

# PREDICTORS OF MICROPORE VOLUMES FOR ACTIVATED CARBONACEOUS MATERIALS

Gerry O. Wood, Los Alamos National Laboratory  
Mail Stop K-486, Los Alamos, NM 87545

Joseph A. Rehrmann and Christopher J. Karwacki  
U.S. Army Edgewood Research, Development & Engineering Center,  
Aberdeen Proving Ground, MD 21012-5423

## ABSTRACT

Micropore volumes from adsorption isotherms for organic vapors and for nitrogen on activated carbons were compiled from various sources. Organic vapor micropore volumes ( $\text{cm}^3/\text{g}$ ) were proportional to BET surface areas ( $\text{m}^2/\text{g}$ ) by a constant of  $0.00041 \pm 10\%$ . The correlation with nitrogen micropore volumes was about 10% lower. Butane gas saturations of six activated carbons at ambient temperatures gave even lower micropore volumes when normal liquid densities were used to calculate micropore volumes from capacities. Ethyl acetate saturations gave higher pore volumes than the first correlation, presumably due to supermicropore and macropore volume filling.

## INTRODUCTION

Models have been published<sup>1,2</sup> for estimating adsorption capacities and adsorption bed service lives for organic vapors removed by activated carbon beds, such as in military gas mask or commercial respirator cartridges. An essential input to these estimation models is the micropore volume per gram of the activated carbon. The Dubinin/Radushkevich (D/R) isotherm equation<sup>3</sup> is used to calculate adsorption capacities at the average exposure vapor concentration.

Micropore volumes for organic vapors are not commonly measured and reported by manufacturers and suppliers of carbons and cartridges. If any characteristic is reported, it is the surface area measured with nitrogen at its boiling point ( $77^\circ\text{K}$ ) and calculated using the Brunauer, Emmett, and Teller (BET) adsorption isotherm equation.<sup>4</sup> Equipment is

commercially available for automatically measuring BET surface area, as well as micropore and total pore volumes. These are usually measured with nitrogen.

The question this work addresses is: Are these BET surface areas measured by adsorption of the small nitrogen molecule representative of D/R micropore volumes filled with condensed organic vapors?

### LITERATURE DATA

BET surface areas are often reported in experimental studies as important characteristics of adsorbents. Adsorption isotherms have been reported in many studies, too. These can be fit to the D/R equation. However, unless the isotherms extend to high concentrations approaching saturation, the micropore volumes obtained by data fitting may not be accurate. We have accumulated such BET surface area and corresponding D/R micropore volume data from several sources<sup>1, 5-7</sup> for many types of activated carbons and degrees of activation.

Figure 1 shows a comparison of these two types of data. Most of the data fall within 10% of a proportionality with a slope of 0.00041 mL/g micropore volume per m<sup>2</sup>/g surface area.

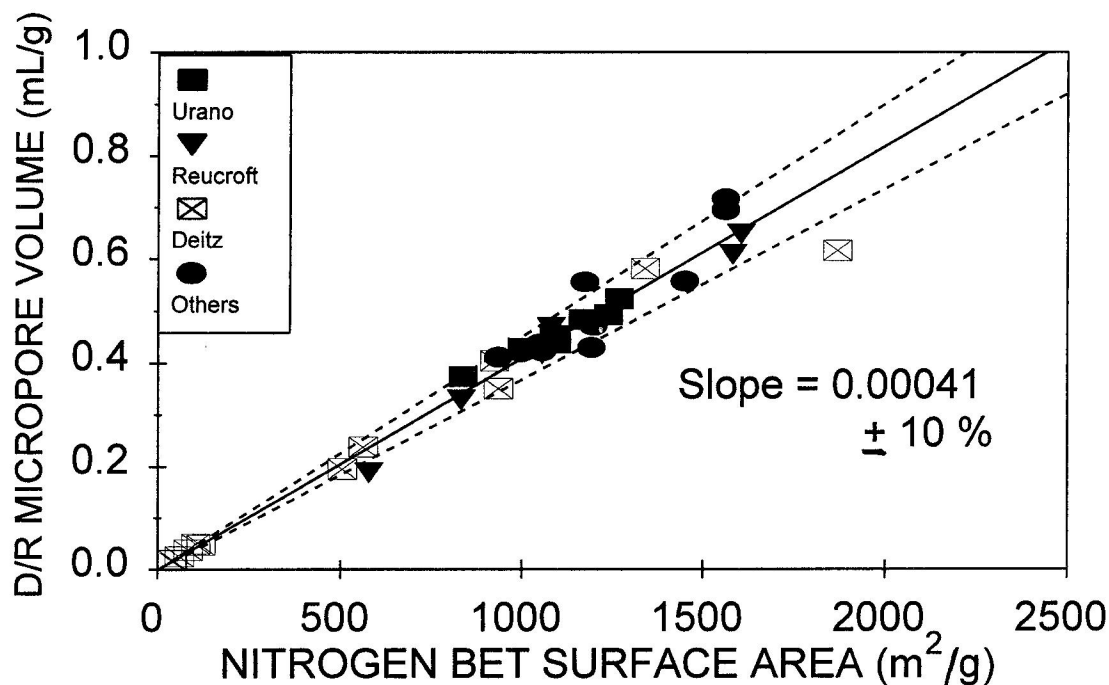


Figure 1. D/R isotherm micropore volumes compared with BET surface areas.

## NITROGEN ADSORPTION

Twelve unimpregnated and variously chemically-impregnated activated carbons were collected and studied for adsorption properties, including nitrogen BET surface areas, micropore volumes, and total pore volumes. Such data was also collected from published sources<sup>7-10</sup> for a variety of original and impregnated bone chars, activated carbons, superactivated carbons (Maxsorb), and carbonized resins (Ambersorb).

Figure 2 shows a comparison of nitrogen micropore volumes with BET surface areas. The solid and dashed lines represent the average and  $\pm 10\%$  ranges, respectively, in Figure 1. These data show that nitrogen micropore volumes are also proportional to BET surface areas for all these types of carbonaceous materials, but the correlation averages about 10% lower than that obtained for organic vapor D/R micropore volumes. This result qualitatively agrees with the observations of others.<sup>7,11</sup>

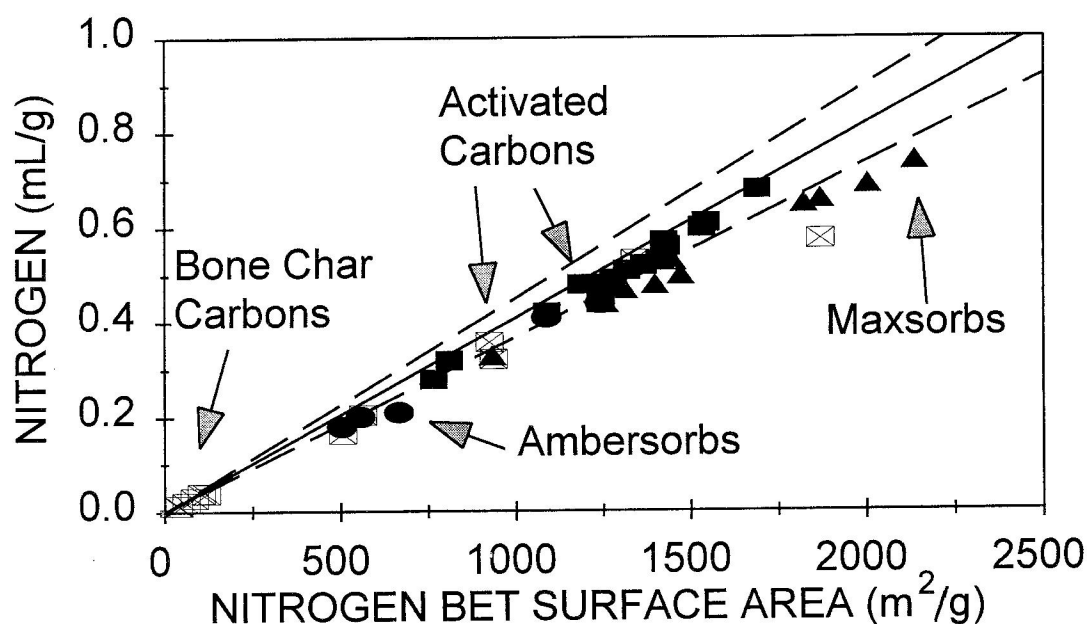


Figure 2. Nitrogen micropore volumes compared with BET surface areas and the correlation from Figure 1.

Figure 3 shows a similar comparison, but using total nitrogen pore volumes. These volumes are consistently higher than the correlation of Figure 1, especially for the Ambersorb and two Maxsorb. These deviations are attributed to filling of larger supermicropores and macropores, as well as the micropores at the experimental conditions.

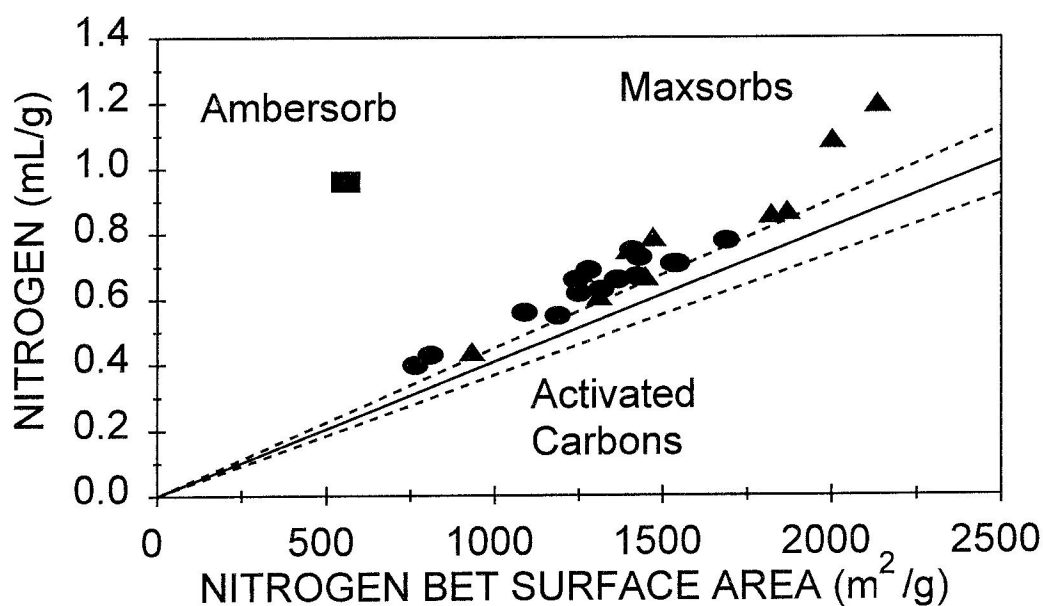


Figure 3. Nitrogen total pore volumes compared with BET surface areas and the correlation from Figure 1.

### GAS AND VAPOR SATURATIONS

We have attempted to estimate micropore volumes by simple procedures saturating carbons with a gas and the vapor of a liquid. First, six unimpregnated carbons were saturated with n-butane gas at  $26 \pm 1^\circ\text{C}$  and 0.77 atm (Los Alamos average barometric pressure). The gas was passed through vials of dried carbon until no further weight gain was noted. Pore volumes filled were calculated from weights of adsorbed butane using the reported liquid density at  $25^\circ\text{C}$ , 0.57 g/mL. Figure 4 shows these volumes to fall below the correlation in Figure 1. This may be due to incomplete micropore filling above the  $-0.5^\circ\text{C}$  boiling point, even at saturation, and/or to lower actual condensed phase density in the open micropores.

Next, twelve activated carbons (six chemically impregnated) and two Maxsorbs were saturated over a period of 163 days with ethyl acetate vapors evaporating from a pool of liquid in a closed container at  $26 \pm 1^\circ\text{C}$ . The samples were weighed repeatedly until constant weights were reached. Adsorbed liquid volumes were calculated from weight gains using the normal liquid density of 0.90 g/mL. Figure 5 shows these ethyl acetate vapor saturation volumes to approximate the micropore volume correlation from Figure 1 for some carbons and to be more than 10 % higher for others, especially for the two superactivated Maxsorbs and the two most highly impregnated carbons (open symbols). Supermicropore and/or macropore volume filling may explain the high values.

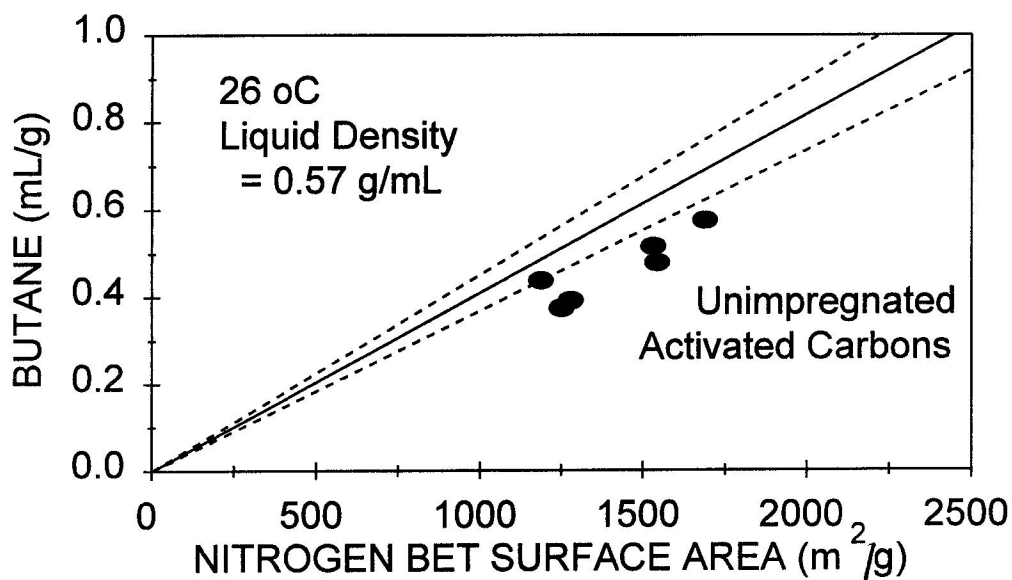


Figure 4. Butane saturation volumes at ambient temperature compared with BET surface areas.

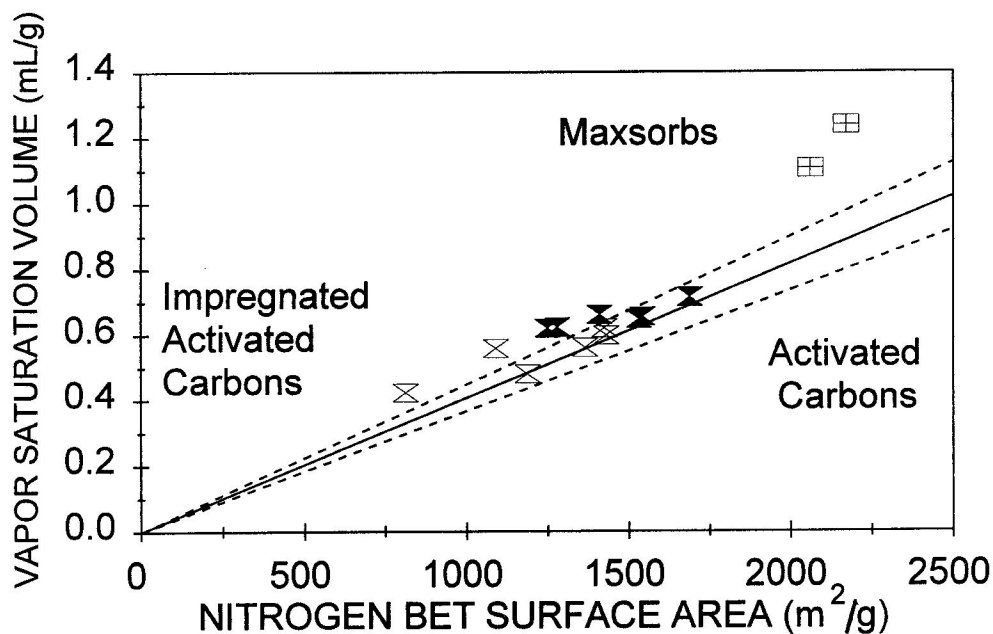


Figure 5. Ethyl acetate vapor saturation volumes compared with BET surface areas and the correlation in Figure 1.

## CONCLUSIONS

Micropore volumes ( $W_o$ ) from Dubinin/Radushkevich adsorption isotherms for organic vapors can be estimated from BET surface areas ( $A_s$ ) or micropore volumes ( $V_N$ ) measured with nitrogen at 77 °K:

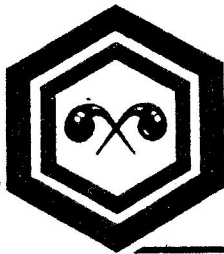
$$W_o \text{ (cm}^3\text{/g)} = 0.00041 A_s \text{ (m}^2\text{/g)}$$

$$W_o \text{ (cm}^3\text{/g)} = 1.1 V_N \text{ (cm}^3\text{/g)}$$

Butane gas saturation capacities at ambient temperature gives low values of micropore volumes when normal liquid density is used to convert from weight to volume adsorbed. Ethyl acetate saturation capacity is a predictor of  $W_o$  for unimpregnated activated carbons, but not for superactivated or highly impregnated carbons.

## REFERENCES

1. G.O. Wood, *Carbon* **30**, 593-599 (1991)
2. G.O. Wood, *Amer. Ind. Hyg. Assoc. J.* **55**, 11-15 (1994).
3. M.M. Dubinin, *Prog. Surf. Membr. Sci.* **9**, 1-70 (1975).
4. S. Brunauer, P.H. Emmett, and E. Teller, *J. Am. Chem. Soc.* **60**, 309 (1938).
5. W.H. Lee, P.J. Reucroft, M. Jagtoyen, and F.J. Derbyshire, *Carbon '95*, Extended Abstracts and Program, San Diego, CA, 484-485 (1995).
6. K. Urano, S. Omori, and E. Yamamoto, *Environ. Sci. Technol.*, **16**, 10-14 (1982).
7. V.R. Deitz, *Carbon '94*, Extended Abstracts and Programme, Granada, Spain, 208-209 (1994).
8. V.R. Deitz and L.F. Gleysteen, *J. Research Natl. Bureau St'ds*, **29**, 191-225 (1942).
9. R.W. Morrison, R.C. Grue, J.A. Rehrman, T.L. Callaghan, and P. Jones, "Evaluation Super-Activated Carbon as a Potential Adsorbent for Chemical Warfare Agents," ERDEC-TR-214, Aberdeen Proving Ground, MD (1994).
10. R.W. Morrison, R.C. Grue, J.A. Rehrman, D.L. Carlile, and P. Jones, "Evaluation of Rhom and Haas Ambersorb Carbonized Resins as Adsorbents for Chemical Warfare (CW) Agents," ERDEC-TR-163, Aberdeen Proving Ground, MD (1994).
11. M.M. Dubinin, A.V. Neimark, and V.V. Serpinsky, *Carbon*, **31**, 1015-1019 (1993).



**EDGEWOOD**

RESEARCH, DEVELOPMENT & ENGINEERING CENTER

U.S. ARMY CHEMICAL AND BIOLOGICAL DEFENSE COMMAND

ERDEC-SP-043

PROCEEDINGS OF THE 1995 ERDEC SCIENTIFIC CONFERENCE  
ON CHEMICAL AND BIOLOGICAL DEFENSE RESEARCH  
14-17 NOVEMBER 1995

Dorothy A. Berg

RESEARCH AND TECHNOLOGY DIRECTORATE

JULY 1996

Approved for public release;  
distribution is unlimited.



Aberdeen Proving Ground, MD 21010-5423