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Separation Science and Technology
Publication details, including instructions for authors and subscription information:
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To cite this Article Kujawski, Wojciech , Adamczak, Piotr and Narebska, Anna(1989) 'A Fully Automated System for the Determination of Pore Size Distribution in Microfiltration and Ultrafiltration Membranes', Separation Science and Technology, 24: 7, 495 — 506
To link to this Article: DOI: 10.1080/01496398908049787
URL: http://dx.doi.org/10.1080/01496398908049787

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SEPARATION SCIENCE AND TECHNOLOGY, 24(7 & 8), pp. 495-506, 1989

A Fully Automated System for the Determination of Pore Size Distribution in Microfiltration and Ultrafiltration Membranes*

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Abstract

An automated system controlled by a Amstrad CPC 6128 microcomputer was designed. The apparatus can be used for a fast characterization of MF and UF membranes by the bubble point method. The theory for a modified bubble-point method is reviewed. The system determines pore size, pore size distribution, and surface porosity for the membranes of pore radii not less than 45 nm. The whole experiment takes 3–5 h to complete. The apparatus was tested on various MF and UF membranes (Nuclepore, Synpor, PVC UF, PAN UF, CA UF).

INTRODUCTION

Pressure-driven separation operations are microfiltration, ultrafiltration, and reverse osmosis. The pressure difference is also a driving force in gas separation and pervaporation techniques (*1–4*).

The type of membrane operation determines which kind of membrane has to be used. In going from microfiltration to pervaporation, the pore diameter, the membrane structure, and the transport mechanism vary (Table 1).

*Presented during the 9th CHISA Congress, Prague, Czechoslovakia, 1987, and during the 4th Summer School in Membrane Science, Chester, England, 1987.

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TABLE 1
Techniques and Membranes for Pressure-Driven Operations

Membrane operation	Type of membrane	Pore radius (nm)	Transport mechanism
Microfiltration	(a) Symmetric, porous	50–10,000	Sieving
Ultrafiltration	(a) Symmetric, microporous	1–100	Sieving
Reverse osmosis	Asymmetric, "skin" type	0.2–2	Solution–diffusion
Gas separation	Homogeneous, nonporous	<0.5	Solution–diffusion
Pervaporation	Homogeneous, nonporous	<0.5	Solution–diffusion

For MF and UF membranes the methods used for the determination of pore size and/or pore structure are based on (*1*, *5–17*):

Electron microscopy
Fluid permeation measurements by use of the Hagen–Poiseuille law and the Knudsen relation
Determination of pore size distribution by means of Hg-intrusion
Bubble-point method
Determination of molecular weight cut-off
Low-angle x-ray scattering

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In this paper we present a fully automated system (bubble-poremeter) designed for the determination of pore sizes and pore size distributions in UF and MF membranes by using a modified bubble-point method.

THEORETICAL

A modified bubble-point method is based on two physical laws (*1*, *8–13*).

(1) Pressure drop appearing over a curved surface according to the Laplace–Young equation:

$$r_{max} = \frac{2\sigma \cos\theta}{\Delta p_{min}} \tag{1}$$

where r_{max} = maximum pore radius opened by pressure Δp_{min}
θ = wetting angle
σ = interfacial surface tension

(2) Hydrodynamic flow in a capillary according to the Hagen–Poiseulle equation:

$$V = \frac{(r_{max})^4 N \pi (\Delta p_{min}) A}{8 \eta \lambda} \tag{2}$$

where V = hydrodynamic flow through a wetted membrane
N_i = number of opened pores
η = viscosity
A = membrane area
λ = membrane thickness (for asymmetric membranes, the thickness of the skin layer)

Equations (1) and (2) were derived by assuming that the pores of membranes are circular capillaries.

A typical effluent gas flow–pressure curve for a wet MF/UF membrane is presented in Fig. 1 (left). At pressures below $\Delta P_{min} = 2\sigma \cos\theta / r_{max}$, the membrane is impermeable. At the pressure ΔP_{min} a flow through the largest pores (r_{max}) begins. At higher pressures (ΔP_{i+1}) the gas flow (V_{i+1}) consists of three components:

$$V_{i+1} = V_i + \Delta V'_{i+1} + \Delta V''_{i+1} \tag{3}$$

where V_i = flow at pressure ΔP_i
$\Delta V'_{i+1}$ = increase of flow according to the Hagen-Poiseulle equation
$\Delta V''_{i+1}$ = increase of flow caused by opening new pores (an active flow)

At the pressure ΔP_{max} the smallest pores are opened. With further increases in pressure the gas flow increases linearly according to the Hagen-Poiseulle law (an active flow, $\Delta V''_{i+1}$ becomes zero). The active flow–pressure curve is presented in Fig. 1 (right).

The following parameters characterizing the porosity of MF/UF membranes can be computed by combining Eqs. (1)–(3):

1. Pore radius:

$$r_m = \frac{2\sigma \cos\theta}{\Delta P_m} \tag{4}$$

where $\Delta P_m = (\Delta P_i + \Delta P_{i+1})/2$.

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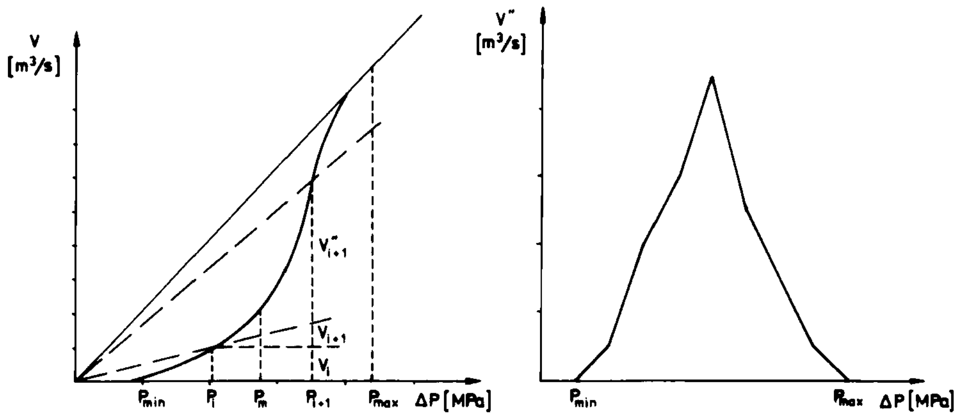

FIG. 1. Left: A typical effluent flow-pressure curve for wet MF/UF membranes. Right: An Active flow vs pressure difference.

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2. Pore density (number of pores per unit area):

$$N_m = \frac{\eta\lambda}{2\pi\sigma^4 \cos^4\theta A} \Delta p_m^3 \Delta V''_{i+1} \tag{5}$$

3. Surface porosity:

$$P_s = \frac{\sum A_m}{A} 100\% \tag{6}$$

where A_m = area occupied by pores of r_m radius.

4. Percentage contribution of pores of radius r_m in an active area of the membrane:

$$U_m = \frac{A_m}{\sum A_j} 100\% \tag{7}$$

The minimum pore radius (r_{min}) calculated by the bubble-point method is a function of pressure, wetting angle, and surface tension (Eq. 1). Values of r_{min} are very often misquoted in the literature (*1, 8, 10*). In Table 2 we present correct values of r_{min} for different wetting-permeating systems. Figure 2 presents the influence on the wetting angle (θ) on r_{min}. Calculations of pore radius were performed according to Eq. (1).

TABLE 2
A Minimum Pore Size Determined by a Bubble-Point Method Using Different Wetting-Permeating Systems

System	ΔP (MPa)	σ (10^{-3} N/m)	θ (degree)	r_{min} (nm)
Water–nitrogen	1.0	72.77 (*18*)	0	145
Ethanol–nitrogen	1.0	22.30 (*18*)	0	45
Isobutanol–water	1.0	1.53[a]	0	4

[a]Surface tension was determined by using the stalagmometric method (*19*).

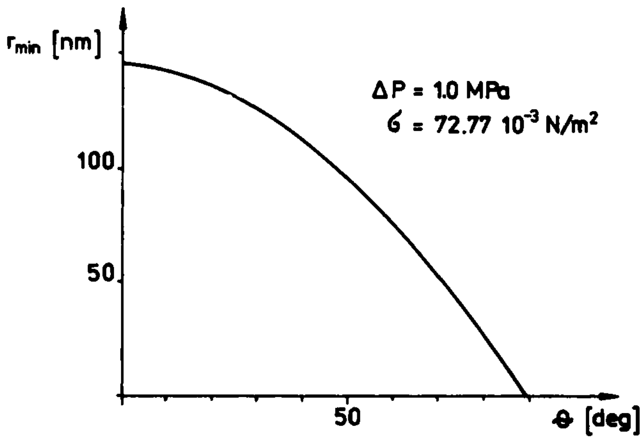

FIG. 2. The dependence of minimum pore radii on the wetting angle for the water–nitrogen system.

HARDWARE

Following the theoretical outline offered by the bubble-point method, a fully automated system (bubble-poremeter) has been designed. It consists of (Fig. 3):

Amstrad CPC 6128 microcomputer
8-Bit parallel interface
Electronic pressure converter
Pressure controller and pressure regulator gauges
Test cell
Gas flow-rate electronic gauge

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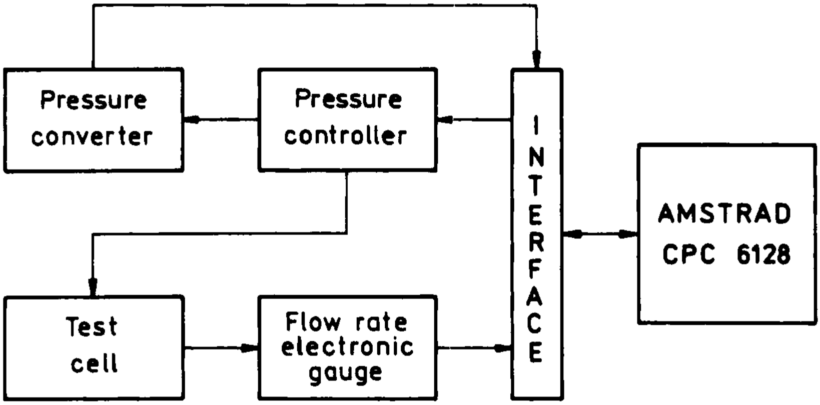

FIG. 3. Schematic diagram of the system.

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Interface, pressure controller, pressure regulator gauges, test cell, and gas flow-rate electronic gauge were designed and produced in the Institute of Chemistry at N. Copernicus University, Torun.

An Amstrad CPC microcomputer is an 8-bit micro with a fast Basic interpreter (BASIC 1.1 Locomotive Software Ltd.). Amstrad controls the system using the controlling, data acquisition, and data processing program.

The 8-bit parallel interface enables information to be transferred between a computer and the system.

The scheme of a test cell is presented in Fig. 4.

In the gas flow-rate gauge the anemometric rule has been applied. The bubble-poremeter can measure a gas flow up to 8×10^{-4} m^3/s (3000 dm^3/h) with an accuracy of ±0.5%.

SOFTWARE

The controlling, data acquisition, and data processing program is written in BASIC. This program needs 17 kB of random access memory of the microcomputer. A flow chart of the program is presented in Fig. 5.

EXPERIMENTAL

Direct measurements of a gas flow across a wetted membrane should be preceded by determination of the wetting angle (θ) and interfacial tension (σ).

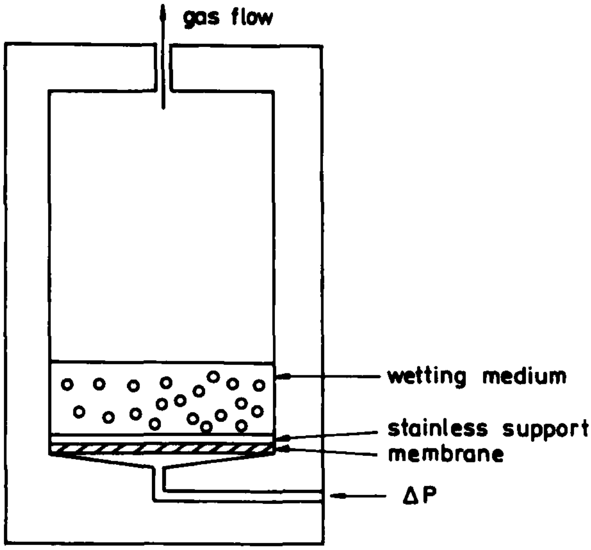

FIG. 4. Scheme of the testing cell.

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Membranes

The bubble-poremeter was tested on the following MF/UF membranes:

Nuclepore N 080 (USA)
Synpor (Czechoslovakia)
PVC UF (made in Technical University, Szczecin, Poland)
PAN UF (made in Silesian Technical University, Gliwice, Poland)
CA UF (made in Technical University, Wroclaw, Poland)

The Determination of a Wetting Angle

The wetting angle between a membrane, imbibed liquid, and penetrating gas was measured by an inverted bubble technique (*20*). The apparatus employed for the measurement is described elsewhere (*21*). The wetting angle has a great influence on the determination of a correct pore size, especially when it exceeds 20° (Fig. 2).

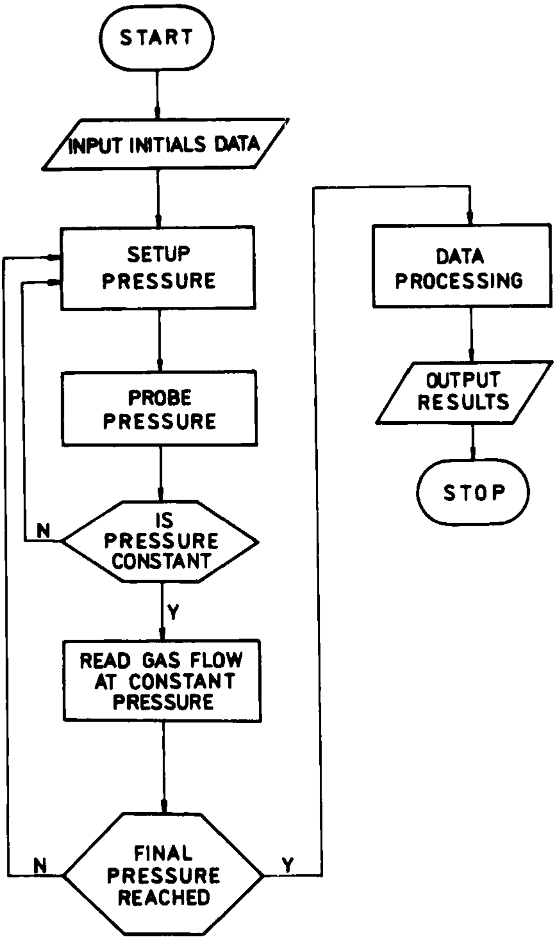

FIG. 5. Flow chart of the program.

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Determination of Pore Size and Pore Size Distribution

The measurement starts by clamping a membrane in a vessel, turning on the valve of the nitrogen pressure bottle, and carrying out the computer program. After 3 to 5 h the results are available. Each point on the experimental curve is the average of 50 separate measurements of pressure and gas flow.

The final display of the results is composed of:

A gas flow versus pressure (V vs ΔP)
An active gas flow versus pressure (ΔV vs ΔP)
Pore size distribution
Average pore size
Surface porosity of a membrane
Percentage contribution of pores in an active surface of the membrane

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RESULTS AND DISCUSSION

The results obtained for a PVC UF membrane are presented in Figs. 6–8 and in Table 3.

The designed system allows for a fast, precise, reproducible, and fully automated determination of the parameters characterizing the surface porosity of MF and UF membranes.

The software determines the correct values of pore radii. The wetting

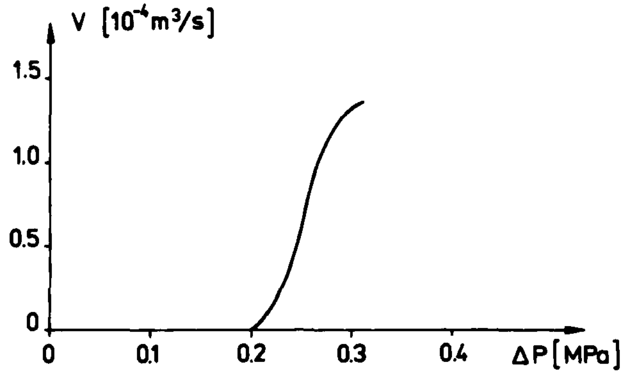

FIG. 6. An experimental effluent flow-pressure curve for the PVC-UF membrane.

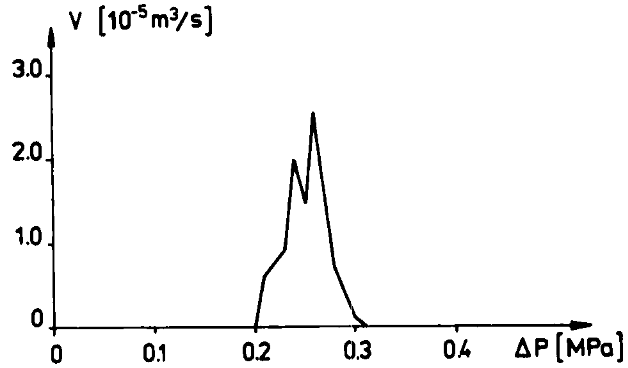

FIG. 7. An active flow vs pressure difference for the PVC-UF membrane.

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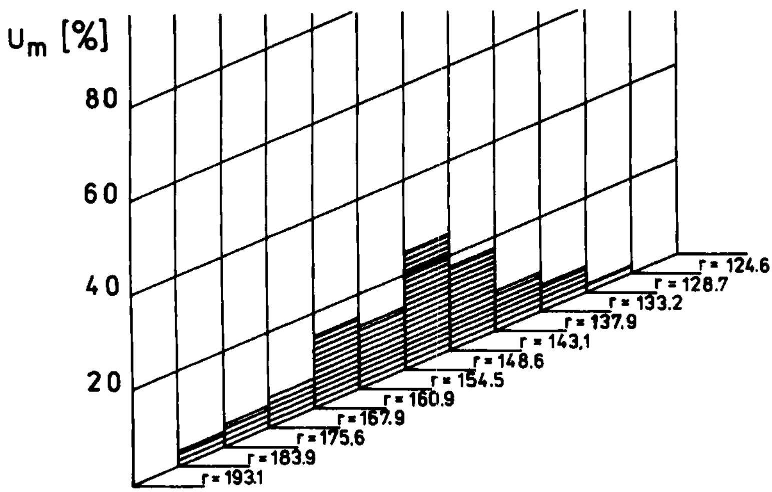

FIG. 8. Percentage contribution of pores in the active surface of an PVC-UF membrane.

TABLE 3
Characteristics of Porosity of PVC-UF Membrane[a]

No.	r (nm)	U_m (%)	N (1/m^2)
1	193.1	0.0	0.00E + 00
2	183.9	3.1	1.76E + 08
3	175.6	4.5	2.57E + 08
4	167.9	6.1	3.50E + 08
5	160.9	15.2	8.68E + 08
6	154.5	12.9	7.36E + 08
7	148.6	24.8	1.41E + 09
8	143.1	17.5	9.98E + 08
9	137.9	8.7	4.94E + 08
10	133.2	5.6	3.20E + 08
11	128.7	1.6	9.37E + 07
12	124.6	0.0	0.00E + 00

[a]P_s (%) = 0.04. Average pore size = 151.6.

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angle should be taken into account in calculation of the parameters of membrane porosity.

The system can be easily adapted to other kinds of measurements.

Acknowledgments

The authors are grateful to Eng. Witold M. Fredrych and Mr. Marek Chachowski (Institute of Chemistry, N. Copernicus University, Torun) for their technical assistance. The work was supported by the project CPBP 02.11 "MEMBRANES."

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Received by editor April 18, 1988

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