REDUCED FOULING OF ULTRAFILTRATION MEMBRANES
VIA SURFACE FLUORINATION

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ABSTRACT

Surface fluorination can affect significantly the performance of an ultrafiltration membrane used to concentrate a food-related stream. Membranes which have been fluorinated under appropriate conditions and tested as flat sheets exhibit higher initial fluxes, and do not foul as rapidly as untreated membranes. We link this improvement to increased hydrophilicity of the surface, as shown by the decrease we observe in contact angle with water. This increased hydrophilicity, in turn, we link to the addition of fluorine and oxygen to the surface.

Our pilot plant study did not show the clear difference in membrane flux and fouling that we observed in the flat sheet study. Instead, fluorinated and unfluorinated modules behaved in a substantially similar manner. Fouling by the potato waste feed was severe, and resulted in the formation of an extensive gel layer within the module on the surface of the membrane. XPS, SEM and FTIR studies combine to indicate that some build up of organic material occurred on both the fluorinated and unfluorinated membranes, but SEM indicates that a fibrous mat of material was observed only on the non-fluorinated membrane. We conclude that in the pilot study, membrane fouling and gel formation were so extensive that the surface interaction effect on which our approach is based was overwhelmed.

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1.0 INTRODUCTION

Fouling of ultrafiltration membranes is a critical problem in the food processing industry[1-5]. Membrane fouling decreases flux and shortens membrane lifetimes, making them less economical to food processors for concentrating process streams. Membranes foul with organic material (e.g. lipids during soy processing[6] and proteins from processing cheese whey[7]) and this results in a significant decline in flux. The fouling of the membranes may also be irreversible even with extensive cleaning, and as a result membrane lifetime is also decreased.

If fouling could be minimized, membrane separation would be a more economical and energy saving method for concentrating aqueous streams[1,2]. Presently, the food processing industry consumes 2% of the total national energy usage[1]. Most of the processes which consume this energy are thermally driven separations and concentrations where the process streams contain dilute solutions of organic matter. These process streams consist of recyclable organic material such as starch and protein. Present thermal concentration methods inherently use large amounts of energy to concentrate these process streams, due to the latent heat of vaporization of water.

Fouling of the membrane can be changed either by varying the hydrodynamics over the membrane or by varying the physico-chemical interaction between the foulant and the membrane[8-11]. By varying hydrodynamics (i.e. increasing the crossflow velocity), foulant can be swept away from the membrane before adsorption can occur. This is illustrated in Figure 1. Alternatively, the adsorption of foulant may be reduced by decreasing the physico-chemical interaction between foulant and membrane thus allowing the foulant to diffuse away and be swept from the surface.

Various pretreatments of the membrane surface have been used to modify the interactions between the foulant and membrane. These treatments were intended to produce membranes with more hydrophilic surfaces that would interact less strongly with proteins. Membranes have been modified via plasma treatment to make the surface more hydrophilic by introducing more hydroxyl groups to the surface[12] or by polymerizing monomeric substrates to the surface of the membranes to produce a thin

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layer of hydrophilic polymer on top of the hydrophobic membrane[13]. The latter approach reduced the permeate flux through the membrane, perhaps by decreasing the effective pore size of the membrane. This might have occurred because of coating of the inside surface of some pores with the hydrophilic polymer or occlusion of the smallest pores by the polymer.

In another approach, Speaker et al[14] used a fluorinated amphiphilic surfactant to coat the surface of membrane. This treatment increased the hydrophilicity of the surface and reduced fouling at the surface, but the surfactant treatment also severely reduced permeate flux through the membrane. In one study, a surfactant treated membrane had substantial fouling reduction, but the permeate flux decreased to nearly zero. In another study[15], this flux decline was avoided by using a nonionic surfactant. All surfactant-based approaches, however, suffer the disadvantage that the surfactant is consumed, and must be replenished periodically.

Fluorination has been used to modify polymer surfaces[16-22]. The goal of these studies was to change the permeation rates of gases through the polymer by changing the solubility of the gases inside a thin layer at the polymer surface. This change in solubility was reported to have had a direct influence on the permeability of gases through the membrane. Fluorination has also been used to improve the wettability of fibers[22]. The authors attributed the increase in wettability to partial fluorination of the membrane surface.

Our study reports on an investigation of the effect of surface fluorination on the fouling characteristics of membranes prepared from non-fluorinated polymers. Fluorination of the membrane chemically modifies the physico-chemical interaction between solution species and the membrane, and this modification can result in a decrease in fouling characteristics of the membranes. At the same time, fluorination should also help improve the lifetime of the membrane by providing an easier surface to clean during the cleaning cycle.

Spiral wound modules can be prepared more easily by the use of surface fluorination on a non-fluorinated membrane than by the use of fluorinated polymers directly. Casting membranes using perfluorinated polymers is a difficult process[23].

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Further processing of fluorinated membrane into industrial type configurations is also difficult due to the non-wetting nature of the fluorinated polymer. Surface treatments are often necessary to allow adhesives to bond with these polymers in the construction of spiral modules[24]. The fluorination process in this study affects only the surface of the membrane without changing the bulk properties of the underlying polymer. Surface fluorination can be used to treat controlled areas, such that further processing is easily accomplished. The surface-fluorinated membranes investigated in this study can be incorporated easily into currently available membrane modules if fluorination is introduced as a pre-treatment to the membranes before the construction of modules.

Ultrafiltration of potato-processing waste is a process where fouling has been noted. A schematic of the typical overall potato process is shown in Figure 2. The potato processing industry produces 25 billion gallons of potato waste annually, and this aqueous waste stream contains about 0.6 % solids, mainly starch, protein and ash[1]. A significant amount of energy would be needed to concentrate this dilute stream by thermal concentration. Presently, the waste is treated at a secondary waste water treatment center or sprayed onto farm fields. With increased environmental concerns about biological oxygen demand (BOD) of waste products, waste streams must be pretreated before effluent can be released to any secondary waste water treatment. Membrane concentration appears to be an energy-efficient way of concentrating the potato waste streams.

2.0 EXPERIMENTAL

2.1 Membrane Preparation

Various membranes were fluorinated at the onset of this study. The membranes fluorinated were polyethylene, polysulfone and cellulose acetate. The polyethylene membranes were DuPont Tyvek T-988 membranes and the polysulfone and cellulose acetate membranes were manufactured by Allied-Signal Fluid Systems (San Diego). The polyethylene membrane was received and stored dry. The polysulfone and cellulose acetate membranes were received and stored wet. The pore sizes of the membranes varied significantly. The polyethylene membrane had a pore size distribution that

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could exclude 99.6% of 0.624 micron latex spheres. The molecular weight cutoff of the untreated polysulfone membrane was typically 100,000 daltons while the molecular weight cutoff of the cellulose acetate membrane was typically 50 daltons. This study will primarily focus on the effects of fouling on polysulfone ultrafiltration membranes, but the effects of surface fluorination on the other membranes surface properties will be noted.

The various membranes to be fluorinated were cut to size from larger sheets of stock membrane. Since membranes must be dried to undergo the fluorination process, the polysulfone and cellulose acetate membranes were first pretreated with an aqueous methanol solution and subsequently dried. The methanol pretreatment aided in recovering permeate flux in the dried polysulfone membranes as will be discussed in Section 3.1.

Membranes were fluorinated at a facility in Allied-Signal's Morristown Laboratories by the Exploratory Research Group. The process for all three membranes used elemental fluorine mixed with nitrogen. Oxygen was excluded from the reaction mixture. A schematic of the fluorination reactor is given in Figure 3. The dry membranes were placed inside the reactor and treated at various residence times from 0 to 120 minutes and concentrations from 0.0125 to 0.05 % fluorine in nitrogen. The flow rate of reaction mixture in the reactor was 4 liter/minute at ambient pressure. The high flow rate of gas guaranteed that the concentration of fluorine in the atmosphere over the membrane was constant. After fluorination, the treated membrane was quickly exposed to air. One large sheet of membrane was treated at each set of fluorination conditions and the treated sheets were used for both the performance experiments and further surface analysis.

2.2 Membrane Permeation System

2.2.1 Single Flat Sheet Module

Potato-waste filtration was carried out at room temperature in a standard closed-loop filtration system of three or six cells mounted in series, each with an effective cross-sectional area of 3 in². A schematic of a related system containing

one membrane module is shown in Figure 4. Filtrate and permeate were recycled to insure that feed composition remained constant. The feed tank contained 3 liters of potato feed. To reduce concentration polarization and minimize gel-layer formation (14), the unit was run in a cross-flow configuration with Reynolds number greater than 1600 for turbulent flow. The applied trans-membrane pressure was 100 psi.

2.2.2 Spiral Modules

Spiral modules were constructed by Fluid Systems from large sheets of membrane prepared as described above. The fluorinated membrane used in the pilot studies was fluorinated with 0.025 F_2 in N_2 for 30 minutes. Fluorinated and untreated membrane sheets were built into spiral modules with an average effective surface area of 87 in^2. The thickness of the feed and permeate spacers were 0.031 and 0.018 inches, respectively. A schematic of a typical spiral module is shown in Figure 5. The spiral modules tested in the pilot plant were run in parallel, as shown in the schematic in Figure 6. A photograph of the completed bench-scale spiral module pilot plant is shown in Figure 7. The spiral modules were placed inside the stainless steel housings, and the filtrate and permeate were recycled to ensure that the feed composition was not concentrated due to permeation. The feed tank for the pilot study contained 18.9 liters (5 gallons) of feed. The flow rate through each spiral was one liter/minute during the first pilot study and three liters/minute during the second. The trans-membrane pressure drop in the spiral module was 20 psi and the trans-spiral pressure drop was 2 psi at 1 liter/minute, and 6 psi at 3 liter/minute. The pilot plant was run on a twenty-four hour cycle for five days a week. During such a run, the pilot plant was on-line approximately 21 hours and then cleaned for 3 hours. The cleaning procedure will be discussed in Section 3.3. On weekends, the pilot plant was cleaned and subsequently filled with DI water for storage over the weekend.

2.3 Potato Waste Stream Feed

2.3.1 Simulated Feed Stream

The simulated potato waste stream was prepared by blending 432 grams of washed unpeeled potatoes with 1 liter of DI water in a Waring blender at high speed for three minutes. The blend was then heated to 60 °C and held at that temperature for 5 minutes. This step was intended to solubilize a portion of the potato starch. Subsequently, the mixture was strained through cheese cloth and the resulting filtrate was stored in the refrigerator until used. The total solids of this master batch was 0.95 %. The feed used in the filtration unit was prepared by dilution of this master batch to a value of 0.6 % total solids.

2.3.2 Process Potato Feed

Basic American Foods (Blackfoot, ID) kindly provided an industrial potato waste stream from water-gun slicing of potatoes. The total solids of the waste stream was 1.1 wt. %. The potato waste was kept in cold storage until the feed was to be tested. Even with cold storage, the potato waste in the flat cell study degraded, resulting in a drop of pH from 6.7 to 3.9 between shipment and end use. Before an experimental run, the waste water was treated with 200 ppm sodium benzoate as a preservative to prevent further degradation. For the pilot study, fresh feed (25 gallons) was shipped by overnight air on the Friday preceding each week's run. The potato feed during the first pilot study was prefiltered with a 50 μm filter the morning of the run to prevent end plugging of the spiral module, while the potato feed during the second pilot study was prefiltered with a 25 μm filter.

2.4 Analytical Procedures

2.4.1 COD measurements

Chemical oxygen demand (COD) measurements were made using a colorimetric method, following digestion with potassium dichromate[25]. The COD measurement is an indirect analysis of the amount of organic carbon present in the retentate and

permeate. The analysis was done with a commercially available HACH COD digestion reactor with the appropriate reagents for a particular COD range. COD results were read directly from a HACH DR 100 Colorimeter.

2.4.2 Total Organic Nitrogen

The total organic nitrogen of the permeate and feed streams were measured using a chemiluminescence technique (ASTM method D 4629-86). Total organic nitrogen is a direct measure of total protein in this study.

2.4.3 Turbidity

Turbidity of the permeate samples was measured with a DRT-15C Portable Turbidimeter from H F Scientific Inc. The turbidimeter measures the nephelometric turbidity via scattered light from suspended solids present in the permeate. Measurements are reported in standardized NTU units The feed samples needed to be diluted to lower the turbidity into the measurement range of the turbidimeter.

2.4.4 Contact Angle Measurements

Contact angle measurements were taken with a Ramé-Hart Inc. (New Jersey) comparator microscope (NRL C.A. Goniometer 100-00) fitted with a goniometer scale for measuring the angle directly from a drop of water on the membrane. The contact angle measured is illustrated in Figure 8. The contact angle measurements were made on 1" by 1" representative samples of membrane using de-ionized water as the boundary liquid. The reported values are the average of at least three independent measurements on the membrane where the contact angle measurement was taken on both sides of the water drop. The measurements were taken within 2 minutes of placing the drop on the membrane surface. The contact angle provides a measure of the hydrophilicity of the membrane[26].

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2.4.5 X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) was used to analyze the surface composition of the membranes. XPS data were recorded with an HP 5950 ESCA system. Small rectangular samples were covered with a gold plated mask, containing a window 3 mm by 7 mm. Samples were introduced into the vacuum chamber and set to an angle of 38 degrees relative to the x-ray beam. This corresponds to an analysis depth of ca. 50 Å. The samples were flooded with electrons produced by a hot filament to minimize charge buildup. A survey scan of 0-1000 eV was taken to identify all the elements present on the membrane surface. Peak fitting routines were used to obtain accurate area and binding energy information for all the peaks located in the high resolution windows. Adventitious carbon is seen on the samples exposed to air and has a binding energy equal to that of graphite or hydrocarbons. The binding energies reported have offset corrections to force adventitious carbon to 284.6 eV. The atomic percentages reported were corrected for the sensitivity of the instrument to the transition of each element. The atomic percentages will be presented as ratios with respect to the total number of carbon atoms. This procedure allows us to directly compare the atomic ratios found for the various treated membranes. This assumes that the number of carbons remains constant in the 50 Å layer that is being analyzed. Since no carbon is added to the surface and fluorination occurs under mild conditions, this assumption is presumed to be valid.

2.4.6 ATR - Fourier-Transform Infrared Spectroscopy

Attenuated Total Reflectance - Fourier-Transform Infrared Spectroscopy (ATR-FTIR) was utilized to analyze the functional groups present on the surface of the starting and fouled membranes. The fouled membrane samples from the pilot study were washed for one hour in DI-water in a mechanical shaker before analysis. The DI-water was changed and the membrane was shaken for an additional hour. The samples were subsequently air dried in a hood. A 30° germanium crystal was utilized with an effective penetration depth of 3.0 to 0.3 μm over the infrared wavelengths of 2.5 to 25 μm. The spectra were measured on a Perkin-Elmer 16PC FTIR configured with the ATR specimen rig. Each specimen was scanned from 400 to 4000 cm^{-1} at 2 cm^{-1} resolution for 64 scans. The spectra were normalized and were reported in

absorbance mode.

2.4.7 Scanning Electron Microscopy

The surface appearance of the membranes was analyzed via scanning electron microscopy (SEM). The fouled membrane samples for the SEM were washed as in Section 2.4.6. Additionally, the membranes were prepared by critical point drying, which is believed to conserve the integrity of the pores. The process consists of solvent exchanging the water in the pores sequentially with ethanol, amyl acetate and finally liquid carbon dioxide under high pressure. The carbon dioxide is flashed off leaving the pore structure intact.

2.4.8 Gel Permeation Chromatography

Gel permeation chromatography (GPC) was performed on feed and permeate samples to estimate the initial pore size distribution and the effect of fluorination on the pore size distribution of the treated membrane[27,28]. Two feed mixtures of a high and low molecular weight distribution of dextran were fed to the membranes in the flat cell rig and the permeate was collected at 100 psi trans-membrane pressure. The feed and permeate were analyzed with a Waters 150C chromatograph equipped with a refractive index detector. The column was a combination of two Shodex Ion-Pak S803 columns and one S804 column. The mobile phase was 0.1M sodium nitrate and the flow rate was 0.94 ml/min. The column and injector temperature were set at 80 °C. The column was calibrated with dextran standards. The sample concentrations were 0.2 wt%.

3.0 RESULTS AND DISCUSSION

3.1 Surface Fluorination

All of the membranes which were modified in this study were fluorinated at Allied Signal's Exploratory Research Group (Morristown, NJ). Membranes were fluorinated dry as batch samples in a flow reactor through which was passed a dilute mixture of elemental fluorine in nitrogen. Oxygen was carefully excluded from the reactor during fluorination, and all fluorinations were done at room temperature in

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the dark. The principal variables studied with respect to fluorination conditions were the exposure time and concentration of fluorine in the flow gas, and the degree of fluorination was judged principally by XPS analysis of the membranes. Comparison of scanning electron micrographs of fluorinated and untreated membranes revealed no apparent surface damage due to the fluorination process.

Pretreatment of the polysulfone membranes was necessary before fluorination, since these membranes are normally shipped and stored wet. If the membrane is allowed to dry, we observe very little water flux through the membrane, even at applied pressures up to 400 psi. To aid in rewetting the membrane, the membranes were pretreated with a 50% aqueous solution of methanol and then air dried in the hood. The deionized (DI) water flux in the dry methanol-treated membrane returned to a reasonable value, as illustrated in Figure 9, while a dry untreated membrane exhibited very little flux at a trans-membrane pressure of 100 psi. The methanol treatment of the membrane is believed to prevent pore collapse in the membrane during the drying process, thus allowing the membrane to re-wetted under moderate pressures. Before use, t'? fluorinated membranes were wetted by subjecting the membranes to DI water at 100 psi for at least 15 minutes.

Elemental fluorine is a powerful electrophile, and is capable of reacting with essentially all organic compounds, including alkanes. For the polymeric materials discussed in this work, the major mechanisms for attack are assumed to be free radical halogenation and electrophilic substitution. Free radical halogenation was probably the only mechanism by which fluorine was introduced into polyethylene, and would also be the mechanism by which fluorine would be introduced into methyl or methylene groups in polysulfone and cellulose acetate. Attack is presumably initiated by hydrogen abstraction by a fluorine radical (1) and occurs by a chain reaction (1-2). Fluorination of aromatic rings presumably occurs via a carbonium ion mechanism (3).

$$F\cdot \; + \; R-CH_3 \; \rightarrow \; HF \; + \; RCH_2\cdot \qquad\qquad (1)$$

$$R-CH_2\cdot \; + \; F_2 \; \rightarrow \; RCH_2F \; + \; F\cdot \qquad\qquad (2)$$

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$$\text{(benzene ring)} + F_2 \longrightarrow \quad \longrightarrow + HF \qquad (3)$$
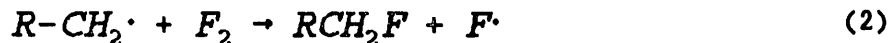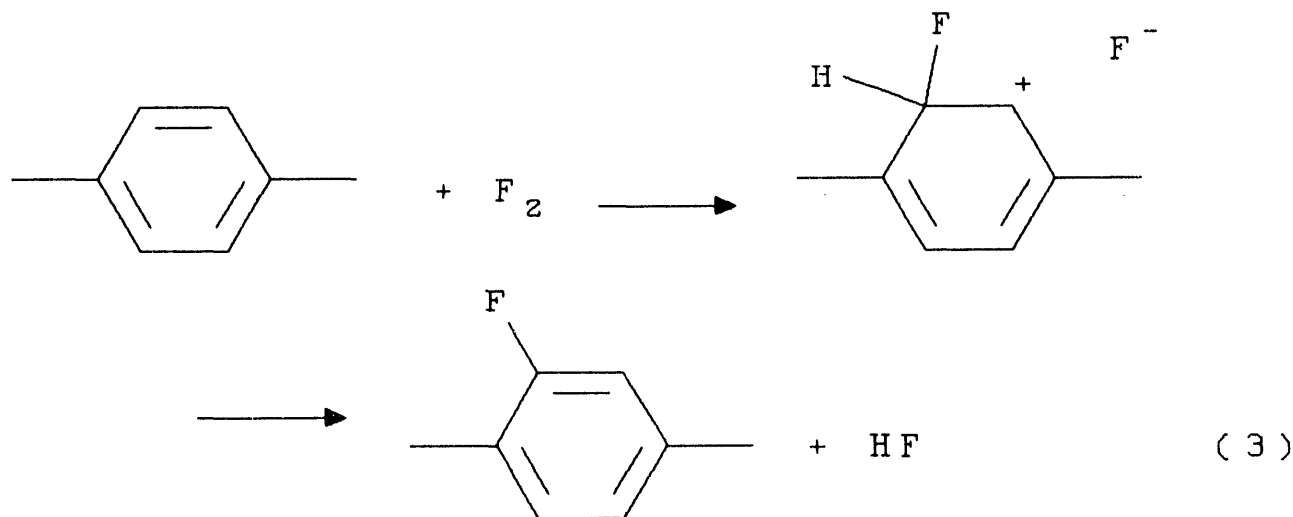
Elemental fluorine is a strong enough electrophile to cleave carbon-carbon single bonds. For a material with as much fine structure as an ultrafiltration membrane, such cleavage reactions might result in significant damage to the membrane structure. Later in this report, we will discuss experiments designed to test whether such damage occurs. The use of very dilute fluorine streams and low temperatures was designed to avoid as much carbon cleavage as possible. As a result of either carbon cleavage or homolysis of C-H bonds, formation of relatively stable free radical sites within the membrane is possible. As we will note later in this report, these free radical sites may be implicated in the introduction of oxygenated functionality into the membrane.

Strong evidence for the formation of such stable free radical sites within the membrane and the importance of quenching them by reaction with air components was presented by an experiment in which a polysulfone membrane was carefully protected from air, not only during fluorination, but also afterwards. This membrane became extremely brittle, and shattered into numerous small pieces on handling. Our hypothesis is that the unquenched free radical sites resulted in cross-linking within the membrane structure, and this made the membrane brittle.

3.2 Flat Sheet Results

3.2.1 Surface Properties of Various Fluorinated Membranes

Polysulfone, cellulose acetate and polyethylene membranes were surface fluorinated and the surface properties were analyzed via contact angle measurements and XPS. The contact angle measurements were used to quantify the hydrophilicity of the membranes, while XPS analyses provided a measure of the amount of fluorine and other elements added to the membrane. The effect of fluorination on pore size was analyzed via dextran permeation experiments.

3.2.1.1   Contact Angle Measurements

Contact angle measurements of water on the membranes were performed to provide a measure of the surface energy of untreated membranes and membranes after treatment under various fluorination conditions. The effect of fluorine treatment time on the contact angle of polysulfone is shown in Figure 10, which shows the contact angle of water on polysulfone membranes treated at 0, 5, 30, and 60 minutes at 0.025 vol% fluorine in nitrogen. The contact angle decreased from an initial value of 90° to a value of 56° after fluorine treatment for 60 minutes with a concentration of 0.025 vol% fluorine in nitrogen. This observation was at first surprising, since it indicated that the membrane had become more hydrophilic, not more hydrophobic, as would have been expected if the membrane were perfluorinated.

The effect of fluorine treatment on a polyethylene membrane is shown in Figure 11. As with the polysulfone membrane, the membrane became more hydrophilic with increased fluorination treatment. The contact angle decreased from an initial value of 99° to a value of 77° after fluorine treatment for 30 minutes with a concentration of 0.025 vol% fluorine in nitrogen. With a more intensive fluorine treatment of 0.25 vol % fluorine in nitrogen for thirty minutes, no contact angle measurement could be taken because the water wetted the surface completely, and was absorbed into the pores.

No contact angle measurements were possible on the untreated or fluorinated cellulose acetate membranes because extensive surface damage occurred during the drying procedure. The entire surface was cracked and curled, and no representative 1" by 1" samples could be obtained.

3.2.1.2 XPS of Fluorinated Membranes

The surface composition of the untreated and fluorinated membranes was analyzed by XPS. XPS has previously successfully been applied to the analysis of membrane properties[27,29,30]. The XPS results on fluorinated polysulfone, polyethylene and cellulose acetate are listed in Tables 1, 2, and 3, respectively. The theoretical elemental concentrations for the untreated membranes (based on the empirical formulae of the polymers) are also listed in parentheses in the Tables. XPS is generally considered to be sensitive to a depth of 50 Å into the surface examined. We assumed that the number of carbon atoms near the surface remains the same, and therefore report atomic ratios with respect to carbon in order to give a clear indication of the chemistry occurring at the surface.

For polysulfone, the atomic ratio for sulfur remains relatively constant for all treatment times as seen in Figure 12 and listed in Table 1. This indicates that the fluorination process does not remove the sulfur from the surface. The atomic ratios with respect to carbon show that the fluorine content does increase on the surface, as expected, with an atomic ratio of 0.44 F/C at 60 minutes. Note, however, that Figure 12 also shows that the level of oxygen increases on the membrane to an atomic ratio of 0.36 O/C at 60 minutes. Since the reaction was completed in oxygen-free reaction gas, the increase in oxygen on the membrane surface must be a result of reaction with water or oxygen absorbed in the membrane present from the start of the reaction or reaction with atmospheric water or oxygen after removal from the fluorination reactor.

For the polyethylene membrane, similar surface changes were evident with increased fluorination treatment, as the concentrations of atomic fluorine and oxygen increased on the surface (Table 2). The atomic ratios with respect to carbon show that the fluorine content does increase on the surface as expected, with a

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atomic ratio of 0.235 F/C for 30 minutes (0.025 vol% fluorine in nitrogen), and that the level of oxygen increased on the membrane to an atomic ratio of 0.13 O/C. At a higher concentration of fluorine (0.25%) in the reaction mixture, the amount of fluorine on the surface did not increase substantially over the amount of fluorine present on the surface at the lower concentration, while the amount of oxygen increased almost threefold.

Untreated and fluorinated cellulose acetate membranes were analyzed via XPS and the composition of the surface is given in Table 3. The atomic ratios with respect to carbon show that the fluorine content increased on the surface, as expected, with an atomic ratio of 0.15 F/C at 30 minutes. The level of oxygen decreased on the membrane to an atomic ratio of 0.46 O/C versus 0.49 for the untreated cellulose acetate membrane. This decrease in oxygen on the surface may not be statistically significant.

Based on our XPS results, we can advance two possible rationales for the increase in hydrophilicity we observe in the contact angle experiments on the polysulfone and polyethylene membranes: polar interactions resulting from partial fluorination, and surface oxygenation. Fluorination of a surface can lower its hydrophilicity as the surface becomes more like a perfluorinated polymer, but, at incomplete fluorination, the hydrophilicity may increase. For example, the estimated Hildebrand interaction parameters[31] for the methyl pendant group ($-CH_3$) of the polysulfone molecule and the related fluorine-substituted methyl groups ($-CH_2F$, $-CHF_2$ and $-CF_3$) are 11.9, 16.4, 16.4 , and 13.4 $MPa^{1/2}$, respectively. We observe that, with increasing fluorination, these methyl groups first become more hydrophilic as revealed by the increase in the Hildebrand parameter, but eventually become more hydrophobic as the methyl group is perfluorinated. Similar Hildebrand parameter results are observed with the methylene groups in polyethylene.

Ring fluorination is expected to have a lesser effect on increasing the hydrophilicity of the surface. Thus, the Hildebrand interaction parameter for phenylene groups on the polysulfone molecule decreases on fluorination, which would have the effect of making a membrane more hydrophobic (i.e. 22.6 $MPa^{1/2}$ for the mono-substituted phenylene versus 24.7 $MPa^{1/2}$ for the phenylene group).

Surface oxygenation may also play a large role on the membrane's hydrophilicity. Oxygenated species, such as acid fluorides, on the surface would greatly increase the wettability of the surface. The increase in hydrophilicity during fluorination has been observed previously by Anand et. al,[18] who observed a minimum in contact angle at the maximum level of atomic % oxygen on a fluorinated poly(ethylene) membrane prepared for gas separation. However, at long treatment times, the membrane surface was eventually perfluorinated and reached the maximum contact angle. Of the two effects, we suspect that the hydrophilicity of the fluorinated membrane is mainly due to the increased oxygen level in the surface. We observed this clearly in the fluorinated polyethylene membranes listed in Table 2, where the amount of fluorine added to the surface was relatively small compared to the amount of oxygen added to the surface at the higher fluorine gas concentration. The associated contact angle measurements in Figure 11 show that the membrane treated at the higher fluorine concentration had a larger decrease in contact angle than the membrane treated at the lower concentration, even though the relative amounts of fluorine on the surface did not vary drastically.

3.2.1.3 Pore Size Analysis via GPC

The effect of our fluorination treatment on the pore size of polysulfone membranes was analyzed via dextran permeation through the membrane. GPC analysis of dextran in the feeds and permeates were used to compare the pore sizes of the untreated membrane to the fluorinated polysulfone membrane. A dextran feed with a low molecular weight distribution (M_w - 5.4 x 10^5 daltons and M_w/M_n - 2.6) was filtered using untreated and fluorinated membranes, and the corresponding GPC chromatograms are given in Figure 13. For this molecular weight distribution of feed, the permeate GPC chromatograms show identical distributions for all the membranes, indicating that the dextran easily passed through the membrane pores. This result indicates that the pore size of the treated membranes did not decrease below 5.5 x 10^4 daltons.

A high molecular weight distribution (M_w - 5.3 x 10^6 daltons and M_w/M_n - 23) dextran feed was subsequently filtered with the same untreated and fluorinated membranes and the corresponding GPC chromatograms are given in Figure 14. The

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molecular weight distribution was bimodal with peaks at approximately 1.0×10^6 and 2.2×10^5 daltons, and these GPC chromatograms show that very little of the dextran has permeated through the membrane. The molecular weight distributions of dextran that permeated through the untreated and fluorinated membranes are identical again, indicating that the pores sizes did not increase past 2.2×10^5 daltons during the fluorination process. We conclude that the fluorination treatment used in this study does not drastically affect the pore size distribution of the polysulfone membrane.

3.2.2 Membrane Performance

Membrane performance in the flat sheet study was evaluated using the permeate flux and the rejection of COD and nitrogen (protein).

3.2.2.1   Permeate Flux

The effect of fluorination treatment time on membrane performance is illustrated in Figure 15. Fluorination has a significant effect on both initial permeate flux and fouling rate. We observe that the initial fluxes of the treated membranes were higher than those of the untreated membrane. In general, we found that the initial flux increased with increased treatment time. We also note that the treated membranes had lower fouling rates when compared to the untreated membrane, as indicated by the decreasing slopes of the data on the Log(Flux) versus Log(Time) plot of Figure 15. In general, the fouling rate of the fluorinated membranes decreased with increasing treatment time. An ideal nonfouling membrane would have a slope of zero. Overall, the fluorinated membranes exhibit better fouling properties than the untreated polysulfone membrane. Membrane performance using simulated potato feed (Section 2.3.1) is given in Appendix A1. Additional studies using other process feeds and treated membranes are given in Appendix A2.

Our observation of increased flux for the fluorinated membrane is interesting, since our dextran experiments have already shown that the pore dimension does not change significantly. The principal change is thus the change in contact angle between the water and the membrane surface, which is in turn linked to increased

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hydrophilicity. We can understand this increase in flux by remembering that our membrane has a distribution of pore sizes, and that the diameter of the smallest pore which is actively involved in flow will be given by the Cantor[6] equation (4), where γ is the surface tension of the liquid, θ is the contact angle with that liquid, and P is pressure.

$$D = \frac{4\gamma\cos(\theta)}{P} \tag{4}$$

Thus decreasing the contact angle will decrease the minimum diameter of useful pores, increasing the total number of pores available for flow.

Increased hydrophilicity also can explain the decrease in fouling rate as shown in Figure 15. Our study is thus in agreement with others[9,12], who have observed that the rate of adsorption of hydrophobic foulants (i.e. proteins) decreased with the increase of hydrophilicity of the membrane surface. Our common interpretation is that a hydrophilic surface layer reduces the number of hydrophobic sites available on the membrane for adsorption and deposition of protein, thus reducing the observed fouling rate.

In particular, we should note that membrane hydrophilicity is likely to have a significant effect on protein adhesion due to the possibility of denaturation. For many proteins, secondary and tertiary structure is dependent on the presence of a hydrophilic external medium. Placed in contact with a hydrophobic surface, these proteins will denature, and adhere strongly to the surface. A hydrophilic surface will adsorb a surface layer of water, thus presenting to proteins which come into contact with it a surface similar to that of water. This effect was recently observed by Chmiel, et. al[32].

3.2.2.2 COD and Nitrogen Rejection

COD and total organic nitrogen rejection were measured for the feed stream and permeates after three hours into the experiment. The COD and total nitrogen of the feed stream were 10,100 mg/l and 0.037 % mass, respectively. COD rejection through

the membranes was $42 \pm 1\%$ and total organic nitrogen rejection was $78 \pm 2\%$. The low rejection in COD is due to the large pore size of this polysulfone membrane. Rejections as measured by COD and total nitrogen were within one standard deviation of each other for fluorinated and untreated membranes, indicating that selectivity was not altered significantly by fluorination. The acceptable rejections of both COD and nitrogen for the potato waste stream need to be at least 75%. The rejection of COD and nitrogen for various potato feeds and treated membranes is given in Appendix A2.

3.2.3 Summary - Flat Sheet Experiments

Our initial studies with flat sheets have shown that surface fluorination can significantly affect the performance of an ultrafiltration membrane used to concentrate a food-related stream. Membranes which have been fluorinated under appropriate conditions exhibit higher initial fluxes, and do not foul as rapidly as untreated membranes. We link this improvement to increased hydrophilicity of the surface, as shown by the decrease we observe in contact angle with water. This increased hydrophilicity, in turn, we link to the addition of fluorine and oxygen to the surface. Partial fluorination can make a surface more hydrophilic due to the strong dipole moment of the C-F bond, while oxygen-containing functional groups can participate in hydrogen bonding interactions.

3.3 Cleaning Study

A preliminary cleaning study was performed to test the stability and cleanability of untreated and treated membranes to various typical cleaning solutions. Membranes were fouled for three hours in the filtration rig with fresh industrial potato waste under rig conditions identical to the flat sheet studies. A fouled and nonfouled membrane were each cut into three pieces and concurrently subjected to the various washes listed in Table 4a for an hour in a shaker bath, followed by a DI-water rinse for an additional hour. The fouled membranes had a gel-like material on the surface before cleaning. The final membrane appearance was noted after cleaning and the results are listed in Table 4a. No permeate flux study was completed on the cleaned membranes.

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Membrane stability to cleaning was analyzed on the washed but not initially fouled membranes from the first portion of this study. The membranes were analyzed via XPS and the results are noted in Table 4b. We observe that, for all the washes, some of the elemental fluorine was removed from the surface. This result was expected, since surface fluorination can lead to a variety of functional groups with varying degrees of hydrolytic sensitivity. In particular, since surface oxidation of any polymer surface is inevitable, some fluorine will be attached to the polymer as -OF or -COF groups which will not survive contact with water. Similar observations have been made by Dixon and Hayes[33] for fluorination of polyolefin films. Of course, hydrolysis of these groups releases hydrophilic functionality, so this reaction should cause no particular harm to our fouling resistance.

With respect to other treatments, we observed that acid washing with sulfuric acid added sulfur and oxygen to the surface. We ascribe this to surface-adsorbed sulfuric acid which was not completely washed off. The bleach wash added chlorine to the surface, perhaps due to light chlorination of the surface. It appears that the acid wash removed more fluorine from the membrane than the basic or bleach wash.

Based on qualitative appearance of the membranes and the XPS results, we decided to use a the cleaning procedure in the spiral module pilot study involving a sodium hydroxide wash followed by a disinfecting bleach wash.

3.4 Scale-up to Spiral Modules

The pilot plant study was used to investigate the effects of increasing the fluorinated membrane surface area, and changing the membrane configuration. It also allowed us to observe long term fouling of membrane under realistic conditions, including a daily cleaning cycle. Two pilot studies were conducted. The first pilot study was run at a feed rate of 1 liter/minute/spiral and the second pilot study was run at a feed rate of 3 liters/minute/ spiral. The second pilot study was conducted at a higher cross-flow velocity to reduce the gel formation and severe fouling observed in the first pilot study at the lower feed rate.

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The feed used in the pilot plant study was shipped fresh from a plant operated by Basic American Foods in Blackfoot Falls, ID once a week, as detailed in the experimental section. According to BAF, the feed came from the potato peeling operation in their plant, and was typical of their normal waste stream from this operation. We filtered the feed through a 50 micron filter immediately before use. Our analyses showed that the organic constituents in the feed consisted primarily of starches. With a total solids loading of 1.24%, it had a COD of 11,500 mg/L, an organic nitrogen content of 0.026 mass % and an ash content of 0.124 mass %. Based on this analysis, we can conclude that the organic components in the feed are primarily starches, with a low concentration of proteins. We estimate that the starches had an average molecular weight of 1.8×10^6 daltons and a dispersity of 2.7. Qualitatively, we found that this was a highly fouling feed in our system.

3.4.1 Membrane Performance

Membrane performance in the pilot plant study was evaluated by monitoring the change in permeate flux with time and the rejection of COD and nitrogen (protein) by the membrane. The turbidities of the initial and final permeates were also measured. Finally, the surface properties of the fouled membranes were measured on samples cut from the spiral module after it had been used in the pilot plant. These properties included visual observations, SEM observations and XPS analysis of the surface composition of the fouled membrane.

3.4.1.1   Permeate Flux

The permeate flux of the untreated and fluorinated membrane modules were monitored throughout both pilot plant studies. In the first pilot study (21 days), the feed rate was 1 liter/minute per spiral, while in the second pilot study (5 days), the feed rate was 3 liter/minute per spiral. The untreated spiral modules in the first pilot study were prepared using membrane which had been methanol treated, then dried. The untreated modules were re-wetted by placing the module into the pilot plant housing and passing a 50% aqueous methanol solution through the membrane. Each module was then rinsed thoroughly with DI water. The fluorinated

membrane did not require this treatment to regain flux.

The permeate fluxes of the untreated and fluorinated membranes during the first pilot study are given in Figure 16. The solid and dashed lines represent the permeate fluxes of the fluorinated and untreated membranes, respectively. The untreated spiral module had to be replaced after nine days; it failed when a misplaced o-ring allowed the feed to flow around the spiral module instead of through the spiral module. This misplaced o-ring resulted in a steep decline in permeate flux in the untreated membrane. We believe that the reduced flow through the untreated membrane also affected the cleanability of the membrane by reducing the cross-flow velocity and allowing foulants to build up at the surface. Also, during the cleaning cycle, less cleaning solution passed through the membrane, allowing bacteria and other solids to build up inside the permeate spacer (See Figure 5).

In all experiments, we noted that very severe drops in permeate flux of the membranes occurred early in each day's cycle. While in typical commercial membrane operation, the flux may drop to 50% of its original value by the time the cleaning cycle is begun, we observed that it fell to one third its original value within 15 minutes of the start of each cycle. These severe drops are undoubtedly due to the high concentration of starches and other foulants in the potato-derived feed.

We found that the permeate flux of the fluorinated spiral module was greater than that of the second untreated spiral module for the first six days of each spiral's operation. After six days of operation, the permeate flux of the fluorinated membrane dropped below the permeate flux of the untreated membrane. The final fluxes for both membranes were very low relative to the starting flux.

We believe that one reason for the drop in the permeate flux of the fluorinated membrane over time was the lack of effectiveness of the cleaning cycle in removing foulants from the surface. After each cleaning cycle, we passed DI water through the membrane and measured the permeate flux. The DI water flux immediately after cleaning and the permeate flux after 15 minutes of operation is given in Figure 17 for various days of the pilot study, and provides a measure of

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the effectiveness of the cleaning cycle and the fouling ability of the potato feed. We see that, in general, the trend for both membranes is that the DI permeate flux declines with the total number of cleaning cycles. In the fluorinated membrane, there is little recovery in the DI water flux after 10 days. The fluorinated membrane may have been affected by bacterial growth in the stagnant fluid in the permeate spacer in the first mis-aligned untreated module which then passed into the fluorinated spiral module. The DI permeate flux does increase on days 19, 20, and 21 in both membranes and this increase is most likely related to variations in the total foulants in the initial potato feed. We observed that the total solids and COD in the feed had decreased on those days (See Appendix B1).

The extent of fouling in the untreated and fluorinated modules by the potato feed is seen in the relative drop in permeate flux after 15 minutes. For example, the flux decline for the fluorinated membrane on the first day (Day 1) is 88 %, while the flux decline for the non-fluorinated membrane on the first day (Day 10) is 82%. These flux declines are very large and are probably indicative of gel layer formation at the surface.

Our flux results at the end of the first pilot plant study did not show the resistance to fouling which we had previously observed in the flat sheet studies. Comparing the two studies, we noted that the cross-flow velocity was much higher in the flat sheet studies than it had been in our spiral wound modules (12,500 cm/min versus 734 cm/min) as listed in Table 6. Since, as we note earlier, fouling is strongly affected by both hydrodynamics and surface interactions, we ran a second pilot plant study to explore the effect of increased cross-flow velocity.

The permeate flux of the untreated and fluorinated membranes during the second pilot study are shown in Figure 18. The solid and dashed lines represent the permeate flux of the untreated and fluorinated membranes, respectively. The untreated membrane had a higher permeate flux than the fluorinated membrane for all five days of the study. The higher flux for the untreated membrane relative to the fluorinated membrane, was due to the wetting behavior of the fluorinated membrane. We believe that the fluorinated membrane was not completely wetted before the start of the run, since we saw the permeate flux through the fluorinated membrane

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increasing continuously throughout the first day of the second pilot study .

We again observed the extent of fouling by the potato feed in the relative drop in permeate flux after 15 minutes in the untreated and fluorinated modules (Figure 19). For example, the flux decline for the fluorinated membrane on the second day is 77%, while the flux decline for the fluorinated membrane on the same day is 50%. These flux declines are very large and are indicative of gel layer formation at the surface.

The cleanability of the untreated and fluorinated membranes can also be deduced from Figure 19. The cleaning procedure used in this study appears to clean the untreated membrane, but does not appear to effectively clean the fluorinated surface. Tragardh[34] has observed that membrane cleaning procedures are dependent on both the type of foulant and the type of membrane used.

Comparing the two pilot plant studies, the effect of the retentate flow rate on the performance of untreated and fluorinated membrane performance is shown in Figures 20 and 21, respectively. For the untreated membrane, the permeate flux increased with the increase in retentate flow rate, while for the fluorinated membrane, the permeate flux did not change with increasing retentate flow rate. The differences in the permeate flux rates for the untreated membrane may not be experimentally significant.

3.4.1.2   Turbidity, COD and Nitrogen Rejection

Turbidity, COD and total organic nitrogen rejection were measured for the feed stream and permeates at various times during both pilot studies. The numerical results for the first and second pilot studies are listed in Appendices B1 and B2, respectively. The variation in the initial daily potato feed is obvious from the change of COD, total organic nitrogen, and total solids over the duration of the pilot studies. For example, the initial COD reading varied from 6800 mg/L to 13,407 mg/L during the first pilot study. At the same time, the COD typically decreased during a daily run for both pilot studies. For example, the COD of the feed at the start and finish of the first day in the second pilot study changed from 5250 mg/L

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to 4850 mg/L, respectively. This decrease in COD may be due to degradation of the high molecular weight starches in the feed to low molecular weight starches which can easily pass through the membrane. Such degradation may result from the high shearing stresses, bacteria action, or thermal degradation[35,36].

The rejections of COD and total nitrogen were similar for the fluorinated and untreated membranes, indicating that the selectivity of the membrane was not altered significantly by the fluorination treatment. For example, the COD rejections of the untreated and fluorinated membranes at the start of day one of the second pilot study were 34% and 36%, respectively. The COD rejections of the untreated and fluorinated membranes at the end of the same day were 24% and 23%, respectively. The membranes behaved identically even though the rejections decreased during the day. This decrease in rejection is a direct effect of starch degradation in the feed during the day. The acceptable rejections of both COD and nitrogen for the potato waste stream need to be at least 75%. The low COD and low nitrogen rejection is due to the large pore size in this polysulfone membrane.

Finally, COD rejections for the mis-aligned untreated spiral module of the first pilot study indicate that bacterial growth or mass build-up may have occurred in the permeate spacer. The COD rejection values were very low or negative. A negative rejection would imply that mass was being produced in the permeate.

The turbidity of the feed and permeate were taken at the start and conclusion of the experiment, and the results are listed in Appendix B. The feed was typically very cloudy and the permeate through the membranes was visually clear. The feed turbidity varied from about 90 to 1000 NTU and was reduced to 0.2 to 20 NTU in the permeate. The turbidity of the feed increased from the first sample to the final sample indicating that the composition of the feed did vary with time, most likely due to degradation of the feed with temperature, or degradation by bacterial growth.

3.4.1.3   Gel Permeation Chromatography Analysis of Process Potato Starch

Feed and permeate samples from both the untreated and fluorinated spiral modules, taken at the beginning of the run (1st day, 2nd pilot study) and at the conclusion of the run, were analyzed via GPC to determine the molecular weight distribution of potato starch rejected by the membranes. The molecular weight distributions were evaluated using polysaccharide calibration standards.

The GPC chromatograms for feed samples taken at the beginning (lower curve) and end (upper curve) of the run are shown in Figure 22. The initial feed had a high molecular weight fraction at 8.4×10^6 daltons, while the final feed did not contain this high molecular weight component. The initial feed also had a large peak at 3.8×10^5, but in the final sample, this peak had increased in magnitude and shifted to longer retention times indicating that the overall molecular weight distribution had decreased. These results indicate that the feed stream degraded significantly over the 21 hr daily run period and that degradation of the starch in the feed resulted in a decrease in the overall molecular weight distribution of the starch.

The GPC chromatograms of the permeates from each module and the feed at the start of the pilot study are shown in Figure 23. The feed had a GPC peak at 8.4×10^6 daltons, which did not appear in both permeate samples. The disappearance of this peak indicates that the untreated and fluorinated membranes removed the high molecular weight starch. The remaining regions of the GPC chromatograms were identical for all the curves, indicating that the lower molecular species were not rejected by the untreated and fluorinated membranes.

The GPC chromatograms of the two permeates and feed at the conclusion of the pilot study are shown in Figure 24. The GPC chromatograms are identical over all retention times, indicating that the entire molecular weight distribution had passed through both the untreated and fluorinated membranes. Since starch degradation had eliminated the highest molecular weight starch component, a greater fraction of the starch passed through the membrane, and the rejection of the membranes decreased. This result explains our results in section 3.4.1.2, where we observed that the COD

rejection decreased over each daily run in the pilot plant.

3.4.2 Surface Properties

3.4.2.1   Final Appearance

The spiral modules were dissected at the conclusion of each pilot plant study. Photographs of the front and back of the membranes from the spiral modules of the first and second pilot study are shown in Figures 25 and 26, respectively. A solid gel-like material is seen in the feed spacer close to the permeate tube. A greater build up of gel material occurred in the fluorinated spiral in Figure 25. We link this increased accumulation to the longer time the fluorinated spiral module spent on-line in the filtration rig. The gel builds up preferentially near the permeate tube because this is where there is the least resistance to flow through the permeate spacer.

3.4.2.2   SEM Micrographs

SEM micrographs were taken of the untreated and fluorinated membranes after the first pilot plant study. The membrane samples were extensively washed with DI water and dried via critical point drying to preserve the pore structure. A small representative sample was cut from the final dried membranes and observed by SEM.

Micrographs of the untreated and fluorinated membranes are shown in Figures 27 and 28, respectively. A fibrous material with a characteristic dimension of 500 Å is seen on the surface of the untreated membrane in Figure 27, which we believe is most likely an accumulation of starch. This fibrous material did not cover the surface evenly, and photographs taken from other parts of the membrane showed no sign of it. The entire surface of the fluorinated membrane is clean of the fibrous material. The fluorinated membrane does exhibit fissures in the surface, which are most likely due to the drying process. Overall, the surfaces of the untreated and fluorinated membranes have similar appearance.

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3.4.2.3   XPS Analysis of Fouled Surfaces

XPS results for the membranes from the first pilot plant study are presented in Table 5. We see that there is fluorine left on the membrane surface even after extended continuous operation. The fluorinated membrane was online for 22 days while the untreated membrane was online for 13 days. While the fluorine level appears to have dropped from about 0.12 F/C for a cleaned membrane to 0.04 F/C for a pilot tested membrane, this is probably an artifact of our data treatment. In earlier studies, we assumed that the number of carbon atoms in the 50 Å layer being analyzed would remain constant during fluorination, but this is no longer true when carbon-containing materials adsorb on the surface (i.e. protein, starch). Any additional carbon material adsorbed would dilute the number of fluorine atoms present in the analyzed layer. The presence of this adsorbed carbon is clearly indicated by the S/C ratio, which decreased after extended use.

We can also evaluate fluorine content on the surface by comparing the F/S ratio of a water-washed fluorinated membrane (Table 4b) with the fluorinated membrane from the pilot study (Table 5). Since sulfur and fluorine should be present at the same depth, the amount of sulfur to fluorine would be expected to remain constant even with the fouled layer present. We observe that the F/S ratio decreased from 5.2 for the water-washed fluorinated membrane to 2.4 for the fluorinated membrane from the pilot study. The decrease in F/S indicates that the fluorination decreased by 50 % over the 21 day period.

3.4.2.4   ATR-FTIR Analysis of Surface

The spectra of clean untreated and fluorinated polysulfone membranes are given in Figures 29 and 31, respectively. The peak in the region between 3100 and 3000 cm^{-1} is indicative of the C-H stretch of an aromatic hydrogen and the peak in the region between 3000 and 2870 cm^{-1} is indicative of the C-H stretch of an aliphatic hydrogen[27]. The aromatic nature of the polysulfone is confirmed by the aromatic bands at 1592 and 1492 cm^{-1}. The 1334/1304 cm^{-1} doublet and the 1159 cm^{-1} are attributed to RSO_2R groups of the polysulfone backbone. The spectra are in agreement with spectra of other polysulfone membranes[27,30,31].

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The spectra of fouled untreated and fluorinated polysulfone membranes from the first pilot study are given in Figures 30 and 32, respectively. The membranes were extensively washed with DI water and dried in air. The spectra exhibit all of the functional groups present in the starting polysulfone membranes. Additional peaks are observed at 3313, 1663, and 1549 cm^{-1} in the fouled membrane. The 3313 cm^{-1} peak can be associated with the N-H stretch in proteins or with an O-H stretch, and the 1663 and 1549 cm^{-1} peaks may be associated with the amide I and amide II bands[27]. The appearance of the amide bands is indicative that proteins have adsorbed on the surface during the pilot plant study, and that long term fouling of the membranes is controlled by protein deposition. Direct quantitative analysis of the degree of protein fouling is difficult to calculate due to the difference in run times of the various membranes used in the first pilot study.

The effect of fluorination on the polysulfone spectra can be seen by comparing Figures 29 and 31. The decrease in the peak at 2954 cm^{-1} indicates that the number of aliphatic C-H bonds has decreased, while the number of C-F bonds has increased as indicated by the absorbance increase[37] in the region of 1350-1000 cm^{-1}. The C-F bonds are detected in the 1100-1000 cm^{-1} region and the CF_2/CF_3 groups show broad peaks in the region of 1350-1120 cm^{-1}.

3.4.3 Summary -- Spiral Wound Module Study

Our pilot plant study does not show the clear difference in membrane flux and fouling that we observed in the flat sheet study. Instead, fluorinated and untreated modules behaved in a substantially similar manner. Fouling by the potato waste feed was severe, and resulted in the formation of an extensive gel layer within the module on the surface of the membrane. As a result, permeate fluxes decreased to less than 50% of their original values within the first 15 minutes of each cycle. XPS, SEM and FTIR studies combine to indicate that some build up of organic material occurred on both the fluorinated and unfluorinated membranes, but SEM indicates that a fibrous mat of material was observed only on the non-fluorinated membrane. We conclude that in the pilot study, membrane fouling and gel formation were so extensive that the surface interaction effect on which the fouling technique is based was overwhelmed.

Reconciliation of the results of the spiral module study with those in the flat sheet study will be discussed in section 4.0.

3.5 Economic Analysis

The ultimate objective of our program was to reduce energy consumption by the food processing industry by providing an alternative to evaporative concentration of aqueous streams. In order for such a process to be considered by the food processing industry, it must be reasonably low in cost, and offer significant savings to the processor in energy and other costs. In this section we analyze these costs.

Since surface fluorination represents an added treatment to an existing ultrafiltration membrane, analysis of the costs of the modified membrane is relatively simple. Conventional ultrafiltration membranes of the type used in our work are normally sold for $3.5-4.5/sq. ft. as spiral wound modules[38]. Surface fluorination would most conveniently be accomplished by treating the formed, unrolled membrane with fluorine in either a batch or continuous mode. Fluorine is commercially available at $40-50/lb,[39] and based on the amount of fluorine on the surface we estimate that this would contribute $1.3 x 10^{-5}/sq. ft. to the cost of the membrane. The principal cost of fluorination will therefore be the capital, labor and environmental costs associated with using fluorine safely. By way of comparison, the cost of fluorinating the interior of a one gallon polyethylene container was estimated[40] at 5.5 - 6 ¢ per container in 1978, and this cost included a royalty fee for the proprietary process used. Clearly, surface fluorination is an inexpensive treatment and can be also be applied inexpensively to fluorinating other polymeric surfaces, including membranes.

The economics of an increase in permeate flux through a fluorinated membrane were analyzed[39] for a hypothetical ultrafiltration plant running on a 365 day, 24 hour operating cycle which included daily cleaning of the membrane. The plant would be operated 20 to 22 hours per day with a cleaning cycle varying between 2 to 4 hours per day. A 25% increase in permeate throughput through a membrane would result in a 23% reduction in capital costs as illustrated in

Appendix D. The decrease in capital costs is directly related to a decrease in both the number of modules, pressure tubes and pumps needed to provide a given plant output. In addition to reduced capital costs, operating costs would decrease as illustrated in Appendix D. Utility costs would also be reduced by 20-25%. For example, electrical costs would decrease from $52,700 to $39,500 due to decreased pumping requirements. Steam and water costs were not estimated due to large regional price differences. The amount of steam used remains constant and is directly related to the total amount of feed treated. Cleaning costs would be reduced 15-20%, mainly resulting from a reduction in the quantity of chemicals and water used to clean the modules. There would be no reduction in labor costs and no reduction in pretreatment procedures. Annual replacement costs of the membranes would also decrease due to the decrease in the number of membrane modules present in the ultrafiltration system for a specified permeate flux. The replacement cost of the improved membranes listed in Appendix D does not include fluorination costs.

In conclusion, the 25% increase of permeate flux decreased both the initial capital investment and the annual operating costs of the ultrafiltration plant. An original equipment manufacturer stated that a fluorinated membrane with a 25% increase in permeate flux would be attractive due to the increased efficiency it would provide to the overall membrane process.

By reducing the costs of using membranes, surface fluorination is an enabling technology for energy conservation. Fluorinated membranes can be used to reduce the energy required to concentrate final food products or aqueous waste streams in industries like those involved in meat and poultry, fruits and vegetables, dairy, and grain milling processes. Examples of food processes where membranes can be applied include ultrafiltration (UF) of poultry brine, UF fractionation of milk to produce cheese, and UF of potato waste streams. As a concentration method, our technology thus offers an alternative to evaporation and distillation, which require large quantities of energy to due to the latent heat of vaporization of water.

4.0 CONCLUSIONS AND RECOMMENDATIONS

Our flat sheet study has shown that in the filtration of potato waste streams, permeate flux increased and the fouling rate of the polysulfone membrane was reduced by surface fluorination. Analysis of the fluorinated membrane showed that the fluorination process added both fluorine and oxygen to the surface. We believe that the increased oxygen and fluorine on the surface of the membrane increased the hydrophilic nature of the membrane, and this increase in hydrophilicity increased the initial flux by decreasing the contact angle in the pores of the membrane. It also decreased the fouling rate by decreasing the interactions of foulants with the membrane. Avoiding denaturation of proteins and glycoproteins on the hydrophobic surface may be important to this effect.

The permeate flux results in the spiral module pilot study did not agree with the flat sheet results. No significant difference was observed between the performance of the fluorinated module and an untreated module, and neither module worked well with the realistic feed. Analytical results with respect to degree of fluorination and contact angle, however, were similar to those in the flat sheet study.

The decrease we observed in permeate flux in the spiral module may have been due to (1) operating conditions (crossflow velocity, trans-membrane pressure, etc.) (2) cleaning procedures, or (3) changes in the composition of the potato feed. Membrane fouling was more severe in the spiral module than in the flat sheet runs as evidenced by the sharp decrease in permeate flux at the start of each run. The operating conditions of the flat sheet studies and the spiral modules runs differed since cross flow velocities in the flat sheet were greater than those in the spiral module by an order of magnitude. The increased crossflow velocity in the flat sheet study could have swept away any gels formed on the surface of the membrane, while in the spiral modules, the gels would have built up at the surface. The spiral module also contained a feed spacer which was not present in the flat sheet studies. This spacer could have aggravated gel formation by entrapping and concentrating gels that had formed inside the spacer. Spacer sizing and design are critical in controlling the build-up of

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foulants inside the module.

We found that the cleaning procedure used in this study did not effectively clean the spiral modules. This was made evident by the hardened gel that formed inside both the untreated and fluorinated modules after extended use. The long term build up of foulant would result in a short lifetime for the membrane.

In retrospect, we also believe that the feed composition also varied between the flat sheet study and the spiral module runs. Feed degradation occurred continuously on receipt of each feed sample, but the potato feed was clearly further degraded in the flat sheet study than in the spiral module study, judging from the pH values of the samples. Degradation results in a lower molecular weight distribution of starch, and associated with the lower molecular weight, a higher critical gel concentration. With a higher critical gel concentration, we would expect a gel layer to first occur at a higher surface concentration (or at longer filtration times), as was in fact observed in our flat sheet study.

As a result of these problems, severe gel formation on the spiral modules prevented us from observing the effects of surface fluorination on the membrane surface in the pilot study. The permeate flux dropped over 50 % in the first 15 minutes of each cycle, indicating that a gel layer formed quickly on the surface. After gel formation, the permeate flux through the membrane was probably controlled by the presence of the gel layer rather than by the membrane surface.

We recommend that further studies be completed to establish whether surface fluorination is a viable approach to reducing fouling in ultrafiltration membranes. These studies should focus on the three hypotheses described above, and determine whether each is involved, separately or in combination, in obviating the surface fluorination effect we observed in the flat sheet study. In particular, further studies should refine our identification of the foulants on or near the membrane surface. They should also define the gelling properties of potato starch and map the critical gel concentration as a function of concentration, pH, ionic strength and other factors. Membrane cleaning also

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needs a much closer examination, including pilot plant trials with alternative cleaning agents. The net effect of these studies would be a much more clearly defined picture of the benefits of surface fluorination, and a concrete resolution of the question of whether its benefits are sufficient to justify commercial development.

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40. <u>Plastics Technology</u>, <u>24</u>, September, 23 (1978)
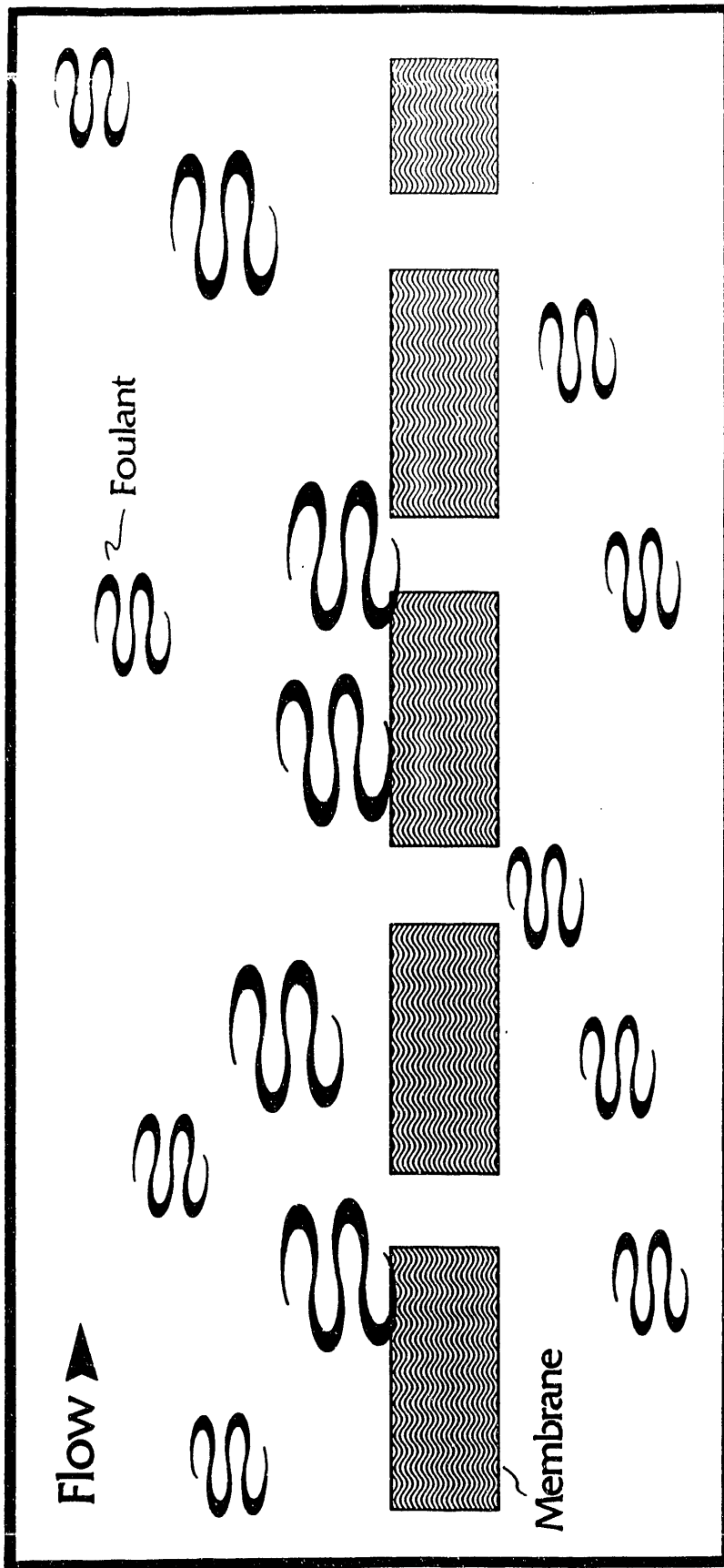
Figure 1: Schematic of Ultrafiltration Membrane Separation
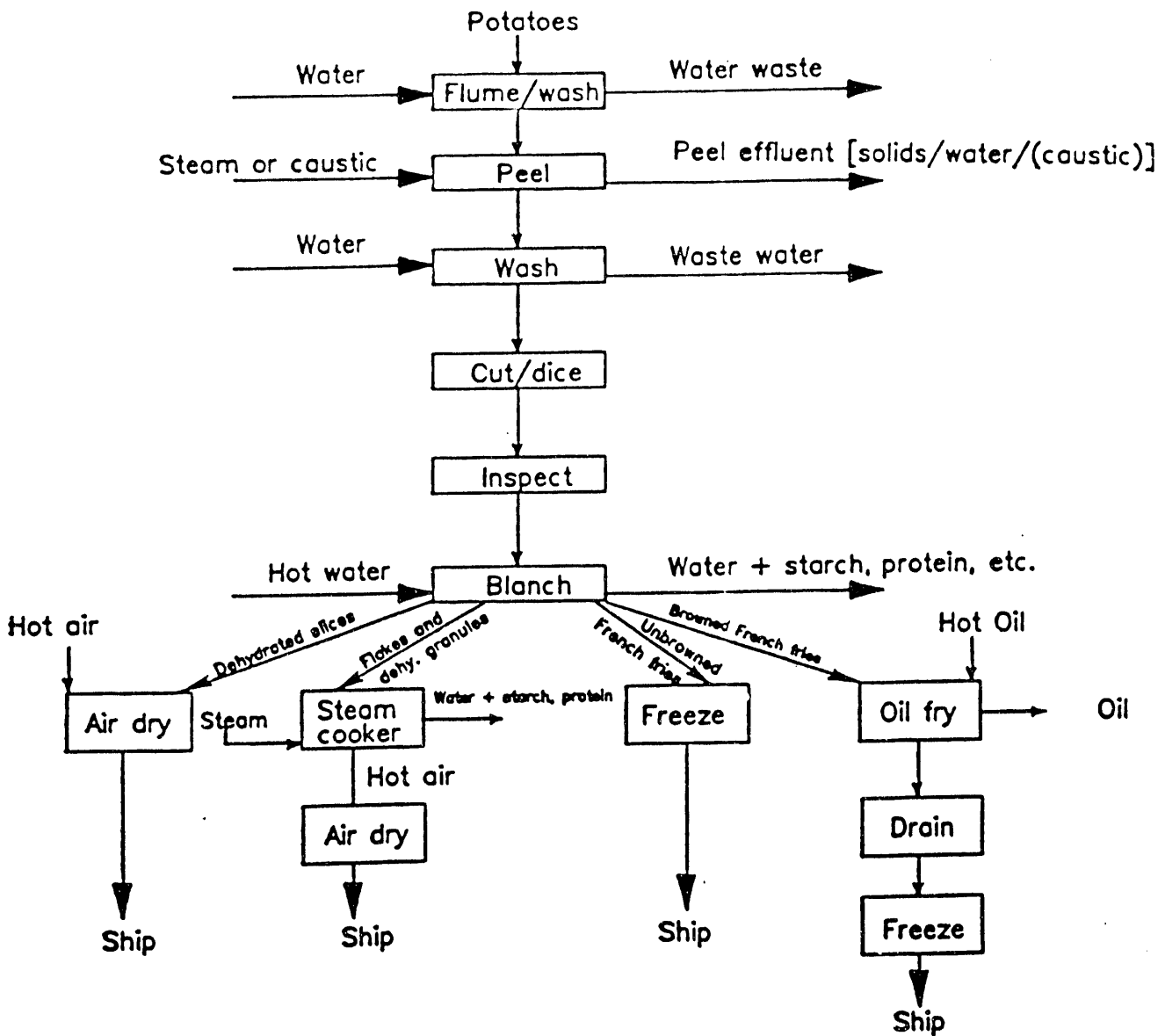
Figure 2: Flowsheet of a Typical Potato Processor[1]

Fluorination Apparatus

POWER SUPPLY

25 AMP

UV LIGHT

FEP COATED QUARTZ

TEMP PROBE

MONEL SPARGER

FLUORINE INLET

TEMP BATH

FLOW CONTROL

MIXER

HELIUM

FLUORINE

VOLATILE TRAP

F_2 SCRUBBER

HF SCRUBBER

VENT
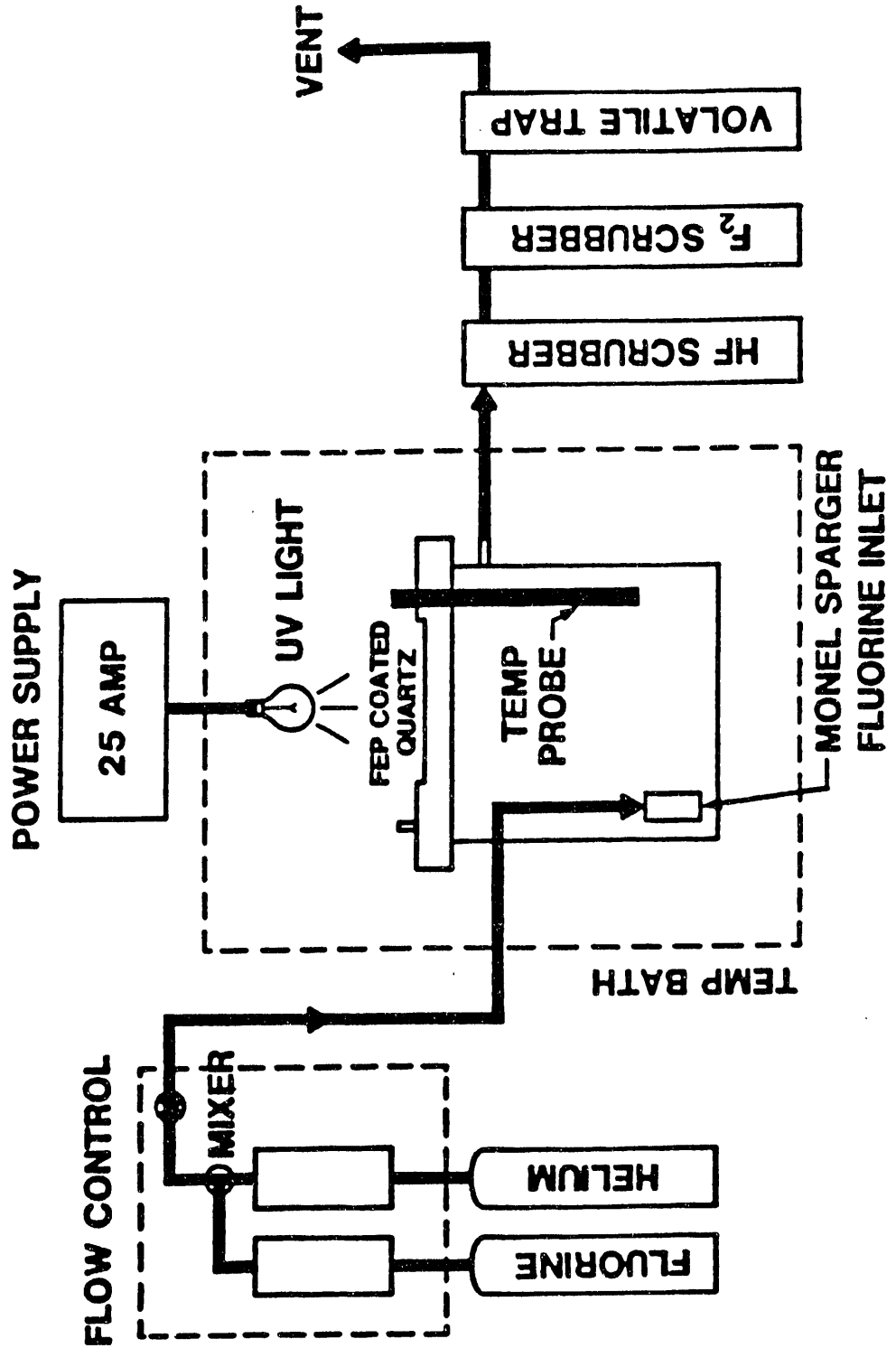
Figure 3: Schematic of the Fluorination Apparatus

39
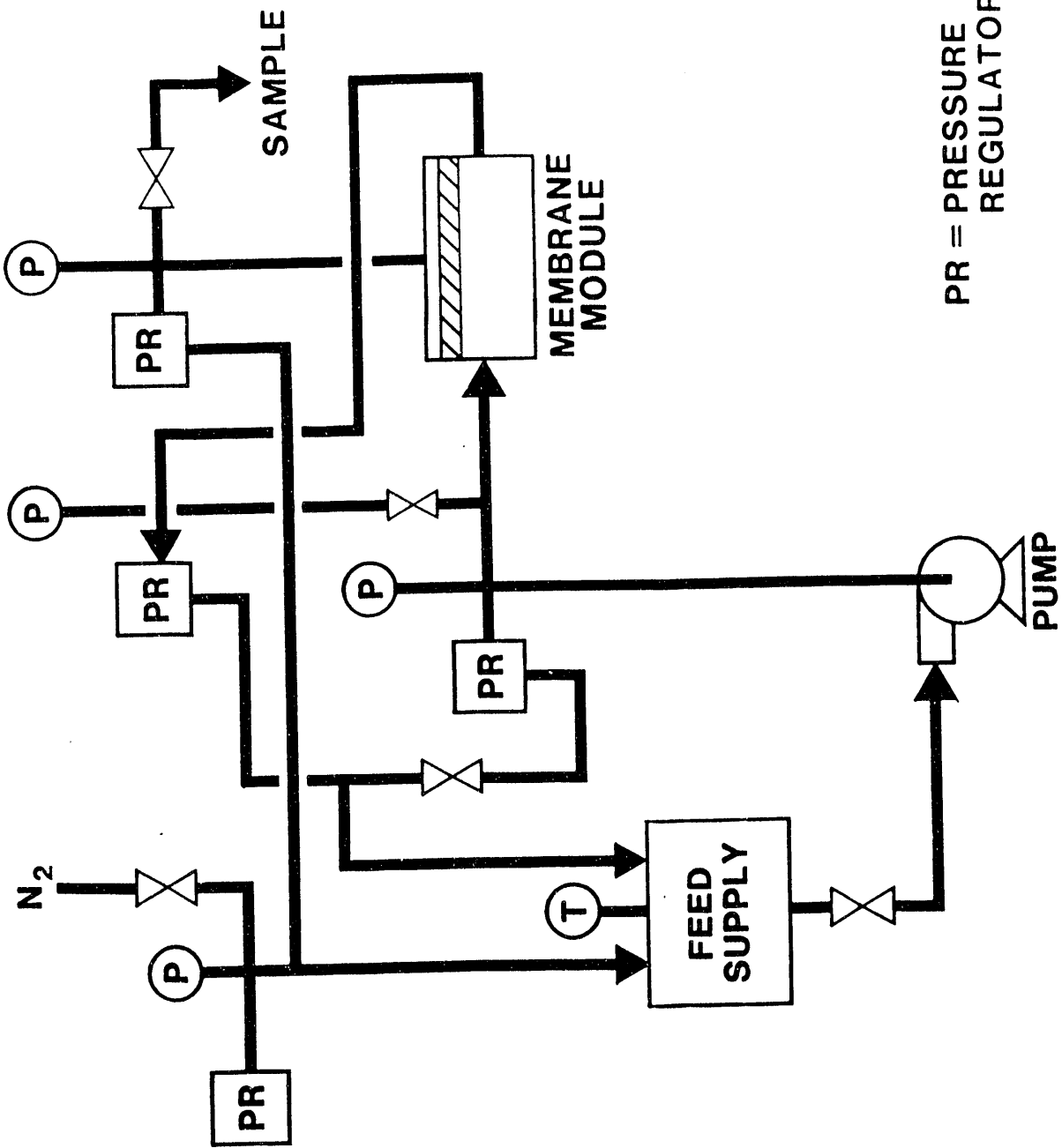
Figure 4: Schematic of a Test System with a Single Ultrafiltration Cell

PR = PRESSURE REGULATOR

ROLL TO
ASSEMBLE

FEED SIDE
SPACER

FEED IN

PERMEATE
OUTLET

PERMEATE FLOW
(AFTER PASSAGE
THROUGH MEMBRANE)

PERMEATE
SPACER

FEED OUT

MEMBRANE ON EACH
SIDE OF PERMEATE
SPACER, GLUED TO
SEAL AROUND THREE
FREE EDGES AND
TO TUBE

A-82307
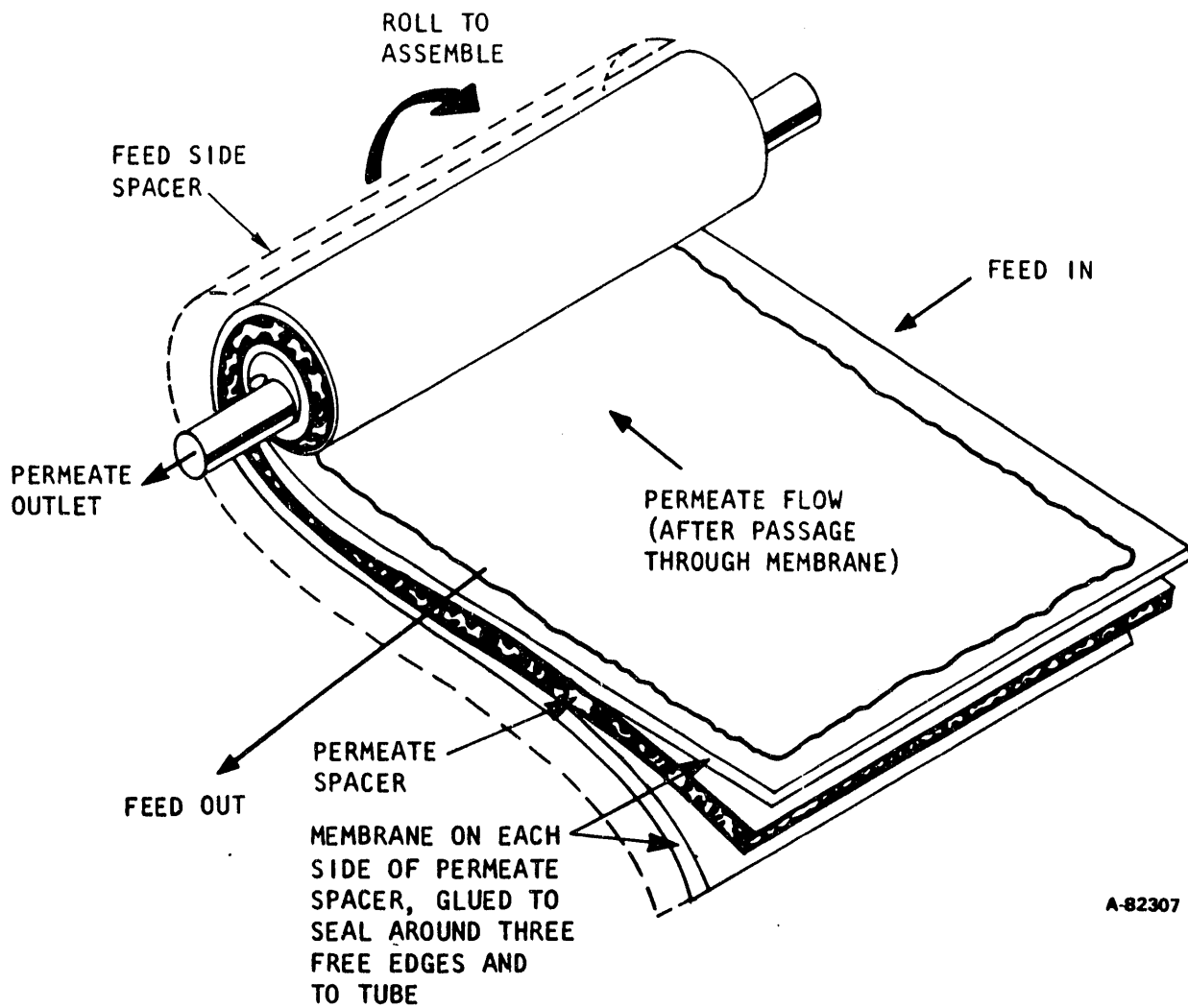
Figure 5:   Diagram of Unrolled Spiral-Wound Membrane Module

41
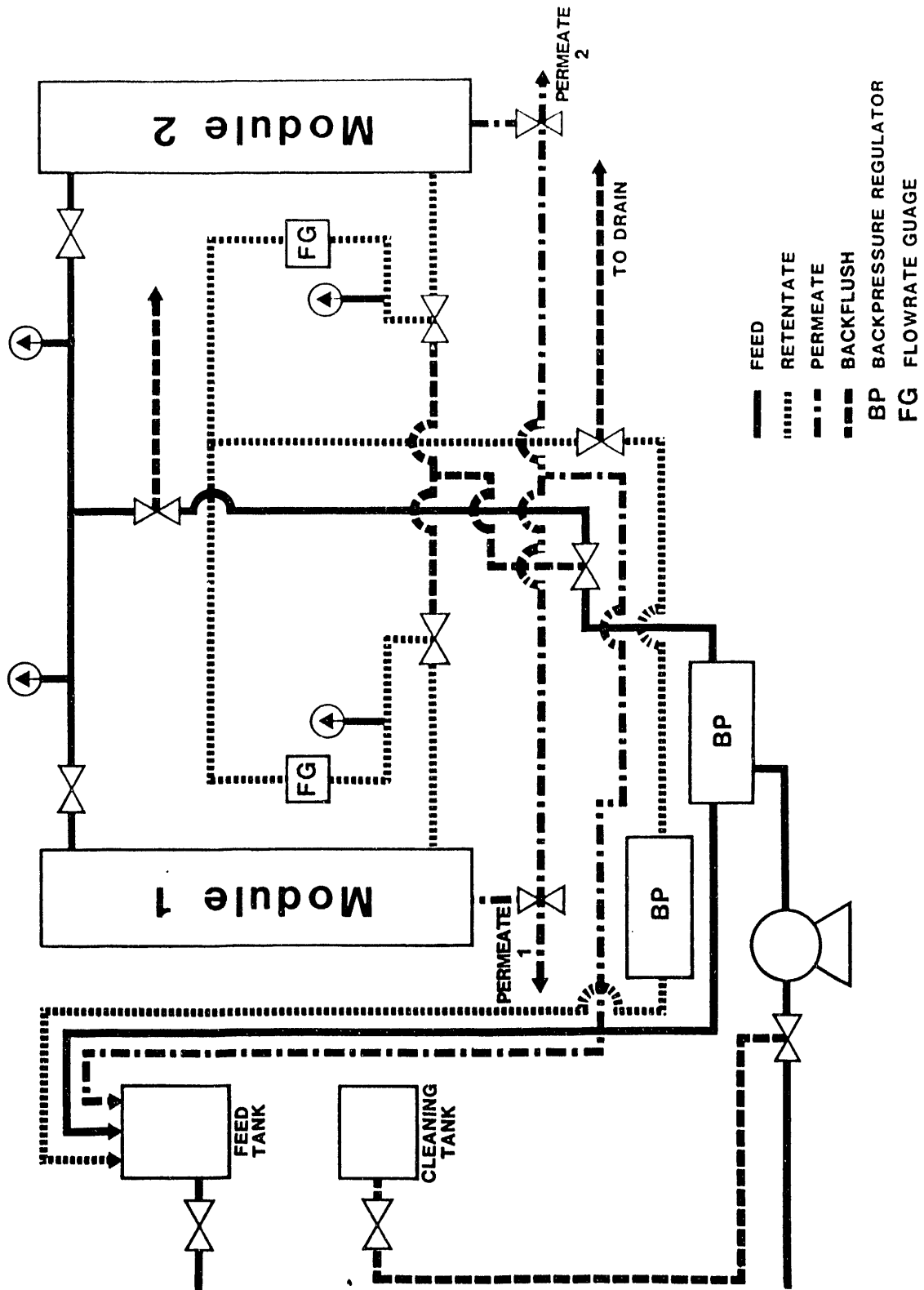
Figure 6: Flowsheet of the Spiral Module Pilot Plant

42
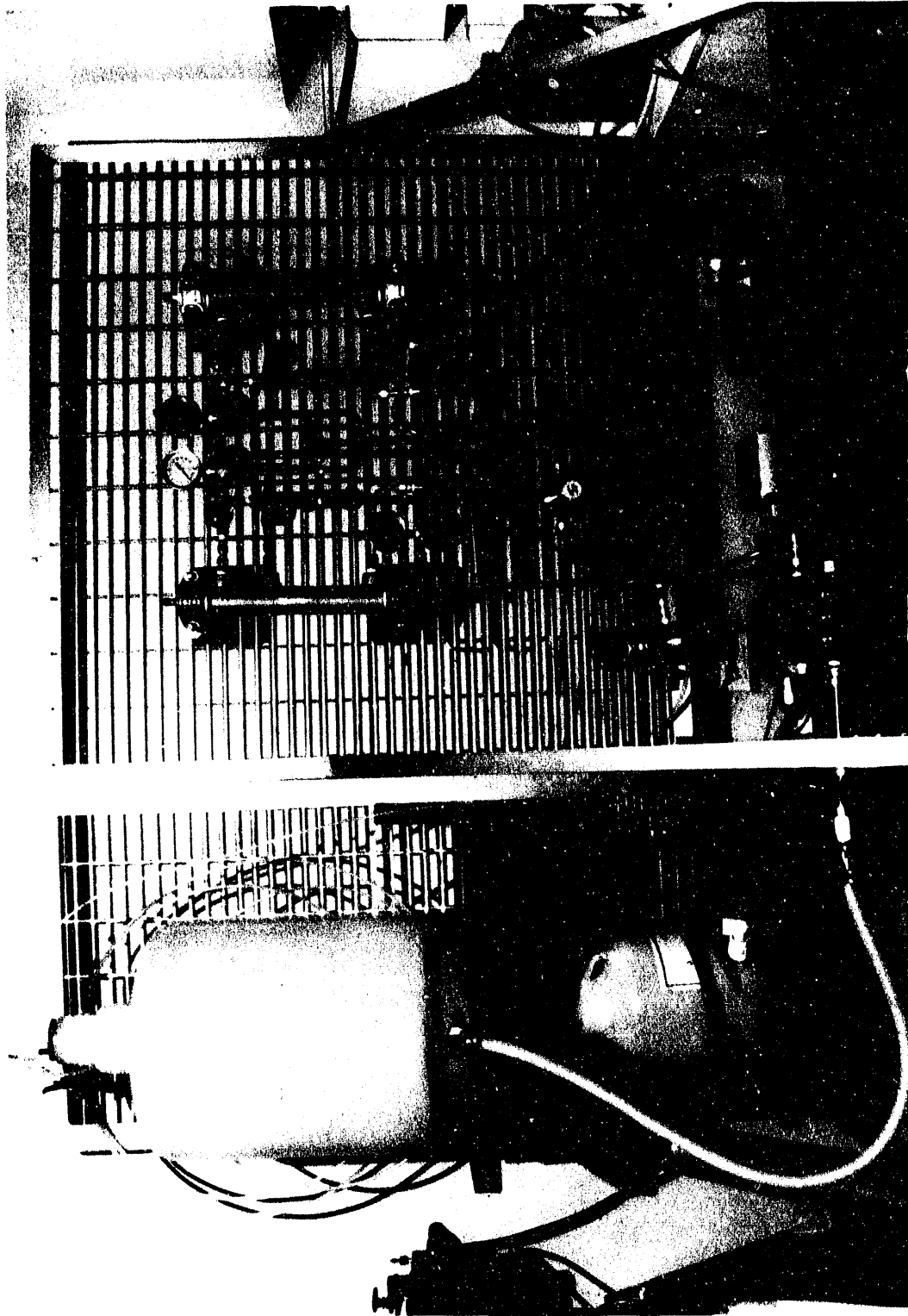
Figure 7: Photograph of the Spiral Module Pilot Plant
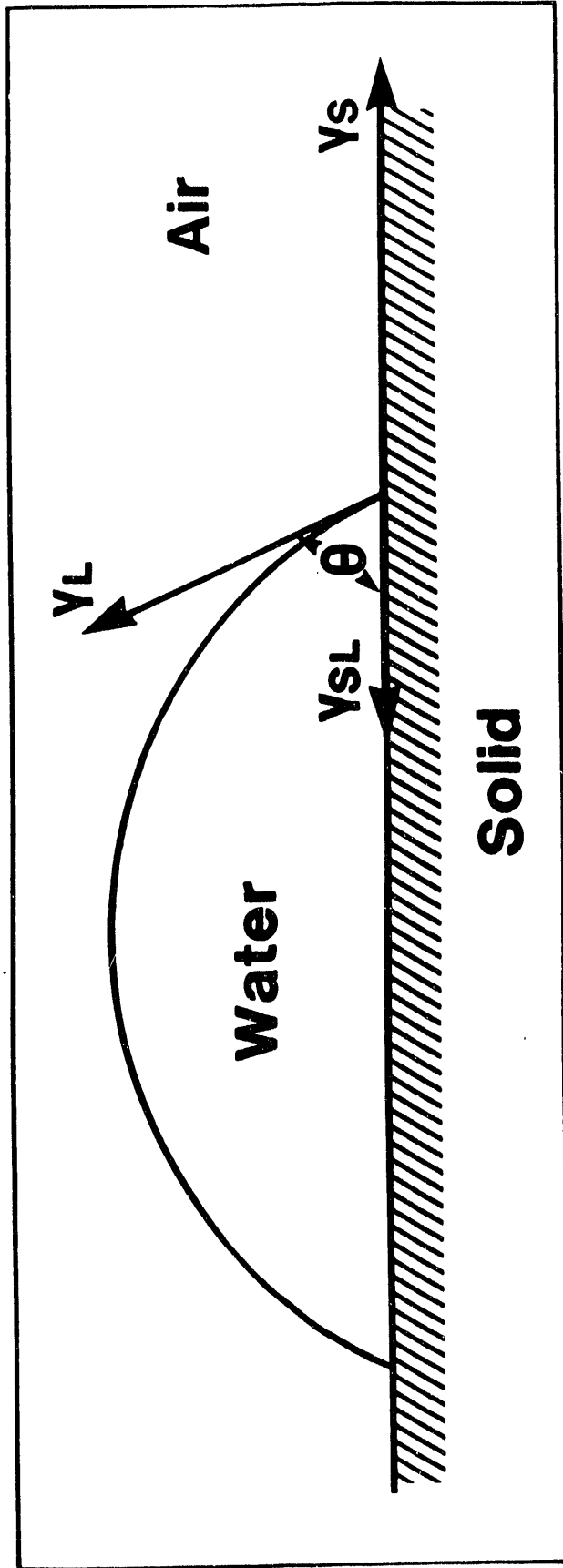
Figure 8:   Definition of Contact Angle θ at Water-Solid Interface

44
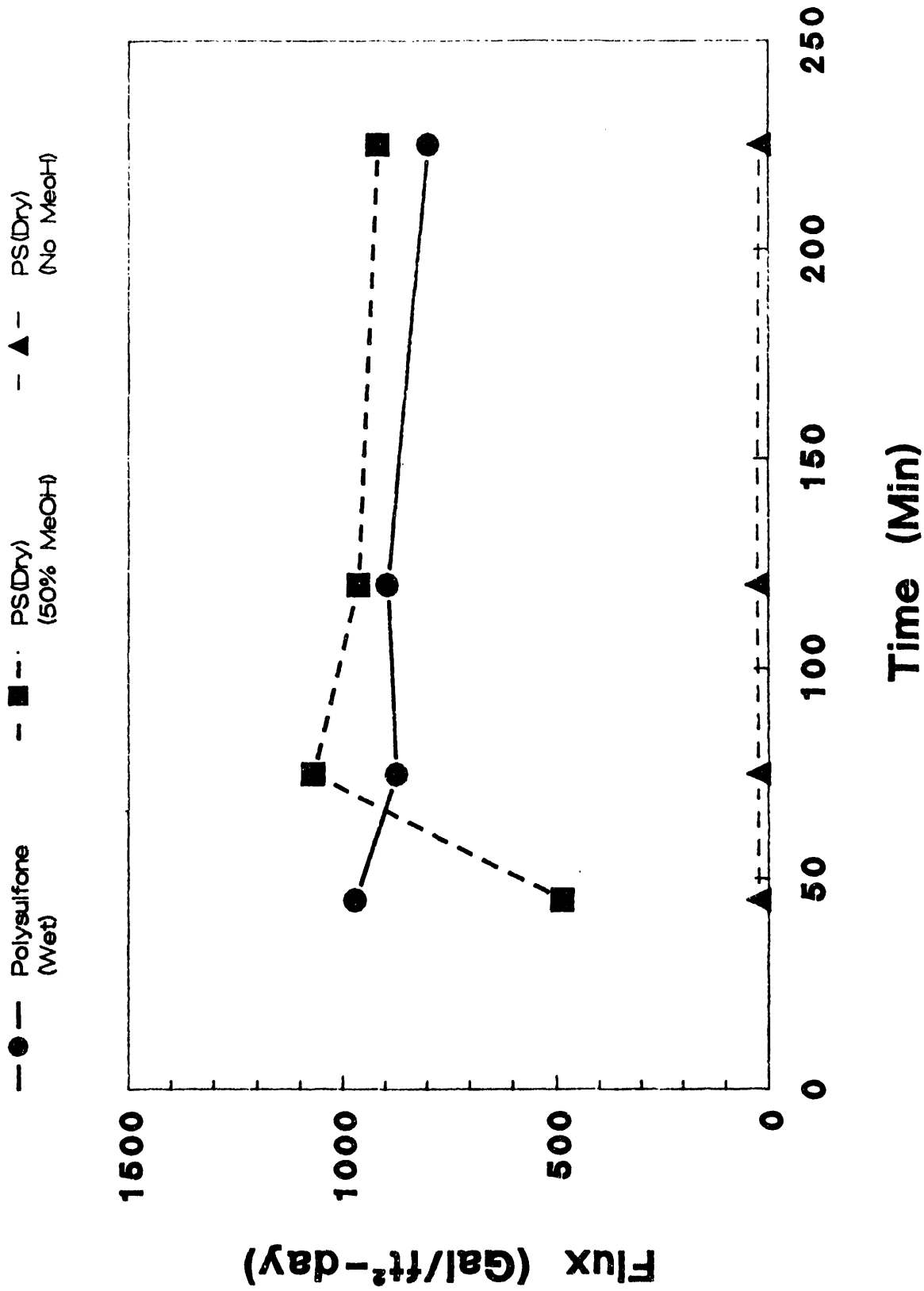
Figure 9: Comparison of DI Water Flux Through Pretreated Membranes

45
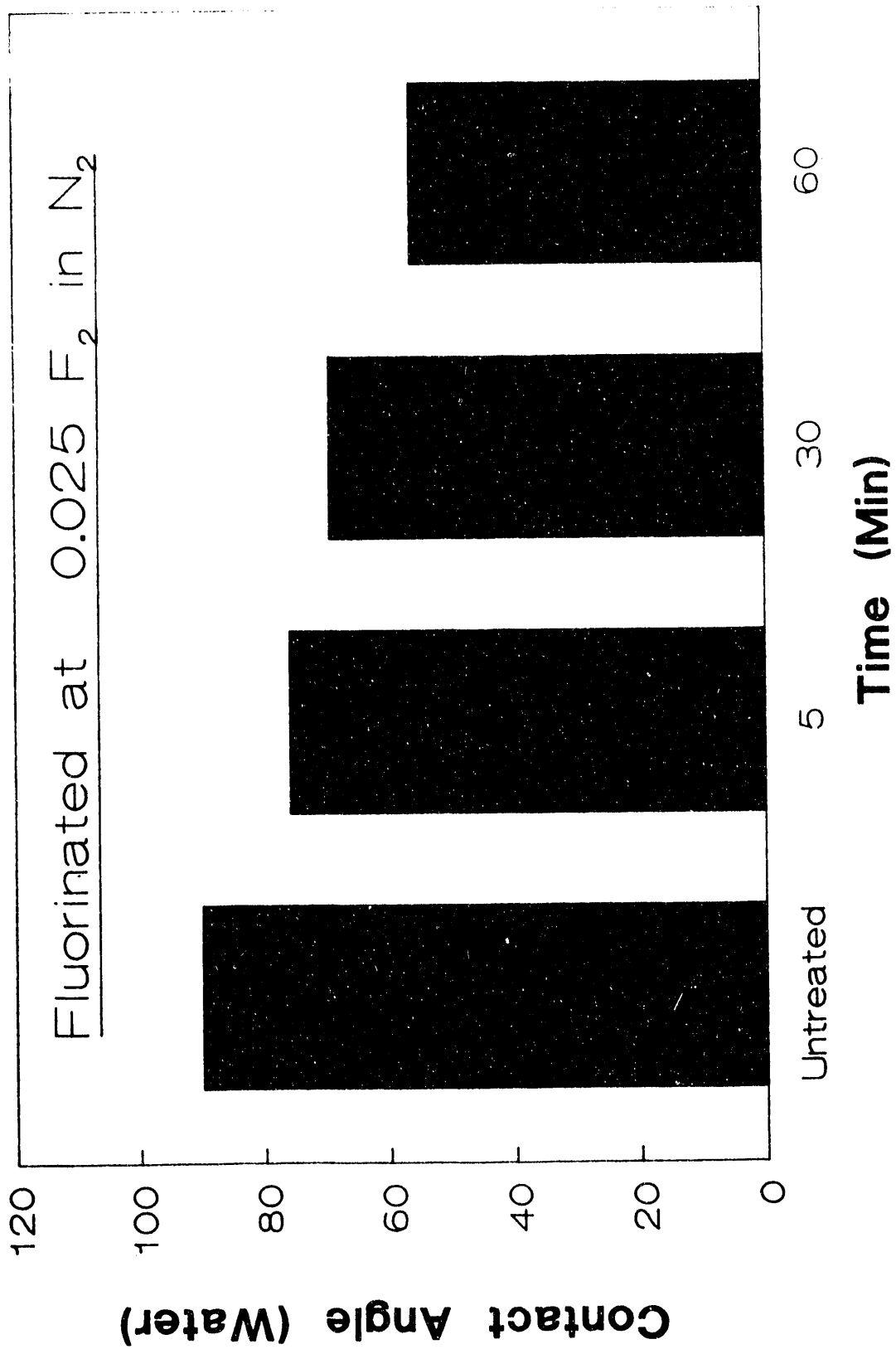
Figure 10: Contact Angle Measurements of Untreated and Fluorinated Polysulfone Membranes
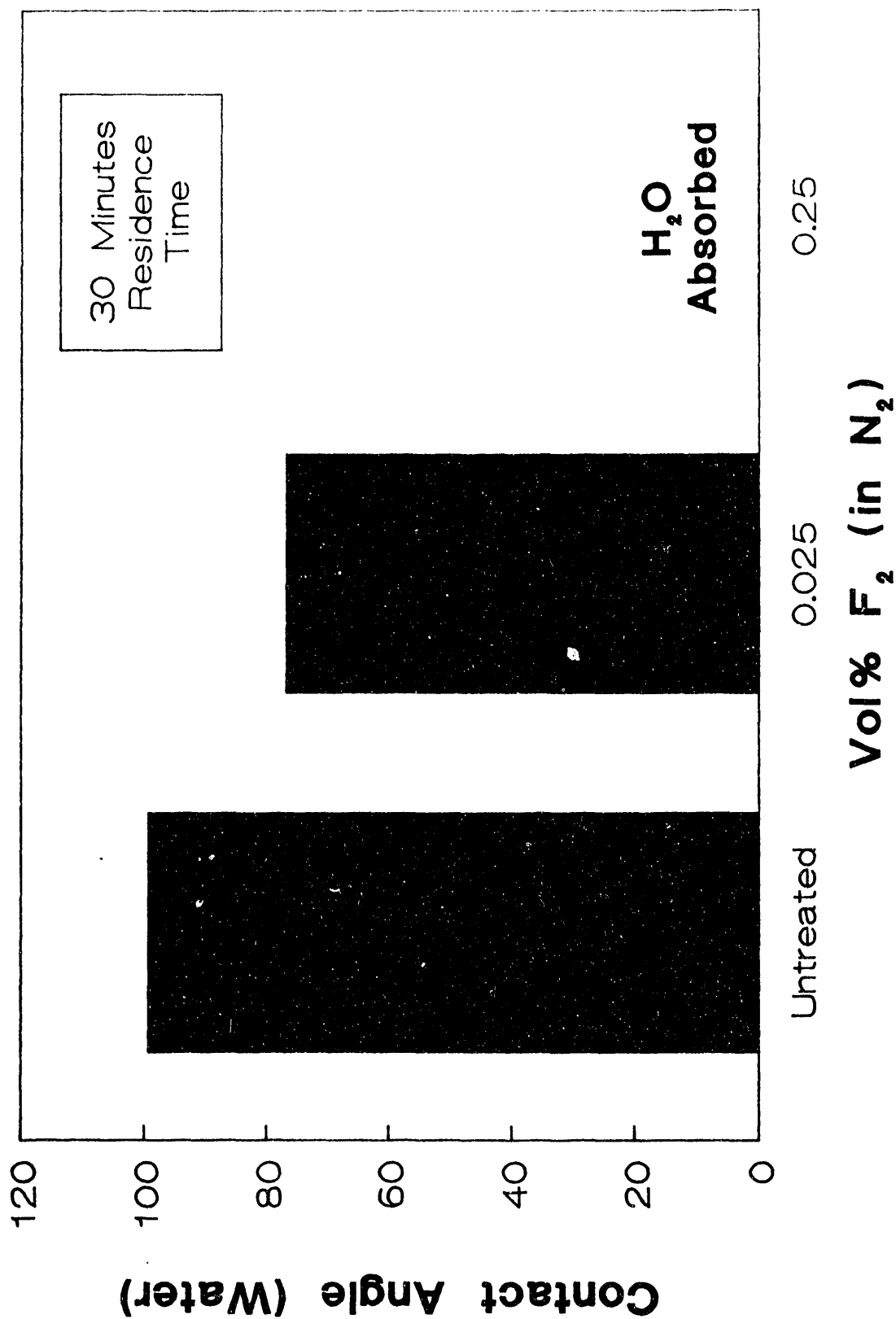
Figure 11: Contact Angle Measurements of Untreated and Fluorinated Polyethylene Membranes
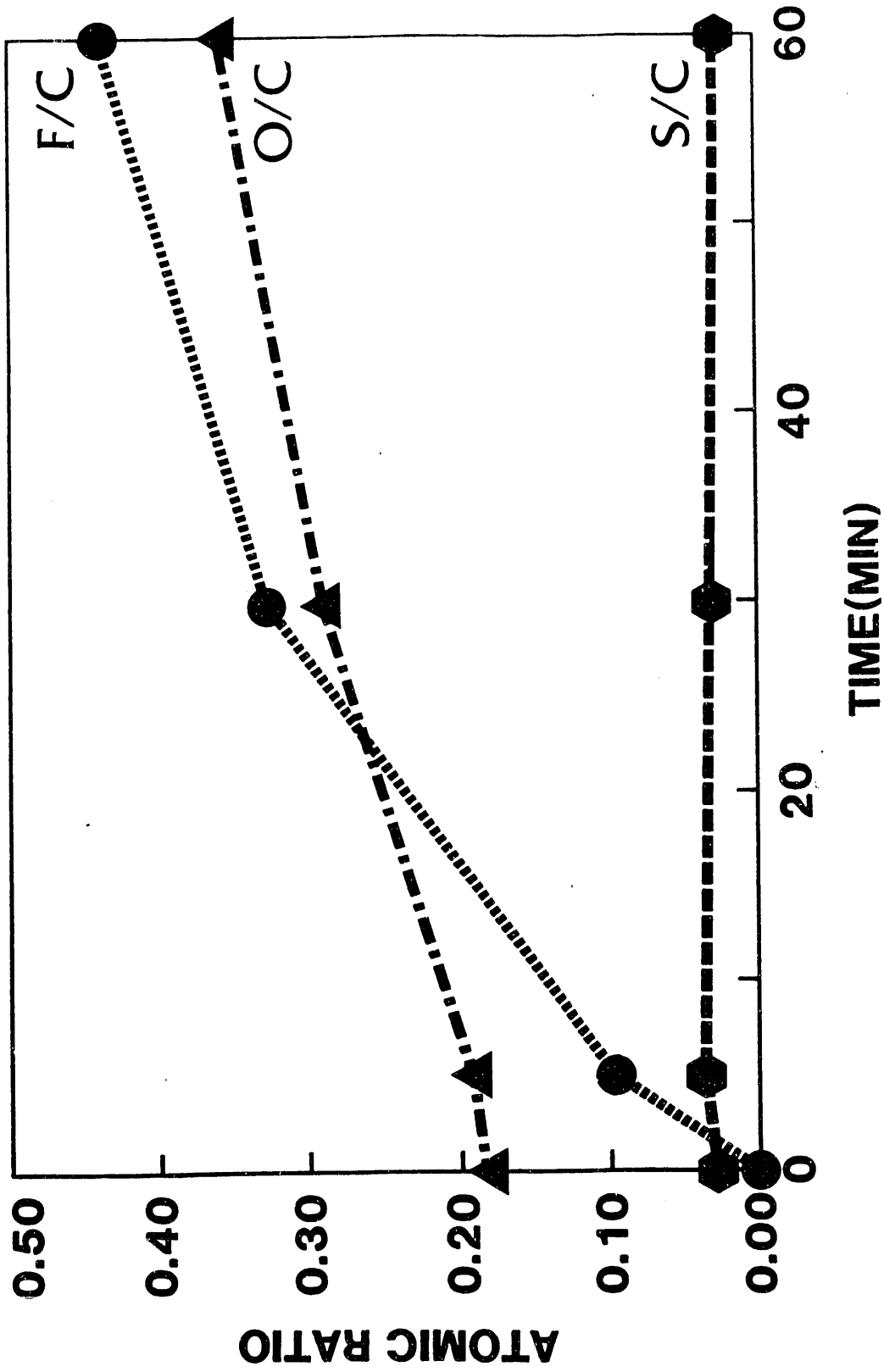
Figure 12: Atomic Ratios for Untreated and Fluorinated Polysulfone Membranes as Determined by X-ray Photoelectron Spectroscopy.

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Feed

Untreated

$0.025 \ F_2/He$
30 Minutes

$0.025 \ F_2/He$
60 Minutes

5.5×10^4

Amplitude

Increasing MW
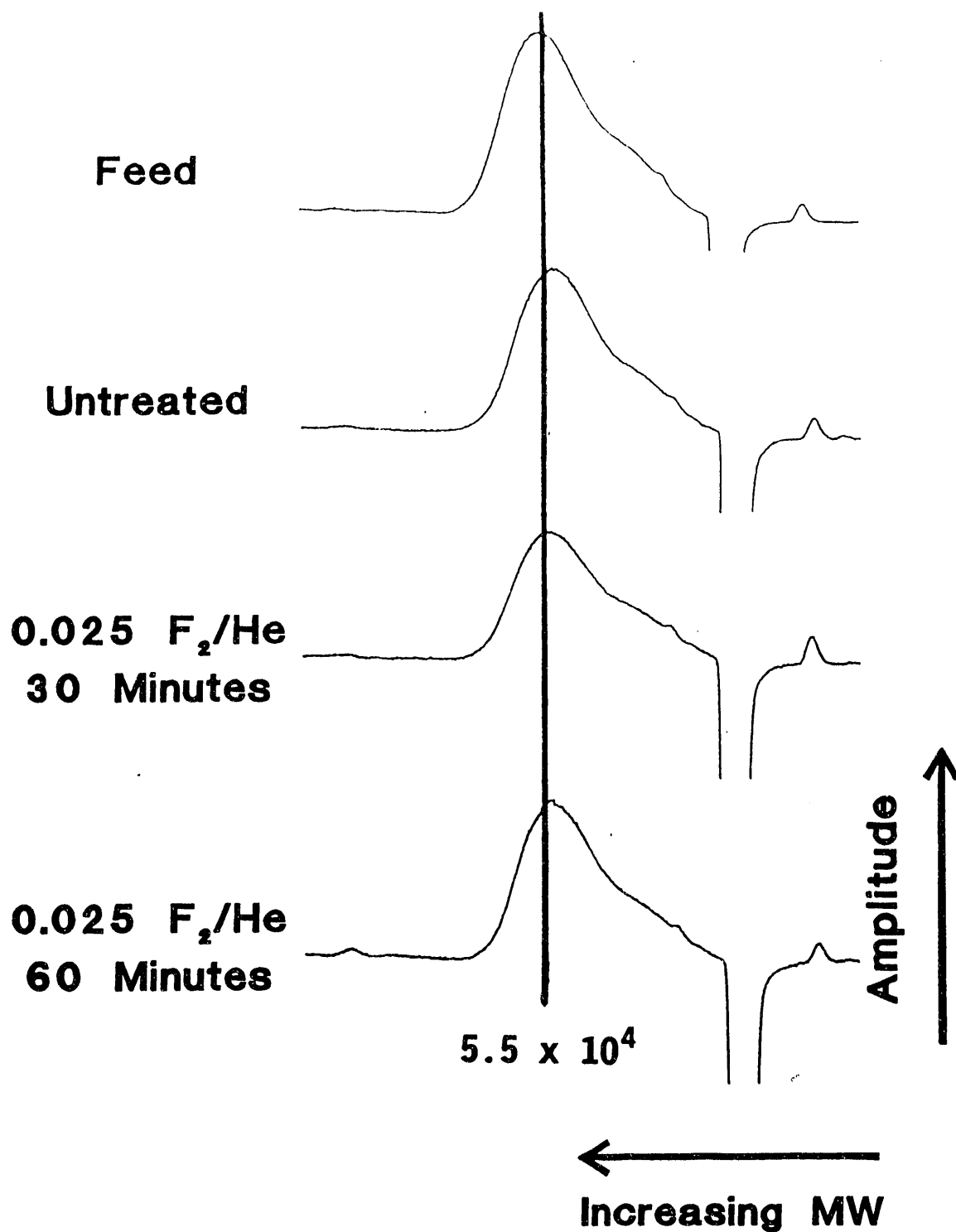
Figure 13: Gel Permeation Chromatograms of Low Molecular Weight Dextran Feed Through Untreated and Fluorinated Polysulfone Membranes

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Feed

Untreated   3X

0.025 F$_2$/He
30 Minutes   3X

0.025 F$_2$/He
60 Minutes   3X

1.0 x 10^6

2.2 x 10^5

Increasing MW
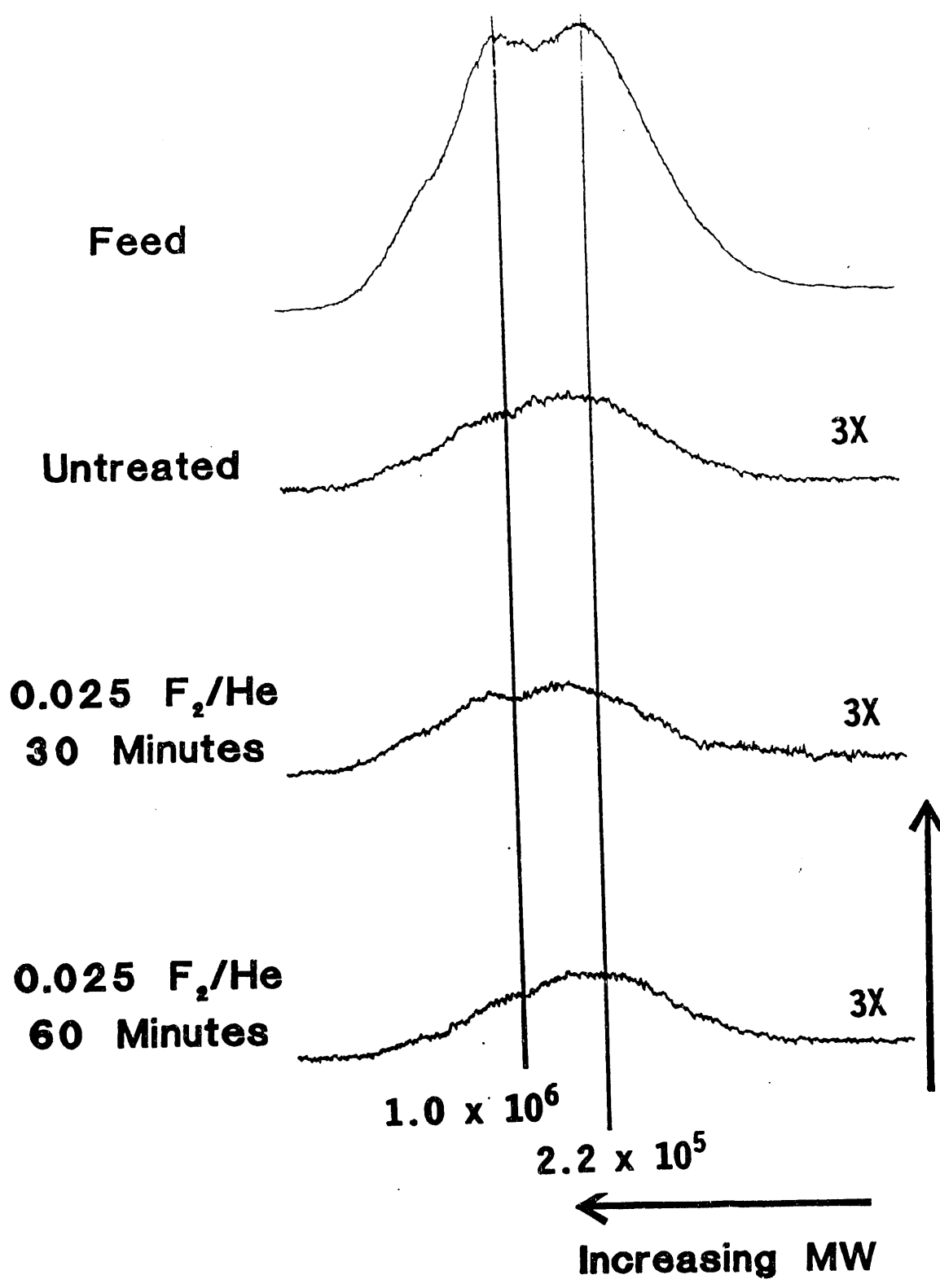
Figure 14: Gel Permeation Chromatograms of High Molecular Weight Dextran Feed Through Untreated and Fluorinated Polysulfone Membranes

50
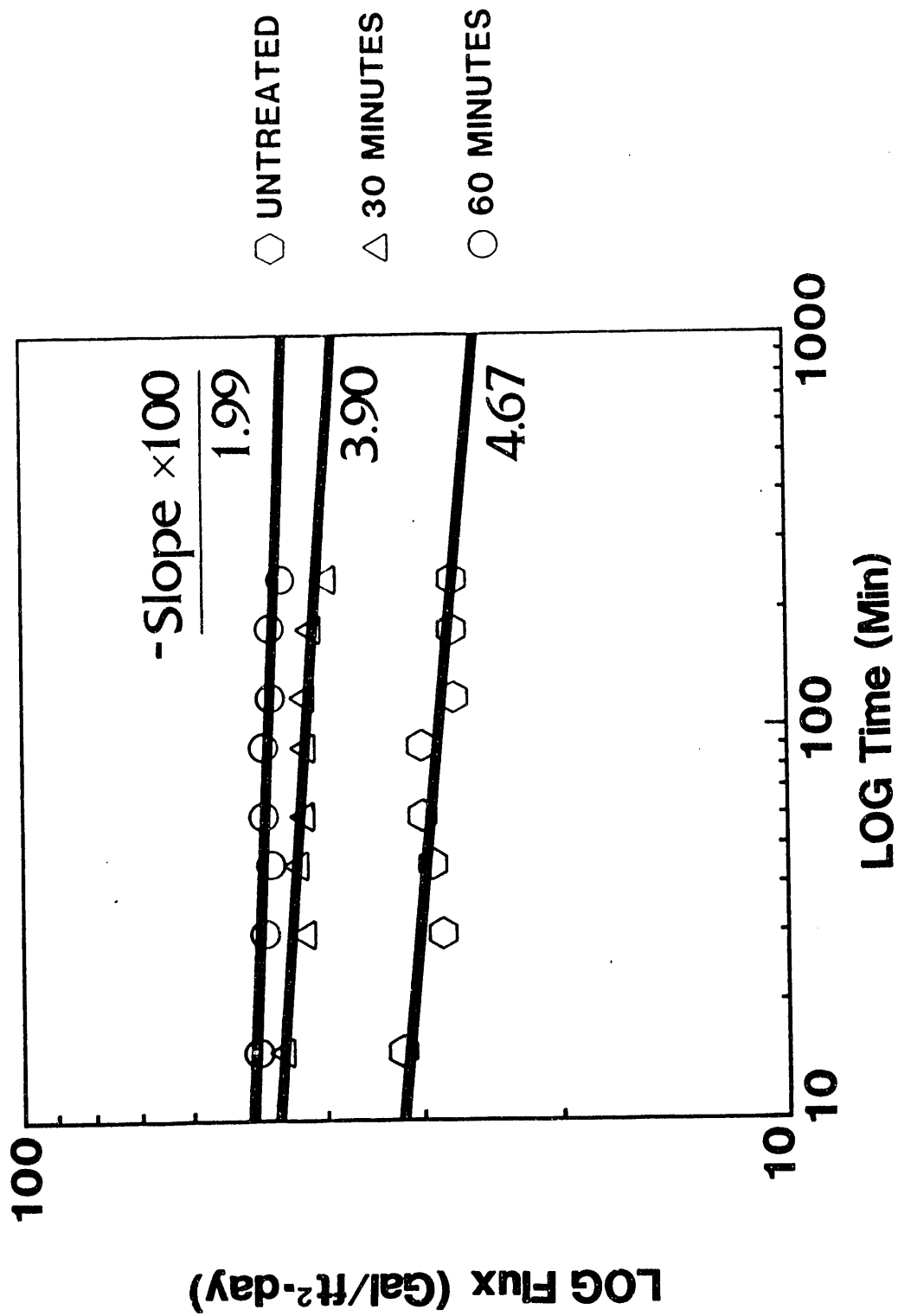
Figure 15: Performance Results of Untreated and Fluorinated Polysulfone Membranes In Flat Sheet Study
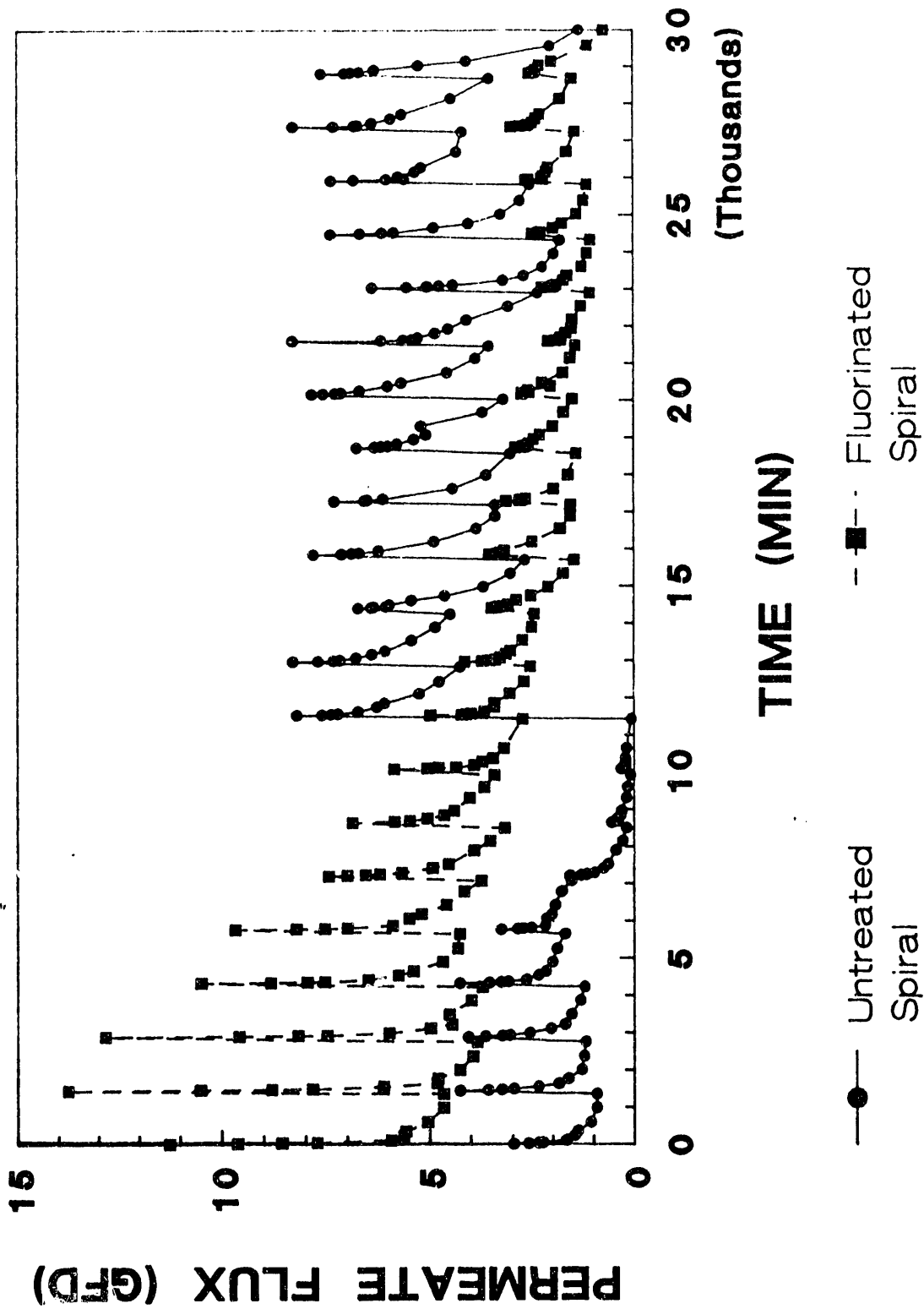
Figure 16: Performance Results of Untreated and Fluorinated Polysulfone Membranes In Pilot Study #1
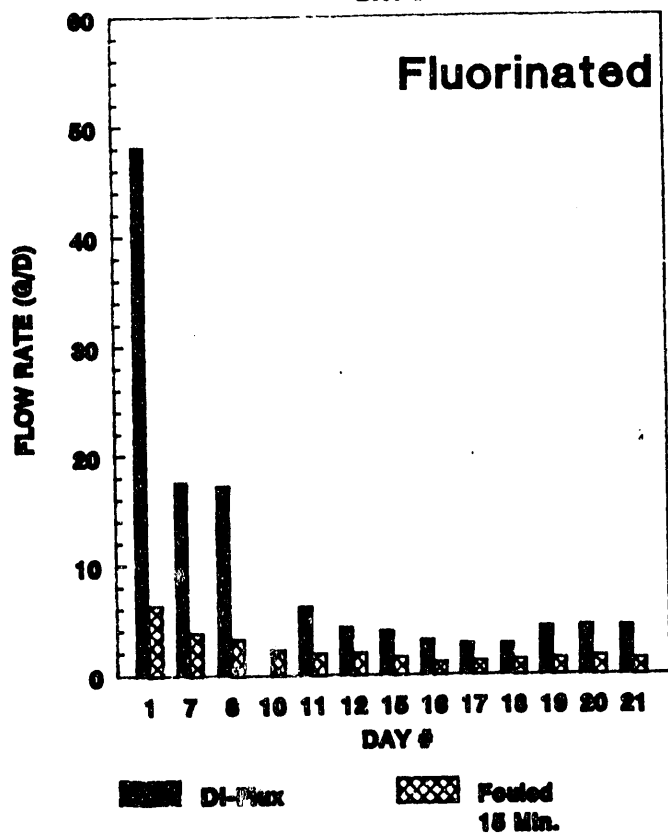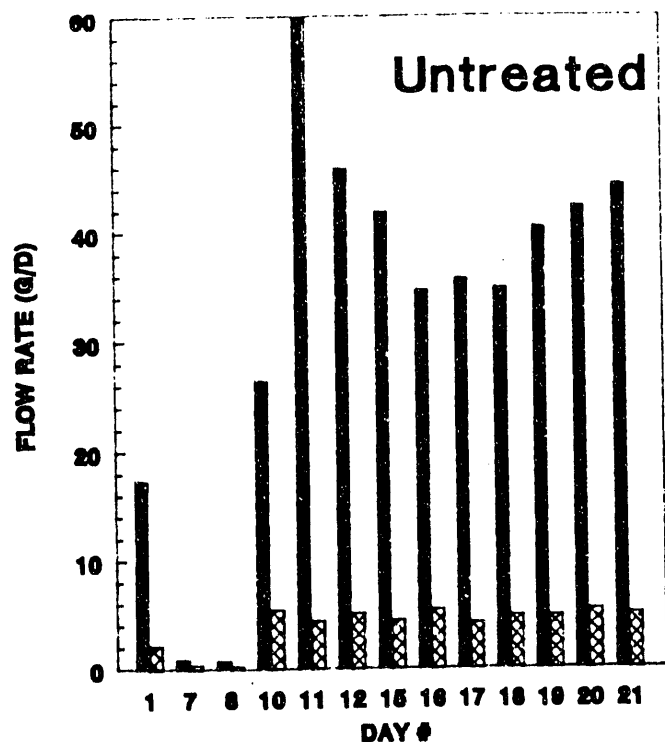
Figure 17: DI Water and Permeate Flow Rates (15 Minute) of Untreated and Fluorinated Polysulfone Membranes In Pilot Study #1
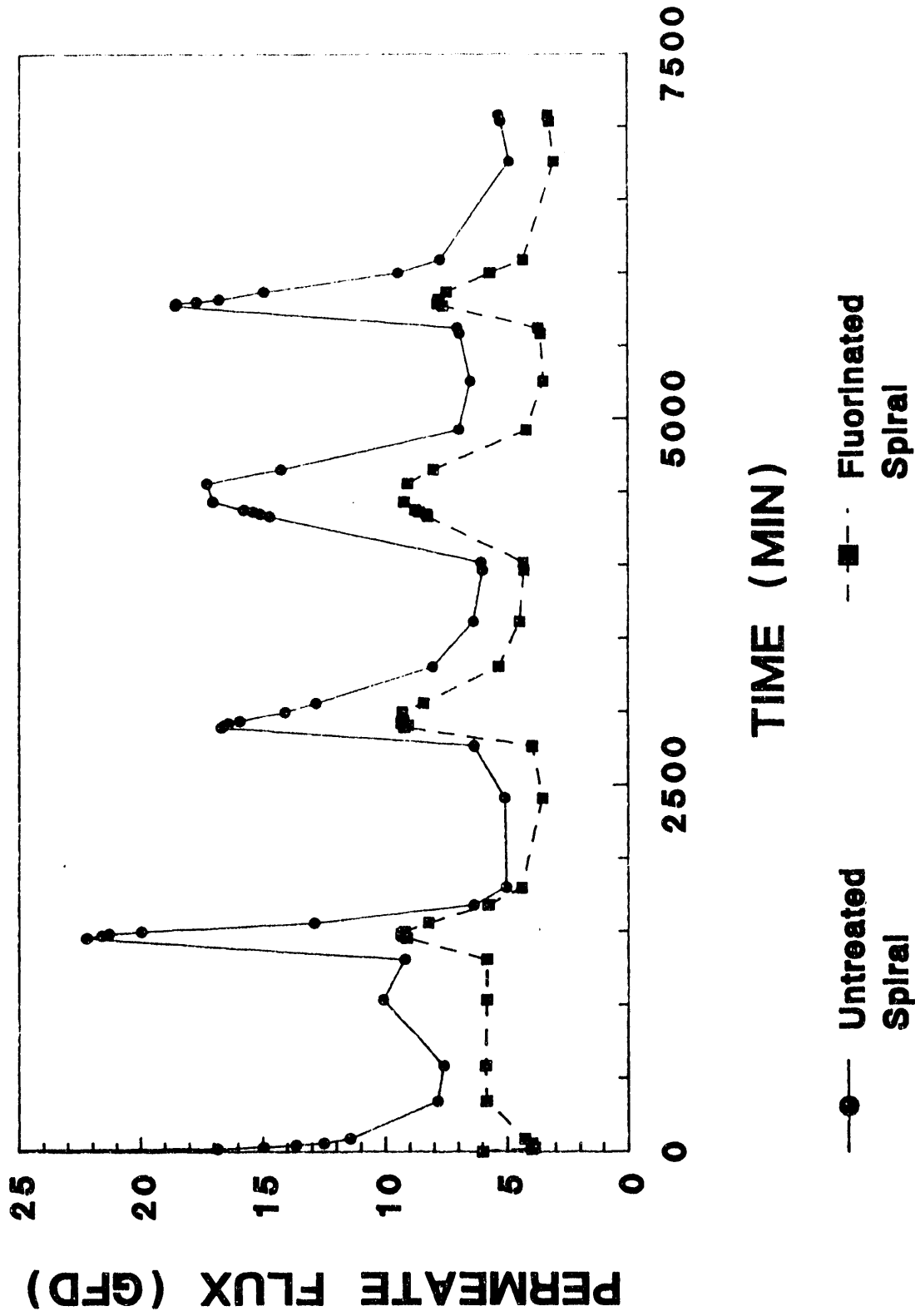
Figure 18: Performance Results of Untreated and Fluorinated Polysulfone Membranes In Pilot Study #2

54
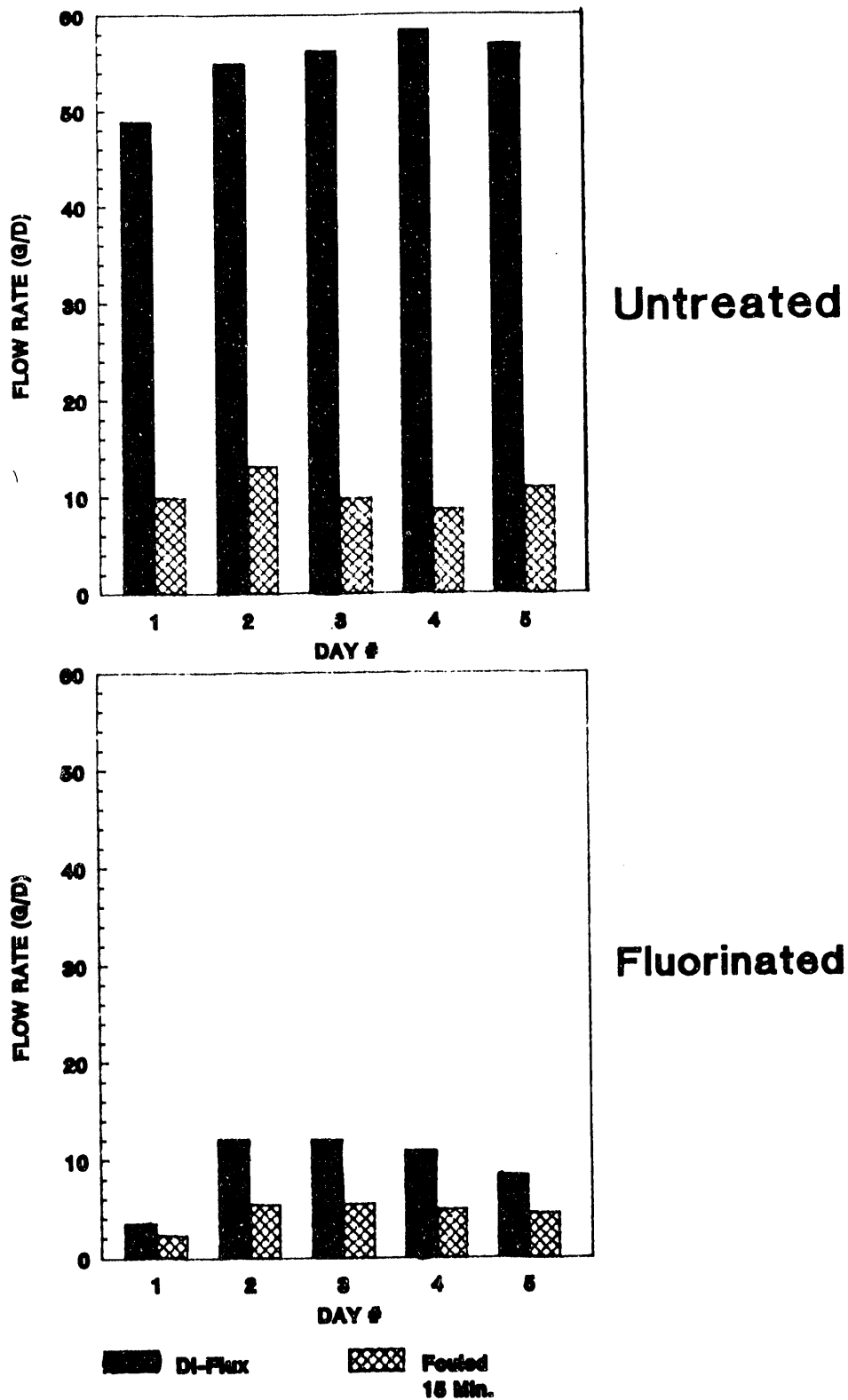
Figure 19: DI Water and Permeate Flow Rates (15 Minute) of Untreated and Fluorinated Polysulfone Membranes In Pilot Study #2
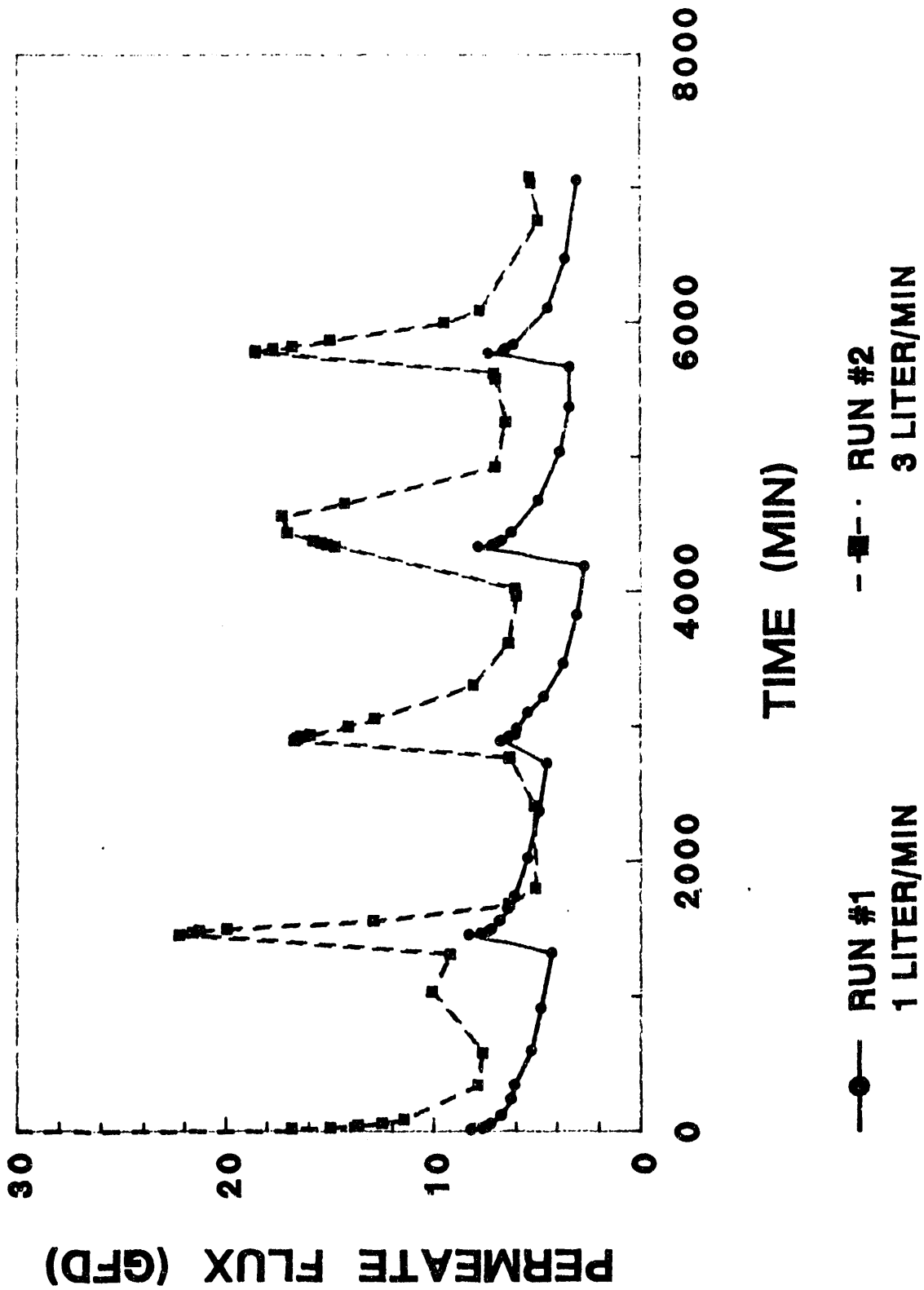
Figure 20: Comparison of Untreated Polysulfone Membranes From Pilot Studies #1 and #2
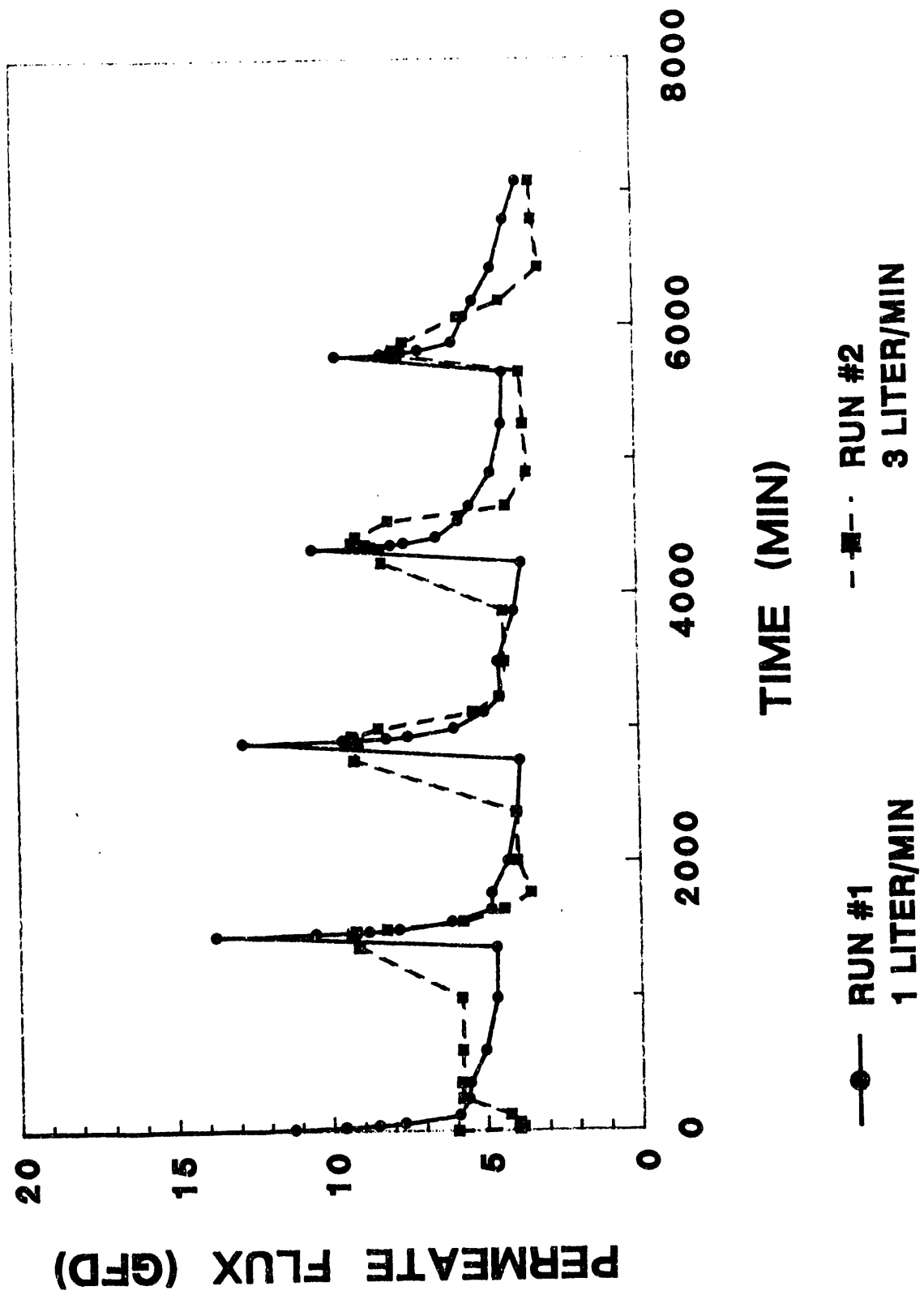
Figure 21: Comparison of Fluorinated Polysulfone Membranes From Pilot Studies #1 and #2

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RI Amplitude

Molecular Weight

2.0 x 10⁵

8.4 x 10⁶

Feed
(1310 Min. Reading)
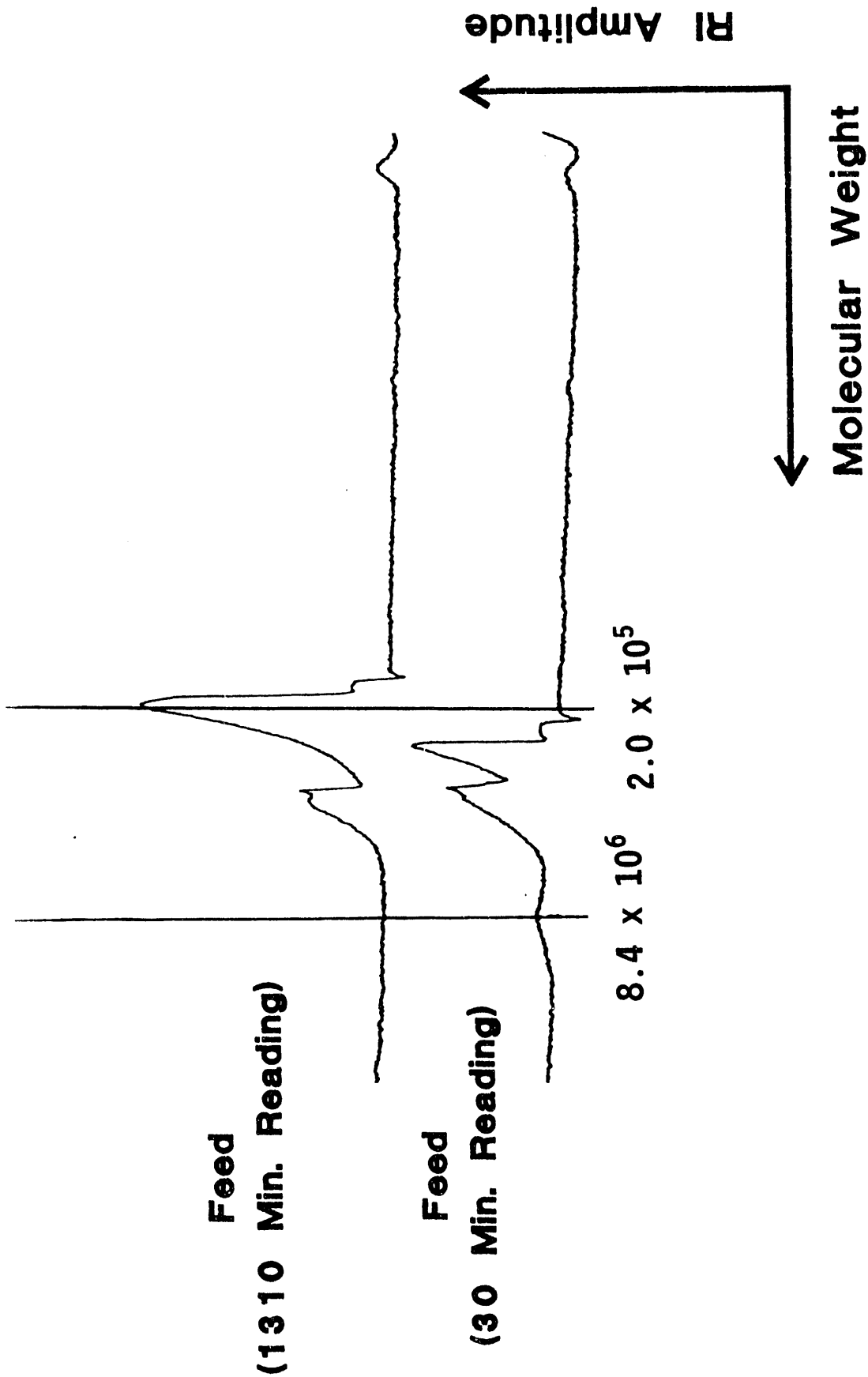
Feed
(30 Min. Reading)

Figure 22: Gel Permeation Chromatographs of the Degradation of
the Industrial Potato Waste Feed During Run
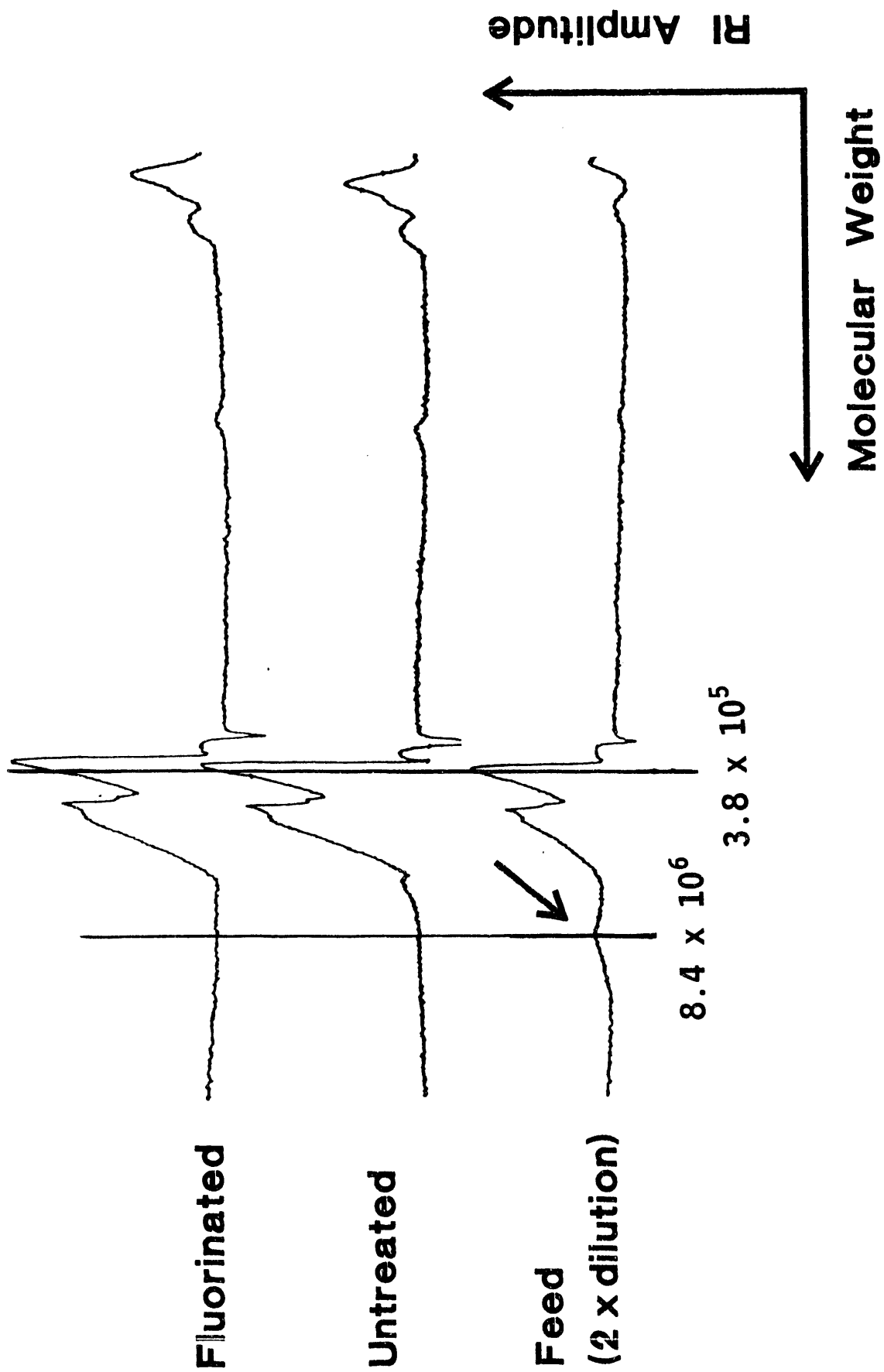
Figure 23: Gel Permeation Chromatographs of Industrial Potato Feed Through Untreated and Fluorinated Polysulfone Membranes (30 Minute Reading)

RI Amplitude

Molecular Weight

Fluorinated

Untreated

Feed
(2 x dilution)

2.0×10^5

2.0×10^5

8.4×10^6

60
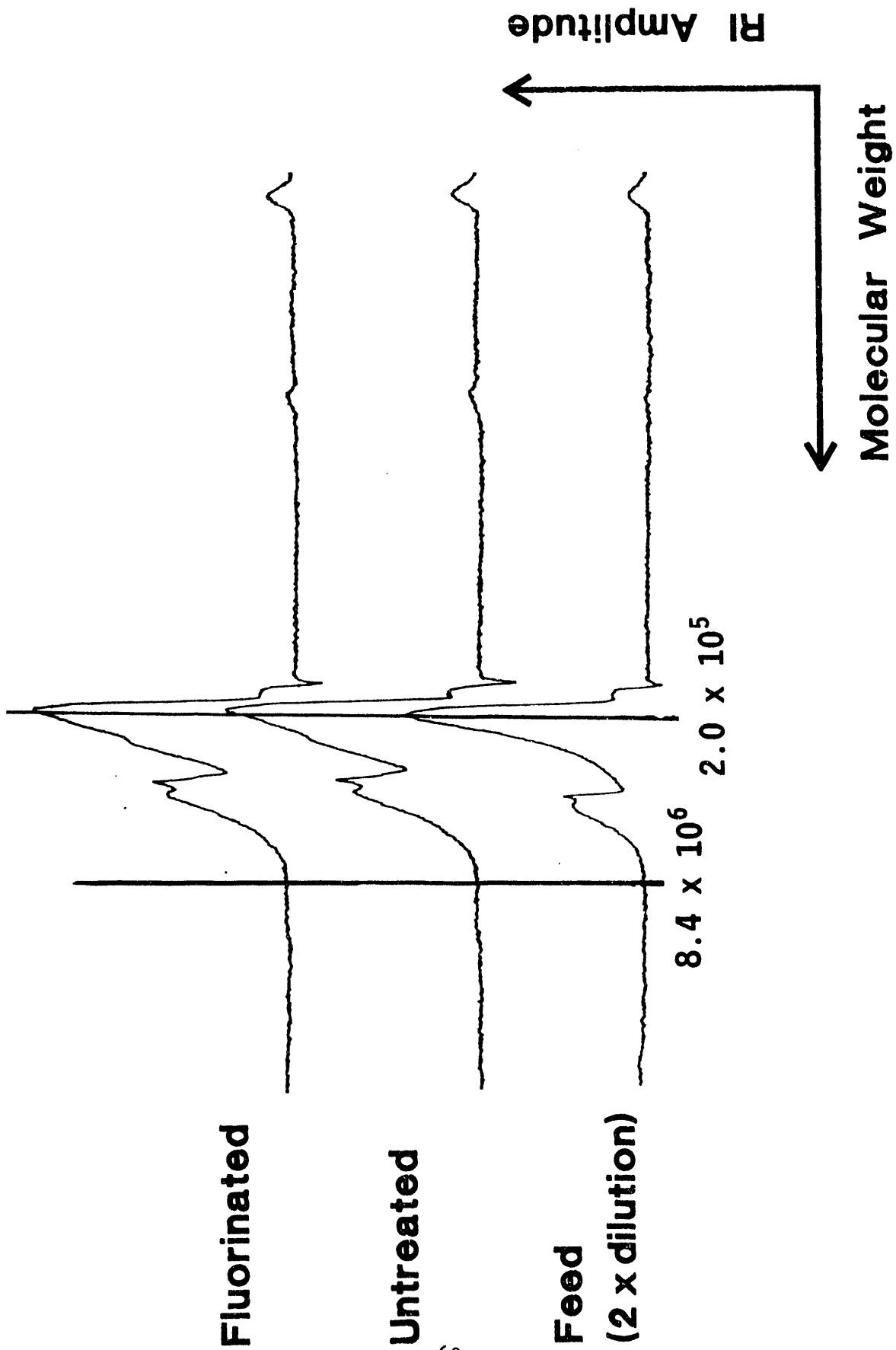
Figure 24: Gel Permeation Chromatographs of Industrial Potato Feed
Through Untreated and Fluorinated Polysulfone Membranes
(Final Reading)

Figure 25:   Photographs of Opened Spiral Modules at Conclusion of Pilot Study. The Left and Right Photographs are the Untreated and Fluorinated Membranes of Pilot Study #1, Respectively.
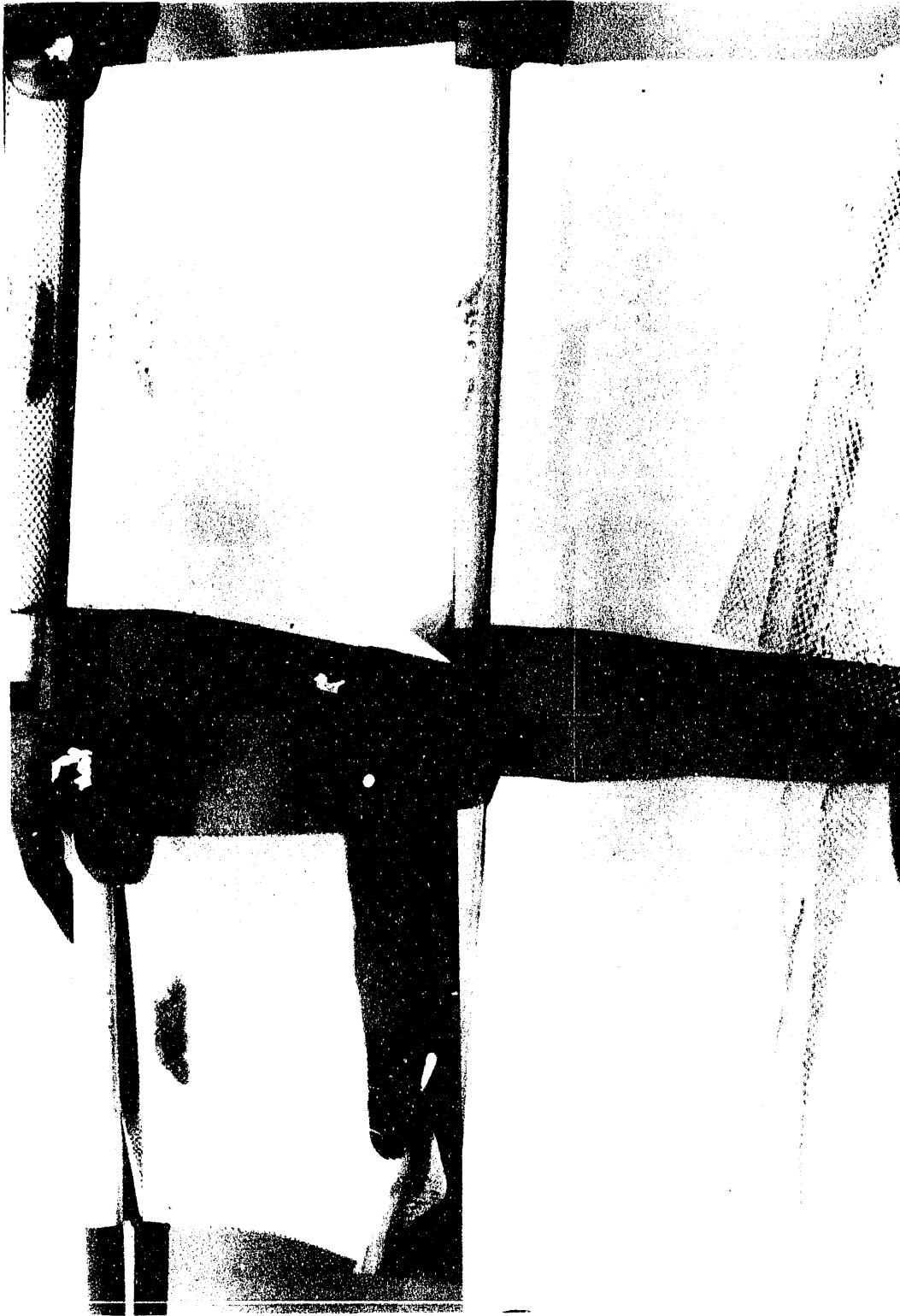
Figure 26: Photographs of Opened Spiral Modules at Conclusion of Pilot Study. The Left and Right Photographs are the Untreated and Fluorinated Membranes of Pilot Study #2, Respectively.
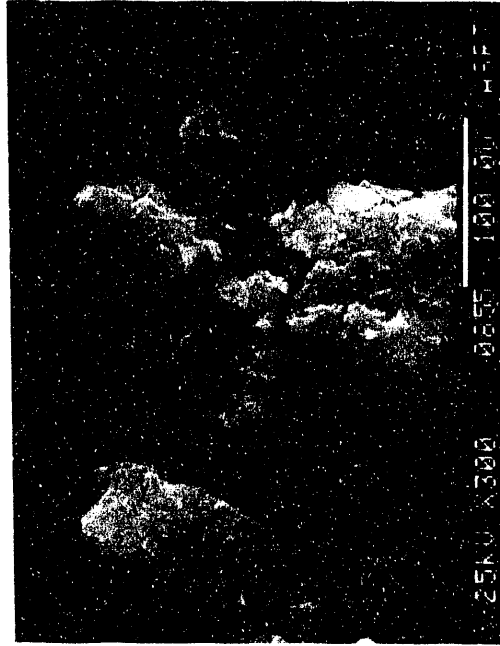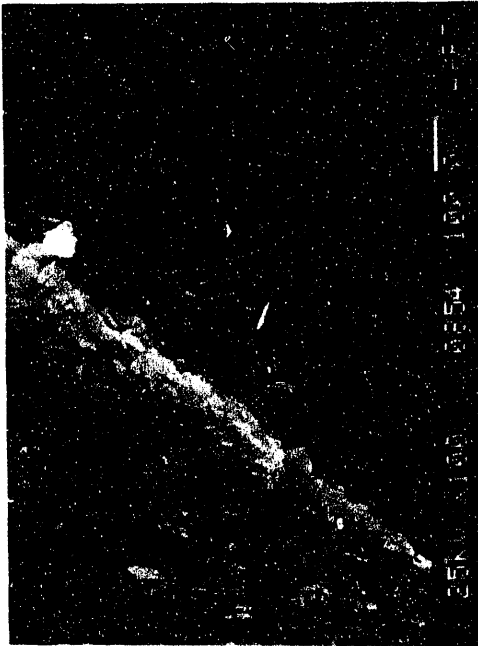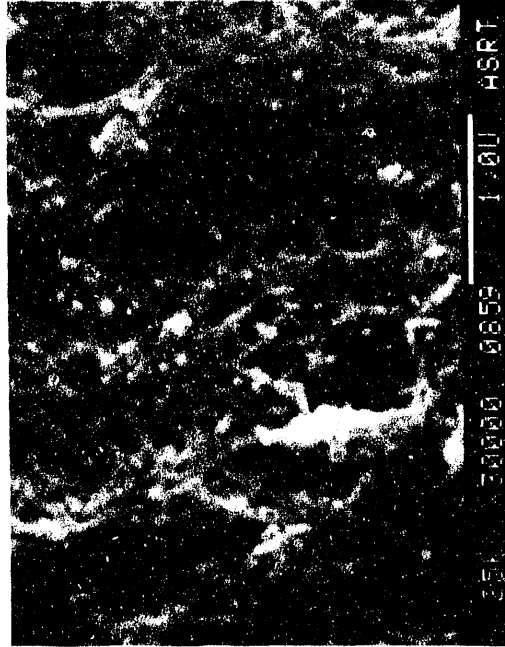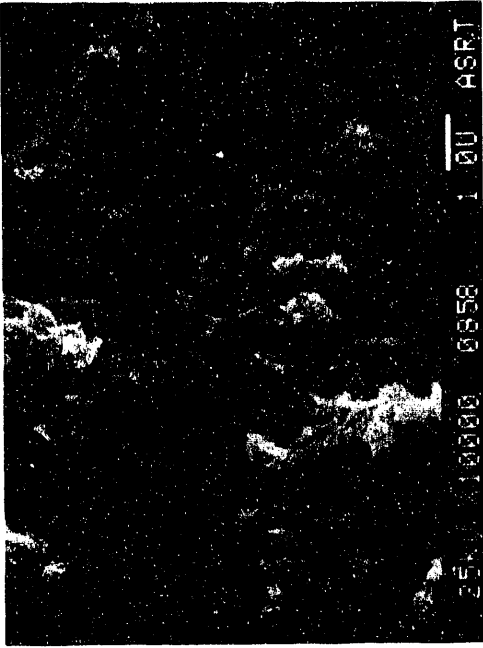
Figure 27: SEM Micrographs of the Untreated Membrane at the Conclusion of Pilot Study #1.
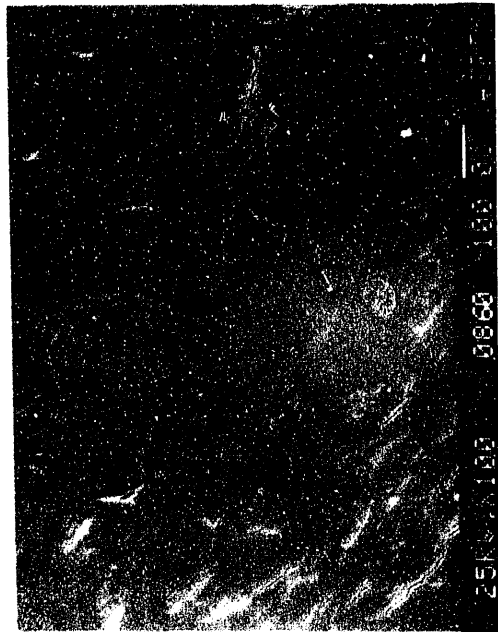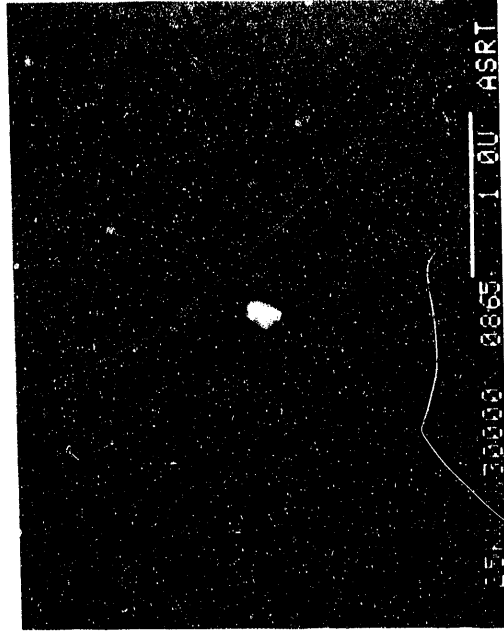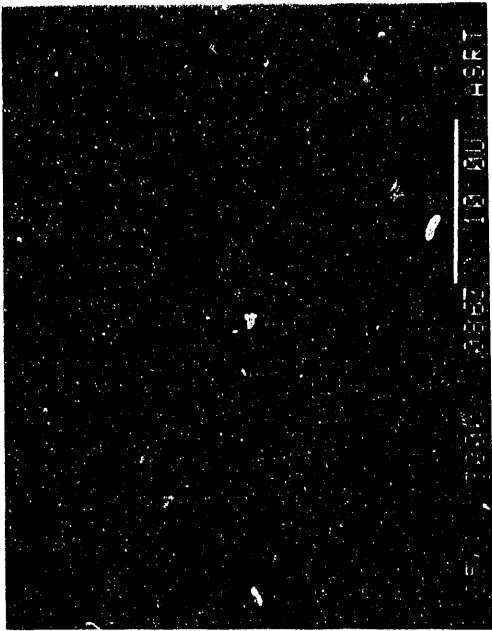
Figure 28: SEM Micrographs of the Fluorinated Membrane at the Conclusion of Pilot Study #1.
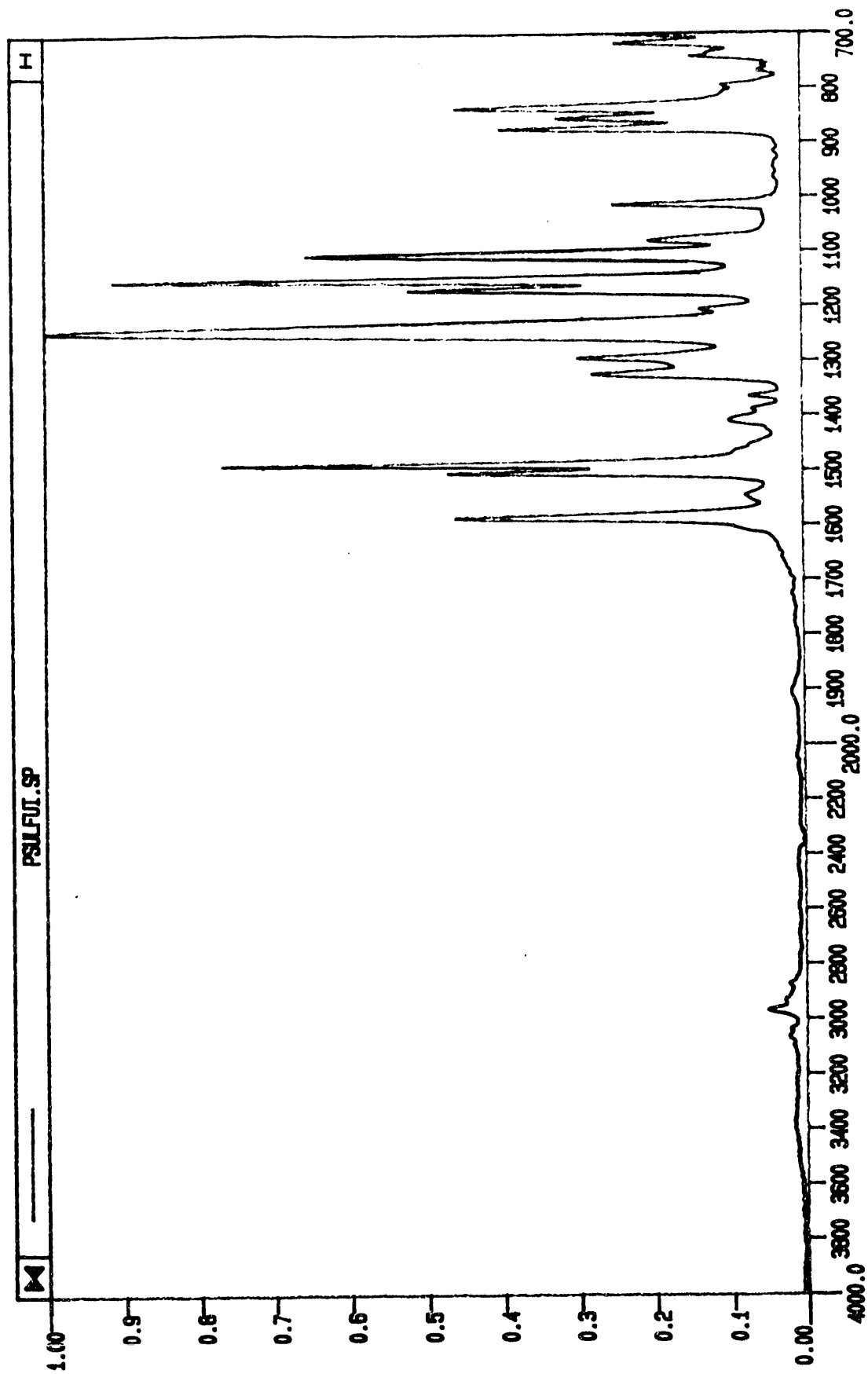
Figure 29: ATR-FTIR Spectra of the Non-Fouled Untreated Membrane
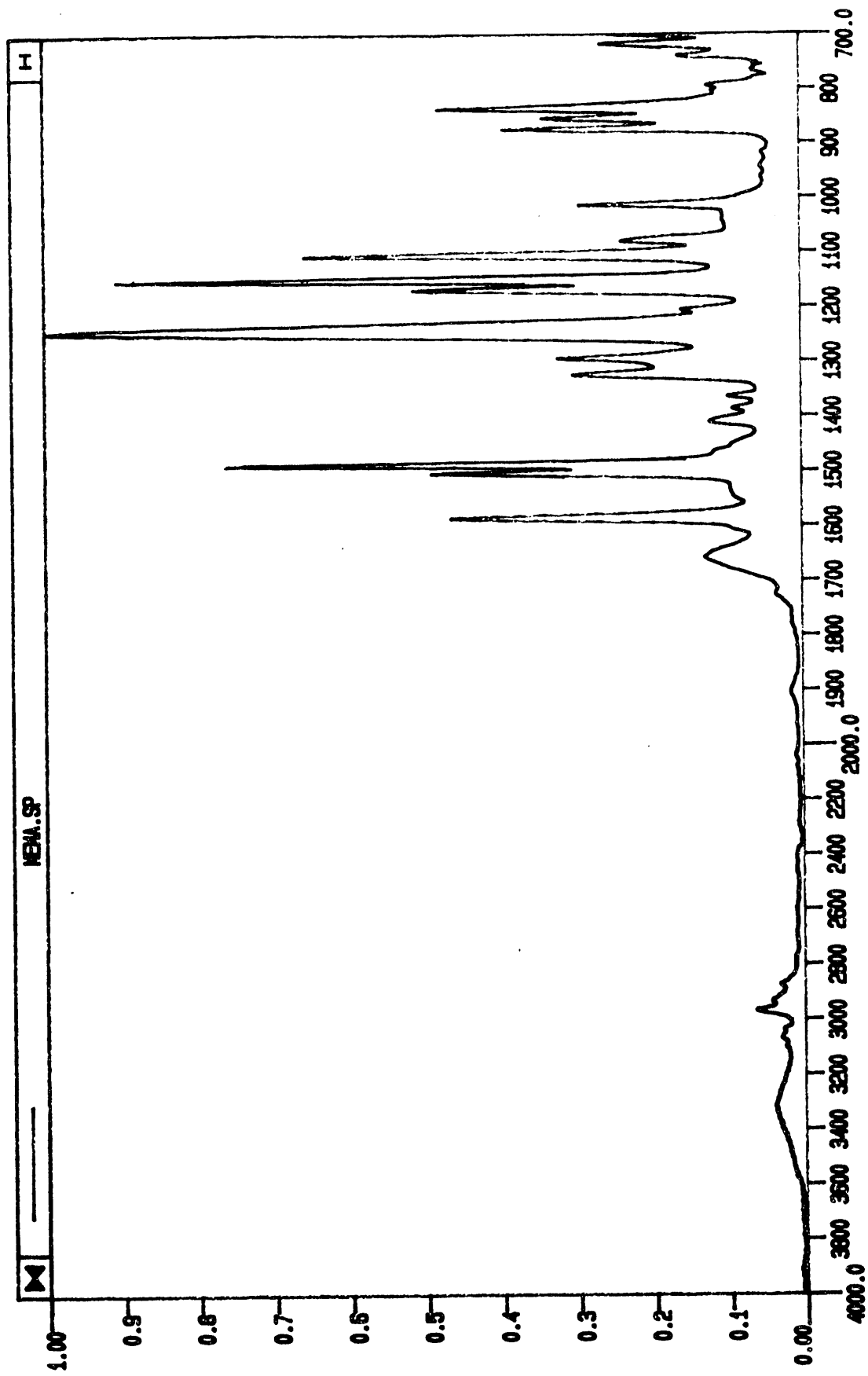
Figure 16. ATR-FTIR Spectra of the Fouled Untreated Membrane

66
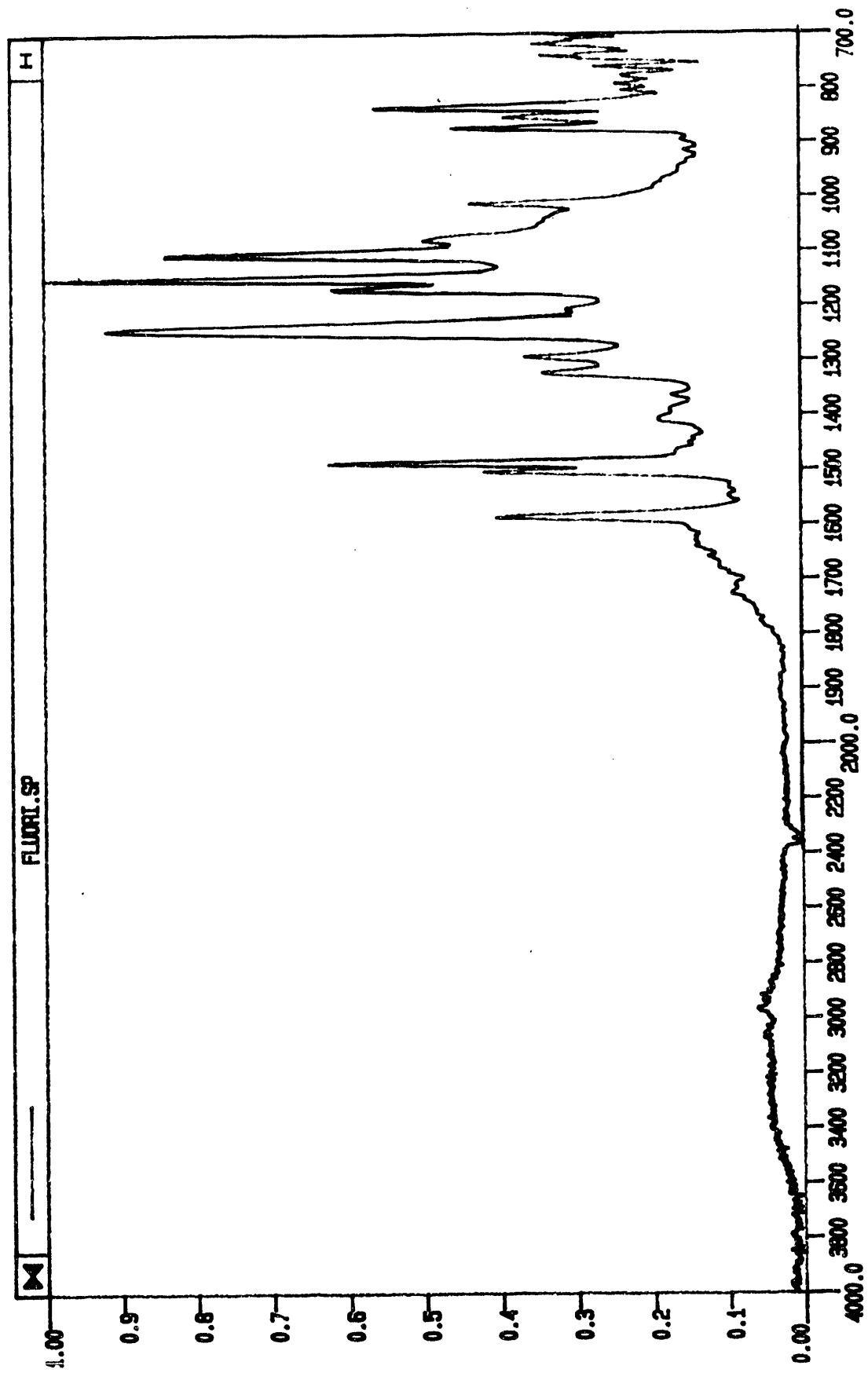
Figure 31: ATR-FTIR Spectra of the Non-Fouled Fluorinated Membrane

67
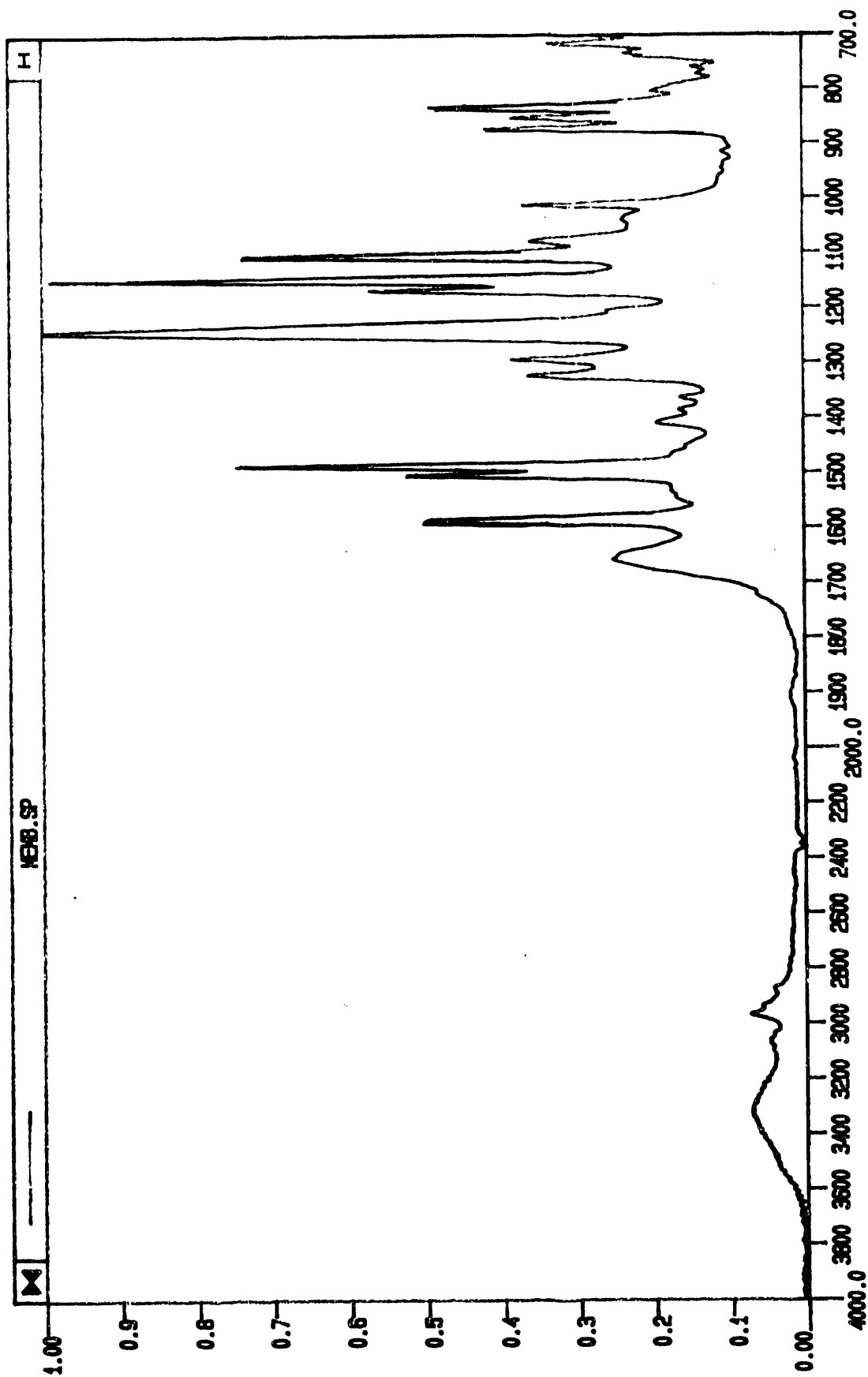
Figure 32: ATR-FTIR Spectra of the Fouled Fluorinated Membrane

	Untreated (Theoretical)	Fluorinated 0.025 F_2/N_2 5 Min	Fluorinated 0.025 F_2/N_2 30 Min	Fluorinated 0.025 F_2/N_2 60 Min
C	82.4 (84.4)	77.4	60.6	54.8
O	15.1 (12.5)	17.4	17.5	19.7
F	0.0 (0)	3.1	19.9	24.0
S	2.46 (3.1)	2.1	1.9	1.5
F/C	0.000	0.040	0.328	0.438
O/C	0.183	0.225	0.289	0.359
S/C	0.030	0.028	0.031	0.027

Table 1:   XPS Analysis of Fluorinated Polysulfone Membranes

	Untreated (Theoretical)	Fluorinated 0.025% F_2/N_2 30 Min	Fluorinated 0.25% F_2/N_2 30 Min
C	95.36 (100.0)	73.2	60.5
O	4.57 (0)	9.6	22.8
F	0.0 (0)	17.2	16.6
F/C	0.000	0.235	0.274
O/C	0.048	0.131	0.377
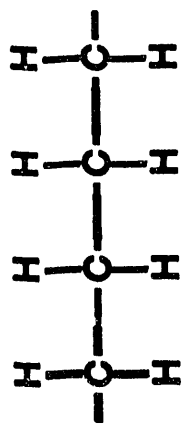
Table 2: XPS Analysis of Fluorinated Polyethylene Membranes

70

	Untreated (Theoretical) (Atom %)	Fluorinated 0.025% F_2/N_2 30 Min (Atom %)
C	67.2 (59.9)	62.1
O	32.8 (40.1)	28.5
F	0.0 (0)	9.4
F/C	0.000	0.152
O/C	0.489	0.459

Table 3: XPS Analysis of Fluorinated Cellulose Acetate Membranes

TABLE 4A: SURFACE APPEARANCE OF CLEAN AND FOULED MEMBRANES

CLEANING PROCEDURE	NON-FOULED MEMBRANE	FOULED MEMBRANE
H_2SO_4 (0.8 %)	CLEAN GLOSSY	CLEAN POWDERY APPEARANCE
NaOH (0.8 %)	CLEAN GLOSSY	CLEAN GLOSSY
CLOROX (0.05%)	CLEAN GLOSSY	CLEAN SLIGHT POWDERY APPEARANCE

TABLE 4B: XPS ANALYSIS OF WASHED POLYSULFONE MEMBRANES

	CONTROL	WATER WASH	H_2SO_4 0.8%	NaOH 0.8%	CLOROX 0.05%
SULFUR	1.7	2.1	3.5	2.4	2.0
CARBON	61.0	69.1	68.1	72.1	70.9
NITROGEN	1.5	1.7	1.2	1.9	1.7
OXYGEN	18.1	16.7	19.6	15.4	15.6
FLUORINE	17.6	10.5	7.5	8.7	8.9
CHLORINE	0	0	0	0	1.0
S/C	0.028	0.0291	0.0536	0.0339	0.0286
N/C	0.0244	0.0252	0.0182	0.0189	0.0233
O/C	0.2972	0.2419	0.2876	0.2137	0.2193
F/C	0.2884	0.1514	0.1096	0.1213	0.1254
CL/C	0	0	0	0	0.0140

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TABLE 5: XPS ANALYSIS OF FINAL PILOT STUDY MEMBRANES

	Untreated Membrane	Fluorinated Membrane
SULFUR	1.9	1.2
CARBON	75.3	68.5
NITROGEN	6.3	7.9
OXYGEN	16.0	19.6
FLUORINE	0.0	2.8
CHLORINE	Trace	Trace
S/C	0.0246	0.0172
N/C	0.0837	0.1159
O/C	0.2128	0.2854
F/C	-	0.0413

TABLE 6: OPERATING CONDITIONS FOR PILOT STUDIES

TEST	ΔP (psi)	Q (ml/min)	SPACER THICKNESS (in)	<v> (cm/min)	FEED pH	% TOTAL SOLIDS FEED
FLAT SHEET	100	2500	None	12,500	4.3	0.9
PILOT STUDY #1	20	1211	0.031	734	5.5	1.2
PILOT STUDY #2	20	2900	0.031	1760	6.0	0.6

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APPENDIX A

Append A: Flat Sheet Trials

4. Industrial Feed (Blancher)

A2

Flat Sheet Module Set-up

The flat sheet module set-up consisted of 3 or 6 single cell modules (See Figure 4) connected in series. The feed stream flow went sequentially from membrane cell #1 to membrane cell #6 and back to the feed tank. The flow rate of feed was approximately 2.5 liters/minute. A typical permeate flow rate during a run with the potato waste was 2.2 ml/min (40 GFD) through the membrane, and the trans-membrane pressure drop was 100 psi.

Initial Flat Sheet Test
Data Sheet

Date of Run - 11/7/89

Membrane #1 - Dry Methanol-Treated Fluid System's PS #1
Membrane #2 - Dry Methanol-Treated Fluid System's PS #2
Membrane #3 - Fluorinated PS with 0.05 vol % F_2 in N_2 for 60 Minutes
(where PS = Polysulfone)

Flow Rate = 2500 ml/minute

ΔP(Cross-membrane) = 100 psi

Total Solids in Feed = 0.19 wt%

Water Flux
Through
Polysulfone Membranes
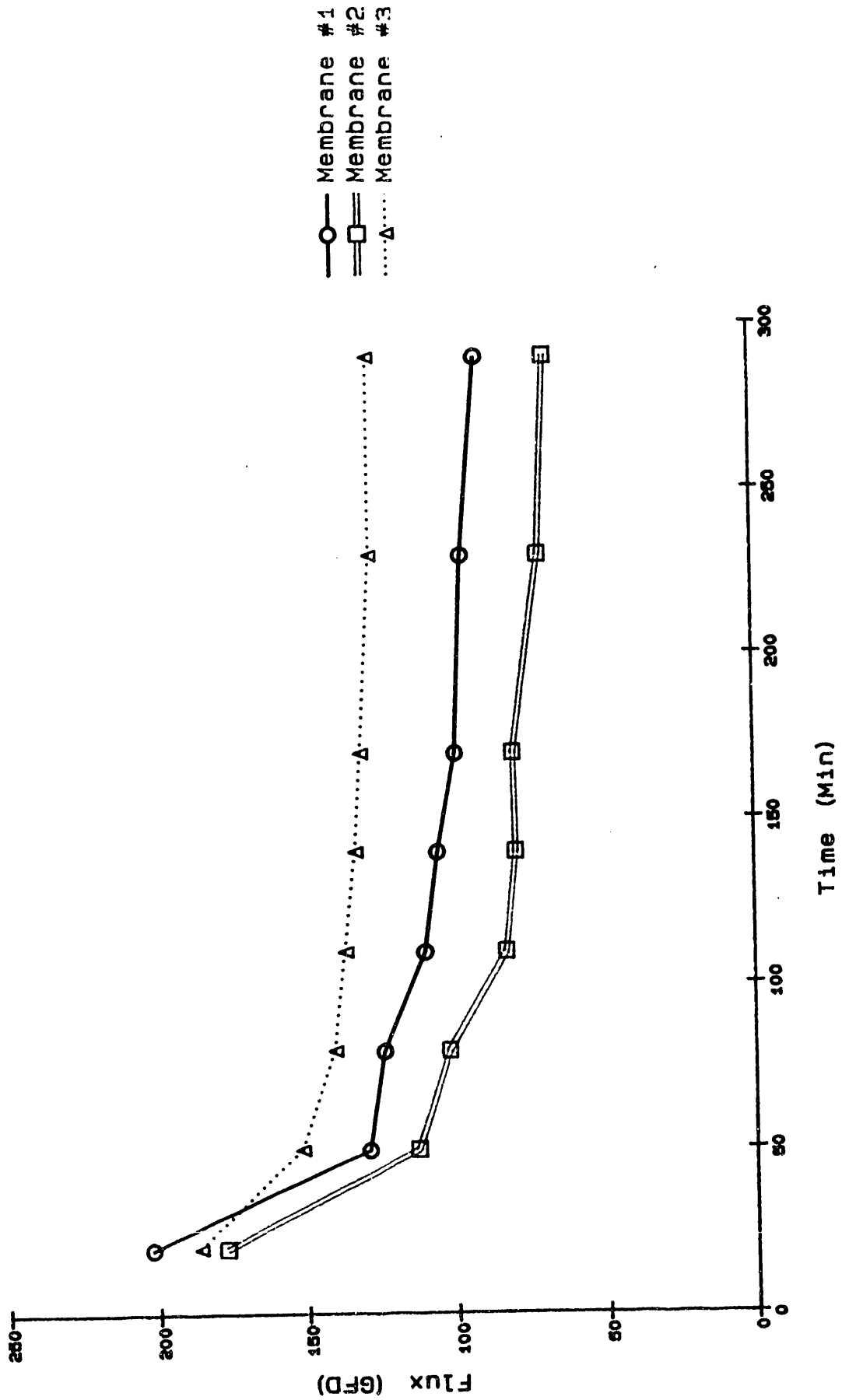
Flux (GFD)

Time (Min)

Membrane #1
Membrane #2
Membrane #3

A4

Potato Waste Stream
Filtrate Flux
Through
Polysulfone Membranes

Membrane #1
Membrane #2
Membrane #3

Flux (GFD)

Time (Min)

A5

Normalized Flux
of
Potato Waste Stream Filtrate
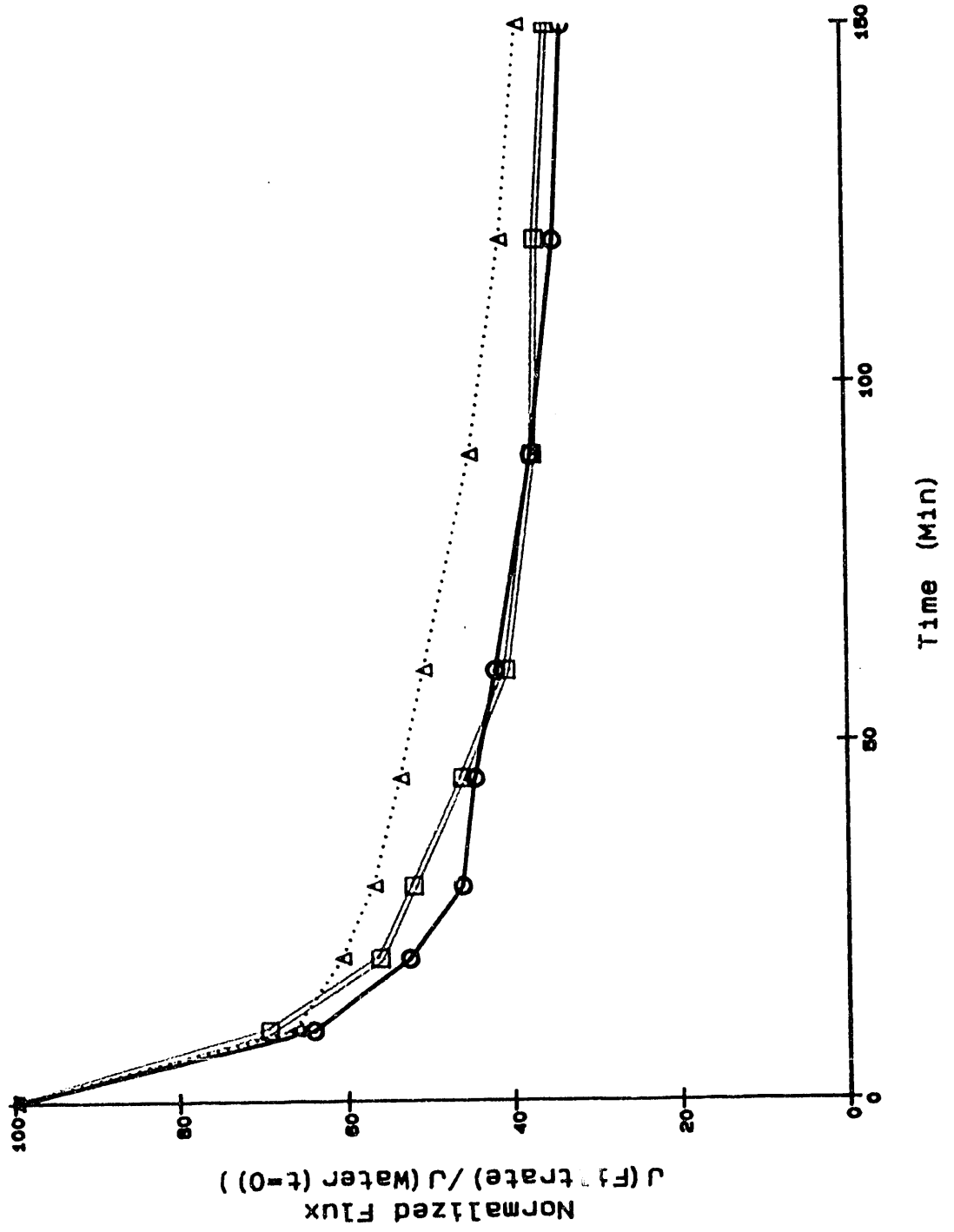
Membrane #1
Membrane #2
Membrane #3

Normalized Flux
J (Filtrate)/J (Water (t=0))

Time (Min)

A6

Potato Waste Stream
Filtrate Flux
Through
Polysulfone Membranes

Membrane #1   -0.232859*X +1.988515
Membrane #2   -0.254511*X +1.92048
Membrane #3   -0.199629*X +2.147973

Log (Flux) (GFD)

2.0
1.8
1.6
1.4
1.2

Log(Time) (Min)

1.0 1.2 1.4 1.6 1.8 2.0 2.2
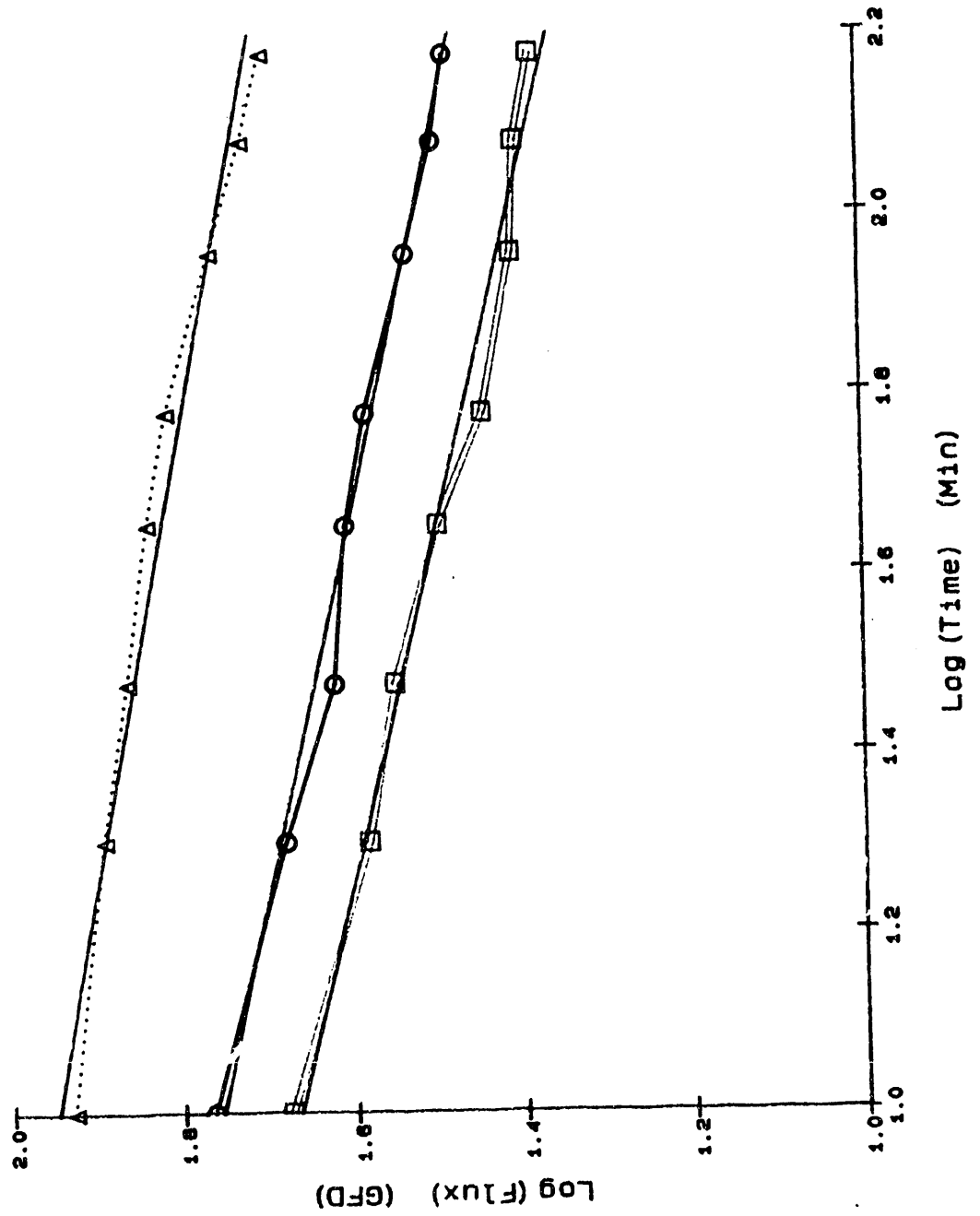
Flat Sheet Screening Runs I:
Data Sheet

Date of Run - 04-12-90

Membrane #1 - Wet PS (as delivered)
Membrane #2 - Fluorinated PS with 0.025 vol % F_2 in N_2 for 60 Min
Membrane #3 - Fluorinated PS with 0.025 vol % F_2 in N_2 for 30 Min
Membrane #4 - Fluorinated PS with 0.025 vol % F_2 in N_2 for 5 Min
Membrane #5 - Fluorinated PS with 0.050 vol % F_2 in N_2 for 5 Min
Membrane #6 - Fluorinated PS with 0.050 vol % F_2 in N_2 for 120 Min
(where PS = Fluid System's Polysulfone)

Flow Rate = 2500 ml/minute

ΔP(Cross-membrane) = 100 psi

Total Solids in Feed = 0.53 wt%
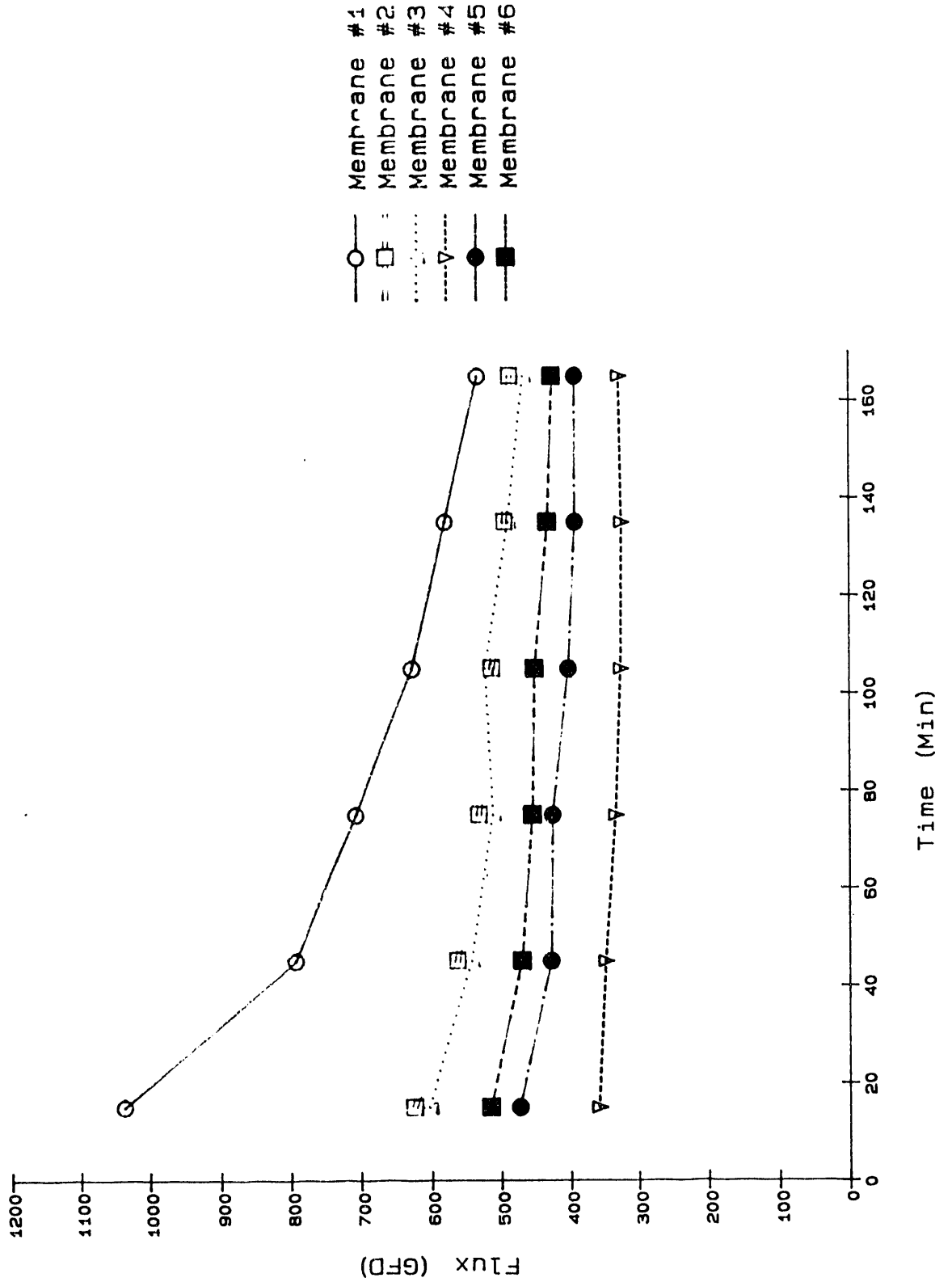
DI Water Flux
Through
Fluorinated Membranes

Potato Waste Stream
Through
Fluorinated Membranes
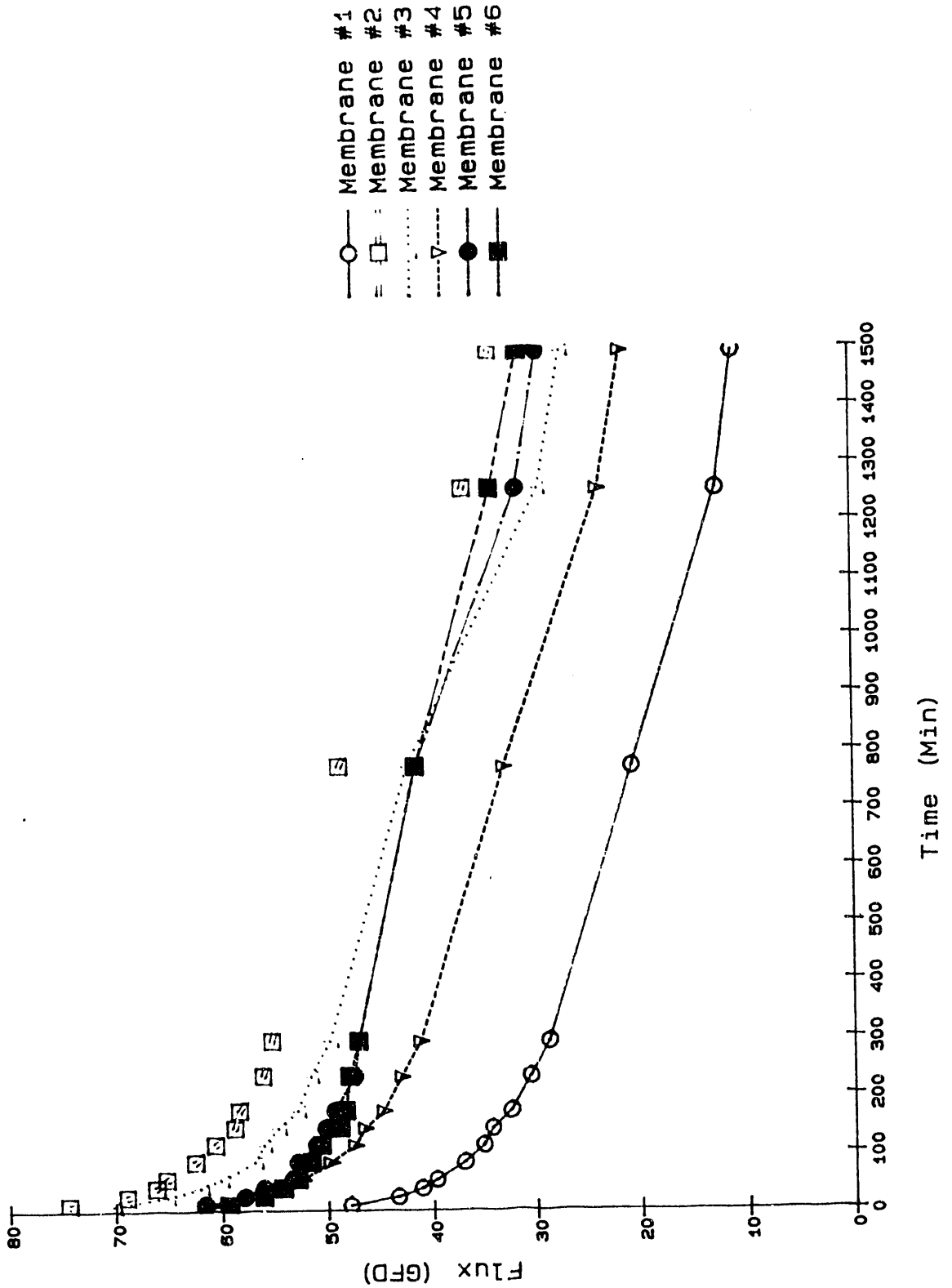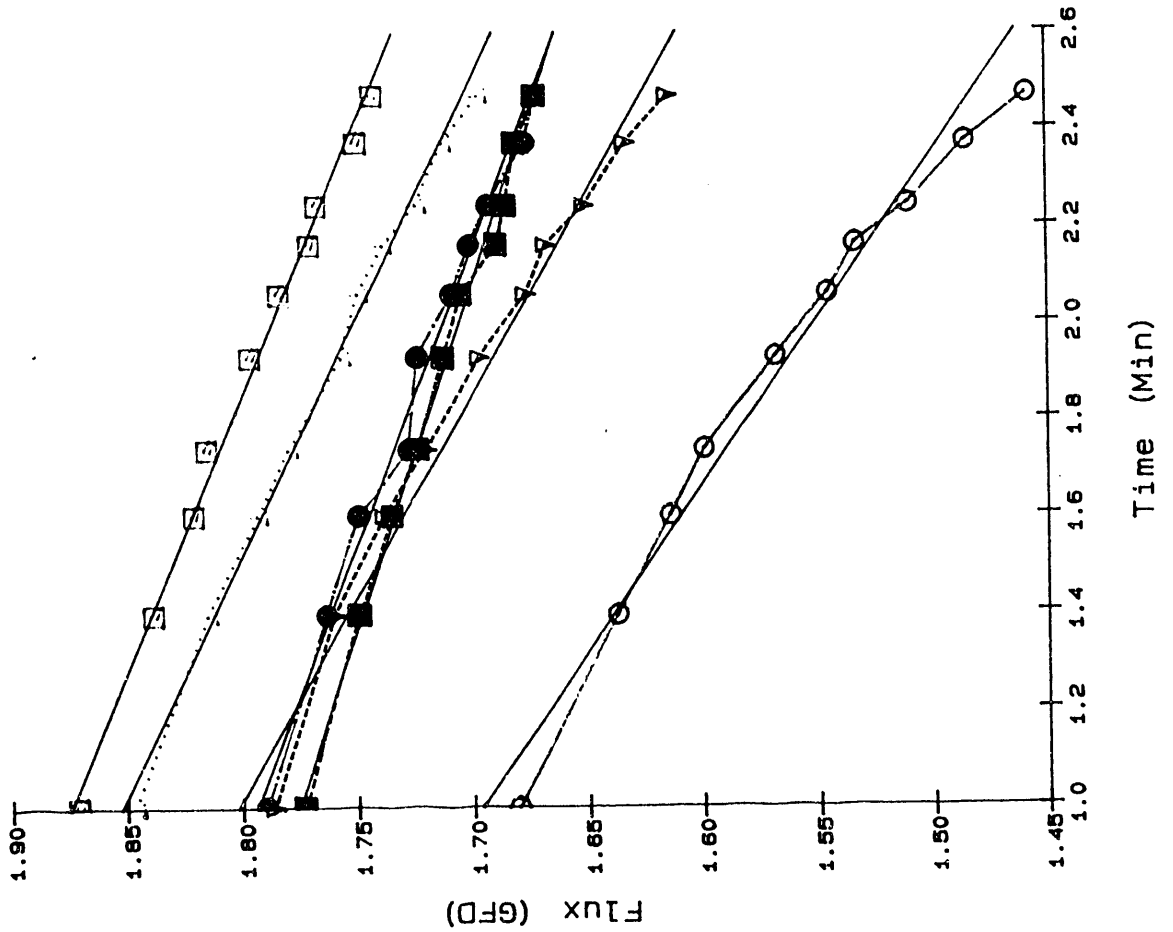
Membrane #1
Membrane #2
Membrane #3
Membrane #4
Membrane #5
Membrane #6

Flux (GFD)

Time (Min)

A10

Potato Waste Stream
Through
Fluorinated Membranes

Membrane #1   -0.145621*X +1.841977
Membrane #2   -0.088483*X +1.963234
Membrane #3   -0.10173*X +1.954265
Membrane #4   -0.120317*X +1.922654
Membrane #5   -0.081727*X +1.875594
Membrane #6   -0.070635*X +1.846568

Flux (GFD)

Time (Min)

A11

Flat Sheet Screening Runs II:
Data Sheet

Date of Run -   05-07-90

Membrane #1 - Fluorinated PS with 0.0125 vol % F_2 in N_2 for 5 Min
Membrane #2 - Fluorinated PS with 0.0125 vol % F_2 in N_2 for 120 Min
Membrane #3 - Dry Methanol- Treated PS
Membrane #4 - Wet PS (as delivered)
Membrane #5 - Fluorinated PS with 0.025 vol % F_2 in N_2 for 30 Min
Membrane #6 - Fluorinated PS with 0.025 vol % F_2 in N_2 for 60 Min
(where PS = Fluid System's Polysulfone)

Flow Rate =   2500 ml/minute

ΔP(Cross-membrane) = 100 psi

Total Solids in Feed = 0.67 wt%

Note: The membranes fluorinated at 0.0125 vol % F_2 in N_2 did not
recover initial flux when subjected to the DI water. Subsequently,
these membranes were still wetting out when subjected to the
simulated potato feed. The data have been removed from the figures
for clarity.

DI Water Flux
Through
Fluorinated Membranes

Membrane #1
Membrane #2
Membrane #3
Membrane #4
Membrane #5
Membrane #6

Flux (GFD)

500
400
300
200
100
0

Time (Min)

0 10 20 30 40 50 60 70 80 90 100 110 120 130 140 150 160 170

A13

Potato Waste Stream
Through
Fluorinated Membranes

△ ······ Membrane #3
▽ ----- Membrane #4
● —— Membrane #5
■ —··— Membrane #6

Flux (GFD)

Time (Min)

A14

Potato Waste Stream
Through
Fluorinated Membranes

Flux (GFD)

Time (Min)

△······ Membrane #3
▽---- Membrane #4
●—·— Membrane #5
■---- Membrane #6

A15

Potato Waste Streams
Basic American Foods
Blackfoot Falls, ID

Feed Stream	Total Solids %	COD (mg/L)	Total Nitrogen Mass %	pH
Barrel	1.1	30000	0.036	3.9
Slicer	0.9	10100	0.039	4.3
Blancher	3.2	32000	0.11	5.0

Barrel Feed - High Temperature for 30 seconds
Slicer Feed - Water Gun Cutting at Room Temperature
Blancher   - High Temperature for 45 minutes

A16

Table A2-1A: Membrane Specifications
(Slicer Stream)

Membrane	Membrane Treatment
#1	Wet PS (as delivered)
#2	Fluorinated PS with 0.025 vol % F_2 in N_2 for 60 Min
#3	Fluorinated PS with 0.025 vol % F_2 in N_2 for 30 Min
#4	Wet PS (as delivered)
#5	Fluorinated PS with 0.050 vol % F_2 in N_2 for 5 Min
#6	Fluorinated PS with 0.050 vol % F_2 in N_2 for 120 Min

Flux of DI Water
(Slicer)

Flux (Gal/ft²-day)

Time (Min)

Membrane #1
Membrane #2
Membrane #3
Membrane #4
Membrane #5
Membrane #6

Permeate Flux of Potato Waste Stream
(Slicer)

- ● Membrane #1
- ■ Membrane #2
- ◄ Membrane #3
- ◆ Membrane #4
- ► Membrane #5
- + Membrane #6

Flux (Gal/ft²-day)

Time (Min)
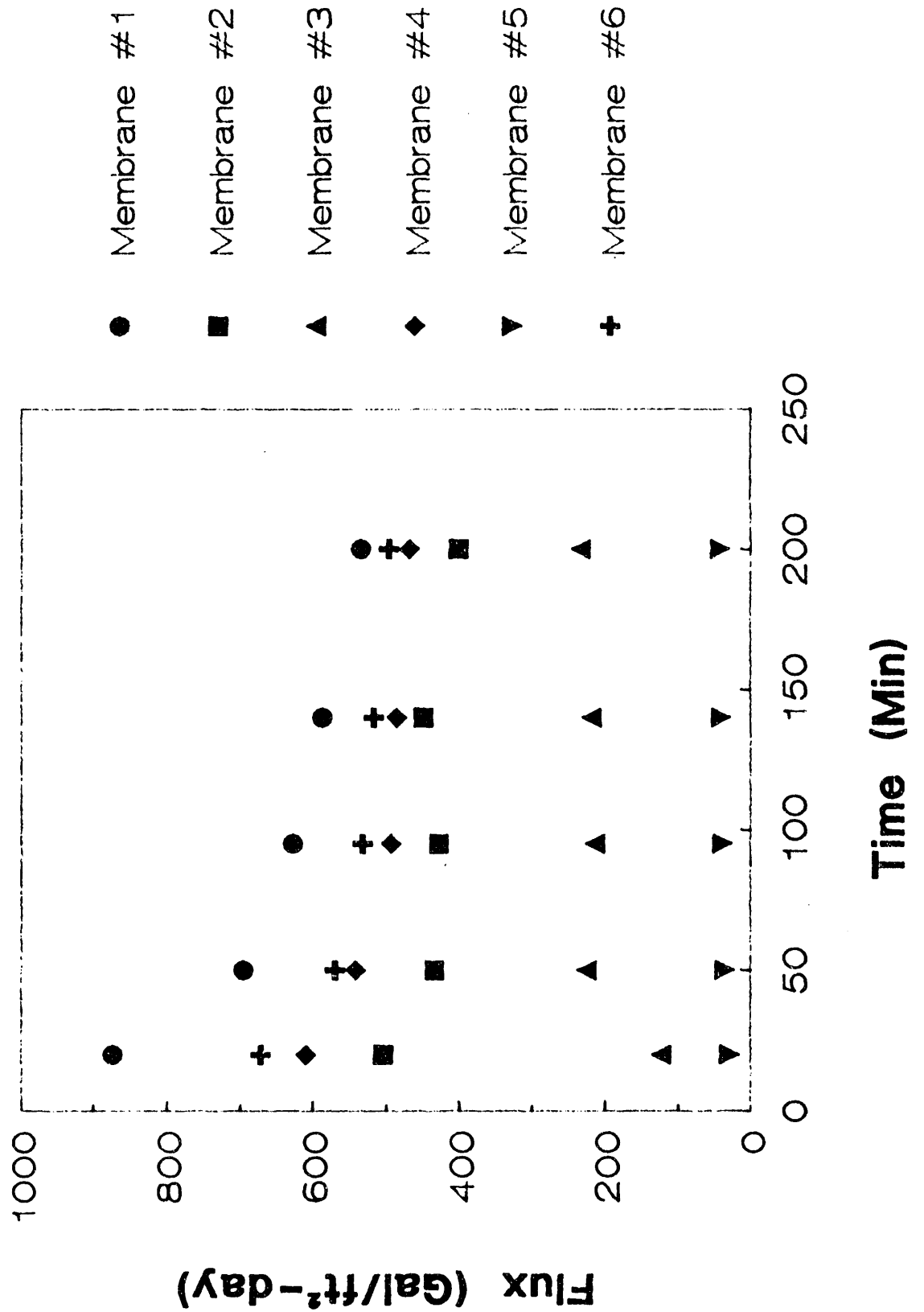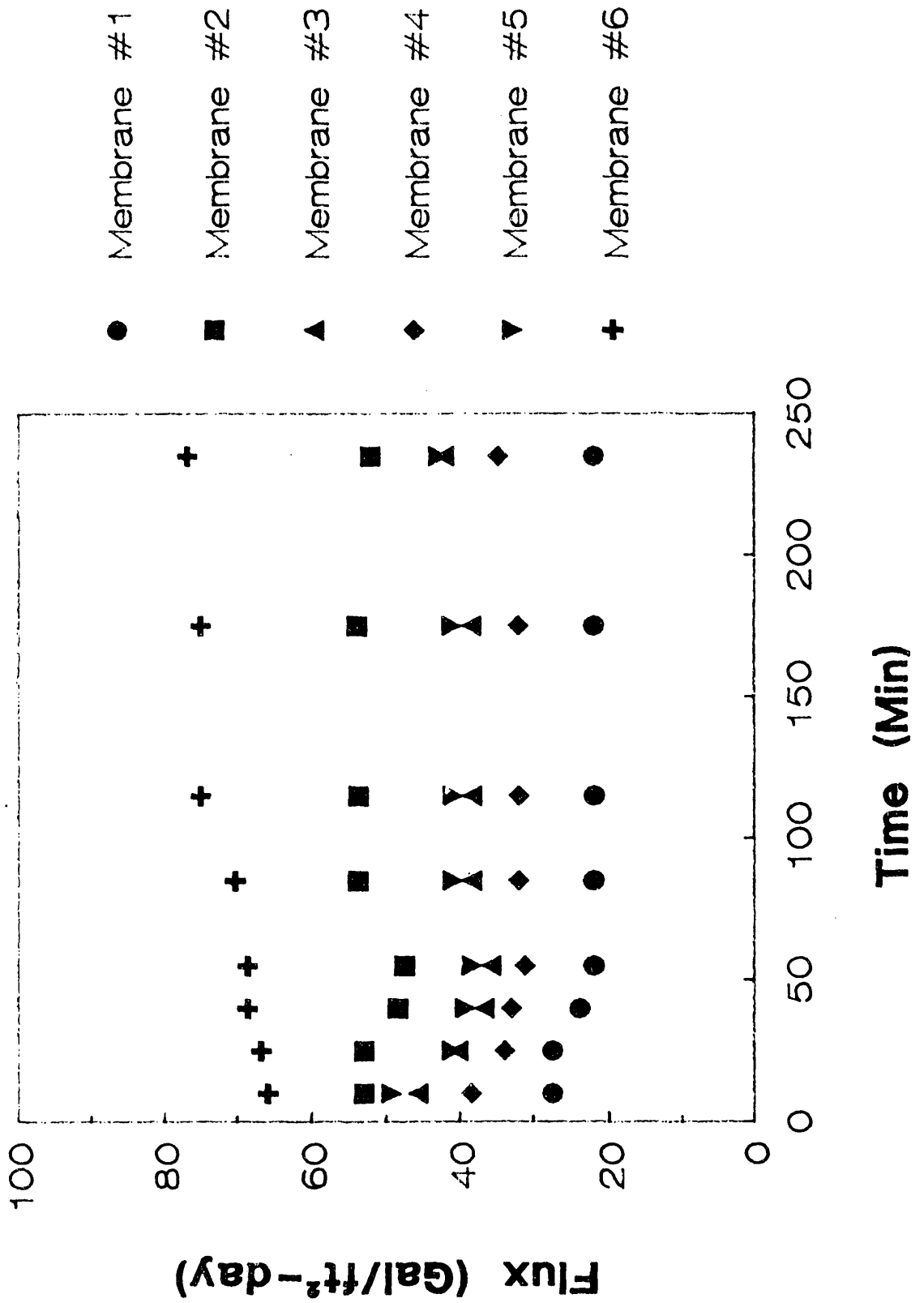
Table A2-1B: COD and Nitrogen Rejection
(Slicer Stream)

Run Date 7-10-90
Start Time 12:00 PM

Membrane	COD (mg/l)	% Rejection	Total Nitrogen Mass %	% Rejection
12:15 PM				
Feed	10100	–	3.9e-2	–
1	5300	48	7.8e-3	80
2	5500	46	8.8e-3	78
3	5700	44	8.0e-3	80
4	5100	50	8.1e-3	80
5	6500	36	9.6e-3	76
6	6000	41	8.5e-3	78
3:00 PM				
Feed	10,000	–	3.7e-2	–
1	5900	41	8.2e-3	78
2	5500	45	7.9e-3	79
3	5900	41	8.4e-3	78
4	6100	38	8.2e-3	78
5	7000	30	1.0e-2	73
6	6500	35	8.0e-3	79

Table A2-1C: DI Water and Permeate Fluxes (Slicer)

DI Water Flux

Time (Min)	Membrane #1 (GFD)	Membrane #2 (GFD)	Membrane #3 (GFD)	Membrane #4 (GFD)	Membrane #5 (GFD)	Membrane #6 (GFD)
20	873.4	504.3	122.6	609.0	28.8	671.4
50	695.4	434.3	224.7	541.6	35.1	569.5
95	627.0	428.0	213.3	493.4	38.0	532.5
200	535.3	400.8	233.2	468.7	41.7	496.8
1400	587.2	449.8	218.1	486.0	40.2	517.6

Permeate Flux

Time (Min)	Membrane #1 (GFD)	Membrane #2 (GFD)	Membrane #3 (GFD)	Membrane #4 (GFD)	Membrane #5 (GFD)	Membrane #6 (GFD)
10	27.4	53.0	45.7	38.4	49.4	65.8
25	27.4	53.0	40.2	33.8	41.1	66.7
40	23.8	48.4	36.6	32.9	39.3	68.6
55	21.9	47.5	35.7	31.1	38.4	68.6
85	27.4	53.8	38.3	31.9	41.0	70.2
115	21.0	49.4	36.6	31.1	39.3	69.5
175	21.9	53.9	38.4	32.0	41.1	75.0
235	21.9	53.8	52.1	34.7	43.0	76.8

Table A2-2A: Membrane Specifications
(Barrel Stream)

Membrane	Membrane Treatment
#1	Wet PS (as delivered)
#2	Fluorinated PS with 0.025 vol % F_2 in N_2 for 60 Min
#3	Fluorinated PS with 0.025 vol % F_2 in N_2 for 30 Min
#4	Wet PS (as delivered)
#5	Fluorinated PS with 0.050 vol % F_2 in N_2 for 5 Min
#6	Fluorinated PS with 0.050 vol % F_2 in N_2 for 120 Min

Flux of DI Water (Barrel)

Flux (Gal/ft²-day)

Time (Min)

- ● Membrane #1
- ■ Membrane #2
- ◄ Membrane #3
- ◆ Membrane #4
- ► Membrane #5
- + Membrane #6

Permeate Flux of Potato Waste Stream
(Barrel)

Membrane #1 ●
Membrane #2 ■
Membrane #3 ◄
Membrane #4 ◆
Membrane #5 ►
Membrane #6 +

Flux (Gal/ft²-day)

Time (Min)

A24

Table A2-2B: COD and Nitrogen Rejection
(Barrel Stream)

Run Date 7-12-90
Start Time 12:00 PM

Membrane	COD(mg/l)	% Rejection	Total Nitrogen Mass %	% Rejection
12:15 PM (7-13-90)				
Feed	30000	—	3.6e-2	—
1	7500	75	6.2e-3	83
2	6100	80	8.6e-3	76
3	6200	79	8.5e-3	76
4	5900	80	8.1e-3	78
5	8400	72	9.5e-3	74
6	6900	77	9.8e-3	73

Table A2-2C: DI Water and Permeate Fluxes (Barrel)

DI Water Flux

Time (Min)	Membrane #1 (GFD)	Membrane #2 (GFD)	Membrane #3 (GFD)	Membrane #4 (GFD)	Membrane #5 (GFD)	Membrane #6 (GFD)
20	218.6	149.4	116.8	196.8	116.6	164.0
45	138.5	109.3	94.7	127.5	91.1	116.6
70	116.6	113.0	91.1	120.3	89.3	113.0
100	100.2	98.4	78.3	94.7	78.3	94.7
145	87.5	94.7	74.7	87.5	76.5	94.7
190	65.6	89.3	67.4	76.5	72.9	82.0

Permeate Flux

Time (Min)	Membrane #1 (GFD)	Membrane #2 (GFD)	Membrane #3 (GFD)	Membrane #4 (GFD)	Membrane #5 (GFD)	Membrane #6 (GFD)
15	31.9	49.2	49.5	41.9	45.6	49.2
30	28.2	48.3	42.8	40.1	44.6	45.6
45	29.2	47.4	43.7	39.2	42.8	45.6
60	30.1	48.3	42.8	39.2	43.7	45.6
90	30.1	48.3	42.8	39.2	43.7	45.6
120	27.3	47.4	42.8	38.3	41.0	44.6
180	27.3	47.4	41.9	41.9	42.8	43.7
240	27.3	45.6	40.1	34.6	41.0	41.0
720	22.5	41.3	37.1	32.8	34.6	34.6
1200	22.8	43.7	41.0	33.7	32.8	36.4
1440	21.9	41.9	41.0	31.9	31.0	32.8

Table A2-3A: Membrane Specifications
(Blancher Stream)

Membrane	Membrane Treatment
#1	Wet PS (as delivered)
#2	Fluorinated PS with 0.025 vol % F_2 in N_2 for 60 Min
#3	Fluorinated PS with 0.025 vol % F_2 in N_2 for 30 Min
#4	Wet PS (as delivered)
#5	Fluorinated PS with 0.050 vol % F_2 in N_2 for 5 Min
#6	Fluorinated PS with 0.025 vol % F_2 in N_2 for 5 Min

Flux of DI Water (Blancher)

Flux (Gal/ft²-day)

Time (Min)

Membrane #1 ●
Membrane #2 ■
Membrane #3 ◄
Membrane #4 ◆
Membrane #5 ►
Membrane #6 +
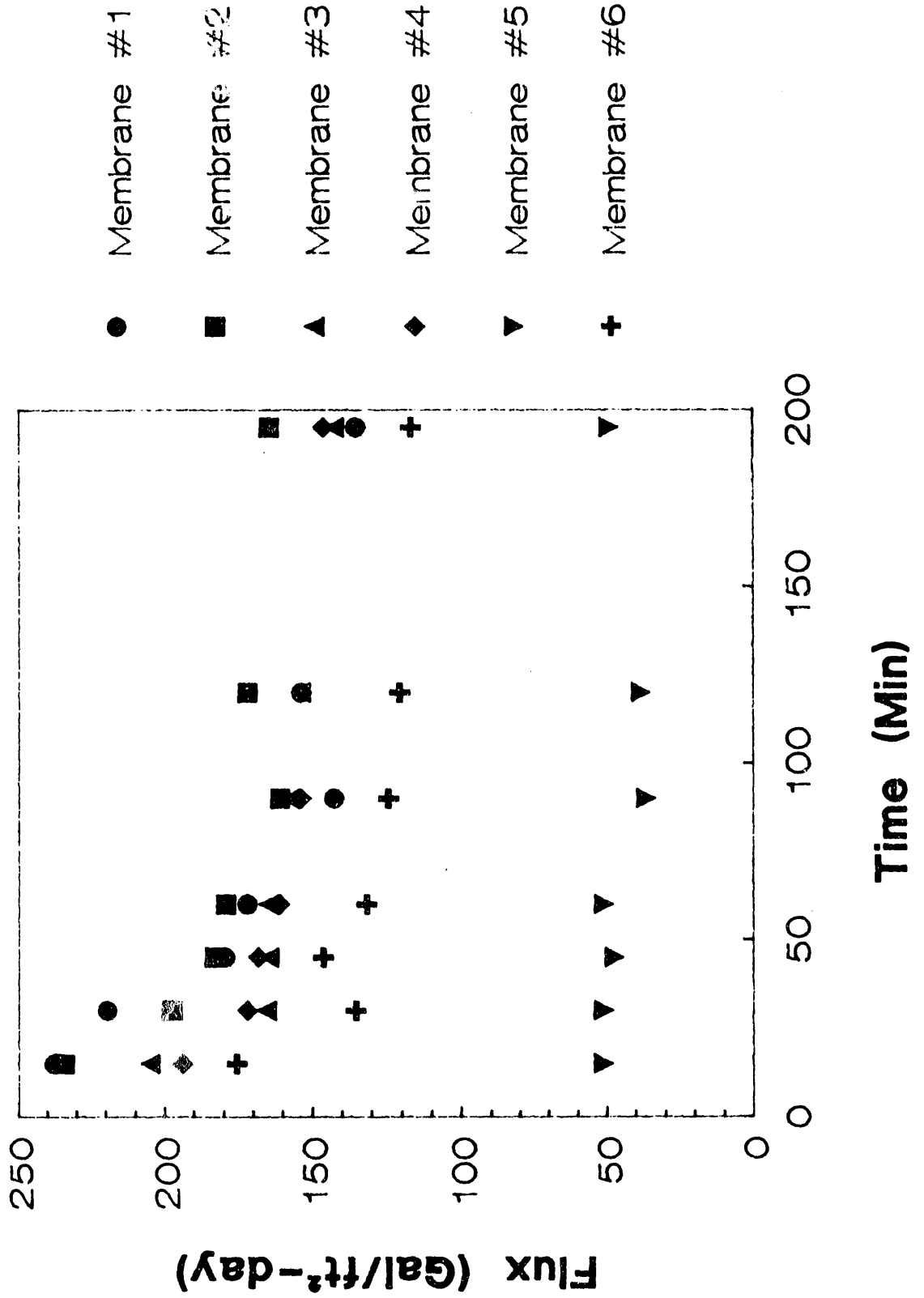
Permeate Flux of Potato Waste Stream (Blancher)

Flux (Gal/ft²-day) vs Time (Min)

Membrane #1 ●
Membrane #2 ■
Membrane #3 ◀
Membrane #4 ◆
Membrane #5 ▶
Membrane #6 +
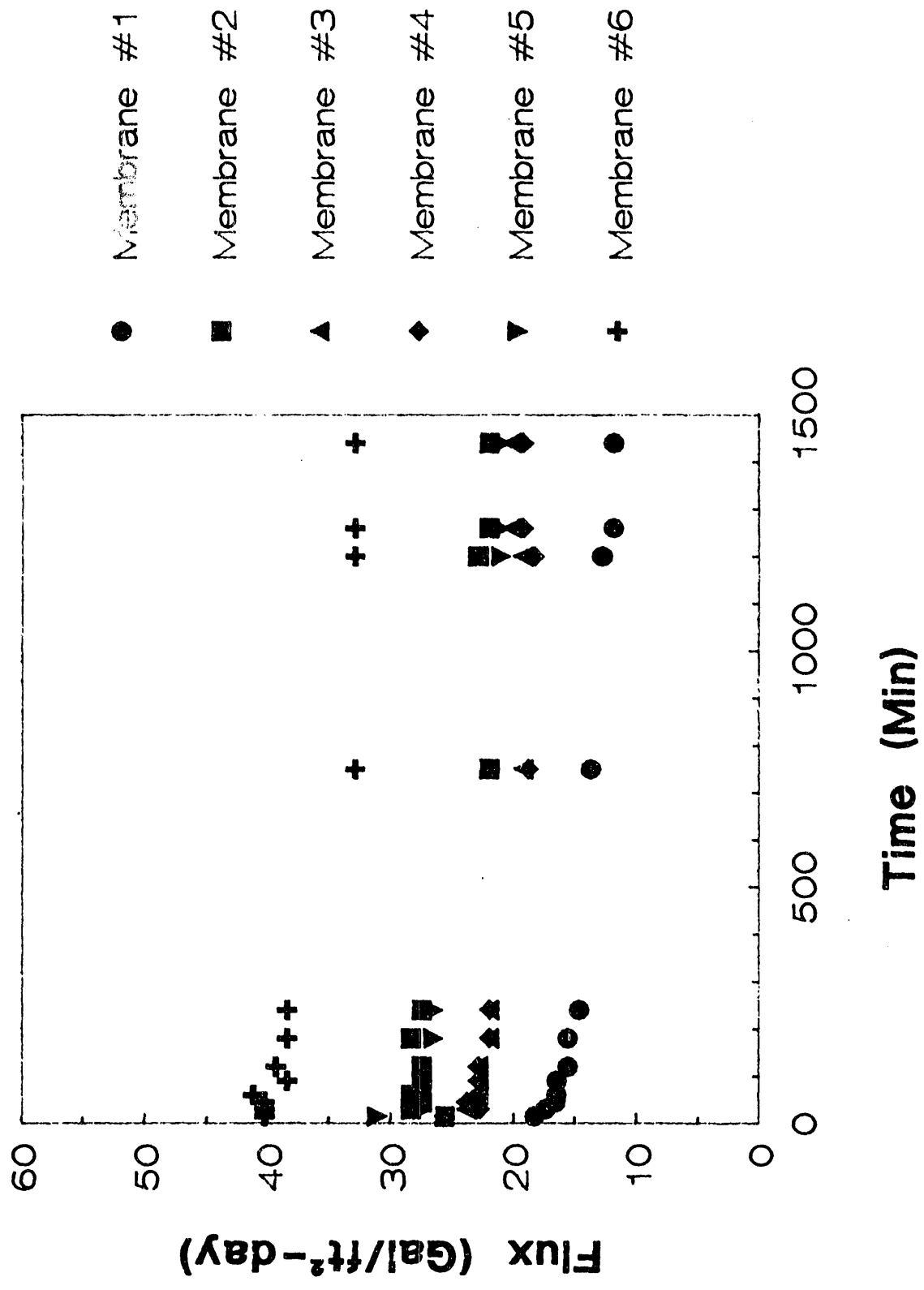
Table A2-3B: COD and Nitrogen Rejection
(Blancher Stream)

Run Date 7-19-90
Start Time 12:00 PM

Membrane	COD (mg/l)	% Rejection	Total Nitrogen Mass %	% Rejection
2:00 PM				
Feed	31500	–	0.110	–
1	6500	79	0.069	33
2	10500	67	0.066	34
3	8750	72	0.067	34
4	10500	67	0.059	42
5	10000	68	0.063	38
6	10000	68	0.067	34
8:00 AM (7-20-90)				
Feed	35000	–	0.110	–
1	9500	73	1.1e-2	90
2	9100	74	1.4e-2	87
3	8900	75	1.2e-2	89
4	9200	74	1.5e-2	86
5	7000	80	1.3e-2	88
6	10000	71	1.1e-2	90

Table A2-3C: DI Water and Permeate Fluxes (Blancher)

DI Water Flux

Time (Min)	Membrane #1 (GFD)	Membrane #2 (GFD)	Membrane #3 (GFD)	Membrane #4 (GFD)	Membrane #5 (GFD)	Membrane #6 (GFD)
15	237.6	234.0	204.7	193.8	51.2	175.5
30	219.4	197.4	165.4	171.8	51.2	135.3
45	179.4	182.8	164.5	168.2	47.5	146.2
60	171.8	179.1	164.5	160.9	51.2	131.6
90	142.6	160.9	157.2	153.6	36.6	124.3
120	153.6	171.8	153.6	153.6	38.4	120.7
195	135.3	164.5	142.5	146.2	49.4	117.0

Permeate Flux

Time (Min)	Membrane #1 (GFD)	Membrane #2 (GFD)	Membrane #3 (GFD)	Membrane #4 (GFD)	Membrane #5 (GFD)	Membrane #6 (GFD)
15	18.3	25.5	25.6	25.6	31.1	40.2
30	17.4	28.3	23.8	22.8	27.4	40.2
45	16.5	27.4	23.8	23.8	28.3	40.2
60	16.5	28.3	22.9	22.9	27.4	41.1
90	16.5	27.4	22.9	22.9	27.4	38.4
120	15.5	27.4	22.9	22.9	27.4	39.3
180	15.5	28.3	21.9	21.9	26.5	38.4
240	14.6	27.4	21.9	21.9	26.5	38.4
750	13.7	21.9	19.2	18.8	21.9	32.9
1200	12.8	22.9	19.2	18.3	21.0	32.9
1260	11.9	21.9	20.1	19.2	21.0	32.9
1440	11.9	21.9	20.1	19.2	21.0	32.9

APPENDIX B

Appendix B

ULTRAFILTRATION MEMBRANES: PILOT STUDY #1
21-DAY PILOT RUN: SEPTEMBER 4 - OCTOBER 3, 1991

	TIME (Min.)	MEMBRANE A (GFD)	MEMBRANE B (GFD)
SEPT 4: (DAY 1)	0	17.48	48.25
	15	2.18	6.45
	30	1.91	5.51
	45	1.73	4.90
	60	1.64	4.42
	120	1.22	3.40
	240	1.08	3.22
	360	1.02	3.19
	600	0.78	2.89
	990	0.67	2.67
	1365	0.67	2.67
SEPT 5: (DAY 2)	0	—	—
	15	3.12	7.88
	30	2.62	6.02
	45	2.38	5.04
	60	2.17	4.48
	120	1.72	3.50
	210	1.35	2.76
	330	1.19	2.75
	570	0.95	2.44
	930	0.90	2.26
	1320	0.87	2.20

ULTRAFILTRATION MEMBRANES: PILOT STUDY #1 (CONT)
21-DAY PILOT PLAN RUN: SEPTEMBER 4-OCTOBER 3, 1991

	TIME (Min.)	MEMBRANE A (GFD)	MEMBRANE B (GFD)
SEPT 6: (DAY 3)	0	—	—
	15	2.97	7.35
	30	2.67	5.49
	45	2.37	4.68
	60	2.24	4.28
	120	1.88	3.42
	240	1.49	2.85
	350	1.24	2.55
	615	1.13	2.59
	990	0.97	2.28
	1350	0.89	2.13
SEPT 9: (DAY 4)	0	—	—
	15	3.12	6.01
	30	2.60	5.05
	45	2.39	4.55
	60	2.27	4.31
	105	1.94	3.71
	225	1.72	3.29
	335	1.58	3.08
	585	1.46	2.68
	945	1.38	2.47
	1335	1.24	2.44

ULTRAFILTRATION MEMBRANES: PILOT STUDY #1 (CONT)
21-DAY PILOT PLAN RUN: SEPTEMBER 4-OCTOBER 3, 1991

	TIME (Min.)	MEMBRANE A (GFD)	MEMBRANE B (GFD)
SEPT 10: (DAY 5)	0	—	—
	15	2.39	5.54
	30	2.10	4.70
	45	2.00	4.31
	60	1.85	4.00
	120	1.59	3.37
	310	1.57	3.14
	430	1.47	2.97
	675	1.41	2.63
	1035	1.30	2.38
	1320	1.13	2.14
SEPT 11: (DAY 6)	0	—	—
	15	1.16	4.26
	30	0.96	4.00
	45	0.86	3.75
	60	0.86	3.55
	105	0.71	3.24
	225	0.54	2.82
	335	0.46	2.60
	705	0.32	2.24
	955	0.20	2.02
	1305	0.13	1.82

ULTRAFILTRATION MEMBRANES: PILOT STUDY #1 (CONT)
21-DAY PILOT PLAN RUN: SEPTEMBER 4-OCTOBER 3, 1991

	TIME (Min.)	MEMBRANE A (GFD)	MEMBRANE B (GFD)
SEPT 12: (DAY 7)	0	0.91	17.65
	15	0.40	3.93
	45	0.34	3.34
	60	0.29	3.13
	120	0.30	2.89
	210	0.24	2.66
	330	0.22	2.52
	680	0.13	2.30
	965	0.11	2.10
	1290	0.06	1.96
SEPT 13: (DAY 8)	0	0.76	17.33
	15	0.23	3.35
	30	0.21	2.89
	45	0.17	2.74
	60	0.15	2.49
	120	0.15	2.24
	210	0.15	2.13
	305	0.15	1.98
	570	0.13	1.83
	1350	0.04	1.57

ULTRAFILTRATION MEMBRANES: PILOT STUDY #1 (CONT)
21-DAY PILOT PLAN RUN: SEPTEMBER 4-OCTOBER 3, 1991

	TIME (Min.)	MEMBRANE A (GFD)	MEMBRANE B (GFD)
SEPT 16: (DAY 9)	0	—	—
	15	5.40	2.85
	30	5.00	2.41
	45	4.86	2.35
	60	4.75	2.28
	120	4.43	2.10
	240	4.13	1.96
	345	4.01	1.96
	600	3.45	1.75
	915	3.14	1.55
	1320	2.80	1.46
SEPT 17: (DAY 10)	0	26.62	1.94
	15	5.46	2.37
	30	5.06	2.13
	45	4.82	2.02
	60	4.72	1.95
	120	4.46	1.88
	210	4.21	1.80
	300	4.00	1.74
	585	3.57	1.57
	935	3.20	1.44
	1290	2.96	1.40

ULTRAFILTRATION MEMBRANES: PILOT STUDY #1 (CONT)
21-DAY PILOT PLAN RUN: SEPTEMBER 4-OCTOBER 3, 1991

	TIME (Min.)	MEMBRANE A (GFD)	MEMBRANE B (GFD)
SEPT 18: (DAY 11)	0	60.61	6.31
	15	4.43	2.00
	30	4.22	1.94
	45	4.18	1.90
	60	3.98	1.84
	105	3.93	1.77
	225	3.57	1.66
	345	3.05	1.45
	585	2.43	1.20
	945	2.00	0.99
	1305	1.77	0.84
SEPT 19 (DAY 12)	0	46.08	4.46
	15	5.14	2.03
	30	4.69	1.93
	45	4.53	1.85
	60	4.41	1.88
	120	4.10	1.82
	360	3.22	1.43
	720	2.54	1.03
	1050	2.24	.89
	1350	2.24	.89

	TIME (Min.)	MEMBRANE A (GFD)	MEMBRANE B (GFD)
SEPT. 20 (DAY 13)	0	―――	―――
	15	4.81	1.80
	30	4.33	1.61
	45	4.28	1.58
	75	4.03	1.52
	350	2.92	1.12
	715	2.38	.92
	1295	2.00	.81
SEPT 23 (DAY 14)	0	42.00	4.10
	15	4.45	1.67
	30	4.16	1.56
	45	4.06	1.56
	60	3.95	1.52
	120	3.80	1.48
	240	3.53	1.41
	360	3.34	1.32
	595	3.42	1.13
	970	2.44	0.98
	1320	2.11	0.86

ULTRAFILTRATION MEMBRANES: PILOT STUDY #1 (CONT)
21-DAY PILOT PLAN RUN: SEPTEMBER 4-OCTOBER 3, 1991

	TIME (Min.)	MEMBRANE A (GFD)	MEMBRANE B (GFD)
SEPT 24: (DAY 15)	0	38.92	3.33
	15	5.16	1.58
	30	4.98	1.58
	45	4.79	1.58
	60	4.70	1.47
	120	4.40	1.49
	240	3.95	1.16
	330	3.73	1.29
	600	3.01	0.99
	990	2.55	0.89
	1320	2.34	0.82
SEPT: 25 (DAY 16)	0	34.82	3.21
	15	5.46	1.20
	30	4.06	1.09
	45	3.70	1.04
	60	3.56	1.02
	105	3.47	1.02
	225	3.20	0.95
	345	2.99	0.87
	585	2.69	0.86
	945	2.03	0.74
	1305	1.55	0.61

	TIME (Min.)	MEMBRANE A (GFD)	MEMBRANE B (GFD)
SEPT: 26 (DAY 17)	0	—	—
	15	4.20	1.29
	30	3.64	1.15
	45	3.32	1.12
	60	3.13	1.12
	90	2.91	1.08
	210	2.11	0.98
	330	1.78	0.
	570	1.47	0.
	930	1.28	0.65
	1290	1.18	0.60
SEPT: 27 (DAY 18)	0	35.01	2.89
	15	4.86	1.43
	30	4.39	1.34
	45	4.04	1.33
	60	3.85	1.30
	180	3.22	1.12
	300	2.66	1.00
	545	2.15	0.80
	905	1.84	0.70
	1335	1.68	0.65

ULTRAFILTRATION MEMBRANES: PILOT STUDY #1 (CONT)
21-DAY PILOT PLAN RUN: SEPTEMBER 4-OCTOBER 3, 1991

	TIME (Min.)	MEMBRANE A (GFD)	MEMBRANE B (GFD)
SEPT: 30 (DAY 19)	0	40.64	4.46
	15	4.85	1.52
	30	4.49	1.48
	45	3.97	1.26
	60	3.68	1.29
	120	3.78	1.27
	245	3.51	1.22
	360	3.41	1.19
	780	2.85	0.93
	1320	2.76	0.82
OCT: 1 (DAY 20)	0	42.47	4.56
	15	5.45	1.72
	30	4.81	1.60
	45	4.48	1.51
	60	4.43	1.49
	120	4.20	1.42
	240	3.90	1.37
	360	3:72	1.31
	780	2.94	1.02
	1320	2.33	0.86

	0	44.49	4.51
OCT: 2 (DAY 21)	15	5.01	1.47
	30	4.63	1.42
	45	4.54	1.42
	60	4.40	1.39
	120	4.16	1.37
	240	3.45	1.32
	360	2.69	1.14
	780	1.34	0.64
	1270	0.88	0.41

5-DAY PILOT RUN: OCT 11 - OCT 17, 1991: STUDY #2

	TIME (Min.)	MEMBRANE A (GFD)	MEMBRANE B (GFD)
OCT: 11 (DAY 1)	0	31.50	5.99
	20	16.83	3.98
	30	14.96	3.86
	45	13.64	4.00
	60	12.51	3.98
	90	11.43	4.28
	345	7.83	5.83
	585	7.58	5.86
	1035	10.08	5.81
	1310	9.18	5.81
OCT: 14 (DAY 2)	0	92.27	20.29
	15	22.23	9.12
	30	21.61	9.27
	45	21.30	9.34
	60	19.94	9.21
	120	12.90	8.21
	240	6.33	5.74
	360	5.03	4.39
	972	5.10	3.53
	1325	6.33	3.96
	1330	6.33	3.9

B13

5-DAY PILOT RUN: OCT 11 - OCT 17, 1991: PLANT #2 (CONT)

	TIME (Min.)	MEMBRANE A (GFD)	MEMBRANE B (GFD)
OCT: 15 (DAY 3)	0	95.14	20.19
	15	16.68	9.21
	30	16.56	9.06
	45	16.38	9.34
	60	15.92	9.24
	120	14.08	9.29
	180	12.83	8.41
	426	8.04	5.34
	736	6.35	4.48
	1085	5.98	4.30
	1140	6.04	4.33
OCT: 16 (DAY 4)	0	98.97	18.43
	15	14.97	8.26
	30	15.11	8.29
	45	15.40	8.61
	60	15.77	8.77
	115	17.03	9.22
	240	17.27	9.07
	335	14.25	8.01
	607	6.96	4.20
	940	6.48	3.50
	1265	9.94	3.61
	1305	7.04	3.71

5-DAY PILOT RUN: OCT 11 - OCT 17, 1991: PLANT #2 (CONT)

	TIME (Min.)	MEMBRANE A (GFD)	MEMBRANE B (GFD)
OCT: 17 (DAY 5)	0	93.74	14.05
	15	18.57	7.62
	30	18.54	7.86
	45	17.69	7.77
	60	16.78	7.81
	110	14.96	7.46
	240	9.45	5.68
	330	7.73	4.33
	1000	4.91	3.05
	1275	5.27	3.25
	1320	5.35	3.31

Appendix B2 Nomenclature

Sample Type

A = Permeate Sample (Untreated Spiral Module)
B = Permeate Sample (Fluorinated Spiral Module)
F = Feed Sample

Time Interval

1 = 30 minutes into experiment
2 = 60 minutes into experiment
3 = 360 minutes into experiment
4 = Final reading

ULTRAFILTRATION MEMBRANE PILOT PLANT
RUN #1

CHEMICAL OXYGEN DEMAND (mg/L)

	DAY 1	DAY 2	DAY 3	DAY 4	DAY 5	DAY 6	DAY 7
1-A	5813	6533	6525	8084	9611	3675	4176
1-B	5133	5983	5833	6826	7141	2475	2527
1-F	11976	11677	11826	11868	11800	12125	13407
2-A	5480	6717	6525	6886	7665	3575	3324
2-B	5240	6300	5850	6707	7156	2400	2308
2-F	10679	11377	11826	11528	11800	11900	11703
3-A	-	8508	8303	10550	11000	3900	3516
3-B	-	6958	3527	6646	7750	2550	2445
3-F	-	12076	12575	11264	11900	11875	11978
4-A	11329	11375	12471	8832	11350	4700	3434
4-B	7433	7855	7705	8234	8425	3200	2637
4-F	9980	11976	11527	8901	11700	12050	11648

REJECTION

	DAY 1	DAY 2	DAY 3	DAY 4	DAY 5	DAY 6	DAY 7
1-A	51.46	44.05	44.82	31.88	18.55	69.69	68.85
1-B	57.14	48.76	50.68	42.48	39.48	79.59	81.15
2-A	48.68	40.96	44.82	40.27	35.04	69.96	71.60
2-B	50.93	44.63	50.53	41.82	39.36	79.83	80.28
3-A	-	29.55	33.97	6.34	7.56	67.16	70.65
3-B	-	42.38	71.95	41.00	34.87	78.53	79.59
4-A	-13.52	5.02	-8.19	0.78	2.99	61.00	70.52
4-B	25.52	34.41	33.16	7.49	27.99	73.44	77.36

ULTRAFILTRATION MEMBRANE PILOT PLANT
RUN #1 (CONT.)

CHEMICAL OXYGEN DEMAND (mg/L)

	DAY 8	DAY9	DAY 10	DAY 11	DAY 12	DAY 13	DAY 14
1-A	3104	3709	2525	3025	2250	1975	2625
1-B	2582	2473	2225	2450	1975	1300	1850
1-F	17253	11648	11300	12850	11450	12250	11350
2-A	4396	2550	2650	2325	2500	-	-
2-B	2390	2450	4475	1925	1975	-	-
2-F	10950	11150	11050	12200	11250	-	-
3-A	4973	2600	2800	2350	-	-	-
3-B	-	2450	2525	1975	-	-	-
3-F	11319	11175	11300	12250	-	-	-
4-A	6731	2725	2825	2875	2800	3200	2925
4-B	2665	2650	2875	2500	2075	2750	2500
4-F	11593	11550	11175	12300	10850	11000	10950

REJECTION

	DAY 8	DAY9	DAY 10	DAY 11	DAY 12	DAY 13	DAY 14
1-A	82.01	68.16	77.65	76.46	80.35	83.88	76.87
1-B	85.03	78.77	80.31	80.93	82.75	89.39	83.70
2-A	59.85	77.13	76.02	80.94	77.78	-	-
2-B	78.17	78.03	59.50	84.22	82.44	-	-
3-A	56.07	76.73	75.22	80.82	-	-	-
3-B	100.00	78.08	77.65	83.88	-	-	-
4-A	41.94	76.41	74.72	76.63	74.19	70.91	73.29
4-B	77.01	77.06	74.27	79.67	80.88	75.00	77.17

ULTRAFILTRATION MEMBRANE PILOT PLANT
RUN #1 (CONT.)

CHEMICAL OXYGEN DEMAND (mg/L)

	DAY 15	DAY 16	DAY 17	DAY 18	DAY 19	DAY 20	DAY 21
1-A	2750	3150	3150	3925	3475	3200	3725
1-B	2100	1450	1875	3050	2900	2400	3075
1-F	11000	15000	13250	12350	11050	9400	6800
2-A	-	-	-	-	-	-	-
2-B	-	-	-	-	-	-	-
2-F	-	-	-	-	-	-	-
3-A	-	-	-	-	-	-	-
3-B	-	-	-	-	-	-	-
3-F	-	-	-	-	-	-	-
4-A	3100	3725	4250	5050	4400	3600	4000
4-B	2775	3350	3600	4550	4150	3125	3450
4-F	10750	13850	12050	11550	10600	9200	6500

REJECTION

	DAY 15	DAY 16	DAY 17	DAY 18	DAY 19	DAY 20	DAY 21
1-A	75.00	79.00	76.23	68.22	68.55	65.96	45.22
1-B	80.91	90.33	85.85	75.30	73.76	74.47	54.78
2-A	-	-	-	-	-	-	-
2-B	-	-	-	-	-	-	-
3-A	-	-	-	-	-	-	-
3-B	-	-	-	-	-	-	-
4-A	71.16	73.10	64.73	56.28	58.49	60.87	38.46
4-B	74.19	75.81	70.12	60.61	60.85	66.03	46.92

PERCENT TOTAL SOLIDS: RUN #1

	DAY 1	DAY 2	DAY 3	DAY 4	DAY 5	DAY 6	DAY 7
FEED							
1-F	1.25	1.22	1.24	1.16	1.23	1.29	1.28
4-F	1.17	1.22	1.17	1.22	1.21	1.24	1.2
PERMEATES							
1-A	-	-	1.14	0.97	1.06	0.36	0.74
1-B	-	-	0.76	0.66	0.80	0.4	0.7
4-A	-	-	0.026	0.205	0.124	0.710	0.383
4-B	-	-	0.350	0.459	0.339	0.677	0.417

PERCENT TOTAL SOLIDS: RUN #1 (CONT.)

	DAY 8	DAY 9	DAY 10	DAY 11	DAY 12	DAY 13	DAY 14
FEED							
1-F	1.25	1.2	1.2	1.33	1.25	1.22	1.25
4-F	1.18	1.17	1.12	1.28	1.19	1.24	1.22
PERMEATES							
1-A	0.28	0.81	0.34	0.48	-	0.44	0.33
1-B	0.29	0.33	0.3	0.3	-	0.27	0.33
4-A	0.763	0.308	0.696	0.625	1.000	0.645	0.730
4-B	0.754	0.718	0.732	0.766	1.000	0.782	0.730

PERCENT TOTAL SOLIDS: RUN #1 (CONT.)

FEED

	DAY 15	DAY 16	DAY 17	DAY 18	DAY 19	DAY 20	DAY 21
1-F	1.14	1.54	1.4	1.28	1.15	1.07	0.86
4-F	1.36	-	1.26	1.13	1.13	0.94	0.71

PERMEATES

	DAY 15	DAY 16	DAY 17	DAY 18	DAY 19	DAY 20	DAY 21
1-A	0.38	0.39	0.4	0.5	0.57	0.63	0.49
1-B	0.29	0.27	0.41	0.51	0.61	0.39	0.33
4-A	0.721	-	0.683	0.558	0.496	0.330	0.310
4-B	0.787	-	0.675	0.549	0.460	0.585	0.535

B21

ULTRAFILTRATION MEMBRANE PILOT PLANT: RUN #1

NITROGEN ANALYSIS

	DAY 1	DAY 2	DAY 9	DAY 21
1-A	-	-	197	315
1-B	225	223	213	291
1-F	247	-	230	365
4-A	240	245	-	321
4-B	237	236	181	315
4-F	235	258	227	379

% REJECTION

	DAY 1	DAY 2	DAY 9	DAY 21
1-A	-	-	14.3	13.7
1-B	8.9	-	7.4	20.3
4-A	-2.1	5.0	-	15.3
4-B	-.9	8.5	20.3	16.9

B22

ULTRAFILTRATION MEMBRANES: PILOT STUDY #1
TURBIDITY

DAY	1-A	1-B	A-F	4-A	4-B	4-F
1	1.0	0.2	101	0.6	0.4	111
2	0.1	0.2	80	0.7	0.4	87
3	0.7	0.2	58	0.8	5.8	89
4	1.0	1.2	75	1.1	1.9	90
5	0.6	0.7	80	1.1	1.1	110
6	1.7	0.7	374	9.6	1.7	407
7	2.3	0.2	316	19.2	3.1	314
8	5.0	1.5	328	-	6.1	448
9	0.3	0.5	339	1.7	2.4	336
10	0.3	0.9	342	0.6	4.4	341
17	0.8	2.9	1016	1.0	1.5	1093
18	0.7	0.3	586	5.5	5.4	1524
20	6.1	25.6	624	0.9	15.0	604
21	0.5	22.3	331	1.2	10.3	207

ULTRAFILTRATION MEMBRANE PILOT PLANT
RUN #2

CHEMICAL OXYGEN DEMAND (mg/L)

	DAY 1	DAY 2	DAY 3	DAY 4	DAY 5
1-A	3475	4275	2150	2175	2400
1-B	3350	4125	2000	1900	2050
1-F	5250	6050	8800	7900	6500
4-A	3675	4700	4325	4400	3650
4-B	3750	4550	4025	4725	3450
4-F	4850	5700	8400	7450	6050

REJECTION

	DAY 1	DAY 2	DAY 3	DAY 4	DAY 5
1-A	33.81	29.34	75.57	72.47	63.08
1-B	36.19	31.82	77.27	75.95	68.46
4-A	24.23	17.54	48.51	40.94	39.67
4-B	22.68	20.18	52.08	36.58	42.98

PERCENTAGE TOTAL SOLIDS: RUN #2

	DAY 1	DAY 2	DAY 3	DAY 4	DAY 5
FEED					
1-F	0.58	0.67	0.96	1.31	0.76
4-F	0.48	0.63	0.89	0.75	0.67
PERMEATES					
1-A	0.33	0.5	0.53	0.47	0.44
1-B	0.34	0.49	0.51	0.49	0.41
4-A	0.31	0.21	0.40	0.37	0.34
4-B	0.29	0.22	0.43	0.35	0.39

B25

ULTRAFILTRATION MEMBRANE PILOT PLANT: RUN #2

NITROGEN ANALYSIS

	DAY 1	DAY 2	DAY 3	DAY 4	DAY 5
1-A	355	446	269	227	276
1-B	373	446	219	544	268
1-F	369	443	360	359	345
4-A	367	313	298	228	199
4-B	359	314	294	301	208
4-F	352	346	372	306	252

% REJECTION

	DAY 1	DAY 2	DAY 3	DAY 4	DAY 5
1-A	3.8	-0.7	25.3	36.8	20.0
1-B	-1.1	-0.7	39.2	-51.5	22.3
4-A	-4.3	9.5	19.9	25.5	21.0
4-B	-2.0	9.2	21.0	1.6	17.5

ULTRAFILTRATION MEMBRANES: PILOT STUDY #2
TURBIDITY

DAY	1-A	1-B	1-F	4-A	4-B	4-F
1	19.3	19	419	126.2*	11.3*	292*
2	45.4*	40.4*	267*	14.6	5.1	217
3	13.5	8.6	384	0.8	0.9	419
4	0.8	0.4	305	0.7	1.0	461
5	49.6	48.5	266	0.9	0.8	389

* Stored for 5 days in refrigerator

APPENDIX C

Appendix C : ESCA Survey Spectra of Fluorinated Membranes

MRS Region:	1	Run Date:	12/18/1989	Flood Gun: 1.0eV / 0.30mA
		# of Scans:	10	Sample Angle: 38 Degrees
				Aperture: CLOSED

Sample Description: Fluid Systems Polysulfone Membrane(washed w/H2O)

5000

O(A) Counts:

C 1s

O 1s

N 1s

S 2s

S 2p

O 2s

0.0

1000.0

Binding Energy (eV)

Figure 1a. ESCA Spectra of Dried Polysulfone (PS) (as delivered)

MRS Region:	1	Run Date:	3/15/1990	Flood Gun: 1.0eV / 0.3mA
		# of Scans:	5	Sample Angle: 38 Degrees
				Aperture: CLOSED

Sample Description: Fluid Systems Membrane

2000

Counts:

F 2s —

Si2p —

Si2s —
S 2p —

S 2s —

C 1s —

Na(A) —

O 1s —

F 1s —

F(A) —

O(A) —
O(A) —

Na1s —

0.0

1100.0

Binding Energy (eV)

Figure 1b. ESCA Spectra of Fluorinated PS with 0.025 vol % F_2 in N_2 for 5 Min

MRS Region: 1

Run Date: 3/16/1990

Flood Gun: 1.0eV / 0.30mA
Sample Angle: 38 Degrees
Aperture: CLOSED

# of Scans: 10

Sample Description: Fluid Systems Mem.w/F2/He

Counts: 10000

F 1s

O 1s

C 1s

S 2s

S 2p

F 2s

F(H)

F(A)

F(A)

O(A)

1000.0

0.0

Binding Energy (eV)

Figure 1c. ESCA Spectra of Fluorinated PS with 0.025 vol % F$_2$ in N$_2$ for 30 Min

MRS Region:	1	Run Date:	3/19/1990	Flood Gun: 1.0eV / 0.30mA
		# of Scans:	10	Sample Angle: 38 Degrees
				Aperture: CLOSED

Sample Description: Fluid Systems Mem.w/F2/He

Binding Energy (eV)

Figure 1d. ESCA Spectra of Fluorinated PS with 0.025 vol % F_2 in N_2 for 60 Min

MRS Region: 1

Run Date: 6/4/1990

# of Scans: 15

Flood Gun: 1.0eV / 0.30mA
Sample Angle: 38 Degrees
Aperture: CLOSED

Sample Description: Polysulfone membrane(.05 F2/He:120min.)

10000

Counts:

1000.0

F 2s

S 2p

S 2s

C 1s

O 1s

F 1s

F(A)

F(A)

O(A)

0.0

Binding Energy (eV)

Figure 1e. ESCA Spectra of Fluorinated PS with 0.050 vol % F_2 in N_2 for 120 Min

Table C1: Summary of Atomic Percentages and Binding Energies (PS)

Atomic Percents					
Membrane	Ia	Ib	Ic	Id	Ie
S 2p	2.41	2.13	1.90	1.46	1.31
C 1s	58.20	59.19	29.35	17.93	16.79
C 1s	22.62	18.16	25.09	27.58	24.29
C 1s	-	-	6.20	9.31	10.09
N 1s	1.92	-	-	-	-
O 1s	14.85	8.08	17.55	19.69	3.42
O 1s	-	9.32	-	-	12.76
F 1s	-	3.11	19.91	17.08	-
F 1s	-	-	-	6.95	31.34

Corrected Binding Energies					
Membrane	Ia	Ib	Ic	Id	Ie
Offset	1.16	0.87	0.07	-0.24	-0.89
S 2p	168.29	168.19	168.24	168.28	167.87
C 1s	284.60	284.60	284.60	284.60	284.60
C 1s	286.04	286.08	287.23	287.26	287.03
C 1s	-	-	289.46	289.35	289.09
N 1s	399.65	-	-	-	-
O 1s	532.05	531.55	532.62	532.49	530.70
O 1s	-	533.08	-	-	532.22
F 1s	-	686.45	686.67	686.23	-
F 1s	-	-	-	687.32	686.13

MRS Region:	1	Run Date:	6/7/1990	Flood Gun: 1.0eV / 0.30mA
		# of Scans:	10	Sample Angle: 38 Degrees
				Aperture: CLOSED

Sample Description: Polyethelene(Tyvek 988)untreated

10000

Counts:

1000.0

C 1s

O 1s

0.0

Binding Energy (eV)
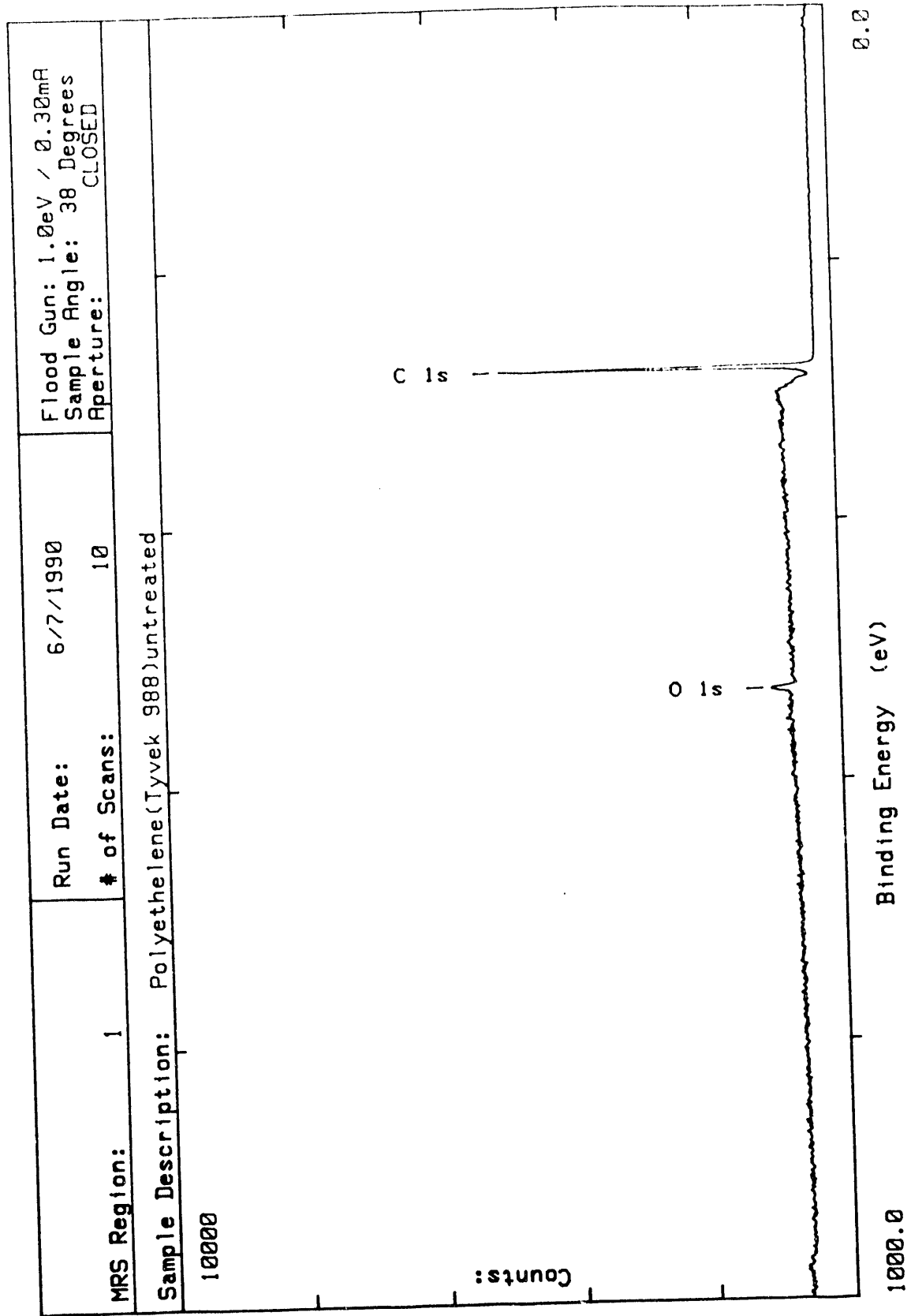
Figure IIa. ESCA Spectra of Untreated Polyethlyene (PE)
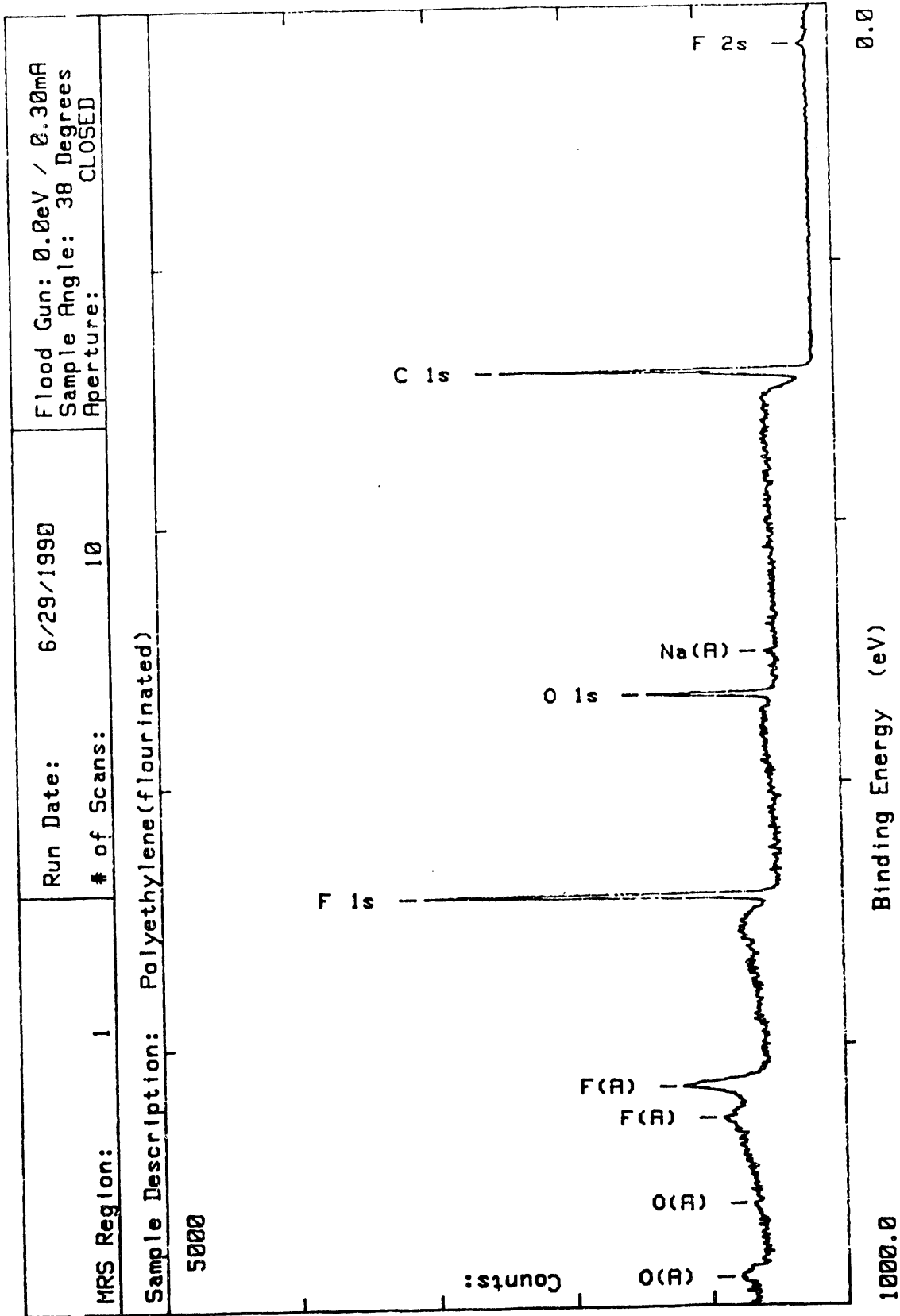
Figure IIb. ESCA Spectra of Fluorinated PE with 0.025 vol % F_2 in N_2 for 30 Min

C9

MRS Region: 1   Run Date: 7/23/1990   Flood Gun: 0.0eV / 0.30mA
                                # of Scans: 10   Sample Angle: 38 Degrees
                                                                 Aperture: CLOSED

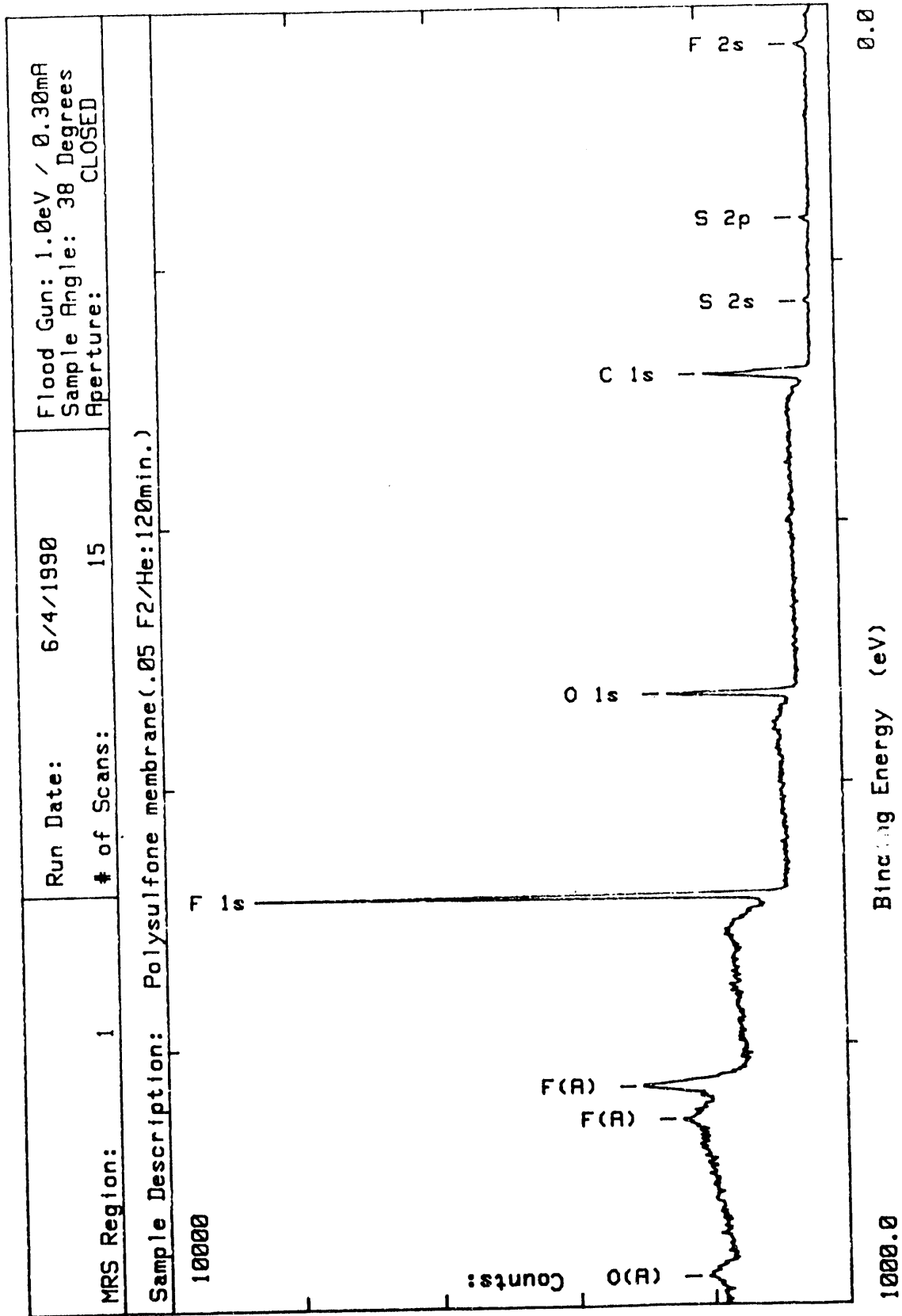Sample Description: Polyetylene(Flourinated)

Figure IIc. ESCA Spectra of Fluorinated PE with 0.250 vol % F₂ in N₂ for 30 Min

Table C2: Summary of Atomic Percentages and Binding Energies (PE)

Atomic Percents			
Membrane	IIa	IIb	IIc
S 2p	0.07	-	0.14
C 1s	83.59	44.19	35.70
C 1s	11.77	25.67	20.74
C 1s	-	3.36	4.03
O 1s	4.57	9.61	3.64
O 1s	-	-	19.17
F 1s	-	14.7	13.84
F 1s	-	2.47	2.74

Corrected Binding Energies			
Membrane	IIa	IIb	IIc
Offset	1.02	0.90	0.30
S 2p	169.9	-	169.01
C 1s	284.60	284.60	284.60
C 1s	285.56	287.14	287.07
C 1s	-	289.74	289.39
O 1s	532.25	532.75	530.99
O 1s	-	-	532.53
F 1s	-	686.44	686.52
F 1s	-	687.85	687.92

MRS Region: 1

Run Date: 9/4/1990

Flood Gun: 0.0eV / 0.30mA
Sample Angle: 38 Degrees
Aperture: CLOSED

# of Scans: 10

Sample Description: Cellulose acetate membrane

5000

Counts:

O 1s —

C 1s —

O 2s —

O(A) —

Binding Energy (eV)

1000.0

0.0
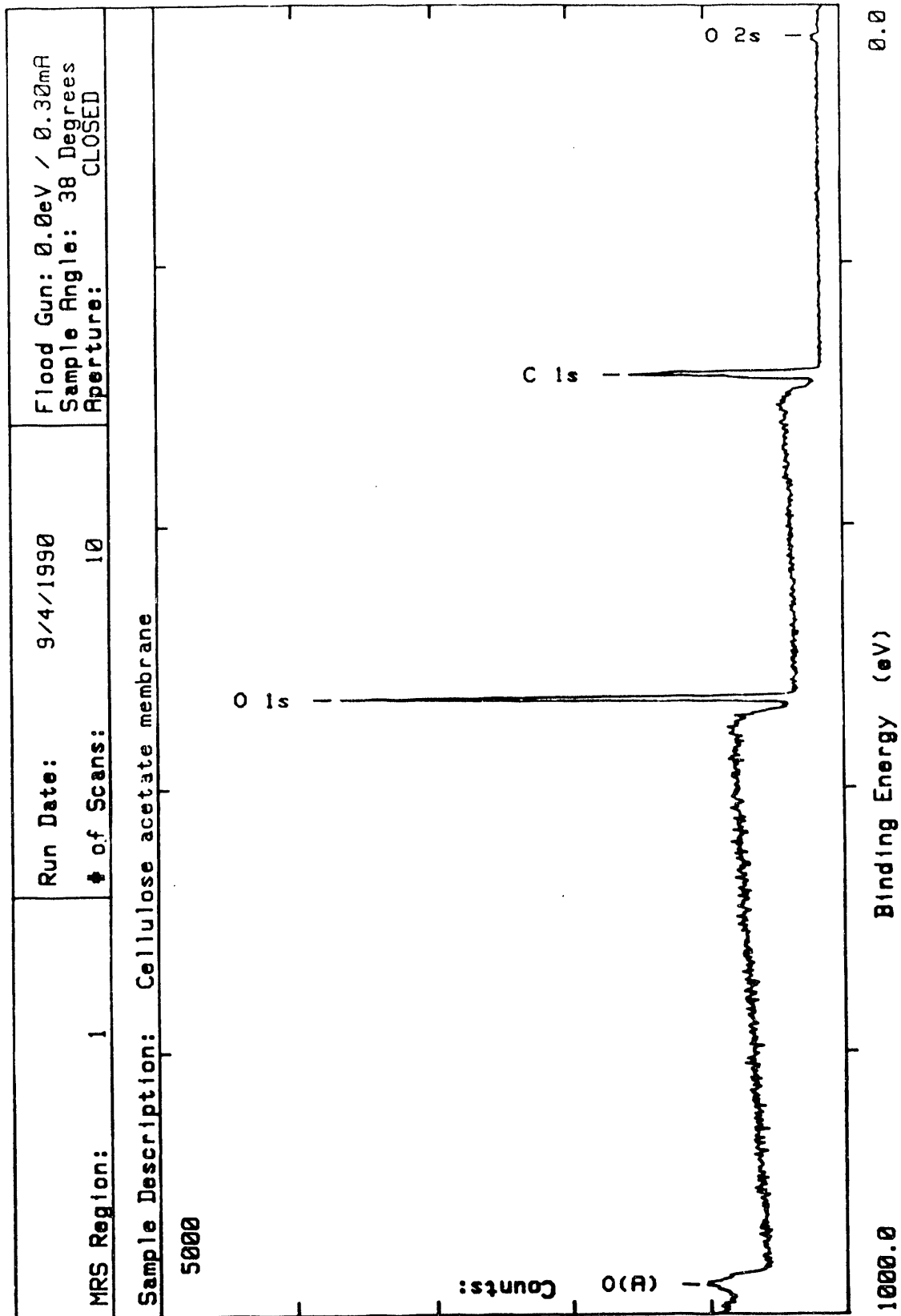
Figure IIIa. ESCA Spectra of Untreated Cellulose Acetate (CA)

MRS Region:	1	Run Date:	9/4/1990	Flood Gun: 0.0eV / 0.30mA
		# of Scans:	10	Sample Angle: 38 Degrees
				Aperture: CLOSED

Sample Description: Cellulose acetate membrane

Counts: 5000

O 2s

C 1s

N 1s

Na(A)
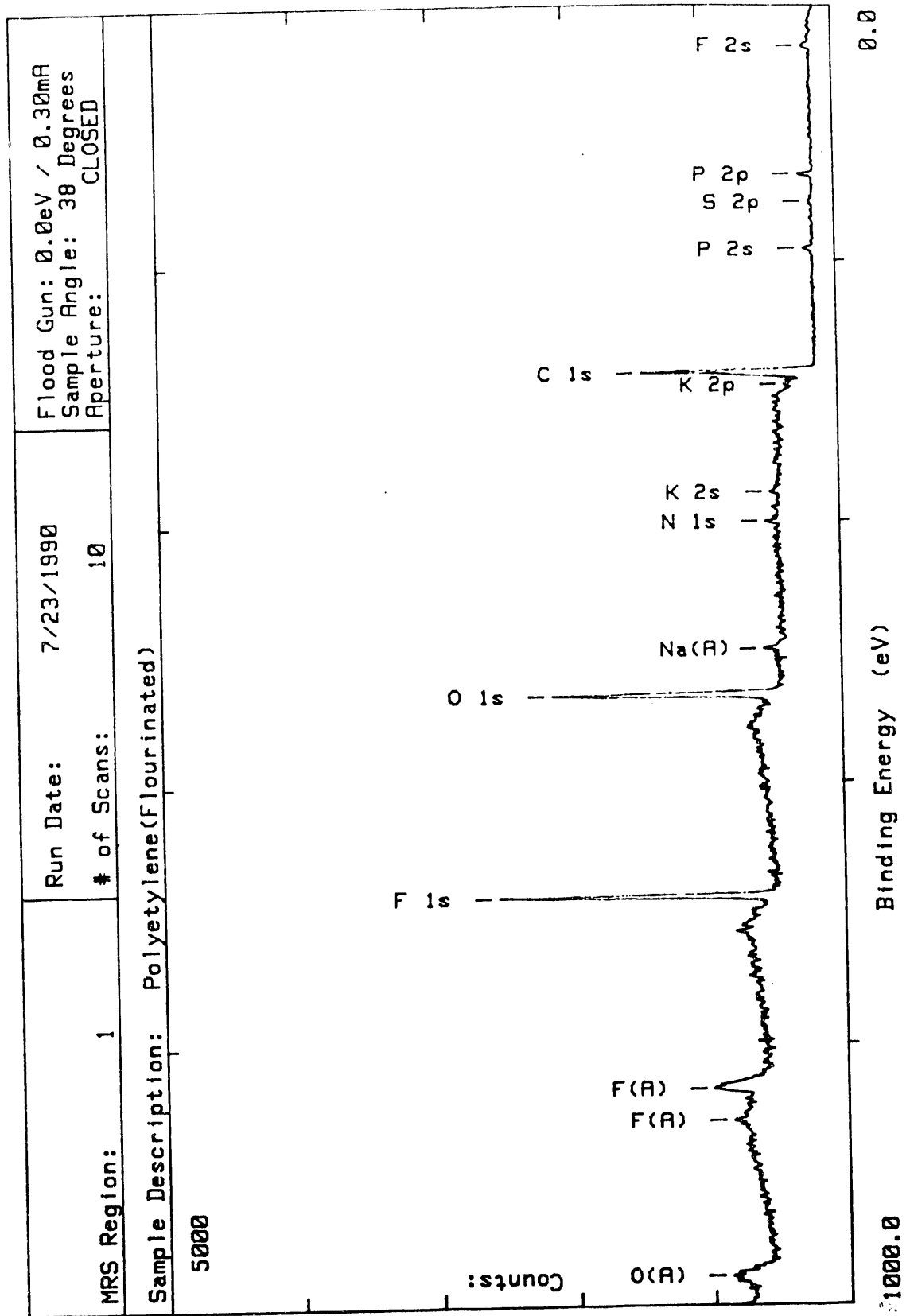
O 1s

F 1s

F(A)

O(A)

0.0

Binding Energy (eV)

1000.0
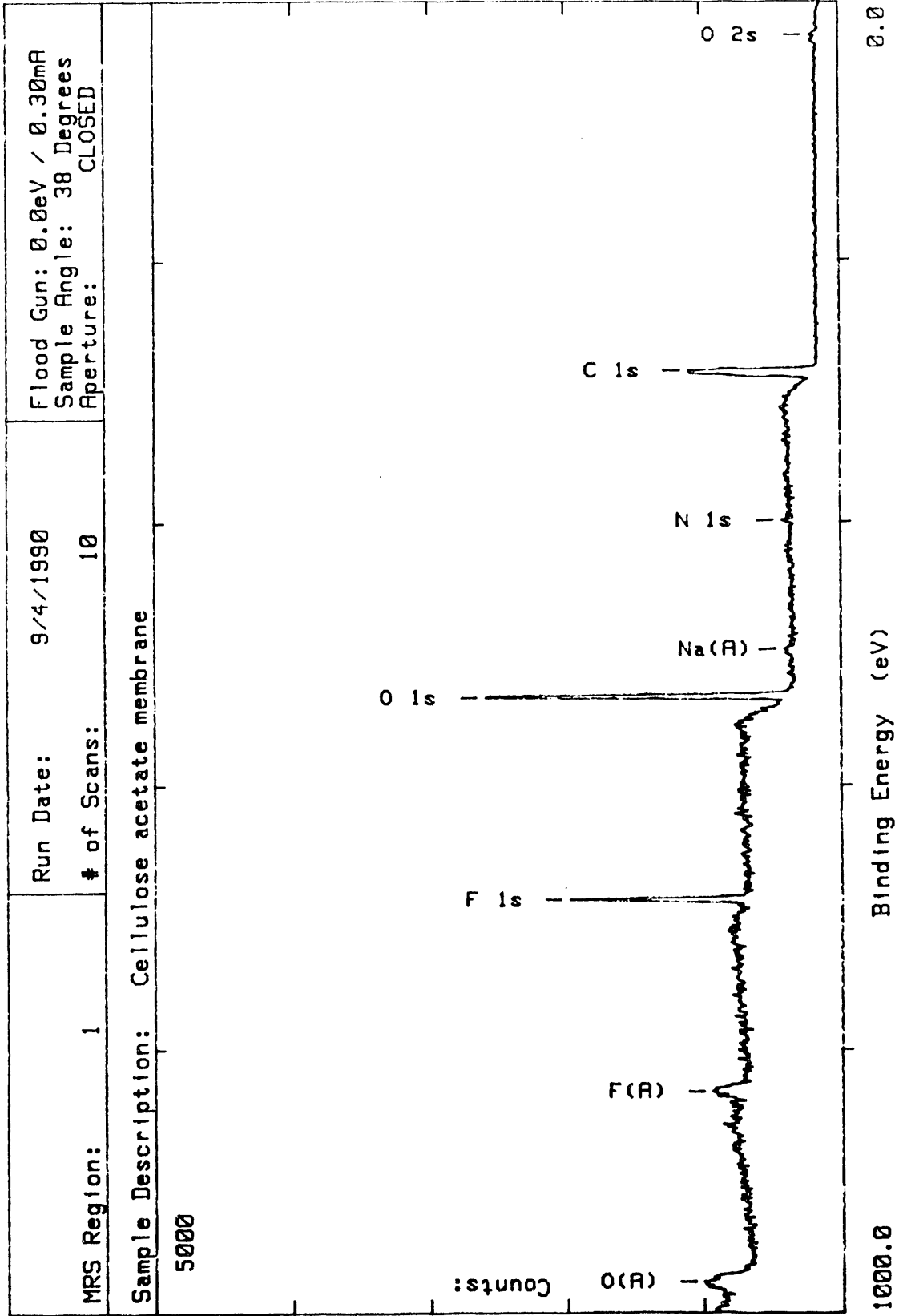
Figure IIIb. ESCA Spectra of Fluorinated CA with 0.025 vol % F_2 in N_2 for 30 Min

Table C3: Summary of Atomic Percentages and Binding Energies (CA)

Atomic Percents		
Membrane	IIIa	IIIb
C 1s	19.94	21.90
C 1s	31.90	24.53
C 1s	15.33	15.70
O 1s	32.82	7.47
O 1s	-	20.98
F 1s	-	9.42

Corrected Binding Energies		
Membrane	IIIa	IIIb
Offset	0.81	0.41
C 1s	284.60	284.60
C 1s	286.35	286.55
C 1s	288.76	288.70
O 1s	532.62	531.54
O 1s	-	532.84
F 1s	-	686.50
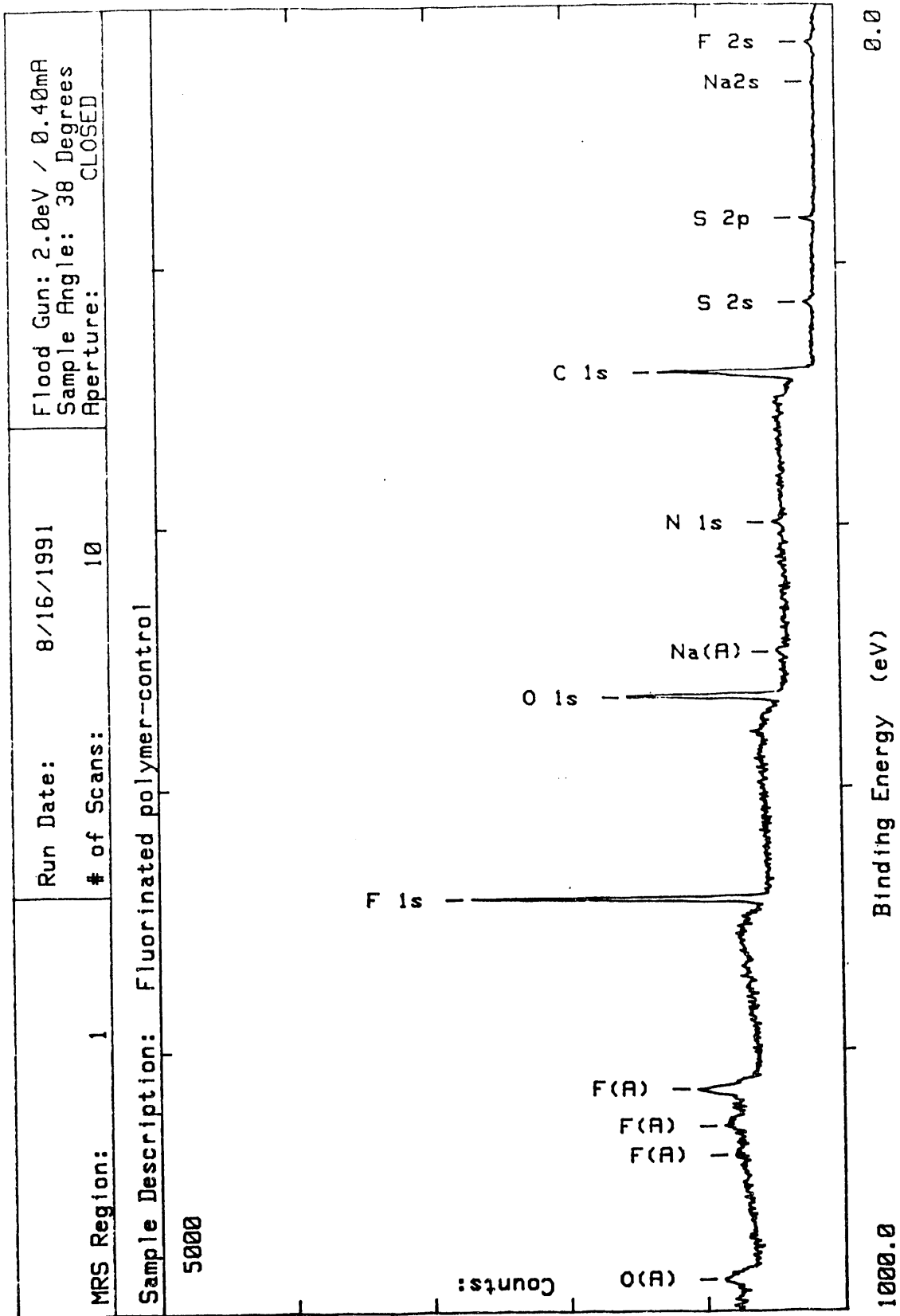
Figure IVa. ESCA Spectra of Dried Polysulfone (PS) (as delivered)
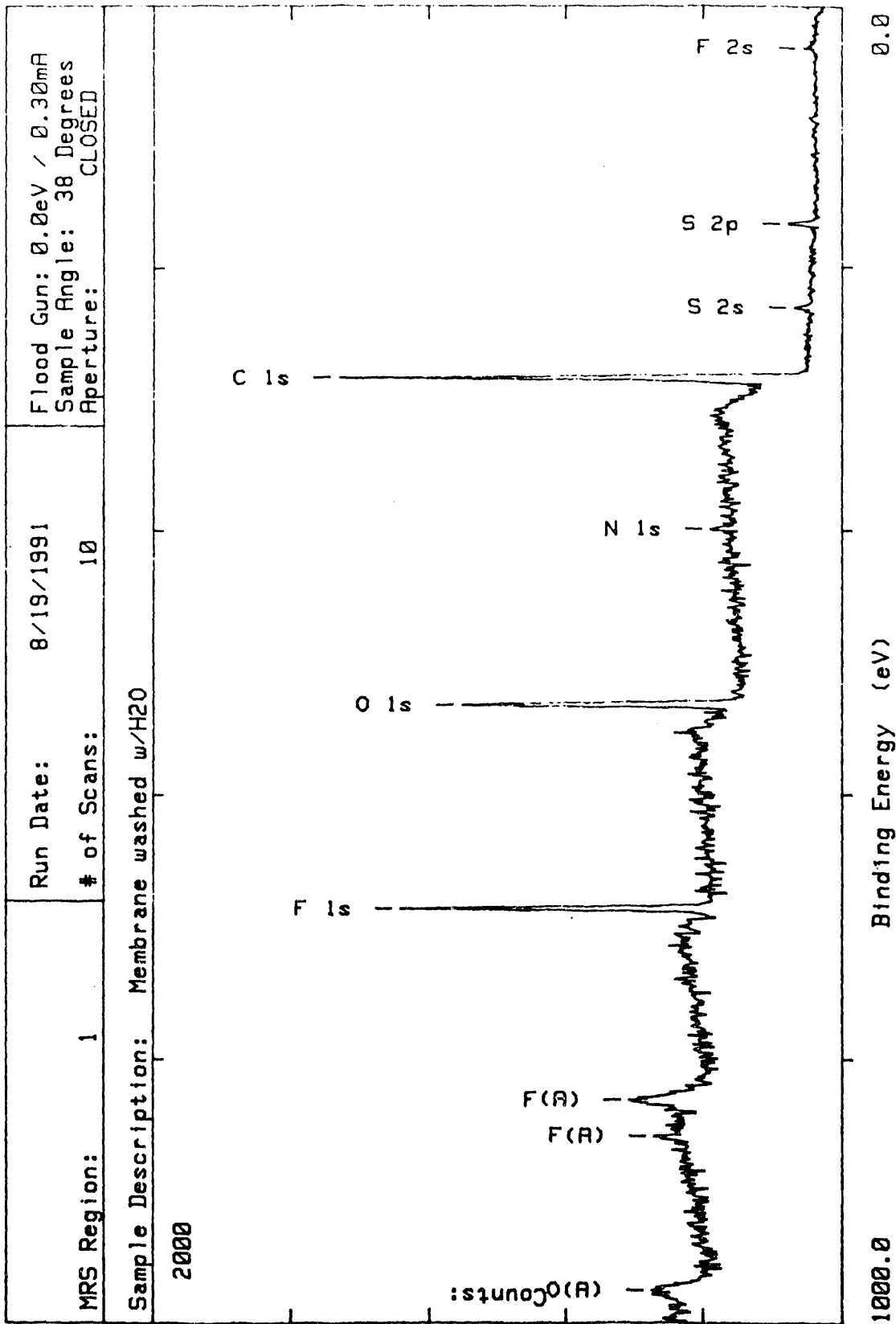
Figure IVb. ESCA Spectra of Washed and Dried PS

The chart includes the following labels and annotations:

MRS Region: 1 | Run Date: 8/19/1991 | Flood Gun: 0.0eV / 0.30mA
# of Scans: 10 | Sample Angle: 38 Degrees
Aperture: CLOSED

Sample Description: Membrane washed w/H2O

Counts: 2000

Peaks labeled: F 2s, S 2p, S 2s, C 1s, N 1s, O 1s, F 1s, F(A), F(A), O(A)

Binding Energy (eV)

0.0 ... 1000.0

C16
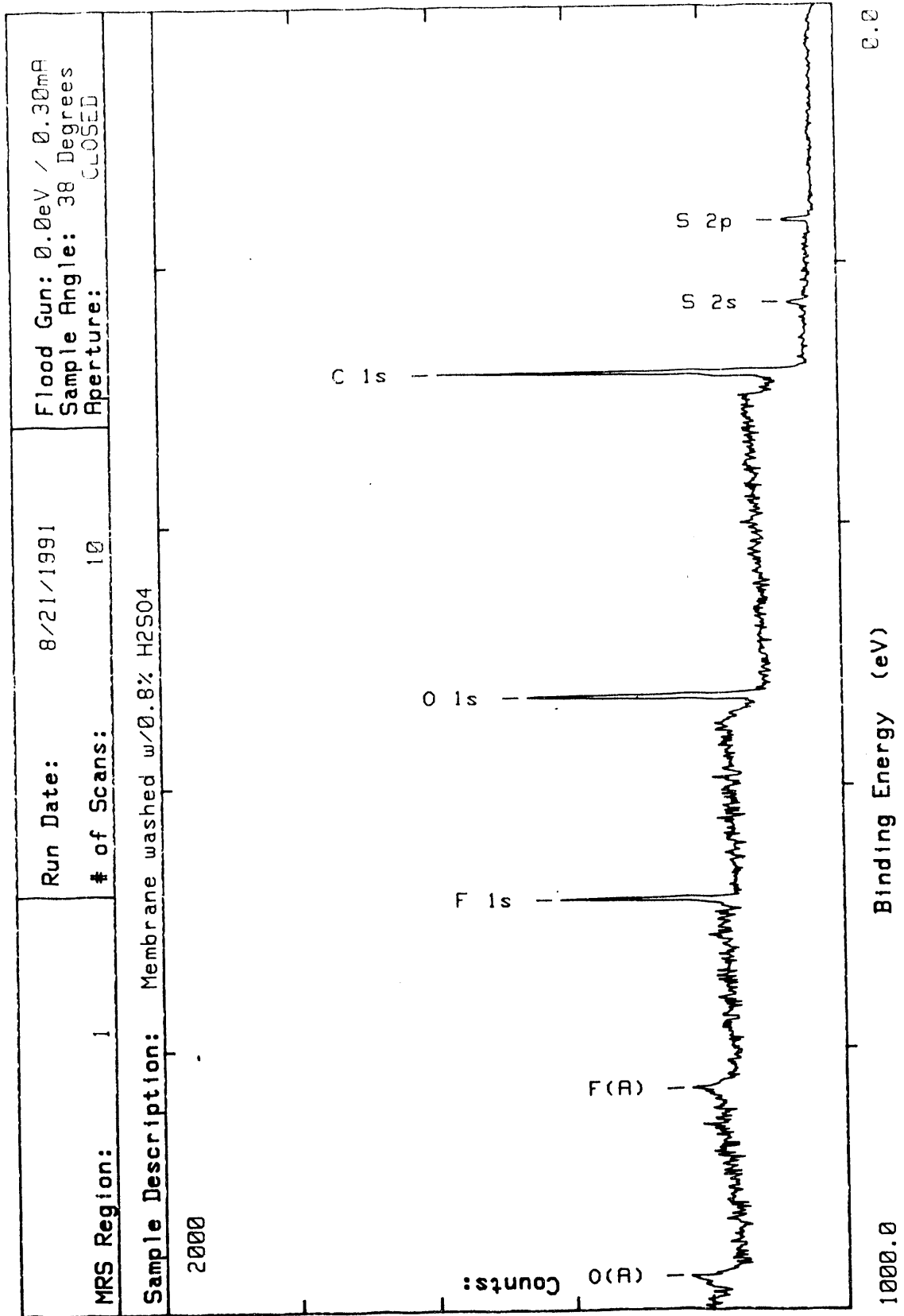
Figure IVc. ESCA Spectra of Fluorinated" PS washed with 0.8% H_2SO_4
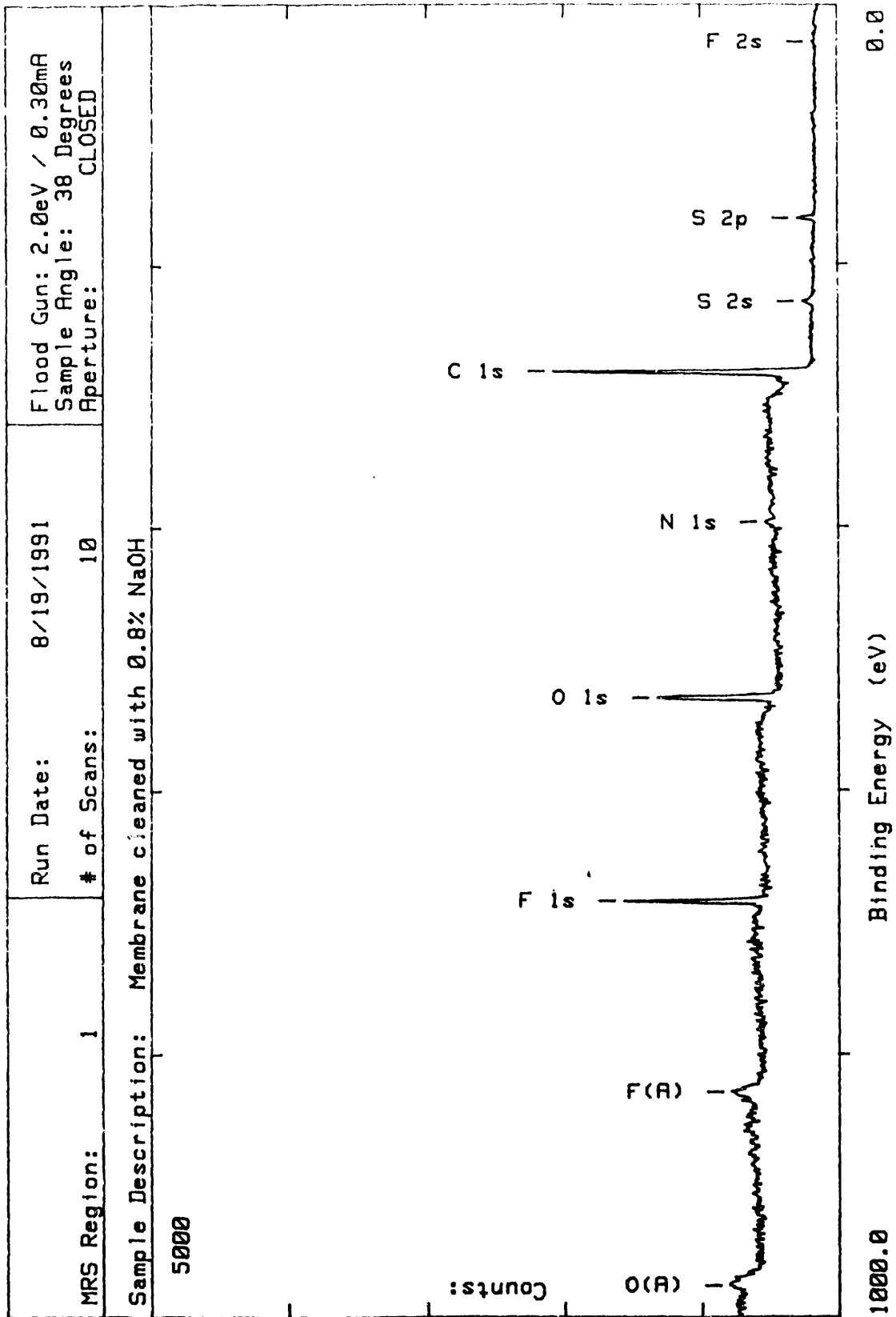
Figure IVd. ESCA Spectra of Fluorinated" PS washed with 0.8% NaOH
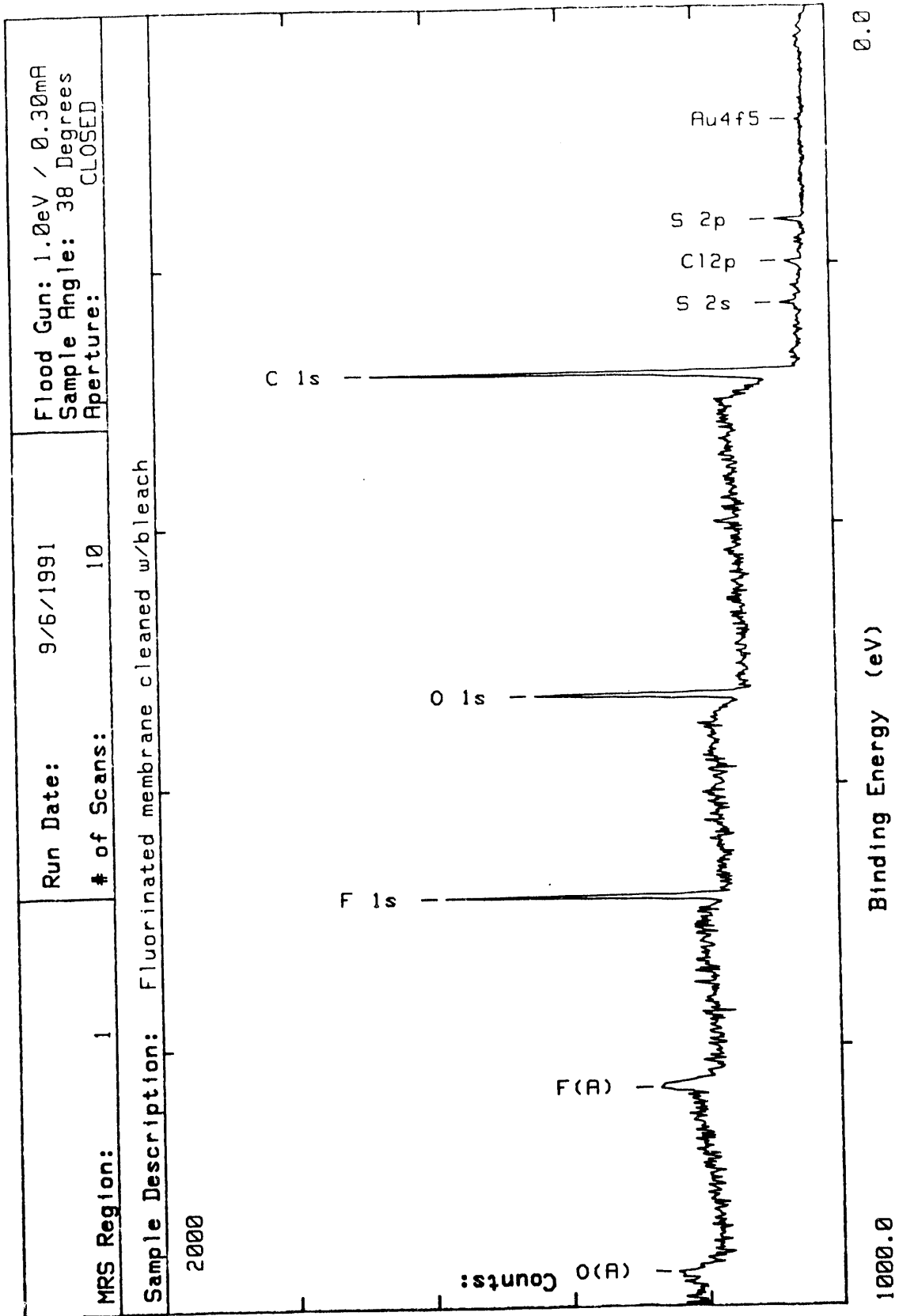
Figure IVe. ESCA Spectra of Fluorinated PS washed with 0.05% Clorox

MRS Region:	1	Run Date:	9/6/1991	Flood Gun: 1.0eV / 0.30mA
		# of Scans:	10	Sample Angle: 38 Degrees
				Aperture: CLOSED

Sample Description: Fluorinated membrane cleaned w/bleach

2000

Counts:

Au4f5 —
S 2p —
Cl2p —
S 2s —
C 1s —
O 1s —
F 1s —
F(A) —
O(A) —

1000.0   Binding Energy (eV)   0.0

C19

Table C4: Summary of Atomic Percentages and Binding Energies
(Cleaning Study)

Atomic Percents					
Membrane	IVa	IVb	IVc	IVd	IVe
S 2p	1.74	2.01	0.24	2.44	2.03
S 2p	-	-	3.41	-	-
Cl 2p	-	-	-	-	0.99
C 1s	34.39	41.13	37.47	47.23	45.11
C 1s	22.62	27.95	30.61	24.83	25.79
C 1s	4.02	-	-	-	-
N 1s	1.49	1.74	1.24	1.36	1.65
O 1s	9.78	8.44	8.55	7.88	6.95
O 1s	8.36	8.27	11.03	7.52	8.60
F 1s	17.6	10.46	7.46	8.74	8.89

Corrected Binding Energies					
Membrane	IVa	IVb	IVc	IVd	IVe
Offset	0.38	1.01	1.21	0.59	0.67
S 2p	168.28	168.25	165.12	168.19	168.19
S 2p	-	-	168.62	-	-
Cl 2p	-	-	-	-	201.01
C 1s	284.60	284.60	284.60	284.60	284.60
C 1s	287.01	286.28	285.81	286.05	286.32
C 1s	289.26	-	-	-	-
N 1s	399.40	399.58	400.70	399.71	399.55
O 1s	531.73	531.75	531.76	531.63	531.72
O 1s	533.11	533.21	533.16	533.16	533.19
F 1s	686.74	686.83	687.00	686.83	686.91
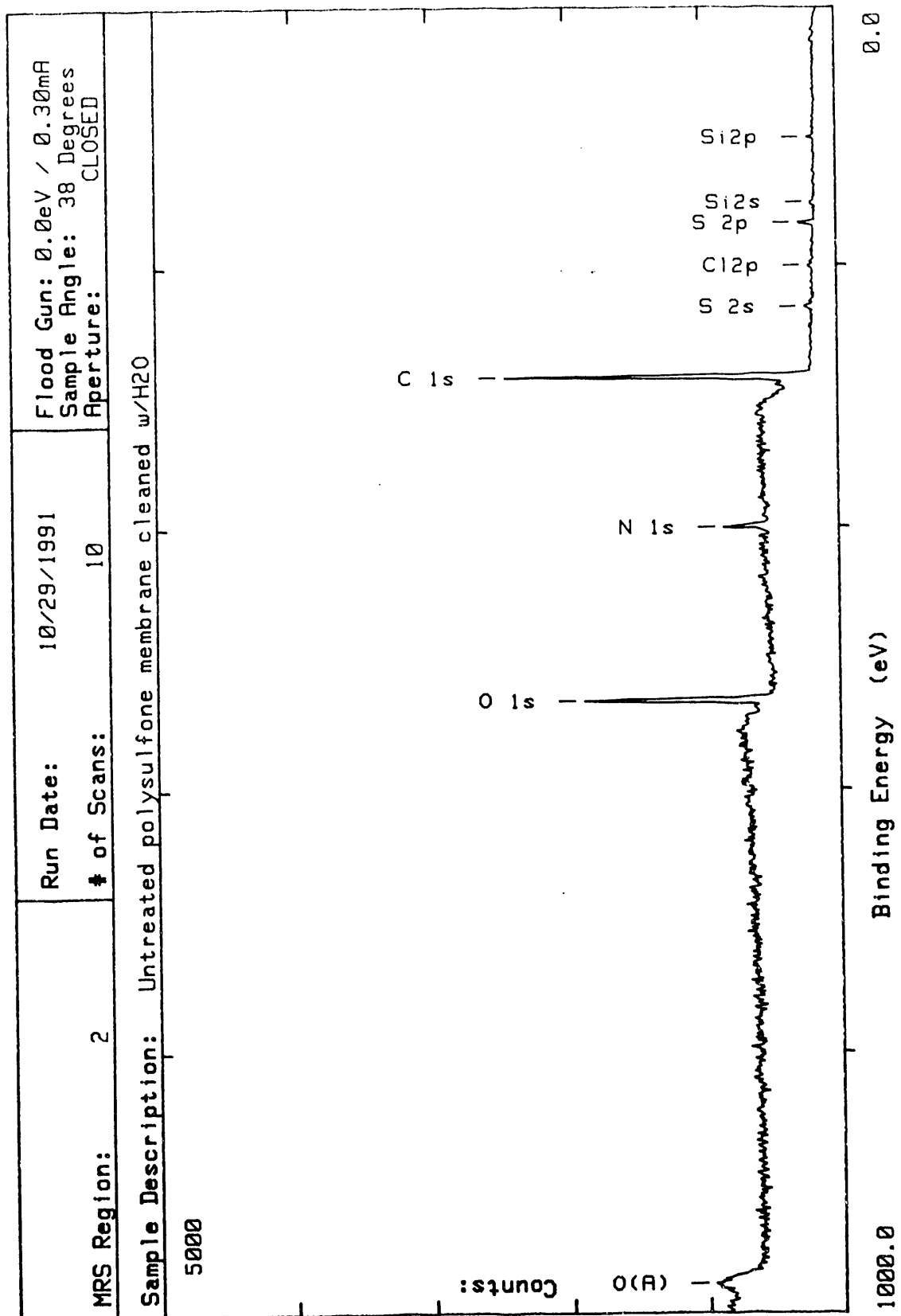
Figure Va. ESCA Spectra of Fouled Untreated Polysulfone Figure

MRS Region:	2	Run Date:	10/29/1991	Flood Gun: 0.0eV / 0.30mA
		# of Scans:	10	Sample Angle: 38 Degrees
				Aperture: CLOSED

Sample Description: Untreated polysulfone membrane cleaned w/H2O

5000

Counts:

Binding Energy (eV)

C21

MRS Region:	2	Run Date:	11/1/1991	Flood Gun: 0.0eV / 0.30mA
		# of Scans:	10	Sample Angle: 38 Degrees
				Aperture: CLOSED

Sample Description: Fluorinated polysulfone cleaned w/H2O
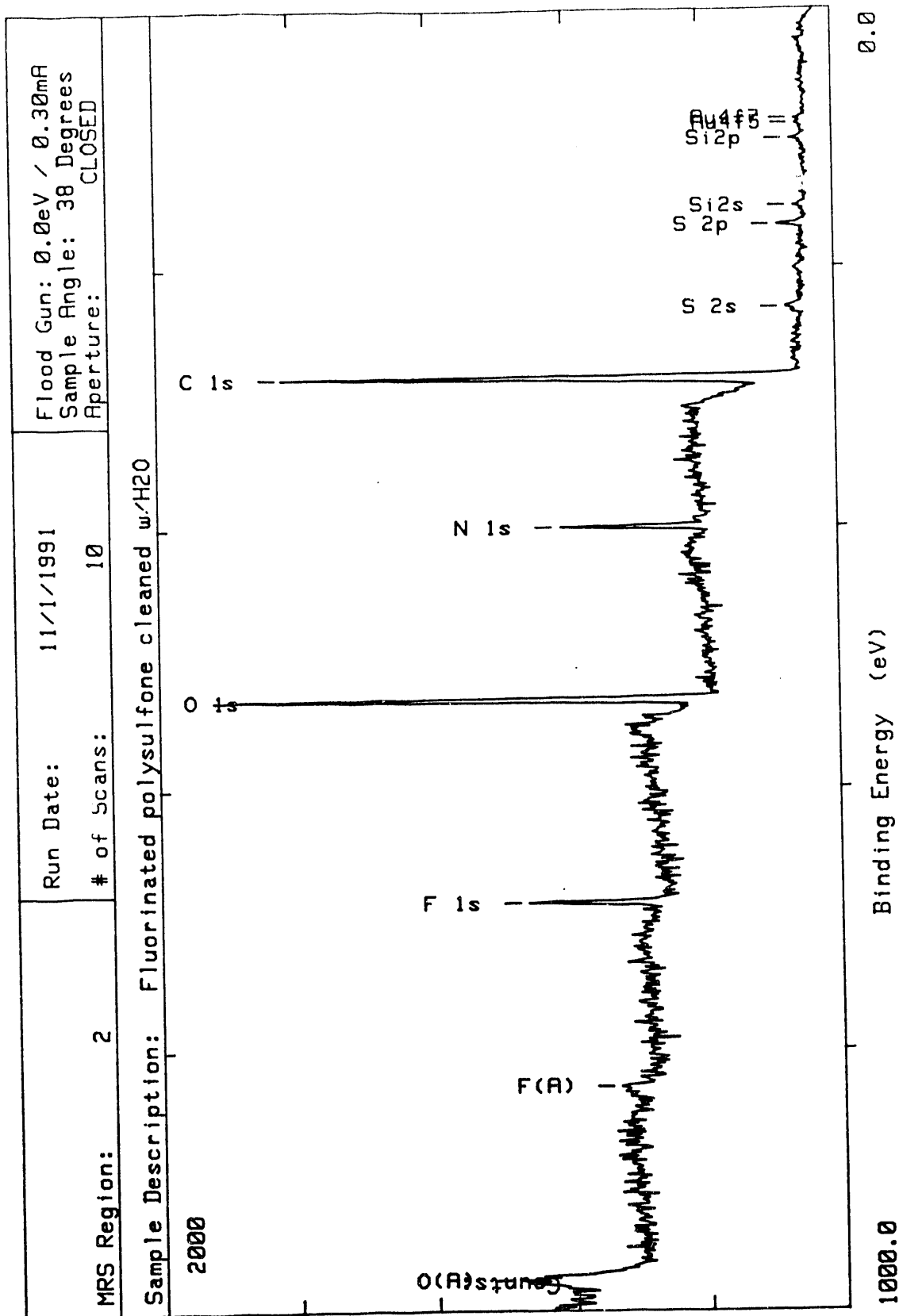
Binding Energy (eV)

Figure Vb. ESCA Spectra of Fouled Fluorinated PS with 0.025 vol % F_2 in N_2 for 30 Min

Table C5: Summary of Atomic Percentages and Binding Energies
(Pilot Plant Studies)

Atomic Percents		
Membrane	Va	Vb
S 2p	1.85	1.18
C 1s	51.28	41.72
C 1s	15.61	11.52
C 1s	8.36	15.26
N 1s	6.30	7.94
O 1s	12.59	17.78
O 1s	4.01	1.77
F 1s	-	2.83

Corrected Binding Energies		
Membrane	Va	Vb
Offset	0.22	0
S 2p	168.79	168.07
C 1s	284.60	284.60
C 1s	286.02	285.97
C 1s	287.47	287.47
N 1s	400.33	399.71
O 1s	531.81	531.72
O 1s	533.41	533.49
F 1s	-	686.27

APPENDIX D

Appendix D: Economic Analysis of Ultrafiltration Systems

D1

Capital Costs of Ultrafiltration System

(5.5-FOLD CONCENTRATION OF PROTEIN IN 1,500,000 POUNDS OF WHOLE WHEY)

Present ultrafiltration membranes:

Equipment Type	Costs ($)	Percentage of Total Cost(%)
Membranes	77,000	24
Hardware (Pressure tubes, pumps, etc.)	215,000	66
Peripherals (Controls, instrumentation, etc.)	35,000	10
Total Costs	327,000	100

Improved ultrafiltration membrane with 25% increase in permeate flux:

Equipment Type	Costs ($)	Percentage of Total Costs(%)
Membranes	57,500	22
Hardware (Pressure tubes, pumps, etc.)	161,000	64
Peripherals (Controls, instrumentation, etc.)	35,000	14
Total Costs	253,500	100
Savings in Capital Costs	73,500	23

Annual Operating Costs of Ultrafiltration System

(5.5-FOLD CONCENTRATION OF PROTEIN IN 1,500,000 POUNDS OF WHOLE WHEY)

Operating Costs	Standard Membrane	Improved Membrane
Electrical ($0.038/kw)	$52,700	$39,500
Steam	438,000 lbs	No Change
Cleaning Water	5,400,000 gal	4,320,000 gal
Cleaning Chemicals	$60,000	$48,000
Membrane Replacement	$60,000	$45,015
Labor	1095 hours	No change

END

DATE
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