# Wicking technique combined with electrical resistance measurements for determination of pore size in ceramic membranes

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An easy, fast and inexpensive method to determine the mean pore size of a microfiltration ceramic membrane is offered by the wicking technique combined with electrical resistance measurements. Mean pore size is derived from the measured rates of capillary rise of different liquids of known surface tension through the ceramic membrane, via the Washburn equation. We used low-energy liquids for which the contact angle $\theta \approx 0$, such as hydrocarbons, and we determined the tortuosity of the membrane pores from electrical resistance measurements so that the mean pore radius was the only unknown in the Washburn equation. The mean pore diameter of the ceramic membrane was also determined from Mercury Intrusion Porosimetry (MIP) for comparison. It was found to be in very good agreement with that afforded by the wicking technique. © *1999 Kluwer Academic Publishers*

## 1. Introduction

Membrane technology provides an economical and reliable separation process in many industrial applications. Flourishing interests in the development of this technology make it imperative to tailor membrane with better separation characteristics for specific industrial applications.

The separation characteristics are affected by the physical properties of the membrane such as porosity, mean pore size, pore size distribution, surface area and tortuosity, as well as by the electrochemical properties of the membrane (zeta-potential and surface charge density).

Pore size plays an important role in determining permeability and permselectivity of a membrane. The size of the crystallites forming the network of membranes pores and the porous nature of this network affect the permeation and separation properties of porous inorganic membranes. The network of the inter-connected membrane pores formed during preparation and fabrication may be tortuous or nearly straight depending on the synthesis and subsequent heat treatment and conditions.

Methods of characterizing the pore size distribution or its mean value of porous inorganic membranes can be assessed by a number of physical methods [1]. These include electron microscopy, mercury penetration, the bubble point method, nitrogen adsorption-desorption, molecular weight cut-off... Among these methods, only electron microscopy, mercury penetration and the bubble point method are suitable to describe pore diameters of ∼1 $\mu$m.

Electron microscopy is only able to sample a very small area fraction, can only see surface pores and is destructive. However, microscopy is a very important tool and gives very valuable insight.

Mercury Intrusion Porosimetry (MIP) is widely used [2, 3] because it is a relatively easy experiment to perform, pore size can be derived by simple calculation, and the values obtained are usually reproducible. Ambiguity in the pore sizes derived from MIP results from pore shape and non-interconnectivity assumptions as well as the uncertainty of the wetting behavior of the mercury at the liquid/solid interface. This latter consideration is manifested as questionable mercury contact angle values. Moreover the mercury intrusion is based on artificial and simple models of the porous structure (e.g., straight cylindrical non-intersecting pores of uniform and invariable radii).

The bubble point method [4, 5] is used to determine the largest pore size in a crack-free membrane. Considerable care must be taken to receive reproducible and meaningful results.

Finally, most of these techniques involve relatively elaborate and time consuming procedure. So, it is necessary to improve the development of simple and inexpensive methods accessible to membrane fabricators, investigators and users.

Described in this paper is an alternative method for measuring mean pore sizes (incorporating small as well as large pores [6]) of a ceramic microfiltration membrane (microfiltration is the separation of dispersed materials in the size range of 0.1–1 $\mu$m using polymeric or inorganic membranes). This method requires no special equipment, the reagents are inexpensive and easy to handle, making it an attractive alternative for the routine measurement of pore sizes in ceramic materials.
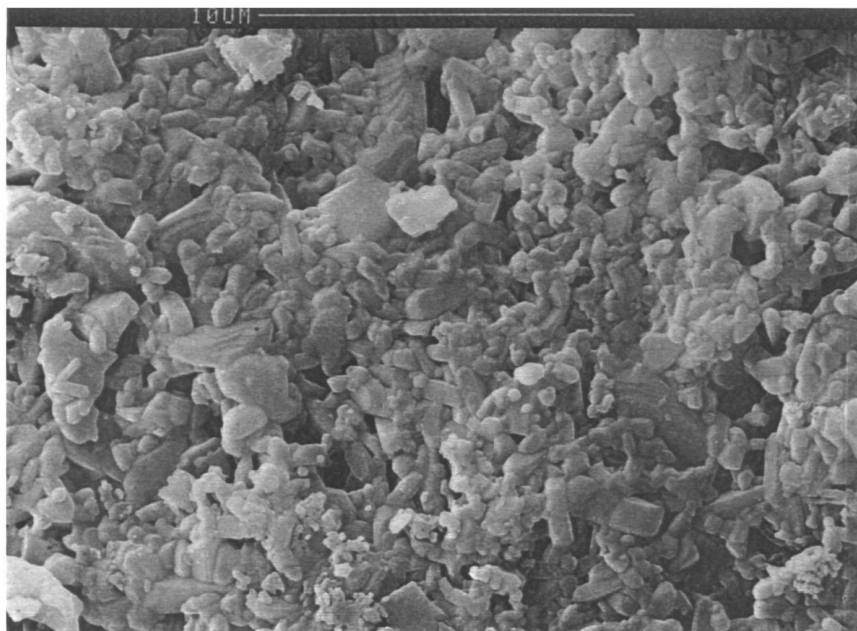
*Figure 1* Scanning micrograph of the ceramic membrane (×5000).

## 2. Materials and methods

The microporous membranes studied in the present paper were produced by TAMI, Nyons, France. On bulk analysis, these membranes consist of ca. 64% aluminium oxide ($Al_2O_3$) ca. 27% titanium dioxide ($TiO_2$), and ca. 9% silica.

The scanning micrograph (Fig. 1) suggests that the membrane consists of a percolation system with a spongy structure. The pore sizes are ~1 $\mu$m.

The porosity of the membrane was determined by the usual method described by Helfferich [7]. The porosity $\varepsilon$ (fractional void volume of the membrane) was calculated from the relationship:

$$\varepsilon = \frac{V_p}{V_g} = \frac{W_w - W_d}{w V_g} \qquad (1)$$

where $V_p$ is the volume of water in the pores, $V_g$ the geometric membrane volume, $W_w$ and $W_d$ the weights of wet and dried membranes and $w$ the water density. The mean porosity of the ceramic membrane is about 25%.

Membranes in the form of 47 mm discs were used for electrical resistance measurements. For wicking experiments, rectangular samples were cut from the membrane discs with a diamond saw.

## 2.1. Wicking technique for determination of mean pore size

The wicking technique [8, 9] is an alternative method to measure mean pore sizes (including small as well as large pores). It is based on the capillary rise of a low surface tension liquid into pores.

When a porous body with randomly oriented capillary pores, is placed in contact with the surface of a liquid, the liquid rises through the pore system with a velocity that is related to the mean size of the pores, surface tension and viscosity of the liquid and contact angle that a drop of the liquid makes when placed on a smooth surface of the solid [10–13]. The relation between these quantities is given by the Washburn equation:

$$h^2 = \frac{r\gamma \cos\theta}{\chi^2 2\eta} t \qquad (2)$$

where $h$ is the height traveled by the liquid in time $t$, $r$ is the mean pore radius, $\gamma$ and $\theta$ have the usual meaning of surface tension and contact angle and $\chi$ is the tortuosity factor which is defined as the ratio between the distance traveled by the liquid i.e., the effective length of path, and the height of the wetting front. The tortuosity factor of the ceramic membrane was determined from electrical resistance measurements (Section 2.2).

### 2.1.1. Experimental procedure
Rectangular ceramic membrane samples were suspended in a closed cell and equilibrated for one hour with the vapor of the wicking liquid (Fig. 2). This is important because it prevents the effects of excessive evaporation of the solvent during the wicking process which would depress the rate of rise in the porous body. The samples were then placed in contact with the surface of the liquid, in the vertical position. By means of thin lines drawn on the samples, it was possible to measure the different times elapsed for the liquid front to reach the various heights. The rising front was easily visible because the tint darkened as imbibing took place.

## 2.2. Electrical resistance measurements for determination of the tortuosity factor
Electrochemical impedance spectroscopy is a procedure that is well adapted to obtaining information about the structure of a porous non-conducting material [14, 15].

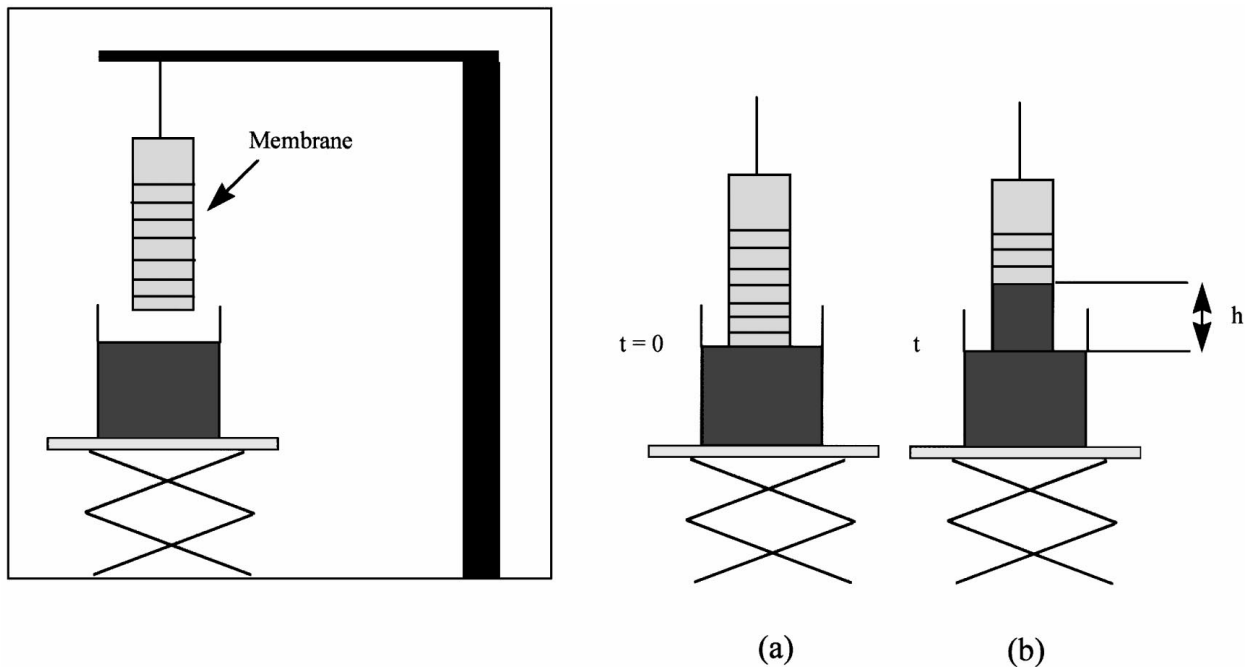Electrical resistance measurements were performed using electrochemical impedance spectroscopy.

*Figure 2* Principle of wicking technique for determining mean pore size of the ceramic membrane.
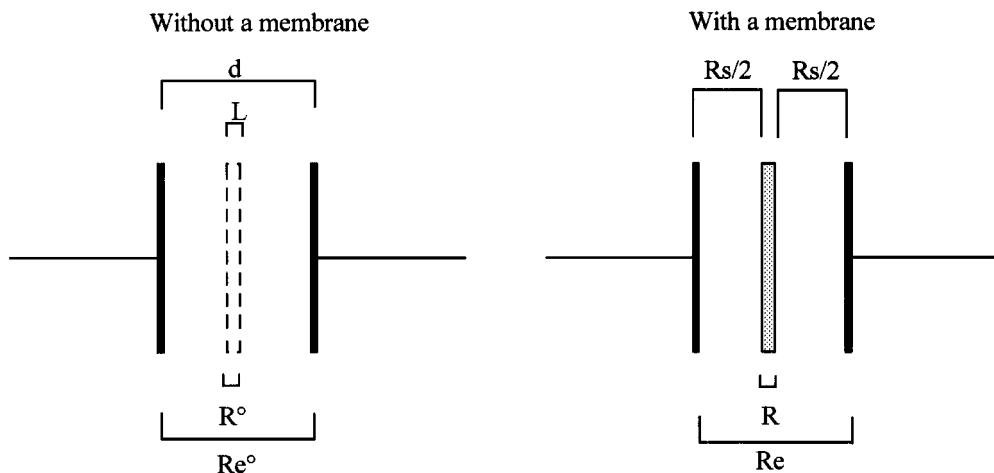


*Figure 3* Experimental procedure for determining electrical resistance of ceramic membrane.

The equipment used was a Solartron 1286 electrochemical interface linked to a solartron 1255 frequency response analyzer, controlled by a personal computer. We used the galvanostatic four-electrode mode to measure the resistance of the solution in the pores of the ceramic membrane.

The ceramic membrane was held between two half compartments filled with the same solution. The cell was equipped with two Ag/AgCl discs, parallel to the membrane, in the end of each half compartment, and firmly held by O-rings and polycarbonate discs. The cell also included two other Ag/AgCl wire electrodes placed on either side of, and equidistant from the membrane. These wires were used to measure the voltage in galvanostatic mode.

Resistance measurements were performed as a function of KCl concentration in the range of $10^{-3}-1$ M. The ceramic membrane was first equilibrated with the solution to be used, before each measurement, and before mounting in the cell. All measurements were then carried out at $20\,°C$ ($\pm1\,°C$) at the frequency of 4 kHz and with an ac amplitude voltage of 15 mV.

The resistance $Re$ of the measuring cell is the sum of the resistance of the membrane $R$ and the solution $Rs$ (Fig. 3). The $Rs$ value was determined from the resistance measured without a membrane. $R$ was then obtained by subtracting the value of $Rs$ from $Re$.

## 3. Results and discussion
### 3.1. Tortuosity factor
Fig. 4 shows an example of the dependence of the logarithm of the membrane resistance ($\log R$) on the logarithm of KCl resistivity ($\log \rho$). The analysis of the $\log R$ vs. $\log \rho$ plot shows that the resistance $R$ follows the equation:
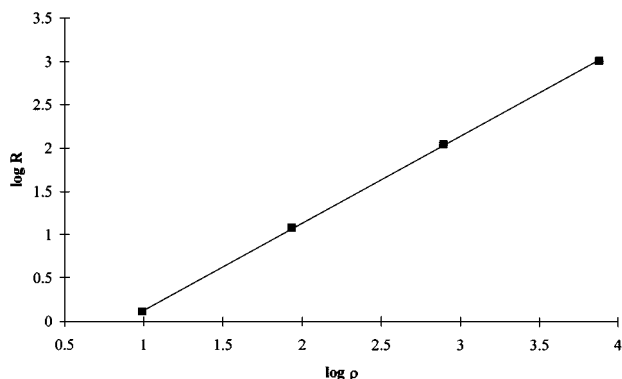
$$R = \beta\rho^{\alpha} \qquad (3)$$

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*Figure 4* Plot of log $R$ versus log $\rho$.

The $\alpha$ values of three membrane samples tested were close to one (0.98, 0.99, 0.98). This implies that the resistivity of the solution in the pores of the ceramic membrane is the same as that of the bulk solution. This result allows determining the tortuosity factor [16, 17].

This one is defined as follows:

$$\chi = \frac{L'}{L} \qquad (4)$$

where $L$ is the membrane thickness and $L'$ the distance traveled by the liquid for crossing the membrane, i.e. the effective length of path.

### 3.1.1. Theoretical basis for relating tortuosity to electrical resistance measurements

Electric current ($I$) flowing through unit area of non conducting porous bodies such as ceramic membranes the pores of which are filled with an ionic conductor of specific resistance ($\rho$), may be expressed as follows:

$$\rho I = \frac{\varepsilon}{\chi} \, \text{grad } E \qquad (5)$$

where $E$ is the potential.

Equation 5 states that the current flowing through unit area is a function of the potential gradient and two determining structural dimensions of the membrane network. These dimensions are the porosity $\varepsilon$ and the tortuosity $\chi$. Equation 5 may be rewritten as follows:

$$R \frac{\varepsilon}{\chi} = \rho L \qquad (6)$$

Besides, we may express the electric resistance $R^0$ per unit area of an ionic conductor occupying the same bounds of space as the membrane:

$$R^0 = \rho L \qquad (7)$$

Finally, combination of Equations 6 and 7 yields:

$$\frac{R}{R^0} = \frac{\chi}{\varepsilon} \qquad (8)$$

The measure of $R/R^0$, if $\varepsilon$ is known, allows the determination of the tortuosity. $R/R^0$ was calculated from the following equation:

$$\frac{R}{R^0} = \left[ \frac{Re}{Re^0} - 1 \right] \cdot \frac{d}{L} + 1 \qquad (9)$$

where $d$ is the distance between the two Ag/AgCl wires (Fig. 3). $Re$ and $Re^0$ were directly obtained from impedance results.

The tortuosity factor is different from one: it is in the range of 2.4–2.7. This result clearly indicates that the membrane pores are not straight. So, the membrane consists of a tortuous pore system. A series of tortuosity factor measurements on bonded porous alumina was carried out by Little [18]. The tortuosity factor ranged from 2 to 6, which is in good agreement with our result.

### 3.2. Mean pore radius

Wicking experiments were performed with three liquids for which the contact angle $\theta \approx 0$. Table I lists the physical characteristics of these liquids. Each liquid was wicked in triplicate; i.e. three membrane samples were examined. Fig. 5 shows an example of a typical plot obtained for decane. The linearity of the plot $h^2$ versus $t$ confirmed that the Washburn equation (Equation 2) is applicable. The values of $h^2/t$ were calculated by regression for each sample and liquid.

Fig. 6 shows, for all wicking liquids used, that the Washburn equation is linear in $2\eta\chi^2 h^2/t$ and $\gamma$. The mean pore radius, which is determined from the slope of the linear plot $2\eta\chi^2 h^2/t$ versus $\gamma$ is ~0.4 $\mu$m.

The mean pore size of the ceramic membrane was also determined by MIP in a Micromeristics 9310 poresizer. The results obtained are presented in Fig. 7. The pore size distribution is large and is in the range 13.24–0.01 $\mu$m with a mean pore diameter of ~0.9 $\mu$m, that is to say a pore radius of ~0.45 $\mu$m.

TABLE I Surface tension and viscosity of liquids used to determine mean pore radius

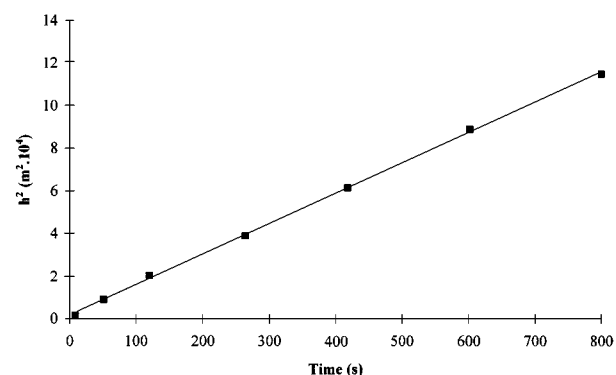| Liquid | $\gamma$ (mJ/m$^2$) | $\eta$ (mPa·s) |
|---|---|---|
| Hexane | 18.4 | 0.326 |
| Decane | 13.83 | 0.907 |
| Distilled water | 72.2 | 1 |



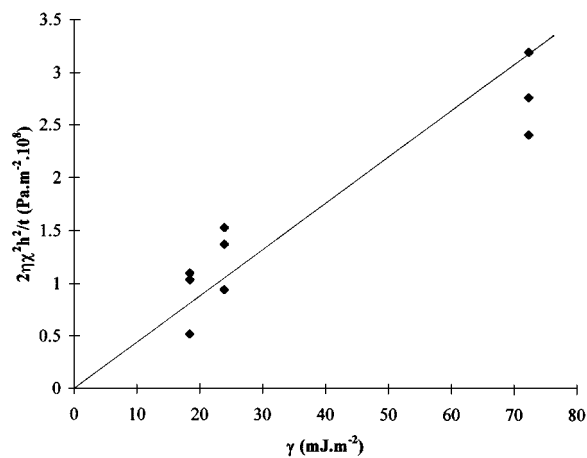*Figure 5* Plot of $h^2$ versus $t$ for decane.

*Figure 6* Plot of $2\eta\chi^2 h^2/t$ versus $\gamma$ of three liquids used for wicking experiments.

This value is in very good agreement with that obtained by the wicking technique. It is important to keep in mind that the tortuosity of the membrane pores is essential to determine correctly the pore size of a porous material. Indeed, when the tortuosity of the pores is not considered ($\chi = 1$) the mean pore radius is underestimated (Equation 2). In our study, a value of 0.05 $\mu$m, that's to say smaller by a factor of 8, is obtained when $\chi$ is taken equals to 1. Determining mean pore size by wicking technique has already been reported in the litterature [8, 9] but the authors doesn't usually take into account the tortuosity of their porous material. For example, Li *et al.* [8] used the wicking technique and MIP for determining mean pore size in ceramic materials. Pore diameters obtained from wicking were found to be smaller than those afforded by MIP by a factor of ~2. To explain this result, the authors pointed out that MIP is based on assumptions relative to pore shape. So, irregular, too small or too large pores are the source of errors in determining mean pore size. Moreover, high-energy liquids, such as mercury, are, by their nature, more susceptible to contamination than are the low-energy liquids employed in wicking experiments. This contamination can reduce the interfacial surface ten-

sion between mercury and the porous material, leading to an overestimate of the mean pore size. Although these arguments are quite valuable, the difference observed by Li *et al.* between the wicking technique and MIP may be partially due to the fact that they considered the tortuosity of the pores equals to 1 in the Washburn equation (Equation 2).

## 4. Conclusion

The technique of wicking combined with electrical resistance measurements as a method for determining mean pore size has been demonstrated for a ceramic microfiltration membrane.

Experiments with different liquids showed the validity of the standard Washburn equation in describing the rate of wetting of the membrane as measured by the linearity of the distance squared versus time plot.

The mean pore size of the ceramic membrane was also determined from mercury intrusion porosimetry.

Comparison of the results obtained from the wicking technique and MIP revealed that the mean pore sizes are in very good agreement. We showed the importance to take into account the tortuosity of the membrane pores to determine correctly the mean pore size of a porous material by the wicking technique.

So, the wicking technique combined with electrical resistance measurements is well suited for routine determination of pore size in other ceramic systems.

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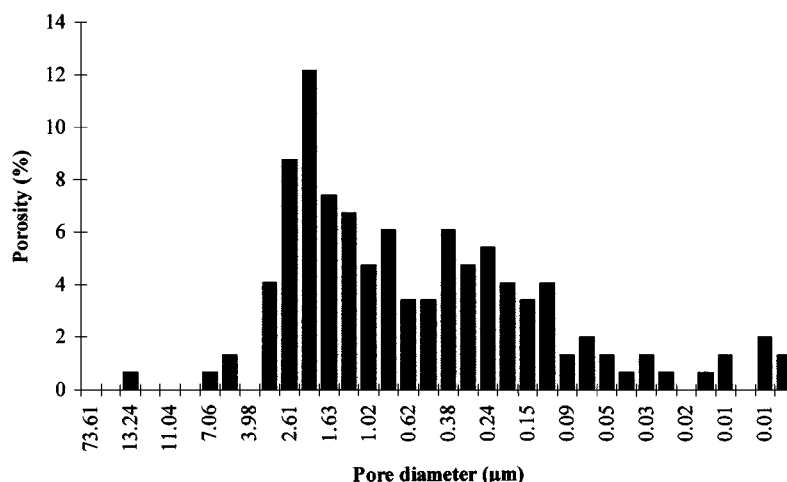
*Figure 7* Pore size distribution of the ceramic membrane.

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