7.1 min.
s = 9.5 min
Frequency
20
15
10
5
0
0
Nelson
n = 65
d = 0.2 min.
s = 14.3 min.
15
10
5
0
−44
−36
−28
−20
−12
−4
0
4
12
20
28
36
44
d = t (calc) − t (ëxp)

$$\frac{t_m}{t_d} = \frac{k}{w+k}$$

where t_m = breakthrough time using moist charcoal and moist air
t_d = breakthrough time using dry charcoal and dry air
w = weight of water adsorbed
k = a constant

Burrage and Allmand report that in some cases, moisture has a beneficial effect on the adsorption capacity of charcoal. They theorize that this is caused by the moisture's removal of oxide contamination from the charcoal surface.

Robell et al [3] studied the effect of humidity on removal of contaminants from spacecraft air. Their data show that adsorption capacity decreases with increasing humidity, and that the amount of change is temperature-dependent. They attribute this decrease in adsorption capacity to blockage of the adsorption sites by water molecules. Table 9, taken from reference [3] shows the percent blockage at different humidities and temperatures. Using the modified Polanyi theory that will be discussed in paragraph 3.4, they obtained reasonably good correlation of the moisture-contaminant adsorption data.

The most comprehensive work done on the effect of humidity on breakthrough times has been done by Nelson and coworkers at the Lawrence Livermore Laboratory [1,21,24]. In their most recent paper [24], they conclude that storage (preconditioning) and use humidities above 65 percent greatly reduce the service life of respirators. In addition, they conclude:

> "1. Both the precondition and use humidity alter the cartridge service life.
>
> 2. The use humidity has a greater effect than the preconditioning humidity.
>
> 3. Service life is approximately the same between 0 and 50 percent humidity.
>
> 4. Humidity has a greater effect on cartridge performance at lower concentrations (of solvent vapor)."

In this paper, Nelson compares experimental breakthrough times with those calculated from the Mecklenburg (Klotz) and Wheeler equations and states that no way has been found to modify these equations to account for the effect of moisture.

Contaminant	(°C)	(ppm)	at 25° C	(%)
n-Butane	26	25	42	28
n-Butane	27	26	63	79
n-Butane	26	26	89	95
n-Butane	67	26	42	0
n-Butane	65	26	63	0
n-Butane	64	26	89	0
Ethanol	26	24	42	5
Ethanol	27	27	63	30
Ethanol	27	20	89	65
Ethanol	66	20	42	56
Ethanol	66	16	63	73
Ethanol	66	28	89	71

The potential factor, as written by Robell, is

$$A = \frac{T}{V_m}\log(P°/P)$$

where A = potential factor
T = absolute temperature
V_m = molar volume
P = partial pressure
$P°$ = vapor pressure

Substituting Raoult's law into the potential factor equation, we have:

$$A = \frac{T}{V_m}\left[\log X_i(P_i°/P_i)\right]$$

From the Polanyi potential theory, the following holds, since all curves are superimposable to one:

$$\frac{1}{(V_m)_1}\log\left[X_1(P_1°/P_1)\right] = \frac{1}{(V_m)_2}\log\left[X_2(P_2°/P_2)\right], \text{ etc.}$$

Since, by definition

$$X_1 = \frac{P_1}{\sum_{i=1}^{n} P_i}$$

then $X_1 + X_2 + X_3 \cdots X_n = 1$

Robell and coworkers used this treatment to correlate solvent-water data, and propane-butane, ethylene-propane, and butane-toluene data.

where N_i = number of moles of component i

N_i' = adsorption capacity for pure component i (moles)

Lewis reports that this relationship gave mixture adsorption values within 6 percent of the experimental value in most cases tested.

This method is self-explanatory and obviously the least desirable because of the large amount of testing required. This method would, of course, give the most reliable results.

4.2 Method 2 - Test each device against certain gases and vapors representative of chemical structure groups.

Under this method, all organic compounds would be divided into groups, according to chemical structure. Examples of such structural groups are alcohols, alkanes, amines, ketones, aldehydes, and aromatics. The lowest molecular weight compound from each group which gives an acceptable service life could be chosen as the test compound from that group. Then, if the device is certifiable against the test compound, it would be certified against all compounds of higher molecular weight within that group.

4.3 Method 3 - Test each device against gases and vapors classified according to the service time they give against commercially available sorbents.

Organic compounds would be divided into groups according to service life against commercially available respirator cartridges. For example, in the paper by Nelson [1] on the effect of solvent vapor, those compounds tested against type I cartridges could be grouped as follows:

0-19 minutes - 5 compounds
20-40 minutes - 11 compounds
50-69 minutes - 11 compounds
70-89 minutes - 24 compounds
90-115 minutes - 14 compounds

One compound would be chosen from each group for testing. If the device being tested is certifiable against the test vapor, it would be certified against all compounds from its group.

4.4 Method 4 - Test each device against selected gases and vapors and calculate service life for other pertinent gases and vapors.

A compound or compounds would be chosen which would act as predictors for all organic compounds. Mathematical prediction of service life could be made with the modified Wheeler equation. If only one test

4.5 Method 5 - Other schemes which may seem practical as well as various combinations of schemes.

Some possibilities are as follows:

(1) Continue testing as present and rely on published literature for service lives against compounds other than carbon tetrachloride.

(2) Calculate service lives from equations which do not require experimental data. For example, Nelson's [21] empirical equation requires only that the weight of carbon be known, and the Klotz equation requires only cartridge dimensions and various carbon properties.

(3) Use of different equations for different circumstances. For instance, the Klotz equation might be used to predict the service lives of the compounds for which it is accurate. Another method would be found for the small, low-boiling compounds for which the Klotz equation is inaccurate.

example, if a device could be tested one time against two different vapors per day, then it would require 8 months' work and 1,200 man-hours to test the device against 300 different organic vapors. After initial testing, quality control tests would have to be performed on a routine basis to ensure that previously determined service lives are being maintained. This method would put an even greater burden on NIOSH Testing and Certification Laboratory (TCL), since it would have to test each type of device from each manufacturer against all toxic organic vapors.

5.2 Method 2

The testing of one compound from each structural group would require a great deal of testing without giving very much information in return. If the test compound were chosen as described in paragraph 4.2, then only the minimum service life, not the actual service life, would be known for the other compounds in the group.

5.3 Method 3

The grouping of compounds according to the service life they give against commercially available sorbents is not a promising certification scheme. It has the following disadvantages: (1) a lot of testing would be required, (2) it would be difficult to assign previously untested compounds to the proper group, and (3) it is not known if the rankings by service life would be the same for all types of cartridges and canisters.

5.4 Method 4

The use of one or a few compounds as predictors for all other compounds would be the ideal method, since testing would be minimized. However, the success of this method depends on the use of accurate predictive formulae, and none have been found. If the modified Wheeler equation were used for prediction, the accuracy of the results would depend on the choice of a reference compound. Since not all gases and vapors are adsorbed at the same rate, it would not give accurate breakthrough results for all gases and vapors, using the same rate constant for all gases and vapors. If a reference compound with a low rate constant were chosen, then the service lives against strongly adsorbed vapors would be underestimated; this would be preferable, however, to the use of a compound with a large rate constant, which would cause overestimation of service life for weakly adsorbed compounds. More

The main drawback to the dependence on published literature for information on cartridge and canister service life is that not all devices have been tested against a large number of vapors. Even those devices that have been tested most extensively have not been tested against all toxic organic gases and vapors.

The use of predictive equations which do not require experimental data would be satisfactory, of course, if the equations give accurate results. Nelson's empirical equation fits his data for a number of compounds, but the equation was probably fitted to this data. The Klotz equation gives accurate breakthrough times for certain types of compounds, if charcoal and cartridge parameters are accurately known. These parameters would have to be determined for each different type of device.

The apparatus works as follows: compressed air passes through a pressure regulator into a constant differential flow controller. The regulated airflow is filtered and passed through the humidifier. The humidifier is a three-neck flask encapsulated in a heating mantle; any desired humidity can be obtained by appropriate control of water level and temperature. The humidified air flows out of the humidifier through the sensor of a Hastings Model AHL mass flowmeter with a range of 0 to 100 liters per minute. Solvent is injected into the airstream by a Sage Model 355 syringe pump; the needle of the syringe is heated to the boiling temperature of the solvent by a cartridge-heated block, the temperature of which is regulated by a proportional temperature controller. Just downstream of the syringe needle is a pulsation dampener which consists of activated carbon between two glass wool plugs. The pulsation dampener smooths out concentration pulsations caused by the tendency of the solvent to form droplets on the needle. Until conditions of flowrate, concentration, and humidity are stabilized, the vapor-air stream flows through a bypass leg; pressure drop in the bypass is adjusted with a valve to match the pressure drop of the test cartridge. Pressure is measured with an oil manometer calibrated in inches of water. After conditions have stabilized, the gas flow is routed through the test cartridge. Concentration of organic vapor in the gas stream may be measured either upstream or downstream of the test cartridge by analysis with a flame ionization detector. Samples are removed from the system by a stainless-steel-bellows sampling pump and 1/8-inch stainless-steel sampling lines. The system manifold is fabricated from 1/2-inch stainless-steel lines and A/N fittings.

The cartridge holder is shown in Figure 4. Basically, it is a cylindrical plexiglass tube large enough to accommodate standard-sized commercially available respirator cartridges. The back-end and the adjustable backing plate are stepped to fit cartridges of different diameters. After the test cartridge is inserted between the back-end of the holder and the adjustable backing plate, the end-plate is screwed down against the backing plate until the test cartridge is sealed in place.

The reusable test cartridge is shown in Figure 5. It was designed by Bendix and fabricated by the NASA prototype shop at the Kennedy Space Center. This cartridge has a diameter of 7.0 centimeters, a depth of 2.2 centimeters, and a volume of 85 cubic centimeters. It is fabricated from Teflon with gauze filters and stainless-steel screen. One retaining ring is held in place by screws, while the other wedges in and is held in place by the cartridge holder. The metal rings at each end of the cartridge were added after initial testing indicated that channeling was taking place along the walls of the cartridge. The addition of these rings effectively minimized the channeling problem.

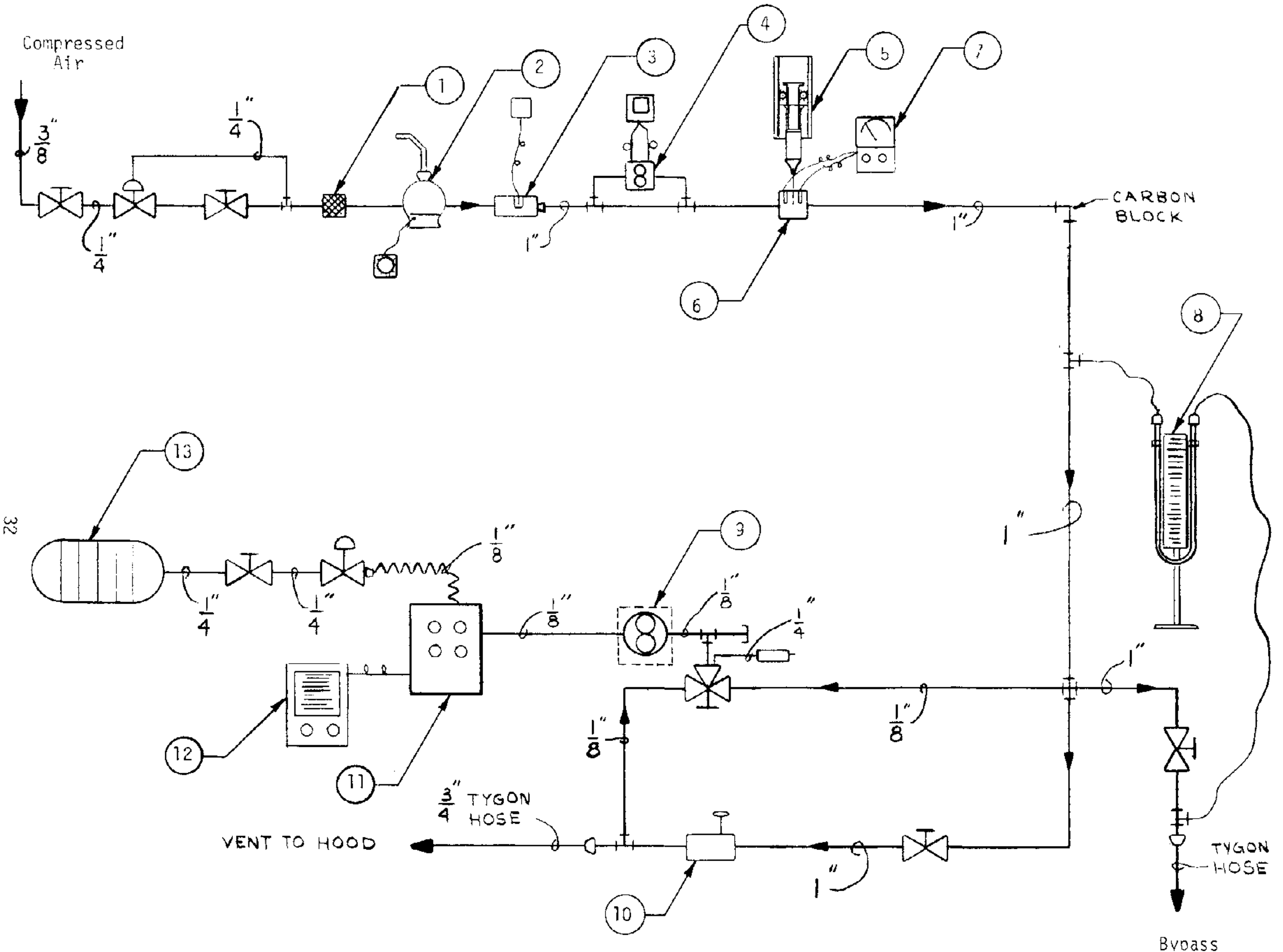


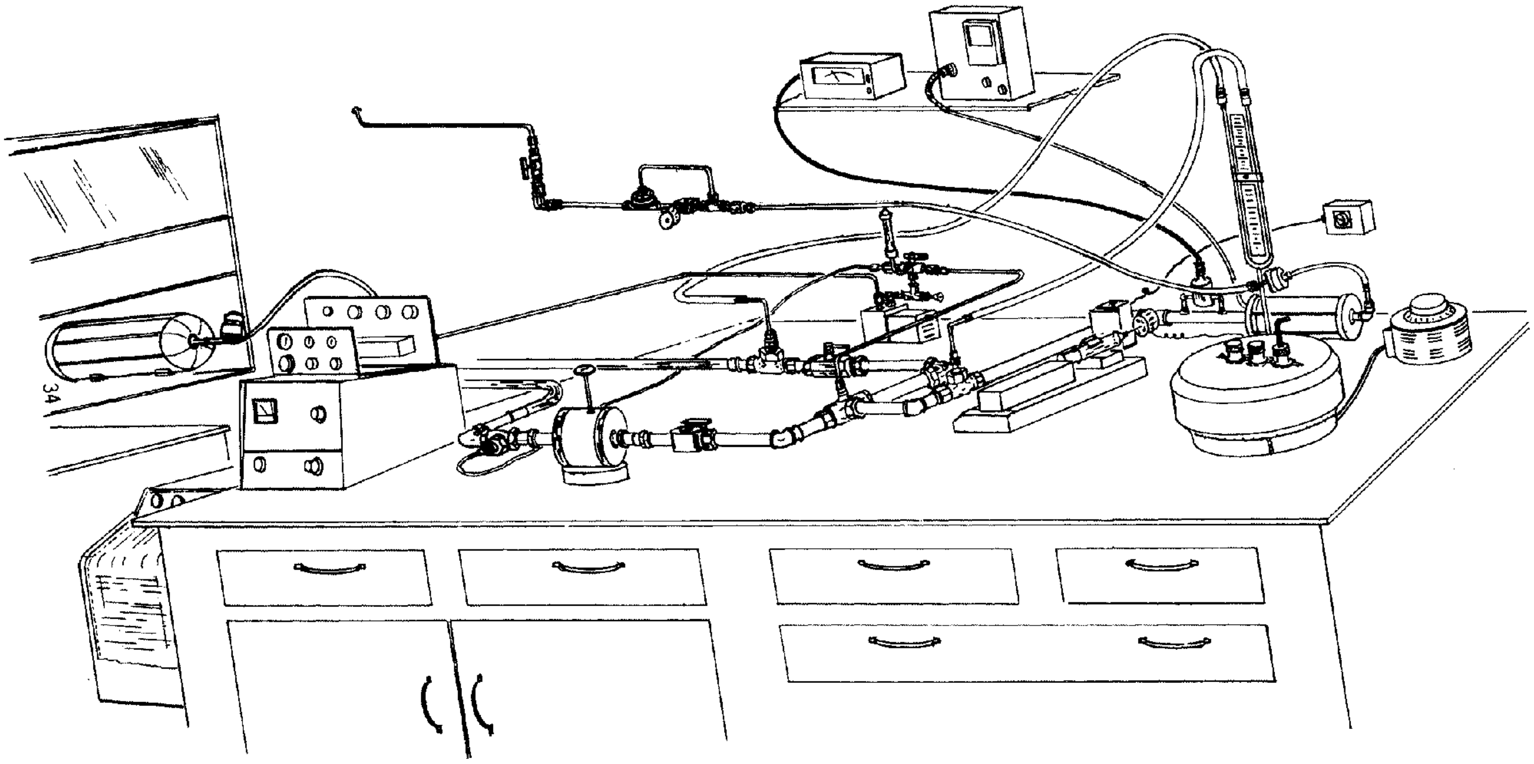
FIGURE 3 (Sheet 1 of 2)
TEST APPARATUS SCHEMATIC

2. Humidity generator
3. Humidity sensor
4. Mass flowmeter
5. Syringe pump
6. Heated block
7. Proportional temperature controller
8. Manometer
9. Sampling pump
10. Cartridge holder
11. Hydrocarbon analyzer (F.I.D.)
12. Integrating recorder
13. Calibration gas for F.I.D.

FIGURE 3 (Sheet 2 of 2)
TEST APPARATUS SCHEMATIC

FIGURE 4

TEST APPARATUS, PICTORIAL



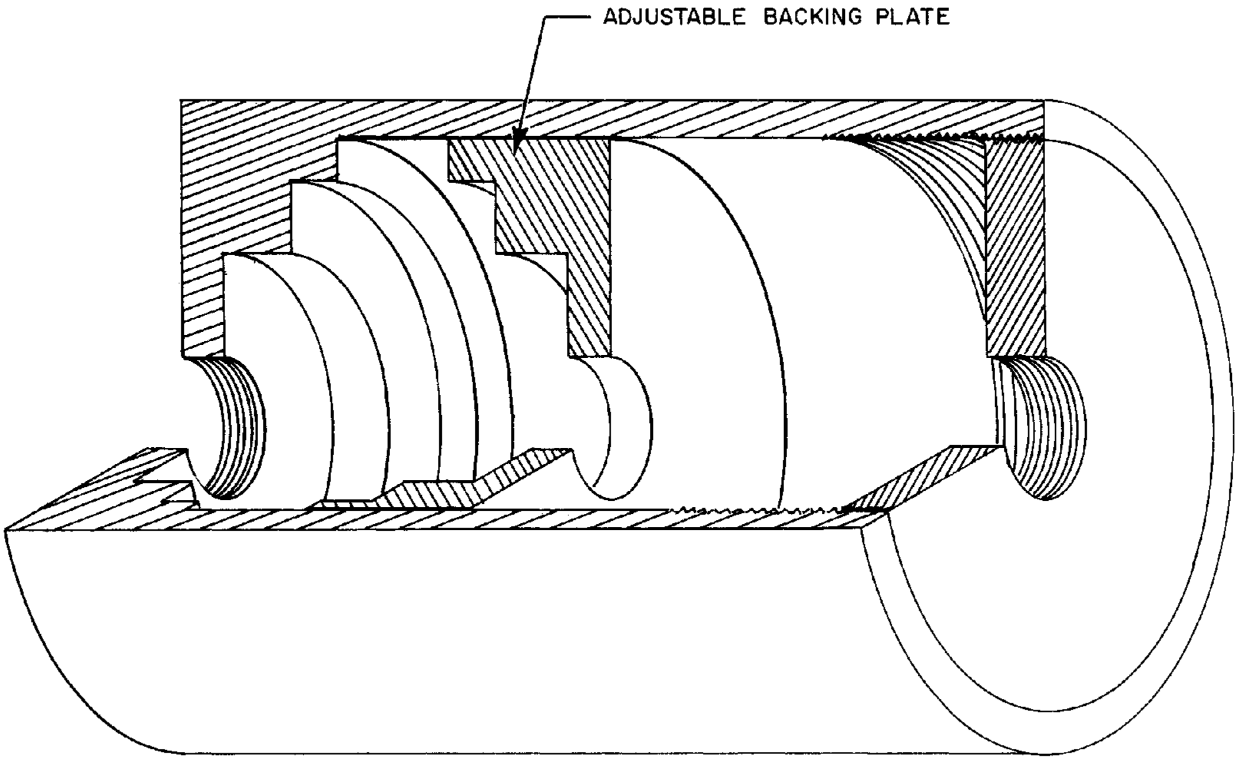


FIGURE 5

TEST CARTRIDGE CONTAINER (ALL PLEXIGLASS)

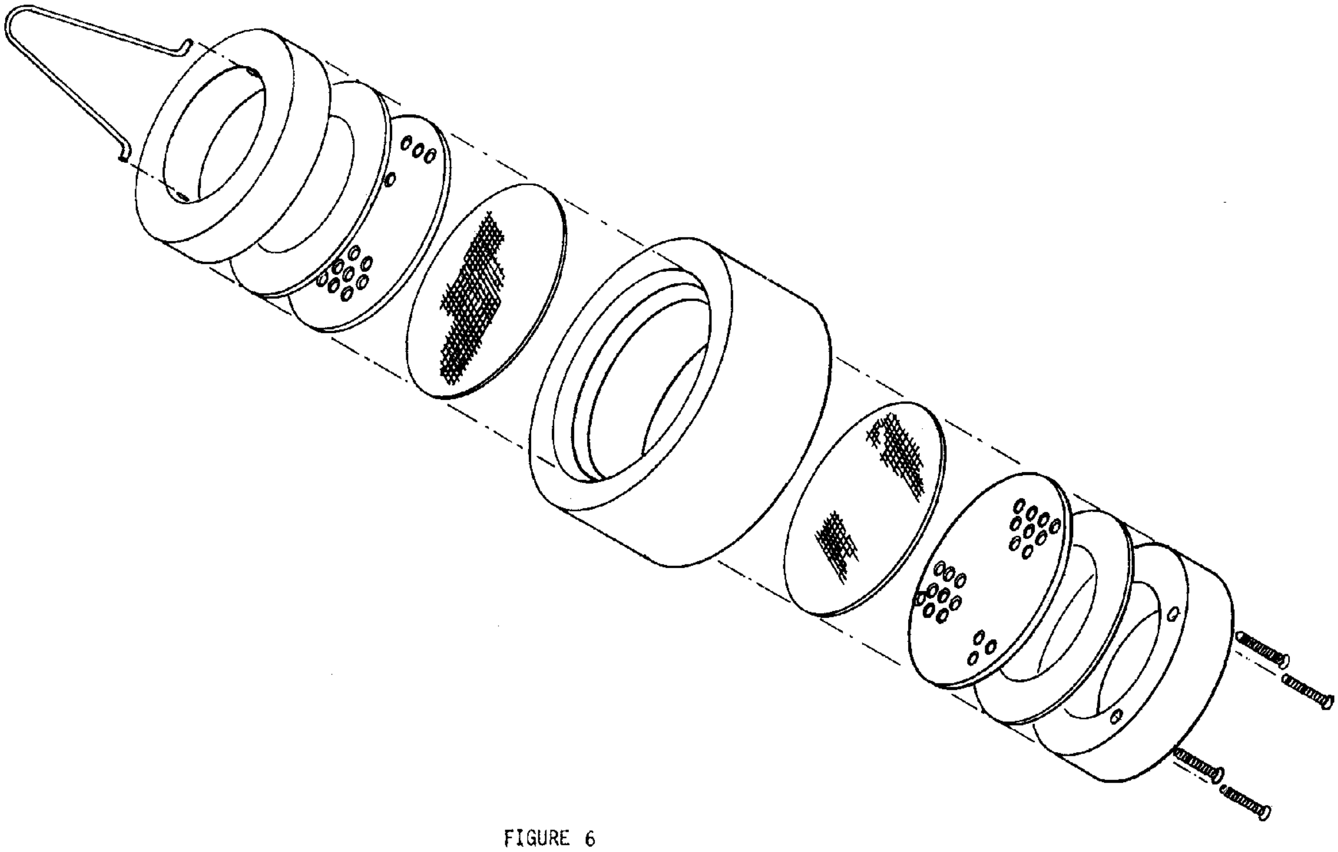


FIGURE 6

TEST CARTRIDGE

Preliminary testing with the reusable cartridge revealed a severe channeling problem. Data from these tests are shown in Table 10. While the reusable cartridge was being modified to minimize channeling, a few commercial cartridges were tested. This data is presented in Table 11. The modified reusable cartridge was tested against 1000 ppm of 12 different organic vapors at 0, 50, and 80 percent relative humidity and a flowrate of 32 liters/minute. This data is presented in Table 12.

Solvent	Carbon (g)	Capacity (g/g)	1%	10%	99%
Benzene	35.55	.292	57	70	128
	33.81	.292	54	65	126
	34.88	.291	48	62	126
	34.66	.293	45	60	133
	33.18	.294	51	71	133
Ethanol	34.25	.120	18	36	122
	34.31	.122	29	42	198
	34.22	.128	29	42	164
	34.19	.125	28	41	138
	34.06	.124	29	44	149
Carbon Tetrachloride	34.20	.540	47	69	131
	34.20	.580	53	69	131
	34.20	.548	59	72	119
	34.23	.550	47	61	119
	34.13	.554	58	83	134
	34.22	.551	51	73	134
	34.28	.547	51	64	125
Trichloroethylene	34.30	.555	59	75	137
	34.28	.541	70	93	148
	34.31	.540	74	88	144
	34.36	.541	60	72	139
	34.03	.541	71	90	143
	34.05	.545	64	76	120
	Averages				
Benzene	34.42	.292	51.0	65.6	129
Ethanol	34.21	.124	26.6	41.0	154
Carbon Tetrachloride	34.21	.553	52.3	70.1	128
Trichloroethylene	34.22	.544	66.3	82.3	138
	Standard Deviations (%)				
Benzene	2.7	0.4	9.3	7.4	2.8
Ethanol	0.3	2.4	18.1	7.3	18.8
Carbon Tetrachloride	0.1	2.3	9.2	10.1	5.1
Trichloroethylene	0.4	1.1	9.4	10.9	7.1

Flowrate of dry air: 32 liters/minute
Temperature: 25° C
Cartridge type: Willson R21

Methyl Ethyl Ketone Data

	Adsorption Capacity (g/g)	Weight of Carbon (g)	Breakthrough Times (min)	
			1%	10%
	0.250	48.58	106	113
	0.249	48.76	110	119
	0.249	47.82	99	107
	-	46.49	103	113
	0.256	47.80	116	121
Average	0.251	47.89	106.8	114.6
Std. Dev.	±1.3%	±1.9%	±6.1%	±4.8%

Benzene Data

	Adsorption Capacity (g/g)	Weight of Carbon (g)	Breakthrough Times (min)	
			1%	10%
	0.270	46.08	90	116
	0.272	49.19	127	136
	0.273	47.33	118	126
	0.275	47.04	116	122
	0.273	47.73	110	119
Average	0.273	47.47	112	124
Std. Dev.	±0.7%	±2.4%	±12.3%	±6.3%

TABLE 12

DATA FROM MODIFIED REUSABLE CARTRIDGE

Solvent vapor concentration:	1000 ppm
Flowrate of dry air:	32 liters/minute
Temperature:	25° C
Carbon type:	Witcarb 337, 12 x 20 mesh

Carbon Tetrachloride Data

	Relative Humidity (%)	Solvent Adsorbed (g/g)	Water Adsorbed (g/g)	Weight of Carbon (g)	Breakthro
					1%
	0	0.505	-	34.38	85
	0	0.549	-	34.45	93
	0	0.534	-	34.33	66
	0	0.519	-	34.48	90
	0	0.526	-	34.38	90
	0	0.511	-	34.41	90
	0	0.533	-	34.25	-
	0	0.511	-	34.29	91
Average	0	0.524	-	34.37	86.4
Std. Dev. (%)	0	±2.8	-	±0.2	±10.8
	50	0.567	-	34.27	79
	50	0.553	-	34.28	77
Average	50	0.560	-	34.28	78.0
	80	0.508	0.063	34.27	69
	80	0.533	0.035	34.34	68
Average	80	0.521	0.049	34.30	68.5

TABLE 12
DATA FROM MODIFIED REUSABLE CARTRIDGE
(continued)

Ethanol Data

	Relative Humidity (%)	Solvent Adsorbed (g/g)	Water Adsorbed (g/g)	Weight of Carbon (g)	Breakthr	
					1%	1
	0	0.097	-	34.24	42	5
	0	0.092	-	34.28	39	4
	0	0.094	-	34.27	39	4
	0	0.090	-	34.31	40	5
	0	0.094	-	34.25	36	4
	0	0.092	-	34.35	36	4
Average	0	0.093	-	34.28	38.7	4
Std. Dev. (%)	0	±2.6	-	±0.1	±6.0	±
	50	0.181	0.006	34.31	39	6
	50	0.184	0.007	34.28	37	5
	50	0.178	0.007	34.27	39	6
Average	50	0.181	0.007	34.29	38.3	6
	80	0.174	0.247	34.29	39	5
	80	0.172	0.259	34.24	38	5
Average	80	0.173	0.253	34.26	38.5	5

TABLE 12
DATA FROM MODIFIED REUSABLE CARTRIDGE
(continued)

Trichloroethylene Data

	Relative Humidity (%)	Solvent Adsorbed (g/g)	Water Adsorbed (g/g)	Weight of Carbon (g)	Breakthr	
					1%	1
	0	0.522	-	34.34	118	1
	0	0.523	-	34.44	107	1
	0	-	-	34.40	97	1
	0	0.526	-	34.36	91	1
	0	0.534	-	34.38	102	1
	0	0.527	-	34.36	108	1
	0	0.531	-	34.31	104	1
	0	0.523	-	34.34	110	1
	0	0.528	-	34.30	104	1
Average	0	0.527	-	34.36	105	1
Std. Dev. (%)	0	±0.8	-	±0.1	±7.3	±4
	50	0.539	-	34.32	99	1
	50	0.532	-	34.33	92	1
	50	0.545	-	34.18	105	1
	50	0.533	-	34.30	113	1
	50	0.527	-	34.32	98	1
	50	0.535	-	34.17	105	1
Average	50	0.535	-	34.27	102	1
Std. Dev. (%)	-	±1.2	-	±0.2	±7.1	±5
	80	0.549	-	34.27	98	1
	80	0.558	-	34.27	94	1
	80	0.583	-	34.29	100	1
	80	0.553	-	34.30	98	1
Average	80	0.561	-	34.28	97.5	1
Std. Dev. (%)	-	±2.7	-	0.0	±2.6	±1

TABLE 12
DATA FROM MODIFIED REUSABLE CARTRIDGE
(continued)

Benzene Data

	Relative Humidity (%)	Solvent Adsorbed (g/g)	Water Adsorbed (g/g)	Weight of Carbon (g)	Breakthr	
					1%	10%
	0	0.286	-	34.35	78	8
	0	0.286	-	34.33	70	8
	0	0.291	-	34.34	81	8
	0	0.285	-	34.33	79	8
	0	0.291	-	34.29	86	9
	0	0.290	-	34.27	69	8
	0	0.292	-	34.40	67	8
	0	0.287	-	34.25	82	91
	0	0.283	-	34.39	84	9
	0	0.285	-	33.48	77	84
	0	0.283	-	34.36	86	94
Average	0	0.287	-	34.25	78.1	8
Std. Dev. (%)	0	±1.1	-	±0.8	±8.7	±
	50	0.344	-0.052	34.34	84	94
	50	0.346	-0.052	34.31	87	100
	50	0.322	-0.033	34.35	90	97
Average	50	0.337	-0.046	34.33	87.0	97
	80	0.316	0.006	34.27	80	88
	80	0.291	0.034	34.27	77	84
Average	80	0.304	0.020	34.27	78.5	86

TABLE 12
DATA FROM MODIFIED REUSABLE CARTRIDGE
(continued)

2-Butanone Data

	Relative Humidity (%)	Solvent Adsorbed (g/g)	Water Adsorbed (g/g)	Weight of Carbon (g)	Breakthr	
					1%	1
	0	0.253	0.004	34.25	89	9
	0	0.258	-0.007	34.27	89	9
	0	0.252	0.003	34.27	82	9
Average	0	0.254	0.000	34.26	86.7	9
	50	0.248	0.021	34.32	81	9
	50	0.247	0.025	34.32	84	9
Average	50	0.248	0.023	34.32	82.5	9
	80	0.219	0.191	34.29	80	8
	80	0.225	0.186	34.29	79	8
Average	80	0.222	0.189	34.29	79.5	8

TABLE 12
DATA FROM MODIFIED REUSABLE CARTRIDGE
(continued)

2-Propanol Data

	Relative Humidity (%)	Solvent Adsorbed (g/g)	Water Adsorbed (g/g)	Weight of Carbon (g)	Breakthr 1%	1
	0	0.254	-0.001	34.26	76	8
	0	0.258	-0.014	34.23	79	9
	0	0.244	-0.007	34.26	76	8
Average	0	0.252	0.007	34.25	77.0	8
	50	0.272	0.050	34.28	78	9
	50	0.276	0.053	34.20	80	91
Average	50	0.274	0.052	34.24	79.0	91
	80	0.227	0.216	34.24	73	8
	80	0.215	0.228	34.14	72	8
	80	0.238	0.201	34.25	76	8
	80	0.232	0.205	34.22	74	8
Average	80	0.228	0.213	34.21	73.8	8
Std. Dev. (%)	0	±4.3	±5.7	±0.1	±2.3	±

TABLE 12
DATA FROM MODIFIED REUSABLE CARTRIDGE
(continued)

Chloroform Data

	Relative Humidity (%)	Solvent Adsorbed (g/g)	Water Adsorbed (g/g)	Weight of Carbon (g)	Breakthro 1%	 1
	0	0.354	-	34.25	55	65
	0	0.357	-	34.13	56	65
Average	0	0.356	-	34.19	55.6	65
	50	0.350	0.043	34.02	56	64
	50	0.365	0.025	34.12	56	66
Average	50	0.358	0.034	34.07	56.0	65
	80	0.319	0.090	34.16	49	56
	80	0.317	0.095	34.03	47	55
Average	80	0.318	0.093	34.10	48.0	55

TABLE 12
DATA FROM MODIFIED REUSABLE CARTRIDGE
(continued)

Acetone Data

	Relative Humidity (%)	Solvent Adsorbed (g/g)	Water Adsorbed (g/g)	Weight of Carbon (g)	Breakthr	
					1%	1
	0	0.122	-	34.28	41	4
	0	0.126	-	34.25	45	5
	0	0.122	-	34.32	41	4
	0	0.124	-	34.28	44	4
Average	0	0.124	-	34.28	42.8	4
Std. Dev. (%)	0	±1.5	-	±0.1	±4.8	±
	50	0.140	0.024	34.35	44	5
	50	0.136	0.032	34.27	41	4
	50	0.129	0.037	34.32	39	4
	50	0.135	0.036	34.27	46	5
Average	50	0.135	0.032	34.30	42.5	4
Std. Dev. (%)	0	±3.4	±18.5	±0.1	±7.3	±
	80	0.123	0.215	34.31	38	4
	80	0.123	0.229	34.27	39	4
	80	0.116	0.257	34.29	38	4
	80	0.117	0.229	34.31	38	4
Average	80	0.120	0.233	34.30	38.2	4
Std. Dev. (%)	0	±3.2	±7.6	±0.1	±1.3	±

TABLE 12
DATA FROM MODIFIED REUSABLE CARTRIDGE
(continued)

Ethyl Acetate Data

	Relative Humidity (%)	Solvent Adsorbed (g/g)	Water Adsorbed (g/g)	Weight of Carbon (g)	Breakthro 1%	1
	0	0.313	-0.004	34.30	61	8
	0	0.304	0.009	34.23	61	8
	0	0.311	-0.005	34.26	60	8
Average	0	0.309	0.000	34.26	60.7	8
	50	0.310	0.016	34.21	63	8
	50	0.324	0.001	34.24	62	8
	50	0.322	0.001	34.29	64	8
Average	50	0.315	0.006	34.25	63.0	8
	80	0.286	0.127	34.25	63	7
	80	0.284	0.136	34.26	65	8
	80	0.284	0.129	34.24	67	8
Average	80	0.285	0.131	34.25	65.0	7

TABLE 12
DATA FROM MODIFIED REUSABLE CARTRIDGE
(continued)

Hexane Data

	Relative Humidity (%)	Solvent Adsorbed (g/g)	Water Adsorbed (g/g)	Weight of Carbon (g)	Breakthr	
					1%	1
	0	0.250	0.007	34.13	69	7
	0	0.262	-0.005	34.14	72	7
	0	0.262	-0.001	34.09	63	7
	0	0.258	-0.001	34.17	70	7
Average	0	0.258	0.000	34.13	68.5	7
Std. Dev. (%)	0	±2.2	-	±0.1	±5.6	±
	50	0.261	.004	34.24	71	7
	50	0.260	.010	34.20	73	7
Average	50	0.261	.007	34.22	72.0	7
	80	0.219	0.078	34.18	58	(
	80	0.253	0.048	34.15	61	(
	80	0.234	0.064	34.18	63	(
Average	80	0.235	0.063	34.17	60.7	(

TABLE 12
DATA FROM MODIFIED REUSABLE CARTRIDGE
(continued)

3-Chloropropene Data

	Relative Humidity (%)	Solvent Adsorbed (g/g)	Water Adsorbed (g/g)	Weight of Carbon (g)	Breakthr	
					1%	1
	0	0.182	-	34.20	43	5
	0	0.188	-	34.13	48	5
	0	0.182	-	34.17	49	5
Average	0	0.184	-	34.17	46.7	5
	50	0.167	0.023	34.20	51	5
	50	0.173	0.020	34.07	50	5
Average	50	0.170	0.022	34.14	50.5	5
	80	0.133	0.157	34.10	41	4
	80	0.121	0.121	34.12	39	4
Average	80	0.127	0.139	34.11	40.0	4

TABLE 12
DATA FROM MODIFIED REUSABLE CARTRIDGE
(continued)

1,2-Dibromoethane Data

	Relative Humidity (%)	Solvent Adsorbed (g/g)	Water Adsorbed (g/g)	Weight of Carbon (g)	Breakthro	
					1%	10
	0	1.08	-	34.18	126	13
	0	1.08	-	34.21	129	13
Average	0	1.08	-	34.20	128	13
	50	1.07	-	34.10	125	13
	50	1.12	-	34.18	124	13
	50	1.09	-	34.22	137	14
Average	50	1.09	-	34.17	129	13
	80	1.08	-	34.00	113	13
	80	0.988	-	34.33	99	11
Average	80	1.03	-	34.16	106	12

the calculations. The data used for the calculations is summarized in Table 13, while the results are tabulated in Table 14. As can be seen from the correlation coefficients and the standard errors of estimate, the fit is best at 0 humidity and gets progressively worse with increasing humidity.

TABLE 13

DATA FOR DUBININ EQUATION CALCULATIONS

	Adsorption Capacity at Different Humidities			Solvent Density	β	p_s/p
	0%	50%	80%			
2-butanone	0.254	0.248	0.222	0.8054	0.93	92.89
ethyl acetate	0.309	0.315	0.285	0.9005	1.01	97.89
hexane	0.258	0.261	0.235	0.6594	1.35	159.2
2-propanol	0.252	0.274	0.228	0.7851	0.80	42.63
chloroform	0.356	0.358	0.318	1.4916	0.83	209.6
trichloroethylene	0.527	0.535	0.561	1.462	0.93	77.11
acetone	0.124	0.135	0.120	0.8422	0.71	403.9
carbon tetrachloride	0.524	0.560	0.521	1.5942	1.00	121.2
ethanol	0.093	0.181	0.173	0.7893	0.60	57.37
benzene	0.287	0.337	0.304	0.8787	0.92	95.26
1,2-dibromoethane	1.08	1.09	1.03	2.180	0.89	15.04
3-chloropropene	0.184	0.170	0.127	0.9397	0.84	394.7

TABLE 14

DUBININ EQUATION RESULTS

Humidity (%)	W_o (cc/g)	B	r	$S_{y \cdot x}$
0	0.51 ± 3.6%	1.09×10^{-6} ± 5.8%	0.985	0.061
50	0.53 ± 5.3%	1.10×10^{-6} ± 8.1%	0.969	0.089
80	0.50 ± 8.8%	1.19×10^{-6} ± 12.5%	0.931	0.148

times calculated from the Klotz, Wheeler, and Nelson equations. As can be seen from the table, the Klotz and Wheeler equations give similar results. Table 19 contains carbon data and cartridge and test parameters used to make the breakthrough calculations. The histograms in Figure 7, page 58, graphically depict the results in Table 18. For this set of data, the average deviation from the experimental result is 1.2 minutes for the Wheeler equation, 2.2 minutes for the Klotz equation, and -4.6 minutes for the Nelson equation. The standard deviations (s) of these deviations are, respectively, 13.2, 13.6, and 20.7 minutes.

7.3 Effect of Humidity

Table 20 compares adsorption capacities at three different humidities. Adsorption capacity at first increases with increasing humidity and then decreases at higher humidities. This is in agreement with the data of Burrage and Allmand [23]. Table 21 shows the quantity of water adsorbed (grams of water per gram of carbon) at 50 and 80 percent relative humidity. The quantity of water adsorbed is related to the water solubility of the organic solvent being tested and is greater for more soluble compounds. Table 21 also shows the percent decrease in service life in going from 50 percent to 80 percent relative humidity. In general, service life decrease is greater for the water-insoluble compounds.

TABLE 15

EXPERIMENTAL VS CALCULATED BREAKTHROUGH TIMES AT ZERO HUMIDITY

				Breakthrough Times (mi			
				1%			
	w_s (g/g)	W (g)	$c_o \times 10^6$ (g/cc)	exp	calc	Δ%	exp
acetone	0.124	34.28	2.42	42.8	45.4	+6.1	48.2
2-butanone	0.254	34.26	3.00	86.7	75.0	-13.5	95.7
ethanol	0.093	34.28	1.92	38.7	42.9	+10.8	49.2
2-propanol	0.252	34.25	2.50	77.0	89.2	+15.8	87.3
ethyl acetate	0.309	34.26	3.66	60.7	74.7	+23.1	84.3
3-chloropropene	0.184	34.17	3.18	46.7	51.1	+9.4	54.7
chloroform	0.356	34.19	4.97	55.6	63.3	+13.8	65.0
trichloroethylene	0.527	34.36	5.46	105.0	85.8	-18.3	116.0
carbon tetrachloride	0.524	34.37	6.40	86.4	72.8	-15.7	93.4
hexane	0.258	34.13	3.59	68.5	63.3	-7.6	76.2
benzene	0.287	34.25	3.25	78.1	78.2	+0.1	88.5
1,2-dibromoethane	1.08	34.20	7.82	128.0	122.0	-4.7	138.0

w_s = adsorption capacity (grams of solvent/gram of carbon)
W = weight of carbon in cartridge (grams)
c_o = input concentration of solvent vapor (grams/cm^3)

TABLE 16

EXPERIMENTAL VS CALCULATED BREAKTHROUGH TIMES AT 50% RELATIVE HUMIDITY

				Breakthrough Times (mi			
				1%			
	w_s (g/g)	W (g)	$c_o \times 10^6$ (g/cc)	exp	calc	Δ%	exp
acetone	0.135	34.30	2.42	42.5	49.5	+16.5	49.8
2-butanone	0.248	34.32	3.00	82.5	73.3	-11.2	93.0
ethanol	0.181	34.29	1.92	38.3	83.6	+118.0	60.0
2-propanol	0.274	34.24	2.50	79.0	97.0	+22.8	91.5
ethyl acetate	0.315	34.25	3.66	63.0	76.2	+21.0	87.0
3-chloropropene	0.170	34.14	3.18	50.5	47.1	-6.7	56.0
chloroform	0.358	34.07	4.97	56.0	63.3	+13.0	65.0
trichloroethylene	0.535	34.27	5.46	102.0	86.8	-14.9	114.0
carbon tetrachloride	0.560	34.28	6.40	78.0	77.5	-0.6	86.0
hexane	0.261	34.22	3.59	72.0	64.3	-10.7	78.5
benzene	0.337	34.33	3.25	87.0	92.0	+5.7	97.0
1,2-dibromoethane	1.09	34.17	7.82	129.0	123.0	-4.7	139.0

w_s = adsorption capacity (grams of solvent/gram of carbon)
W = weight of carbon in cartridge (grams)
c_o = input concentration of solvent vapor (grams/cm^3)

TABLE 17

EXPERIMENTAL VS CALCULATED BREAKTHROUGH TIMES AT 80% RELATIVE HUMIDITY

				Breakthrough Times (m			
				1%			
	w_s (g/g)	W (g)	$c_o \times 10^6$ (g/cc)	exp	calc	Δ%	exp
acetone	0.120	34.30	2.42	38.2	44.0	+15.2	44.2
2-butanone	0.222	34.29	3.00	79.5	65.6	-17.5	87.0
ethanol	0.173	34.26	1.92	38.5	79.8	+107.0	55.0
2-propanol	0.228	34.21	2.50	73.8	80.6	+9.2	83.0
ethyl acetate	0.285	34.25	3.66	65.0	68.9	+6.0	79.3
3-chloropropene	0.127	34.11	3.18	40.0	35.2	-12.0	44.0
chloroform	0.318	34.10	4.97	48.0	56.3	+17.3	55.5
trichloroethylene	0.561	34.28	5.46	97.5	91.0	-6.7	108.0
carbon tetrachloride	0.521	34.30	6.40	68.5	72.2	+5.4	76.5
hexane	0.235	34.17	3.59	60.7	57.8	-4.8	66.3
benzene	0.304	34.27	3.25	78.5	82.8	+5.5	86.0
1,2-dibromoethane	1.03	34.16	7.82	106.0	116.0	+9.4	120.0

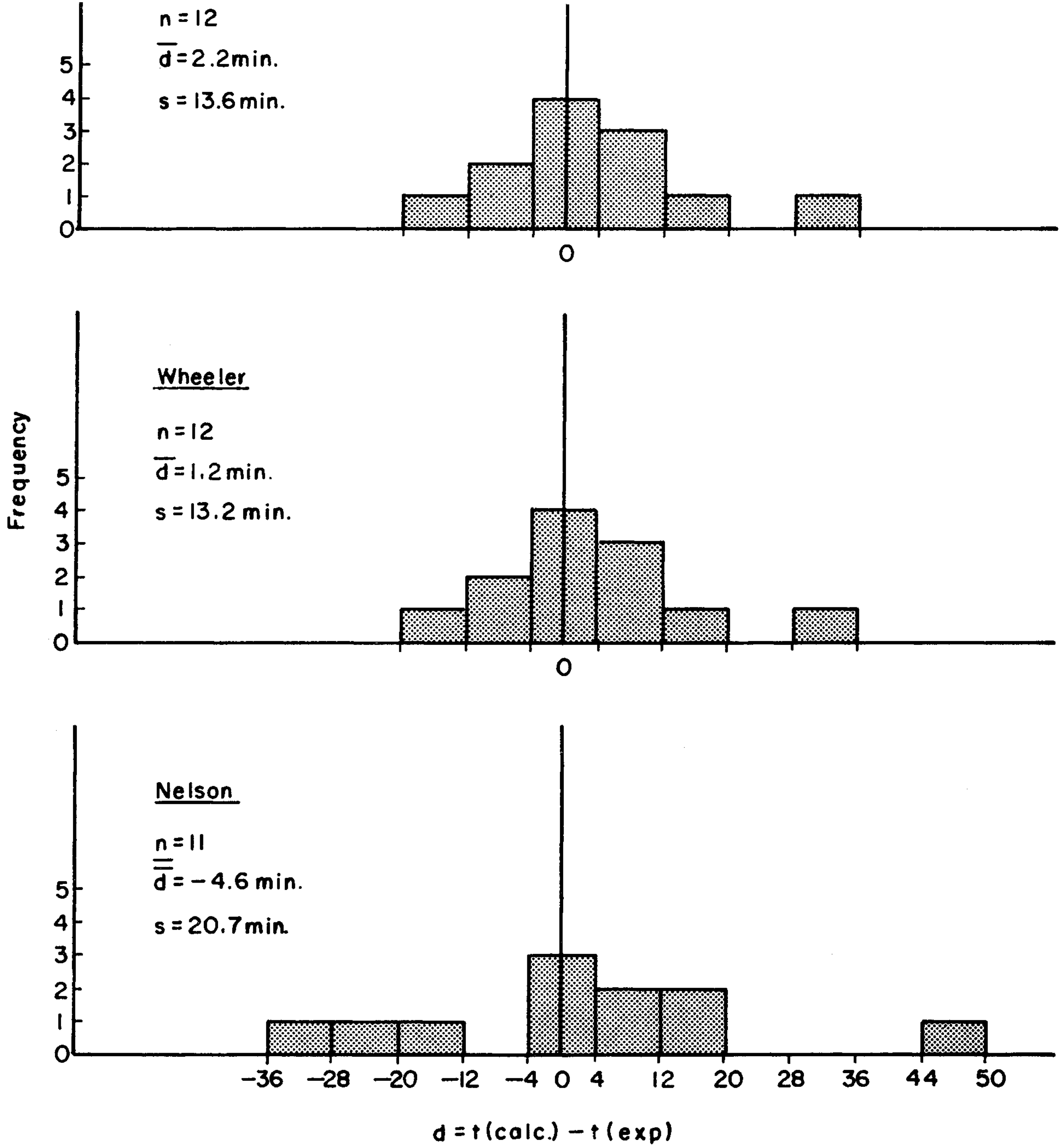
w_s = adsorption capacity (grams of solvent/gram of carbon)
W = weight of carbon in cartridge (grams)
c_o = input concentration of solvent vapor (grams/cm^3)

acetone	49.8	55.5	54.6	87.1
2-butanone	93.0	81.6	81.0	94.4
ethanol	60.0	94.2	92.3	53.9
2-propanol	91.5	109.0	107.0	53.2
ethyl acetate	87.0	84.8	84.1	65.4
3-chloropropene	56.0	53.0	52.1	60.0
chloroform	65.0	71.1	70.0	58.9
trichlorcethylene	114.0	96.6	95.8	82.7
carbon tetrachloride	86.0	86.0	85.6	94.7
hexane	78.5	71.0	71.0	73.4
benzene	97.0	103.0	102.0	103.0
1,2-dibromoethane	139.0	137.0	136.0	-

TABLE 19

CARBON AND CARTRIDGE DATA USED FOR CALCULATING BREAKTHROUGH TIMES FROM THE KLOTZ AND WHEELER EQUATIONS

Bed depth	2.2 cm
Cartridge volume	85 cm^3
Carbon density	0.40 g/cm^3
Average particle diameter	0.12 cm
Flowrate	32 liters/min.
Cross-sectional area of bed	38.5 cm^2
Void volume	0.4 cm^3/g
Specific surface area	71 cm^2/g
Viscosity of air-vapor stream	1.83×10^{-4} g/cm sec.
Density of air-vapor stream	1.2×10^{-3} g/cm^3
Wheeler equation constant	9987


n = 12
$\overline{d}$ = 2.2 min.
s = 13.6 min.
Wheeler
n = 12
$\overline{d}$ = 1.2 min.
s = 13.2 min.
Nelson
n = 11
$\overline{d}$ = − 4.6 min.
s = 20.7 min.
Frequency
0
1
2
3
4
5
0
−36
−28
−20
−12
−4
0
4
12
20
28
36
44
50
d = t (calc.) − t (exp)

acetone	0.124	0.135	0.120
2-butanone	0.254	0.248	0.222
ethanol	0.093	0.181	0.173
2-propanol	0.252	0.274	0.228
ethyl acetate	0.309	0.315	0.285
3-chloropropene	0.184	0.170	0.127
chloroform	0.356	0.358	0.318
trichloroethylene	0.527	0.535	0.561
carbon tetrachloride	0.524	0.560	0.521
hexane	0.258	0.261	0.235
benzene	0.287	0.337	0.304
1,2-dibromoethane	1.08	1.09	1.03

TABLE 21

WATER ADSORBED AT DIFFERENT HUMIDITIES (G/G) AND PERCENT DECREASE IN 10% BREAKTHROUGH TIMES

	50%	80%	%Δt
acetone	0.032	0.233	11.2
2-butanone	0.023	0.189	6.5
ethanol	0.007	0.253	8.3
2-propanol	0.052	0.212	9.3
ethyl acetate	0.006	0.131	8.9
3-chloropropene	0.022	0.139	21.4
chloroform	0.034	0.093	14.6
trichloroethylene	-	-	5.3
carbon tetrachloride	-	0.049	11.0
hexane	0.007	0.063	15.5
benzene	-	0.020	11.3
1,2-dibromoethane	-	-	13.7

some types of compounds, precautions can be taken to overcome this problem. It is therefore recommended that a certification program be adopted which utilizes the Dubinin equation to calculate adsorption capacity and the modified Wheeler equation to calculate the service life of organic vapor respirator cartridges. Table 22 gives estimated service lives against 80 selected organic vapors of the reusable cartridge used in this study. These estimated service lives were calculated according to the proposed certification program given in Section 9.0. Adsorption capacities were calculated from the Dubinin equation using the values of W_0 and B for 50 percent relative humidity given in Table 14. The input concentration used for the calculations is 10 times the Threshold Limit Value (TLV) for the compound or 1,000 ppm, whichever is least. The input concentration for compounds having no listed TLV is 1,000 ppm. As a safety factor, the calculated service lives of compounds having high adsorption potentials ($A^2>60$) were divided by 2. (A is defined on page 3 of this report.) The estimated cartridge service lives for the 80 compounds in Table 22 fall into time ranges as follows: less than 1 hour, 18 percent; 1-2 hours, 60 percent; 2-4 hours, 10 percent; and greater than 4 hours, 12 percent.

8.2 Further Research Required

It is recommended that research be carried out in the following areas:

(1) Determination of the best compound for adsorption capacity prediction. When a single compound is used at different concentrations to determine the Dubinin constants W_0 and B, the values of the constants thus obtained will not necessarily be the same as those obtained by statistical treatment of a large group of solvents. Perhaps a single solvent can be found which will approximate these "best" values of the constants. If it is necessary to use more than one test solvent, Jonas [5] method of dividing organic compounds into groups (nonpolar, weakly polar, and strongly polar) and choosing a reference compound from each should be tested.

(2) Effect of solvent-solvent interaction. Very little work has been done on the effect of two or more solvents on the adsorption capacity and service life of respirator cartridges and canisters. Workers in industry are probably more likely to be exposed to mixtures of solvent vapors than to pure solvent vapors. Once sufficient data has been generated, the modified potential theory and the method of Lewis, discussed in paragraph 3.4 of this report, can be tested for correlation of mixed adsorption data.

toluene	100	3.83	0.387	16.7	96.1
ethylbenzene	100	4.42	0.434	5.6	93.4
m-xylene	100	4.41	0.438	4.9	94.5
cumene	50	2.50	0.439	4.1	167
mesitylene	-	4.99	0.455	0.6	86.8
p-cymene	-	5.57	0.453	0.2	77.4
methanol	200	1.33	0.036	240	12.9
ethanol	1,000	1.92	0.181	80.6	44.8
2-propanol	400	2.50	0.275	40.3	105
allyl alcohol	2	0.048	0.063	190	624
propanol	200	2.50	0.322	24.4	122
sec-butanol	150	3.08	0.365	15.7	113
butanol	50	1.54	0.370	14.6	229
2-pentanol	-	3.67	0.411	4.3	107
3-methyl-1-butanol	100	3.67	0.421	1.9	109
4-methyl-2-pentanol	25	1.07	0.386	9.4	343
pentanol	-	3.67	0.425	1.1	110
2-ethyl-1-butanol	-	4.25	0.437	0.6	97.8
methyl chloride	100	2.10	0.009	395	2.1
vinyl chloride	1	0.026	0.001	578	18.3
ethyl chloride	1,000	2.68	0.080	174	14.2
2-chloropropane	-	3.27	0.200	80.5	29.1
allyl chloride	1	0.032	0.027	283	402
1-chloropropane	-	3.27	0.106	145	15.4
2-chloro-2-methylpropane	-	3.85	0.280	46.9	69.2
1-chlorobutane	-	3.85	0.334	33.3	82.5
2-chloro-2-methylbutane	-	4.43	0.370	21.1	79.5
1-chloropentane	-	4.43	0.407	13.6	87.4
chlorobenzene	75	3.51	0.516	12.4	140
1-chlorohexane	-	5.02	0.445	4.5	84.3
o-chlorotoluene	50	2.63	0.547	4.6	198
1-chloroheptane	-	5.60	0.463	0.8	78.7
dichloromethane	200	3.53	0.145	155	19.6
t-1,2-dichloroethylene	200	4.03	0.249	96.2	29.4
1,1-dichloroethane	200	4.12	0.312	67.6	36.1
c-1,2-dichloroethylene	200	4.03	0.297	80.3	35.1
1,2-dichloroethane	50	2.06	0.330	69.2	76.0
1,2-dichloropropane	75	3.52	0.438	32.5	118
1,4-dichlorobutane	-	5.28	0.597	2.8	108
o-dichlorobenzene	50	3.06	0.685	0.9	213
chloroform	25	1.24	0.235	118	180

methylchloroform	350	5.55	0.465	41.8	79.7
trichloroethylene	100	5.46	0.518	39.2	90.3
1,1,2-trichloroethane	10	0.555	0.423	57.8	725
1,2,3-trichloropropane	50	3.06	0.707	4.4	220
carbon tetrachloride	10	0.640	0.334	90.7	248
perchloroethylene	100	6.90	0.748	13.6	103
1,1,2,2-tetrachloroethane	5	0.349	0.854	35.3	2328
methyl acetate	200	3.08	0.217	84.5	33.5
vinyl acetate	-	3.58	0.312	45.0	80.3
ethyl acetate	400	3.66	0.327	36.8	85.0
isopropyl acetate	250	4.16	0.373	20.9	85.3
propyl acetate	200	4.25	0.402	15.4	90.0
butyl acetate	150	4.83	0.443	5.4	87.3
isopentyl acetate	100	5.41	0.452	1.9	79.5
pentyl acetate	100	5.41	0.457	1.4	80.4
acetone	1,000	2.41	0.133	112	26.2
2-butanone	200	3.00	0.276	42.9	87.5
2-pentanone	200	3.58	0.350	20.3	93.0
3-pentanone	-	3.58	0.355	19.1	94.4
4-methyl-2-pentanone	100	4.16	0.384	10.0	87.8
mesityl oxide	25	1.02	0.379	17.8	354
2,4-pentanedione	-	4.16	0.478	7.3	109
2-heptanone	100	4.75	0.424	1.4	84.9
cyclohexanone	50	2.04	0.486	8.3	227
pentane	600	3.00	0.197	50.5	62.5
2,3-dimethylbutane	-	3.58	0.257	30.2	68.3
hexane	100	3.58	0.270	25.2	71.8
methylcyclopentane	-	3.50	0.283	32.8	76.9
cyclohexane	300	3.50	0.302	30.7	82.1
cyclohexene	300	3.41	0.305	33.5	85.1
2,2,4-trimethylpentane	-	4.75	0.333	9.5	66.7
heptane	400	4.17	0.322	11.5	73.5
methylcyclohexane	-	4.08	0.348	15.4	81.2
nonane	-	5.33	0.376	1.1	67.1
methyl iodide	5	0.295	0.033	357	53
acrylonitrile	20	0.441	0.097	143	104
1,2-dibromoethane	20	1.56	0.791	36.7	482
epichlorohydrin	5	0.192	0.244	91.5	604

*Calculated from the modified Wheeler equation according to the procedure given on page 65.

was directed toward cartridges. Research should be performed to determine if the proposed cartridge certification program can be adapted to canisters.

the proposed certification program following, it is possible to gain certification information adequate to ensure the protection of workers using organic vapor respirator cartridges.

9.2 Certification Program

(a) Cartridges will be tested on an apparatus that allows the test atmosphere at 50±5 percent relative humidity and room temperature, approximately 25° C, to enter cartridges continuously at predetermined concentrations and a flowrate of 20 liters/minute per cartridge (minimum of 40 liters/minute for single cartridge respirators). The apparatus will have a means of accurately measuring both the input solvent vapor concentration and the effluent solvent vapor concentration.

(b) Sufficient cartridges of each type will be disassembled and measurement made to determine the average cartridge volume, bed depth, internal diameter, and weight of carbon.

(c) Determine the average particle size of the carbon by sieving a representative sample and measuring the distribution in each mesh range.

(d) Eight cartridges will be tested on the test apparatus, two each at solvent vapor concentrations of 5,000, 1,000, 200, and 50 ppm of carbon tetrachloride.

(e) Record the time of 10 percent breakthrough, but continue the test to complete saturation. Measure the weight gain of the cartridge and calculate adsorption capacity, w_s by dividing this weight gain by the weight of carbon in an untested cartridge. Duplicate runs are made at each concentration.

(f) Using the Dubinin equation and the four adsorption capacities determined above, calculate (using the method of least squares) the quantities W_o and B for the carbon. These values of W_o and B will be used to calculate adsorption capacities for other vapors.

(g) Using the Dubinin equation with the constants calculated above, and affinity coefficients calculated from molar volumes, calculate adsorption capacities for other organic compounds.

modified Wheeler equation:

$$t_b = \frac{w_s}{C_o Q}\left[W - \frac{\rho Q}{k} \ln C_o/C\right]$$

where t_b = calculated service life
w_s = calculated adsorption capacity
C_o = input concentration = 10 x TLV or 1,000 ppm, whichever is least (1,000 ppm if the compound has no listed TLV)
W = weight of carbon in cartridge
ρ = carbon density = $\frac{\text{carbon weight}}{\text{cartridge volume}}$
Q = 20 liters/minute/cartridge
C_o/C = 10
k = rate constant determined in (h)

(j) If the compound in question has a high adsorption potential ($A^2>60$) and a low TLV, divide the calculated service life by 2.

(k) The subject test cartridge will not be certified for organic vapors having calculated service lives of 30 minutes or less; it will be certified for limited use against vapors having calculated service lives of 31-60 minutes, and will be fully certified against vapors having calculated service lives of 60 minutes or greater, if they meet the criteria of (l) following.

(l) The use of organic vapor cartridges may be inappropriate even though the calculated service life appears adequate. Other factors such as substance warning properties, eye irritation, flammability of the vapor, skin irritation or adsorption, and dangerous use concentrations should also be considered when determining application. These factors have been incorporated into a "respirator decision logic" developed and used by the joint NIOSH/OSHA Standards Completion Program to write substance standards on toxic substances identified in 42CFR1910.1000.

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W_2. The test weight of carbon, W, is given by: $W = W_2 - W_1$.

(5) Install the test cartridge in the cartridge holder of the test apparatus.

(6) Turn on airflow and adjust to the desired flowrate.

(7) Measure and record the pressure drop across the test cartridge.

(8) Route airflow through the bypass leg of the apparatus.

(9) Adjust the pressure drop of the bypass leg to match that of the test cartridge.

(10) Adjust heat to the humidifier to give the desired humidity, as measured on the hygrometer; maintain a constant water level in the humidifier during the test.

(11) Adjust the syringe heating block to the boiling temperature of the solvent.

(12) Fill a gas-tight syringe of appropriate size with the test solvent.

(13) Install the solvent-filled syringe on the test apparatus.

(14) Adjust the syringe pump speed to give the desired flowrate of solvent. Calculate solvent flowrate from the formula:

$$q = \frac{MPCQ}{dRT \times 10^6}$$

where q = solvent flowrate (ml/min)
m = molecular weight of solvent (grams/mole)
P = system pressure (atmospheres)
C = desired vapor concentration of solvent (ppm)
Q = flowrate of air (liters/min)
d = density of solvent
R = gas constant (atmospheres-liter/°K mole)
T = temperature (°K)

where C = solvent vapor concentration (ppm)
v = volume of liquid solvent (microliters)
d = solvent density (grams/ml)
R = gas constant (atmosphere-liter/°K mole)
T = temperature (°K)
P = pressure (atmospheres)
V = volume of standard (liters)
M = molecular weight of solvent (grams/mole)

(16) Turn on the syringe pump.

(17) Calibrate the analyzer by analyzing a standard mixture containing a known concentration of the solvent vapor in question. Obtain the factor, f, given by the formula:

$$f = \frac{k\,C}{C_1}$$

where f = calculation factor
k = calibration factor (counts/minute for the standard, taken from integrator)
C = test vapor concentration (ppm)
C_1 = concentration of calibration mixture (ppm)

(18) Position the three-way sampling valve to monitor upstream solvent vapor concentration.

(19) After the solvent vapor concentration has stabilized, readjust syringe pump speed if necessary, as determined by calibration, to obtain the desired concentration.

(20) After the desired stable concentration has been reached, route the test gas mixture to flow through the test cartridge.

(21) Immediately position the sampling valve so that the analyzer monitors the exit gas from the test cartridge.

tration to ascertain that it has not changed during the test.

(26) Remove the test cartridge and reweigh it. Record this weight, W_3.

(27) Calculate the weight of solvent plus water, W_4 adsorbed on the cartridge.

$$W_4 = W_3 - W_2$$

(28) Calculate weight of solvent adsorbed on the cartridge from the following formula:

$$w = \frac{(ft-A)\ MCQP}{fRT \times 10^6}$$

where w = weight of solvent adsorbed (grams)
f = calculation factor (counts/min)
t = time (minutes)
A = area under breakthrough curve (counts)
M = molecular weight of solvent (grams/mole)
C = concentration of solvent vapor (ppm)
Q = flowrate of air (liters/min)
P = system pressure (atmospheres)
R = gas constant (liter-atmospheres/°K mole)
T = temperature (°K)

(29) Calculate weight of water, W_5 adsorbed on cartridge:

$$W_5 = W_4 - w$$

(30) Calculate adsorption capacity, w_s of the charcoal (grams/gram):

$$w_s = \frac{w}{W}$$

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