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The Abundance, Diversity, and Stratigraphy of the Upper Crab Orchard Formation, Lewis County, Kentucky by Patrick M. Higgins

The Modification of Flemion for Use in a Solid Electrolyte Battery by Timothy Howard

Simple Analog Computers by Leah Carol Ross

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SIMPLE ANALOG COMPUTERS

A Senior Thesis

Presented to the

Department of Physical Sciences of

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In Partial Fulfillment of

the Requirements for a Degree

in

Physics

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by

Leah Carol Ross

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INTRODUCTION

General Discussion

Computers can be classified into two categories -analog and digital. A digital computer had inputs of only zero and one and is simply a machine that does arithmetic calculations (Technical Education and Management, Inc., 1962, p.17). An analog computer, however, has a range of inputs. The analog computer was so named because it simulates, or makes an analogy of, some sort of physical quantity or event. The output is then the solution to the problem (Batter, 1987, p.1). Although analog computers are very useful in many situations, there is always some error in the final result because the input voltage is never an absolute number unlike the digital computers of today. The components of the analog circuits also always have inherent errors in their values.(Technical Education and Management, Inc., 1962, p.18). As with the digital computers used today, the analog computer can be built to solve many different types of problems where the problems are only limited by the available equipment (Rummer, 1969,p.3). This investigation is concerned with simple analog computer circuits, their usefulness, and the errors involved.

Method of Investigation

To build the analog circuits under investigation very few computer components were needed. Resistors, capacitors, diodes, and operational amplifiers, or op-amps were, the necessary parts of all the circuits which were made. Resistors are the components of the circuit that impede energy flow. Capacitors store the electricity.(Faissler, 1991). Diodes keep the current from flowing in both directions(Blum, 1969, p.87). The final component, the op-amp, is the component that does the mathematical operations in the system. Op-amps multiply the input voltage using a very high input impedance which causes a very low input current(Rummer, 1969,p.8). These four components are shown in Fig.1.

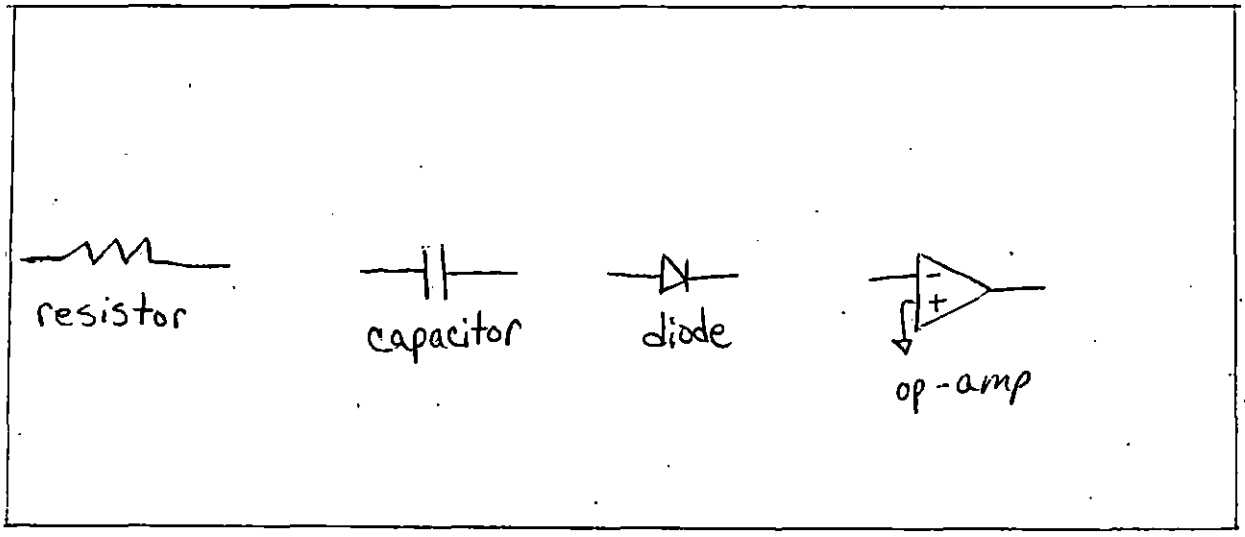

Figure 1. Circuit Components.

Together, these four components can make up the two most important parts of an analog computer circuit-inverting amplifiers and

integrator. They are shown in Fig.2.

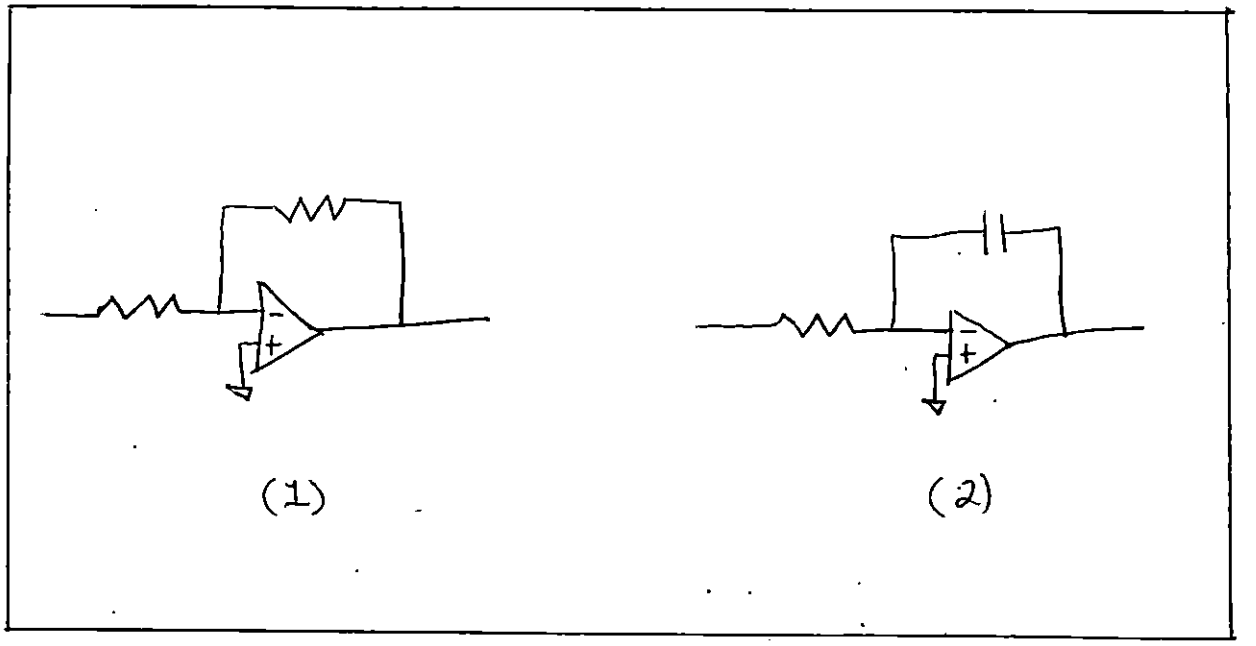

Figure 2. Inverting Amplifier (1) and Integrator (2).

Inverting amplifiers take the negative of the input (Rummer, 1969, p.11). Integrator do the function that they are named for- they integrate. They integrate by constantly adding up the input(Technical Education and Management, Inc., 1962, p.126). Because the input impedance is so high, virtually no current can't get through the capacitor. The only thing that the current can do is continually build up, or add, as it tries to go into the op-amp. This is exactly like the integration which is just a continual summing process. By using resistors, capacitors, diodes, op-amps, inverting amplifiers, and integrator, it is possible to build circuits to solve almost any type of equation or problem.

MASS-ON-A-SPRING CIRCUIT

Set Up

The first circuit that was investigated was one to simulate the motion of a mass on a spring-oscillations up and down. To accomplish this mathematically the equation would be $\frac{d^2x}{dt^2} = \frac{-kx}{m}$ where K is the force constant, X is the position, and M is the mass. By integrating this equation once, it is possible to determine the velocity. By integrating it twice, the position can be found which was the goal-to see the position of the mass as it oscillated on the spring. In order to do this, the circuit had to contain two integrator and an inverting amplifier to make the output positive. The circuit diagram is shown in Fig. 3.

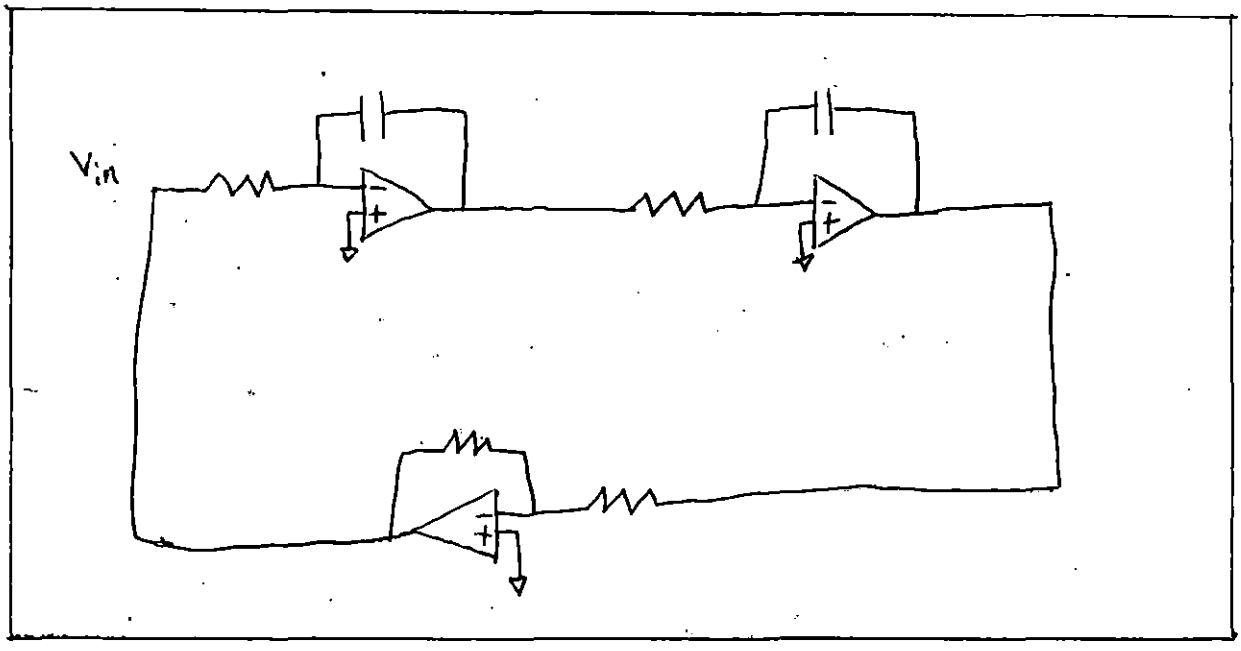

Figure 3. MASS-ON-A-SPRING CIRCUIT DIAGRAM.

The resistors used were 100 kilo-ohm. The capacitors were 1 microfarad. And the op-amps were 741's. All of these components were off-the -shelf and inexpensive. Once the circuit was wired and connected to an oscilloscope, it was possible to watch the results. The final result was the expected up and down oscillations yet they damped down quite quickly (approximately one minute to damp down to 37% of the original value). It was obvious that there was a problem in the system since no frictional factor had been taken into account in the equation. A rough sketch of the result is shown in Fig.4.

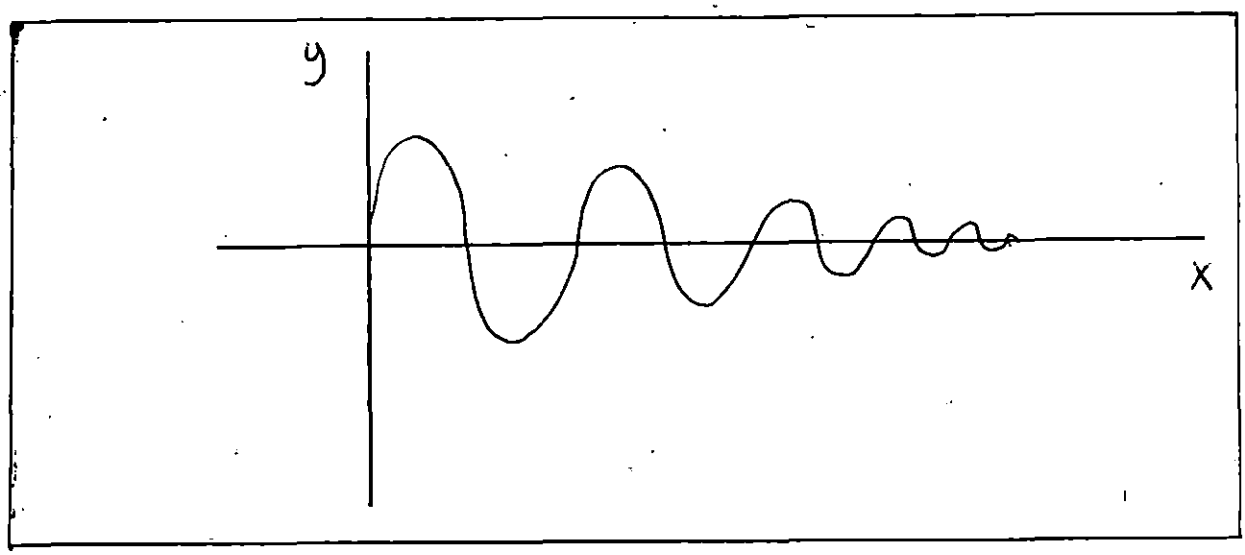

Figure 4. MASS-ON-A-SPRING CIRCUIT RESULT

Errors

Because the 741's were the least accurate op-amps int he lab, it seemed possible that they were the cause of the damping. To check this, they were replaced with ICL 7641's which had a much higher input impedance. This higher impedance should cause less current to leak through the op-amp into the system and therefore reduce the damping. However, the result was essentially unchanged. Next the resistors were checked. They were good to +/- 1% of their value of 100 kilo-ohms so the problem was not with them. Finally, the capacitors were measured using an impedance bridge. Although they were good to +/- 1% of 1 microfarad, one of the capacitors had a dissipation factor that was so high it was basically off the scale. Since leakage is a major concern when dealing with the usefulness of a capacitor, the one with the high dissipation factor might as well not have been in the circuit. It was allowing the electricity to leak through into the system much too quickly causing the output to damp down much faster than was expected. Once the capacitor was replaced in the circuit with one that had a low dissipation factor, the damping occurred much more slowly (approximately 10 minutes to damp down to 37% of the original value). Although no frictional factor had been accounted for in the circuit, it was not unexpected that some damping would occur since there were errors in all the components. Until this point, all measurements were taken using a stop-watch. In an effort to get the measurements to greater accuracy, a frequency counter was

used; however, it wouldn't measure frequencies low enough for this circuit. In an effort to increase the frequency, different capacitors were placed into the circuit to change the time constant and therefore the frequency. After the frequency was increased, the system damped down so quickly that the frequency counter was unable to get a reading. This led to the relationship between the dissipation and frequency: dissipation is directly proportional to the frequency. As the frequency increased, so did the leakage through the capacitors which caused the system to damp down so quickly that no measurements were able to be taken. The stop-watch measurements had to be sufficient.

ACCELERATION OF GRAVITY CIRCUIT

Set Up

The second analog computer circuit that was investigated was one that would find the value of the acceleration of gravity. The equation to do this mathematically was $\frac{d^2x}{dt^2}=g$ (Rummer, 1969,p.85). To compute g with a circuit called for two integrator, an oscilloscope to view the results, and a digital computer to check the accuracy of the result. The circuit diagram is shown in Fig.5.

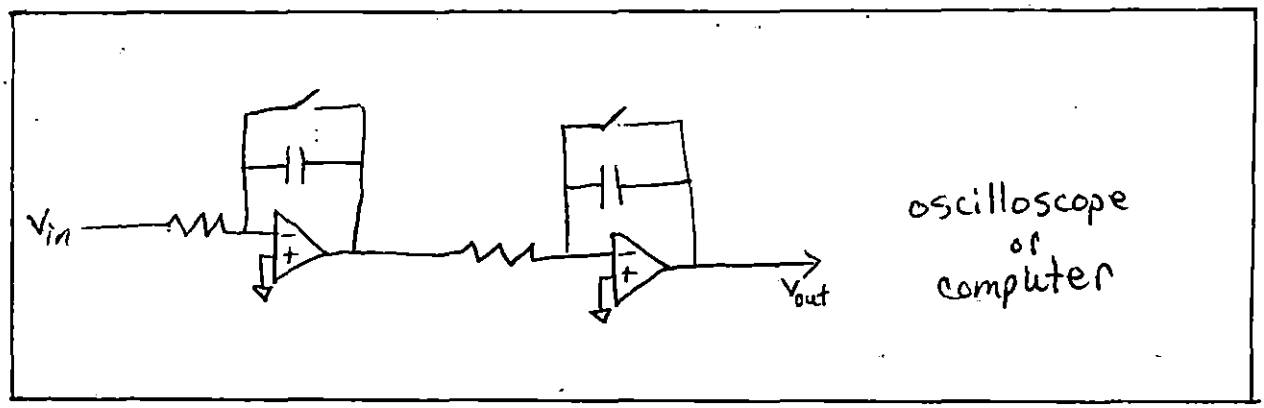

Figure 5. Acceleration of gravity Circuit Diagram

Once the circuit was wired and hooked to an oscilloscope the results were what was expected-a parabola and then zero. This is shown in a rough sketch in Fig.6.

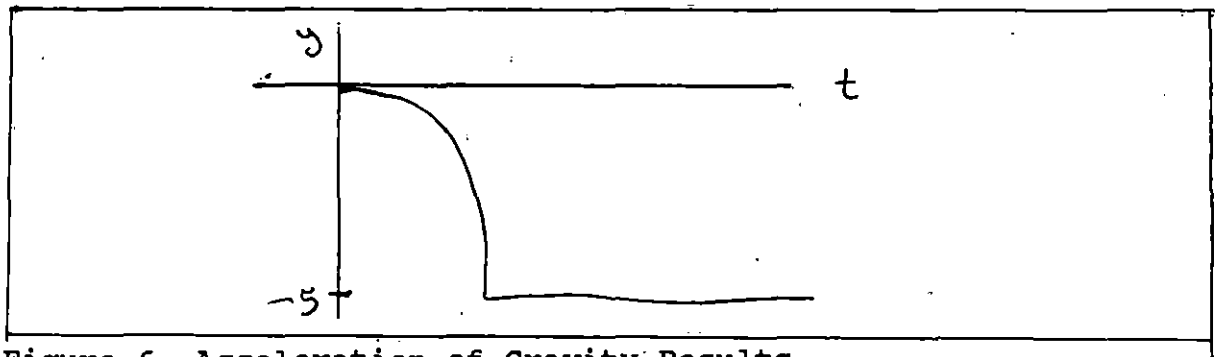

Figure 6. Acceleration of Gravity Results

To see how accurately the analog circuit was working, a digital computer was used. First, the calibration of the digital computer was checked with a Weston cell and voltmeter. Next it was programmed to take measurements of the time and position for fifteen different positions. Once the data was collected, a least squares gave a result of 9.6 or 98% of the true value of the acceleration of gravity after it was scaled up from 5V. A correlation coefficient of 0.9998 was obtained.

Errors

As with the first circuit, the resistors and capacitors were measured to be within +/- 1% of their stated values which could have accounted partially for the value being low. Also, although the correlation coefficient was so high, there might have been systematic errors that caused the value to be off that the random statistics could not catch. The timing of the computer was done in 1/60's of a second. In the worst case scenario, the computer could have been off in its timing by 1/60 of a second or about +/- 2% total. The cumulative error of the system was approximately +/- 3%. The result of 9.6 was well within that range.

CHAOTIC MOTION CIRCUIT

The third and final analog circuit that was investigated was one that would graph chaotic motion on the oscilloscope screen. A nonlinear equation was needed to mathematically describe chaos: $\frac{d^2x}{dt^2} = -a(e^{bx} - 1)$. To solve this using an analog circuit, two integrator, one inverting amplifier, and one potentiometer were needed. The circuit diagram is pictured in Fig.7.

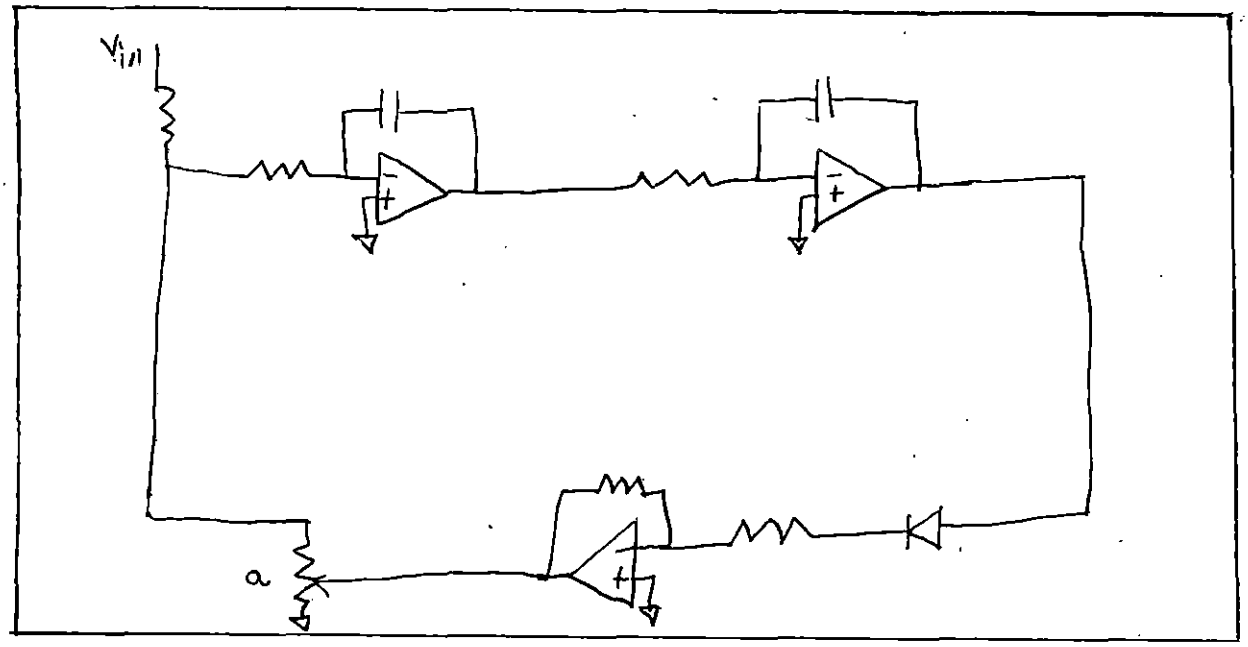

Figure 7. Chaotic Motion Circuit Diagram.

Once the circuit was wired, it was possible to measure the value of b which turned out to be 1.5. Also, a was determined by the potentiometer so it had a range of values. The equation was able to simulate chaotic motion because the exponential term tried to shoot the function to infinity at the same time that the -a tried

to bring it back down. There were three distinct regions determined by a. When a was near one, the output was fairly stable and saturated and the output rose straight up on the screen. However, when a was 0.7, chaotic motion occurred. It was not possible to predict where the output would show up on the oscilloscope screen.

CONCLUSIONS

Although digital computers are used universally now, analog computer circuits are simple and fairly efficient ways to solve many problems and simulate many events. Analog computers will always have that inherent error of +/- 1% or +/-2%, but for many situations that error can be virtually neglected. Simple harmonic motion, the acceleration of gravity, and chaotic motion are all easy to solve for and graph using simple analog circuits and an oscilloscope.

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THE ABUNDANCE, DIVERSITY, AND STRATIGRAPHY OF THE UPPER CRAB ORCHARD FORMATION LEWIS COUNTY, KENTUCKY

A Senior Thesis Presented to the
Department of Physical Sciences
Morehead State University

In Partial Fulfillment
of the Requirements
for the Degree of Bachelor of Science
in Geology

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by
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MACROFOSSIL AND MICROFOSSIL ABUNDANCE AND DIVERSITY OF THE CRAB ORCHARD SHALE, LEWIS COUNTY, KENTUCKY.

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ABSTRACT

The Crab Orchard section in Lewis County Kentucky provided the interval of study. Eight, one meter samples were taken from a 17.53 meter section located 1/2 mile east of Charters, Kentucky along State Route 546, to determine the abundance and diversity of macrofossils and microfossils.

The samples were disaggregated with Stoddard's Solution, or kerosene, then flushed through sieves to concentrate macrofossils and microfossils. The samples were then further concentrated by using the heavy liquid Acetylene Tetrabromide. The macrofossils and microfossils sample residues were then examined.

Macrofossils were found throughout the section, with the most abundant being crinoids and brachiopods. Also found were bryozoans, clams, gastropods, trilobites, and one Sphenothallus worm tube. Two modes of preservation were present, replacement by pyrite, and recrystallization. Pyrite replacement was the dominant mode of preservation overall, but in the upper samples, recrystallization was the dominant mode.

Microfossils were also found throughout the section, with the most abundant forms being graptolites and ostracodes. Also found were chitinizoans, scelecodonts and conodonts, brachiopod fragments, clams, echinoderm fragments, gastropods, sponge spicules and Sphenothallus worm tubes, and three questionable foraminifera. scelecodonts, chitinizoans and graptolites are all carbonized, while conodonts are phosphatic and ostracodes are either pyrite replaced, or recrystallized.

The Charter section shows all the characteristics of a good subtidal, low energy, open marine environment. Storm deposits, or Tempestites, indicate a resuspension of sediments. The mode of preservation of the fauna present indicates a dissolved oxygen content near the dysaerobic/aerobic boundary. In comparison with the Knob Lick section, the Charters section contains green and maroon shales, while the Knob Lick section has only green shales present. The Knob Lick section also contains fewer and thinner Tempestite deposits. It also shows an abundance of Forams, while the Charters section has almost a complete absence of Forams due to turbidity and rapid sedimentation, as well as abundant resuspension of sediments due to storm activity. There is also no significant differences in the

macrofossil content or mode of preservation in the green and maroon beds of the Charters section.

INTRODUCTION

The study of the Crab Orchard began as a Special Problems class during the summer of 1991. I became very interested in dysaerobic environments and decided to continue work on it for my senior thesis. I chose this project because it would give me an opportunity to examine a variety of Siluirian age microfossils and macrofossils from the area. It also gave me the chance to examine a dysaerobic environment (between 1.0 and 0.1 ml/L dissolved oxygen content) firsthand. This study also gave me the chance to gain experience collecting and processing samples, as well as working with laboratory equipment used in this type of project.

Locality

The section used for this study is located near the small town of Charters in Lewis County, Kentucky (Fig. 1). It can be located in the northeast corner of rectangle 5, on the Charters 7.5 minute topographic or geologic quadrangle (Morris, 1965). The section is a roadcut on the North side

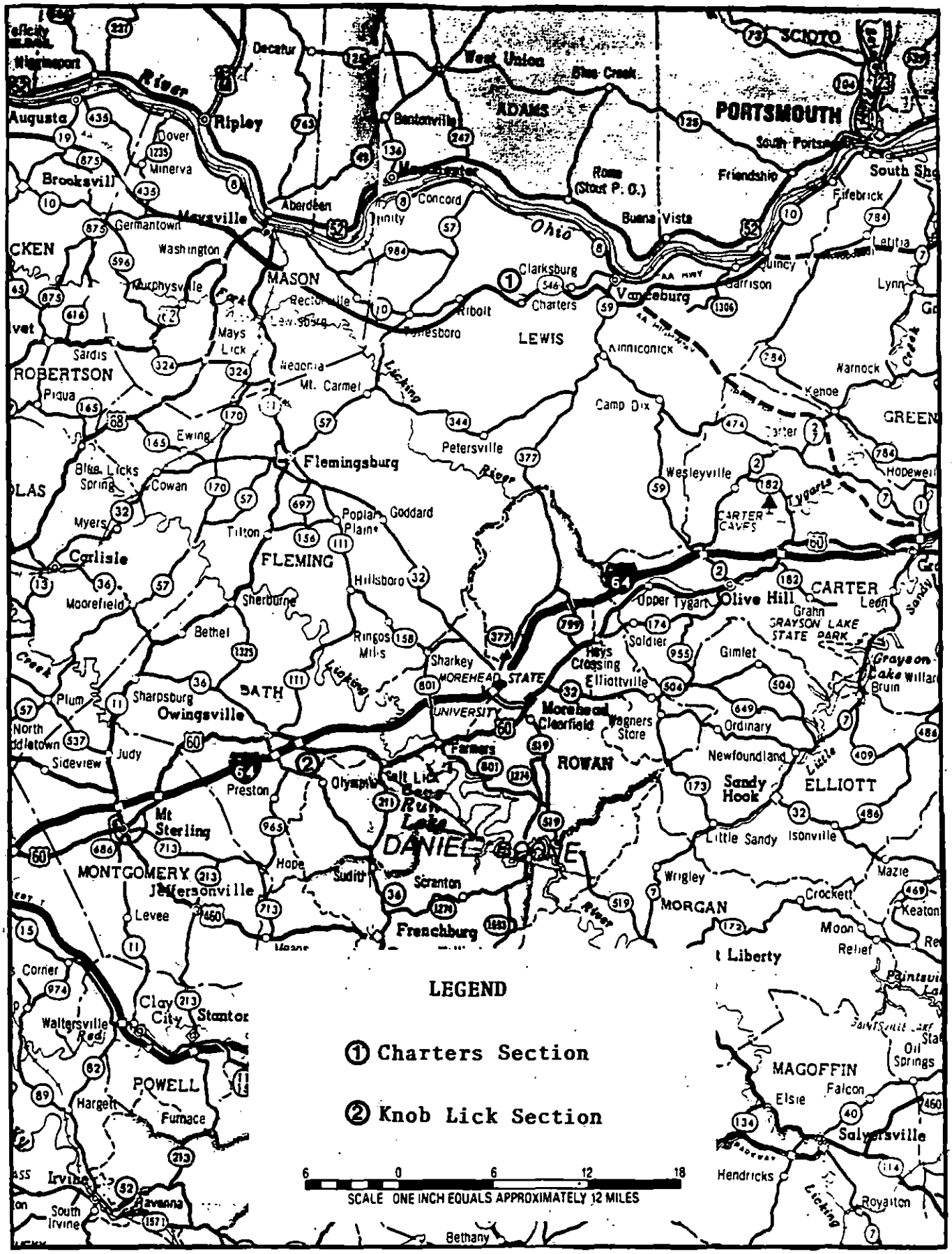


Figure 1. Charter's and Knob Lick Section Localities

of the road, which is located 0.5 kilometers (0.4 miles) north east of Charters on State Route 10 and 546. It lies approximately 83 degrees 25′ 50" west longitude and 38 degrees 35′ 45" north latitude (Morris, 1965).

Stratigraphy

The Charters section is located in the Upper Shale Member of the Crab Orchard Formation (Fig. 2). The Crab Orchard Formation is normally overlain by the Bisher Formation, and underlain by the Brassfield Formation, both Silurian in age (Peck, 1967). Although, in the study area the Crab Orchard base is covered (Morris, 1965).

Lithology

The interval of study is composed of green shales at the top of the section, and maroon colored shales at the bottom, with mixed maroon-green layers toward the middle. The shale is fissile to chunky, and slightly bioturbated. Dolostone beds up to four or five centimeters thick are also found scattered throughout the section (Fig. 3).

Purpose of Study

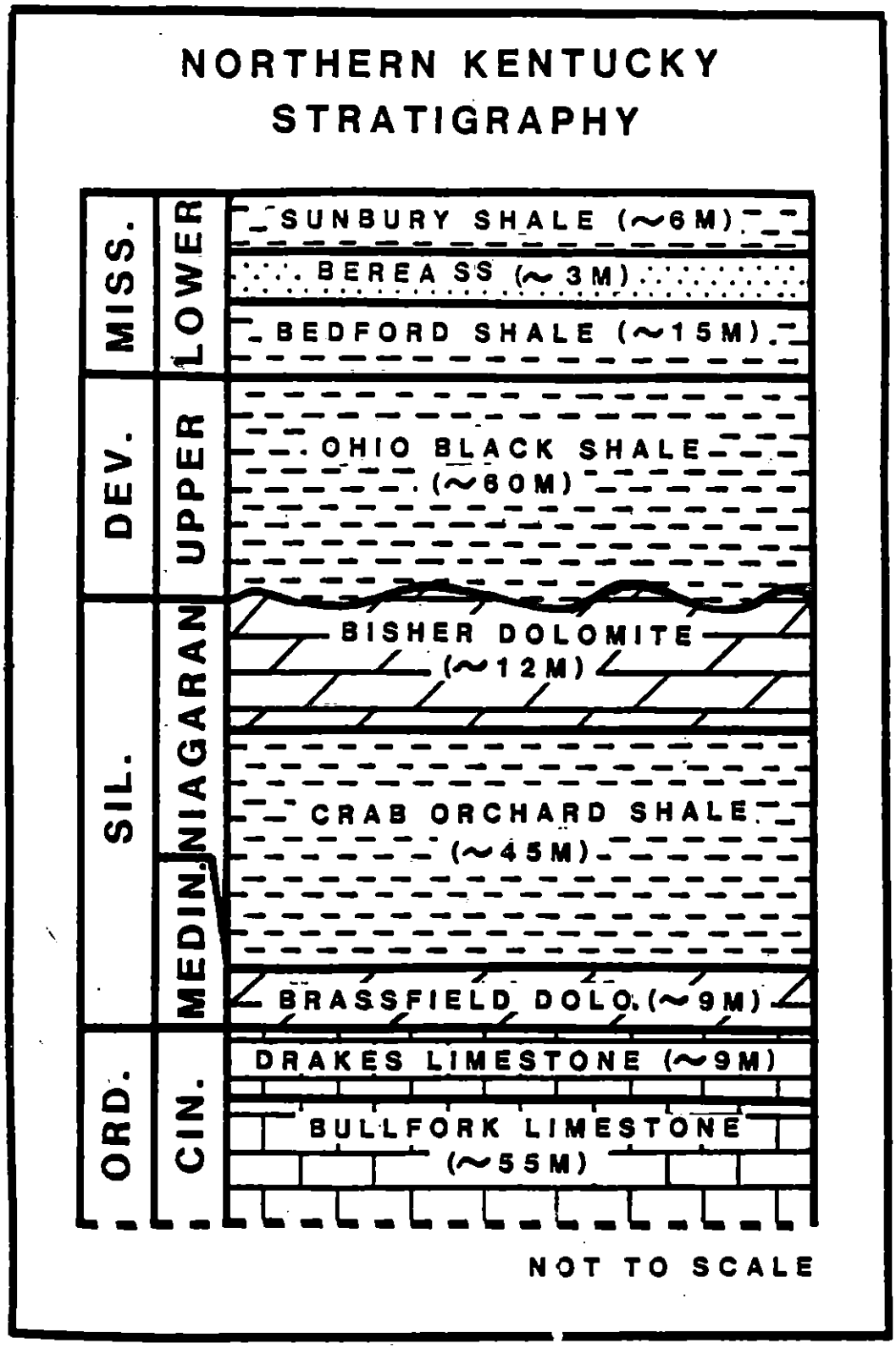
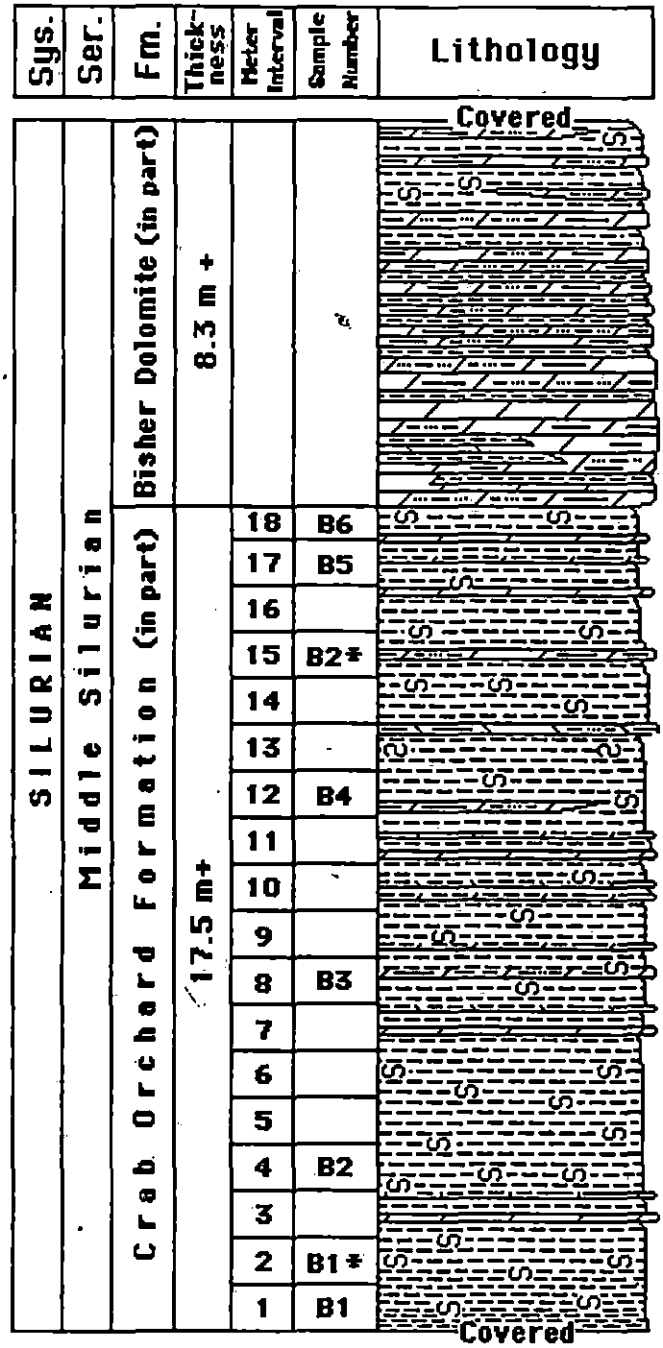


Figure 2.- Northern Kentucky stratigraphy in the vicinity of Lewis County, Kentucky (after Morris and Pierce, 1967).

Figure 3. Charters Stratigraphic Section Lewis County Kentucky



Legend

Shales, partly bioturbated

Argillaceous or silty dolostone

Interbedded shale and argillaceous dolostone

Sample Series

C. E. M.- 6-18-91--B1 through B6

C. E. M.-10-10-91--B1* and B2*

Scale

ft. 16 — 5.0 m

0 — 0

The primary purpose of the study was to determine the abundance and diversity of the fossil fauna present. Comparisons were also made to previous studies (Jones, 1990, Manley, 1991) done on the same formation and approximately same stratigraphic interval, at Knob Lick Kentucky (Fig. 1) 33 miles southwest of Charters. The Knob Lick section proved to be a dysaerobic environment, which can be defined as having 1.0 to 0.1 ml/L dissolved oxygen, where as aerobic environments have greater than 1.0 ml/L dissolved oxygen and anaerobic ones have less than 0.1 ml/L dissolved oxygen (Kramer, et.al. 1986).

Also, a secondary purpose was to compare the abundance, diversity and mode of preservation of fossils present between the maroon and green colored shales. Typically the maroon color indicates a more oxygenated environment, while the green color indicates a more oxygen depleted environment.

METHODS OF INVESTIGATION

Sample Collection

Six spot samples were taken from the upper most 17.53 meters of the exposed formation (Fig. 3). A fault was also discovered while measuring the section. It is a normal fault with .7 meters of vertical displacement. Evidence for the fault includes, 1.) Slickenslides along the fault plane, and 2.) The offset of beds. Starting at the base of the outcrop, a hand level and meter stick were used to measure the height of the section. A hoe pick was then used to clear weathered material from the interval selected for sampling, and a fresh sample was then collected in small increments from the base of one meter to the base of the following meter. This procedure was repeated at regular intervals throughout the section, with the last sample coming from the top meter (Fig.3). Taking samples in this manner allows for thorough mixing, and was repeated for each sample collected. A samples of green shale and a sample of maroon shale were also taken later in the study for comparitive purposes (Fig.3). At least five kilograms of material was collected, and placed in labeled sample bags for transport to the laboratory.

Drying Samples

After the samples were brought back to the laboratory, they were placed in seperate metal trays, labeled, and oven dried at 120 degrees Celcius for 24 hours. Table one below shows the total dry weights of the samples collected.

Figure 4. Total dry weights of samples collected for study.

Sample #	Dry Weight (Kg.)
CEM 6-18-91 B1	8.242
CEM 6-18-91 B2	8.390
CEM 6-18-91 B3	7.035
CEM 6-18-91 B4	6.804
CEM 6-18-91 B5	5.418
CEM 6-18-91 B6	6.650
CEM 10-10-91 B1	6.035
CEM 10-10-91 B2	6.550

Disaggregation of Samples

A five kilogram portion was weighed from each sample, then broken down into three equal parts and placed into metal buckets. The buckets were then filled with Stoddard's Solution (Kerosene) and allowed to soak for 24 hours. The kerosene was then decanted and replaced with water, and allowed to soak for an additional 24 hours. This same procedure was followed for all samples.

Wet Sieving

After disaggregation of each sample, it was washed through a set of standard sieves (#20 for macrofossils and #140 for microfossils). The clay and silt sized materials were removed by washing the sample through the sieves. The material in the sieves was then flushed into an evaporation bowl, and dried in a oven for 24 hours. The samples were then weighed seperately in kilograms. Table two lists the dry weights of the samples after wet sieving.

Figure 5. Dry weights of samples after wet sieving, in Kgs.

Sample #	Total	#20	#140
CEM 6-18-91 B1	.497	.441	.056
CEM 6-18-91 B2	.134	.035	.099
CEM 6-18-91 B3	.162	.069	.093
CEM 6-18-91 B4	.375	.280	.095
CEM 6-18-91 B5	.943	.906	.037
CEM 6-18-91 B6	.230	.204	.026
CEM 10-10-91 B1	.193	.101	.092
CEM 10-10-91 B2	.513	.422	.091

The #20 and #140 dried retained residue was then were labeled according to sieve size and sample number, and placed in seperate vials for later examination. The material caught in the #20 sieve was ready for examination, the material caught in the #140 sieve underwent heavy liquid seperation to further concentrate the microfossils.

Heavy Liquid Separation

To seperate the heavy material from the light material of the #140 sieve samples, specific gravity seperation was performed using the heavy liquid Acetylene Tetrabromide. It is carcinogenic and should be handled with extreme caution. Three funnels were set up on a laboratory stand, and filled with 1500 ml. of the heavy liquid. The specific gravity of Acetylene Tetrabromide is 2.96. A #140 sieve sample was added to each funnel, and allowed to seperate, with the lighter fractions, those having a specific gravity of less than 2.96 floating and the heavier fractions, those having a specific gravity of higher than 2.96 sinking to the bottom. The sample was stirred frequently and allowed to seperate for one hour. Then, filter paper was placed in a seperate funnel and placed beneath the funnel containing the heavy liquid. The heavy materials were then reaeased by opening the stopcock on the seperating funnel. The filter paper in the funnel below caught the solid material and allowed the liquid to pass on through into a beaker beneath it. The filter paper was labeled "heavies", along with sample number with pencil so it could be distinguished from the other samples.

The lighter fraction was caught on a second filter paper labeled "lights" after the heavy fraction had been filtered off. The filter paper and residue was then washed

with acetone to remove the excess heavy liquid. It was then allowed to dry. The heavy and light samples were weighed, put into vials, and labeled according to sample number and fraction. This process was repeated for all eight #140 samples. Figure six lists all the dry weights of the solids left after heavy liquid seperation.

Figure 6. The dry weights of materials left after heavy liquid seperation (in Kgs.).

Sample No.	Heavy	Light
CEM 6-18-91 B1	.003	.021
CEM 6-18-91 B2	.006	.083
CEM 6-18-91 B3	.011	.081
CEM 6-18-91 B4	.005	.095
CEM 6-18-91 B5	.003	.047
CEM 6-18-91 B6	.003	.019
CEM 10-10-91 B1	.005	.086
CEM 10-10-91 B2	.002	.100

SAMPLE PICKING AND SORTING

Macrofossils

The #20 sieve collections were picked and sorted for macrofossils. The sample was placed in a picking tray, and a binocular scope and light source was used to sort through it. Macrofossils found were removed, and placed in vials labeled by sample number and later identified.

Microfossils

Material collected in the #140 sieve (heavies and lights) were then examined with a binocular scope and light source. A moistened #5-0 picking brush was used to remove and place specimens onto picking slides. The slides were labeled by sample number and if they were light or heavy. The specimens were later identified.

RESULTS

Macrofossils

Macrofossils are found throughout the section (Fig.7). Samples found in CEM 6-18-91 B1 through CEM 6-18-91 B6 contain Brachiopods, Bryozoans, Clams, Crinoids, Gastropods, Trilobites and one Sphenothallus worm tube. Two modes of preservation of macrofossils are present, replacement by pyrite and recrystallized forms, which were subsequently dolomitized. Brachiopods are 67% pyrite replaced, Byozoans are 100% pyrite replaced, Clams are 100% pyrite replaced Crinoids are 58% pyrite replaced, Gastropods are 100% pyrite replaced and Trilobites are 0% pyrite replaced. The percent of recrystallized macrofossils increases significantly up section. Pyrite is the dominant mode of preservation in the lower samples, where recrystallization is dominant up section. CEM 6-18-91 B2 has the most abundance and diversity of any sample. Crinoids and Brachiopods are the two most abundant macrofossils found throughout the section.

Microfossils

Microfossils are found throughout the section (Fig.8). Graptolites and Ostracodes are the most abundant, followed

Figure 7. **List of Macrofossils from the Charters Section in Lewis County, KY.**

Fossils	B1	B2	B3	B4	B5	B6	B1*	B2*	Totals
Brachiopods	1	9	0	4	1	0	0	0	15
Bryozoans	0	6	0	0	0	2	0	0	8
Clams	0	2	0	0	0	0	0	0	2
Crinoids	9	100	6	33	7	0	0	0	155
Gastropods	0	2	0	0	0	1	0	0	3
Sphenothallus	0	0	0	1	0	0	0	0	1
Trilobites	0	0	1	4	1	0	0	0	6
Worm Burrows	38	308	29	6	35	47	0	0	463
Unknown Frag.	0	97	0	1	3	1	0	0	101
Totals	48	525	38	51	53	54	0	0	754

Note: Sample numbers are CEM-6-18-91 B1 through B6 and CEM-10-10-91 B1* to B2*.

Figure 8. **List of Microfossils from the Charters Section in Lewis County, KY.**

Fossils	B1	B2	B3	B4	B5	B6	B1*	B2*	Totals
Chitinizoans	10	4	0	11	0	0	1	4	30
Conodonts	6	0	0	0	0	1	4	6	17
Foraminifera	0	0	0	0	0	?3	0	0	?3
Graptolites	21	5	3	16	8	6	8	44	111
Ostracodes	10	2	1	1	22	7	2	1	46
Scolecodont	10	5	0	6	2	2	1	7	33
Unknown Frag.	4	1	7	6	8	2	3	16	47
Brachiopods	1	0	0	3	5	1	0	1	11
Echinoderms	21	26	7	20	16	0	0	0	90
Sphenothalus	1	0	0	0	0	0	2	1	4
Worm Burrows	22	15	22	17	16	26	6	10	134
Totals	106	58	40	80	77	48	27	90	526

Note: Sample numbers are CEM-6-18-91 B1 through B6 and CEM-10-10-91 B1* to B2*.

by, Chitinizoans, Scelecodonts and Conodonts. CEM 6-18-91 B1 has the most abundant microfossill fauna, and also the most diverse. Chitinizoans, Scelecodonts, and Graptolites are all carbonized, while Conodonts are phosphatic and Ostracodes are either pyrite replaced or recrystallized. Juvenile macrofossils also found were Echinoderm and Brachiopod fragments, Clams, Gastropods, Sphenothallus worm tubes, Sponge Spicules and one Tentaculites.

DISCUSSION

Comparison to Knob Lick Dysaerobic Environment

The Charters section shows all the characteristics of an offshore open marine environment. It is subtidal with slow rate of sedimentation in a low energy setting below mave base. The Charters section has green beds at the top, maroon beds at the bottom, with mixed red and green bed mixed in its middle part, where as the Knob Lick section contains only green beds. The number of dolostone beds (tempestites) are fewer and they are relatively thinner at the Knob Lick section(Jones 1990, Manley,1991). Tempestites are found throughout the Charters section in relative abundance, the number of tempestites also increases significantly up section. Tempestites indicate storms, when wave base deepens, sediments are agitated and resuspended, coarser particles settle out first and creates a fining upward sequence. This forms dolostone or tempestite beds. These tempestite beds tell us that the Charters Section is more proximal, or closer to the shore, due to the way storms affect it, it is closer to wave base. Also, the absence of these tempestite beds at the Knob Lick section tell us it is further away from wave base and more distal from the shore.

In the Knob Lick section all preservation of macrofossils is pyrite replacement, no recrystallization(Jones 1990, Manley 1991). Recrystallization, as suggested above, indicates a higher oxygen content, due to the storm activity and the mixing of the water column.

Macrofossils of the Charters section compare well with macrofossils of the the Knob Lick section, Echinoderms, Brachiopods and Gastropods all being dominant. Knob Lick showed an increase up section, where the Charters section does not show an increase of macrofossils up section.

Microfossils show a significant difference in abundance and diversity. Knob Lick had abundant Forams and Ostracodes. Charters had no Forams, Graptolites and Ostracodes were the two most abundant microfossils. Tony Bryant, a Foram specialist from the United States Geological Survey, pointed out that turbidity affects the prescence of benthic life. We know that there was turbid water due to the storm deposits present. This is based on Cretaceous times, marine sediments contain no Forams due to storm activity and high sedimentation rates. I believe that this holds true for the Charters section, and inhibits Forams from occuping this portion of the Silurian Epicontinental Sea.

Comparisons of Maroon Green Shales

Comparisons of the green shales found at the top of the section and the maroon shales found at the bottom of the section, showed no significant differences in the macrofossil content, as none were recovered from the greater than #20 sieve. However, macrofossils were caught on the #140 sieve and these showed no significant differences. At first I thought that the red color indicated a more oxygenated environment, while the green color indicated a more oxygen depleted environment. The two shale samples also show no difference in mode of preservation.

These conclusions may be due to an error in sampling. A broad sample was taken, and there may have ben maroon-green shales mixed into each sample. The sample should have been smaller. Also, Dr. Frank Ettensohn from the University of Kentucky thought that the source area may have bed red beds. Sediments were eroded, transported, then deposited as red beds. It may have nothing at all to do with environment. It could, possiibly be Ordivician age red beds located to the East.

CONCLUSIONS

1.) Macrofossils are found throughout the Charters Section

2.) The fossil fauna present indicates an open marine environment.

3.) Crinoids and Brachiopods are the two most abundant macrofossils

4.) Macrofossils have two modes of preservation, replacement by pyrite, or recrystallization.

5.) The percent of recrystallized macrofossils increases significantly up section.

6.) Microfossils are found throughout the Charters section.

7.) Graptolites and Ostracodes are the two most abundant microfossils

8.) The Kob Lick section contains fewer and thinner Tempestite deposits.

9.) The Knob Lick section contains only green shales, while the Charters section contains red and green shales.

10.) The Knob Lick section has an abundance of Forams. The The Charters section shows an almost complete absence of Forams due to turbidity and rapid sedimentation as well as abundant resuspension of sediments due to

storm activity.

11.) There is no significant difference between the macrofossil content, or mode of preservation in the green and maroon shales of the Charters section.

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The Modification of Flemion

for use in a Solid Electrolyte Battery

A Research Paper

Presented to

the Department of Physical Sciences

Moerhead State University

In Partial Fulfillment

of the Requirements for

Science 471

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by

Timothy Howard

April 1992

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INTRODUCTION

General Discussion

This investigation is primarily concerned with modifying the functional groups on a Flemion membrane so it can be used in an aluminum/chlorine solid electrolyte battery. Flemion is a perfluorocarbon polymer having a general structure of

$$Rf=[CF_2=CFOCF_2CFCFO(CF_2)_3]COOCH_3$$
$$|$$
$$-CF_3$$

Flemion was developed by the Asahi Glass Company in Japan. The largest scale application of Flemion is in the chlor-alkali industry. The Flemion cell used for the production of caustic soda is more efficient than the diaphragm or mercury processes previously used. As of 1986 Flemion cells contributed over 10% of the worlds caustic soda production (Ukihashi, 1986, p. 263).

The use for Flemion depends on Flemion's chemical inertness and its ability to selectively conduct positive ions in its carboxylate form in a basic solution. The carboxylate form of Flemion has the same structure as unmodified Flemion except the $RfCOOCH_3$ is converted to RfCOOH. The conversion of Flemion to its carboxylate form is carried out in a two step process. First, the Flemion is reacted with concentrated NaOH at 90° for twenty-four hours.

$$RfCOOCH_3 + NaOH \text{ -----> } RfCOONa + CH_3OH$$

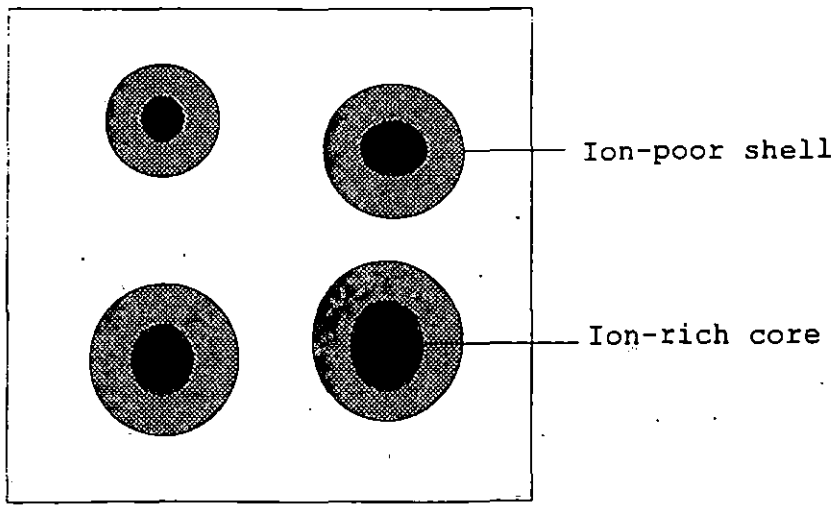
Next, an ion exchange with 6M HCl is carried out for 24 hours at room temperature.

$$RfCOONa + HCl \text{ -----> } RfCOOH + NaCl$$

I hoped to take advantage of the chemistry of Flemion. My goal was to make the Flemion into an anionic conductor rather than a cationic conductor. I tried to accomplish this goal by converting the Flemion $COOCH_3$ functional group to a $CHNH_3^+$ site.

Previous Work

Hashimoto et. al.using small angle X-ray scattering(SAXS), verified the existence of ion clusters in Flemion membranes. The ion clusters were proposed as an explanation for some perfluorinated acid polymer qualities, like swelling in aqueous solutions (Cooper and MacKnight, 1973. p.344) . The core-shell model, which included the idea of ion clusters, predicted that the polymer would orient itself in such a way that some of the ions would be grouped together in ion clusters. These clusters would in turn be surrounded by ion-poor regions that is mostly fluorocarbon (Figure 1). The clusters were connected by channels, the feature that allows ion transport. Direct verification of clusters and channels was given when Ag^+ and Sn^{2+} ions were counter diffused across a Nafion(a membrane very similar to Flemion except it has SO_3 for functional groups) membrane and it was examined with a transmission electron microscope (Gierke, 1983, p. 307) (Figure 2). It was estimated the channel diameter to be 4.2nm. The small channel size combined with ion clusters explains the perfluorinated acid polymer's ion selectivity. In a basic solution, the acid groups lose most of their protons (Figure 3). The high concentration of negative charges around such a small channel allows positive ions to



Flemion

Figure 1: The microstructure of Flemion as predicted by the ion cluster theory.

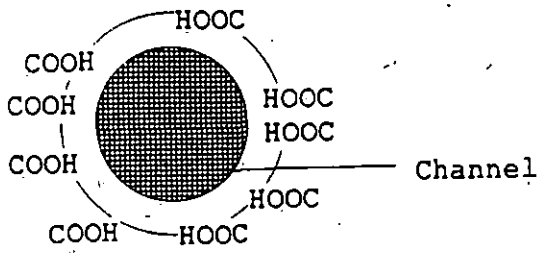


Figure 2: Channel structure of the carboxylic acid derivative of Flemion.

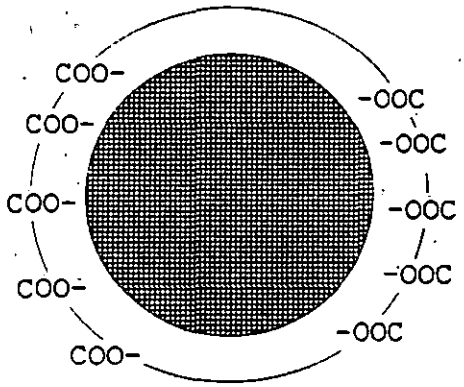


Figure 3: Channel structure of the carboxylic acid derivative of Flemion in strong base.

pass through, but repels negative ions, by preventing their entry into the channels

Some time ago the Air Force developed a novel battery. It used aluminum at one electrode and chlorine gas at the other electrode. The electrolyte was a solid, 1-methyl-3-ethylimidazolium ion. The battery was rechargeable and produced 1315 W-hr/kg as compared to 180 W-hr/kg for a standard $Pb/PbSO_4$ battery(Newman, 1991, p. 12). Unfortunately, over a period of time the chlorine gas reacted with the electrolyte destroying its ability to store energy.

Purpose of Investigation

The purpose of my experiments was to alter the functional group on the Flemion membrane in such a way that the membrane could be used as a separator in the Al/Cl_2 battery. A separator for this battery must have three characteristics: it must be chemically inert to the environment in the battery, it must control the passage of Cl_2 and it must be able to conduct Cl^- ions. The first work in this project was done at Bowling Green State University by Dr. David Newman(Newman, 1991, p. 15). Newman et. al. devised the following reaction scheme for accomplishing their goal.

First the membrane was soaked in NaOH for 24 hours at 90° C.

$$RfCOOCH_3 + NaOH \text{ ----------> } RfCOONa + CH_3OH$$

Next, the membrane was reacted in 1M HCl for 24 hours at room temperature.

$$RfCOONa + HCl \text{ ----------> } RfCOOH + NaCl$$

Then the membrane was refluxed in $SOCl_2$ for 24 hours.

$$RfCOOH + SOCl_2 \text{ ----------> } RfCOCl + SO_2 + HCl$$

Finally, the acid chloride derivative was reacted with dibenzo-18-crown-6 in an attempt to attach one of the benzene rings in the crown ether to the aryl group on the membrane. The last reaction was suggested by an earlier experiment that showed dibenzo-18-crown-6, when combined with lithium chloride in the solid phase, was a chloride ion conductor (Newman, 1981,p . 389-392) . Newman et. al. hoped to combine the chemical stability of the Flemion and the chloride conducting ability of the dibenzo-18-crown-6 for use in the aluminum/chlorine battery. However, after a series of experiments, it was hypothesized that only about 2-3% of the sites had a crown ether attached. I repeated the original experiments and obtained a similar low yield of acylated sites. The photophysical studies in Flemion(Blatt, 1988, 4151), suggested that the crown ethers were too large to fit through the channels once some of the acid chlorides had been replaced by the bulky crown ethers. I immediately began to search for another group to attach to the membrane that offered small size and the possibility of being able to conduct anions. A reasonable method would be to attach some small group that was either positive or could be made positive once it was incorporated into the membrane. My hypothesis was that a positive group would have just the opposite effect of the COO- in strong base. A positive group should repel positive charges while allowing negative ions to pass through. Because of its small size and ability to acquire a proton in acidic solution a simple amine group was suggested. We decided to use the first three reactions developed by Dr. Newman et. al. The acid chloride membrane would then be reacted with an amine to form an amide.

$$RfCOCl + NR_1R_2H \text{ ----------> } RfCONR_1R_2 + NH_2R_1R_2^+Cl^-$$

where R_1= H, CH_3, CH_2CH_3, $CH_2CH_2CH_3$ or $(CH_2)_3CH_3$ and where R_2= H or CH_2CH_3. Then the amide can be reduced to an amine by a reduction reaction it with lithium aluminum hydride.

$$RfCONR_1R_2 + LiAlH_4 \text{ ----------> } RfCNR_1R_2$$

Experimental

All infrared spectra were taken on a Nicolet 5MX Fourier transform infrared spectrophotometer. In an attempt for reproducibility, membranes were held in place by a pair of salt plates. The salt plates were lightly tightened in the same way for each spectra keeping the membranes at the original thickness. A small groove was cut on the edge of the salt plates and the edge of the holder to insure the reproducible orientation of the salt plates with respect to the infrared beam.

A Barnsted water deionizer was used in the experiments where deionized water was used to remove ions from the membranes.

A National Appliances vacuum oven set at approximately 100° C was used to dry all membranes. All membranes were dried in a vacuum.

The reaction of Flemion with NaOH is carried out to produce the Na^+ derivative of Flemion. Small pieces of Flemion, around 60mg in weight, approximately 1.5cm, are cut from the membrane sample donated for this research by Asahi Glass Company. The Flemion is then dried in a vacuum oven for 24 hours. Then the Flemion is removed and placed in a 50 mL flask with a magnetic stirrer and 20 mL of approximately 6 M NaOH.

The reaction mixture is heated to 90°C for twenty four hours. The membranes are rinsed off with distilled water and placed in another flask with 30mL of deionized water for 24 hours. The membranes are dried in the vacuum oven for 24 hours at which time their infrared spectra are obtained.

The dry Na^+ derivative membranes are placed in a 50 mL flask with 6M HCl to produce the RfCOOH or carboxylic acid derivative of Flemion. The reaction mixture is left at room temperature for 24 hours with a magnetic stirrer. The membranes are rinsed off with distilled water and placed in a 50 mL flask with 30 mL of deionized water for 24 hours. The membranes are then removed and dried in the vacuum oven for 24 hours, after which time their infrared spectra are observed.

The carboxylic acid derivative of Flemion is refluxed with 20 mL of $SOCl_2$. The membranes are refluxed at least 24 hours before use. After 24 hours a membrane is selected and its infrared spectra is taken to insure that the conversion was essentially complete. The membranes are left in a stoppered flask with the excess $SOCl_2$ until they are needed for other reactions.

A quantitative experiment to determine an estimate the number of reactive sites per milligram of membrane was done in the following way. Two membranes were removed from the $SOCl_2$, quickly wiped with a Kimwipe, placed between two salt plates and their infrared spectra were taken. Then the membranes were placed in the vacuum oven for 1 hour. They were removed and their infrared spectra were taken. The spectra showed no change. The membranes were placed in scintillation vials with 20 mL of deionized water. The membranes were left for 24 hours. The water was then decanted off the membranes into two 50 mL volumetric flasks. Twenty milliliters of deionized water was added to the membranes for 24 hours to remove any chloride left in the membranes. This water was added into the same 50 mL volumetric flask as used the day

before. The vials were carefully rinsed with small amounts of deionized water, which were also added to the volumetric flasks. The flasks were filled to the mark and a Mohr titration was done to determine the amount of chloride released from each membrane. This allowed us to estimate the number of sites, because the amount of chloride ions released equals the number of reactive sites on the membrane.

$$RfCOCl + H_2O \text{ ----------> } RfCOOH + HCl$$

To prove that an infrared peak at 1420cm^{-1} was due to an absorption by the COOH group, an acid chloride membrane was taped across the infrared machine's window and was left in the purge for four days. The purge consisted of air pushed through a flask of anhydrous calcium sulfate and then through a drying column containing both silica gel and molecular sieves. The purge gas was used to slow the reaction of the acid chloride membrane with water in the air so good records of shifting peaks and new infrared peaks could be obtained. Spectra were at first taken each minute, then each hour, then each day.

All amine reactions were done in the following way. An acid chloride membrane was reacted with an amine. After the reaction was finished, a Kimwipe was use to wipe off the surface of the membrane and an infrared spectrum was taken. Then the membrane was soaked in deionized water for 24 hours and dried in the vacuum oven. When the membrane was dry another infrared spectrum was taken. This process was developed for two reasons. The infrared spectrum of the membrane is usually much sharper after the $NH_2R_1R_2{}^+Cl^-$ salt (produced in the reaction), and excess amine are removed. Also, unreacted acid chloride sites reacted with water and form COOH sites on the membrane. If my hypothesis about the COOH functional group on the membrane causing the absorption at 1420 cm^{-1} is correct, I should have seen an appearance of the

$1420cm^{-1}$ peak after soaking the membrane in deionized water, if there are acid chloride groups that did not react with the amine.

A gas bubbler with a wire basket fitted to the fritted glass end (Figure 4) was used in the reaction of an acid chloride membrane with gaseous anhydrous ammonia. The gas was passed through the apparatus for three hours. The resultant membrane was treated in the standard way.

The reaction of three acid chloride membranes with methylamine was carried out in benzene while methylamine was bubbled through (Figure 5). NaOH was added to methylamine hydrochloride to form methylamine. The methylamine was passed through the drying tube and bubbled into the benzene. When the membranes were removed they were treated exactly in the standard way.

The reaction of RfCOCl with propylamine, diethylamine and ethylenediamine was carried out in the same way. The amines were dried by adding barium oxide to a small amount of amine in a scintillation vial. The barium oxide was allowed to settle out and the amine was decanted into another clean scintillation vial. The membrane surfaces were quickly wiped with Kimwipes after they were removed from the $SOCl_2$. The membranes were then dropped into the scintillation vial and left to react for at least 24 hours at room temperature. The membranes were removed and treated exactly in the standard way.

Results and Discussion

Infrared spectra and observations on flexibility and stiffness were made for each reaction. I will list them in reaction order.

Figure 4: Apparatus used for the reaction of ammonia with acid chloride membrane.

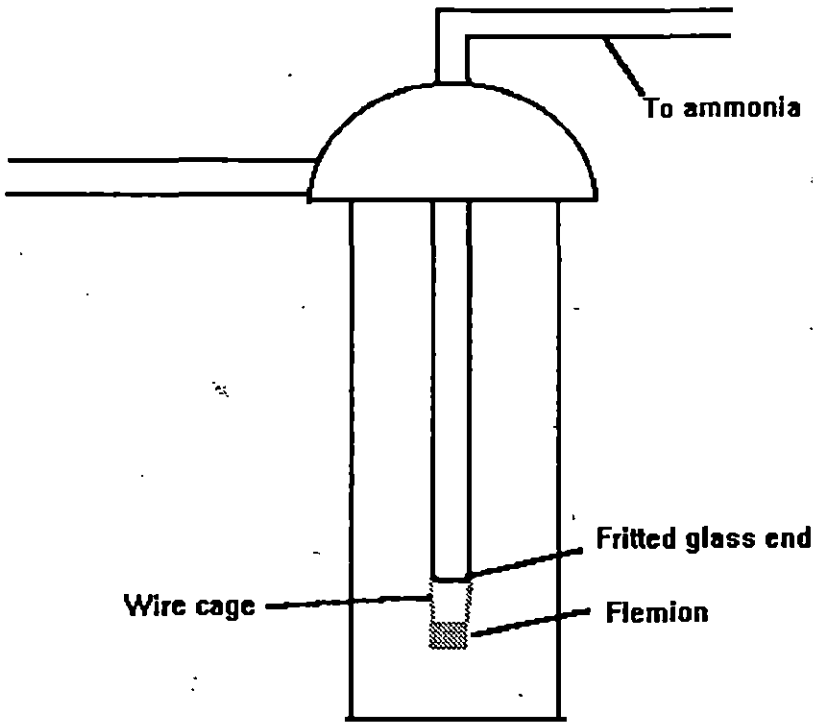
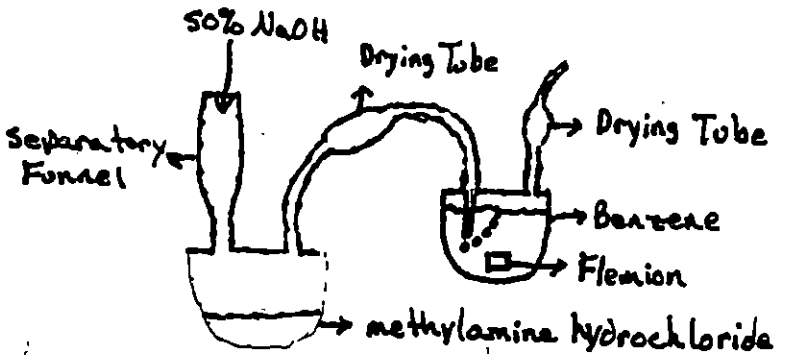


Figure 5: Apparatus used for the reaction of methylamine with acid chloride membrane.



Unaltered Flemion

Useful characteristic infrared absorptions: C-H 3000cm^{-1}(sharp),

C=O 1780-1805cm^{-1}, C-H 1450-1440cm^{-1}, C-F 2600-2200cm^{-1}

The spectrum was taken after the Flemion was dried in the vacuum oven for 24 hours (Figure 6). The C-F absorption is in all spectra and will be omitted from further listings of infrared peaks.

	before washing	after washing
Flexibility:	very flexible	very flexible
Clarity of membrane:	clear	clear

RfCOONa Flemion

Useful characteristic infrared absorption peaks: C=O at 1740-1635cm^{-1} (broad),

COONa 1440-1400cm^{-1}

The spectrum was taken after the membrane was soaked in NaOH for 24 hours at 90° C, soaked in deionized water for 24 hours and dried (Figure 7).

	before washing	after washing
Flexibility:	stiff	very stiff
Clarity of membrane:	cloudy	clear

RfCOOH Flemion

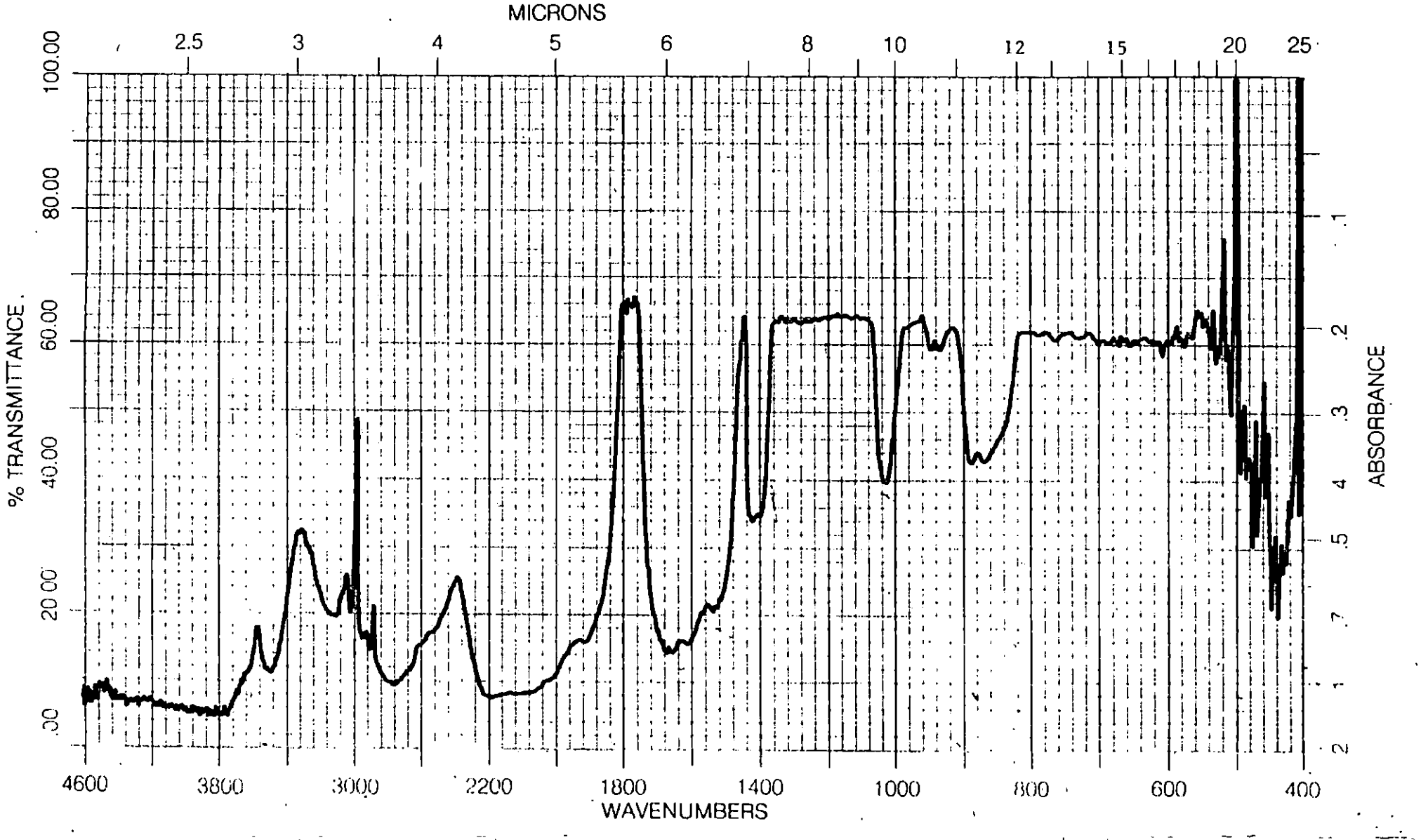
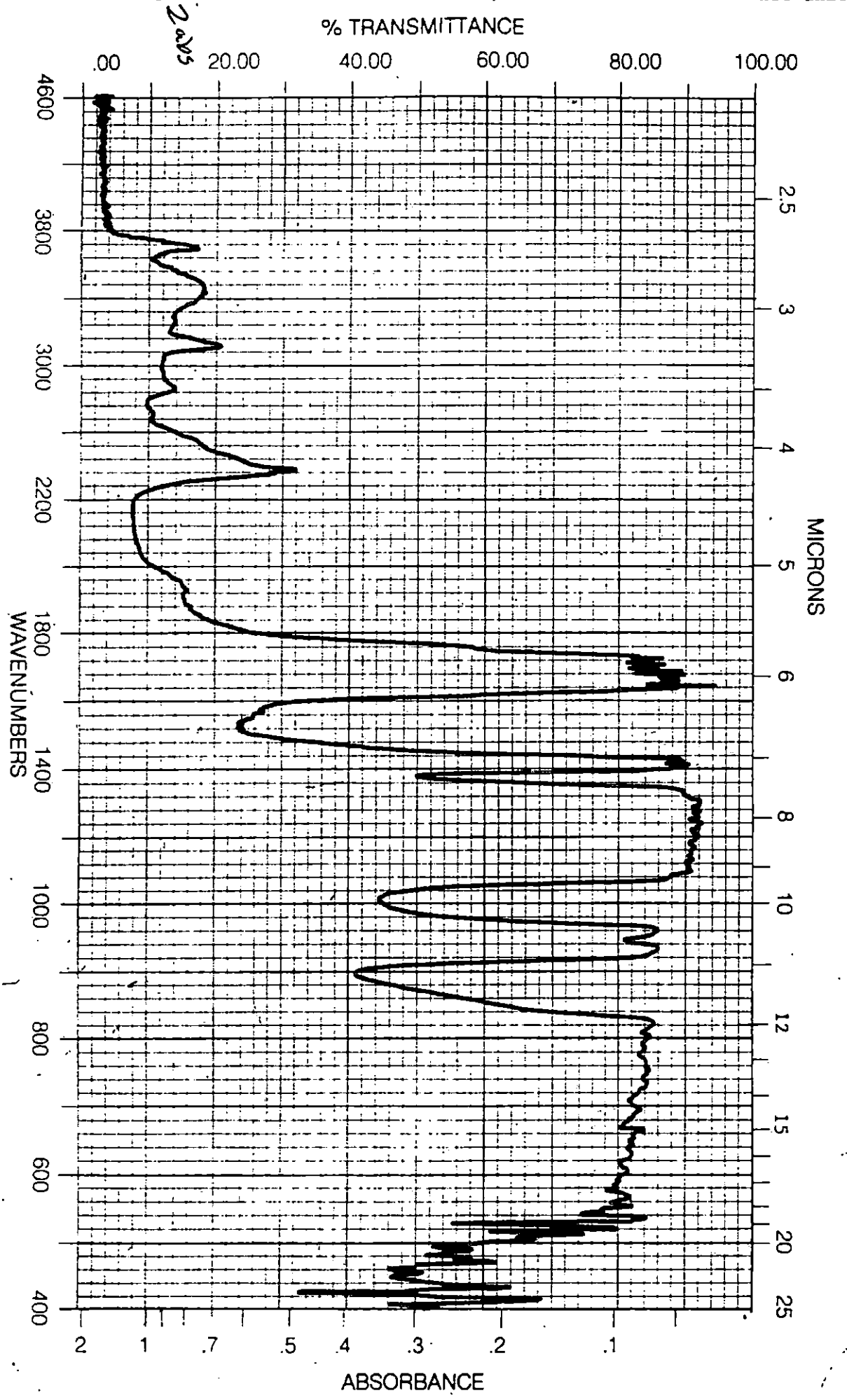

MICRONS
2.5
3
4
5
6
8
10
12
15
20
25
100.00
80.00
60.00
40.00
20.00
.00
% TRANSMITTANCE
.1
.2
.3
.4
.5
.7
1
2
ABSORBANCE
4600
3800
3000
2200
1800
1400
1000
800
600
400
WAVENUMBERS

Figure 7: Sodium ion derivative; full scale two absorbance units



Useful characteristic infrared absorption peaks: O-H 2280-3340cm^{-1}(broad),

C=O 1680-1780cm^{-1}, COOH 1400-1450cm^{-1}

The spectrum was taken after the membrane was soaked in HCl for 24 hours at room temperature, soaked in deionized water for 24 hours and dried in the vacuum oven (Figure 8).

	before washing	after washing
Flexibility:	very stiff	very stiff
Clarity of membrane:	cloudy	clear

Other observations: After membranes were removed from the HCl solution and dried they had a frosty appearance. I proposed that the white color was due to NaCl trapped in the channels. To show this, I soaked a white membrane in a small amount of deionized water for 5 hours. I decanted the deionized water into a scintillation vial and dried the membrane. It was now clear. I took an sample of the decant and performed a flame test on it. The flame glowed bright orange indicating the presence of Na^+. I took another portion of the decant and added some silver nitrate solution. A little white precipitate formed indicating the presence of chloride. The COONa membranes were also white when I dried them so I began to soak both the COONa and COOH membranes in deionized water to remove all ions.

RfCOCl Flemion

Useful characteristic infrared absorption peaks: C=O 1790-1830cm^{-1}

The spectrum was taken after the membrane was refluxed for 24 hours and wiped off with a Kimwipe (Figure 9).

Figure 8: Carboxylic acid derivative; full scale two absorbance units

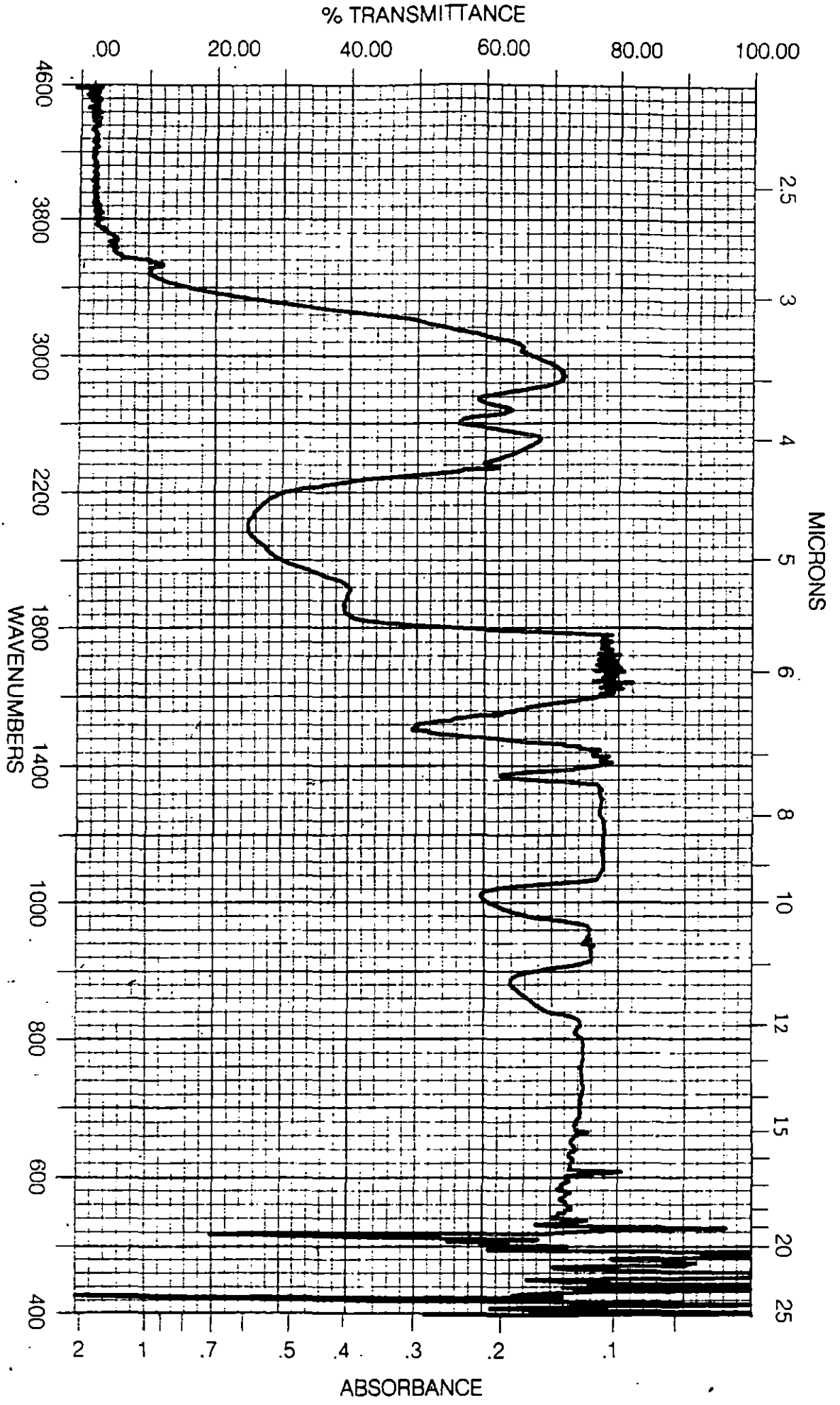
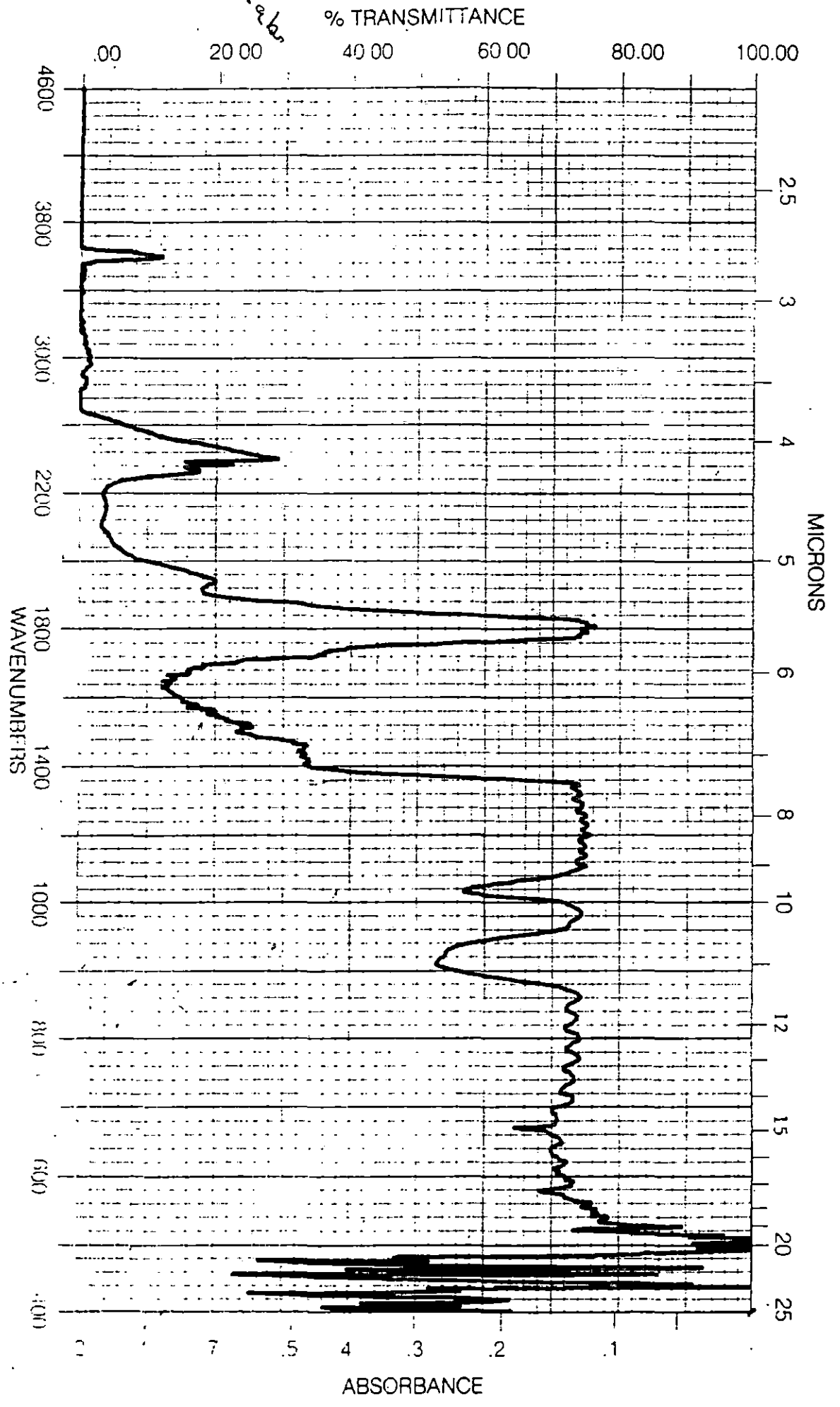


Figure 9: Acid chloride derivative; full scale one absorbance unit



	before washing
Flexibility:	very flexible
Clarity of membrane:	light brown

Mohr Titration

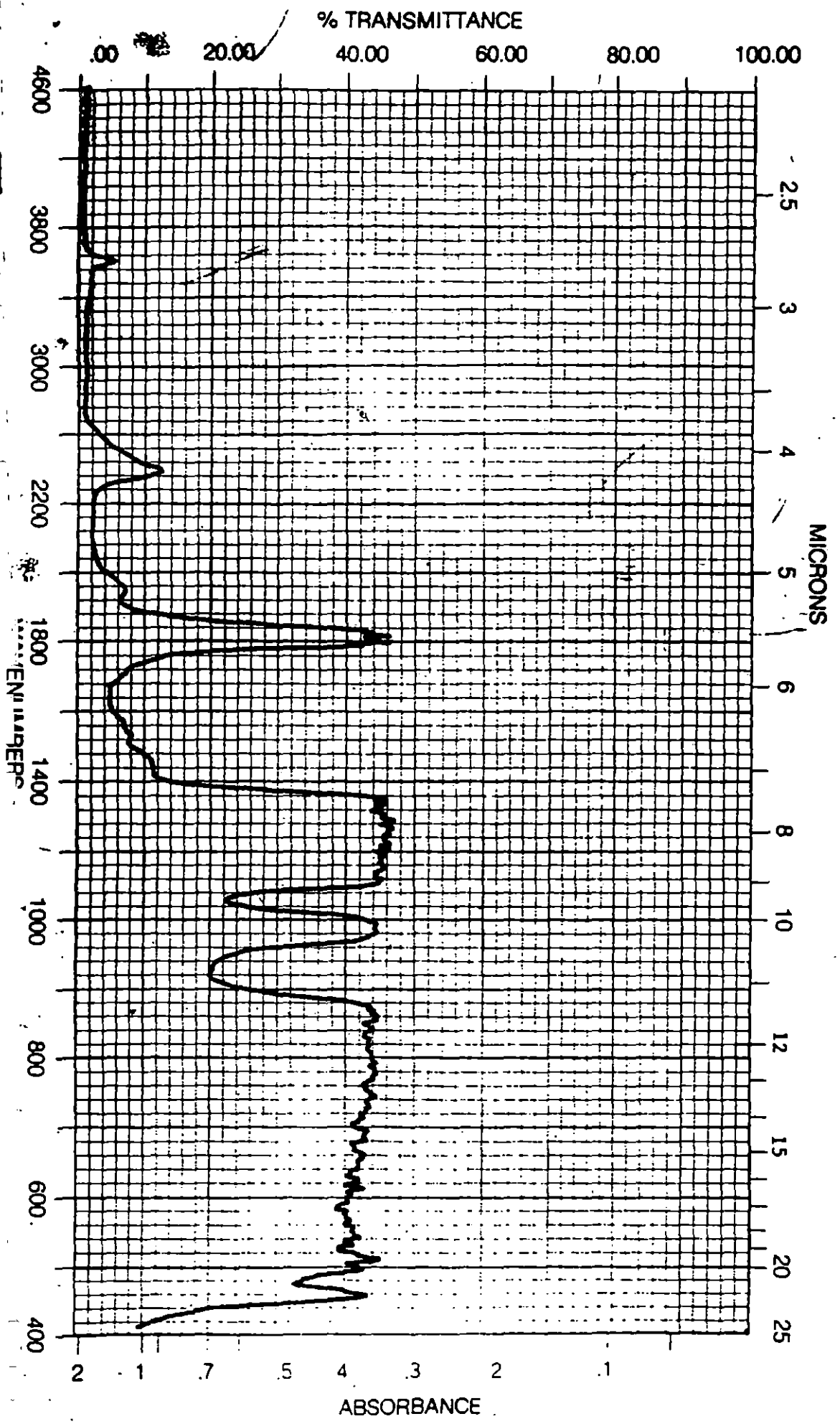
I completed titrations of two separate membranes and found an average of 600 g/ moles of sites.

Determination of 1420cm^{-1} peak

The membrane used in this experiment had the characteristic infrared spectrum of a RfCOCl membrane and was assumed to be at least 98% RfCOCl based on the absence of any other peaks and the accuracy of the fourier transform spectrophotometer used(figure 10).

The purge gas had a low concentration of water vapor which helped me obtain a very slow reaction between the acyl chloride membrane and the water vapor. Infrared spectra were taken every minute for 5 minutes and every hour for 2 hours until it was seen that there was not perceptible change in the spectra. The first spectra in which there was a detectable change was after 24 hours (Figure 11). Notice the sharp peak appearing at about 1440cm^{-1}. This peak grew slightly sharper and shifted to between 1440-1400cm^{-1}. The final spectrum was taken five days after the membrane had been left in the purge gas (Figure 12). The absorption band between 1440-1400cm^{-1} was broader than usual. I think this may have been due to the hydrogen bonding of water absorbed into channels with the RfCOOH groups. Simple proof of this theory would have been to dry the membrane out and take another spectrum and notice any changes. Unfortunately,

Figure 10: Peak determination experiment; start



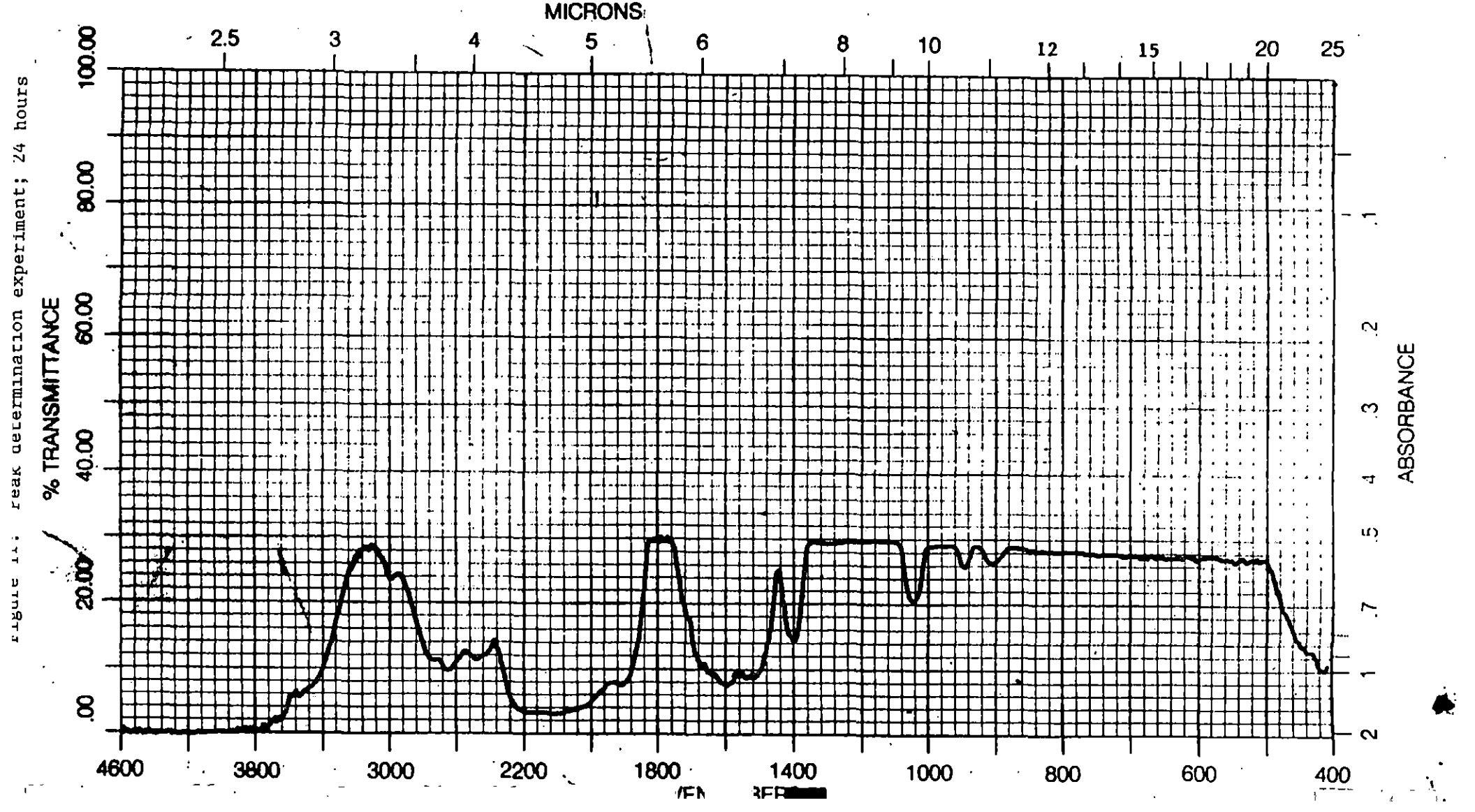
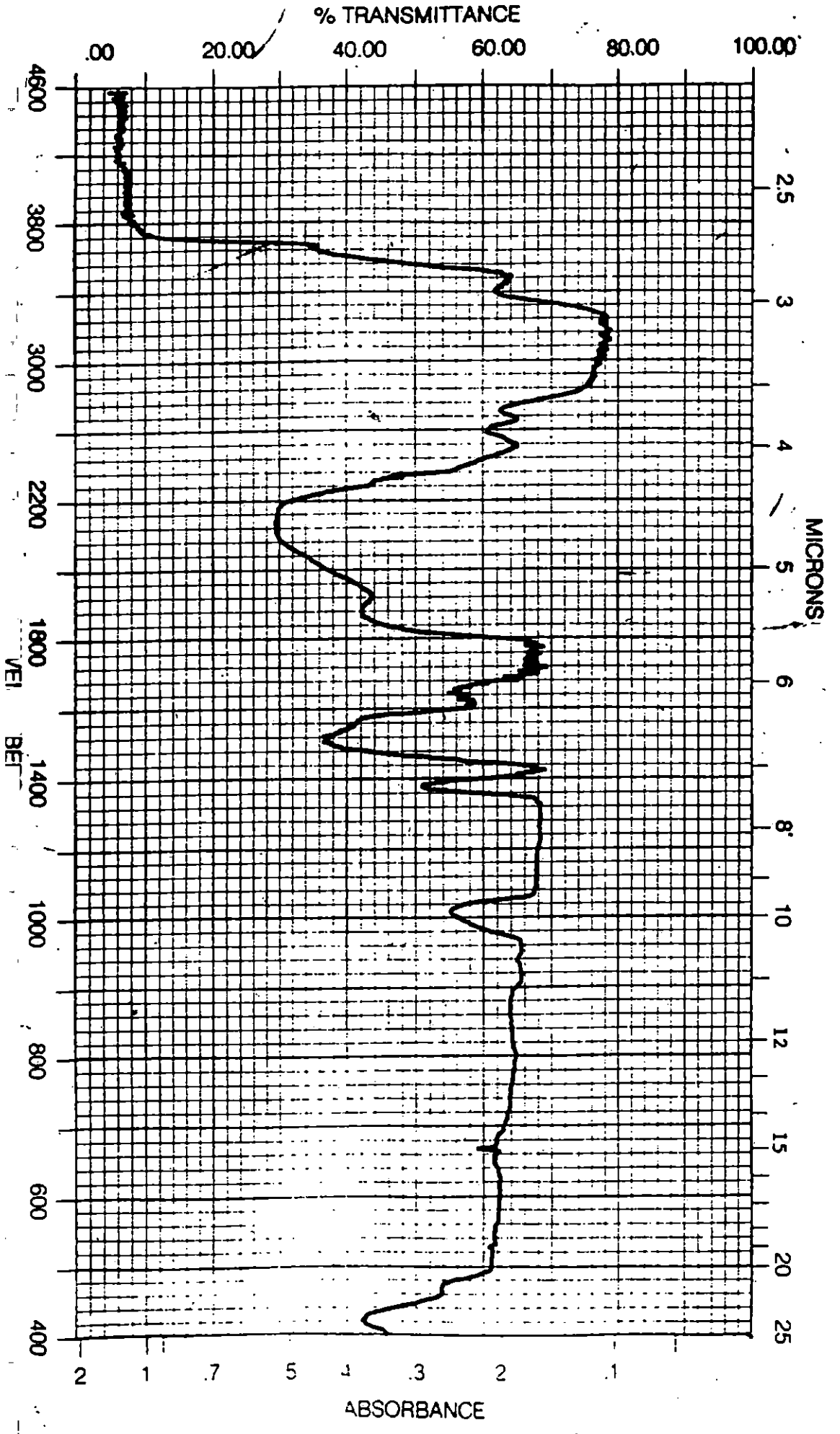


Figure 11. Peak determination experiment; 24 hours

Figure 12: Peak determination experiment; five days.



research on my project ended before I could do this.

$$RfCOCl + NH(CH_2CH_3)_2 \text{ ---------> } RfCON(CH_2CH_3)_2 + NH_2(CH_2CH_3)_2^+Cl^-$$

Useful characteristic infrared absorption peaks: possible amide 1600cm^{-1}(sharp) ,

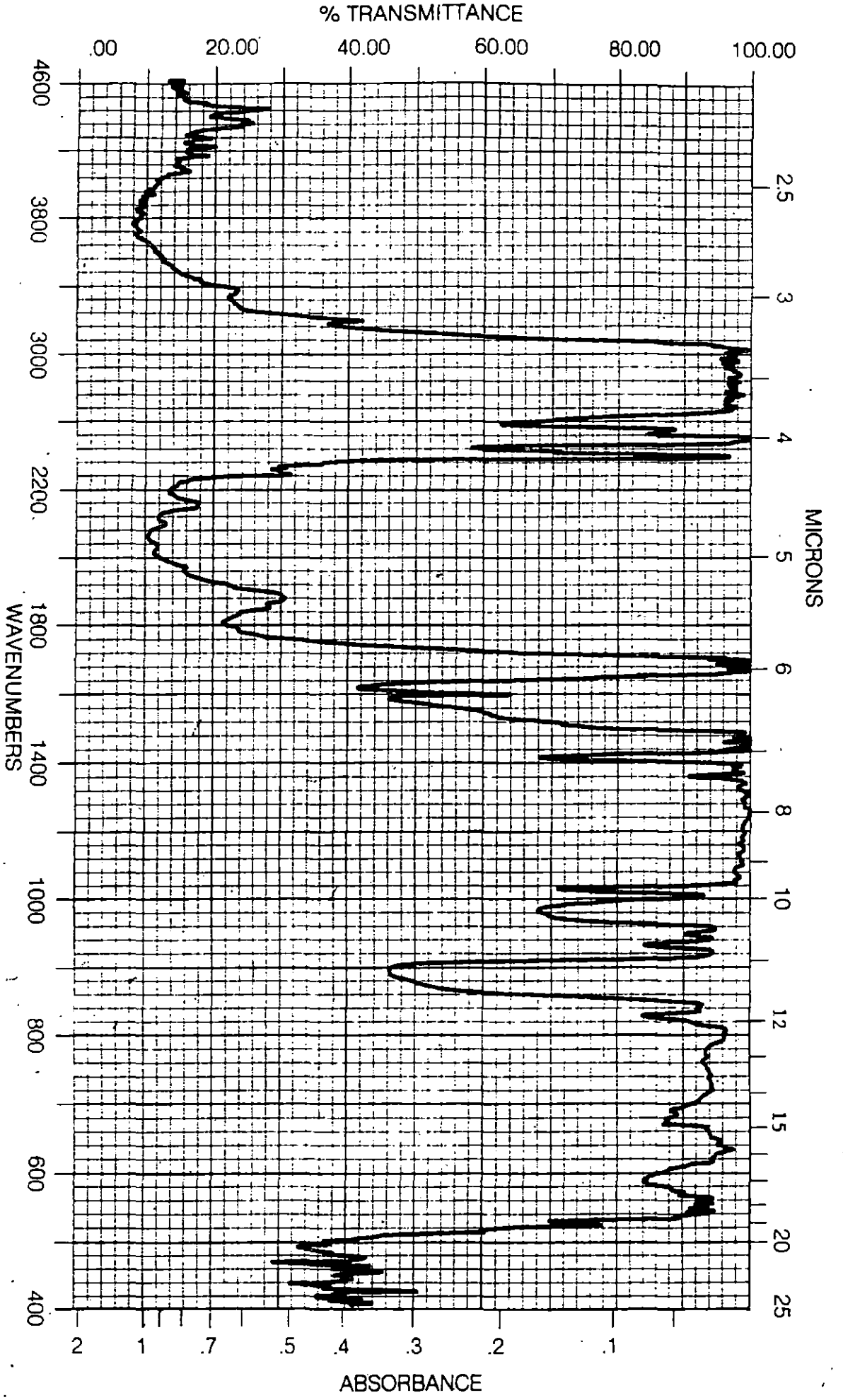
C=O 1720-1680cm^{-1}, C-H 1500-1440cm^{-1}, C-H 2680-3080cm^{-1}

The spectrum was taken after the membrane was soaked in diethyl amine for 24 hours, soaked in deionized water for 24 hours and dried (Figure 13). The spectrum was indistinguishable to the one taken before the membrane was soaked in water so I do not include it.

	before washing	after washing
Flexibility:	flexible	flexible
Clarity of membrane:	white	white

Other observations: About 5 minutes after the membrane was dropped in the diethyl amine the membrane turned white. Small white crystals were floating in the amine. The white color of the membrane in the other experiments meant suggested salts were trapped in the membranes, so I made the assumption the crystals were $NH_2(CH_2CH_3)_2^+Cl^-$. Later the amine was decanted off and the crystals and a drop of nitric acid were added to a solution of silver nitrate. A white precipitate was formed indicating the crystals contained chloride ions. I soaked the diethyl amide membrane in deionized water for 24 hours. Soaking in deionized water for 24 hours usually removes the white color of the membrane. The diethyl amide membrane was clear when I removed it from the water but, after it dried regained its frosty color. I theorized that the ethyl groups on the surface amide groups were blocking the channels and not allowing the $NH_2(CH_2CH_3)_2^+Cl^-$, formed as a by product of the amide reaction, to exit the channels.

Figure 13: Diethylamide derivative? Full scale two absorbance units



The water was able to enter the channels and dissolve the salt making the membrane clear. Then when the membrane was dried in the vacuum oven the small water molecules, that could enter the channels, was evaporated leaving the salt behind. In a rigorous attempt to dissolve the salt, I dropped a membrane in boiling deionized water. After about 30 minutes I returned to examine the membrane. To my surprise the membrane had swelled to about double it original size. There were blisters of trapped liquid of various sizes >1 mm. The membrane was now clear. I dried the membrane again and it returned to its original size, although distorted and was white again. I think the swelling effect may have been due to the fact that the interior of the membrane contained a high concentration of ions. This, combined with the high temperature probably made it easier for water to enter the channels, would explain why so much water forced itself into the interior of the membrane.

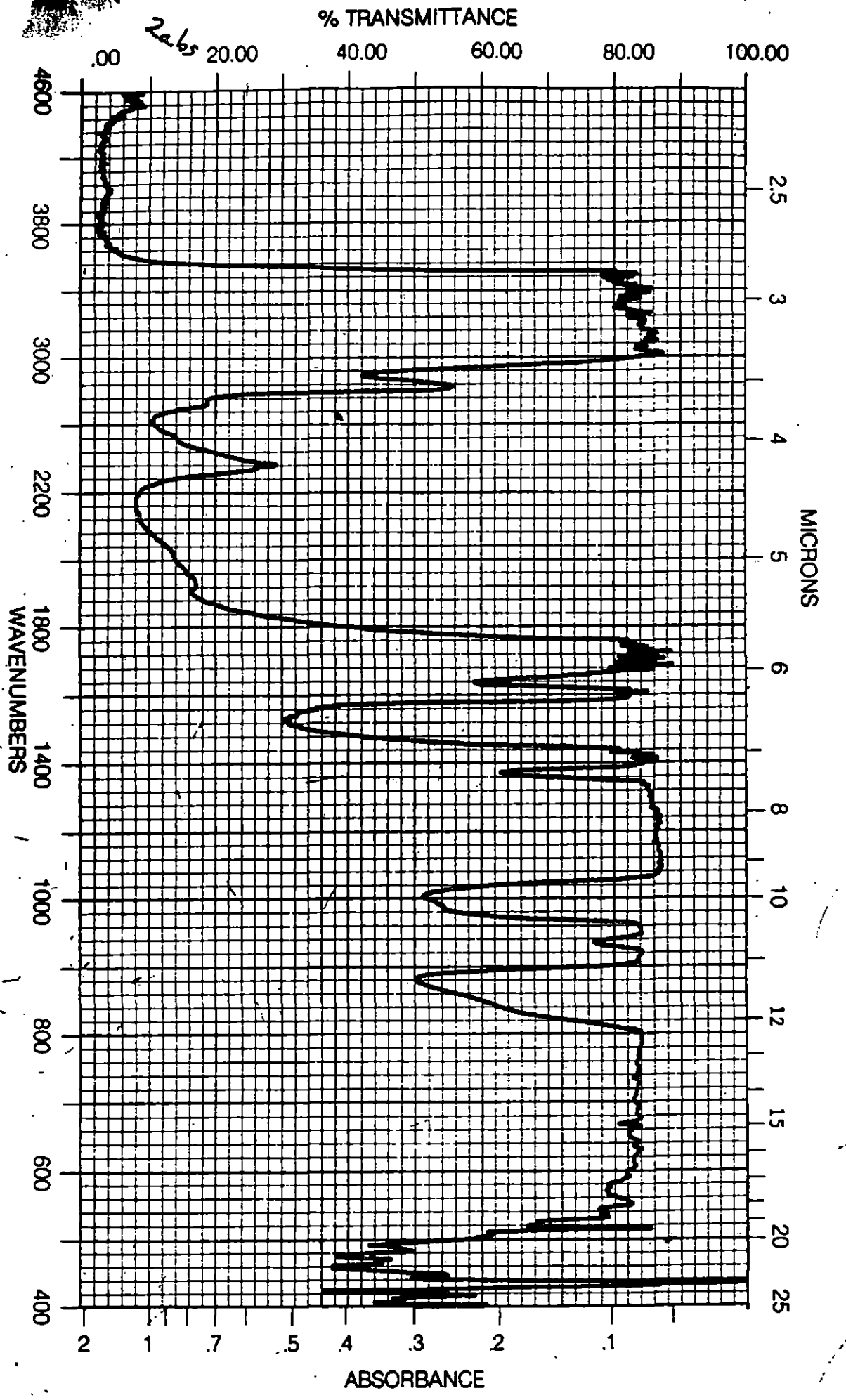
$$RfCOCl + NH_3 \text{ ----------> } RfCONH_2 + NH_4Cl$$

Useful characteristic infrared peaks: Probable COOH 1440-1400, probable amid 1620-1580cm^{-1}, C=O 1760-1680cm^{-1}, ? 2840cm^{-1}, possible O-H,N-H 3700-3000cm^{-1}

The spectrum was taken after the membrane had been reacted with anhydrous ammonia, soaked in deionized water for 24 hours and dried (Figure 14). I did not include the spectrum taken before the membrane was soaked in deionized water because the membrane was covered in crystals, probably ammonium chloride from the reaction, which did not allow a spectrum of the film to be taken.

	before washing	after washing
Flexibility:	flexible	stiff
Clarity of the membrane:	white	clear

Figure 14: Amide derivative? Full scale two absorbance units



Other observations: After 6-7 minutes the membrane was covered in crystals. The crystals dissolved easily in water. I concluded based on my earlier experiences with crystals during the amine reactions that these crystals were NH_4Cl. The spectrum shows the peak around 1420cm^{-1} that I attribute to COOH. One possibility for its appearance in the spectrum, even though the membrane was never reacted with water, is another gas bubbler was used following the bubbler in which the membrane was contained. The second bubbler contained concentrated H_2SO_4 to absorb the ammonia that did not react. Since the flow rate of the ammonia was slow, some water vapor may have diffused back into the bubbler contained the membrane. There were also several occasions when there was some back suction. Some water vapor may have entered the reaction bubbler at this time.

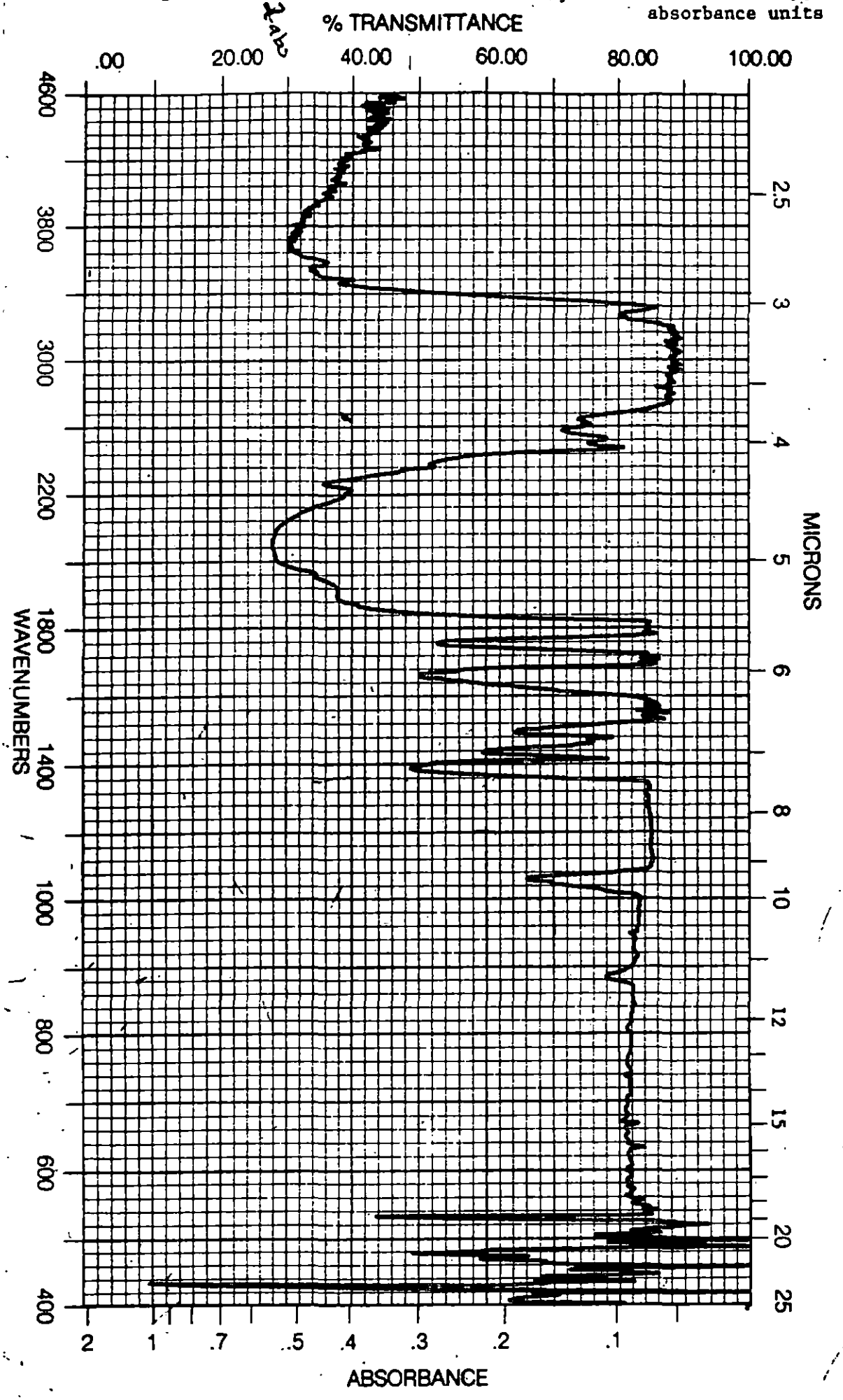
$$RfCOCl + NH_2CH_3 \text{ ----------} > RfCONHCH_3 + NH_3CH_3^+Cl^-$$

Note there are two separate sections for infrared data because one membrane was removed early in an attempt to get an infrared of a membrane before the reaction was complete and one was taken three hours later after the reaction was assumed to be complete.

Useful characteristic infrared peaks for membrane removed early: COCl 1820-1780cm^{-1}, C=O 1740-1720cm^{-1}, C-H 1480-1460cm^{-1}, COOH? 1415cm^{-1}(sharp), N-H, O-H 3600-2600cm^{-1}, amide 1600-1520cm^{-1}

The membrane was soaked in benzene while methylamine was being bubbled through, for approximately 5 minutes then the membrane was removed, wiped with a Kimwipe and its spectrum taken (Figure 15).

Figure 15: Membrane removed from methylamine reaction early; full scale two absorbance units



Useful characteristic infrared peaks for membrane reacted for 24 hours: COOH ? 1420cm^{-1}, C-H 1490-1460cm^{-1}, amide ? 1620-1520cm^{-1}, C=O 1740-1700cm^{-1}

The spectrum was taken after a membrane had been soaked in the benzene for 24 hours and wiped off with a Kimwipe (Figure 16).

	before washing	after washing
Flexibility:	flexible	stiff
Clarity of membrane:	white	clear

Other observations: White crystals floating in benzene. Again the peak at 1420cm^{-1} is in the spectrum. I think, due to the COOH peak observed at 1420cm-1, there was not sufficient drying materials between the reaction mixture of NaOH plus methylamine hydrochloride to prevent water vapor from entering the flask containing the benzene and the membranes. The flow of the evolved gas was hard to control and at times it bubbled really fast through the benzene. It was at the times that the methylamine gas evolved in large amounts that the water entered the benzene and reacted with the membrane.

$RfCOCl + NH_2(CH_2CH_2CH_3)$ ----------> $RfCONH(CH_2CH_2CH_3) + NH_2(CH_2CH_2CH_3)^+Cl^-$

Useful characteristic infrared peaks: C-H 1480-1440cm^{-1}, $CONH(CH_2CH_2CH_3)$? 1560-1520cm^{-1}, C=O 1720-1670cm^{-1}, ? 2840cm^{-1}, aliphatic 2990-2920cm^{-1}, aliphatic 3000cm^{-1}, N-H stretch 3320-3240cm^{-1}, O-H stretch 3460cm^{-1}

The first spectrum was taken after the membrane had reacted with propylamine for 24 hours at room temperature and was wiped off with a Kimwipe (Figure 17).

The second spectrum is the same membrane after it was soaked in deionized water

Figure 16. Acetylamide derivative. Full scale four absorbance units

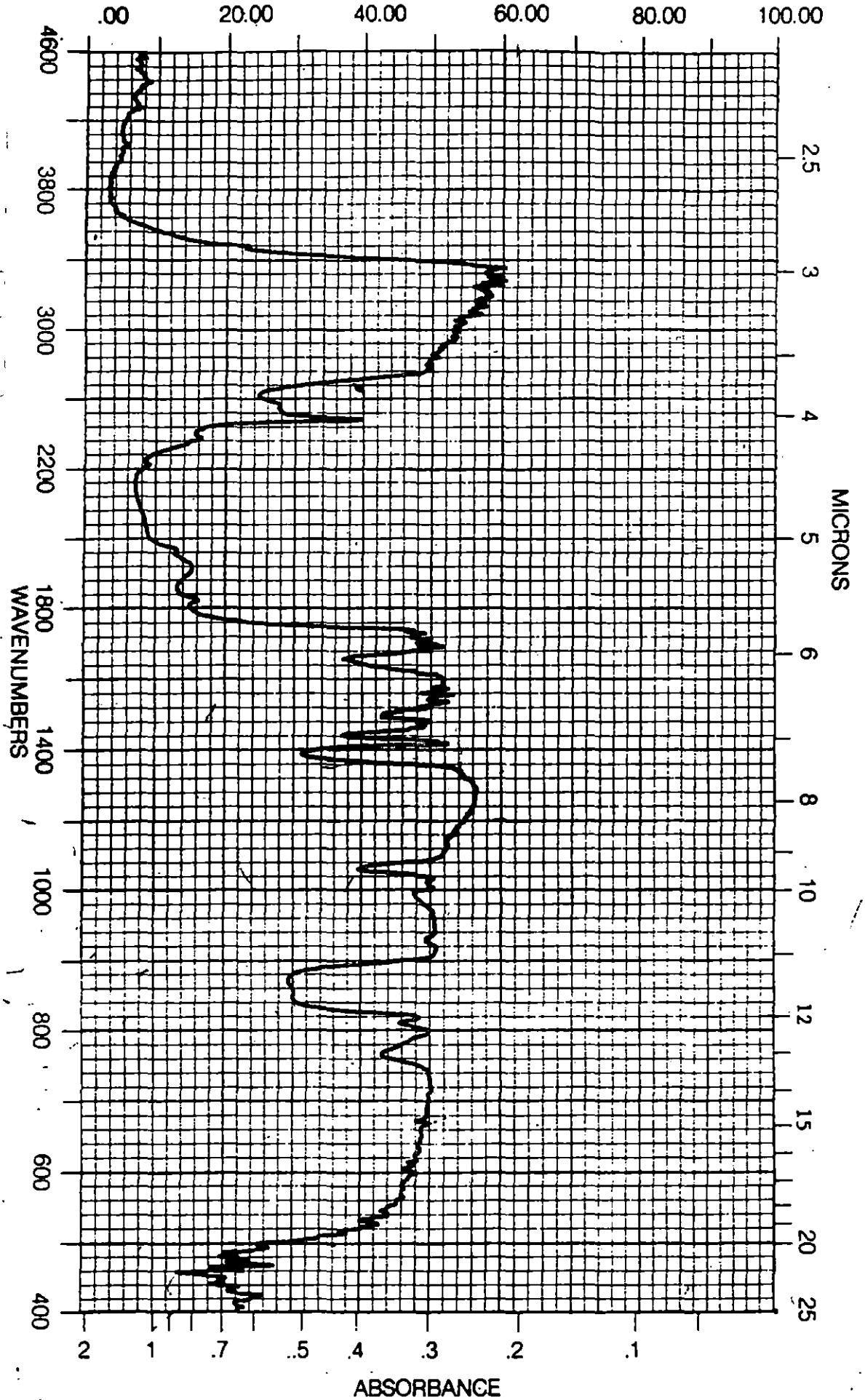
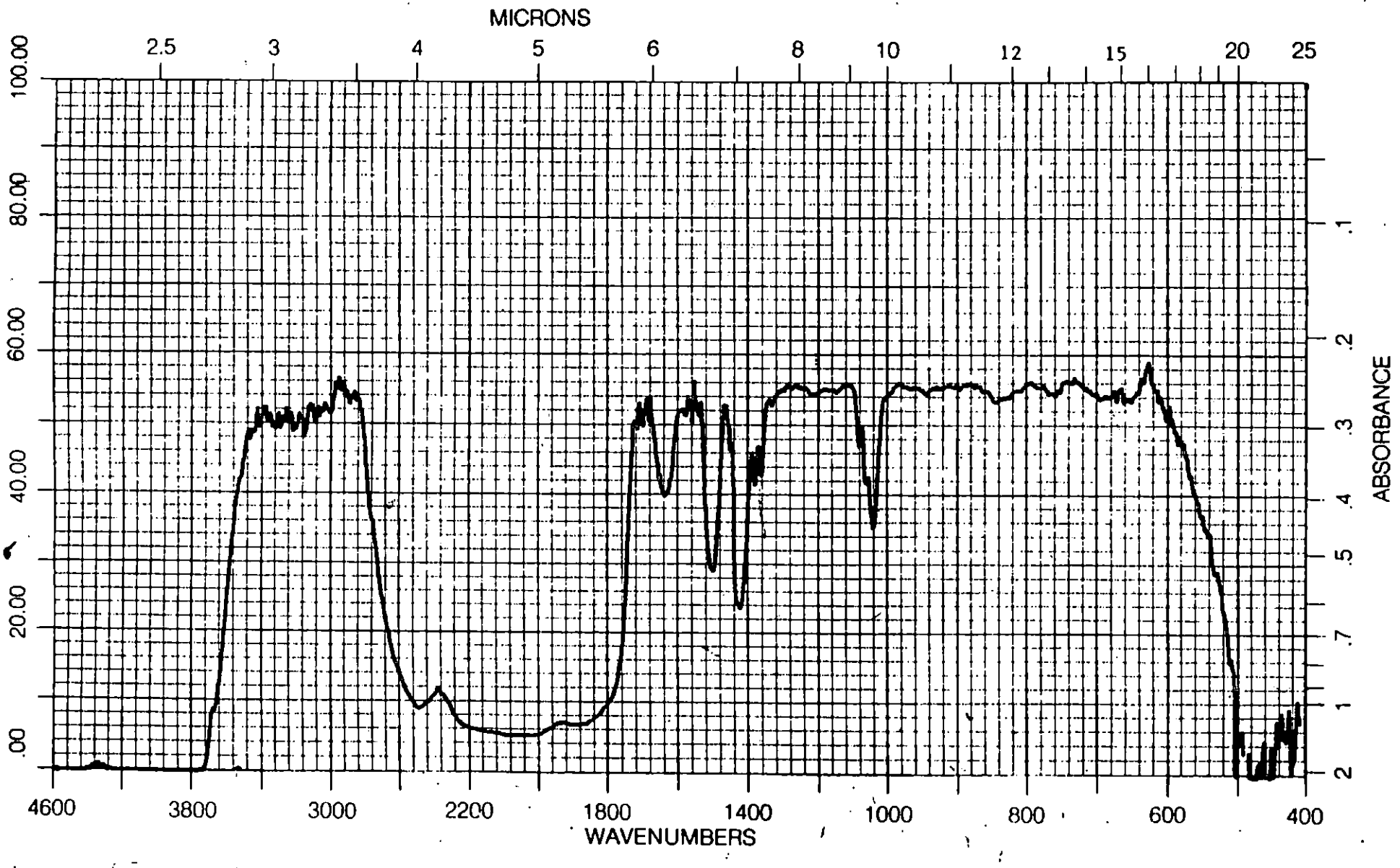


Figure 17: Propylamide derivative? Before drying; full scale four absorbance units 30



and dried (Figure 18). Notice the better separation of peaks after the membrane was flushed with deionized water and dried especially between 3800-2600cm^{-1}. Also there is no peak at 1420cm^{-1}.

	before washing	after washing
Flexibility:	flexible	stiff
Clarity of membrane:	white	clear

Other observations: White crystals floating in amine. The membrane curled at the edges.

Reaction with Ethylenediamine

Useful characteristic infrared peaks: C-H 1440cm^{-1}, amide ? 1560-1520cm^{-1},

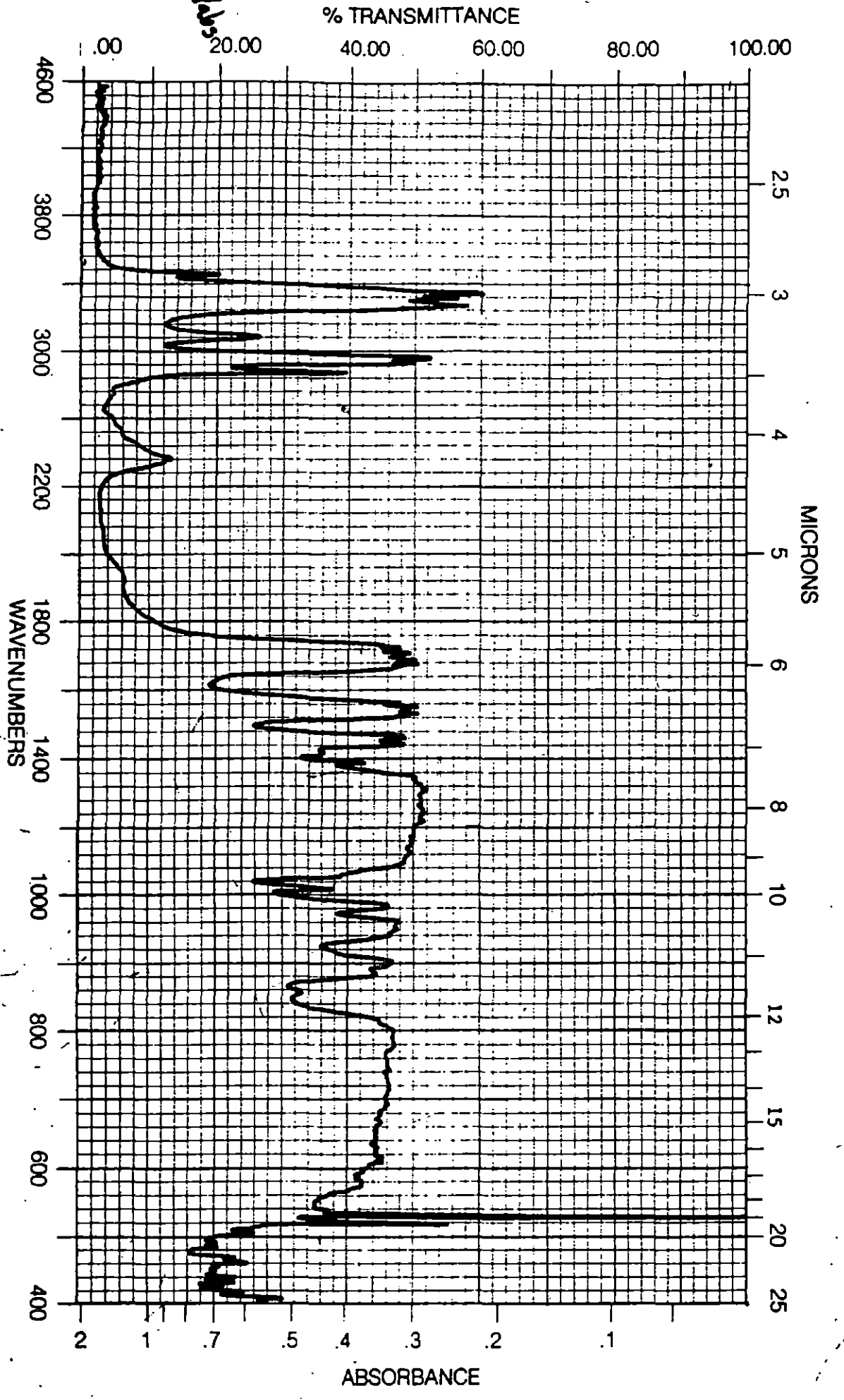
C=O 1720-1680cm^{-1}, C-H, N-H? 3320-2840cm^{-1}

The first spectrum is the membrane after it was reacted in ethylene diamine for 24 hours and wiped off with a Kimwipe (Figure 19).

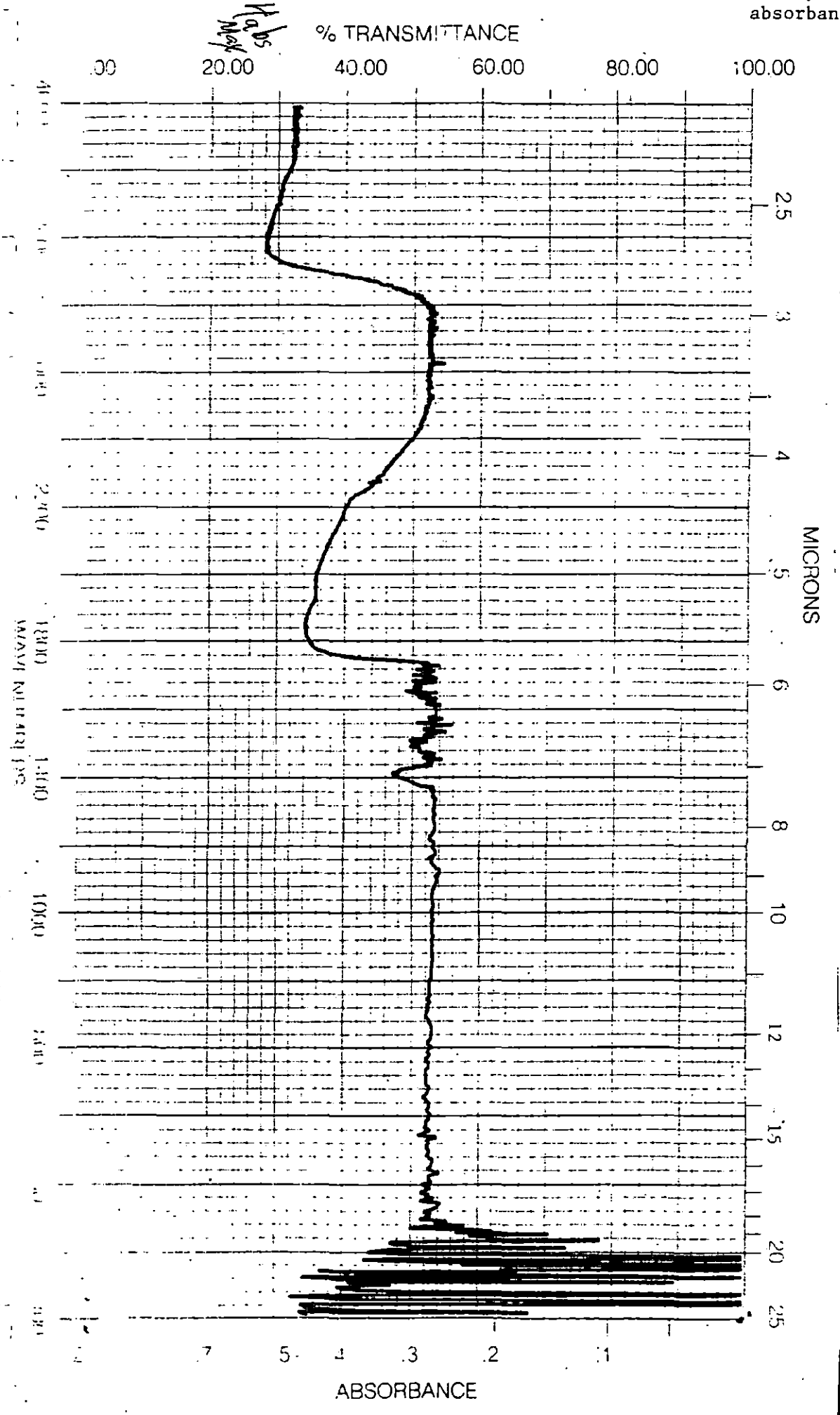
The second spectrum is the same membranes after it was soaked in deionized water for 24 hours and dried (Figure 20). Notice the dramatic improvement in the second spectrum.

This membrane does not fit into any of the other categories of amine reactions. The membrane was soaked in ethylene diamine for 24 hours at room temperature, just like the other amine reactions. However, when I removed the membrane appeared fibrous like paper. The membrane was white, could be easily broken in two parts or even ripped. The infrared spectrum shows no peculiar features. The only explanation I can offer is that the ethylenediamine reacted till it swelled the channels to the point, that it pulled apart the layers of the membrane.

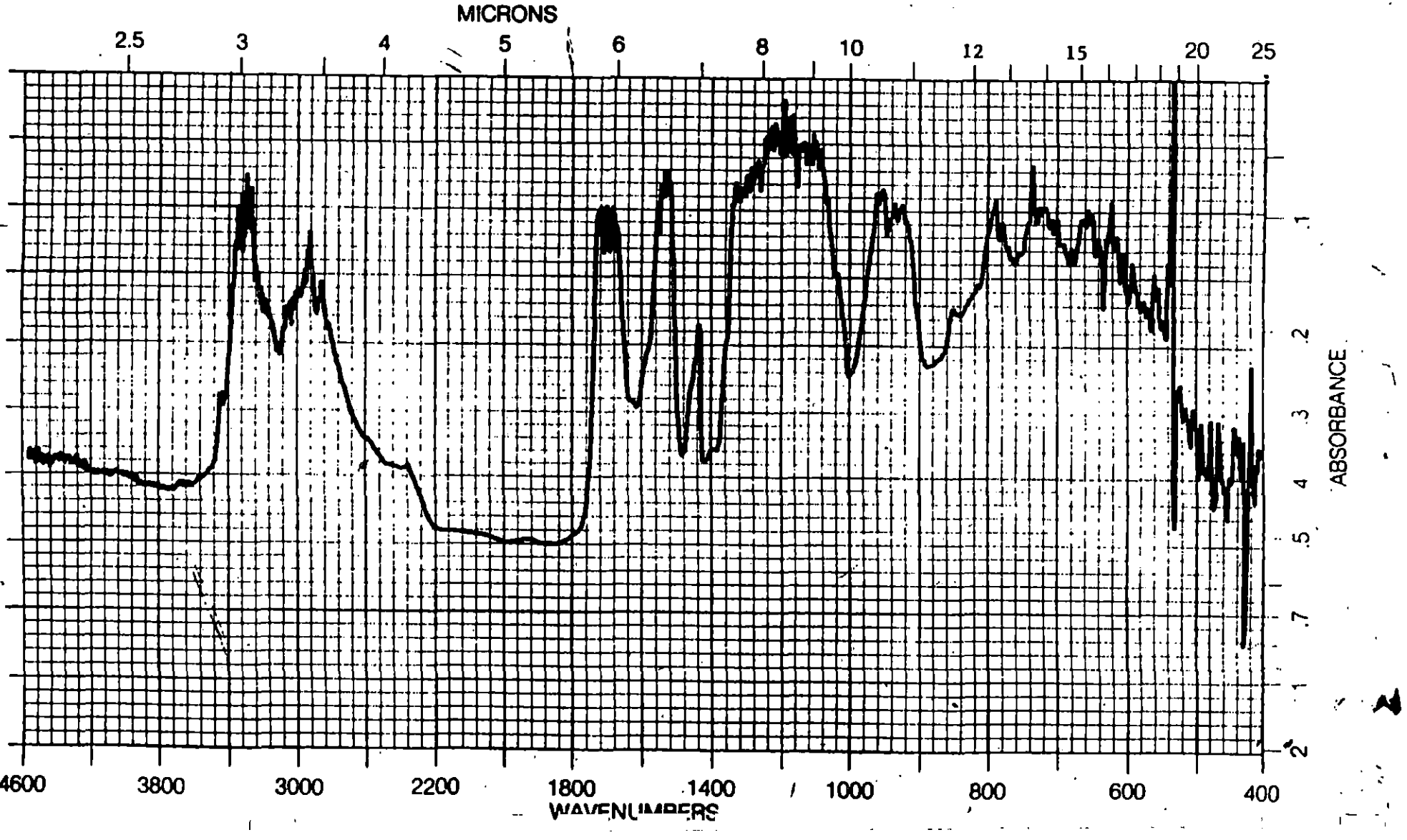
Figure 18: ? Propylamide derivative? After drying; full scale four absorbance units



absorbance units



absorbance units



Conclusion

The sodium hydroxide and hydrochloric acid reactions were well known, but the observations are not well characterized in the literature. We have established these reactions generated water soluble salts in the membranes. The opacity made in these membranes could not be duplicated by soaking a membrane in a saturated salt solution although some opacity could be reproduced. This suggests that once the salt is in the membrane it is difficult to remove it and once it has been removed it is difficult to penetrate the membrane.

I am sure that reaction with $SOCl_2$ went to completion because of the complete disappearance of the broad O-H peak that was in the COOH spectrum. The membranes, for some reason, become very flexible after the reflux with $SOCl_2$. I have not been able to produce a good model of what makes a membrane stiff or flexible.

I tried several different amines in an attempt to get an amide. The ammonia and methyl amine reactions did not seem to go very well. The main problem with these reactions is that they either have to be reacted in the gas phase or in an organic solvent. The crystals of the salts formed from the amines may block the channels since the organic solvent cannot flush them out of the channels.

The reaction with the propyl amine seemed to go very well. The infrared bands in the 3500-3000cm^{-1} region are sharp suggesting all the bands are due to C-H and N-H bonds and not due to O-H absorptions. I would have expected O-H absorptions after I soaked the amide membrane in deionized water if the reaction with the amine had not gone to completion because of the reaction:

$$RfCOCl + H_2O \text{ ----------> } RfCOOH + HCl$$

The reaction with diethylamine is puzzling. Their is only a small sharp absorption in the region I claim is the amide 1600-1540cm^{-1}, yet there was no change in spectra taken before and after the membranes were soaked in deionized water. This suggests that the membrane has completely reacted. The broad absorption between 3080-2600cm^{-1} suggests there are some O-H bonds in the membrane. Perhaps there was some water remaining in the diethylamine after drying, or the broad band absorbed so strongly that even if the membrane reacted with water, I could not detect the difference. I have no explanation as to why this membrane remained flexible while the others went stiff after soaking in deionized water.

The Mohr titration enabled me to calculate the moles of sites per gram of membrane. This information could be useful if used in conjunction with an elemental analysis of the amide membranes, because it would allow me to calculate the extent the reaction went to completion.

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