Ion track filters: Properties, development and applications

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Ion track filters (ITFs) are produced by physico-chemical treatments to thin films of polymers and mica irradiated by heavy ions. These ion track filters have many applications in the fields of science and technology. In the present article, we report some applications of ITFs, like microhydrodynamical flow studies, conduction of bacteria and blood cells, development of metal and metal–semiconductor microstructures.

DURING the past several years, various new microporous membranes and filters have been developed for use in the fields of science and technology, viz. health, medicine, air pollution, beverage industries, development of microtubules, material science characterization, etc. These filters are generally made from polymeric materials, ceramics and minerals. The technique that led to the development of etched track membranes was first discovered by Price and Walker[1]. They found that the damage trails in insulating materials caused by the ionization as a result of the passage of travelling charged particles can be revealed by the chemical etching to form the cylindrical pores. They observed the fine pores due to fission fragments in 12 μm thick layer of synthetic mica. Since 1972, fission fragments from various radioactive sources have been used for the commercial manufacture of nuclear track filters up to 10 μm track length[2]. Heavy ion accelerators are a promising alternative for generating these filters.

In order to produce ion track filters, thin sheets of plastics are exposed to a collimated beam of particles from an accelerator having different energies. When heavy charged particles pass through these thin foils, they produce continuous damage along their path and thus leave behind a trail of radiation-damaged material. The chemical etching of these irradiated foils leads to the formation of fine hollow channels along the path of the charged particles due to preferential etching along the latent trail. If the thickness of the sheet is less than the particle range in it, the above process leads to the formation of the fine pores in the irradiated sheet. The porosity of these membranes can be controlled by the flux of the ion beam and pore diameter can be controlled by ion characteristics and etching parameters like etching time, etching temperature, etchant concentration, etc. Filters of diameter from 50 Å to a few microns can be produced by this method in minerals and various plastics. Ion track filters are mainly divided into two categories: (a) Single pore filters and (b) Multi-pore filters. Single pore track filters can be produced from the accelerator by controlling the beam optics and fluence of the heavy ion beam.

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Materials

The materials used for the production of single and multi-pore ion track filters and their etching conditions are summarized in Table 1.

Development of ion track filters

Samples of various polymer films and mica have been irradiated by different heavy ion beams from the UNILAC accelerator at GSI, Darmstadt, Germany. Details of ion beams, irradiation and chemical etching parameters are as follows:

Filters in Makrofol-KG

The samples of Makrofol-KG have been irradiated by the ^{132}Xe (14.5 and 5.9 MeV/u), ^{208}Pb (13.6 MeV/u) and ^{238}U (14.0 MeV/u) heavy ions. All the irradiations were made at an angle of 90° with respect to the surface of the detector. The irradiated samples were cut into small pieces and etched in 6.0 N NaOH solution at various temperatures, viz. 40, 50, 60 and 70°C. The etched samples were dried in the folds of a tissue paper. The etched and dried samples were scanned under a Carl Zeiss optical microscope. The bulk etch rate (V_b) of the film is determined by using the thickness measurement technique[3]. The bulk etch rate V_b has an exponential dependence on the temperature of the etching solution as given by the relation[4]

$$V_b = A_b e^{-E_b/kT},$$

Table 1. Some ion track recording films with typical etching conditions used for production of ITFs

Material	Etching condition
Makrofol (N, KG, SKG)	5.0–7.0 N NaOH at 40–70°C
Kapton-H and F $[C_{22}H_{10}O_5N_2]_n$	(a) 1.0 N KOH in 80% ethanol and 20% H_2O (b) Sodium hypochlorite (NaOCl)
Polyvinylidene fluoride ($PVDF, CH_2CF_2$)	(a) 5–10 N NaOH (b) KOH + $KMnO_4$ at 70°C
CR-39 ($C_{12}H_{18}O_7$)	6.25 N NaOH at 70°C
Lexan polycarbonate ($C_{16}H_{14}O_3$)	5.0–7.0 N NaOH at 50–70°C
Muscovite mica	48 vol% HF at 23°C
Cellulose nitrate	2.5–5.0 N NaOH at 40–60°C

Table 2. Activation energies for bulk etching, E_b, for different track recording films

Film	Etchant	E_b (eV)
Makrofol-KG	6.0 N NaOH	0.61
	6.5 N KOH	0.62
SR-86	6.0 N NaOH	0.67
	6.5 N KOH	0.62
Kapton	NaOCl	0.41
Lexan polycarbonate	6.25 N NaOH	0.68
CR-39	6.25 N NaOH	0.74
	6.5 N KOH	0.76

where A_b is the pre-exponential constant, E_b the activation energy for the bulk etching, k the Boltzmann constant and T the temperature of the etchant. The value of activation energy for the bulk etching, E_b, is calculated (Figure 1) by plotting $\ln(V_b)$ vs 1000/T (K^{-1}). The activation energies for SR-86, lexan polycarbonate, CR-39 and Kapton have been determined by a similar way (Table 2). All the films were etched at different temperatures of 40, 50, 60 and 70°C in different recommended solutions. The photomicrograph of the observed ion (^{132}Xe) track pores in Makrofol-KG is shown in Figure 2. The variation of pore diameter (for ^{132}Xe heavy ion) with etching time at different temperatures is shown in Figure 3.

Filters in muscovite mica

The samples of mica irradiated by ^{132}Xe ions (14.5 MeV/u and 5.9 MeV/u) were etched in 48 vol% HF at room temperature (29°C). The etched samples were scanned under the optical microscope. As the irradiation was at an angle of 90° w.r.t. the surface, the etched tracks are rhombic in shape (photomicrograph of the etched pore for ^{132}Xe ion of energy 5.9 MeV/u is shown in Figure 4). The measured etched pore parameters, viz. major axis, minor axis and their mean for both the sides of the sample are given in Table 3.

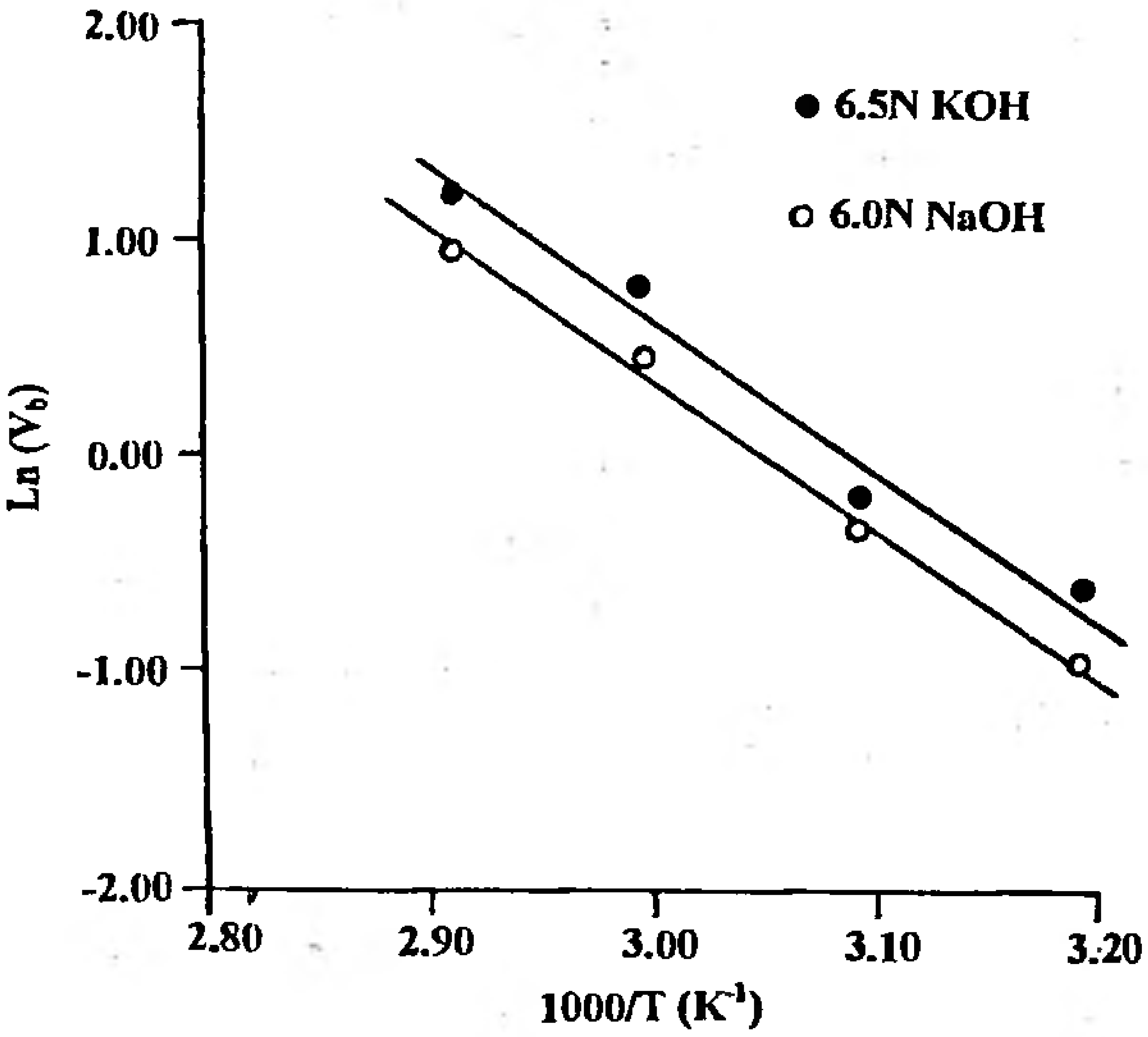

Figure 1. Variation of $\ln(V_b)$ versus 1000/T (K^{-1}) for Makrofol-KG.

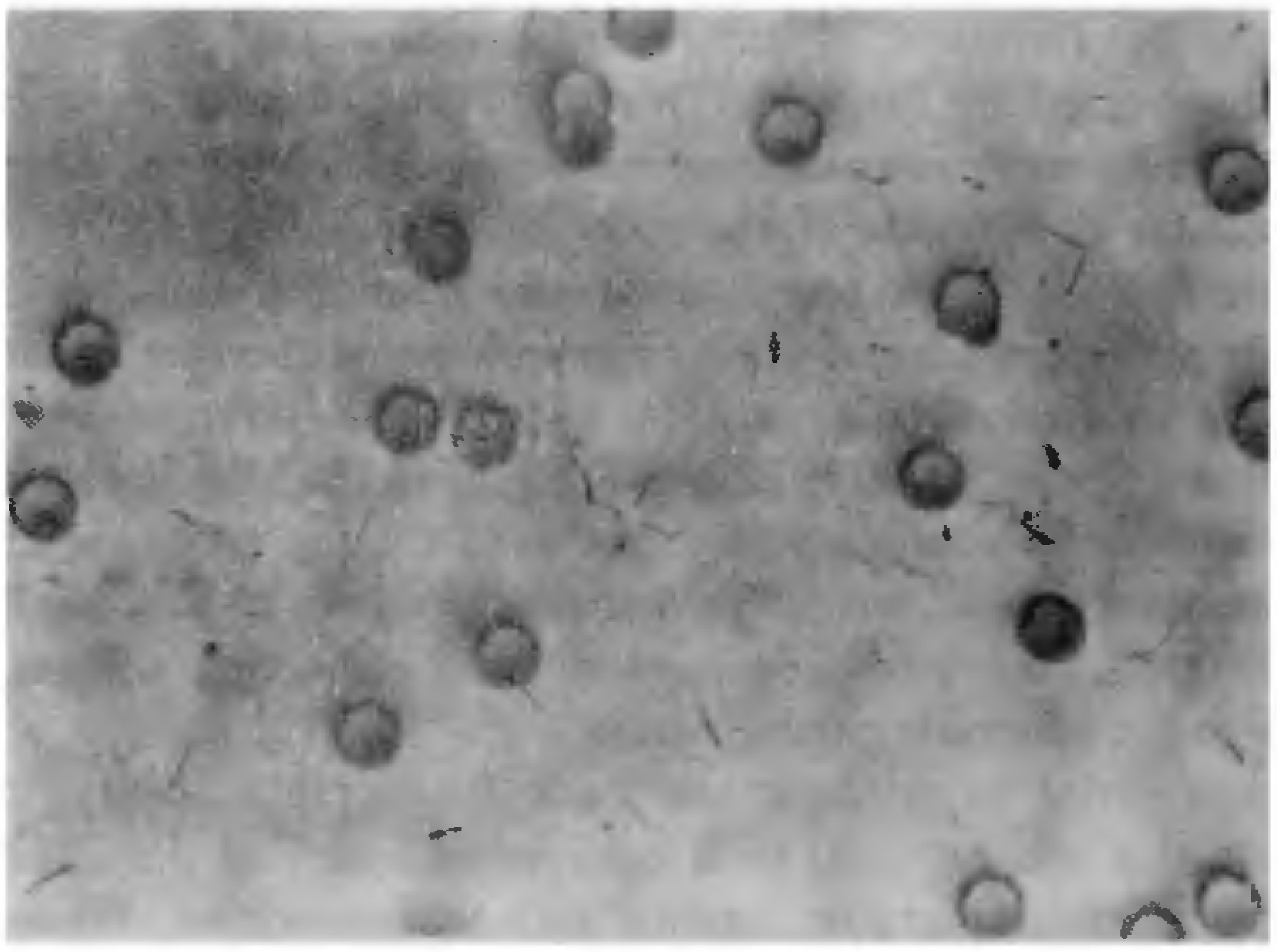

Figure 2. Photomicrograph of ^{132}Xe (14.5 MeV/u) ion track pores (~13.3 μm) in Makrofol-KG.

The samples of Kapton-H were etched in NaOCl at different temperatures. Similarly, the samples of polyvinylidene fluoride (PVDF) irradiated by ^{238}U (11.6 MeV/u) ions were etched in a solution of KOH + $KMnO_4$ at 70°C for about 90 h. The mean value of observed diameter of the etched pores is 10.12 μm.

Applications of ion track filters

Microhydrodynamical flow studies in various liquids using ion track filters

Ion track membranes have been used for various microhydrodynamical studies, like separation of circulating

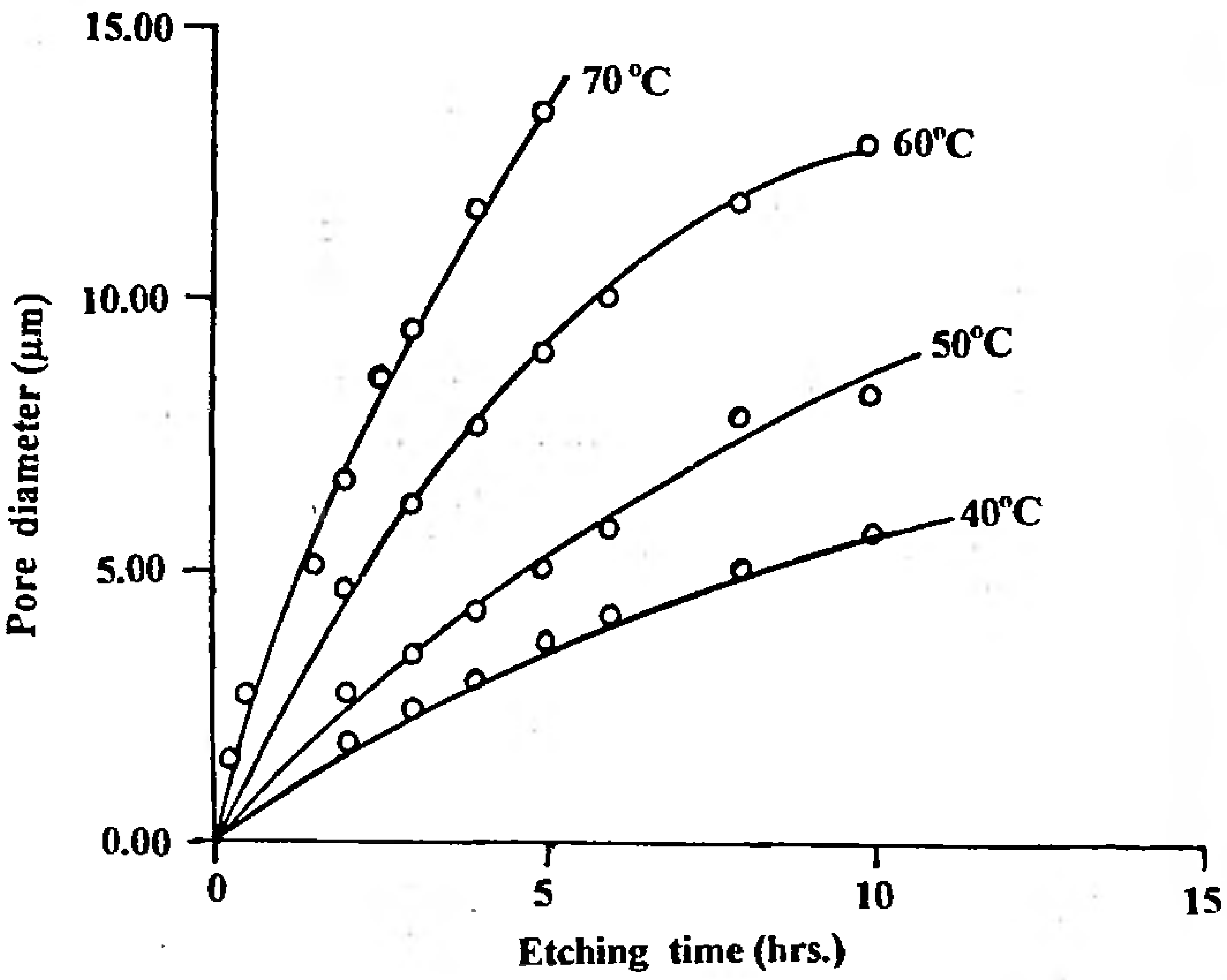

Figure 3. Variation of pore diameter with etching time for ^{132}Xe (14.5 MeV/u) at various temperatures of the etching solution in Makrofol-KG.

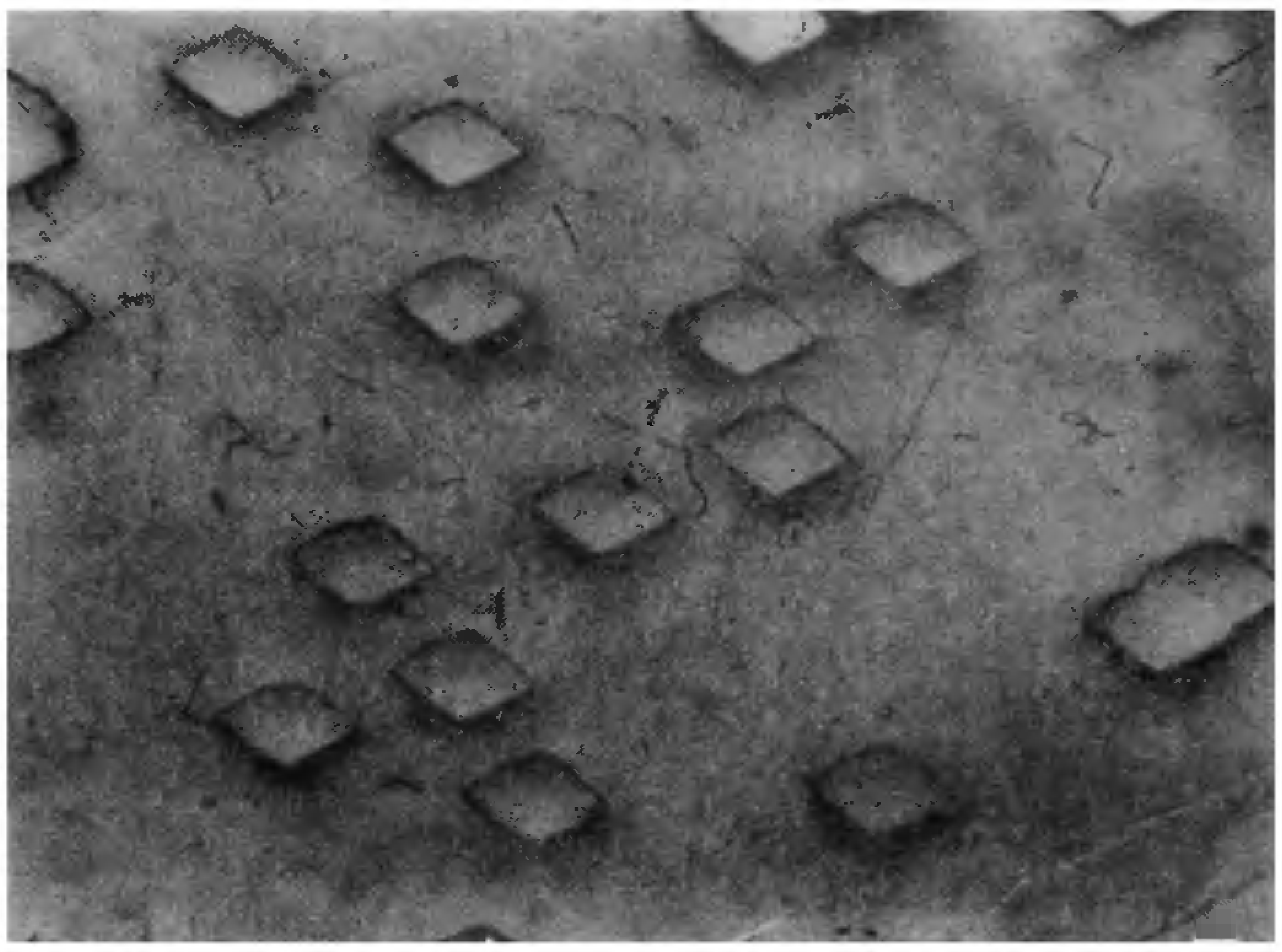

Figure 4. Photomicrograph of ^{132}Xe (5.9 MeV/u) ion track pores (major axis ~26.9 µm and minor axis ~17.71 µm) in muscovite mica.

Table 3. Major-axis, minor-axis and their mean for ^{132}Xe (5.9 MeV/u) ion pores in muscovite mica (etched in 48 vol.% HF at 29°C)

	Side A			Side B		
Etching time (min.)	Track size along the axis (µm) Major	Minor	Mean	Track size along the axis (µm) Major	Minor	Mean
10	3.65	3.43	3.54	3.27	2.68	2.98
20	6.79	4.83	5.81	5.66	4.14	4.90
30	9.10	6.13	7.60	7.93	5.33	6.63
40	11.04	7.47	9.44	10.35	6.44	8.39
50	13.92	8.75	11.36	12.25	8.57	10.41
60	15.53	10.46	12.99	14.20	9.39	11.79
80	20.58	12.60	16.59	18.19	12.92	15.56
100	25.87	14.89	20.39	22.54	15.73	19.13
120	28.84	17.74	23.29	26.69	16.79	21.74
140	32.78	20.31	26.55	30.94	18.53	24.73
160	36.87	22.77	29.82	33.58	18.99	26.29

*Statistical error in experimental data is within ± 7%.

cancer cells from blood[5], characterization of submicron particles in human blood[6,7], filtration of unwanted microparticles from liquid and gaseous media[8,9], purification of aerosol particles in the atmosphere of industrial plants[10,11], etc. Above all, there exist a variety of techniques for understanding the solute–solvent interaction. We have made microhydrodynamical flow studies on various fluids (water, alcohol, acetone) using ion track filters (ITFs) of Makrofol-KG (thickness = 60 µm). The apparatus used for this study is designed and fabricated in such a way that the filter acts as a partition between the upper and lower parts (Figure 5). The variation of rate of flow (dV/dt) with concentration has been studied for two miscible solutions (solute + solvent) at constant pressure. It has been observed that the flow rate decreases with increasing concentration of solutes keeping water as a base in both cases, i.e. propan-2-ol and acetone (Figure 6).

Conduction of bacteria and blood cells through polycarbonate filters

The conduction of bacteria and malignant cells has been studied through the single and multi-pore track filters. The method used here for the growth of bacteria (*E. coli* and *Colon bacillus*) is Luria broth (LB). For the preparation of culture, the requirement is trypton 5 g, yeast extract 10 g, NaCl 10 g and distilled water 500 ml. The grown cells of *E. coli* (ball shaped) and *C. bacillus* (rod shaped) have diameter of the order of 1 µm. The malignant blood cells of size 7–15 µm were collected from Sri Guru Ramdas Hospital and Medical Research

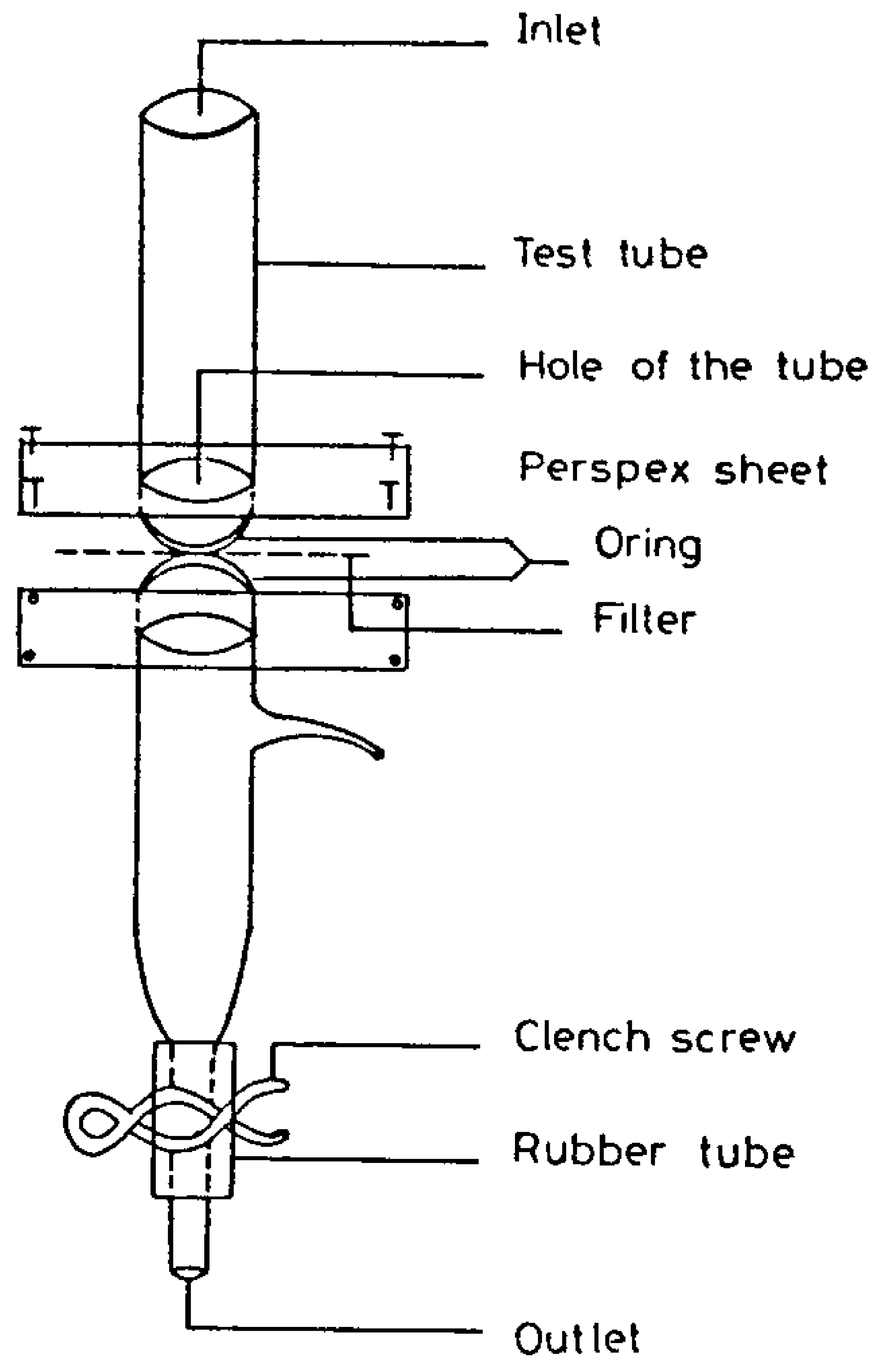

Figure 5. Block diagram of filter apparatus used in microhydrodynamical flow studies.

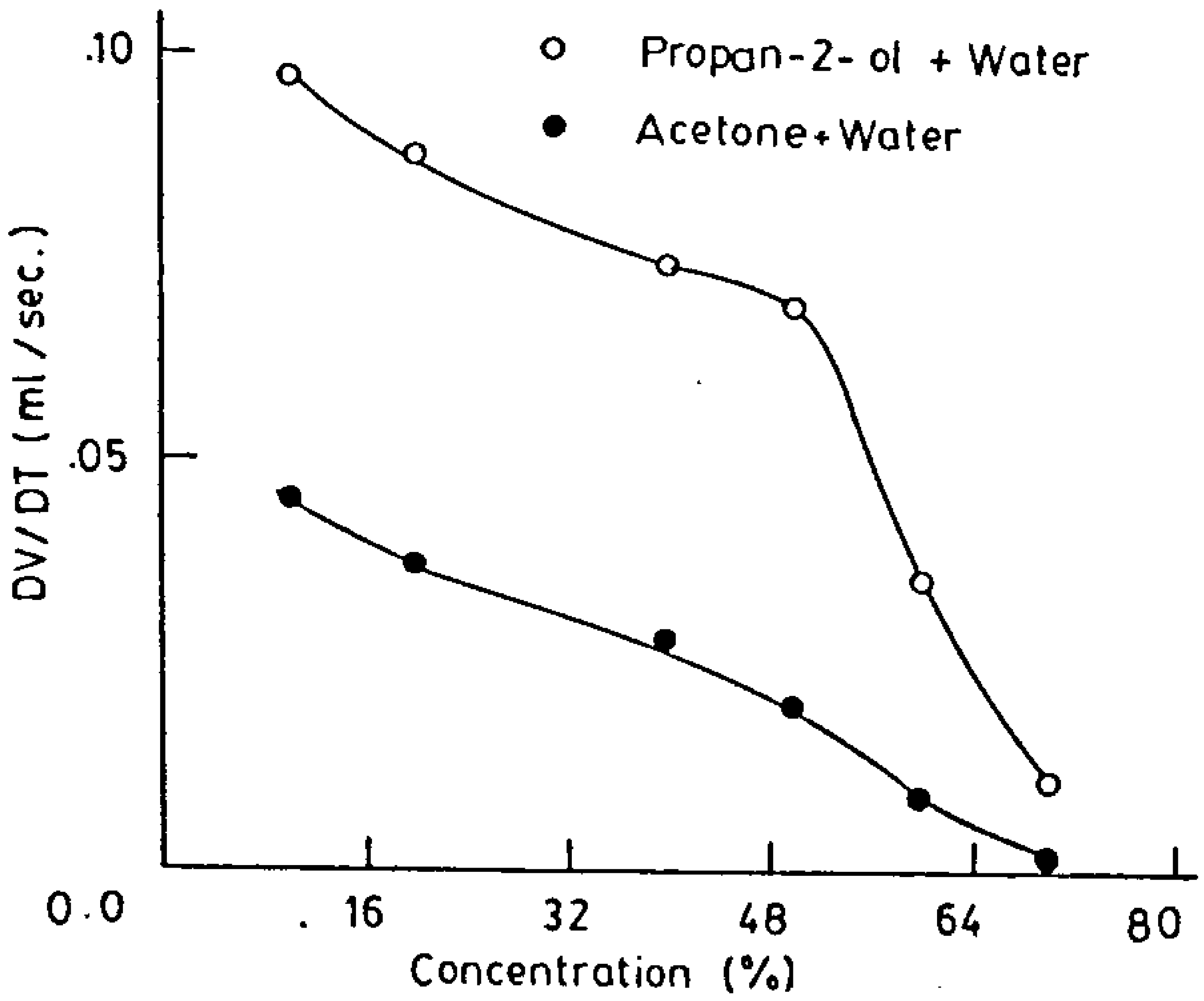

Figure 6. Variation of flow rate, dV/dt with concentration of solutes in water at a constant pressure difference.

Institute, Amritsar. The conduction effect through the polycarbonate pores (sieves) has been observed by using the conductivity cell[12] (Figure 7). A membrane partition between the two chambers served as a barrier to bacteria and cell migration and the change in current shows the resistance to the flow of the contaminants through the

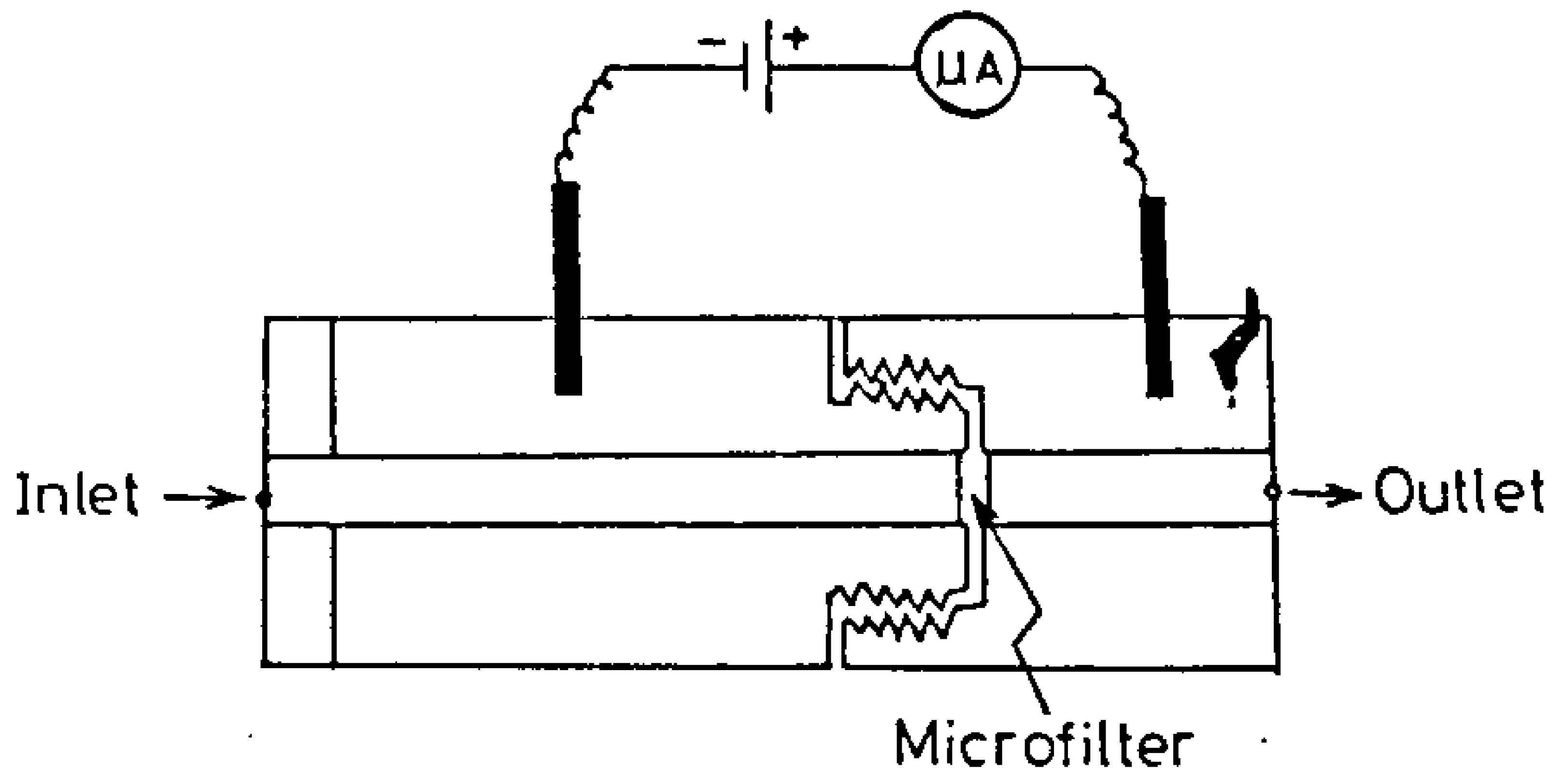

Figure 7. Block diagram of conductivity cell.

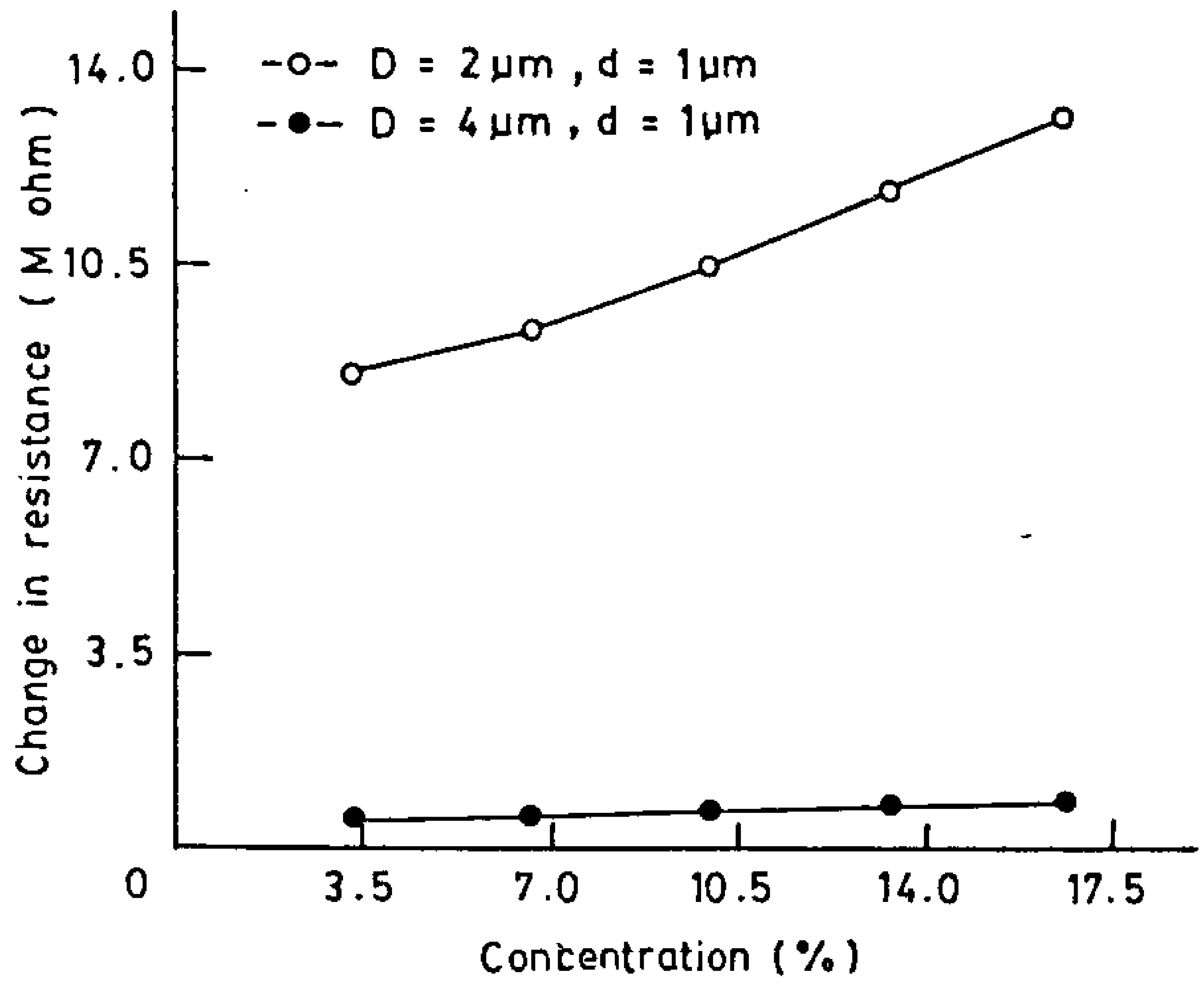

Figure 8. Variation of change in resistance with concentration using single pore filter for *E. coli* and *C. bacillus* in water.

pores. The resistance through the pores of different diameters is measured using Ohm's law and the change in resistance[2], ΔR, w.r.t. pore diameter is obtained by using the relation $\Delta R = 4\rho d^3/\pi D^4$ and the corresponding resistivity of the solution is found by $\rho = RA/l$, where R is the resistance, A the area of cylindrical shaped conductivity cell and l the length of the hole inside the cell. It had been observed that the resistance between the two electrodes depends primarily on the conducting path through the pore. As a particle enters, the resistance increases by an amount proportional to the volume of the particle. It is observed that conduction is reduced progressively with increasing concentration of pollutants if the negative polarity is given to the polluted water and positive polarity to the clean water. Taking different concentrations of the contaminated water and human blood, the conduction through the pores of different diameters has been studied. The diameters of microfilters used here are: multi-pore (2 and 4 μm) and single pore (5, 7 and 10 μm). The resistance through the pore is highly

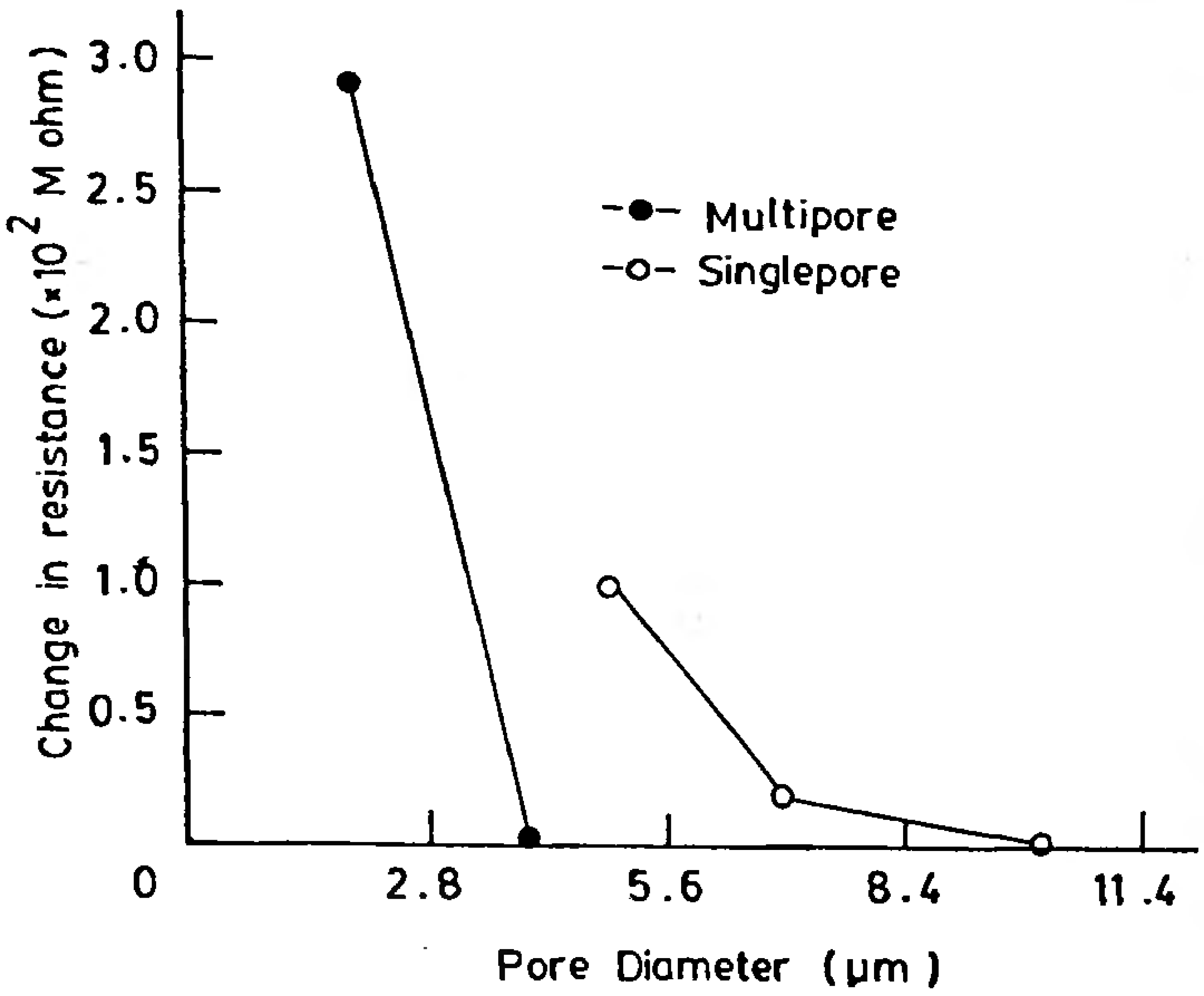

Figure 9. Variation of change in resistance with pore diameter for *E. coli* and *C. bacillus* in water.

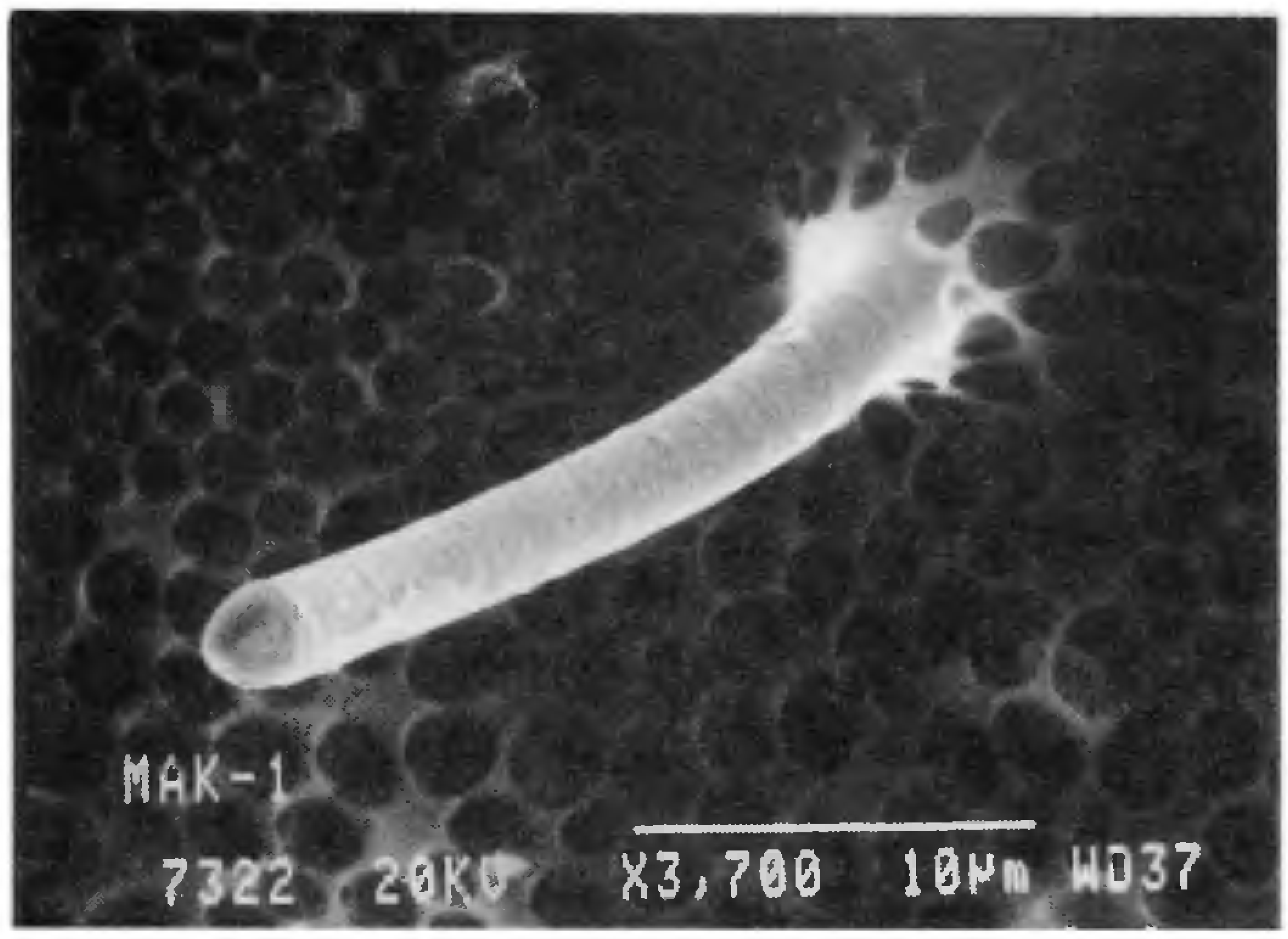

Figure 10. Microstructure (scanned by SEM) ensembles of Cu grown electrochemically through single-pore of Makrofol-KG.

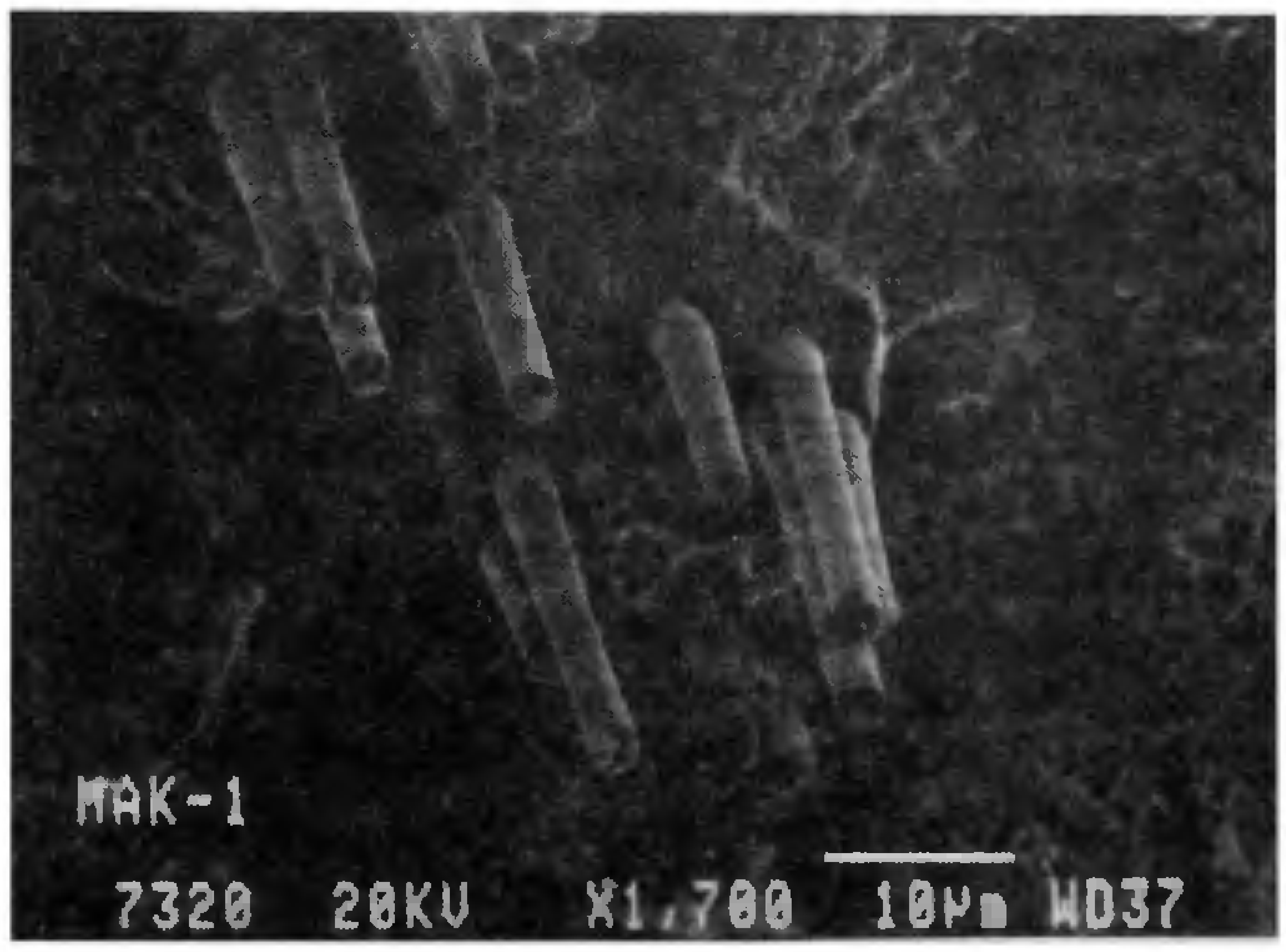

Figure 11. Microstructure (scanned by SEM) ensembles of Cu grown electrochemically through multipore filters of Makrofol-KG.

sensitive to geometry and is proportional to d^3/D^4, where d is the diameter of the particle and D is the diameter of the pore. The variation of change in resistance with concentration and pore diameter for single pore filter is shown in Figures 8 and 9, respectively. A similar variation is observed in the case of multipore filters.

It is observed that the conduction is reduced progressively with increasing concentration of bacteria and blood cells. The change in resistance encountered by the bacteria and blood cells through a 10 μm pore is found to be lower than that through a 5 μm pore in case of a single pore filter, and in case of multipore filters, 4 μm pore is found to conduct better than a 2 μm pore. But since the blood cells have the property of deforming their shape while traversing through the pores, the conduction in case of blood sample is better than in case of *E. coli* and *C. bacillus* in water.

Development of metal and metal–semiconductor microstructures through ion track filters

Fabrication of microstructures is being considered a potential technology not only for use in micromechanics and microelectronics but also in the studies pertaining to behaviour of materials at micro and nano levels. Microstructures comprising microdimensional devices, dots, fibrils, wires, cones, tubules and whiskers have invited attention for use in multidisciplinary areas[13]. There are different techniques for the development of microstructures[14] but template growth through the etched pores considered to be very simple and microstructures with extraordinary low dimensions have been reported by Wu and Bein[15]. The methodology of the development of microstructures is based upon the earlier work of Possin[16] and Penner and Martin[17] producing thin metal wires, etc. This simple and well known underlying concept of electrodeposition of metals is described as an electrochemical process in which metallic ions in supporting solution are reduced to the metallic state at the cathode if it is covered by an ion track membrane, and thus would lead to the formation of growth of plated film as embodiment of micro and nano-structures. After chemical dissolution or peeling off the polymer film from the metal substrate, the free metallic whiskers are obtained.

In the present work, we describe the simple method of electrodeposition of copper into the etched pores of polymeric ITFs by using an electrochemical cell[18]. The

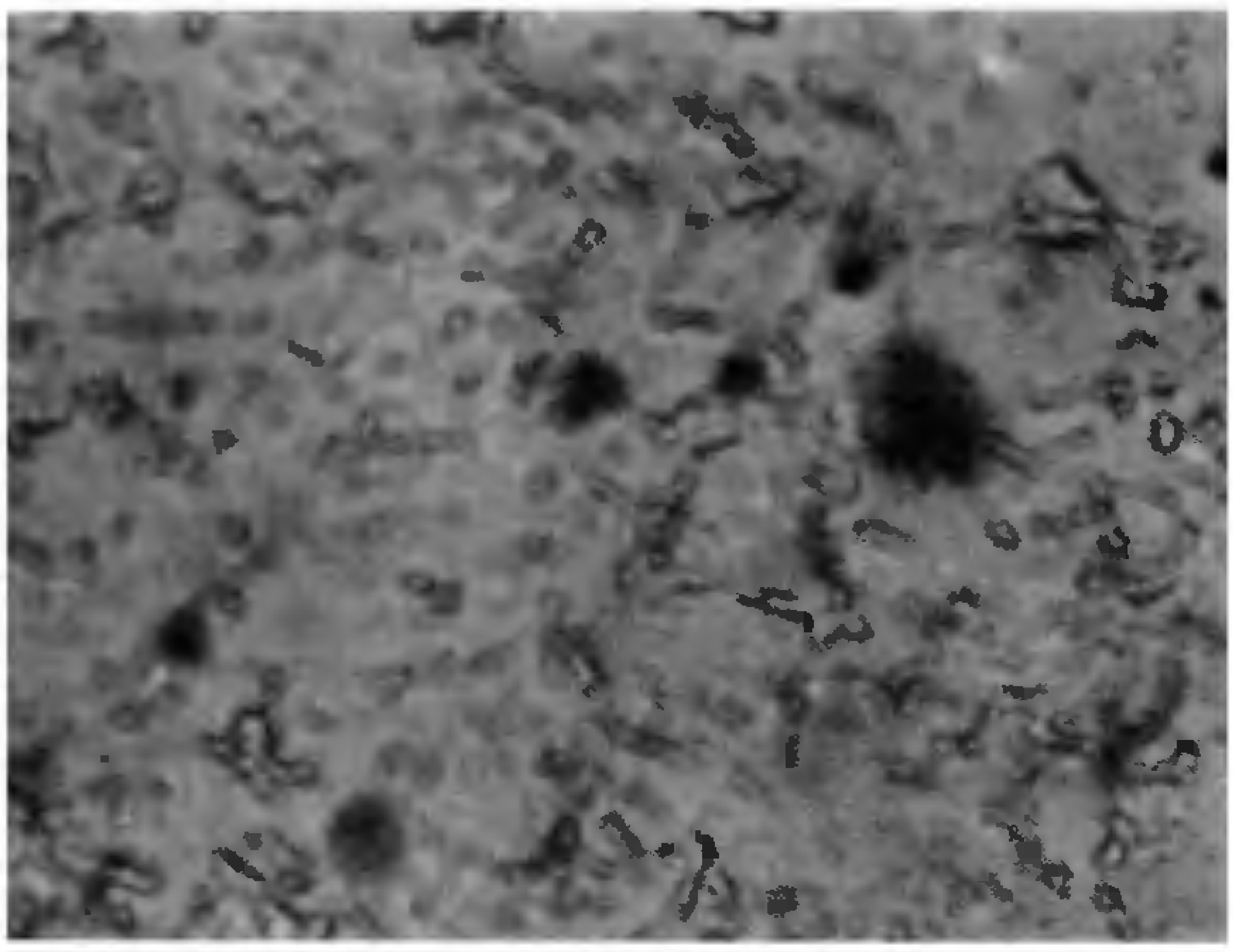

Figure 12. Photomicrograph of filtered *E. coli* and *C. bacillus* bacteria separated by a Makrofol-KG microfilter.

electrolyte used here is $CuSO_4 \cdot 5H_2O$ acidic solution in high resistivity ion-free water + 25% vol. H_2SO_4. A current of 0.05 A/cm^2 was applied for 20 min. After the electrodeposition was over, the electrolyte was drained out and the copper electrode was detached from the copper substrate. After drying, the Makrofol-KG thin film was removed from the microstructure substrate by dissolving in chloroform ($CHCl_3$) followed by rinsing with water and ethanol. The developed microstructures were coated with gold by the sputtering method and then scanned under scanning electron microscope (SEM) (Jeol, JSM-6100) for morphological and structural studies. The microstructures of copper (Cu) grown through the single and multipore ITFs of Makrofol-KG are shown in Figures 10 and 11 respectively. The metallic needles developed by this technique have various possible applications, e.g. field ion emitters, as a stylus in STM, cantilever of AFM, etc.

Filtration applications

Filtration is the process of removing physically-suspended matter from a given volume of liquid or gas by forcing the material through a porous, mechanical barrier or a filter. This facilitates the extraction and analysis of the material separated from the fluid or gas. The filtration efficiency is defined as the ability of the media to distinguish between particles of different specific sizes. Ion track filters have advantages over the other conventional filters due to their well-defined pore size which makes it possible to remove all particles bigger than its pore size. In this investigation, the contaminated water was filtered using a filter apparatus fabricated in our laboratory (Figure 5). The photomicrograph (Figure 12) shows the filtered *E. coli* and *C. bacillus* by ITF. The removal efficiency depends upon the pore size of the microfilter and also on the diameter of the pollutant.

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