Thermochimica Acta, 51 (1981) 67—75
Elsevier Scientific Publishing Company, Amsterdam — Printed in The Netherlands

COMPUTERISED REDUCTION OF THE WEIGHING TIME REQUIRED FOR THE DETERMINATION OF ADSORPTION ISOTHERMS ON ACTIVATED CARBONS[*]

Olavi Jäntti (University of Technology, Helsinki;
Revontulentie 2 G 79, SF-02100 Espoo, Finland)
Erich Robens (Battelle-Institut e.V., Am Römerhof 35,
D-6000 Frankfurt am Main, Federal Republic of Germany)

ABSTRACT

The method of extrapolation of equilibrium values of adsorbed mass to determine the nitrogen isotherm as presented in Berlin involves application of an exponential equation. This method has been found suitable for determinations in the meso- and macropore region. For the micropore range transformation using a quadratic equation and subsequent application of linear regression is preferable in several cases. The resultant values are evaluated by means of the Dubinin-Radushkevich method. The results of the determinations by these two extrapolation methods are in good agreement.

Linear regression is also suitable for the evaluation of adsorption kinetics measurements.

METHODS OF REDUCING THE MEASURING TIME

The measurement of adsorption isotherms is very time-consuming. Therefore, several methods of reducing the measuring time have been developed. These include:

- automation of the measuring apparatus,
- reduction of the number of measuring points,
- continuous measurement,
- extrapolation of the mass adsorbed at each measuring point,
- calculation of the results by means of a computer (ref. 1, 2).

---

[*] The results of these investigations will be published in: Mikhail/Robens: Structure Analysis and Thermogravimetry of Solid Surfaces; Heyden, London 1982

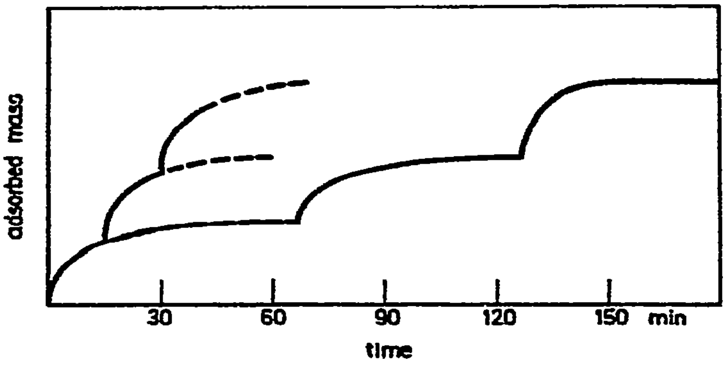


Fig. 1: Extrapolation of equilibrium values of mass adsorbed.

A wide variety of automatic instruments, both volumetric and gravimetric, are in use; some of them are commercially available. Single-point measurement is a reasonable means of making routine measurements of specific surface area. Continuous measurement of pore size distribution by slow increase and subsequent decrease of the pressure cannot be recommended because the error involved cannot be estimated and because the fine structure of the isotherm gets blurred.

In the following it will be shown that extrapolation of the equilibrium value of the adsorbed mass (or volume) at each point of the isotherm is an effective means of speeding up the measurement without loss of accuracy (Fig. 1).

PREVIOUS EXTRAPOLATION METHODS

Some extrapolation methods for the evaluation of thermogravimetric experiments have been published. Jäntti, Junttila and Yrjänheikki presented an extrapolation method for adsorption measurements based on model concepts of the adsorption process at the Ninth Conference on Vacuum Microbalance Techniques 1969 in Berlin (ref. 3). They arrived at the following equation suitable for numerical calculation:

$$Y_\infty = \frac{Y(2)^2 - Y(1)\cdot Y(3)}{2\cdot Y(2) - Y(1) - Y(3)} \qquad (1)$$

with Y(1), Y(2), Y(3) being the adsorbed mass measured 5, 10 and 15 min after a pressure change and Y_∞ the extrapolated mass adsorbed in equilibrium.

A drawback of this equation is that for very low adsorption velocities the denominator may become zero; this can be avoided, however, by adding small artifical values to the denominator.

Whereas in the BET region and in the region of mesopore filling very good results have been obtained (ref. 4-7), remarkable differences were observed in the micropore range. This is attributed to the fact that adsorption theories made for the mesopore region fail for microporous activated carbons. As Inhola (ref. 7) pointed out, reliable results will be obtained, however, by using the Dubinin-Radushkevich equation. For the region of applicability of this equation (lower part of the isotherm), the extrapolation method presented in the following is well suited.

Extrapolation by Linear Regression

A widely used method to extrapolate values is linear regression (method of smallest squares). According to this method, the straight line is calculated which best approximates the measured scattering data. This method exhibits some advantages:

- Linear regression programs are generated by most computers and even by some pocket computers.
- Statistical deviations of the experimental data are calculated.
- Systematic deviations are visualised.
- The desired equilibrium value becomes visible as the ordinate intercept.

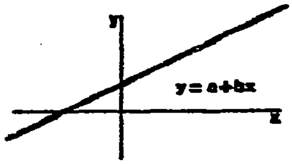
According to this method it is necessary first of all to transform the experimental adsorption curve plotted under isothermal and isobaric conditions as a function of time T. This curve, which is asymptotic towards an equilibrium value, is transformed into a straight line. The equation used need not be valid for the whole curve, but only for the part of interest between the mass Y_o before the pressure change and the mass Y_∞ adsorbed at equilibrium. The following equations have been considered:

$$Y = A + BT \tag{2}$$

$$Y = A \cdot e^{BT} \tag{3}$$

$$Y = A \cdot T^{B} \tag{4}$$

$$Y = A + B/T \tag{5}$$



(9)

$$b = \frac{\sum x_i y_i - \frac{\sum x_i \sum y_i}{n}}{\sum x_i^2 - \frac{(\sum x_i)^2}{n}} \qquad (10)$$

$$a = \left[\frac{\sum y_i}{n} - b\frac{\sum x_i}{n}\right] \qquad (11)$$

$$r^2 = \frac{\left[\sum x_i y_i - \frac{\sum x_i \sum y_i}{n}\right]^2}{\left[\sum x_i^2 - \frac{(\sum x_i)^2}{n}\right]\left[\sum y_i^2 - \frac{(\sum y_i)^2}{n}\right]} \qquad (12)$$

Fig. 2: Linear regression program CURFIT.

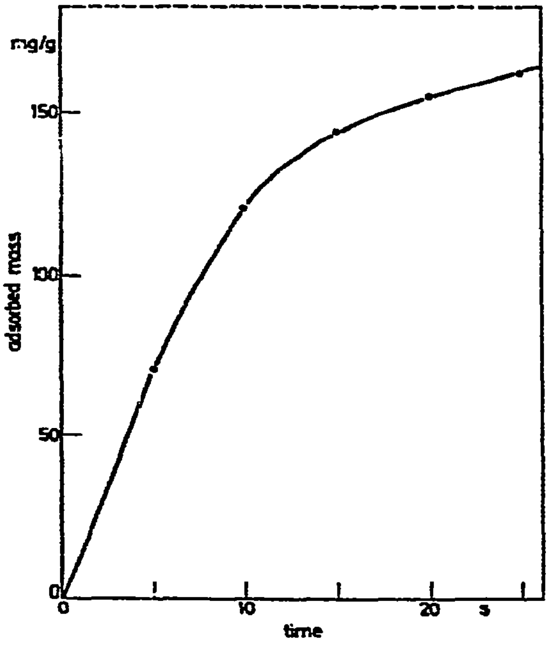


Fig. 3: Adsorption of nitrogen at 77 K and a relative pressure of 0.0013 on activated carbon as a function of time.

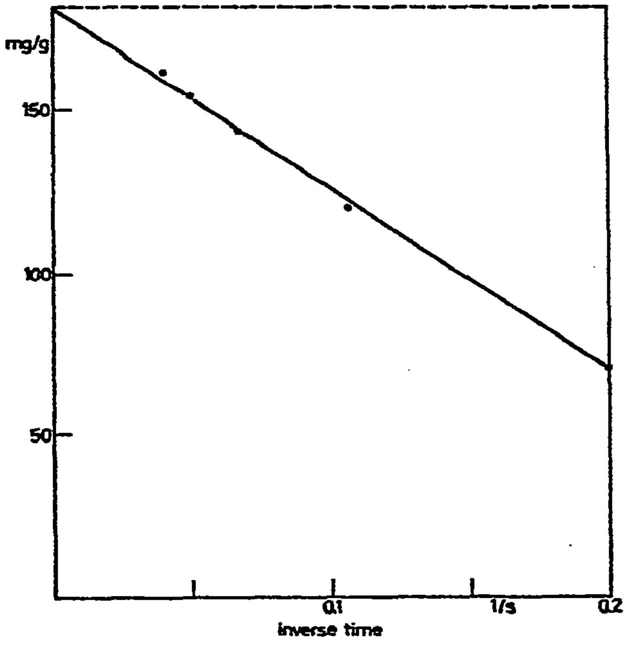


Fig. 4: Linearisation of the adsorption curve (Fig. 2) using the inverse time scale as abscissa.

$$Y = 1/(A + BT) \qquad (6)$$

$$Y = T/(A + BT) \qquad (7)$$

$$Y = A + B \cdot \log T \qquad (8)$$

The suitability of the equations was tested using experimental data of nitrogen adsorption at 77 K on activated carbon at a relative pressure of $p/p_o = 0.0013$ (ultramicropore region) as shown in Fig. 2. For the calculation the CURFIT program of Hewlett-Packard written in BASIC was used (Fig. 3). The squares of correlation (determination index) are given by equation (12).

In most cases, the best approximation was achieved with equation (5). In our example the transformation is shown in Fig. 4: Using 1/T as abscissa, the equilibrium mass adsorbed is given by the ordinate intercept.

Results of the adsorption measurements as a function of the observation time (s) at a relative pressure of 0.0013 on different activated carbons are shown in Table I together with the equilibrium values obtained by exponential extrapolation and linear regression. The difference between the two extrapolated values is under 10 percent. At a relative pressure of 0.01 and above, the difference was found to be below 1 percent.

FURTHER APPLICATIONS

Time derivation of equation (5) yields the adsorption velocity

$$dY/dX = - B/X^2 \qquad (13)$$

Application of the extrapolation method to the desorption process during degassing can help to detect any bulk decomposition, which in general is connected with a change of the surface area, and thus to find the optimum degassing temperature. To speed up the degassing process, the highest possible degassing temperature has to be chosen which does not damage the sample material. Plotting of the transformed experimental values in the Y-1/T diagram (Fig. 4) reveals systematic deviations from the straight line which may be due to a decomposition process superposed to the degassing process.

An extension of the method can be used to calculate the decomposition velocity; this may be useful for thermogravimetric applications.

Table I: Measurement and extrapolation of the nitrogen mass adsorbed in equilibrium at 77 K, $p/p_0 = 0.0013$ as a function of time

Sample material / Time/s	5	10	15	20	25	Y_∞/mg·g^{-1} using (5)	extrapolated using equation (1) (mean values)	Δ %
	mg·g^{-1}							
SAP	70.23	119.56	143.63	154.43	161.86	181.8	169.3	6.9
Caldacarb A2/10	80.67	132.75	159.64	176.29	185.50	205.7	196.2	4.6
Caldacarb A6/10	75.99	124.39	143.48	152.49	157.54	177.4	160.2	9.7
Darco KB	69.66	123.77	154.60	174.19	185.94	206.3	202.4	1.9
Grade CA 10	68.02	126.15	157.69	174.49	183.30	207.2	193.5	6.6
Grade 3/61	67.84	120.99	140.85	156.04	165.50	184.5	179.8	2.5
Norit SA 2		122.77	139.80	145.52	148.08	166.6	149.3	10.4
Norit Supra	81.30	132.82	156.16	167.80	173.94	195.2	178.6	8.6
Koe 112	83.12	129.18	150.06	159.97		183.4	168.1	8.3
Sol 11 Actibon	46.83	77.26	93.94	100.10	103.31	116.8	108.2	7.4
Sol 61 Actibon	50.84	81.66	95.56	102.05	105.00	118.1	107.4	9.1

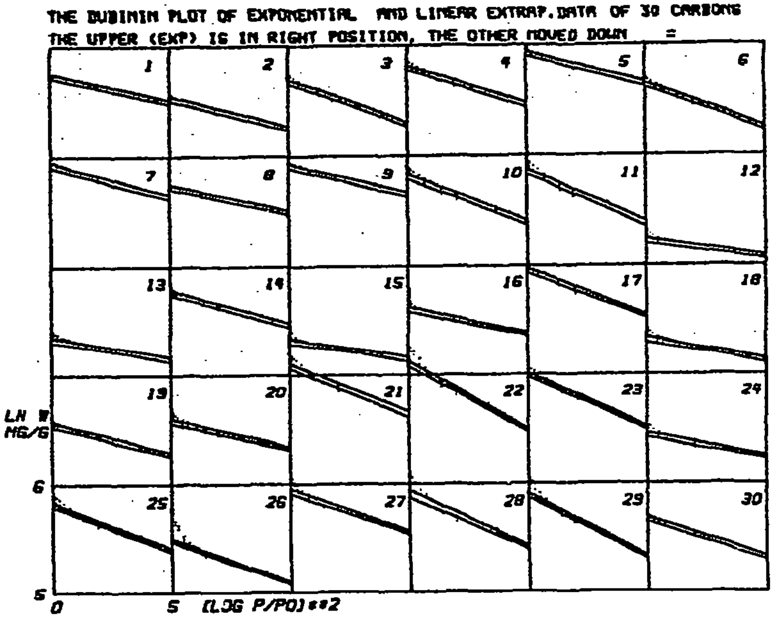


Fig. 5: The Dubinin-Radushkevich plot for various charcoals.

It should be noted that linear regression can also be applied to the Dubinin-Radushkevich equation

$$\ln W = \ln W_o - B \frac{T^2}{\beta^2} (\ln p/p_o)^2 \qquad (14)$$

If the experimental results are plotted in an ln W versus ln p/p_o diagram, a straight line should be obtained. Using the equation

$$t = 0.61 - 0.247 \ln p_o/p \quad (\mathrm{nm}) \qquad (15)$$

for the layer thickness, we obtain the micropore volume by multiplying the layer thickness by the specific surface area of the mesopore region

$$W_i = t \cdot S_{meso} \qquad (16)$$

In the D-R diagram (Fig. 5) the ordinate intercept gives the micropore volume W_o. In our measurements on activated carbons this value was found to be in good agreement with values obtained by conventional calculation. The slope of the regression curve gives information on the pore width (ref. 6). In Fig. 5 the second line has purposely drawn parallel and below its correct position in order to facilitate comparison with the line of exponential extrapolated data. The degree to which it has been lowered is noted after the title.

GENERAL RESULTS

Our evaluation of nitrogen isotherms is based on Juhola's procedure (ref. 7). The equilibrium value of nitrogen adsorbed on activated carbons at low relative pressures (micropore range) can be extrapolated using a quadratic equation followed by linear regression. At higher relative pressures (mesopore range), approximation using an exponential equation is more favorable.

Using these extrapolation methods the measuring time to obtain nitrogen adsorption isotherms can be remarkably reduced. With regard to the heterogeneity of surfaces and pore systems it is suspected that a generally applicable extrapolation method does not exist. The calculation methods described allow easy comparison of different extrapolation methods and thus selection of the most suitable method.

ACKNOWLEDGEMENT

The measurements were made at the Fuel and Lubrication Laboratory of the Technical Research Centre of Finland and the Research Center of the Finnish Defense Forces, Helsinki. Dr. J. Ochs of Battelle-Institut e.V., Frankfurt am Main, gave us valuable advice. We are very grateful for this help.

REFERENCES

1 J. Kankare, O. Jäntti, The Determination of Pore Structures from Physical Adsorption Isotherms. Part II. Digital Computer Program, Suomen Kemistilehti 40(1967)51.

2 M. Büchner, E. Robens, R.Sh. Mikhail, Computer Program for Surface Area and Pore Size Analysis from Sorption Isotherms, in C. Eyraud, M. Escoubes (Eds.): Progress in Vacuum Microbalance Techniques, Vol. 3, Heyden, London, 1970, p. 324.

3 O. Jäntti, J. Junttila, E. Yrjänheikki, On Curtailing the Microweighing Time by an Extrapolation Method, in Th. Gast, E. Robens (Eds.): Progress in Vacuum Microbalance Techniques, Vol. 1, Heyden, London, 1970, p. 345.

4 O. Jäntti, V. Peltonen, On the Pore Distribution of Activated Carbon and its Measurement (finnish), Kemian Teollisuus 25(1968)65.

5 E. Ekman, O. Jäntti, J. Ranta, Peat as Raw Material for Activated Carbon. Properties of Activated Carbons. Report 17 of Fuel and Lubricant Research Laboratory of the Technical Research Centre of Finland 1978 (finnish).

6 J. Ranta, The Role of Microporosity on Evaluation the Properties of Activated Carbon, Lisentiate study (finnish) University of Jyväskylä 1980, Finland

7 A.J. Juhola, Manufacture: Pore Structure and Application of Activated Carbon, Kem-Kemi 4(1977)543, 653.