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Springborn Laboratories, Inc.
Department of Analytical Chemistry
Ten Springborn Center
Enfield, CT 06082

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F. Mikes

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TABLE I*

DC 1200 Primer Lots Used at Springborn Laboratories

| <u>Springborn Labs ID #</u> | <u>DC Primer Lot #</u> | <u>Date Received at Springborn</u> | <u>Additional Description and Further Sample Labeling</u> |
|---------------------------------|----------------------------|--|--|
| A** | QL033703 | 5/11/83 | red, opaque |
| B** | QL071621 | 11/29/83 | red, leaked |
| C** | QL093752 | 11/29/83 | clear, sealed |
| 1*** | EN057367 | 3/30/84 | clear |
| 2*** | QL033705 | 3/30/84 | red |
| 3*** | 063711 | 3/30/84 | red, S/L Exp 6/84, Temp 50/90F, RS3.900324, 7/83 MMSK343AO25 83G382 |
| 4*** | 093713 | 3/30/84 | red, S/L Exp. 09/84, Temp 50/90F, RS3.794481, 09/83 MMSK343AO25 83G530 (hold for J Mills) |
| 5*** | 093733 | 3/30/84 | red, S/L Exp 09/84, Temp 50/90F, RS3.794481, 09/83 MMSK343AO25 83G529 |
| 6*** | 071620 | 3/30/84 | red, S/L Exp 7/82, Temp 50 to 90F, RS1:705481, 08/81 MMSK343AO25 81G464 |

*A sample identification table is included as the first page in each report.

**Three (3) DC1200 Primer Lots acquired by Springborn Laboratories for initial tests (see monthly reports 1, 2 and 3).

***Six (6) DC1200 Primer Lots received from NASA, Management Division Bldg. 4471, on March 30, 1984.

7th and 8th MONTHLY PROGRESS REPORT

8/1/84 - 10/31/84

I. Description of Work Proposed

The following testing studies were proposed in the last report.

1. Continuation of HPLC studies
2. GC-MS analyses
3. GPC analyses of all nine DC-1200 primer lots (after naphtha removal)
4. Specific gravities/viscosities

II. Description of Work Performed1. Continuation of HPLC Studies

HPLC studies are being conducted to determine whether variations in alcohols' concentrations can be considered as acceptance criteria for different lots of silanes.*

As indicated in the 3rd Progress Report (item 3, pg 7) the following alcohols were found in DC-1200 silane primer lots using gas chromatography-mass spectrometry:

- 2 - propanol
- 1 - propanol
- 2 - methoxyethanol
- 1 - butanol

No suitable HPLC method has yet been found for the separation of these alcohols on a silicagel support using an HPLC method.

Two major problems were encountered by HPLC:

- High back pressure build-up in the HPLC system due to the silicates and titanates present.
- Difficulty in separating individual alcohols using a non-aqueous mobile phase (i.e. hexane/methylene chloride/acetonitrile).

* Alcohols are released during the silane aging process: $Y Si(OR)_3 \xrightarrow{H_2O} Y Si(OH)_3 + 3ROH$ (R= propyl, isopropyl, butyl, methoxyethyl groups)

A new method is being developed to analyze free alcohols in silanes as their 3,5-dinitrobenzoyl derivatives using a non polar mobile phase.

2. GCMS Comparison Study of Alcohols in DC 1200 Primer Lots

The objective of this study is to determine the alcohols' content in different silane primer lots, compare them with FTIR results, and conclude whether gas chromatography can be selected as an evaluation method for different silane primers.

A series of nine DC-1200 silane primer lots were analyzed by GCMS for their alcohols' content.

Individual GCMS profiles, as well as their mass ionograms at m/z 31 (characteristic for alcohols) are shown in Figures 1 through 7. The peak areas at m/z 31 of three alcohols in the silane lots studied are summarized in Table 1.

Analyses and comparison of the results indicate that:

- the small differences in alcohols released are not significant enough to distinguish between individual silane lots,
- no correlation was found between OH-absorption band intensities* and alcohols released in different silane primer lots.

Two explanations are suggested for the absence of detectable differences using gas chromatography as the analytical method: heat treatment and catalytic effect during analysis. All substances separated by GC are carried in the gas phase through a hot injector and over active centers in the stationary phase maintained at elevated temperatures. These factors may be responsible for additional cleavage of alkoxy functional groups. Thus, concentration differences present in the original liquid DC 1200 silane lots might be lost.

Temperature was the only factor studied during the silane GC runs. A lower injector temperature (100°C) resulted in lower concentrations of released alcohols, whereas an injector temperature of 300° released substantially higher quantities of alcohols.

This method will not be considered as a candidate for acceptance criteria test on silane lots.

* The OH-absorption band is considered as an "analytical marker" for aged DC 1200 silane primers (see item 6).

TABLE 1

DC 1200 Silane Primers - Their Area Counts for Mass Fragment at m/z 31

| Alcohol Studied | Area Counts for DC 1200 Sample ID # | | | | | | | | |
|--------------------------|-------------------------------------|------|------|------|------|--------------|---------------|--------|--------|
| | 1 | 2 | 3 | 5 | 6 | B | C | B | C |
| 1 - Propanol | 6409 | 6590 | 5628 | 7266 | 6397 | 4784 5692 | 9664 10652 | 12,345 | 14,776 |
| 2- Methoxyethanol | 1426 | 1515 | 1909 | 1165 | 1744 | 1252 1705 | 2201 2909 | 3,861 | 4,565 |
| 1- Butanol | 1357 | 1686 | 1890 | 1557 | 1737 | 1705 2537 | 3290 3993 | 4,953 | 4,698 |
| Figure No. | 1 | 1 | 2 | 2 | 3 | 4 | 5 | 6 | 7 |
| Temperature/ Injector | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 300 | 300 |

3. GPC Method

After naptha solvent removal from DC 1200 silane primer samples, the residues were found to be crosslinked and thus very difficult to dissolve for GPC analyses. The GPC method was then excluded as a candidate method for determining silane lot acceptability.

4. Viscosities

The viscosities of silane primers were measured by the ASTM procedure. Results are summarized in Table 2.

TABLE 2
Viscosities of DC 1200 Primer Lots

| <u>Sample I.D. #</u> | <u>Viscosity (in cps)</u> | <u>Notes</u> |
|----------------------|-------------------------------|---|
| 1 | 0.716 | Specific gravity constant taken from the supplier. |
| 2 | 0.756 | |
| 3 | 0.734 | For DC 1200 clear primer : 0.763 g/mL @ 25°C |
| 4 | 0.751 | |
| 5 | 0.760 | For DC 1200 red primer : 0.773 g/mL @ 25°C |
| 6 | 0.698 | |
| B | 0.718 | |
| C | 0.716 | |

The viscosity results for silane primers do not correlate with the differences in the hydroxyl absorption region measured by the FTIR method (see item 6 of this report).

FURTHER TEST METHODS USED FOR CHARACTERIZATION OF
SILANE PRIMER LOTS

5. Thermogravimetric Analyses (TGA)

The objective of TGA measurements was to try an additional method (since GPC was not successful), where testing could be conducted on silane primers after drying. The results would be evaluated and compared with the FTIR spectroscopy data (see item 6 below).

A series of seven DC 1200 silane primers were evaporated to dryness at 105°C (solvent removal). Approximately 20 mg of each sample was then analyzed by TGA. The seven TGA profiles are enclosed as Figures 8 through 14.

Three characteristic profile similarity patterns can be selected from the TGA figures as indicated below.

| <u>Similarity Groups</u> | <u>TGA^a of DC 1200 Sample ID</u> | <u>See Figure No.</u> |
|--------------------------|---|-----------------------|
| I | 1, 2, 3 | 8, 9, 10 |
| II | 4, 5, 6 | 11, 12, 13 |
| III | C | 14 |

The TGA profile of sample C indicated the largest differences in comparison with the other silane samples. The TGA differences between the other six samples were minimal.

The final TGA tests will be concluded in the next report. Duplicate TGA analyses of samples B and C will be performed and evaluated.^b

6. FTIR Analysis - A Comparison Study Between Aging Silane Lots

6.1 FTIR Analysis of Silane Liquid Samples

The infrared absorption differences of silane primers in the OH region was the subject of a previous FTIR study described in the 3rd progress report (pg 3-4). An objective of the present work was the completion of this FTIR study. It was decided to obtain FTIR spectra of differently aged DC 1200 primer silanes and compare the results in a final evaluation of the method as a selective procedure. Based on this study, the final decision was made to select the FTIR method as an instrumentation procedure

a. TGA conditions are given in each TGA figure (Figures 8 through 14).

b. i.e. compared with FTIR analyses

which will be utilized for DC 1200 silane primer system evaluation, i.e. for measurement of typical acceptance levels (minimum/maximum values).

Four different IR absorption bands were selected* for measurement in the silane primers and their absolute values compared between five differently aged series of primers, as is shown in Table 3.

A graphic presentation of these four absorption bands and their increase with time in silane lots are given for better visual comparison in three differently aged primer lot series, (Figures 15 through 23).

The first series of silane primer analyses were conducted on the samples "as received" (taken in March 1984). Samples were pipetted from the original cans and kept under nitrogen. Absorption values were found to be extremely small in the six samples received from NASA (ID #1 to 6). Our own DC 1200 primers have already shown some significant differences. Sample A (received in May '83 and closed under an air atmosphere) exhibited the highest absorption of all the samples examined.

The second silane group (ID of samples indicated with one apostrophe, e.g. 1' - 6' and a' - C') represents the same series of primer silanes described above, but analyzed 6 months later (in October 84). Furthermore, these cans were opened during this period, at least 3 times, and samples pipetted for different analytical tests. The graphs and FTIR spectra indicate large increases in the OH-absorption region, which can be explained by crosslinking of the silanes due to moisture functioning as a catalyst during this time period. The metal lid was found to be not hermetically closed in sample 3' and, thus, air contact with this sample caused increased OH absorption values. The progressive aging of sample A (e.g. $A=0.45 \rightarrow A' = 0.99$, at 3360 cm^{-1}) can also be seen from Table 3 and Figure 21. A further dramatic aging change was observed in sample C ($C = 0.028 \rightarrow C' = 1.86$, at 3360 cm^{-1}) due to leakage in the tin lid.

A third series of primers designated with two apostrophes (1'', 3'', 4'', 5'', C'') represent samples introduced from original containers into 30 mLs vials, sealed with teflon lined septums, and kept under nitrogen. Sample septa were then pierced with a needle (0.5 mm O.D.) and kept in the laboratory at ambient temperature with varying humidity (i.e. as in real field conditions). Chronic deterioration was found in Sample A. An already colloidal sample separated into two layers (upper solvent, lower crosslinked product) and it was no longer considered for FTIR analysis.

* i.e. bands characteristic for the OH region at 3360, 3380, 3420 and 3470 cm^{-1}

TABLE 3

FTIR Absorption in OH-Region of Five Series of
Differently Aged DC 1200 Silane Primers

| Sample DC-1200 Lot # | Au (Abs. units) = Hmm X $\frac{\Delta \text{ Abs unit}/(\text{inch})}{25}$ (conversion 25 mm = 1") @ 4 different cm^{-1} | | | | | | | |
|-------------------------|---|---------|-------------------------|---------|-------------------------|---------|-------------------------|---------|
| | 3360 cm^{-1} | | 3380 cm^{-1} | | 3420 cm^{-1} | | 3470 cm^{-1} | |
| | Dupl. | Average | Dupl. | Average | Dupl. | Average | Dupl. | Average |
| 1 (3/30/84) | $\frac{0.0616}{0.0504}$ | 0.0560 | $\frac{0.028}{0.042}$ | 0.035 | $\frac{0.0252}{0.0224}$ | 0.0238 | $\frac{0.0392}{0.0448}$ | 0.042 |
| 2 (3/30/84) | $\frac{0.0196}{0.0532}$ | 0.0364 | $\frac{0.0252}{0.0252}$ | 0.0252 | $\frac{0.0252}{0.0308}$ | 0.028 | $\frac{0.0336}{0.0364}$ | 0.035 |
| 3 (3/30/84) | $\frac{0.0288}{0.0544}$ | 0.0832 | $\frac{0.0224}{0.0224}$ | 0.0224 | $\frac{0.0352}{0.0032}$ | 0.0192 | $\frac{0.032}{0.016}$ | 0.024 |
| 4 (3/30/84) | $\frac{0.0384}{0.0512}$ | 0.0448 | $\frac{0.0288}{0.0384}$ | 0.0336 | $\frac{0.0096}{0.0224}$ | 0.016 | $\frac{0.048}{0.0576}$ | 0.0528 |
| 5 (3/30/84) | — | 0.0 | — | 0.0 | — | 0.0 | — | 0.0 |
| 6 (3/30/84) | $\frac{0.0176}{0.026}$ | 0.0218 | $\frac{0.008}{0.010}$ | 0.009 | $\frac{0.0128}{0.006}$ | 0.0094 | $\frac{0.0144}{0.0140}$ | 0.0142 |
| A (3/30/84) | $\frac{0.3456}{0.558}$ | 0.4518 | $\frac{0.6144}{0.3276}$ | 0.471 | $\frac{0.5952}{0.5328}$ | 0.564 | $\frac{0.5808}{0.342}$ | 0.4614 |
| B (3/30/84) | $\frac{0.21}{0.2128}$ | 0.2114 | $\frac{0.21}{0.2156}$ | 0.2128 | $\frac{0.2324}{0.238}$ | 0.2352 | $\frac{0.266}{0.2576}$ | 0.2618 |
| C (3/30/84) | $\frac{0.0264}{0.0288}$ | 0.0276 | $\frac{0.0192}{0.0192}$ | 0.0192 | $\frac{0.0096}{0.0096}$ | 0.0096 | $\frac{0.024}{0.0336}$ | 0.0456 |
| 1' (10/8/84) | $\frac{0.1144}{0.112}$ | 0.1132 | $\frac{0.1056}{0.1232}$ | 0.1144 | $\frac{0.1232}{0.1344}$ | 0.1288 | $\frac{0.1848}{0.1792}$ | 0.182 |
| 2' (10/8/84) | $\frac{0.2112}{0.1848}$ | 0.198 | $\frac{0.2112}{0.1848}$ | 0.198 | $\frac{0.2304}{0.2016}$ | 0.216 | $\frac{0.2688}{0.2436}$ | 0.2562 |
| 3' (10/8/84)* | $\frac{0.47}{0.484}$ | 0.477 | $\frac{0.47}{0.484}$ | 0.477 | $\frac{0.46}{0.5016}$ | 0.4808 | $\frac{0.48}{0.5104}$ | 0.4952 |
| 4' (10/8/84) | $\frac{0.1872}{0.1408}$ | 0.164 | $\frac{0.1872}{0.132}$ | 0.1596 | $\frac{0.208}{0.1584}$ | 0.1832 | $\frac{0.26}{0.2112}$ | 0.2356 |
| 5' (10/8/84) | $\frac{0.3132}{0.2392}$ | 0.2762 | $\frac{0.3248}{0.2484}$ | 0.2866 | $\frac{0.348}{0.276}$ | 0.312 | $\frac{0.406}{0.3312}$ | 0.3686 |
| 6' (10/8/84) | $\frac{0.1176}{0.1144}$ | 0.116 | $\frac{0.1176}{0.1056}$ | 0.1116 | $\frac{0.1428}{0.1232}$ | 0.133 | $\frac{0.1932}{0.176}$ | 0.1846 |

* Suspected leakage from container

TABLE 3 - Continued
 FTIR Absorption in OH-Region of Five Series of
 Differently Aged DC 1200 Silane Primers

| Sample DC-1200 Lot # | Au (Abs. units) = $\text{Hm} \times \frac{\Delta \text{ Abs unit}/(\text{inch})}{25 \text{ (conversion } 25 \text{ mm} = 1\text{")}}$ @ 4 different cm^{-1} | | | | | | | |
|-------------------------|--|---------|-------------------------|---------|-------------------------|---------|-------------------------|---------|
| | 3360 cm^{-1} | | 3380 cm^{-1} | | 3420 cm^{-1} | | 3470 cm^{-1} | |
| | Dupl. | Average | Dupl. | Average | Dupl. | Average | Dupl. | Average |
| A' | $\frac{0.9976}{0.9984}$ | 0.998 | $\frac{0.928}{0.884}$ | 0.906 | $\frac{0.754}{0.7592}$ | 0.7566 | $\frac{0.5336}{0.5512}$ | 0.5464 |
| B' | $\frac{0.2052}{0.2300}$ | 0.2176 | $\frac{0.1976}{0.2208}$ | 0.2092 | $\frac{0.2204}{0.2484}$ | 0.2344 | $\frac{0.266}{0.2852}$ | 0.2756 |
| C'* | $\frac{1.856}{1.856}$ | 1.856 | $\frac{1.776}{1.872}$ | 1.824 | $\frac{1.584}{1.44}$ | 1.512 | $\frac{1.28}{0.976}$ | 1.128 |
| 1" | $\frac{0.8624}{1.1368}$ | 0.9996 | $\frac{0.836}{1.1252}$ | 0.9806 | $\frac{0.8712}{1.0092}$ | 0.9402 | $\frac{0.6864}{0.8816}$ | 0.784 |
| 3" | $\frac{2.096}{-}$ | 2.096 | $\frac{2.112}{-}$ | 2.112 | $\frac{1.52}{-}$ | 1.52 | $\frac{1.52}{-}$ | 1.52 |
| 4" | $\frac{0.768}{1.1716}$ | 0.9698 | $\frac{0.752}{1.1136}$ | 0.9328 | $\frac{0.704}{1.0208}$ | 0.8624 | $\frac{0.648}{0.8932}$ | 0.7706 |
| 5" | $\frac{0.5292}{0.484}$ | 0.5066 | $\frac{0.5376}{0.5192}$ | 0.5284 | $\frac{0.5712}{0.5544}$ | 0.5628 | $\frac{0.63}{0.616}$ | 0.633 |
| C" | $\frac{1.824}{1.952}$ | 1.888 | $\frac{1.504}{1.888}$ | 1.696 | $\frac{1.472}{2.0}$ | 1.736 | $\frac{1.296}{1.6}$ | 1.448 |
| 1''' | | 0.1672 | | 0.1716 | | 0.1804 | | 0.198 |
| 2''' | | 0.286 | | 0.286 | | 0.2816 | | 0.2816 |
| 3''' | | 0.534 | | 0.540 | | 0.510 | | 0.450 |
| 4''' | | 0.24 | | 0.232 | | 0.252 | | 0.272 |
| 5''' | | 0.2906 | | 0.2948 | | 0.3036 | | 0.3036 |
| 6''' | | 0.1652 | | 0.1652 | | 0.182 | | 0.2044 |
| B''' | | 0.288 | | 0.288 | | 0.2772 | | 0.2772 |
| C''' | | 1.3804 | | 1.276 | | 1.0672 | | 0.812 |

* A leak developed during storage period.

TABLE 3 - Continued

FTIR Absorption in OH-Region of Five Series of
Differently Aged DC 1200 Silane Primers

| Sample DC-1200 Lot # | Au (Abs. units) = $Hmm \times \frac{\text{Abs unit}/(\text{inch})}{25 \text{ (conversion } 25 \text{ mm} = 1\text{)}} @ 4 \text{ different } cm^{-1}$ | | | | | | | |
|-------------------------|---|---------|----------------|---------|----------------|---------|----------------|---------|
| | 3360 cm^{-1} | | 3380 cm^{-1} | | 3420 cm^{-1} | | 3470 cm^{-1} | |
| | Dupl. | Average | Dupl. | Average | Dupl. | Average | Dupl. | Average |
| 1''' | | 0.0704 | | 0.0688 | | 0.0832 | | 0.1072 |
| 2'''* | | 0.66 | | 0.6204 | | 0.7392 | | 0.9636 |
| 3''' | | 0.144 | | 0.1464 | | 0.156 | | 0.1752 |
| 4''' | | 0.0936 | | 0.096 | | 0.108 | | 0.1368 |
| 5''' | | 0.0384 | | 0.036 | | 0.042 | | 0.0624 |
| 6''' | | 0.046 | | 0.04 | | 0.052 | | 0.072 |
| B''' | | 0.1764 | | 0.1792 | | 0.1876 | | 0.196 |
| C'''* | | 0.5644 | | 0.5508 | | 0.5236 | | 0.4692 |

* A leak developed during storage period.

Samples 1-6 , A, B, C - Analysis done 3/30/84 (samples taken from original cans).

Samples 1' - 6', A' B', C' - Analysis done 10/8/84 (Samples stored under nitrogen in original cans)

Samples 1'', 3'', 4'' 5'', C'' - Analysis done 10/8/84 (samples stored in teflon lined sealed vials, stored under nitrogen, but septa pierced with needles providing air contact)

Samples 1'''-6''', B''', C''' - Analysis done 11/21/84 (original cans under nitrogen, B and C samples transferred to glass jars on 10/8/84. All samples stored under nitrogen.

Samples 1'''-6''', B''', C''' - Analysis done 11/21/84 (samples sealed under nitrogen on 7/11/84 from original cans).

6031.2

A large increase in OH absorptions was also found in sample #4 ($4' = 0.16 \rightarrow 4'' = 0.97$ at 3360 cm^{-1}).

Closer investigation of the sample revealed that the hole in the vial septum was larger than that of other samples - thus sample contact with air moisture was enhanced.

The fourth series of silanes analyzed by FTIR ($1''' - 6'''$, B''', C''') were the original samples (i.e. enclosed in cans) analyzed one month later (in Nov.'84) than samples designated with one apostrophe (analyzed in Oct.'84). In this series sample A''' had already deteriorated so much, that it was found divided into two layers (upper = naphtha solvent, lower = crosslinked primer) and its FTIR analysis was not further pursued. The metal lid on sample 3''' was found to be leaking during measurements in Oct.'84.

A further increase in its OH absorption was found ($3' = 0.48 \rightarrow 3'' = 0.53$ at 3360 cm^{-1}). Sample C''' indicated a smaller IR absorption in the OH region compared to its analyses one month earlier ($C' = 1.86 \rightarrow C'' = 1.38$). This variance can be explained by non-homogeneity of the silane analyzed in Oct.'84. (i.e. Sample was not sufficiently stirred).

The last (5th) series of aged silane samples represents silane lots ($1'''' - 6''''$, A'''' - C''') transferred into glass vials from the original cans after their FTIR measurements in March'84. Silane primers were pipetted into the glass containers, purged with dry nitrogen, and hermetically sealed. No substantial increase in OH-absorption was expected after analyzing them in Oct.'84. The table of results (Table 3) confirms this anticipation. The absorptions are only slightly different (i.e. higher due to the aging process only) compared with the original series (except samples 2'''' and C''', where microleaks developed in the sealed vials during their storage period).

All FTIR spectra obtained during the study period August - November 1984 are enclosed in Figures 24 - 66.

The following conclusions have been made following this FTIR study:

1. FTIR is suggested as the testing method for silane lot evaluation.
2. The FTIR method has the capacity to function as a Quantitative Indicator for typical acceptance levels or minimum/maximum values for the DC 1200 silane primers if further developed as described in B Phase 2, scope of work of Exhibit "A". (See "Changes" clause submitted to MSFC-AP29-F on 9/6/84).

There is good reason to expect that the results from actual adhesion tests of DC 1200 primer system will quantitatively correlate with the the FTIR method.

3. The proposed FTIR method is:

- o Simple (direct liquid measurement, 0.2 mL/sample)
- o Fast (32 scans/1 minute; whole analysis takes only 5-10 minutes)
- o Can be operated by skilled analytical technician only
- o Relatively inexpensive*

6.2 FTIR Analysis of Silanes as Solids

A comparison study of FTIR spectra was also performed on nine vacuum dried DC 1200 silane primer samples. Approximately 1 mg of each sample was used for KBr pellet preparation and the FTIR run immediately in order to keep contact with moisture to a minimum.

The FTIR absorbance values at 3360 cm^{-1} of all nine samples are summarized in Table 4 and their spectra shown in Figures 67-75. The IR values obtained do not correlate with the IR values obtained under similar FTIR conditions, but with liquid silane samples (see chapter 6.1 above). Thus, values received are not considered significant and the method used is not being suggested as a candidate for a silane lot acceptance test. The explanation is an observation made during GPC analyses (see therein), i.e. during solvent removal the silanes are found to crosslink. This may be an explanation for the scattered values of the absorption readings obtained.

TABLE 4

UV Absorbance Values at 3360 cm^{-1} of Nine DC 1200 Silane Primers
Analyzed as KBr Pellets

| Sample | UV Absorbance at 3360 cm^{-1} |
|--------|---|
| 1 | 0.394 |
| 2 | 0.308 |
| 3 | 0.324 |
| 4 | 0.249 |
| 5 | 0.440 |
| 6 | 0.566 |
| A | 0.378 |
| B | 0.517 |
| C | 0.216 |

* The cost for a benchtop FTIR instrument suitable for the suggested tests is presently about \$20-25,000.

III . Plan For Future Work

1. Concluding work on an HPLC method (i.e. separation of alcohols as 3,5-dinitrobenzoylestere on an HPLC column) for different silane lots and their correlation with FTIR studies.
2. TGA analyses of samples B and C (in duplicate).

These two items will conclude the original (non-amended) proposed work.

If the "Changes" clause (submitted to MSFC, AP29-F on September 6, 1984) is approved* , the following program will start concurrently with items 1 and 2:

3. Ms. Carol A. Mowrey, a junior chemist, will be sent to NASA-MSFC Materials and Processing Laboratory for 2 working days to learn lay-up and bonding technique involving silane primer system (i.e. aluminum substrate - DeSoto Primer - DC 1200 as coupling reagent and GX 3000 silicon rubber).

Our earliest proposed date for this 2 day training visit is December 1984.

4. After Phase 3 is completed, ten test panels for adhesive bond tests will be prepared at our Enfield location. The DC 1200 silane primer lots used for our FTIR studies will be used as silane primer testing batches, if no other DC 1200 will be made available from MSFC.

IV. Financial Status

The total cumulative expenditures incurred as of the report date (8/31/84) is \$30,808 (i.e. material and labor). Estimated percentage of contract completion is 85%.

* In order to speed up the project work, an initial verbal approval from ACO would be satisfactory for initiating the task.

LIST OF FIGURES

- Figures 1 - 7 Total and extracted ion current mass chromatograms of silane primer lots.
- Figures 8 - 14 TGA profiles of 9 silane primer samples
- Figures 15 - 23 Bar graphs comparing OH region IR absorbances of differently aged series of silane primer lots.
- Figures 24 - 66 FTIR spectra of all silane liquid samples used for analytical evaluation in this study.
- Figures 67 - 75 FTIR spectra of silane samples analyzed as solids.

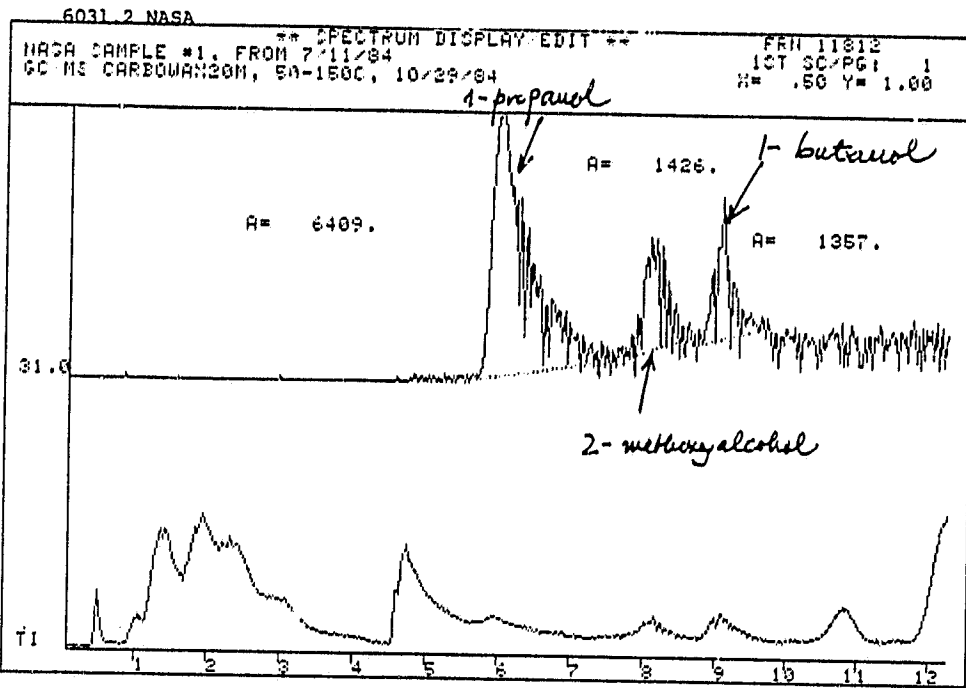


FIG 1

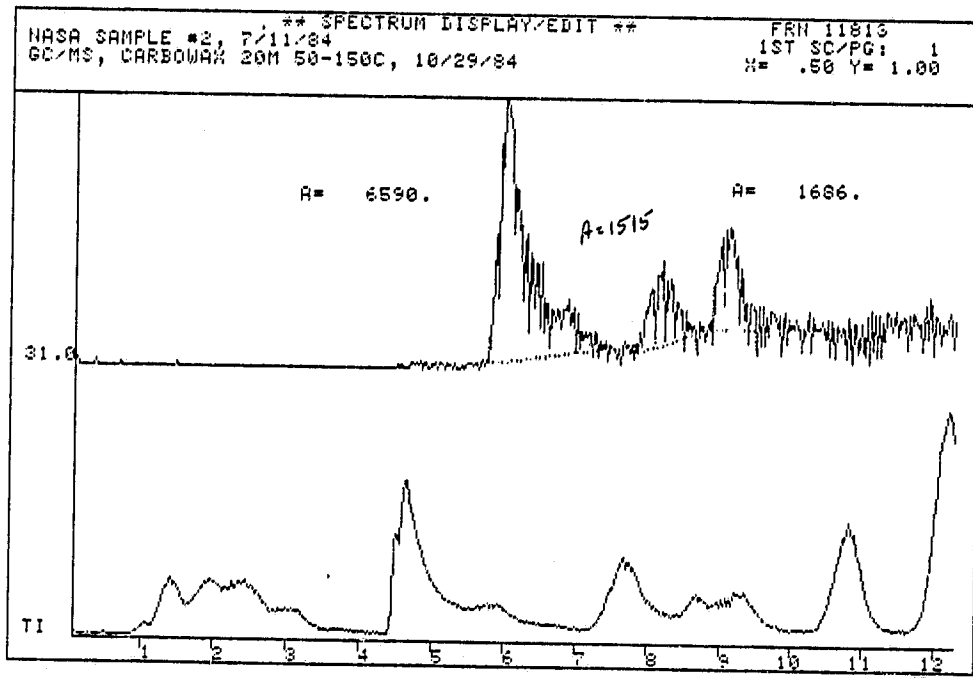
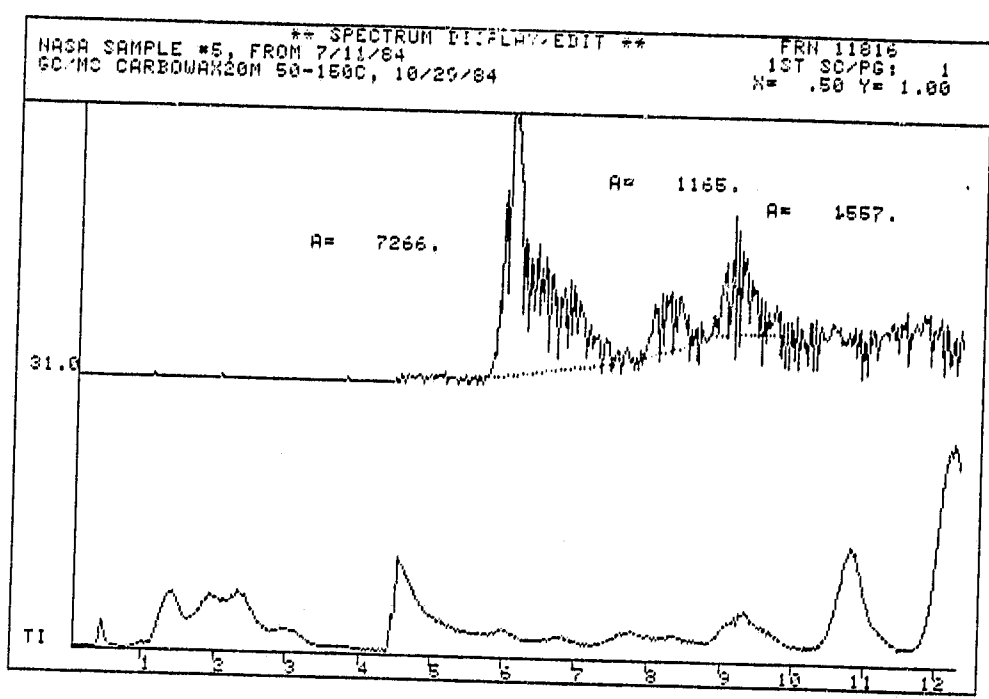
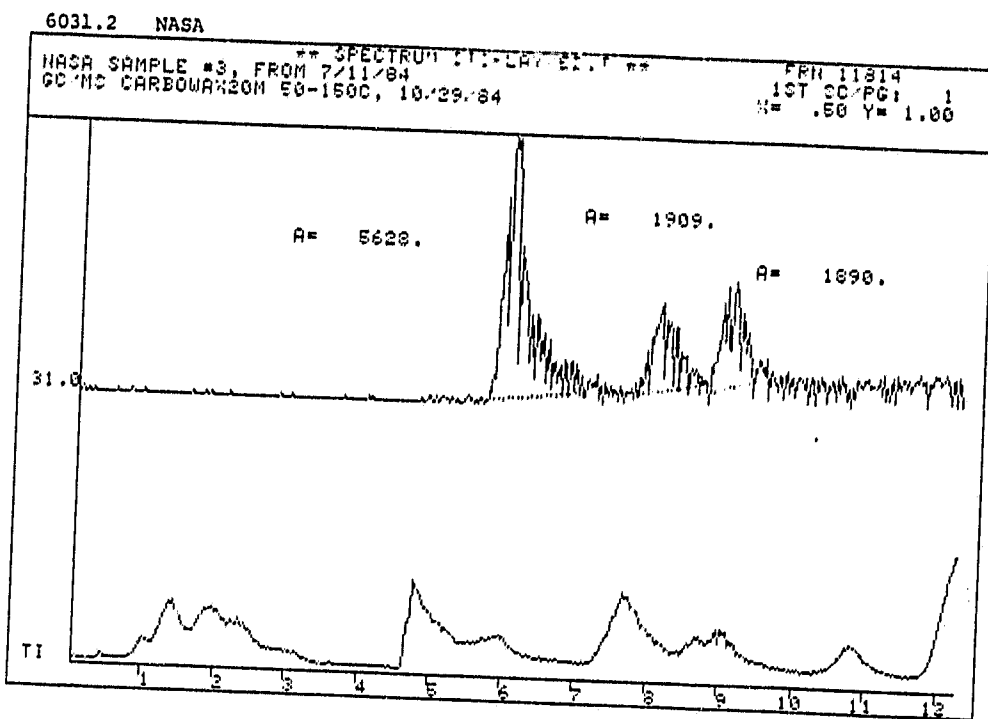


FIG 2



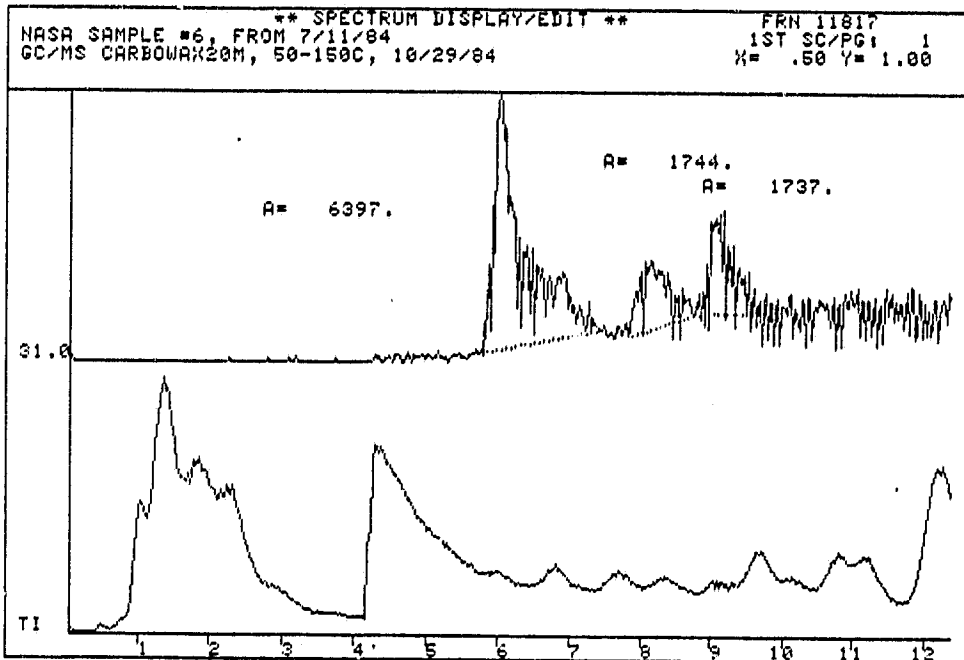


FIG. 4

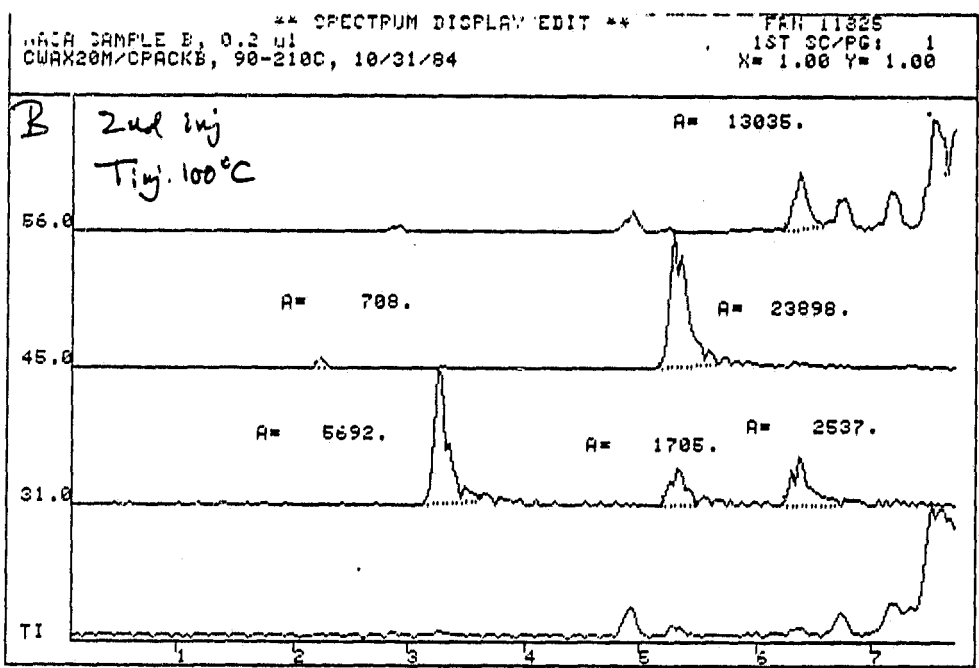
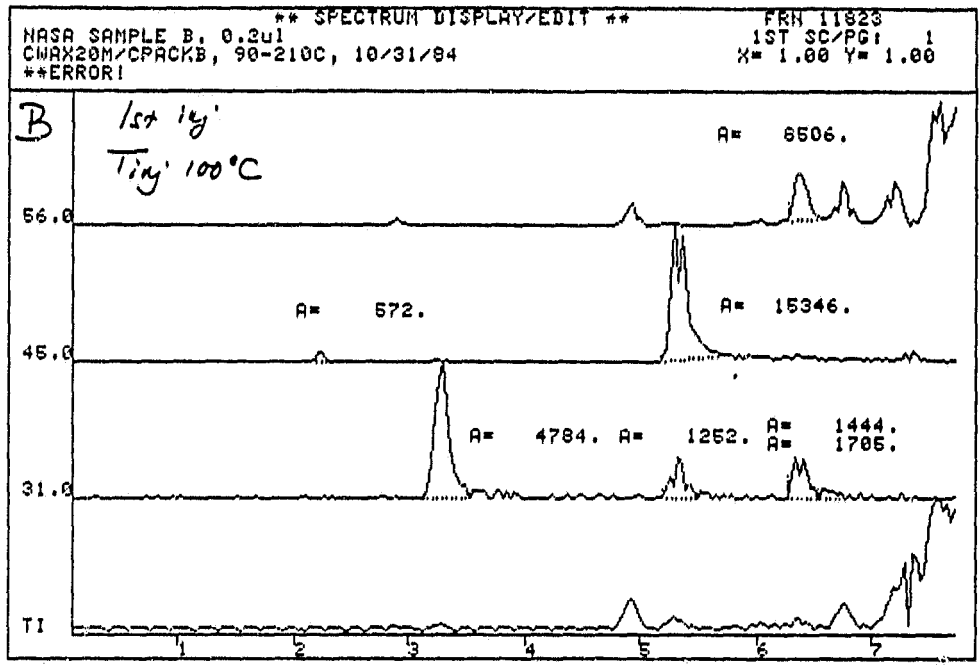


FIG. 5

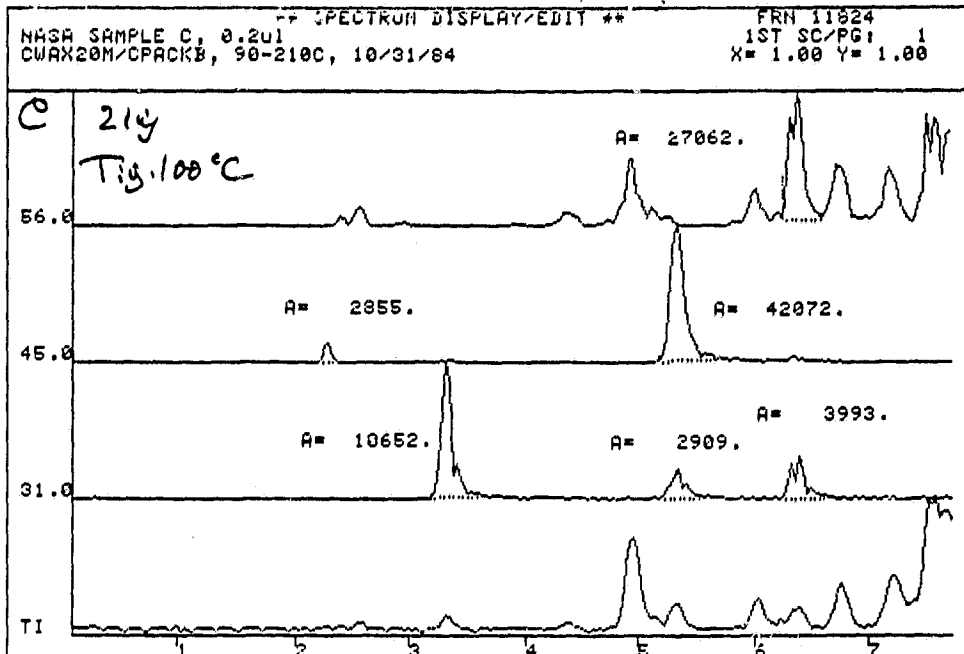
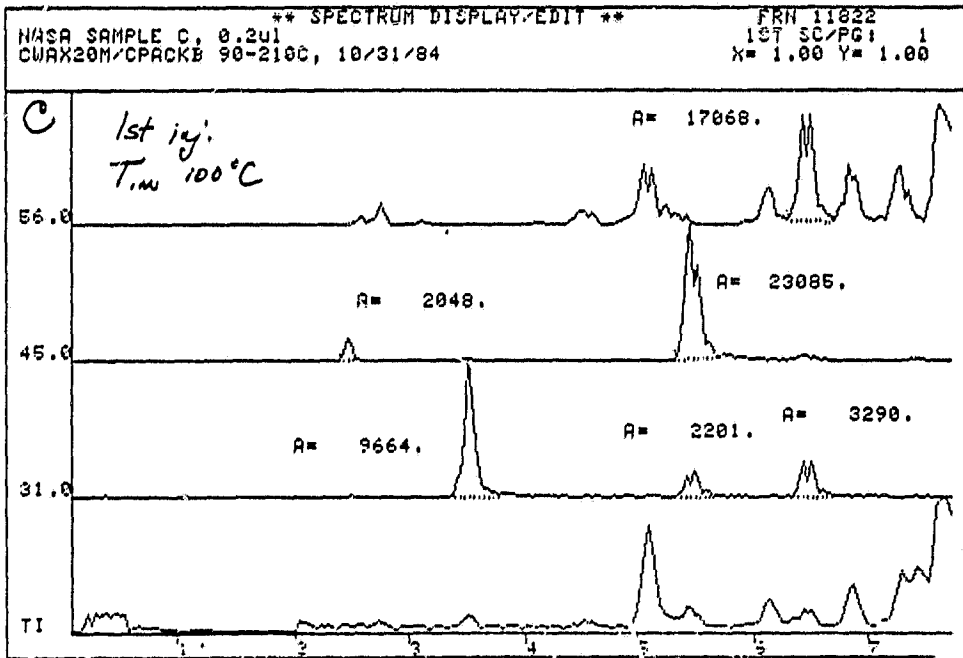
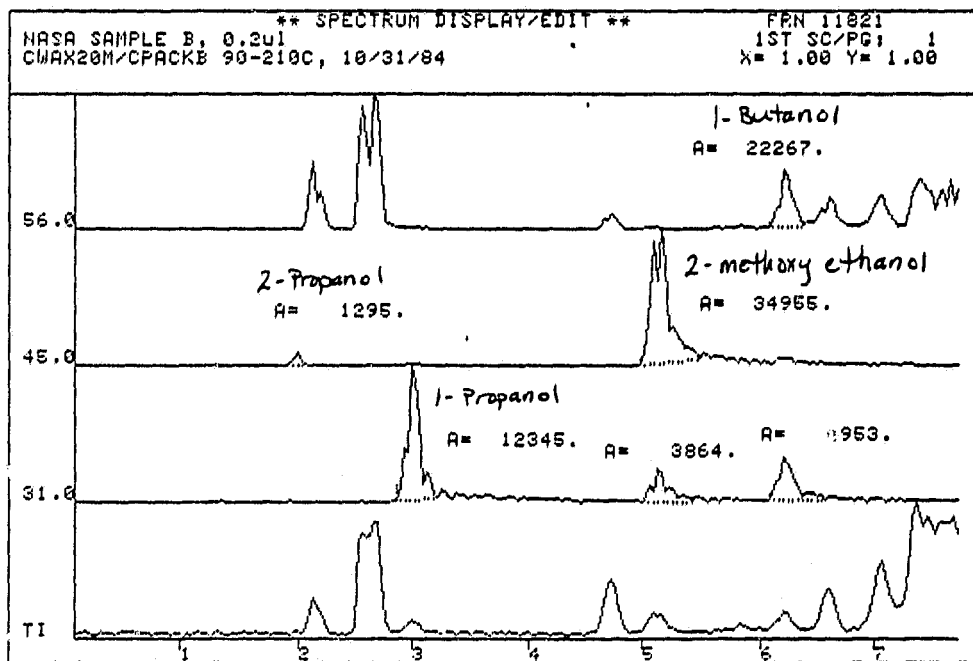
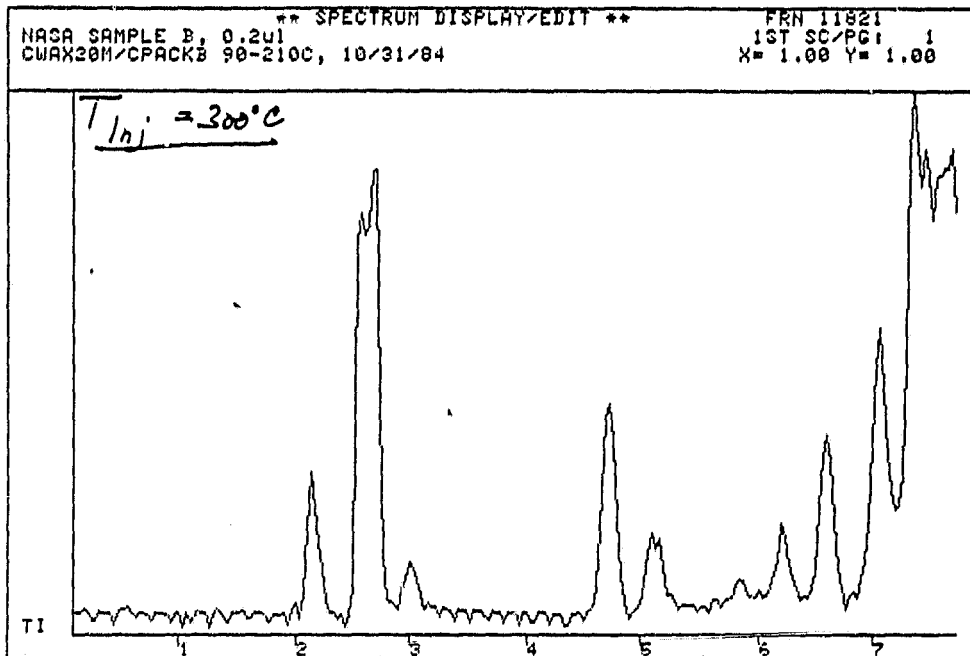
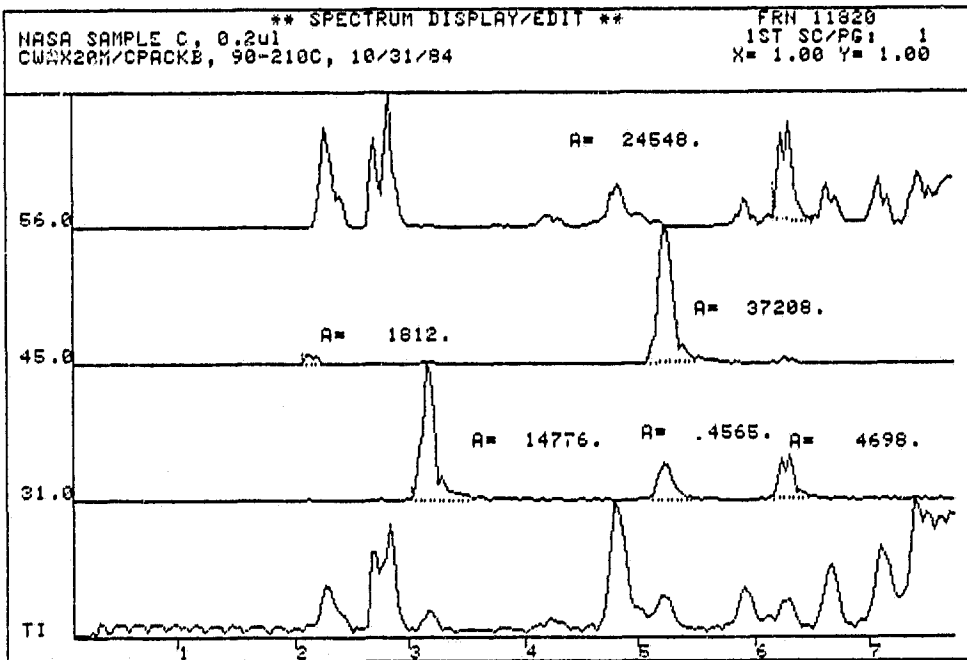
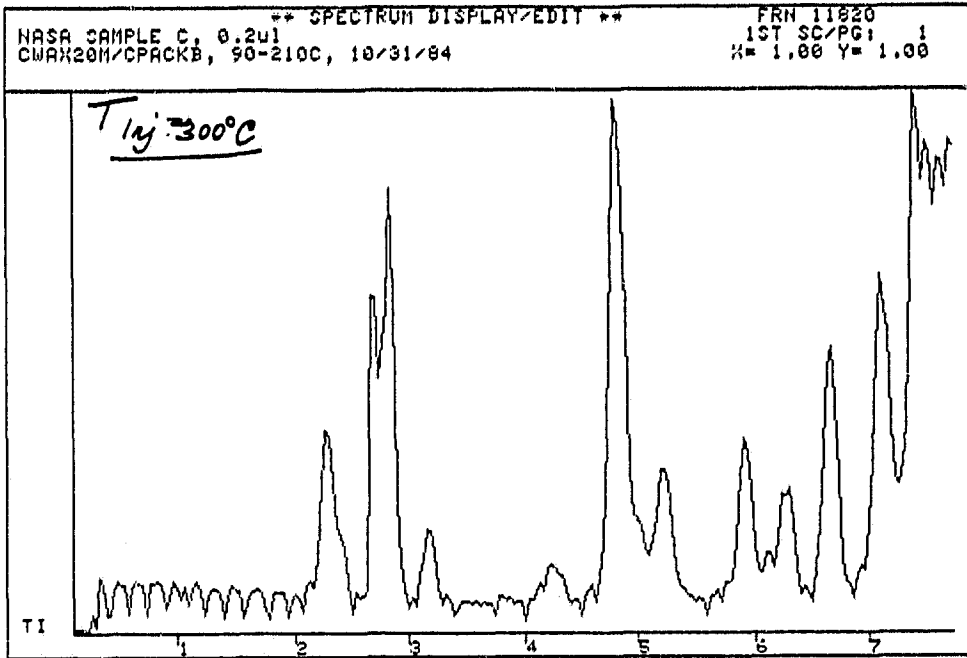


FIG. 6







OMNITHERM CORPORATION

FIG. 8

NASA 6031-2

PN-25680

ORIGINAL PAGE IS
OF POOR QUALITY

SAMPLE:
Sample #1
(white)

ORIGIN:

X-AXIS

TEMP. SCALE ^{amb} 500 °C
inch

Spl wgt
SHIFT 20.6 mg/inch

TIME SCALE (ALT.)

Y-AXIS

SCALE ^{amb} 50 mg.
inch
(SCALE SETTING X 2)

SUPPRESSION 10.6 mg.

RUN NO. 2123 DATE 10-8-84

OPERATOR Chris F

HEATING RATE 20 °C/min.

ATM. N₂ @ 40 cc/min

TIME CONSTANT 2 sec.

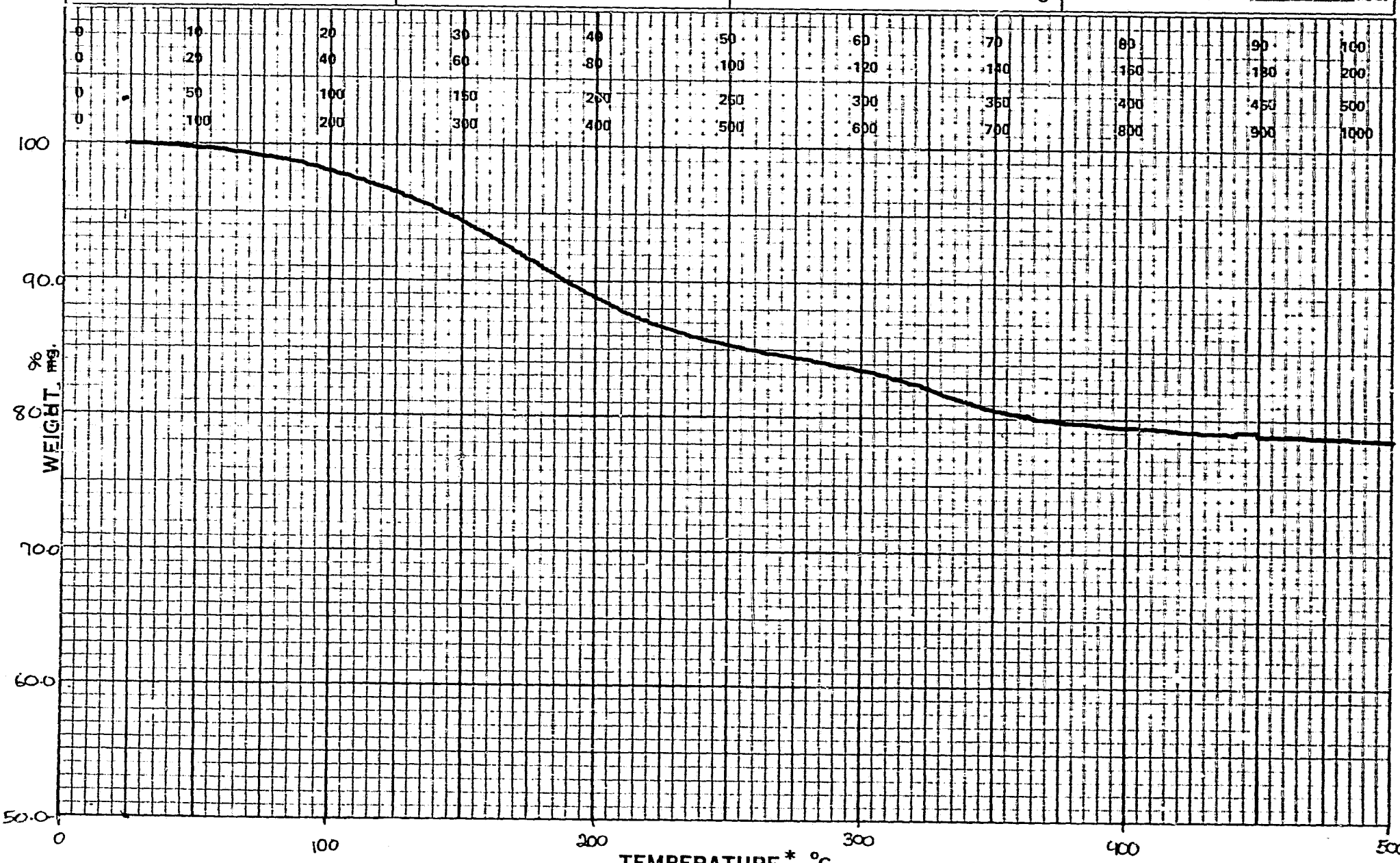


FIG 8



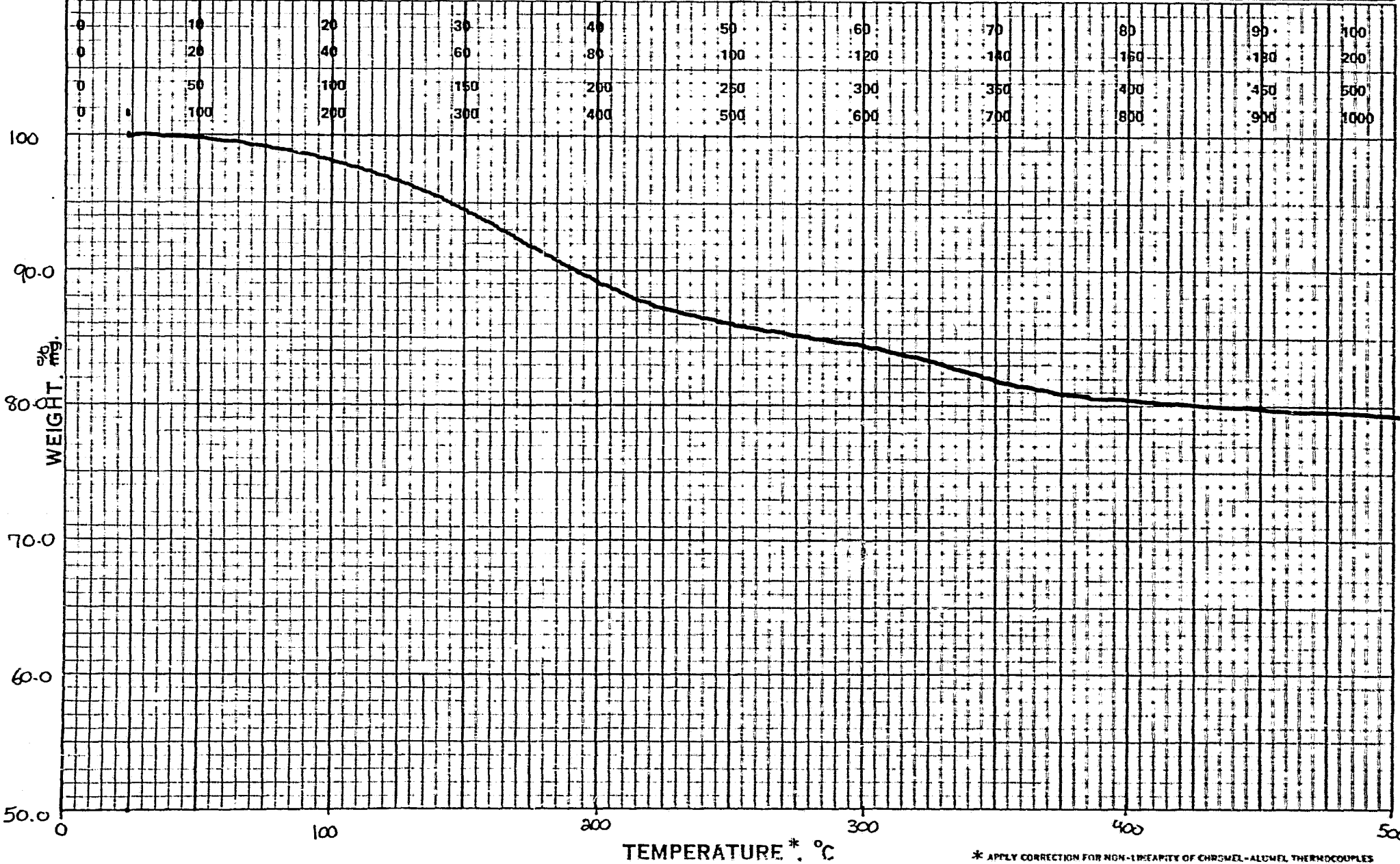
FIG. 9
OMNITHERM CORPORATION

Nasa 6031.2

PN-25680

| | X-AXIS | Y-AXIS | |
|----------------|---|--|---|
| SAMPLE: | TEMP. SCALE $\frac{\text{amb}}{500} \frac{^{\circ}\text{C}}{\text{inch}}$ | SCALE $\frac{\text{mg.}}{\text{inch}}$ | RUN NO. <u>2124</u> DATE <u>10-8-84</u> |
| Sample # 2 | SHIFT $\frac{\text{plwgt}}{20.3 \text{ mg inch}}$ | (SCALE SETTING X 2) | OPERATOR <u>Chris F.</u> |
| ORIGIN: | TIME SCALE (ALT.) | SUPPRESSION <u>10.3</u> mg. | HEATING RATE <u>20</u> $\frac{^{\circ}\text{C}}{\text{min.}}$ |
| (pink) | | | ATM. <u>N₂ @ 40 cc/min</u> |
| | | | TIME CONSTANT <u>2</u> sec. |

ORIGINAL PAGE IS OF POOR QUALITY



* APPLY CORRECTION FOR NON-LINEARITY OF CHRMEL-ALUMEL THERMOCOUPLES

FIG. 9



OMNITHERM CORPORATION

FIG. 10

Nasa 6031.2

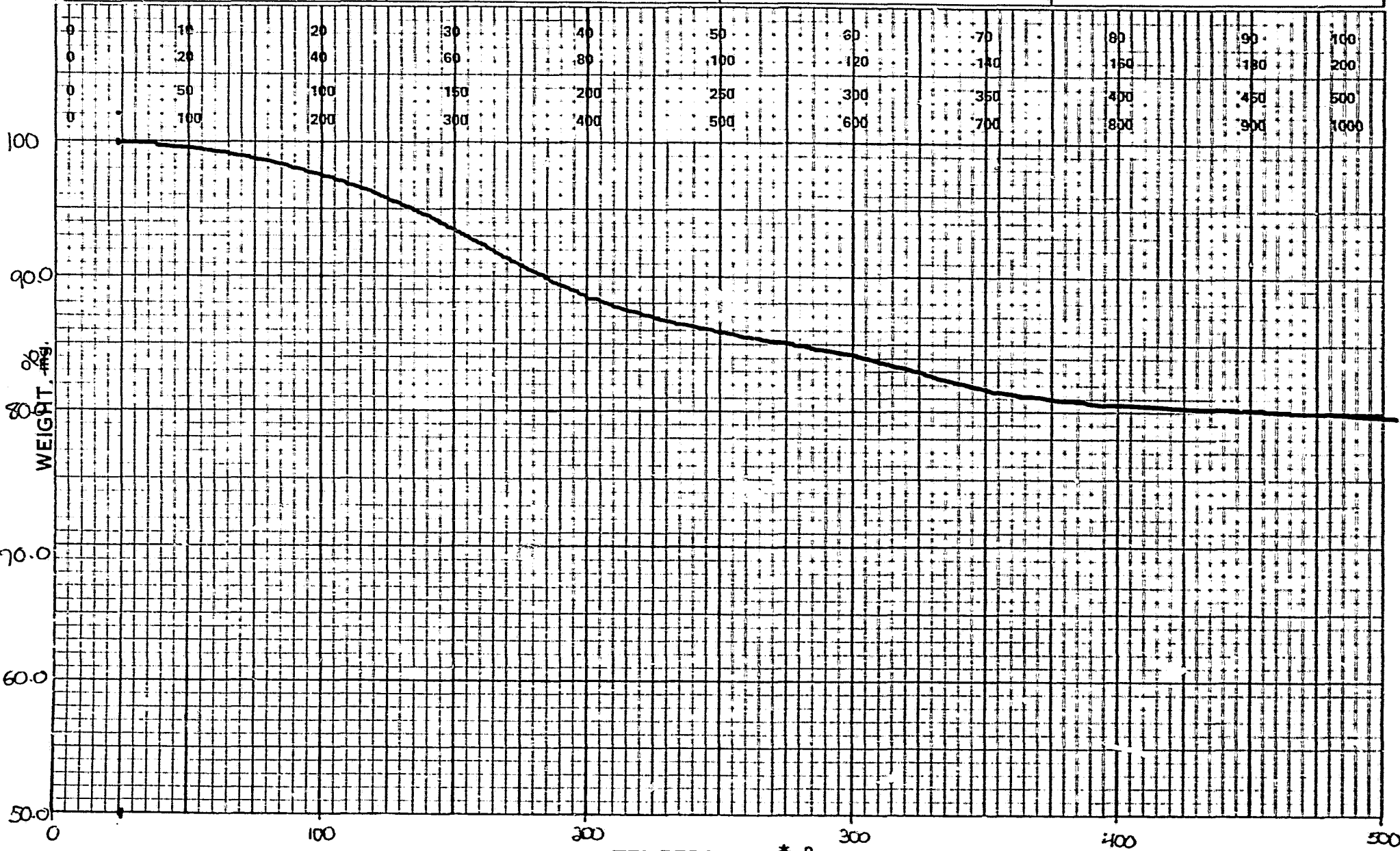
PN-25680

SAMPLE: Sample # 3
 ORIGIN: bright pink-red

X-AXIS
 TEMP. SCALE $\frac{\text{amb-}^\circ\text{C}}{500}$
 SHFT $\frac{\text{spl wgt}}{20.4 \text{ mg}} \frac{\text{inch}}{\text{inch}}$
 TIME SCALE (ALT.)

Y-AXIS
 SCALE $\frac{\text{mg.}}{\text{inch}}$
 (SCALE SETTING X 2)
 SUPPRESSION 10.4 mg.

RUN NO. 2124 DATE 10-8-84
 OPERATOR CHRIS F
 HEATING RATE 20 $\frac{^\circ\text{C}}{\text{min.}}$
 ATM. $\text{N}_2 @ 40 \text{ cc/min}$
 TIME CONSTANT 2 sec.



* APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES

FIG. 10



OMNITHERM CORPORATION

Fig. 11

NASA 6031.2

PN-25680

SAMPLE:

Sample # 4

ORIGIN:

(pink-red)

X-AXIS

TEMP. SCALE $\frac{\text{amb-}}{500} \frac{^{\circ}\text{C}}{\text{inch}}$

SHIFT $\frac{\text{split}}{20.3} \frac{\text{mg}}{\text{inch}}$

TIME SCALE (ALT.)

Y-AXIS

SCALE $\frac{\text{mg.}}{\text{inch}}$
(SCALE SETTING X 2)

SUPPRESSION $\frac{10.3}{\text{mg.}}$

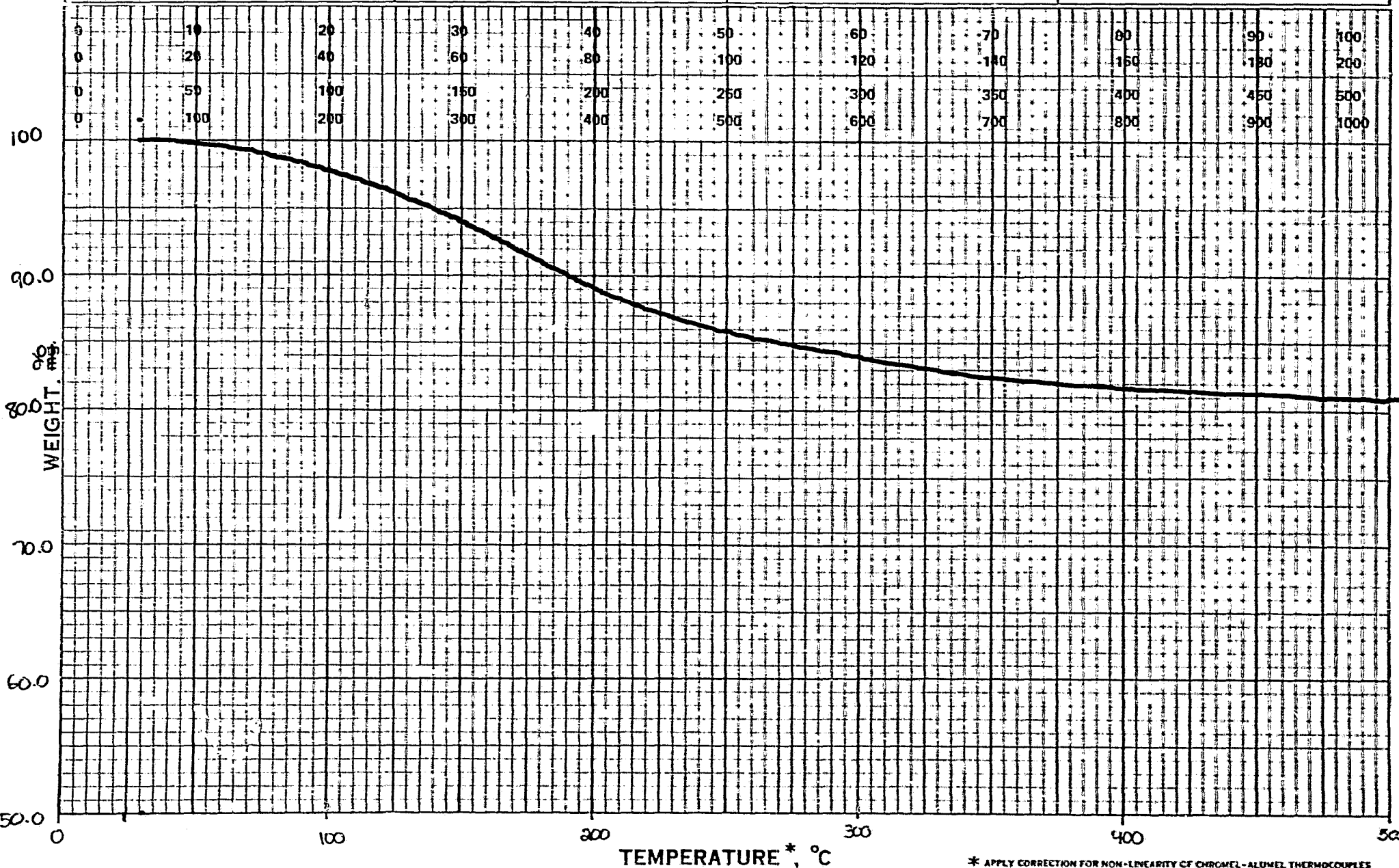
RUN NO. 2125 DATE 10-10-84

OPERATOR Chris F.

HEATING RATE $\frac{20}{\text{min.}}$ $^{\circ}\text{C}$

ATM. $\text{N}_2 @ 40 \text{ ml/min}$

TIME CONSTANT $\frac{2}{\text{sec.}}$



* APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES

Fig. 11

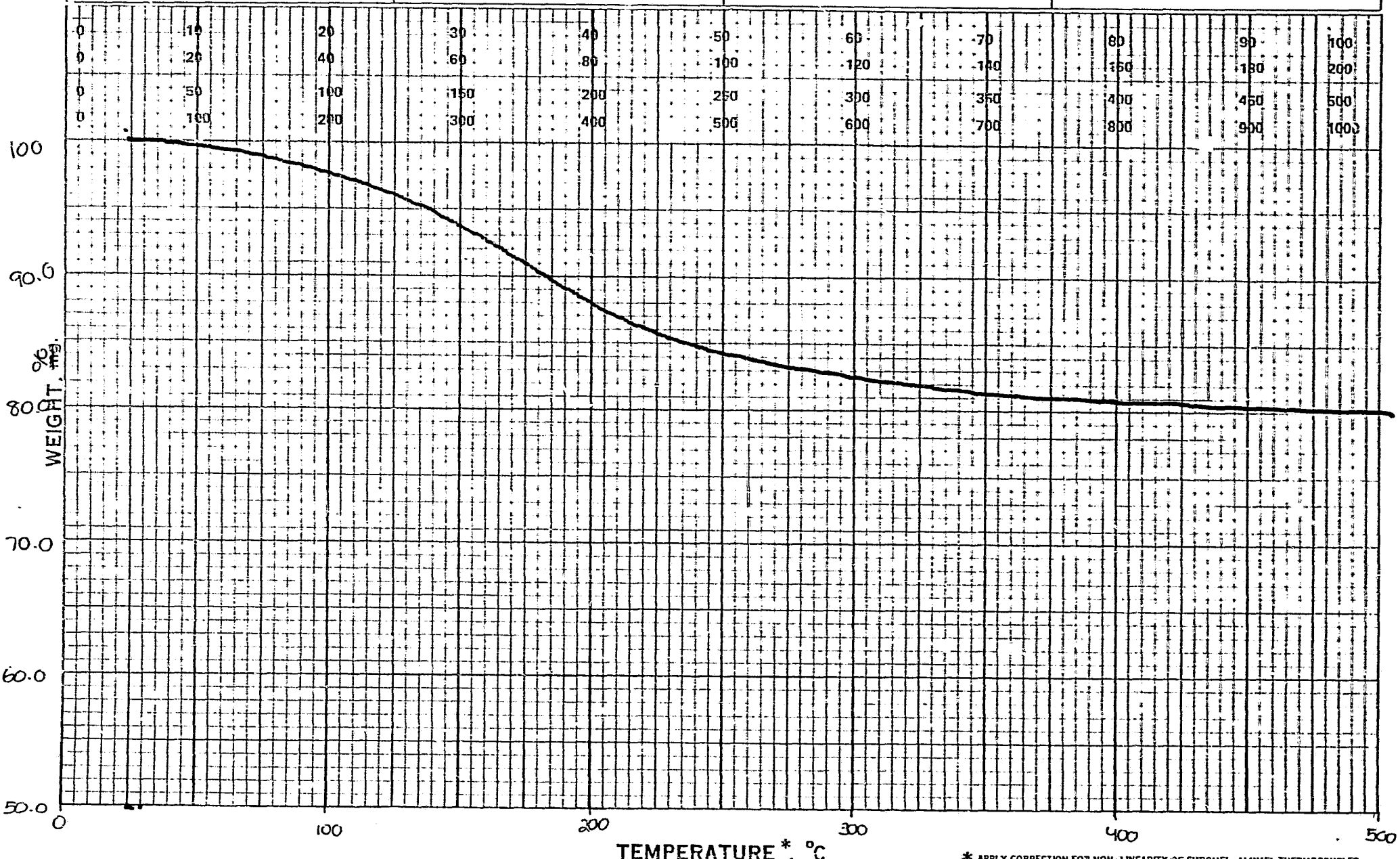


OMNITHERM CORPORATION

FIG. 12 Nasa 6031.2

PN-25680

| | | | |
|-----------------------|--|---------------------------------|--|
| SAMPLE: # Sample 5 | TEMP. SCALE <u>amb</u> °C <u>500</u> inch | SCALE <u>mg.</u> <u>inch</u> | RUN NO. <u>2126</u> DATE <u>10-10-84</u> |
| | SHIFT <u>20.1 mg</u> inch | (SCALE SETTING X 2) | OPERATOR <u>Chris F.</u> |
| ORIGIN: | TIME SCALE (ALT.) | SUPPRESSION <u>10.1</u> mg. | HEATING RATE <u>20</u> °C/min. |
| | | | ATM. <u>N₂ @ 40 cc/min</u> |
| | | | TIME CONSTANT <u>2</u> sec. |



* APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES



OMNITHERM CORPORATION

FIG. 13

NGSA 6031.2

PN-25680

SAMPLE:

Sample #6

ORIGIN:

(dark red)

X-AXIS

 TEMP. SCALE $\frac{\text{Amb-}}{500} \frac{^{\circ}\text{C}}{\text{inch}}$
 Spt wgt
 SHIFT 20.4 mg inch

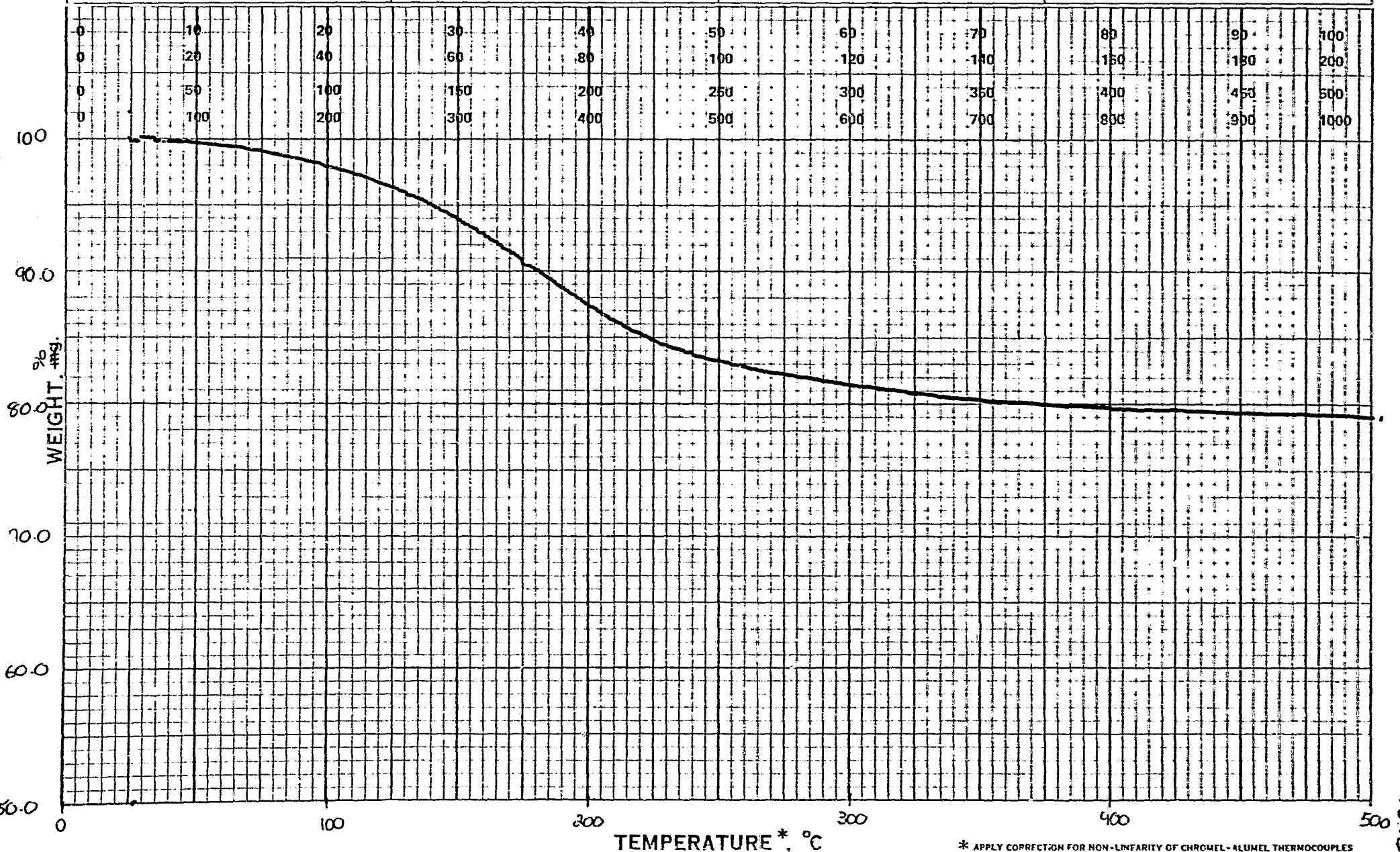
TIME SCALE (ALT.)

Y-AXIS

 SCALE $\frac{\text{mg.}}{\text{inch}}$
 (SCALE SETTING X 2)
SUPPRESSION 10.4 mg.

RUN NO. 2126 DATE 10-10-84

OPERATOR Chris F

HEATING RATE $20 \frac{^{\circ}\text{C}}{\text{min.}}$ ATM. $\text{N}_2 @ 40 \text{ cc/min}$ TIME CONSTANT 2 sec. 

* APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES



OMNITHERM CORPORATION

FIG. 14 NASA 6031.2

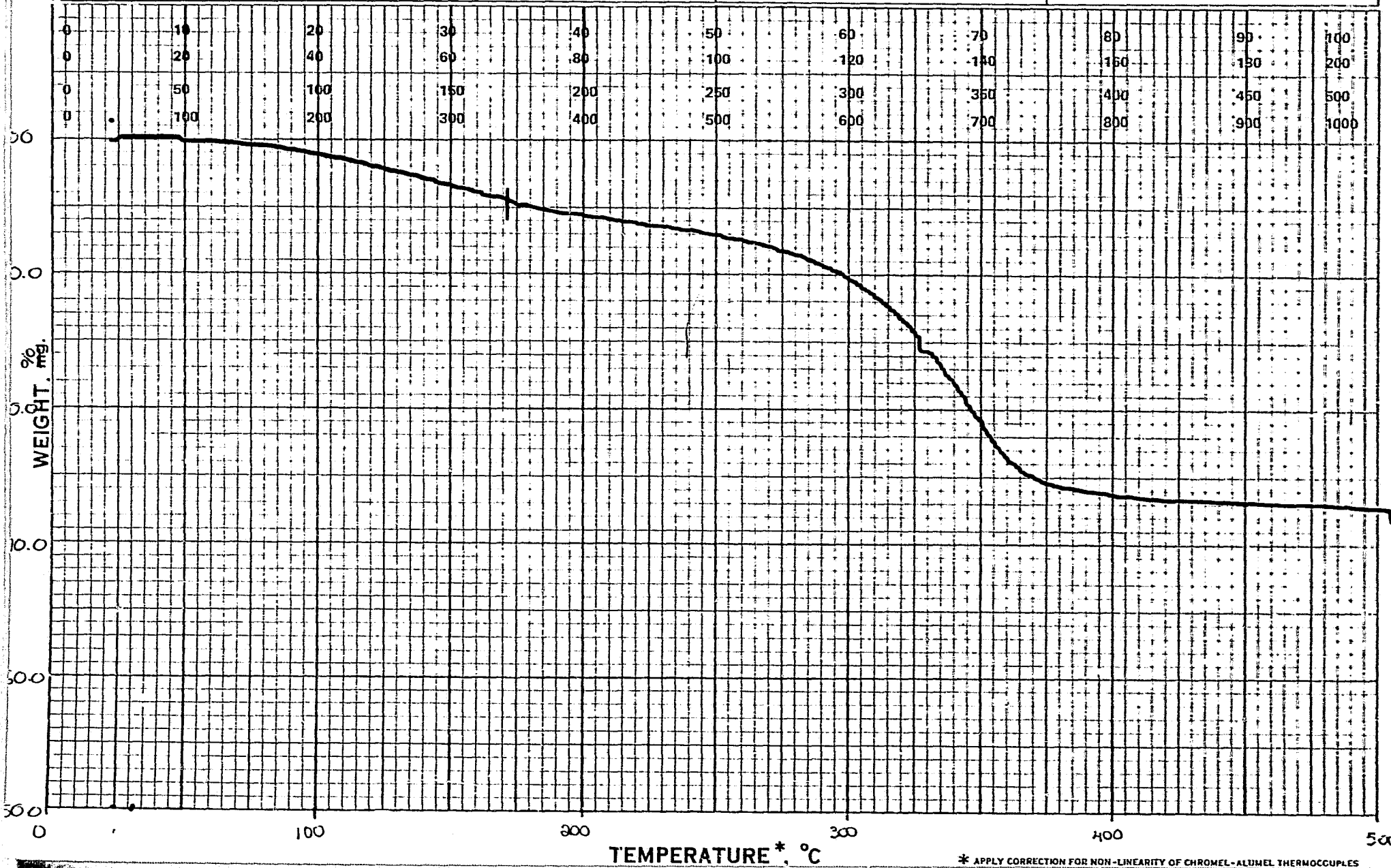
PN-25680

SAMPLE: Sample C (white)
ORIGIN:

X-AXIS
TEMP. SCALE ^{amb-} 500 °C
Sp. weight
SHIFT 20.3 mg. inch
TIME SCALE (ALT.)

Y-AXIS
SCALE _____ mg.
inch
(SCALE SETTING X 2)
SUPPRESSION ≈ 10.3 mg.

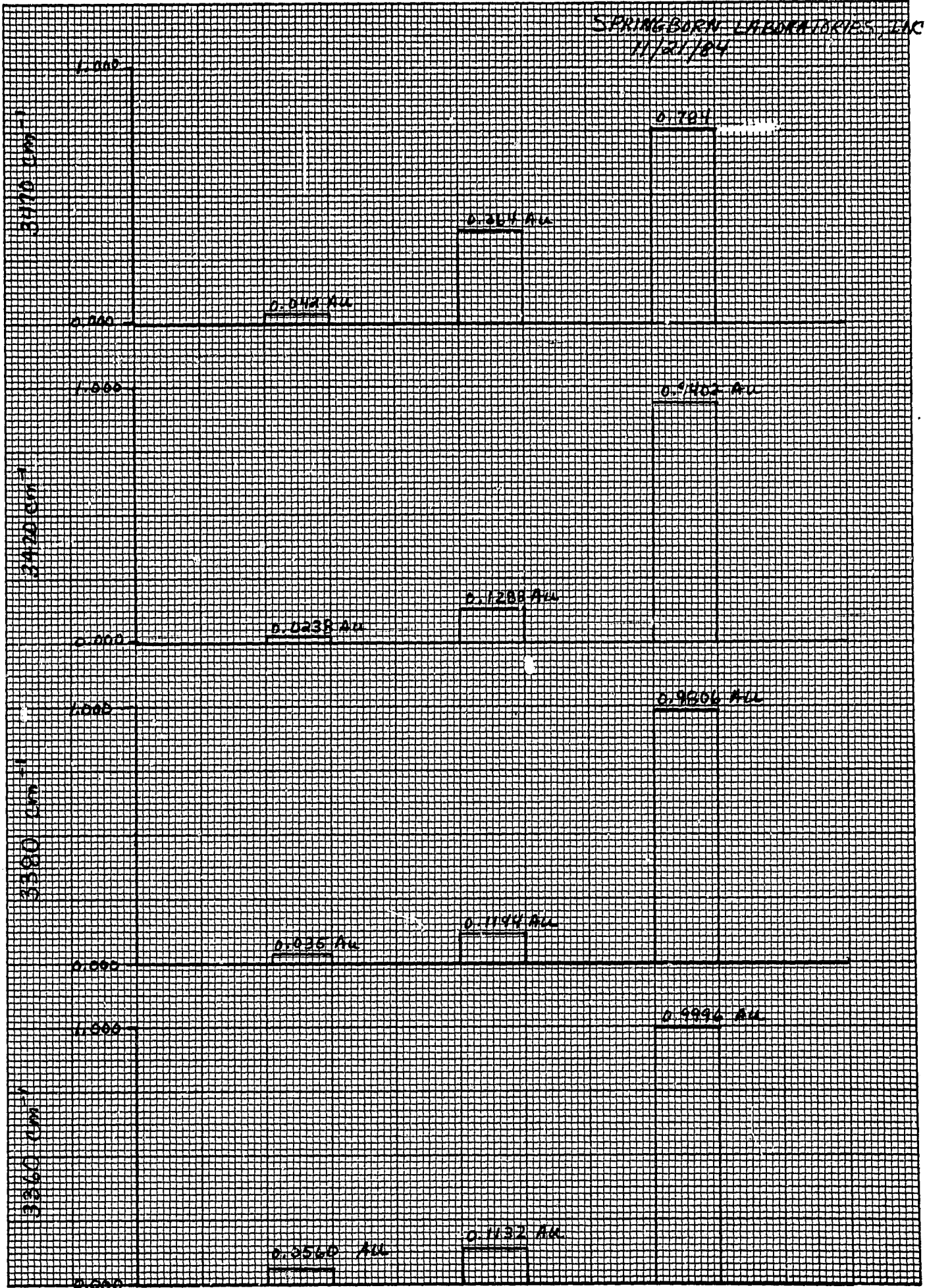
RUN NO. 2122 DATE 10-8-84
OPERATOR CHRIS F.
HEATING RATE 20 °C/min.
ATM. N₂ @ 40 cc/min
TIME CONSTANT 2 sec.



* APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES

FIG. 14

SPRINGBORN LABORATORIES, INC.
11/21/84



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Graph Paper

S3 83 HG

20 DIVISIONS PER INCH BOTH WAYS. 140 BY 200 DIVISIONS.

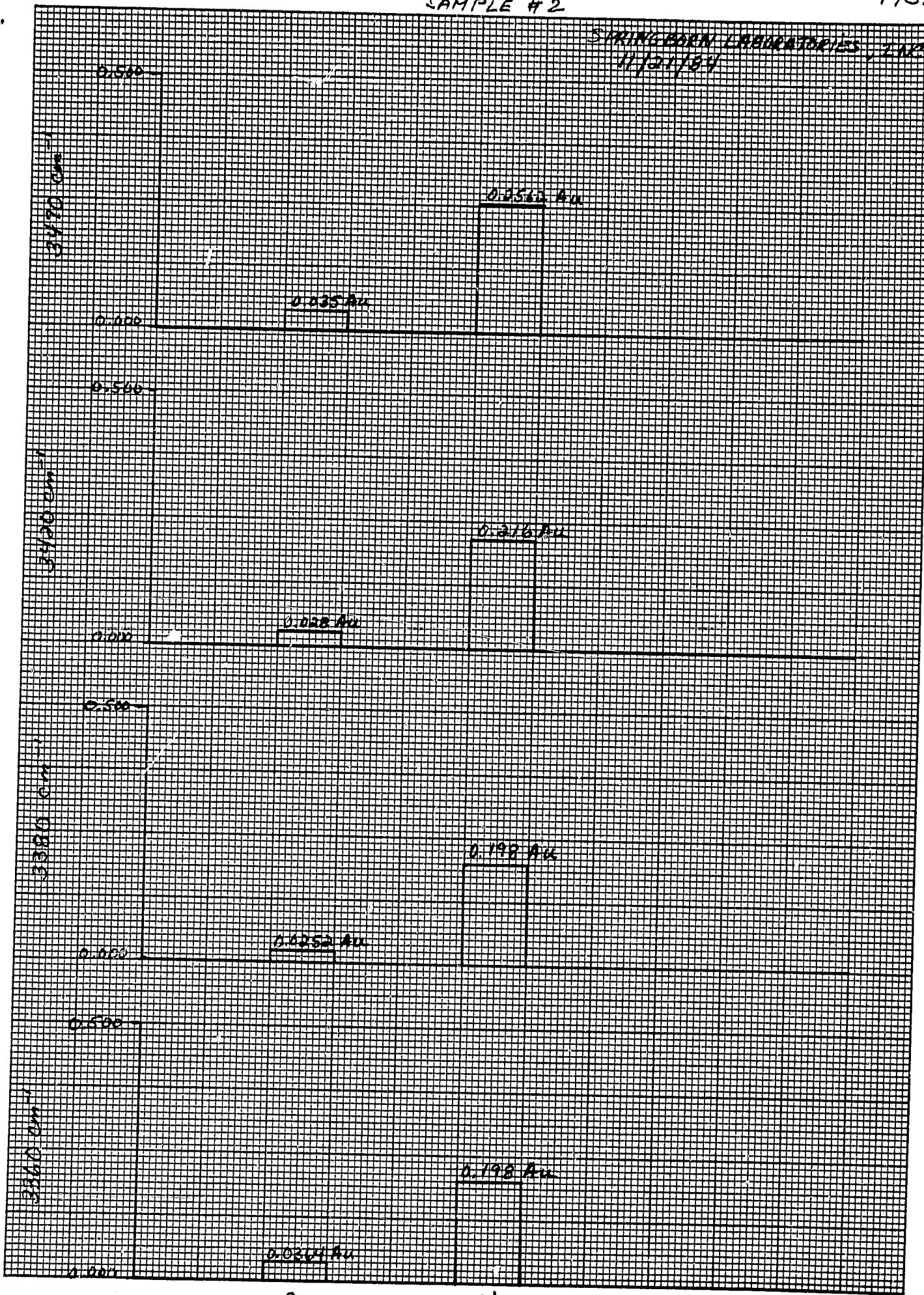
SAMPLE

1

1"

1"

SPRINGBORN LABORATORIES, INC.
11/21/54



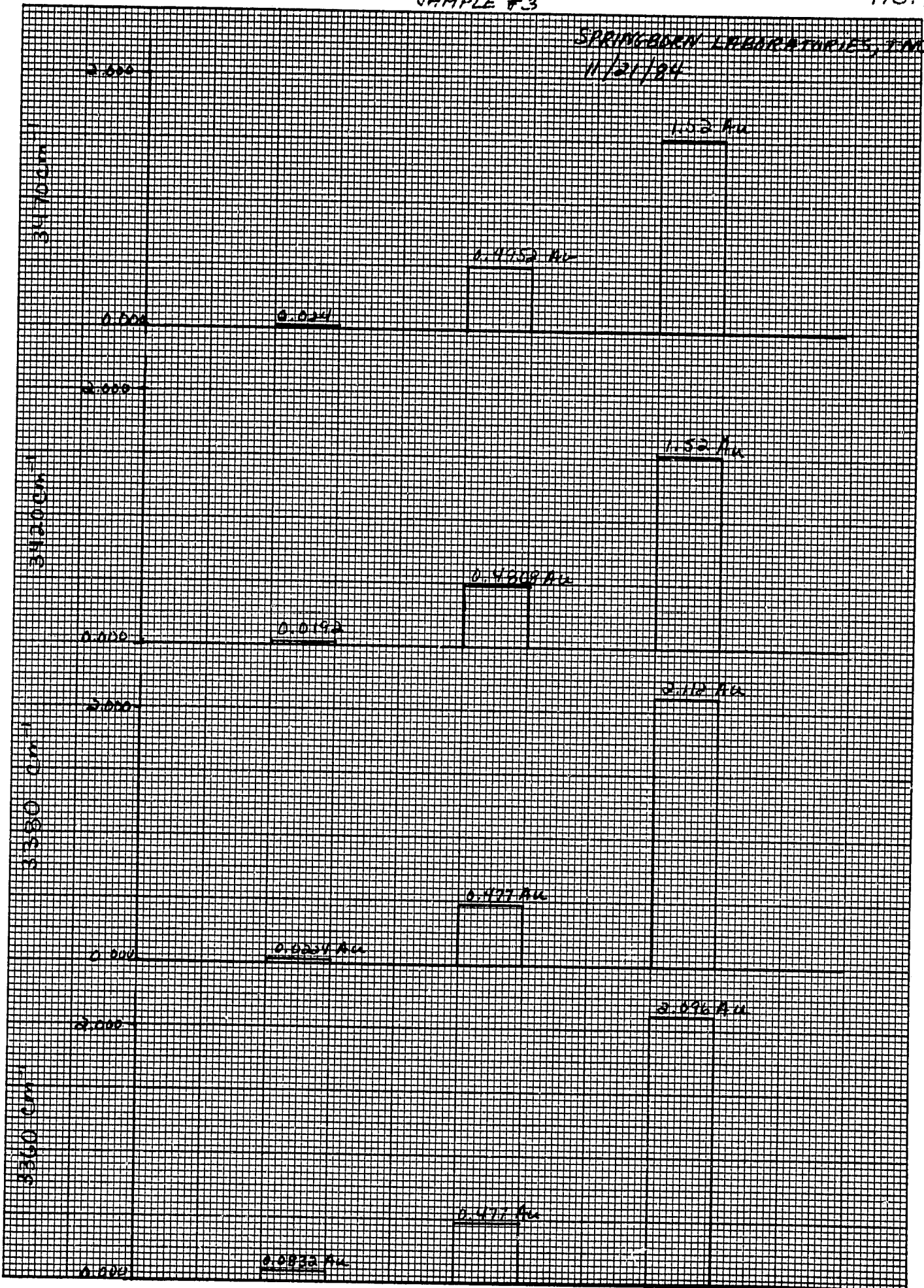
UNIVERSITY MICROFILMS CO., NORTHWOOD, MASS. 02062
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Graph Paper

2

2'

SPRINGDEN LABORATORIES, INC.
11/21/24



3

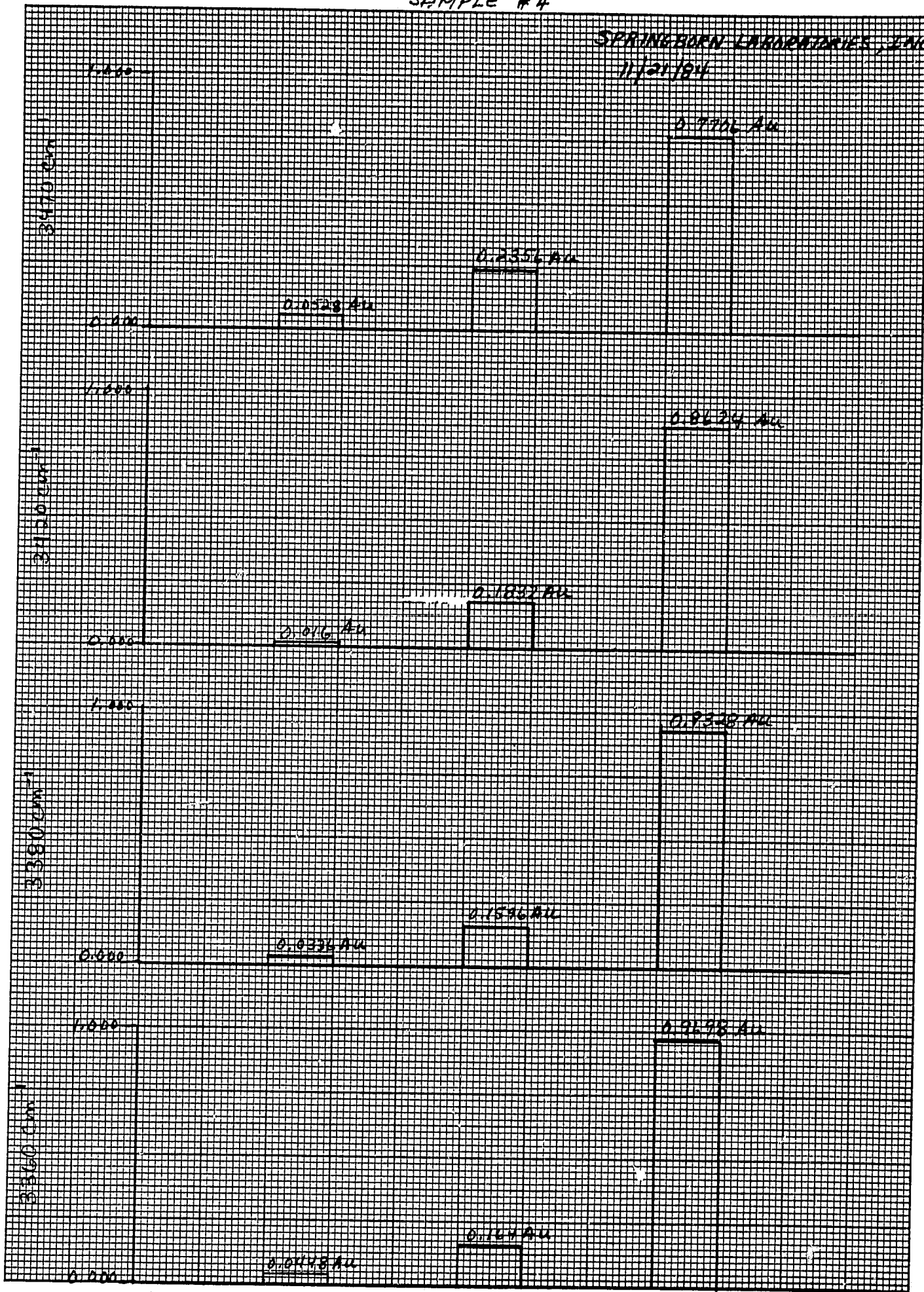
3'

3"

SPRINGBORN LABORATORIES, INC

7/21/84

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Graph Paper
PRINTED IN U.S.A.



4

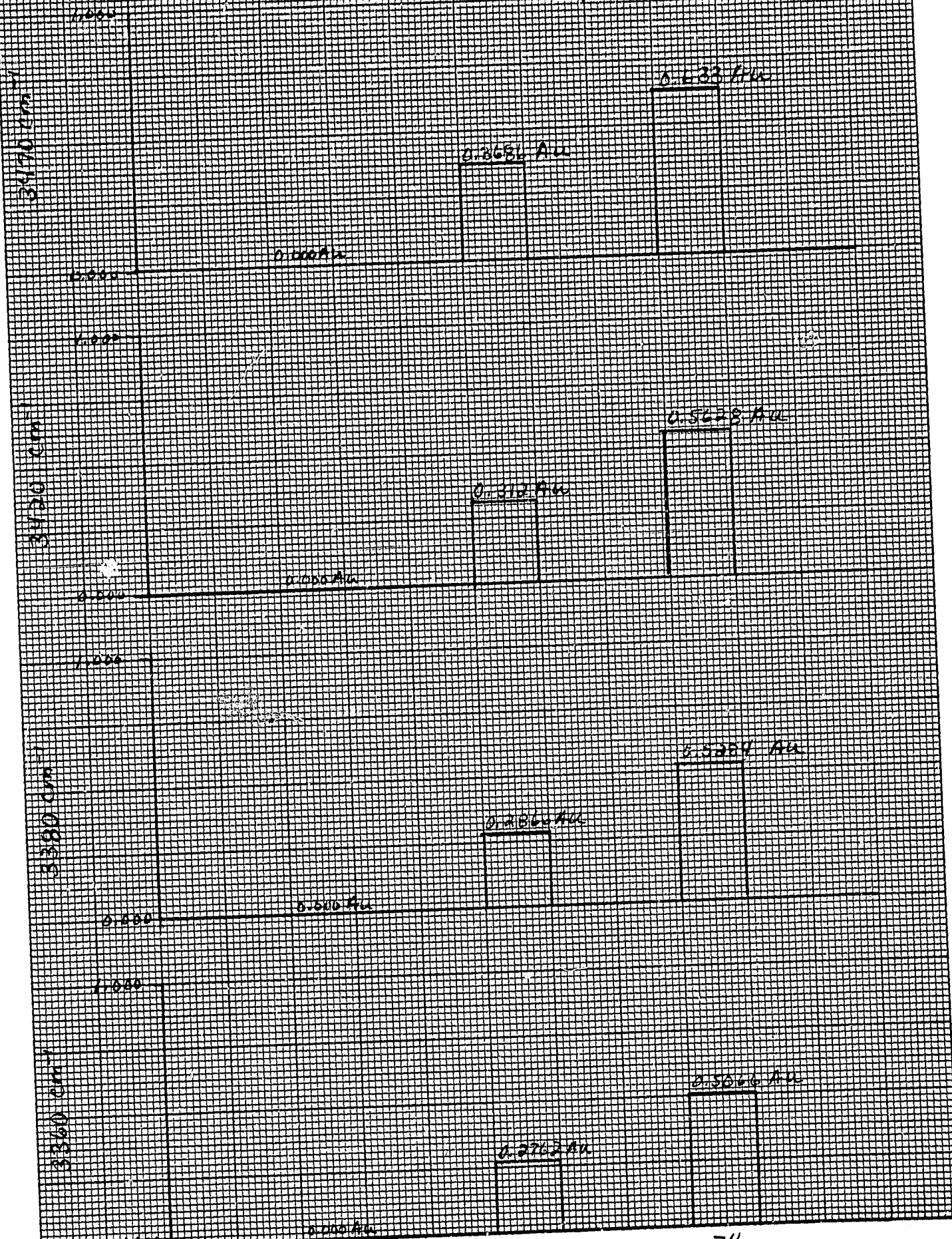
4'

4''

SAMPLE #5

SPRINGBORN LABORATORIES, INC.

11/21/84



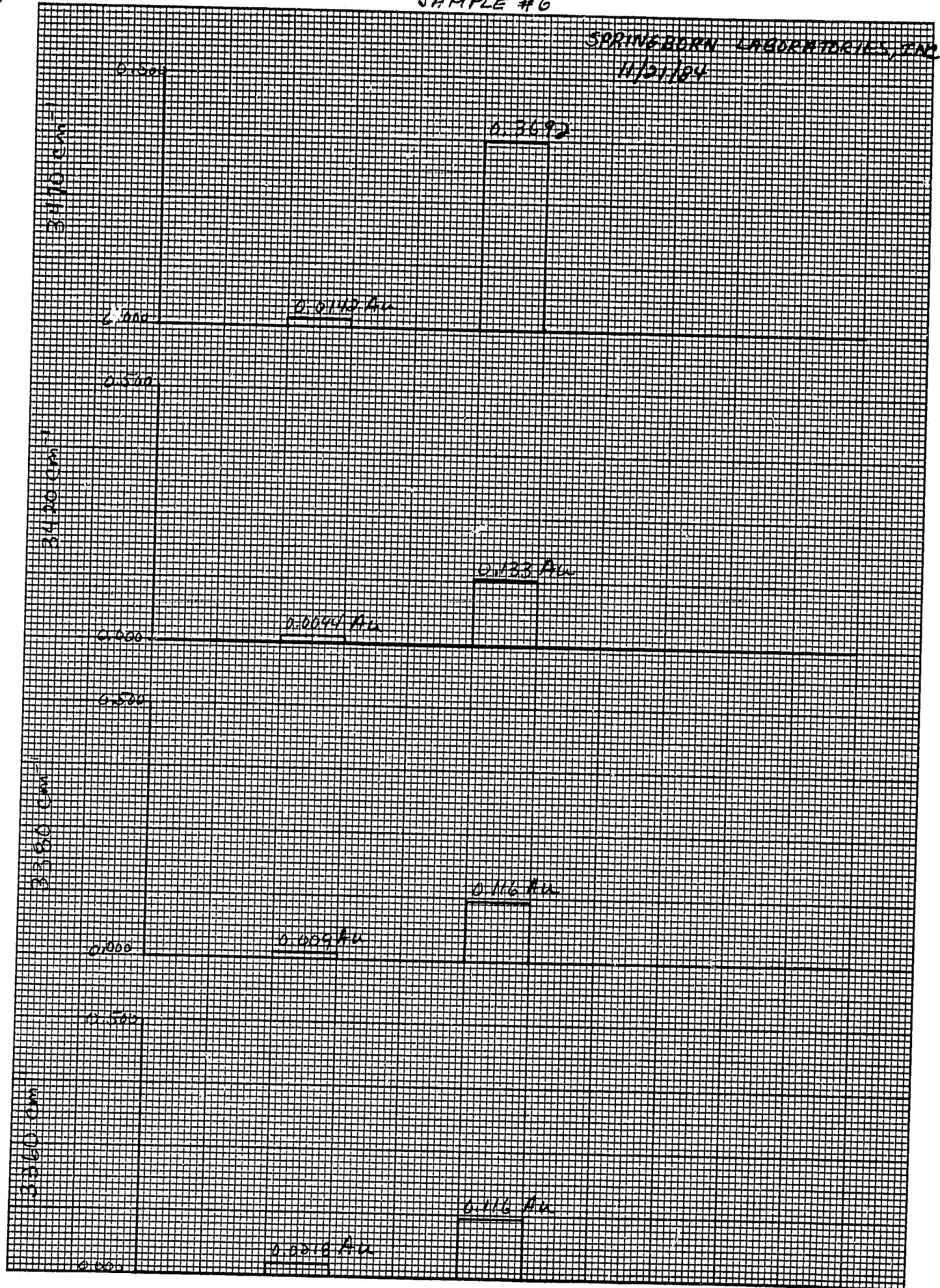
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CODEX Graph Paper

S3 83 HG

20 DIVISIONS PER INCH BOTH WAYS. 140 BY 200 DIVISIONS.

SPRINGBORN LABORATORIES, INC
11/21/84



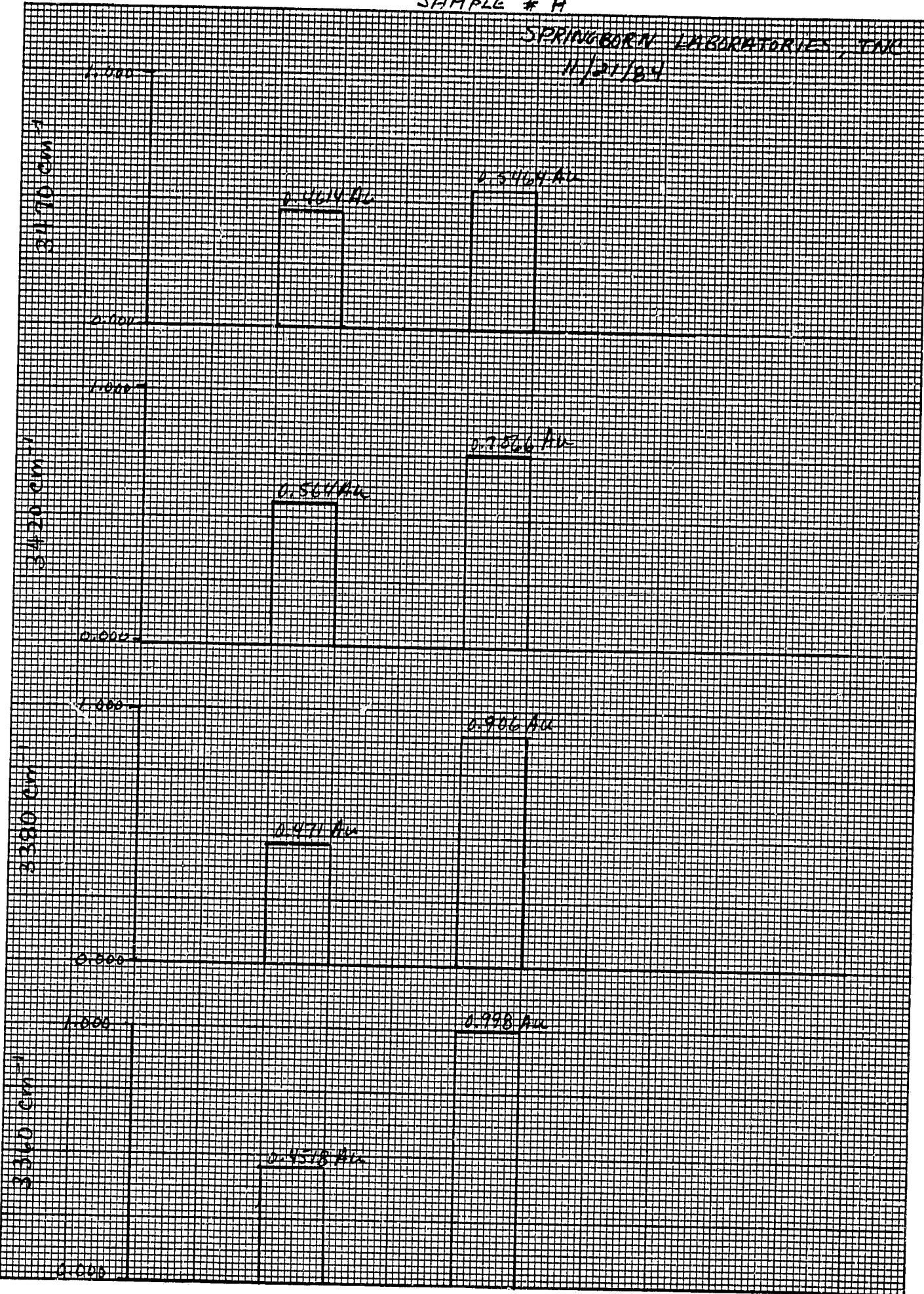
A

FIG. 21

SAMPLE # A

SPRINGBORN LABORATORIES, INC

11/21/54



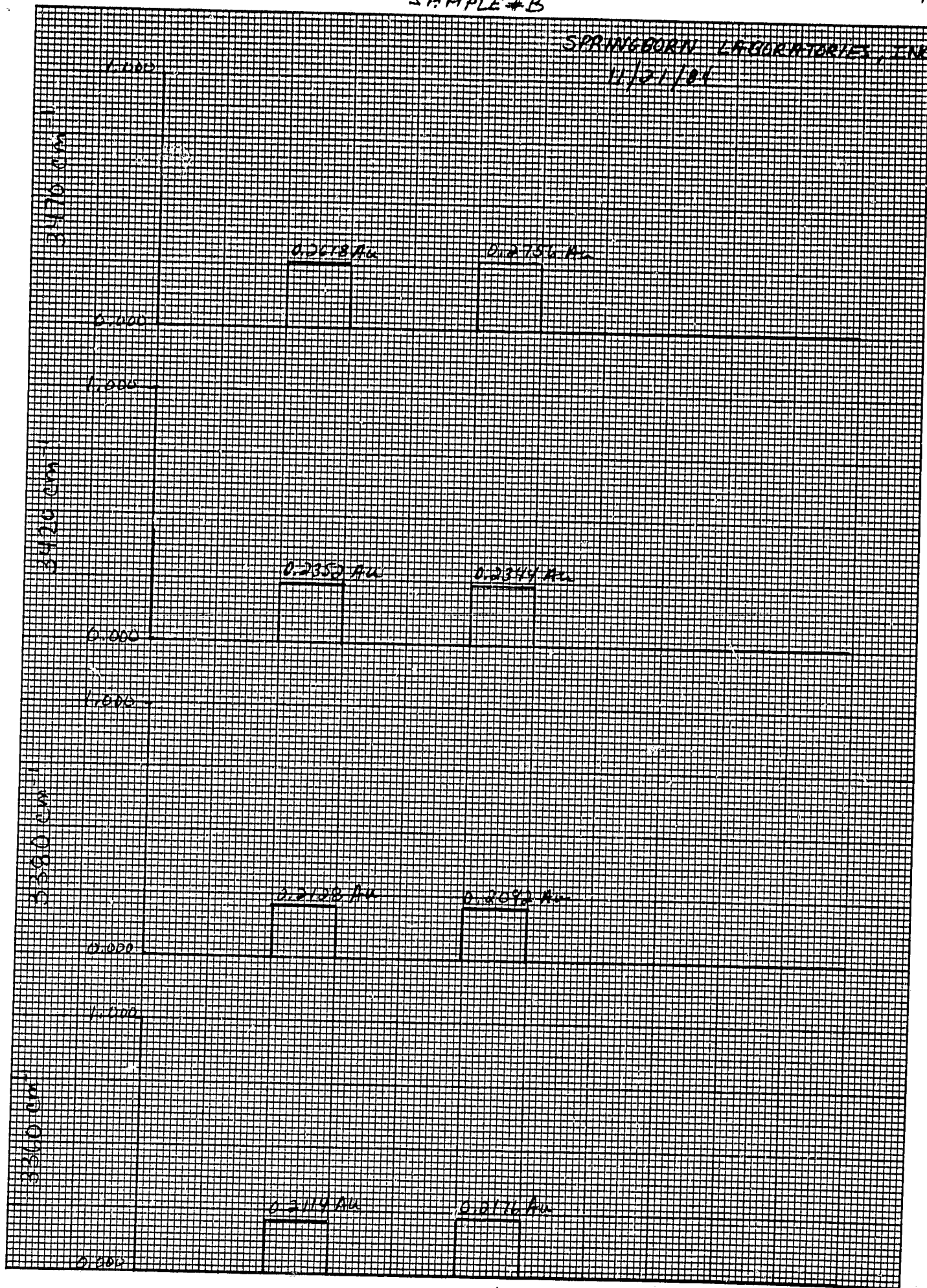
A

A'

SAMPLE #B

FIG. 21

SPRINGBORN LABORATORIES, INC.
11/21/04



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Graph Paper

S3 83 HG

LETTERS PRINTED BOTH WAYS. 140 BY 200 DIVISIONS.

SAMPLE # C

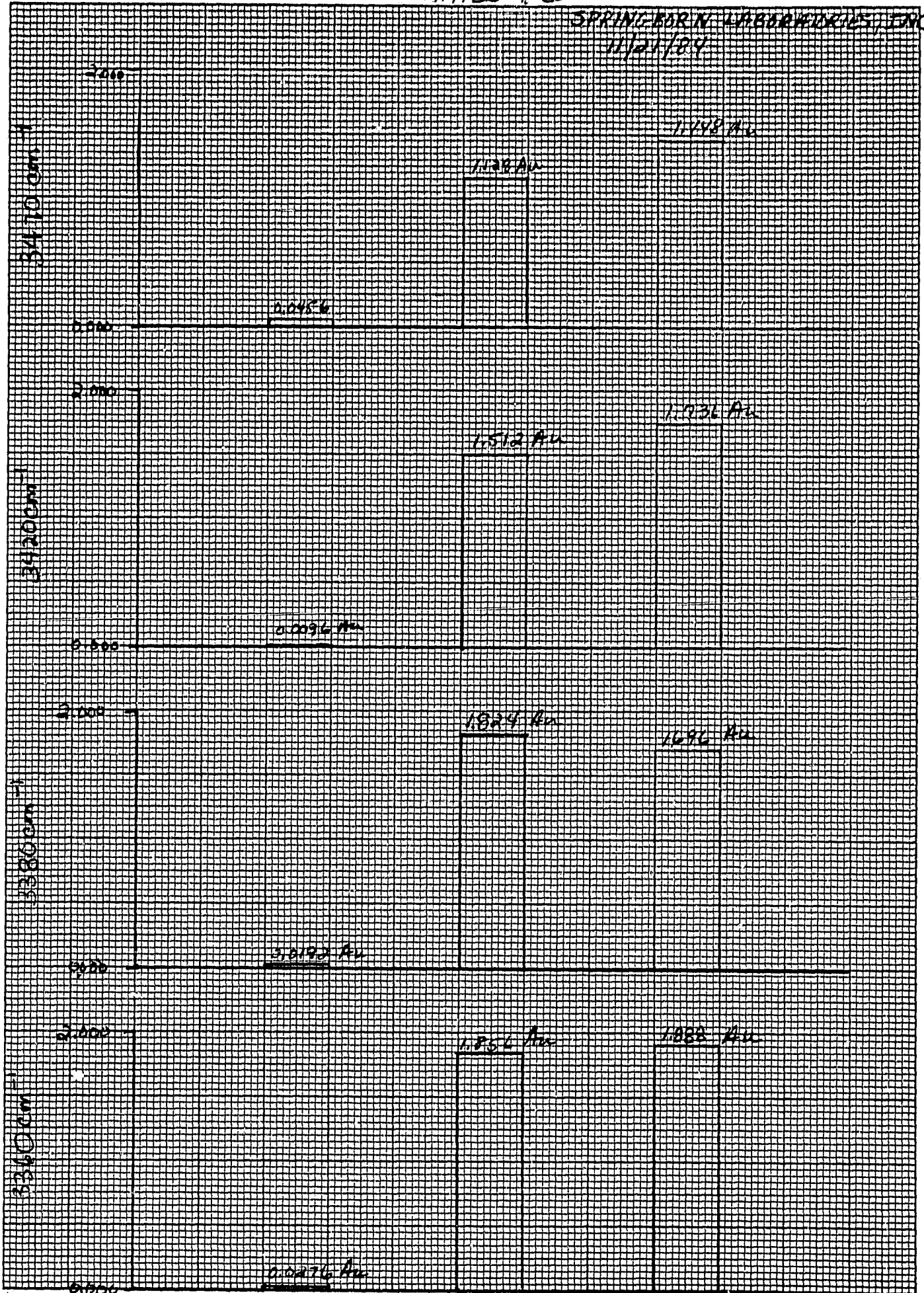
SPRINGBORN LABORATORIES, INC
11/21/84

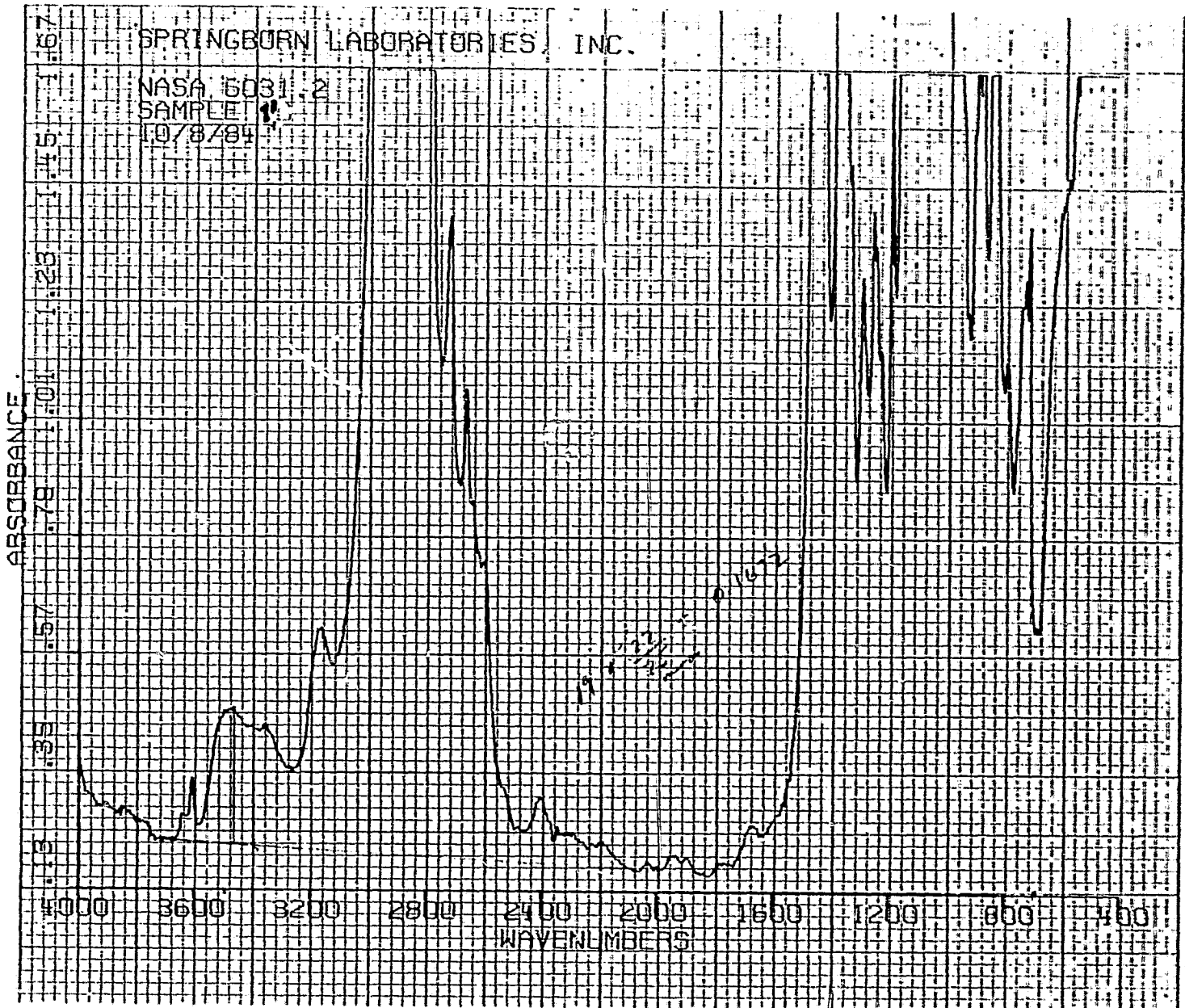
DIRECT FROM CODEX BOOK CO., NORWOOD, MASS. 02062
PRINTED IN U.S.A.

CODEX
Graph Paper

S3 83 HG

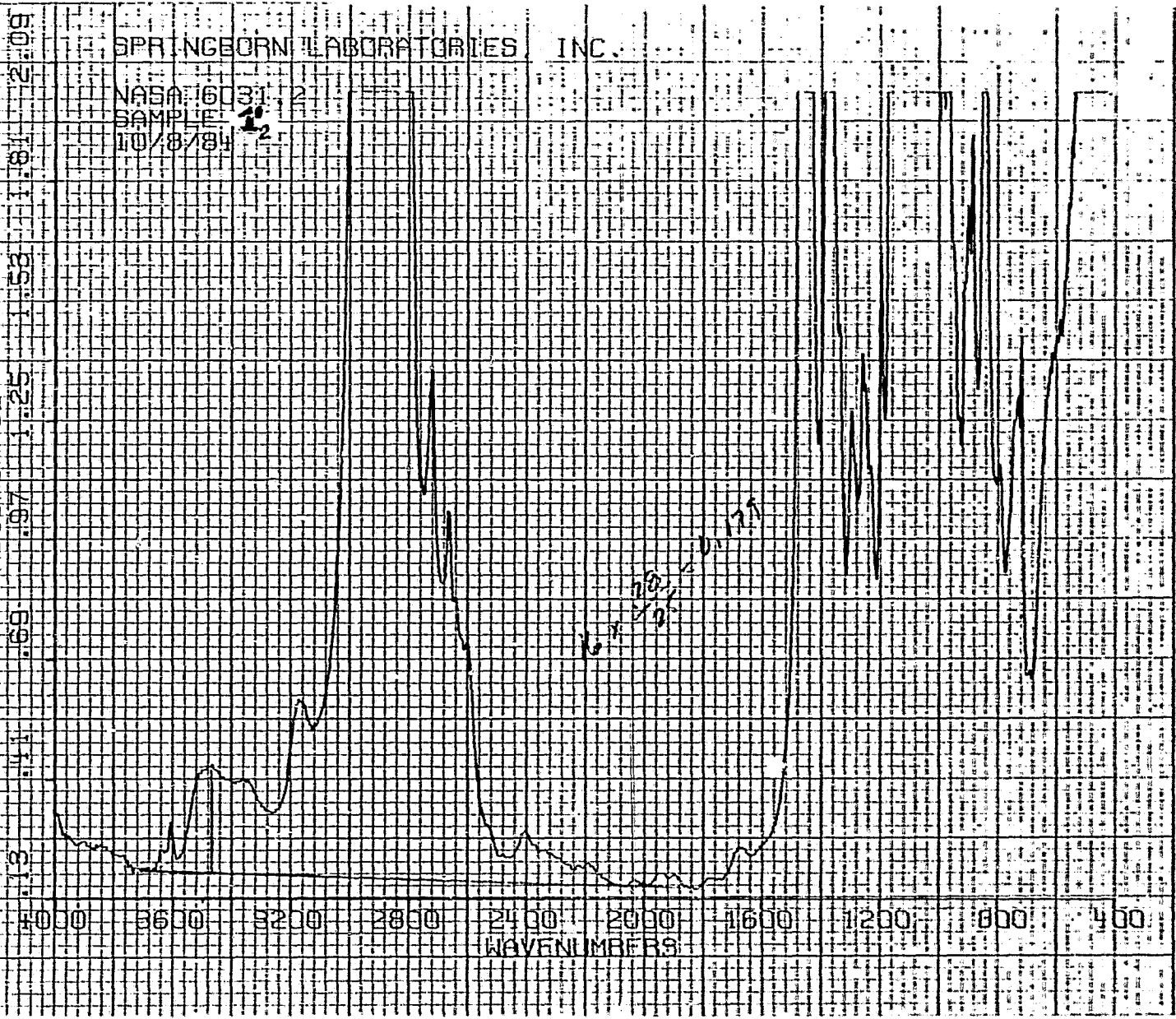
20 DIVISIONS PER INCH BOTH WAYS. 140 BY 200 DIVISIONS.





76 24

ABSORBANCE

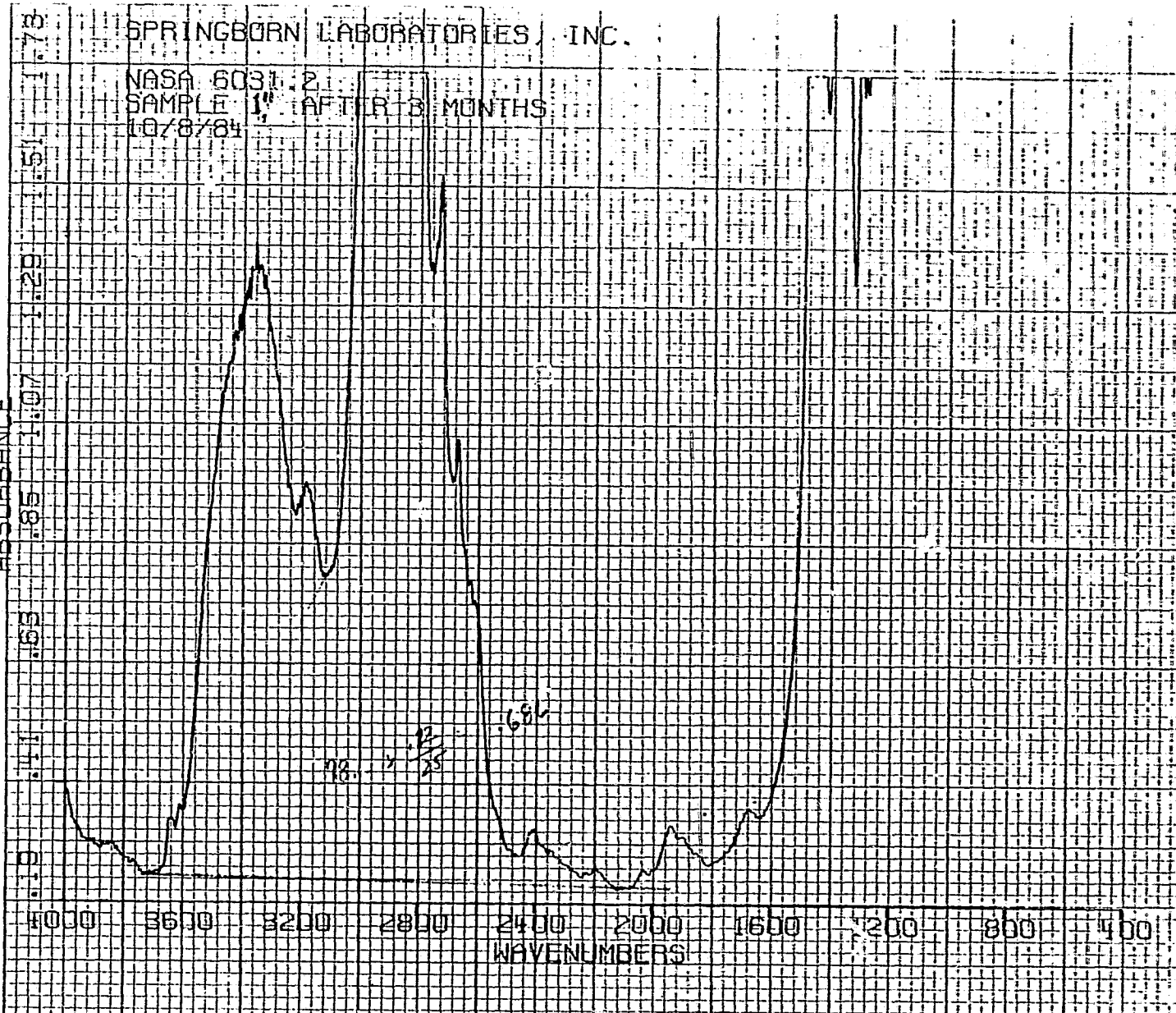


7625

SPRINGBORN LABORATORIES, INC.

NASA 6031-2
SAMPLE 1 AFTER 3 MONTHS
1078784

ABSORBANCE



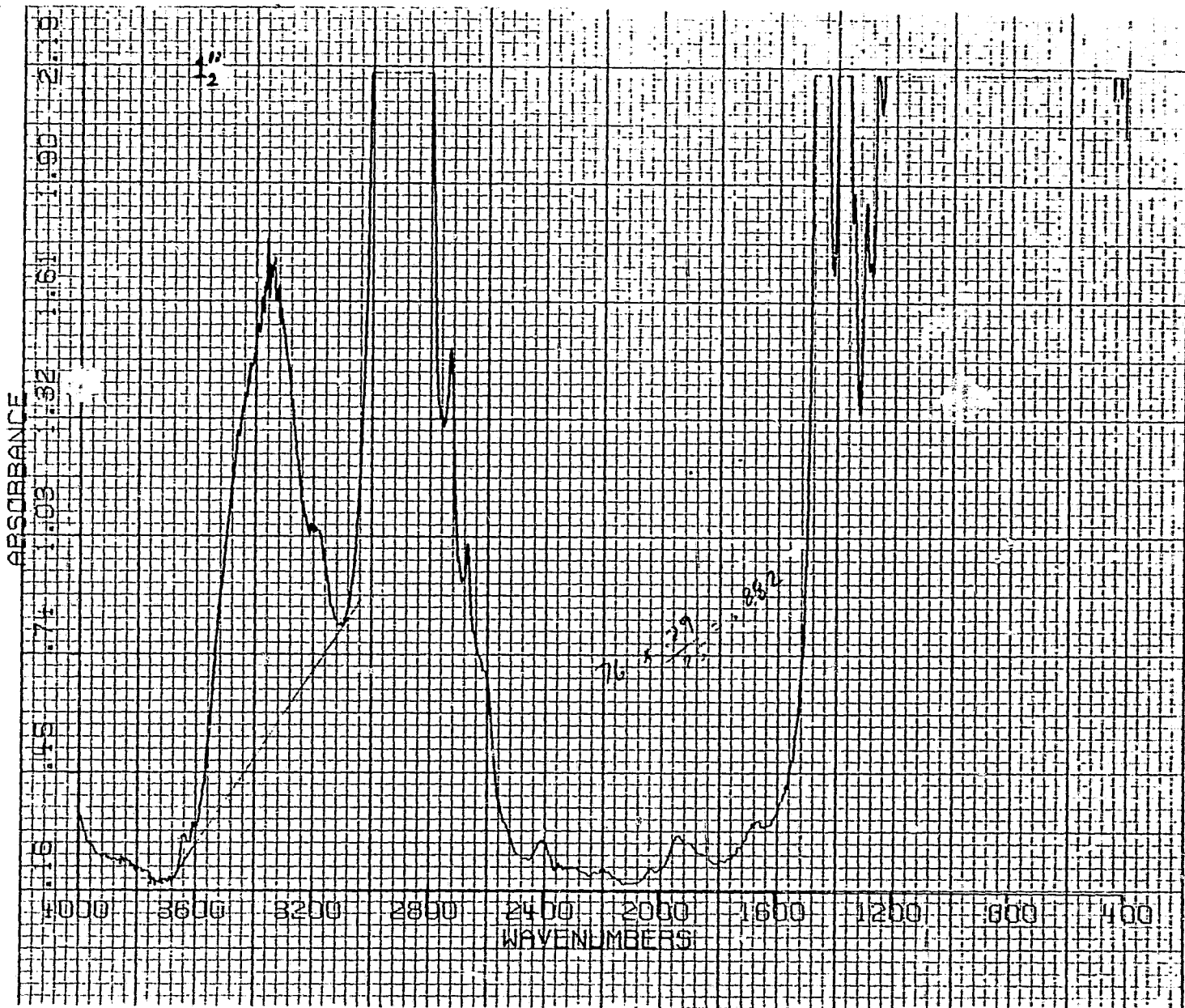
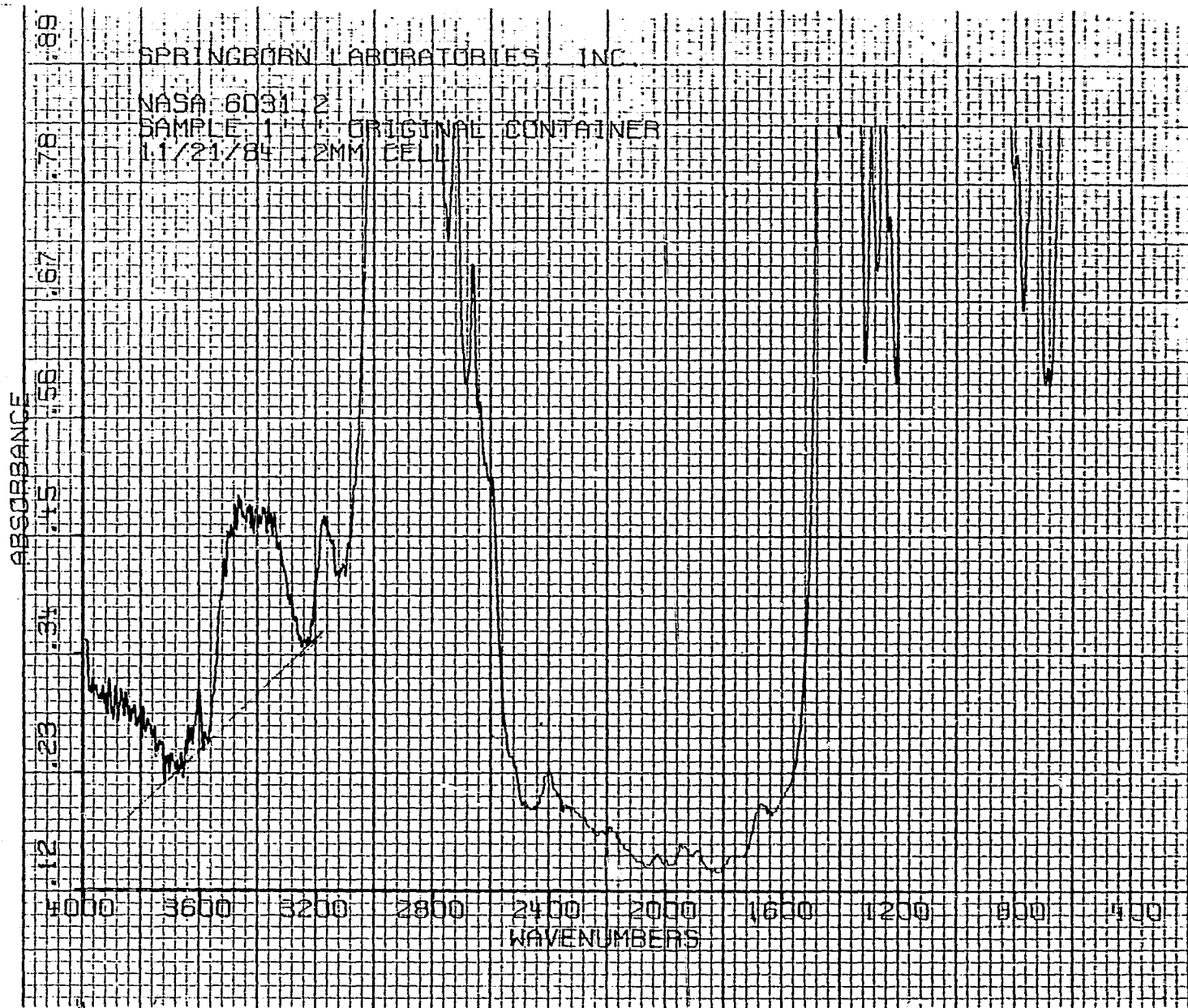


Fig 27



SPRINGBORN LABORATORIES, INC.

NASA 60301-2
SAMPLE 1-1 SEALED VIAL UNDER NO. 771170

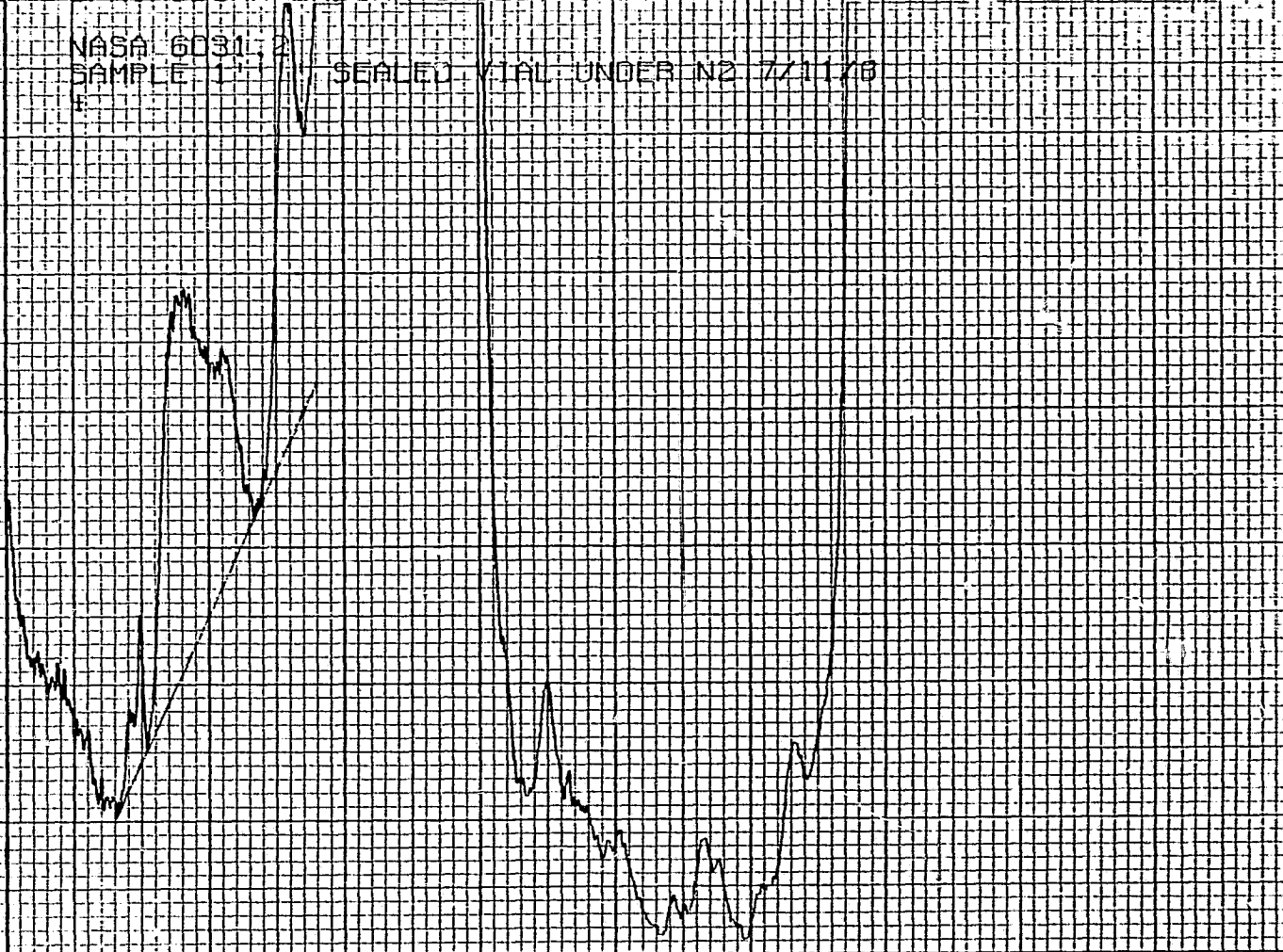
ABSORBANCE

.44
.40
.35
.31
.27
.22
.18
.14

4000 3600 3200 2800 2400 2000 1600 1200 800 400

WAVENUMBERS

HC 29

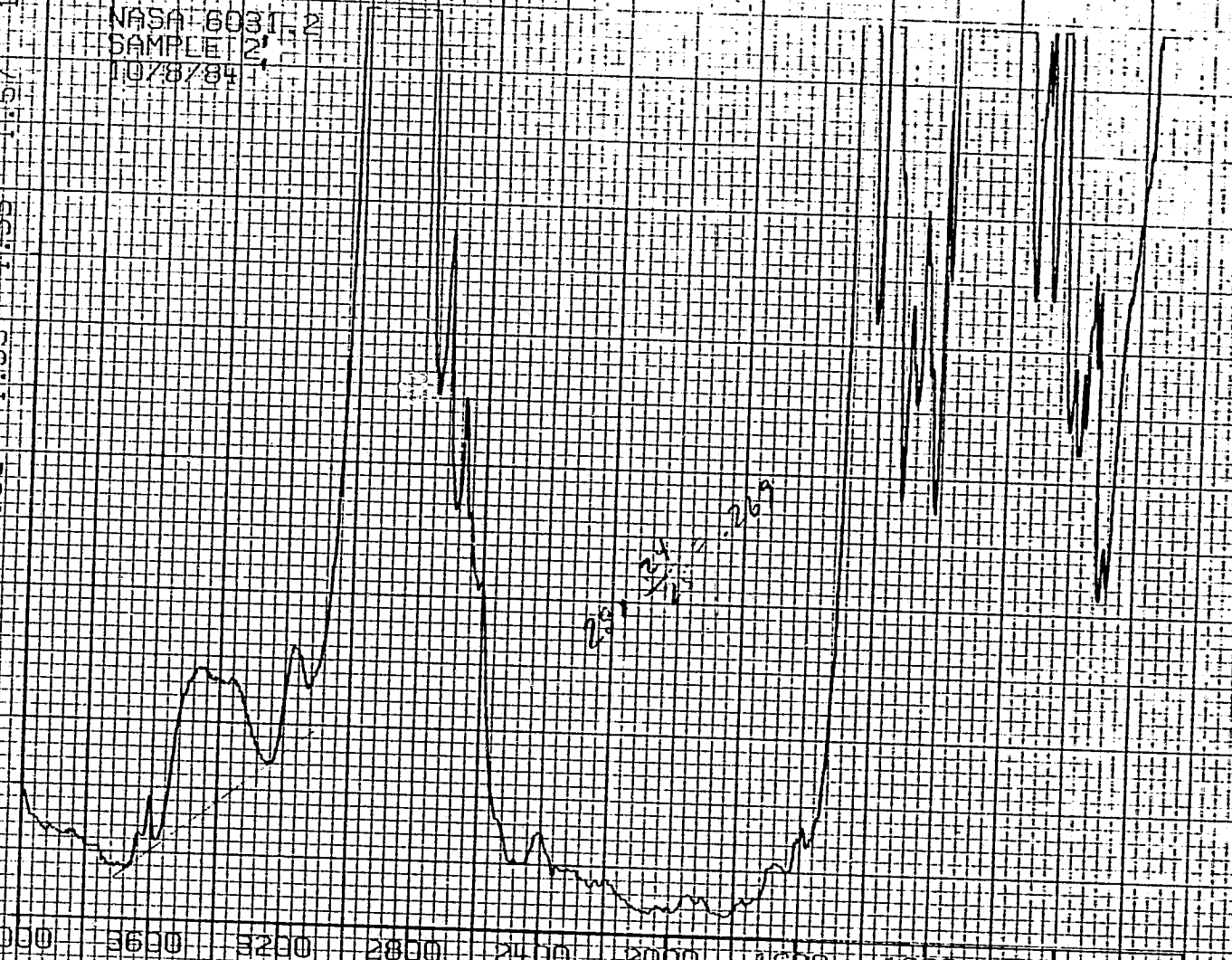


SPRINGBORN LABORATORIES, INC.

NASA 6031-2
SAMPLE 2
1078784

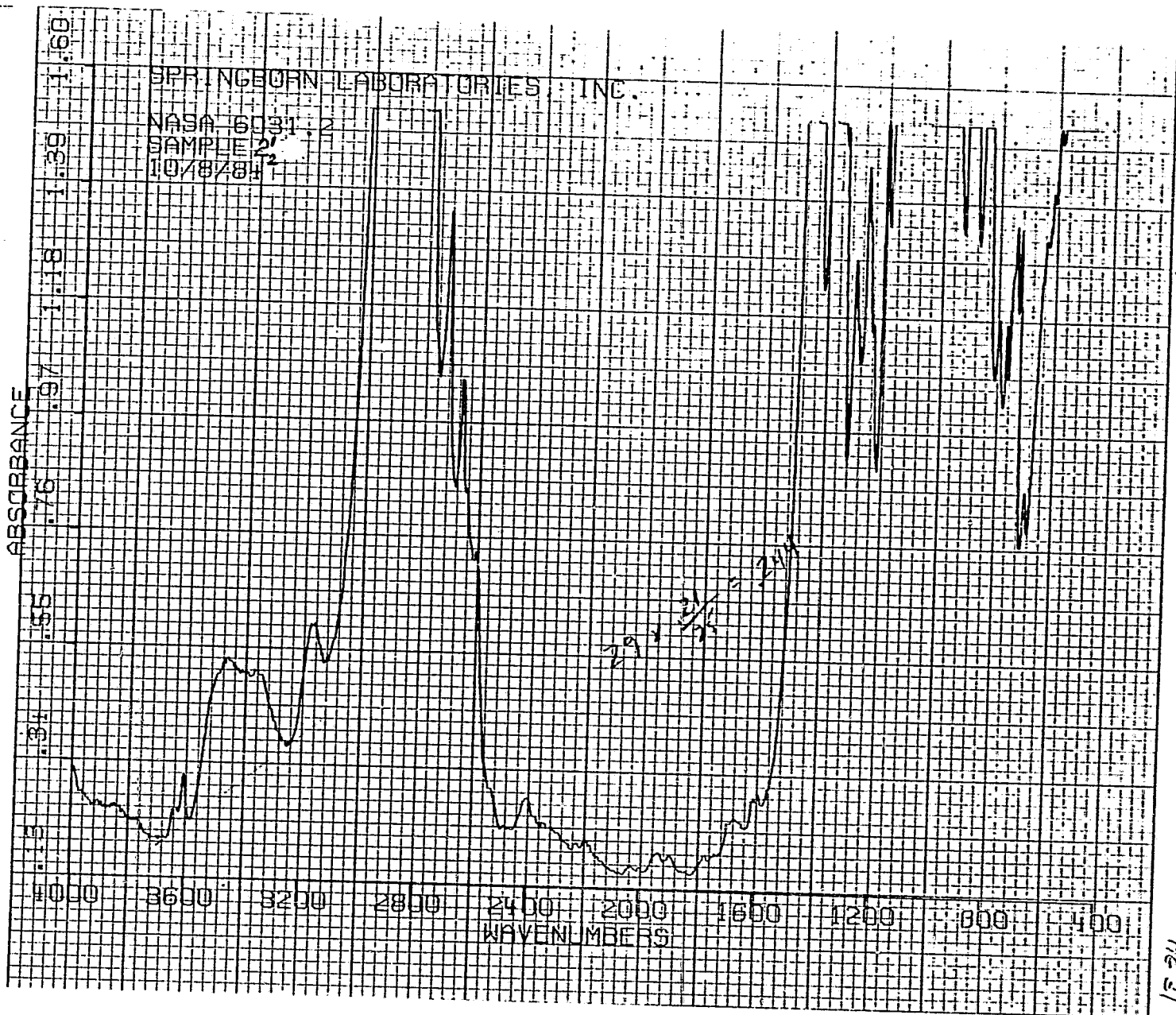
ABSORBANCE

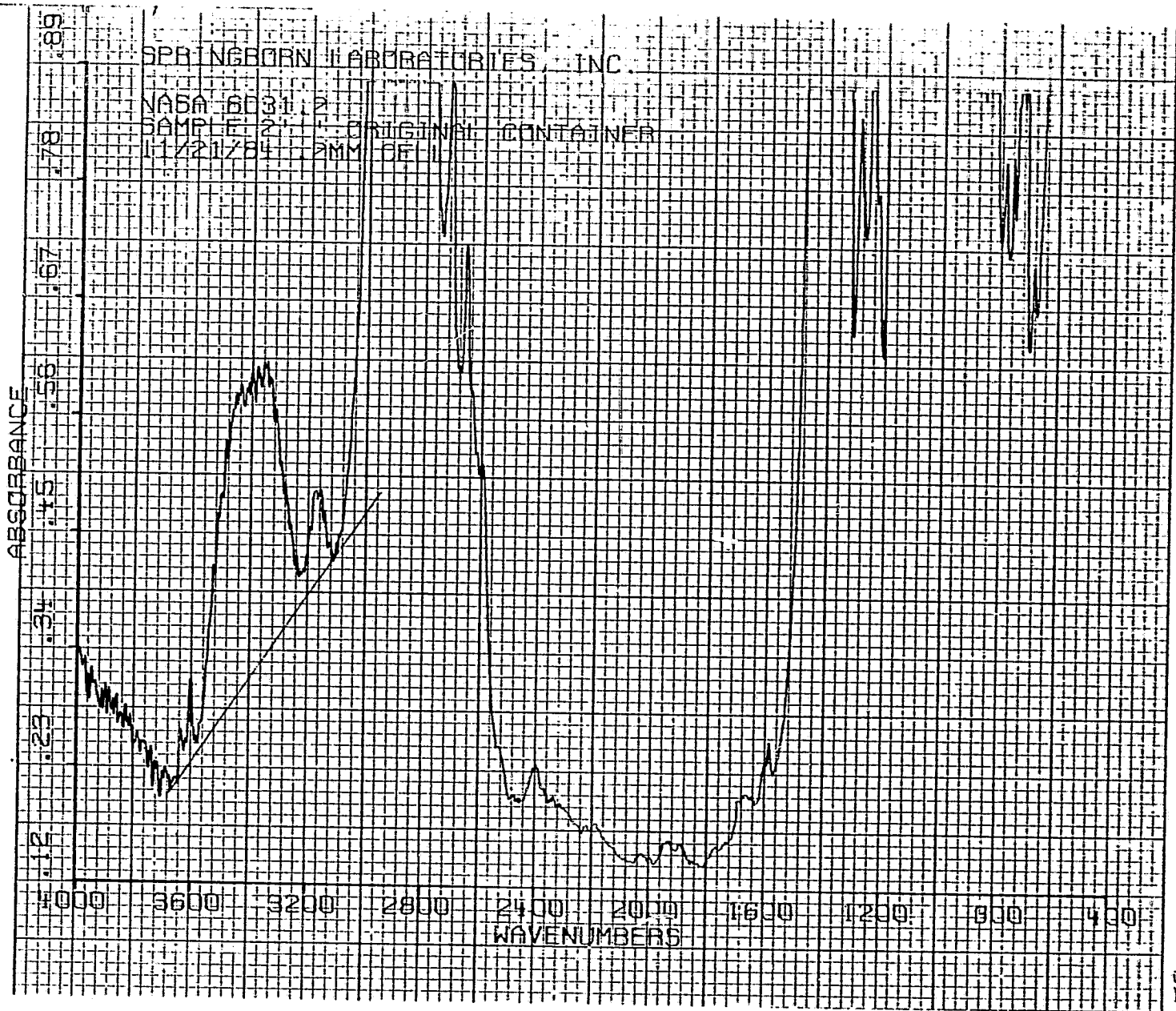
1.81
1.57
1.33
1.09
.85
.61
.37
.13

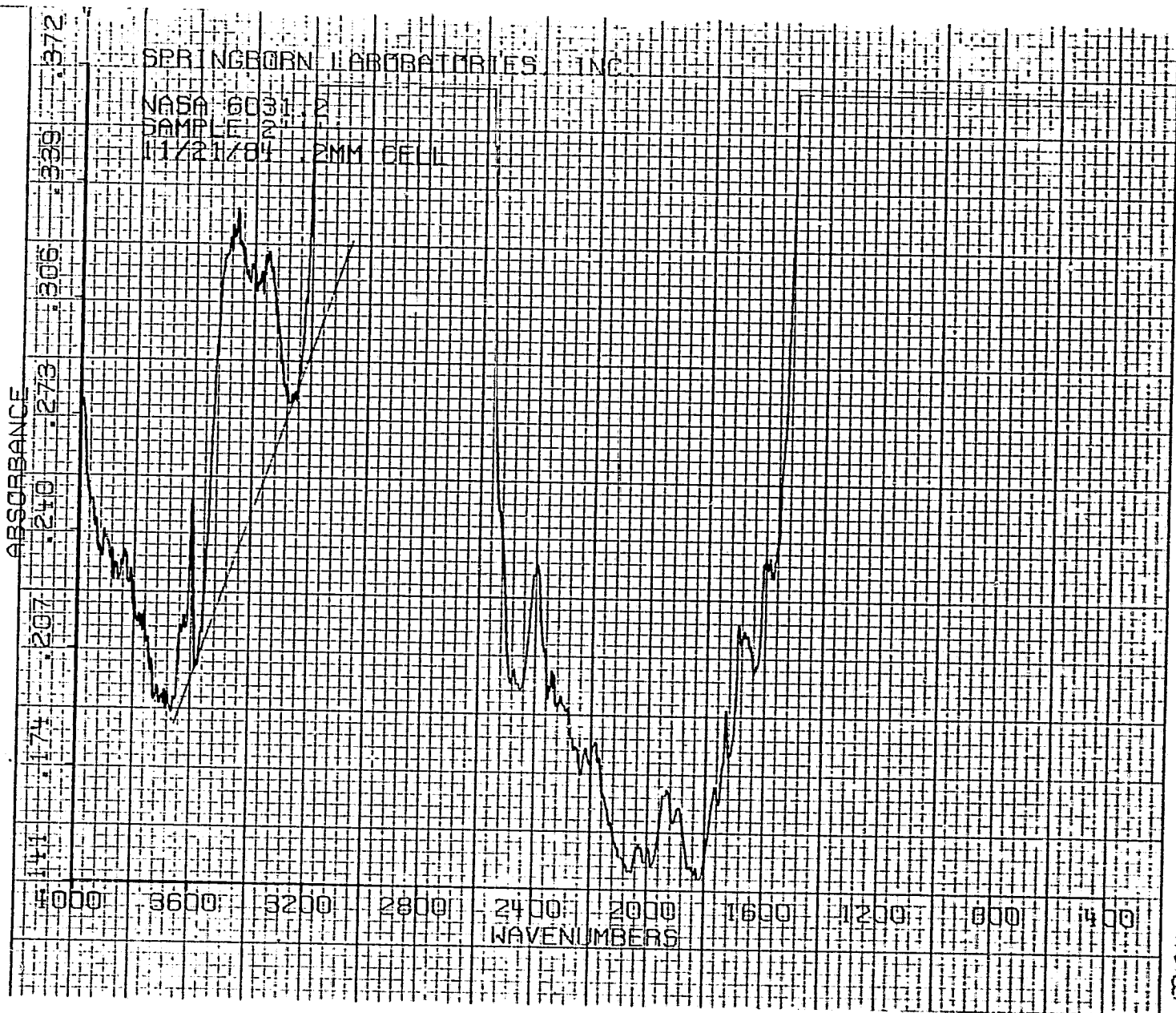


4000 3600 3200 2800 2400 2000 1600 1200 800 400
WAVENUMBERS

76.30







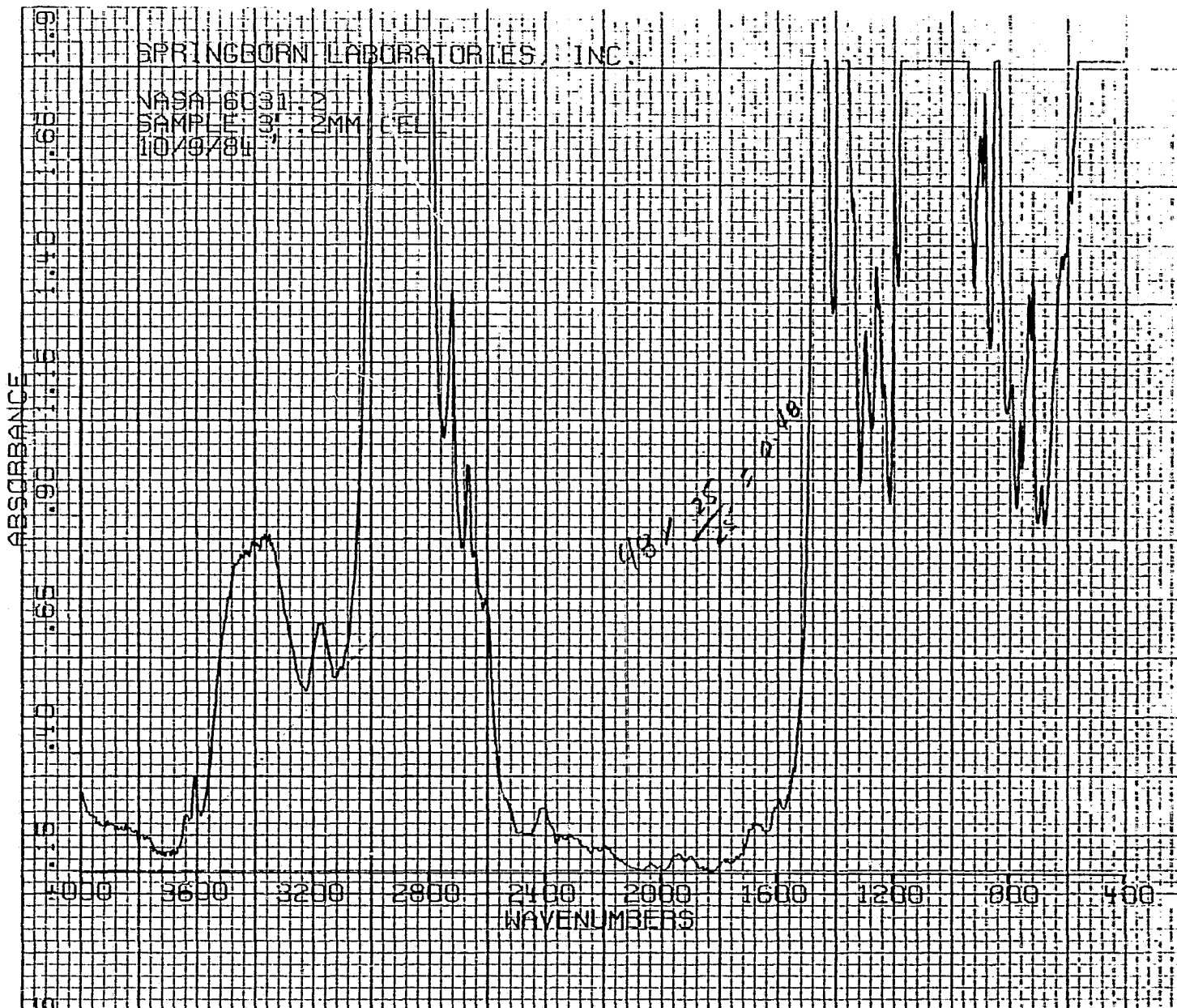
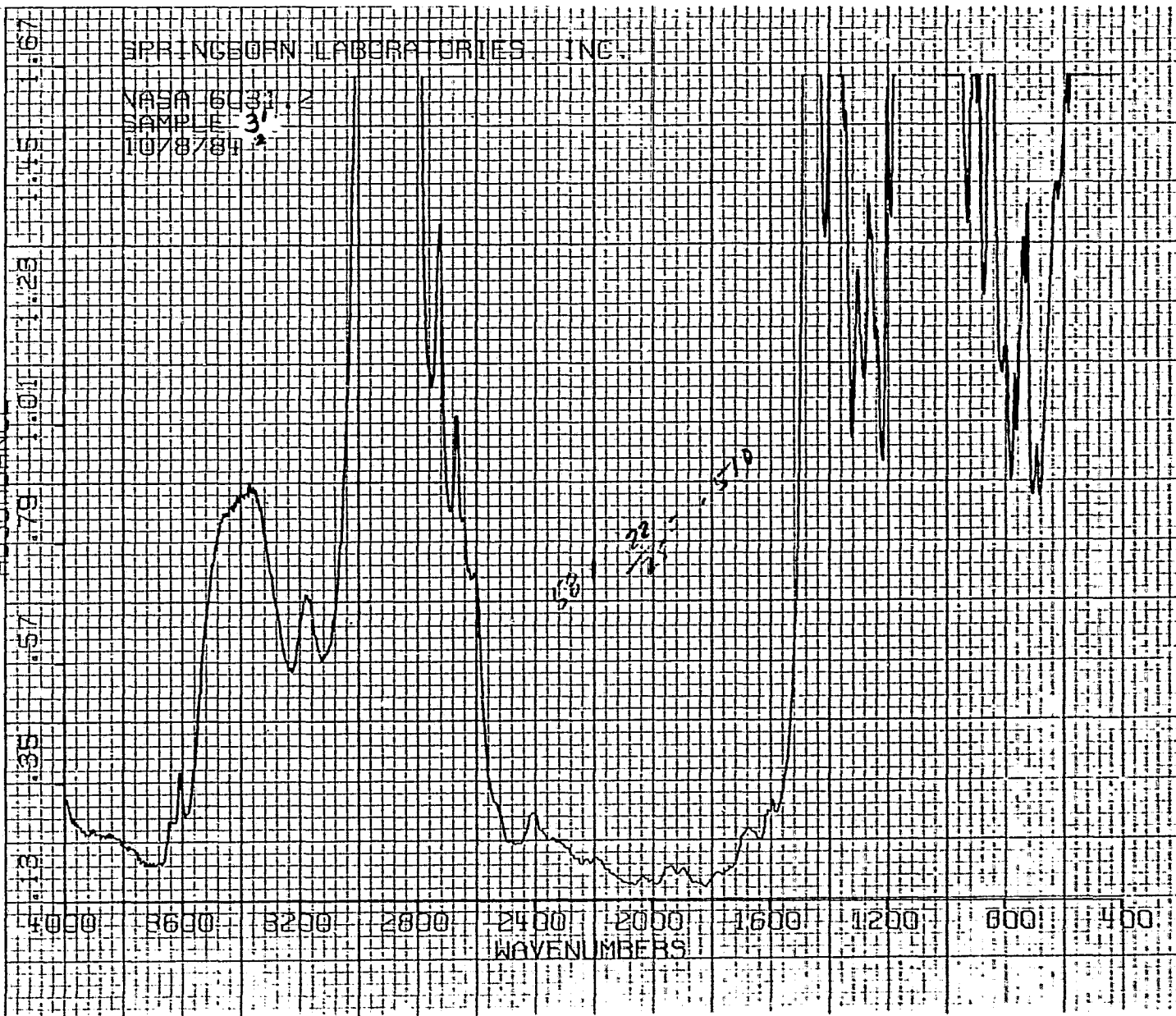


Fig 34

ABSORBANCE



5635

SPRINGBORN LABORATORIES, INC.

NASA 160 31 2
SAMPLE 37 2
1078784

ABSORBANCE

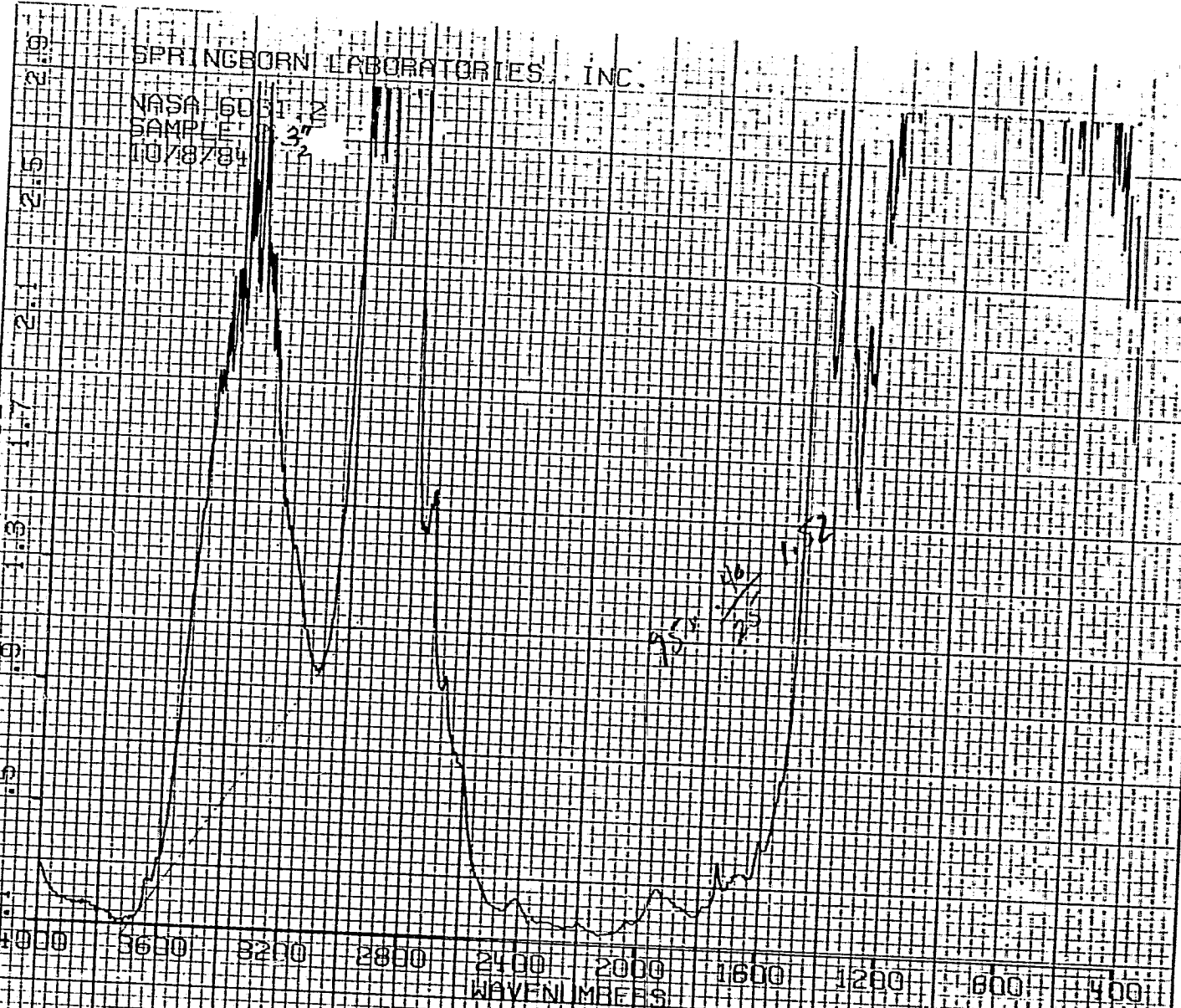
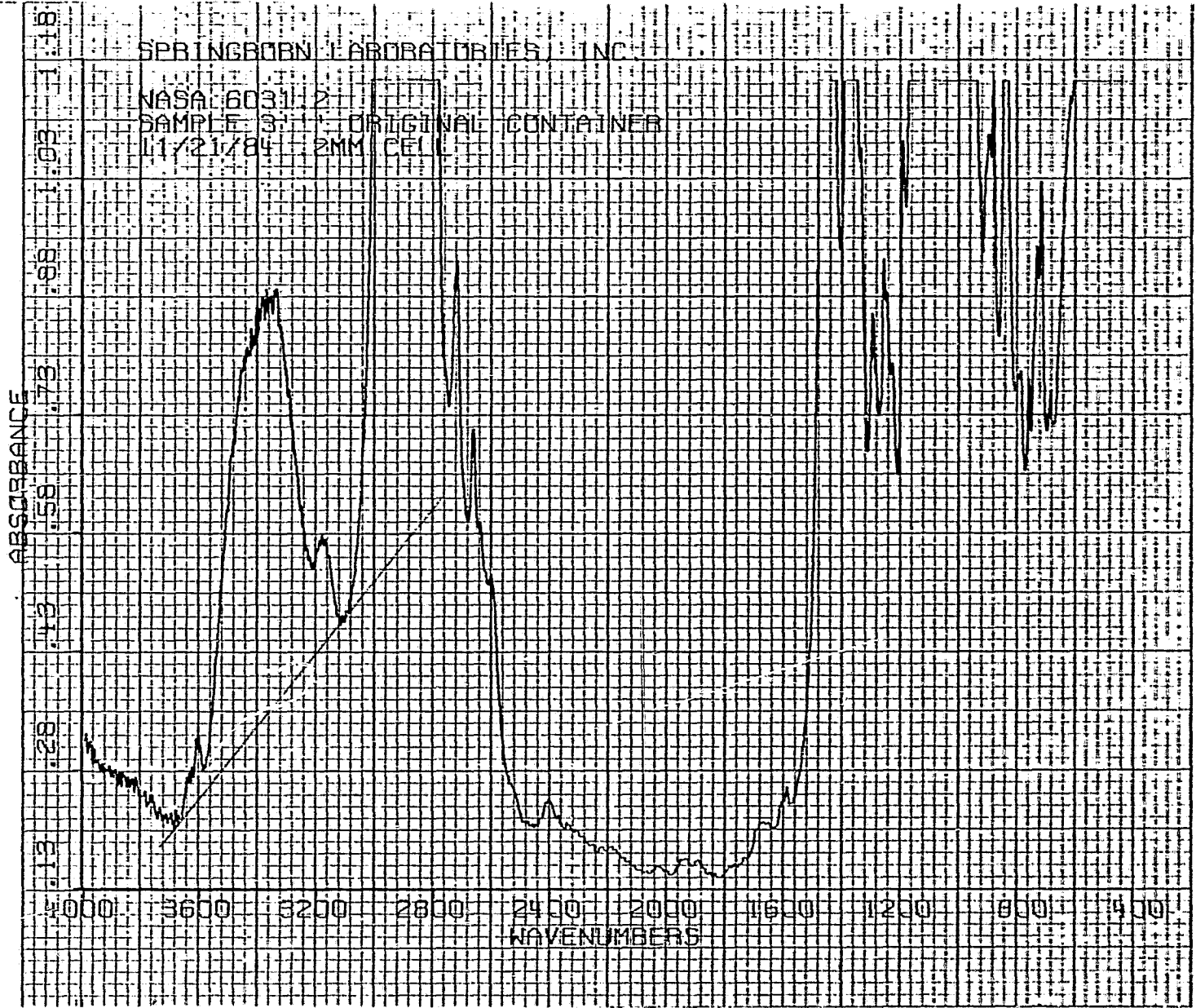
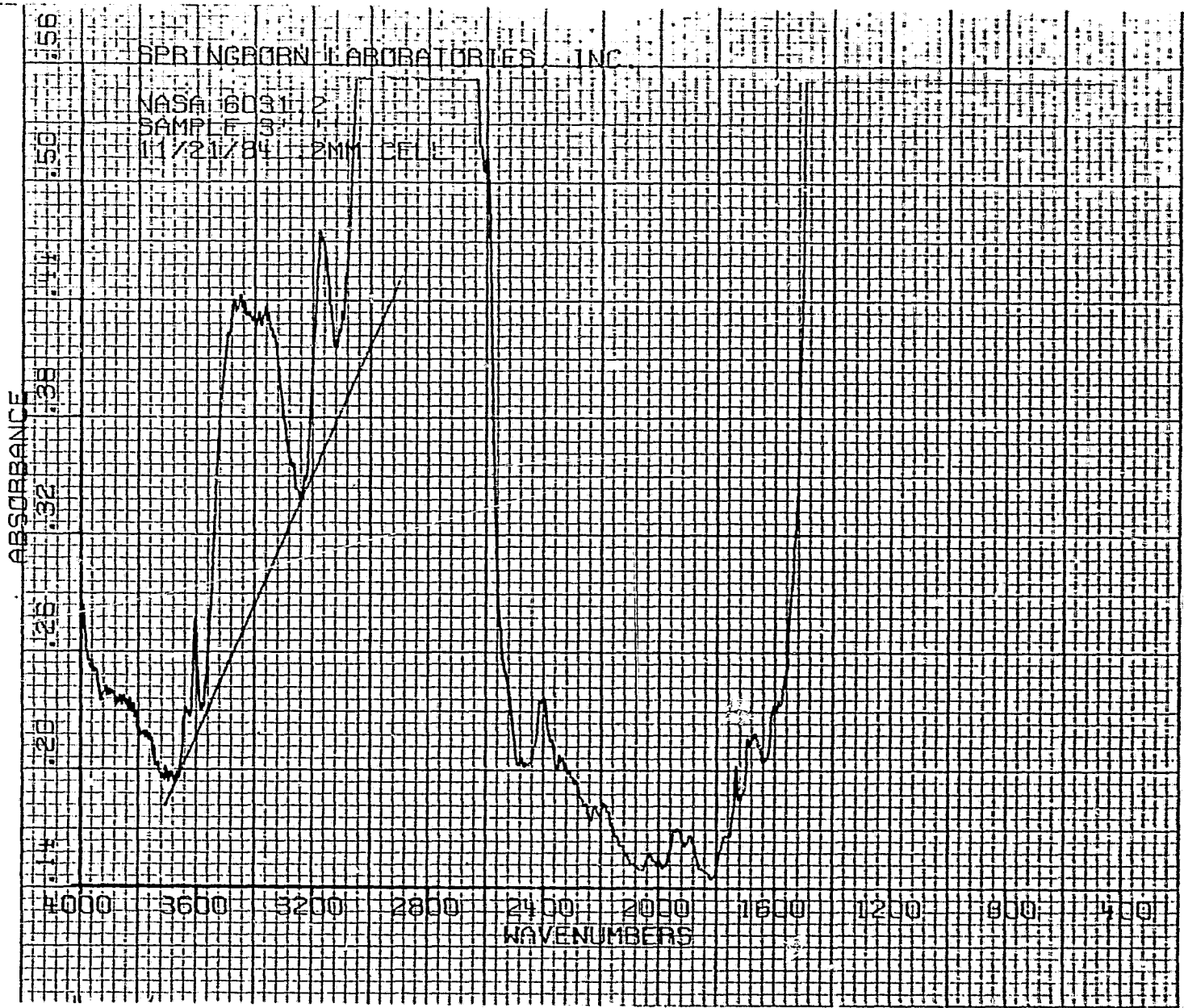


Fig 36

SPRINGBORN LABORATORIES, INC.



7637



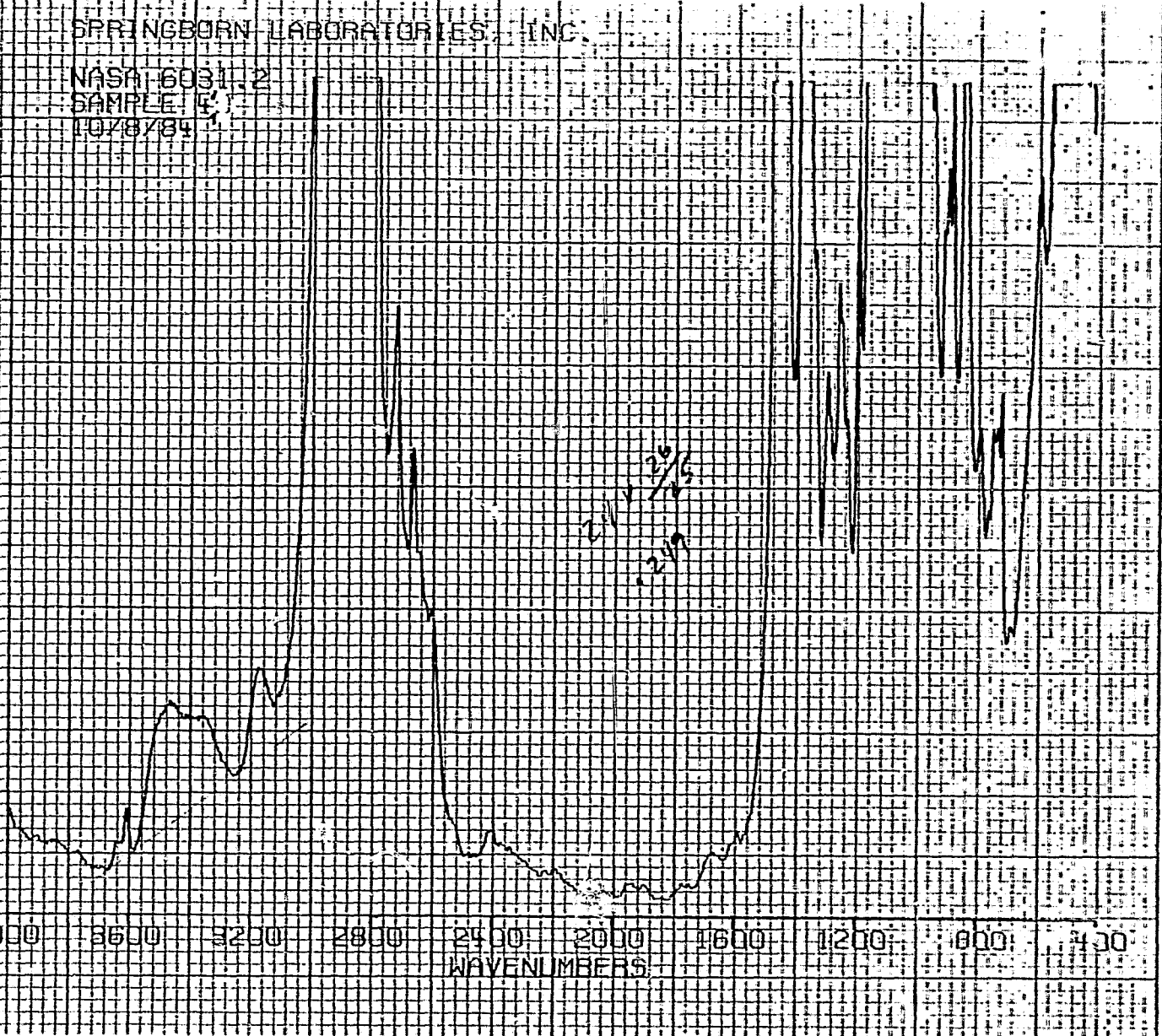
7c.38

SPRINGBORN LABORATORIES, INC.

NASH 6031-2
SAMPLE #
10/18/84

ABSORBANCE

1.2
1.15
1.1
1.05
1.0
0.95
0.9
0.85
0.8
0.75
0.7
0.65
0.6
0.55
0.5
0.45
0.4
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0.0



WAVENUMBERS

Fig 39

SPRINGFIELD LABORATORIES, INC.

NASA 6031-2
SAMPLE 41
107878-2

ABSORBANCE

1.00
1.10
1.20
1.02
1.00
0.80
0.58
0.38
0.18

WAVENUMBERS

4000 3600 3200 2800 2400 2000 1600 1200 800 400

2.18
 $\frac{32}{100}$ = 0.32

FIG 4b

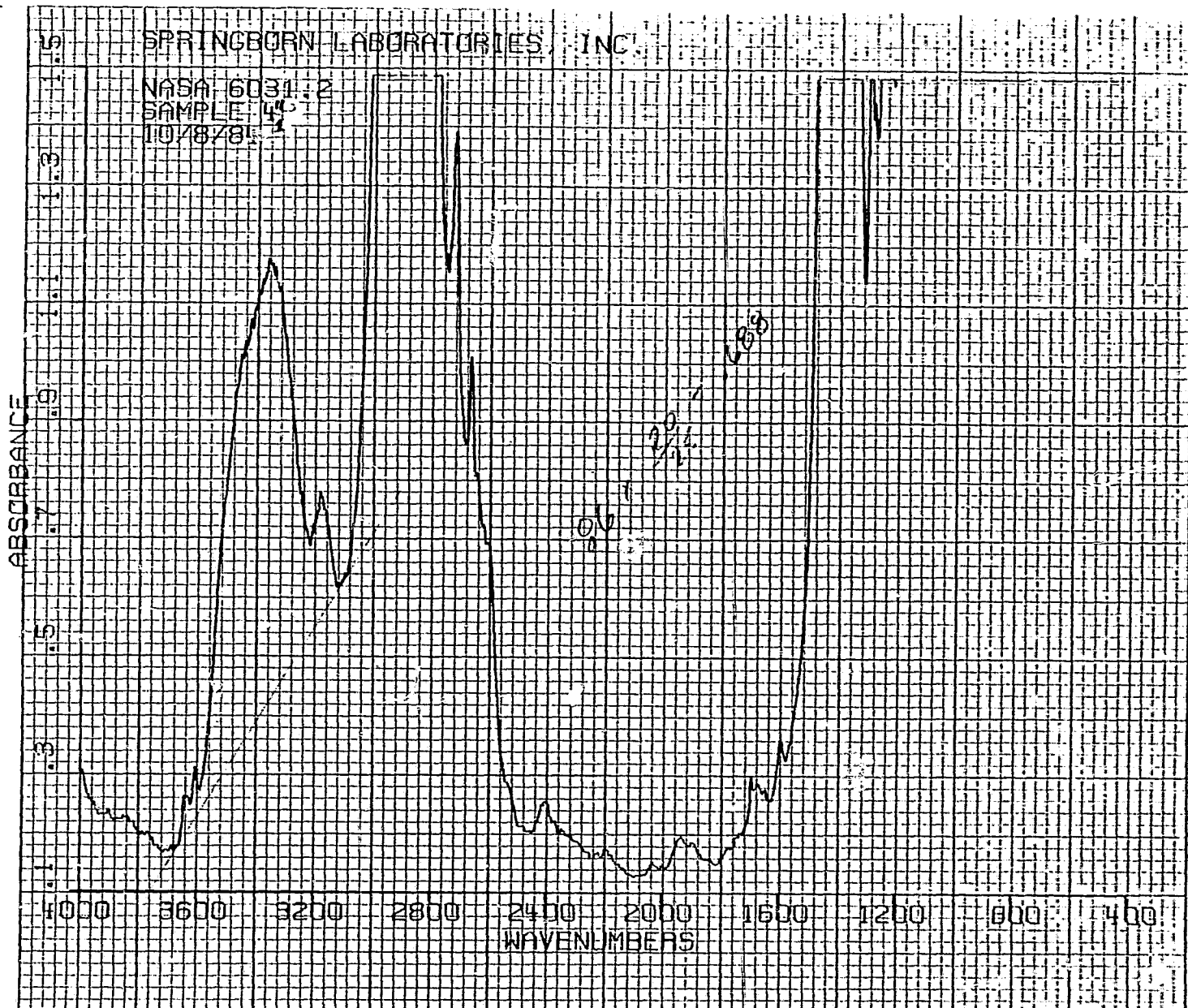


Fig 41

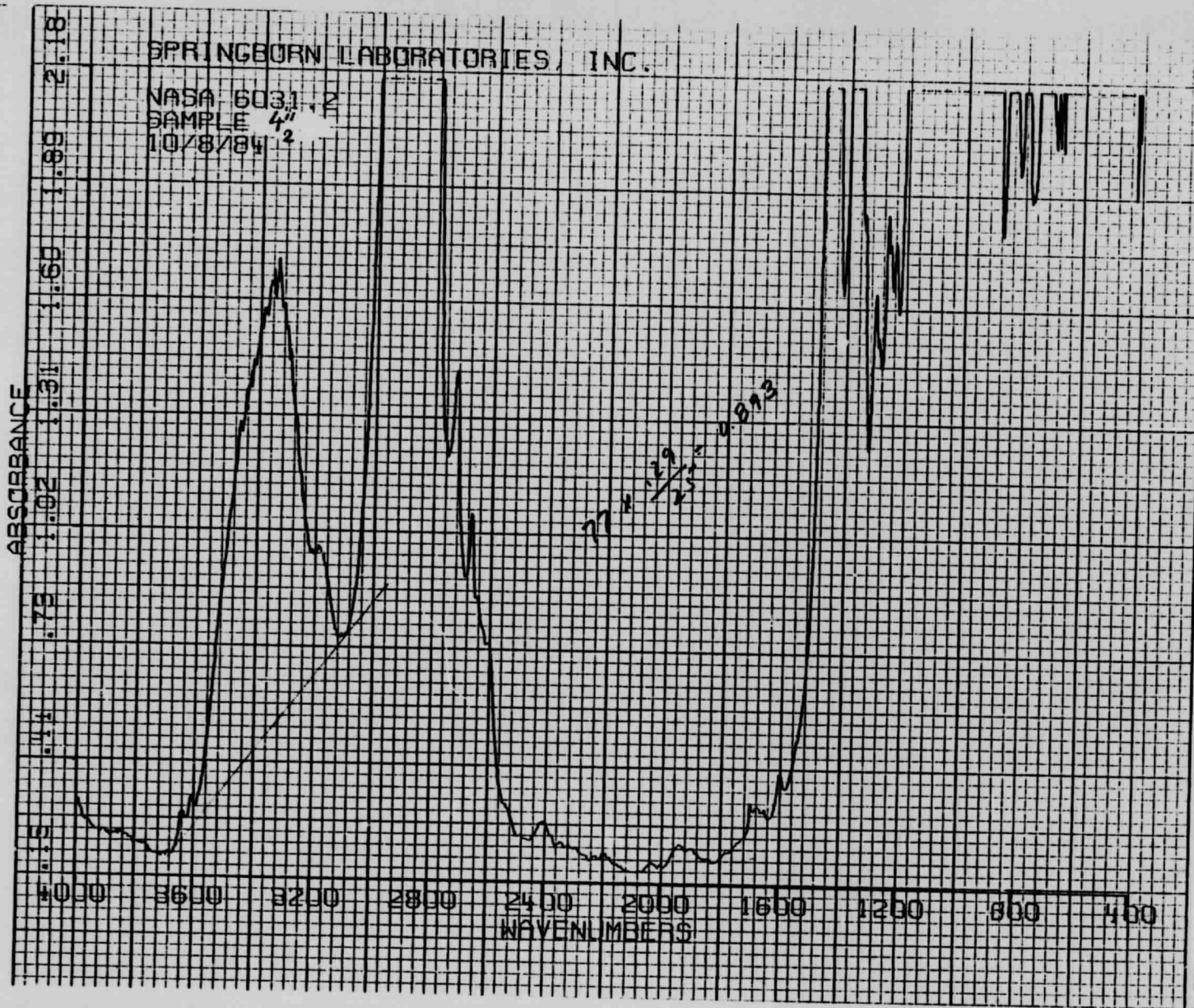


Fig 42

SPRINGBORN LABORATORIES, INC.

NASA 16031, 2

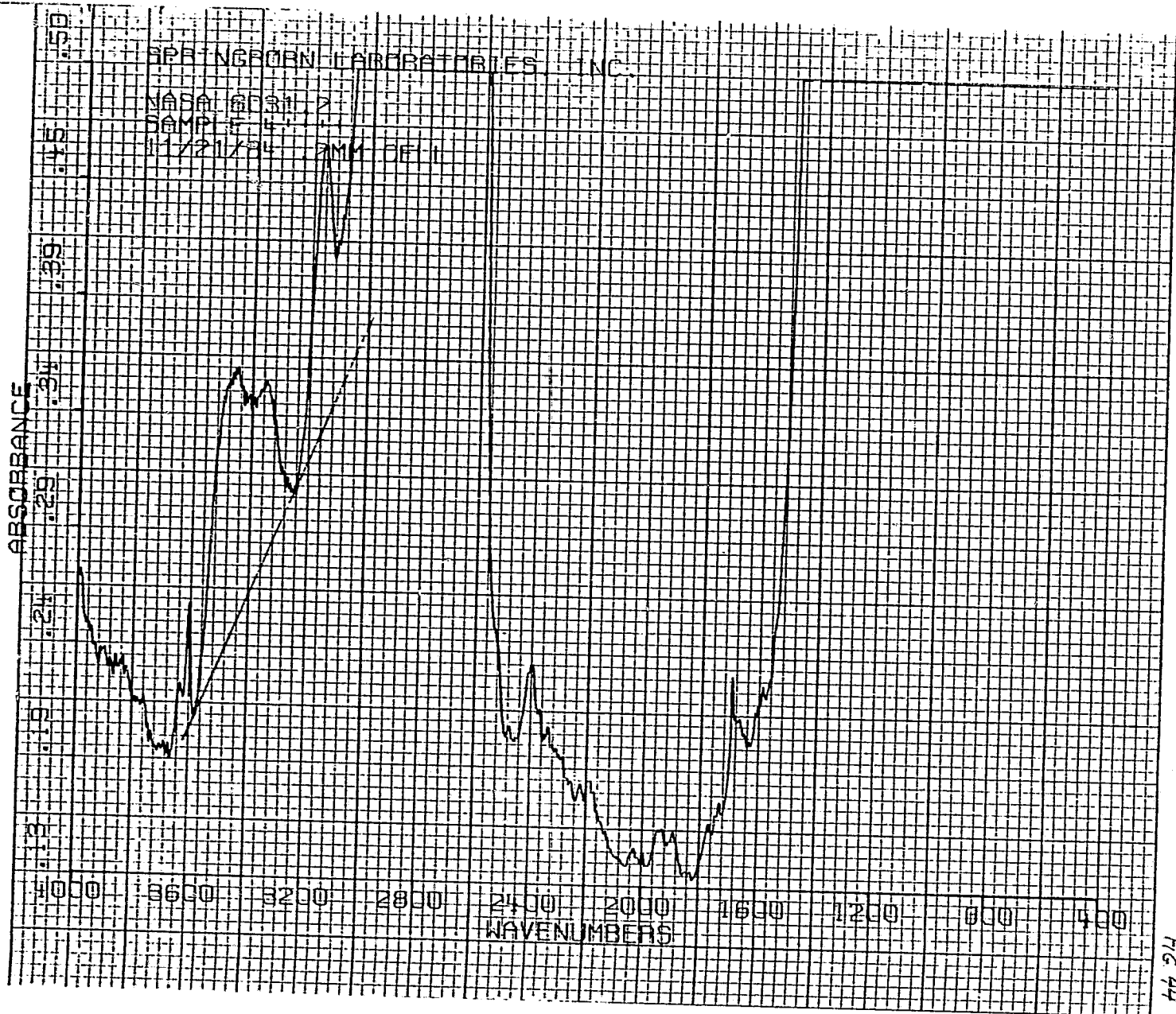
SAMPLE # ORIGINAL CONTAINER
11/21/74 2MM CELL

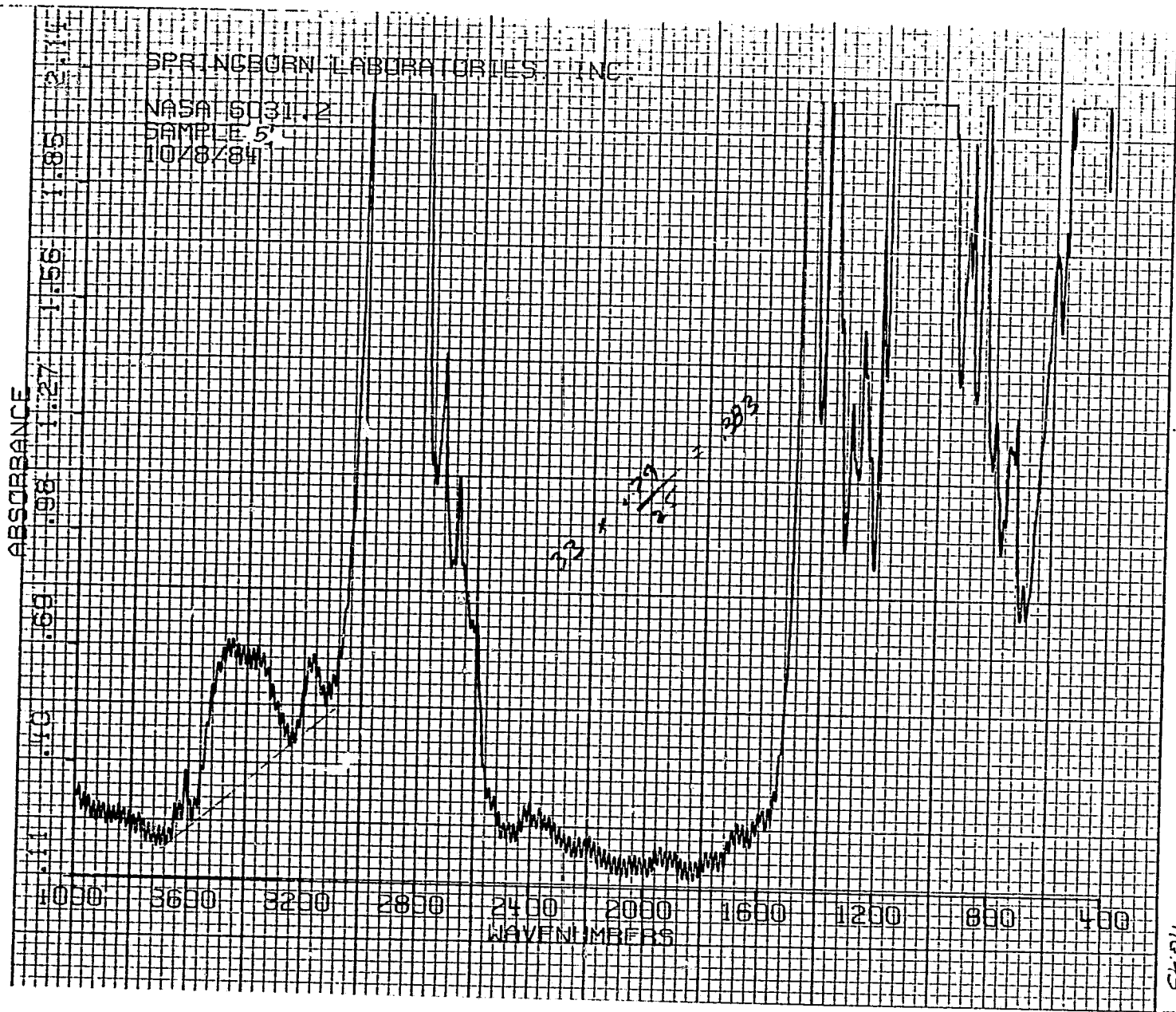
ABSORBANCE

0.70
0.51
0.32
0.13

4000 3600 3200 2800 2400 2000 1600 1200 800 400
WAVENUMBERS

7c 43





Fe 45

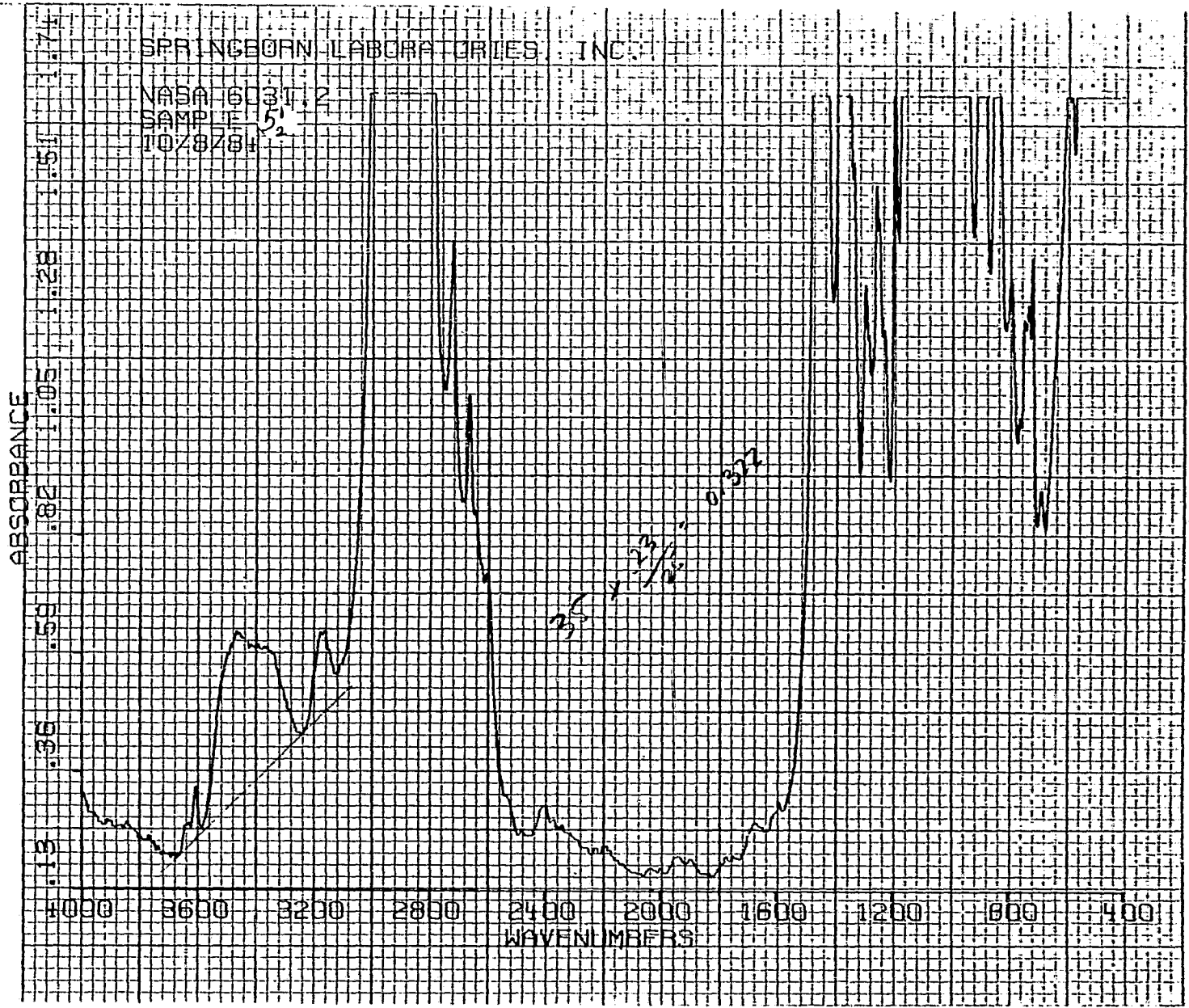


Fig 46

SPRINGBORN LABORATORIES, INC.

NASA 6031-2

SAMPLE 5

10/8/84

ABSORBANCE

1.00
1.10
1.20
1.30
1.40
1.50
1.60
1.70
1.80
1.90
2.00

WAVENUMBERS

4000 3600 3200 2800 2400 2000 1600 1200 800 400

$\frac{21}{25}$
 $\frac{22}{25}$
0.522

Field

100-10-0000-0000-0000-0000

SPRINGBORN LABORATORIES, INC.

NASA 6031, P
SAMPLE 5⁷
10/8/84

ABSORBANCE

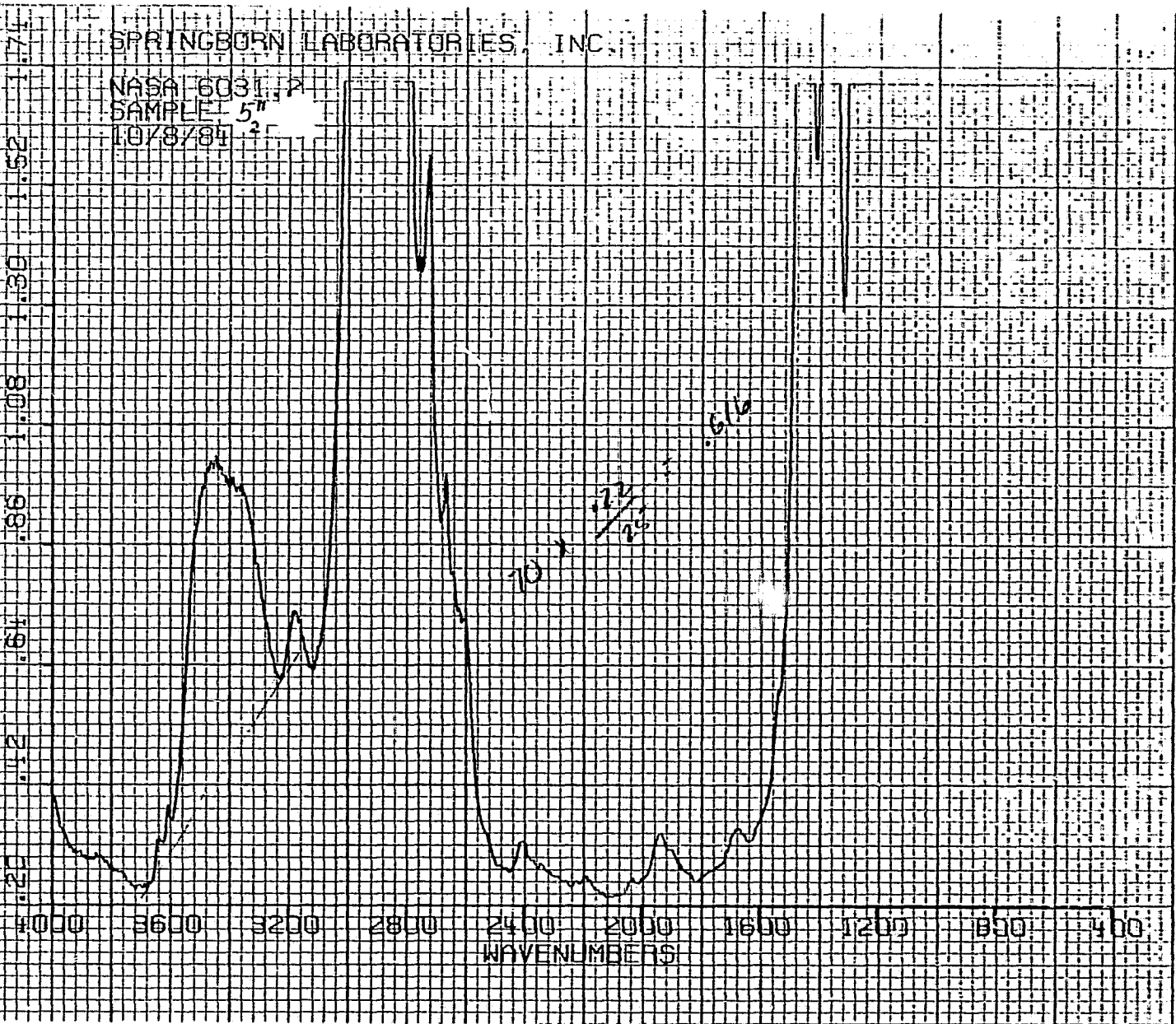


FIG 48

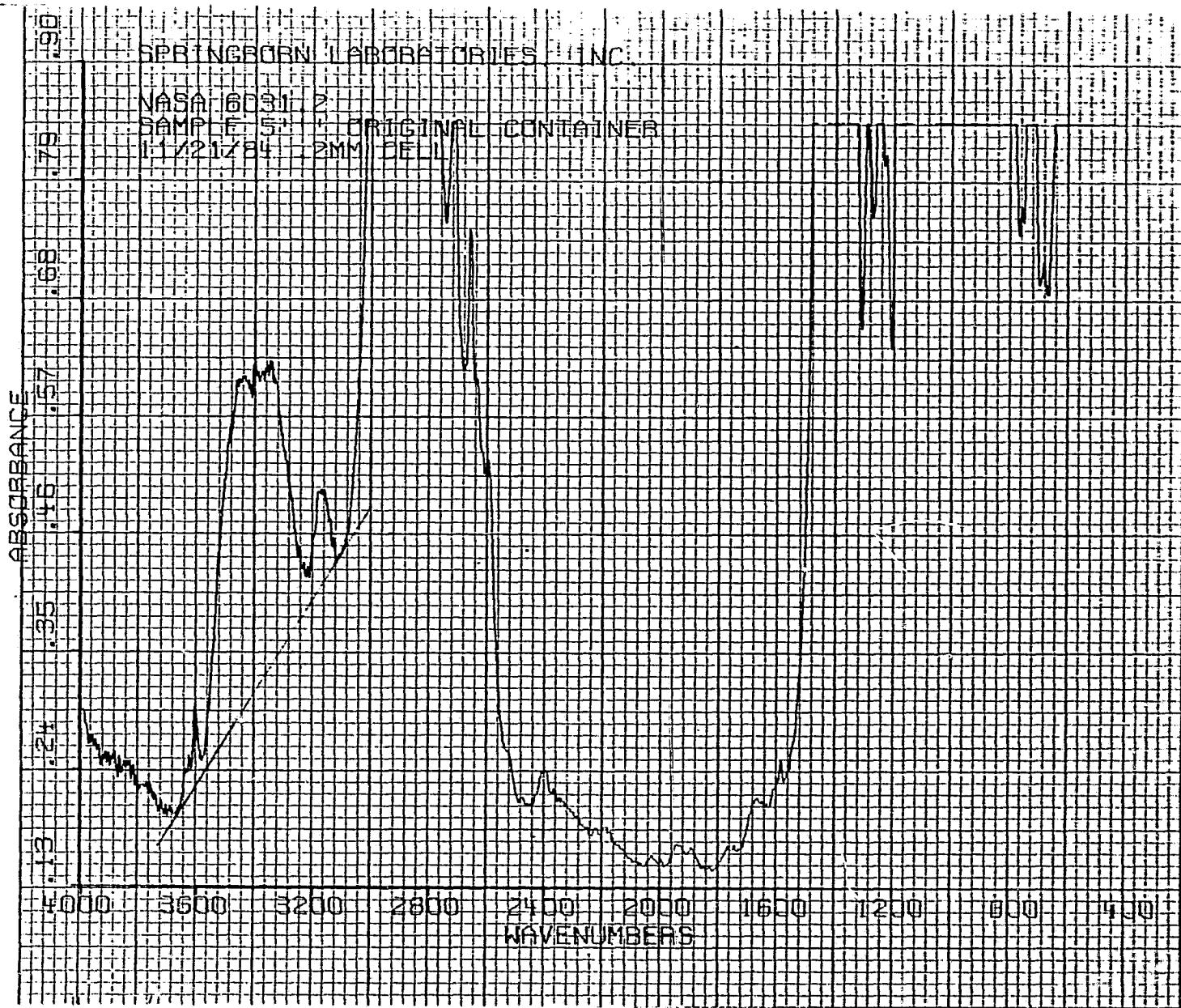


FIG. 49

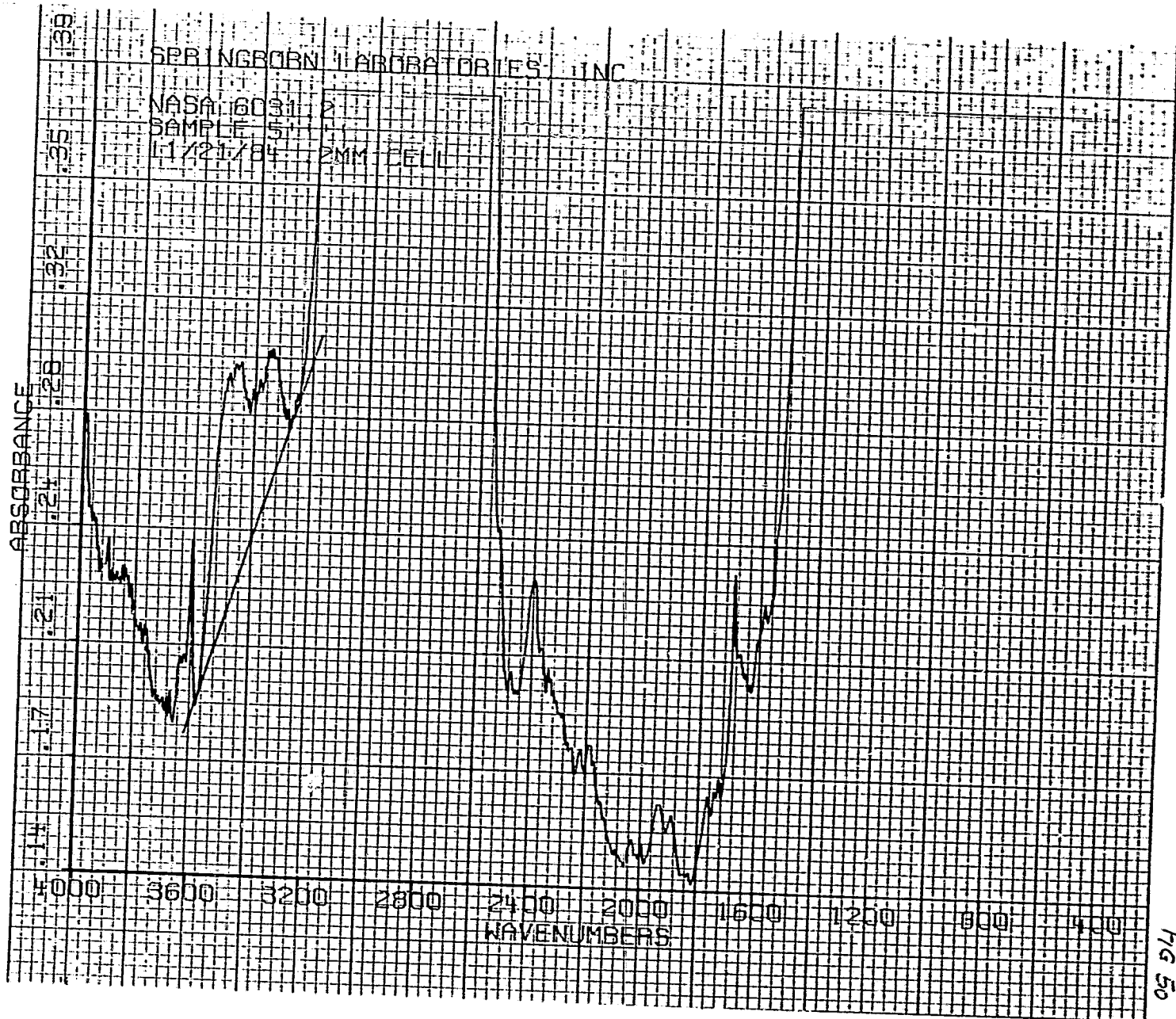


FIG 50

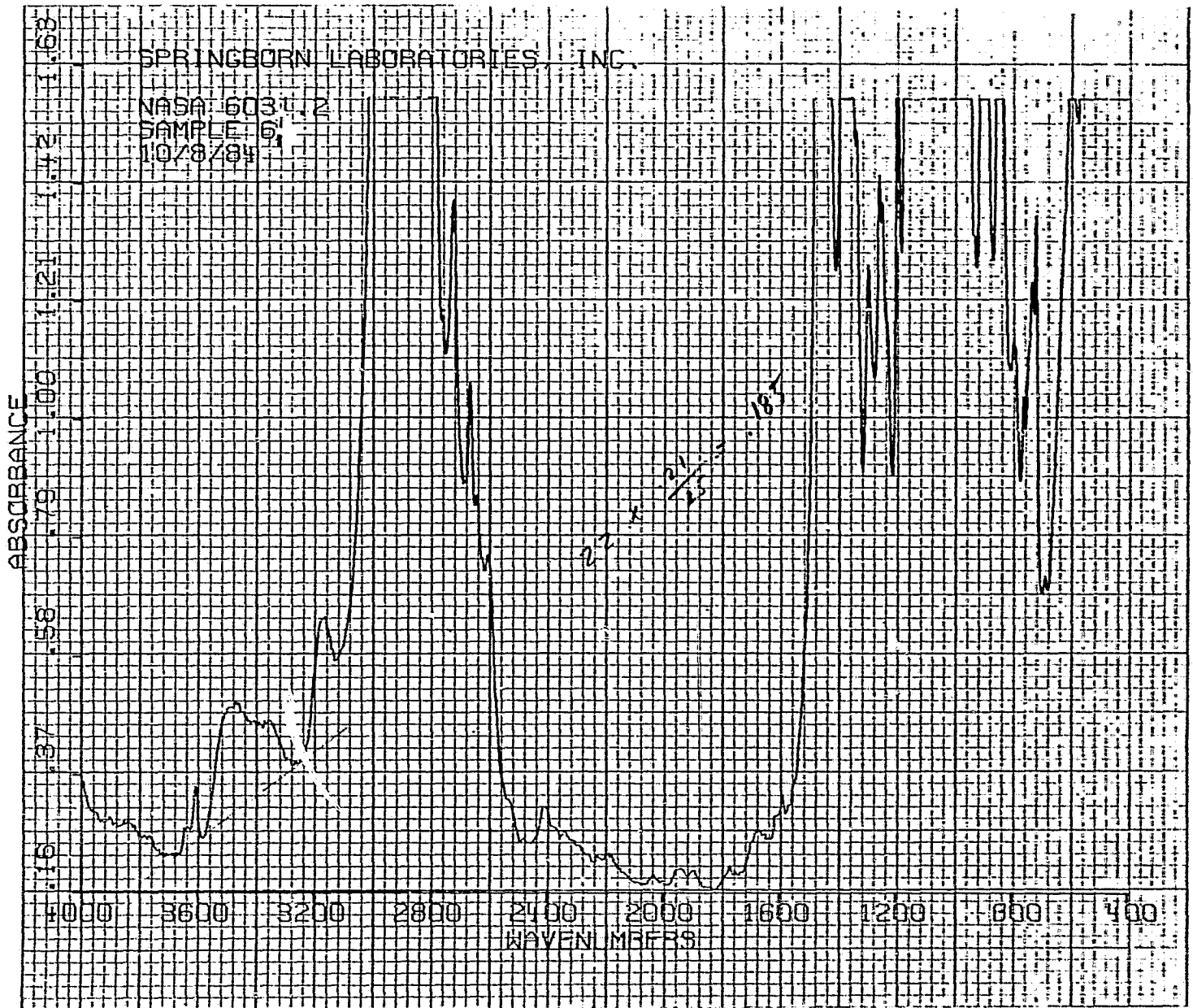


Fig 51

SPRINGBORN LABORATORIES, INC.

NASA 6031-2
SAMPLE 6-2
1078784

ABSORBANCE

1.68
1.45
1.24
1.02
.80
.58
.36
.14

WAVENUMBERS

4000 3600 3200 2800 2400 2000 1600 1200 800 400

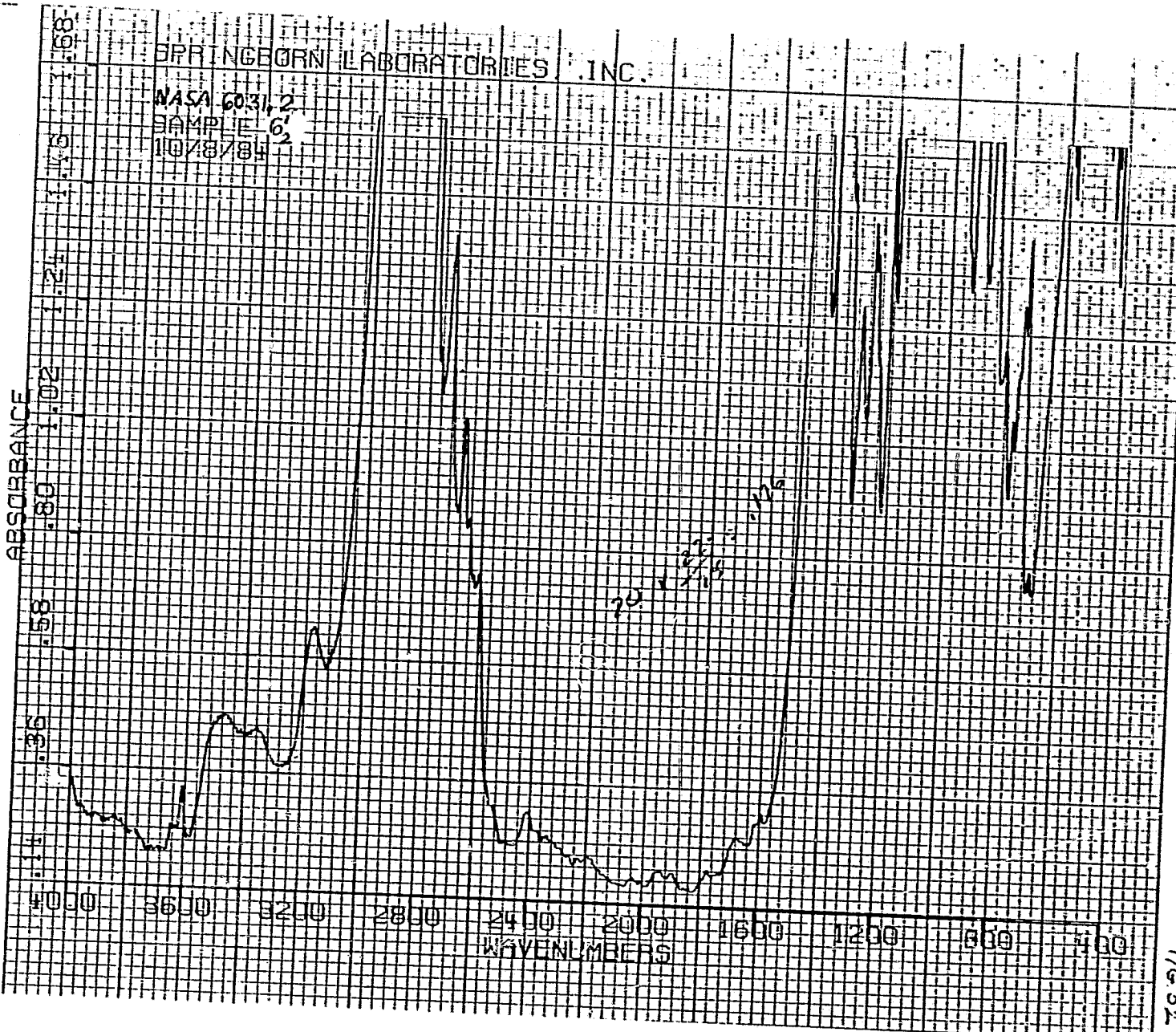
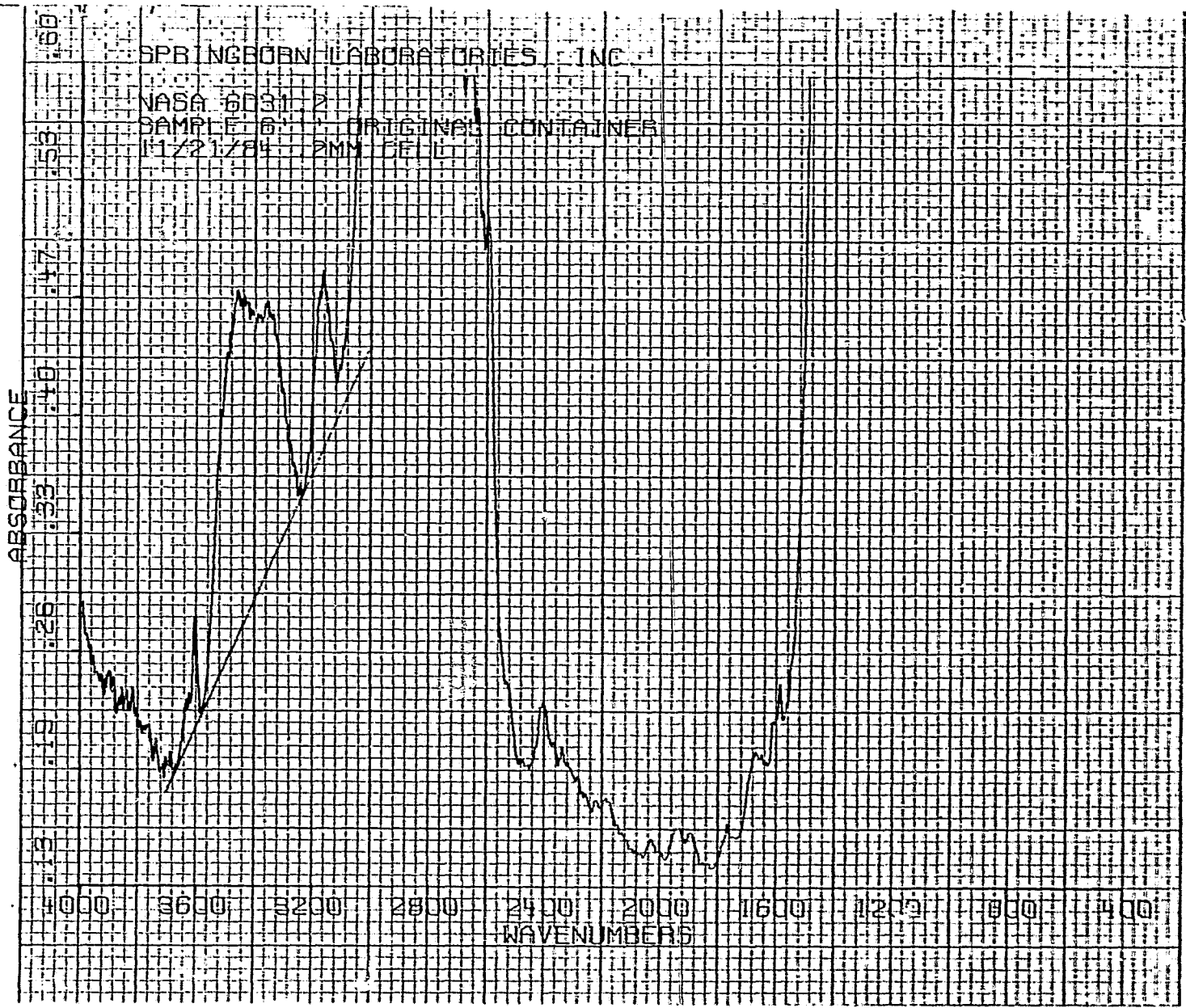


Fig 52



7653

SPRINGBORN LABORATORIES, INC.

NASA 60311 P
SAMPLE 6
11721784 - 2MM FILM

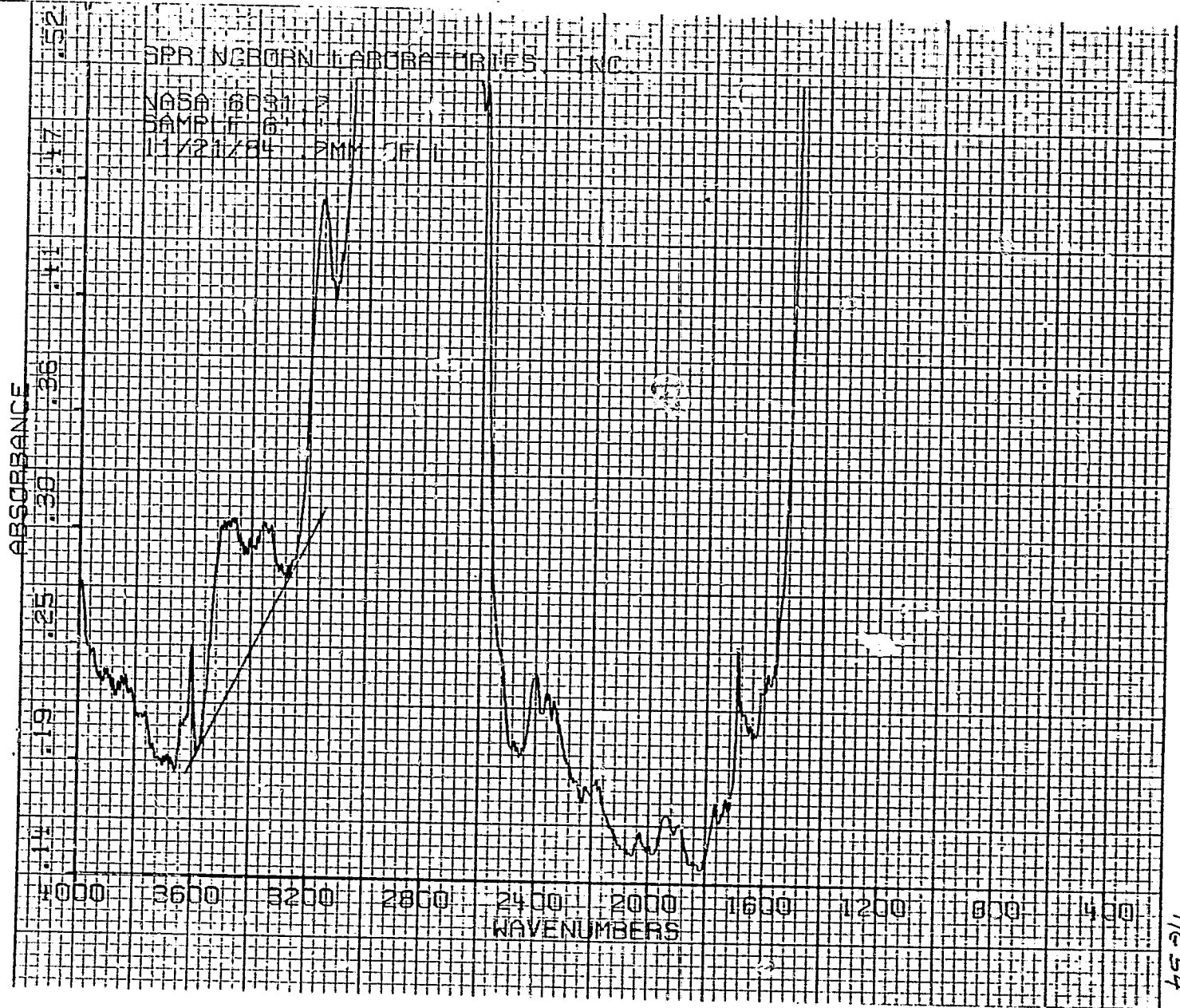


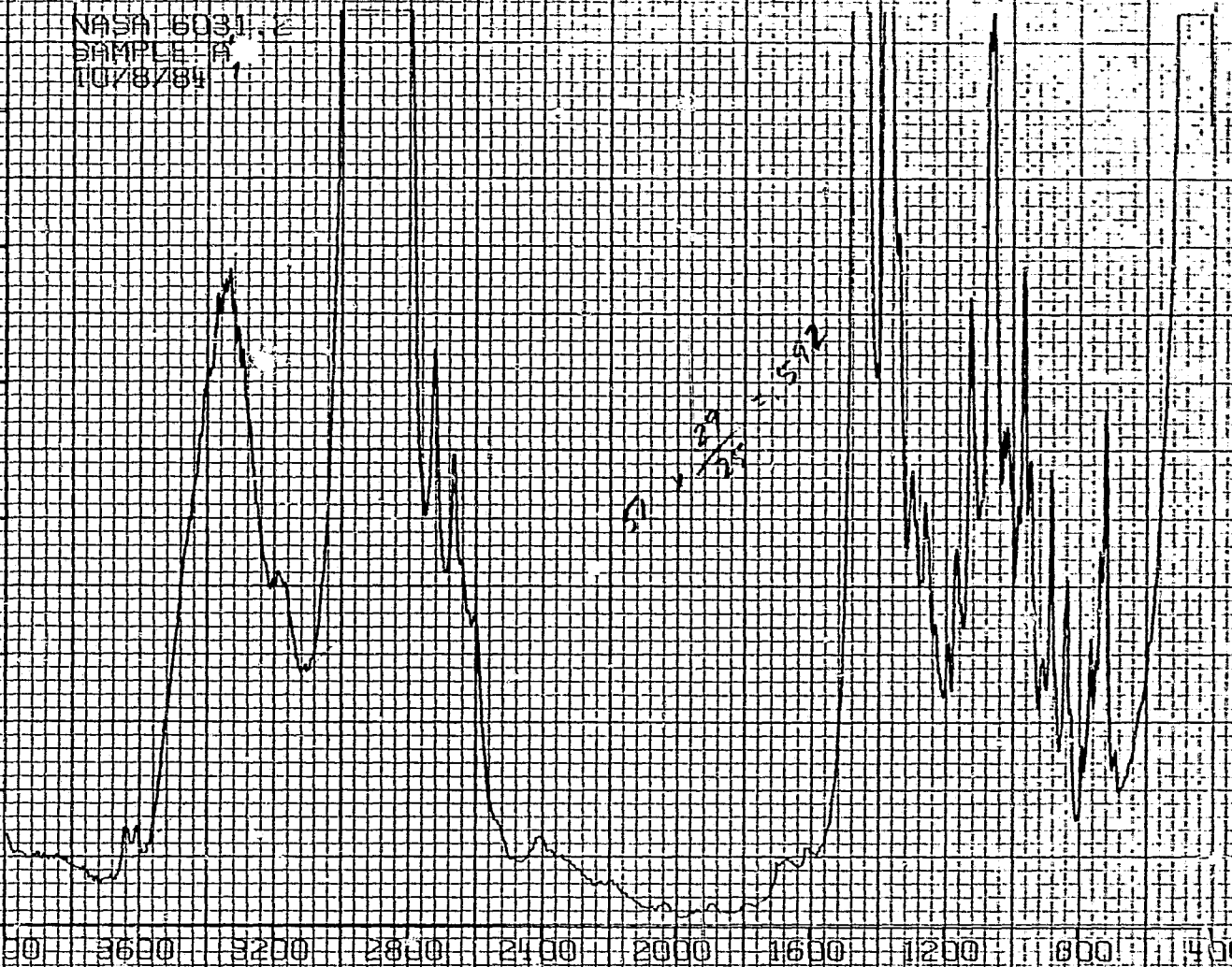
FIG 54

SPRINGBURN LABORATORIES, INC.

NASA 6031, 2
SAMPLE 1A
1078784

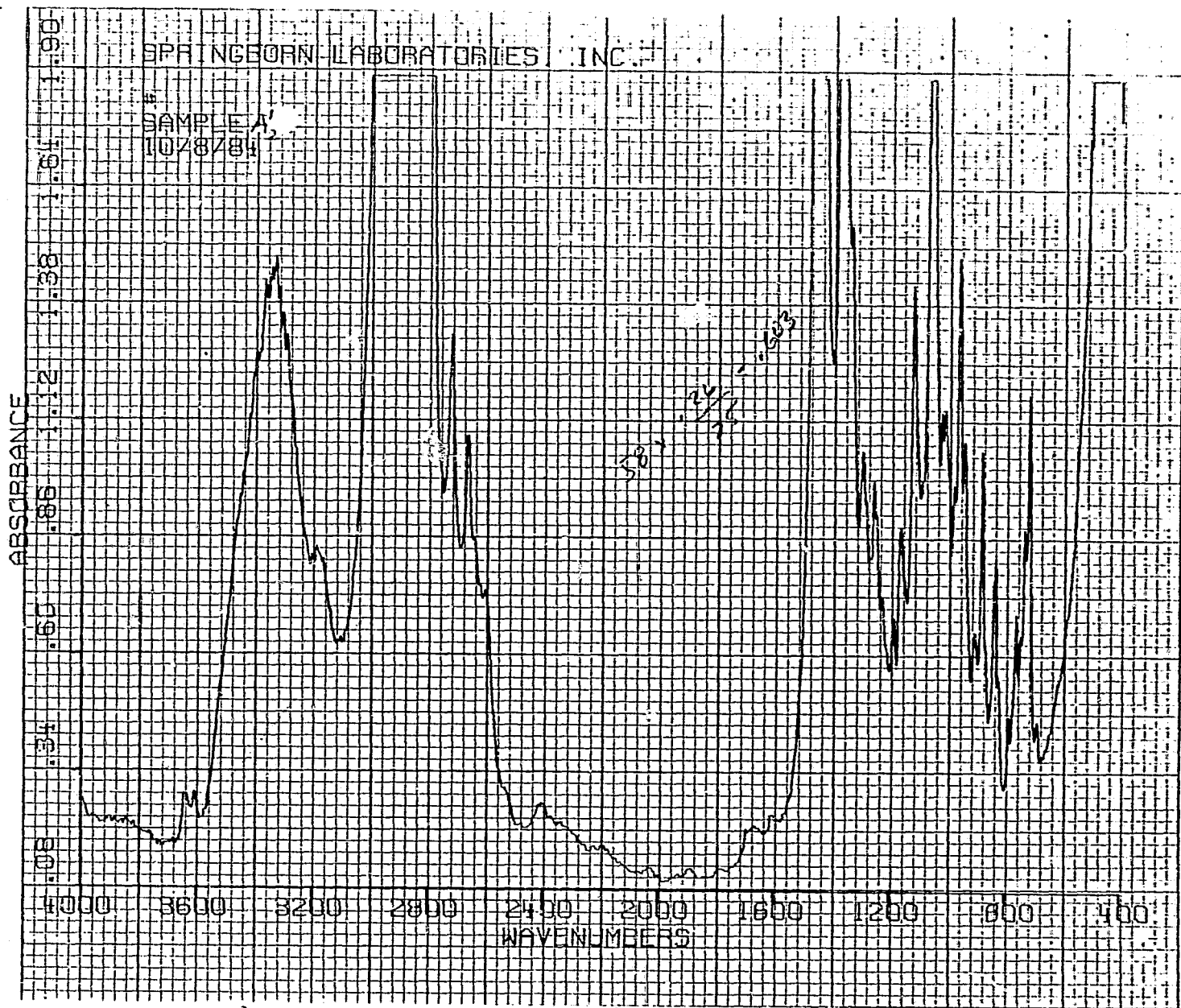
ABSORBANCE

2.11
1.82
1.53
1.24
0.95
0.66
0.37
0.09



WAVENUMBERS

1555



FG 56

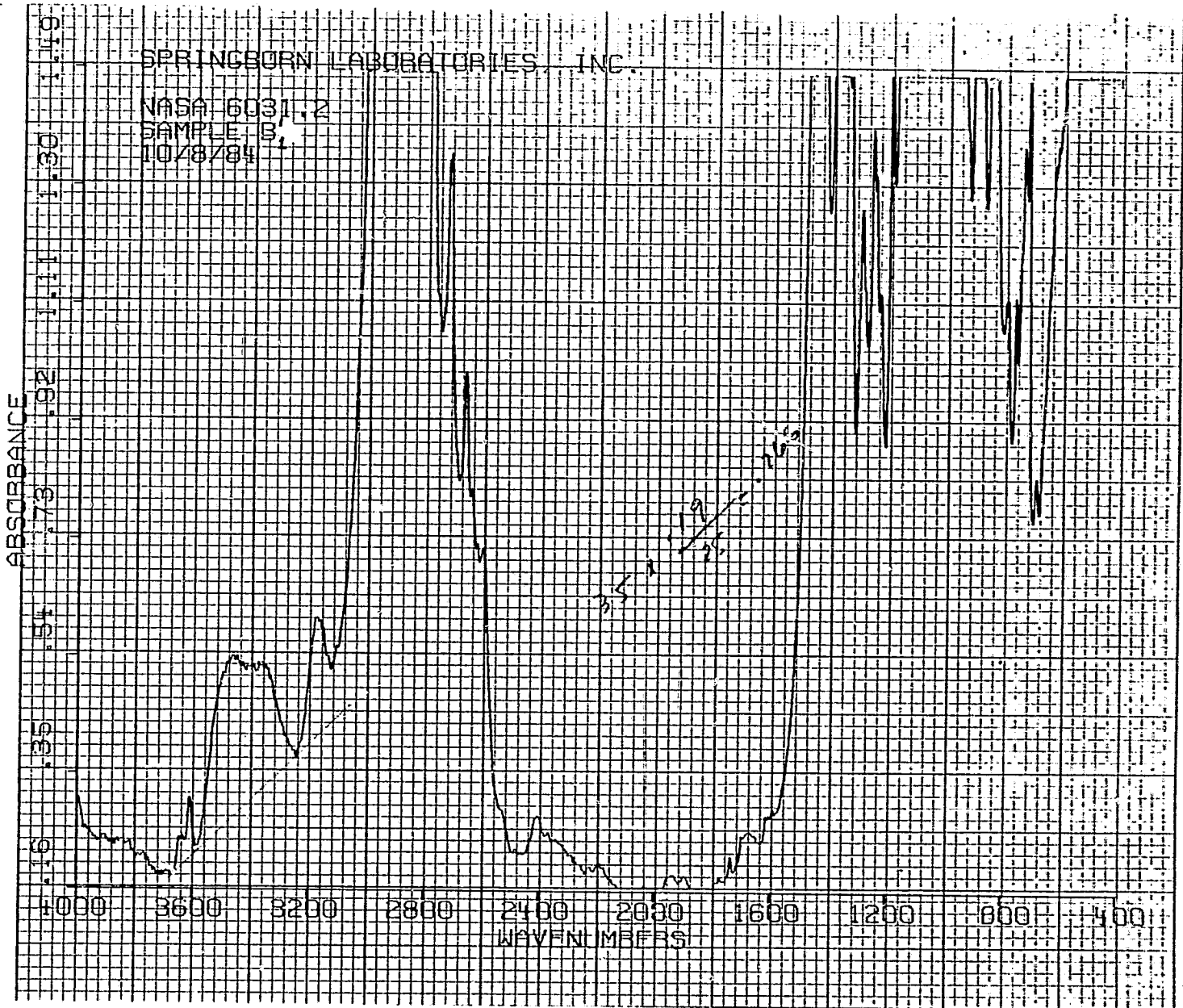


Fig 57

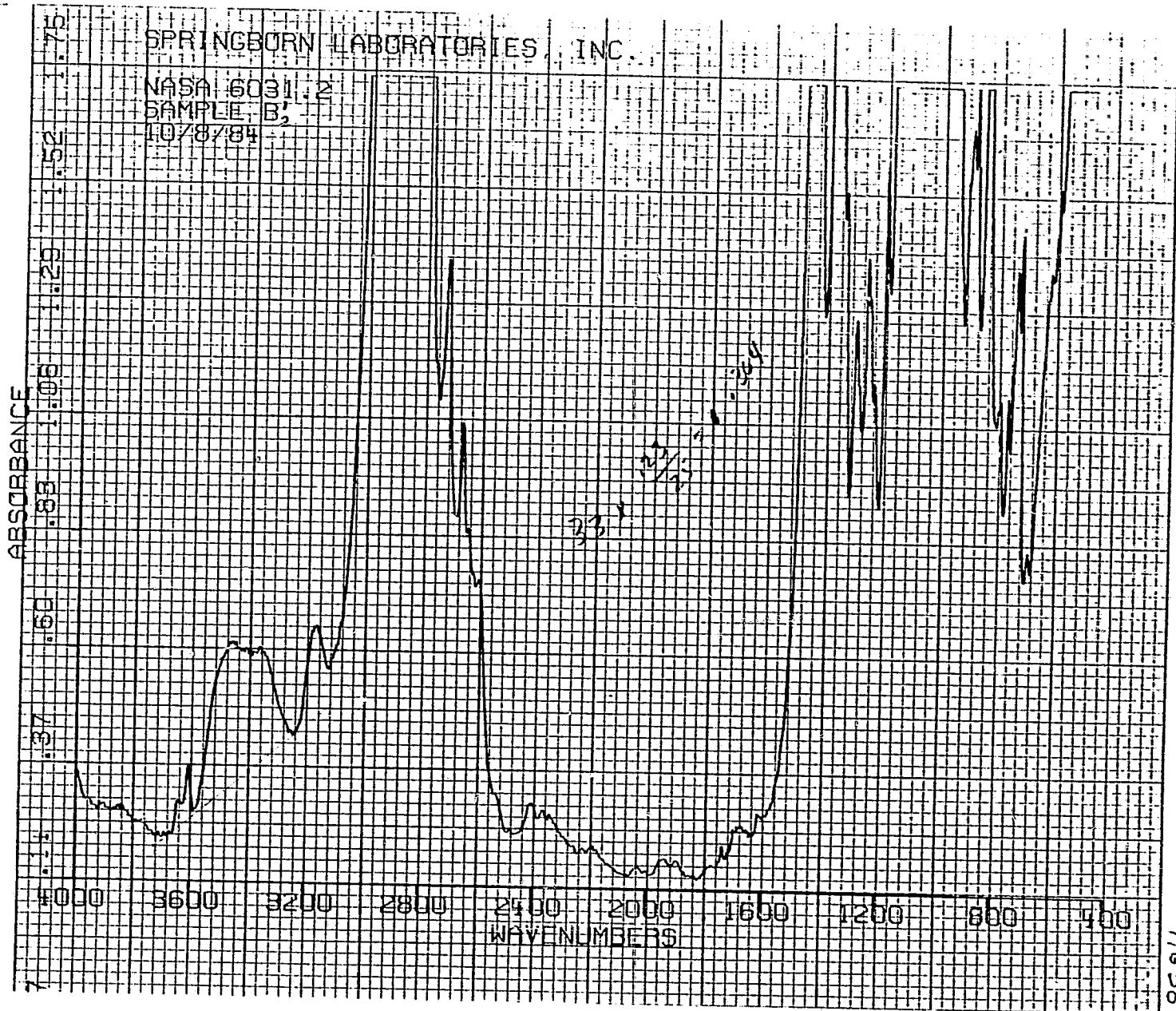
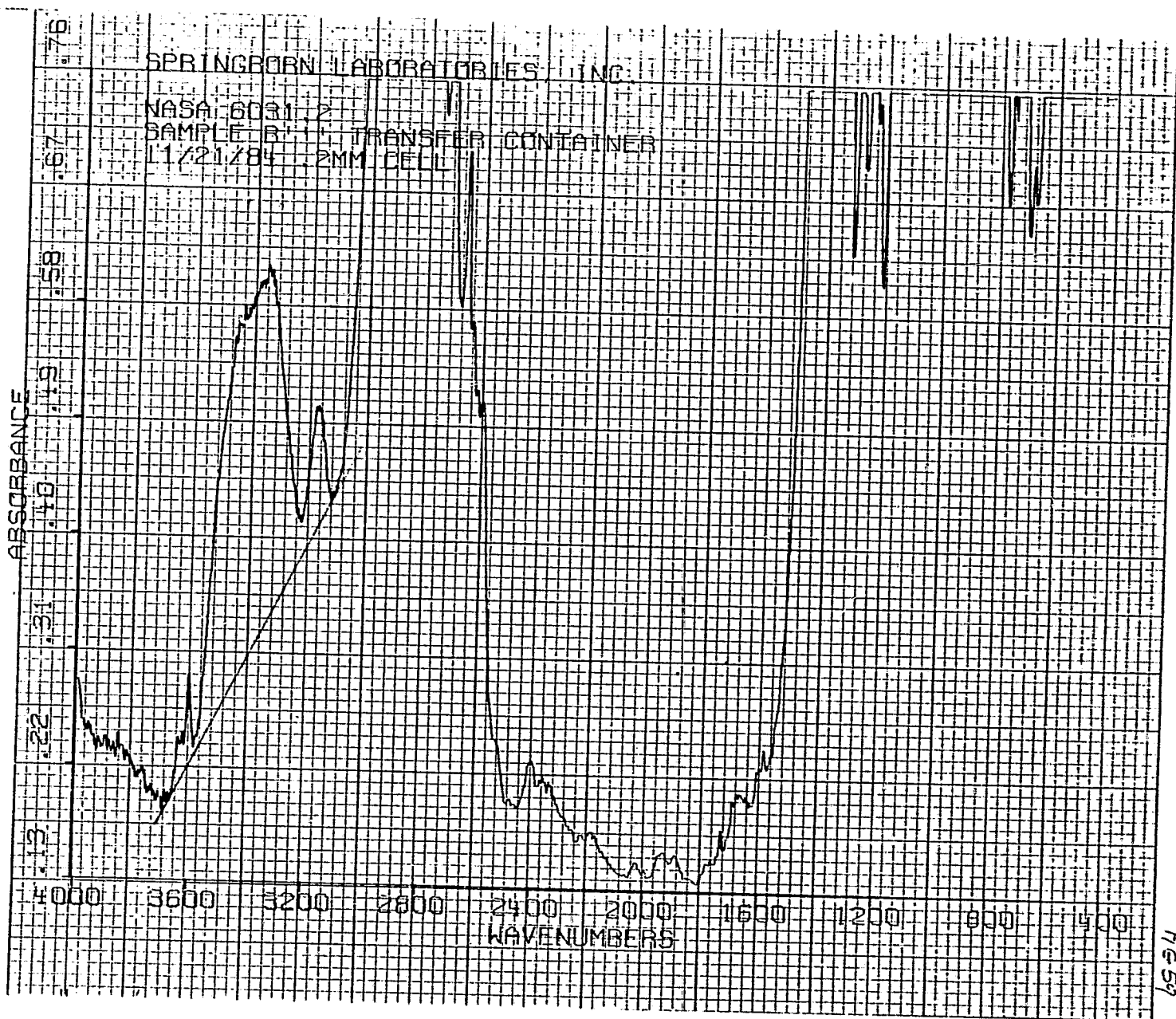


FIG 58



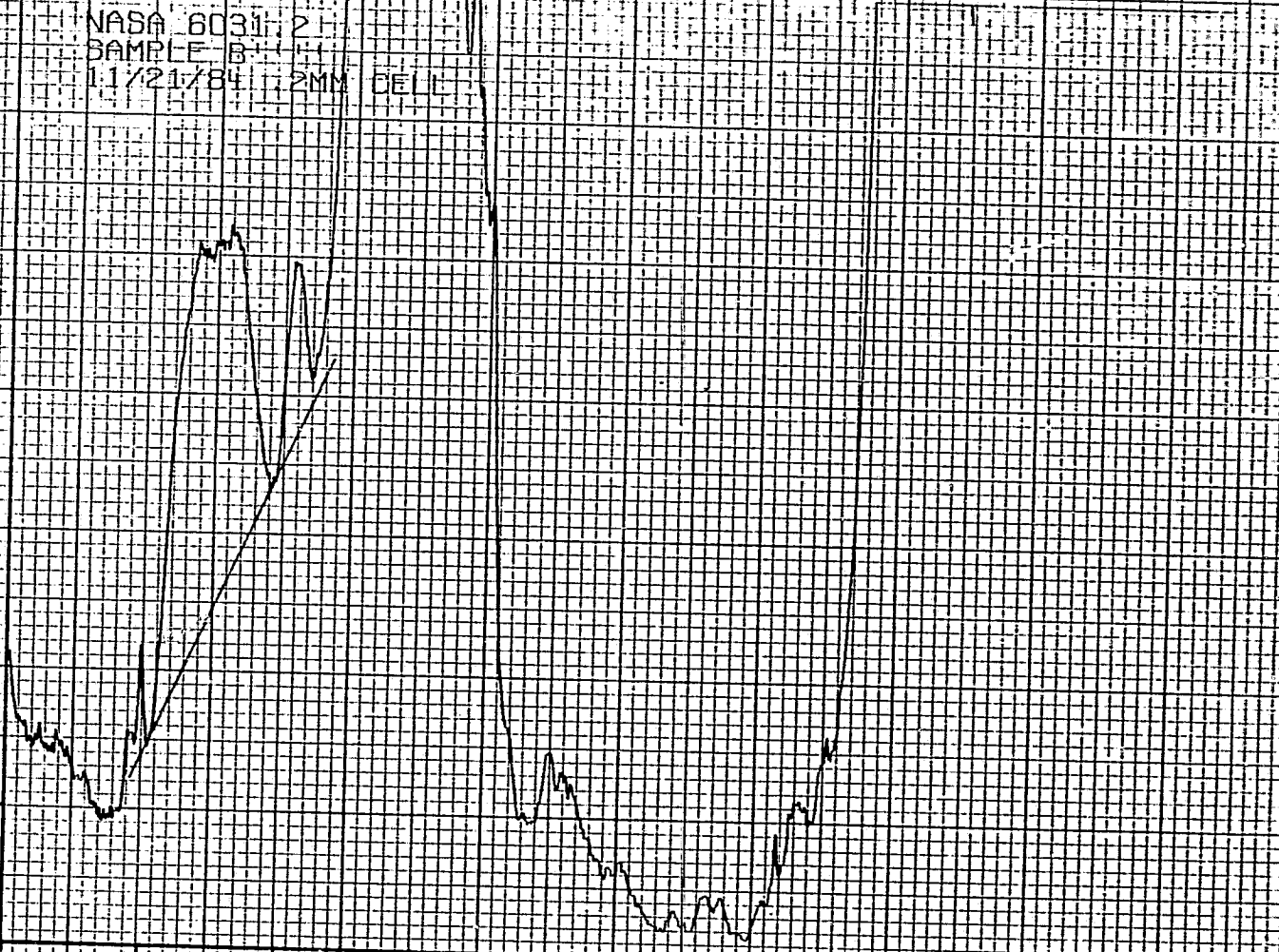
7c59

SPRINGBORN LABORATORIES, INC.

NASA 6031-2
SAMPLE B
1.1721784 2MM CELL

ABSORBANCE

0.62
0.55
0.48
0.41
0.34
0.27
0.20
0.13



4000 3600 3200 2800 2400 2000 1600 1200 800 400
WAVENUMBERS

7960

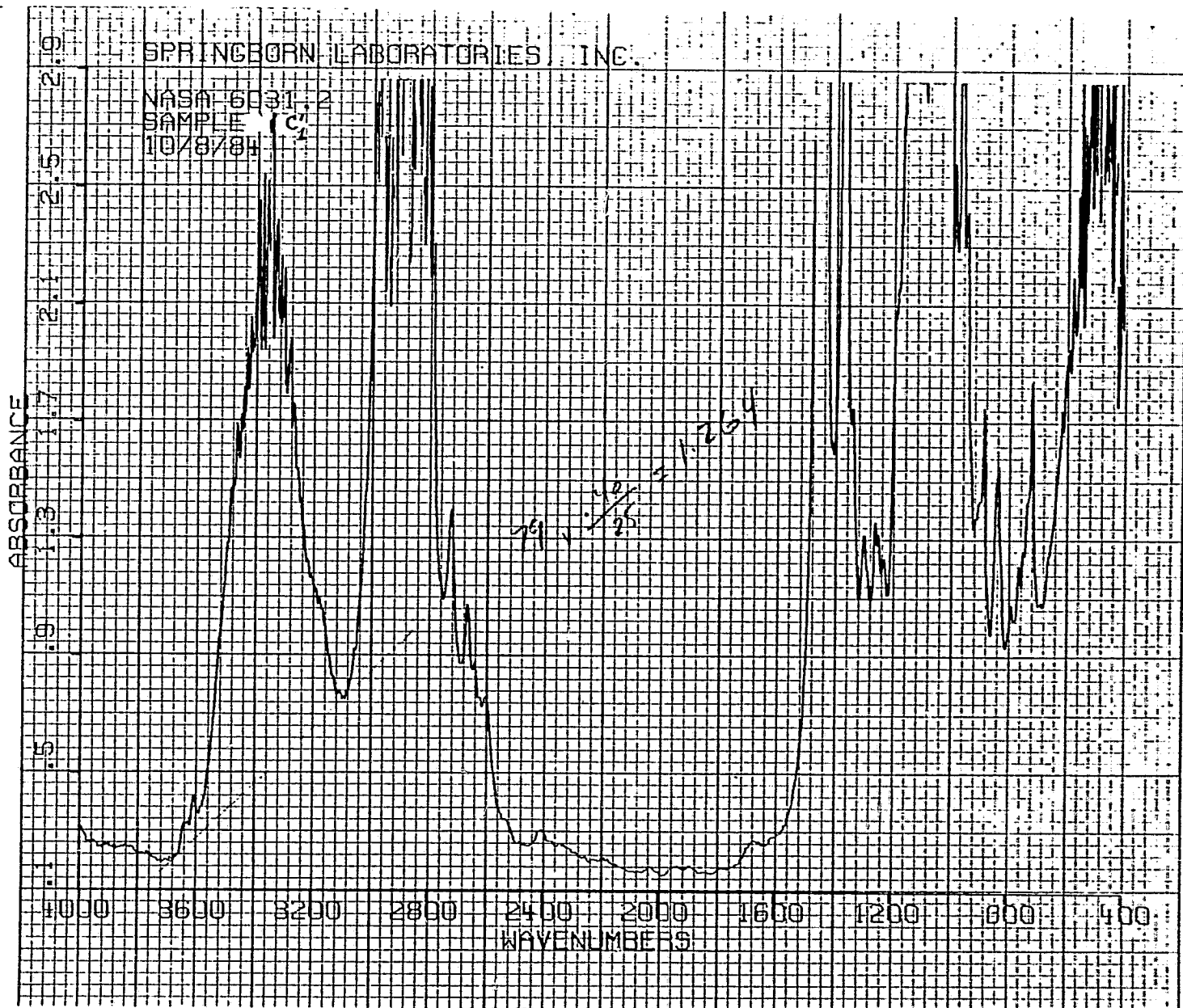


Fig 61

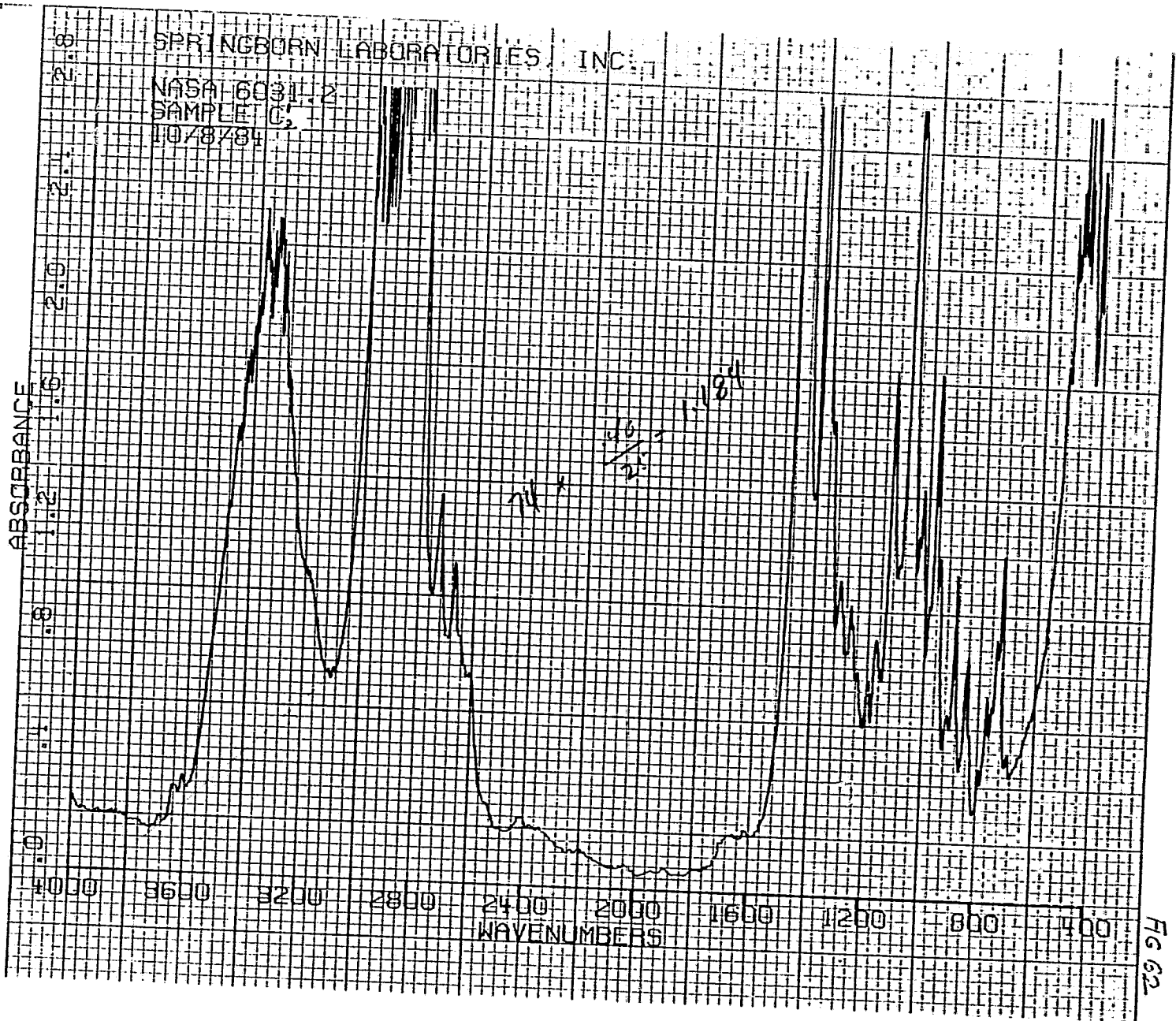
SPRINGBORN LABORATORIES, INC.

NASA 6031.2
SAMPLE C
1078784

ABSORBANCE

WAVENUMBERS

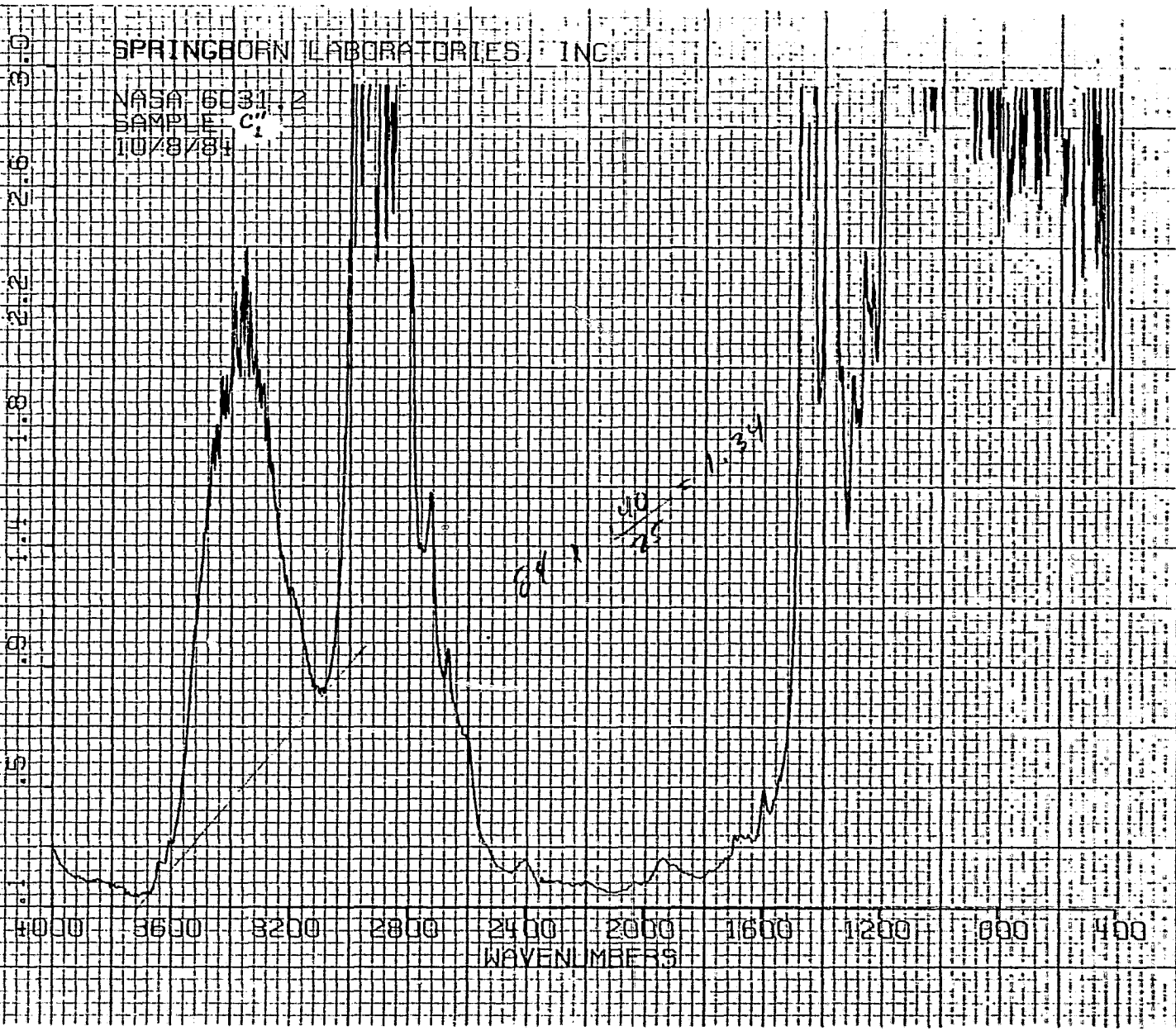
Fig 62



SPRINGBORN LABORATORIES, INC.

NASA 6031.2
SAMPLE C:
10/8/84

ABSORBANCE



FG 63

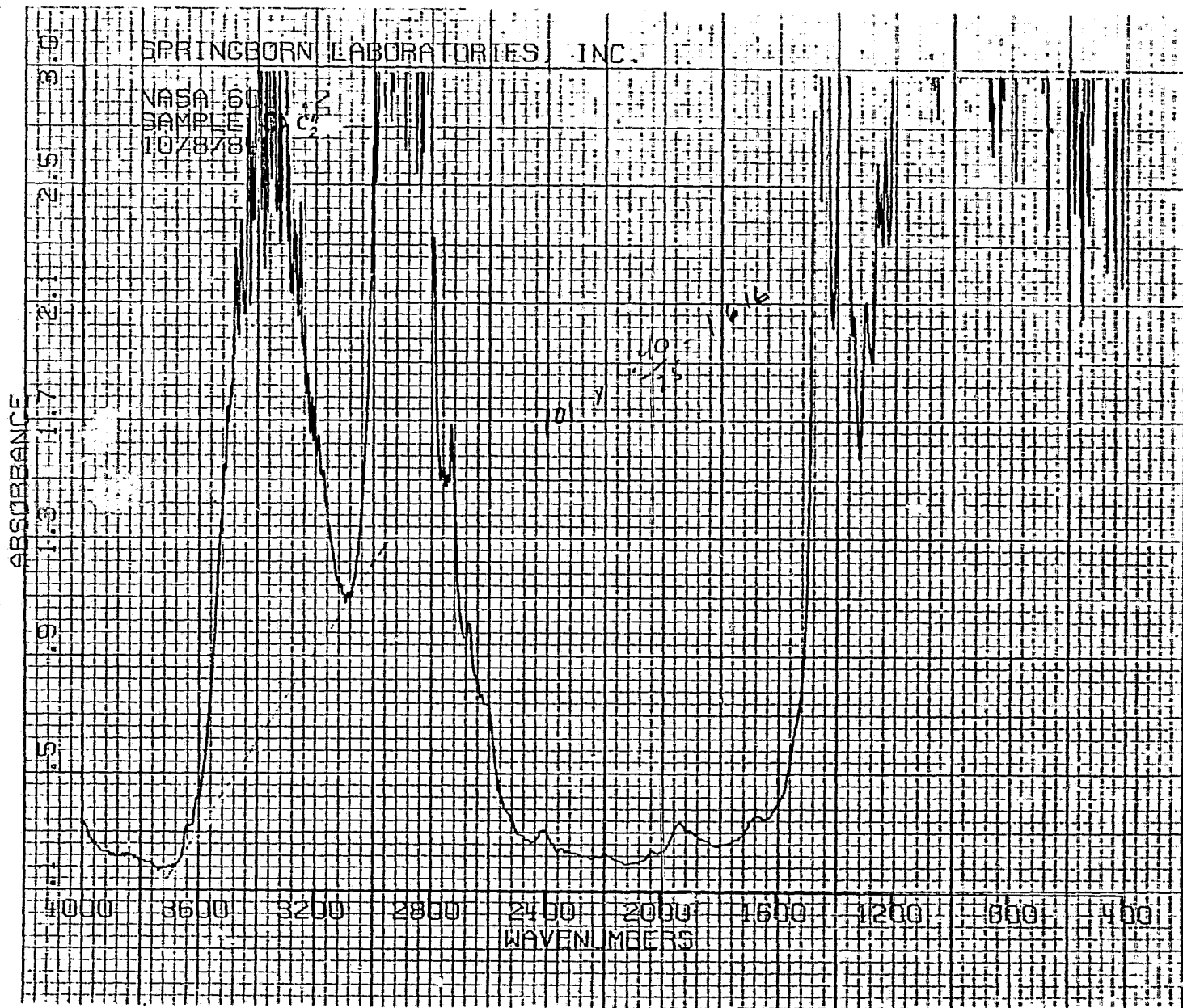
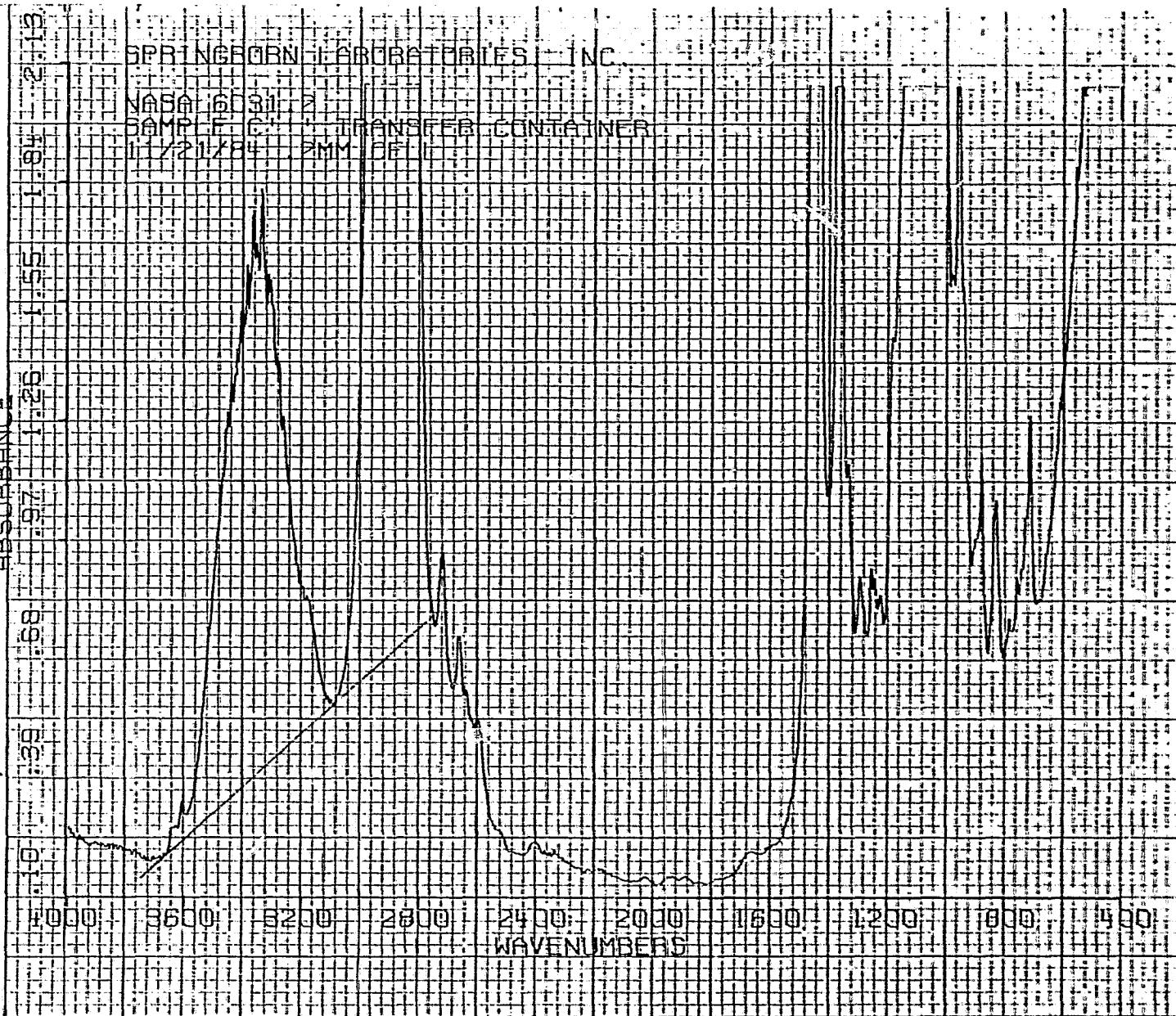


FIG 64

ABSORBANCE



HC 65

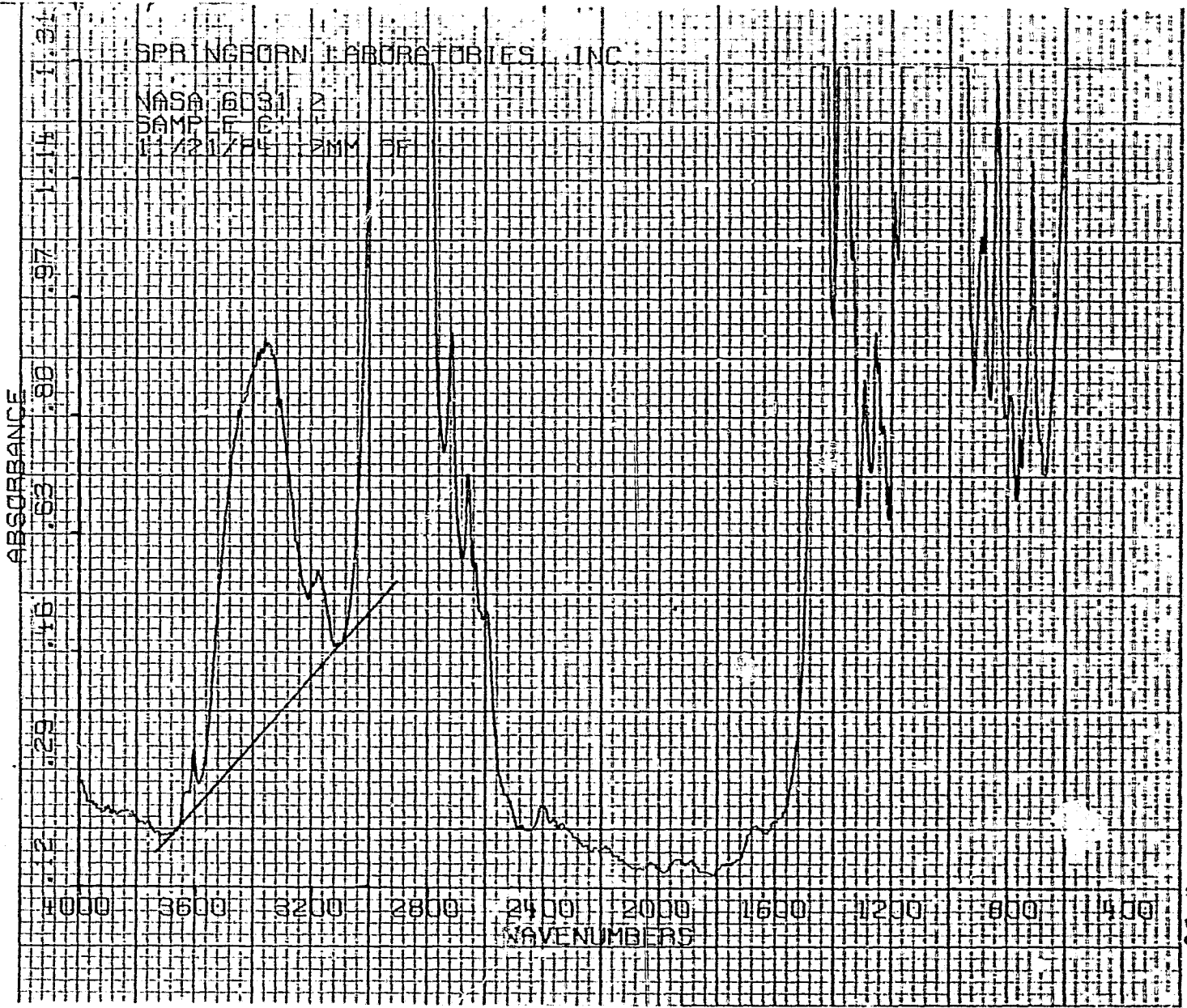


Fig 66

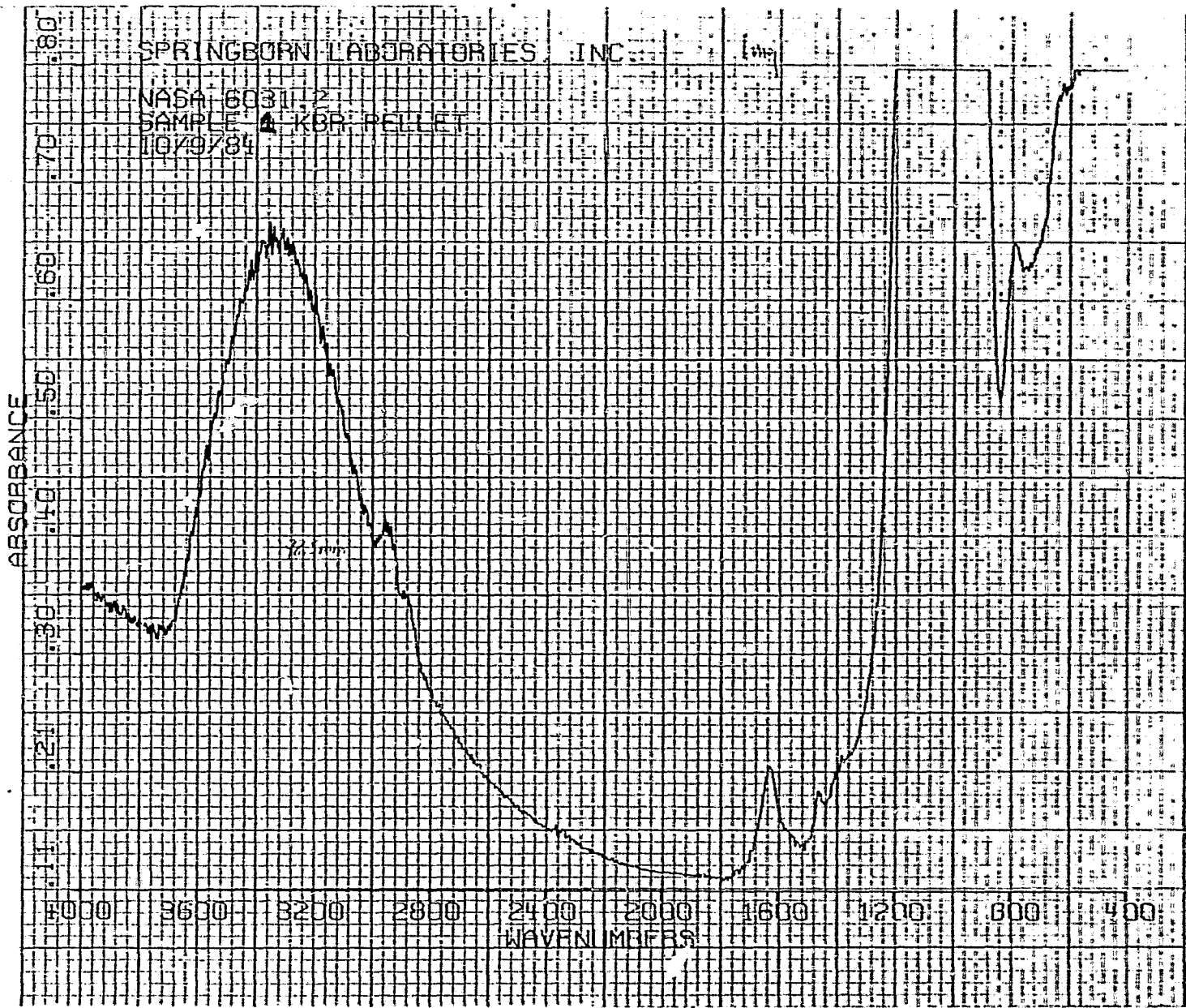


FIG 67

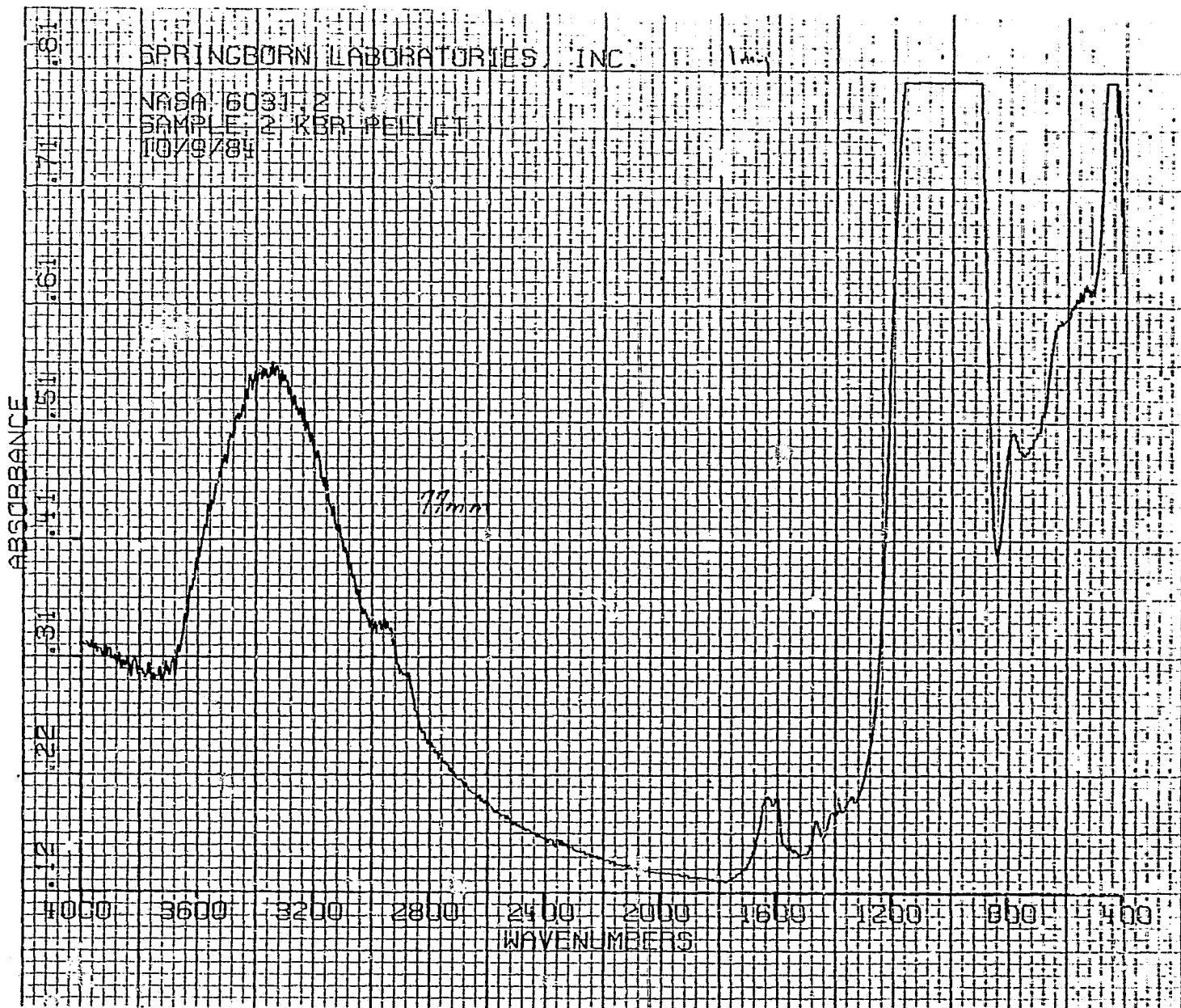
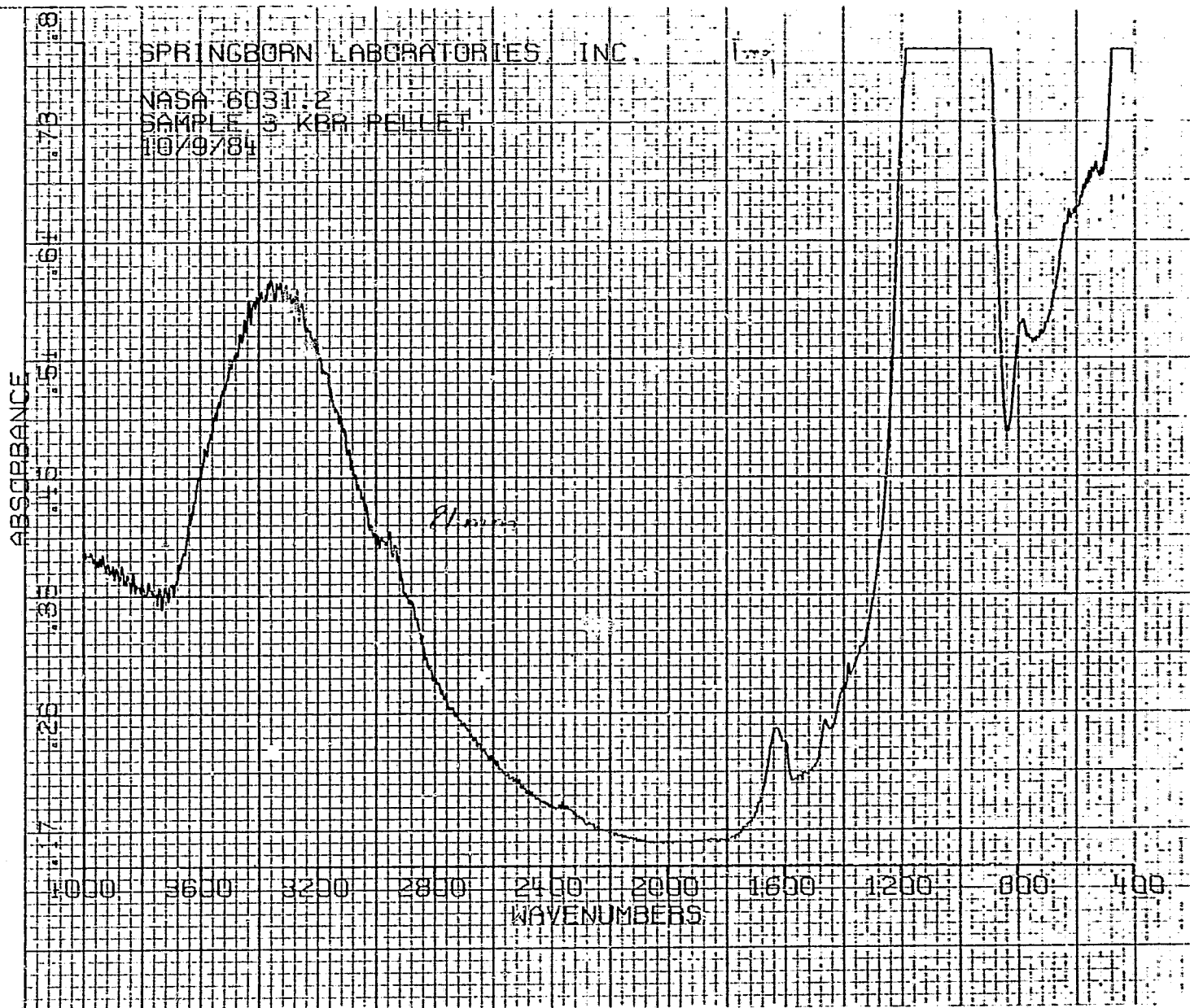


FIG. 68



File 69

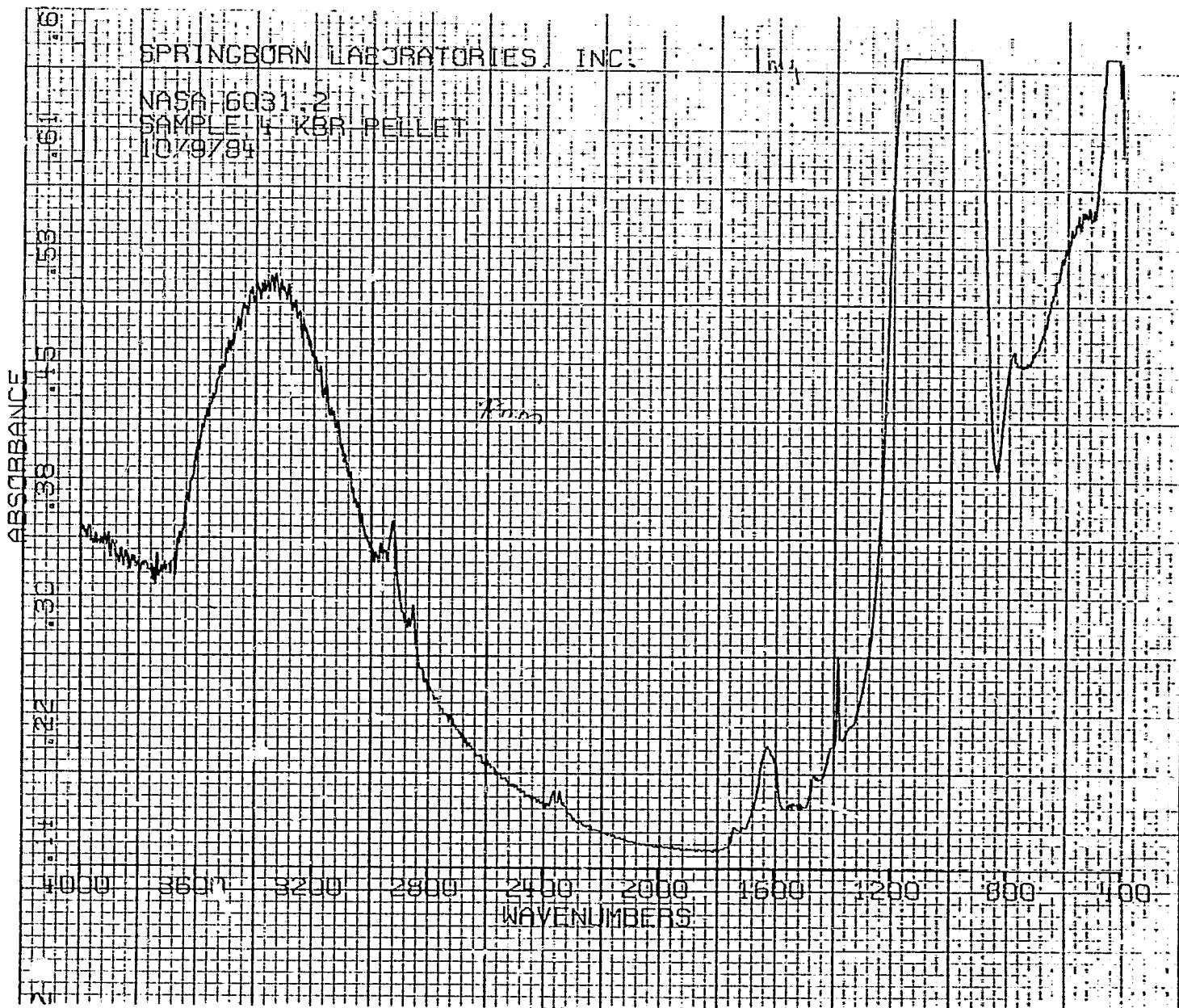
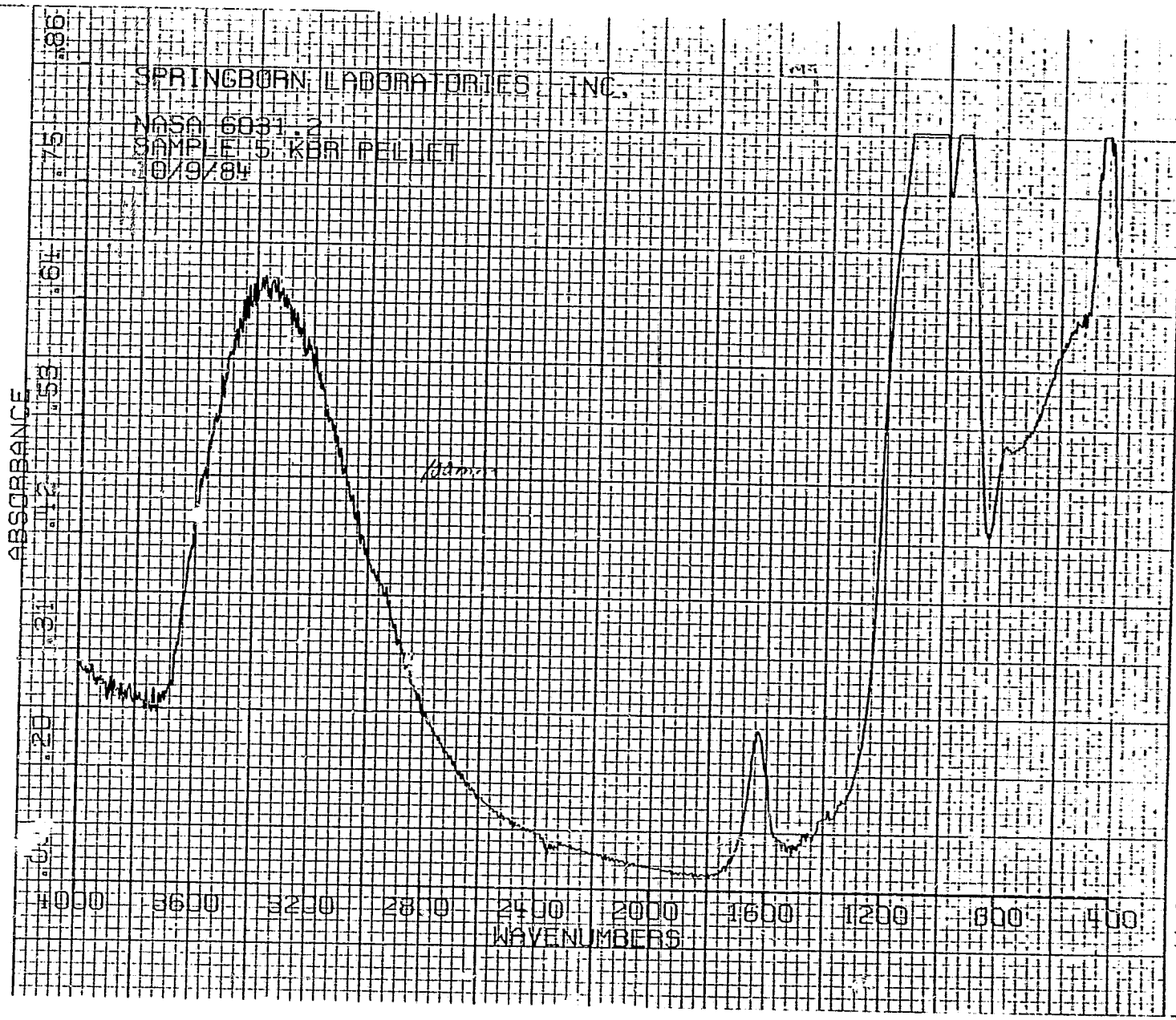


FIG 70



TG 71

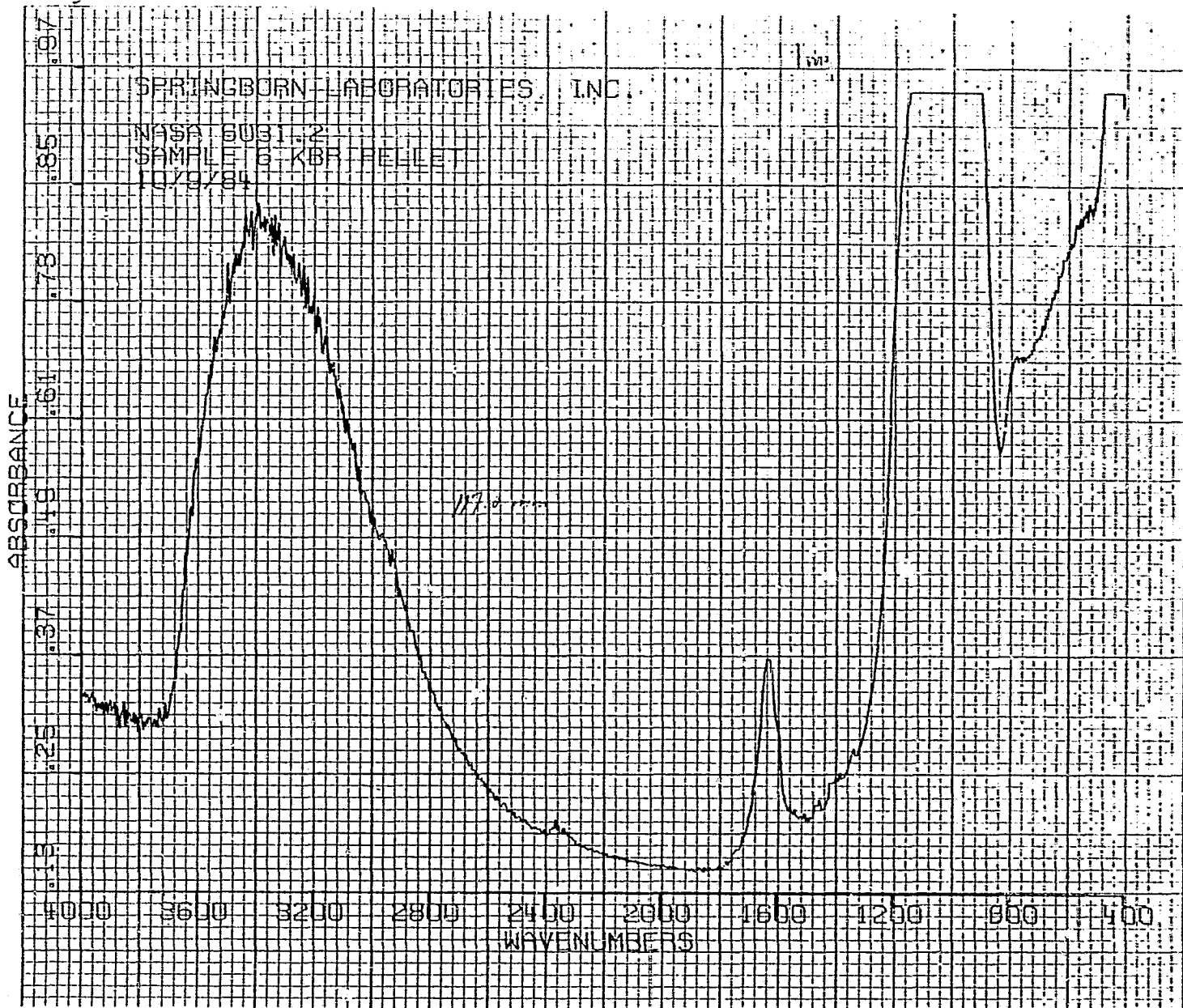


FIG 72

SPRINGBORN LABORATORIES, INC.

NASA 603112
SAMPLE A KBR PELLETS
1079781

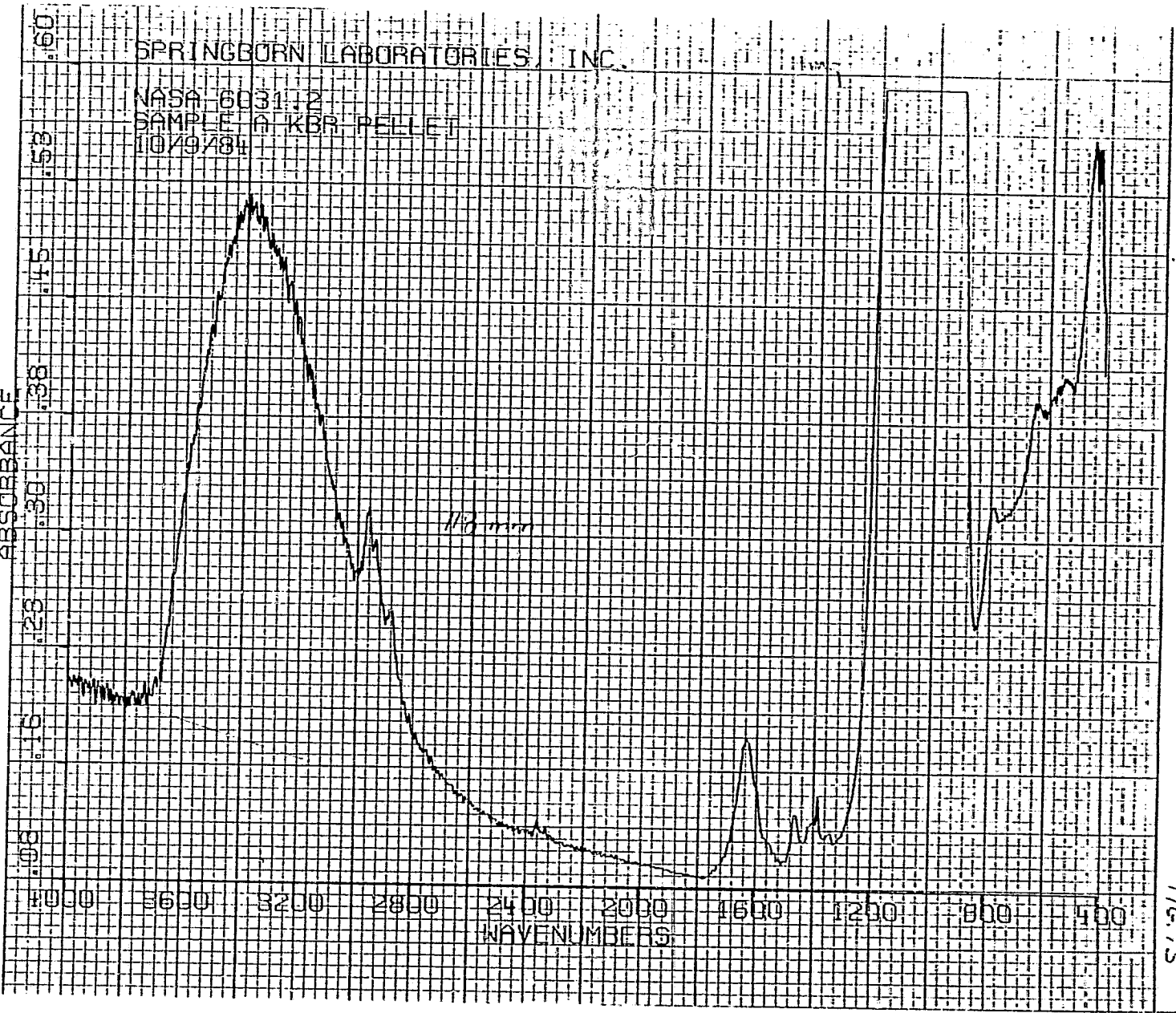
ABSORBANCE

.60
.45
.30
.23
.16
.08

11.2 microns

4000 3600 3200 2800 2400 2000 1600 1200 800 400
WAVENUMBERS

FIG. 73



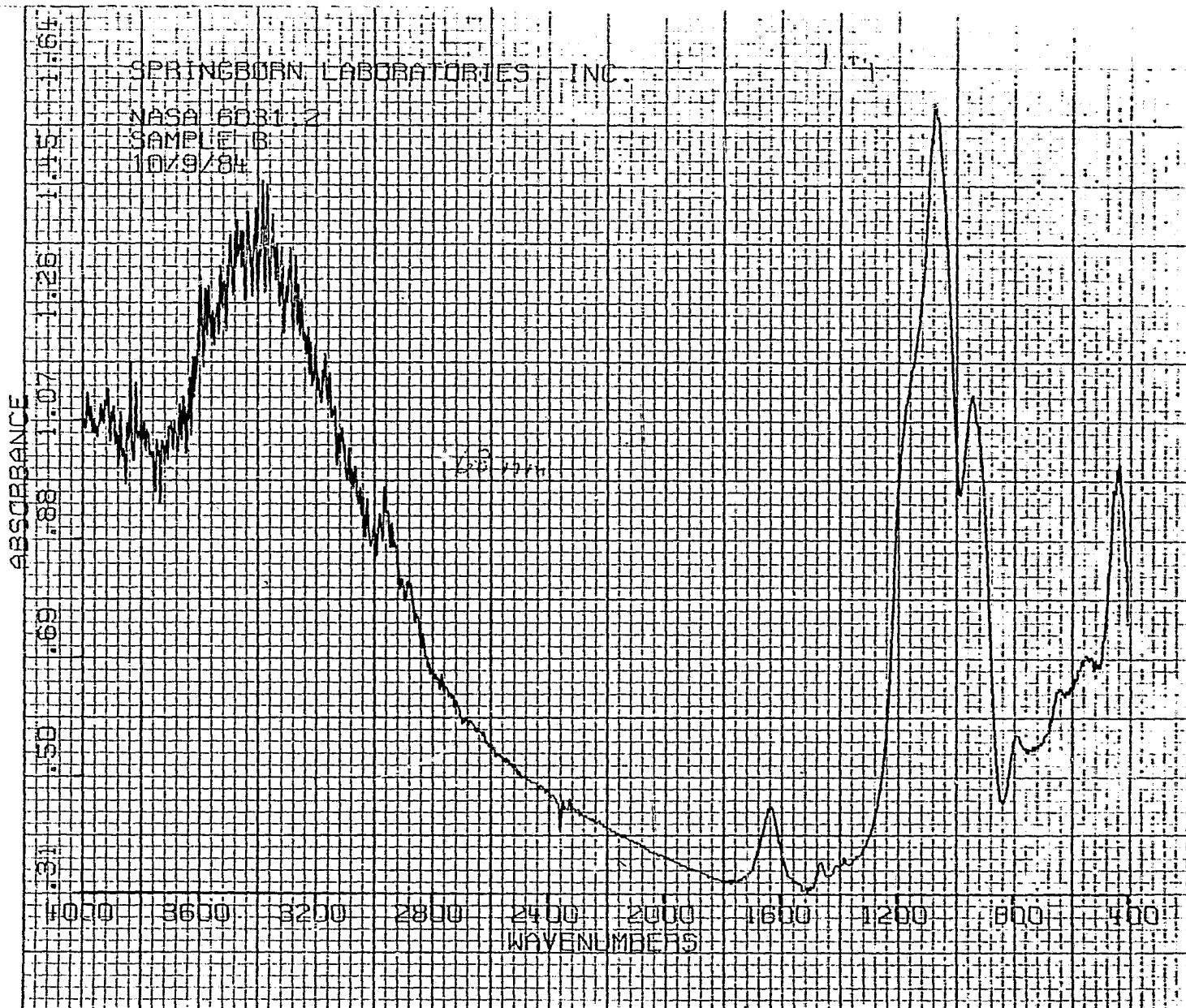
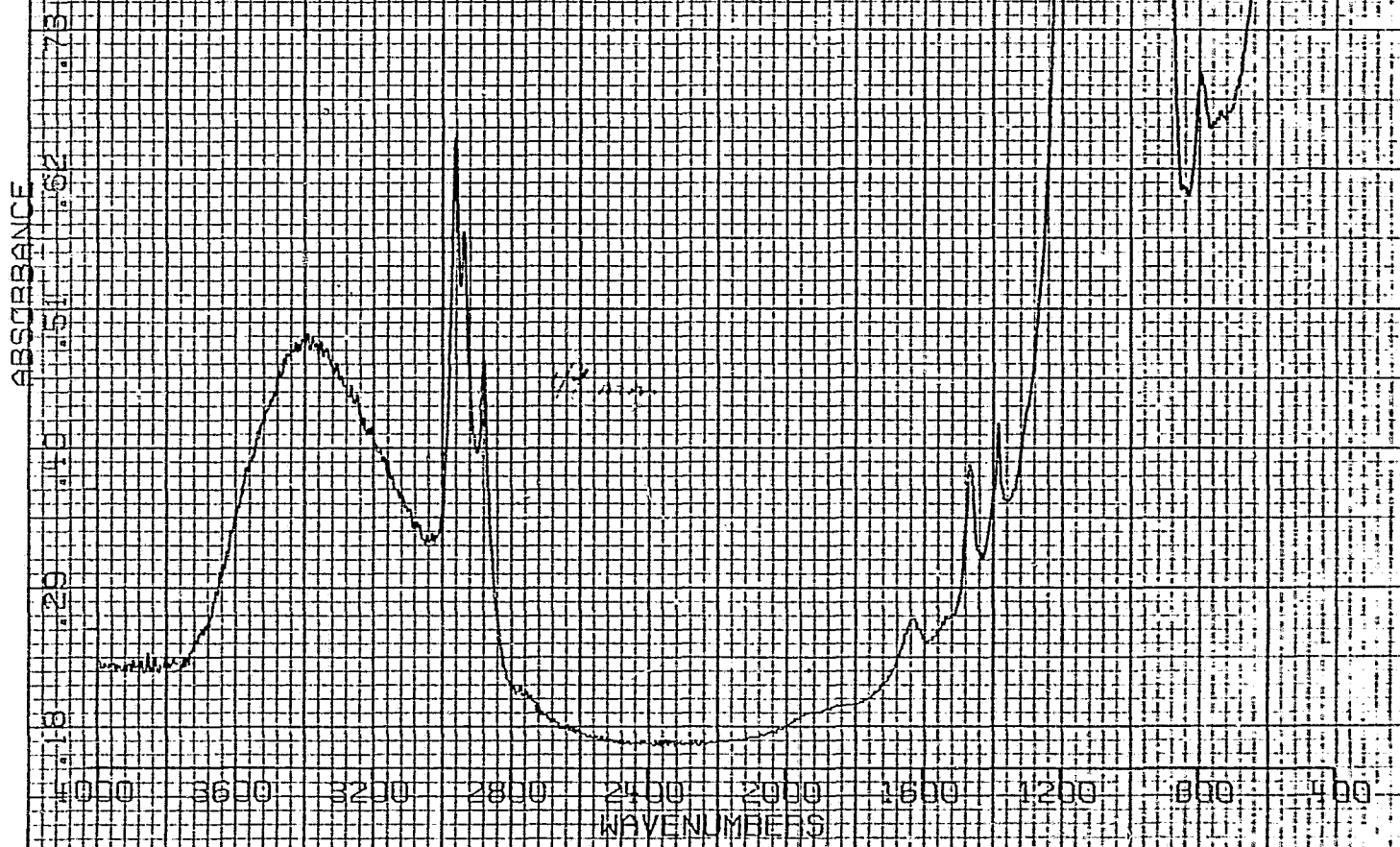


FIG. 74

SPRINGBORN LABORATORIES, INC.

NASA 6031.2
SAMPLE C: KBR PELLETS
10/9/84



76.75