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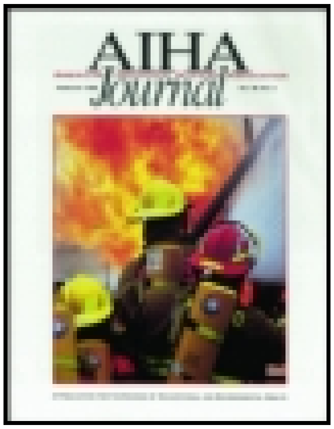

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Effects of Adsorbed Water Vapor on the Adsorption Rate Constant and the Kinetic Adsorption Capacity of the Wheeler Kinetic Model

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A recent trend in occupational safety and health has focused on the use of respiratory protective equipment to supplant engineering controls as the primary means of protecting workers from toxic substances. Respirator adsorbent cartridges have been demonstrated to have a finite capacity to adsorb toxic vapors. The knowledge of when this limit is approached or has been exceeded is crucial to the user. The Wheeler kinetic breakthrough model has been shown to describe accurately organic vapor penetration through beds of activated carbon. The model, however, does not account for competitive adsorption of water vapor or other organic vapors. The investigations reported here demonstrate the effect of adsorbed water vapor on the kinetic adsorption parameters (kinetic rate constant and kinetic saturation capacity) of the Wheeler equation. Adsorbent beds were equilibrated at varying concentrations of water vapor and then challenged with carbon tetrachloride vapor-laden air. Dry carbon had an initial rate constant of 62.5 s^{-1} and a kinetic adsorption capacity of 0.36 g of adsorbed CCl_4/gram (g/g) of adsorbent. These parameters decreased in proportion to the amount of water vapor adsorbed, with the minimum predicted values occurring at 100% relative humidity. The minimum experimental value for the kinetic rate constant was 17.6 s^{-1}, a decrease of 73% from the dry carbon values. The minimum predicted value for the kinetic adsorption capacity was 0.16 g/g, a decrease of 45%.

Introduction

In 1983 the Office of Technology Assessment, Committee on Control Technologies in the Workplace, estimated that there were as many as seven million workers in the United States who used respirators to control exposures to environmental contaminants.(1) Many of these users relied on activated carbon-containing respirator cartridges. Although activated carbon is considered to be an excellent sorbent, it does not adsorb all substances equally nor does it have an unlimited adsorption capacity. The National Institute for Occupational Safety and Health (NIOSH) recommended method for determining cartridge exhaustion relies on the user's physiological response to the penetrating substance (odor, taste, or irritation).(2) Since physiological response, *e.g.*, olfactory or irritation, to air contaminants can be highly variable within individuals and groups of individuals, the NIOSH approved method for determining cartridge penetration could result in worker overexposure while wearing approved respirators.

An alternative approach is to make a prediction of the time to cartridge exhaustion based on an applicable theoretical model and to replace the cartridges at the predicted time. A number of plausible models have been proposed.(3-5) In a NIOSH-sponsored review of the available models, it was concluded that the Wheeler-Dubinin model showed the most promise as a predictor of respirator performance.(6)

The effect of adsorbed or adsorbing water vapor on the subsequent adsorption of contaminant vapors largely is unknown.(3,6-8)) Nelson, *et al.*(7) demonstrated the effects of water vapor on the subsequent adsorption of 35 common industrial air contaminants. The predicted time to 10% breakthrough for nonpolar adsorbates was overestimated severely in the presence of water vapor at concentrations greater than 50% relative humidity (RH). For a model to be useful, it must account for competitive adsorption of water vapor.

The Wheeler-Dubinin model assumes an unoccupied adsorption space. Under environmental conditions, where water vapor is present, this assumption may not be fulfilled, resulting in deviations from the predicted time to breakthrough of the activated carbon adsorbent bed. The work reported here focuses on the effect of adsorbed water vapor on the Wheeler parameters: k_v, the kinetic rate constant, and W_e, the kinetic adsorption capacity.

The Wheeler-Dubinin model(9) was developed during the 1960s from a mass balance analysis of contaminant-laden air passing through an adsorbent bed. The model assumes an adsorption process which is described by a pseudo-first-order kinetics reaction between the adsorbing molecules, the adsorbent and an unoccupied adsorption space. The first assumption is fulfilled when the adsorption sites greatly exceed the number of contaminant molecules entering the bed ($C_x/C_o < 3$–4%). The second assumption is true when the carbon is clean, *i.e.*, little or nothing is adsorbed on its micropore surfaces. The Wheeler equation is

$$t_B = W_e/(C_o\,Q)\,[W - (\rho_B\,Q\,\mathrm{Ln}\,C_o/C_x)/k_v] \qquad (1)$$

t_B = time to breakthrough (sec);
W_e = the kinetic adsorption capacity (g/g);
C_o = contaminant inlet concentration (g/cm^3);
W = weight of carbon adsorbent (g);
ρ_b = packed bed density (g/cm^3);
k_v = the pseudo-first-order rate constant (s^{-1});
C_x = the concentration exiting the adsorbent bed (g/cm^3); and
Q = volumetric flow rate (cm^3/min).

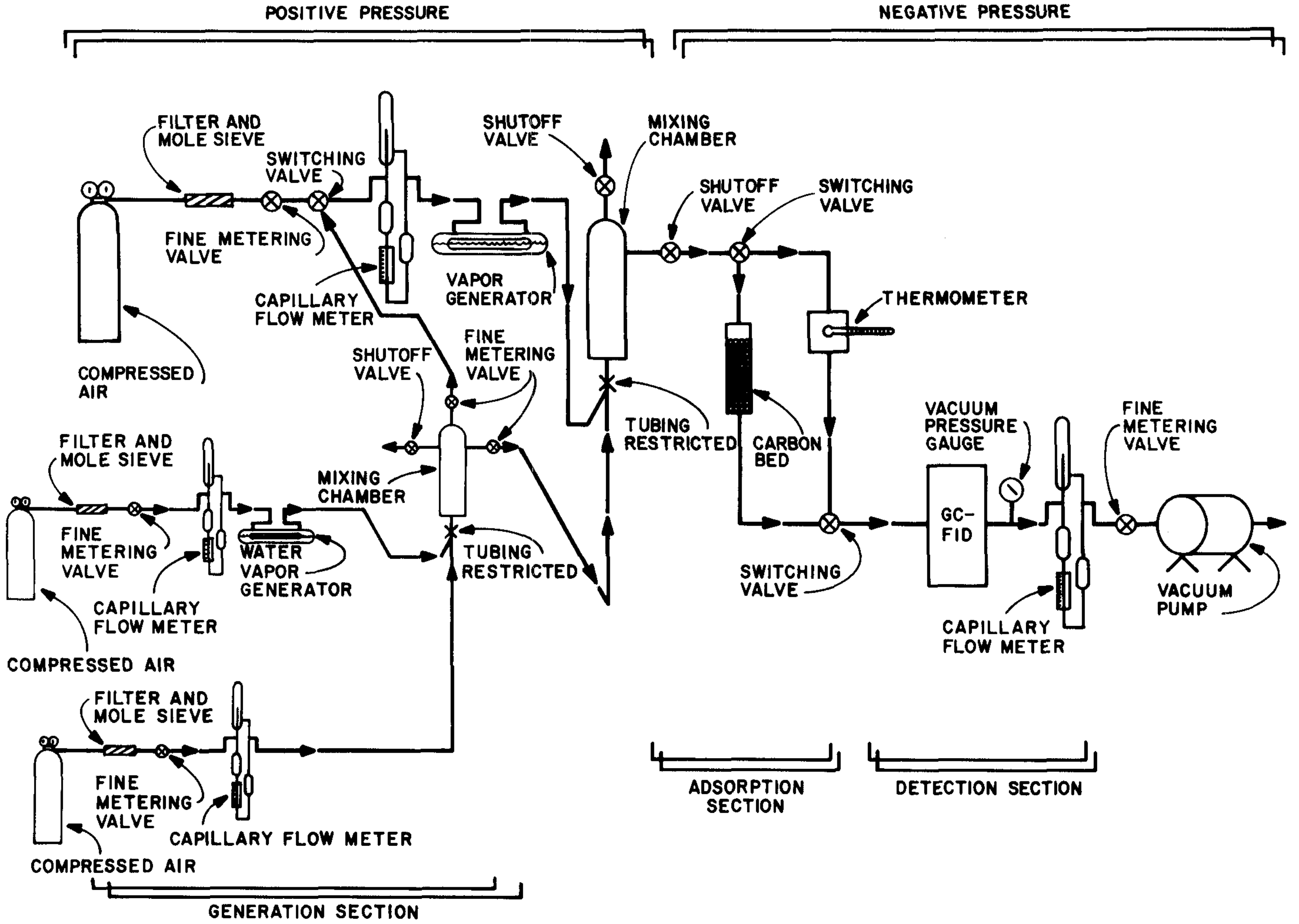

Figure 1—Vapor generation/carbon adsorption system

The Wheeler-Dubinin model has been shown to be a reliable predictor of small carbon bed performance.(9-12) The reliability of its predictive power under field conditions has not been demonstrated. In addition, the effects of multiple adsorbable vapors and varying contaminant concentrations largely are unknown.

Materials and Methods

The adsorbates used in these investigations were carbon tetrachloride (Fisher Certified, Fisher Scientific, Pittsburgh, Pa.) and triple distilled water. The adsorbent was a 12-20 mesh petroleum-based granular activated carbon. The carbon is a standard respirator carbon used by a major supplier of respirator cartridges. The humidity test chambers were established using saturated salt solutions in small plastic desiccators. The salt solutions used were magnesium chloride, 33%; magnesium nitrate, 52%; lithium acetate, 68%; potassium chloride, 86%; barium chloride, 90% RH (23°C).

Adsorption Apparatus

The adsorption apparatus is shown in Figure 1. The apparatus consists of three functionally discrete sections: vapor generation, adsorption and detection.

The flow through the vapor generation section is produced by three compressed air lines. Two provide vapor generation air and the other a dilution air source. Airstreams pass through in-line filters and molecular sieve/drying tubes and are regulated with stainless steel, fine-metering valves. The volumetric flow rates are measured using capillary flow meters.

Organic and water vapors are generated separately by passing air through a boat generator, which is a glass cylinder (approximately 230 cm^3) half filled with the liquid to be evaporated. To increase the surface area for evaporation, a porous cellulose cylinder is placed inside the generator. The airstream enters one end of the generator and becomes vapor laden as it sweeps across the liquid surface and the wetted cellulose cylinder. Vapor-laden air is mixed with dilution air in a 250 cm^3 mixing chamber. The vapor steam enters the mixing chamber through a constriction that produces turbulent flow, ensuring good mixing. The vapor stream can be drawn off to challenge a carbon bed or pass through the chamber and exit the system. As depicted in Figure 1, the generation section is under positive pressure. The remainder of the apparatus is under negative pressure with the challenged vapor being drawn from the generation section using a vacuum pump. Generating excess vapor under positive pressure and challenging under negative pressure allows the flow rate through the carbon bed to be changed without affecting the generation rate or the challenge concentration. In this system, the vapor concentration can be set by adjusting the flow rate through the generator and/or by adjusting the dilution airflow by using the fine metering valves placed in each of these lines. The vapor concentration will remain stable for long periods of time as long as the liquid in the generator is kept roughly half full. The temperature of the vapor is monitored by an in-line thermometer.

The adsorption section of the apparatus consists of a carbon bed and associated plumbing. The vapor, drawn from the generation sections, can pass through a carbon adsorbent bed or be diverted around the bed using switching valves. Bed bypass is used when starting the system or whenever the concentration is to be adjusted. The carbon bed holder is a 1-cm O.D. glass tube approximately 14 cm in length and can hold up to 1.2 g of carbon. The carbon is retained by a coarse glass frit located approximately 4 cm from the bottom of the holder.

The flow rate through the negative pressure side of the apparatus is measured using a capillary flow meter and regulated with a fine metering valve. A Millipore vacuum pump (Millipore Corporation, Bedford, Mass.) is used to draw the air through the negative pressure side of the system.

The apparatus was constructed primarily with stainless steel tubing (small sections contained copper tubing) and borosilicate glass. All valves were stainless steel, and glass unions are ball and socket. Liquid leak detector was used to test for leakage in the positive pressure side. The negative pressure side was tested for leakage by closing off one end and drawing approximately 3 times the normal operating vacuum (25 cm Hg). It was determined to have negligible leakage when after 5 min the vacuum had not decreased by more than 10% (2.5 cm Hg).

System water vapor concentrations were determined using an electric hygrometer equipped with narrow-range, lithium chloride coated wire probes.

A gas chromatograph equipped with a flame ionization detector (GC–FID) was used in the detection section of the apparatus. The GC was equipped with a 30 M, 530 μM I.D. capillary column. Samples were injected using a heated gas sampling valve (GSV, 0.5 cm^3).

Procedure

The adsorbent bed weights used in these investigations ranged from 0.8 to 1.2 g (dry weight) of activated carbon. The carbon adsorbent used was equilibrated at the desired test humidity by storage in a saturated salt solution chamber maintained at 23°C. The adsorbent was considered saturated when no weight gain was noted on 3 consecutive measurements (72 hr). After equilibration with water vapor, the adsorbent was gravity packed into the carbon holder. The bulk density of packing (dry) of the adsorbent was 0.401 g/cm^3.

An airstream containing 90 μg/cm^3 carbon tetrachloride vapor (relative pressure of 0.01) was drawn through the adsorbent bed at 285 cm^3/min. Carbon tetrachloride and water vapor were introduced simultaneously into the adsorbent bed. The carbon tetrachloride concentration for each run was kept constant while the water vapor concentration was varied to match the equilibration concentration of the adsorbent. A series of at least 3 repetitive experimental trials were conducted at each relative humidity point (0%, 30%, 52%, 60%, 86%, 90% RH).

As the test vapor passed through the bed, the exit concentration was monitored as a function of time. The log C_x/C_o versus time can be plotted according to Equation 2. Equation 2 can be derived from algebraically manipulating Equation 1. Equations 1 and 2 are valid only in the region $0 < C_x/C_o < 0.04$. This is the region of pseudo-first-order kinetics.$^{(9)}$ Using a personal computer and statistics package, a regression line was calculated for each run. The rate constant k_v and the saturation capacity W_e can be calculated from the regression coefficients of the polynomial:

$$\text{natural logarithm (Ln)} \ (C_x/C_o) = a + b\,t_B$$

according to Equations 3 and 4.

$$\mathrm{Ln}(C_x/C_o) = (-Wk_v/Q\rho_B) + (C_o\,k_v/W_e\,\rho_B)\,t_B \qquad \textbf{(2)}$$

$$k_v = -(aQ\rho_B/W) \qquad \textbf{(3)}$$

$$W_e = (C_o\,k_v/b\,\rho_B) \qquad \textbf{(4)}$$

Results

Water Vapor–Carbon Isotherm

The water vapor–carbon isotherm is shown in Figure 2. At each relative humidity point, the mass (g) of water vapor adsorbed was determined. The mass was plotted against the relative water vapor pressure (at 23°C). It is a typical Type V isotherm.$^{(13)}$ The isotherm consists of 2 legs, an adsorption leg, and a desorption leg (the upper curve). From the adsorption leg, one can see that little vapor is adsorbed until the relative vapor pressure (P/Ps) exceeds 0.5. Of particular interest is the desorption isotherm which shows a significant

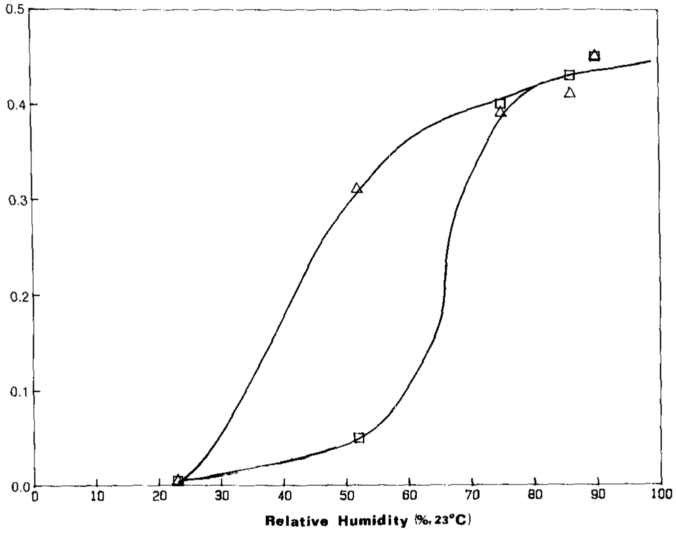

Figure 2—Water vapor/carbon isotherm: □—adsorption △—desorption

TABLE I
Adsorption Parameters of Respirator Activated Carbon for Carbon Tetrachloride at Various Humidities

Relative Humidity (23° C)	Adsorption Rate Constant K_v, (s^{-1})	Kinetic Adsorption Capacity, W_e (g/g)
0	65	0.361
30	68	0.286
52	63	0.271
60	48	0.248
86	25	0.203
90	18	0.194

hysteresis effect. The importance of this phenomenon is that once water vapor has adsorbed onto the adsorbent, it is not desorbed readily. The maximum mass of water vapor adsorbed for this carbon was 0.46 g of vapor per gram of adsorbent. This isotherm agrees with other published data.(8,12,13)

Carbon Tetrachloride and Water Vapor

The effect of adsorbed water vapor at 0%, 30%, 52%, 60%, 86% and 90% relative humidity (23° C, corresponding to 0, 7, 14, 18 and 21 mg/L) on k_v and W_e was determined. These data are presented in Table I. Coefficients of correlations for the regression equations ranged from 0.95 to 0.99. High correlation coefficients indicate good linearity when the data are plotted according to Equation 2.

The family of regression lines used to develop the data in Table I are presented in Figure 3. Once the water vapor concentration exceeded 50% RH, there was a shift to the left in each of the regression lines. In all but one case, this shift resulted in a lower observed k_v and W_e. The 30% RH regression curve exhibited a slightly increased k_v, 68 versus 65 s^{-1}, when compared to dry carbon. This is consistent with other investigations which have reported enhanced adsorption of contaminants at low water vapor concentrations when compared to adsorption on dry carbon.

As the water vapor concentration exceeded 50% RH (12 mg/L, 23° C), the rate constant decreased in a linear fashion. The relationship of k_v to %RH was evaluated by plotting k_v against the relative humidity (Figure 4). For relative humidities exceeding 50%, the data can be described by the line:

$$k_v = 129.9 - 1.23\% \text{ RH}$$

Using this relationship, the minimum k_v predicted would be 6.3 s^{-1} at a water vapor concentration equal to 100% RH. This is 90% reduction from the dry carbon value.

The kinetic adsorption capacity, W_e, for the carbon tetrachloride–dry carbon system was found to be 0.36 g/g. As the system water vapor concentration was increased, the adsorption capacity showed a decrease which was linear when plotted against %RH (Fig. 5). The equation of the regression line was the following:

$$W_e = 0.36 - 0.002\% \text{ RH}$$

This line predicts a minimum W_e of approximately 0.16 g/g, a 45% reduction from the dry carbon value.

Using experimental data, the time to 1% breakthrough was calculated and plotted against the equilibrium relative humidity (Figure 6). The result of this plot indicates that the protective capacity of a one-gram adsorbent bed has been reduced by approximately 80%.

Conclusions and Discussions

Adsorbed moisture has been demonstrated to have a profound effect on the parameters in the Wheeler equation. The ability of the Wheeler-Dubinin Model to predict service life is dependent on the accuracy of the Wheeler equation. Predictions based upon dry carbon values of W_e and k_v would overestimate severely the protective capacity of an adsorbent cartridge.

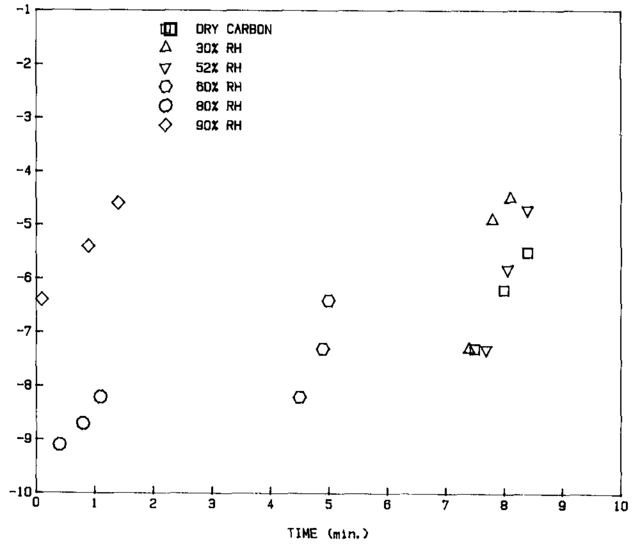

Figure 3—Kinetic regression curves for experimental trials

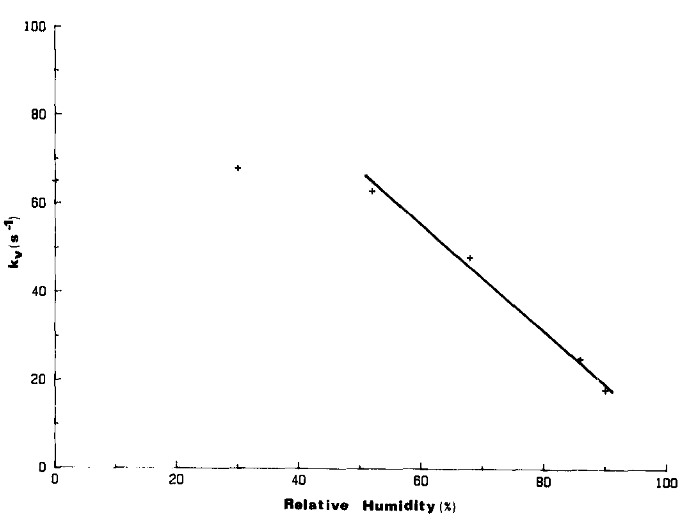

Figure 4—k_v versus % RH (23° C)

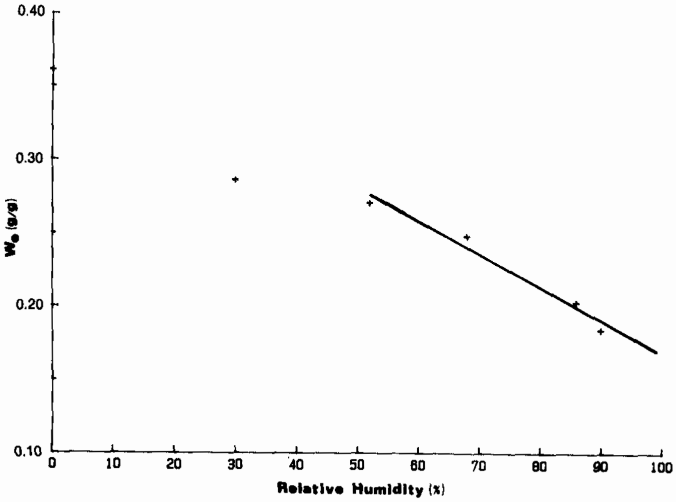

Figure 5—W_e versus % RH (23° C)

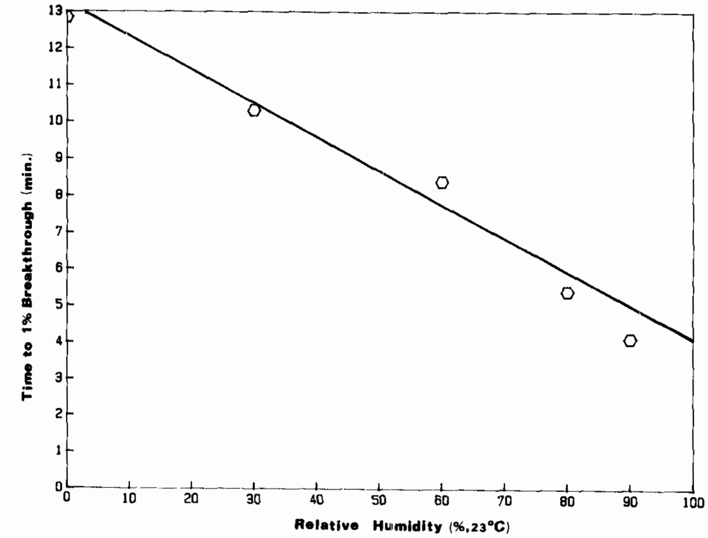

Figure 6—1% Breakthrough versus % RH

The data presented in this paper represent the worst case, *i.e.*, a cartridge fully saturated with water vapor and an adsorbate with poor water solubility. If an estimate of respirator cartridge protective capacity were based upon this data, a significant margin of safety for the cartridge would exist. The use of the worst case analysis is supported by consideration of the water vapor isotherm. When the environmental water vapor concentration exceeds 80% RH, the adsorbent bed nearly is saturated, and the maximum reduction in bed capacity can be expected. This still would hold if the ambient water vapor concentration declined to 60% or 70% RH.

Acknowledgment

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