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Adsorption Characteristics of Volatile Anesthetics on Activated Carbons and Performance of Carbon Canisters

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The adsorption characteristics, such as the adsorption capacity, the nature of the mass transfer zone, and heats of adsorption, are important for evaluating the performances of carbon canisters for removal of waste anesthetic vapors. The adsorption capacities and the natures of the mass transfer zones were measured for halothane, methoxyflurane, enflurane, isoflurane, and trichloroethylene on Witcarb 965 activated carbon. In addition, adsorption capacities and heats of adsorption for nitrous oxide, cyclopropane and oxygen were measured on the same carbon. The data indicate that high adsorption capacities of dilute anesthetic vapors on this activated carbon permit the use of carbon canisters for removal of these volatile anesthetics from mixtures with oxygen or nitrous oxide. In contrast, high concentrations of anesthetics such as nitrous oxide and cyclopropane cannot be removed economically by disposable canisters. A simplified procedure using the "characteristic curve" concept and "LUB/equilibrium section theory" for approximate prediction of the adsorption capacities and evaluation of the performance of a canister is outlined. (Key words: Physics, carbon adsorbents; Equipment, anesthetic adsorbents; Anesthetics, volatile, trace concentrations.)

THERE IS A GROWING CONCERN regarding the contamination of the operating room atmosphere by volatile anesthetics. Recent studies¹⁻⁵ suggest that the incidences of spontaneous abortion, congenital abnormalities, cancer, and hepatic and renal diseases are increased among personnel undergoing prolonged exposure to waste anesthetics, even at trace quantities. Several procedures have been proposed to reduce the level of this pollution.⁶ A simple and effective method is the use of a canister containing activated carbon, which selectively

removes the anesthetic from the waste gas.⁷⁻⁹ Published literature on this subject is limited to descriptions of general performances of such commercial devices with respect to a few selected anesthetic vapors. A more basic understanding of the adsorption characteristics of volatile anesthetics on the carbon adsorbent is necessary for the judicious selection and use of this procedure. Questions such as, "Can the same canister be used with equal effectiveness for removal of different anesthetics under different conditions of operation?" may be answered only on the basis of a fundamental analysis of the process. The purpose of this article is to provide such background and to outline a simplified procedure for the selection and evaluation of the canister.

Selective separation of gas mixtures by the phenomenon of adsorption is caused by differences in the intermolecular attraction between the components of the mixture and the solid adsorbent. Consequently, selected components of the gas mixture are concentrated at the solid surface in excess of the others, resulting in their removal from the gas phase. This is different from absorption, where the gas molecules penetrate into the bulk of the solid/solvent adsorbent molecules.

Determinants of adsorptive properties of adsorbent canisters include: a) equilibrium adsorption capacity of anesthetics on the carbon; b) nature of the mass transfer zone; c) heat of adsorption.

EQUILIBRIUM ADSORPTION CAPACITY

The equilibrium capacity represents the maximum amount of the anesthetic vapor/gas that can be removed by a given quantity of carbon under a given condition. It depends on the nature of the anesthetic, its concentration (partial pressure) in the feed stream, the natures and concentrations of other

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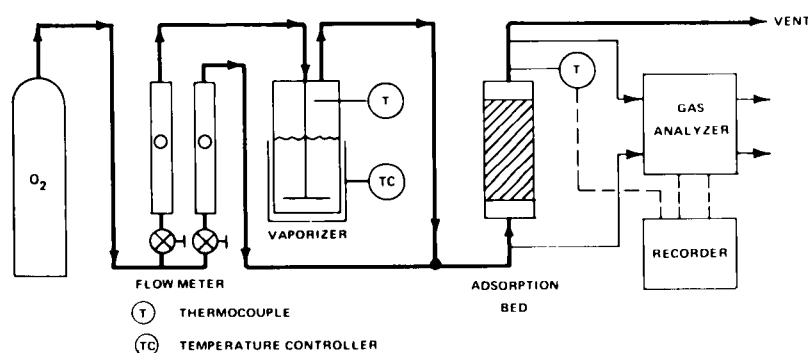


FIG. 1. Schematic of the continuous flow system for measurement of adsorption capacities and mass transfer characteristics of dilute volatile anesthetics.

components in the stream, and the temperature of the system. Typically, the higher the concentration of the anesthetic vapor, the larger is the adsorption capacity, while the higher the temperature of the canister (or feed stream), the lower is the equilibrium capacity.

NATURE OF MASS TRANSFER ZONE

A mass transfer zone is formed at the inlet end of the canister soon after the contaminated stream is fed into it. Selective adsorption (removal) of the contaminant takes place only in this zone. The concentration of the contaminant varies from that of the feed stream to zero across the zone. The zone propagates through the canister as more feed is passed. The carbon behind the zone remains loaded with the contaminant at its equilibrium capacity under the superincumbent condition (feed condition for dilute contaminants) and the carbon ahead of the zone stays virtually free of the contaminant. The contaminant begins to appear at the exit end of the canister when the front of the zone reaches

that end. This is commonly known as the breakthrough of the contaminants, which represents the point at which the canister is no longer able to produce a contaminant-free effluent stream (life of the canister) without reactivation of the adsorbent.

It follows that one must know the shape and the size of the mass transfer zone in order to evaluate canister performance, because the carbon in the zone realizes an adsorption capacity less than its equilibrium capacity. In other words, the canister offers less than its maximum possible capacity (equilibrium capacity) for the contaminant at breakthrough due to the presence of a finite mass transfer zone. The nature of the zone may depend on various factors, such as adsorption kinetics, gas flow rate, gas composition, temperature, and size of adsorbent particles. The wider the zone, the less is the effectiveness of the canister. The user, therefore, should choose the carbon with the thinnest mass transfer zone for the anesthetics of interest.

HEAT OF ADSORPTION

Adsorption is an exothermic process. The temperature of the adsorbent in the canister rises during adsorption of an anesthetic. This, in turn, causes a reduction in the equilibrium capacity of the adsorbent, making the situation more complex. However, for most dilute contaminants, the operation of the canister is approximately isothermal because the velocity of the heat transfer zone is faster than the velocity of the mass transfer zone. Consequently, the equilibrium capacity realized by the carbon behind the zone is approximately at feed temperature and concentration. This is fortunate in view of the fact that most anesthetic vapors are dilute in concentration. Even the presence of nitrous oxide as the carrier gas does not create a problem because of high selectivity of anesthetic vapors from such mixtures (see text later).

In summary, the desired characteristics of the carbon adsorbent are: a) large equilibrium capacity and selectivity for the anesthetic; b) thin mass transfer zone for the anesthetic; c) low heat of adsorption (for bulk contaminants). The choice of the carbon must be made only after a careful investigation of these properties.

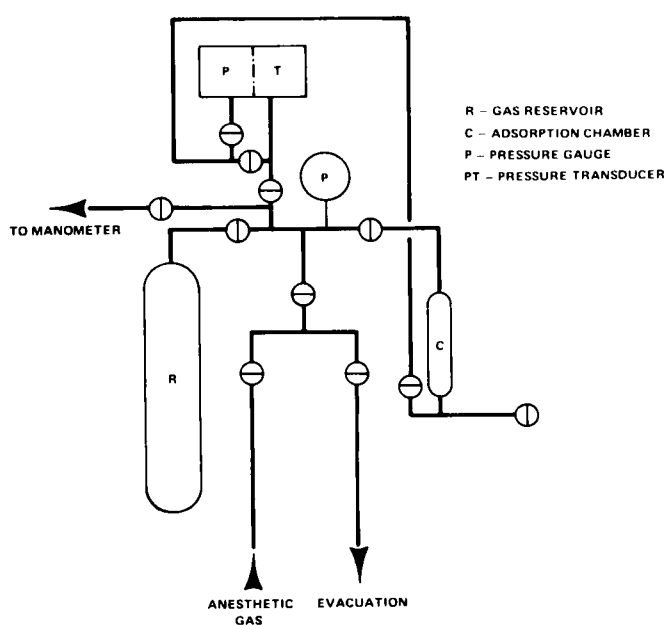


FIG. 2. Schematic of the volumetric adsorption apparatus for measurement of adsorption capacities of gaseous anesthetics.

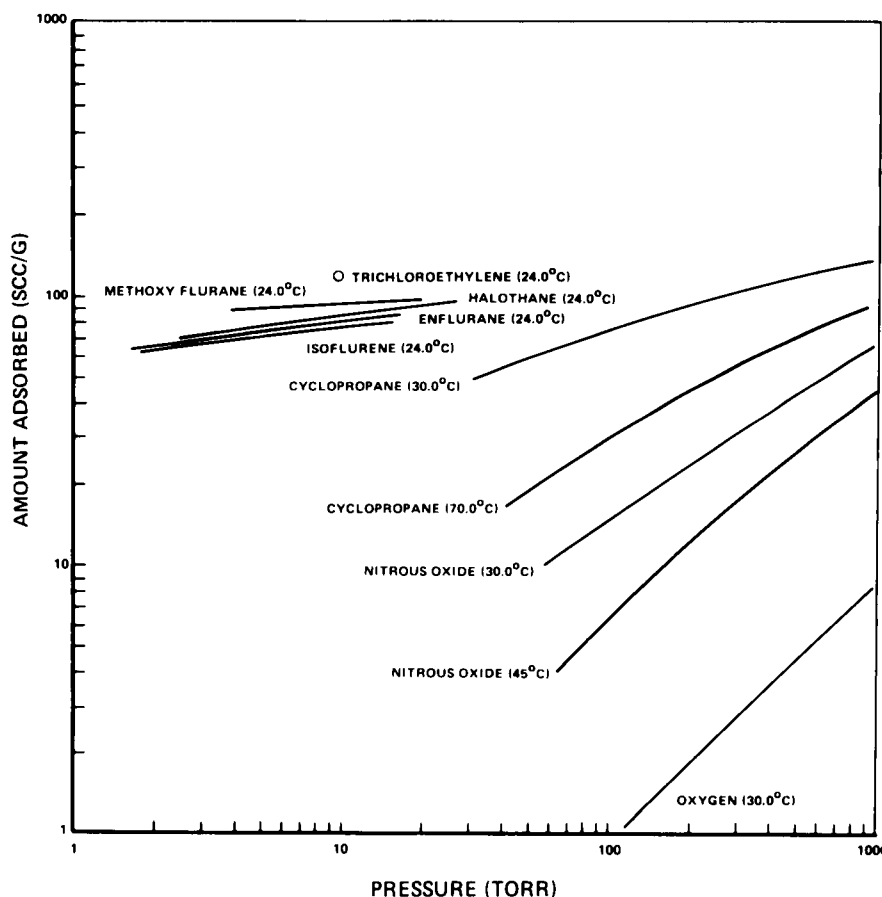


FIG. 3. Adsorption isotherms for various anesthetics plotted as a function of equilibrium partial pressure of the anesthetic on Witcarb 965 activated carbon.

Methods and Materials

Having outlined the criteria for a desired adsorbent, we measured the properties of a particular commercial carbon, Witcarb 965 (12–20 mesh), manufactured by Witco Chemical Company, New York. This carbon was arbitrarily chosen for demonstrating the concepts discussed in this article. However, the results show (see Appendix) that this carbon is adequate for efficient and economic removal of dilute anesthetics. We briefly summarize the experimental methods used for these measurements.

The adsorption capacities and breakthrough characteristics for halothane, methoxyflurane, enflurane, isoflurane, and trichloroethylene were measured using a flow system (fig. 1). Different mixtures of anesthetic vapors and oxygen were passed at a constant flow rate through a tubular carbon bed containing a known quantity of carbon. (Although these experiments were carried out using mixtures of anesthetic vapors and oxygen, similar experiments can be carried out using mixtures of nitrous oxide and oxygen as a carrier gas.) The effluent gas concentration was monitored as a function of time by using a mass spectrometer (Perkin-Elmer MGA-1100A) for halothane and methoxyflurane and by using a katharometer (Gow-Mac 20-150) for the others. The carbon bed was

removed from the system and weighed when the column was saturated with the feed, *i.e.*, when the effluent concentration became equal to that of feed. The concentration–time read-out provided the breakthrough characteristics, while the increase in weight of the carbon column gave the equilibrium capacity at feed conditions.

In experiments in which the flow system was used (fig. 1), the bed used for breakthrough experiments was 4.2 cm in internal diameter and 5.2 cm in length. It contained 30 grams of dry carbon. A different bed (internal diameter 1.5 cm, length 8 cm) containing 3 grams of carbon was used for determination of equilibrium capacities at concentrations below 1.5 per cent. Anesthetic vapors of different concentrations were generated by flowing oxygen through a Copper Kettle® vaporizer while maintaining the total flow rate at approximately 1 liter/min.

The equilibrium capacities for 100 per cent nitrous oxide, cyclopropane and oxygen at different gas pressures were measured using an isothermal volumetric adsorption apparatus (fig. 2). The principle involved in these measurements consisted of exposing a known volume of anesthetic gas at a given initial pressure from reservoir R with a specific quantity of carbon in the adsorption chamber C and measuring the resulting pressure change in the system due to adsorption using

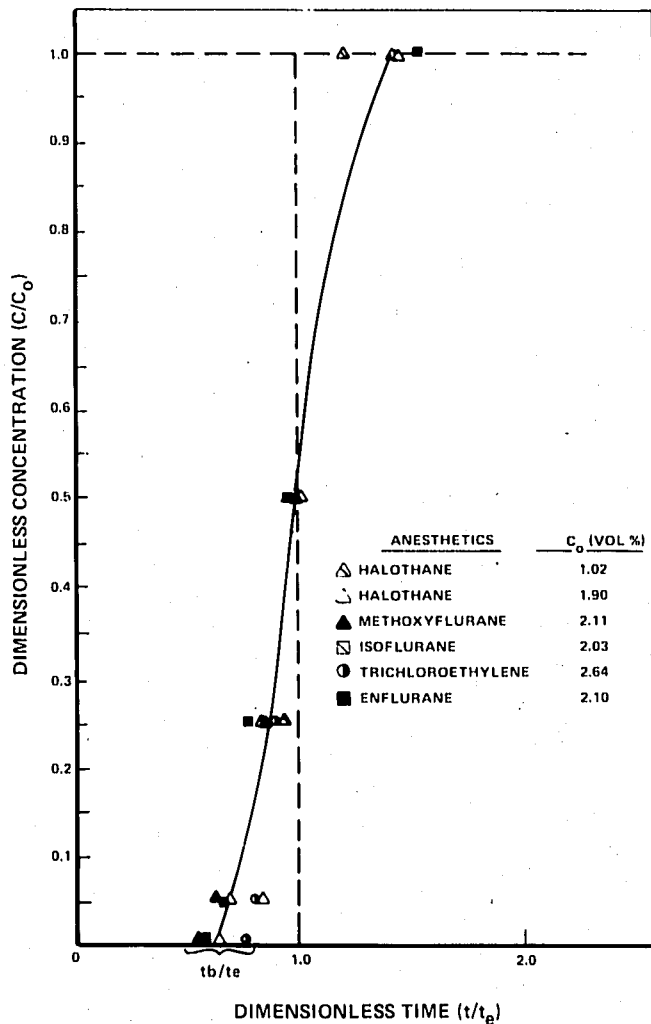


FIG. 4. Breakthrough characteristics of dilute anesthetic vapors from mixtures with oxygen on Witcarb 965 activated carbon. (See text for explanation.)

pressure transducer PT and the gauge P. The amount adsorbed at the final equilibrium pressure of the system was then calculated from the pressure changes using a material balance to account for the anesthetics removed by the carbon. A more detailed account of this experimental procedure may be found in the literature.¹⁰ Heats of adsorption were evaluated by using the isothermal equilibrium data at different temperatures.¹¹

Results and Discussion

EQUILIBRIUM CAPACITIES

The adsorption capacities of the anesthetic vapors at various concentrations in mixture with oxygen were measured at about 24 C. The adsorption capacities for nitrous oxide, cyclopropane and oxygen were determined at 30, 45, and 70 C. Figure 3 shows the experimental equilibrium isotherms plotted as the amount adsorbed in

standard cubic centimeters per gram of the carbon, n (scc/g), as a function of the equilibrium partial pressure, P (torr), of the gas/vapor. The figure shows that the carbon offers very large capacities for the anesthetic vapors even at a very low partial pressure. On the other hand, the capacities for the gases, nitrous oxide and cyclopropane, are relatively low at low pressures, but they become moderate to high at elevated pressures. In comparison, oxygen capacity remains low even at large pressures.

The adsorption capacity of a component of a gas mixture is, however, not equal to its equilibrium capacity as pure gas at its partial pressure in the mixture. The capacity of a component depends on its relative selectivity of adsorption with respect to the other components of the mixture. Theories to predict the selectivity and the consequent mixed gas capacity from pure component adsorption data have been developed.¹² It can be shown from these theories that anesthetic vapors studied in this report will be adsorbed on the carbon almost exclusively from mixtures with nitrous oxide and/or oxygen due to their large selectivity even at dilute concentration.

MASS TRANSFER ZONE

The characteristics of the mass transfer zones for adsorption of the anesthetic vapors from dilute mixtures in oxygen were measured at approximately 24 C and at a total pressure of 760 torr. Figure 4 shows the complete breakthrough characteristics. The ordinate represents the ratio of the exit

TABLE 1. Important Physical Properties of Anesthetic Agents

| Anesthetics | Mol. Wt. | Liquid Molar Volume at 20 C (v, cc/mol) | Vapor Pressure at 20 C (P_0 , Torr) |
|-------------------|----------|---|--|
| Chloroform | 119.4 | 81.2 | 159 |
| Diethyl ether | 74.1 | 102.9 | 442 |
| Divinyl ether | 70.1 | 91.0 | 580 |
| Enflurane | 184.5 | 121.4 | 180 |
| Fluroxene | 126.0 | 111.5 | 286 |
| Halothane | 197.4 | 105.6 | 242 |
| Isoflurane | 184.5 | 123.8 | 250 |
| Methoxyflurane | 165.0 | 117.9 | 26 |
| Trichloroethylene | 131.5 | 87.8 | 58 |
| Cyclopropane | 42.0 | 67.6 | 4,256 |
| Ethyl chloride | 64.0 | 70.6 | 1,000 |
| Ethylene | 28.0 | Above critical | Above critical |
| Nitrous oxide | 44.0 | 59.9 | 39,520 |

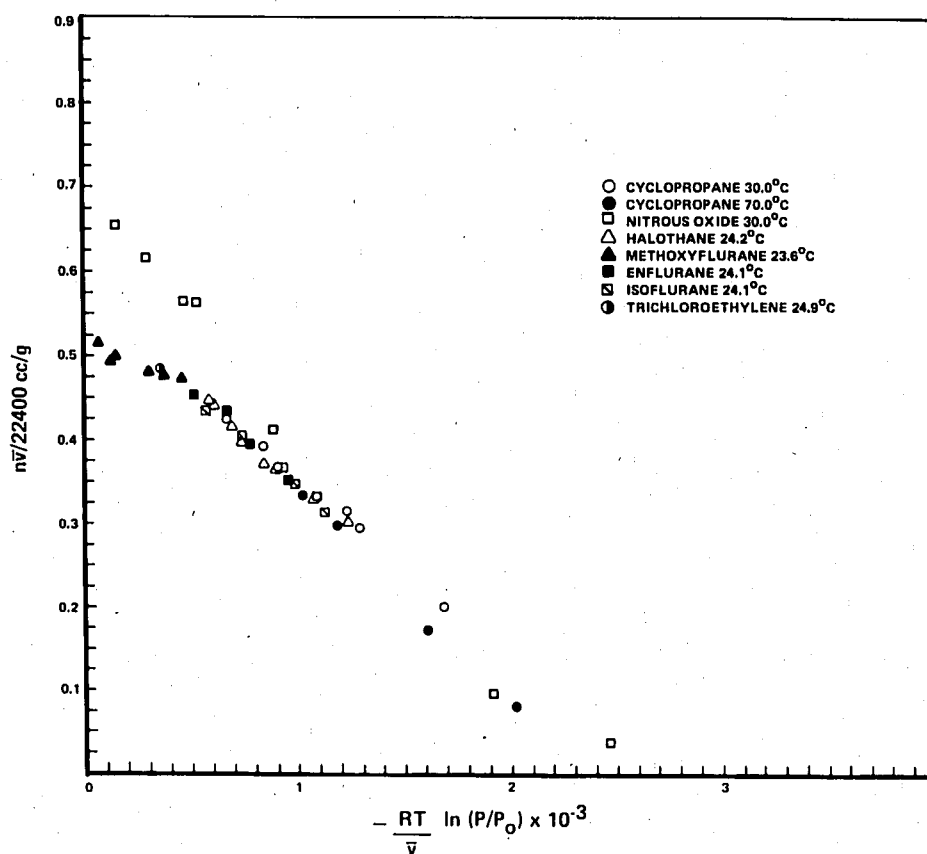


FIG. 5. Characteristic curve for adsorption of anesthetics on Witcarb 965 activated carbon. (See text for explanation.)

anesthetic composition, C (volume per cent) to the concentration of the feed, C_0 (volume per cent). The abscissa represents the ratio of the actual elapsed time since the beginning of the experiment, t , to the equilibrium breakthrough time, t_e (minutes). t_b is the time required for the canister to break through if the mass transfer zone is infinitely thin, and its value can be estimated by simply dividing the total equilibrium capacity, $W \cdot n$, of the canister by the flow rate of the anesthetic, $F \cdot C_0$, where W (g) is the total amount of carbon in the canister, n (cc/g) is the equilibrium capacity of the carbon at the feed condition, and F (cc/min) is the total flow rate of the feed stream to be cleaned. t_b is the actual breakthrough time due to the presence of a mass transfer zone.

Following this convention, the shape of the curve in figure 4 must be a vertical line at $t/t_e = 1$ ($t_b = t_e$) as shown by the dashed line if the mass transfer zone is infinitely thin. Any deviation from this behavior ($t_b/t_e < 1$) indicates the presence of a finite mass transfer zone thickness which causes the anesthetic to break through before the entire equilibrium capacity of the canister is utilized.

Indeed, figure 4 shows that such is the case for the anesthetics studied in this evaluation. Figure 4 also shows that these anesthetics have very similar mass transfer zones since they all break through at values of approximately 0.6–0.8 for t_b/t_e .

HEAT OF ADSORPTION

Heats of adsorption were not measured for the anesthetic vapors in this study because they are commonly used in very dilute concentrations and their removal can be carried out under nearly isothermal conditions. The heats of adsorption for the gases nitrous oxide and cyclopropane were evaluated to be approximately 8–12 kcal/mol, depending on their loading on the carbon. The heat effects for these gases, which are commonly used in bulk concentrations, cannot be ignored for their separation from mixtures with oxygen. This is, however, not a problem for removal of diluent anesthetic vapors from mixtures with nitrous oxide and/or oxygen because of their large selectivity.

DESIGN AND PERFORMANCE OF THE CANISTER

We now briefly describe a simple procedure for evaluation of the carbon canister for isothermal operation utilizing the adsorption characteristics discussed above. The concept is known as the "LUB (length of unused bed)/equilibrium section concept" proposed by Collins.¹³ It consists of attributing a parameter "LUB" as a measure of the ineffectiveness of the mass transfer zone in removing the anesthetics at the equilibrium capacity. It represents an equivalent length of the bed that is incapable

of any separation due to the presence of a finite mass transfer zone if one assumes equilibrium loading at feed conditions as the capacity of the entire carbon bed. LUB can be obtained from the breakthrough data (fig. 4) by the equation:

$$\text{LUB} = (1 - t_b/t_c) L_0$$

where t_b/t_c is the dimensionless breakthrough time at which the anesthetic agents appear in the effluent from the test canister, and L_0 is the length of the carbon bed in the test canister.

This concept may be used to design a canister by determining the size of the carbon bed necessary for removing all of the feed anesthetic contaminant at the equilibrium capacity under feed conditions and then by adding an extra length equal to LUB for the system of interest. The shape and geometry for most systems and, therefore, LUB obtained from a test bed can be used for scale up. The test bed, however, should be long enough to contain the entire mass transfer zone so that LUB can be experimentally measured.

The usefulness of this design concept is illustrated by the examples given in the Appendix, together with an explanation of why the same carbon canister cannot be used with equal effectiveness for removal of different anesthetics under different operating conditions.

PREDICTION OF ADSORPTION CHARACTERISTICS

The importance of the adsorption characteristics of anesthetics in evaluating the performance of the canister is evident. Unfortunately, these properties are not always available in the literature and the user must determine them experimentally for the system of interest. Such measurements are often tedious and time-consuming. However, it may be possible to predict these properties at least approximately, using theories designed to coalesce equilibrium adsorption capacities for different gases under different conditions into a single "characteristic curve" for a given adsorbent.¹⁴ This enables prediction of the equilibrium capacity for any gas simply by generating the characteristic curve for the adsorbent of interest using a reference gas.

We evaluated the correlation proposed by Maslan and co-workers¹⁵ using our experimental data. According to this theory, a plot of the quantity $n\bar{v}/22,400$, versus $(RT/\bar{v}) \ln (P/P_0)$ would generate a characteristic curve that would be independent of the nature of the gas, its pressure and the temperature. The parameters are as follows: n = volume of the anesthetic (scc) adsorbed per gram of the adsorbent at an equilibrium partial pressure P (torr) of the anesthetic at temperature T (degrees K). \bar{v} = liquid molar volume (cc/mol) of the anesthetic at temperature T . P_0 = vapor pressure (torr) of the gas at temperature T . R = gas constant, 82 cc-atm/mol degrees K.

Figure 5 shows the test of this theory for our

data on the carbon. Table 1 summarizes the values of \bar{v} and P_0 for most of the important volatile anesthetics. It may be seen from figure 5 that the correlation helps to coalesce the data into a single curve fairly well, particularly in the region of large P . The only significant deviation is manifested by nitrous oxide at its high loading region, indicating a much larger capacity for this gas. This is possibly due to the adsorption of nitrous oxide, which is the smallest molecule in the group, in some of the smaller pores of the carbon not accessible to the other gases because of their larger molecular sizes.

It may be concluded that the equilibrium capacities of the anesthetic vapors on the Witcarb carbon can be predicted reasonably well from the characteristic curve in figure 5. The procedure is to calculate the dimensionless group in the abscissa of figure 5 for the desired gas at the P and T of interest and then predict n from the ordinate. It should be noted here that the characteristic curve is a property of a particular carbon and will differ from carbon to carbon.

In contrast, there is no simple and adequate theory for predicting the LUB. The best that one can do in the absence of this information is to evaluate the minimum equilibrium requirement for the canister under a specific condition of operation and overdesign the canister by a certain percentage. At least the adequacy of a given canister for a desired operation can be evaluated.

Conclusions

1) Knowledge of equilibrium capacity and nature of the mass transfer zone is necessary for efficient selection and operation of an adsorbent canister for removal of anesthetics. 2) The carbon canisters may be used to remove most of the volatile anesthetics, such as halothane, methoxyflurane, enflurane, isoflurane, and trichloroethylene, from waste gases on a disposable basis, but this approach cannot be used economically to remove bulk contamination of gaseous anesthetics such as cyclopropane and nitrous oxide. 3) Equilibrium adsorption characteristics of anesthetics on activated carbons can be approximately predicted from the characteristic curve.

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APPENDIX

Examples of the Use of Adsorption Characteristics of Anesthetics on Activated Carbon for Evaluating Canister Performance

Example 1:

Consider a case where the waste gas contains 1.02 vol per cent (C_0) of halothane in oxygen at a temperature of 24 C and a total pressure of 760 torr. The waste gas flow rate (F) is 5 l/min and the duration (t_0) of operation is 6 hours.

a. *Calculation of Minimum Equilibrium Canister Size:*

$$\begin{aligned} &\text{The total amount of halothane to be removed during the operation, } FC_0t_0 \\ &\times \frac{273}{(273 + 24)} = 16,876 \text{ scc} \end{aligned}$$

$$\text{The partial pressure of halothane feed} = 7.75 \text{ torr}$$

$$\text{The equilibrium capacity of the carbon for halothane at 24 C and 10 torr (from figure 3)} = 82 \text{ scc/g}$$

$$\text{Therefore, the size of the canister based on equilibrium capacity, } W_e = 205 \text{ g}$$

This quantity of carbon (bulk density, 0.44 g/cc) can be packed into a canister 6.7 cm in diameter and 13.4 cm in length. This, of course, is an example; other geometries may be chosen.

b. *Calculation of LUB:*

$$t_b/t_e \text{ for halothane at feed conditions (from figure 4)} = 0.8$$

$$\begin{aligned} \text{Length of test bed} &= 5.4 \text{ cm} \\ \text{Therefore, LUB for halothane} &= 1.08 \text{ cm} \end{aligned}$$

c. *Actual Canister Size:*

The actual canister size required for the desired operation is 6.7 cm internal diameter and $(13.4 + 1.08) = 14.48$ cm length. This canister would contain 224.8 g of carbon, which is 10 per cent larger than the minimum equilibrium quantity. It should be mentioned here that the longer the canister, the smaller is the ratio, LUB/total length, and, hence, better is its efficiency.

Example 2:

How long would the above-designated canister last if methoxyflurane at a concentration of 2.11 vol per cent were used instead of halothane under the same conditions of operation?

a. *Calculation of LUB:*

$$t_b/t_e \text{ for methoxyflurane under feed conditions (from figure 4)} = 0.55$$

$$\text{Length of test bed} = 5.4 \text{ cm}$$

$$\text{Therefore, LUB for methoxyflurane} = 2.4 \text{ cm}$$

This shows that the canister would have $(14.5 - 2.4) = 12.1$ cm of equilibrium section containing 188 g of carbon for methoxyflurane.

b. *Calculation of Equilibrium Capacity:*

$$\begin{aligned} \text{Partial pressure of methoxyflurane in feed} &= 15 \text{ torr} \\ \text{Capacity of methoxyflurane at 24 C and} & \\ \text{15 torr (from figure 3)} &= 95 \text{ scc/g} \end{aligned}$$

Therefore, the canister can handle 17,860 scc of methoxyflurane prior to its breakthrough, which corresponds to 3 hours of operation at the given feed rate.

Example 3:

Consider the case of a waste gas containing 60 per cent by volume of nitrous oxide in oxygen at 30 C. Other conditions are the same as in Example 1.

a. *Calculation of Minimum Canister Size:*

$$\begin{aligned} &\text{The total amount of nitrous oxide to be removed, } FC_0t_0 \times \frac{273}{(273 + 30)} = 973,069 \text{ scc} \end{aligned}$$

$$\text{Partial pressure of nitrous oxide in feed} = 456 \text{ torr}$$

$$\text{Capacity of nitrous oxide at 30 C and 456 torr (from figure 3)} = 41 \text{ scc/g}$$

$$\text{Minimum quantity of carbon required for isothermal operation} = 23,733 \text{ g}$$

Such a large quantity of carbon required for this separation rules out the applicability of disposable canisters for economic reasons.