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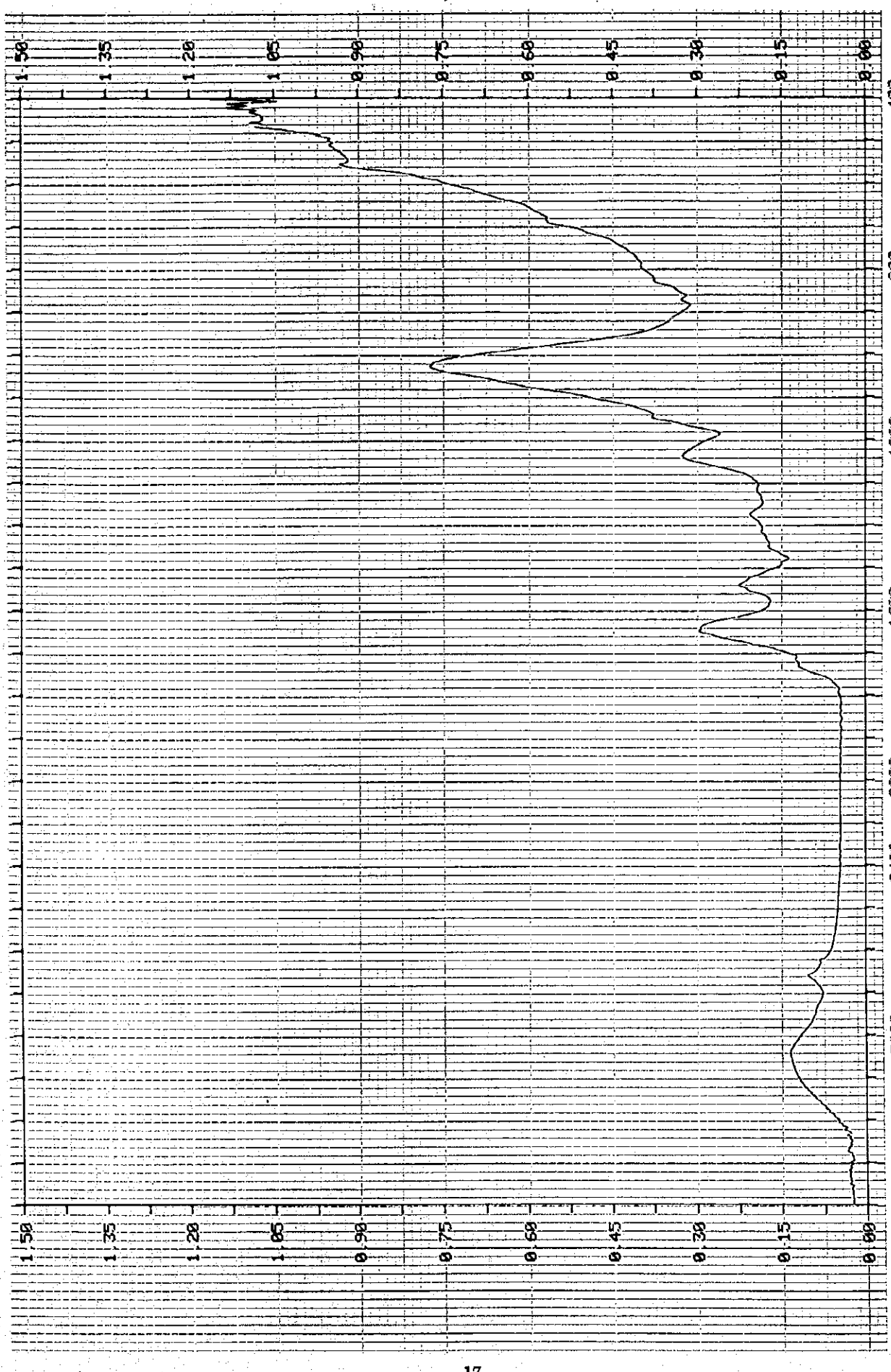

Fig. 7 IR CHART OF THE HCl CLEANED MEMBRANE

(7.1.2.B)

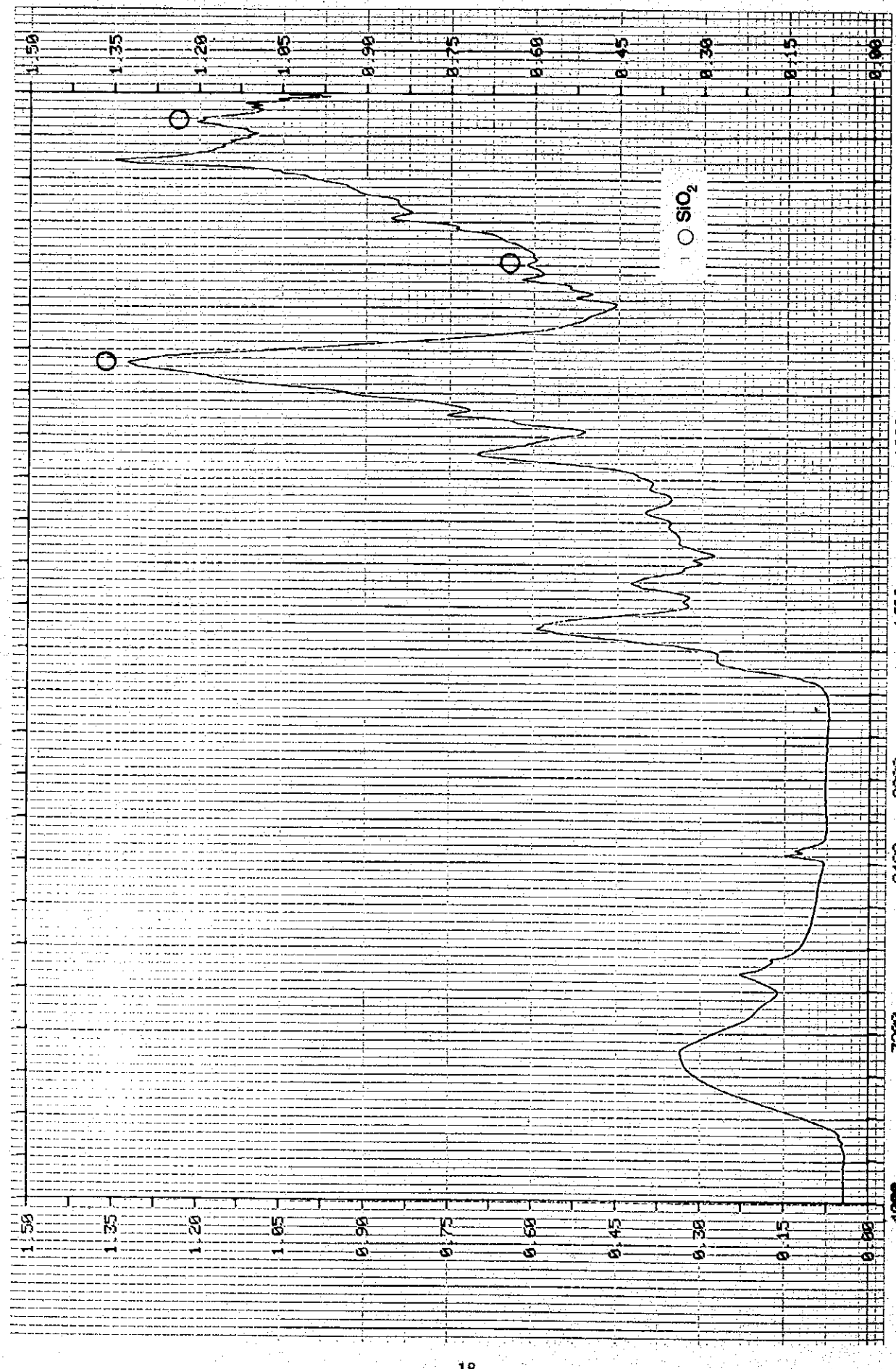

Fig. 8 IR CHART OF THE OXALIC ACID CLEANED MEMBRANE

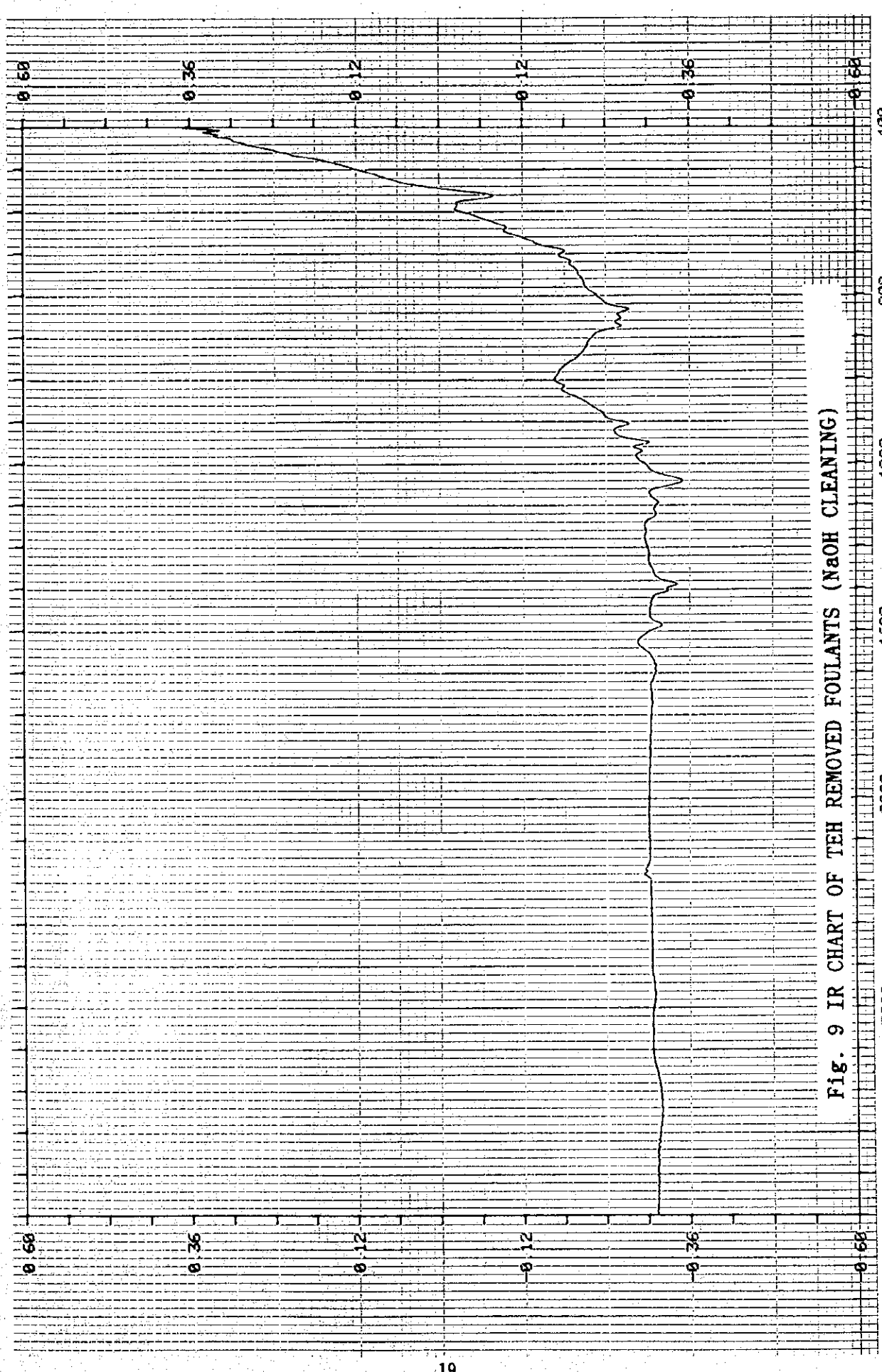

Fig. 9 IR CHART OF TEH REMOVED FOULANTS (NaOH CLEANING)

(7.1.2.B)

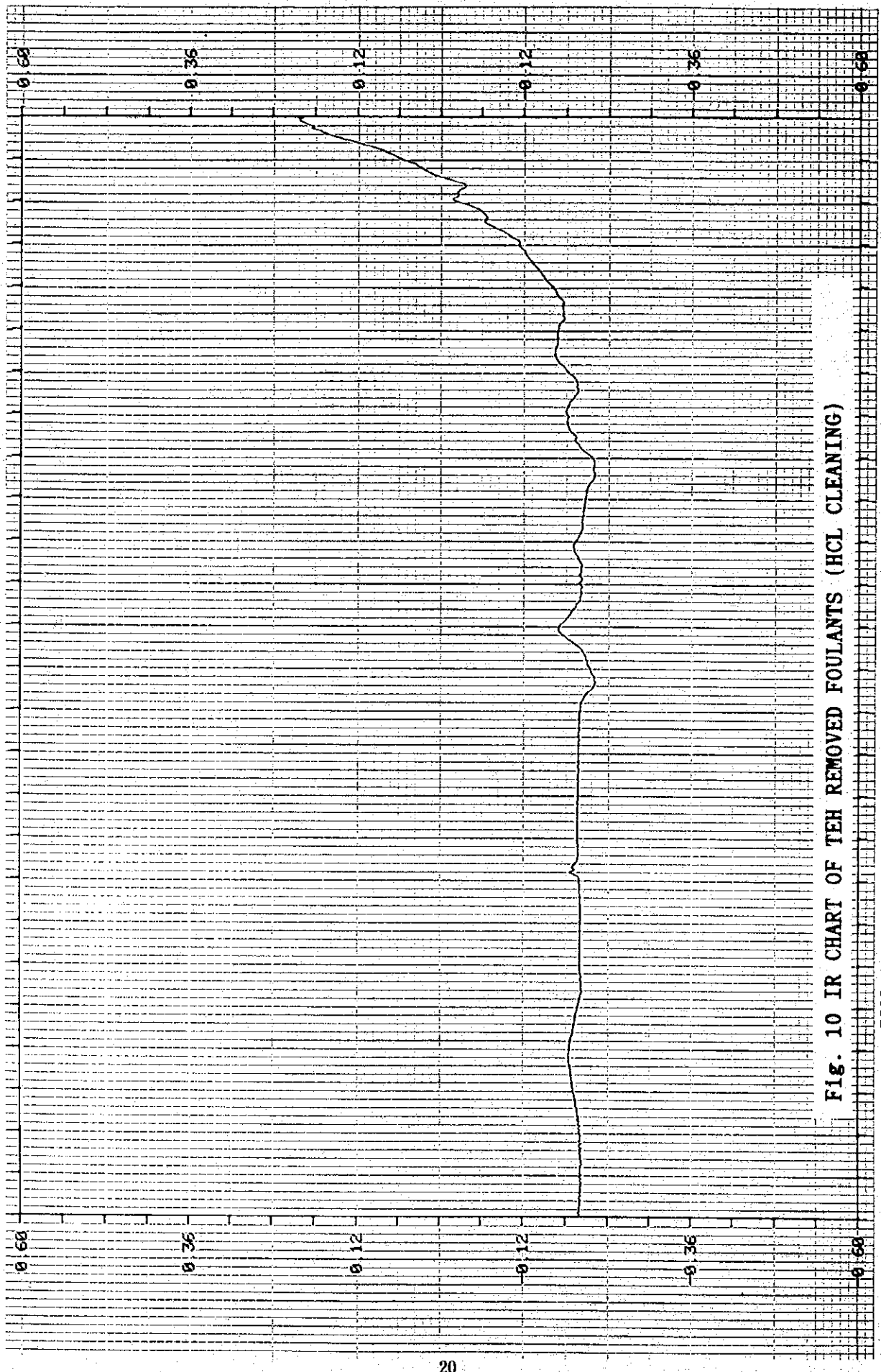

Fig. 10 IR CHART OF TEH REMOVED FOULANTS (HCL CLEANING)

(7.1.2.B)

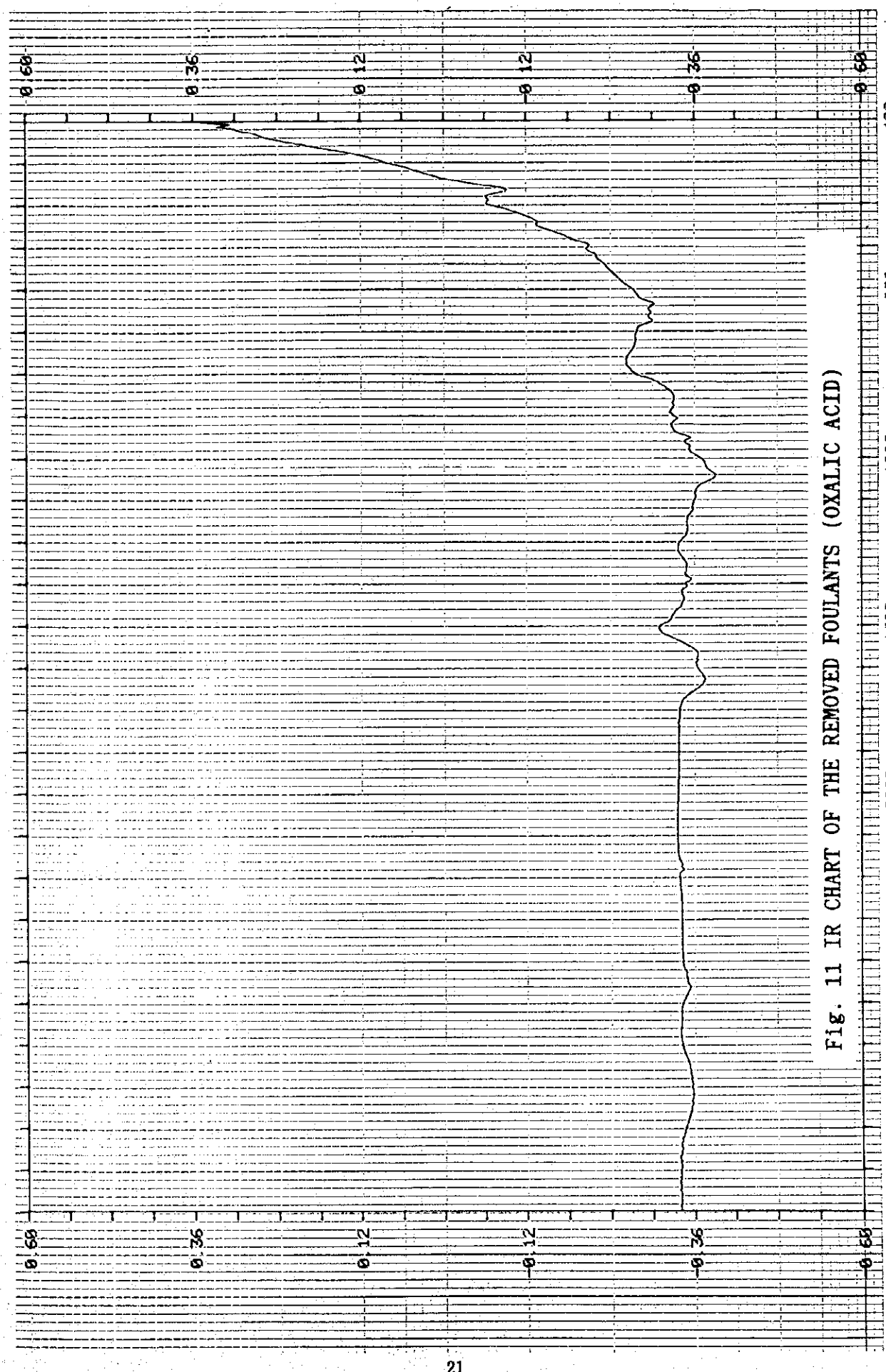

Fig. 11 IR CHART OF THE REMOVED FOULANTS (OXALIC ACID)

7.1.2.C. Fouled Membrane Analysis of Duba SWRO Plant (1)

Contents

List of Tables

List of Figures

1. OBJECTIVES

Performance deterioration of SWRO membranes by chemical and biological fouling are a major concern for the desalination by RO process. The present study aims at identifying the foulants on the fouled membrane surfaces and also causes of membrane deterioration. In addition to visual inspection of membrane surface, various techniques such as scanning electron microscope (SEM), energy dispersive X-ray (EDX) spectroscopy, atomic absorption spectroscopy (AAS) and ion chromatography were used to analyze membranes with poor performance and the foulants on their surfaces. Also the effectiveness of various chemical cleaning agents which can be used for the performance restoration of the fouled membranes was evaluated. This report describes the autopsy and analysis of a SWRO hollow fine fiber membrane obtained from Jeddah SWRO plant and a brackish water spiral wound membrane obtained from Duba second stage SWRO plant.

2. EXPERIMENTAL METHOD

(1) Equipment

Scanning electron microscope (SEM) and energy dispersive X-ray spectroscope (EDX) were used for foulants analysis. Quantitative analysis of the inorganic foulants was done using atomic absorption spectroscope (ASS) and ion chromatograph.

(2) Materials

Autopsy was performed on the hollow fine fiber Toyobo HM 10155 membrane element from module No. 91 of Train E of Jeddah SWCC, SWRO Plant which was in operation for about 5 years and a spiral wound element which was obtained from Duba plant. The latter membrane was removed long time ago and was not preserved for proper autopsy and analysis.

Sodiumhexametaphosphate (SHMP) (1% wt), oxalic acid (0.2% wt, pH = 4), hydrochloric acid (pH = 4), citric acid (2% wt, pH = 4) and ethylenediamenetetra-acetic acid disodium salt (EDTA) (1.5%) were used in the membrane cleaning.

(3) Experimental Procedure

The spiral wound element was analyzed for the foulants using SEM and EDX. The hollow fine fiber element was cut open and physically examined. Samples of fibers of length 50cm were cut from the inner (closer to the feed tube), the middle and the outer portion and it was preserved in 0.5% formalin in a plastic bag.A portion of heavily

fouled membrane was cleaned by immersing in for 24 hours in one of the above mentioned cleaning agents prior to SEM and EDX analysis along with the uncleaned membranes. AAS and ion chromatograph analysis were conducted on samples dissolved in water, or oxalic acid or HCI.

3. RESULTS AND DISCUSSION

(1) Results

A general overview of the spiral wound membrane surface obtained at SEM magnification of 750 is shown in Figure 1 which also gives the elemental analysis of the foulant as determined by EDX the method. The X-ray elemental dot mapping gave the elements distribution in the fouled areas as given in Figure 2.

The general appearance of hollow fine fiber element at various stages of autopsy are shown in Figures 3. The physical examination of the membrane fibers reveal that the fibers close to the feed tube were deepest in color and largest amount of the deposits. Both the color intensity and the amount of deposits decrease as the fiber distance from the feed tube is increased. The fibers at the peripheral part of the element are slight yellowish in color and contains negligible amount of deposits. Qualitative analysis of this reddish brown deposits reveal that it was composed mainly of iron (Fe3) deposits. In addition to the reddish brown deposits, some black particles and some fibrous sticky materials were also observed on the feed tube of the element. Results of SEM and EDX for the fibers from inner, middle and outer portion, the cleaned fibers, the black particles and the sticky fibrous materials are shown in Figures 4 to 14. Results of quantitative inorganic analysis of foulant collected from the hollow fine fiber Toyobo are given in Table 1.

(2) Discussion

Main foulants present on spiral wound membranes were: C,O,Si,Al,Fe and Cr. Other elements such as Na, Mg, CI,K and Ca were found at low concentration. The Fe and Cr distribution on the surface of the fouled membrane are not only similar but also has the same general appearance as that sown for the back scattered electron image, the first photo in Figure 2. The same general distribution is noticed for the Al and Si elements and to a lesser extent C and O which tend to have similar distribution. Similar elements distribution could indicate their presence in a combined or associated form. Thus, the Fe and Cr could arise from the accumulation on the membrane surface of stainless steel corrosion products. The other possibility that the

Fe could arise from the accumulation of trace of the ferric coagulant (Fe2SO4)3) used in the pretreatment step, can be ruled out since the Duba second stage membranes are fed the product from the SWRO first stage which should not allow for Fe passage. The C and O are likely to originate from the CO3 molecules accumulated on membrane surface.

SEM results on the hollow fine fiber fouled membrane shows heavy deposits of foulants which mainly consists of C,O,Fe,Al and Si and also Na and Cl from the salt crystals and to lesser extent Mg,K, and Ca. Micrographs shows that the fiber closer to the feed tube (Figure 4) is heavily fouled whereas fibers away from feed tube, viz, from middle (Figure 5) and top (Figure 6) portions are less fouled. Cleaning using various chemical cleaning agents did not completely remove the foulants as can be seen from the SEM micrographs as well as from EDX (Figure 7 to 12). Oxalic acid was found to be the most efficient cleaning agent as it removes most of the foulants (see Figure 12).

The chemical analysis of the deposits of fiber which was extracted using water, oxalic acid and hydrochloric acid are given in Table 1. In addition to the elements obtained using EDX, chemical analysis revealed the presence of trace amounts of Mn,Zn,Cu,Ni,Sr,Cr and P. It is surprising to observe the absence of SO4 in the chemical analysis of deposits. The high amount of C and O could be due to the presence of carbonates or organic matter from the fiber itself or decayed biological matter. The Fe is from the usage of FeCl3 as coagulant which were collected on the fiber passing through the media filters. The elements Al,Si and Mg originate from silt. Analysis of the black particle by using EDX reveal that it consists of mainly carbon, which could be anthracite particle from the media filter. whereas the fibrous material consists of mainly Si, Mg and Fe of which former two are the major constituents of asbestos.

4. CONCLUSION

The analysis of foulants on Duba second stage spiral wound membrane using SEM and EDX reveal that it contains mainly Fe,Cr,C and O which are produced as a result of corrosion of stainless steel part and also due to deposition of carbonates on membrane.

The analysis of hollow fine fiber reveals that it has large deposits of ferric from the coagulant. Also it has silt, anthracite and asbestos like material on the membrane surface. The study also reveals that oxalic could be used as cleaning agent as it removes most of the foulants.

TABLE 1: QUANTITATIVE INORGANIC ANALYSIS DATA OF MEMBRANE DEPOSITS ON HOLLOW FINE FIBER TOYOBO
(Amount with respect to fiber)

Analyte	Water extract (ppm)	Oxalic acid (2%) extract (ppm)	Hydrochloric acid (1:1) extract (ppm)
Fe	19	14963	17449
Mn	5	5.5	5.4
Zn	ND	3.3	3.4
Cu	1	8.5	8.4
Ni	ND	6.6	9.2
Na	3994	2752	6011
Ca	154	224	327
Mg	360	468	589
K	231	170	192
Al	ND	481	483
Sr	18	30	37
Cr	ND	17	18
Cl	7135	4826	NA
Po_4	131	150	141
SiO_2 (insoluble)	ND	664	560
NO_3-N	16	20	52

Note: *ND = Not Detected*
NA = Not Analyzed

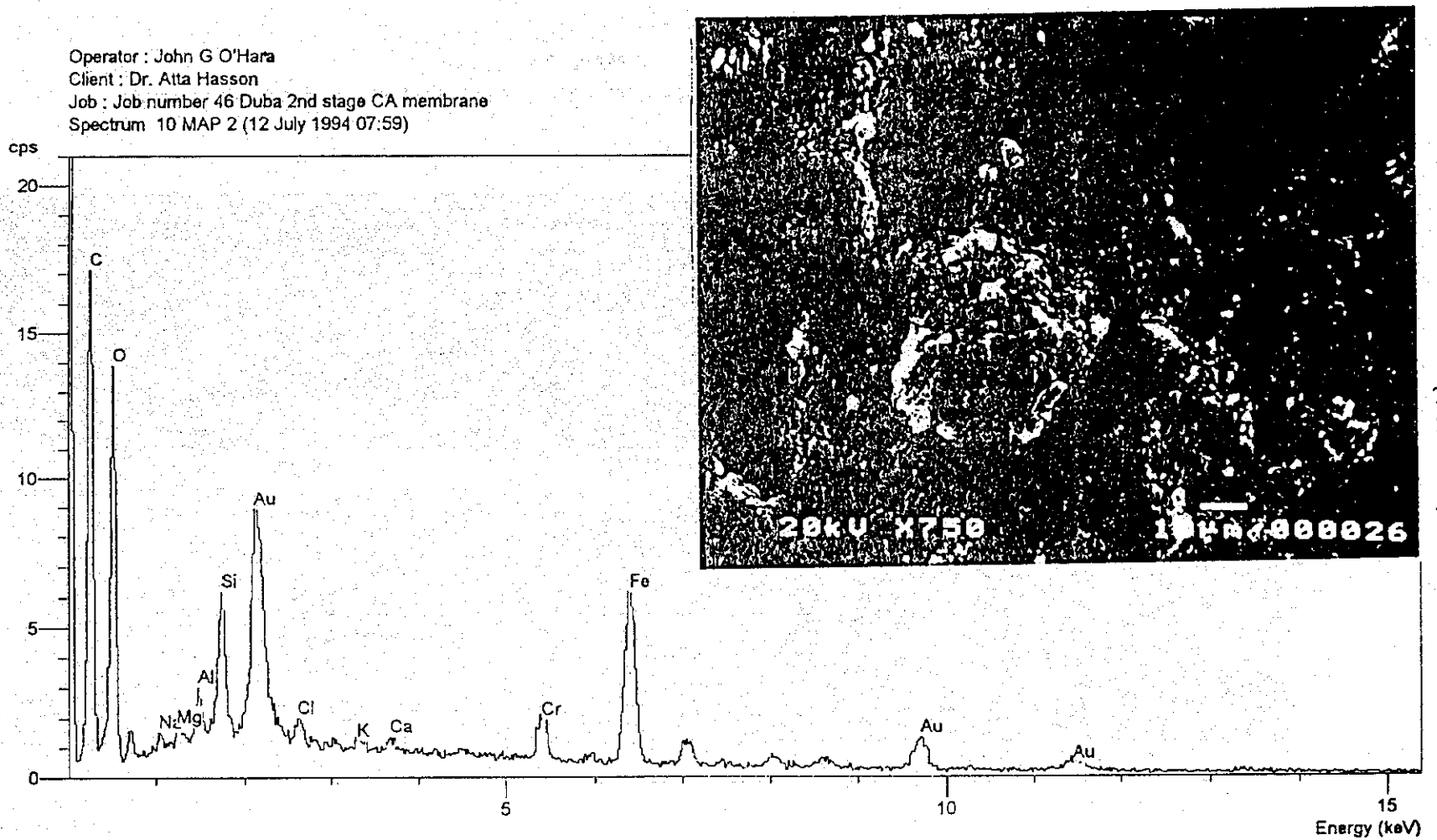

Figure 1 : SEM Micrograph and EDX Spectrum of Fouled Spiral Wound Membrane

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Client: Dr. Atta Hasson
Job: Job number 46 Duba 2nd stage CA membrane
Label: MapGroup 2 (3 Jul 94 13:07:25)

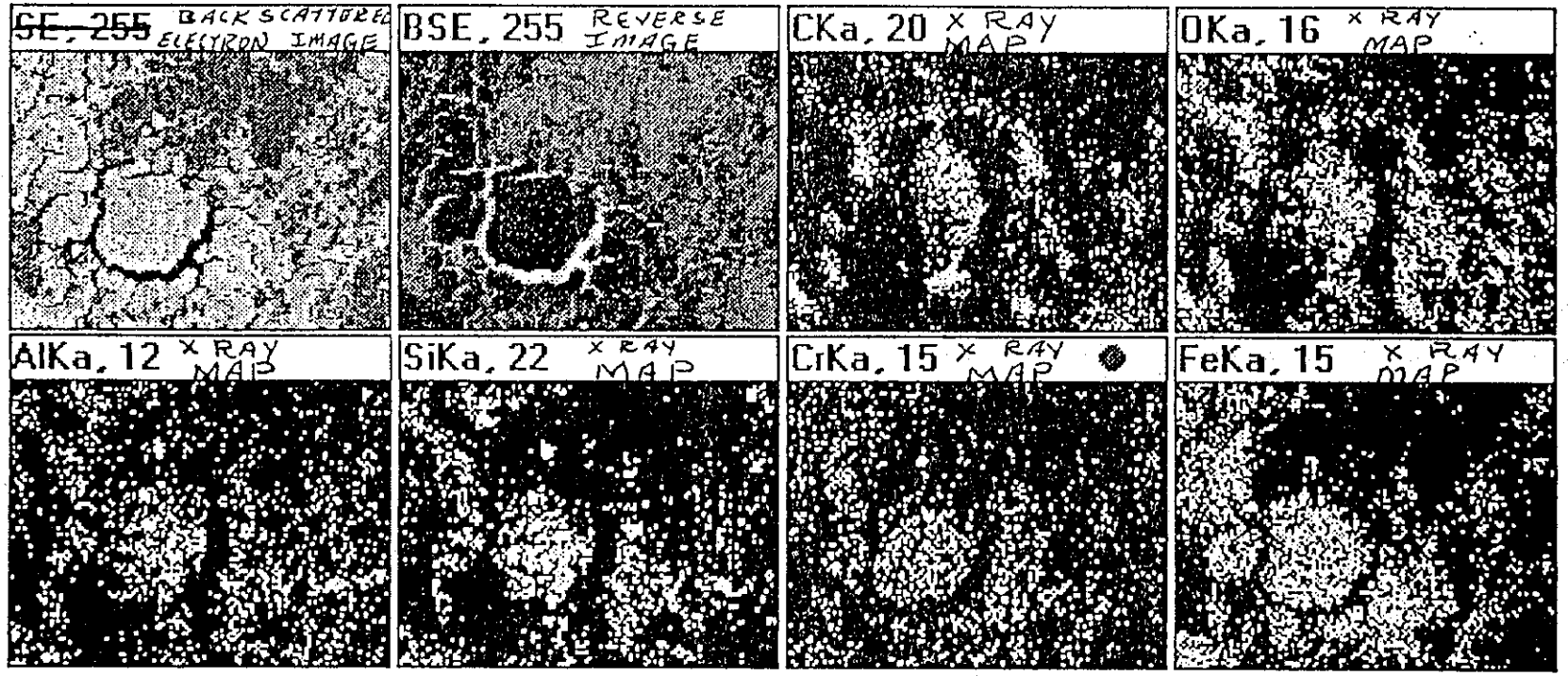
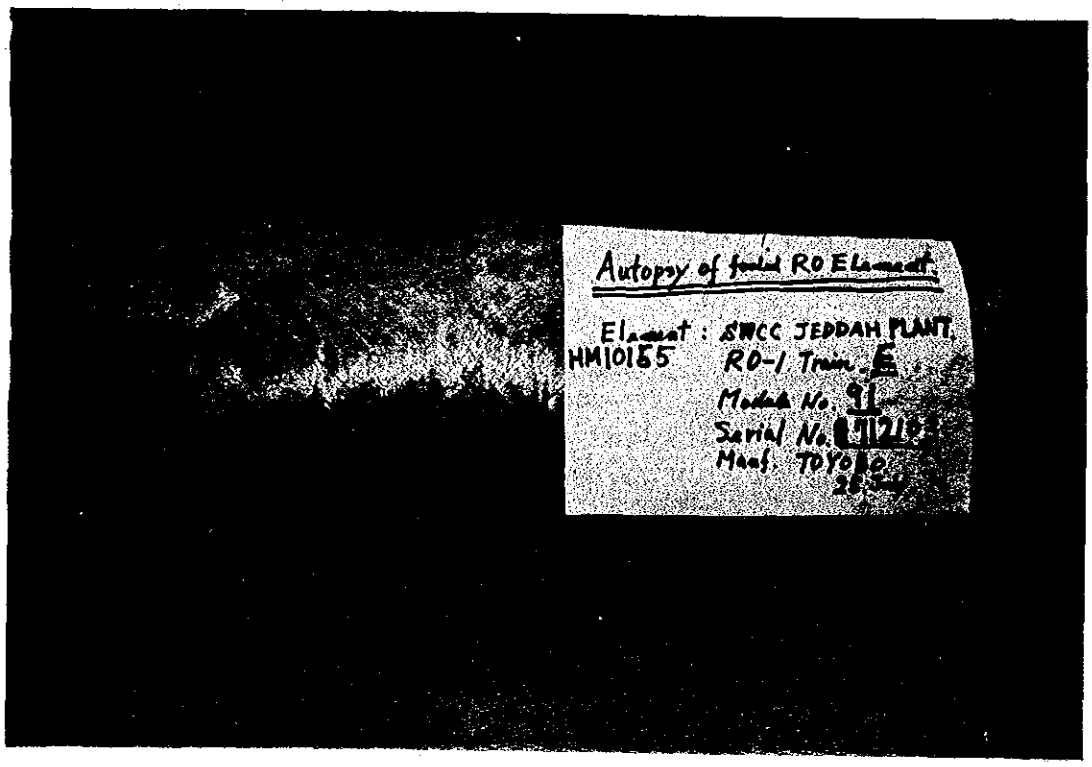


Figure 2 : The X-ray Dot Mapping of Elements Accumulated on the Surface of Fouled Spiral Wound Membrane

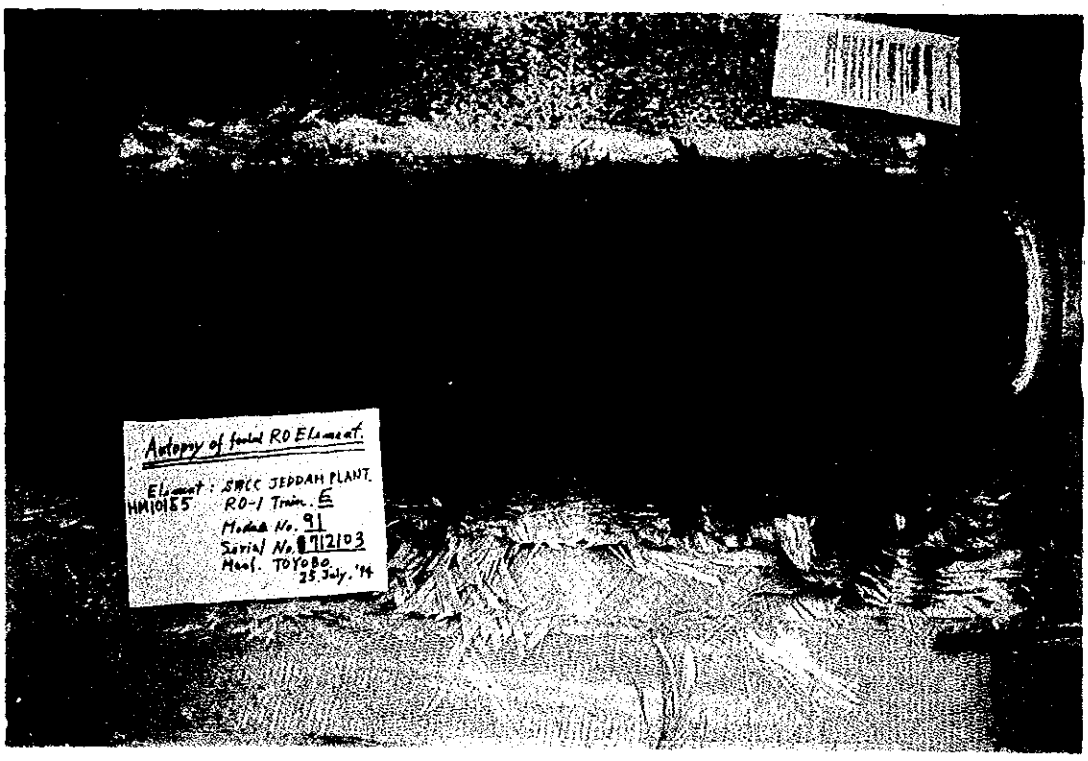
(7.1.2.C.)



Photograph 2

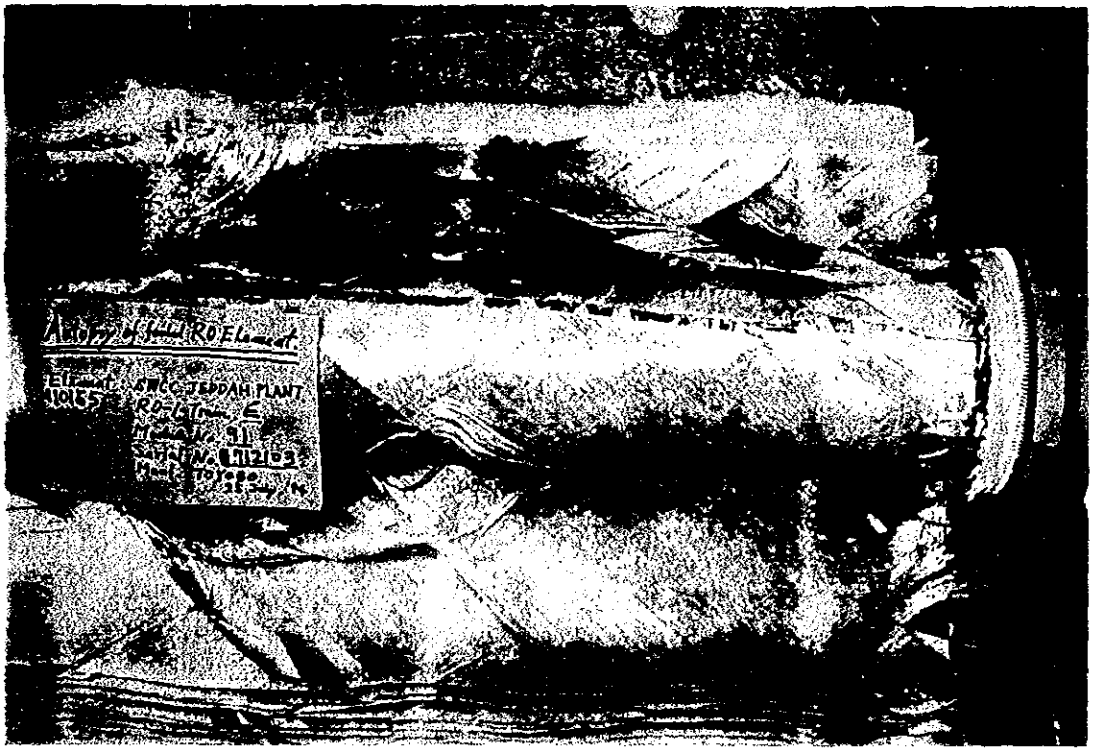
Photograph 1

Fig. 3 Various Stages of Fouled Hollow Fine Fiber Autopsy



Photograph 3

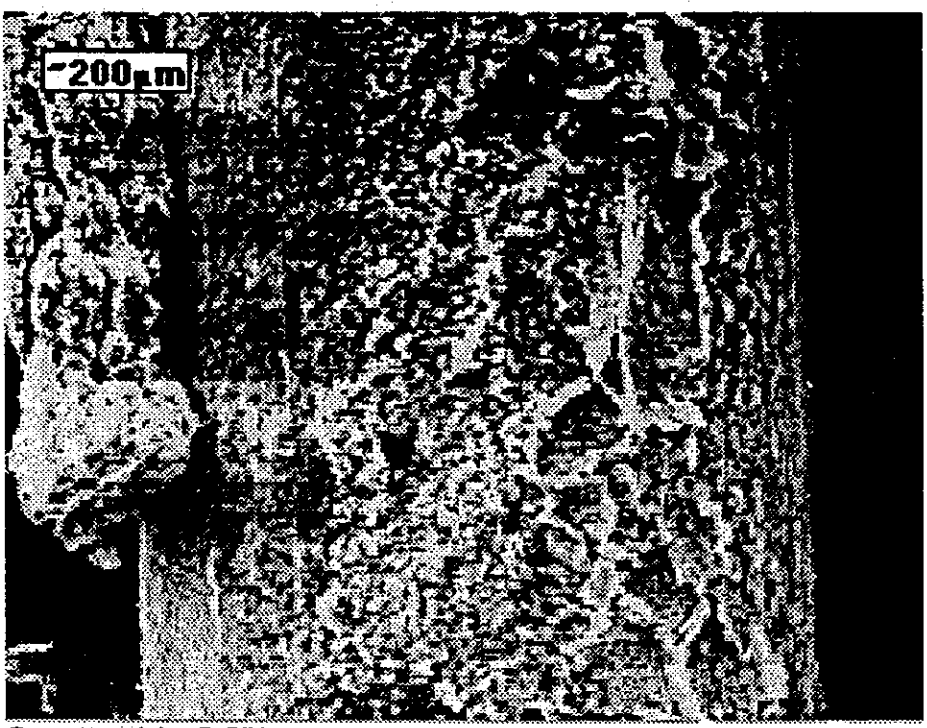
Fig. 3 Various Stages of Fouled Hollow Fine Fiber Autopsy



Photograph 4

Photograph 3

Fig. 3 Various Stages of Fouled Hollow Fine Fiber Autopsy



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Client : Dr. A. M. Farooque
Job : Job number 3 Hollow fibers from Jeddah
Spectrum 3 speciman U scale (08 August 1994 08:44

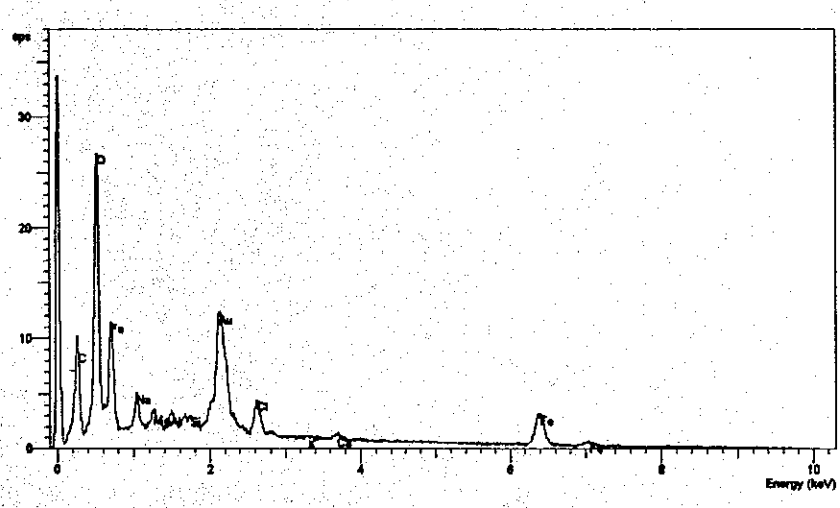

Figure 4 : SEM Micrograph and EDX Spectrum of Fouled Inner Hollow Fine Fiber

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Client : Dr. A. M. Farooque
Job : Job number 3 Hollow fibers from Jeddah
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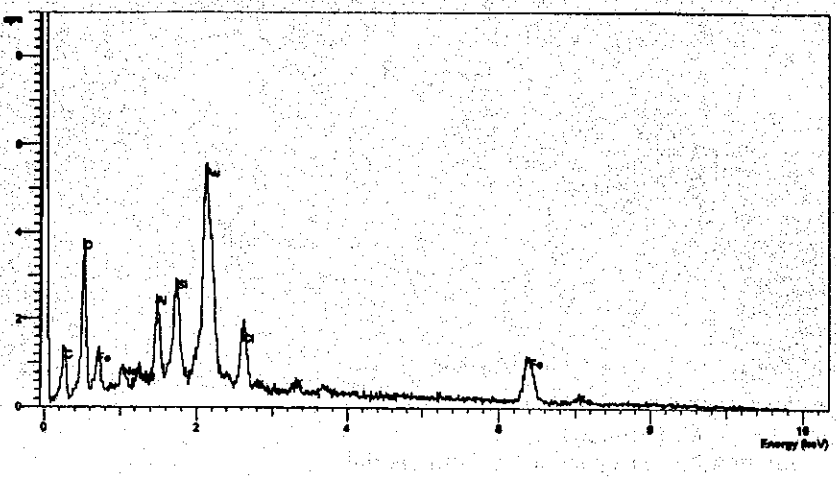

Figure 5 : SEM Micrograph and EDX Spectrum of Fouled Middle Hollow Fine Fiber

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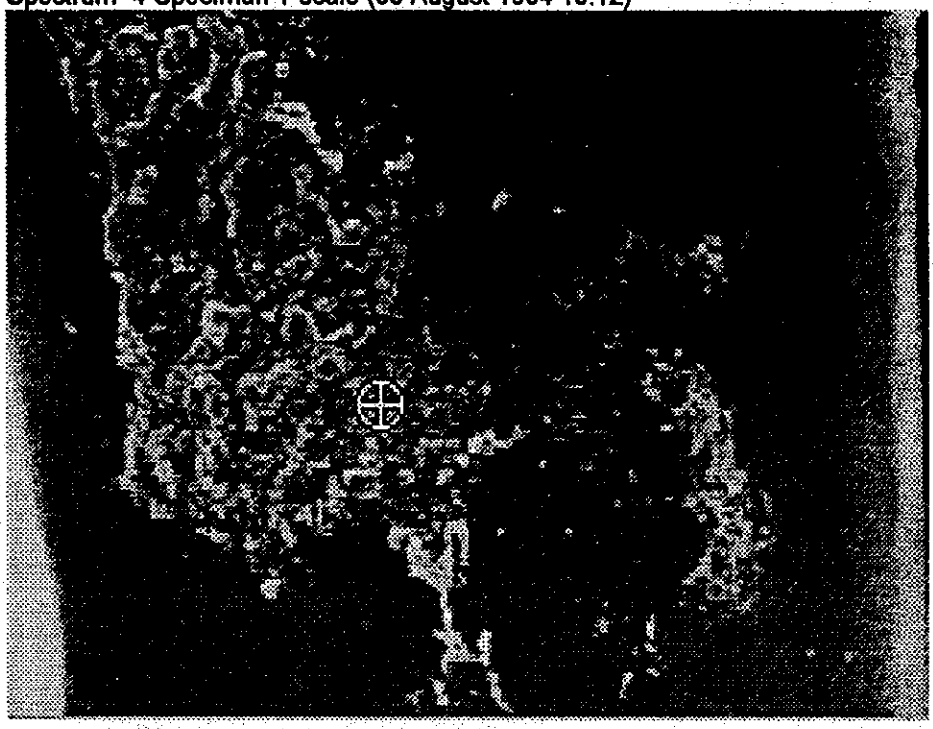
Client : Dr. A. M. Farooque
Job : Job number 3 Hollow fibers from Jeddah
Spectrum 4 Speciman T scale (08 August 1994 10:12)



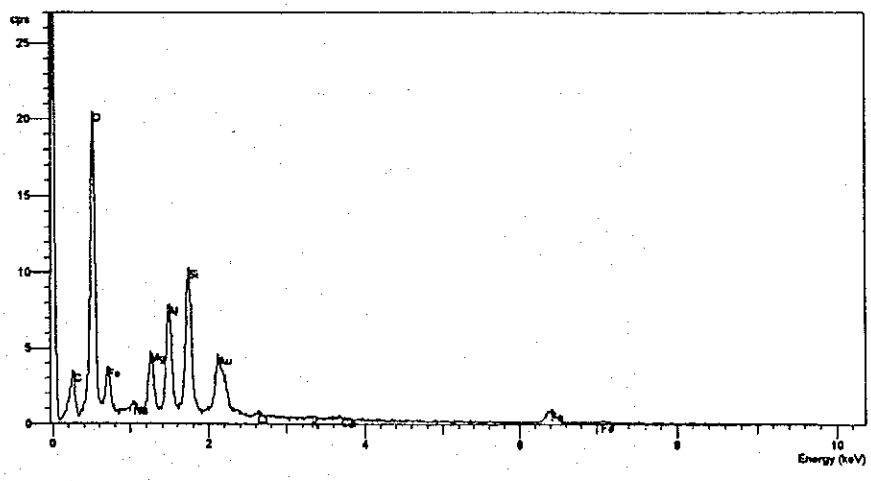


Figure 6 : SEM Micrograph and EDX Spectrum of Fouled Outer Hollow Fine Fiber

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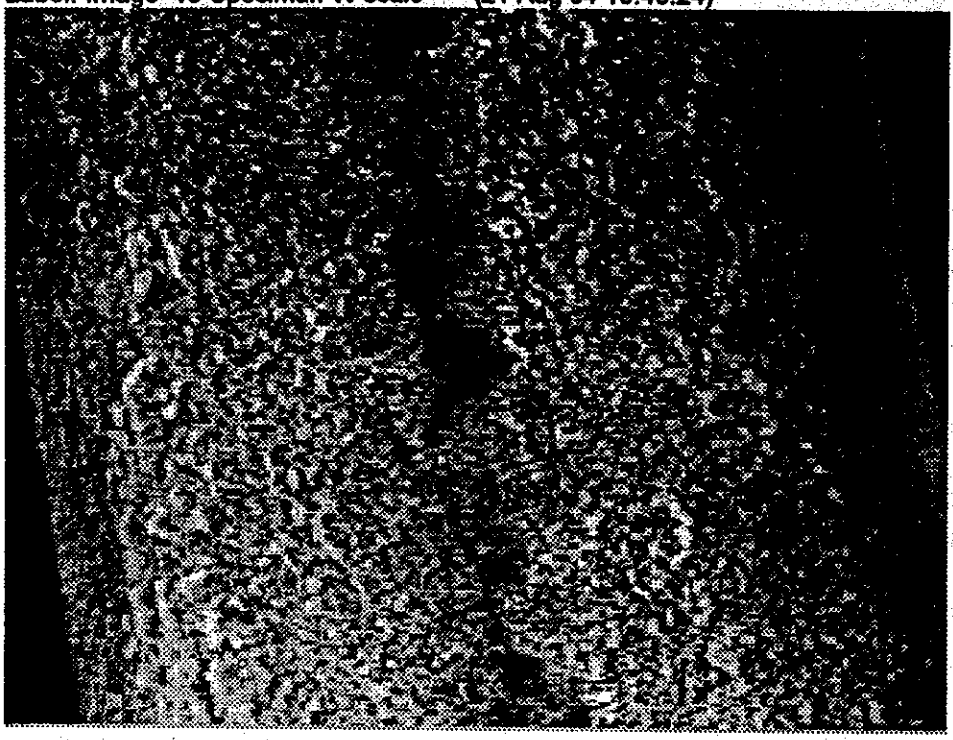

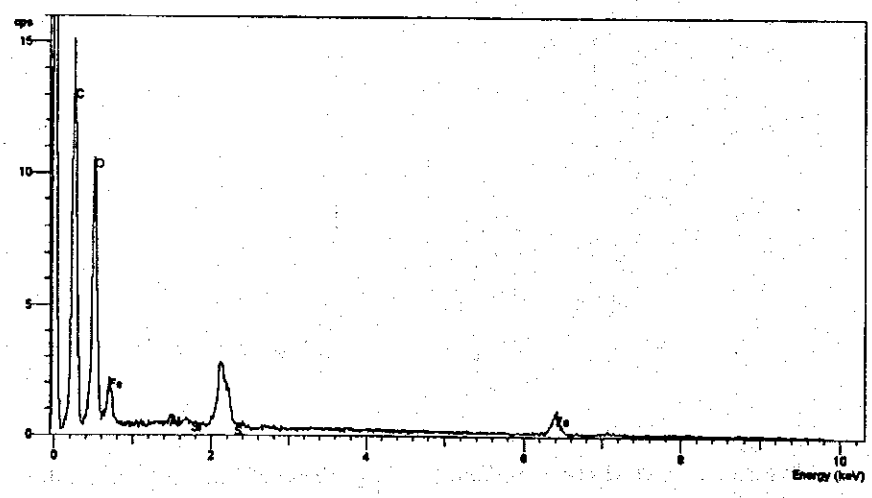

Figure 7 : SEM Micrograph and EDX Spectrum of Water Cleaned Fouled Hollow Fine Fiber

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Client : Dr. A. M. Farooque
Job : Job number 3 Hollow fibers from Jeddah
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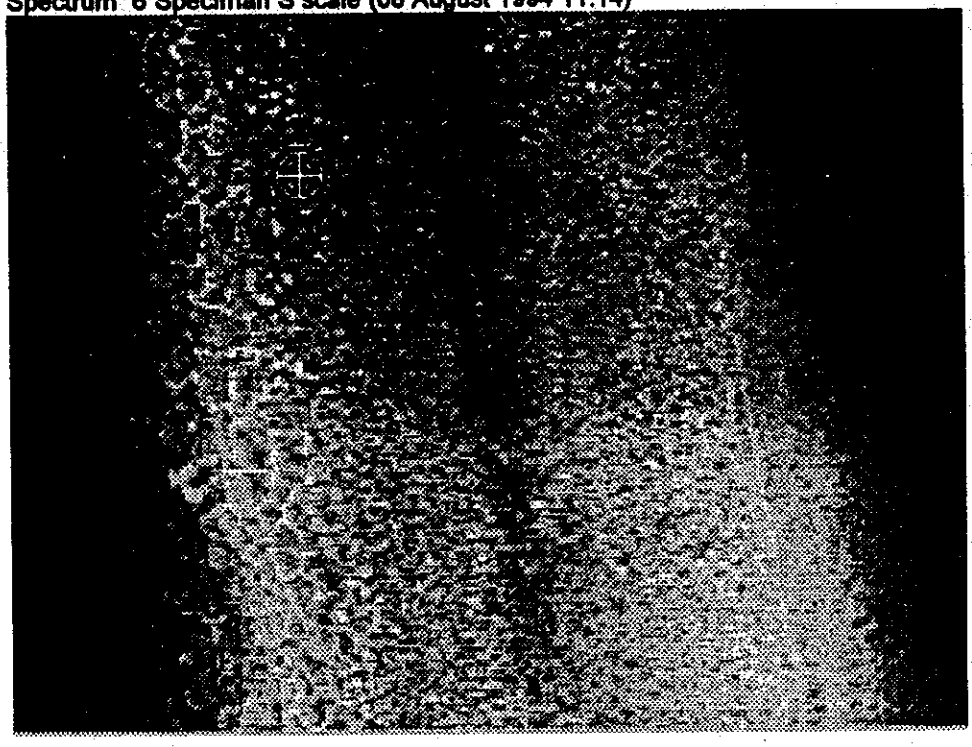

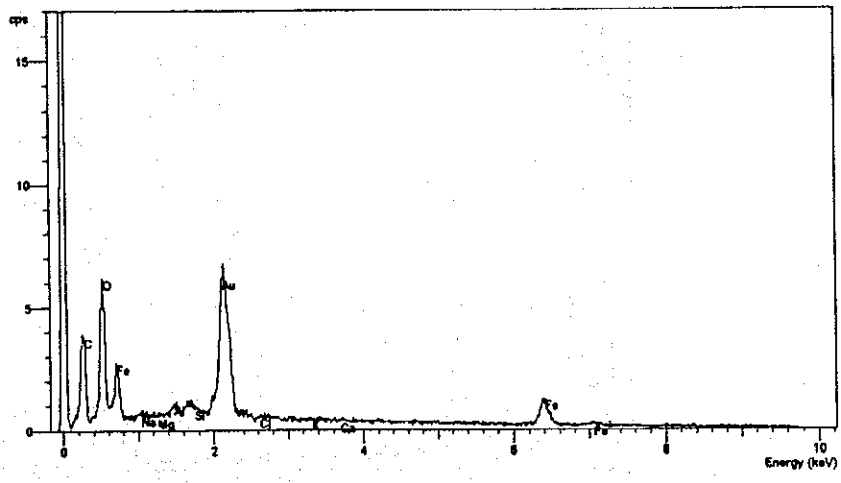

Figure 8 : SEM Micrograph and EDX Spectrum of SHMP Cleaned Fouled Hollow Fine Fiber

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Client : Dr. A. M. Farooque
Job : Job number 3 Hollow fibers from Jeddah
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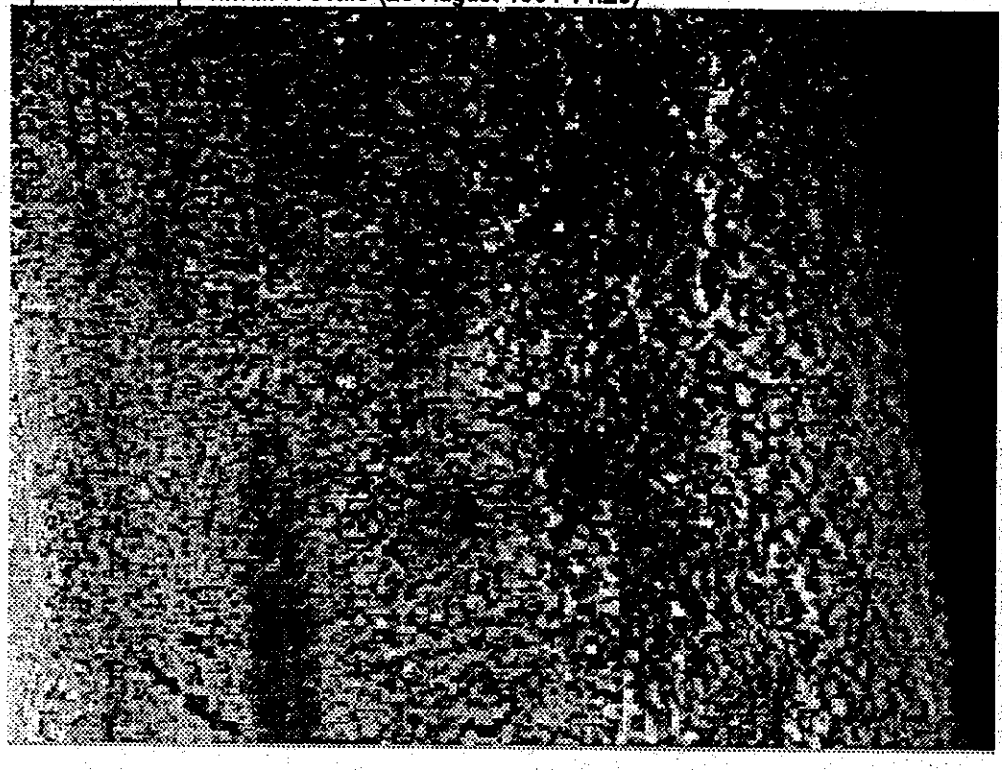

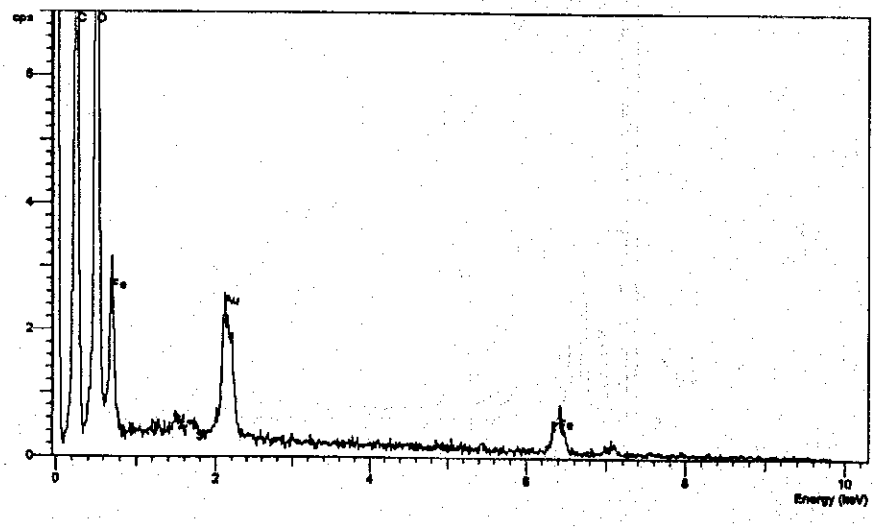

Figure 9 : SEM Micrograph and EDX Spectrum of HCl Cleaned Fouled Hollow Fine Fiber

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Client : Dr. A. M. Farooque
Job : Job number 3 Hollow fibers from Jeddah
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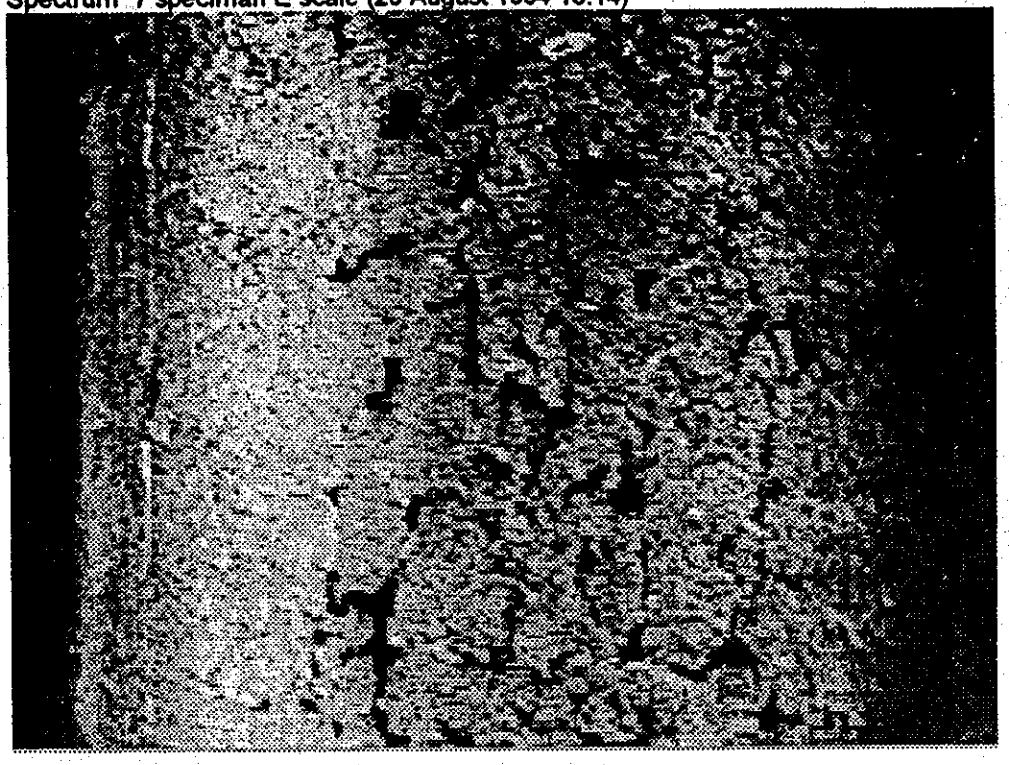

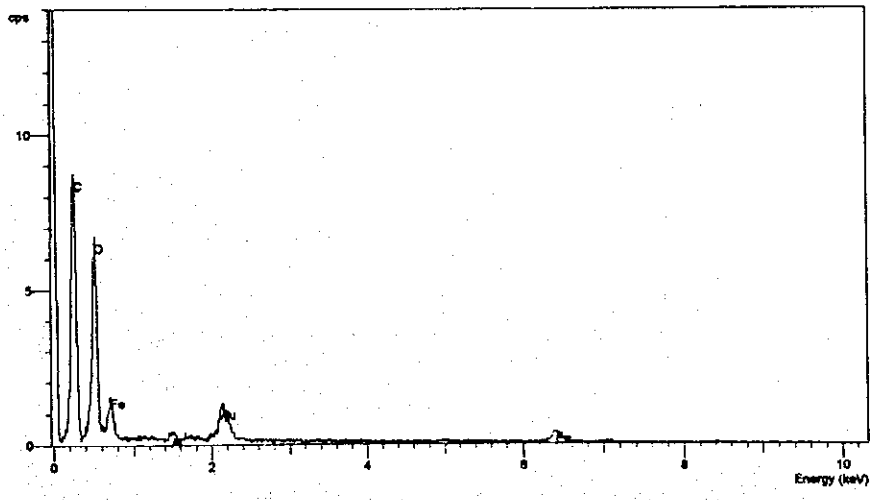

Figure 10 : SEM Micrograph and EDX Spectrum of EDTA Cleaned Fouled Hollow Fine Fiber

(7.1.2.C)

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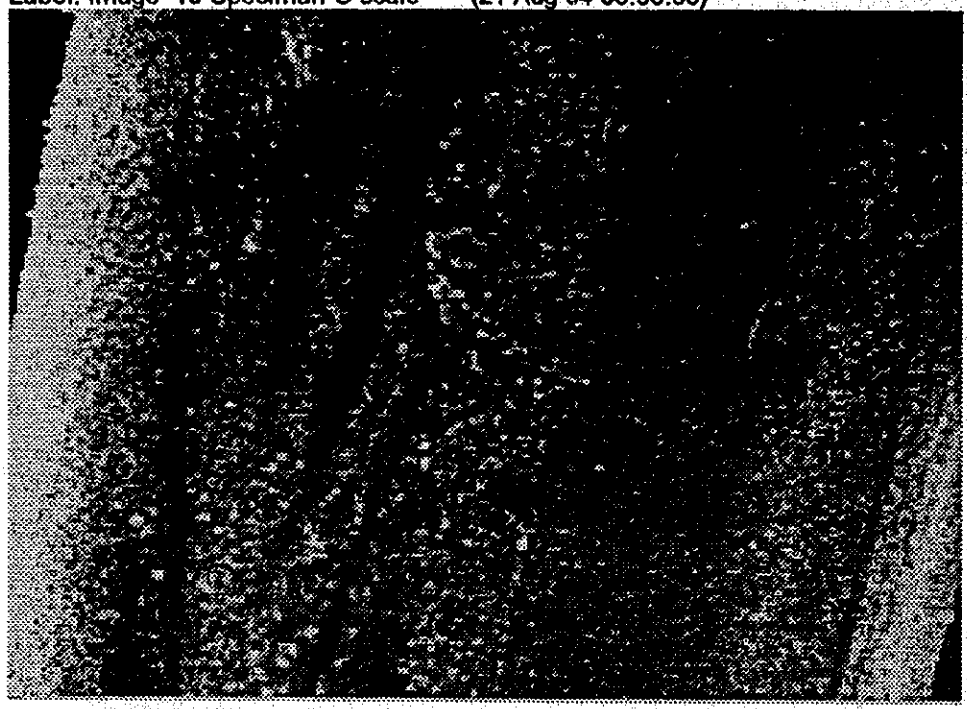

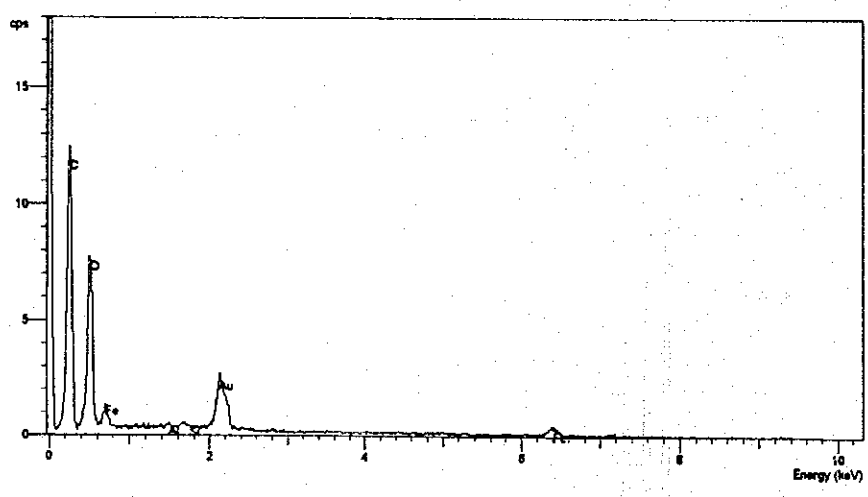

Figure 11 : SEM Micrograph and EDX Spectrum of Citric Acid Cleaned Fouled Hollow Fine Fiber

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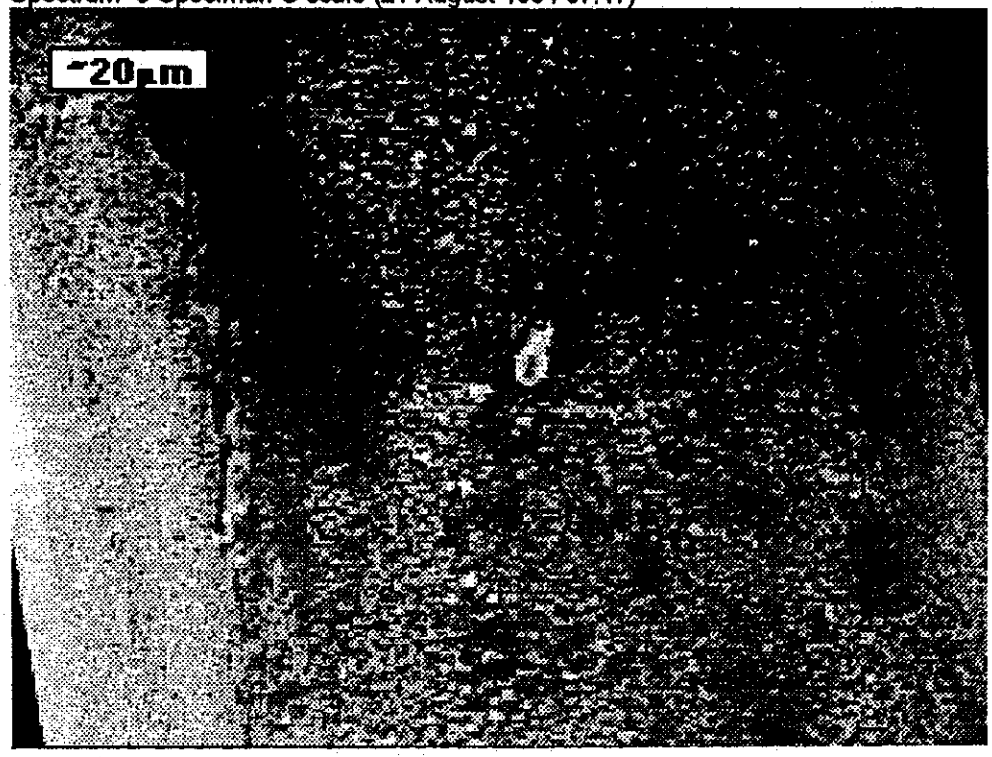


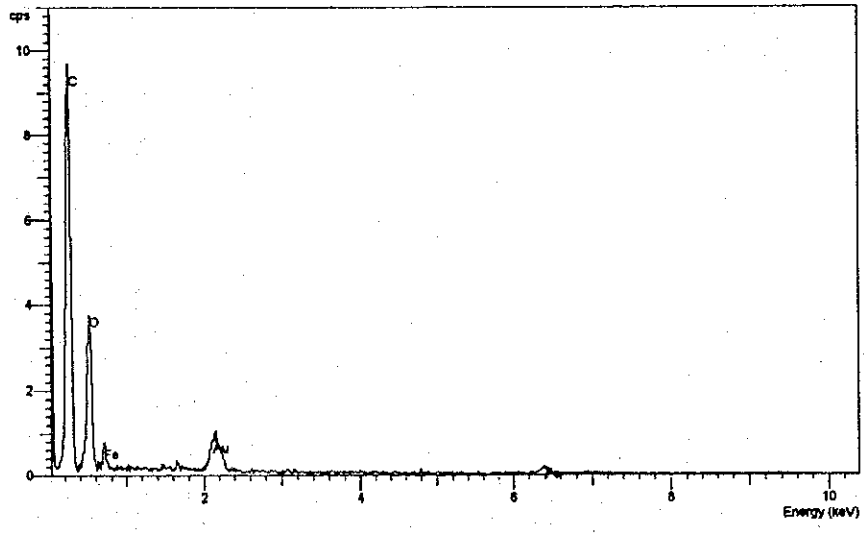


Figure 12 : SEM Micrograph and EDX Spectrum of Oxalic Acid Cleaned Fouled Hollow Fine Fiber

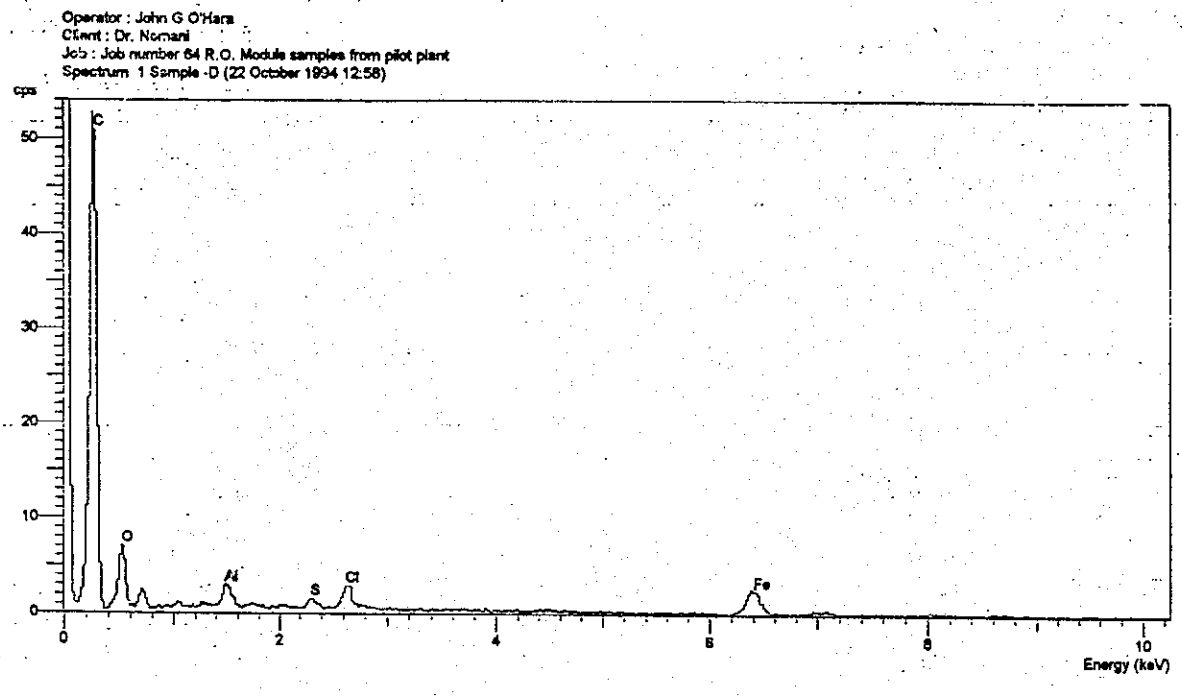


Figure 13 : EDX Spectrum of Black Particle on the Fouled Hollow Fine Fiber

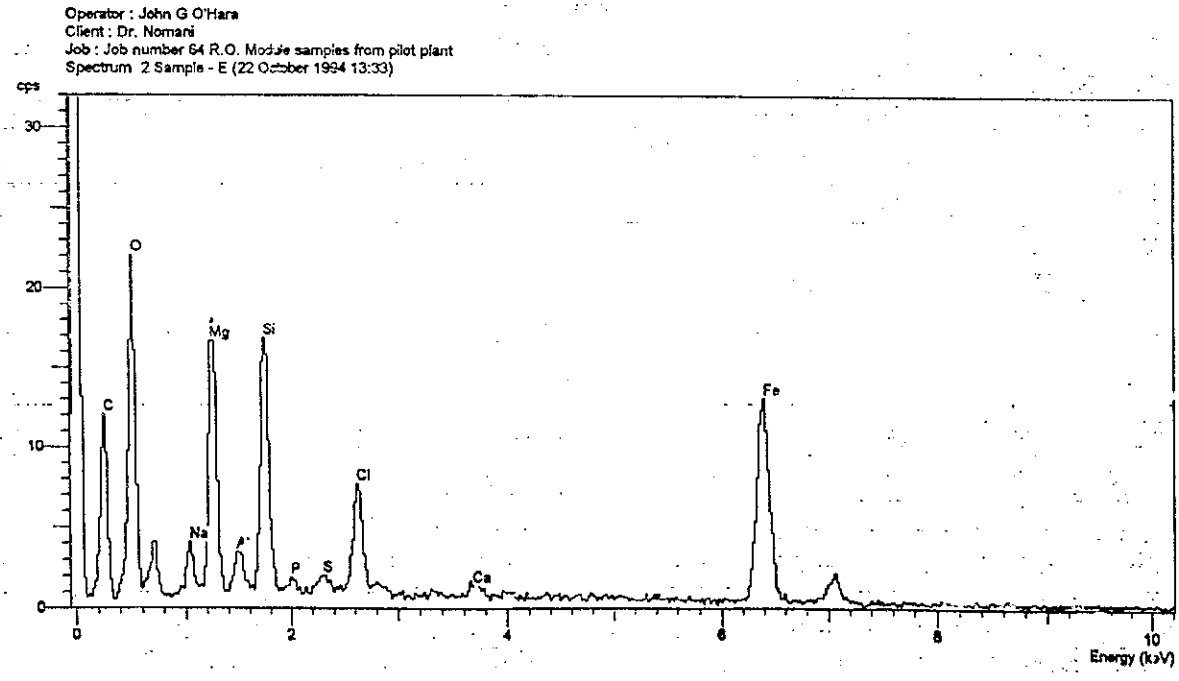


Figure 14 : EDX Spectrum of Fibrous Sticky Material on the Fouled Hollow Fine Fiber

7.1.2.D. Fouled Membrane Cleaning of Duba SWRO Plant

Contents

List of Tables

The present study was taken as exercise for establishing a standard method for cleaning of fouled membranes. The fouled membrane used for this study was procured by Research center from Duba desalination plant for the analysis of foulant chemicals on the surface of the membrane. Since this membrane was removed long time ago and was not preserved for autopsy and analysis, it is expected that the present study would not yield proper results.

1. Objectives

This study aims at evaluating the effectiveness of various chemical cleaning agents which can be used for the performance restoration of the fouled membranes.

2. Experiment Methods

2.1 Equipment

Mini-module Tester(2)- Flat sheet membrane tester RUW-5 made by Nitto Denko Corporation,Japan. The test cells used in the tester were Nitto RO/UF test cell.

2.2 Cleaning solution

Sodiumhexametaphosphate(SHMP,1 Wt%), oxalic acid(0.2 wt.%,pH=4),hydrochloric acid(pH=3) and citric acid(2 wt.%, pH=4).

2.3 Procedure

The performance(flux and salt rejection) of the fouled membranes were determined using feed water having conductivity of 2000 μS/cm. The membranes were then cleaned with various cleaning agents(by immersing for 24 hours) and performance were determined at similar condition.

3. Result and discussion

3.1 Results

The results obtained for the performance evaluation of fouled membranes before and after cleaning with various cleaning agents are shown in the Tale 1.

Table 1 Membrane Performance Before and After Cleaning

CLEANING SOLUTION	REJECTION (%) BEFORE CLEANING	REJECTION (%) AFTER CLEANING	FLUX ($m^3/m^2/day$) BEFORE CLEANING	FLUX ($m^3/m^2/day$) AFTER CLEANING
SHMP	84.1	85.6	5.3×10^{-2}	6.1×10^{-2}
OXALIC ACID	86	85.4	4.1×10^{-2}	4.2×10^{-2}
HCl	89.3	---	3.1×10^{-2}	---
CITRIC ACID	87	85.5	4.9×10^{-2}	4.7×10^{-2}

3.2 Discussion

It can be understand from the results that all the chemicals used for cleaning did not improve the salt rejection and flux of the fouled membranes except sodiumhex–ametaphosphate(SHMP) which was found to improve the flux by about 15%. Hydrochloric acid(HCl) was found to damage the membrane. This could be due to the low pH(3) which aids the hydrolysis of the membrane.

4. Conclusion

The cleaning solution used in the study are not effective in improving the performance of the fouled membranes. This could be expected due to the fact that the membrane is deteriorated as it was not properly preserved.

7.1.2.E. Foulant Analysis and Flat Membrane Performance of Duba SWRO Plant

Contents

List of Tables

List of Figures

List of Figures

1. Objective

Obtaining the deteriorated membrane element from Duba 3 Desalination Water Plant, analysis of foulants and observation on the membrane surface and RO performance tests with the flat sheet membrane' samples were conducted. The result on the investigation of the membrane performance deterioration was shown in the following chapter.

2. Experimental

(1) RO Sample

A leaf of the flat sheet membrane sample taken from a spiral wound element was used in Duba Desalination Plant.

The RO element had been operated for 2 years at the second stage in the RO Plant.

Detailed identification of the membrane is as follows;

Date removed	:	October 1, 1994
Type of Membrane	:	At the second stage in the double pass desalination, cellulose acetate derivative membrane is used.
Manufacturer	:	Fluid system (UOP) supplied.
Distributor	:	American Engineering Service.
Model No.	:	CA/CTA 898–54
Serial No.	:	261955
Operation time	:	16 months at the front end of upstream, then 8 months at the back end in #8 Pressure vessel, (2 years in total).
Final performance	:	The final rejection performance which was reported in the attached sheet from Duba shows; Salt rejection as electroconductivity basis = 61.59 % at 20 bar, Feed water conductivity = 5780 micro–S/cm.

(2) Autopsy of RO element

At SWCC RDTC, Al Jubail the RO element was autopsied and the appointing 6 position–RO membrane samples were obtained from the leaf membrane, as shown in Figure 1.

The two sheets of RO samples, 15cm x 15cm, were obtained from the same places from No.1 to 6 in the leaf, in order to cross–check between JICA and SWCC. These samples were sealed with 0.1% formaldehyde solution in plastic bags and stored and/or transported to be analyzed.

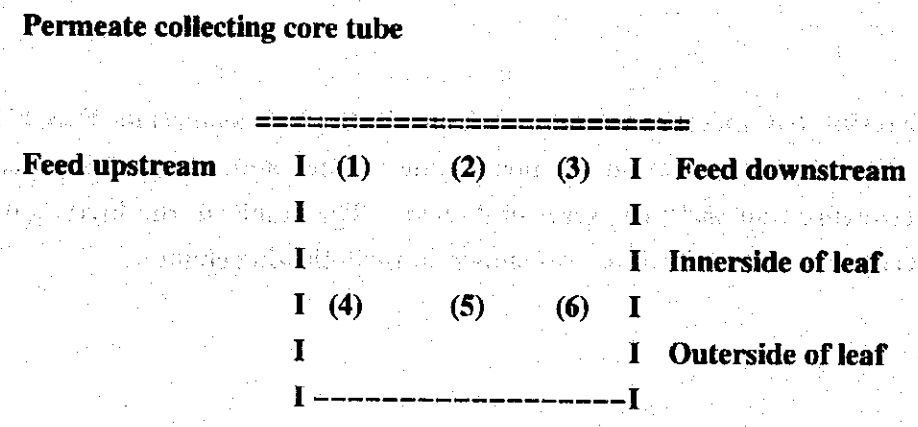


Figure 1. Obtained RO samples' location in the autopsied membrane leaf

(3) Preparation of flat sheet membrane for performance check

The each flat sheet membrane sample was cut into 2 sheets of round pieces with 75 mm in diameter and used for the RO performance check.

(4) RO performance evaluation test

The RO performance of round pieces membrane samples were tested with the following conditions;

Device : Tangential flow flat sheet test cell
Test solution : 3.5% NaCl
Conditions : Feed pressure; 30 kgf/cm^2
Feed flow rate; 5 L/min

Permeate samples were taken from the cell after 30 minutes of operation.

3. Items analyzed

(1) Chemical cleaning

The obtained sample of membrane at this time has almost no foulant on the membrane surface because of being used at the second stage of the double pass RO treatment. Accordingly, the following evaluation and surface analysis were conducted without any chemical cleaning.

(2) Observation and identification of inorganic foulants

Inorganic foulants on the membrane surface were observed and identified by using SEM and EDX.

(3) Identification of organic foulants

Mainly organic foulants on the membrane surface were analyzed and identified by using FT-IR.

4. Results

(1) Appearance check

Prior to the autopsy, appearance of the element was visually checked at SWCC RDTC. No significant change like stain or deformation was observed. The flat sheet membrane leaf itself had no remarkable stain.

(2) SEM and EDX

SEM photos and EDX charts of the membrane samples were shown in Figure 2-1(1)~(6) and Figure 2-2(1)~(6). These results showed that no deposition of microorganism significantly existed on the membrane surfaces. Since inorganic foulant also did not exist on the surfaces, so called membrane fouling did not occur.

Also, since the EDX results among the No.(1) to (6) samples showed no remarkable changes, it indicated that no site specific fouling existed on the leaf membrane.

As shown in Figure 3(1)~(6), the surface observation of higher magnification with low accelerated voltage SEM photos showed wave-strips looked any likelihood of physical damage.

Since there are two possibilities, either mechanical damage during RO operation or electronic beam-damage during SEM operation, the final judgment should be done after checking the referenced SEM photo of unused new RO membrane sample which should be observed under the same condition as these samples.

However, since the trial dying test with red dye solution on the flat sheet membrane leaf indicated that mechanical damage existed remarkably, when the autopsy was conducted, it is very possible that larger pores than RO levels' size were created on the surface of the RO membrane during the RO operation.

(3) FT-IR

The IR spectrum of the membrane samples were shown in Figure 4(1)~(6). Since the membrane material consisted of amylosic triacetate derivative (see Figure 5.) and no unused new membrane sample was available so far, the differential IR spectrum could not be obtained.

It is essential to obtain a reference sample for the control (or blank) analytical data to

conduct the micro-structural investigation. In future, provided new sample membrane available, the above mentioned FT-IR analytical information will enable to examine the membrane deterioration on the stand point of the analytical chemistry.

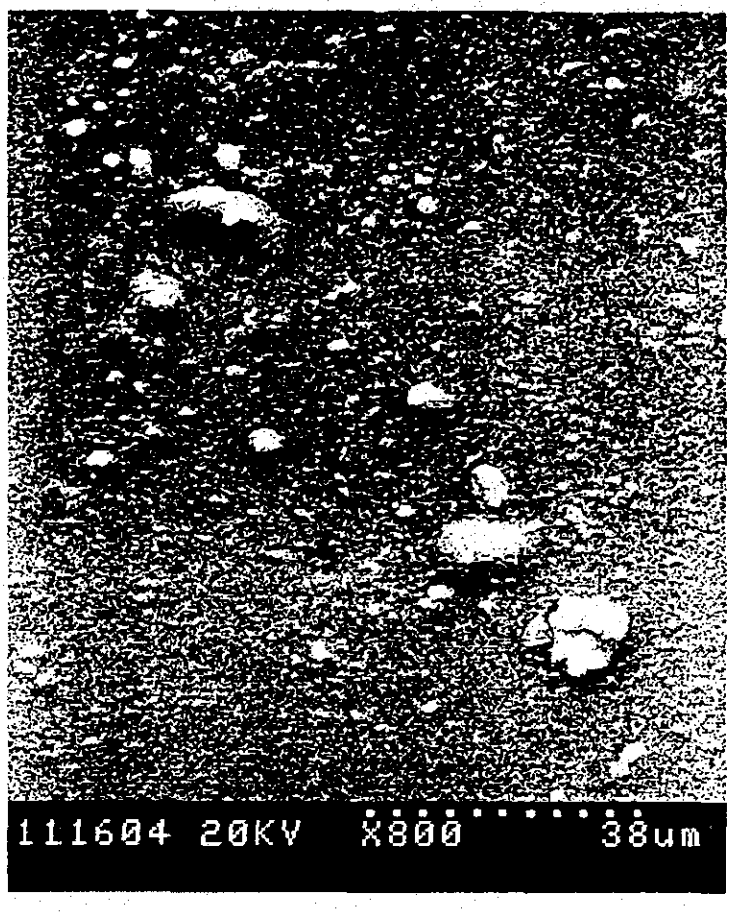
(4) RO performance of flat sheet membrane samples

As shown in Table 1, comparing between the locational performance with flat sheet membrane samples in the leaf of the autopsied element(see Figure 1) and RO performance, it was obvious that the gradient of rejection performances existed from upstream to down stream side changing bigger. In other words, the upstream portion was severely damaged than the down stream side, showing the tendency that the upper stream portions had the lower rejections and the higher fluxes than down portions. On the other hand, there were no changes between outer and inner side within the leaf.

If the wave strips on the membrane surface of SEM photos are concluded that these come from the RO operation, the ultrasonic sound generated from high pressure feed pump mostlikely created the mechanical damage and it should meet the typical membrane deterioration. Because it is well corresponded that the strength of ultrasonic sound affects upper stream side more stronger than the down stream side.

Table 1. RO performances of flat sheet membrane samples

Sample No.	Sample location	Rejection	Flux(m3/m2/d) Ave./ Observ.	Ave. / Observ.
1	Upstream /Inner	57.9/ 58.62	1.06 / 1.04	
			57.20	1.08
2	Midstream/Inner	61.9/ 62.00	0.92 / 0.95	
			61.83	0.88
3	Downstream/Inner	67.6/ 67.84	0.66 / 0.68	
			67.31	0.63
4	Upstream / Outer	58.6/ 56.05	1.09/ 1.18	
			61.19	0.99
5	Midstream/ Outer	65.2/ 65.75	0.78/ 0.76	
			64.66	0.80
6	Downstream/Outer	68.1/ 67.93	0.65/ 0.66	
			68.29	/ 0.64



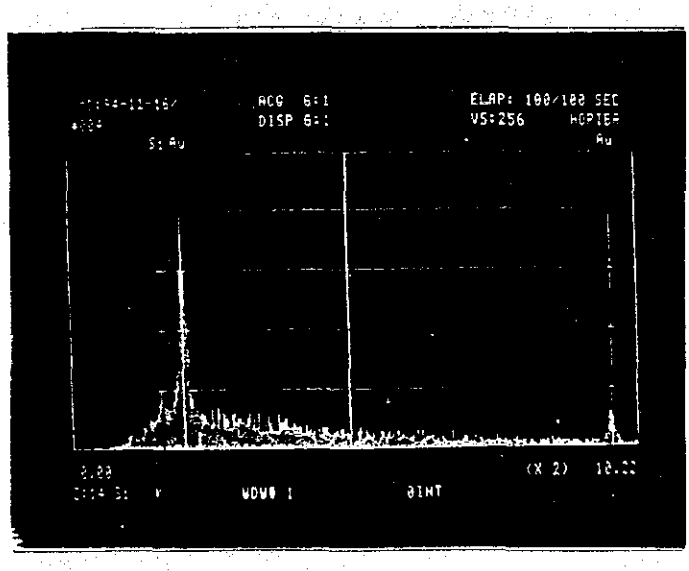
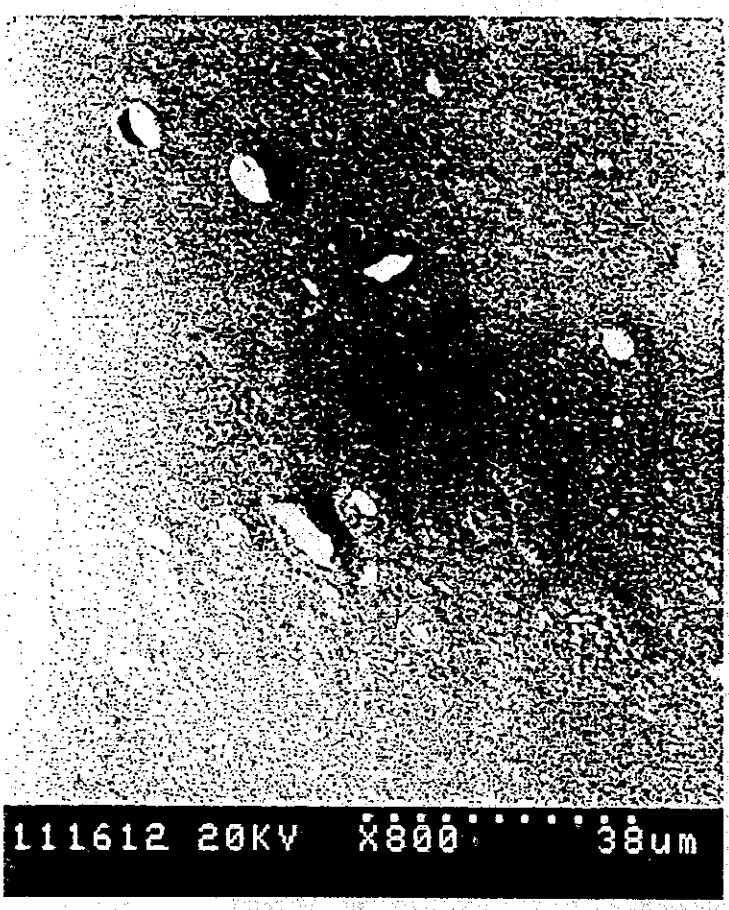


Fig. 2-1(1) SEM(X 800) & EDX Analysis with Membrane Surface of Sample No.1



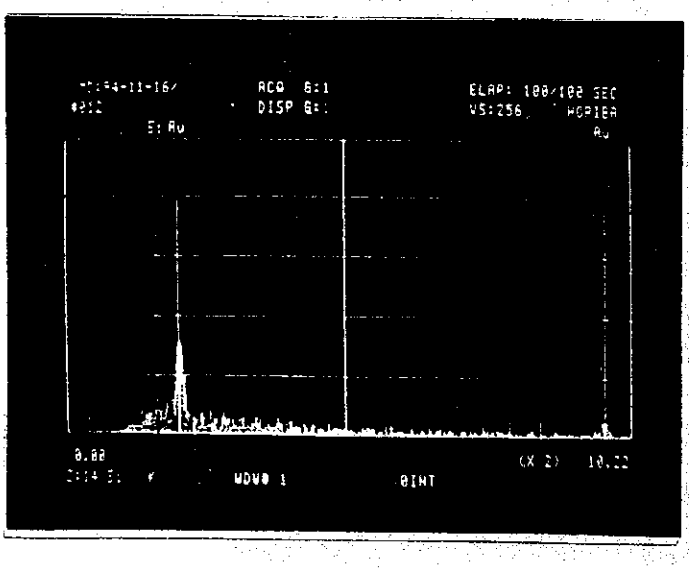
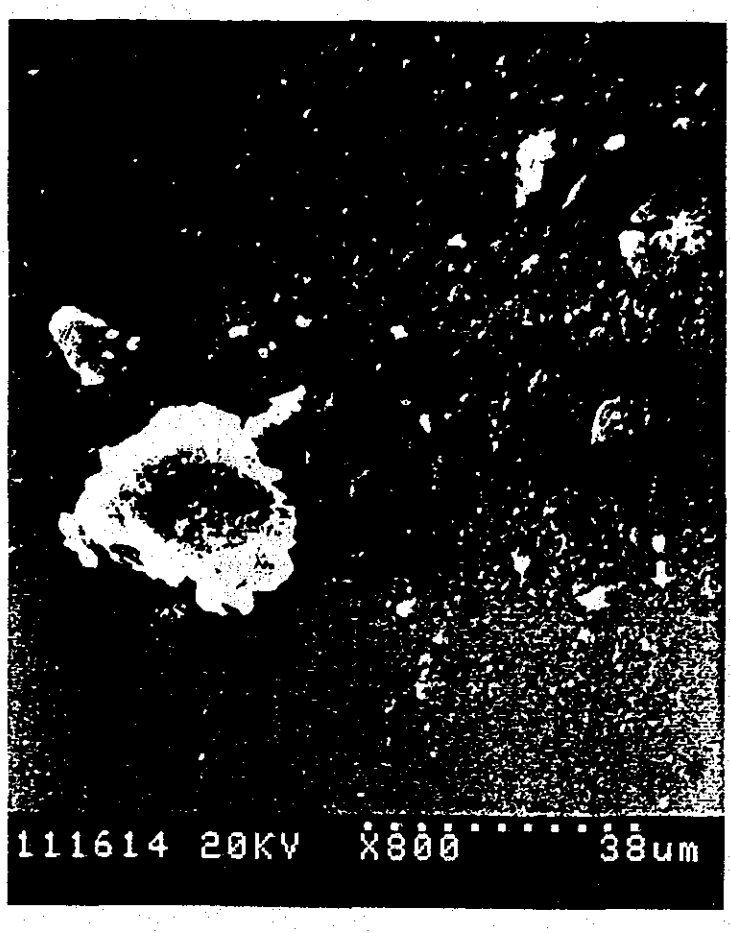


Fig. 2-1(2) SEM(X 800) & EDX Analysis with Membrane Surface of Sample No.2



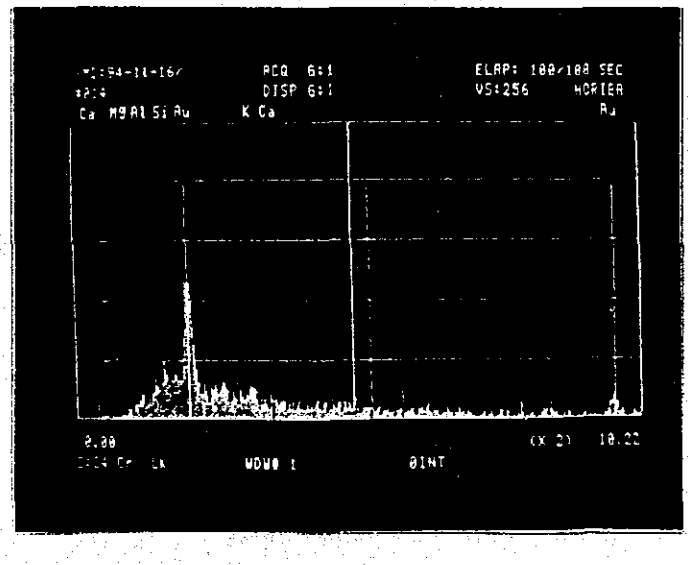
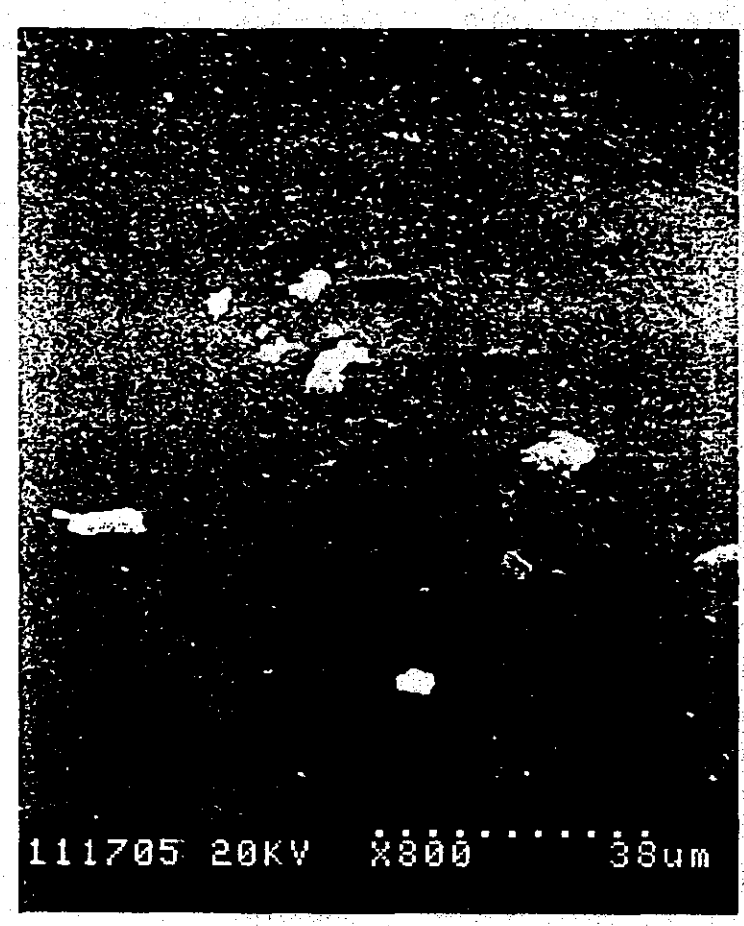


Fig. 2-1(3) SEM(X 800) & EDX Analysis with Membrane Surface of Sample No.3

(7.1.2.E)



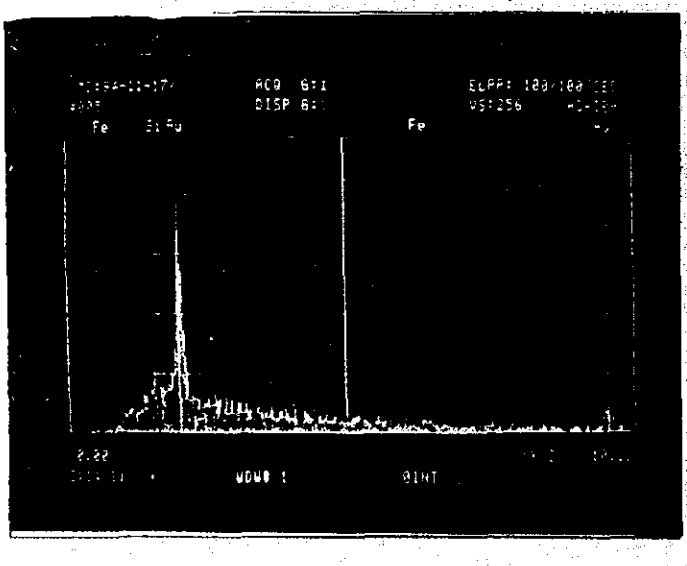
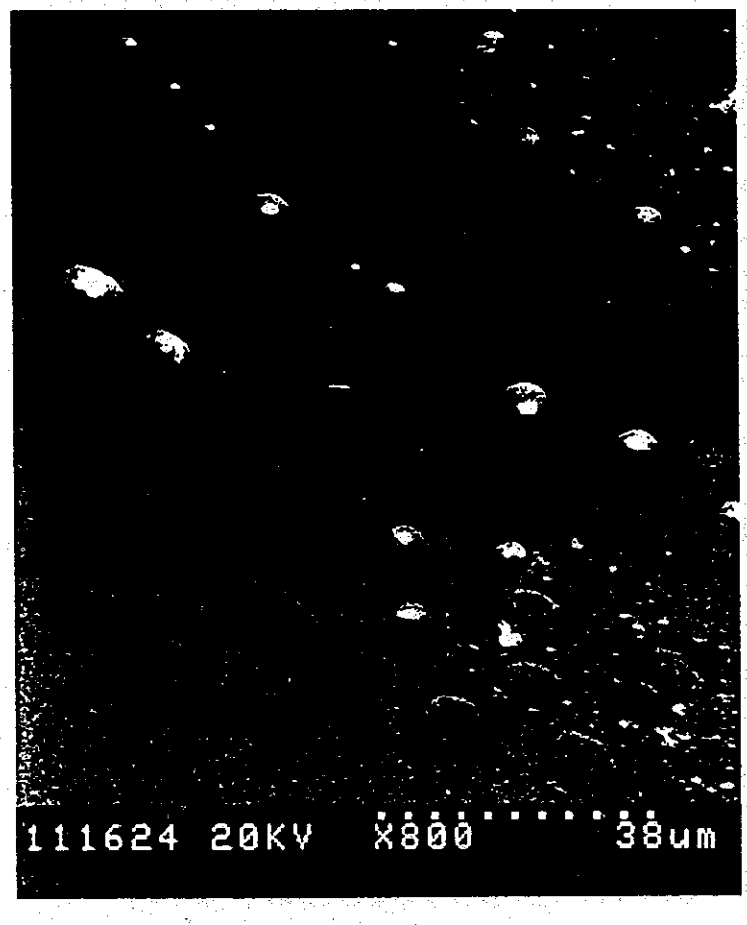


Fig. 2-1(4) SEM(X 800) & EDX Analysis with Membrane Surface of Sample No.4

(7.1.2.E)



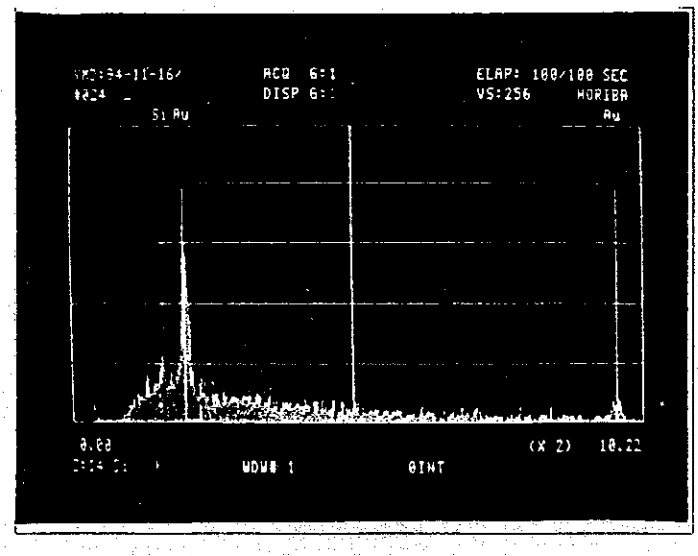
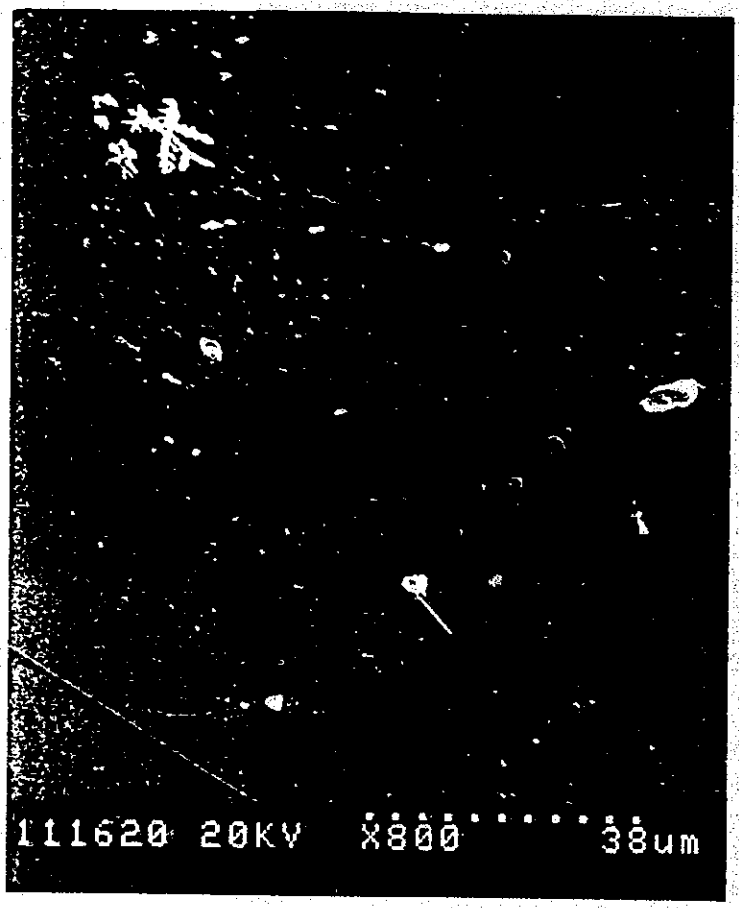


Fig. 2-1(5) SEM(X 800) & EDX Analysis with Membrane Surface of Sample No.5

(7.1.2.E)



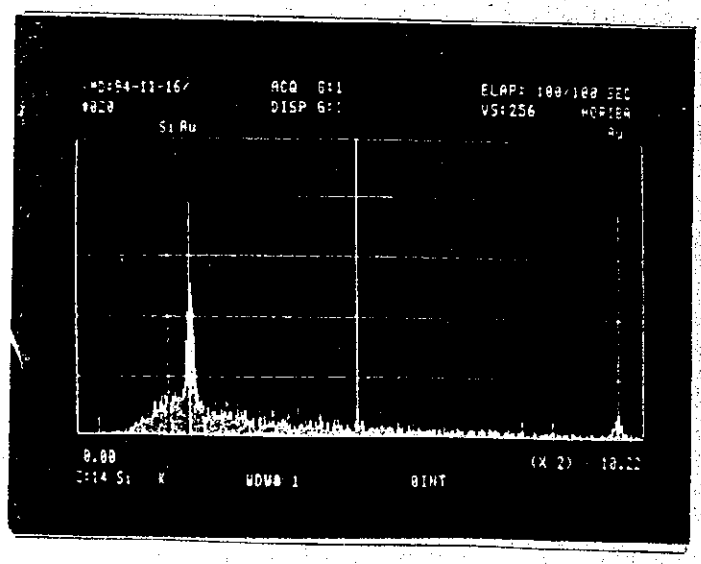


Fig. 2-1(6) SEM(X 800) & EDX Analysis with Membrane Surface of Sample No.6

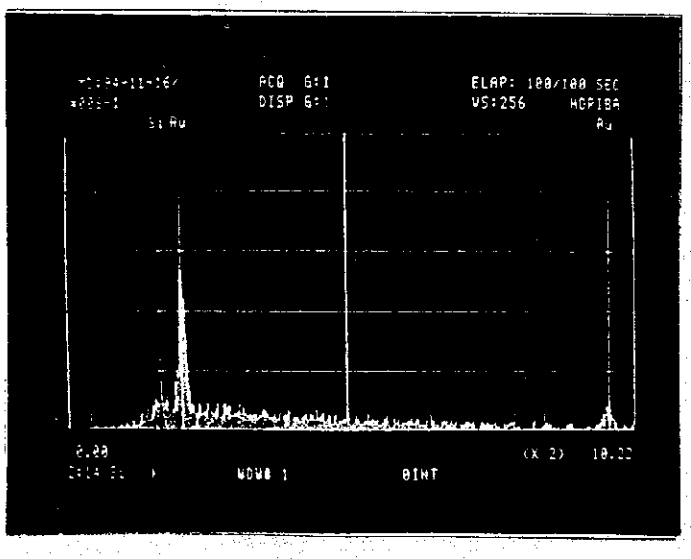
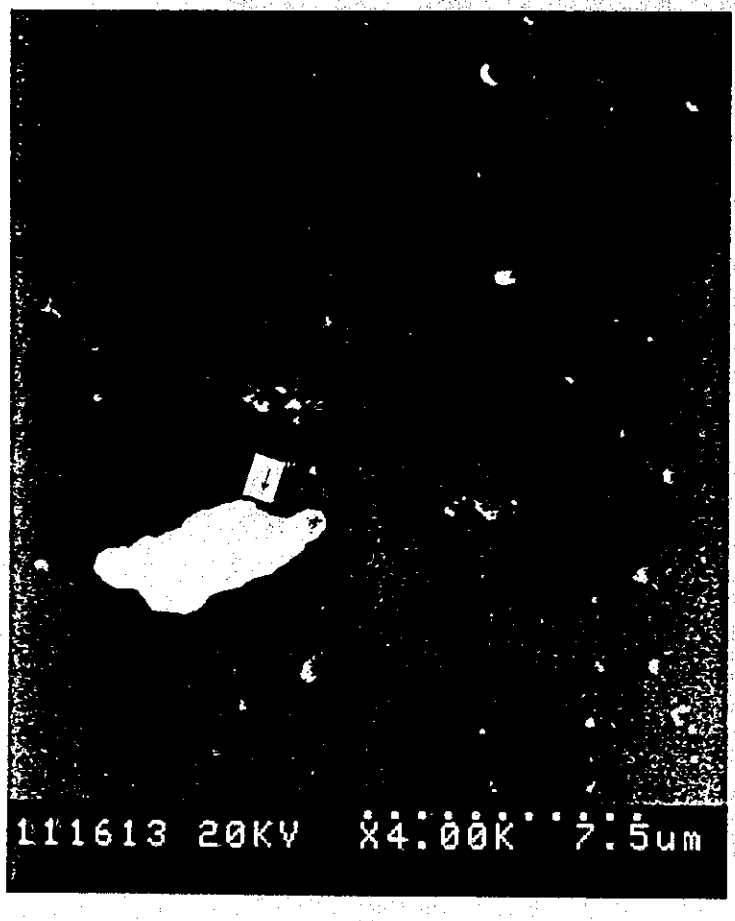


Fig. 2-2(1) SEM(X 4000) & EDX Analysis with Membrane Surface of Sample No.1



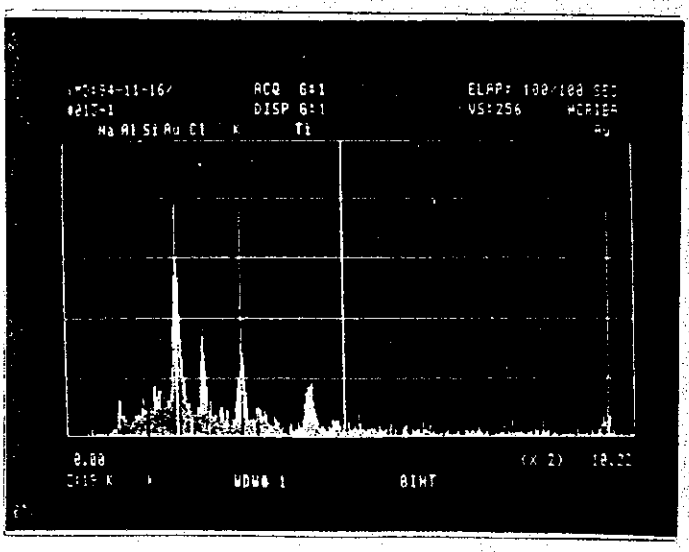


Fig. 2-2(2) SEM(X 4000) & EDX Analysis with Membrane Surface of Sample No.2

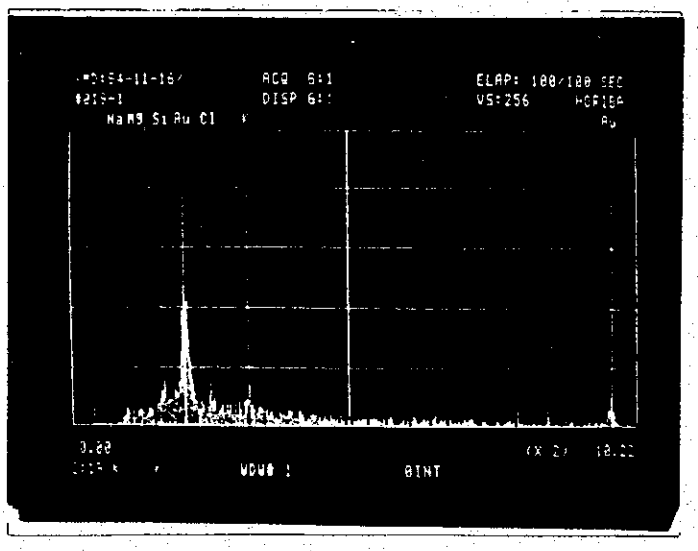
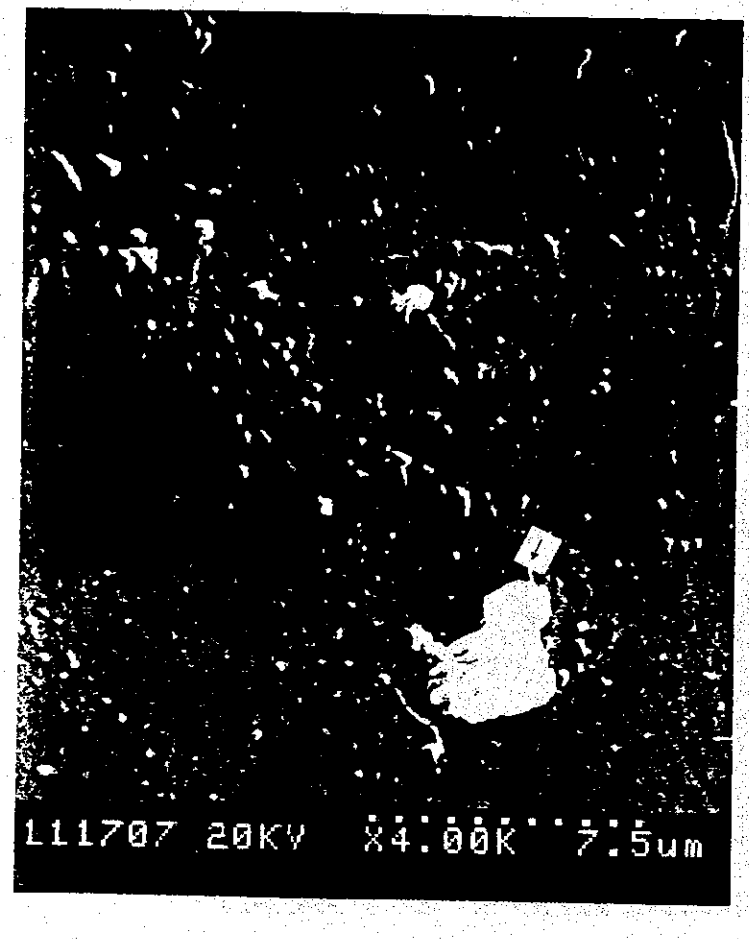


Fig. 2-2(3) SEM(X 4000) & EDX Analysis with Membrane Surface of Sample No.3



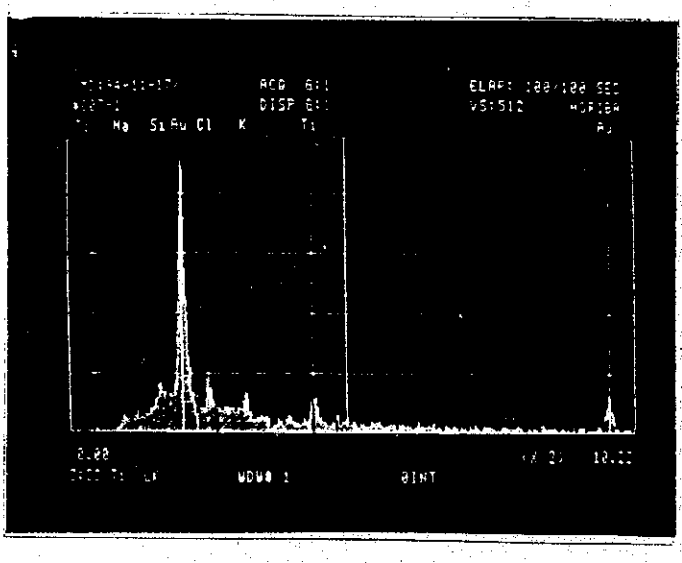
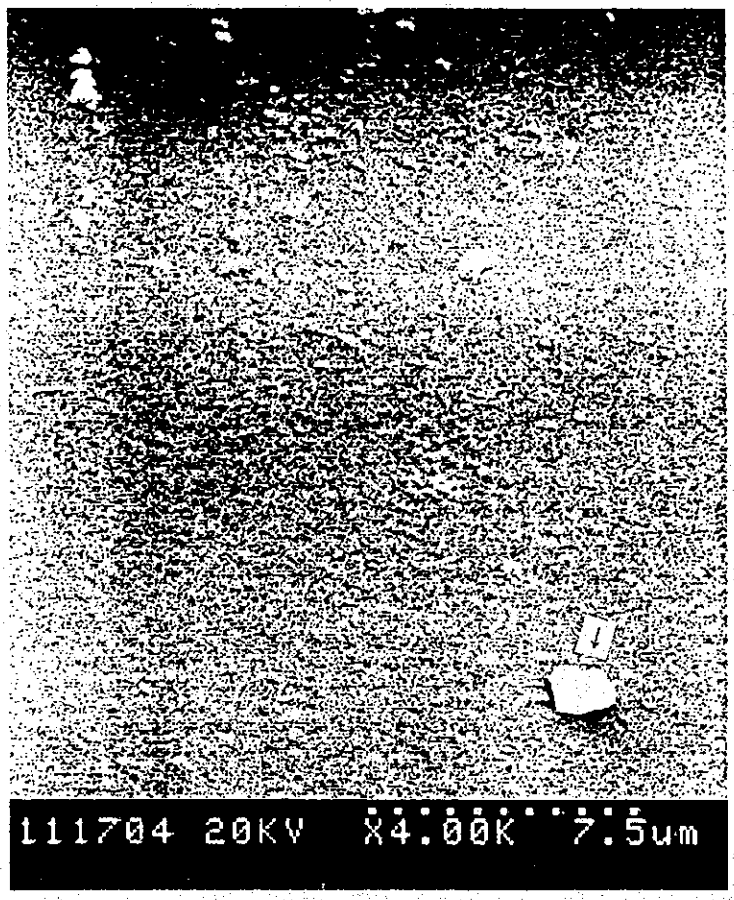


Fig. 2-2(4) SEM(X 4000) & EDX Analysis with Membrane Surface of Sample No.4



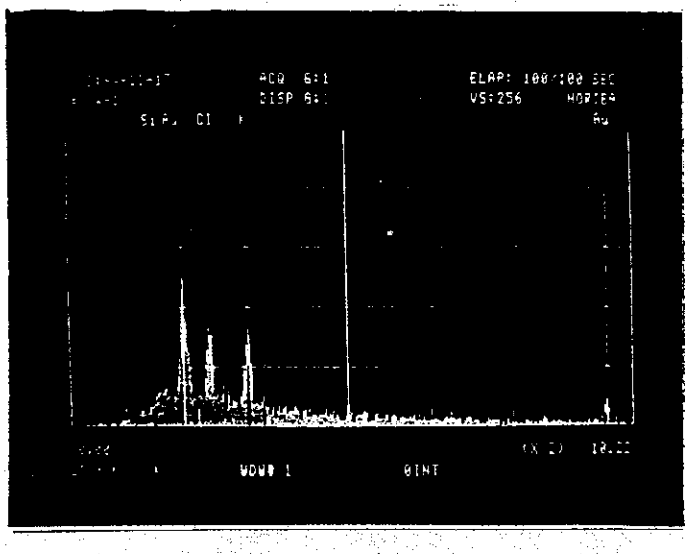


Fig. 2-2(5) SEM(X 4000) & EDX Analysis with Membrane Surface of Sample No.5

(7.1.2.E)

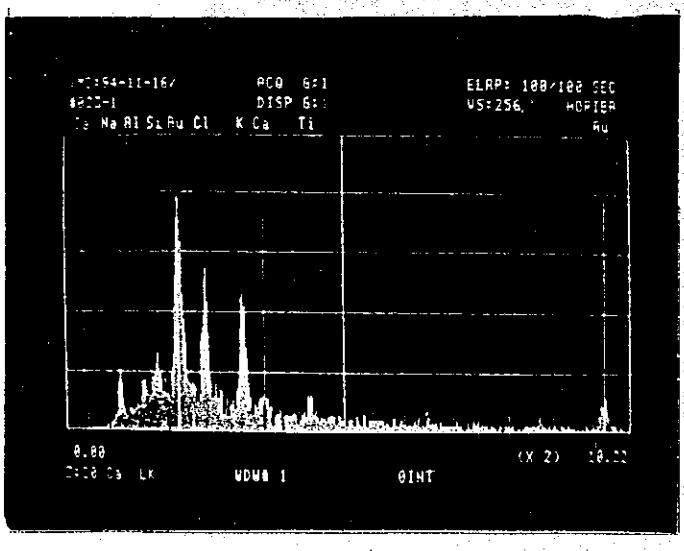


Fig. 2-2(6) SEM(X 4000) & EDX Analysis with Membrane Surface of Sample No.6