



DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
PUBLIC HEALTH SERVICE
NATIONAL INSTITUTES OF HEALTH

December 4, 1978

68
dup
NATIONAL INSTITUTE OF
ENVIRONMENTAL HEALTH SCIENCES
P.O. BOX 12233
RESEARCH TRIANGLE PARK, N.C. 27709

Dr. John F. Brown
Manager, Life Sciences Branch
Physical Chemistry Laboratory
Bldg. K1, Rm. 3B35
GE Company
Research and Development Center
P.O. Box 8
Schenectady, NY 12301

RECEIVED

J. F. BROWN

Dear Dr. Brown:

I have just a few qualifying final comments with regard to your summarization of our data and views.

1) Perhaps some quantitative comparison of the chlorinated benzenes present in such a used mixture with that in an unused mixture (both prepared by random chlorination of benzene in same way) should be made before chlorine distribution in this class of compounds is assumed not to occur. I think the possibility still remains that chlorinated diphenylethers could be formed by oxidative coupling of the highly chlorinated benzenes (see below).

2) I can not accept the possibility that the chlorinated diphenylethers were original contaminants of the chlorinated benzenes used since the levels are sufficiently high to have been easily mistaken for PCBs in gas chromatographic analysis. In addition, there are substantial amounts of hepta and octachloro diphenylethers suggesting involvement of penta and above homologs of chlorinated benzenes.

3) While it would appear that the PCBs themselves are not substantially altered in use, this can only be said with any confidence with respect to PCBs found in Aroclor 1260. In addition, one can not say that this is or is not the case with the other chlorinated components of the mixture.

4) The inability to detect the dibenzofurans in the used fluid is somewhat surprising in view of the data that is now appearing in the literature on their formation from PCBs under "model" conditions. However, this suggest to me again that there are other significant oxygen depleting reactions which are attenuating dibenzofuran formation (such as diphenyl-ether formation).

783219

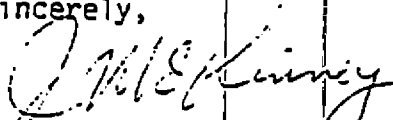
GENP 010408

5) Finally, the diphenylethers are still a potential problem from a disposal viewpoint regardless of how they get there. As pointed out in my previous letter of September 22, they can be converted both photolytically and thermally to dibenzofurans under certain conditions.

6) The raw data that I have enclosed is not all that we have, but it is representative and supportive of the conclusions drawn.

We trust that these comments and information meet with your approval and thank you for our involvement in an interesting analytical chemistry problem.

Sincerely,



James D. McKinney, Ph.D.
Head, Chemistry Section

cc: Dr. Moore
Dr. Albro
Dr. Hass

MASS SPECTROMETRY FACILITY

TO: HEAD, CHEMISTRY SECTION, EECB

THRU: RESEARCH CHEMIST, EECB

FROM: CHEMIST

SUBJECT: PCDF'S IN TRANSFORMER FLUID

IN RESPONSE TO POINT THREE OF MR. BROWN'S LETTER OF OCTOBER 17, 1979
 PLEASE FIND ENCLOSED SEVERAL PIECES OF DATA. THERE ARE TWO RECONSTRUCTED CHROMATOGRAMS
 SHOWING LIMITED MASS SEARCHES FOR IONS FROM HEXACHLOROCYCLOPENTADIENE AT M/Z 372, 374, AND 376
 FROM FRACTION 42 OF OLD AND NEW TRANSFORMER FLUIDS. ALSO INCLUDED IS A MASS SEARCH
 FOR M/Z 444, THE M+2 ISOTOPE OF OCTACHLOROCYCLOPENTADIENE AND M/Z 410, THE M+2 OF HEPTACHLOROCYCLOPENTADIENE.
 THE OLD TRANSFORMER FLUID HAS PEAKS FOR M/Z 374 AND 376, BUT NOT AT 372. THIS IS
 INDICATIVE OF CYCLOPENTADIENE, NOT FURANS. THE NEW TRANSFORMER FLUID HAS PEAKS FOR ALL
 THE ISOTOPE PEAKS OF THE HEXACHLOROCYCLOPENTADIENE, WHICH INDICATES THE PRESENCE OF THIS
 COMPOUND. ONE SHOULD ALSO NOTE IN THE OLD TRANSFORMER FLUID THE LARGE PEAK
 FOR M/Z 444, WITH CORRESPONDING IONS AT M/Z 372, 374 AND 376. THIS IS PROBABLY THE
 RESULT OF LOSS OF TWO CHLORINES FROM AN OCTACHLOROCYCLOPENTADIENE WHICH GIVE
 RISE TO IONS IDENTICAL TO THOSE OF HEXACHLOROCYCLOPENTADIENE. THIS DOESN'T MEAN THAT ONE
 CANNOT ANALYZE FOR THE HEXACHLOROCYCLOPENTADIENE, ONLY THAT YOU MUST BE AWARE OF THIS POSSIBLE
 PROBLEM, AND MONITOR THE BIPHENYL ETHER IONS AS WELL AS THOSE OF THE FURANS.
 THUS, FOR THE NEW TRANSFORMER FLUID, NO IONS AT M/Z 410 OR 444 WERE OBSERVED.
 THEREFORE, THE PEAKS AT M/Z 372, 374 AND 376 CAN BE ATTRIBUTED TO HEXACHLOROCYCLOPENTADIENE,
 AND NOT TO HEPTACHLOROCYCLOPENTADIENE OR OCTACHLOROCYCLOPENTADIENE.

ALSO INCLUDED ARE TWO MASS SPECTRA FROM THESE GC-MS RUNS.
 THE DISPLAYS ARE DUAL PLOTS; THE UPPER SPECTRUM IS "ENHANCED", I.E., THE
 BACKGROUND HAS BEEN SUBTRACTED. THE LOWER (INVERTED) SPECTRUM IS UNENHANCED
 SO THAT ONE CAN SEE HOW INTERFERENCES CAN BE ELIMINATED BY THE ENHANCEMENT
 PROCESS. SCAN 0293 OF NEW TRANSFORMER FLUID CLEARLY HAS IONS AT M/Z 372,
 374, 376, AND 378 - THE MOLECULAR ION ISOTOPE CLUSTER OF HEXACHLOROCYCLOPENTADIENE. IONS ARE
 ALSO OBSERVED AT 337, 339 AND 341 AND AT 383-385, ARISING FROM LOSS OF ONE AND
 TWO CHLORINES, RESPECTIVELY. SCAN 0312 OF THE OLD TRANSFORMER FLUID ALSO HAS

783221

GENP 010410

AD ATTES FROM LOSS OF ONE CHLORINE FROM THE HEPTA CLOPE PRESENT OBSCURE
S INTERPRETATION OF THE MASS SPECTRUM. THUS, IN THE PRESENCE OF LARGE
ANTITIES OF CLOPE'S, IT IS DIFFICULT TO ANALYZE FOR CLOPE'S.

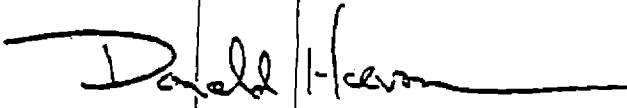
THERE IS NO DOUBT THAT NEW TRANSFORMER FLUID FRACTION 2A
NTAINED CLOPE'S. THIS IS ESTABLISHED BY EXAMINATION OF THE MASS SPECTRA
THE COMPONENTS. HOWEVER, THE LEVELS ARE FROM 5-50 TIMES LOWER THAN IN THE
D TRANSFORMER FLUID.

THE LEVEL OF ¹⁴HEXA CLOPE¹¹ IN NEW TRANSFORMER FLUID FRACTION 49 WAS
STIMATED AT 18 PPM. THIS VALUE REFERRED TO ITS CONCENTRATION IN THAT
ACTION. SINCE THIS WAS THE ONLY FRACTION IN WHICH DIBENZOFURANS
ARE OBSERVED, WE MUST ASSUME THAT THEY WERE CONCENTRATED IN THIS FRACTION
REGARDLESS OF WHERE THEY SHOULD HAVE THEORETICALLY BEEN).
HUS, 18 PPM IN FRACTION 49 WOULD MEAN:

$$\frac{(18 \text{ PPM}) (170 \text{ MG})}{(1000 \text{ MG})} = 1.7 \text{ PPM IN THE ORIGINAL SAMPLE}$$

HIS VALUE IS IN REASONABLE CORRESPONDENCE WITH OTHER INVESTIGATORS' ANALYSES
F AROCLORS FOR DIBENZOFURAN CONTENT.

ALSO INCLUDED ARE THE RECONSTRUCTED CHROMATOGRAMS FOR EACH FRACTION. THESE
EMONSTRATE THE MUCH HIGHER LEVELS OF CLOPE'S IN OLD TRANSFORMER FLUID FRACTION
A AND 49, RELATIVE TO NEW TRANSFORMER FLUID FRACTION 2A.


DONALD HARVAN

12/31/78

783222

GENP 010411

DUAL MASS SPECTRUM

07/14/78 13.18.00 - 19.52

SAMPLE:

ENHANCED (S 15A 2N OT)

100.0 50.0K

DATA: 2780422 (#298)

CALI: 2071478A #1

FL 4B QV17 100/0/260 10U5

BASE M/E: 354/ 56F

RIC: 13199.7 66957E.

3403E

Enhanced
mass spectrum

"Hexachlor"
↓

hepta Cl PCB
↘

M/E 250

300

350

400

450

50.0

Unenhanced
mass spectrum

0.001

GENP 010412

783223

3403E

MASS SPECTRUM

07/07/78 8.29.00 + 20.48

DATA: 2780399 #312

CALI: 2070778 #21

BASE M/E: 394/ 394

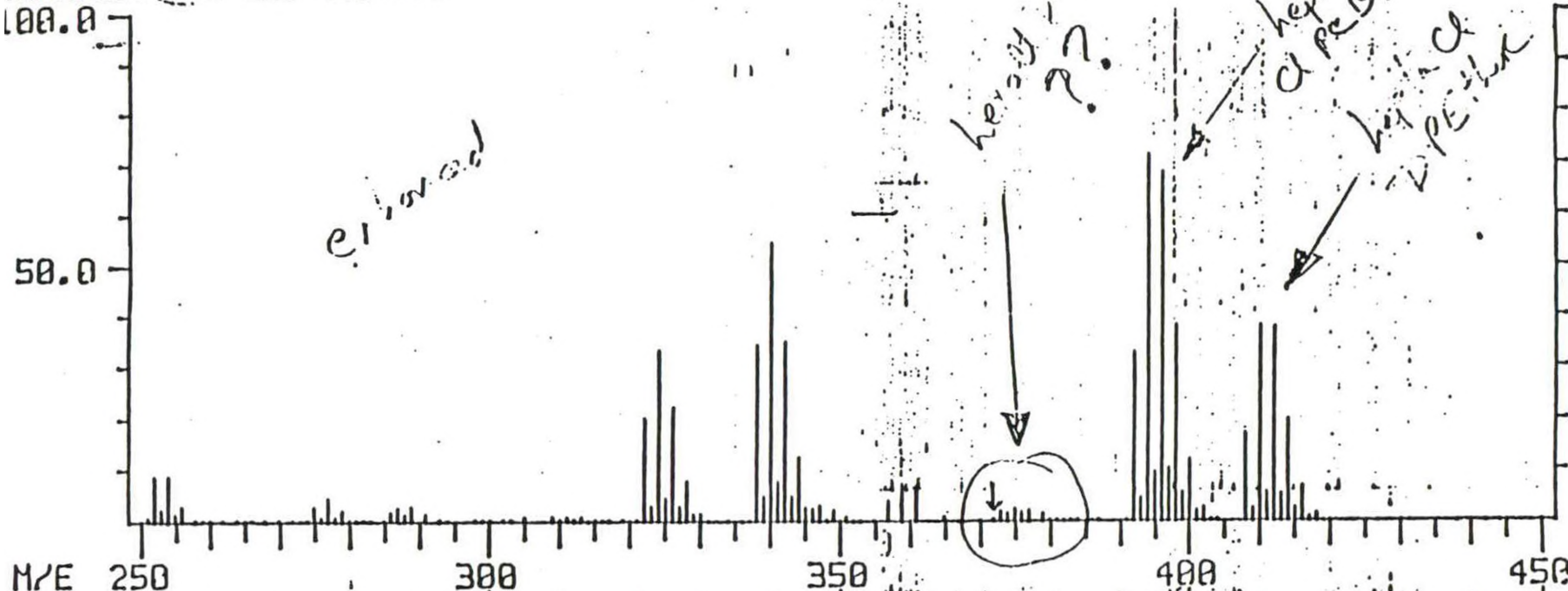
RIC: 1022970. / 1425400.

SAMPLE: (OLD TRANS FC 4B OV17 100/8/280

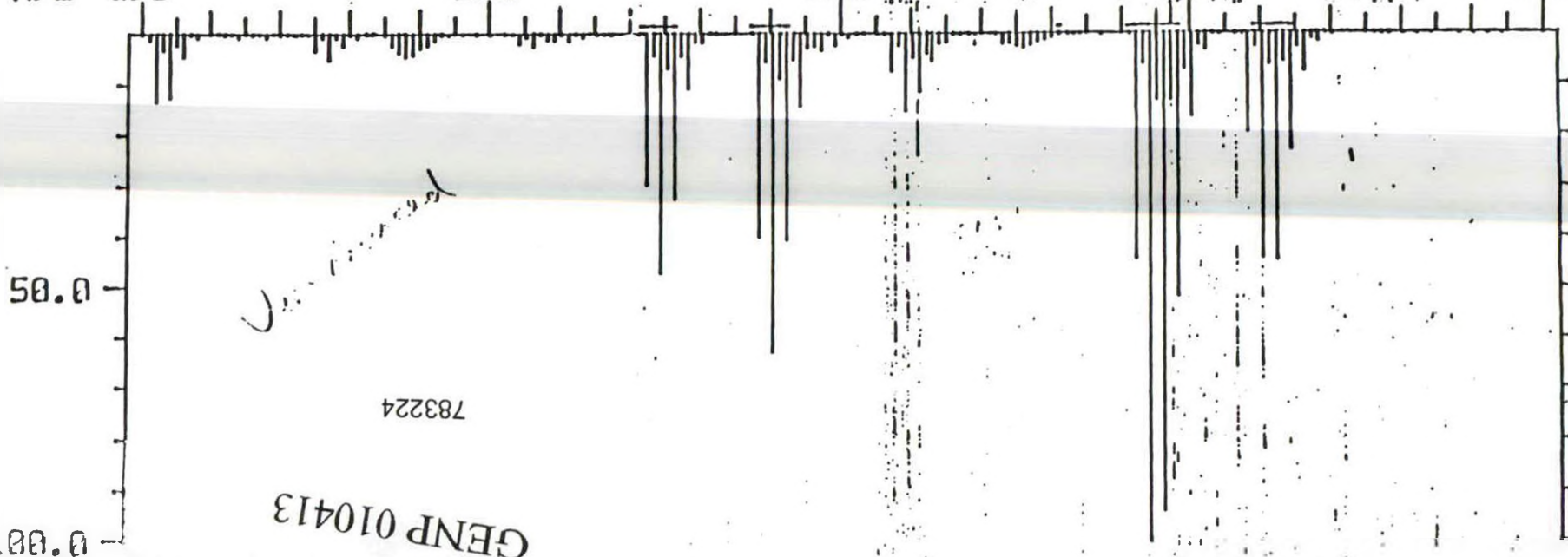
ENHANCED (5 15B 2N 0T)

100.0

98560.



M/E 250 300 350 400 450



783224

GENP 010413

09585

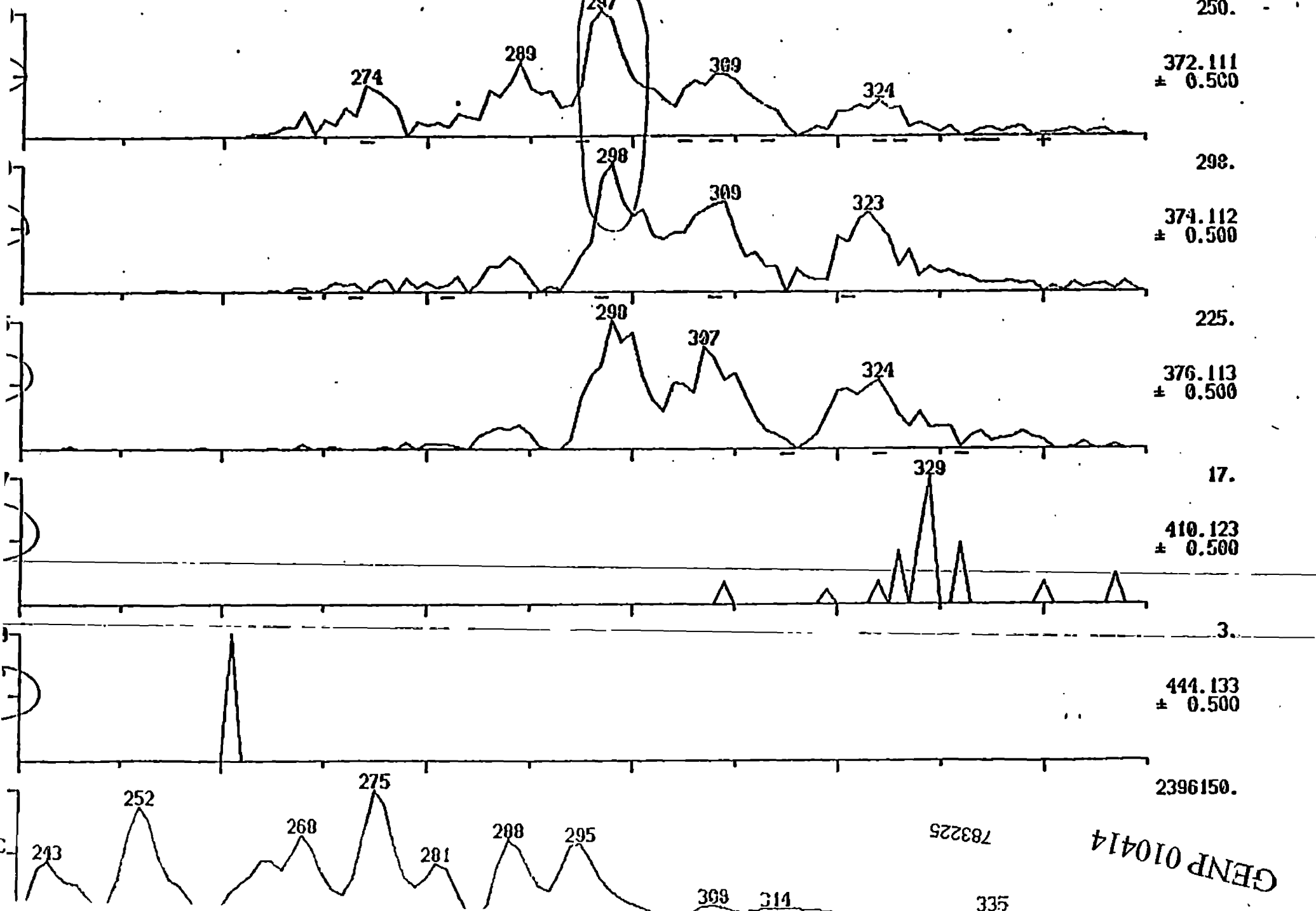
RIC + MASS CHROMATOGRAMS

07/14/78 13:18:00

DATA: 2071478A 01

SAMPLE: NEW TRANS FL 4B OV17 100/8/280 10UG

RANGE: G 1. 191 LABEL: H 2. 4.0 QUAN: A 0. 1.0 BASE: U 20. 3



RIC + MASS CHROMATOGRAMS

07/07/79 8:29:00

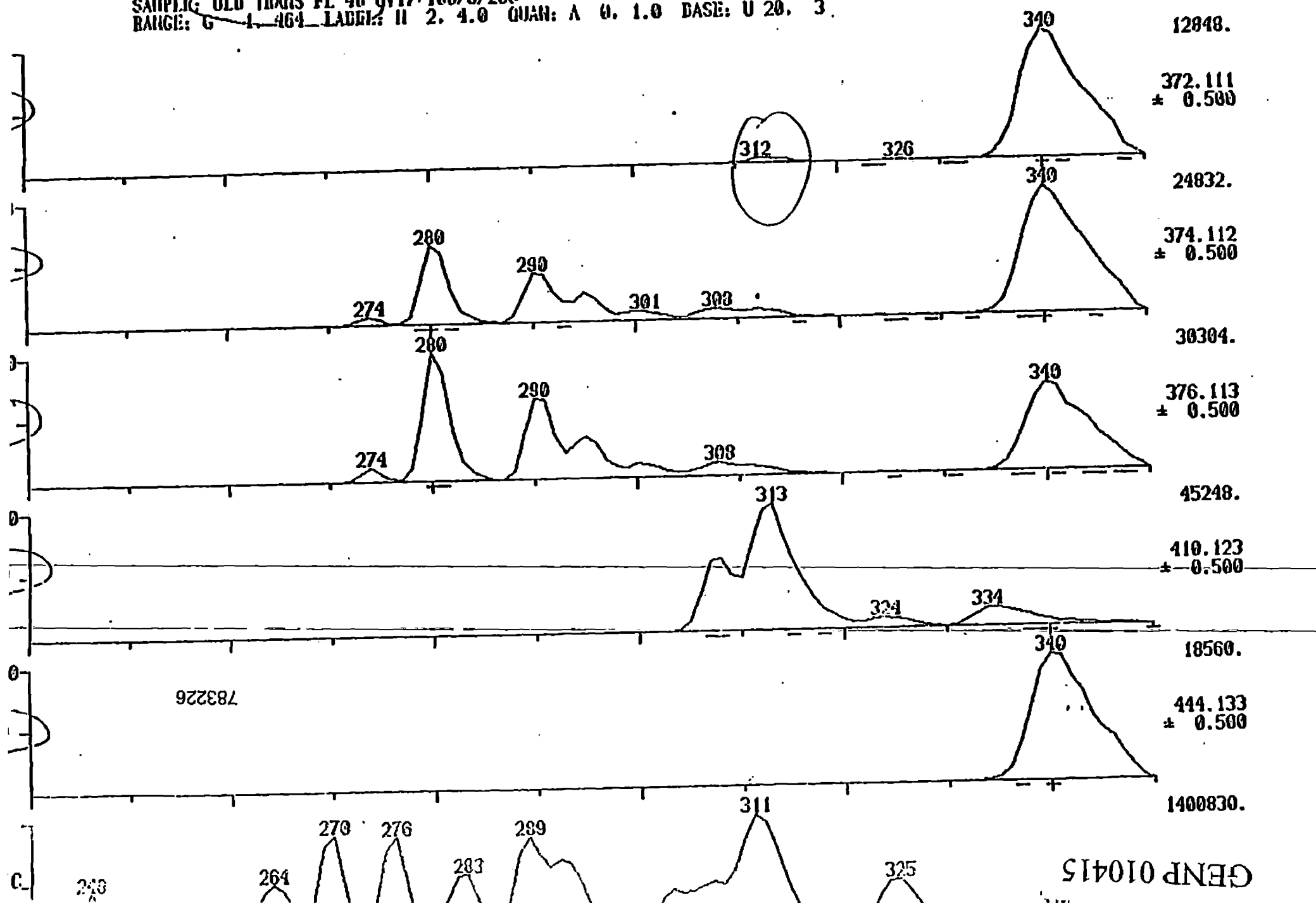
SAMPLE: OLD TRAMS FL 4B QV17.100/8/280

RANGE: G 1.464 LABEL: II 2.4.0 QUAN: A 0.1.0 BASE: U 20. 3.

DATA: Z780399 U1

CAL: Z070770 U2

SCANS 240 TO 350



GENP 010415

RIC

87/12/79 11:13:08

SAMPLE: OLD TRANS FL 2A OV/7 100/8/280 1EUG

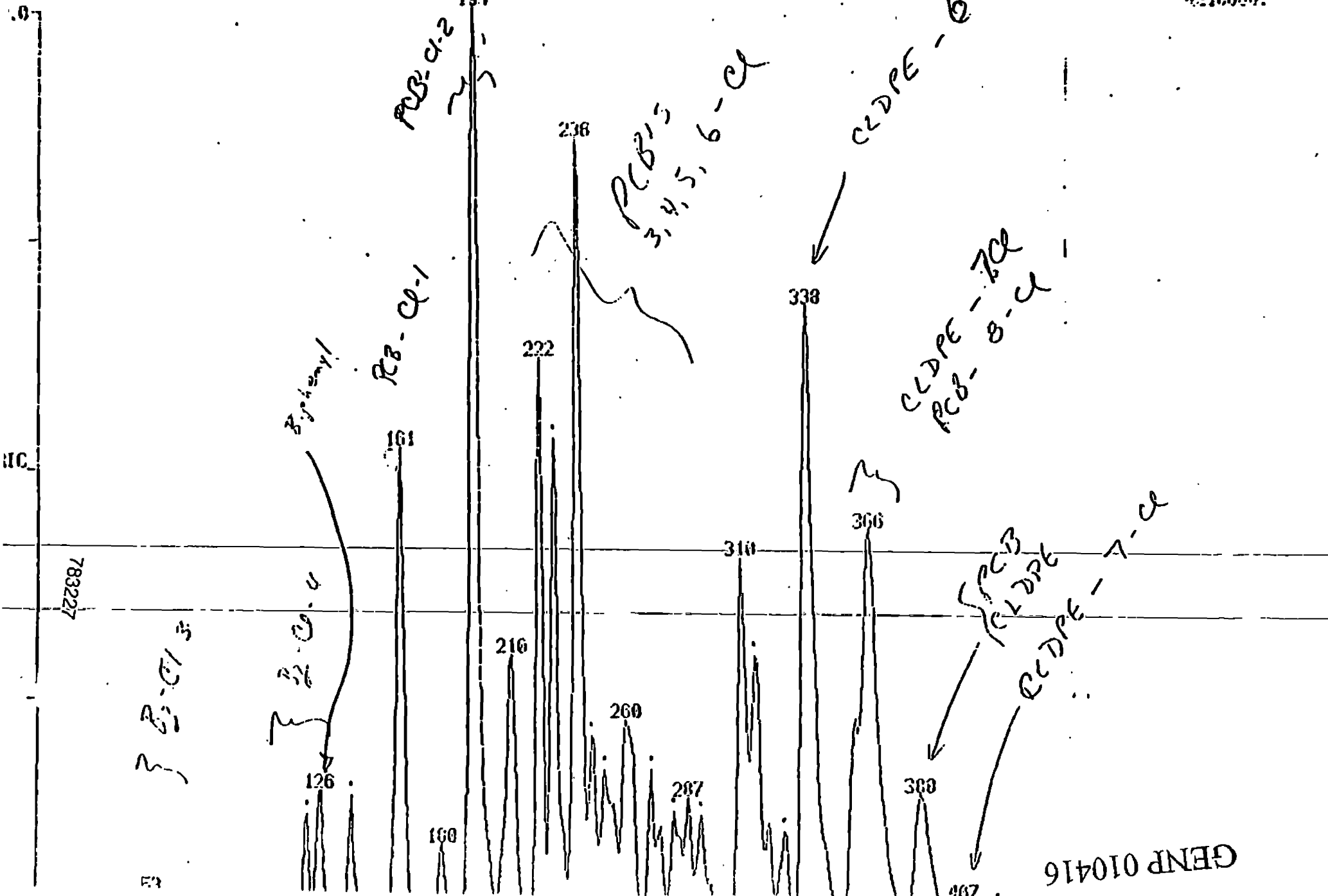
RANGE: 6 1.500 LABEL: H 2.4.0 (UAN: A 0.1.0 BASE: U 20. 3

DATA: Z769420 H1

CALI: Z071479 H3

SCANS 1 TO 539

4210689.



GENP 010416

RIC

07/07/78 8:29:00

SAMPLE: OLD TRANS FL 4D OV:7 100/6/280

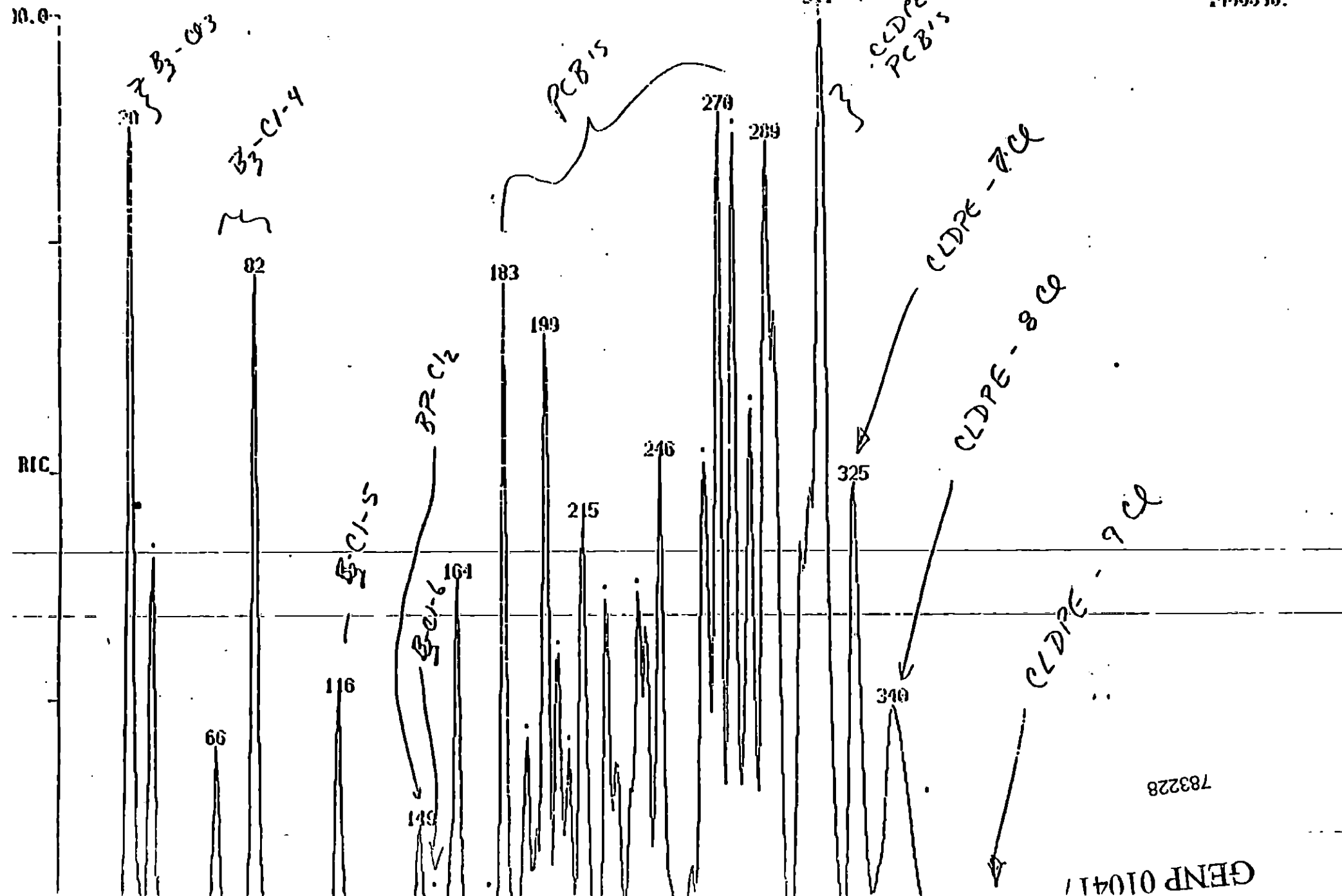
RANGE: G 1. 464 LABEL: H 2. 4.0 QUAN: A 0. 1.0 BASE: U 20. 3

DATA: Z780399 111

CALI: Z670778 112

SCANS 1 TO 481

1499370.



GENP 010418

783229

160. 192. 222. 253. 279. 300. 335. 410. 479.

C₃₄ Hydrocarbon

06/29/78 11:11:00
SAFETY: FGA QUID TRAPS FILLID EC OV17 100/8/200 10UC
RANGE: C 1 500 LABEL: H 5, 2.0 QUANT: A 0. 1.0 BASE: U 20. 3
CALL: 2662678 14

2379770:

MC

0.0

GENP 010419

783230

CLDPC
PC2's

OCB 15
4.4
5.1
6.1
7

phthalate

370
341
255
235
195

DATA: 2/60373 01
CALL: 2662078 61
09/20/78 15:17:03
SAMPLE: 10A OLD THARS FLUID 5B OV17 100/8/209 17/104 ul
INSTR: 6 1.425 LABEL: 11 5. 2.6 QUANT: A 0. 1.0 BASE: 11 20. 3

364032.

GENP 010420

783231

MC

87

C-31 Hydrocarbon

Hydroxy
Triphenyl
Stannane

288
269

RIC
06/26/78 13:45:00
SAMPLE: PVA OLD TRANS FLUID AC OV17 100/6/230
RANGE: 6 1.500 LABEL: H 5. 2.0 QUANT: A 0. 1.0 BASE: U 30. 3
DATA: 2780371 H1
CALL: 2062078 H1

1560710.7

SCANS

RIC
87/14/76 11:55:00

SAMPLE: NEW TRANS FL 2A CY17 169/8 23d

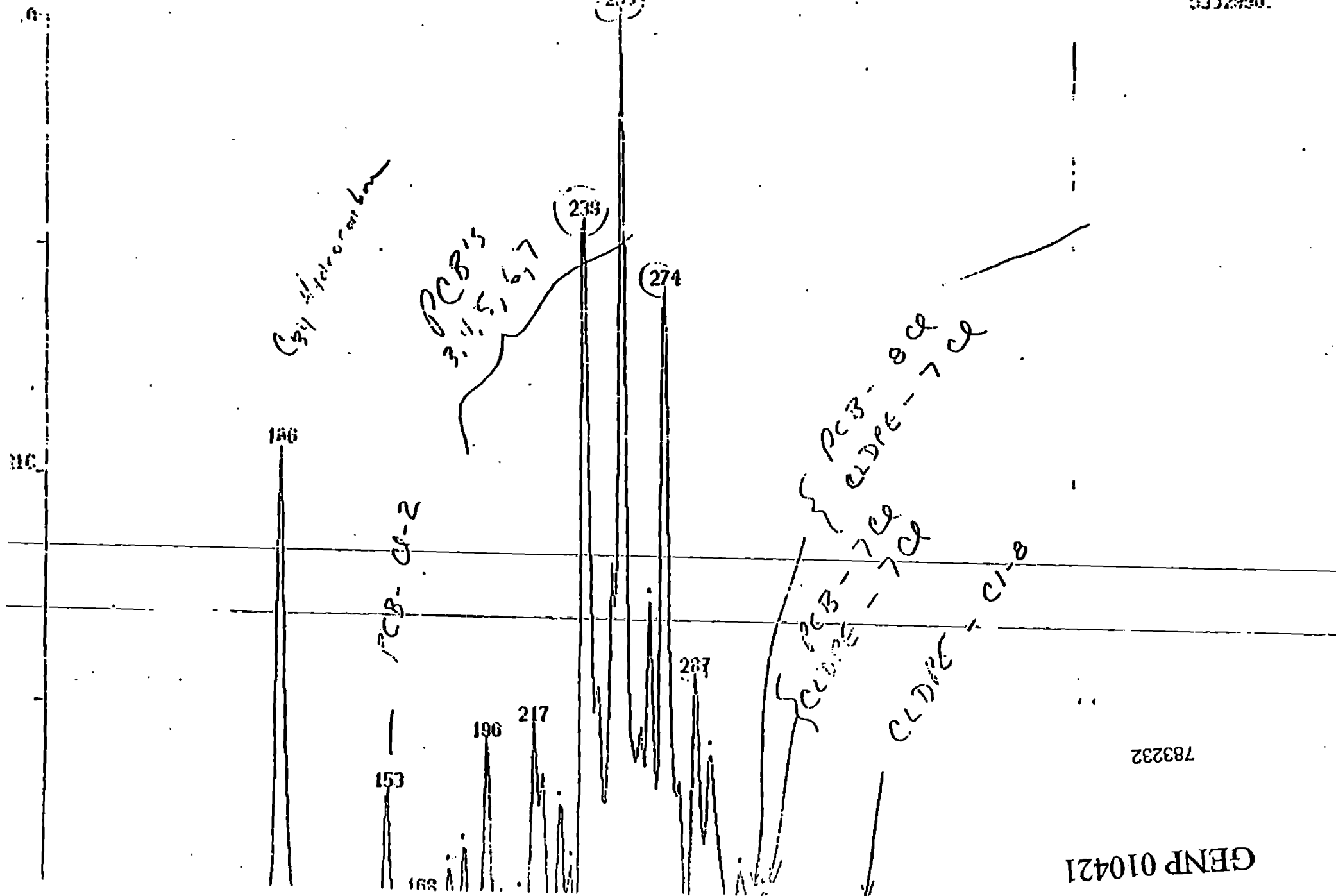
RATE: 6 1.506 LABEL: H 2. 4.0 QUANT: A 0. 1.0 BASE: 0 20. ?

DATA: 2700421 H1

CALI: 2071478 H2

SCANS 1 TO 500

5332920



RIC
07/11/79 13:13:00

SAMPLE: NEW TRANS FL 48 OV17 190/0/200 10UG

RAISE: 6 1. 494 LABEL: H 2. 4.0 QUANT: A 0. 1.0 PAGE: U 20. 3

DATA: 2780122 31
CALI: 2071470A 01

SCANS 1 TO 494

2105150

10.0

43

B3-03

PCB's
3, 4, 5, 6, 7

252

275

288

No CLYPE'S
OBSERVED

RIC

B3-C1-9

220

76

783233

GENP 010422

NIC
06/20/78 14:36:00

SAMPLE: PVA NEW TRANS FLUID 4C 0V17 100/0/230

RANGE: G 1. 450 LABEL: H 5. 2.0 QUANT: A 0. 1.0 BASE: U 20. 3

DATA: Z760372 H1

CAL1: Z062070 H1

SCANS 1 TO 450

1464710.

0.8

NIC

C₃₄ Hydrocarbon

*PCB's
4,5,6,7-α*

246

225

250

275

196

*Hydrocarbon
stems?*

783234

GENP 010423

GENP 010424

783235

RIC
06/20/78 15:59:00
SAMPLE: PVA NEW TRANS FILTH 5M OV17 100/0/200 10MG
RANGE: C 1.450 LABEL: D 5.2.0 GAIN: A 0.1.0
DATA: E70074 RI
CALL: 2062078 RI
SCANS 1 TO 959
1538010.

246

CCBIS
4, 5, 6, 7, 8

226

258

110

92

C₃₄H₁₂O₁₀
C₂H₄

33

71

175

196

275

296

RIC

19.0

GENP 010425

783236

MIC

11.6-

Temp held @ 100°C
for ca. 10 min's

MIC
06/20/78 12:43:09
SAMPLE: PVA NEW TEARS FLUID
RANGE: 6 1.500 LABEL: 11
SC 0V17 100/8/250 10UC
5. 2.0 QUANT: A 0. 1.0
DATA: Z700370 R1
CALL: Z062078 R1
BASE: U 20. 3

951296.

SCANS 1 to 300

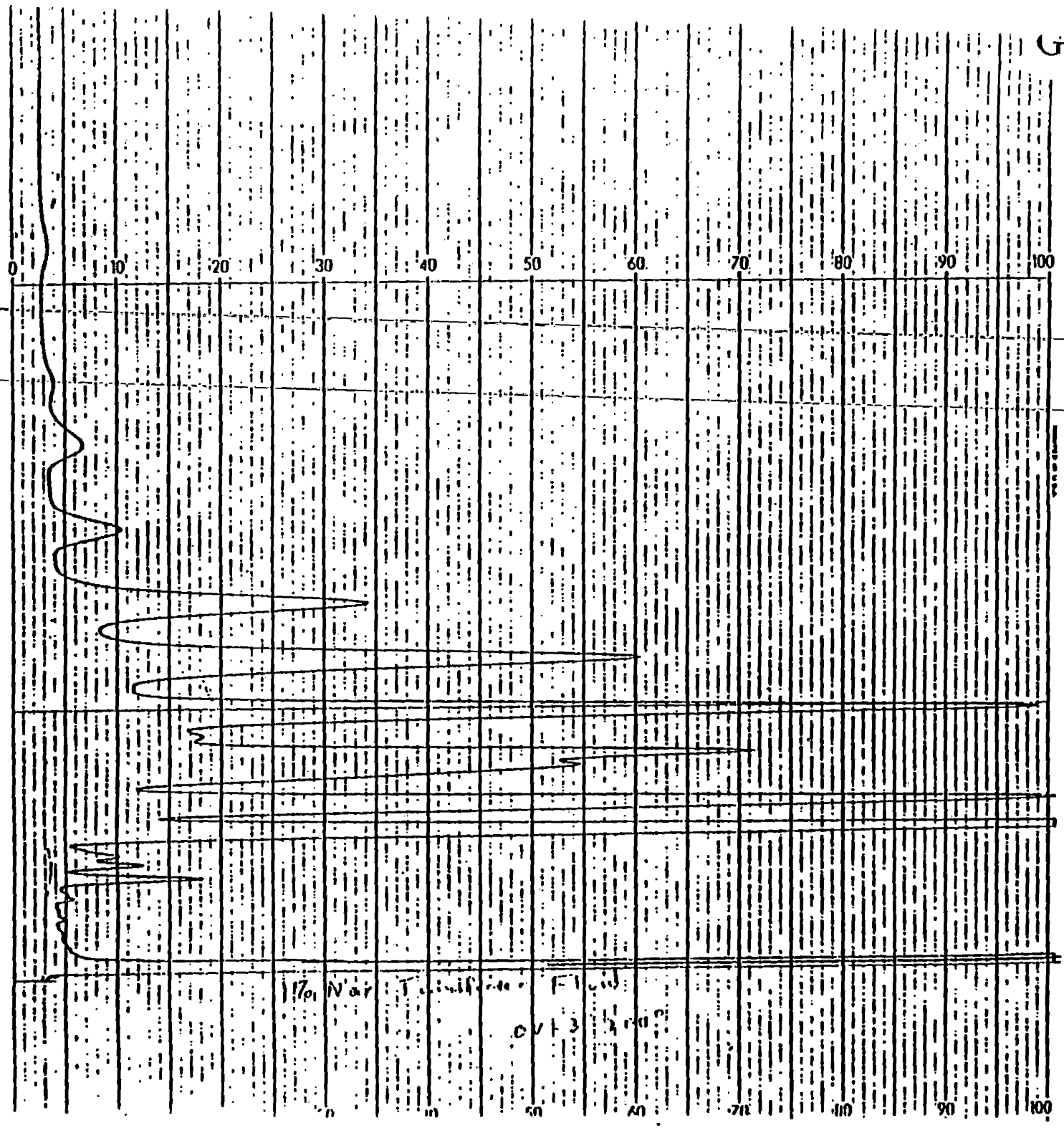
Cy H₂dicca (30.0)

Cy H₂dicca
C₁₀H₁₆
C₁₀H₁₆
C₁₀H₁₆

C₁₀H₁₆

306
305
381
125
150

783237

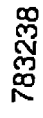


1701 N'ar T. 100000 F. 100000

0013 100000

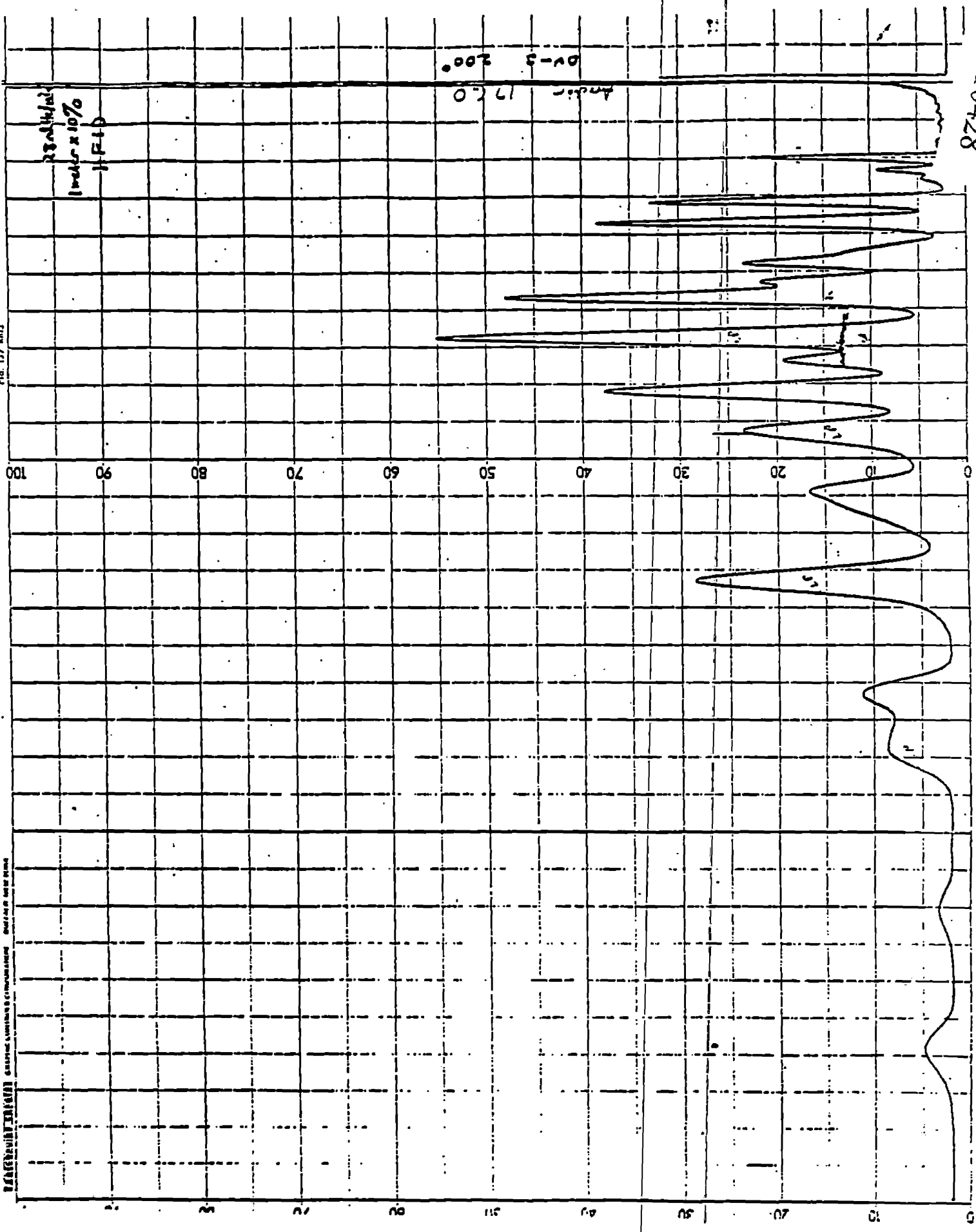
16

No. 159-1093



UNP 010428

783239

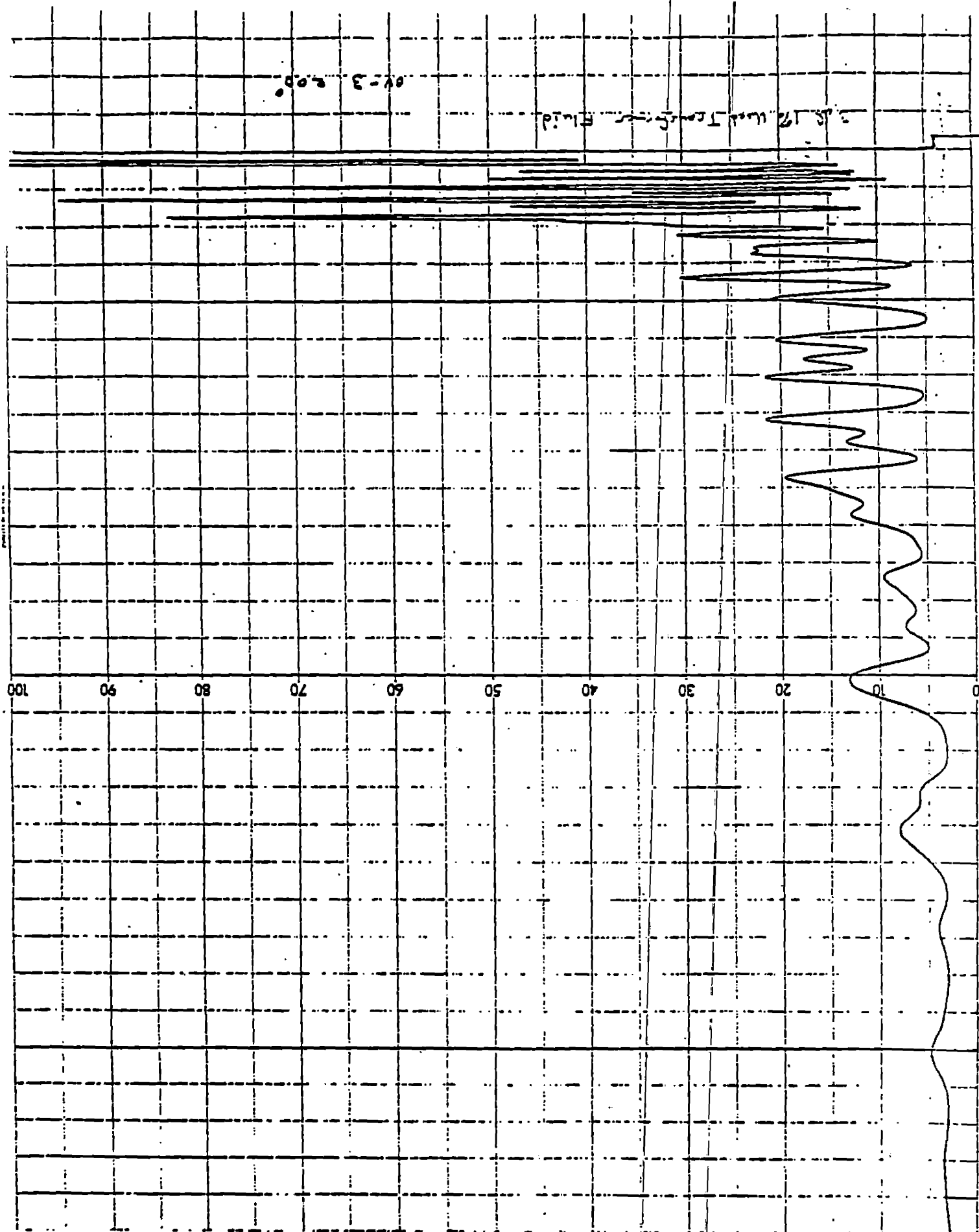


783240

GENE VIVIAN

2.5 17.14.15.16.17.18.19.20.21.22.23.24.25.26.27.28.29.30.31.32.33.34.35.36.37.38.39.40.41.42.43.44.45.46.47.48.49.50.51.52.53.54.55.56.57.58.59.60.61.62.63.64.65.66.67.68.69.70.71.72.73.74.75.76.77.78.79.80.81.82.83.84.85.86.87.88.89.90.91.92.93.94.95.96.97.98.99.100

04-3 2.00°

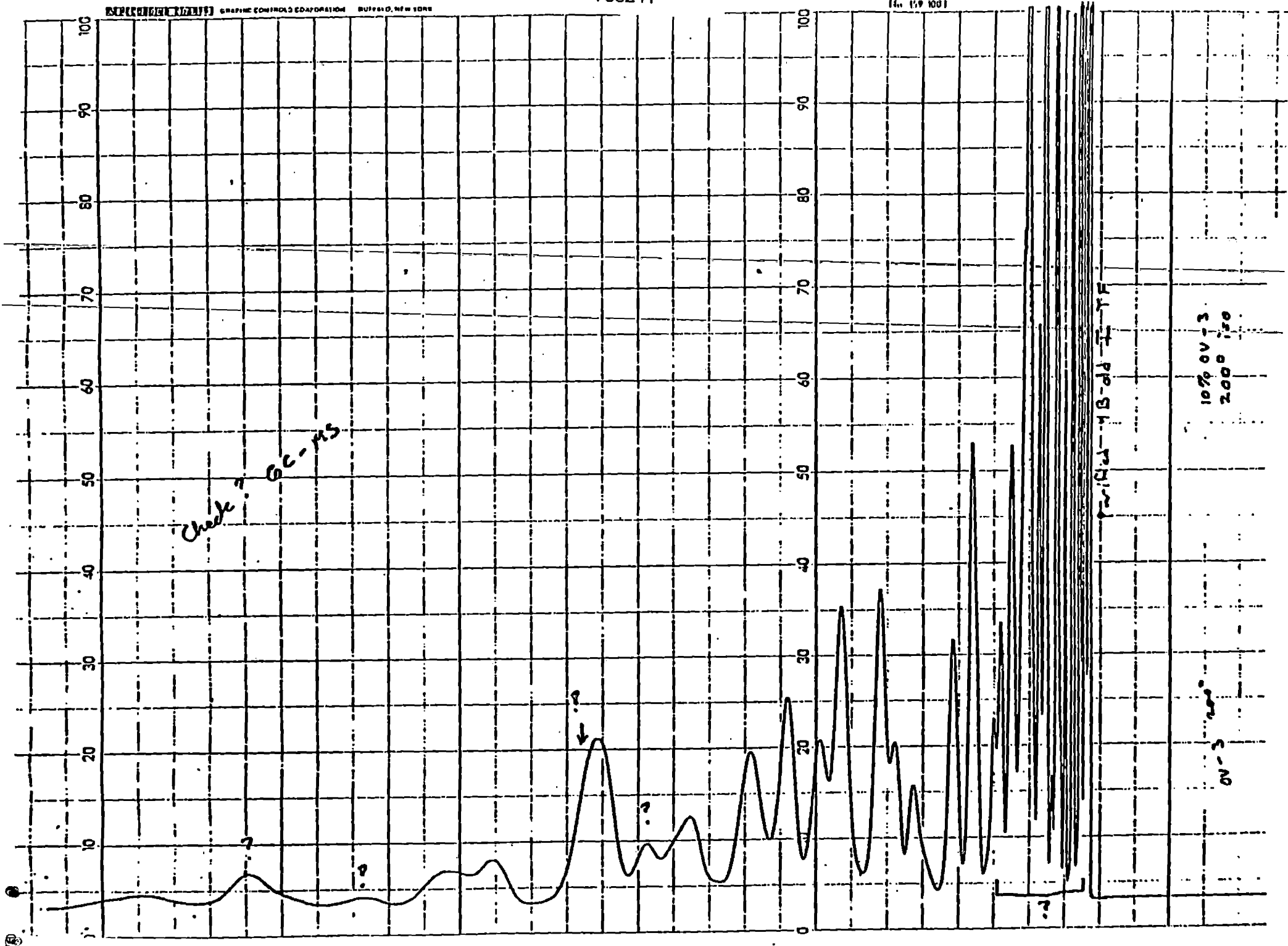


783241

GRAPHIC CONTROLS CORPORATION BUFFALO, NEW YORK

14-15-1001

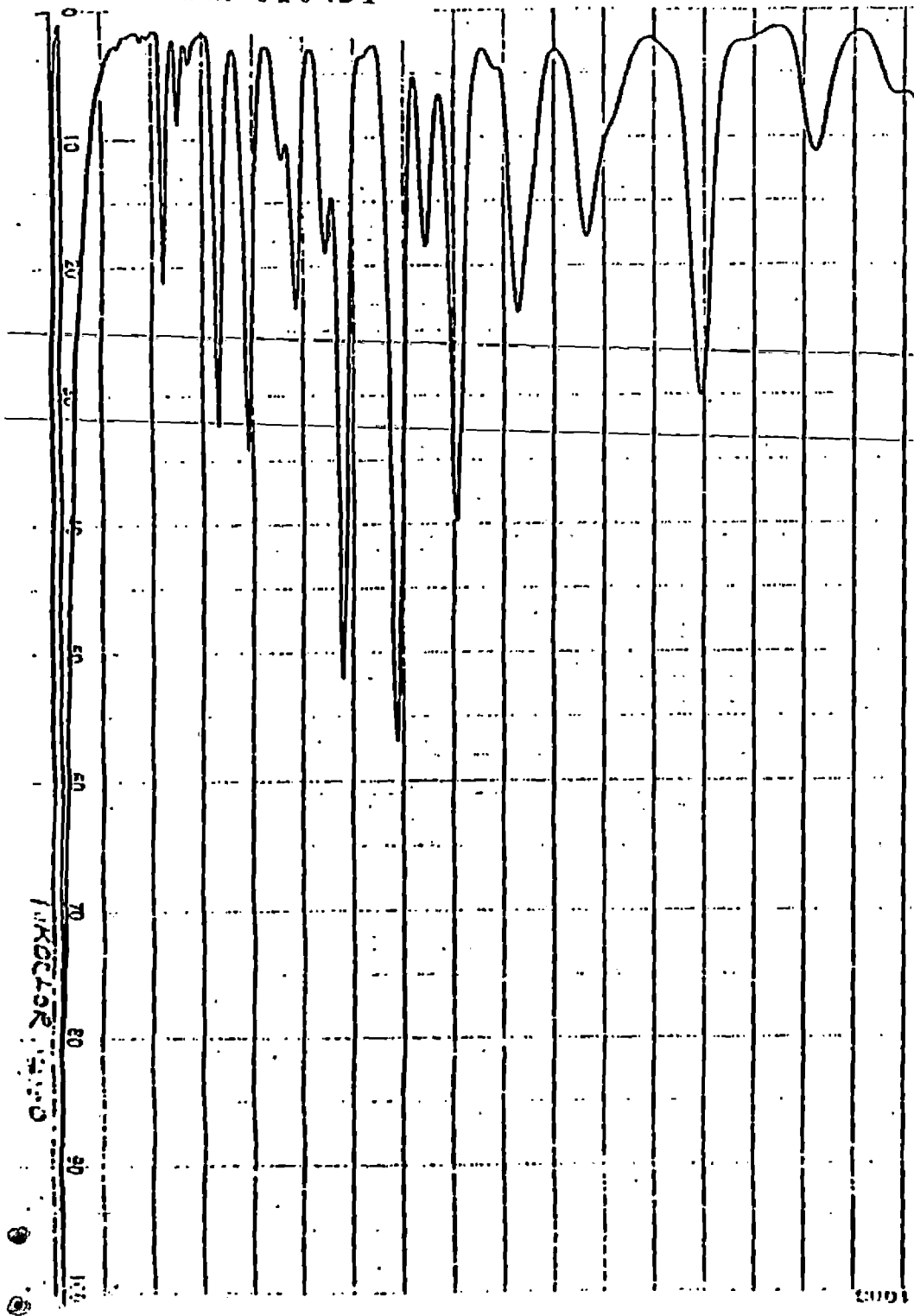
check "GC-MS"



10% OV-3
2000 Hz

OV-3

GENP 010431



783242

10

20

30

40

50

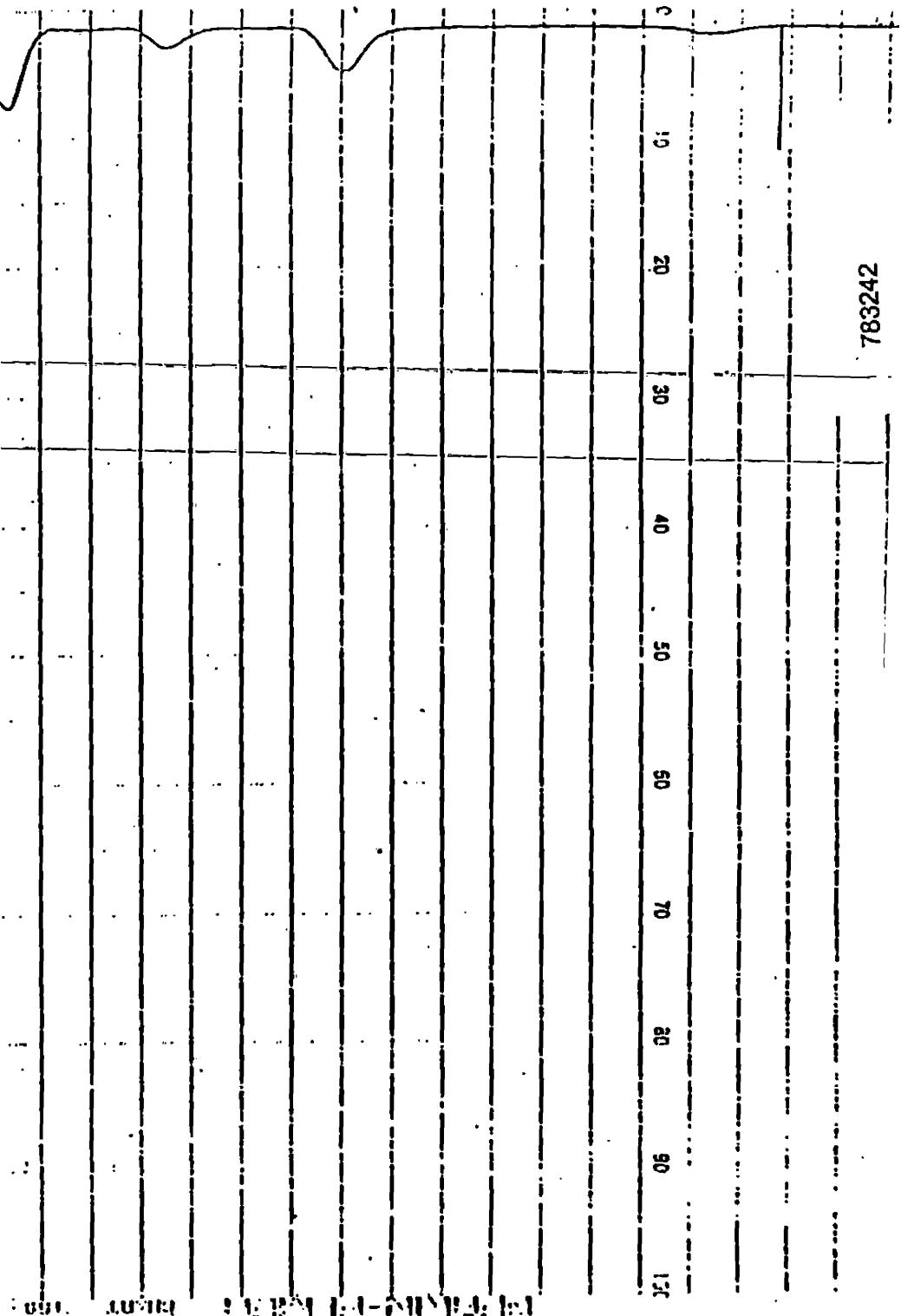
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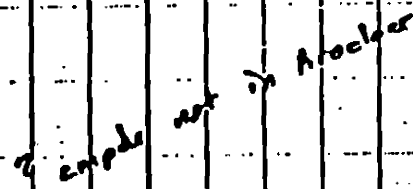
70

80

90

100





1047 1048 1049

PCB
2,3,4,5,2,3,4,6

20

2025.4.29

PCB

[illegible]

NY 961

Stand and Run
Charles
"used" transformer
6/14/68

Transducer
B
11/15/96
11/15/96

11/15/96

PERIOD-ELAPSED

100

50

80

70

60

50

40

30

20

10

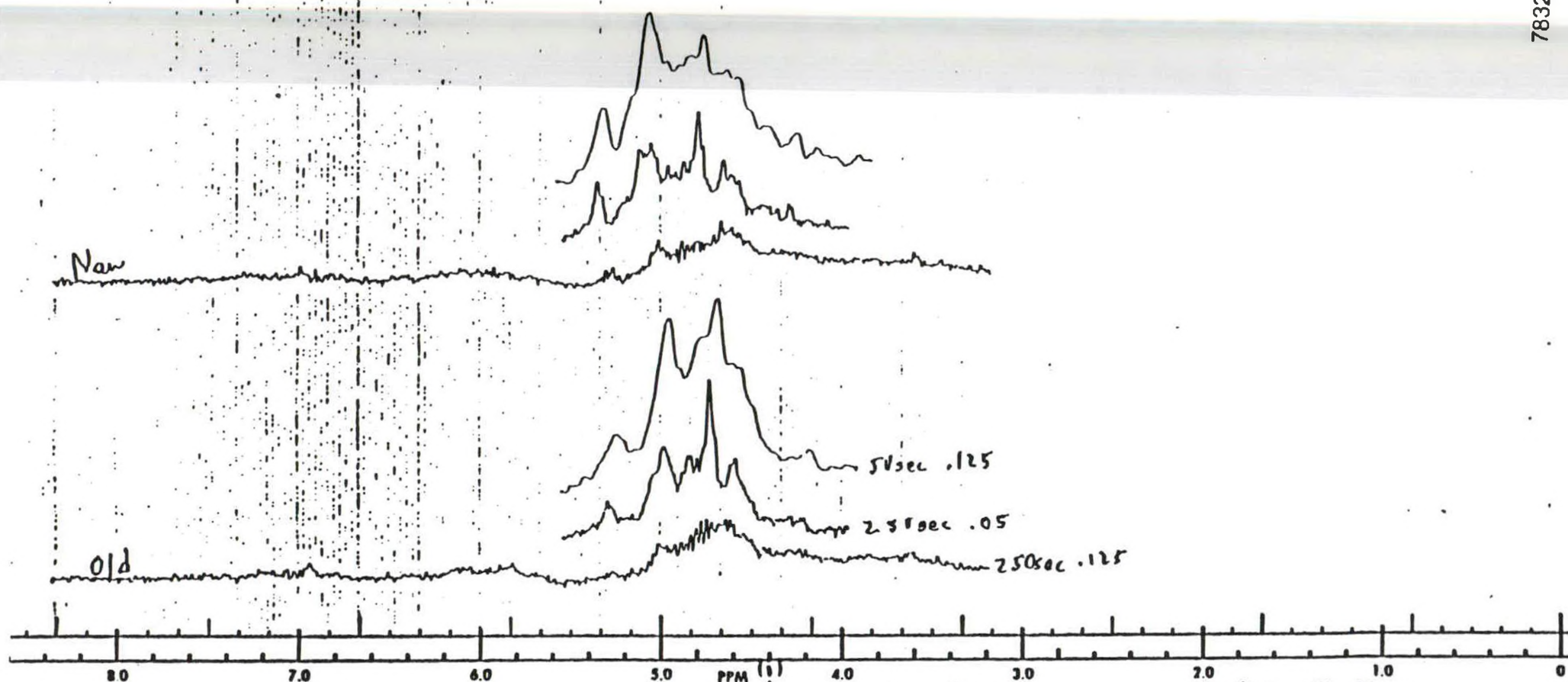
0

UENP 010433

783244

GENP 010434

783245



SWEEP OFFSET (Hz), 30.0
 SPECTRUM AMPLITUDE, 3.2
 INTEGRAL AMPLITUDE,
 SPINNING RATE (RPS), 34

MANUAL
 SWEEP TIME (SEC), 30.24
 SWEEP WIDTH (Hz), 25 50 100 250 500
 FILTER, X 2 3 4 5 6 7 8
 RF POWER LEVEL, 0.125 / 0.5

AUTO ☐
 (250)
 (500)
 (2)
 (.05)

SAMPLE, Transformer
 Fluids

SOLVENT, CDCl₃ TMS

REMARKS, "New" Above
 "Old" Below



STOHLER ISOTOPE CHEMICALS

49 JONES ROAD, WALTHAM, MASS. 02154

DATE,

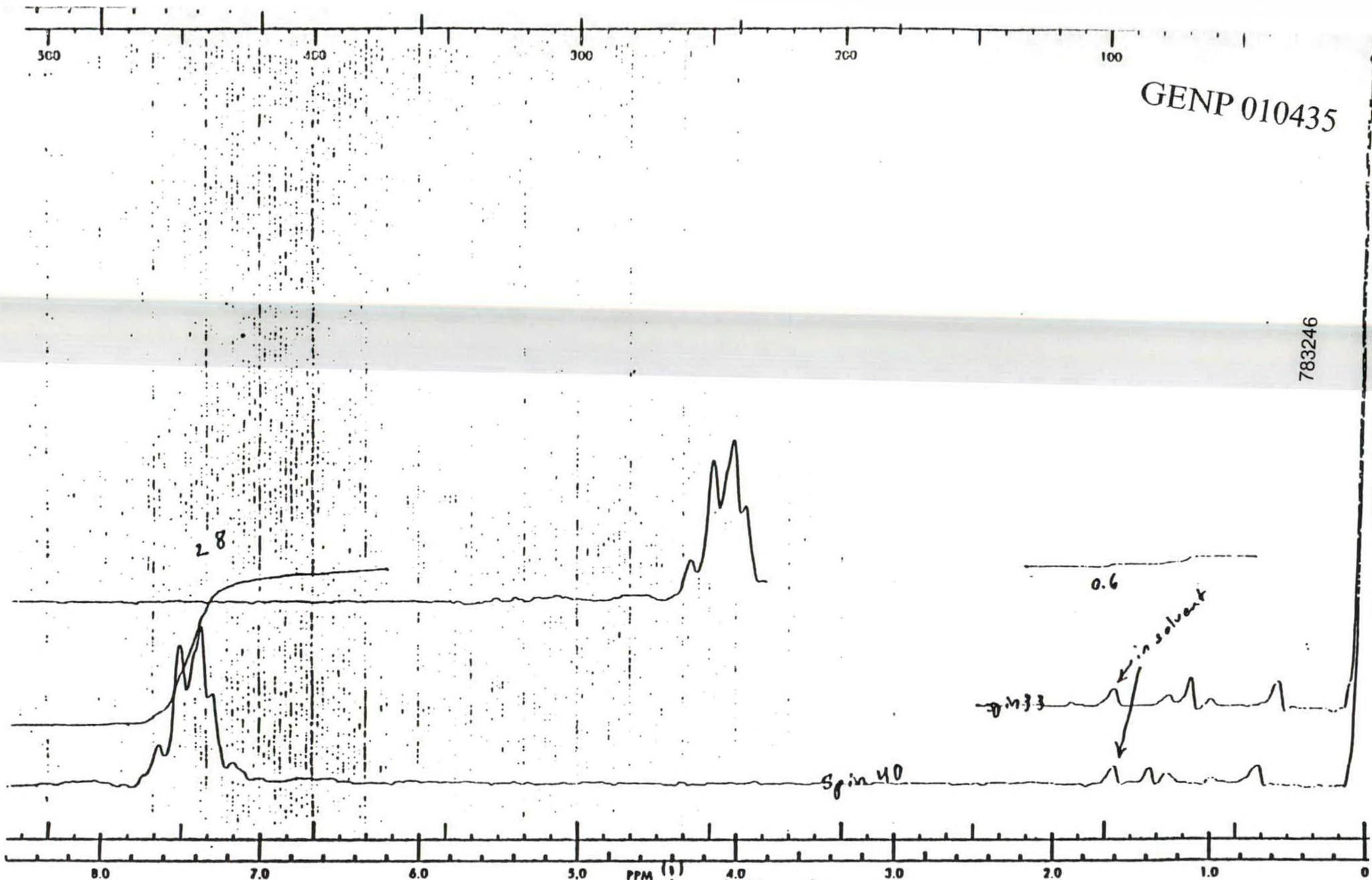
OPERATOR, Albert

60 MHz NMR

SPECTRUM NO.

GENP 010435

783246



SWEEP OFFSET (Hz): 0/200
 SPECTRUM AMPLITUDE: 20
 INTEGRAL AMPLITUDE: 5
 SPINNING RATE (RPS): 40/33

MANUAL
 SWEEP TIME (SEC): 250
 SWEEP WIDTH (Hz): 25 50 100 250 500
 FILTER: 2 3 4 5 6 7 8
 RF POWER LEVEL: 0.125

AUTO ☐
 (250)
 (500)
 (1 2)
 (.05)

SAMPLE: "Old" Transformer Fluid (GE)

SOLVENT: CDCl₃ + TMS

REMARKS:



STOHLER ISOTOPE CHEMICALS

49 JONES ROAD, WALTHAM, MASS. 02154
 25 BECKWITH PLACE, BURLINGTON, N.J. 07070

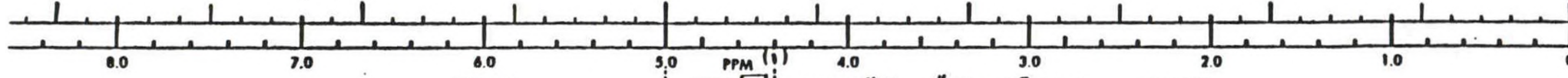
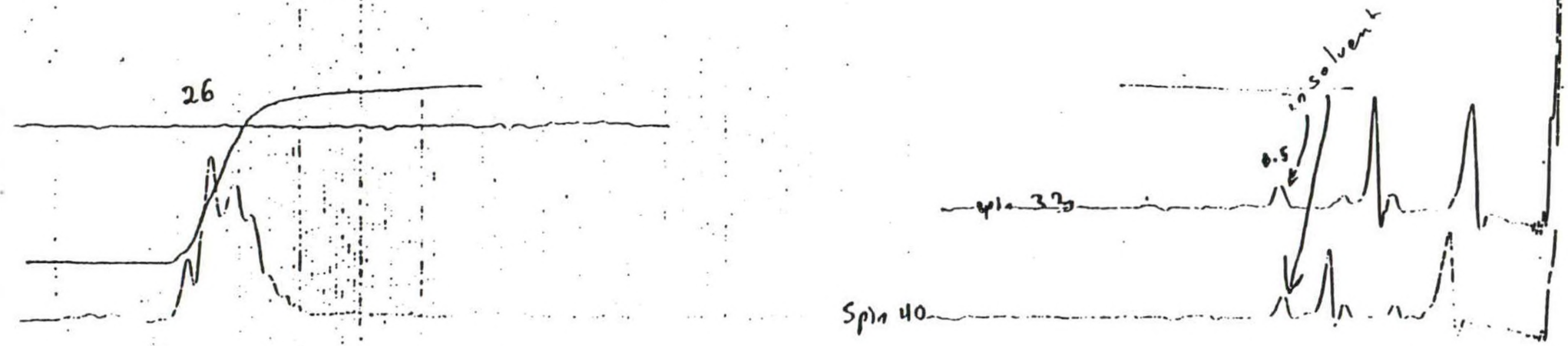
DATE: 3/1/78

OPERATOR: allis

60 MHz NMR
 SPECTRUM NO.

GENP 010436

783247



SWEEP OFFSET (Hz): 0/200
 SPECTRUM AMPLITUDE: 2.0
 INTEGRAL AMPLITUDE: 5
 SPINNING RATE (RPS): 4.0/13.3

MANUAL
 SWEEP TIME (SEC): 30 750
 SWEEP WIDTH (Hz): 25 50 100 250 500
 FILTER: ☒ 2 ☒ 3 ☒ 4 ☒ 5 ☒ 6 ☒ 7 ☒ 8
 RF POWER LEVEL: 0.1 3.5

AUTO ☐
 (250)
 (500)
 (2)
 (.05)

SAMPLE: "New" Transformer Fluid (GE)

REMARKS:

SOLVENT: CCl₃ + TMS

STOHLER ISOTOPE CHEMICALS
 49 JONES ROAD, WALTHAM, MASS. 02154

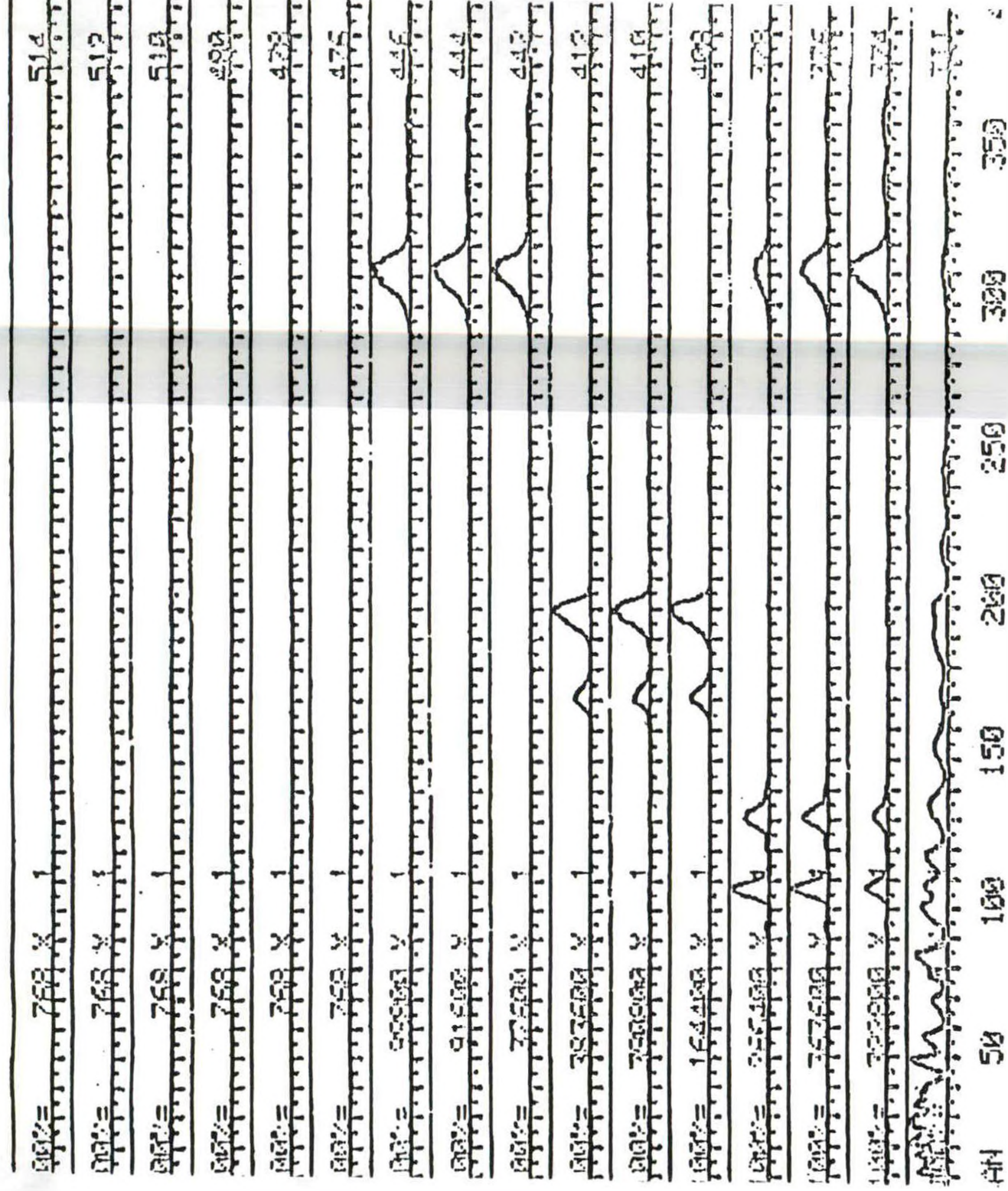
DATE: 3/1/78

OPERATOR: Albus

60 MHz NMR
 SPECTRUM NO. _____

173

IS "PURIFIED OLD 48", QU101 200 DEG. 102673

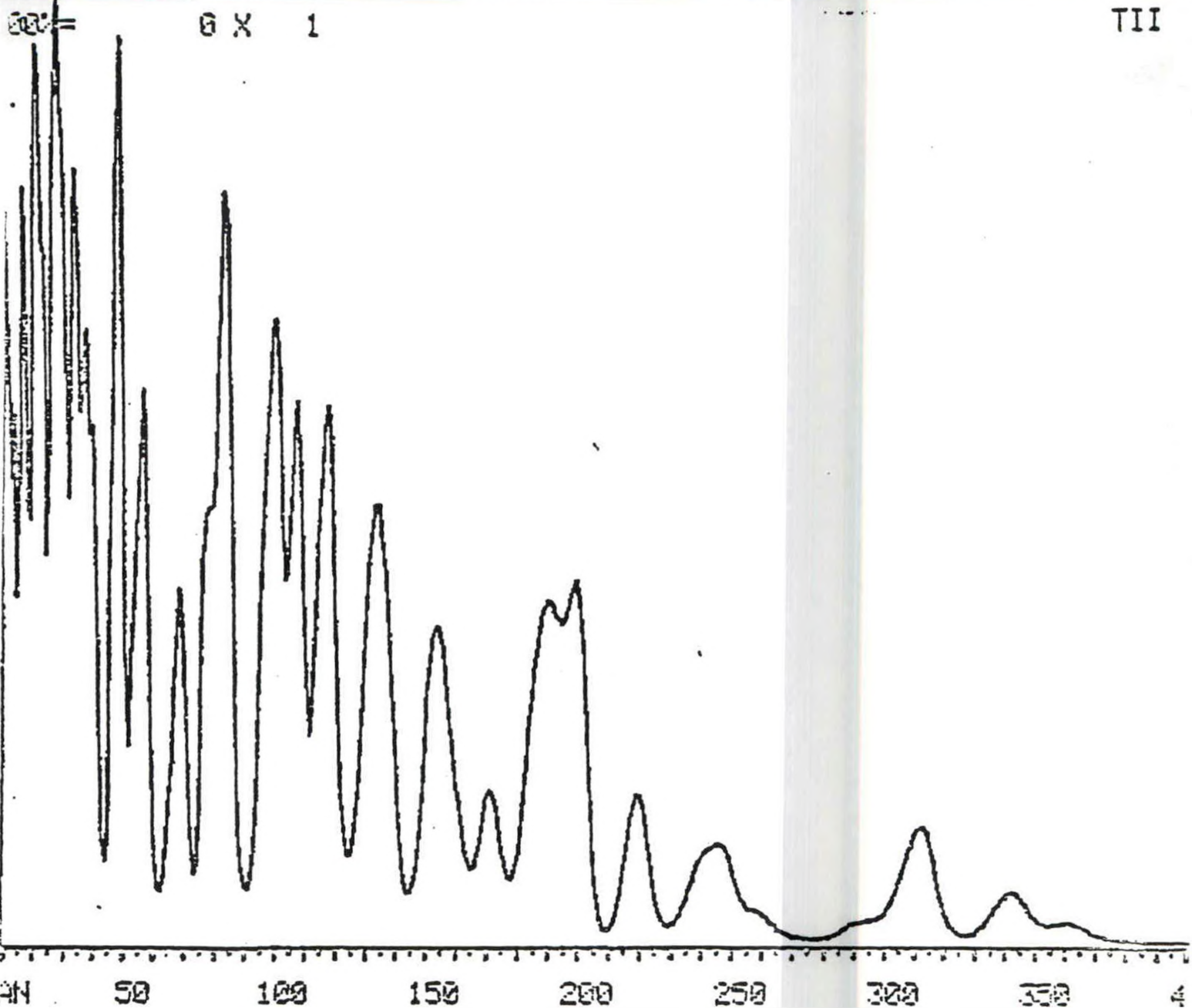


Corrected for DADR

GENP 010437

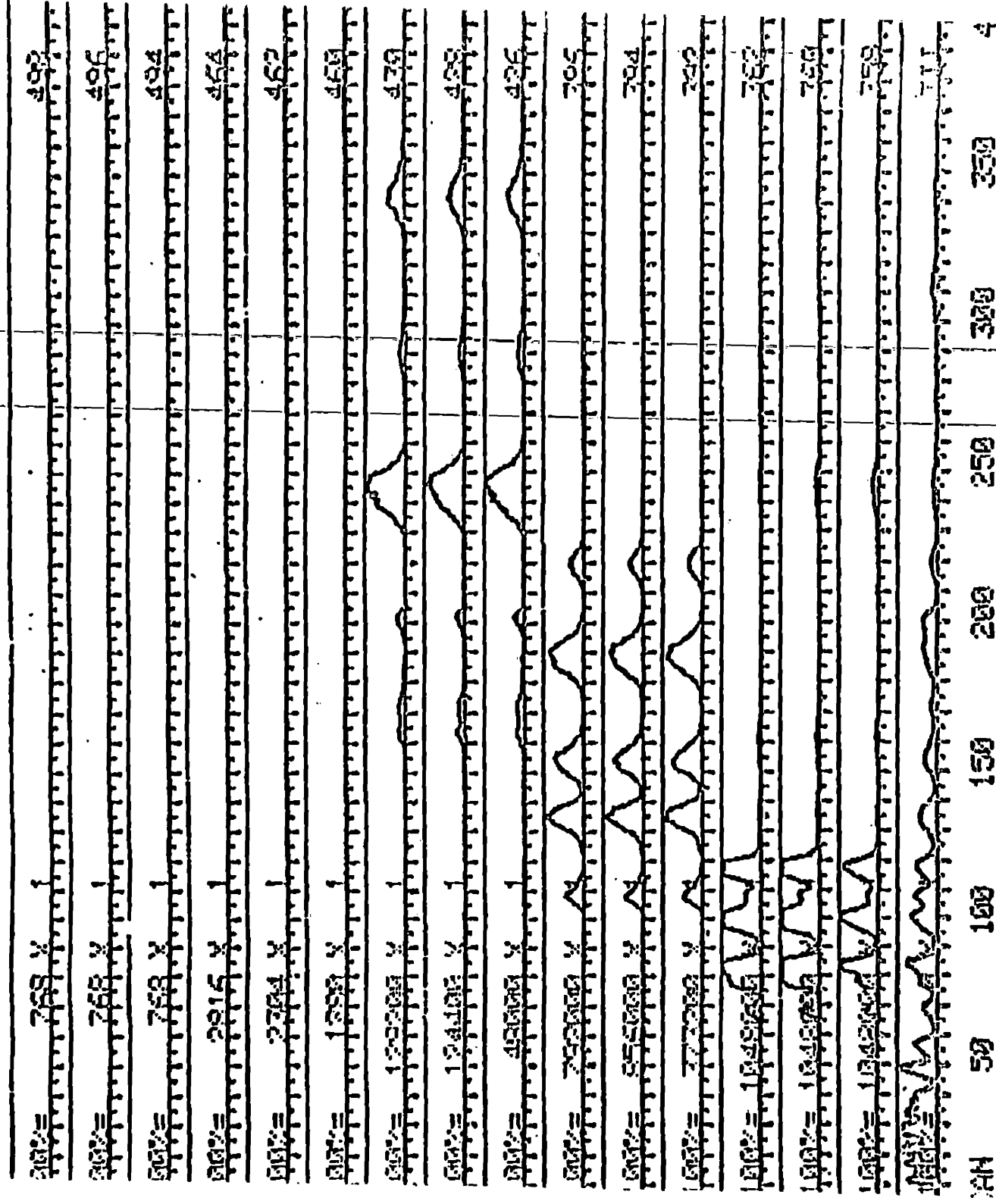
173

1.6 "PURIFIED OLD 4B", QV101 200 DEG. 102678



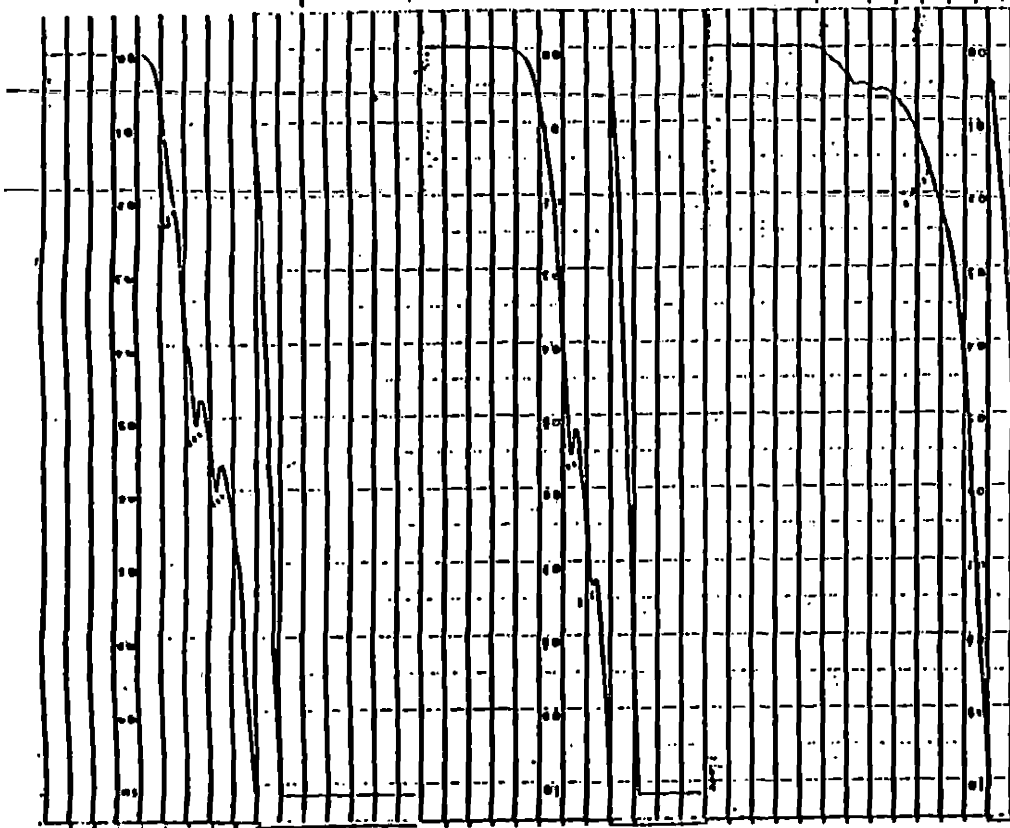
GENP 010438

173
 'S "PURIFIED OLD 45", 00101 200 DEG. 192678



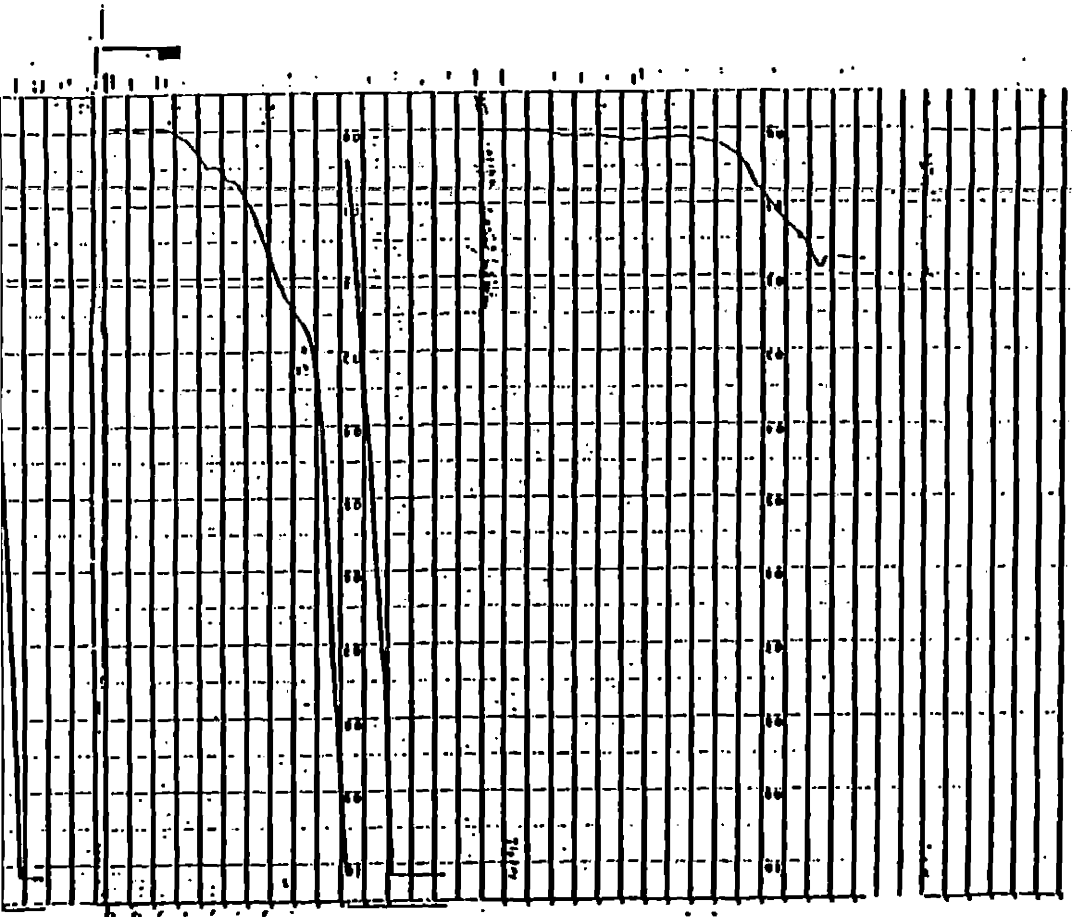
March For 200's

GENP 010439



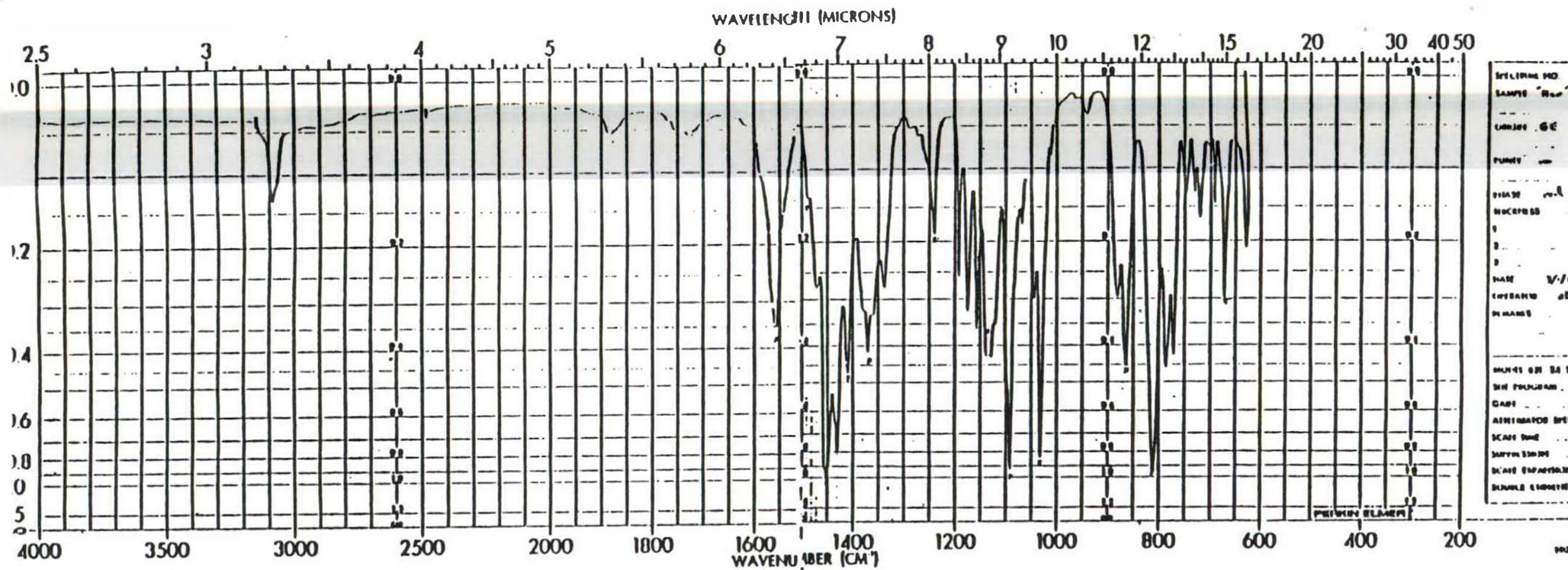
GENP 010440

783251

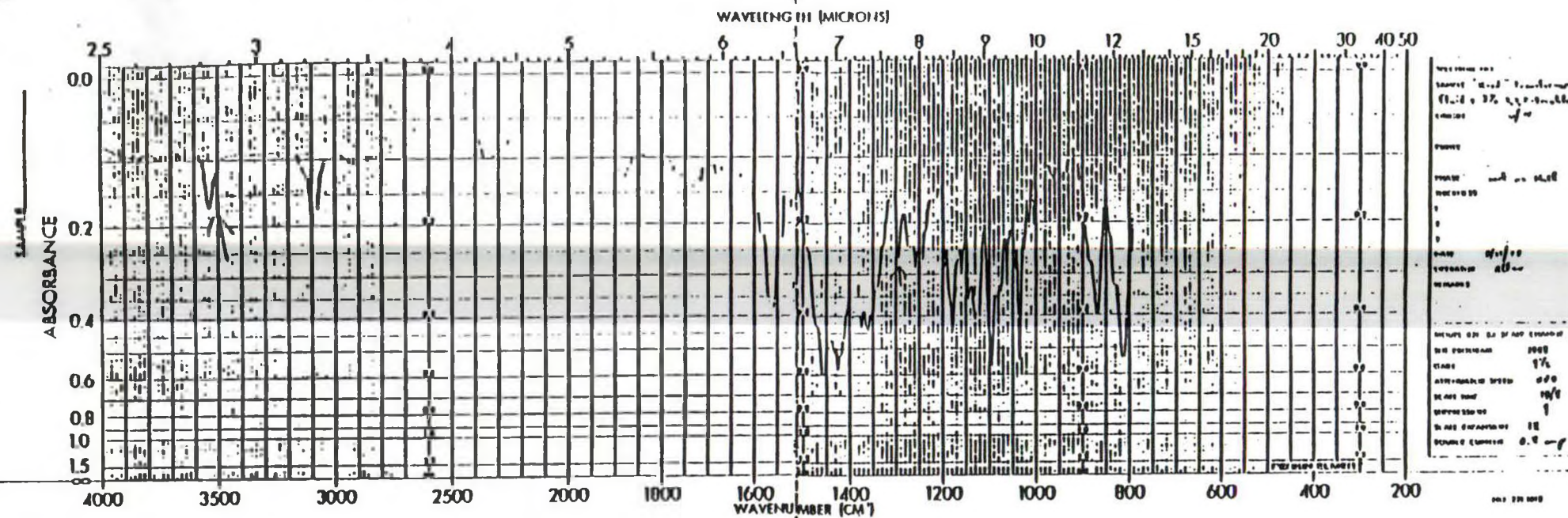


GENP 010441

783252

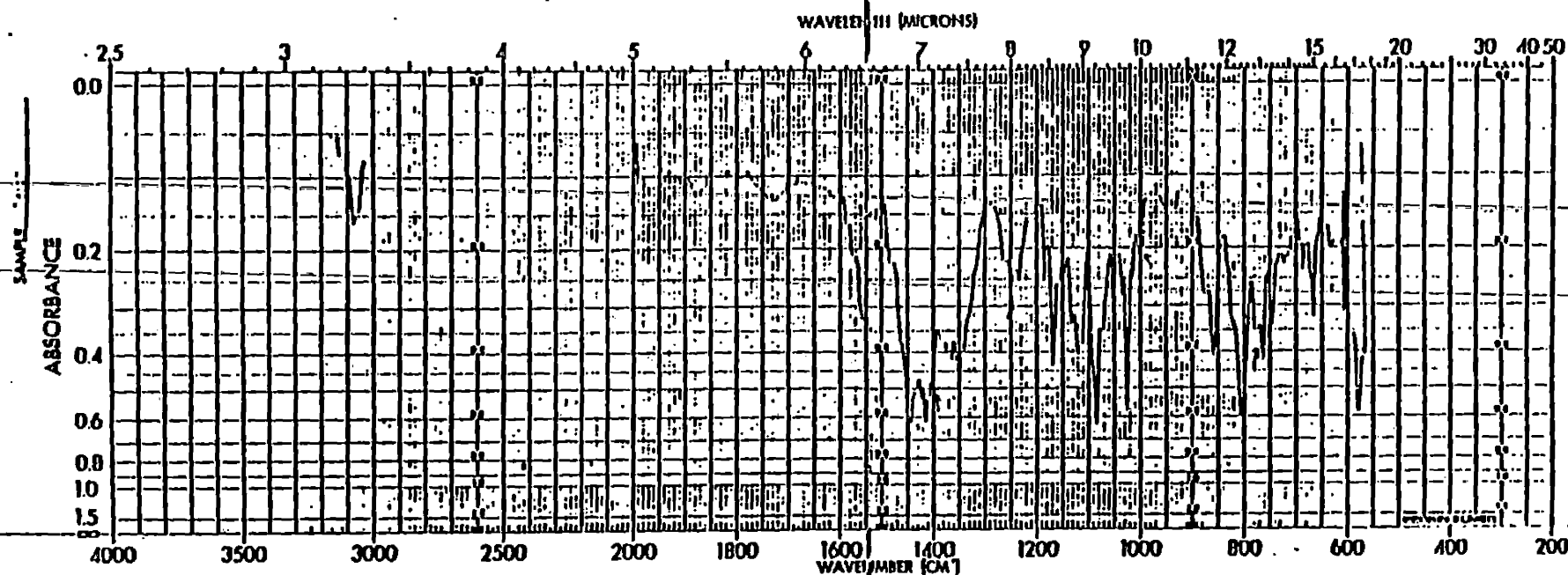


GENP 010442



GENP 010443

783254



DATE	10/10/54
TIME	10:10
OPERATOR	J. L. J.
INSTRUMENT	
SAMPLE	
CONCENTRATION	
THICKNESS	
WAVELENGTH	
WAVENUMBER	
ABSORBANCE	
TRANSMITTANCE	
REFLECTANCE	
SCATTERANCE	
DIFFUSANCE	
REFRACTANCE	
BIREFRINGENCE	
OPTICAL ACTIVITY	
POLARIZATION	
CRYSTALLINITY	
MOLECULAR WEIGHT	
MOLECULAR STRUCTURE	
FUNCTIONAL GROUPS	
ISOMERISM	
POLYMERIZATION	
DEGRADATION	
COMPOSITION	
PURITY	
IDENTIFICATION	
ANALYSIS	
SYNTHESIS	
CHARACTERIZATION	
QUALITY CONTROL	
RESEARCH	
TECHNOLOGY	
INDUSTRY	
ACADEMIA	
GOVERNMENT	
DEFENSE	
SPACE	
ENVIRONMENT	
HEALTH	
AGRICULTURE	
FOOD	
TEXTILES	
CONSTRUCTION	
TRANSPORTATION	
ENERGY	
ENVIRONMENTAL	
BIOTECHNOLOGY	
PHARMACEUTICALS	
COCOS	17
CONCENTRATION	10
THICKNESS	1
WAVELENGTH	10
WAVENUMBER	10
ABSORBANCE	10
TRANSMITTANCE	10
REFLECTANCE	10
SCATTERANCE	10
DIFFUSANCE	10
REFRACTANCE	10
BIREFRINGENCE	10
OPTICAL ACTIVITY	10
POLARIZATION	10
CRYSTALLINITY	10
MOLECULAR WEIGHT	10
MOLECULAR STRUCTURE	10
FUNCTIONAL GROUPS	10
ISOMERISM	10
POLYMERIZATION	10
DEGRADATION	10
COMPOSITION	10
PURITY	10
IDENTIFICATION	10
ANALYSIS	10
SYNTHESIS	10
CHARACTERIZATION	10
QUALITY CONTROL	10
RESEARCH	10
TECHNOLOGY	10
INDUSTRY	10
ACADEMIA	10
GOVERNMENT	10
DEFENSE	10
SPACE	10
ENVIRONMENT	10
HEALTH	10
AGRICULTURE	10
FOOD	10
TEXTILES	10
CONSTRUCTION	10
TRANSPORTATION	10
ENERGY	10
ENVIRONMENTAL	10
BIOTECHNOLOGY	10
PHARMACEUTICALS	10