A Computer Program for Pore Volume and Pore Area Distribution Calculations from Mercury Porosimeter Data on Particulate or Porous Materials*

HILLAR M. ROOTARE and JUDSON SPENCER

University of Michigan, School of Dentistry, Ann Arbor, Mich. 48104 (U.S.A.)

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Summary

A computer program in Fortran IV is described for rapidly determining pore size and pore area distribution calculations from the high pressure mercury porosimeter data. The listing of the program is reproduced as well as the printout of the sample data. Illustrations of the graphic representation of the processed data are given for two samples of fine crystalline precipitated hydroxyapatite and one carbon black—Spheron 6.

INTRODUCTION

Mercury porosimetry is a widely used method today for determining macro pore size distributions of porous or powdered substances1-4, and can be classified as a “standard” method in conjunction with the nitrogen adsorption method.

As the capabilities of commercial instruments have been improved by increasing the maximum attainable pressure limits from the initial 3000 psi5 to the present 60,000 psi6, the method quite often replaced the more elaborate and time consuming gas adsorption method.

At first, the 3000 psi pressure range was satisfactory, because it permits measurements down to 600 Å intruded pore diameter, which is the equivalent starting point for the BJH (Barrett, Joyner, and Halenda method)7 pore size distribution calculations from nitrogen adsorption data. Thus, the large pores from 100 μm to 600 Å in diameter were measured by mercury porosimeter, and the smaller pores from 600 Å down to 14 Å were measured by nitrogen adsorption8. It has been found that a great number of materials have porosities in the high Ångstrom range, which can be intruded by mercury at higher pressures. There has been a demand, therefore, to increase the pressure capability of the mercury porosimeter, thus extending its pore size range downwards. With the increasing awareness of the method and its utility in complementing or substituting for the gas adsorption method, first a 15,000 psi* porosimeter (see Fig. 1)

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and then a 60,000 psi* porosimeter (see Fig. 2) were acquired by this laboratory. Other instruments are also available**.

The 60,000 psi mercury porosimeter can cause mercury to penetrate pores as small as 30 Å in diameter, if $130^\circ$ is taken as the contact angle between mercury and the solid. It can, therefore, frequently and routinely replace the gas adsorption method for pore size distribution determination of materials as a simpler and more rapid way of obtaining the same information.

Nevertheless, the age of automation has provided those who have the funds with an automated adsorption apparatus—the Adsorptomat®*. The "raw data" from the automatic adsorption instrument is reduced by the computer into the final form for evaluation. For this reason there has been a drastic reduction in the time and cost of obtaining pore-size distribution data by nitrogen adsorption method. However, the same type of information is available in less time and at lower cost by high pressure mercury porosimetry, an independent approach to reach the same objective as gas adsorption. Those who have not decided which way to proceed now have an alternative to consider.

Because of the time-consuming hand calculations involved in the treatment of the "raw data" from the mercury porosimeter, a simple but versatile computer program for the pore-size and pore-area distribution calculations has been developed. Machine instructions have been written in Fortran IV (see Fig. 3) for the IBM 1130 computer, which is available at the University of Michigan, School of Dentistry. The program can be readily adapted for use with the IBM 360 or other comparable computers. This program has been successfully used in the analysis of several hundred porosimeter runs, and it has saved hours of labor with the desk calculator. Because of the time requirements, some of the calculations would probably not have been performed at all, if not for the computer (see Figs. 4 and 5).

DESCRIPTION OF PROGRAM

The compilation of the program is reproduced in Fig. 3. At the end of the program, the first statement lists the number 25, which is the number of values at which the pore diameters will be listed for the percent volume and area determinations. The next three cards list the actual pore diameter values for which the computer will calculate the corresponding percent pore volume and pore area distributions, which will be listed on the second page of the printout (Fig. 4).

On the fourth card the weight of the same (W) is listed, and the following card lists the title of the run or the sample identification. These cards are followed by the actual data points—four per card.

* Aminco 60,000 psi porosimeter 5-7125B used in this laboratory.

** Other manufacturers of mercury porosimeters are Carlo Erba Scientific Instruments Division, Via Carlo Imbonati, 24120139 Milano, Italy (porosimeter model 70 has max. pressure 3000 kg/cm² and pore range 37.5 Å to 75 μm) and Micromeritics Instrument Corp., 800 Goshen Springs Road, Norcross, Ga. 30071 (porosimeter model 905 has max. pressure 50,000 psi and pore range 35 Å to 171 μm).

* Adsorptomat 4-4680, American Instrument Co., Silver Spring, Md. 20910.
 COMPUTER PROGRAM FOR MERCURY POROSIMETER DATA

Fig. 3. Computer program listing with two sets of data cards to illustrate the input format.
### Porosimetry Calculations - Pore Area Distribution

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<th>Pore Diameter</th>
<th>Volume</th>
<th>Area</th>
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**SUMMARY TABLE**

1. Median Pore Diameter... 0.0832 Micos
2. Total Pore Volume... 0.5156 CC/g
3. Average Pore Diameter (in μm) 0.746 Pores
4. Total Pore Area... 0.5148 M2/g

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Fig. 4. Computer printout of the calculations of pore size and pore area distribution for the two samples of hydroxyapatite powder.
Fig. 5. Computer printout of the calculations of pore size and pore area distribution for the reference sample number 3, carbon black-Spheron 6.

Each point consists of two values, one for the pressure in psia and the other for the volume in cc. As many points as necessary are listed. All decimal points are punched for the sake of simplicity. The card formats are summarized as follows:

Card Form 1. Cols. 1 & 2: List the number of pore diameter values (in μm) to be used for the percent distribution determination. Cols. 3-9, 10-16, 17-23, 24-30 are used for the values at which pore diameter and the percent pore size distributions are to be determined. If more than one card is required, the next card will have the values listed in columns 1-7, 8-14, 15-21...64-70, and so on.

Card Form 2. Cols. 1-10: List the sample weight (W).

Card Form 3. Cols. 3-80 are used for the title or identification of sample. Card Form 4. Cols. 1-10, 21-30, 41-50, 61-70 are used for pressures in psia, and Cols. 11-20, 31-40, 51-60, 71-80 are used for the volumes in cc.

RESULTS

To illustrate the computer output and to demonstrate the reproducibility of the mercury porosimeter method, the printout is reproduced for two different samples of N-hydroxyapatite powder* in Fig. 4. The printout for reference sample No. 3, carbon black-Spheron 6** is reproduced in Fig. 5. This sample is used by many workers to check the apparatus when measuring BET surface areas with nitrogen. The reported reference value of BET surface area for Spheron 6 is 110 m²/g. The surface area by mercury porosimeter of 109.0 m²/g agrees very well with that of nitrogen adsorption value. The printout consists of two pages; the first page tabulates the original data input in the first two columns, which is followed by columns of corresponding pore diameter (D) in μm and normalized pore volume (SDV) in cc/g. The pore volume versus pore diameter is plotted in the top half of Fig. 6. The fifth column lists the cumulative pore surface area (SA) in m²/g (see Fig. 7 for the plot). The last

* N-Hydroxyapatite sample was provided by the Physical Pharmacy Dept., School of Pharmacy, University of Michigan. Code letter N identifies the preparation.

** One of the reference adsorbents for surface area measurements prepared by Bone Char Research Project, Inc. at the National Bureau of Standards. The project was terminated 1963. Limited quantities of samples and the Technical Report No. 73 may still be available from the American Instrument Co., Silver Spring, Md.
two columns of the first page list the mean pore radius (R BAR) in μm with the corresponding differential distribution function (DV/DR) (see Fig. 6 bottom half).

The second page of the computer printout (Figs. 4 and 5 bottom) lists the percent pore volume and the percent pore area distributions for a selected listing of pore diameters. These pore diameter values are arbitrarily chosen and can be changed to suit individual needs by simply changing the numbers listed on the first set of cards that follows the program listing (Look at the Fig. 3 and the format instructions).

For the convenience of the operator, a Summary Table is printed on the bottom of the second page of the printout. It lists the pertinent information for a quick inspection of results. Median and average (4V/A) pore diameters are given together with the total pore volume and the total pore surface area.

Figures 6 and 7 illustrate some of the graphical representations of data available from the computer output. The top half of Fig. 6 is a plot of cumulative pore volume versus pore diameter in μm or the integral pore-size distribution curve for the N-hydroxyapatite. It shows both the pressurization curve and the depressurization curve for the two samples from Fig. 4, indicating the extent of hysteresis resulting from the characteristic shapes of the pores or rather voids formed by the crystallites of the apatite. The openings to the voids are about six times smaller than the diameters of the voids themselves.

The bottom half of Fig. 6 is a differential distribution curve for the sample P22 showing the results from both the pressurization curve and the depressurization curve. At times it may be important to know not only the mean diameter of the opening to the pores, but also the mean diameter of the voids or pores themselves. These data are obtainable within an hour or two, depending on the sample and the availability of the computer service.

Customarily the DV/DR function is plotted versus the mean radius, which is listed in the next to the last column of the printout as R BAR; however, in order to show the coincidence of the peaks of the differential plot with the sharp rises of the integral curves, DV/DR was plotted as a function of pore diameter.
Pore area distribution is plotted as a function of pore diameter in Fig. 7. Since at times pore area distribution may be of more importance to the investigator studying catalysts than the pore volume distribution, this option is made available by the computer program.

Those who have used Spheron 6 as a reference adsorbent in their work may find Fig. 8 of interest. It is a composite of three curves and is a visual summary of the type of information obtainable by mercury porosimetry. One can quickly observe that the pore volume and the pore area distribution curves are not identical. The smaller pores affect the pore area distribution more than the larger pores. The differential distribution function (DV/DR) shows quite clearly the narrowness and the symmetrical shape of the pore size distribution of the interstitial voids between the particles (in the case of this sample), which may not be as evident from the cumulative pore volume curve.

ACKNOWLEDGEMENTS

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