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A New Working Procedure to Calculate Pore Size Distributions

The complete characterization of a porous solid requires the knowledge of the surface area, pore volume, and pore size distribution. The first two parameters may be easily obtained by means of gas adsorption and mercury porosimetry, but there is no single method to determine the pore size distribution in the whole pore size range; at least two techniques, such as gas adsorption and mercury porosimetry, have to be used. There are several methods to determine the pore size distribution from either gas adsorption or desorption isotherms (*1*). The more widely used methods are those of Pierce (*2*) or Cranston and Inkley (*3*) and, although they are intrinsically different, both can give good information about the evolution of porosity in a series of related samples.

Either of these methods follows the same procedure, i.e., the adsorption data are plotted on a large scale and the amount adsorbed is read at the relative pressure indicated by each method. In this way a pore size distribution with a large number of peaks is obtained and it is not clear if all of these peaks are part of the actual pore size distribution or simply artifacts of the graphical technique. A similar situation occurs with the pore size distributions deduced from mercury porosimetry. Also these pore size distributions are not very reproducible especially if they are calculated by different operators. In order to solve these problems a new working process is proposed to obtain a more consistent pore size distribution independent of the operator and with no false peaks. In order to test the method it will be applied to several adsorption isotherms and mercury porosimetry measurements and the results will be compared with the pore size distributions obtained in the conventional way.

The principal source of errors in the conventional operational mode is the way in which the calculations are carried out. Thus, plotting on a large scale of the adsorption isotherms can result in the experimental uncertainty in adsorption data contributing to the form of the pore size distribution. In the case of mercury porosimetry, the penetrating volume of mercury is increased in discrete amounts; a single volume increment in the apparatus can induce a false peak in the pore size distribution. To avoid these problems in the determination of pore size distributions we propose a new way of treating the experimental data. The experimental results are adjusted by least squares to polynomial functions (or any other type of function). If necessary, the experimental points can be separated into intervals in which the adjustment of the data to the polynomial functions is satisfactory, while ensuring adequate overlapping of the functions to avoid discontinuities. The pore size distributions are obtained by analytical differentiation of these adjusted functions.

In mercury porosimetry a plot of cumulative pore volume as a function of pore diameter is obtained from measurements of the volume of mercury which penetrates a solid as a function of applied pressure (*1*). This plot usually has small steps due to limited sensitivity to increments in volume and, when the plot is used to obtain the pore size distribution, the steps will give rise to corresponding peaks. When a second run is carried out on the same sample the resulting cumulative plot is very similar to the first but the steps are not necessarily the same. Consequently, the pore size distribution will be different to that obtained from the first run.

In order to test this, an activated carbon,

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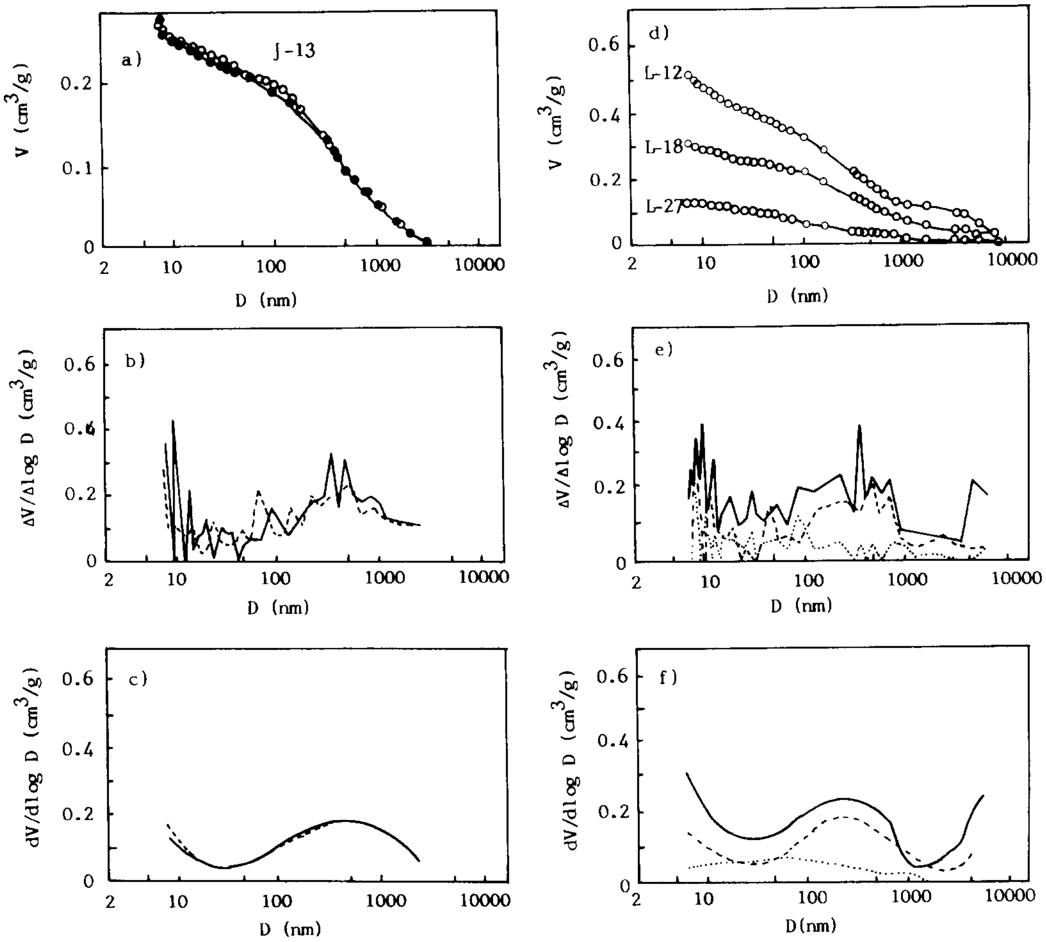

FIG. 1. Mercury porosimetry results for activated carbons. Cumulative plots: (a) J-13, first run (●), second run (○); (d) L-12, L-18, and L-27. Conventional pore size distributions: (b) J-13, first run (—), second run (---); (e) L-27 (···), L-18 (---), L-12 (—). Proposed pore size distributions: J-13, first run (---), second run (—); (f) L-27 (···), L-18 (---), L-12 (—).

J-13, already described (*4*) has been studied using a mercury porosimeter (Carlo Erba, Series 200). The cumulative plots corresponding to two different runs (Fig. 1a), are very similar, especially in the macropore size range. If some data pairs (volume, (V), diameter (D)) are selected to calculated $\Delta V/\Delta \log D$ vs $\log D$ there may be as many peaks in the differential distribution as there were intervals taken (see Fig. 1b). The size and the height of the peaks will depend upon the number of intervals taken, so that the larger the number of intervals the larger the number of peaks. The result is that the pore size distributions obtained from the two plots of Fig. 1a are rather different both in the position of the peaks and in their heights. A further point is that the plots of Fig. 1b show some minima with $\Delta V/\Delta \log D = 0$ besides peaks of up to $\Delta V/\Delta \log D = 0.4$ ($D = 10$ nm, for example); it is most unlikely that in an adsorbent such as activated carbon there would be preferential development of pores of a given size and no development of pores of a neighboring size. To apply the new method the integral plots of Fig. 1a were adjusted to polynomial functions for V vs $\ln D$. The coefficients of the polynomials, the correlation coefficients and the ranges of application can be found in Table 1. In comparison with the experimental curves (Fig. 1b), the derivatives of the polynomial functions (Fig. 1c), are quite reproducible from the first to second run. The small differences in the lower pore size range reflect the small differences in the experimental data (Fig. 1a). The pore size distribution obtained by differentiation of the polynomial functions is smooth with no peaks such as are found in the pore size distribution obtained by the graphical method (Fig. 1b).

In order to further show the validity of these arguments the same method has been applied to mercury porosimetry data for a series of three activated carbons, L-27, L-18, and L-12, of progressively increasing degree of activation (*4*). The cumulative plots of Fig. 1d give an approximate idea of the evolution of the porosity. The corresponding conventional pore size distributions (Fig. 1e), are not easy to interpret, due to the presence of many peaks. However, if the cumulative plots are adjusted to polynomial functions (see Table 1) and the derivatives are plotted (Fig. 1f), the pore size distribution can be more easily interpreted and some semiquantitative comparison between the three curves is possible.

A similar problem is found when the Cranston and Inkley method is applied to the determination of pore size distributions from adsorption isotherms. To obtain a pore size distribution using the method of Cranston and Inkley it is necessary to differentiate graphically the curves of the adsorption isotherm. To obtain a suitable value of $\Delta V/\Delta D$ it is usual to expand the scale of the isotherm. Differentiation using this method can produce spurious peaks for the following reasons: (i) changes in slope due to experimental scatter of data points; (ii) difficulties in interpolating the curve of the expanded isotherm between data points; and (iii) the errors in $\Delta V/\Delta D$ increase rapidly as ΔD approaches zero. The new method has been applied to the N_2 (77 K) isotherms obtained on the samples re-

TABLE 1

Mercury Porosimetry Data. Fitted Polynomials

$V = A_0 + A_1 \ln D + A_2 \ln^2 D + A_3 \ln^3 D + A_4 \ln^4 D$. ($V$, cm^3/g; D, nm).

Sample	Range of D (nm)	A_0	A_1	A_2	A_3	A_4	R^2
J-13 First run	3000–7.4	6.8223×10^{-1}	-4.0349×10^{-1}	1.3559×10^{-1}	-2.0198×10^{-2}	1.0268×10^{-3}	0.999
J-13 Second run	3000–7.4	5.7926×10^{-1}	-3.0797×10^{-1}	1.0627×10^{-1}	-1.6464×10^{-2}	8.5760×10^{-4}	0.998
L-27	7500–750	2.9418	−1.1185	1.4246×10^{-1}	-6.0553×10^{-3}	—	0.985
	1500–50	-1.8684×10^{-1}	3.2245×10^{-1}	-1.1338×10^{-1}	1.5343×10^{-2}	-7.3252×10^{-4}	0.994
	75–7.4	1.4116×10^{-1}	7.7309×10^{-3}	-8.3641×10^{-3}	6.3930×10^{-4}	5.1968×10^{-6}	0.997
L-18	7500–75	−4.0637	2.9030	-7.0360×10^{-1}	7.2175×10^{-2}	-2.6954×10^{-3}	0.995
	150–7.4	5.6552×10^{-1}	-2.0800×10^{-1}	4.6523×10^{-2}	-2.7758×10^{-3}	-2.3361×10^{-4}	0.990
L-12	7500–750	8.0722	−3.1764	4.2477×10^{-1}	1.9046×10^{-2}	—	0.986
	1500–7.4	1.2572	-7.2242×10^{-1}	2.4447×10^{-1}	-3.8210×10^{-2}	2.1001×10^{-3}	0.999

sulting from the reaction in dry air of a graphitized carbon black (V3G) at 798 K to different degrees of burn-off (*5*). The isotherms are in Fig. 2a and the conventional pore size distribution have many peaks, similar to those found using mercury porosimetry (Fig. 1e). The pore size distributions for sample V3G-72.4 obtained from the same experimental data by two operators in Fig. 2b; comparison of the two curves shows that there are apparently distinct differences in the pore size distributions. However, if the experimental data are adjusted to a suitable polynomial function (see Table 2) the resulting pore size distributions are as those given in Fig. 2c. These plots allow a semiquantitative comparison to be made of the evolution of porosity as the oxidation of the carbon black proceeds. It may also be noted that there is only one possible pore size distribution for each sample.

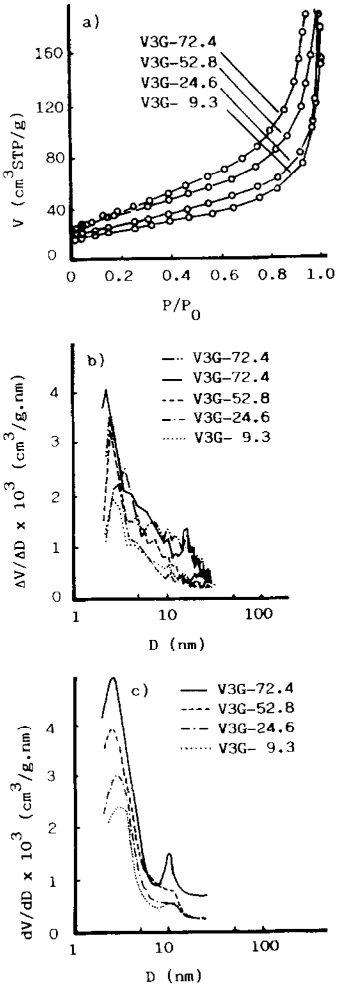

FIG. 2. N_2 (77 K) adsorption on samples of V3G. (a) Adsorption isotherms; (b) conventional pore size distributions; (c) proposed pore size distributions.

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TABLE 2

N_2(77 K) Adsorption Isotherm Data. Fitted Polynomials

$V = A_0 + A_1(P/P_0) + A_2(P/P_0)^2 + A_3(P/P_0)^3 + A_4(P/P_0)^4 + A_5(P/P_0)_5$ (V, cm^3 (STP)/g)

Sample	A_0	A_1	A_2	A_3	A_4	A_5	R^2
V3G- 9.3	15.0779	50.2852	−241.700	1020.49	−1619.40	886.457	0.999
V3G-24.6	18.7640	58.5339	−216.526	840.073	−1259.66	668.083	0.999
V3G-52.8	24.7550	28.6261	149.778	−315.579	242.906	—	0.999
V3G-74.2	12.9868	290.780	−1677.61	5326.57	−7287.03	3604.09	0.999

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