USE OF MULTIPLE TEST TECHNIQUES FOR EVALUATION OF COMPLEX PORE STRUCTURE

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ABSTRACT

Pore structures of a ceramic filtration medium were investigated by liquid extrusion porosimetry, capillary flow porometry and mercury intrusion porosimetry. The results were analyzed and the physical parameters that the techniques measure interpreted. The analysis showed that the filter had through pores with narrow necks and wide mouths. The neck diameters were spread over a wide range. The filter contained appreciable volume percent of blind pores. The blind pores had wide mouths and long and narrow tails.

INTRODUCTION

Filtration media are finding many applications in advanced areas of modern technology. Control of fluid flow characteristics, barrier properties and holding capacities of filter materials are required for such applications. These properties are governed by constricted pore diameters, pore volume, pore distribution and permeability. Therefore, understanding of the pore structure of filtration media is important. Various test techniques are available to evaluate structures of porous materials. However, each technique can determine only certain aspects of pore structure. When several techniques are used, many characteristics of the pore structure are revealed and one obtains a better understanding of the pore structure. Three techniques, liquid extrusion porosimetry, capillary flow porometry, and mercury intrusion porosimetry were used to investigate a commercial ceramic filter. Analysis of results led to useful information on the pore structure characteristics of the filtration material.

NON-MERCURY LIQUID EXTRUSION POROSIMETRY

PRINCIPLE

The sample is placed on a membrane and loaded in the sample chamber. The membrane is such that its largest pore is smaller than the smallest pore of interest in the sample. A wetting liquid is selected. A wetting liquid is such that its surface free energy with the material is lower than the surface free energy of the material with air. The wetting liquid is allowed to spontaneously fill the pores of the sample and the membrane. Pressure of a non-reacting gas over the sample is increased so as to displace the liquid from pores.

Pressure required to displace liquid from a pore is related to the size of the pore [1].

$$p = 4 \gamma \cos \theta / D \qquad (1)$$

where p is the pressure difference across the pore, γ is the surface tension of the liquid, θ is the contact angle of the liquid with the sample and D is the pore diameter. For low surface tension wetting liquids the contact angle is taken as zero [2]. The equation shows that liquid is pushed out of the largest pore of the sample at the lowest pressure and with increasing pressure smaller pores of the sample are emptied at higher pressures. Because the largest pore in the membrane is smaller than the smallest pore of interest in the sample, the gas pressure that empties the pores in the sample cannot remove liquid from the pores of the membrane and permit gas to pass through the membrane. However, all the liquid pushed out of the pores of the sample by the gas passes through the membrane, while its pores remain filled with the liquid. The sketch in Figure 1A illustrates the principle. The pressure of the gas and the amount of liquid flowing out of the membrane are accurately measured. The pressure gives pore diameter and the volume of displaced liquid gives pore volume.

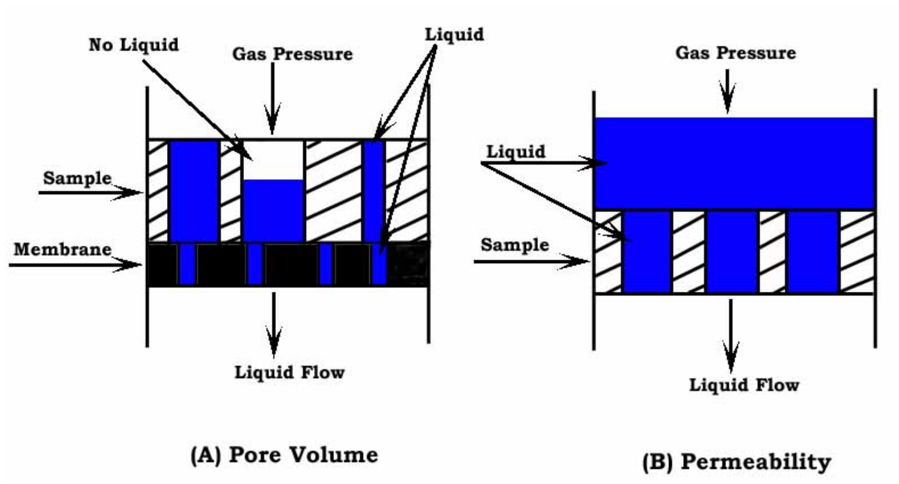

Figure.1. Sketch illustrating the principle of liquid extrusion porosimetry.

For measurement of liquid permeability, the membrane is removed and pressure on excess liquid maintained on the sample is increased (Figure 1B). The pressure and the rate of increase of volume of the displaced liquid are measured. The measured pressure, flow rate and volume are used to compute pore size, pore volume, pore distribution and permeability of pores that permit fluid flow.

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Figure.2: The PMI Liquid Extrusion Porosimeter.

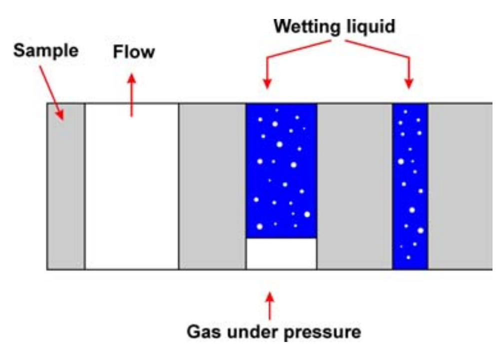

Figure 3. Principle of capillary flow porometry.

INSTRUMENT

The PMI Liquid Extrusion Porosimeter used in this investigation is shown in Figure 2. It is fully automated. Because of the sophisticated and innovative designs incorporated in the instrument, it is possible to increase pressure slowly in small increments and measure pressure and volume of displaced liquid accurately and reproducibly.

CAPILLARY FLOW POROIMETRY

PRINCIPLE

Capillary flow porometry uses samples with their pores filled with a wetting liquid and pressure of a non-reacting gas is used to remove the liquid from pores and permit gas flow (Figure 3). The pressure required to displace the wetting liquid from pores is given by Equation 1. The pressure and flow rates through wet and dry samples are measured. The results are used to compute the largest pore diameter, the mean flow pore diameter, flow distribution and permeability.

Figure 4. The PMI Capillary Flow Porometer

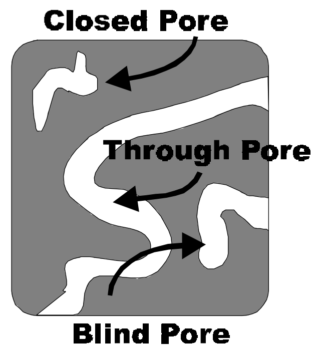

Figure 5. Three different kinds of pores

INSTRUMENT

In this study, the PMI Capillary Flow Porometer was used [3]. The fully automated instrument (Figure 4) yielded highly repeatable and accurate data.

MERCURY INTRUSION POROSIMETRY

In this technique, the non-wetting liquid, mercury is forced into pores of the sample. The pressure needed to intrude mercury in to a pore is given by:

$$p = - 4 \gamma \cos \theta / D \quad (2)$$

where p is pressure on mercury, γ is surface tension of mercury, θ is contact angle of mercury and D is pore diameter. The pressure yields pore diameter and the decrease in volume of mercury due to intrusion gives pore volume. The pressure and intrusion volume are measured. These data are used to compute pore size, pore volume and pore volume distribution. The PMI Mercury Intrusion Porosimeter was used in this investigation.
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RESULTS AND DISCUSSION

KIND OF PORES

Three kinds of pores are found in materials (Figure 5). Closed pores could not be detected by any of these techniques. The through pores permit fluid flow. Therefore, through pores were detected by extrusion porosimetry and flow porometry. Mercury intrusion technique measures all the through and blind pores in the material.

PORE VOLUME

Pore volume measured by extrusion porosimetry is the volume of through pores. Figure 6 shows a typical plot giving variation of the volume of displaced wetting liquid with pressure measured in the PMI Liquid Extrusion Porosimeter. As expected, the volume increases with pressure because liquid is removed from smaller pores at higher pressures. The volume of all through pores is 1.982 cm^3/g.

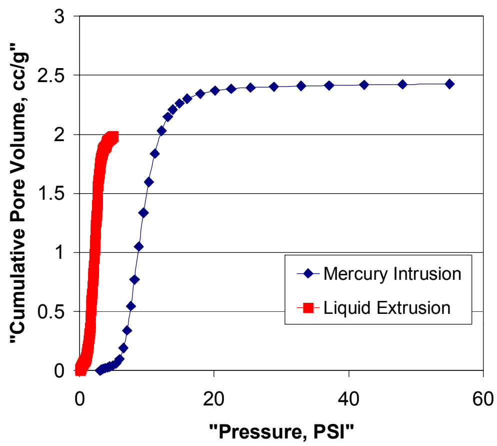


Figure.6. Variation of volume of displaced liquid with pressure measured in the liquid extrusion porosimeter. The result of mercury intrusion porosimetry is also shown.

The pore volume, measured by mercury intrusion porosimetry is due to through and blind pores. The change of pore volume with pressure is also shown in Figure 6. The shape of the curve is similar to that measured by liquid extrusion technique. However, the pressure required for liquid extrusion porosimetry is almost an order of magnitude less than that required for mercury intrusion porosimetry. The measured pore volume, 2.492 cm^3/g corresponds to the volume of through and blind pores.

The volume of blind and through pores measured by intrusion porosimetry is 2.492 cm^3/g compared with the volume of through pores, 1.982 cm^3/g measured by extrusion porosimetry. Hence, the volume of blind pores is 0.51 cm^3/g. 20.5 % of pore volume is due to blind pores.

Through pores:	2.492 cm^3/g,	79.5 % of pore volume.
Blind pores:	0.51 cm^3/g,	20.5 % of pore volume

PORE DIAMETER

The size of a pore changes along its length. At any location along the length of the pore, diameter D of the pore is defined as the diameter of a circular opening whose perimeter to area ratio is the same as that of the pore at the specified location (Figure 7).

$$(\text{Perimeter/Area})_{\text{pore}} = (\text{Perimeter/Area})_{\text{circle of diameter D}} \quad (3)$$

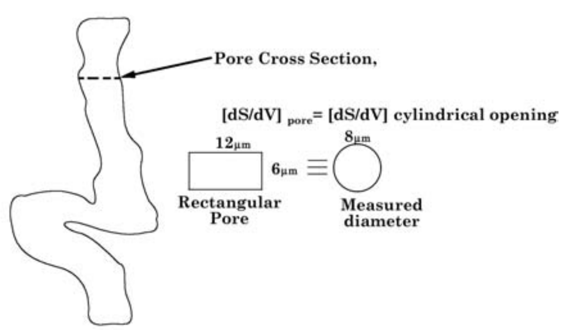


Figure 7. Definition of pore diameter.

Different techniques measure a pore differently. Capillary flow porometry detects the presence of a pore when gas starts flowing through that pore. Gas starts flowing through the pore only when the pressure is high enough to displace liquid from the most constricted part of the pore (Figure 8). Consequently, pore diameter calculated from the pressure is the diameter of the pore at its most constricted part. Thus, each pore is detected as a single pore of diameter equal to the diameter at the most constricted part of the pore.

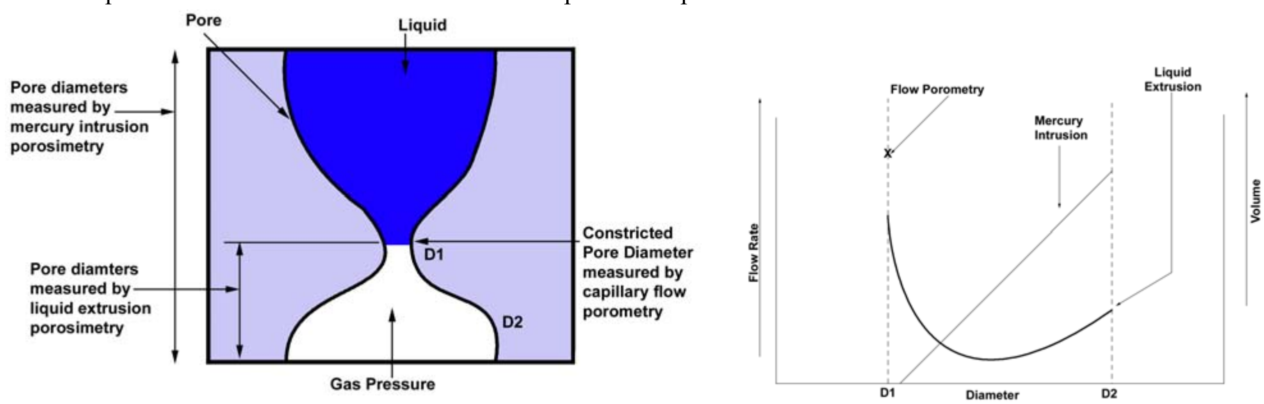


Figure 8. Pore diameters measured by various techniques.

The constricted pore diameters are obtained from the measured gas flow rates as functions of pressure (Figure 9). In this figure the wet curve corresponds to flow through the wetted sample, the dry curve corresponds to flow through the dry sample and the half-dry curve is computed from the dry curve to yield half of the flow through dry sample.

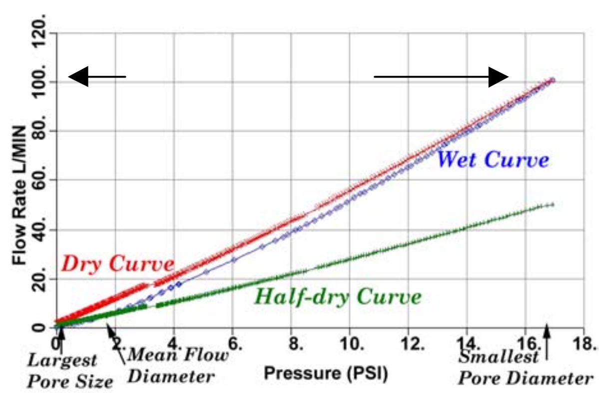


Figure 9. Flow rate as a function of differential pressure measured by flow poromtry.

The largest constricted pore diameter (bubble point) is calculated from the pressure required to initiate flow through a wet sample The mean flow pore diameter is computed from mean flow pressure. The mean flow pressure corresponds to the intersection of the wet curve with the half-dry curve. The mean flow pore diameter is such that half of the flow through the sample is through pores larger than the mean flow pore. The distribution of flow over constricted pore diameter is shown in Figure 10 in terms of the distribution function, f defined by Equation 4.

$$f = -d[(F_w/F_d)\times 100] / dD \quad (4)$$

where F_w and F_d are flow through wet and dry samples respectively at the same differential pressure. It follows from Equation 4 that the area under the curve in any pore size range yields the percentage flow through that pore size range. It has been shown that the distribution is close to the fractional pore number distribution [4]. Most of the pores have constricted diameters close to two microns.

The bubble point (the constricted largest pore diameter) = 450.4 µm.
The constricted mean flow pore diameter = 3.867 µm.
The constricted pore diameter range = 450.4 - 0.39 µm

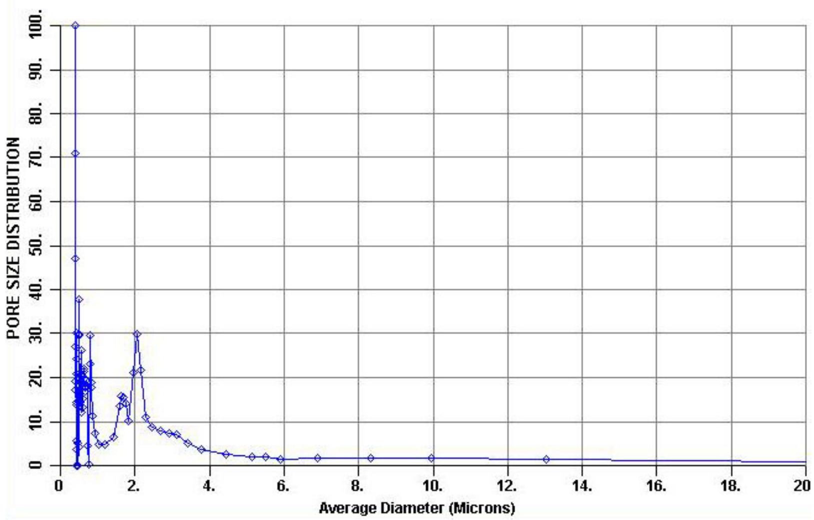


Figure 10. Flow distribution by flow porometry.

Liquid extrusion technique detects a pore when liquid is extruded from the pore due to applied pressure. The pressure required to displace the liquid in the pore at its most constricted part is the highest. Therefore, diameters of the part of pore between the entry point of the gas and the most constricted point are detected as illustrated in Figure 8. Volume of pore beyond the constricted part is detected as volume of pore of the constricted diameter (Figure 8). Thus, if pores are associated with wider parts or wide mouths, the pore distribution by extrusion porosimetry will show a shift to the higher pore diameter. Figure 11 shows the distribution function obtained by extrusion porosimetry. The function, f is such that the area under the curve in a pore size range is the volume of pores in that range.

$$f = - (dV / d \log D) \quad (5)$$

where V is the pore volume. The distribution shows that volume of through pores outside 10-40 micon range is negligible, most of the pores occur at around 18 microns pore size and the distribution of through pores is sharp. Comparison with the distribution obtained by flow porometry suggests that the through pores with large constricted diameters are very few and most through pores have about 2 microns constricted pore diameter and about 18 microns wide mouths.

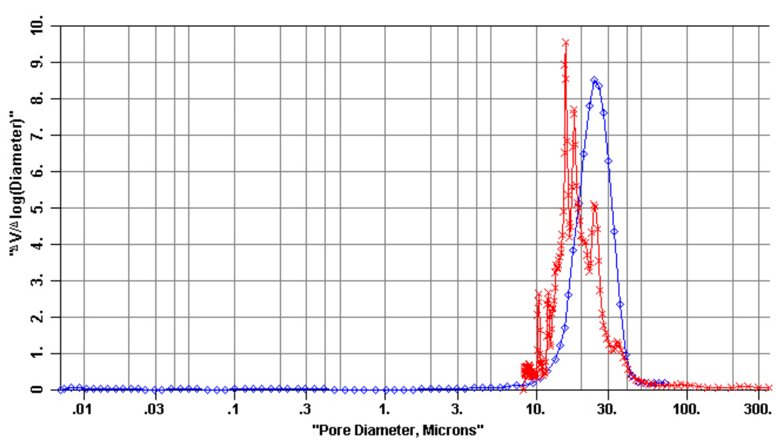


Figure. 11: Pore volume distribution by liquid extrusion technique. The distribution by mercury intrusion technique is also included.

Mercury intrusion technique detects pores when mercury fills pore volume. Since, mercury could enter from both sides of the pore, this technique measures different pore diameters. Figure 8 illustrates the type of measurement expected from this technique. The pore distribution by this technique will be shifted to higher pore diameters for pores with large mouths. Also, the presence of blind pores will shift the position of distribution peak. Blind pores with large openings or mouths will shift the distribution to higher pore diameters and narrow blind pores will shift the distribution to lower pore diameters. The distribution by intrusion porosimetry is also shown in Figure 11. It suggests that the blind pores must have large openings or mouths so that considerable shift of the distribution is observed.

Most through pores: 2 micron constricted diameter
18 microns wide mouths
Blind pores: Wider than 18 micron mouth

One of the unique features of extrusion porosimetry is that converging/diverging pores can be identified as illustrated in Figure 12.

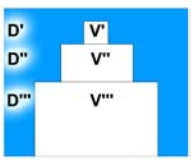
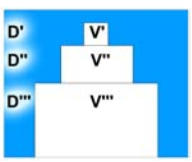
	Pore		Extrusion Porosimetry	Flow porometry	Mercury intrusion porosimetry
(a)			Gas pressure↓	Gas pressure↓	Mercury pressure↓↑
		No. of pores:	1	1	3
		Diameters:	D’	D’	D’, D’’, D’’’
		Pore volume:	(v’+v’’+v’’)	-	v’, v’’, v’’’
(b)			Gas pressure↑	Gas pressure↑	Mercury pressure↓↑
		No. of pores:	3	1	3
		Diameters:	D’’’, D’’, D’	D’	D’’’, D’’, D’
		Pore volume:	v’’’, v’’, v’	-	v’’’, v’’, v’

Figure 12. . Diverging/converging pores detectable by extrusion technique.

PORE SURFACE AREA

Surface area, S is obtainable from extrusion and intrusion porosimetry using the following relation.

$$S = [1/(\gamma \cos \theta)] \int p \, dV \qquad (6)$$

The surface area of through pores computed from the variation of pore volume with pressure is 0.43 m^2/g. The surface area of through and blind pores computed from intrusion porosimetry data is 9.44 m^2/g. Thus, the surface area of blind pores is 9.01 m^2/g. We know that the volume of blind pores is high and the blind pores have wide mouth. Hence, the large contribution to surface from the blind pores can arise if a small volume of blind pores is present as narrow extensions wide mouthed blind pores.

THROUGH PORE CONFIGURATION

The constricted pore diameters of through pores measured by flow porometry are over a wide range of 450.4 & 0.4 microns although the mean flow constricted pore diameter is only 3.867 microns. This result suggests that very few pores have large constricted diameters while many pores have small, constricted diameters. Although the average constricted diameter is around 4 microns, a large part of the pore volume is of pores having diameter between 15 – 30 microns, the median pore diameter based on volume is 18.493 microns and volume of pores larger than 200 microns is negligible. That means, pores with large constricted diameters are very few, pores having small constrictions of about 4 microns have large wide parts of diameter of about 18 microns. The wide parts could constitute wide mouths. Such a pore configuration is consistent with the surface area. The through pore volume measured by extrusion poprosimetry is 1.982 cm^3/g and the median pore diameter based on volume is about 18. Hence, the surface area is 0.44 m^2/g. This is close to the measured value of 0.427 m^2/g.

BLIND PORE CONFIGURATION

The pore volume distributions suggest that both through pores and blind pores have the same range of diameters. However, the median pore diameter of through and blind pores is 22.97 microns much higher than the median through pore diameter of 18.48 microns. Thus, the blind pores must be associated with wide parts and possibly wide mouths. Such pores would have very low surface area. But the surface area of blind and through pores is 9.44 m^2/g compared with through pore surface area of only 0.43 m^2/g. Consequently, the surface area of blind pores, 9.01 m^2/g, is very high. The blind pores must consist of narrow and long parts with wide mouths so that the contributions of blind pores to surface area and to median pore diameter are high. The presence of narrow pores with very small pore volume could account for the large surface area. For example, only ten percent of blind pore volume, 0.05 cm^3/g is associated with the narrow parts of blind pores of diameter 0.02 microns contributes 10 m^2/g to the surface area. This is close to the measured surface area of 9.01 m^2/g. The sketch in Figure 13 illustrates such pore structure in the filter material.

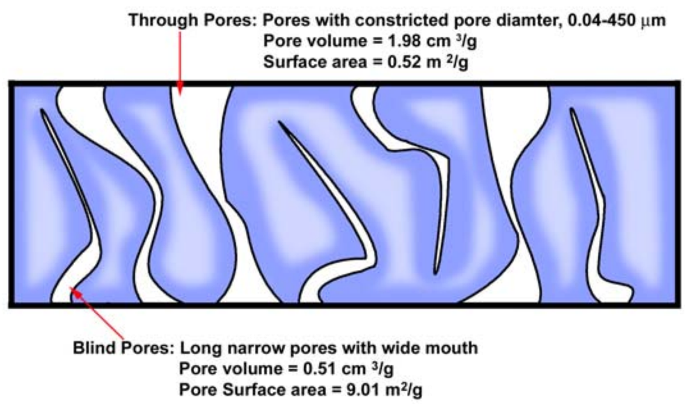


Figure 13. Pore structure of filtration media.

COMPARISON OF TECHNIQUES

Table 1 clearly brings out the capabilities of the three techniques. The liquid extrusion and capillary flow techniques have a number of operational advantages. The pressure required in these techniques is an order of magnitude less than the pressure required for mercury intrusion porosimetry. Also the materials used in these techniques are not toxic and are not harmful to health. Therefore, there is no cost related to sample disposal or safety regulations.

Table 1: Capabilities of the three techniques

Measurable Characteristics	Liquid Extrusion Porosimetry	Capillary Flow Porometry	Mercury Intrusion Porosimetry
Pore diameter	Yes	Yes	Yes
Diameter of pore at its most constricted part	No	Yes	No
Largest constricted pore diameter	No	Yes	No

Mean constricted pore diameter based on flow	No	Yes	No
Median pore diameter based on volume	Yes	No	Yes
Pore volume			
Total pore volume	Yes	No	Yes
Pore volume distribution	Yes	No	Yes
Flow distribution	No	Yes	No
Pore shape			
Through pores only	Yes	Yes	No
Through & blind pores	No	No	Yes
Converging/diverging pores	Yes	No	No
Operational features			
Non-toxic material	Yes	Yes	No
Low pressure	Yes	Yes	No
Permeability			
Liquid Permeability	Yes	Yes	No
Gas permeability	No	Yes	No

CONCLUSIONS

1. Three techniques, liquid extrusion porosimetry, capillary flow porometry and mercury intrusion porosimetry were used to investigate a filter material.
2. Through pore volume, volume distribution, diameter and surface area were measured by liquid extrusion technique.
3. Through pore constricted diameter, largest pore diameter, flow distribution and gas permeability were measured by flow porometry.
4. Blind and through pore volume, volume distribution, diameter and surface area were measured by mercury intrusion.
5. Analysis of the data obtained using the three techniques gave more interesting information on pore configuration of through pores and blind pores.
6. Liquid extrusion and capillary flow techniques did not require the use of any harmful and toxic material. The pressure required was low.

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