Determination of 2,3,7,8-Tetrachlorodibenzo-p-dioxin in Fish Samples from Spring River in Missouri

Laboratory Report to: Missouri Department of Conservation

from

Analytical Chemistry Research Unit
Columbia National Fisheries Research Laboratory
U. S. Fish and Wildlife Service
Route 1
Columbia, MO 65201

Analysts: L. M. Smith and J. L. Johnson
April 11, 1982

JDB
Site: Spurlock Landing
ID # MOD007452154
Break: 3, 4
Other:
4-11-82
0751

40032193
SUPERFUND RECORDS

7 52611

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Laboratory Report to: Missouri Department of Conservation

A request from the Missouri Department of Conservation for the analysis of fish samples for 2,3,7,8-TCDD was made to Dr. Stalling, Chief Chemist and approved by Dr. Richard Schoettger, Laboratory Director. This report includes:

1) Sample history and custody
2) A summary of the analytical results including those for analyses of laboratory control samples
3) Pertinent analytical data including mass chromatograms and molecular ion patterns
4) A description of the contaminant enrichment procedure used to prepare samples for analysis
5) A description of the analytical method
6) Criteria for positive determination of 2,3,7,8-TCDD and determination of the lower limit of detection
7) A discussion of the specificity of the analyses and of the potential for interference or false positive analyses

Sample History, Residue Levels, and Pertinent Data:

Four groups of whole fish were received by L. M. Smith (CNFRL, ACRU) from James Whitley (Fish and Wildlife Research Center, Missouri Department of Conservation, Columbia, MO) on March 18, 1982. The four samples were collected by US Environmental Protection Agency personnel (Kansas City, KN) and subsequently supplied to the Missouri Department of Conservation. One sample was divided into edible (fillets) and non-edible portions and these analyzed separately. Enrichment and analysis were performed on 50 gram aliquots of homogenates of the sample composites. Table 1 documents sample descriptions and analytical results for the determination of 2,3,7,8-TCDD in picograms per gram of tissue or parts-per-trillion (pptr).

In Appendix I are included the mass fragmentograms and reconstructed molecular ion patterns generated in the analyses by high resolution gas chromatography coupled with low resolution mass spectrometry using multiple ion detection (HRGC/LRMS-MID). In each set of data are included the total ion chromatogram (A), selected ion scans for molecular ions of TCDDs (B), selected ion scans for the 13C-TCDD marker (C), expanded scans of B and C used for peak integrations (D) and (E), respectively, and the reconstructed molecular ion clusters for the native TCDD contamination (F) and for the 13C-TCDD (G). The calculations of the concentration of 2,3,7,8-TCDD are included on ion scans B. The calculation involves determination of the ratio of the area of the TCDD residue relative to that of the 13C-TCDD, normalized to the 50 pptr spike concentration and applying a correction factor of 1.24. The correction factor is derived from a determination of the integrated response of the 13C-TCDD internal standard relative to that of a quantitative standard of 2,3,7,8-TCDD. Sample 15C is a

composite fish sample from the Spring River analyzed in December, 1981 for the U. S. Environmental Agency, Kansas City, KN. and was included for comparison with the currently analyzed samples.

$$\text{pptr TCDD in sample} = \frac{\text{area of TCDD}}{\text{area of 13C-TCDD}} \times \frac{50 \text{ pptr}}{1.24}$$

Table 1. Sample Description and TCDD Residue Concentrations.

Description	ACRU/CNFRL #	Concentration pptr 2,3,7,8-TCDD (corrected)
SD 5004 (EPA) seven smallmouth bass	22C	6.2
SD5008 (EPA) nine largemouth bass composite:		
edible portion	23C	1.4
non-edible portion	24C	3.4
whole body calculated sample mean	—	2.5
SD5008 (EPA) four shorthead redhorse	25C	1.1
SD5010 (EPA) two shorthead redhorse and one river redhorse	26C	0.8
Laboratory control (grass carp)	—	0.0
Procedure blank #1	—	0.0
Procedure blank #2	—	0.0

Values for residue levels of 2,3,7,8-TCDD are corrected for recovery using the isotopic dilution technique. The sample is spiked with 50 pptr 13C-2,3,7,8-TCDD before processing. Comparison of the analytical response for native TCDD in the sample with that observed for the 13C-TCDD serves to reduce quantitation errors due to procedural variations. The molecular isotopic patterns were judged to be consistent with a tetrachloro compound in all samples analyzed.

In appendix II, the results of confirmatory GC/MS analyses are given. These data

were generated using a 50 meter OV-17 capillary column in place of the routinely employed DB-5 column. The OV-17 column was provided by Dr. H. R. Buser, Swiss Federal Research Station, Wadenswil, Switzerland, who has demonstrated the isomer specific determination of 2,3,7,8-TCDD using HRGC. By comparison of the retention time of all 22 TCDD isomers (provided by Dr. Buser) on the DB-5 and OV-17 columns, we were able to develop a confirmatory method for 2,3,7,8-TCDD.

Contaminant Enrichment Procedure:

In Appendix III, the procedure used for sample processing and residue enrichment is described.

Analytical Procedure:

Fifty gram samples were processed and reduced to a final analyte volume of 10 microliters. Four microliters of the analyte, equivalent to 20 grams sample, were analyzed by HRGC/LRMS-MID. A Finnigan 4000 GC/MS with an INCOS data system fitted with a 30 meter x 0.25 mm id DB-5 capillary column (J and W Scientific, Inc.) or 50 meter OV-17 column (Buser) was used to analyze the enriched samples. Helium carrier gas at 10 psig and a temperature program from 150 C to 290 C were employed in the analyses. The data were collected using a multiple ion detection (MID) descriptor program to monitor only the nominal mass values corresponding to the molecular ions of the TCDD isomers (m/z 320, 322, 324 and 326) and of the isotopically enriched internal standard 13C-TCDD (m/z 332, 334, and 336). The MID program scan range was set to scan each nominal mass in the range of -.6 amu to +.4 amu (ie. m/z 319.4 to 320.4).

Limits of Detection, Determinative Criteria, and Specificity of the Analyses:

The analytical lower limit of detection was assigned by determining the smallest amount of 2,3,7,8-TCDD necessary to meet the criteria (discussed below) for a positive determination. The analysis of a 20 picogram injection satisfied the criteria of signal-to-noise, GC retention time, nominal molecular mass, and marginally for Cl isotope patterns of the molecular ion. A positive response for 20 picograms of 2,3,7,8-TCDD corresponds to a lower limit of detection of 1.0 part-per-trillion (pptr) in the 20 gram equivalent aliquots that were analyzed in this investigation. The methods lower limit of detection encompasses both the analytical limits and the limits imposed by background interferences which are routinely encountered in a processed sample. Analyses of a large number of samples by the methods described herein demonstrate that the method lower limit of detection is generally defined by the analytical lower limit of detection. In other words the processed samples are usually sufficiently clean that interference from other compounds are rarely encountered.

The criteria used in this laboratory for the assignment of a positive determination of 2,3,7,8-TCDD are:

1) a signal-to-noise ratio of 2.5,

2) the correct retention time relative to the isotopic labeled 13C-TCDD on two complementary HRGC columns (DB-5 and OV-17),

3) the correct nominal masses for the members of the molecular cluster, and

4) the correct relative intensities for the first three members of the molecular isotopic cluster.

The question of the possibility of false positive determinations for 2,3,7,8-TCDD has been addressed in this laboratory. False positive determinations can arise from specific types of interfering compounds; other TCDD isomers and other polychlorinated aromatic compounds which can meet the analytical criteria. There are numerous candidates of both types of interfering compounds. The problems of analytical interference from other TCDD isomers have been largely eliminated by use of two complimentary HRGC analyses discused above. Furthermore, previous determination of 2,3,7,8-TCDD made in this laboratory have been confirmed both by H. R. Buser using a Silar 10C column (1) and by R. K. Mitchum (National Center for Toxicology, Jefferson, AK) using atmospheric pressure negative chemical ionization MS (2). The latter technique provides an independent, isomer specific confirmation for 2,3,7,8-TCDD. The problems associated with other classes of specifically interfering compounds have been addressed by an evaluation in this laboratory of the levels of interferences produced by seven families of compounds which were judged as posing the greatest potential for causing a false positive determination. The chemical families investigated were the following polychlorinated compounds: biphenyls, naphthalenes, diphenyl ethers, methoxy biphenyls, hydroxybiphenyls, methoxydiphenyl ethers, and hydroxydiphenyl ethers. The concentrations of potential specific interferences in analyses for TCDDs were shown to be reduced by a factor of at least 10,000.

The numerous components observed in the fragmentograms in addition to 2,3,7,8-TCDD were identified as procedural background characteristic of hydrocarbons and not chlorinated compounds. These components were identified as trace contaminants in the high purity solvents employed in the enrichment procedure.

References:

1) H. R. Buser and C. Rappe, Analytical Chemistry, 52, 2257-2262 (1980).

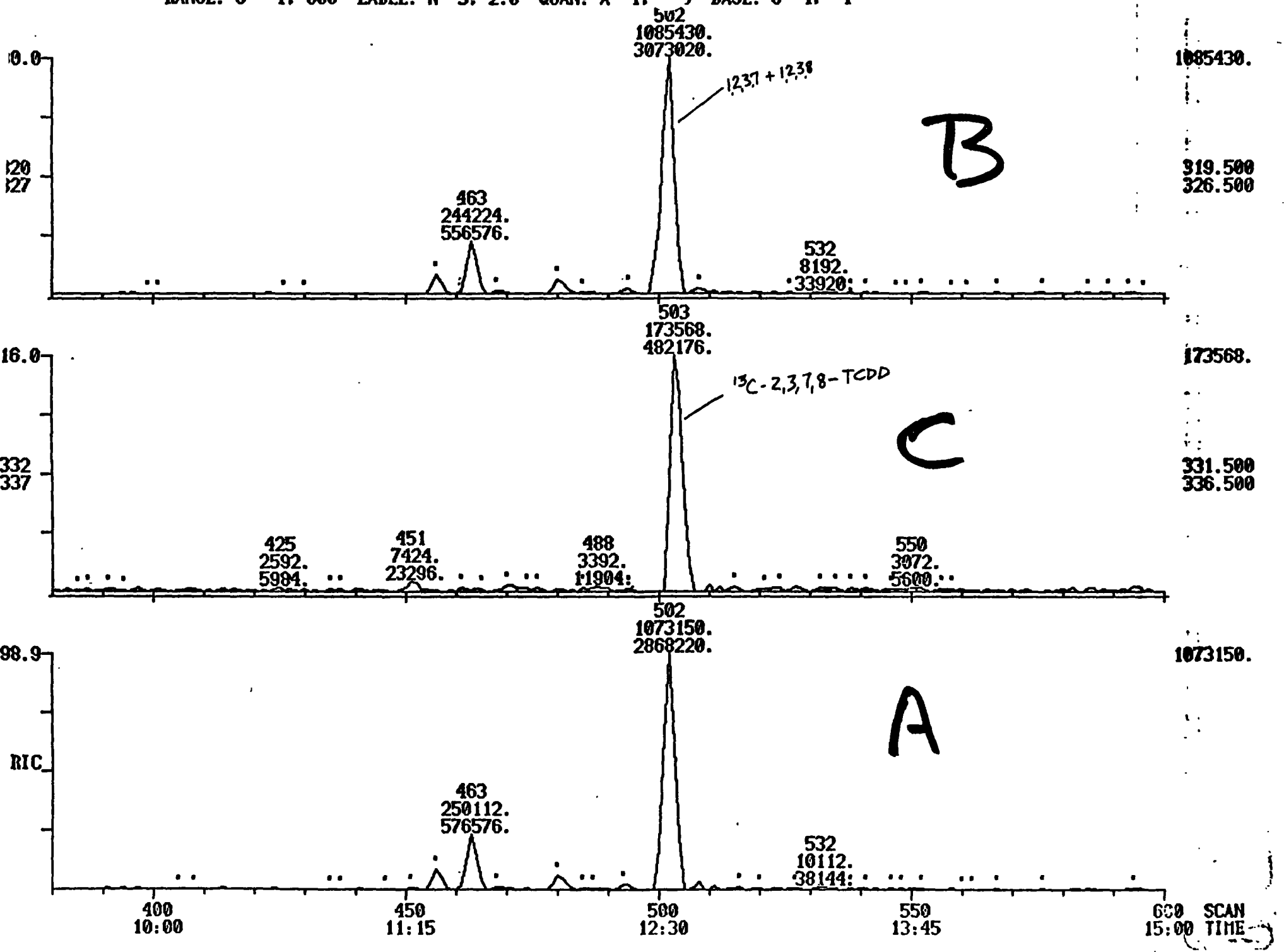
2) R. K. Mitchum, W. A. Korfmacher, G. F. Molar, and D. L. Stalling, Analytical Chemistry, 54, 719-722 (1982).

APPENDIX I

MID RIC + MASS CHROMATOGRAMS
04/04/82 16:16:00
SAMPLE: 2UL BUSER 25+2345 MIX CONT 1237 & 1238 7 +2UL C13 TCDD 200PG
RANGE: G 1. 600 LABEL: N 3. 2.0 QUAN: A 1. BASE: U 4. 1

DATA: TCDD1 01
CALI: C040482B1 05

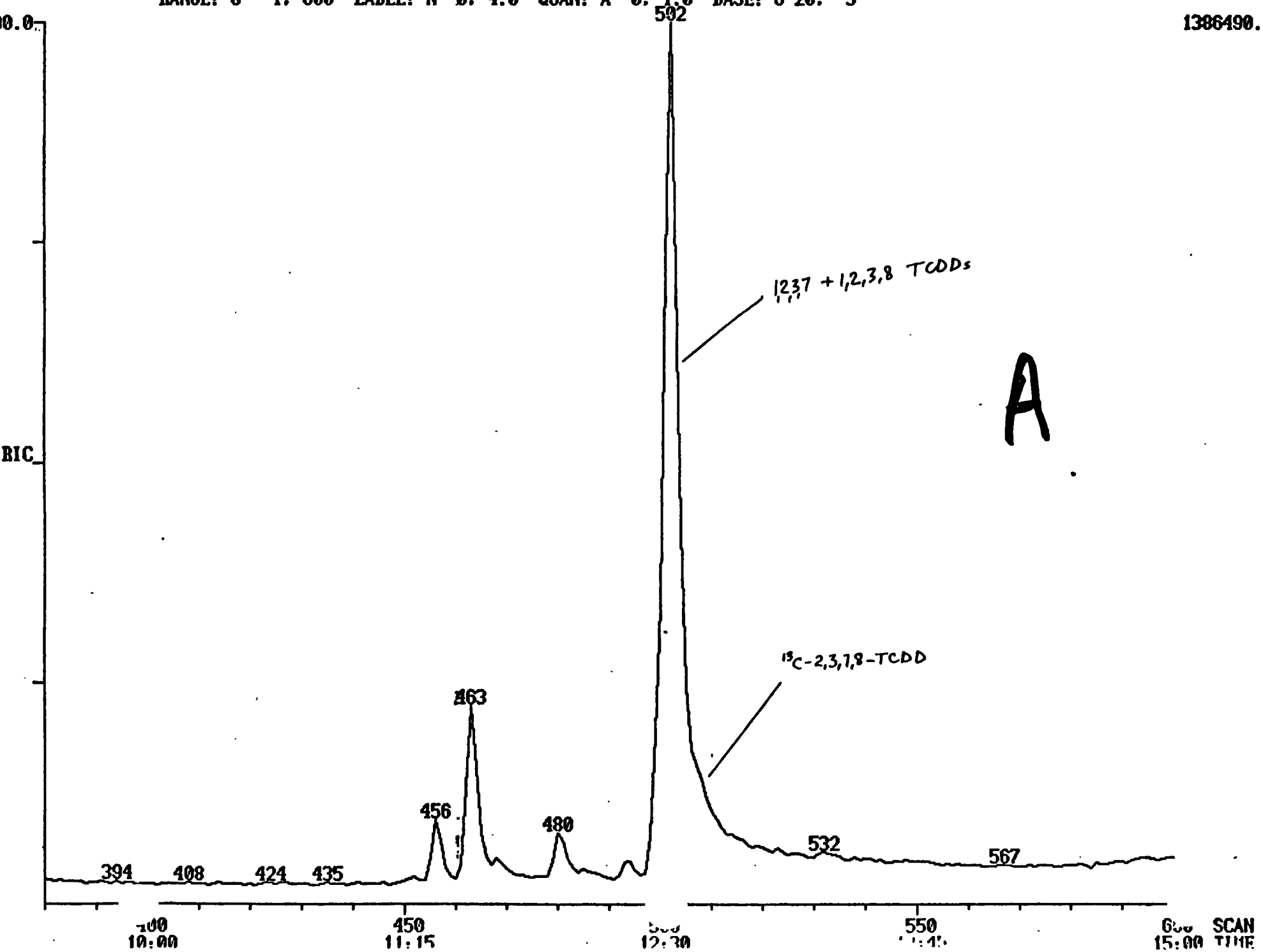
SCANS 380 TO 603



MID RIC
04/04/82 16:16:00
SAMPLE: 2UL BUSER 25+2345 MIX CONT 1237 & 1238 TCDD +2UL C13 TCDD 200PG
RANGE: G 1. 600 LABEL: N 0. 4.0 QUAN: A 0. 1.0 BASE: U 20. 3

DATA: TCDD1 #1
CALI: C040482B1 #5

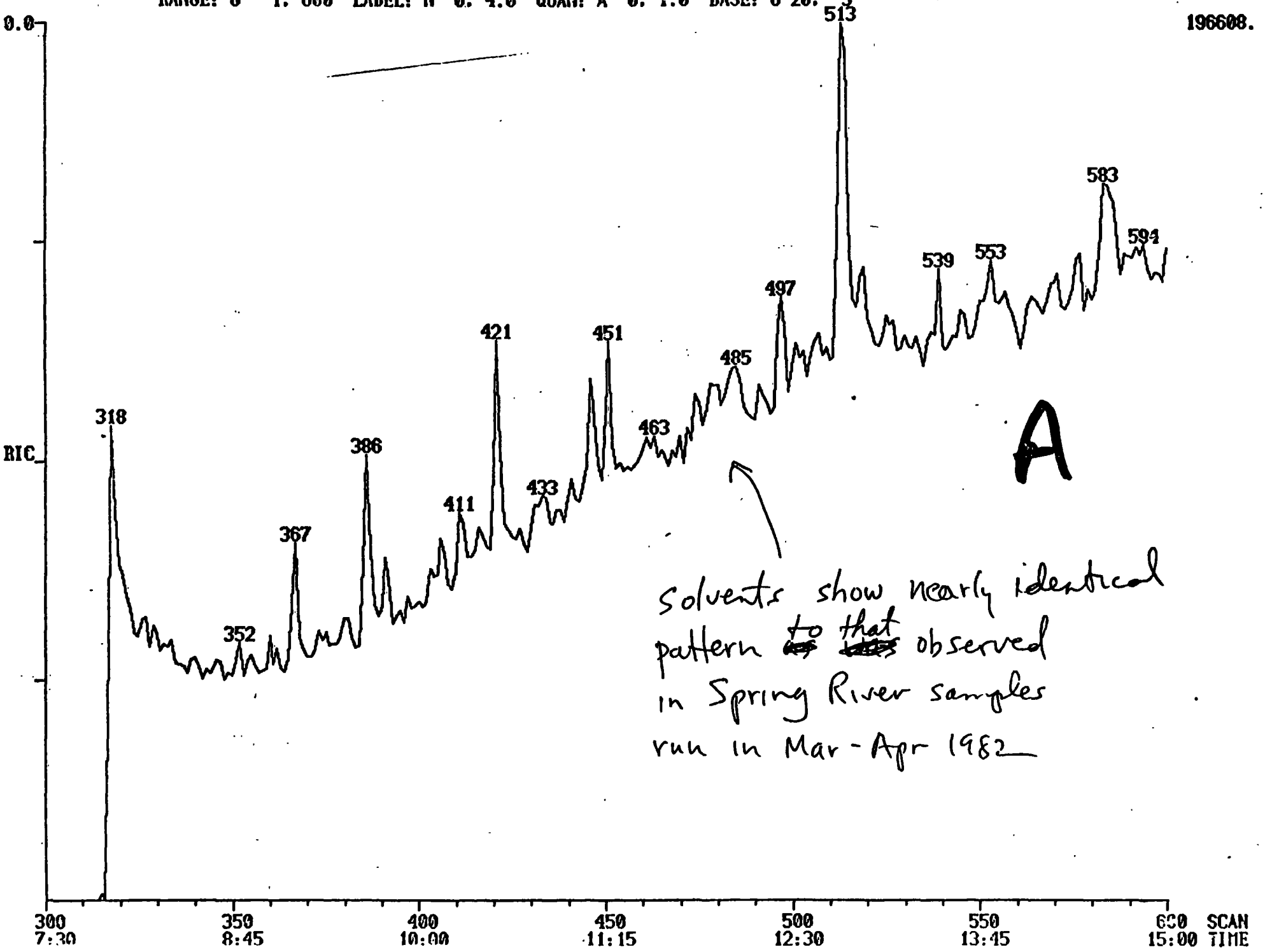
SCANS 380 TO 600



MID RIC
04/06/82 13:07:00
SAMPLE: 4UL LAB SOLVENTS USED IN ALUMIA PRO. 4-6 MID EI
RANGE: G 1. 600 LABEL: N 0. 4.0 QUAN: A 0. ..0 BASE: U 20. 3

DATA: LABSOL1 #1
CALI: C040682B #3

SCANS 300 TO 600

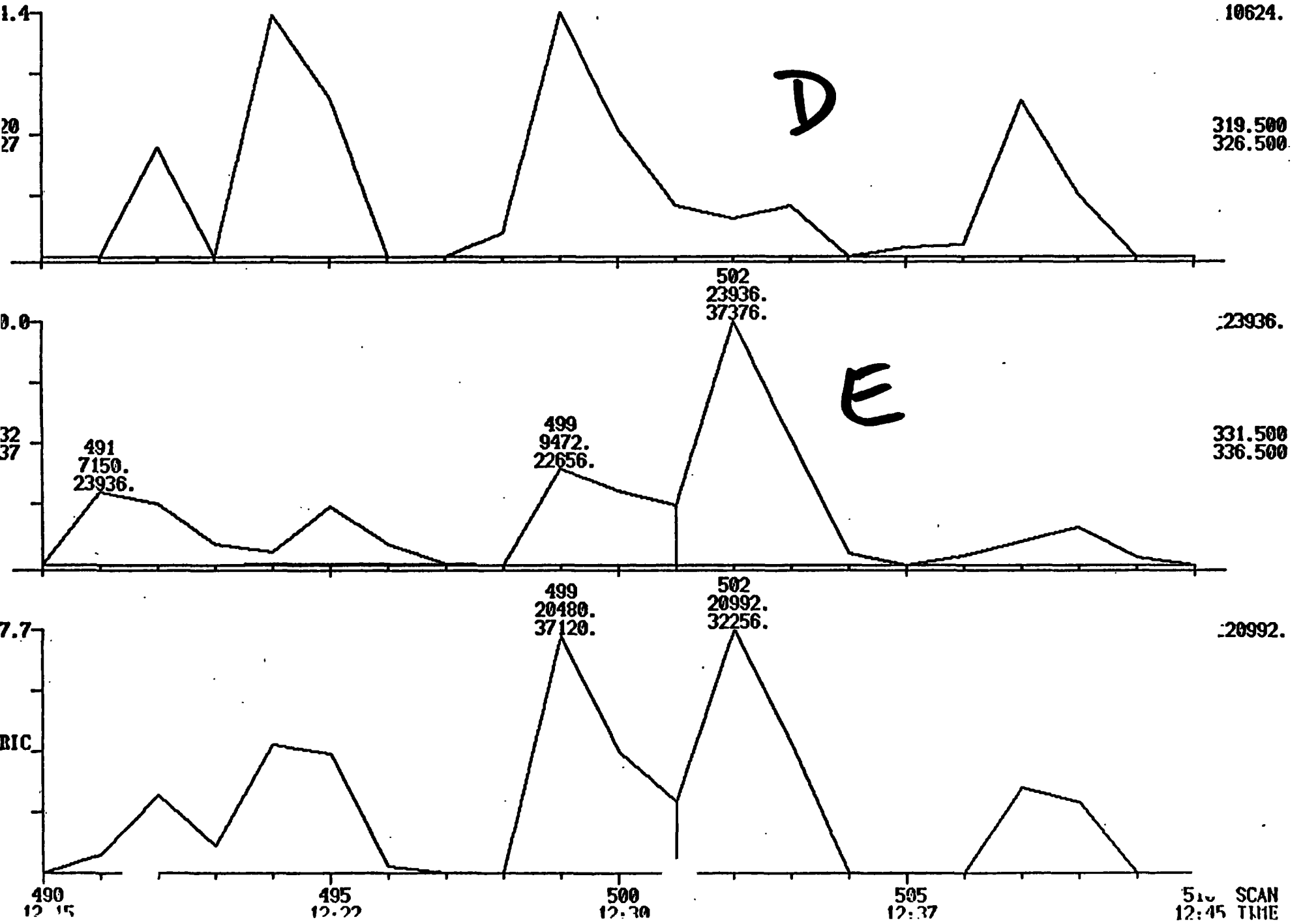


Solvents show nearly identical pattern ~~as~~ ~~this~~ to that observed in Spring River samples run in Mar-Apr 1982

MID RIC + MASS CHROMATOGRAMS
04/04/82 15:41:00
SAMPLE: 4UL SOLV BLK [redacted] SPRING R(3-20-E-4-4-82)10UL VOL 50PPT MARK MI
RANGE: G 1. 600 LABEL: N 3. 2.0 QUAN: A 1. 1.0 BASE: U 4. 1

DATA: SOLBL2 #1
CALI: C040482B1 #5

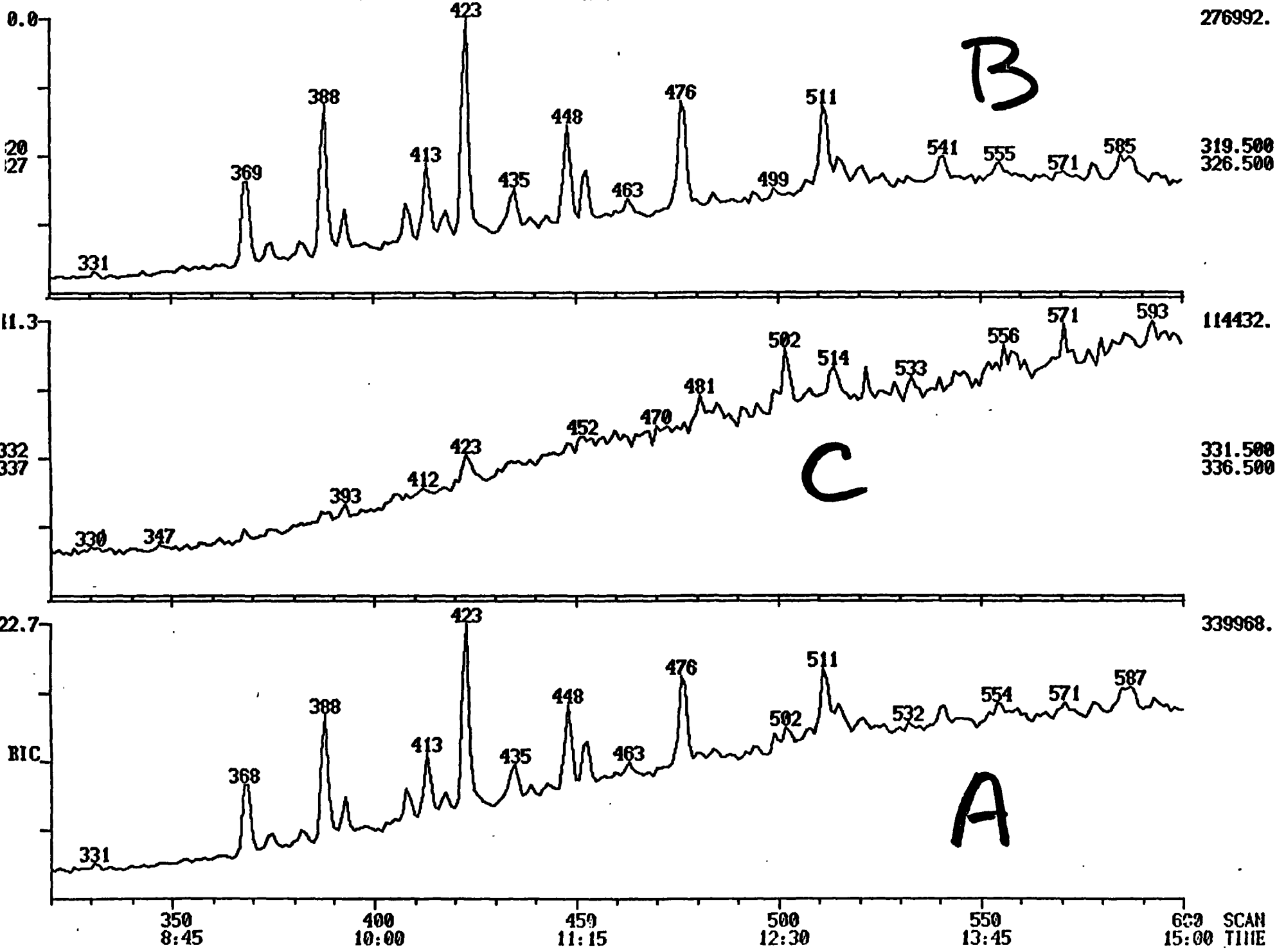
SCANS 490 TO 510



MID RIC + MASS CHROMATOGRAMS
04/04/82 15:41:00 Before
SAMPLE: 4UL SOLV BLK [redacted] SPRING R(3-20-E-4-4-8 UL VOL 50PPT MARK MI
RANGE: G 1. 600 LABEL: N 0. 4.0 QUAN: A 0. BASE: U 20. 3

DATA: SOLBL2 #1
CALI: C040482B1 #5

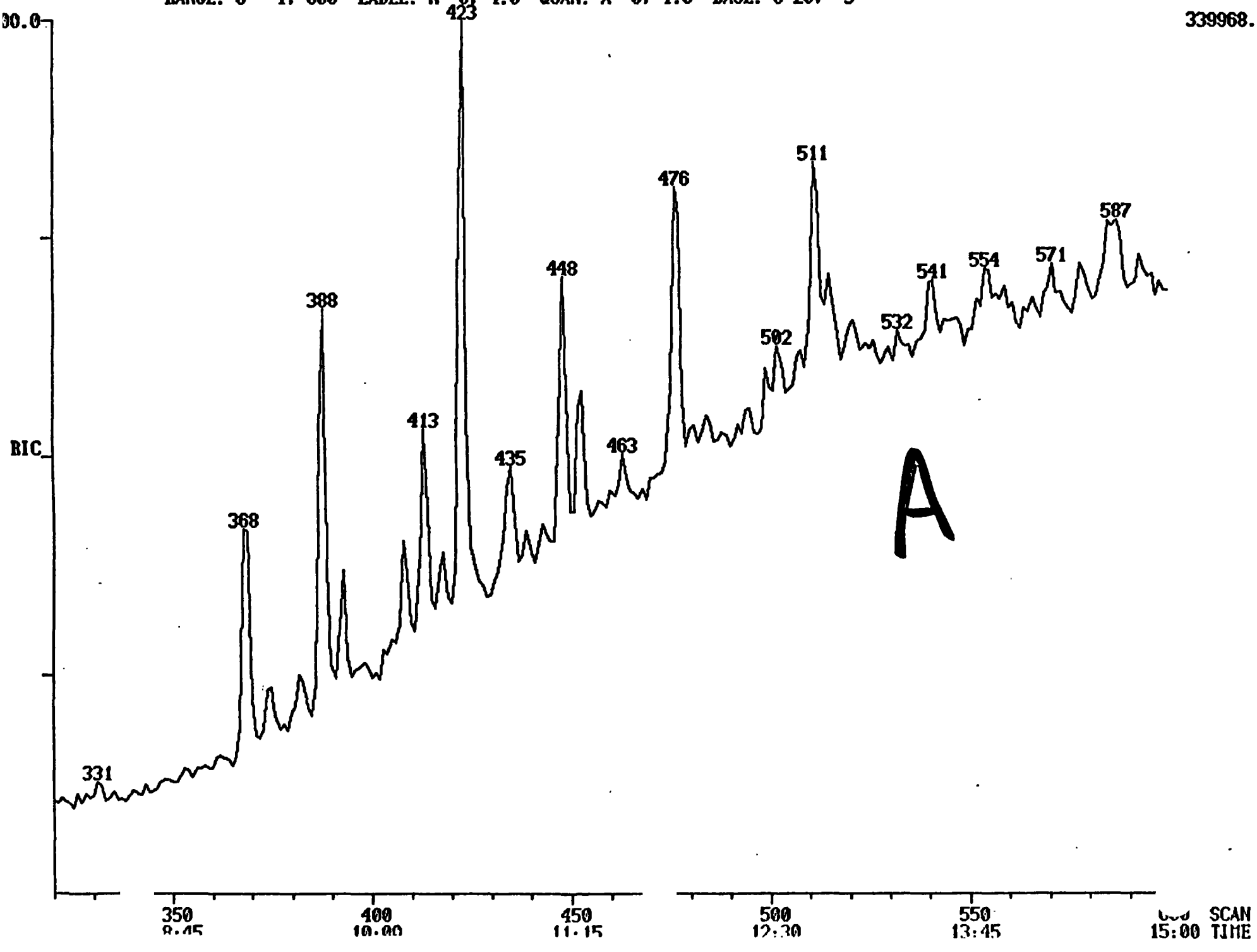
SCANS 320 TO 600



MID RIC
04/04/82 15:41:00 BEFORE
SAMPLE: 4UL SOLV BLK [redacted] SPRING R(3-20-E-4-4-82)10UL VOL 50PPT MARK MI
RANGE: G 1. 600 LABEL: N 0. 4.0 QUAN: A 0. 1.0 BASE: U 20. 3

DATA: SOLBL2 #1
CALI: C040482B1 #5

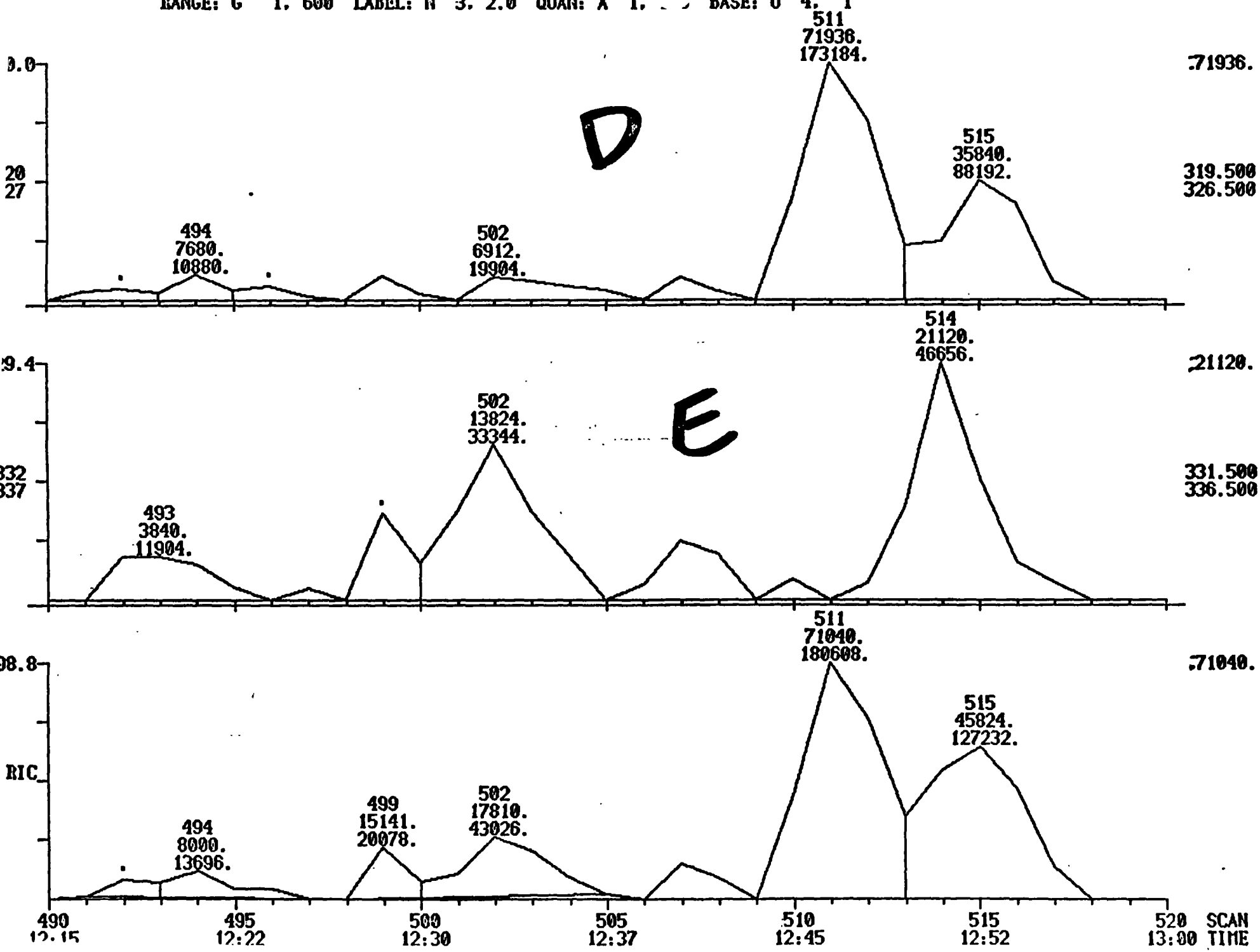
SCANS 320 TO 600



MID RIC + MASS CHROMATOGRAMS
04/04/82 12:46:00
SAMPLE: 4UL SOLVENT BLANK [redacted].(3-20-G-4 2)10UL VOL MID EI 19
RANGE: G 1. 600 LABEL: N 3. 2.0 QUAN: A 1. BASE: U 4. 1

DATA: SOLBL1 #501
CALI: C040482B1 #5

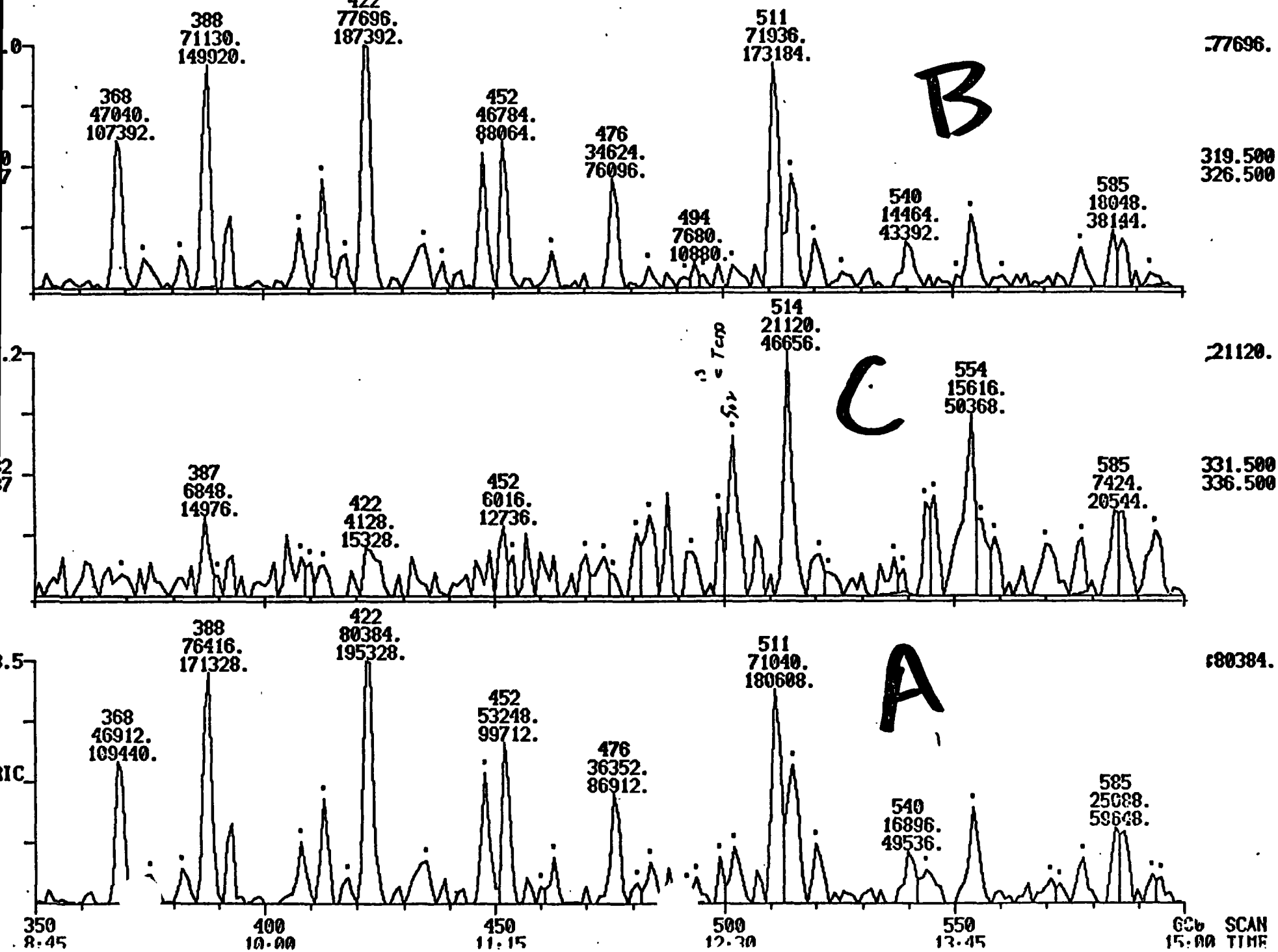
SCANS 490 TO 520



MID RIC + MASS CHROMATOGRAMS
04/04/82 12:46:00
SAMPLE: 4UL SOLVENT BLANK [redacted].(3-20-G-4-3-82)10UL VOL MID EI 19
RANGE: G 1. 600 LABEL: N 3. 2.0 QUAN: A 1. 1.0 BASE: U 4. 1

DATA: SOLBL1 #1
CALI: C040482B1 #5

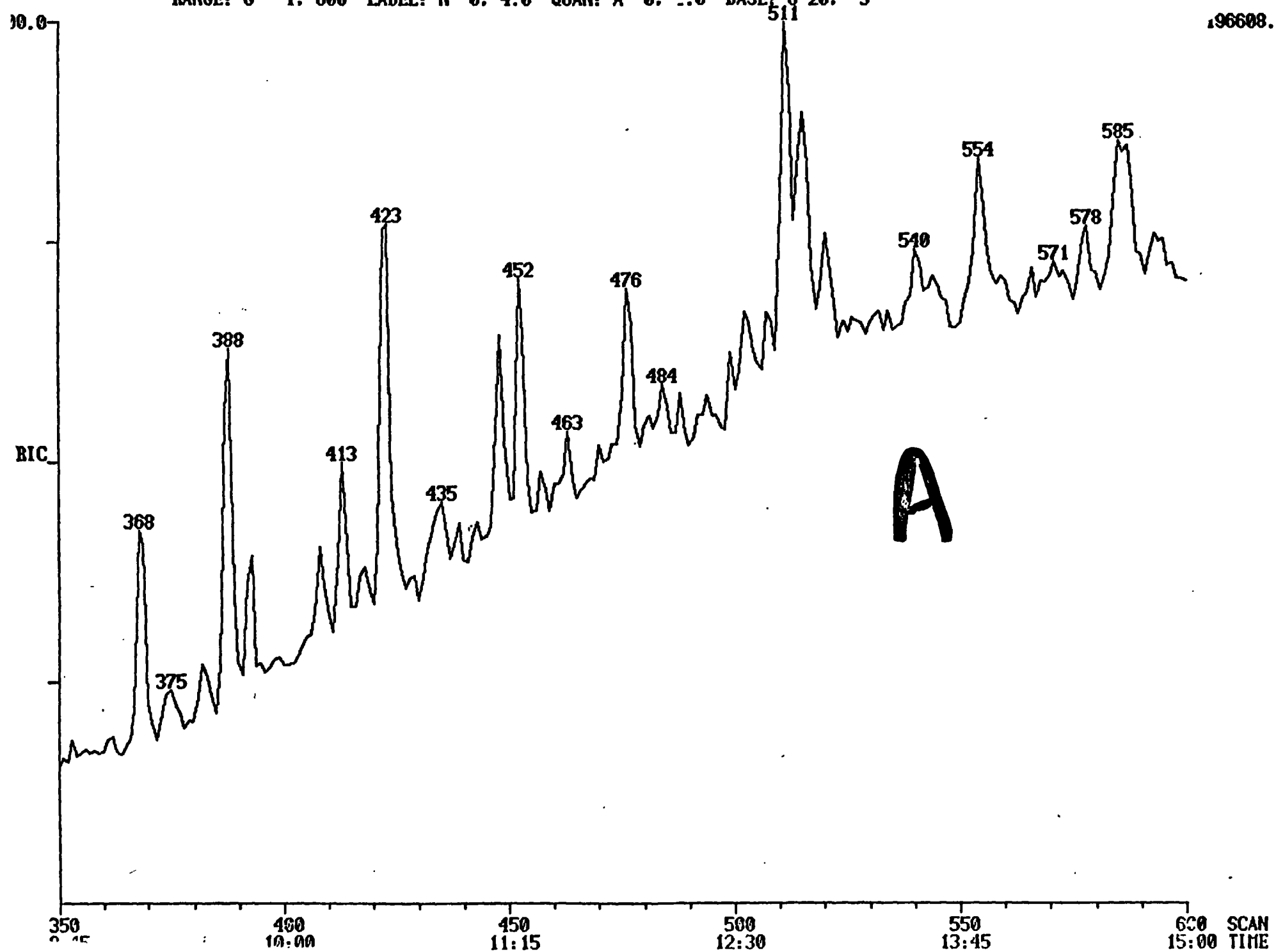
SCANS 350 TO 660



MID RIC
04/04/82 12:46:00
SAMPLE: 4UL SOLVENT BLANK [redacted].(3-20-G-4 82)10UL VOL MID EI 19
RANGE: G 1. 600 LABEL: N 0. 4.0 QUAN: A 0. ..0 BASE: U 20. 3

DATA: SOLBL1 #1
CALI: C040482B1 #5

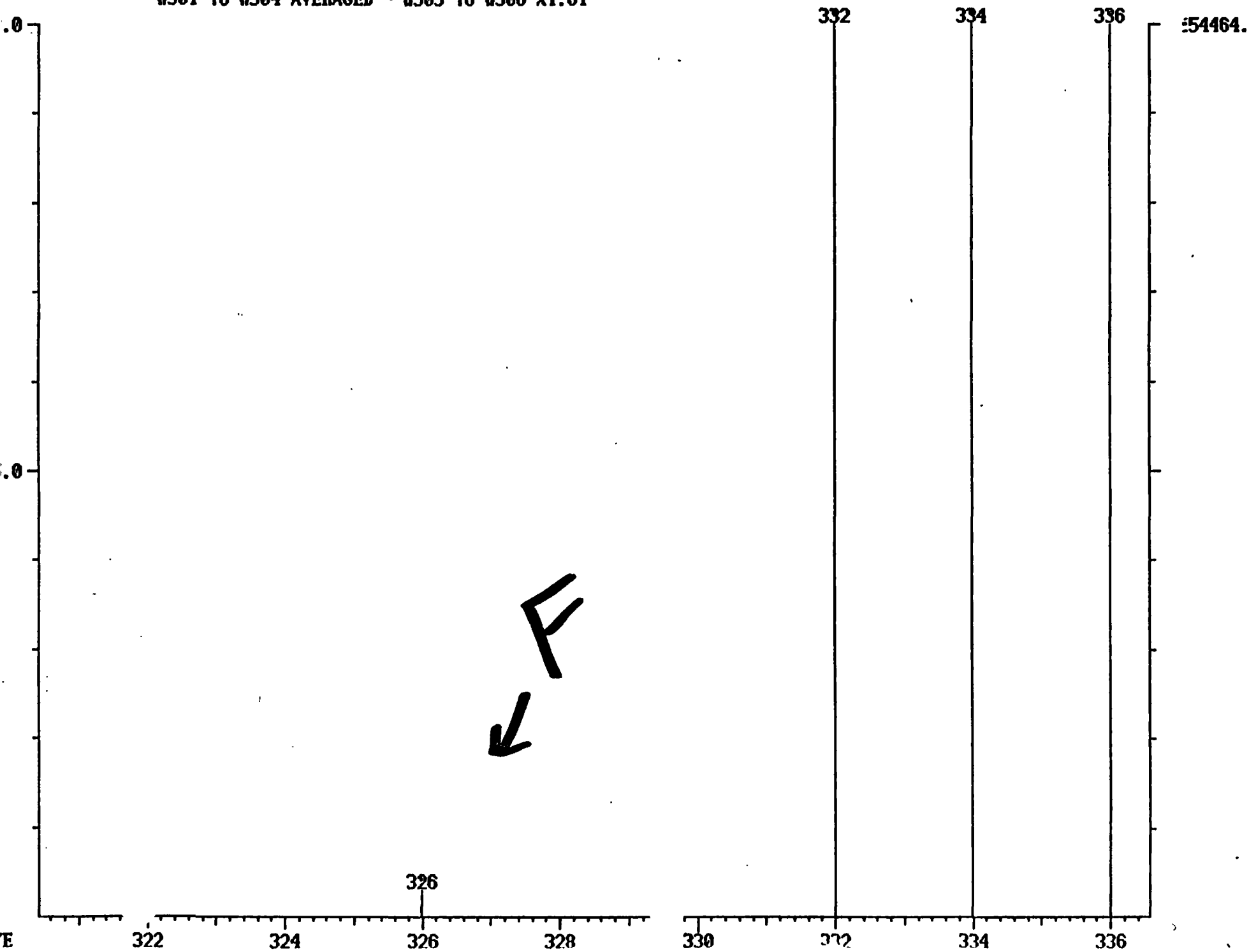
SCANS 350 TO 600



MID MASS SPECTRUM
04/04/82 15:06:00 + 12:33
SAMPLE: 4UL GRASS CARP CONTROL 50G EQ IN 10UL(3-31-E-4-4-82)MID EI 50PPT
#501 TO #504 AVERAGED - #505 TO #506 X1.01

DATA: GRASSCARP #502
CALI: C040482B1 #5

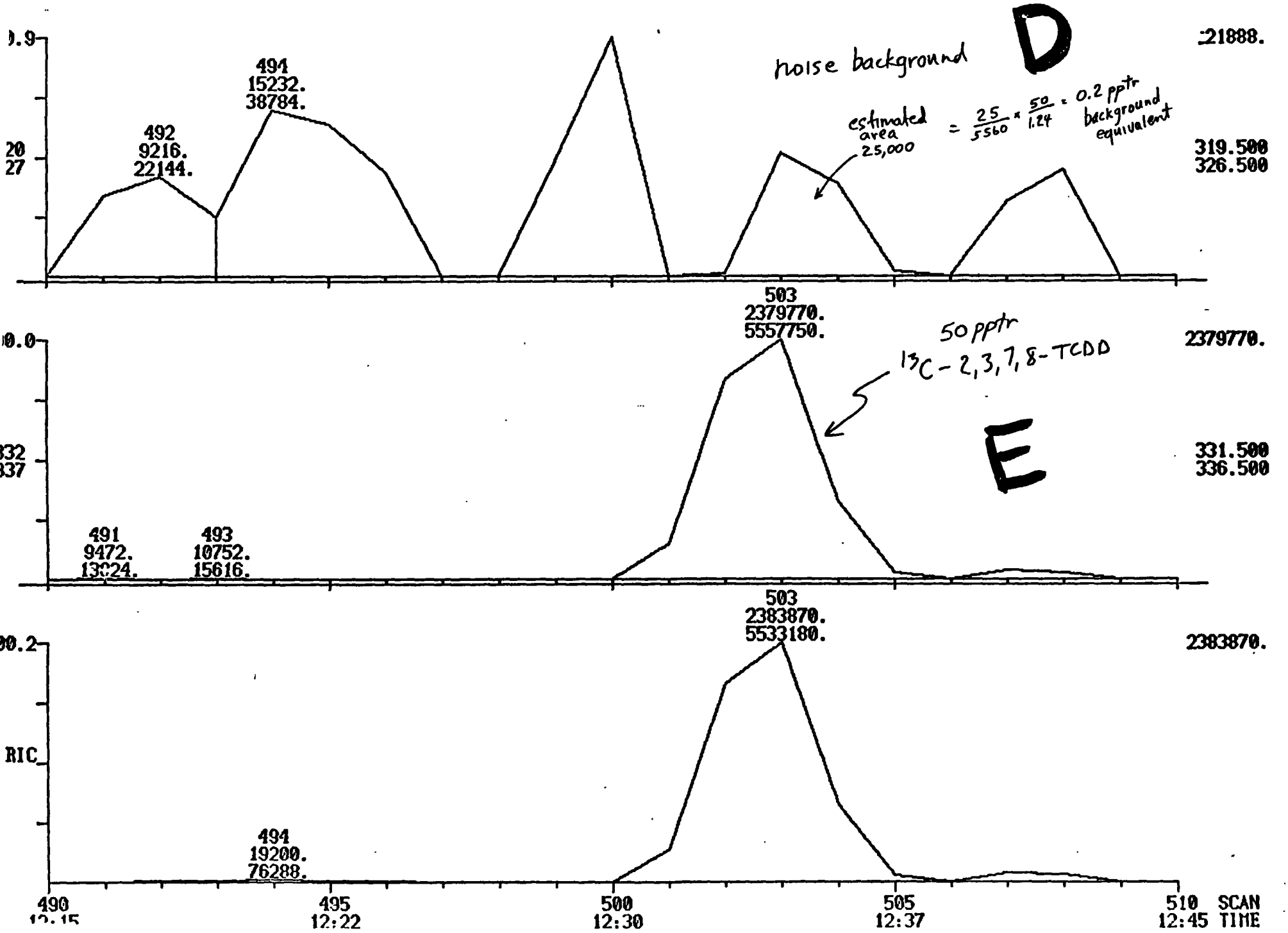
BASE M/E: 334
RIC: 1226750.



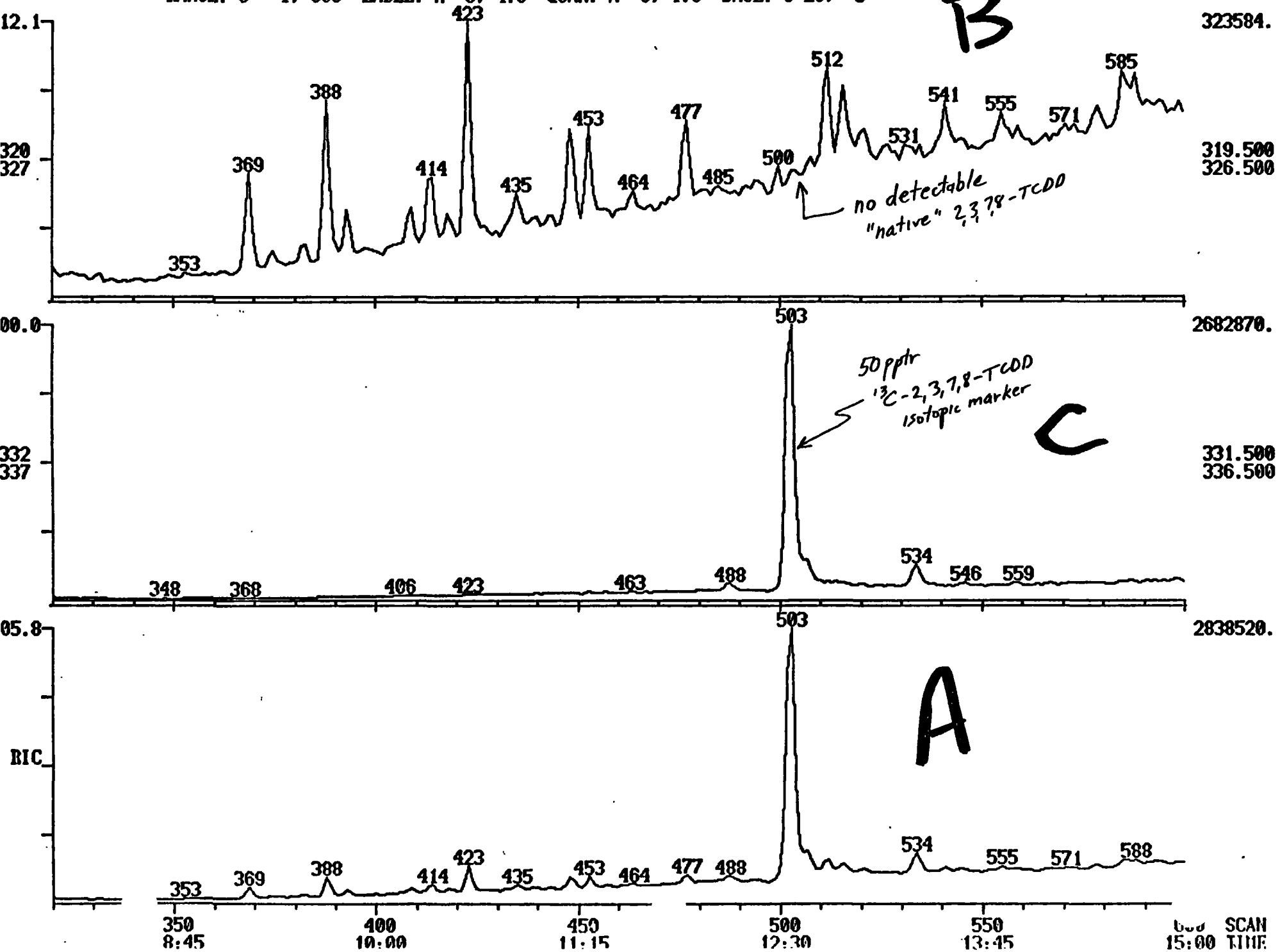
MID RIC + MASS CHROMATOGRAMS
04/04/82 15:06:00
SAMPLE: 4UL GRASS CARP CONTROL 50G EQ IN 10UL(3-
RANGE: G 1. 600 LABEL: N 3. 2.0 QUAN: A 1.

DATA: GRASSCARP 01
CALI: C040482B1 #5
-4-4-82)MID EI 50PPT
BASE: U 4. 1

SCANS 490 TO 510

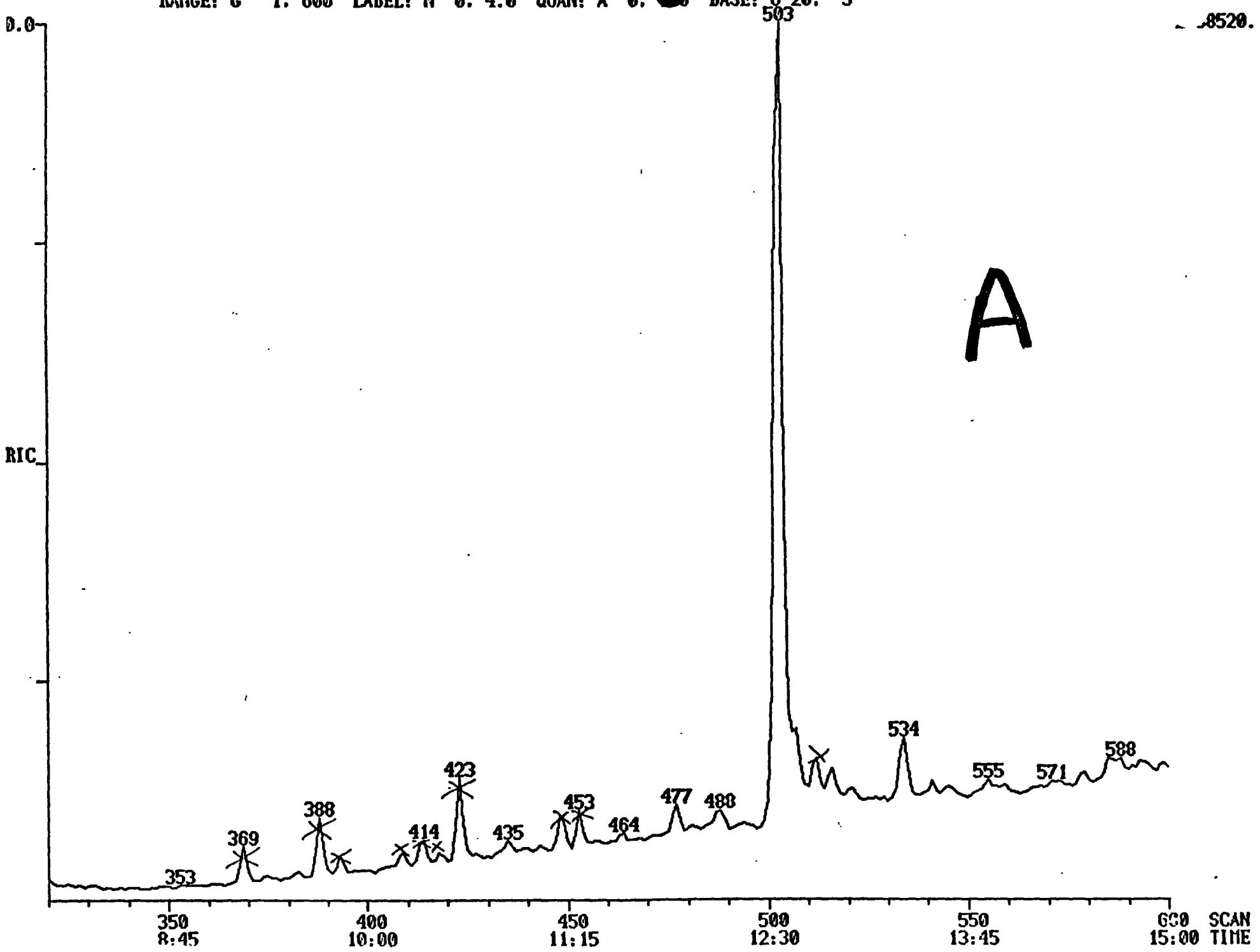


MID RIC + MASS CHROMATOGRAMS DATA: GRASSCARP #501 SCANS 320 TO 600
04/04/82 15:06:00 CALI: C040482B1 #5
SAMPLE: 4UL GRASS CARP CONTROL 50G EQ IN 10UL(3-31-E-4-4-82)MID EI 50PPT
RANGE: G 1. 600 LABEL: N 0. 4.0 QUAN: A 0. 1.0 BASE: U 20. 3



MID RIC
94/04/82 15:06:00
SAMPLE: 4UL GRASS CARP CONTROL 50G EQ IN 10UL(3-3[illegible]E-4-4-82)MID EI 50PPT
RANGE: G 1. 600 LABEL: N 0. 4.0 QUAN: A 0. [illegible] BASE: U 20. 3

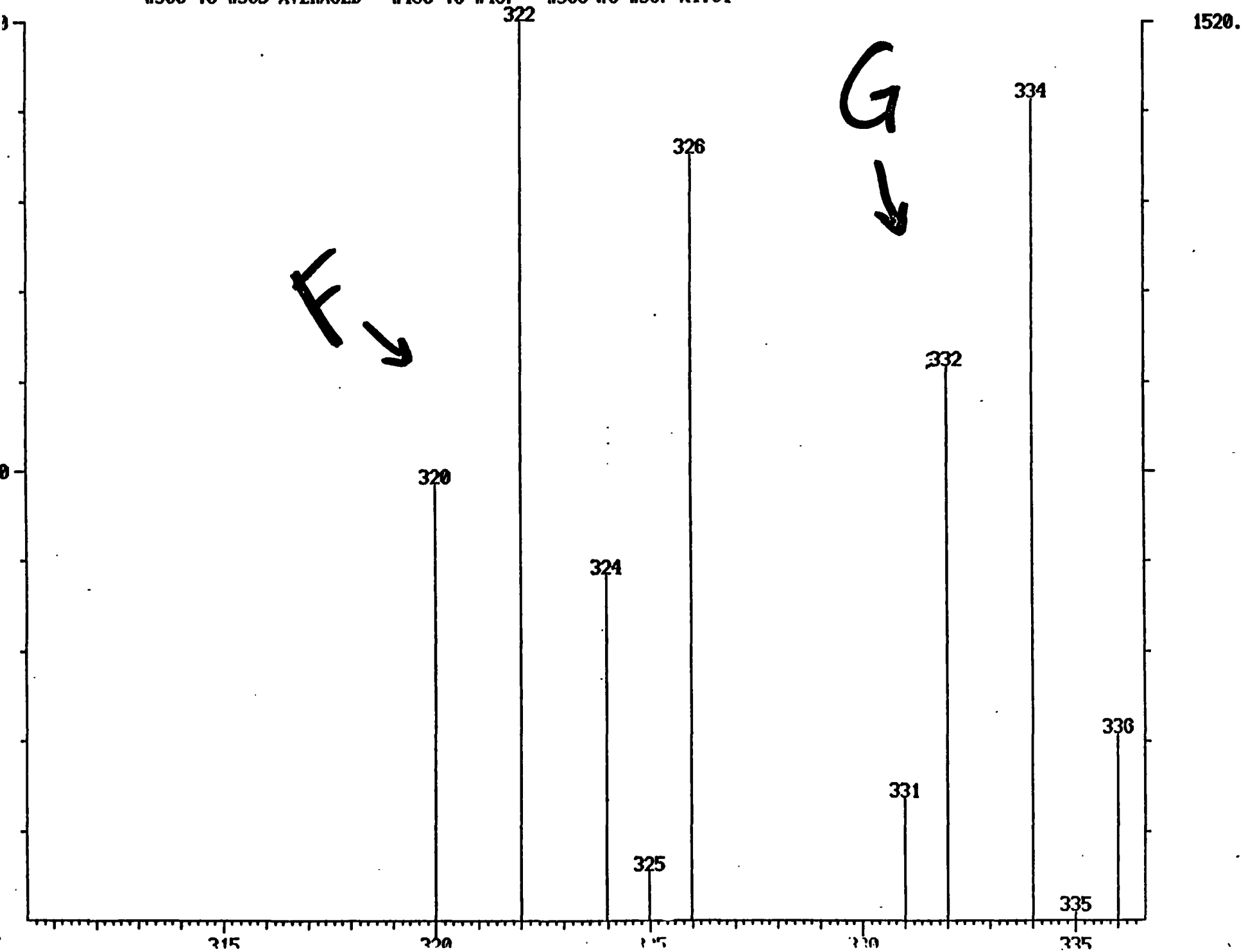
DATA: GRASSCARP H1
CALI: C040482B1 H5
SCANS 320 TO [illegible]



MID MASS SPECTRUM
04/03/82 12:28:00 + 12:31
SAMPLE: 2UL C12 & C13 2378 TCDD STD'7-14-81)10PG/UL MID EI 1900 EMV
#500 TO #503 AVERAGED - #496 TO #497 - #506 TO #507 X1.01

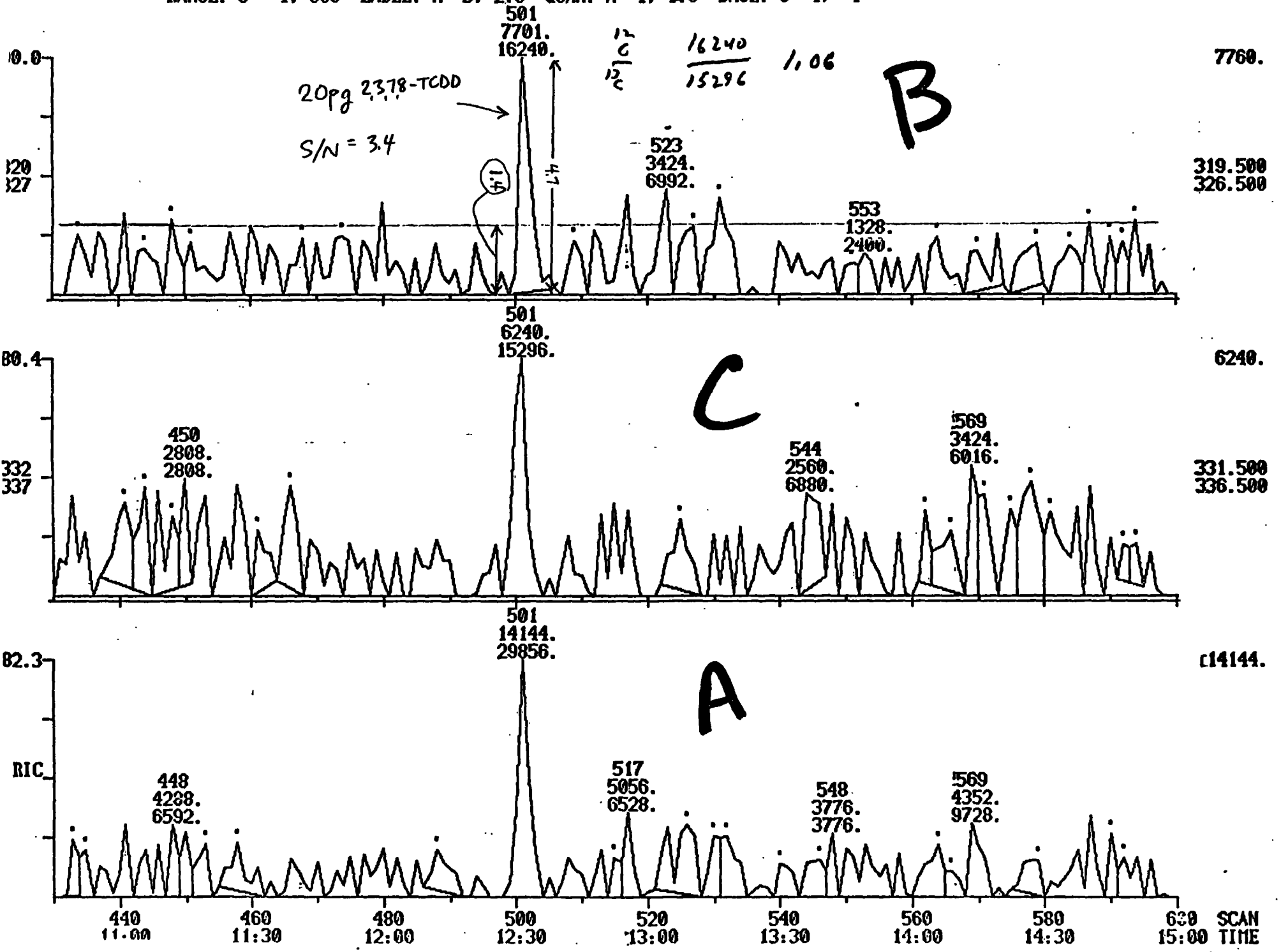
DATA: STD4 #501
CALI: C040382B #3

BASE M/E: 322
RIC: 7080.



MID RIC + MASS CHROMATOGRAMS
04/03/82 12:28:00
SAMPLE: 2UL C12 & C13 2378 TCDD STD'7-14-81)10PG MID EI 1900 EMV
RANGE: G 1. 600 LABEL: N 3. 2.0 QUAN: A 1. 0 BASE: U 4. 1

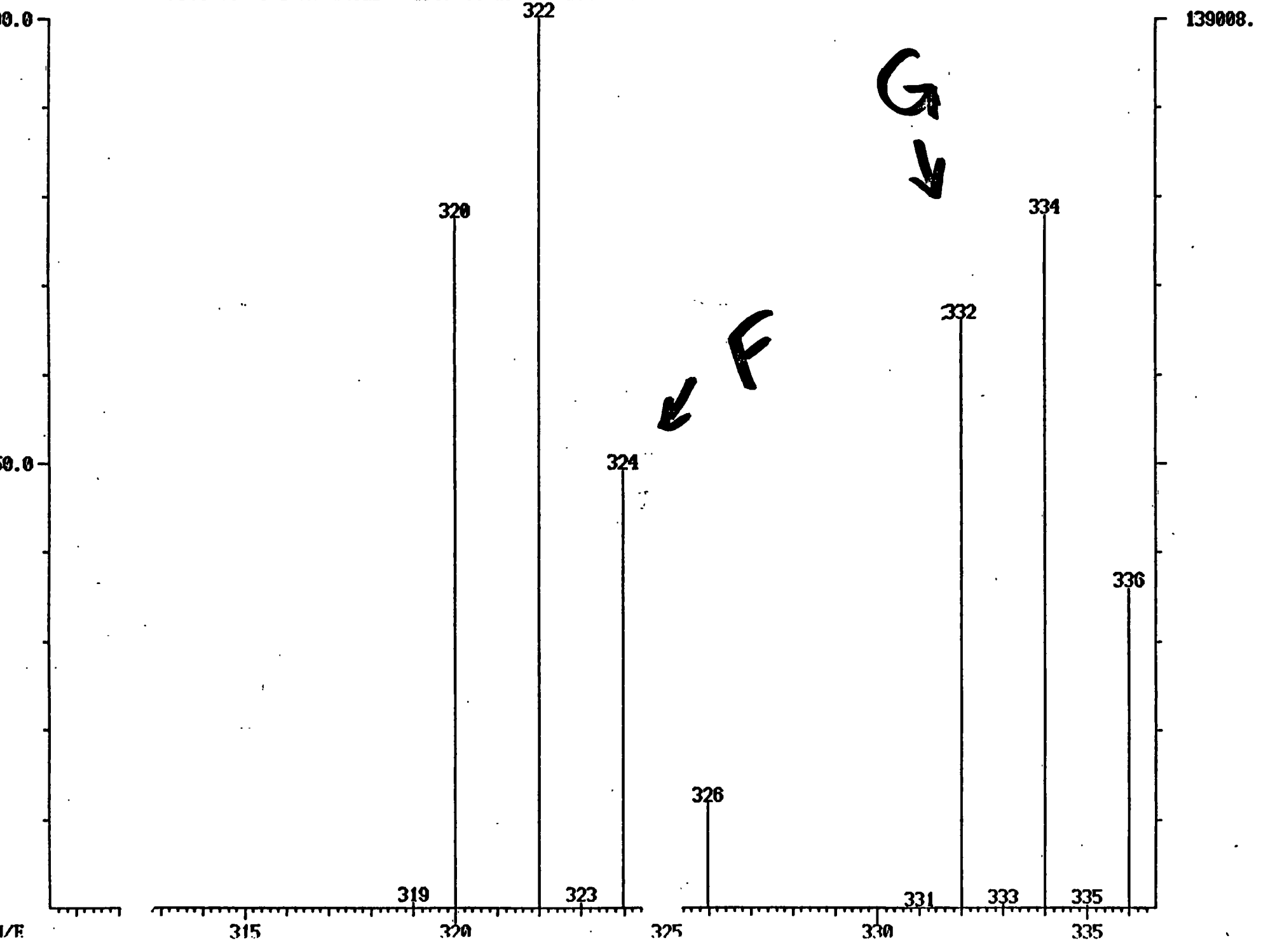
DATA: STD4 #1
CALI: C040382B #3
SCANS 430 TO 600



MID MASS SPECTRUM
04/03/82 15:42:00 + 12:33
SAMPLE: 4UL C12 & C13 STD 2378 TCDD(7-14-81)50PG/UL MID EI 1900EMV
#501 TO #503 AVERAGED - #507 TO #508 - #496 TO #497 X1.01

DATA: STD5 #502
CALI: C040382B #3

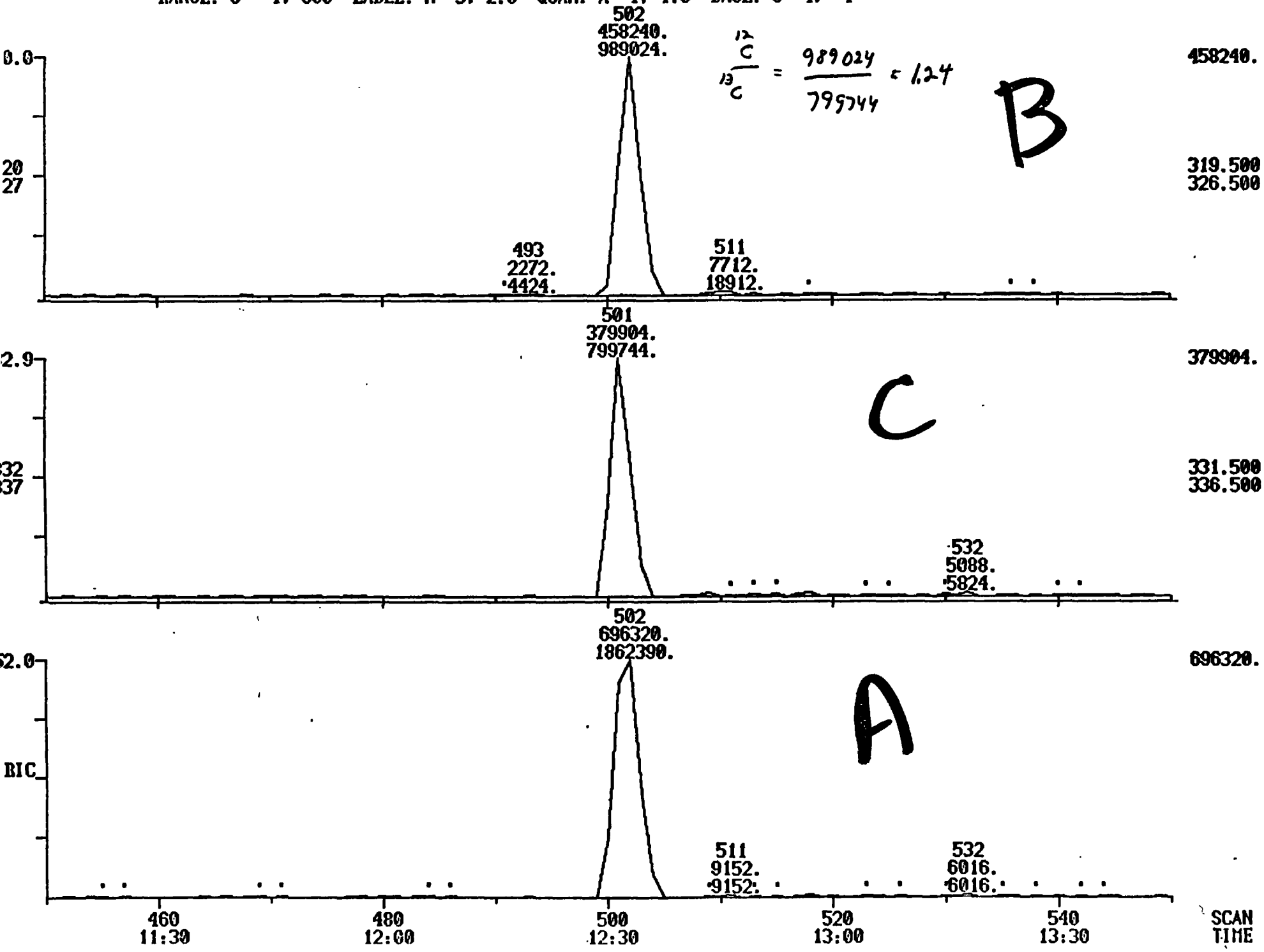
BASE M/E: 322
RIC: 584704.



MID RIC + MASS CHROMATOGRAMS
34/03/82 15:42:00
AMPLE: 4UL C12 & C13 STD 2378 TCDD(7-14-81)50PG. MID EI 1900EMV
RANGE: G 1. 600 LABEL: N 3. 2.0 QUAN: A 1. 1.0 BASE: U 4. 1

DATA: STD5 #1
CALI: C040382B #3

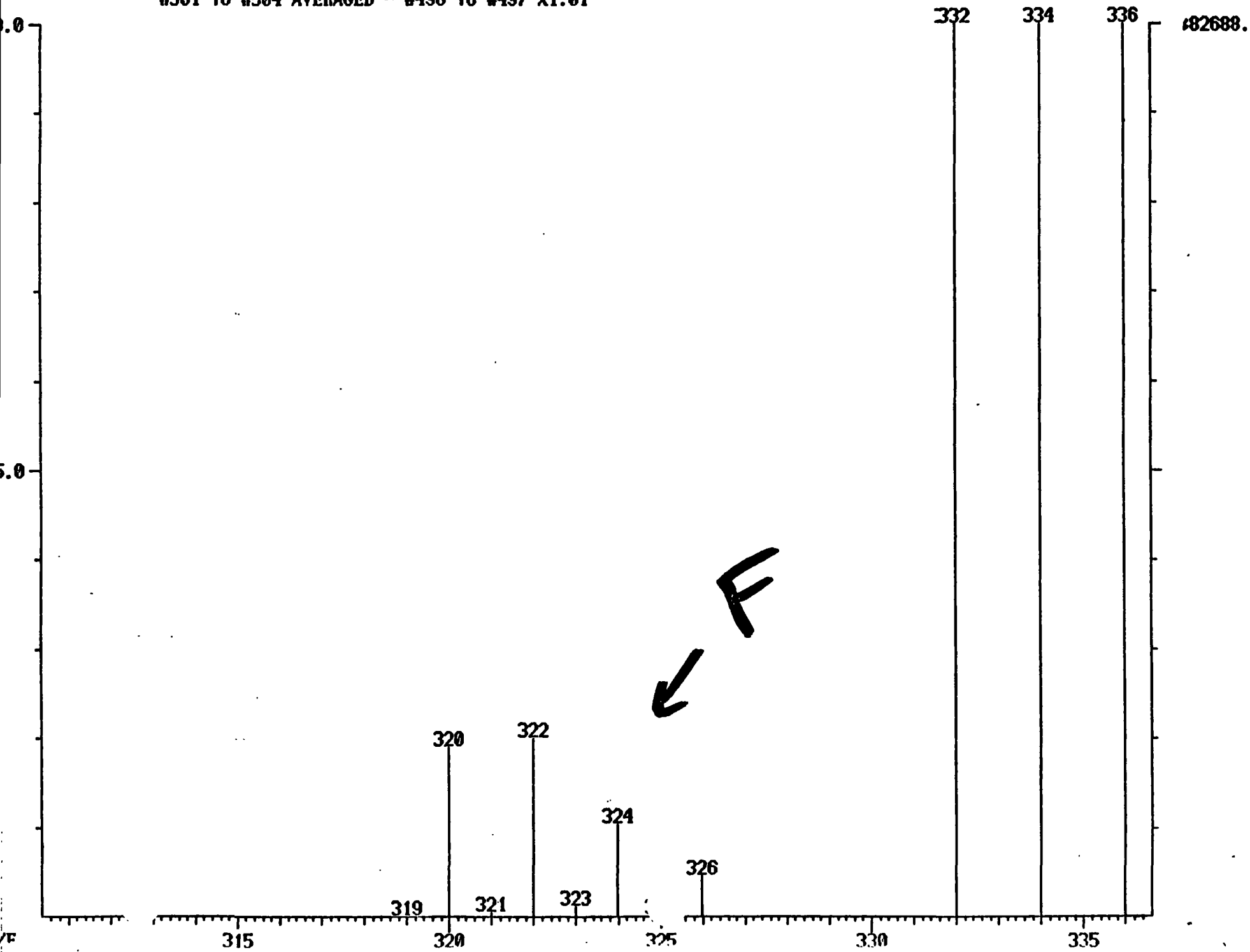
SCANS 450 TO 550



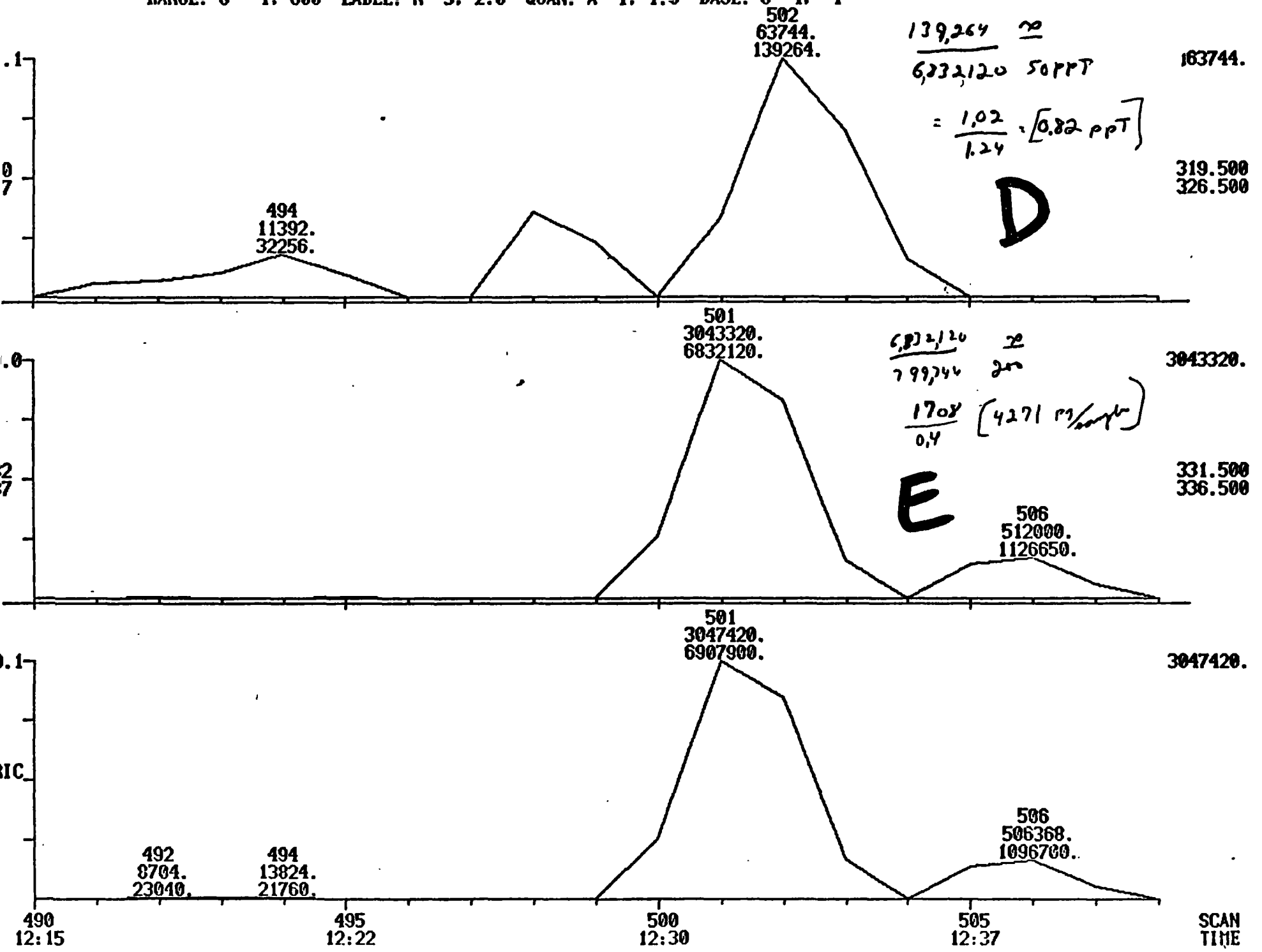
MID MASS SPECTRUM
04/03/82 14:58:00 + 12:33
SAMPLE: 4UL SAMPLE 26C(3-26-G-4-3-82)10UL VOL. 50PPT MARK MID EI SPRING
#501 TO #504 AVERAGED - #496 TO #497 X1.01

DATA: 26C #502
CALI: C040382B #3

BASE M/E: 334
RIC: 1937400.



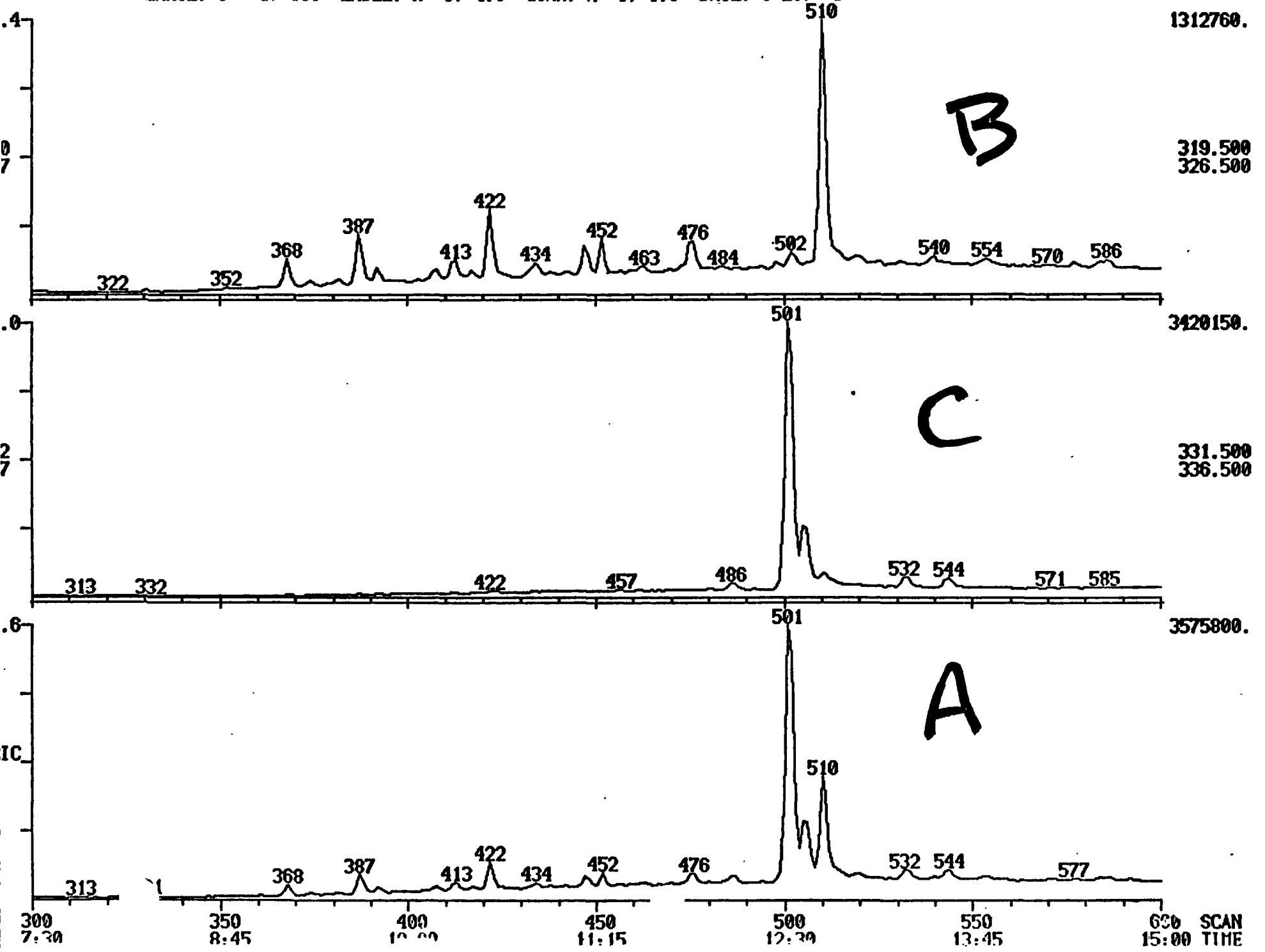
MID RIC + MASS CHROMATOGRAMS
4/03/82 14:58:00
AMPLE: 4UL SAMPLE 26C(3-26-G-4-3-82)10UL VOL. 50
RANGE: G 1. 600 LABEL: H 3. 2.0 QUAN: A 1. 1.
DATA: 26C #509
CALI: C040382B #3
ARK MID EI SPRING
BASE: U 4. 1
SCANS 490 TO 508



MID RIC + MASS CHROMATOGRAMS
04/03/82 14:58:00
SAMPLE: 4UL SAMPLE 26C(3-26-G-4-3-82)10UL VOL. 50PPT MARK MID EI SPRING
RANGE: G 1. 600 LABEL: N 0. 4.0 QUAN: A 0. 1.0 BASE: U 20. 3

DATA: 26C #1
CALI: C040382B #3

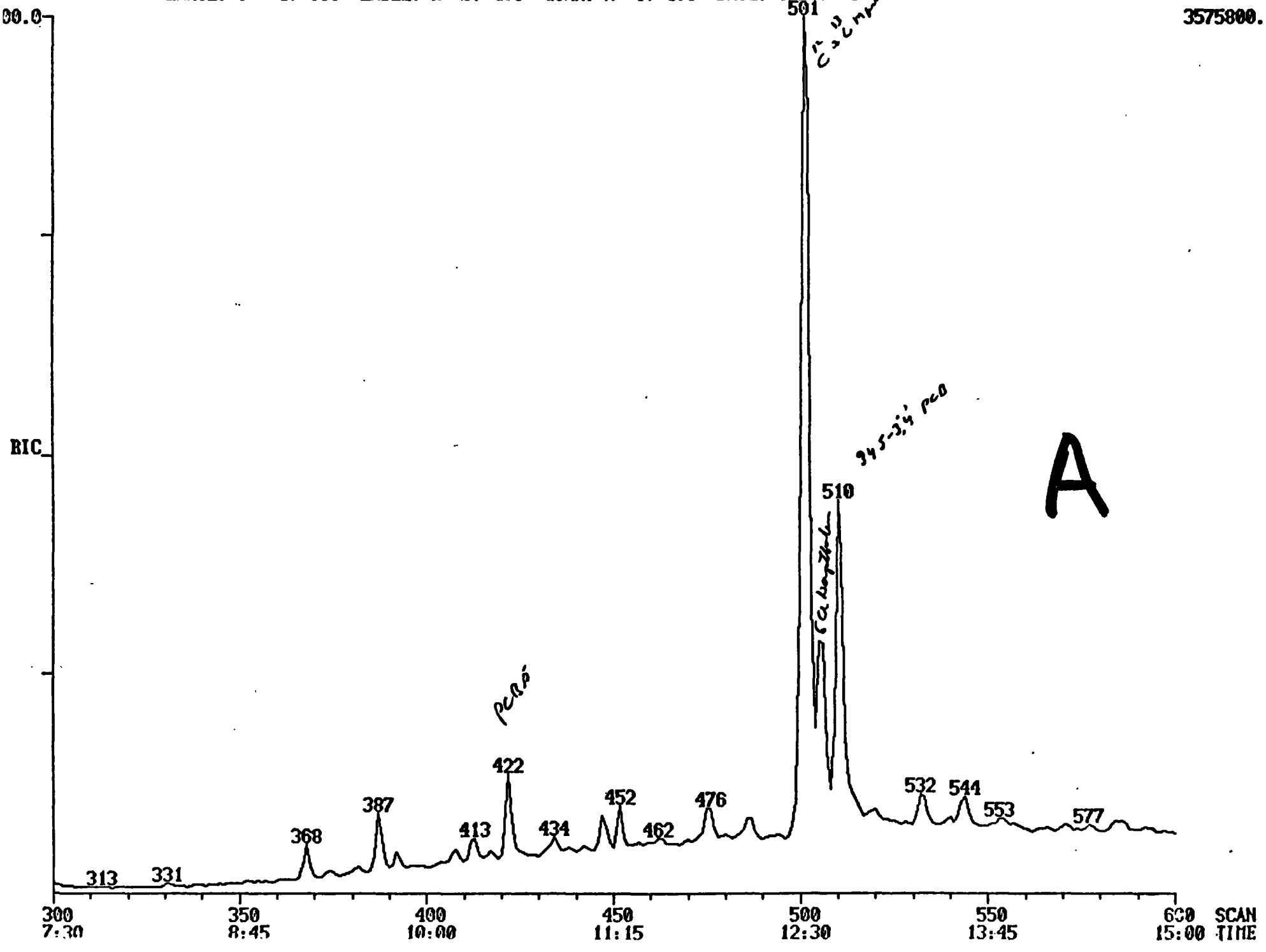
SCANS 300 TO 600



MID RIC
04/03/82 14:58:00
SAMPLE: 4UL SAMPLE 26C(3-26-G-4-3-82)10UL VOL. !
RANGE: G 1. 600 LABEL: H 0. 4.0 QUAN: A 0. ..0 BASE: U 20. 3

DATA: 26C #1
CALI: C040382B #3
T MARK MID EI SPRING

SCANS 300 TO 600

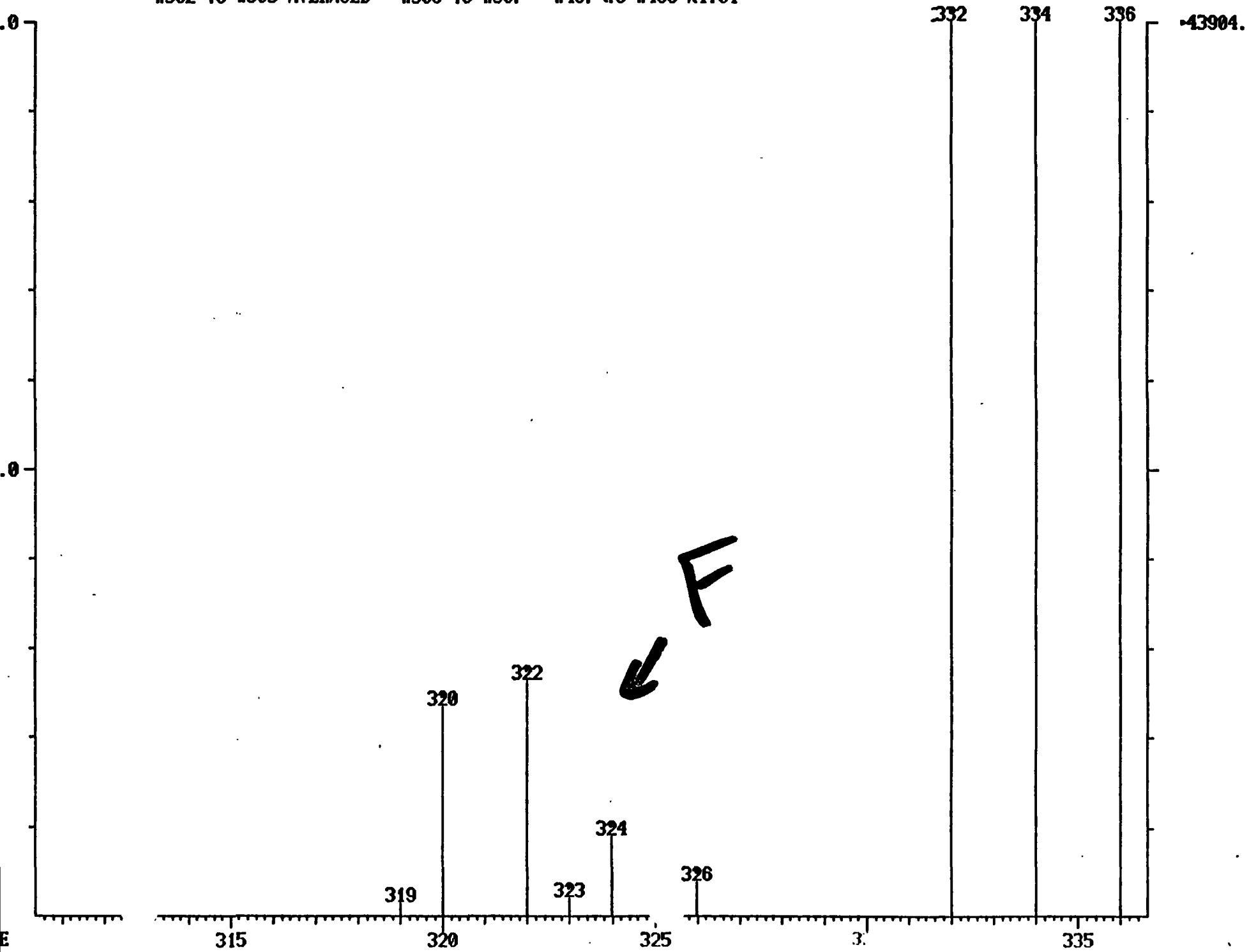


A

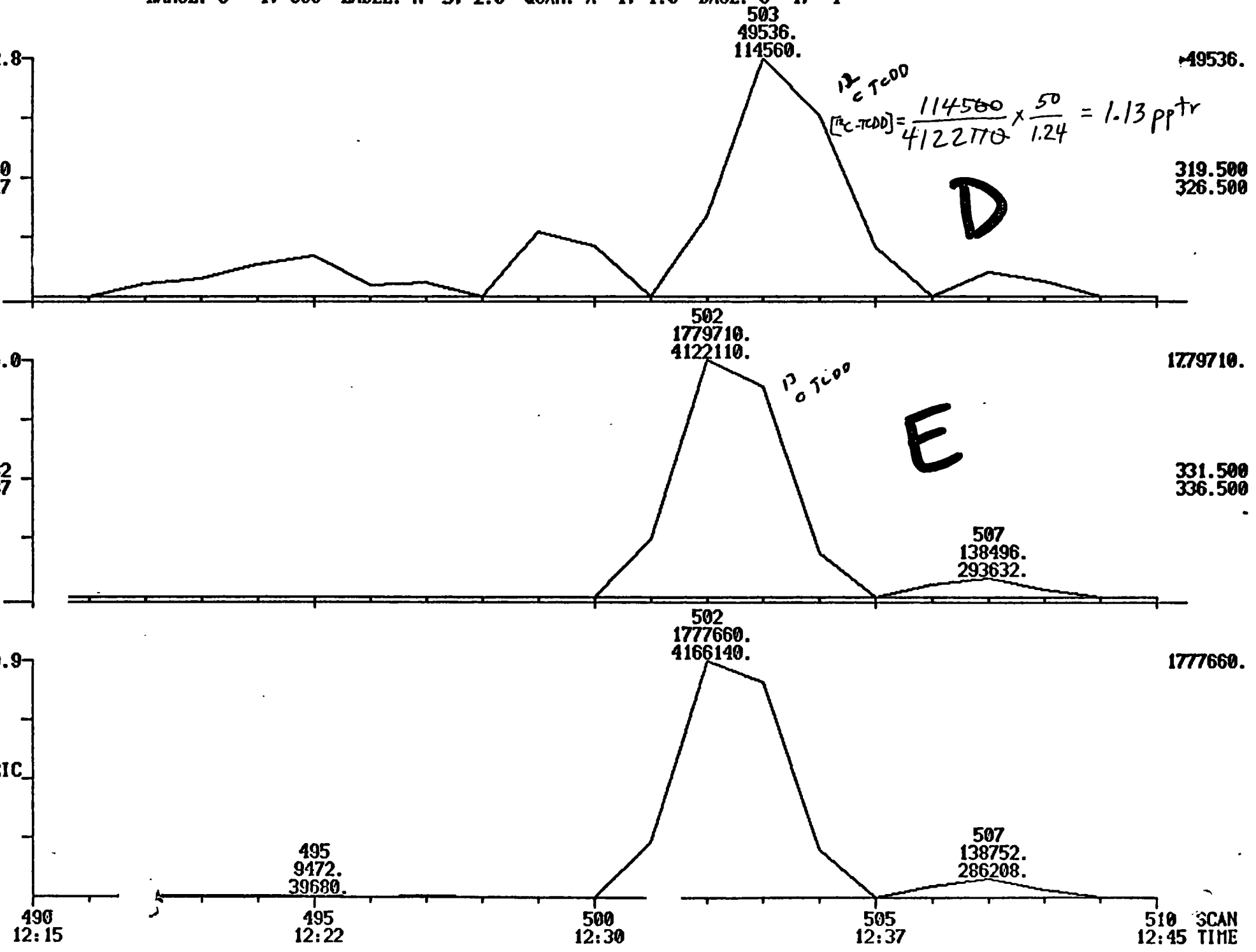
MID MASS SPECTRUM
04/04/82 13:19:00 + 12:34
SAMPLE: 4UL SAMPLE 25C(3-31-G-4-3-82)10UL VOL 50PPT MARK MID EI
#502 TO #505 AVERAGED - #506 TO #507 - #497 TO #498 X1.01

DATA: 25C #503
CALI: C040482B1 #5

BASE M/E: 334
RIC: 1034240.



MID RIC + MASS CHROMATOGRAMS DATA: 25C #1 SCANS 490 TO 510
04/04/82 13:19:00 CALI: C040482B1 #5
SAMPLE: 4UL SAMPLE 25C(3-31-G-4-3-82)10UL VOL 50PPT MARK MID EI
RANGE: G 1. 600 LABEL: N 3. 2.0 QUAN: A 1. 1.0 BASE: U 4. 1



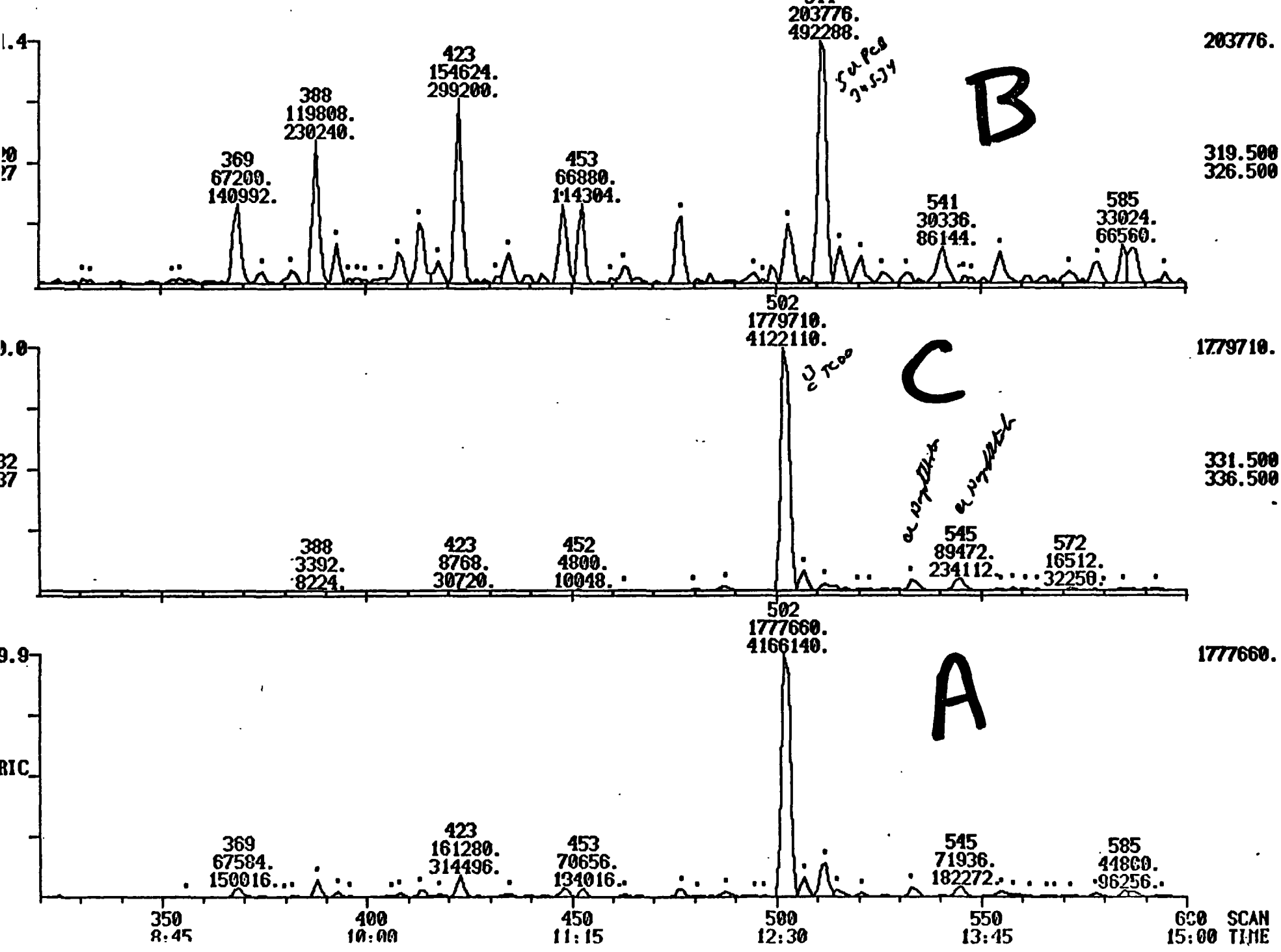
^{13}C TCDD

$$[^{13}C\text{-}TCDD] = \frac{114560}{4122110} \times \frac{50}{1.24} = 1.13\ ppt$$

MID RIC + MASS CHROMATOGRAMS
94/04/82 13:19:00
AMPLE: 4UL SAMPLE 25C(3-31-G-4-3-82)10UL VOL 50I
RANGE: G 1. 600 LABEL: N 3. 2.0 QUAN: A 1. 1.0

DATA: 25C #1
CALI: C040482B1 #5
MARK MID EI
BASE: U 4. 1

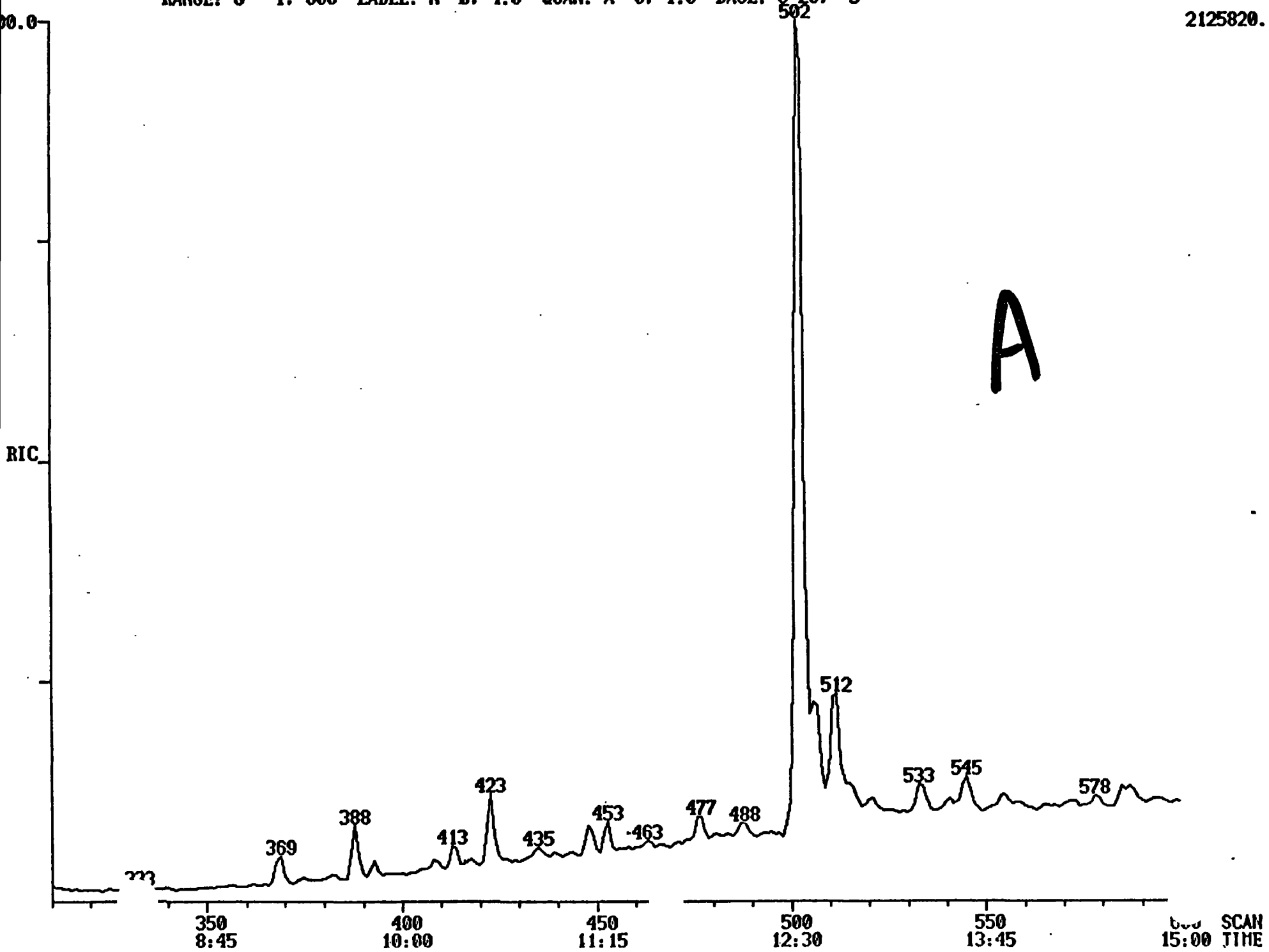
SCANS 320 TO 600



MID RIC
04/04/82 13:19:00
SAMPLE: 4UL SAMPLE 25C(3-31-G-4-3-82)10UL VOL 50PPT MARK MID EI
RANGE: G 1. 600 LABEL: N 0. 4.0 QUAN: A 0. 1.0 BASE: U 20. 3

DATA: 25C #1
CALI: C040482B1 #5

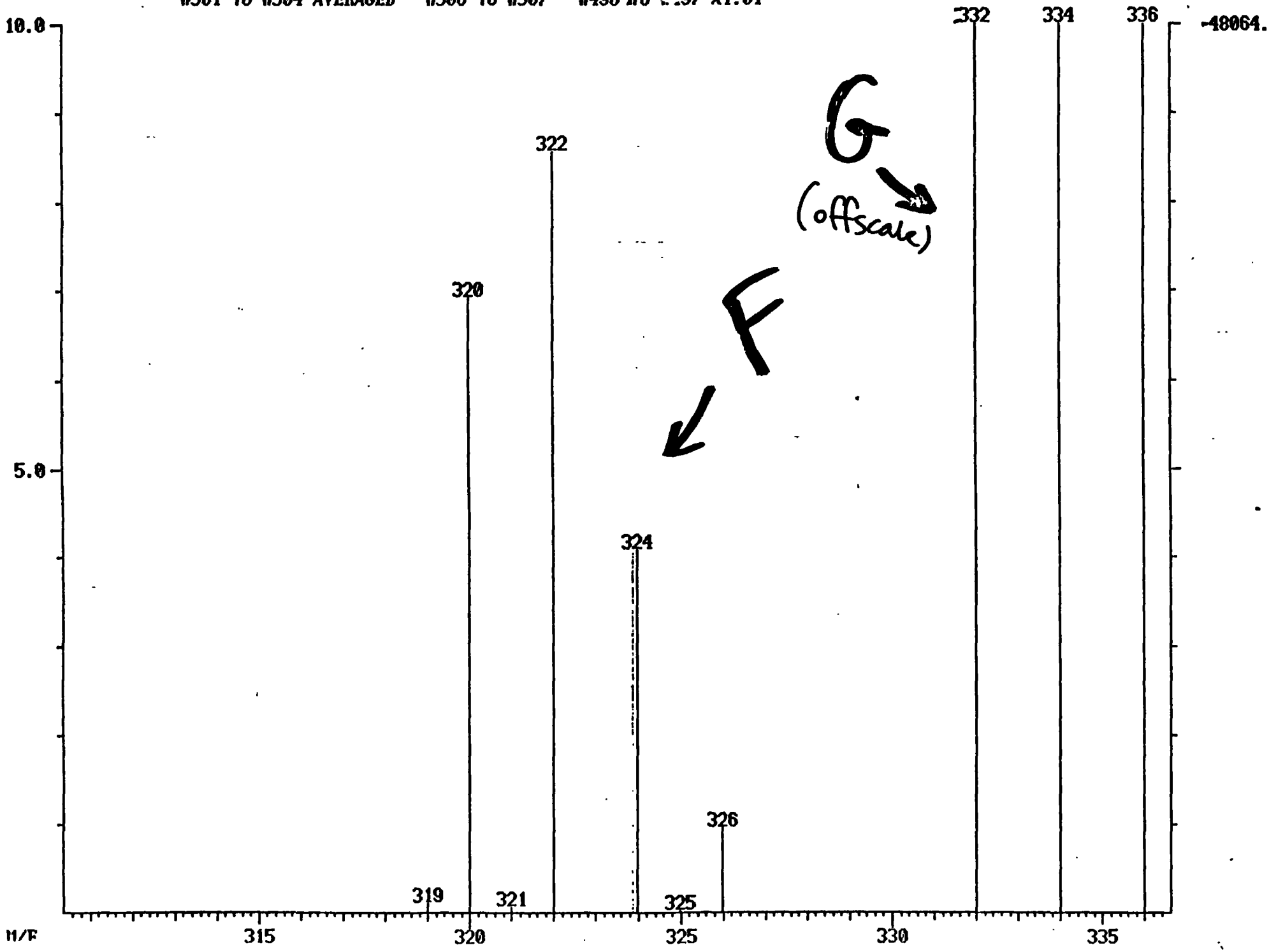
SCANS 310 TO 600



MID MASS SPECTRUM
04/03/82 14:12:00 + 12:33
SAMPLE: 4UL SAMPLE 24C(3-20-G-4-3-82)10UL VOL.
#501 TO #504 AVERAGED - #506 TO #507 - #496 TO ..97 X1.01

DATA: 24C #502
CALI: C040382B #3
T MARK MID EI SPRING

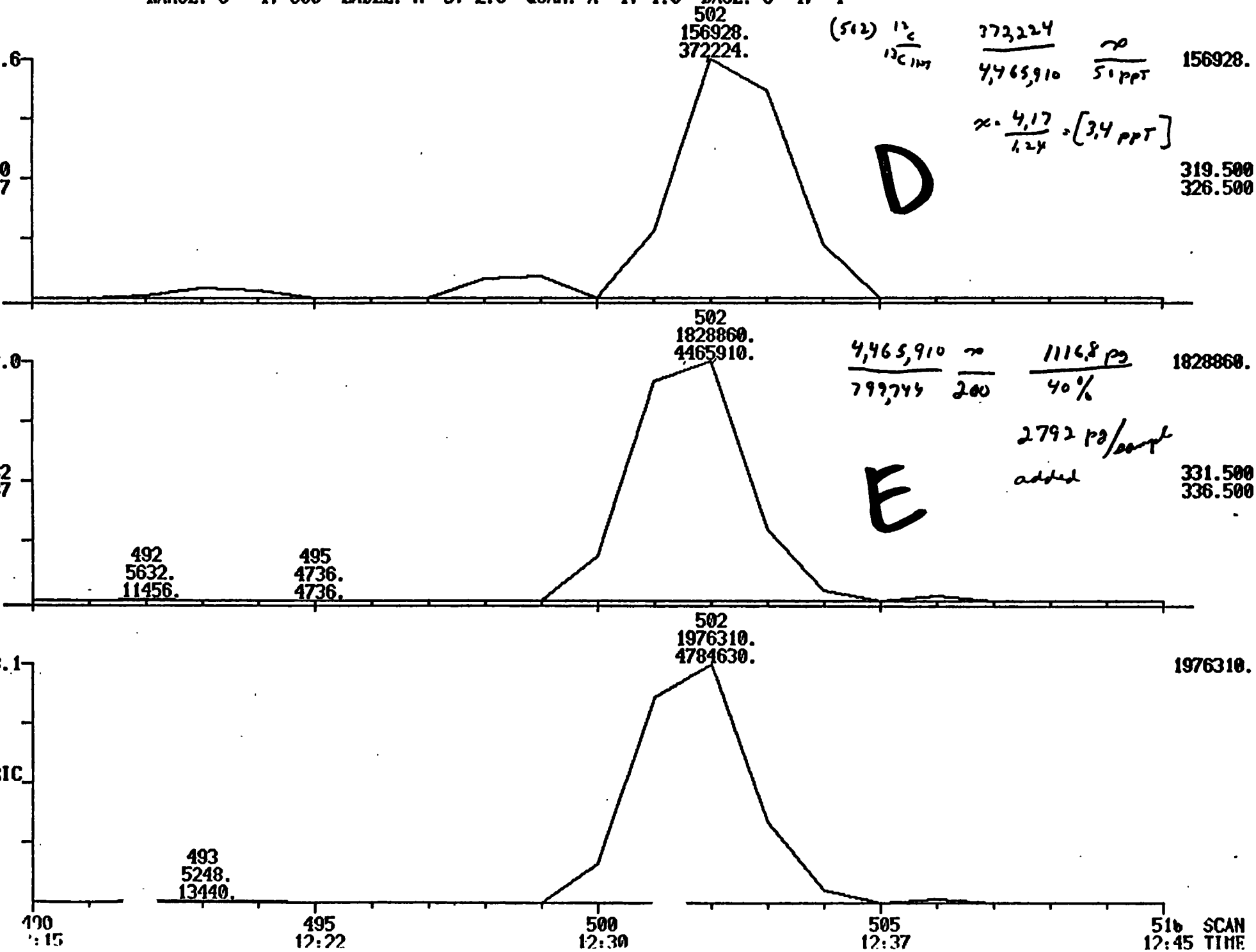
BASE M/E: 334
RIC: 1189880.



MID RIC + MASS CHROMATOGRAMS
04/03/82 14:12:00
SAMPLE: 4UL SAMPLE 24C(3-20-G-4-3-82)10UL VOL. 50PPT MARK MID EI SPRING
RANGE: G 1. 600 LABEL: N 3. 2.0 QUAN: A 1. 1.0 BASE: U 4. 1

DATA: 24C #1
CALI: C040382B #3

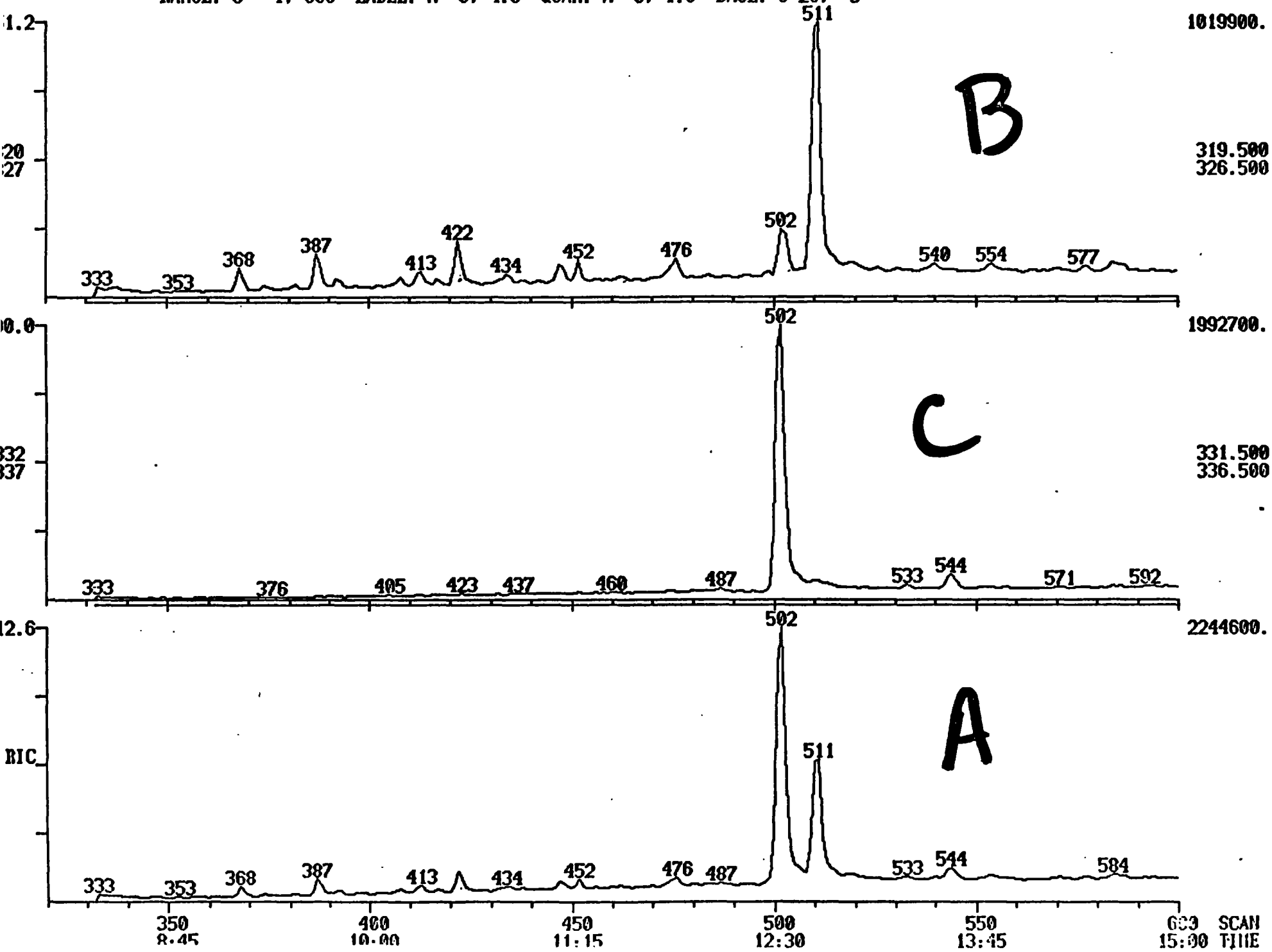
SCANS 490 TO 510



MID RIC + MASS CHROMATOGRAMS
04/03/82 14:12:00
SAMPLE: 4UL SAMPLE 24C(3-20-G-4-3-82)10UL VOL. 5
RANGE: G 1, 600 LABEL: N 0, 4.0 QUAN: A 0, ..0

DATA: 24C #1
CALI: C040382B #3
MARK MID EI SPRING
BASE: U 20, 3

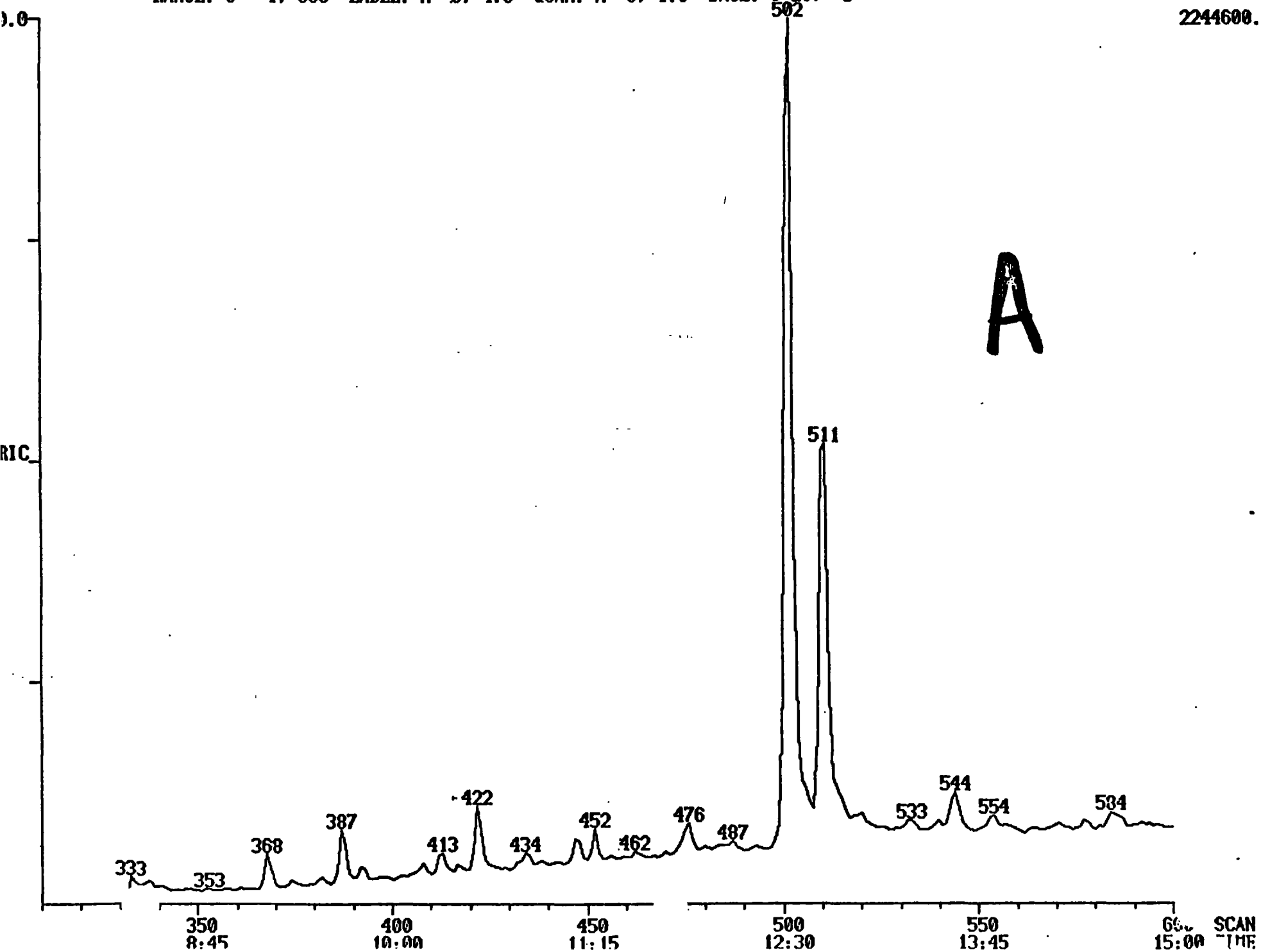
SCANS 320 TO 600



MID RIC
04/03/82 14:12:00
SAMPLE: 4UL SAMPLE 24C(3-20-G-4-3-82)10UL VOL. 50PPT MARK MID EI SPRING
RANGE: G 1. 600 LABEL: N 0. 4.0 QUAN: A 0. 1.0 BASE: U 20. 3

DATA: 24C #1
CALI: C040382B #3

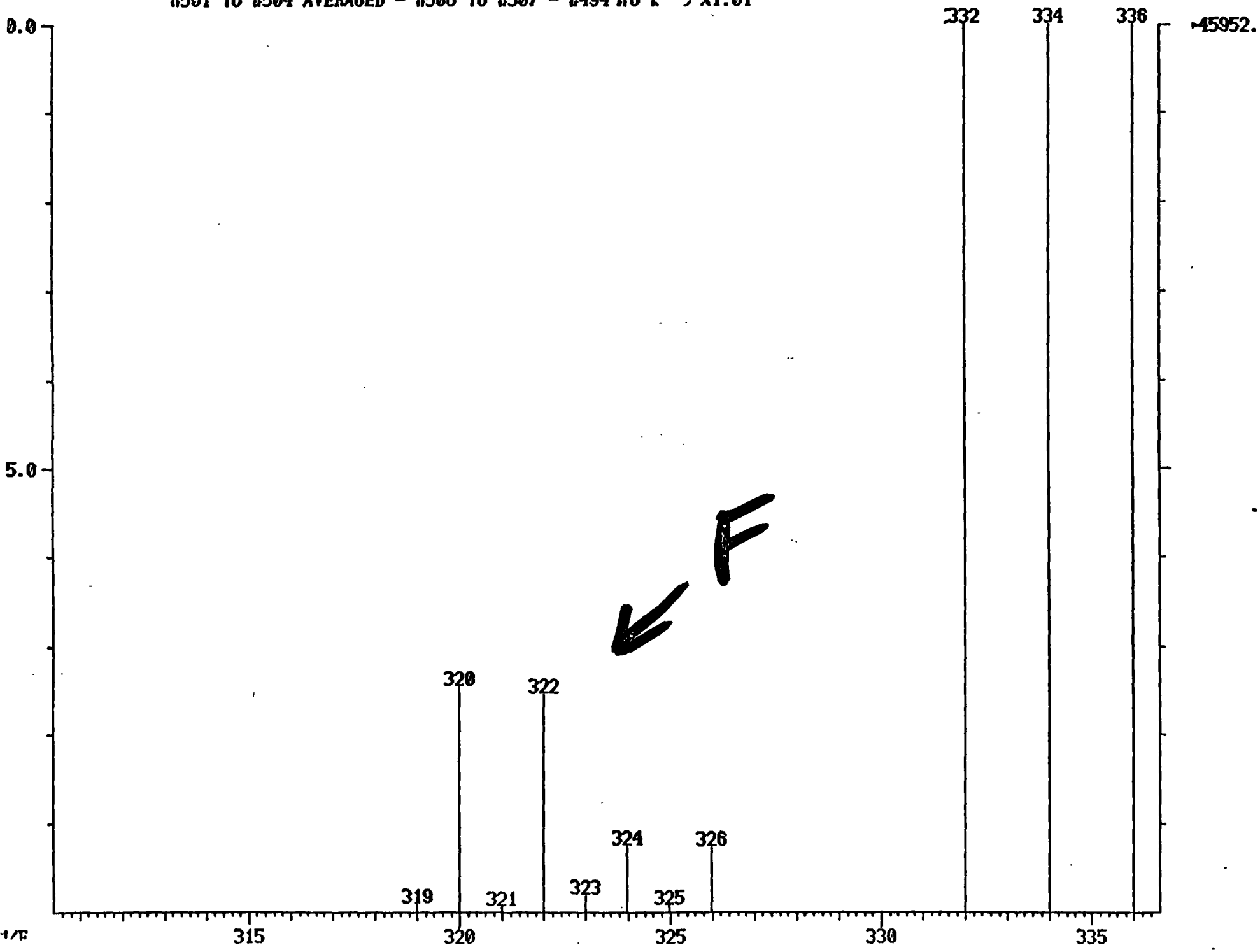
SCANS 310 TO 600



MID MASS SPECTRUM
04/03/82 13:04:00 + 12:33
SAMPLE: 4UL SAMPLE 23C(3-20-E-4-3-82)10UL VOL 50'
#501 TO #504 AVERAGED - #506 TO #507 - #494 TO X1.01

DATA: 23C #502
CALI: C040382B #3
MARK MID EI SPRING R

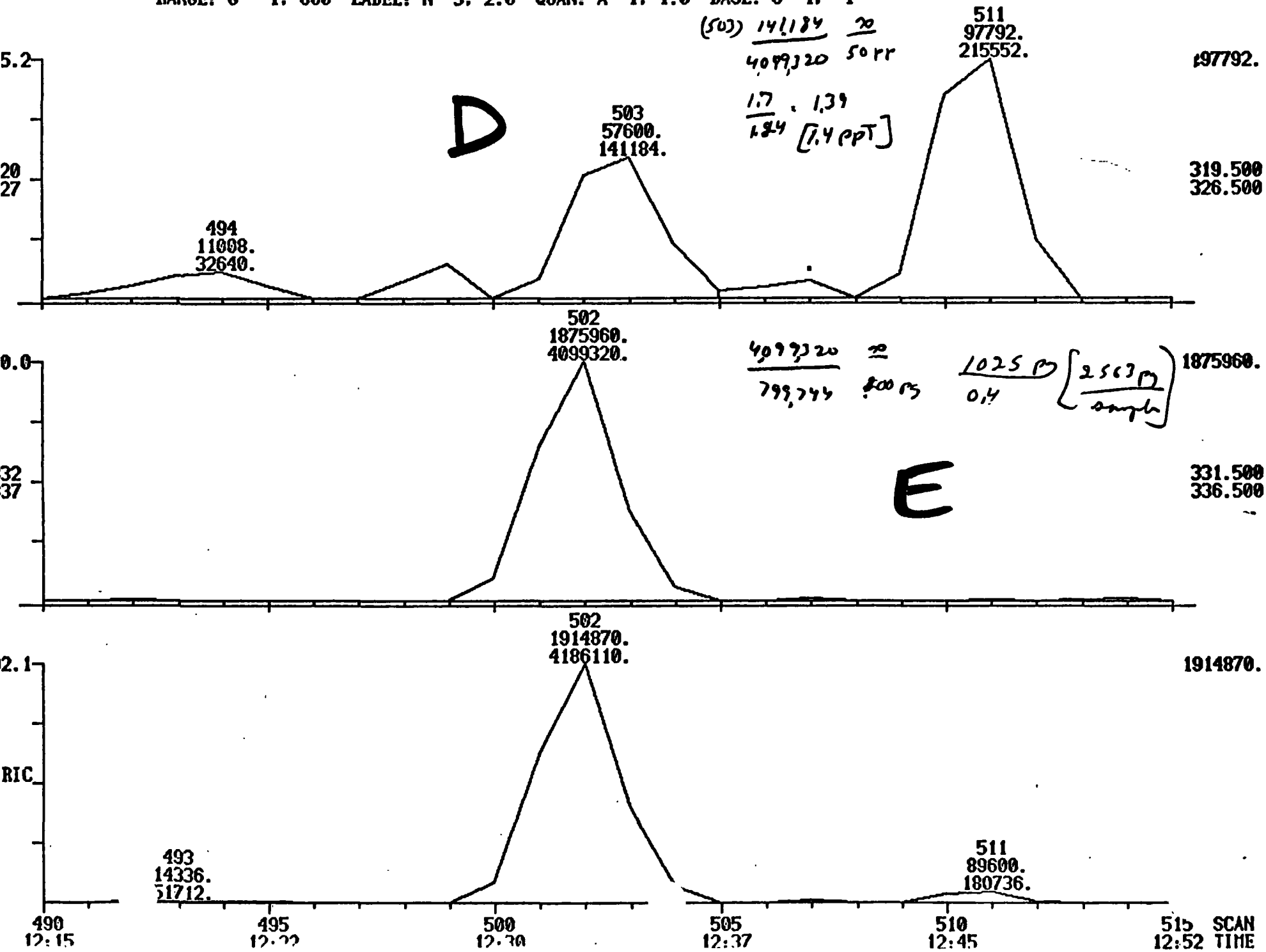
BASE M/E: 334
RIC: 1081340.



MID RIC + MASS CHROMATOGRAMS DATA: 23C #420 SCANS 490 TO 515
04/03/82 13:04:00 CALI: C040382B #3
SAMPLE: 4UL SAMPLE 23C(3-20-E-4-3-82)10UL VOL 50PPT MARK MID EI SPRING R
RANGE: G 1. 600 LABEL: H 3. 2.0 QUAN: A 1. 1.0 BASE: U 4. 1

(503) 141184 / 4099320 ≈ 20 / 50 pr

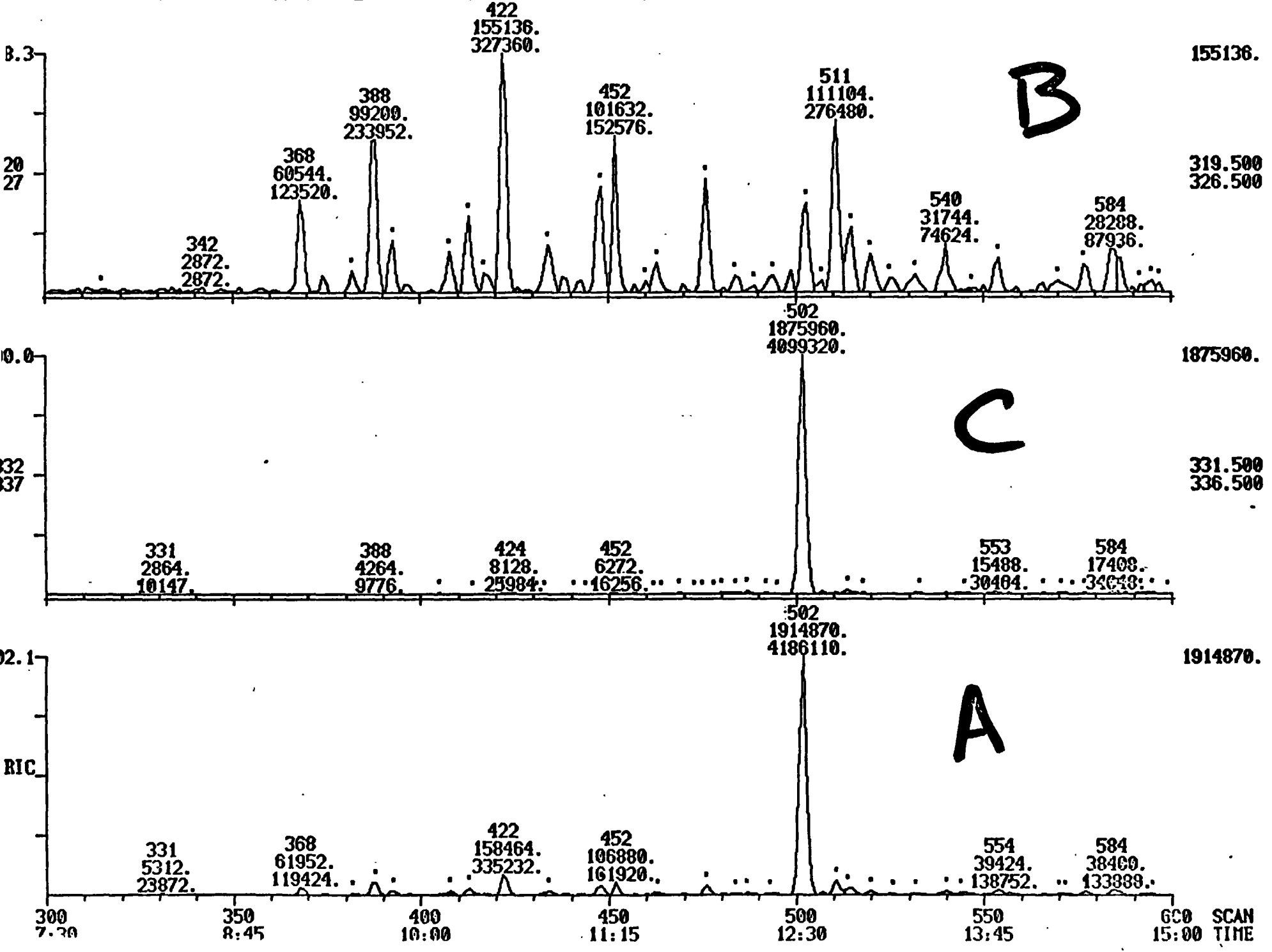
1.7 / 1.24 . 1.39 [1.4 ppT]



4099320 / 799,744 ≈ 800 ng

1025 ng / 0.4 [2563 ng / sample]

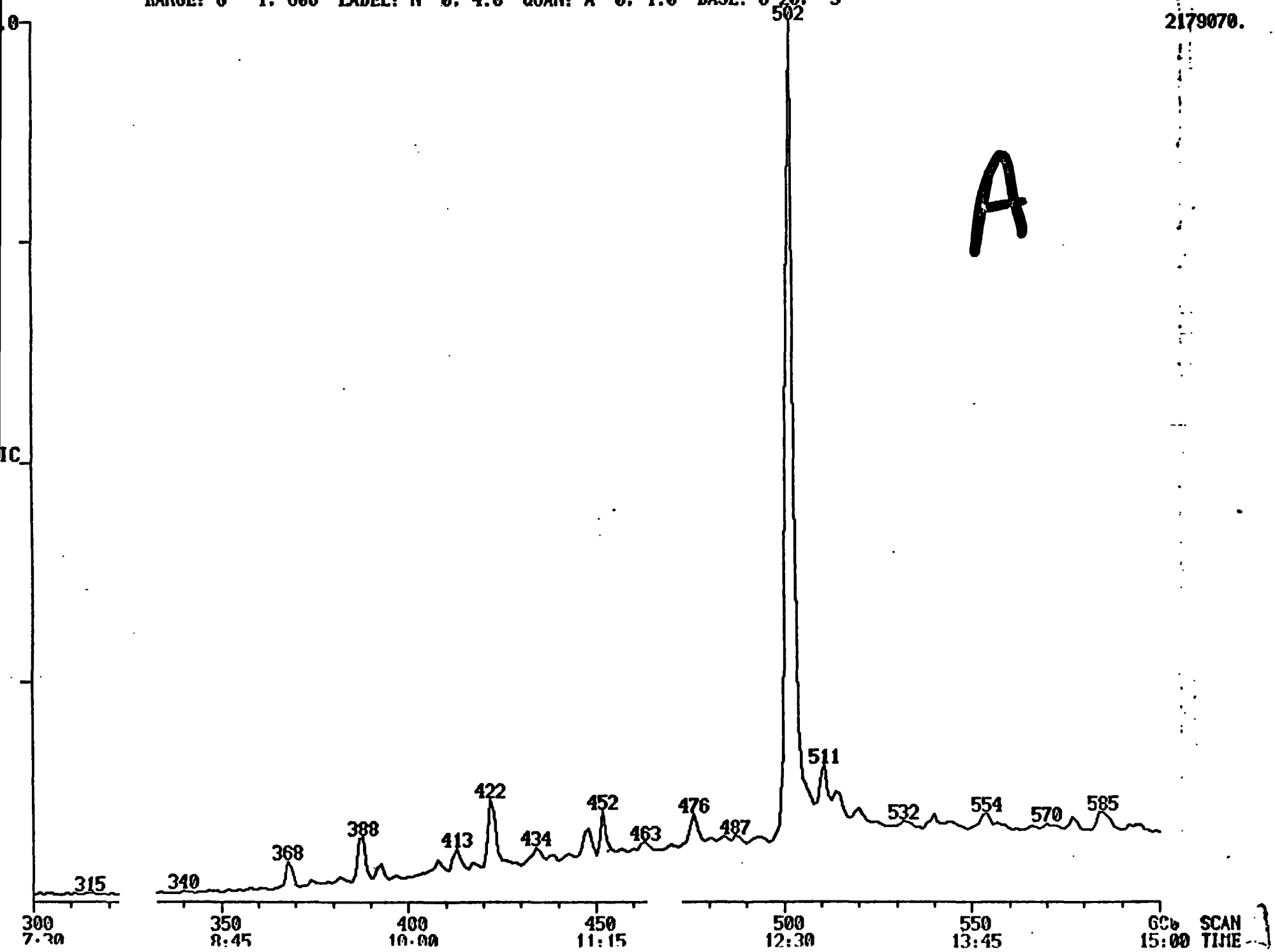
MID RIC + MASS CHROMATOGRAMS DATA: 23C #1 SCANS 300 TO 600
04/03/82 13:04:00 CALI: C040382B #3
SAMPLE: 4UL SAMPLE 23C(3-20-E-4-3-82)10UL VOL 50\ MARK MID EI SPRING R
RANGE: G 1. 600 LABEL: N 3. 2.0 QUAN: A 1. 1.0 BASE: U 4. 1



MID RIC
04/03/82 13:04:00
SAMPLE: 4UL SAMPLE 23C(3-20-E-4-3-82)10UL VOL 50PPT MARK MID EI SPRING R
RANGE: G 1. 600 LABEL: N 0. 4.0 QUAN: A 0. 1.0 BASE: U 20. 3

DATA: 23C #1
CALI: C040382B #3

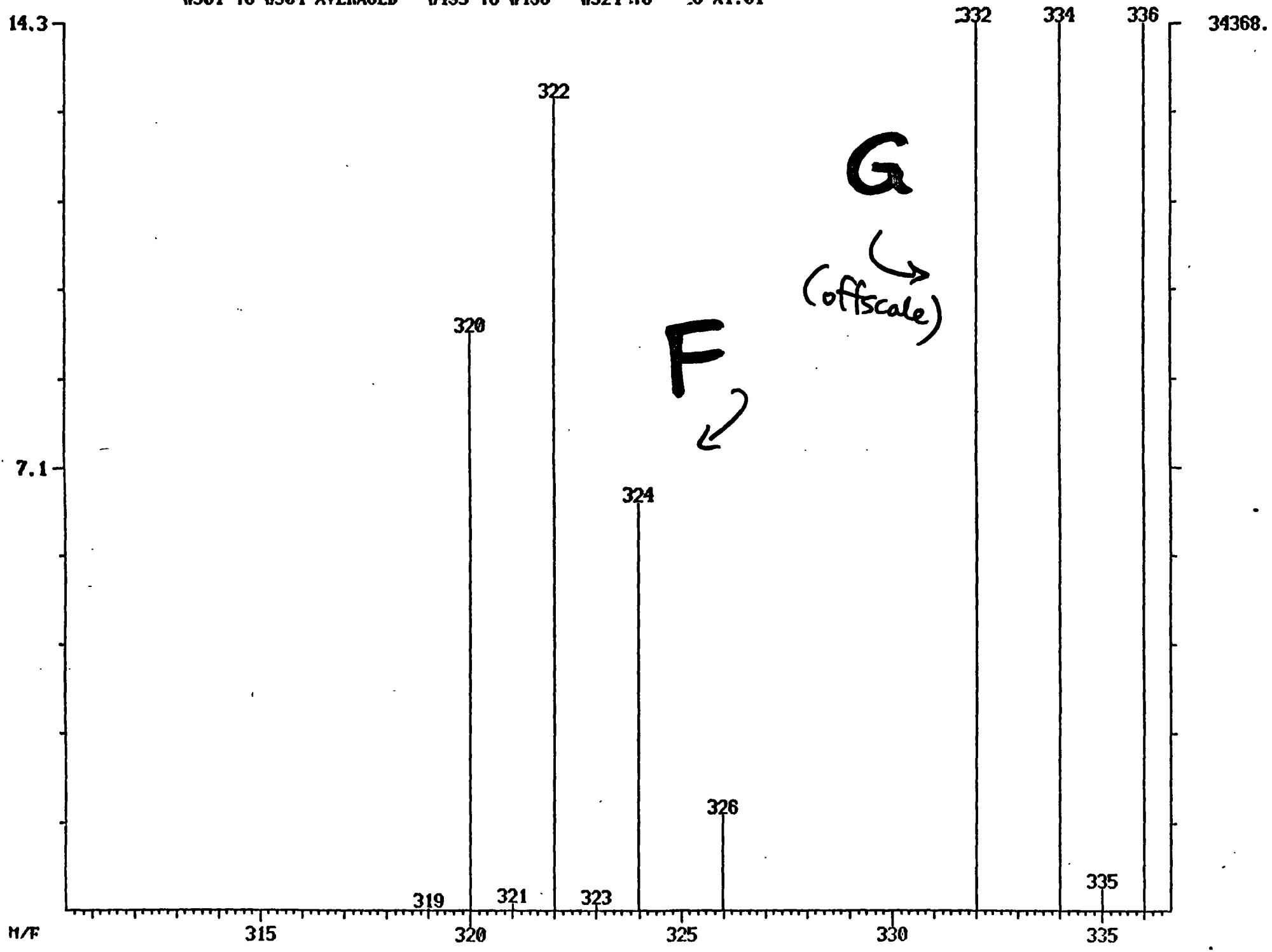
SCANS 300 TO 600



MID MASS SPECTRUM
04/04/82 14:30:00 + 12:33
SAMPLE: 3UL SAMPLE 22C(3-26-E-4-3-82)10UL VOL 5
#501 TO #504 AVERAGED - #495 TO #498 - #524 TO .6 X1.01

DATA: 22C1 #502
CALI: C040482B1 #5
MARK MID EI

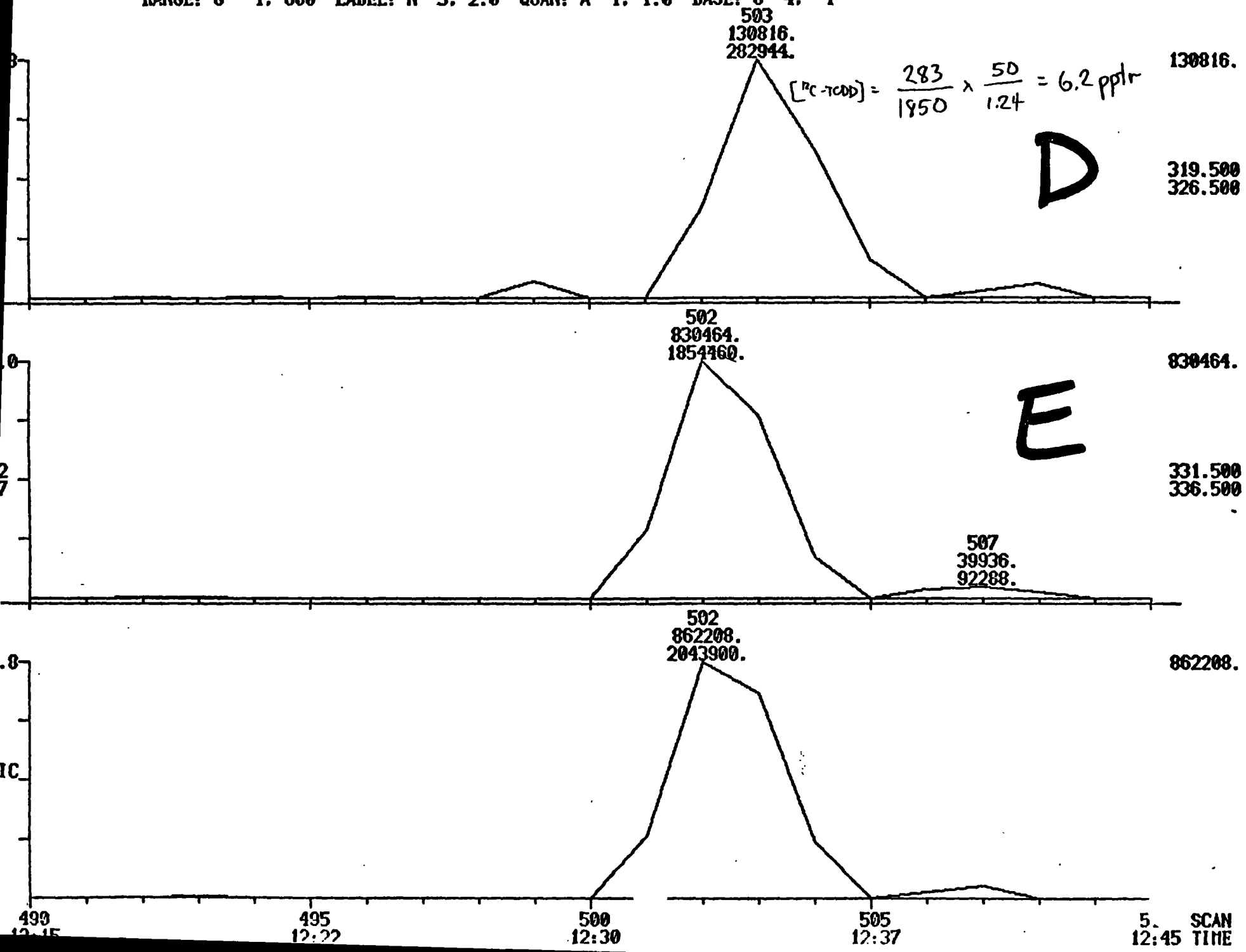
BASE M/E: 334
RIC: 621568.



MID RIC + MASS CHROMATOGRAMS
04/04/82 14:30:00
SAMPLE: 3UL SAMPLE 22C(3-26-E-4-3-82)10UL VOL 50PPT MARK MID EI
RANGE: G 1. 600 LABEL: N 3. 2.0 QUAN: A 1. 1.0 BASE: U 4. 1

DATA: 22C1 #1
CALI: C040482B1 #5

SCANS 490 TO 510



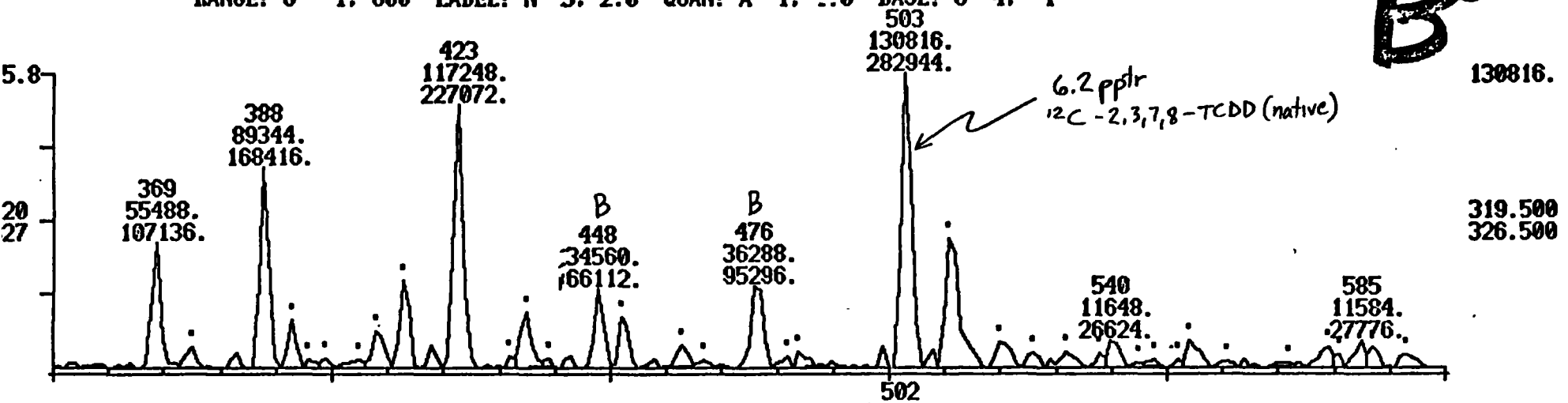
$$[^{13}C\text{-}TCDD] = \frac{283}{1850} \times \frac{50}{1.24} = 6.2\ \text{pptr}$$

MID RIC + MASS CHROMATOGRAMS
04/04/82 14:30:00
SAMPLE: 3UL SAMPLE 22C(3-26-E-4-3-82)10UL VOL 50 MARK MID EI
RANGE: G 1. 600 LABEL: N 3. 2.0 QUAN: A 1. ..6 BASE: U 4. 1

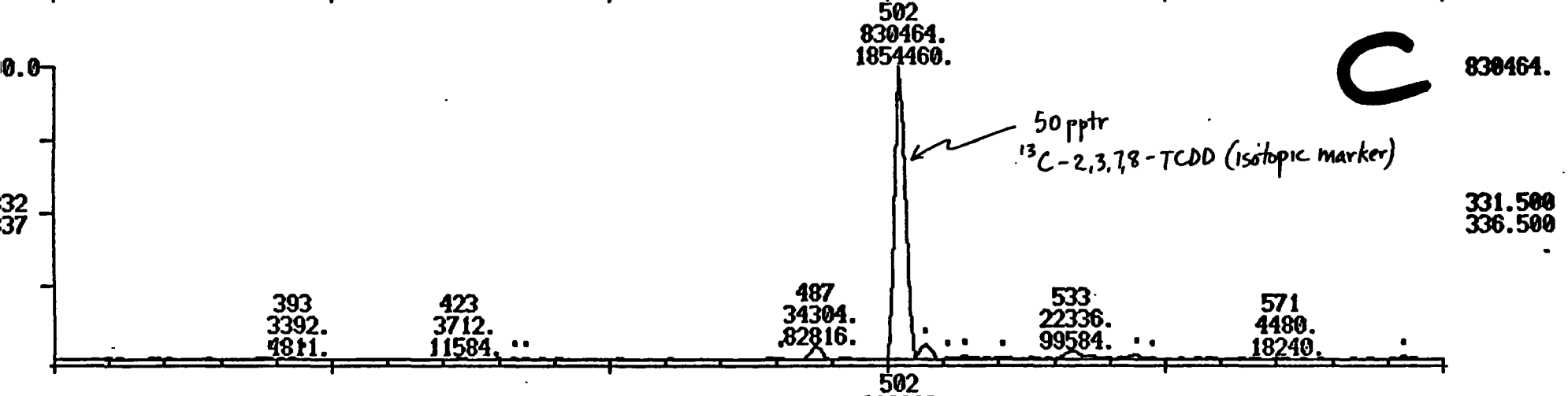
DATA: 22C1 #1
CALI: C040482B1 #5

SCANS 350 TO 600

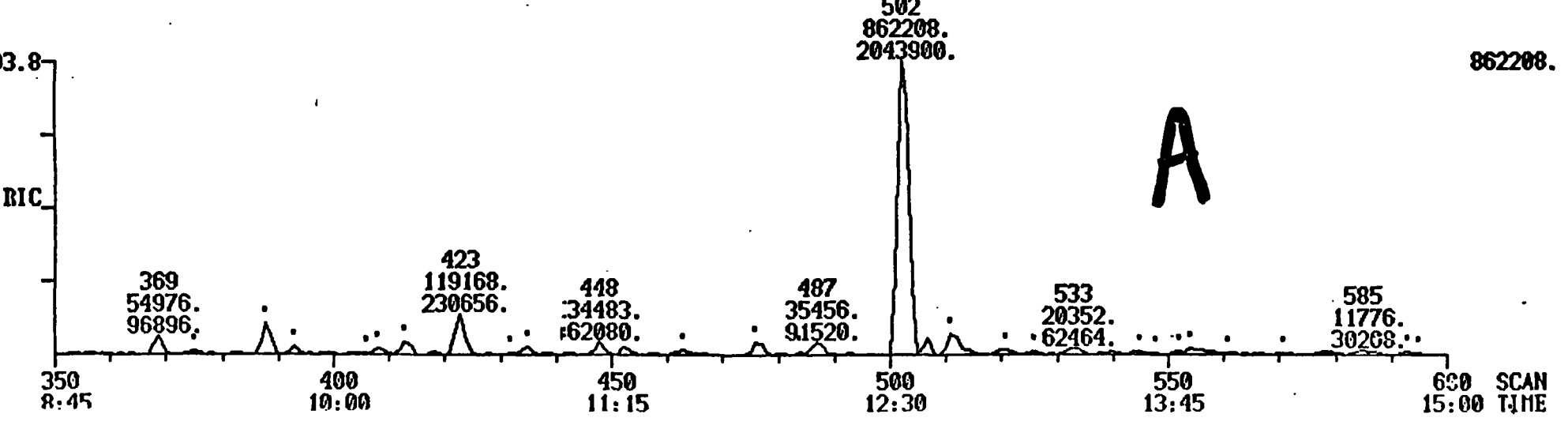
B



C



A

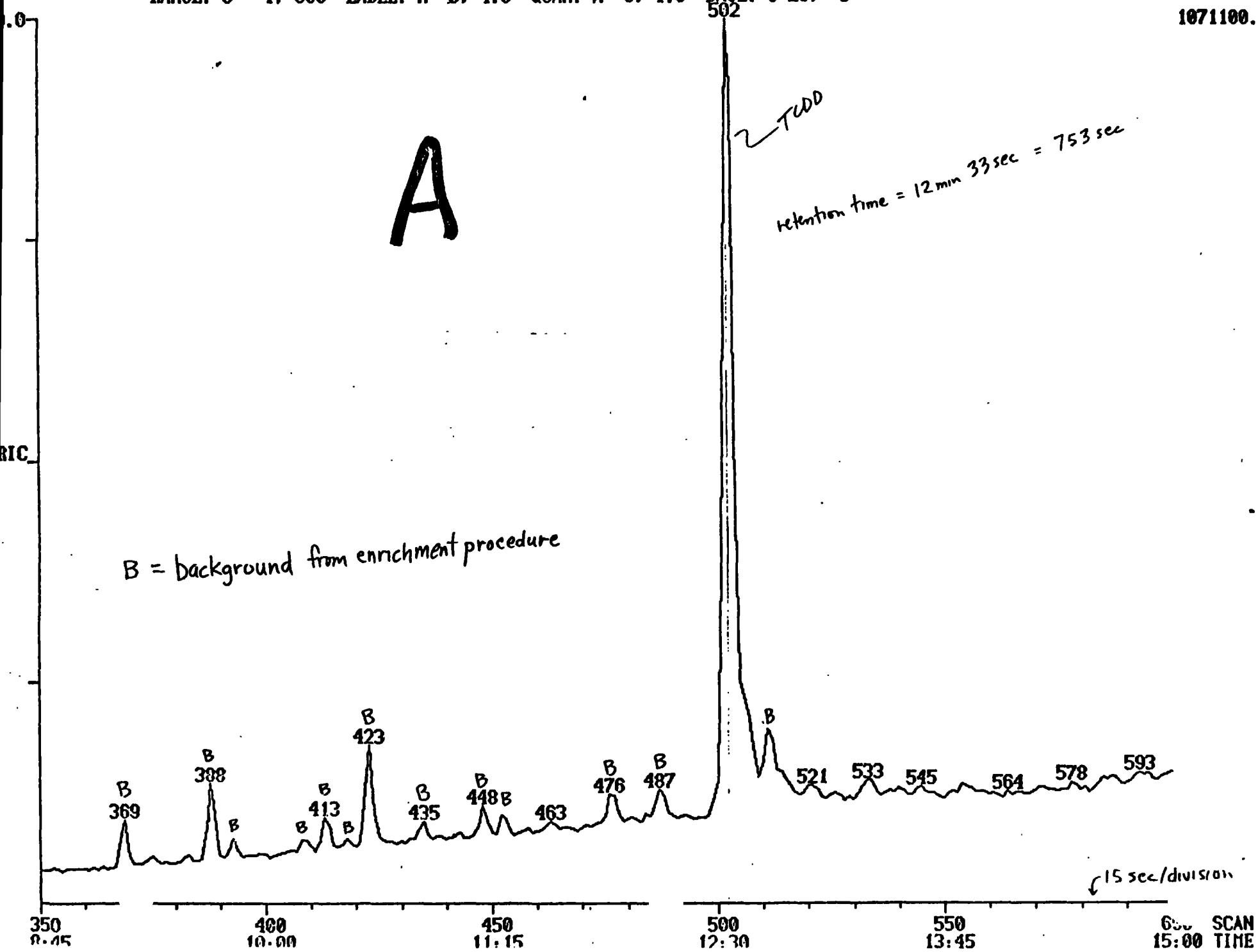


MID RIC
04/04/82 14:30:00
SAMPLE: 3UL SAMPLE 22C(3-26-E-4-3-82)10UL VOL 50PPT MARK MID EI
RANGE: G 1. 600 LABEL: N 0. 4.0 QUAN: A 0. 1.0 BASE: U 20. 3

DATA: 22C1 #1
CALI: C040482B1 #5

SCANS 350 TO 600

1071100.

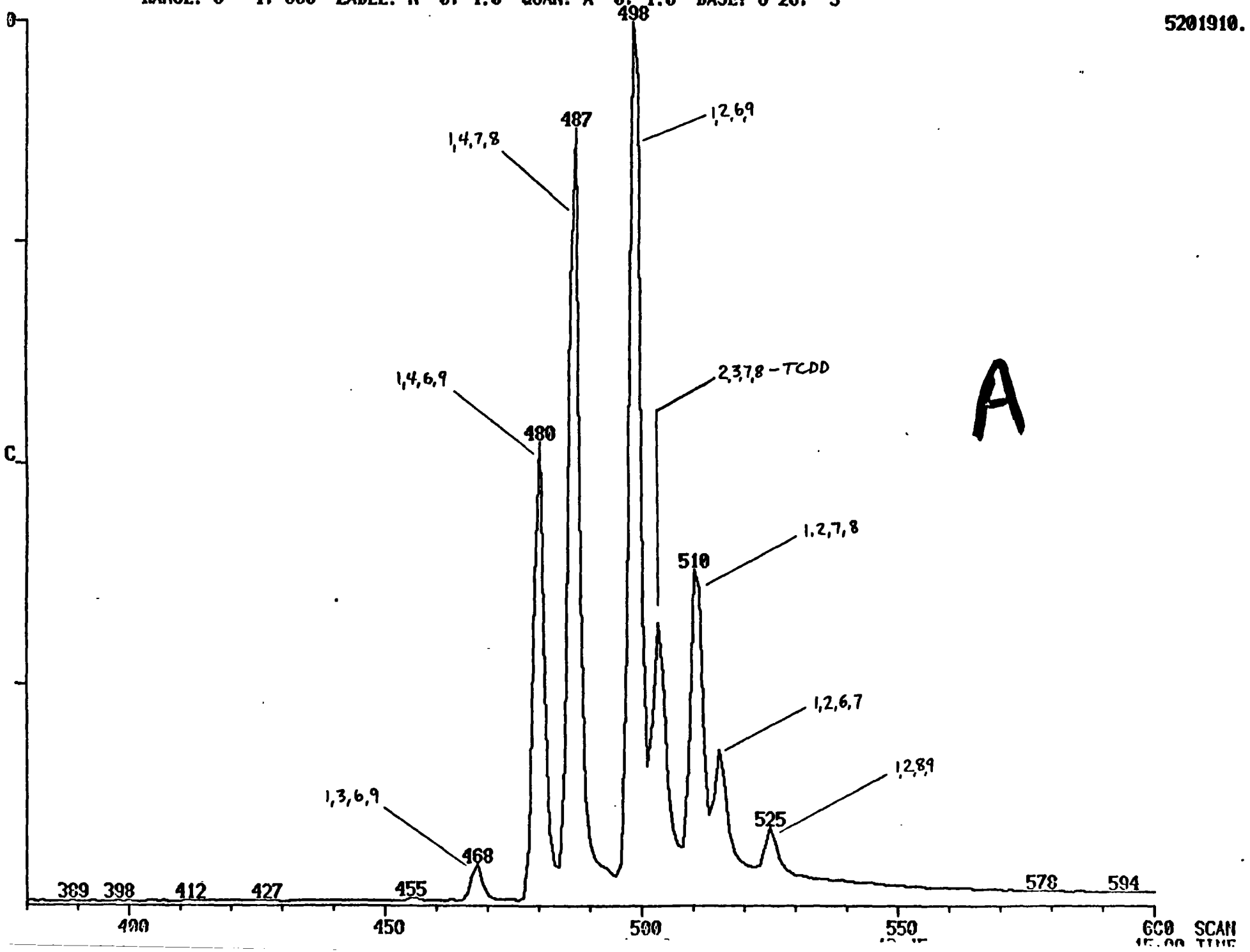


MID RIC
/04/82 16:41:00
AMPLE: 2UL BUSER 245+236 MIX CONT TCDD ISOMERS + C13 TCDD 200PG
RANGE: G 1. 600 LABEL: H 0. 4.0 QUAN: A 0. 1.0 BASE: U 20. 3

DATA: TCDD2 M1
CALI: C040482B1 M5

SCANS 380 TO 600

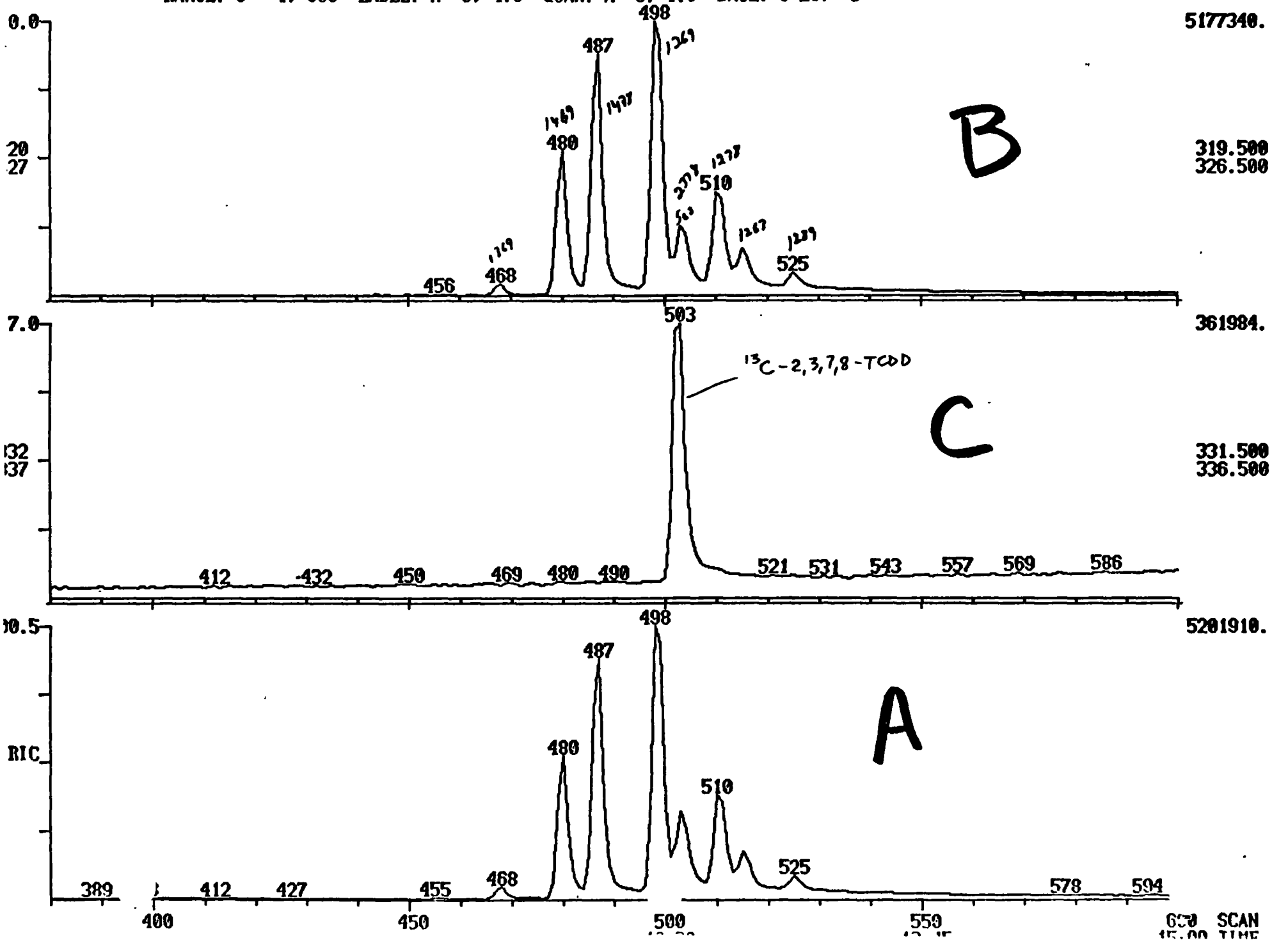
5201910.



MID RIC + MASS CHROMATOGRAMS
04/04/82 16:41:00
SAMPLE: 2UL BUSER 245+236 MIX CONT TCDD ISOMERS + 2UL C13 TCDD 200PG
RANGE: G 1. 600 LABEL: H 0. 4.0 QUAN: A 0. 1.0 BASE: U 20. 3

DATA: TCDD2 #1
CALI: C040482B1 #5

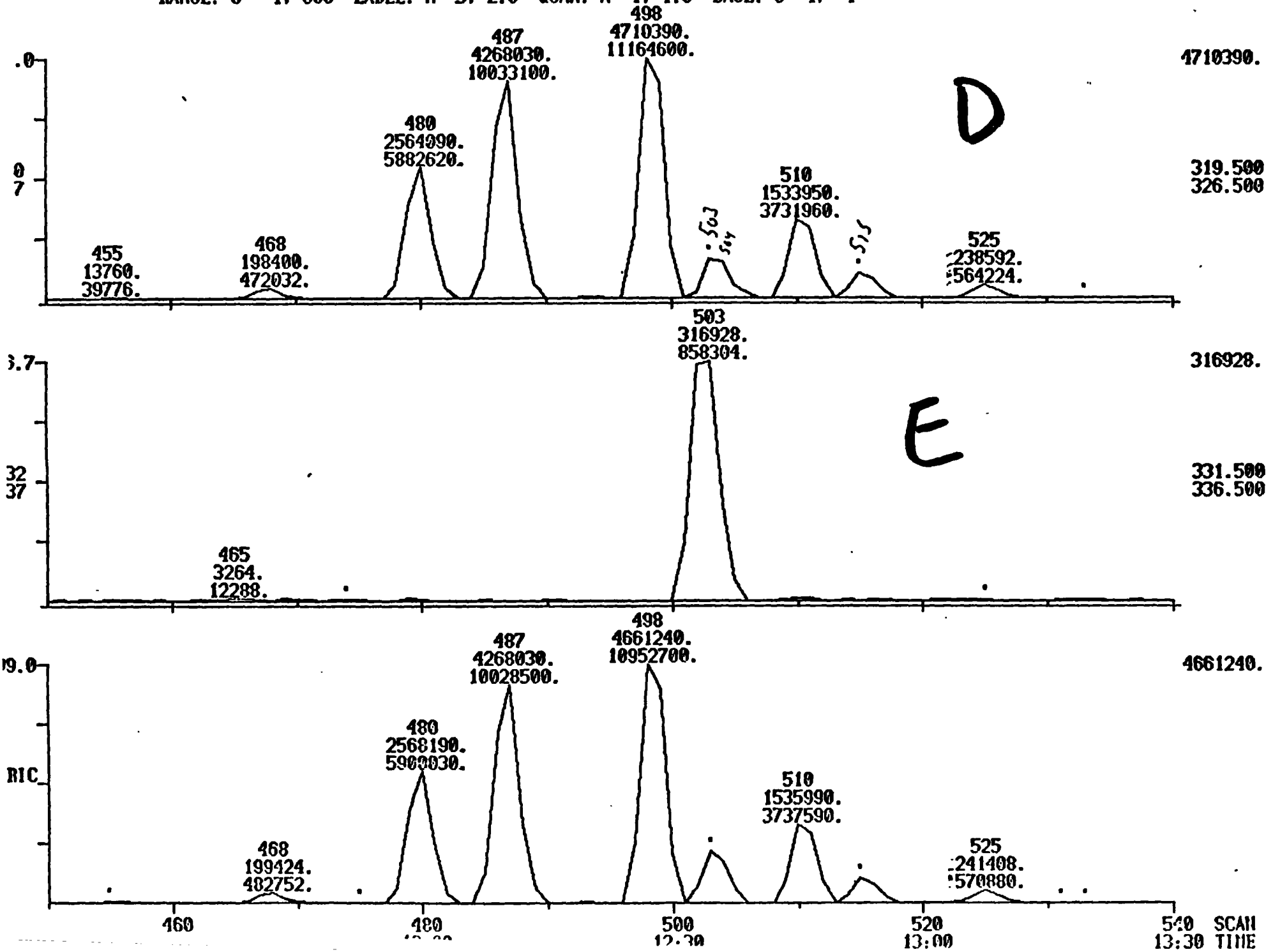
SCANS 380 TO 630



MID RIC + MASS CHROMATOGRAMS
1/04/82 16:41:00
SAMPLE: 2UL BUSER 245+236 MIX CONT TCDD ISOMERS + . C13 TCDD 200PG
RANGE: G 1. 600 LABEL: N 3. 2.0 QUAN: A 1. 1.0 BASE: U 4. 1

DATA: TCDD2 #1
CALI: C040482B1 N5

SCANS 450 TO 540



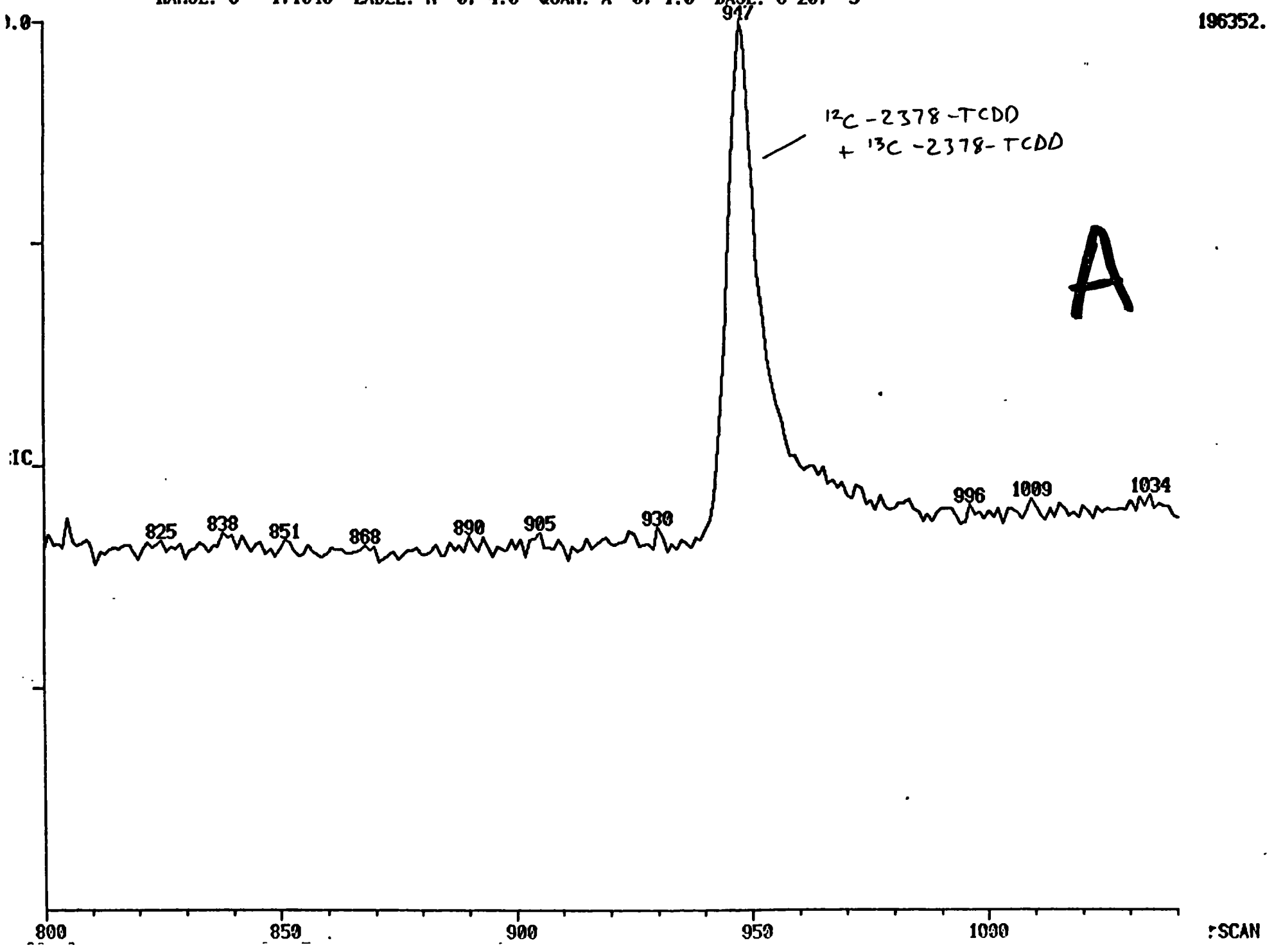
APPENDIX II

MID RIC
04/13/82 11:08:00
SAMPLE: 200PG C13 2378 TCDD + 232PG C12 2378 TCD. / MID OV17
RANGE: G 1.1040 LABEL: N 0. 4.0 QUAN: A 0. 1.0 BASE: U 20. 3

DATA: TSTD2 #1
CALI: C041282B #3

SCANS 800 TO 1040

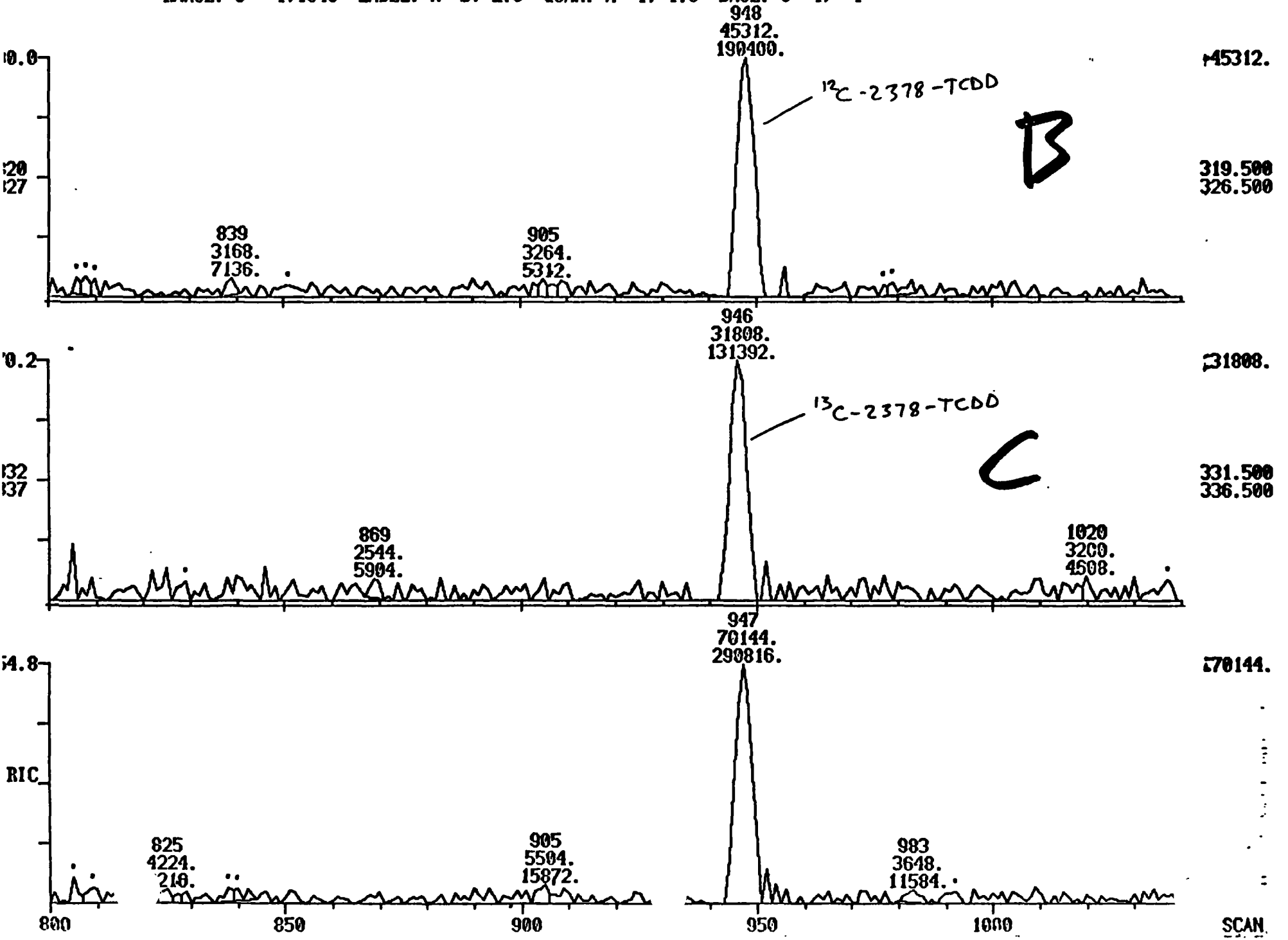
196352.



MID RIC + MASS CHROMATOGRAMS
04/13/82 11:08:00
SAMPLE: 200PG C13 2378 TCDD + 232PG C12 2378 TCDD EI MID OV17
RANGE: G 1.1040 LABEL: N 3. 2.0 QUAN: A 1. 1.0 BASE: U 4. 1

DATA: TSTD2 #1
CALI: C041282B #3

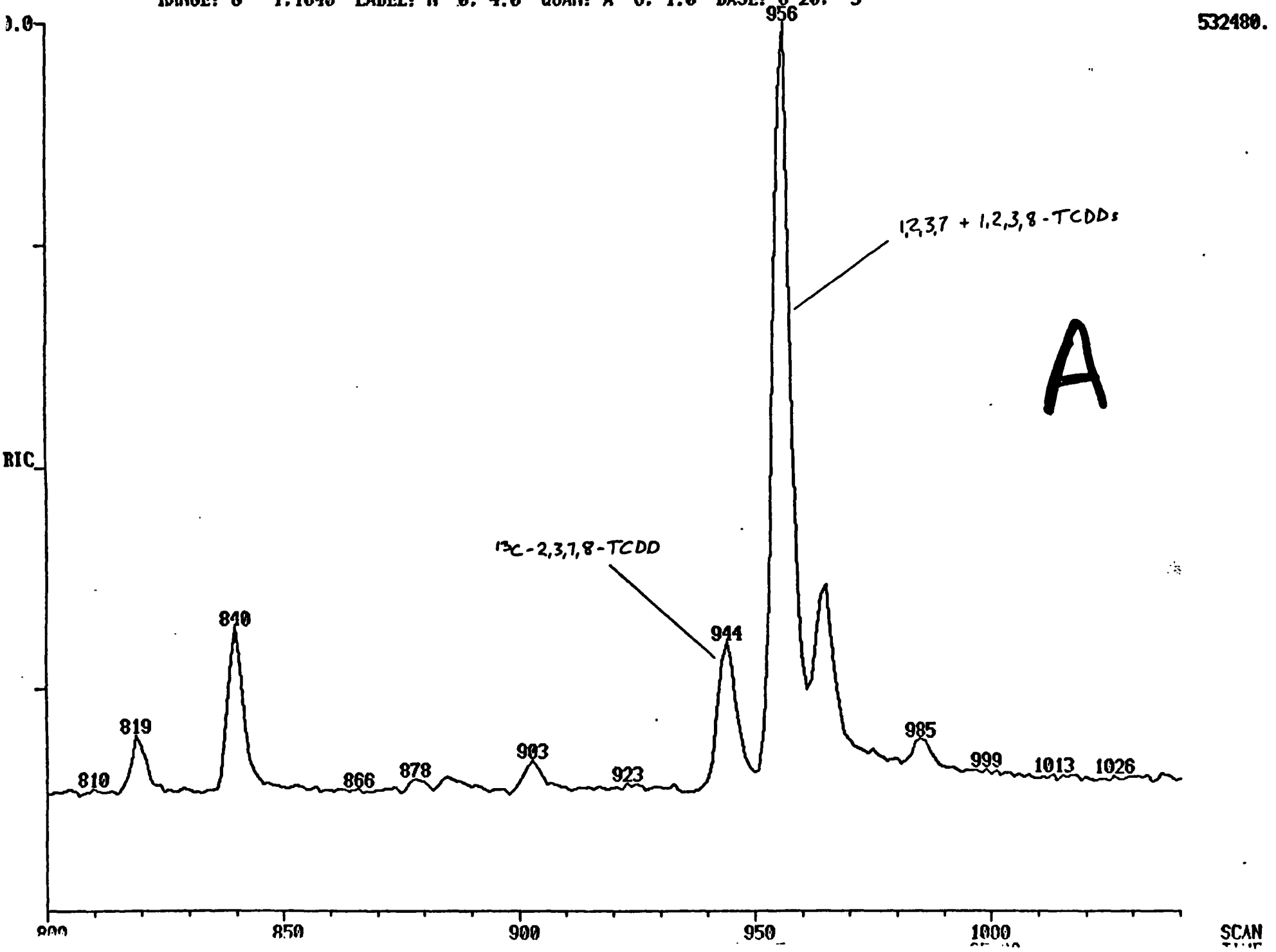
SCANS 800 TO 1040



MID RIC
04/13/02 8:16:00
SAMPLE: 2UL BUSER MIX 25+2345(1237/8)TCDD + 200PG 378TCDD MID EI OV17
RANGE: G 1.1040 LABEL: N 0. 4.0 QUAN: A 0. 1.0 BASE: U 20. 3

DATA: OV17M252345 #1
CALI: C041202B #3

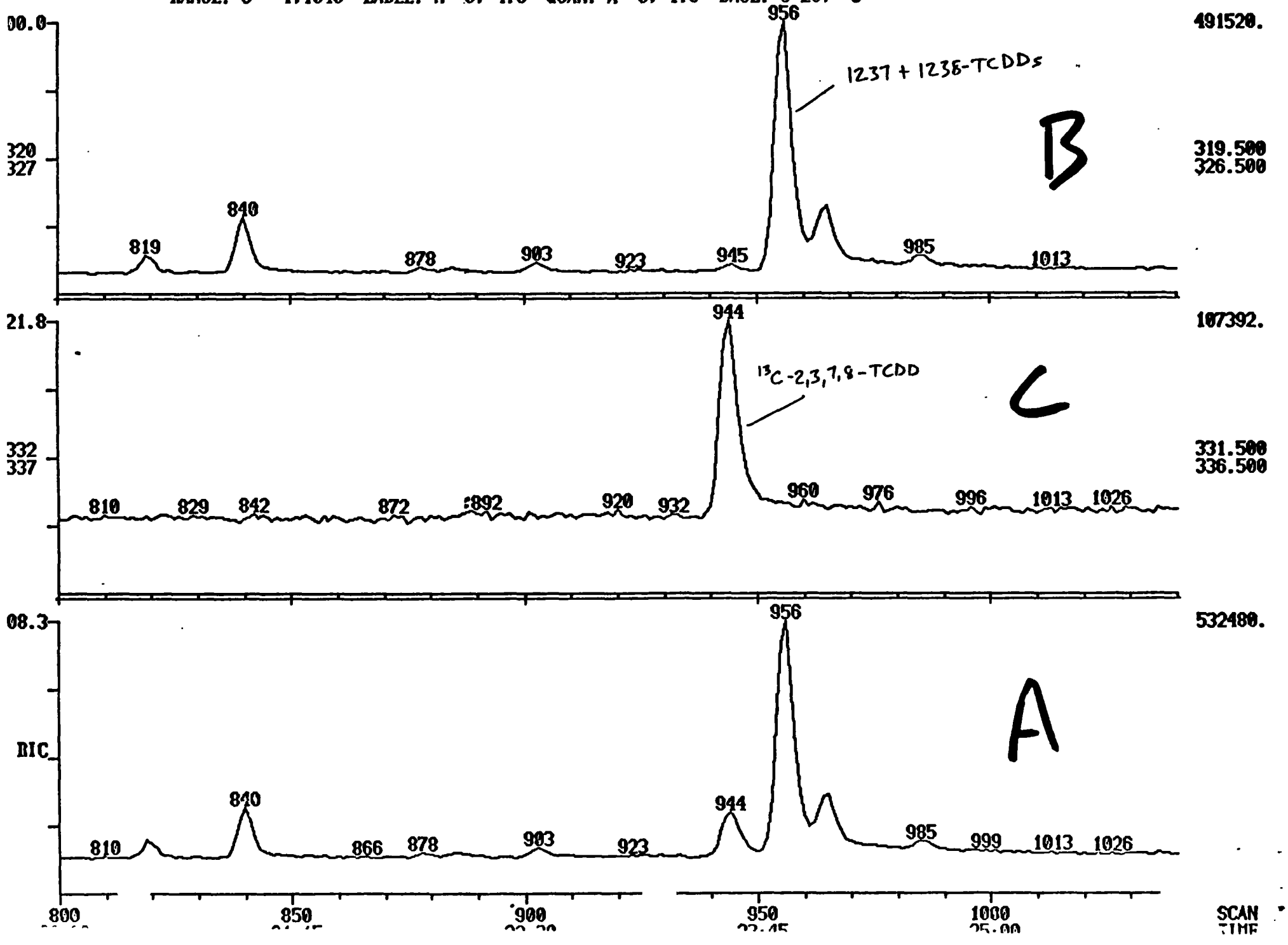
SCANS 800 TO 1040



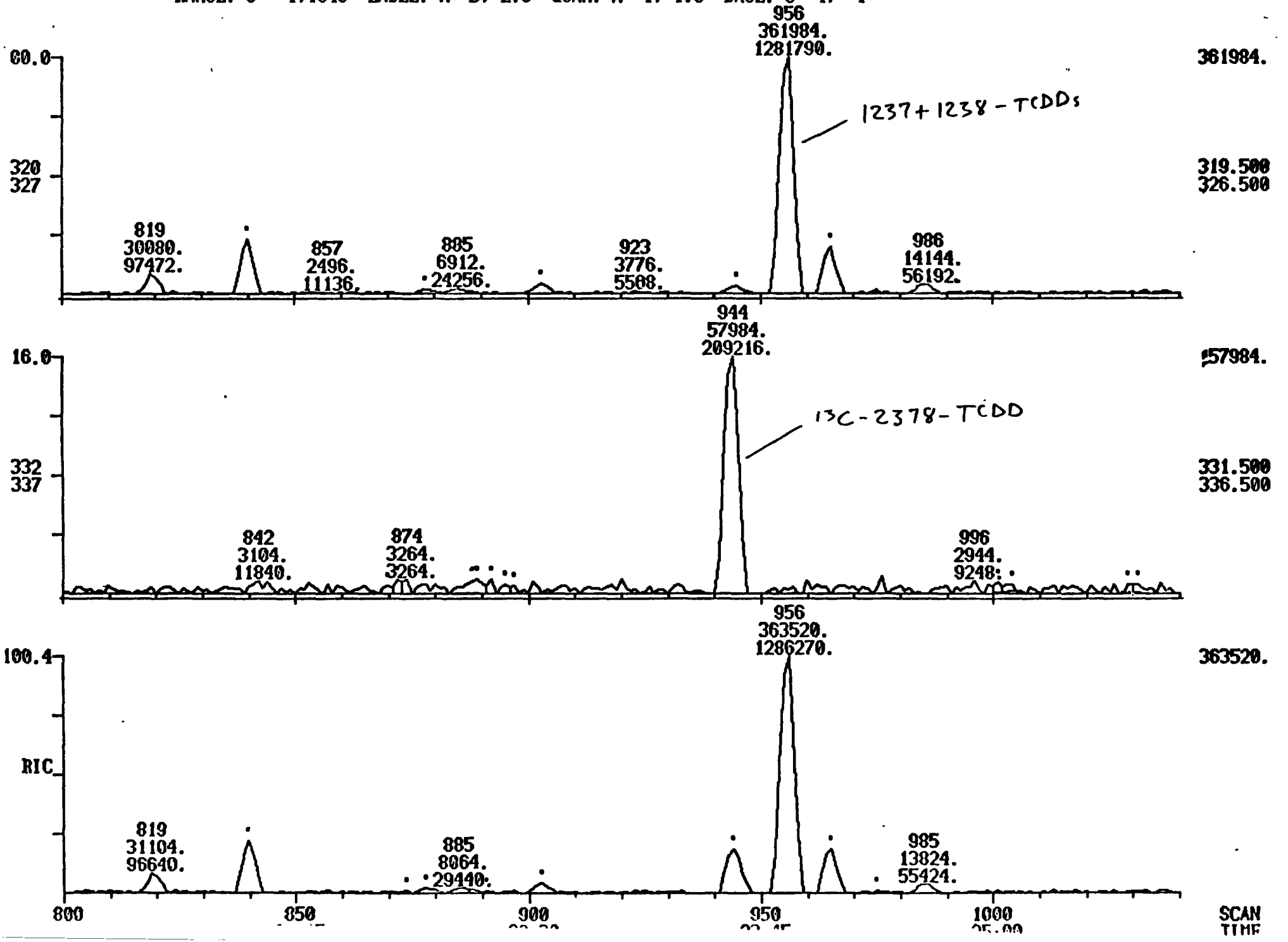
MID RIC + MASS CHROMATOGRAMS
04/13/82 8:16:00
SAMPLE: 2UL BUSER MIX 25+2345(1237/8)TCDD + 200PG 2378TCDD MID EI OV17
RANGE: G 1.1040 LABEL: N 0. 4.0 QUAN: A 0. 1.0 BASE: U 20. 3

DATA: OV17M252345 #1
CALI: C041282B #3

SCANS 800 TO 1049



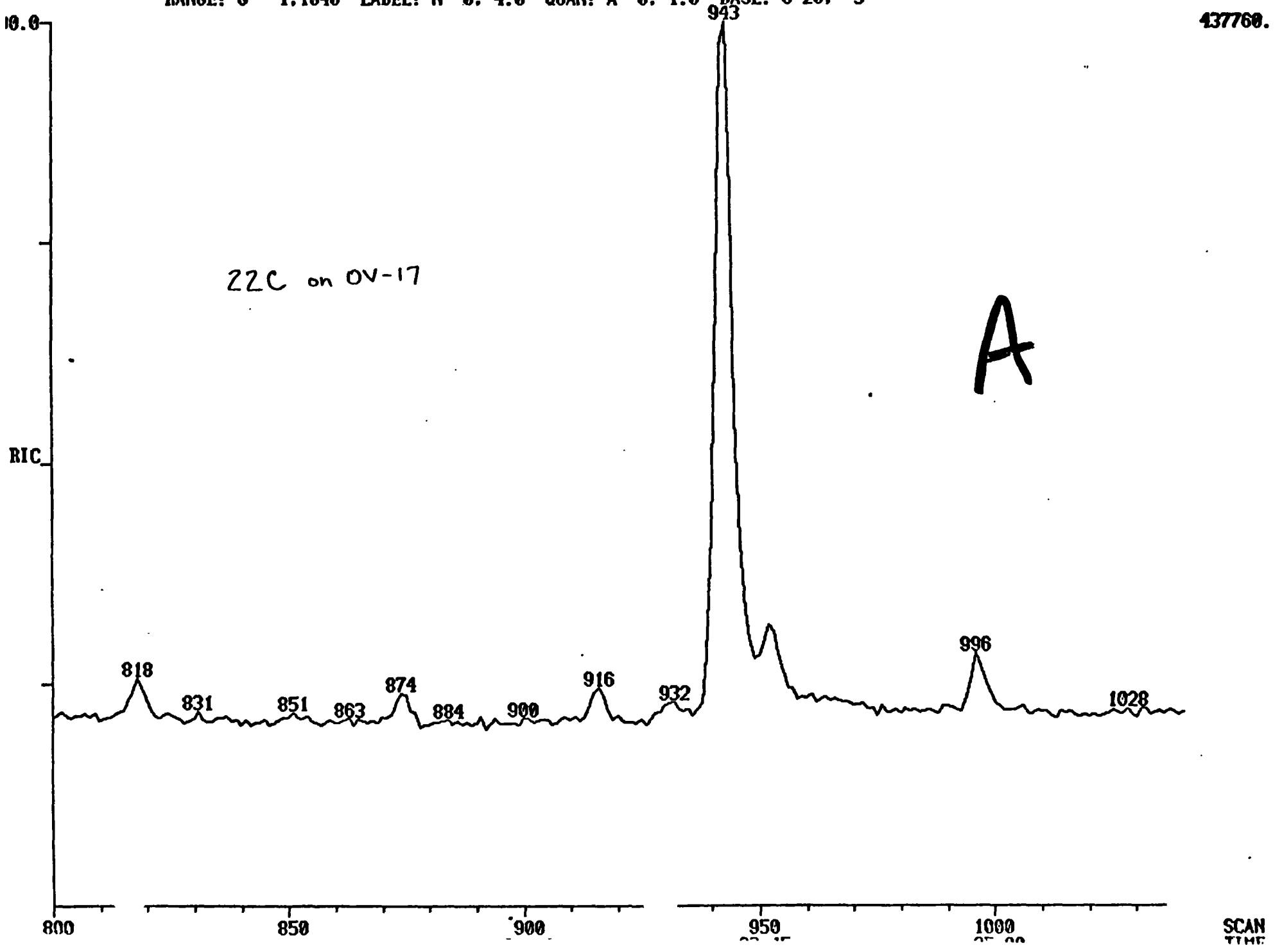
MID RIC + MASS CHROMATOGRAMS DATA: OV17M252345 M1 SCANS 800 TO 1040
04/13/82 8:16:00 CALI: C041282B M3
SAMPLE: 2UL BUSER MIX 25+2345(1237/8)TCDD + 2 3 2378TCDD MID EI OV17
RANGE: G 1.1040 LABEL: M 3. 2.0 QUAN: A 1. 1.0 BASE: U 4. 1



MID RIC
04/12/82 15:37:00
SAMPLE: 30% OF SAMPLE 22C(3-26-E-4-3-82)15G EQ MID EI OV17
RANGE: G 1.1040 LABEL: N 0. 4.0 QUAN: A 0. 1.0 BASE: U 20. 3

DATA: 22CA #1
CALI: C041282B #3

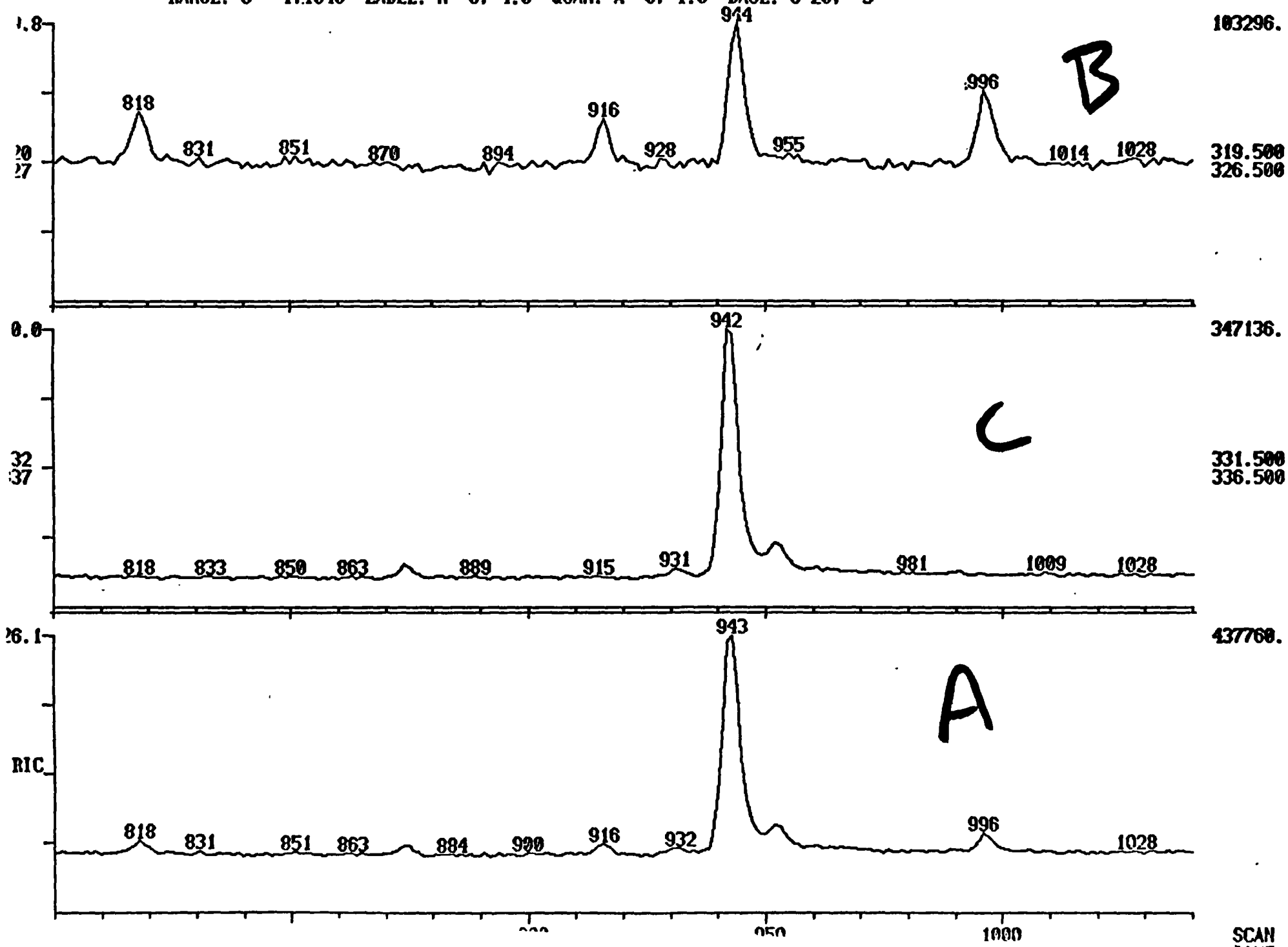
SCANS 800 TO 1040



MID RIC + MASS CHROMATOGRAMS
04/12/82 15:37:00
SAMPLE: 30% OF SAMPLE 22C(3-26-E-4-3-82)15G EQ MID EI OV17
RANGE: G 1.1040 LABEL: N 0. 4.0 QUAN: A 0. 1.0 BASE: U 20. 3

DATA: 22CA #1
CALI: C041282B #3

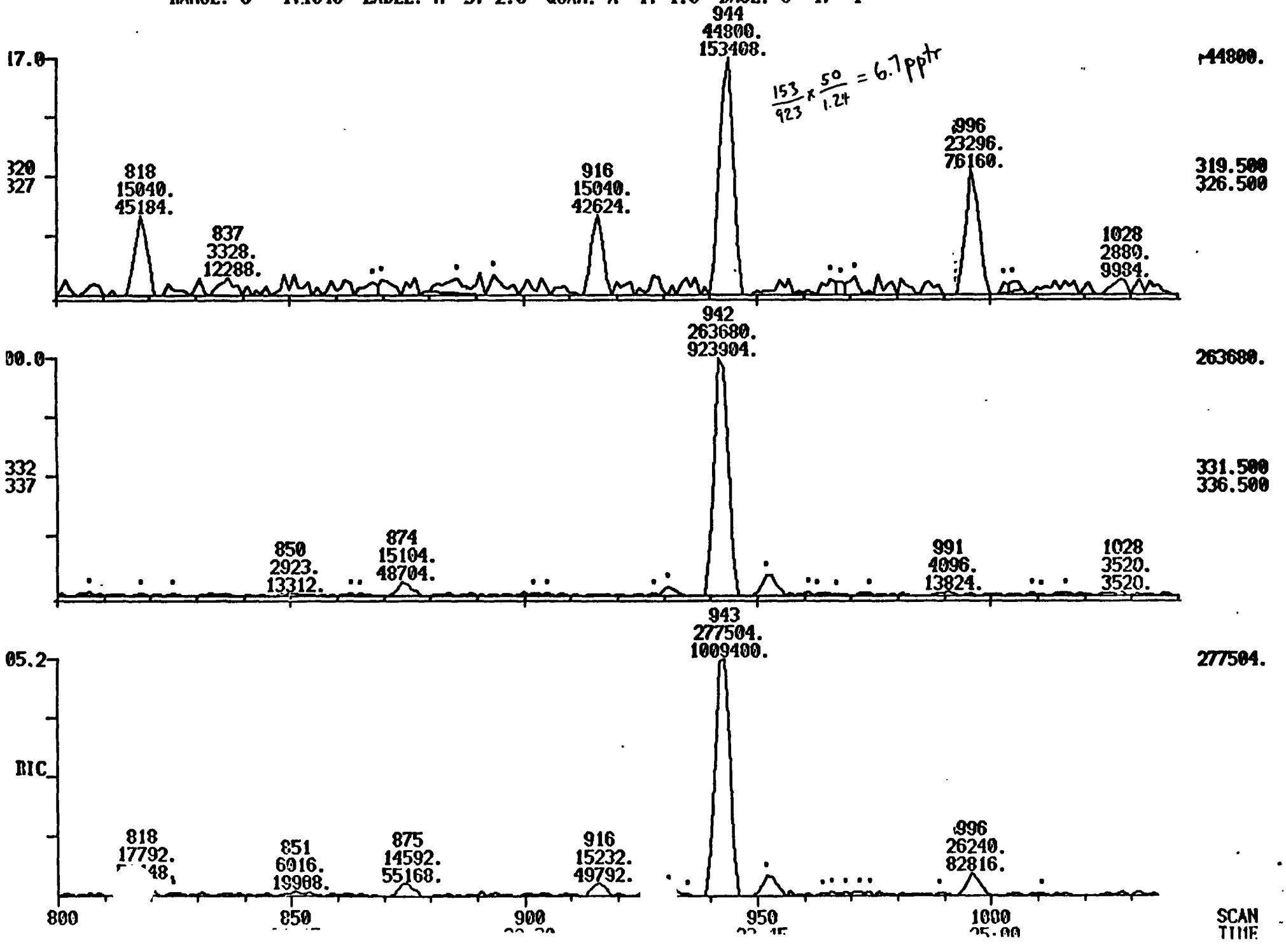
SCANS 800 TO 1040



MID RIC + MASS CHROMATOGRAMS
04/12/82 15:37:00
SAMPLE: 30% OF SAMPLE 22C(3-26-E-4-3-82)15G EQ MID EI OV17
RANGE: G 1.1040 LABEL: N 3. 2.0 QUAN: A 1. 1.0 BASE: U 4. 1

DATA: 22CA N1
CALI: C041282B N3

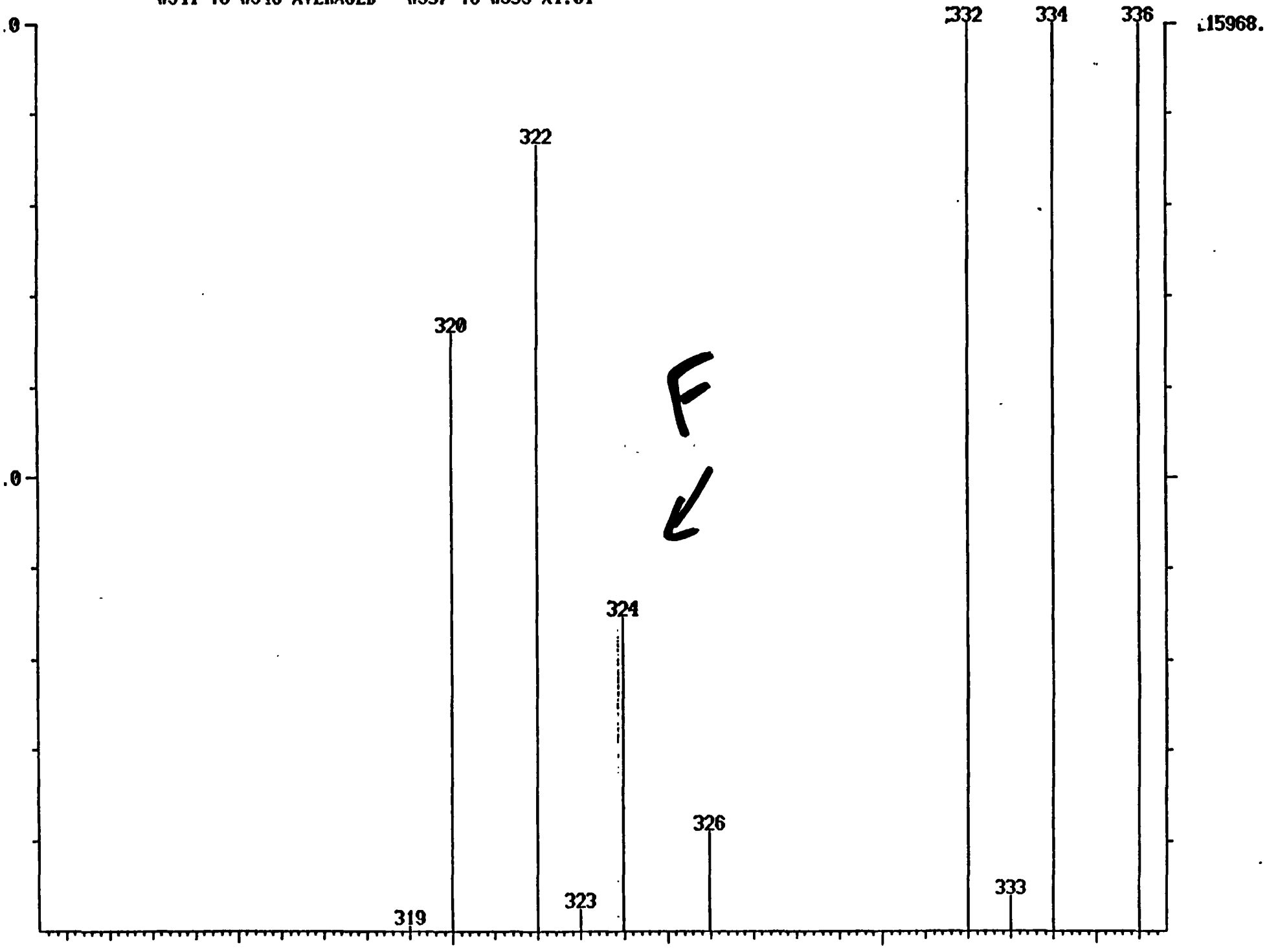
SCANS 800 TO 1040



MID MASS SPECTRUM
4/12/82 15:37:00 + 23:34
SAMPLE: 30% OF SAMPLE 22C(3-26-E-4-3-82)15G EQ MI. .I OV17
#941 TO #946 AVERAGED - #937 TO #939 X1.01

DATA: 22CA #943
CALI: C041282B #3

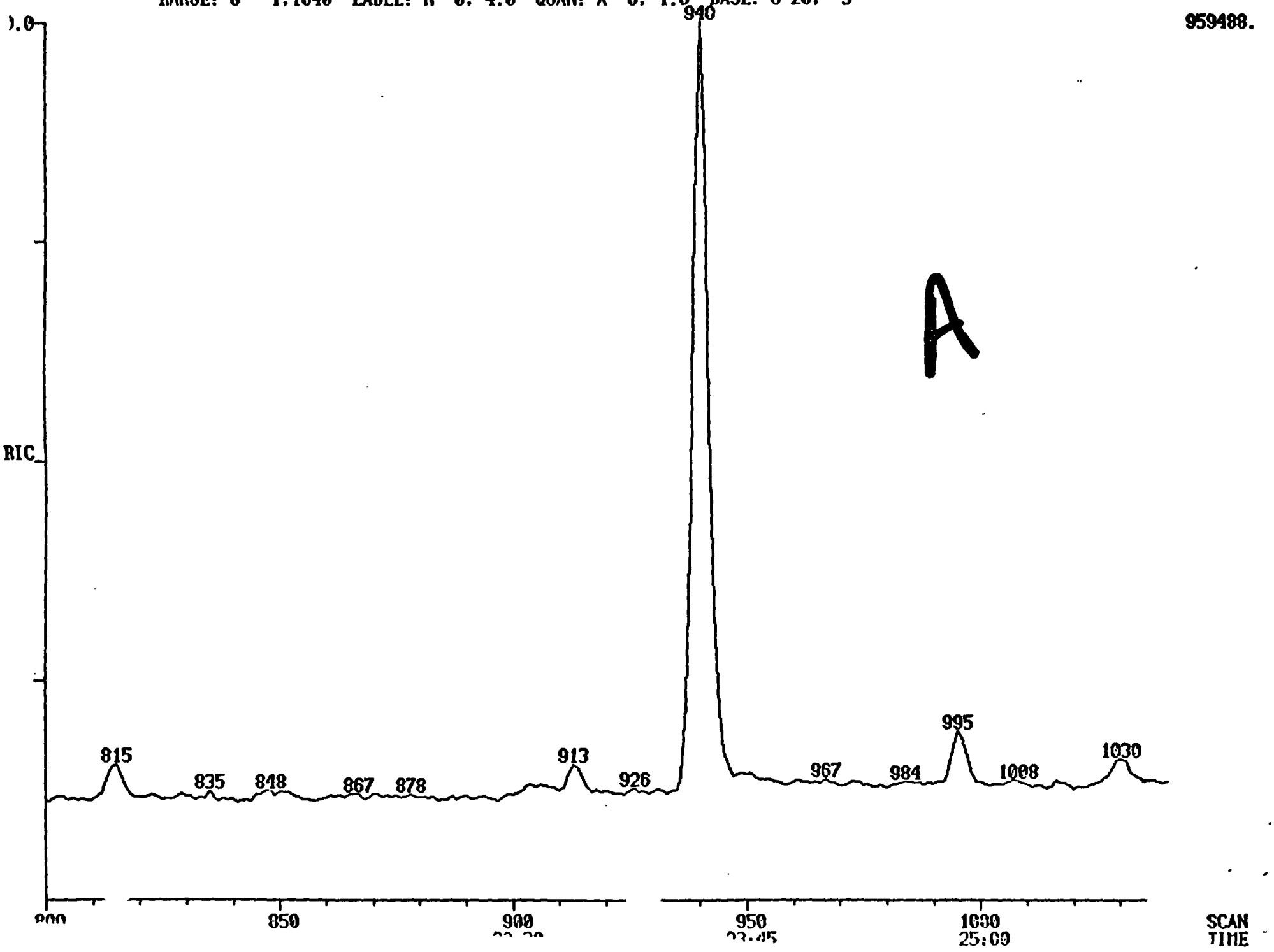
BASE M/E: 334
RIC: 216576.



MID RIC
04/13/82 9:54:00
SAMPLE: 60% SAMPLE 23C SPRING R.(3-20-E-4-3-82)30G EQ MID OV17
RANGE: G 1.1040 LABEL: N 0. 4.0 QUAN: A 0. 1.0 BASE: U 20. 3

DATA: 23COV17 #1
CALI: C041282B 03

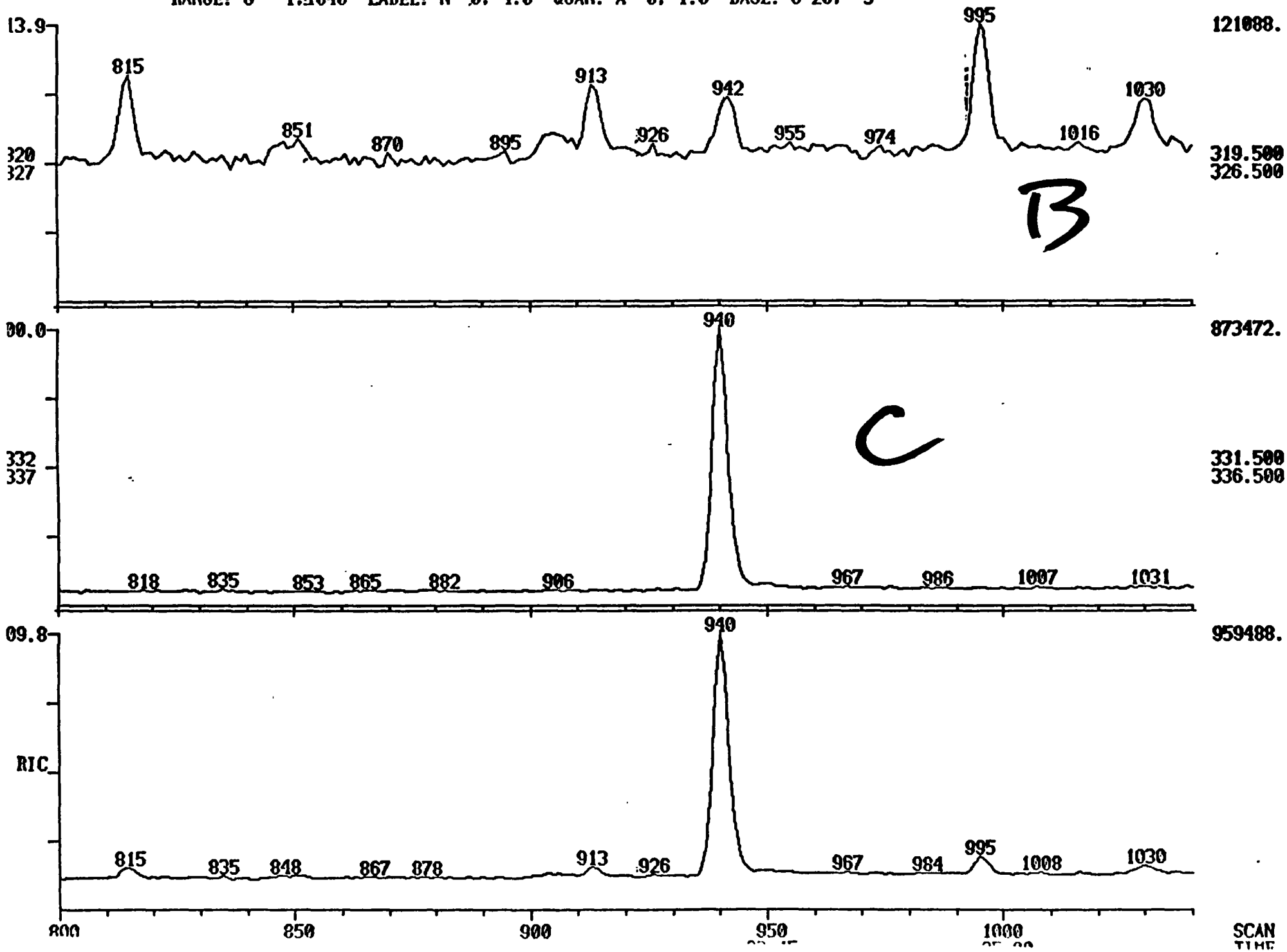
SCANS 800 TO 1040



MID RIC + MASS CHROMATOGRAMS
04/13/82 9:54:00
SAMPLE: 60% SAMPLE 23C SPRING R.(3-20-E-4-3-82, 5 EQ MID OV17
RANGE: G 1.1040 LABEL: N 0. 4.0 QUAN: A 0. 1.0 BASE: U 20. 3

DATA: 23COV17 #1
CALI: C041282B #3

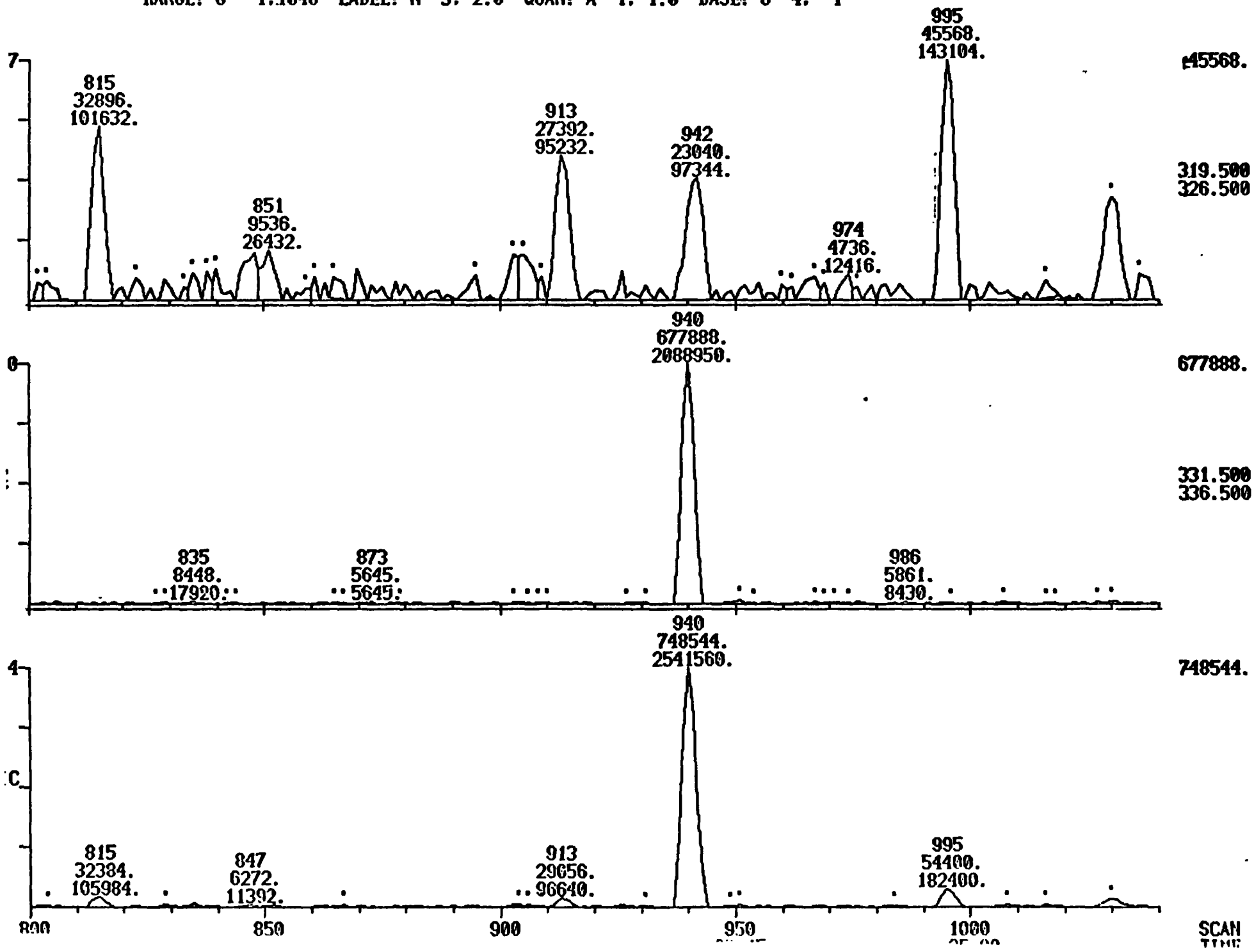
SCANS 800 TO 1040



MID RIC + MASS CHROMATOGRAMS
1/13/82 9:54:00
SAMPLE: 60% SAMPLE 23C SPRING R.(3-20-E-4-3-82)30 MID OV17
RANGE: G 1.1040 LABEL: N 3. 2.0 QUAN: A 1. 1.0 BASE: U 4. 1

DATA: 23COV17 #1
CALI: C041282B H3

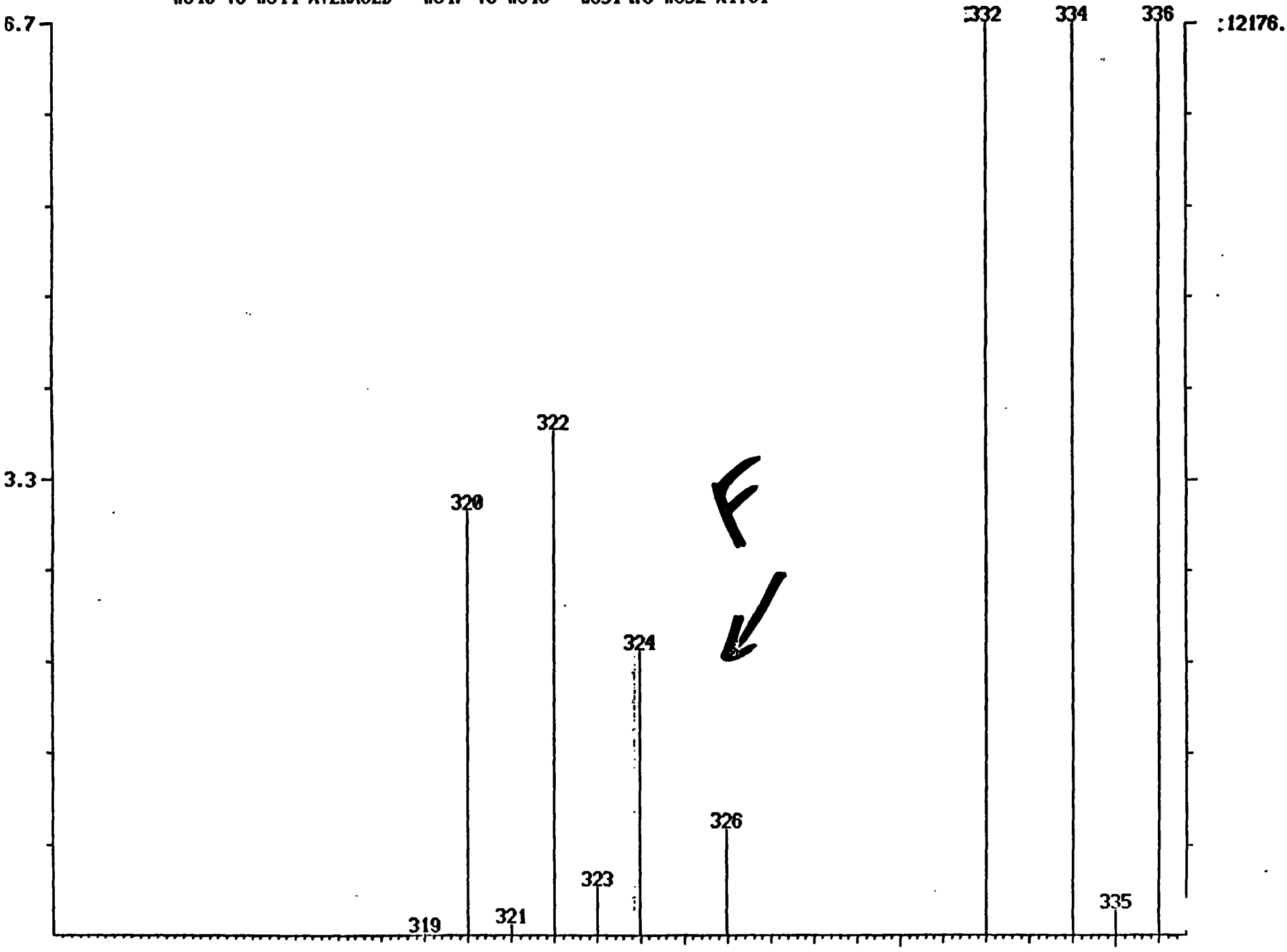
SCANS 800 TO 1040



MID MASS SPECTRUM
04/13/82 9:54:00 + 23:33
SAMPLE: 60% SAMPLE 23C SPRING R.(3-20-E-4-3-82)30G EQ MID OV17
#940 TO #944 AVERAGED - #947 TO #948 - #931 TO #932 X1.01

DATA: 23COV17 #942
CALI: C041282B #3

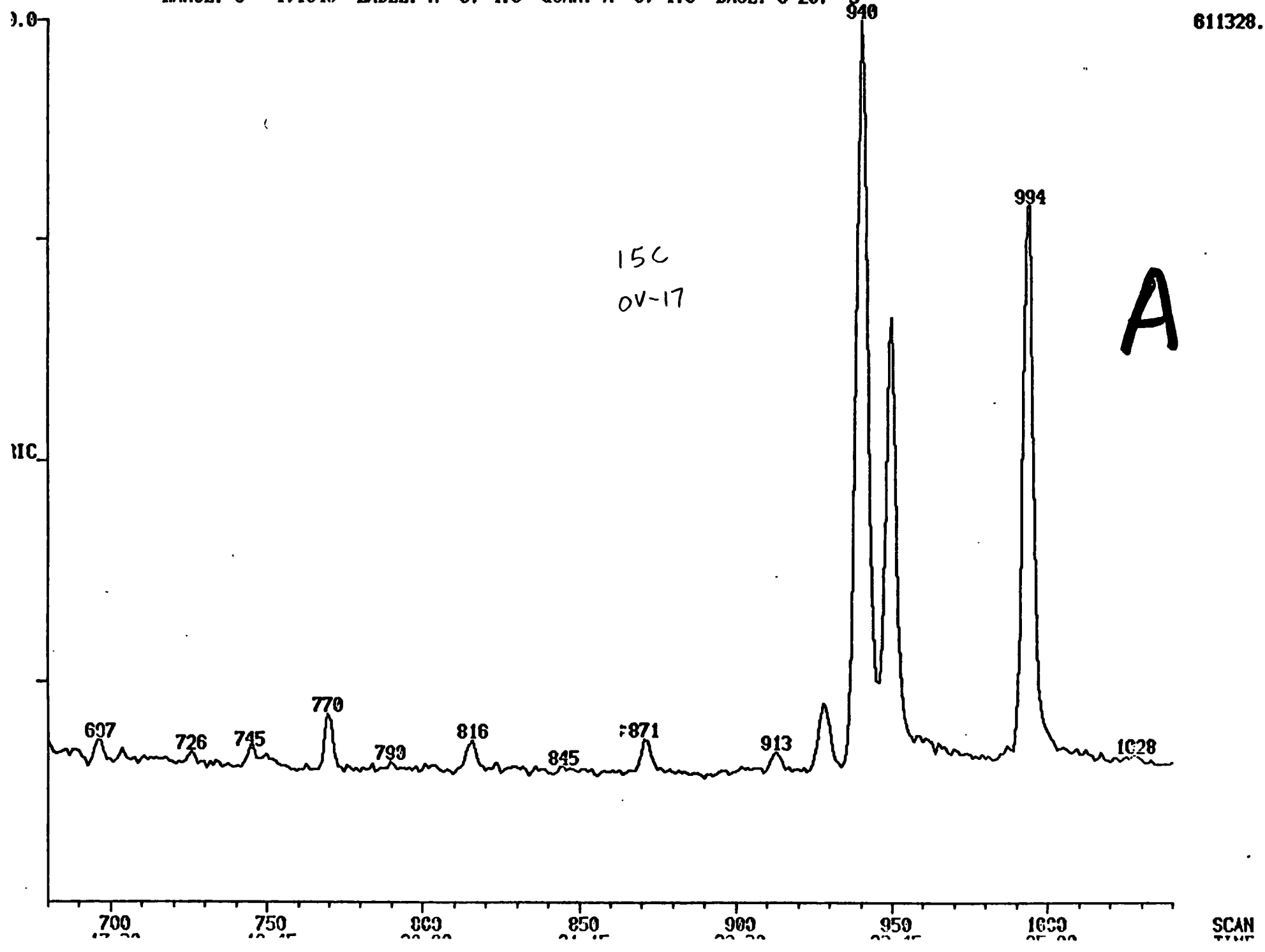
BASE M/E: 334
RIC: 436224.



MID RIC
04/12/82 14:40:00
SAMPLE: 4UL 15C SPRING R. MO.(12-10-81)15UL VOL , EI OV17
RANGE: G 1.1040 LABEL: H 0. 4.0 QUAN: A 0. 1.0 BASE: U 20. 3

DATA: 15CA #1
CALI: C041282B #3

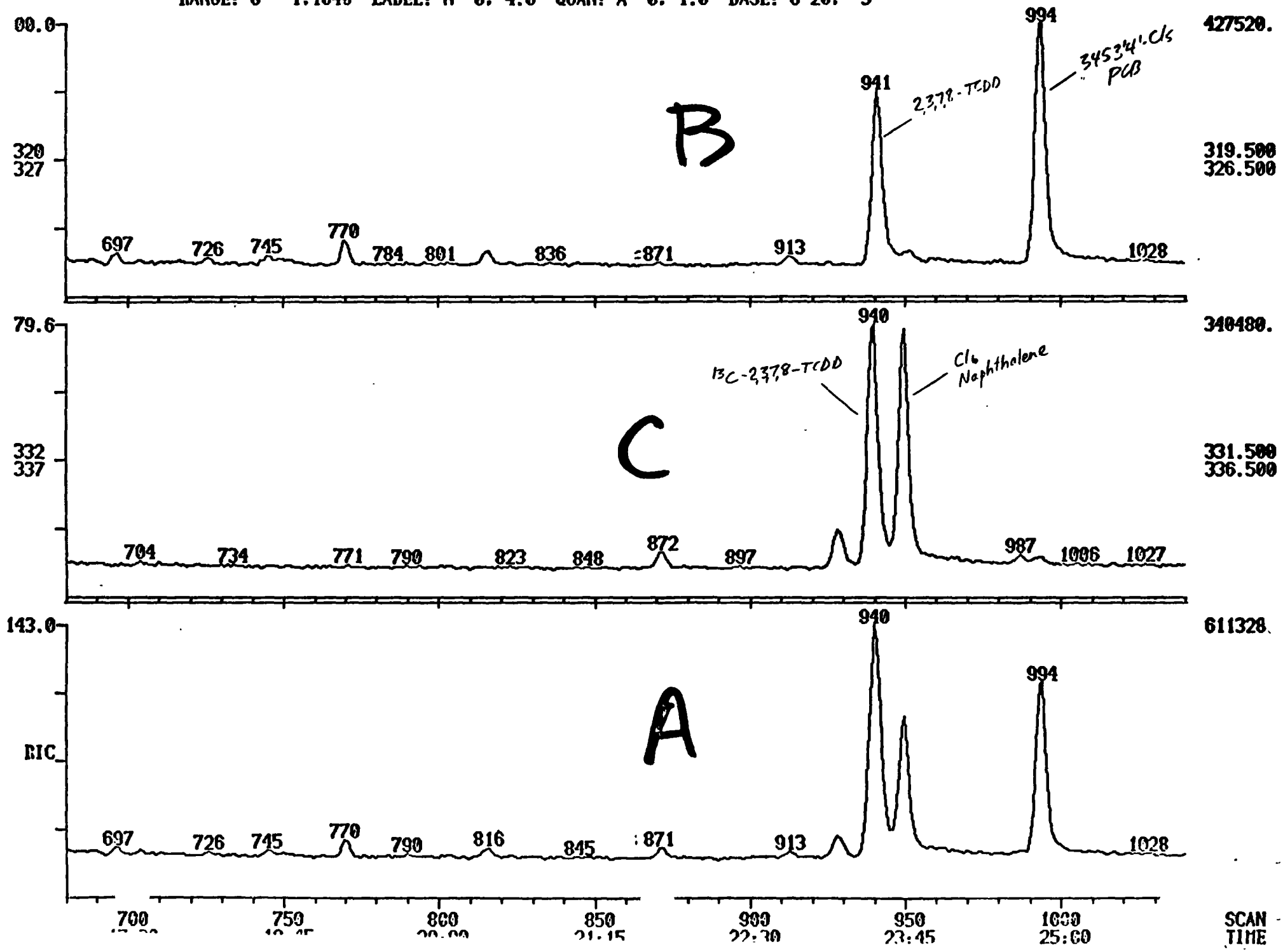
SCANS 680 TO 1040



MID RIC + MASS CHROMATOGRAMS
04/12/82 14:40:00
SAMPLE: 4UL 15C SPRING R. MO.(12-10-81)15UL VOL MID EI OV17
RANGE: G 1.1040 LABEL: N 0. 4.0 QUAN: A 0. 1.0 BASE: U 20. 3

DATA: 15CA #1
CALI: C041282B #3

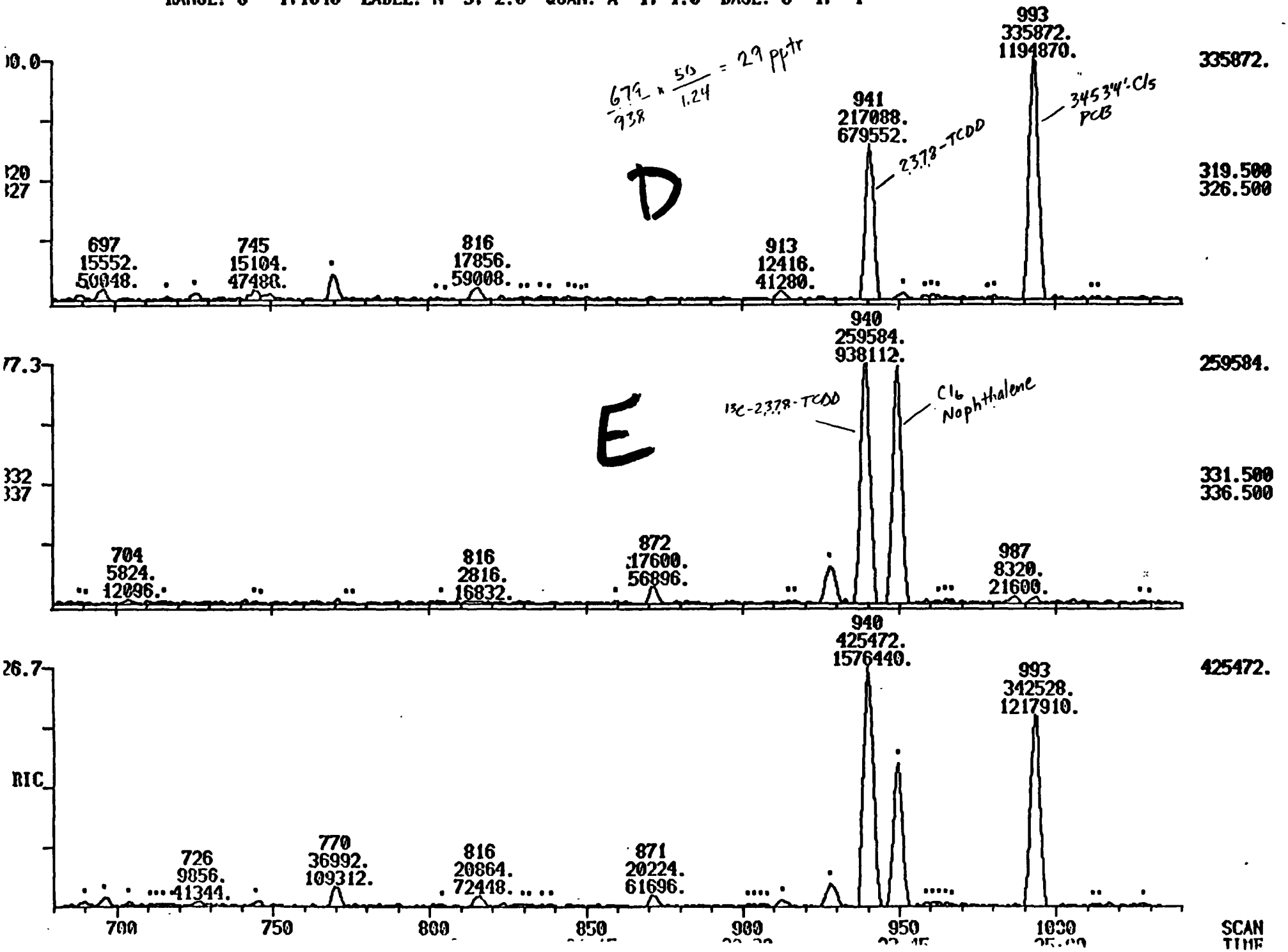
SCANS 680 TO 1040



MID RIC + MASS CHROMATOGRAMS
04/12/82 14:40:00
SAMPLE: 4UL 15C SPRING R. MO.(12-10-81)15UL VOL .0 EI OV17
RANGE: G 1.1040 LABEL: H 3. 2.0 QUAN: A 1. 1.0 BASE: U 4. 1

DATA: 15CA #1
CALI: C041282B #3

SCANS 680 TO 1040

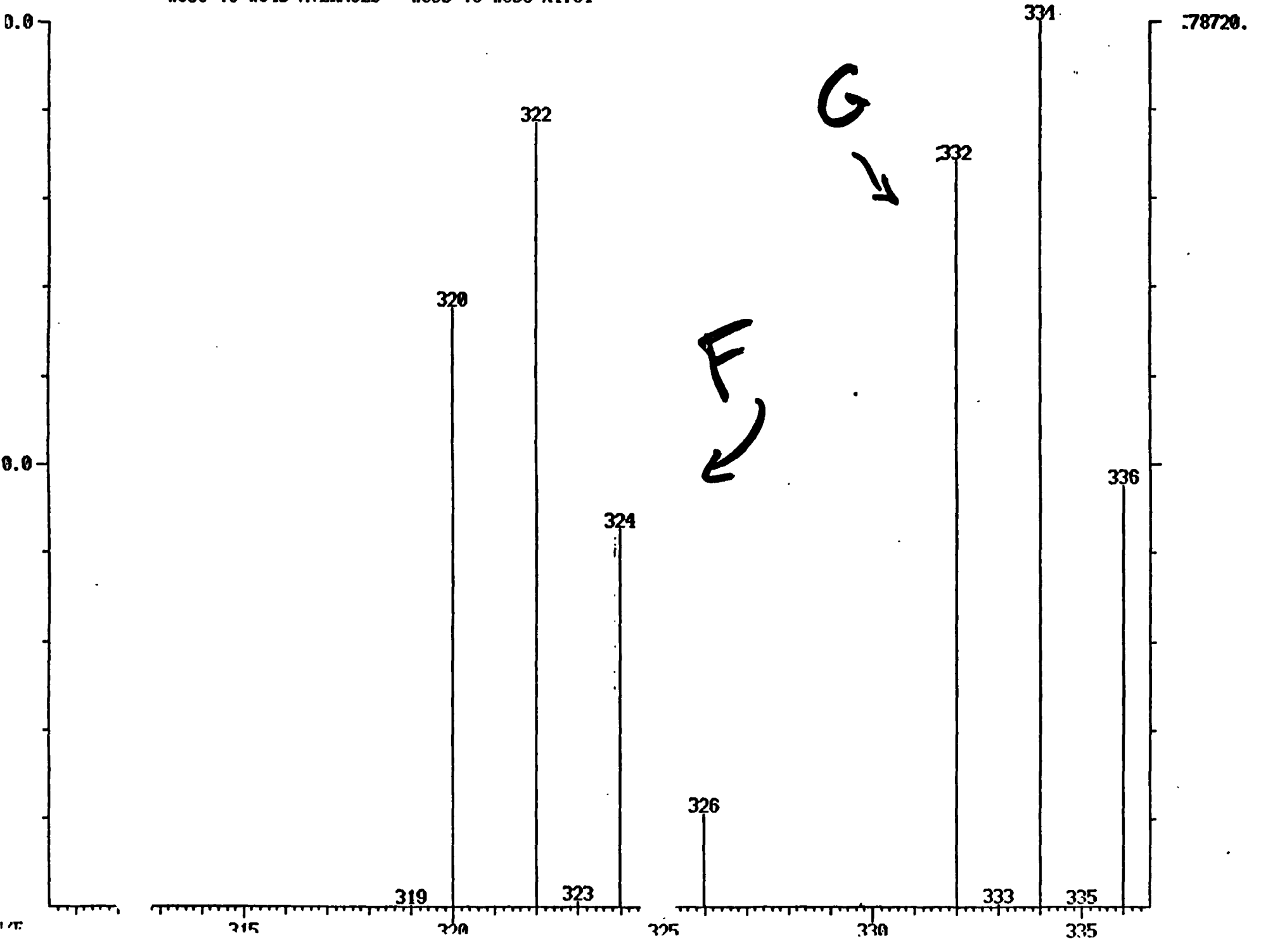


$\frac{679}{938} \times \frac{50}{1.24} = 29$ pptr

MID MASS SPECTRUM
04/12/82 14:40:00 + 23:30
SAMPLE: 4UL 15C SPRING R. MO.(12-10-81)15UL VOL MID EI OV17
#938 TO #943 AVERAGED - #933 TO #936 X1.01

DATA: 15CA #940
CALI: C041282B #3

BASE M/E: 334
RIC: 347648.



APPENDIX III

Procedure the Isolation of Polychloro[illegible]benzofurans and Dioxins in Fish and Other Tissues.

19 Dec. 1980
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FTS 276-3201

Experimental

Synopsis: The tissue sample is processed in a two part procedure. In part I, the sample, in mixture with sodium sulfate, is subjected to solvent extraction and the extract is, in the same process, passed through a series of silica-based adsorbents and then through a carbon/glass fiber adsorbent. The extract passes through the silica-based adsorbents in the following order: potassium silicate, silica gel, cesium silicate, and lastly silica gel. The residues of interest (PCDFs, PCDDs, specific PCB isomers, PCNs, as well as other chemical classes such as PNAHs) will be retained on the carbon adsorbent and are subsequently recovered by reverse elution with toluene. In part II of the procedure, following a change of solvent to hexane the sample is applied to a second series of adsorbents contained in two columns. The first column contains small amounts of cesium silicate and sulfuric acid-impregnated silica gel. The effluent from this column flows directly onto the second column containing activated alumina on which the final fractionation of several classes of residues is accomplished. Following reduction of sample volume, gc/ec and gc/ms analyses are carried out.

Detailed Description:

Part I. The tissue sample (preferable a 3 to 5 fish composite) is cut into small pieces and ground with a meat grinder. One hundred grams of the ground tissue is mixed with 400 grams of anhydrous sodium sulfate which has been heated at ~~300~~ 500°C for 6 to 12 hours. The tissue and sodium sulfate are mixed with a

spoon in a large enough container (glass or ceramic evaporating dishes, for example) that the mixture can be spread to a depth of less than one inch. This is necessary so that when the mass solidifies, it can be broken up without undo difficulty. The mixture is spread out, covered with washed aluminum foil, and allowed to sit overnight. The caked mass is broken up and reduced to a free-flowing powder using a blender.

The first column (column #1, 3 to 5 cm ID and 3 to 4 feet in length) in part I of the process is packed in the following manner: one or two discs of glass microfiber filter [Whatman GF/D or similar material (filter discs are superior to glass wool in this step due to the excessive amount of air trapped in the latter.)], 2 cm depth of anhydrous sodium sulfate, 30 grams of silica gel (Mallinckrodt Silicar CC7, prewashed and activated overnight at 130°C), 30 grams of potassium silicate (silica gel treated with potassium hydroxide, activated at 130°C as described below), 500 grams of the tissue/sodium sulfate (1/4) mixture, and lastly 2 cm depth of anhydrous sodium sulfate. This column and the two columns following are connected by means of teflon tubing (1/16 or 1/8 inch OD using the corresponding tube end fittings from Alltech Assoc. or Rainin Instr. Co.) and a valving system schematized below. The valving system is constructed to permit the following operations to be performed in part I of the process: venting of the solvent line from the column containing the sample and adsorbents (column #1), venting of the solvent reservoir, bypass of the cesium silicate/silica gel column (column #2), delivery of the effluent from column #1 to column #2 and the carbon/glass fibers column (column #3), delivery of solvent from the reservoir to columns #2 and #3 or column #3 only, reversal of solvent flow in columns #2 and #3, and stoppage of solvent flow in all lines. The solvent reservoir is fitted with a ground glass joint so that gas pressure can be applied. Column #2 (22 mm ID x 100 mm Ace Glass Michel-Miller pre-column #5796-34) is packed with equal volumns of cesium silicate and silica gel (E. Merk Silica Gel

60 activated at 130°). ring the operation of part I of the procedure the solvent stream passes first through the silicate and then through the silica gel in column #2. Column #3 is packed with the carbon/glass fibers adsorbent which is washed after each use with 100 ml toluene, then 100 ml methanol, and then 100 ml toluene again. The residual toluene on column #3 is removed later in the washing of freshly packed column #2 with cyclohexane/methylene chloride (50/50) [CH/MC (50/50)]. In any case, the complete displacement of toluene from the carbon by at least 100 ml CH/MC (50/50) is imperative. The bed dimensions of the carbon adsorbent in column #3 are 1.0 cm diameter by 3 to 4 cm length, and 50 mg carbon (Amoco PX-21) is contained in the mixture. The carbon/glass fibers is the only adsorbent which is reused. Column #2, freshly packed with cesium silicate and silica gel, is flushed with CH/MC (50/50) from the reservoir under 5 to 10 psi gas pressure to purge the adsorbents of air and any residual contaminants. Initially, the washing solvent is applied to column #2 so that the effluent does not flow onto the carbon adsorbent, but rather flows through column #3 first and then column #2. Thus, the carbon adsorbent is not exposed to any impurities or air being eluted from column #2. Thus both column #2 and #3 are washed thoroughly with 200 to 300 ml CH/MC (50/50) just before the sample processing in part I is started.

After columns #2 and #3 are properly washed and columns #1 is loaded with adsorbents and sample, the system is ready to be spiked with the internal reference compound (^{13}C-2,3,7,8-TCDD in our case) and to be charged with solvent. A total of 650 to 700 ml CH/MC (50/50) is applied to the system (part I) after inoculation with the internal reference compound. Values are adjusted so that column #1 effluent is vented. The desired amount of the internal reference is applied to the wall of column #1 and washed onto the packed materials below with 15 to 30 ml CH/MC (50/50) using a teflon wash bottle. The washing is repeated four times to insure that the reference compound is completely applied to the

sample mixture, and then 50 ml CH/MC (50/50) is carefu , applied to column #1. As the solvent front runs into the teflon line from column #1 (the line should be 3 or 4 feet in length), significant numbers of air bubbles are usually produced, so the solvent flow is reduced or halted and the line is tapped to force the bubbles past the solvent. After removing the bubbles, the solvent front is allowed to reach valve A and then the effluent is directed through columns #2 and #3 by gravity flow and subsequently collected in a 1 or 2 liter flask. The collecting flask should be positioned above columns #2 and #3 to keep a positive pressure on these columns. The height of column #1 is adjusted so that the flow through the system is no more than 5 ml/minute but sufficient to complete the process overnight. (One ml/minute would require 10 to 12 hours.) Occasionally the solvent flow will slow or stop and this will require the application of one to two psi of gas pressure to column #1. Frequently, the glass fiber filter on the inlet side of the carbon adsorbent, column #3, becomes contaminated with colored biogenic materials and in very "dirty" or oily samples (we've had most trouble with lake trout) can become clogged, but this is rarely encountered. With extremely "dirty" samples, the solvent flow in column #1 may completely stop before the solvent reaches the bottom of the column, and the processing may have to be abandoned. (This has occurred only once in our operations.)

Following completion of the initial extraction/adsorbent operation, column #3 (containing the adsorbed residues of interest) is washed in the forward direction (bypassing column #2) with 75 ml CH/MC (50/50) and then 50 ml methylene chloride/methanol/benzene (75/20/5) at a flow rate of approximately 5 ml/min. The reservoir is then charged with 40 ml toluene and this is passed through column #3 in the reverse flow direction at no greater than 3 to 4 ml/minute. This reverse flow effluent is collected in a 100 ml round bottom (24/40) flask. At this point, part I of the procedure is complete.

The sample in tolue is subjected to rotary evapc ion at 50° to 60° C. The rotary evaporation system must be thorough washed with purified solvents o prevent sample contamination. A vapor trap situated between the sample flask and the rotary evaporation apparatus is very advantageous. The toluene solution is carefully taken to dryness and removed immediately. Approximately 0.5 ml hexane is added to the flask and swirled to wash the bottom half of the flask. The sample is ready for part II of the procedure.

Part II. In part II, the partially enriched sample is applied to two columns in sequence; column #4 contains both cesium silicate and sulfuric acid impregnated silica gel, and column #5 contains activated alumina. Column #4 is prepared with a Pasteur (disposable) pipet, containing a small plug of glass wool and packed first with 3 cm (bed depth) sulfuric acid-impregnated silica gel and then with 3 cm (bed depth) cesium silicate (not oven-activated) and topped with 0.5 cm anhydrous sodium sulfate. This column is washed with 5 to 10 ml hexane to remove air and residual contaminants. Column #5 is constructed from a 5 ml graduated pipet fitted with a 40 ml reservoir and a ground glass joint. Column #5 is packed with a plug of glass wool, followed by 3.50 ml activated alumina, and then 0.5 cm anhydrous sodium sulfate. The air is removed from the alumina by passing 30 to 40 ml hexane through the adsorbent under 2 to 5 psi gas pressure. After columns #4 and #5 are readied, column #4 is partially inserted into column #5 so that the effluent from column #4 passes directly onto the adsorbent bed of column #5. A 50 ml collection vessel is placed at the exit of column #5. The sample is applied to column #4 with four separate 0.5 ml (approximate volume) washes of hexane. Each washing is allowed to pass through column #4 and completely onto the alumina of column #5 before the next wash is applied. The hexane used to apply the sample is drawn from a premeasured volume of 10.0 ml. Hexane is applied to column #4 until a total of 5.0 ml has been used. Column #4 is then removed and the remaining 5.0 ml hexane is applied to column #5.

Then the following sequence of solvents is applied to column #5:

15 ml 2% methylene chloride in hexane

15 ml 5% methylene chloride in hexane

15 ml 8% methylene chloride in hexane

This makes a total of 55 ml effluent from column #5 which is collected in two portions. The first of two collections from column #5 is made from zero to 23 ml, and the second is made from 23 to 55 ml. PCDF's are elute from 23 to 52 ml, 2,3,7,8-TCDD from 39 to 49 ml, and polychloronophthalenes (Halowas 1014) from 12 to 24 ml. Thus the second collection (in a 50 ml tube) is made from 23 to 55 ml; this is the fraction containing the PCDF's and PCDD's. This concludes part II of the procedure.

The sample solution is reduced to approximately 0.5 ml under a stream of nitrogen while warming the solution in a 40° to 45° C water bath. Determination and minimization of sample contamination from the gas system (as well as the rotary evaporation apparatus) is important. Phthalates were detected in large amounts in some samples, and this required establishing some remedial procedures to reduce contamination: the nitrogen line was equipped with a large carbon trap and the rotary evaporator vapor trap is thoroughly washed with glass-distilled solvents before use. In the past, some teflon tubing has been identified as a serious source of phthalate contamination. The carbon trap significantly reduced the level of phthalate contamination in the gas flow evaporation step.

The 0.5 ml volume sample is swirled up the sides of the tube several times and then transfered to a conical mini vial (Alltech 5 ml Mini-Vial #95050, or suitable substitute). Liquid transfers are made with disposable pipets which have been calcined at 475° C. The tube is washed separately with four 0.5 ml portions of methylene chloride which are transfered to the mini vial. The solvent is then completely evaporated under a stream of nitrogen and 10 µL toluene added. The vial is tipped horizontally and rotated to allow the toluene to wet

the sides of the cone. Then 40 µL undecane (purified by treatment with H_2SO_4 and passage through activated alumina) is added and the solvent again washed along the sides of the vial. A vortex mixer facilitates this final mixing. The sample is ready for gc/ec and gc/ms analyses. The sample is stored in a freezer.

After processing of the sample in part I, column #1 is cleaned by first forcing the materials out under air pressure, then rinsing thoroughly with warm water, acetone, and then hexane. Columns #2 and #5 are cleaned in a similar manner. The carbon column, column #3, is washed as described above. Glass collection flasks and tubes are routinely baked at 475° C for 6 to 12 hours and then washed with acetone followed by hexane.

Adsorbents and column preparations:

Potassium and cesium silicates are prepared by the reaction of the corresponding alkali metal hydroxide with silica gel in methanol at 55° C for 90 minutes. The reaction is carried out in a round bottom flask which is rotated and heated by use of a rotary evaporation apparatus (no vacuum applied). The mixture is allowed to cool and then is poured into a large glass column containing a plug of glass wool at the exit end. The adsorbent is washed into the column with methanol, and then 200 ml methanol for every 100 g silica gel is added to the column. The methanol can be pushed through the column under slight gas pressure. As the methanol level reaches the bed of adsorbent, 200 ml methylene chloride for every 100 g silica gel is then added to the column. Nitrogen pressure is applied to push the methylene chloride through and to partially or completely dry the adsorbent. Cesium silicate is dried completely under a nitrogen stream and is not oven-activated; potassium silicate is partially dried under nitrogen and then activated at 130° C. Oven-activated cesium silicate will retain hepta- and octachlorodibenzofurans and dioxins on column #4, and is consequently unacceptable. The following amounts of material are used for the preparations:

60 grams cesium hydroxide (99 + %, Aldrich Chemical Co., Milwaukee, Wis, #19,833-1) and 250 to 350 ml anhydrous methanol for every 100 grams silica gel (E. Merck, Silica Gel 60, 70-230 mesh, activated at 130° C). (The solution of cesium hydroxide in methanol is filtered before addition of silica gel to remove a large amount of suspended solid.)

168 g potassium hydroxide (Baker, Analyzed Reagent, #15-3140) and 700 to 800 ml anhydrous methanol for every 300 grams silica gel (Mallinckrodt, Silicar CC-7).

The carbon/glass fiber adsorbent is prepared from 600 mg fiber filters (Whatman, GF/D) and 50 mg Amoco PX-21 carbon (5 to 20 μm Amoco, Inc., Chicago, Ill). The glass fiber disc is cut into small pieces, suspended in 100 ml methylene chloride, and shredded for approximately 30 seconds with a Polytron homogenizer (Brinkman Instrument, Westburg, NY). The carbon is added to the homogenized fibers and this mixture stirred until the carbon is uniformly distributed on the fibers. Larger carbon particles will not adhere to the fibers and will settle out; consequently only sieved powdered carbon of particle sizes from approximately 5 to 20 microns is employed.

The chromatography columns for the carbon adsorbent were specially designed and consist of 8 cm lengths of thick walled 1.0 cm inside diameter precision bore tubing and are fitted with specially constructed teflon plugs equipped with threaded fittings. The Kontes adjustable chromaflex column (1.0 cm ID x 30 cm length, #K-422350-3010, $145 each) is a suitable substitute. With one end of the column fitted with the teflon plunger or plug, two to four discs of glass fiber filters (Whatman GF/F, 0.7 μm retention, 1.0 cm diameter) are placed in the column flush with the end fitting. The other end of the column is fitted with a funnel and a slurry of the carbon/glass fibers (containing 50 mg carbon) in methylene chloride is added. The adsorbent is packed into the column with a gl rod in small portions. The bed height should measure 3 to 4 cm. Two to four

discs of glass fiber filters are placed on the adsorbent bed, the funnel is removed, and the second end fitting is put in place. The carbon/glass fiber column (column #3) is now ready to be solvent washed. Care must be taken to insure that all the carbon is contained between the glass fiber discs and that none can be dislodged to migrate during solvent flow.

Sulfuric acid-impregnated silica gel (40% w/w) is prepared by adding two parts concentrated sulfuric acid to three parts silica gel in a screw capped bottle and mixing until the mixture is free of lumps. The silica gel (Mallinckrodt Silicar CC-7) is column washed or soxhlet extracted with methylene chloride and activated at 130° C; unactivated silica gel is unsatisfactory. The adsorbent is stored in a screw capped bottle.

SUMMARY

1. PCDDs and PCDFs are recovered from large amounts of co-extracted biogenic materials.

2. All congeners with three or more chlorines are recovered.

3. Good recoveries (75–95%) and good precision (±5% s.d.) at parts-per-trillion levels

4. Rapid: 3 to 4 man-hours per sample with minimum sample manipulation.

5. PCDDs and PCDFs are efficiently separated from compounds that can interfer with GC/MS analysis (PCBs, PCNs, PCDPEs, PCPOPs)

6. Very large Contaminant Enrichment Factor CEF $\approx 10^8$
   Sample size is reduced from 20 g to approximately 200 ng.

$$CEF = \frac{\text{weight of sample before processing}}{\text{weight of sample after processing}} \times \frac{\text{\% recovery of compound}}{100}$$

PART II FRACTIONATION OF AROMATIC RESIDUES

Cesium Silicate (0.54g)

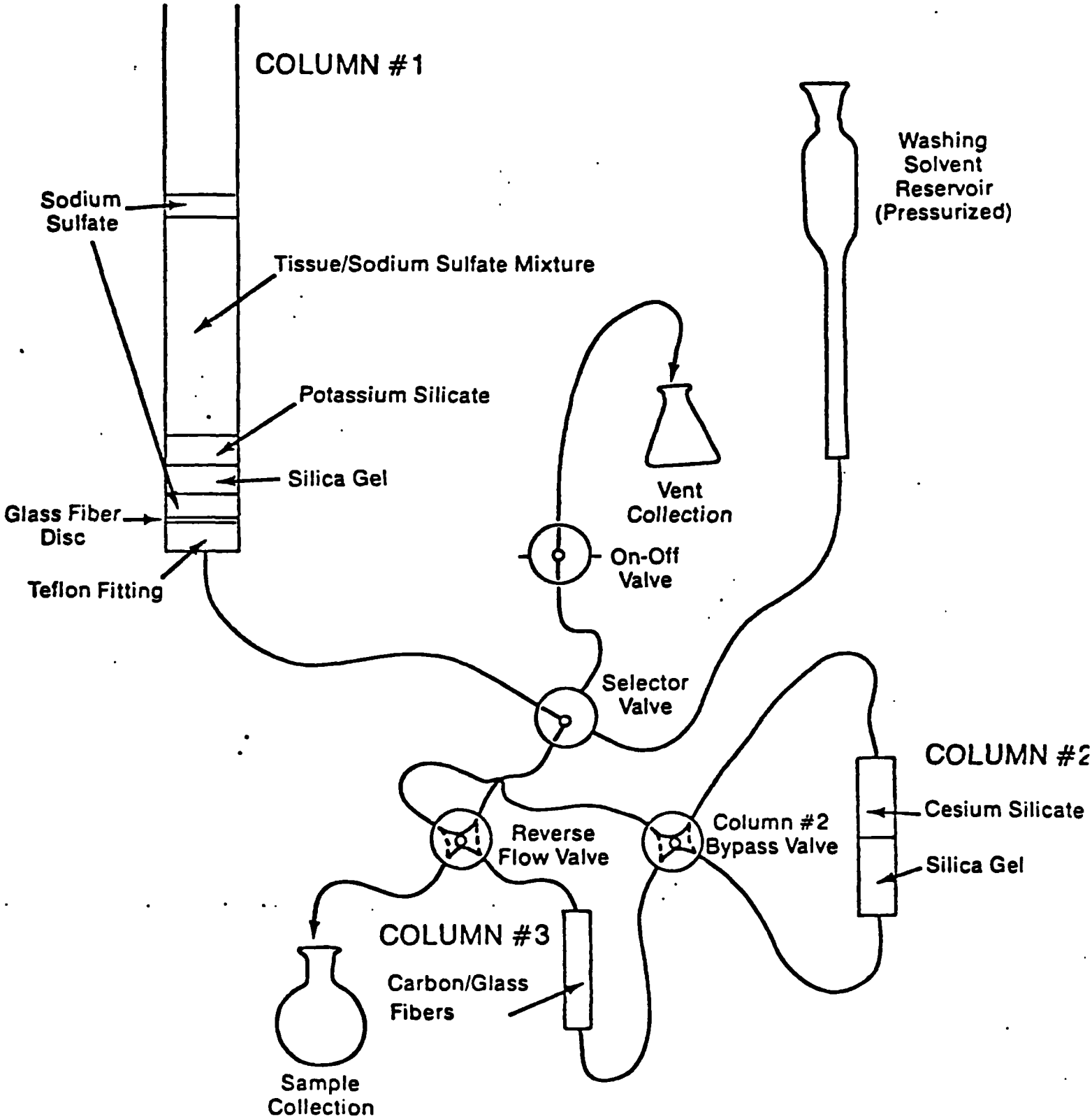
H_2SO_4/Silica Gel (0.47g)

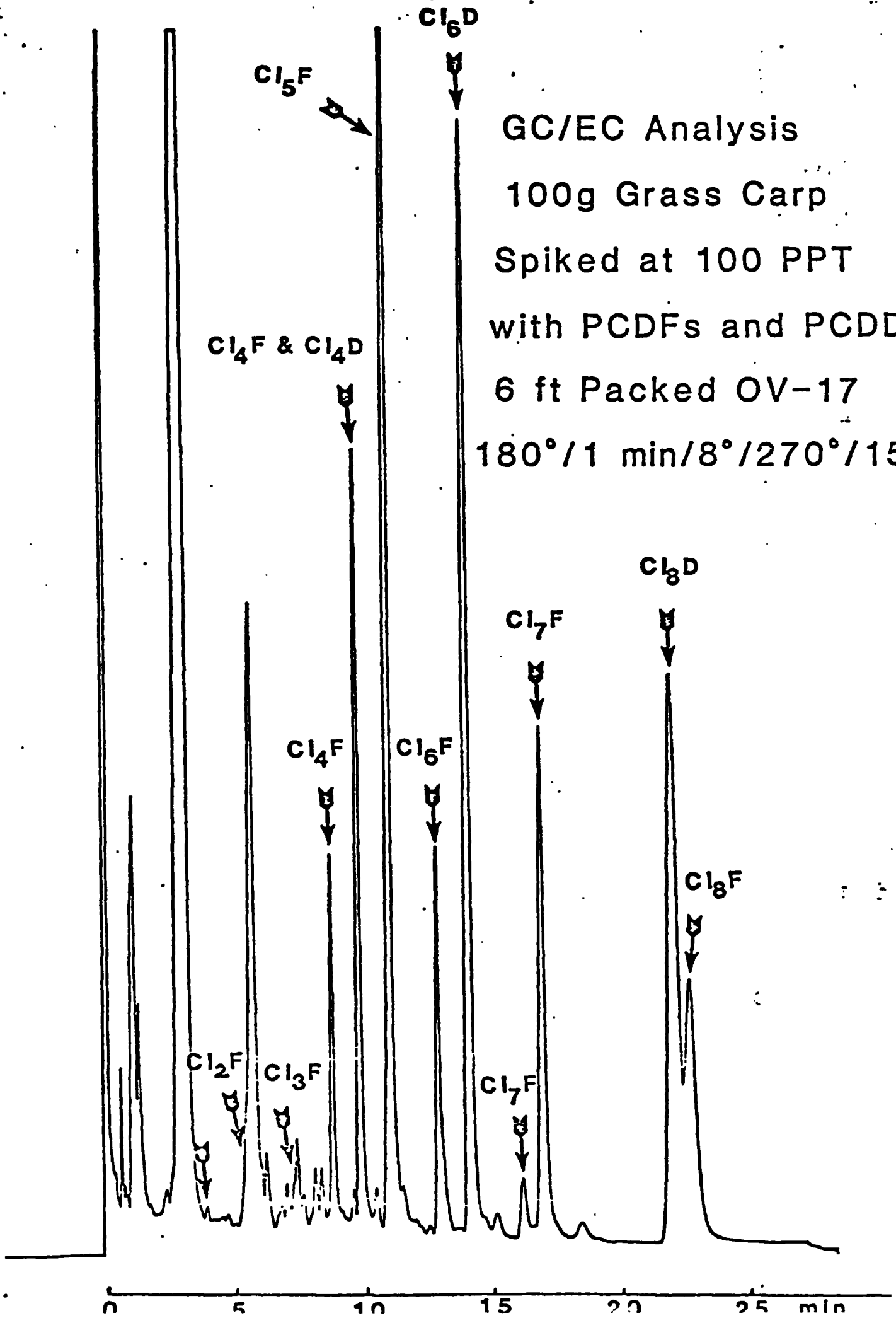
Removal of residual biogenic substances

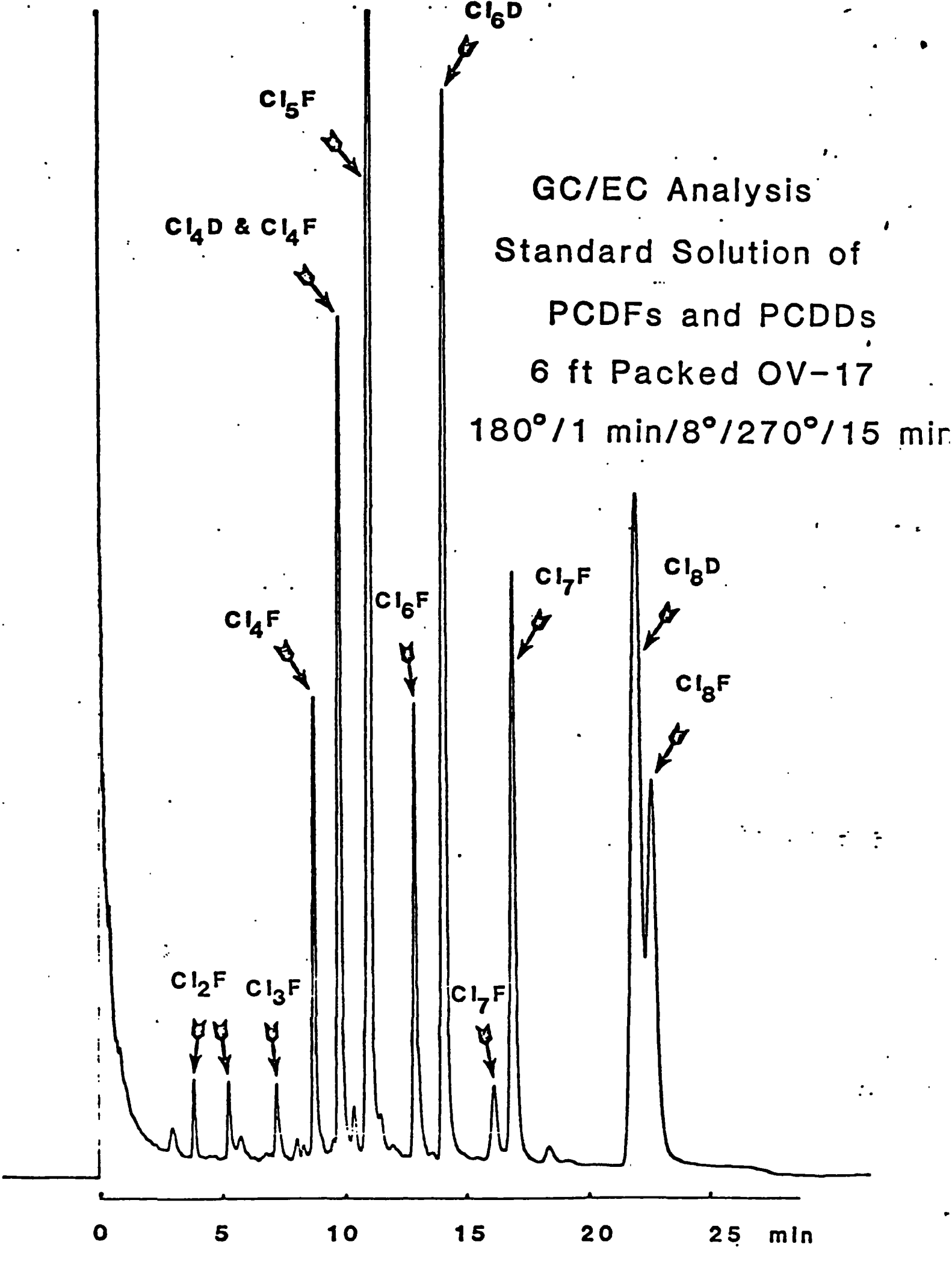
Alumina (3.65g) — Fractionation of xenobiotic residues

Fraction	Solvent	Compounds
0–23 mL	0–2% CH_2Cl_2/C_6H_{14}	PCBs, PCNs
23–55 mL	5–8% CH_2Cl_2/C_6H_{14}	PCDDs, PCDFs

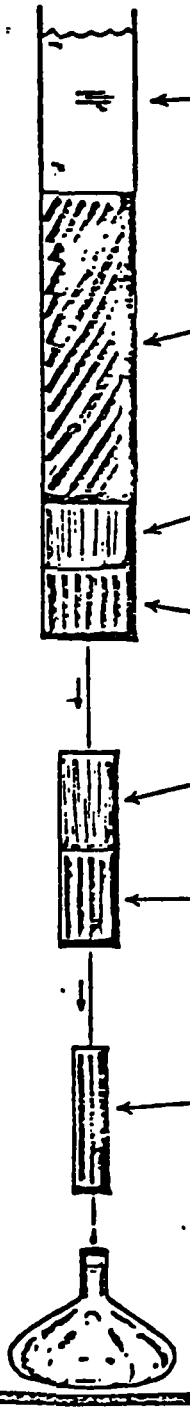
Enrichment Procedure for Polychlorodibenzofurans and Dioxins in Tissue. Part I.




GC/EC Analysis
100g Grass Carp
Spiked at 100 PPT
with PCDFs and PCDDs
6 ft Packed OV-17
180°/1 min/8°/270°/15 r
Cl_6D
Cl_5F
Cl_4F & Cl_4D
Cl_8D
Cl_7F
Cl_4F
Cl_6F
Cl_8F
Cl_2F
Cl_3F
Cl_7F
0
5
10
15
20
25
min


GC/EC Analysis
Standard Solution of
PCDFs and PCDDs
6 ft Packed OV-17
180°/1 min/8°/270°/15 min
Cl_6D
Cl_5F
Cl_4D & Cl_4F
Cl_4F
Cl_6F
Cl_7F
Cl_8D
Cl_8F
Cl_2F
Cl_3F
Cl_7F
0
5
10
15
20
25 min

PART I EXTRACTION and ADSORPTION on CARBON



Solvent
(C_6H_{12}/CH_2Cl_2 1:1 v/v)

Tissue/Na_2SO_4
(500 g 1:4 w/w)

Potassium Silicate
(30g)

Silica Gel (30g)

Remove acidics and other polar biogenic compounds that interfer with adsorption of PCDDs and PCDFs on carbon

Cesium Silicate (10g)

Silica Gel (6g)

Carbon(50mg).
Glass Fibers Mixture

Selective adsorption of PCDDs and PCDFs and similar residues

PCDD, PCDF ENRICHMENT PROCEDURE

1. Prepare mixture of tissue and sodium sulfate.

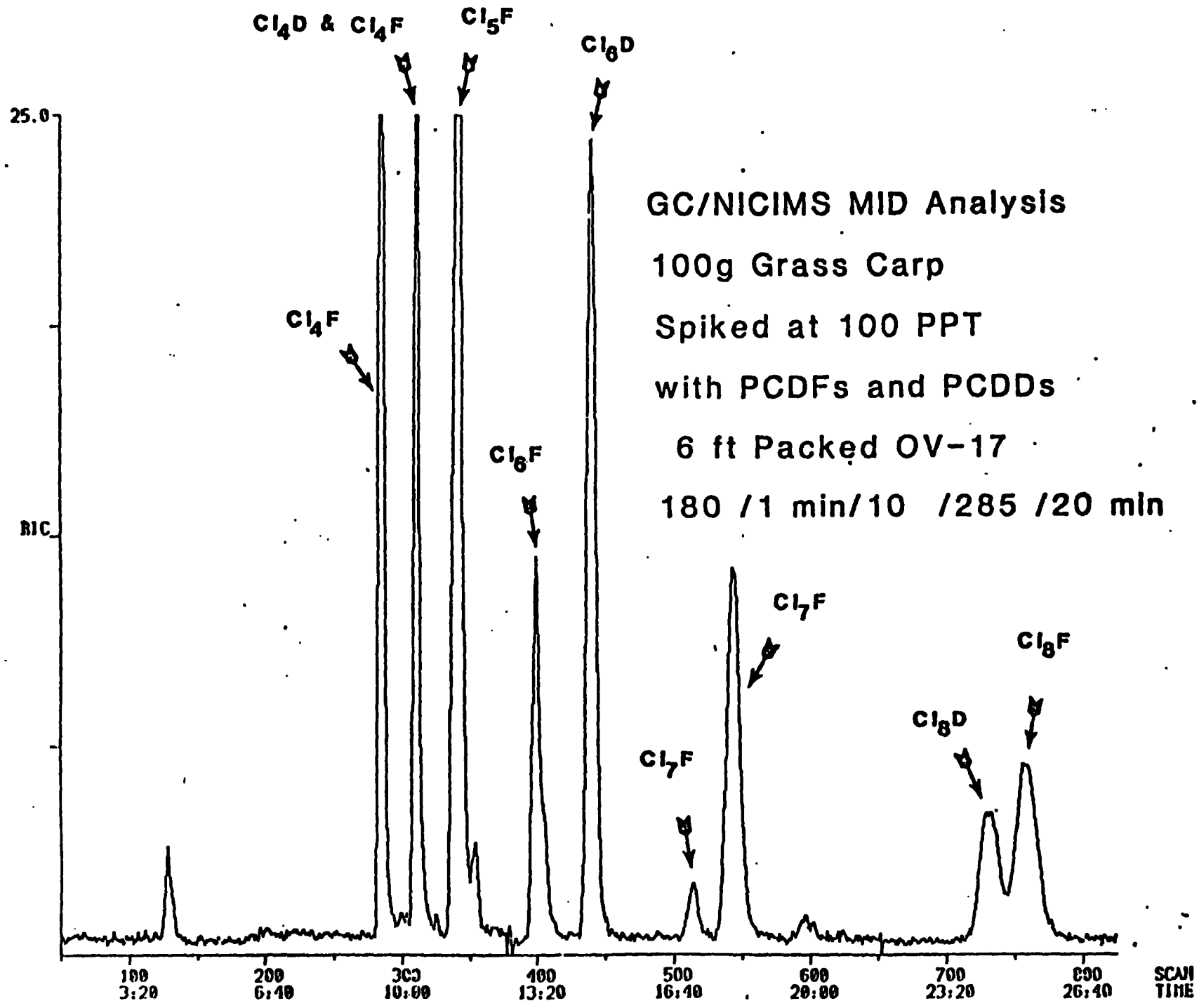
2. Carry out simultaneous extraction and passage of extract through three types of adsorbents. (PART I)

3. Recover PCDFs and PCDDs from carbon (reverse elution with toluene)

4. Apply sample to three-adsorbent system. Fractionation is accomplished on alumina. (PART II)

5. Analyze by GC/EC and GC/MS

Time requirements: 3 to 4 man-hours per sample in sets of 3 to 5 samples.


Cl_4D & Cl_4F
Cl_5F
Cl_6D
Cl_4F
Cl_6F
Cl_7F
Cl_7F
Cl_8D
Cl_8F
25.0
RIC
GC/NICIMS MID Analysis
100g Grass Carp
Spiked at 100 PPT
with PCDFs and PCDDs
6 ft Packed OV-17
180 /1 min/10 /285 /20 min
100 3:20
200 6:40
300 10:00
400 13:20
500 16:40
600 20:00
700 23:20
800 26:40
SCAN TIME

RECOVERY DATA

	TCDD TCDF	PnCDF	HCDF	HCDD	HpCDF	OCDD	OCDF
Spiked Salmon Oil							
25 ppt	81±9%	70±5	75±5	82±3	77±5	87±7	75±5
100 ppt	102±2	97±3	84±4	98±2	87±6	76±3	74±5
250 ppt	66±2	80	68±3	76	72±8	66±3	62±14
Spiked Grass Carp							
100 ppt	92±7	94±3	98±6	104±4	95±8	99±22	91±16