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

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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 substances[1–4], 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 psi[5] to the present 60,000 psi[6], 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 adsorption[8]. 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)

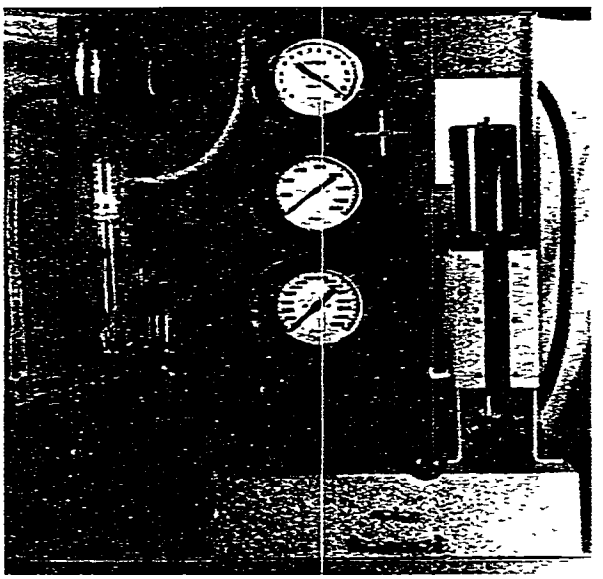

Fig. 1. Aminco 15,000 psi mercury porosimeter 5-7108. This early model has been discontinued and has been replaced with a new instrument that has a motor driven hydraulic pump and digital volume readout.

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* Aminco original 15,000 psi porosimeter 5-7108, still used in this laboratory, has been replaced with a new 15,000 psi motor-driven and digital readout model 5-7121. American Instrument Co., Silver Spring, Maryland 20910.

Fig. 2. Aminco 60,000 psi mercury porosimeter 5-7125B. This high pressure version uses capacitive readout of the mercury volume displacement.

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° 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[9]*. 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, 24 I 20159 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 177 μm).

* Adsorptomat 4-4680, American Instrument Co., Silver Spring, Md. 20910.

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                UNIVERSITY OF MICHIGAN SCHOOL OF DENTISTRY
C
C     PORE VOLUME - AREA DISTRIBUTION CALCULATION PROGRAM
C     FROM MERCURY POROSIMETER DATA
C
      DIMENSION TITLE(72),D(100),PR(100),SD(100),S(100),P2(5),SV2(5)
      READ(2,10)N,(PR(I),I=1,10)
10    FORMAT(I2,10F7.4)
      IF(N-10)7,7,50
50    READ(2,51)(PR(I),I=11,N)
51    FORMAT(10F7.4)
7     AK=0.0225
      SPBDV=0.
      P1=0.
      D1=100.
      SV1=0.
      S(1)=0.
      D(1)=D1
      SD(1)=0.
      J=2
      READ(2,3)W
      WOK=AK/W
      READ(2,8)(TITLE(I),I=1,72)
8     FORMAT(72A1)
      WRITE(5,1)
1     FORMAT(1H1,48H POROSIMETRY CALCULATIONS-PORE AREA-DISTRIBUTION/)
      WRITE(5,8)(TITLE(I),I=1,72)
      WRITE(5,9)W
9     FORMAT(1H ,
     113H INITIAL P=0.,2X,17H INITIAL SUM V=0.,2X,15H INITIAL D=100.,
     22X,3H W=F7.4  ,2X,9H K=0.0225/8X,1HP,6X,3HSDV,8X,1HD,8X,3HSDV/8X,
     32HSA,7X,5HR BAR,5X,5HDV/DR/6X,4HPSIA,6X,2HCC,6X,7HMICRONS,4X,
     44HCC/G,6X,4HM2/G,5X,7HMICRONS)
2     READ(2,3)(P2(NI),SV2(NI),NI=1,4)
3     FORMAT(8F10.4)
      N1=1
52    IF(P2(N1))1,4,4
4     PBAR=(P2(N1)+P1)/2.
      DV=SV2(N1)-SV1
      SPBDV=SPBDV+PBAR*DV
      SA=WOK*SPBDV
      D2=180./P2(N1)
      DR=(D1-D2)/2.
      RB=(D1+D2)/4.
      SDV=SV2(N1)/W
      DVSDR=DV/DR
      D(J)=D2
      SD(J)=SDV
      S(J)=SA
      WRITE(5,5)P2(N1),SV2(N1),D2,SDV,SA,RB,DVSDR
5     FORMAT(F10.2,3F10.4,F10.5,F10.4,E12.4)
      P1=P2(N1)
      SV1=SV2(N1)
      D1=D2
      J=J+1
      N1=N1+1
      IF(N1-5)52,2,2
11    WRITE(5,1)
      WRITE(5,8)(TITLE(I),I=1,72)
      WRITE(5,12)
12    FORMAT(14H PORE DIAMETER,3X,6HVOLUME,5X,4HAREA/4X,7HMICRONS,6X,
     17HPERCENT,3X,7HPERCENT)
      D(J)=D(J-1)
      SD(J)=SD(J-1)
      S(J)=S(J-1)
      JA=J-1
      JB=1
      JC=1
      JD=0
      JE=0
      VPA=0.
13    IF(PR(JC)-D(JB))14,20,21
14    IF(PR(JC)-D(JB+1))15,16,19
15    JB=JB+1
      IF(JB-JA)13,23,23
23    IF(VP-100.)24,25,25
24    IF(JD)25,29,29
29    VP=100.
      AP=100.
      WRITE(5,18)PR(JC),VP,AP
25    TVSA=4.*SD(JA)/S(JA)
      WRITE(5,35)PD,SD(JA),TVSA,S(JA)
35    FORMAT(////16X,14H SUMMARY TABLE/27H 1. MEDIAN PORE DIAMETER...,
     18X,F7.4,4X,7HMICRONS/24H 2. TOTAL PORE VOLUME...,9X,F9.4,
     224X,4HCC/G/35H 3. AVERAGE PORE DIAMETER (4V/A)...,F7.4,3X,
     330H MICRONS/22H 4. TOTAL PORE AREA....,11X,F8.3,5X,4HM2/G)
      IF(P2(N1)+10.)6,7,7
16    VP=100.*(SD(JB+1)/SD(JA))
      AP=100.*(S(JB+1)/S(JA))
17    IF(VP-100.)28,26,24
26    IF(JD)25,27,25
27    JD=1
28    IF(VP-50.)30,31,32
31    PD=PR(JC)
      GO TO 34
32    IF(JE)30,33,30
33    PD=PR(JC-1)+(PR(JC-1)-PR(JC))*(50.-VPA)/(VP-VPA)
34    JE=1
30    WRITE(5,18)PR(JC),VP,AP
18    FORMAT(F11.4,5X,F7.2,3X,F7.2)
      JC=JC+1
      VPA=VP
      GO TO 13
19    FR=(D(JB)-PR(JC))/(D(JB)-D(JB+1))
      VP=100.*((SD(JB)+FR*(SD(JB+1)-SD(JB)))/SD(JA))
      AP=100.*((S(JB)+FR*(S(JB+1)-S(JB)))/S(JA))
      GO TO 17
20    VP=100.*(SD(JB)/SD(JA))
      AP=100.*(S(JB)/S(JA))
      GO TO 17
21    WRITE(5,22)
22    FORMAT(6H ERROR)
      GO TO 7
6     CALL EXIT
      END
```

```
 25 100.    80.    60.    40.    20.    10.     8.     6.     4.     2.
  1.     .8     .6     .4     .2     .1     .08    .06    .04    .02
 .01    .008   .006   .004   .003
.1433
   N   =HAP-POWDER (P12)
 400.     0.    500.   .0015   600.   .0026   750.   .0036
1000.   .0046  1250.   .0071  1600.   .0096  1750.   .0116
1900.   .0172  1950.   .0212  2000.   .0273  2050.   .0313
2100.   .0344  2150.   .0384  2200.   .0394  2250.   .0414
2350.   .0455  2500.   .0505  2650.   .0536  2750.   .0556
3000.   .0606  3250.   .0637  3500.   .0657  3750.   .0677
4000.   .0687  4500.   .0707  5000.   .0717  6000.   .0728
7000.   .0733  8000.   .0738  90000.  .0738  -10.
.1644
   N   =HAP-POWDER (P22)
 300.     .0    400.   .001    500.   .002    800.   .0045
1000.   .0055  1250.   .0071  1500.   .0086  1800.   .0121
1900.   .0177  1950.   .0227  2000.   .0293  2050.   .0348
2100.   .0394  2150.   .0429  2200.   .0459  2250.   .0485
2300.   .0510  2400.   .055   2500.   .0586  2600.   .0616
2700.   .0641  2800.   .0661  3000.   .0702  3100.   .0717
3200.   .0732  3300.   .0742  3500.   .0763  3600.   .0773
3700.   .0783  4000.   .0803  4350.   .0813  4750.   .0823
5100.   .0833  6000.   .0838  7500.   .0848  9000.   .0853
20000.  .0853  -20.
```

Fig. 3. Computer program listing with two sets of data cards to illustrate the input format.

POROSIMETRY CALCULATIONS-PORE AREA-DISTRIBUTION

N -HAP-POWDER (P12)
INITIAL P=0. INITIAL SUM V=0. INITIAL D=100. W= 0.1433 K=0.0225

P PSIA	SOV CC	D MICRONS	SOV CC/G	SA M2/G	R BAR MICRONS	DV/DR
400.00	0.0000	0.4500	0.0000	0.00000	25.1125	0.0000E 00
500.00	0.0015	0.3600	0.0104	0.10598	0.2025	0.3333E-01
600.00	0.0026	0.3000	0.0181	0.20097	0.1649	0.3666E-01
750.00	0.0036	0.2400	0.0251	0.30696	0.1349	0.3333E-01
1000.00	0.0046	0.1800	0.0321	0.44434	0.1050	0.3333E-01
1250.00	0.0071	0.1440	0.0495	0.88594	0.0810	0.1388E 00
1600.00	0.0096	0.1125	0.0669	1.44530	0.0641	0.1587E 00
1750.00	0.0116	0.1028	0.0809	1.97130	0.0538	0.4148E 00
1900.00	0.0172	0.0947	0.1200	3.57597	0.0493	0.1379E 01
1950.00	0.0212	0.0923	0.1479	4.78497	0.0467	0.3293E 01
2000.00	0.0275	0.0900	0.1905	6.67859	0.0455	0.5286E 01
2050.00	0.0313	0.0878	0.2184	7.94839	0.0444	0.3644E 01
2100.00	0.0344	0.0857	0.2400	8.95038	0.0433	0.2965E 01
2150.00	0.0364	0.0837	0.2540	9.62569	0.0423	0.2006E 01
2200.00	0.0394	0.0818	0.2749	10.65020	0.0413	0.3153E 01
2250.00	0.0414	0.0800	0.2889	11.34891	0.0404	0.2199E 01
2350.00	0.0455	0.0765	0.3175	12.82954	0.0391	0.2408E 01
2500.00	0.0505	0.0720	0.3524	14.71332	0.0371	0.2175E 01
2650.00	0.0536	0.0679	0.3740	15.98668	0.0349	0.1521E 01
2750.00	0.0556	0.0654	0.3879	16.83455	0.0333	0.1619E 01
3000.00	0.0606	0.0600	0.4228	19.09162	0.0313	0.1833E 01
3250.00	0.0637	0.0553	0.4445	20.61267	0.0288	0.1343E 01
3500.00	0.0657	0.0514	0.4584	21.67251	0.0267	0.1011E 01
3750.00	0.0677	0.0480	0.4724	22.81086	0.0248	0.1166E 01
4000.00	0.0687	0.0450	0.4794	23.41928	0.0232	0.6666E 00
4500.00	0.0707	0.0400	0.4933	24.75389	0.0212	0.8000E 00
5000.00	0.0717	0.0360	0.5003	25.49970	0.0190	0.5000E 00
6000.00	0.0728	0.0300	0.5080	26.44964	0.0164	0.3666E 00
7000.00	0.0733	0.0257	0.5115	26.95992	0.0139	0.2333E 00
8000.00	0.0738	0.0225	0.5150	27.54873	0.0120	0.3111E 00
30000.00	0.0738	0.0060	0.5150	27.54873	0.0071	0.0000E 00

POROSIMETRY CALCULATIONS-PORE AREA-DISTRIBUTION

N -HAP-POWDER (P22)
INITIAL P=0. INITIAL SUM V=0. INITIAL D=100. W= 0.1644 K=0.0225

P PSIA	SOV CC	D MICRONS	SOV CC/G	SA M2/G	R BAR MICRONS	DV/DR
300.00	0.0000	0.6000	0.0000	0.00000	25.1500	0.0000E 00
400.00	0.0010	0.4500	0.0060	0.04790	0.2624	0.1333E-01
500.00	0.0020	0.3600	0.0121	0.10948	0.2025	0.2222E-01
800.00	0.0045	0.2250	0.0273	0.33188	0.1462	0.3703E-01
1000.00	0.0055	0.1800	0.0334	0.45506	0.1012	0.4444E-01
1250.00	0.0071	0.1440	0.0431	0.70141	0.0810	0.8888E-01
1500.00	0.0086	0.1200	0.0523	0.98369	0.0659	0.1249E 00
1800.00	0.0121	0.1000	0.0736	1.77406	0.0549	0.3500E 00
1900.00	0.0177	0.0947	0.1076	3.19194	0.0486	0.2127E 01
1950.00	0.0227	0.0923	0.1380	4.50923	0.0467	0.4116E 01
2000.00	0.0295	0.0900	0.1782	6.29322	0.0455	0.5719E 01
2050.00	0.0348	0.0878	0.2116	7.61751	0.0444	0.5011E 01
2100.00	0.0394	0.0857	0.2396	9.12385	0.0433	0.4400E 01
2150.00	0.0429	0.0837	0.2609	10.14175	0.0423	0.3511E 01
2200.00	0.0459	0.0818	0.2791	11.03477	0.0413	0.3153E 01
2250.00	0.0485	0.0800	0.2950	11.82652	0.0404	0.2860E 01
2300.00	0.0510	0.0782	0.3102	12.60491	0.0395	0.2875E 01
2400.00	0.0550	0.0750	0.3345	13.89141	0.0383	0.2453E 01
2500.00	0.0586	0.0720	0.3564	15.09852	0.0367	0.2400E 01
2600.00	0.0616	0.0692	0.3746	16.14551	0.0353	0.2166E 01
2700.00	0.0641	0.0666	0.3899	17.05222	0.0339	0.1949E 01
2800.00	0.0661	0.0642	0.4020	17.80495	0.0327	0.1679E 01
3000.00	0.0702	0.0600	0.4270	19.43223	0.0310	0.1913E 01
3100.00	0.0717	0.0580	0.4361	20.05837	0.0295	0.1549E 01
3200.00	0.0732	0.0562	0.4452	20.70504	0.0285	0.1653E 01
3300.00	0.0742	0.0545	0.4513	21.14984	0.0276	0.1173E 01
3500.00	0.0763	0.0514	0.4641	22.12703	0.0264	0.1347E 01
3600.00	0.0773	0.0500	0.4701	22.61208	0.0253	0.1400E 01
3700.00	0.0783	0.0486	0.4762	23.11243	0.0246	0.1480E 01
4000.00	0.0803	0.0450	0.4884	24.16625	0.0234	0.1096E 01
4350.00	0.0813	0.0413	0.4945	24.73765	0.0215	0.5523E 00
4750.00	0.0823	0.0378	0.5006	25.36037	0.0198	0.5739E 00
5100.00	0.0833	0.0352	0.5066	26.03440	0.0182	0.7690E 00
6000.00	0.0838	0.0300	0.5097	26.41419	0.0163	0.1888E 00
7500.00	0.0848	0.0240	0.5158	27.33800	0.0134	0.3333E 00
9000.00	0.0853	0.0200	0.5188	27.90256	0.0109	0.2500E 00
20000.00	0.0853	0.0090	0.5188	27.90256	0.0072	0.0000E 00

POROSIMETRY CALCULATIONS-PORE AREA-DISTRIBUTION

N -HAP-POWDER (P12)

PORE DIAMETER MICRONS	VOLUME PERCENT	AREA PERCENT
100.0000	0.00	0.00
80.0000	0.00	0.00
60.0000	0.00	0.00
40.0000	0.00	0.00
20.0000	0.00	0.00
10.0000	0.00	0.00
8.0000	0.00	0.00
6.0000	0.00	0.00
4.0000	0.00	0.00
2.0000	0.00	0.00
1.0000	0.00	0.00
0.8000	0.00	0.00
0.6000	0.00	0.00
0.4000	1.12	0.21
0.2000	5.76	1.44
0.1000	18.38	9.20
0.0800	56.09	41.19
0.0600	82.11	69.30
0.0400	95.79	89.85
0.0200	100.00	100.00

SUMMARY TABLE

1. MEDIAN PORE DIAMETER...	0.0832	MICRONS
2. TOTAL PORE VOLUME...	0.5150	CC/G
3. AVERAGE PORE DIAMETER (4V/A)...	0.0747	MICRONS
4. TOTAL PORE AREA...	27.548	M2/G

POROSIMETRY CALCULATIONS-PORE AREA-DISTRIBUTION

N -HAP-POWDER (P22)

PORE DIAMETER MICRONS	VOLUME PERCENT	AREA PERCENT
100.0000	0.00	0.00
80.0000	0.00	0.00
60.0000	0.00	0.00
40.0000	0.00	0.00
20.0000	0.00	0.00
10.0000	0.00	0.00
8.0000	0.00	0.00
6.0000	0.00	0.00
4.0000	0.00	0.00
2.0000	0.00	0.00
1.0000	0.00	0.00
0.8000	0.00	0.00
0.6000	0.00	0.00
0.4000	1.82	0.29
0.2000	5.92	1.63
0.1000	14.18	6.35
0.0800	56.85	42.38
0.0600	82.29	69.64
0.0400	95.77	89.54
0.0200	100.00	100.00

SUMMARY TABLE

1. MEDIAN PORE DIAMETER...	0.0832	MICRONS
2. TOTAL PORE VOLUME...	0.5188	CC/G
3. AVERAGE PORE DIAMETER (4V/A)...	0.0743	MICRONS
4. TOTAL PORE AREA...	27.902	M2/G

Fig. 4. Computer printout of the calculations of pore size and pore area distribution for the two samples of hydroxyapatite powder.

POROSIMETRY CALCULATIONS-PORE AREA-DISTRIBUTION page 1.

SPHEROM-6
INITIAL P=0. INITIAL SUM V=0. INITIAL D=100. W= 1.0000 K=0.0225
R BAR DY/DR

P PSIA	SDV CC	D MICRONS	SDV CC/G	SA M**2/G	MICRONS	
1.80	0.0000	100.0000	0.0000	0.00000	50.0000	0.0000E 00
2.60	0.0533	69.2307	0.0533	0.00263	42.3076	0.3464E-02
3.50	0.0867	51.4285	0.0867	0.00355	30.1044	0.1505E-02
15.00	0.0800	12.0000	0.0800	0.00832	15.6571	0.6746E-03
25.00	0.0800	7.2000	0.0800	0.00637	4.8000	0.0000E 00
50.00	0.0933	3.6000	0.0933	0.01754	2.7000	0.7388E-02
100.00	0.1070	1.8000	0.1070	0.04066	1.3500	0.1525E-01
200.00	0.1330	0.9000	0.1330	0.12841	0.6750	0.5777E-01
320.00	0.1600	0.5625	0.1600	0.28836	0.3656	0.1600E 00
670.00	0.2130	0.2686	0.2130	0.87865	0.2077	0.3607E 00
1100.00	0.2670	0.1636	0.2670	1.95192	0.1080	0.1028E 01
2000.00	0.3470	0.0900	0.3470	4.74192	0.0634	0.2172E 01
3500.00	0.4270	0.0514	0.4270	9.69192	0.0353	0.4148E 01
5200.00	0.4870	0.0360	0.4870	15.42642	0.0218	0.7777E 01
6000.00	0.5330	0.0300	0.5330	21.12192	0.0164	0.1533E 02
6400.00	0.6670	0.0281	0.6670	39.81493	0.0152	0.1249E 03
7000.00	0.8670	0.0257	0.8670	68.94693	0.0134	0.1656E 03
8000.00	0.9730	0.0225	0.9730	87.85240	0.0120	0.6595E 02
9000.00	1.0130	0.0200	1.0130	95.50236	0.0106	0.3199E 02
10000.00	1.0330	0.0180	1.0330	98.77740	0.0095	0.2000E 02
12000.00	1.0530	0.0150	1.0530	104.72738	0.0082	0.1333E 02
15000.00	1.0670	0.0120	1.0670	108.97985	0.0067	0.9333E 01

POROSIMETRY CALCULATIONS-PORE AREA-DISTRIBUTION page 2

SPHEROM-6

PORE DIAMETER MICRONS	VOLUME PERCENT	AREA PERCENT
100.0000	0.00	0.00
80.0000	3.24	0.00
60.0000	5.64	0.00
40.0000	6.61	0.00
20.0000	7.24	0.00
10.0000	7.49	0.00
8.0000	7.49	0.00
6.0000	7.91	0.00
4.0000	8.40	0.01
2.0000	9.88	0.03
1.0000	12.19	0.10
0.8000	13.21	0.16
0.6000	14.71	0.24
0.4000	17.74	0.56
0.2000	23.27	1.44
0.1000	31.50	4.00
0.0800	34.46	5.52
0.0600	38.35	7.88
0.0400	44.18	12.79
0.0200	94.93	87.83
0.0100	100.00	100.00

SUMMARY TABLE

1- MEDIAN PORE DIAMETER---	0.0377	MICRONS
2- TOTAL PORE VOLUME---	1.0670	CC/G
3- AVERAGE PORE DIAMETER (4V/A)---	0.0391	MICRONS
4- TOTAL PORE AREA---	108.979	M2/G

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...66–72.

List 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 Pressures in psia are listed, and Cols. 11–20, 31–40, 51–60, 71–80 the volumes in cc are listed for the corresponding pressures. Punch all decimal points.

Each succeeding card will look like the above card except for the last data card. That is, each card will contain four pairs of data points. The last card may end with the last pair of data in columns 61–70 and 71–80. If this is the case, another card should be added which has a $-10.$ in columns 1–4. If the last pair of data does not occur in the last two columns 61–70 and 71–80, then $-10.$ is punched in the first four columns of the ten column field; *e.g.* if the last pair of data points occurs in columns 41–50 and 51–60, then $-10.$ is punched in columns 61–64.

The $-10.$ is a signal to the program that the end of data has been reached, the computation should be done, and that there is another set of data to be processed following the present set. If it is the final set of data, $-20.$ should be substituted for $-10.$ Thus, each set of data starts with the card containing the value of W and continues through the card containing $-10.$ or $-20.$ if it is the last set to be processed.

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[10]** 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 m^2/g. The surface area by mercury porosimeter of 109.0 m^2/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 m^2/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.

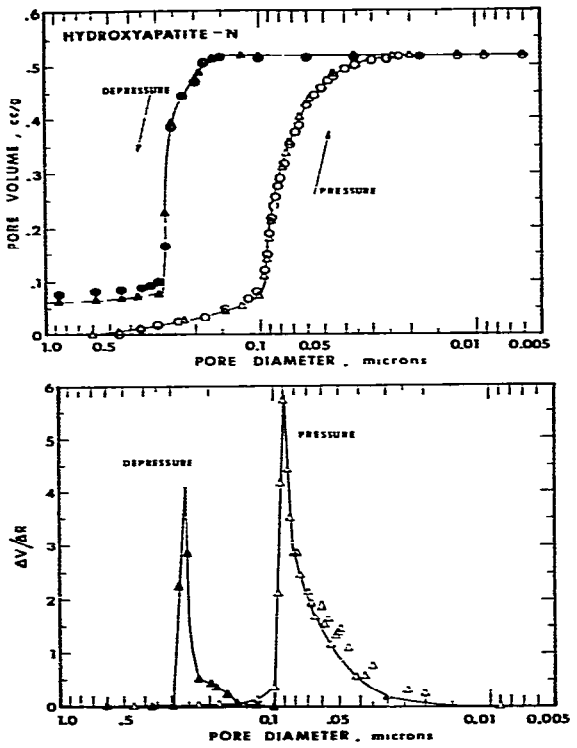

Fig. 6. The top figure shows the pore size distribution in the form of the integral, or the cumulative pore volume vs. pore diameter plot for the two samples of hydroxyapatite samples. ○ first sample P12, △ second sample P22. The bottom figure shows the differential distribution curves for both the pressure and the depressure cycle of the sample P22. The curves for the sample P12 are identical.

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

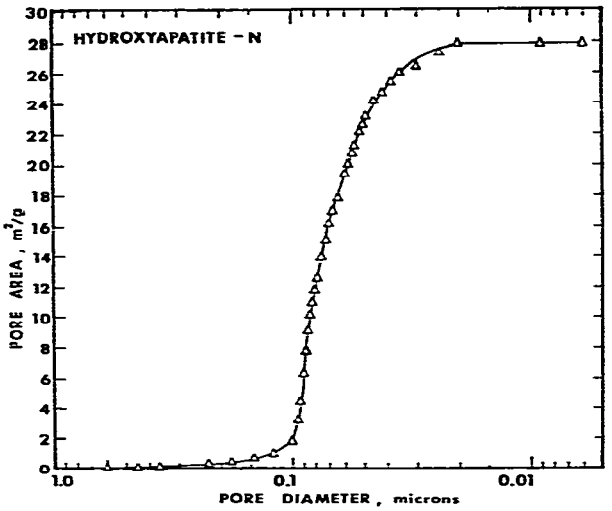

Fig. 7. Pore area (m^2/g) plotted as the function of pore diameter for comparison with the pore volume plot of Fig. 3, for the hydroxyapatite sample.

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.

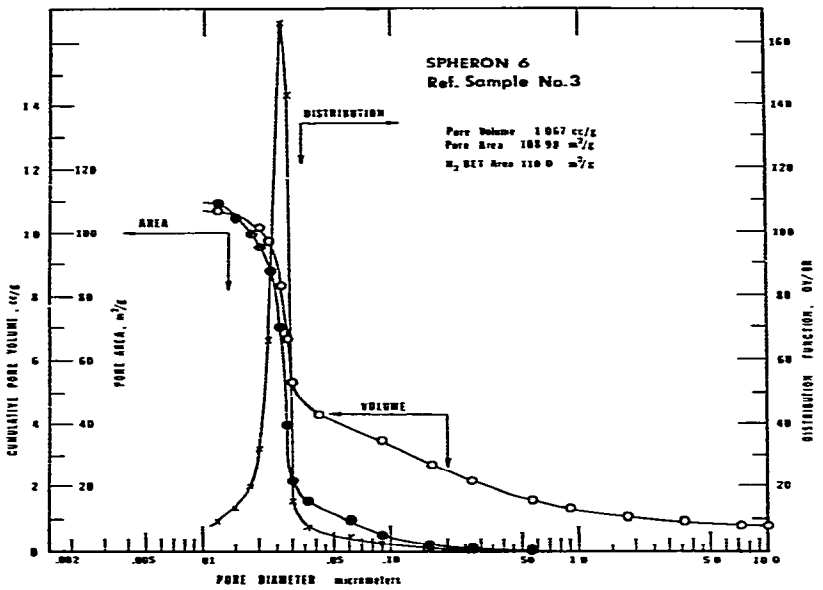

Fig. 8. To illustrate three ways of presenting the data calculated by the computer program, the cumulative pore volume and pore area, as well as the differential distribution function vs. the pore diameter, are plotted on the same graph for Spheron 6.

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.

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