AD-A129 301 INVESTIGATION OF LITHIUM THIONYL CHLORIDE BATTERY SAFETY HAZARDS(U) GTE COMMUNICATIONS PRODUCTS CORP WALTHAM MA POWER SYSTEMS OPERATION R C MCDONALD 1/1

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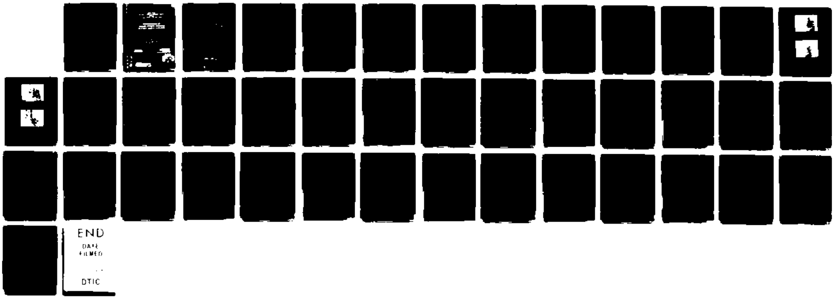

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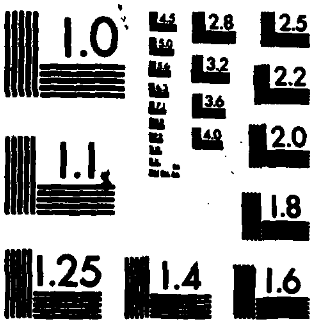

MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

CDRL A002
Quarterly Technical Progress Report
Period
1 April 1982 — 30 June 1982

INVESTIGATION OF LITHIUM THIONYL CHLORIDE BATTERY SAFETY HAZARDS

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Abstract

→ Storage of discharged electrolyte in AgCl cells for infrared analysis leads to artifactual absorbances. However, there are real changes in discharge and overdischarge intermediates as shown by changes in infrared spectra of electrolyte stored in glass. Debye-Scherrer examination of cathodes overdischarged in cathode limited cells indicates the presence of both LiCl and Li_2O_2 as well as at least one other solid. ←

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I. SPECTROSCOPIC STUDIES

A. Results

The glass cell described in QR-I for activation, discharge and analysis in the glovebox was successfully used to sample electrolyte at 85 percent discharge, 50 percent overdischarge and 100 percent overdischarge for FTIR spectra. The cell was anode limited. The spectra are presented in the Appendix: FTIR-1, FTIR-4 and FTIR-7. The final design allows for discharge of either anode or cathode limited cells with an electrolyte quantity of 6 cc/Amp-hour as compared with 2.0-2.6 cc/Amp-hour for commercial $Li/SOCl_2$ cells. No stainless steel is exposed to the electrolyte, only glass, Tefzel and nickel. The principal experimental difference between this cell and the D cells previously discharged to various states is that the discharged electrolyte can be removed immediately at any state of discharge. Disconnecting and opening D cells may consume an hour during which intermediates are in contact with lithium on discharge and on overdischarge in cathode limited cells.

Three spectroscopic differences were observed between the two types of experiments. First, a light pink color could clearly be observed in the discharging electrolyte in the glass cell. This contrasts with a deep brownish orange, or occasionally brownish green, color of discharged electrolyte from discharged and overdischarged D cells.

This pink species persisted throughout overdischarge and after sampling.

The second difference can be seen in the infrared region 2400-2475 cm^{-1} where the three peaks which developed on discharge and overdischarge in the D cell spectra appear as one assymetric peak in the glass cell spectra.

The third difference occurs at 1336 cm^{-1} in the glass cell spectra of overdischarged electrolyte. The comparable spectrum for 90 percent overdischarged electrolyte shows a new peak at 1397 cm^{-1} in addition to the 1336 cm^{-1}.

Small amounts of the three sequential samples pulled from the glass cell were saved for 7-9 days in sealed glass tubes within the glovebox. FTIR spectra were then recorded of the sealed samples as well as the first set still in their AgCl 0.1 mm infrared cells. Spectra FTIR-2, 3, 5, 6, 8 show the effects of this one week storage at each state of discharge.

The AgCl cell stored samples apparently admitted traces of moisture while briefly out of the glovebox as shown by hydrolysis products absorbing at 3360-3370 cm^{-1} and 2755 cm^{-1}. In addition, peaks at 691 cm^{-1} and 767-783 cm^{-1} appear to be artifacts of contact with AgCl. The glass stored electrolyte provides thus a more reliable study of intermediate decomposition.

Lastly, FTIR spectra were recorded of six-week stored electrolyte samples from the anode D cells discharged to 100 percent and overdischarged to 90 percent and the cathode limited cell overdischarged to 50 percent. These spectra are given in the Appendix, FTIR-9, 10, 11. Only one trend is apparent from these and the glass cell storage tests; the infrared absorption at 974-981 cm^{-1} generated by discharge is shifted to 959-966 cm^{-1} by overdischarge or storage in glass for one week.

B. Discussion

Several artifactual infrared peaks have been described. Detailed comparison of spectra from opened D cells and the glass cell allow us to focus our attention on those peaks which reoccur consistently under similar conditions.

The persistent pink color obtained early in discharge of the glass cell was not observed in D cells where the true color is typically masked by a finely divided suspension of LiCl and sulfur. The excess electrolyte in the sampling area at the extreme upper part of the glass cell evidently contains no suspended solid. The changes in spectra of both discharged and overdischarged electrolyte in storage betray other long-lived intermediates.

During the fourth quarter, we hope to describe the simplest mechanistic picture for overdischarge which accounts for the available data. In addition, attempts will be made to assess the effect of high rate discharge and low temperature on the electrolyte spectra.

The last observation to be made at this point is the marked similarity between the spectrum of electrolyte from the glass cell after 100 percent overdischarge and one week storage with that of Li_2SO_4 saturated electrolyte (QR-2). This strongly suggests the formation of an oxidized sulfur species formed on the anode during overdischarge of anode limited cells which is converted with time to sulfate or a sulfate related complex.

II. MORPHOLOGICAL STUDIES

II.A. Results

A.1. Ostwald Ripening of Lithium Dendrites

It has been found during the present project that Li dendrites grow on the surface of the cathode when carbon limited Li/$SOCl_2$ cells are overdischarged.

In principle, over a period of days or even weeks, small Li dendrites could undergo the process of Ostwald ripening during which small dendrites could dissolve and larger dendrites could grow. In overdischarged batteries, this process could lead to sudden unpredictable short circuits during storage resulting in thermal runaway and explosions.

To study Ostwald ripening of Li dendrites, a Li/$SOCl_2$ with a 3.0 x 3.0 x 0.317 cm carbon cathode positioned between two 3.0 x 3.5 cm x .152 cm Li anodes was constructed. The cathode and two Li anodes were parallel and separated by 13 mm. The cathode contained 0.857g of Teflon bonded carbon mix with a 5 Ni 10-2/0 Exmet grid in the center of the sheet without any grid edges exposed to the electrolyte which could stimulate dendrite growth. The cell was vacuum filled with 1.8M $LiAlCl_4/SOCl_2$ electrolyte and discharged at 2 mA/cm^2 at 25^0 to a capacity of 372 mAhr/cm^2 at which time reversal occurred. The cell was then overdischarged 14.6 percent for an additional 55.8 mAhr/cm^2. During overdischarge the cathode potential slowly rose from -0.180 to -0.126V with respect to the Li anode.

When the current was terminated at the end of overdischarge, Li dendrites extended at one point 7 mm from the surface of the carbon cathode towards the Li anode. Microphotographs of the dendrites were then taken at 3.8 and 15.2X magnification through a flat optical glass window in the side of the cell. Photographs were taken immediately at the end of overdischarge and after various intervals of time. By 42 hours the silvery dendrites had turned grey but by 331 hours they had become white and covered with a thick coating of LiCl. However, the 7 mm long dendrite showed no shape changes to within ± 0.02 mm during 331 hours of open circuit storage.

Figures 1 and 2 show the Li dendrites on the carbon electrode after 21 minutes and 16.2 hours on open circuit. The left portion of Figure 2 showing the small dendrites on the edge of the electrode is very dark because the left side was not illuminated as well as in Figure 1. The large mass of dendrites on the right-hand side of the photographs extends about 7 mm from the electrode surface into the electrolyte.

Figure 3 which shows the Li dendrites after 42 hours on open circuit shows the first significant effects of 25°C storage on the appearance of the dendrites. Although no shape change occurred the dendrites turned from a bright silvery color to dull grey. Because of the loss of reflectivity, the exposure time for the microphotographs had to be increased from two to five seconds for Figure 3. The scattered white specks seen on the dendrites to the right side of the electrode in Figure 3 are small portions of the Li dendrites which have retained their original shiny metallic luster.

Figure 4 shows the Li dendrites after 331 hours of open circuit storage. The Li dendrites had turned from the dull grey color observed after 42 hours of storage to a highly reflective white color which suggests that they were coated with a much thicker layer of LiCl. Microphotographs taken at 20X magnification tend to support this conclusion since the very fine structure of the dendrites observed after 16 hours tends to be obscured. At the present time it is not known whether the Li dendrites have been completely or only partially converted to LiCl after 331 hours of 25°C storage. At the end of over 331 hours of storage after overdischarge, the cell was overdischarged an additional 9.18 percent (i.e., 34.4 $mAhr/cm^2$) at 2 mA/cm^2.

The overdischarged cell was disassembled in the dry room and the cathode was placed in a vacuum desiccator within one minute after removal from the $SOCl_2$ electrolyte. It was then vacuum dried for 48 hours at 25°C. The Li dendrites were then scraped off the cathode inside an argon filled glove box (<60 ppm H_2O) and a small portion of the cathode ground with a mortar into a fine powder to fill a capillary for the Debye-Scherrer X-ray diffraction analysis. The diffractions patterns were obtained using CuK∞ radiation from a Phillips X-ray generator with a Ni filter operated at 40 Kv and 20 mA and a 115 mm diameter Debye-Scherrer camera (Phillips). An eight-hour exposure was taken using high speed reflex 25 double coated film (Ceaverken AB, Sweden). The X-ray diffraction pattern obtained for the carbon sample from the overdischarged cathode is shown in Figure 871-5 and the results compared with the known patterns for LiCl, rhombic sulfur and Li_2O_2 in Table I. Similar comparisons for patterns from the literature for Li, Li_2S, Li_2O, $C_{16}Li$, $C_{40}Li$ and graphite intercalation compounds were also carried out. It was concluded that the overdischarged cathode contains only LiCl, rhombic sulfur, and perhaps some Li_2O_2.

A.2. Overdischarge of a Carbon Limited Cell at 20 mA/cm^2, 25°C

A carbon limited $Li/SOCl_2$ cell with a 3.0 x 3.0 cm cathode 0.32 cm thick was discharged then overdischarged at 20 mA/cm^2 at 25°C. Based on the 1.014 mA hour to 0.00V obtained at 20 mA/cm^2 the cell was 76.2 percent overdischarged. However, when a similar cell was discharged at 2 mA/cm^2 at 25°C a capacity of 3.37 Ah was obtained. Thus calculated on the basis of the nominal capacity at 2 mA/cm^2 the overdischarge was only 22.9 percent. Since it is the number of coulombs of overdischarge which determine the amount of lithium deposited on overdischarge the nominal cathode capacity is the preferred base capacity when calculating the amount of overdischarge.

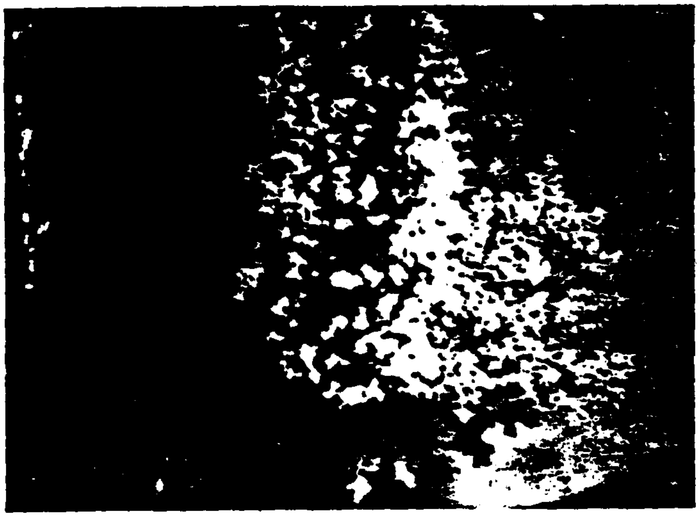


Figure 1. LITHIUM DENDRITES ON OVERDISCHARGED CATHODE (3.8X Magnification); 21 MINUTES ON OPEN CIRCUIT, 2 SEC EXPOSURE.

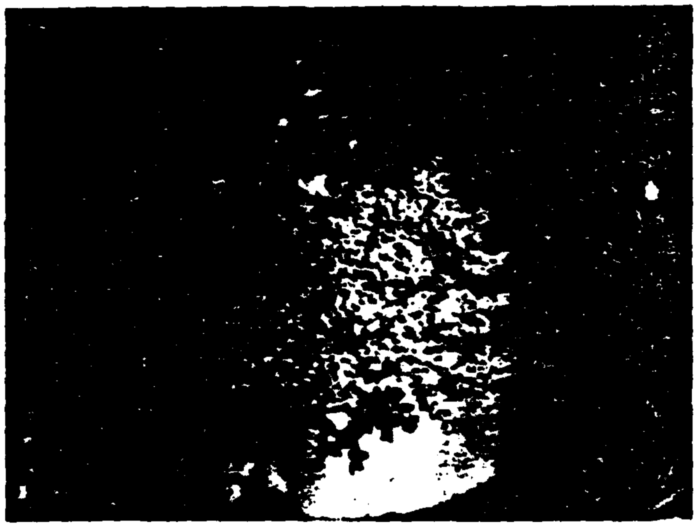


Figure 2. LITHIUM DENDRITES ON OVERDISCHARGED CATHODE (3.8X Magnification); 16.2 HOURS ON OPEN CIRCUIT 1 SEC EXPOSURE.

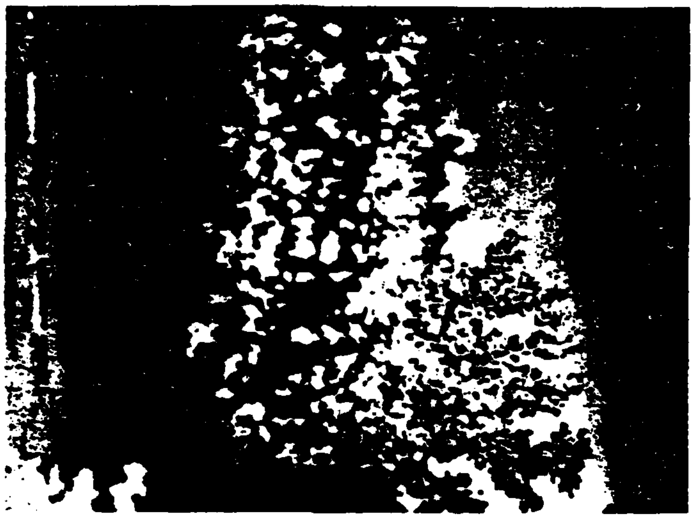


Figure 3. LITHIUM DENDRITES ON OVERDISCHARGED CATHODE (3.8X Magnification); 42 HOURS ON OPEN CIRCUIT, 5 SEC EXPOSURE.

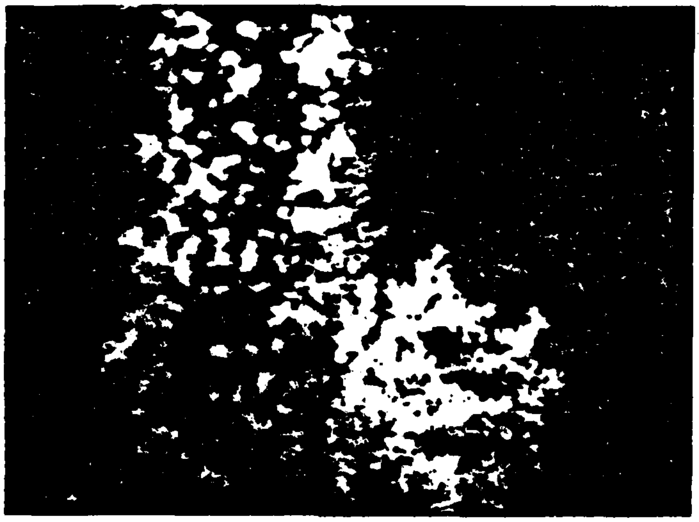


Figure 4. LITHIUM DENDRITES ON OVERDISCHARGED CATHODE (3.8X Magnification); 331 HOURS ON OPEN CIRCUIT, 2 SEC EXPOSURE.

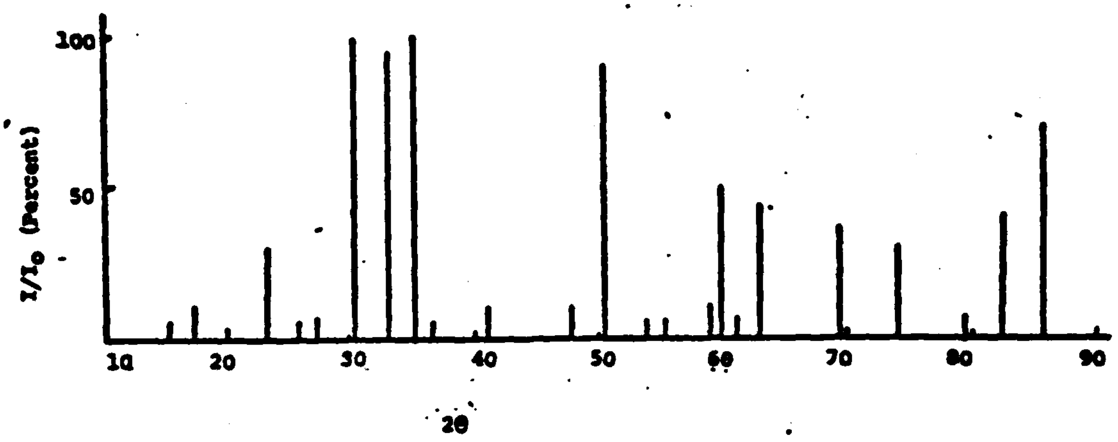


Figure 5. INTENSITIES OF X-RAY DIFFRACTION PATTERN OF CARBON FROM AN OVERDISCHARGED CATHODE.

The carbon cathode was overdischarged 34.4 mAh/cm^2 (9.18%) at 2 mA/cm^2, 25°C.

TABLE I

Debye-Scherrer X-Ray Diffraction Analysis of Carbon from Cathode Overdischarged at 2 mA/cm² at 25°C*

EXPERIMENTAL VALUES			LITERATURE VALUES					
CARBON SAMPLE			LiCl		S RHOMBIC		Li_2O_2	
d (Å)	2θ	I/I_o	d (Å)	I/I_o	d (Å)	I/I_o	d (Å)	I/I_o
5.80	15.26	5			5.46	60		
5.10	17.36	10						
3.80	23.4	30			3.89	100	3.81	60
3.45	25.80	5						
3.25	27.42	5			3.12	80		
2.94	30.38	100	2.967	100				
2.70	33.16	95			2.71	100	2.72	80
2.55	35.16	100	2.570	86			2.561	100+
2.45	36.66	5						
2.20	41.00	10			2.21	40	2.22	80
1.90	47.82	10			2.026	80	1.916	30
1.80	50.66	90	1.817	58			1.875	60
1.70	53.88	5						
1.66	55.30	5					1.572	100
1.56	59.18	10	1.550	29				
1.54	60.00	50						
1.51	61.34	5						
1.475	62.96	45	1.484	16				
1.35	69.58	35			1.352	60	1.335	80
1.275	74.34	30					1.283	40
1.205	79.46	5						
1.17	82.34	50	1.179	10				
1.145	85.56	70	1.149	12				
1.045	94.96	50					1.02	70

*All diffraction results were obtained using CuKα radiation with a Ni filter.

A microphotograph (3.8X magnification) was taken of the Li dendrites at the end of the overdischarge period. The dendrites were similar to those observed at 2 mA/cm^2, 25°C and discussed in detail above.

A.3. Overdischarge of a Carbon Limited Cell at 2.0 mA/cm^2 and -40°C

A carbon limited cell with a 3.0 x 3.0 cm cathode of 3.4 Ahr capacity similar to the cell described in the April report was discharged at -40°C and 2 mA/cm^2. Within 3.43 minutes the cell polarized to 0.00V and to -0.655V after 5.37 minutes when the cell was temporarily disconnected from the constant current supply. Since the cathode and the two lithium electrodes were separated by a 13 mm gap, most of the polarization was caused by concentration polarization and the large IR drop across the gap at -40°C.

The cell was then restarted at 0.5 mA/cm^2 and discharged at an average voltage of approximately 3.00V for three days. Currently the cell has delivered 1.728 Ahr after 192 hours and the potential is 1.352V. Once the cell has been discharged we plan to overdischarge the cell at 2 mA/cm^2 at - 40°C.

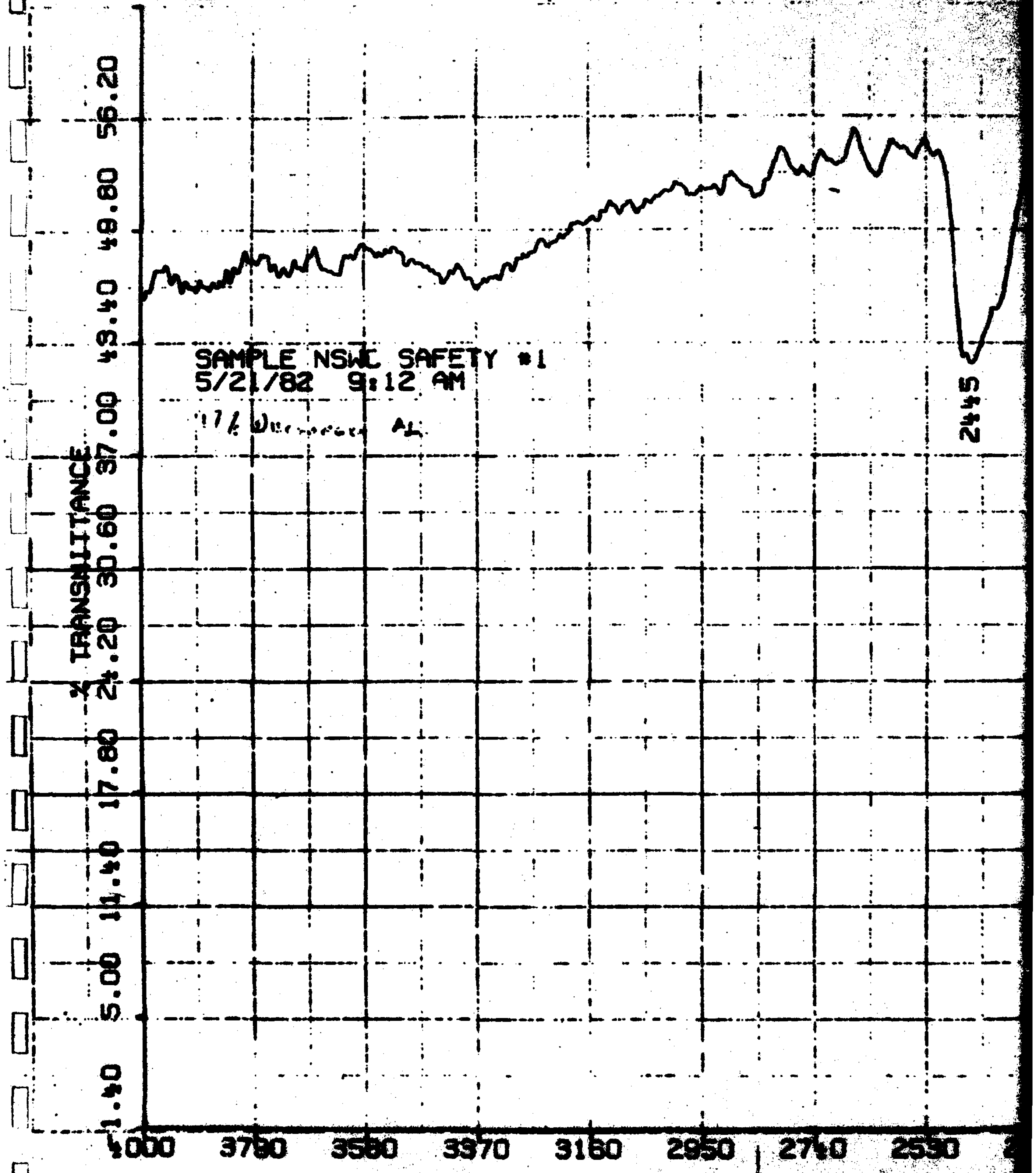
B. Discussion

At discharge rate below about 20 mA/cm^2, dendrite form an overdischarge on the cathode only in cathode limited designs. The dendrite grow during passage of current only. After removal of the power supply, the dendrites corrode in the electrolyte forming more LiCl. This corrosive process prevents any growth or shape changes of metallic lithium dendrite through Ostwald ripening. At room temperature corroded dendrites have insufficient conductivity to initiate an internal short circuit and no exposed lithium to react with $SOCl_2$ or reaction products. Vibration or sudden shock could loosen the dendrite cluster to expose a sufficient quantity of lithium surface area for a rapid reaction with some oxidant in the electrolyte, although this requires further study.

The carbon cathode from the above study was examined with X-ray powder diffraction. All strong and most weak lines could be accounted for by LiCl, rhombic sulfur and Li_2O_2. No evidence was found for Li_2O, Li_2S, $C_{16}Li$, $C_{40}li$, $LiAlCl_4$, or $LiAlO_2$ for which Debye-Scherrer data is available.

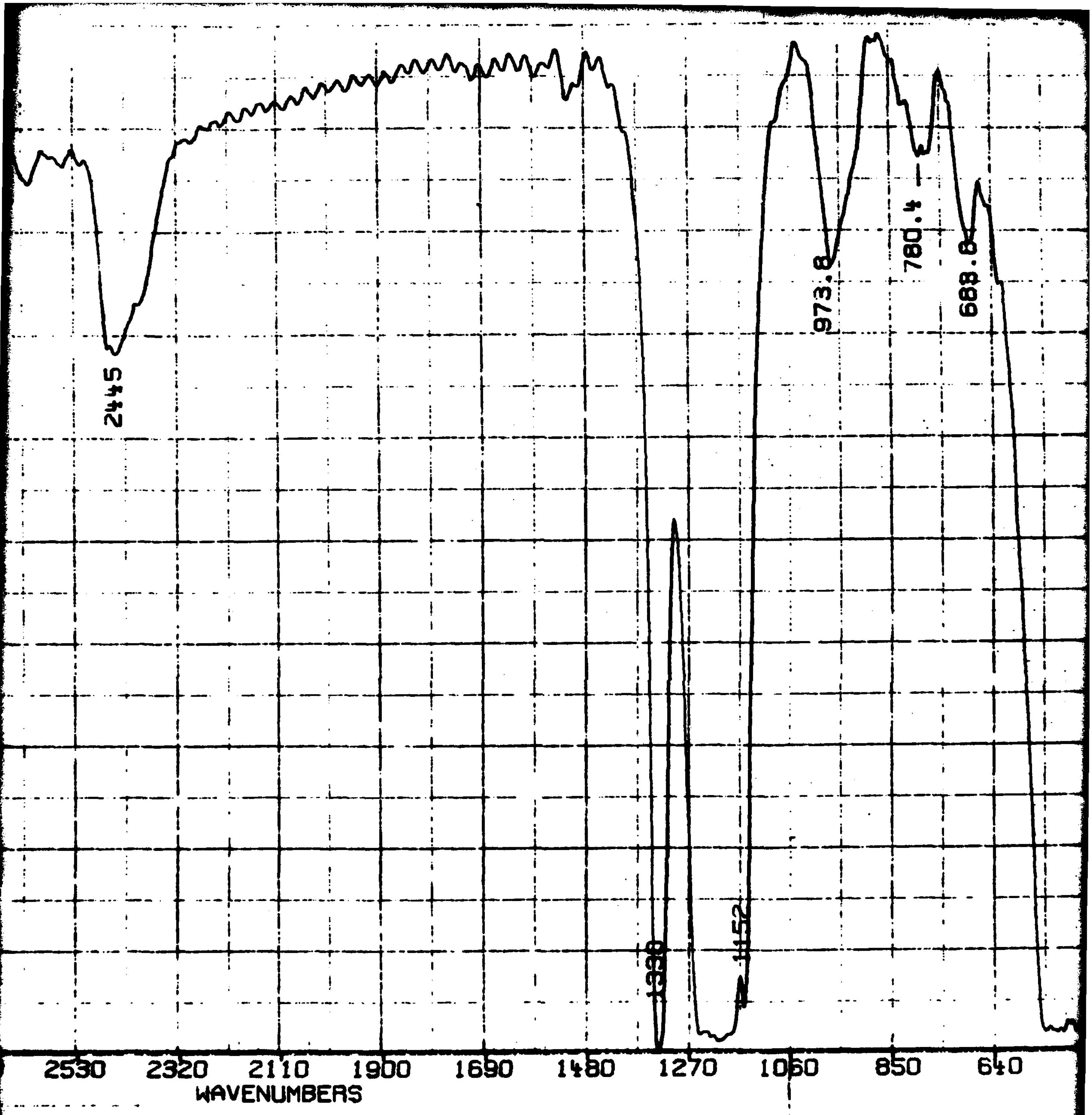
APPENDIX

FOURIER TRANSFORM INFRARED SPECTRA

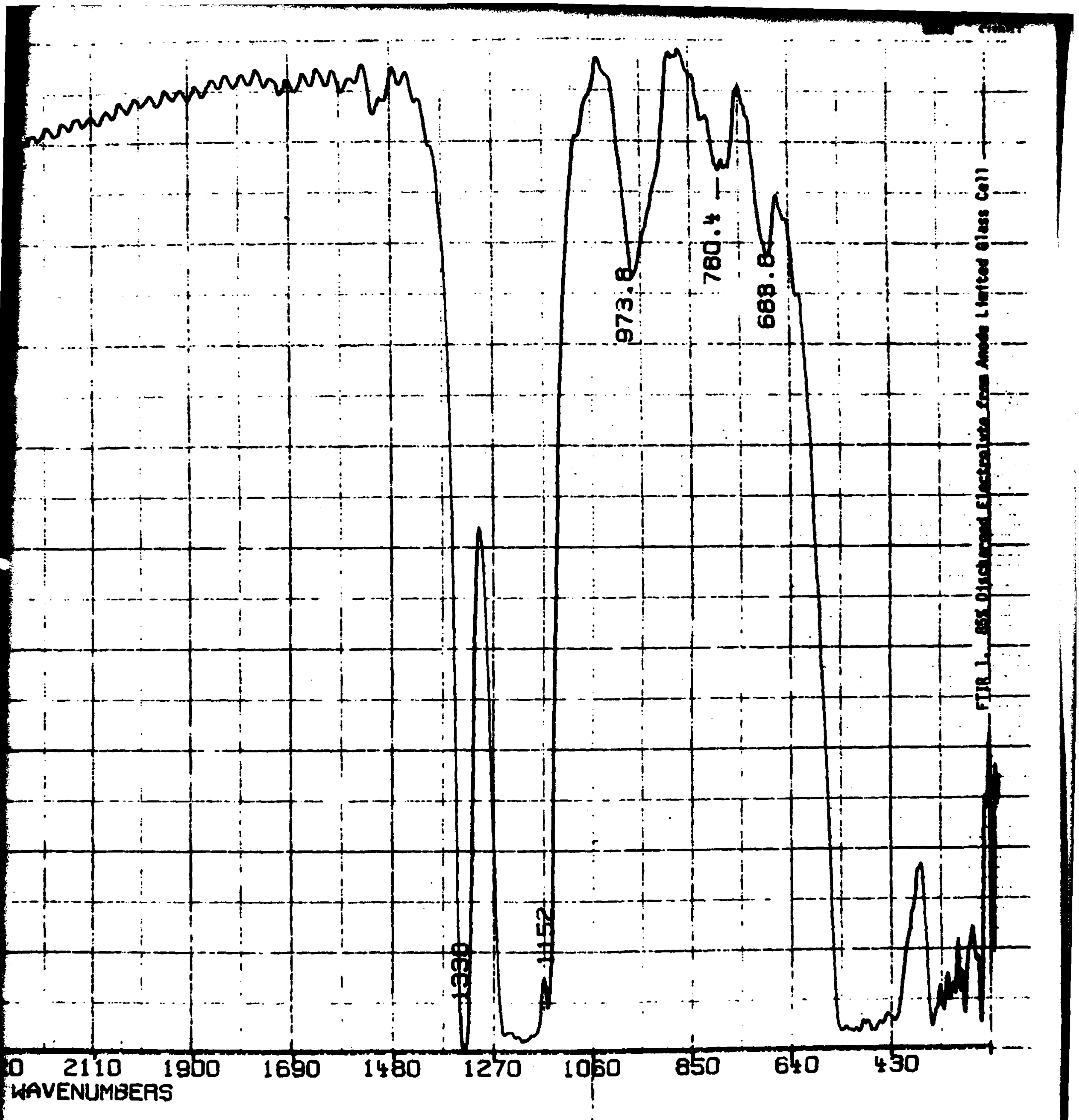


SAMPLE NSWC SAFETY #1
5/21/82 9:12 AM

1% [illegible] Al

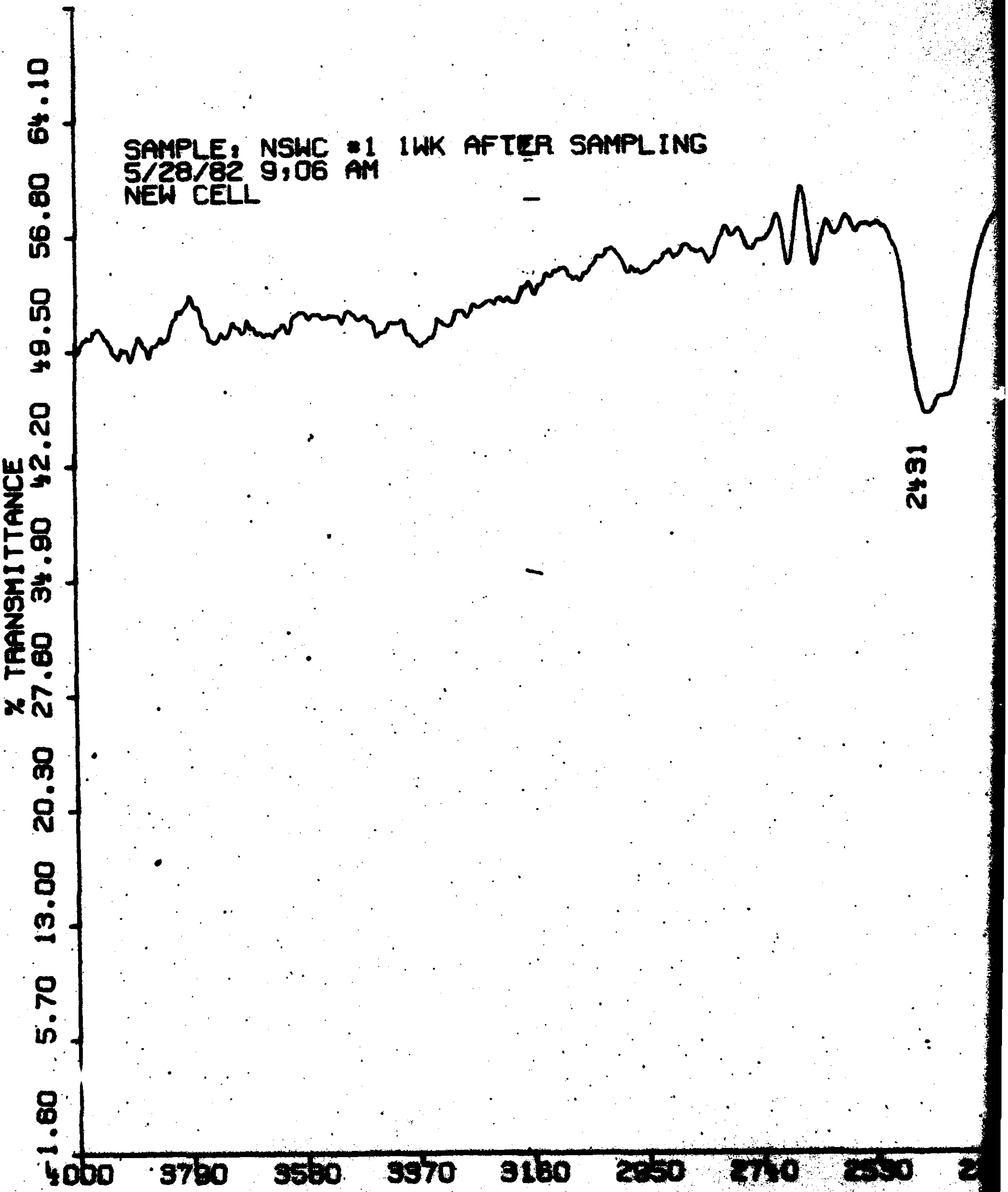

2445
973.8
780.4
688.8
1330
1152
2530
2320
2110
1900
1690
1480
1270
1060
850
640
WAVENUMBERS

2



FTIR 1. 86% Discharged Electrolyte from Anode Limited Glass Cell

2



SAMPLE: NSWC #1 1WK AFTER SAMPLING
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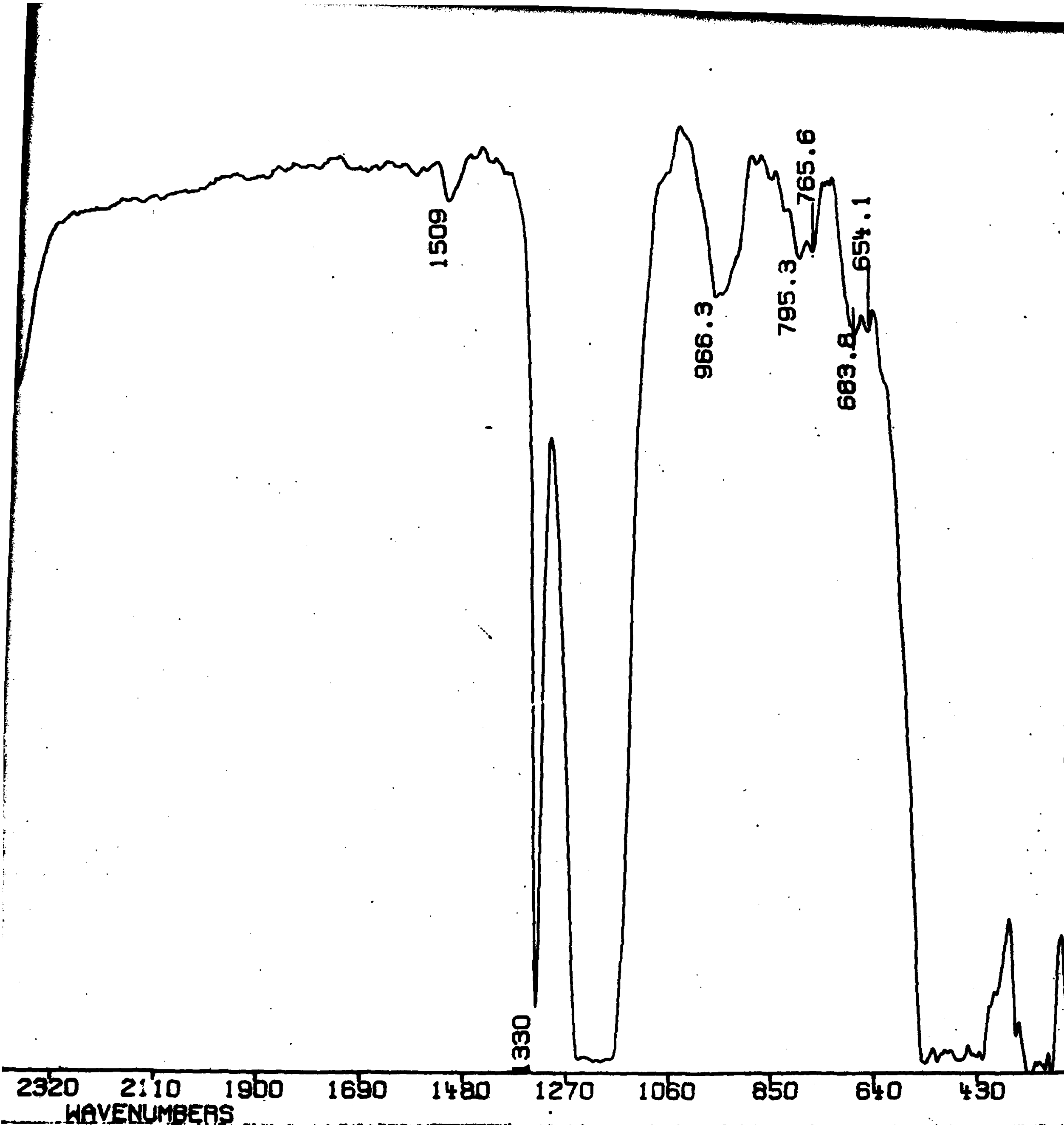
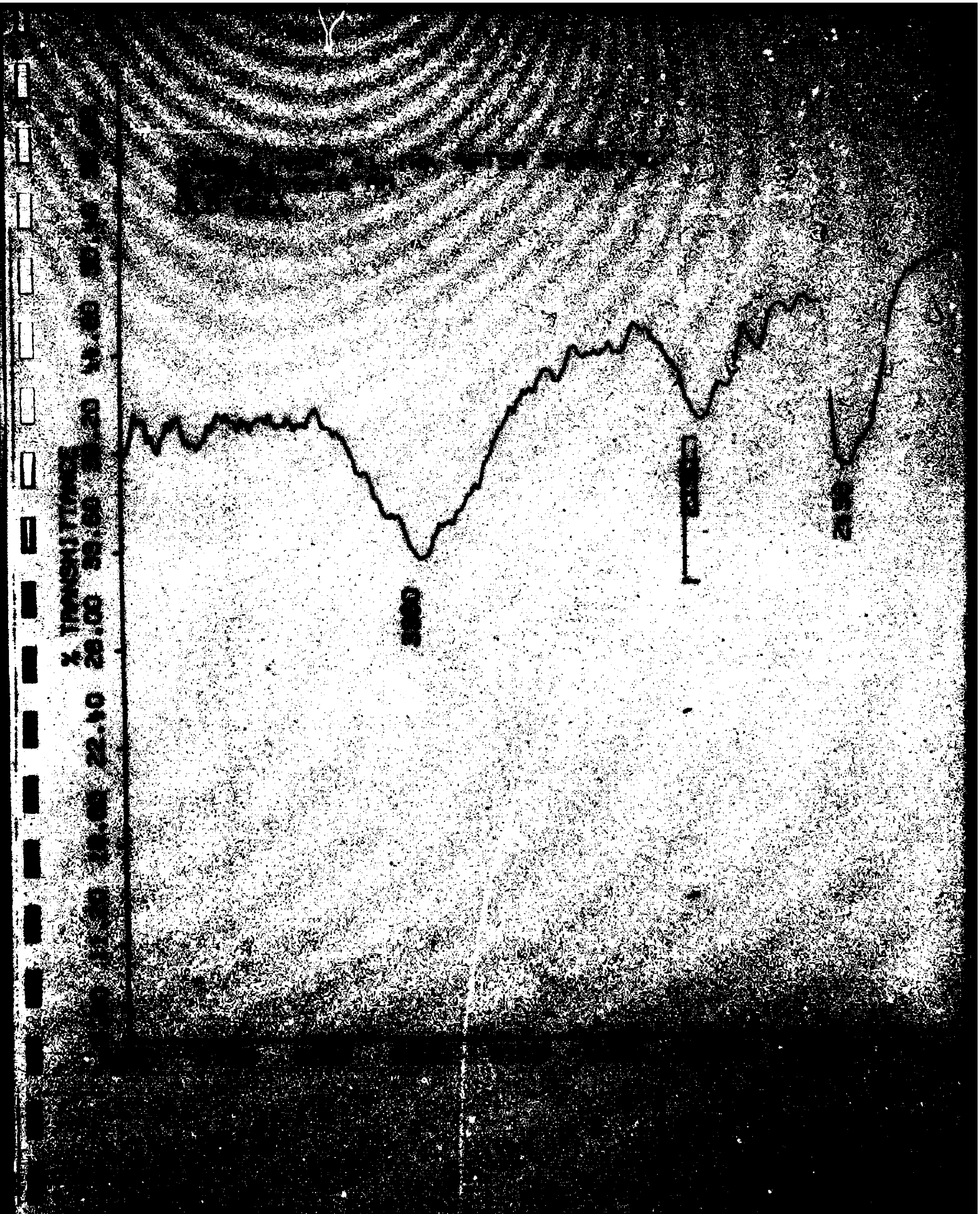
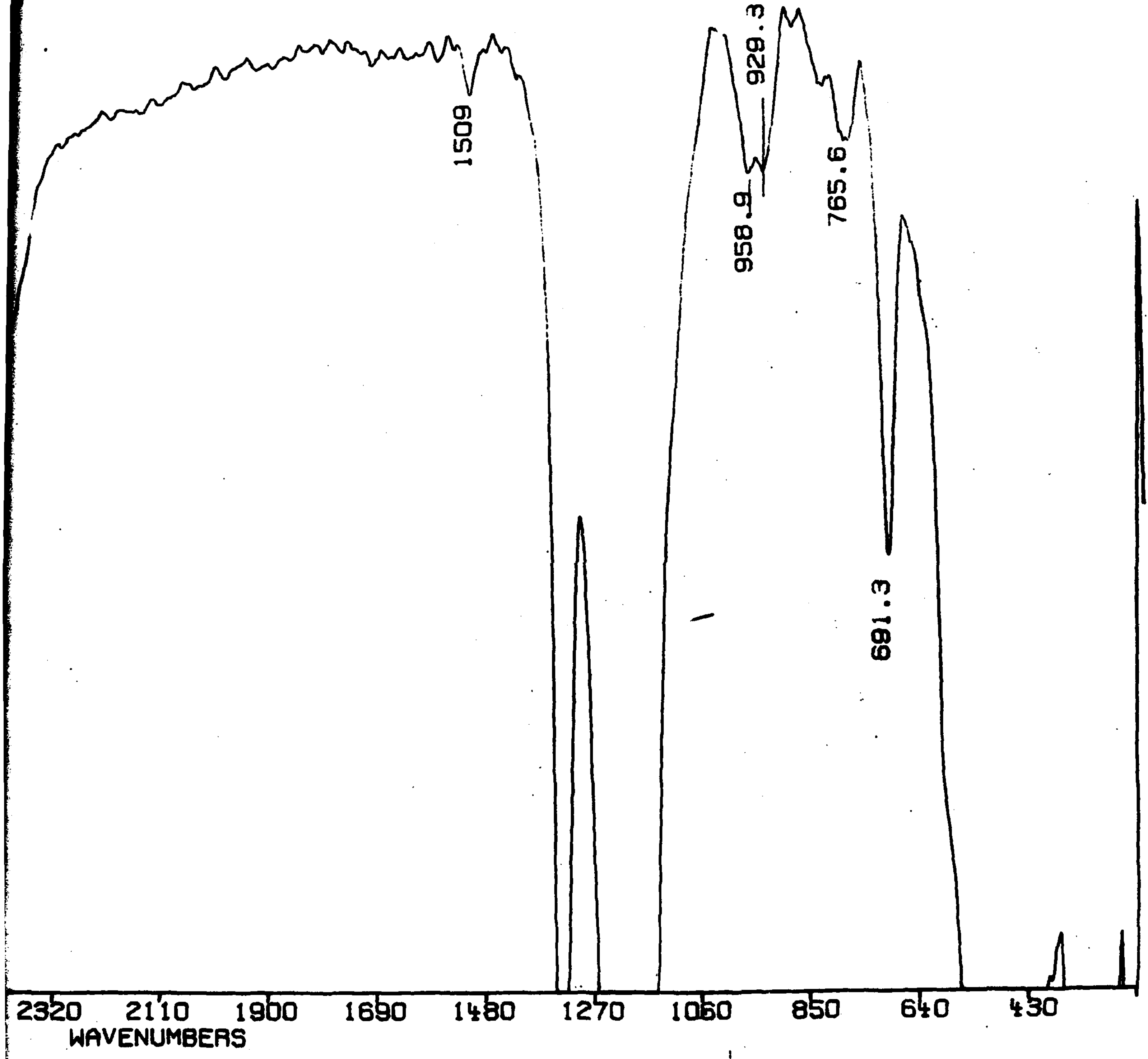
NEW CELL



FTIR 2. Same as No. 1. Stored for 1 Week in Glass

2

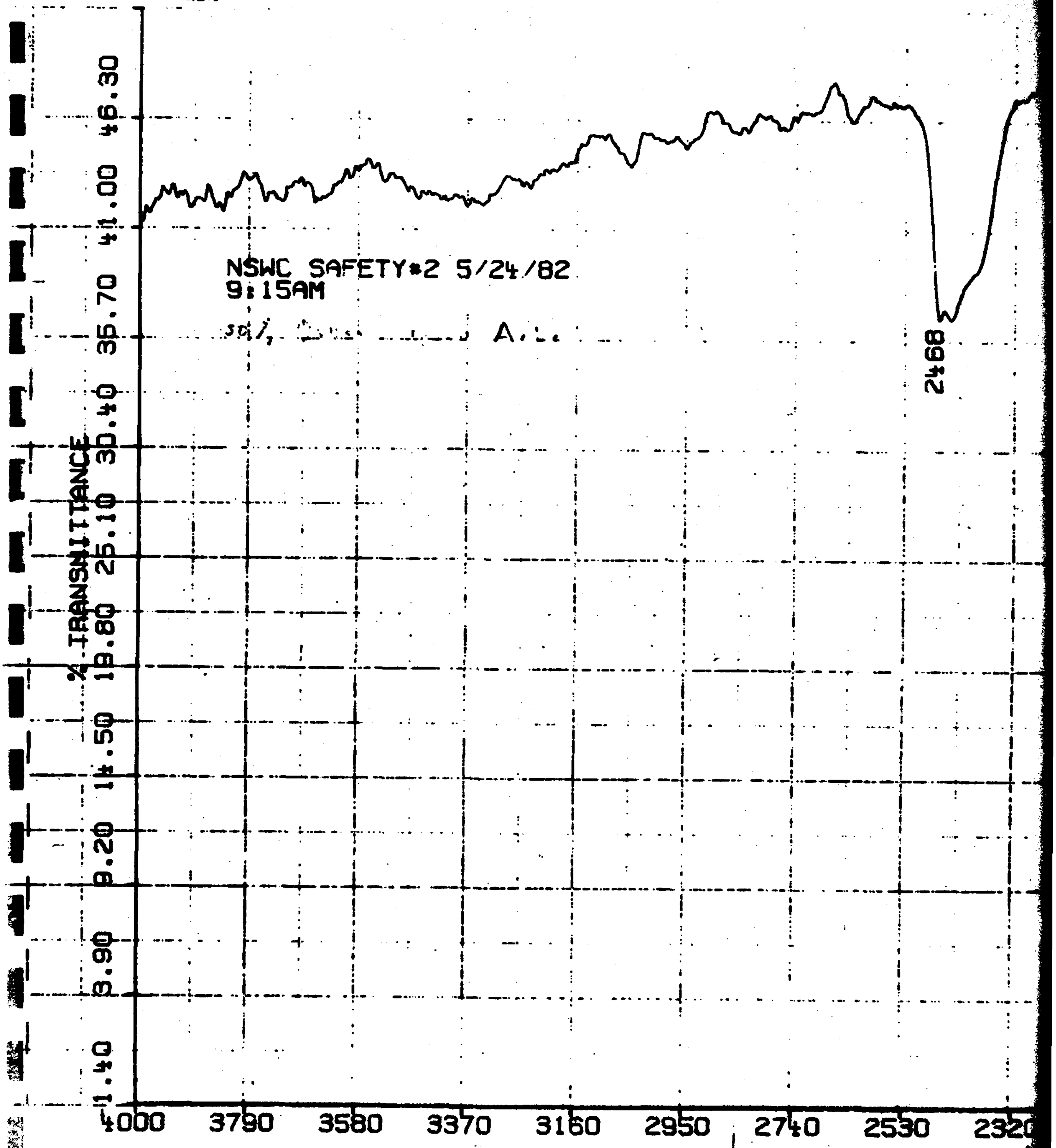

% TRANSMITTANCE



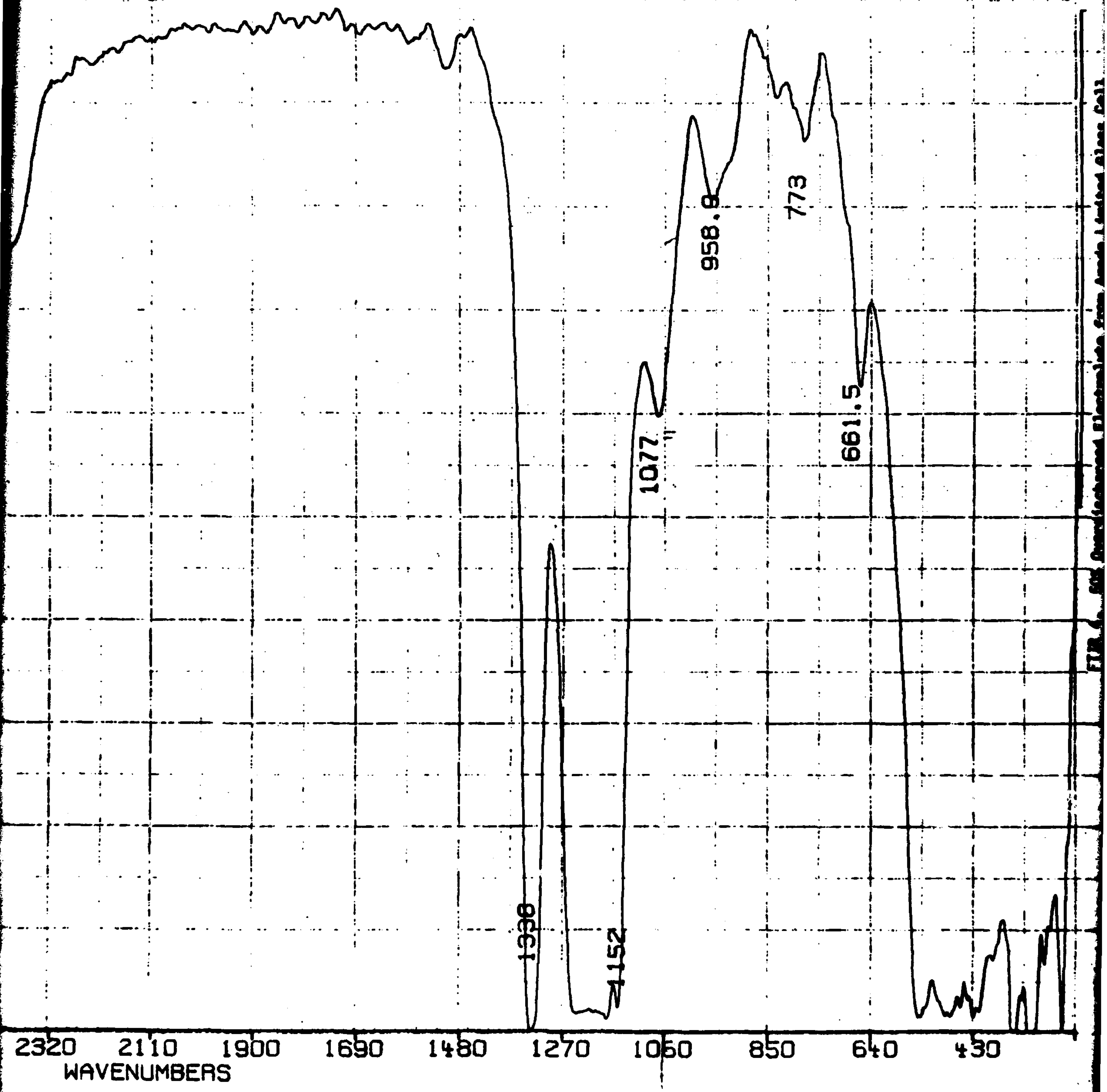
[illegible] 3. Same as No. 1, Stored for 1 Week in AgCl Cell

1

2



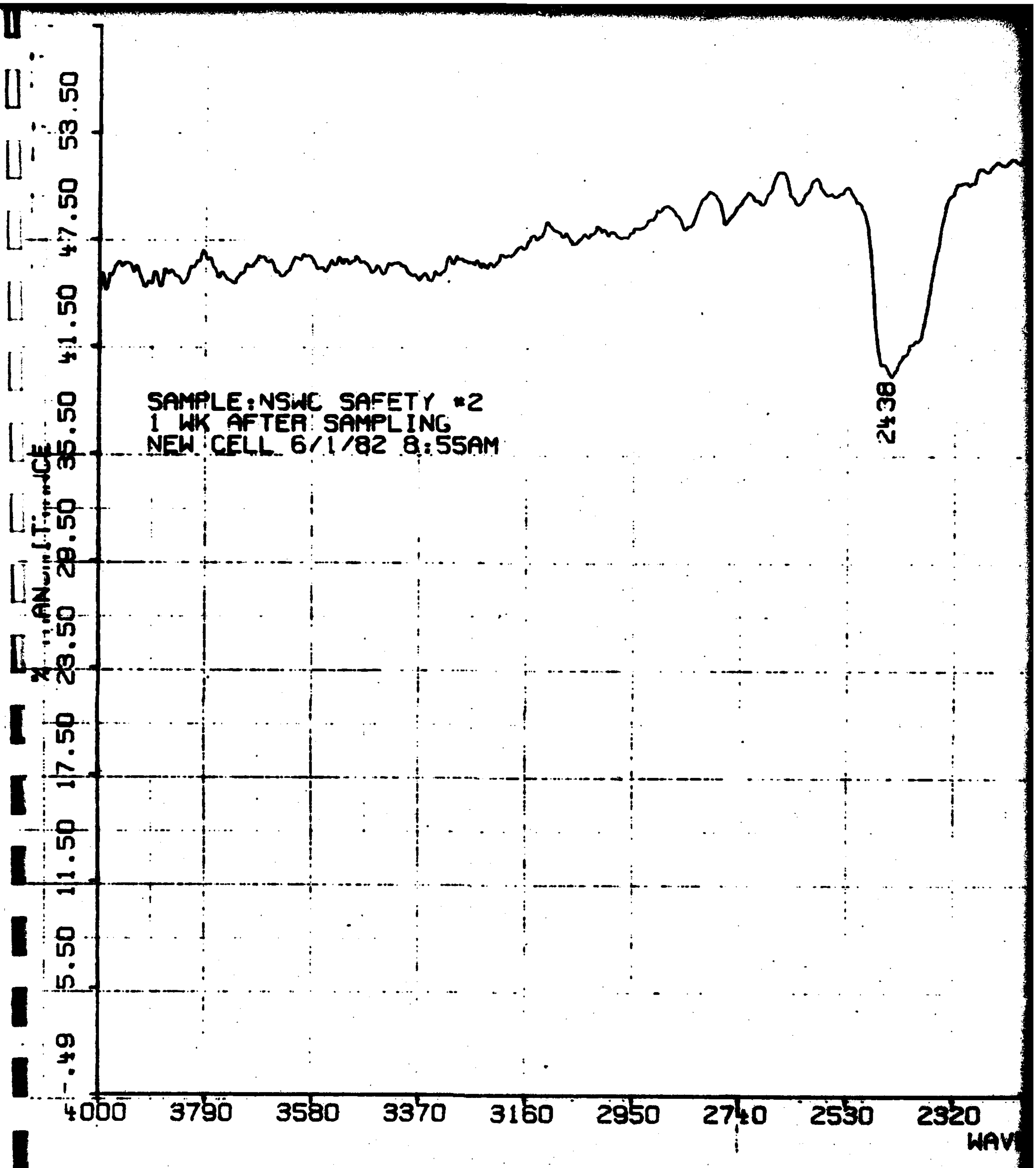
NSWC SAFETY*2 5/24/82
9:15AM



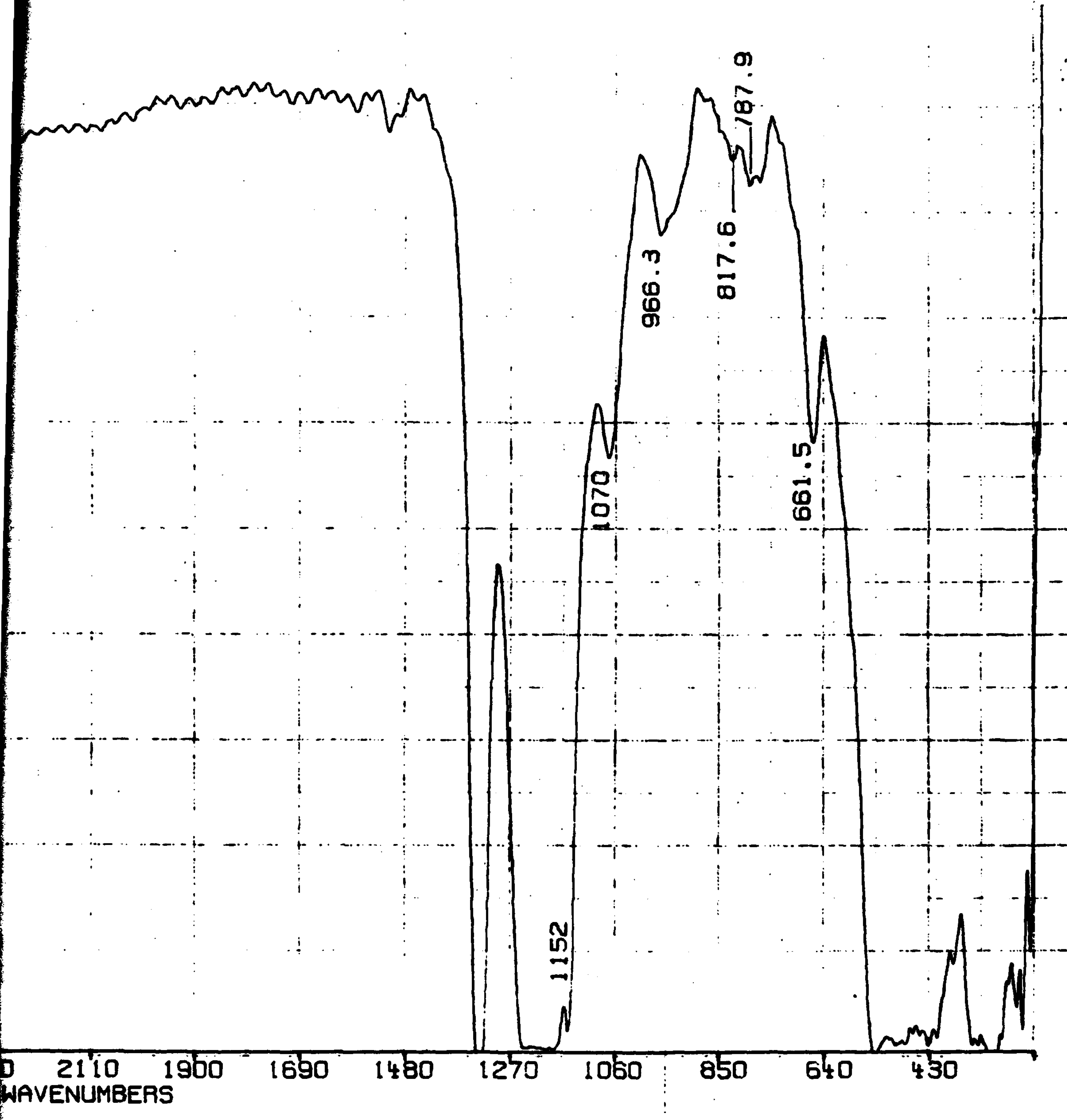
FTIR 6. 50% Overdischarged Electrolyte from Anode Limited Glass Cell

2

1

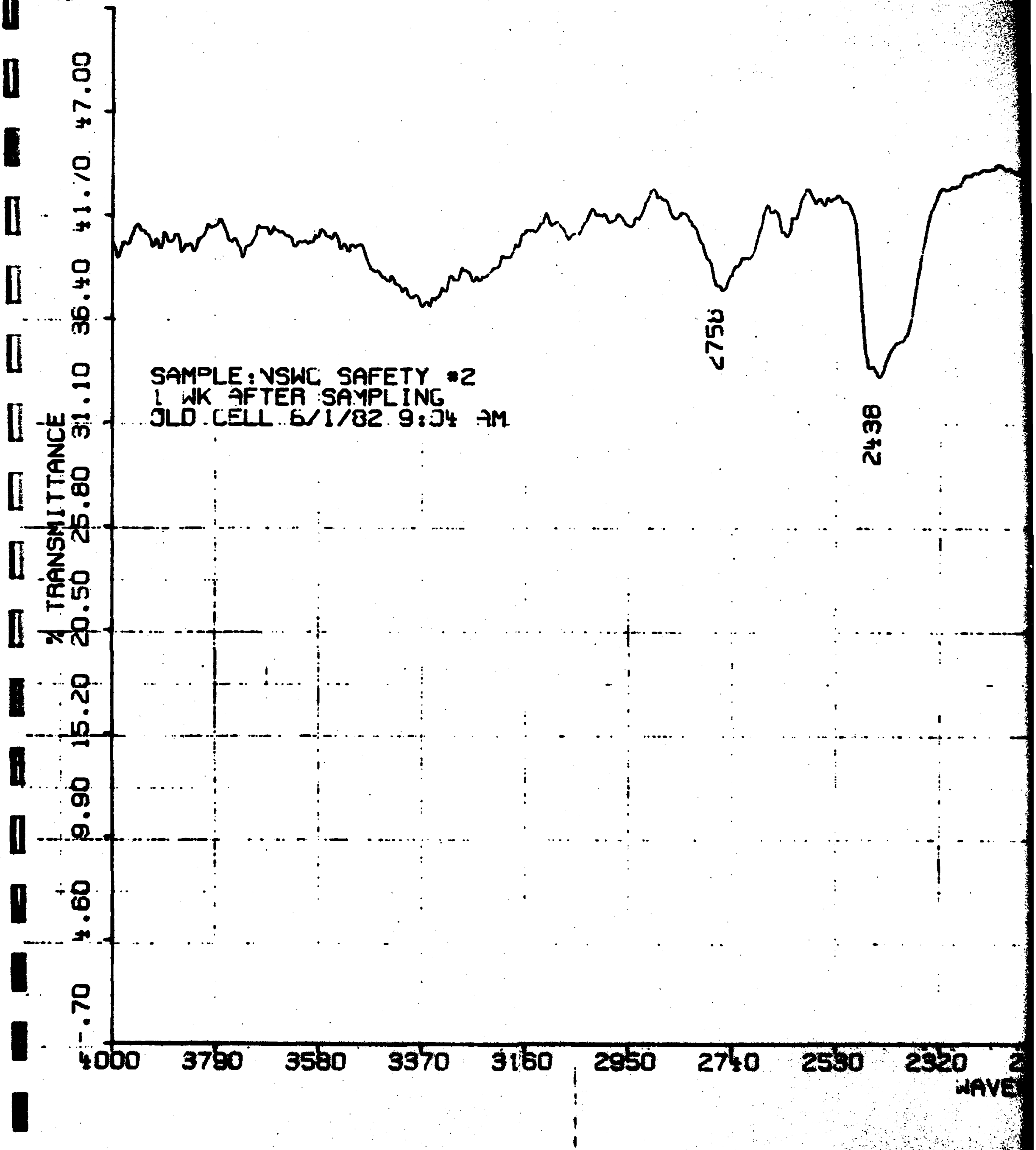


SAMPLE:NSWC SAFETY #2
1 WK AFTER SAMPLING
NEW CELL 6/1/82 8:55AM
2438
% AN..IT..NCE
53.50
47.50
41.50
35.50
29.50
23.50
17.50
11.50
5.50
-.49
4000
3790
3580
3370
3160
2950
2740
2530
2320
WAV



FTIR 5. Same as No. 4, Stored for 8 Days in Glass

2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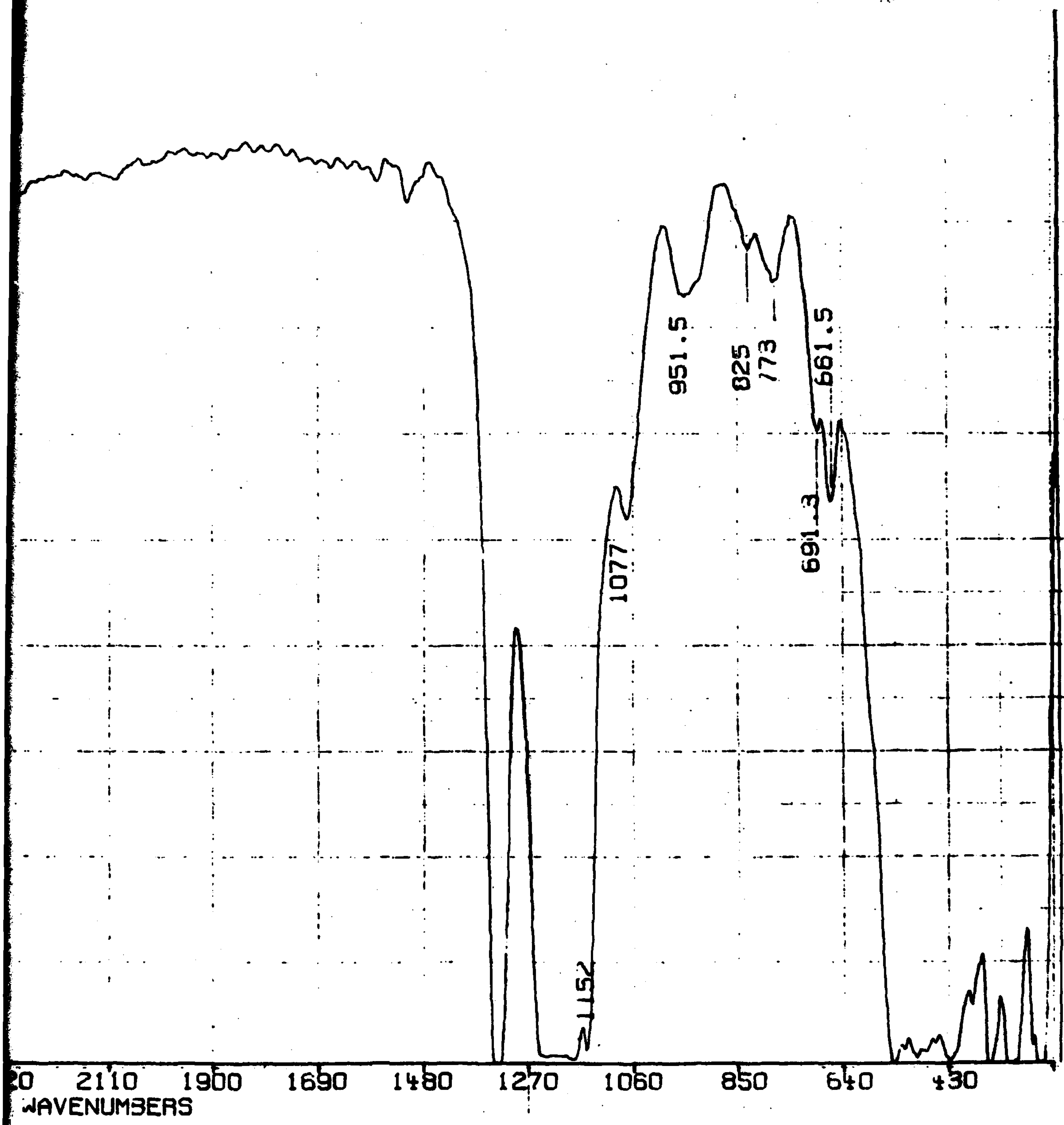
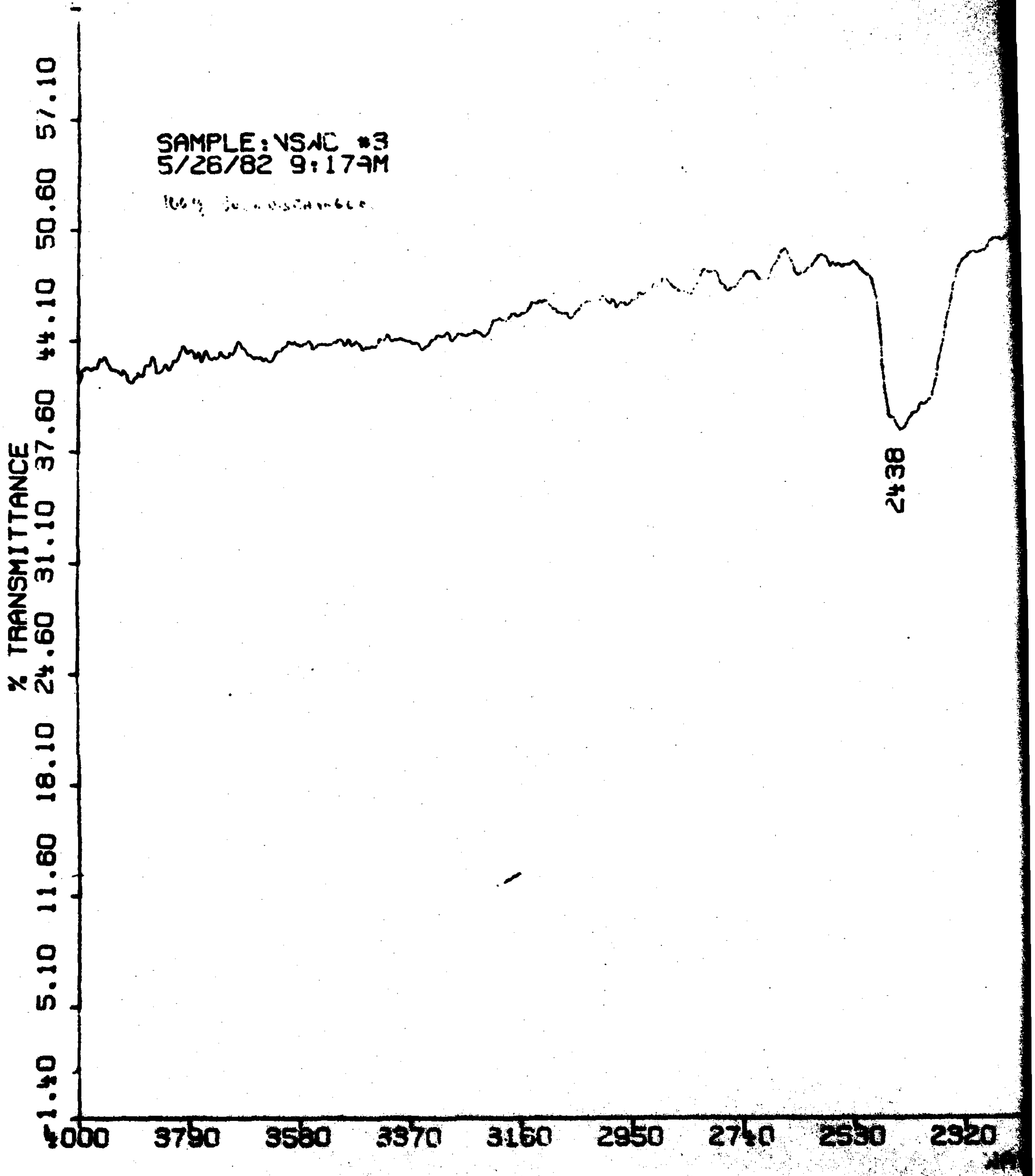
1 WK AFTER SAMPLING
OLD CELL 6/1/82 9:34 AM



FTIR 6. Same as No. 4, Stored for 8 Days in AgCl

2


SAMPLE:NSWC #3
5/26/82 9:17AM
100% [illegible]
% TRANSMITTANCE
1.40
5.10
11.60
18.10
24.60
31.10
37.60
44.10
50.60
57.10
4000
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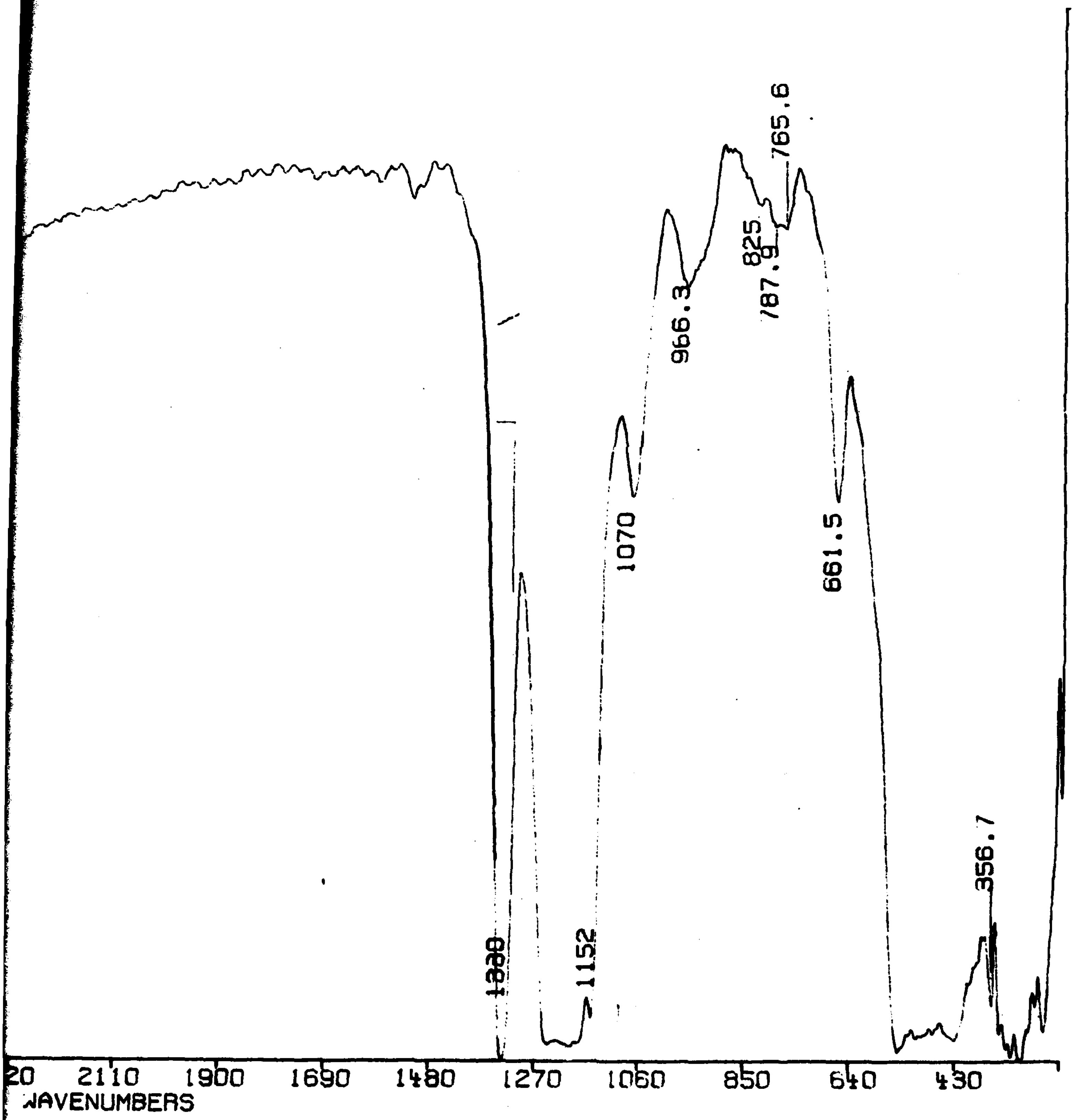
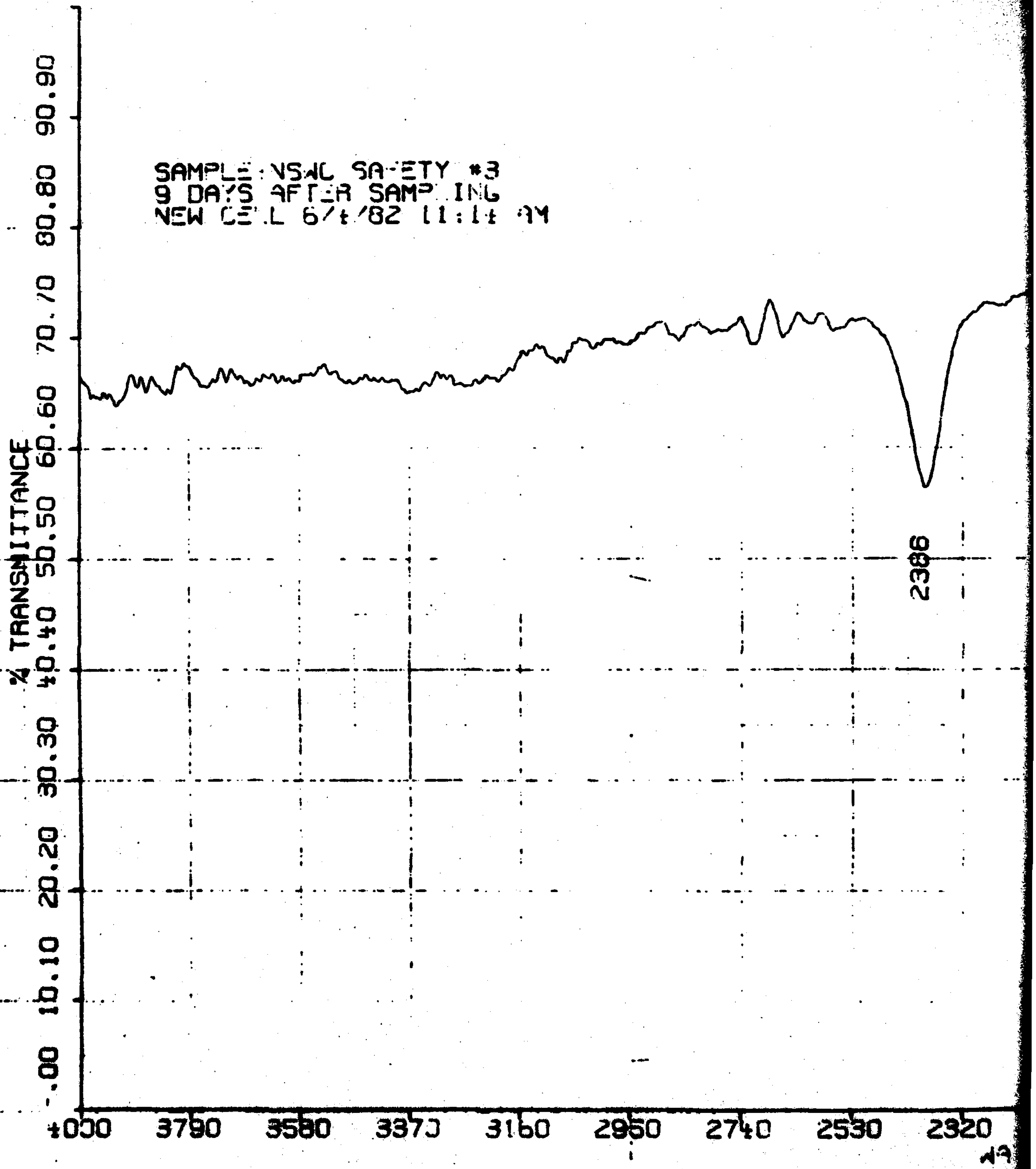
3160
2950
2740
2530
2320
2438

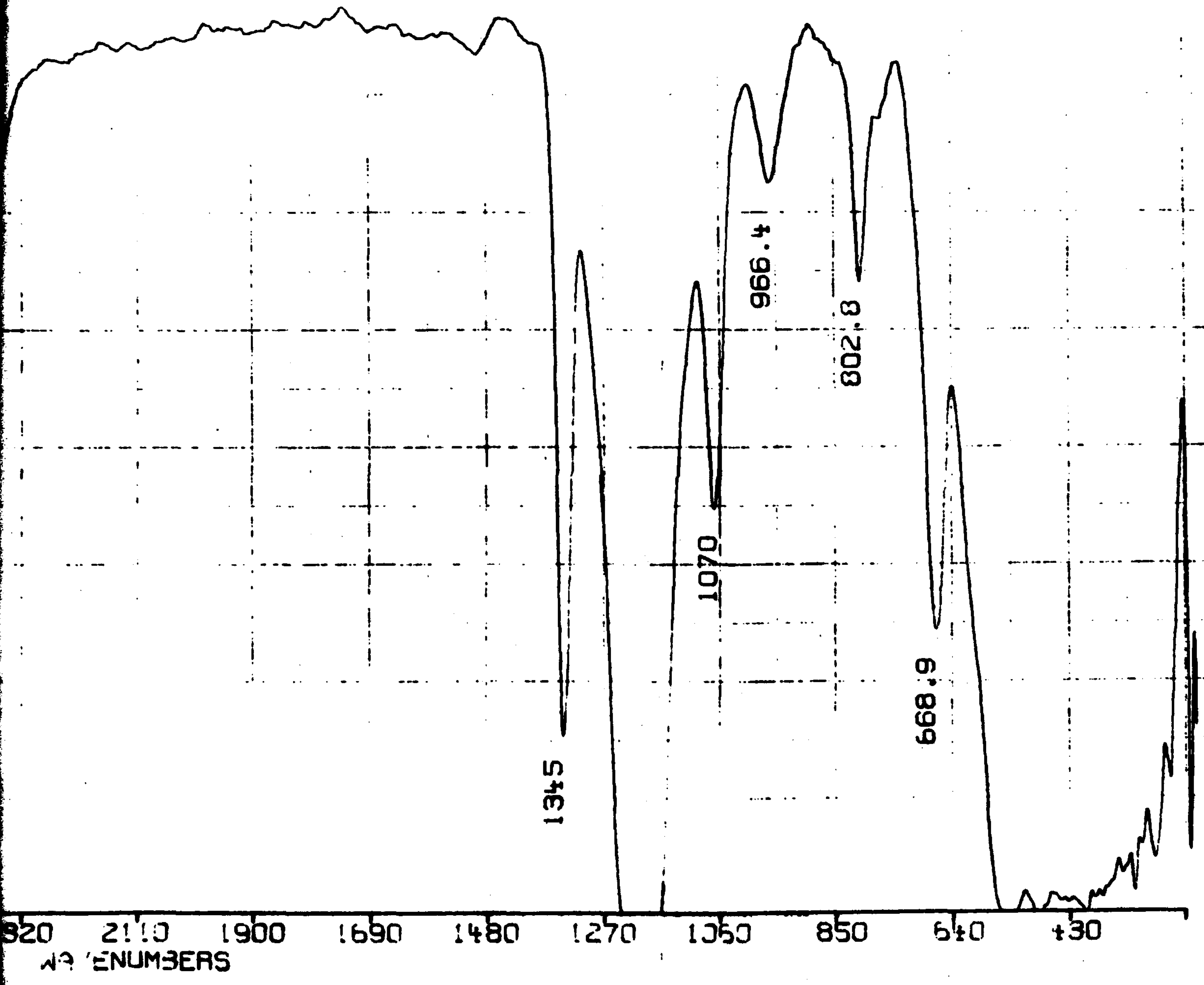


FTIR 7. 100% Overdischarged Electrolyte from Anode Limited Glass Cell

1

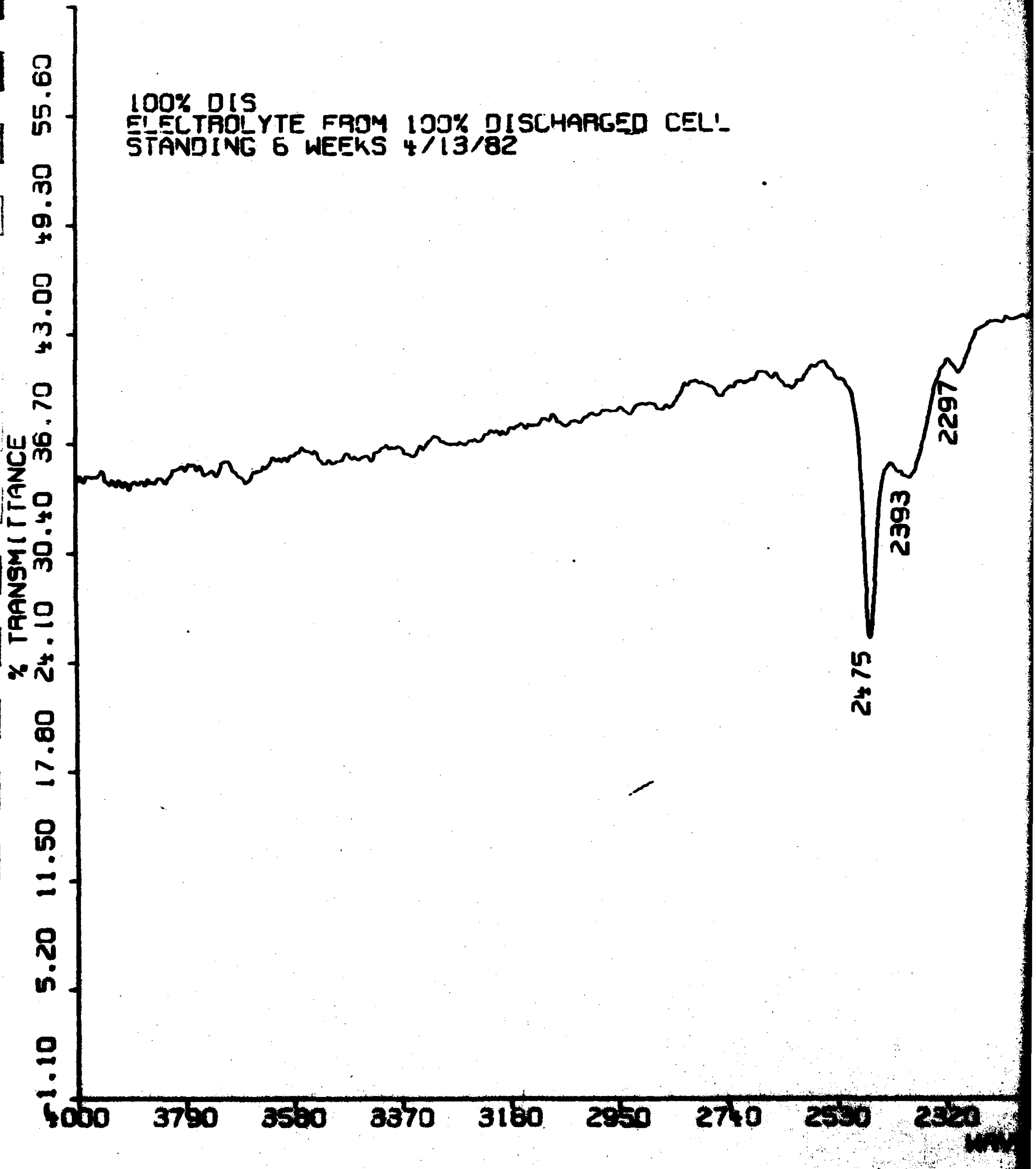
2


SAMPLE: NSWC SAFETY #3
9 DAYS AFTER SAMPLING
NEW CELL 6/4/82 11:14 AM
% TRANSMITTANCE
.00
10.10
20.20
30.30
40.40
50.50
60.60
70.70
80.80
90.90
4000
3790
3580
3370
3160
2950
2740
2530
2320
2386

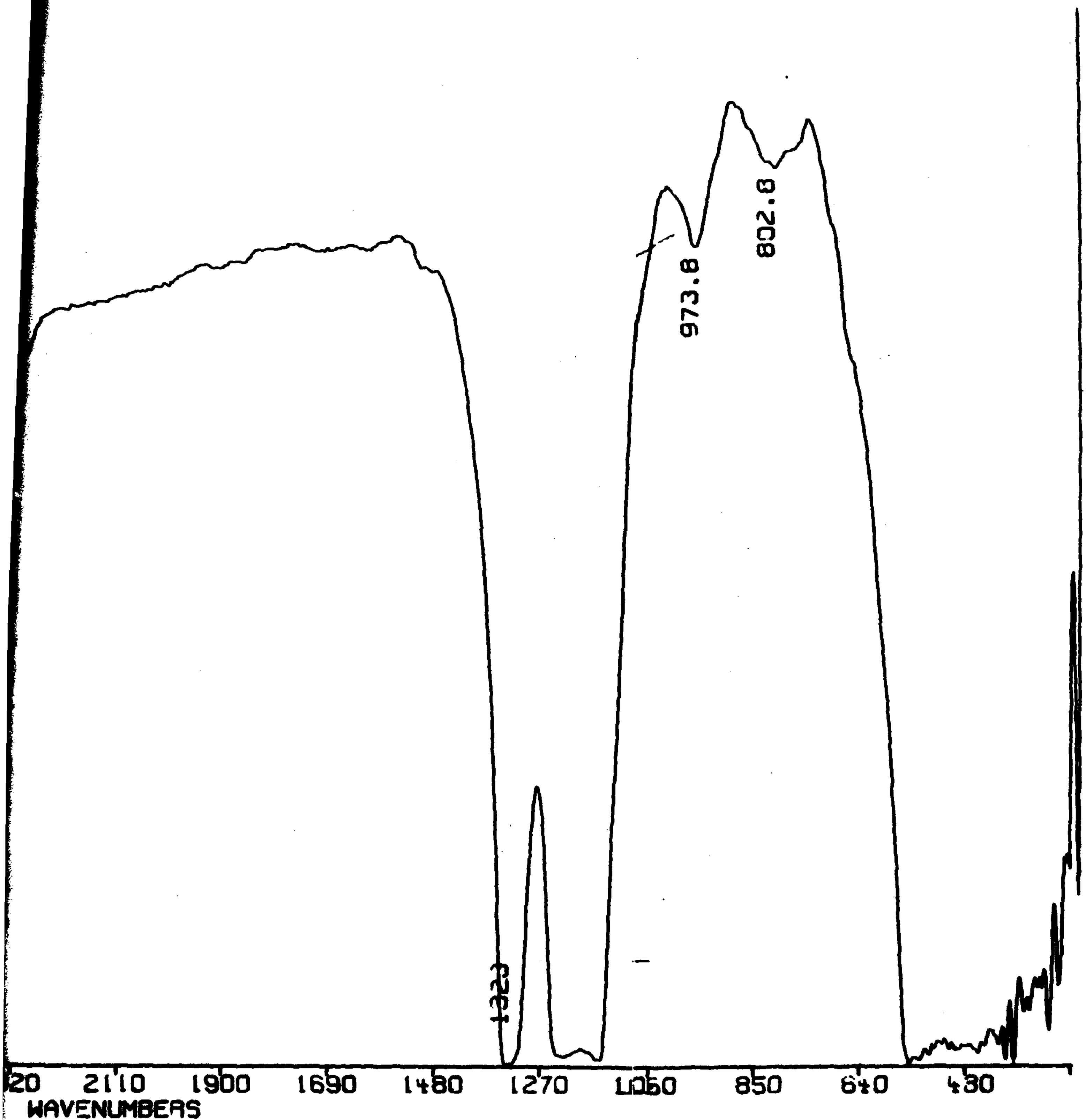


FTIR 8. Same as No. 7. Stored for 9 Days in Glass

2

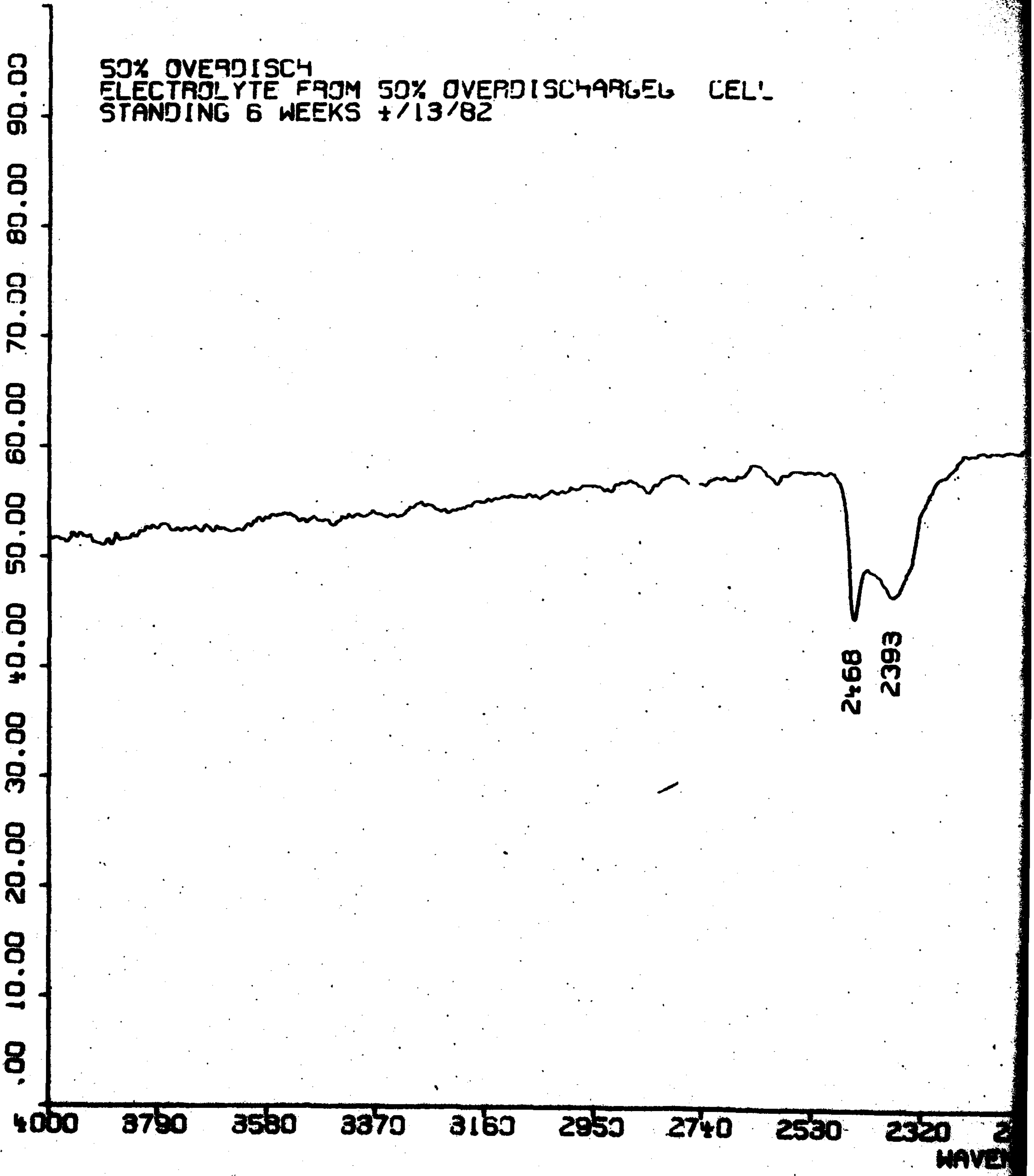


100% DIS
ELECTROLYTE FROM 100% DISCHARGED CELL
STANDING 6 WEEKS 4/13/82



FTIR 9. 100% Discharged Electrolyte from Anode Limited D Cell Stored for 6 Weeks in Glass.

2


50% OVERDISCH
ELECTROLYTE FROM 50% OVERDISCHARGED CELL
STANDING 6 WEEKS 4/13/82
% TRANSMITTANCE
.00
10.00
20.00
30.00
40.00
50.00
60.00
70.00
80.00
90.00
4000
3790
3580
3370
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2530
2320
2
WAVEN
2468
2393

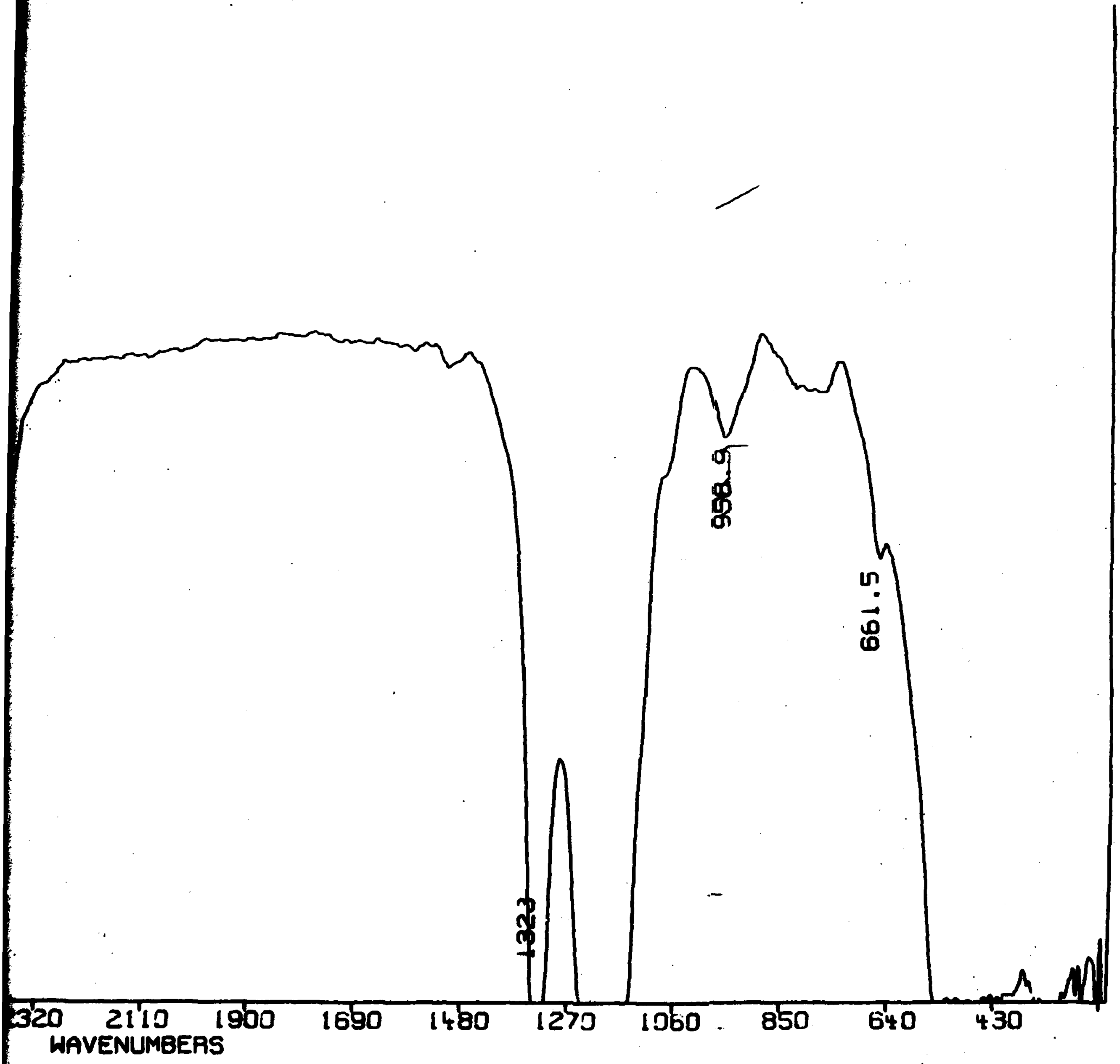
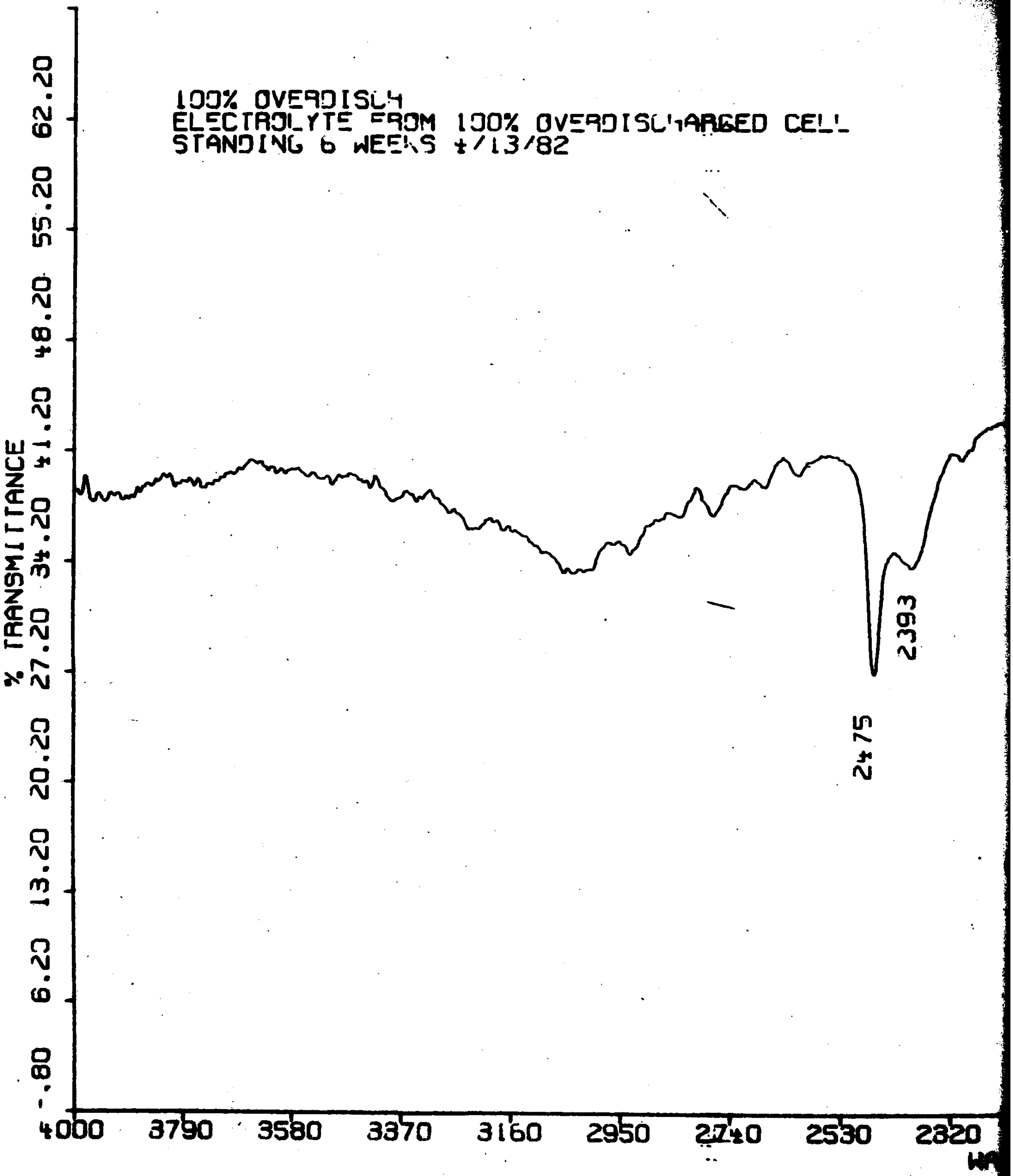


FIG. 10. 30% Overdischarged Electrolyte from Cathode Limited D Cell Stored for 6 Weeks in Glass

2



100% OVERDISCH
ELECTROLYTE FROM 100% OVERDISCHARGED CELL
STANDING 6 WEEKS 4/13/82

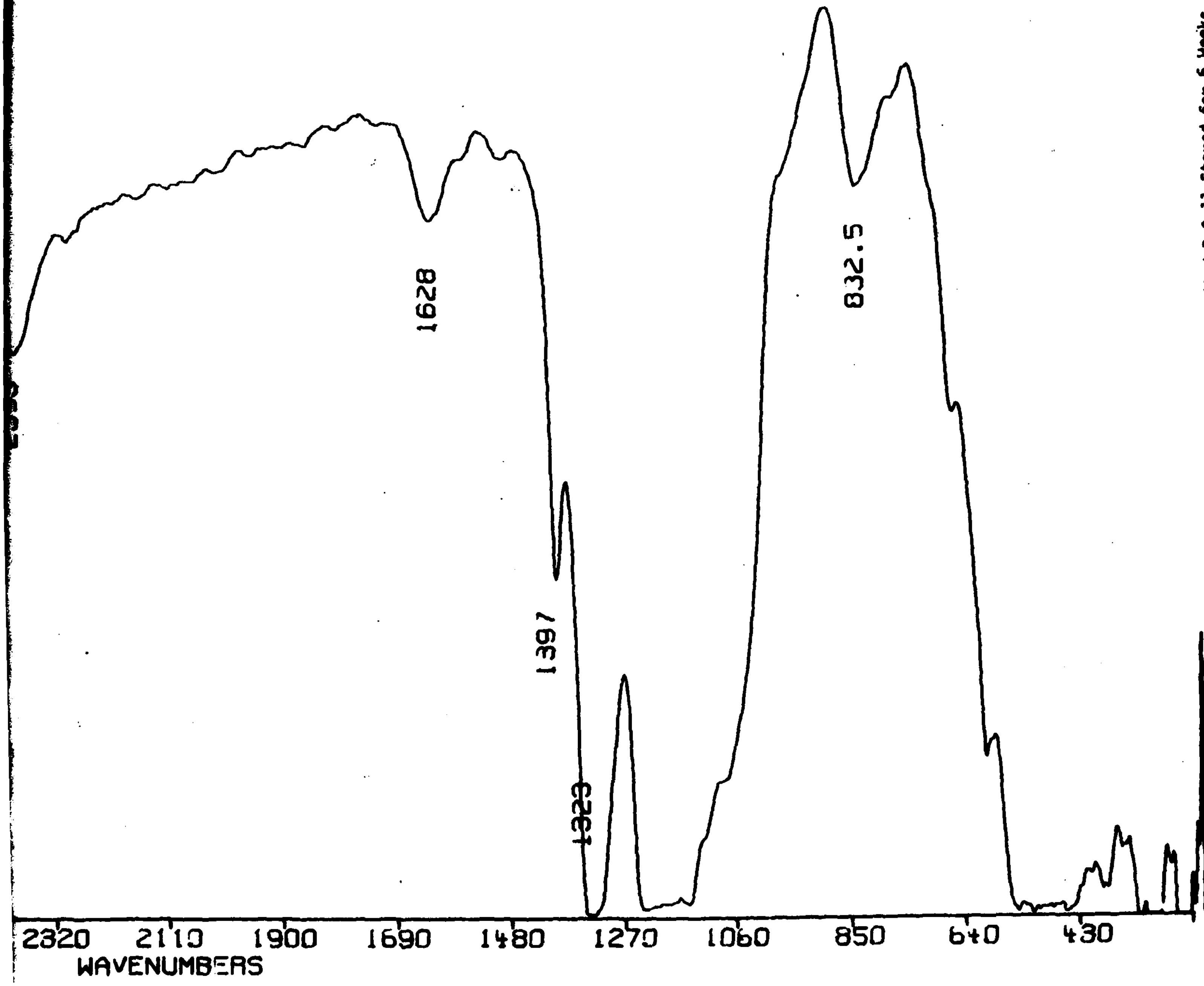


FIG. 11 100% Overdischarged Electrolyte from Anode Limited D Cell Stored for 6 Weeks in Glass

2

1

FILM