Title
METAL COORDINATION CHEMISTRY: REMOVAL AND RECOVERY OF METAL COMPOUNDS FROM HEAVY CRUDE AND SHALE OILS WITH MULTIDENTATE LIGANDS. QUARTERLY PROGRESS REPORT

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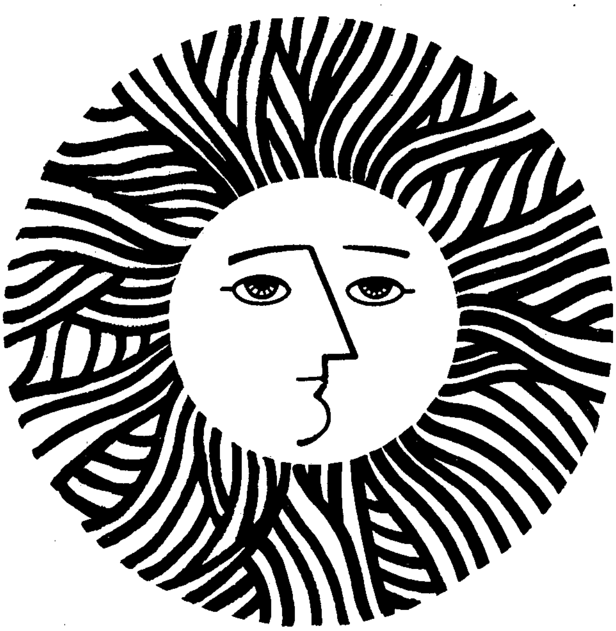

Metal Coordination Chemistry: Removal and Recovery of Metal Compounds from Heavy Crude and Shale Oils with Multidentate Ligands

Quarterly Progress Report for Period

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by

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Introduction

In previous publications,[1,2] we identified methyl and phenylarsonic acid as well as arsenate in oil shale products; namely, shale oil and oil shale retort waters. We believe that the biogeochemical origin of these compounds would be important to elucidate. The reasons being that either these compounds have a biogeochemical origin in oil shale kerogen or that they are formed during the pyrolysis of oil shale kerogen. Additionaly, it is desirable from a process standpoint and for environmental reasons that the origin of these compounds be established.

In this report, we show data that identifies methyl and phenylarsonic acid that was isolated from Green River oil shale kerogen.

In a previous report,[3] we demonstrated the usefulness of HPLC-GFAA analysis for fingerprinting heavy crude oils and utilizing these histograms in defining the molecular weights of various vanadyl compounds found in these oils. In this report, we examined the asphaltenes of several crude oils via HPLC-GFAA analysis and provide a comparison to the data obtained on the whole heavy crude oils.

Indentification of Methyl and Phenylarsonic Acid Found in Green River Oil Shale Kerogen

In earlier experiments, we used the total methanol extracts of a Green River oil shale kerogen sample to identify by HPLC-GFAA and GC-EIMS analysis phenylarsonic acid and, tentatively by HPLC-GFAA, arsenate. We now describe similar experiments with HPLC purified fractions of the methanol extract in which we have derivatized both phenylarsonic acid and the hithertofore unidentified methylarsonic acid with 3-

methylcatechol followed by GC-EIMS analysis. The known compounds from the reaction of 3-methylcatechol and either phenyl or methylarsonic acid, i.e., the five coordinate organoarsenic catecholates (eq. 1) were chromatographed on a 30 m fused silica capillary column interfaced to a electron impact mass spectrometer (GC-EIMS) and gave the following mass spectra and reconstructed ion chromatographs (Figures 1-4).

A similar analysis, as stated above, with the HPLC purified factors provided unequivocal evidence for the identification of methylarsonic acid as well as reconfirmation of the previously indentified phenylarsonic acid (Figures 5-9).

These exciting discoveries open a new field which we have called organometallic geochemistry and which further enhances our original goals of providing polymeric ligands to remove inorganic and organoarsenic compounds from shale oil.

<u>Analysis of Asphaltenes of Cerro Negro, Boscan, Wilmington and Prudhoe Bay Heavy Crude Oils for Vanadyl Porphyrin and Non-Porphyrin Compounds by HPLC-GFAA</u>

In the previous report,[3] we analyzed the heavy crude oils, extracted oils and extracts on size exclusion HPLC columns, which showed the molecular weight distribution for vanadyl compounds in four heavy crude oils. Recently, we have extended this study to the asphaltenes of Cerro Negro, Boscan, Wilmington and Prudhoe Bay isolated via pentane precipitation. Analysis of the vanadium content in the asphaltenes by x-ray fluorescence provided a comparison to the whole heavy crude oils previously studied (Table 1).

As shown in Table 1, the asphaltene fraction, as has previously been understood, has a high concentration of the vanadium present. More importantly, we have examined these asphaltene fractions by SEC-HPLC-GFAA analysis and determined the vanadium distribution with mw > 900; < 900, > 400; < 400. Table 2 states our results and shows conclusively that vanadyl compounds incorporated into molecules with > 900 mw are present in the asphaltenes in very high concentrations as is the porphyrin and non-porphyrin vanadyl compounds. These latter results need to be examined along with an analysis of the maltene fraction (oil remaining after penture precipitation of asphaltenes) and extracts of the asphaltenes.

The fingerprints of the asphaltenes for the heavy crude oils studied are presented in Figures 10-13 and the calibration curve in Figure 14.

We believe these preliminary results on the fingerprinting of asphaltenes for vanadyl compounds will help in future speciation studies for identification of these compounds in the heavy crude oils and components of the oil.

Future Work

We hope to start on the synthesis of polymer-bond catechol derivatives to determine their reactivity with methyl and phenylarsonic acid. In addition, reactions of shale oil with 3-methylcatechol will be performed to see if we can react the coordinated methyl and phenylarsonic acids with this catechol and form the five-coordinate organoarsenic catecholates. This experiment will allow a preliminary view of the feasibility of catechols in competing with the large molecules associated with iron that coordinate the organoarsenic compounds.

The heavy crude oils have been reanalyzed on a combination of 50-100 Å SEC columns and better separations have been offered. More interestingly, the maltenes and extracts of asphaltenes are being analyzed by HPLC-GFAA and should provide some interesting comparisons with the heavy crude oils.

We have also initiated, with the help of three summer students and their professor, a synthesis program to obtain needed vanadyl porphyrin and non-porphyrin model compounds for the speciation studies.

Acknowledgements

We wish to thank John Komlenic, Brian Wines, Carl Weiss, Wyman Walker and Raja Tannous for experimental results reported in this quarterly.

References

(1) R.H. Fish, K.L. Jewett and F.E. Brinckman, Environ. Sci. Tech. 16, 174, (1982).

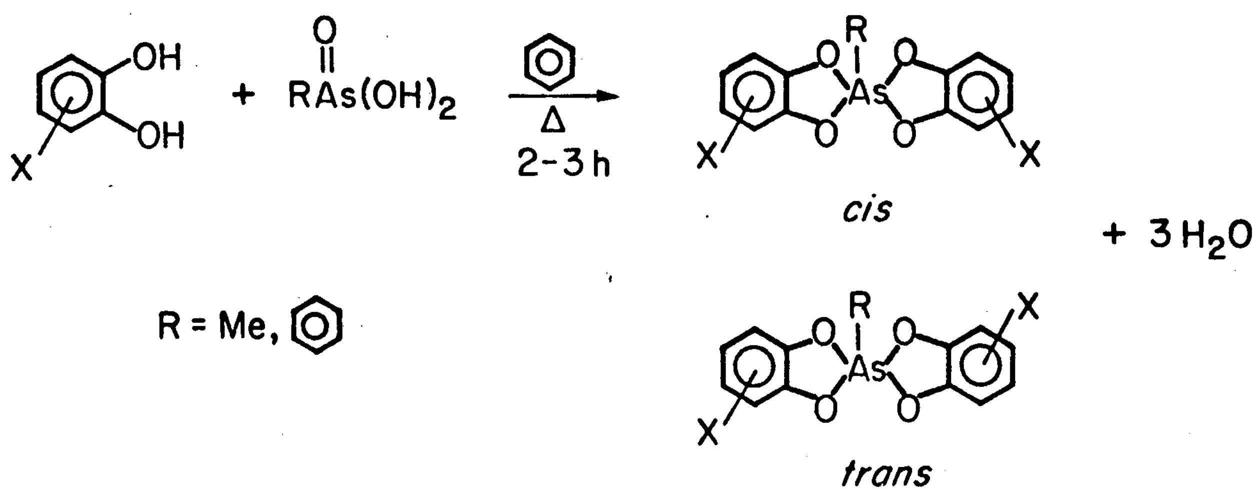
(2) C.W. Weiss, K.L. Jewett, F.E. Brinckman and R.H. Fish, NBS Special Publication 618, 197 (1981).

(3) R.H. Fish, LBID523, Quarterly Report to the Bartlesville Energy Technology Center, Jan. 1, 1982 - April 1, 1982.

Presentations and Publications

R.H. Fish and R.S. Tannous. Synthesis, Structural Elucidation and Stereochemistry of Five-Coordinate Organoarsenic Catecholates, Organometallics, 1982 (in press).

F.E. Brinckman, C.W. Weiss and R.H. Fish, Speciation of Inorganic Arsenic and Organoarsenic Compounds in Fossil Fuel Precursors and Products. Chapter for Chemical and Geochemical Aspects of Fossil Energy Extraction, Ann Arbor Science, Editor T.F. Yen (1982).



EQUATION 1

XBL 818-10978

FIGURE 1

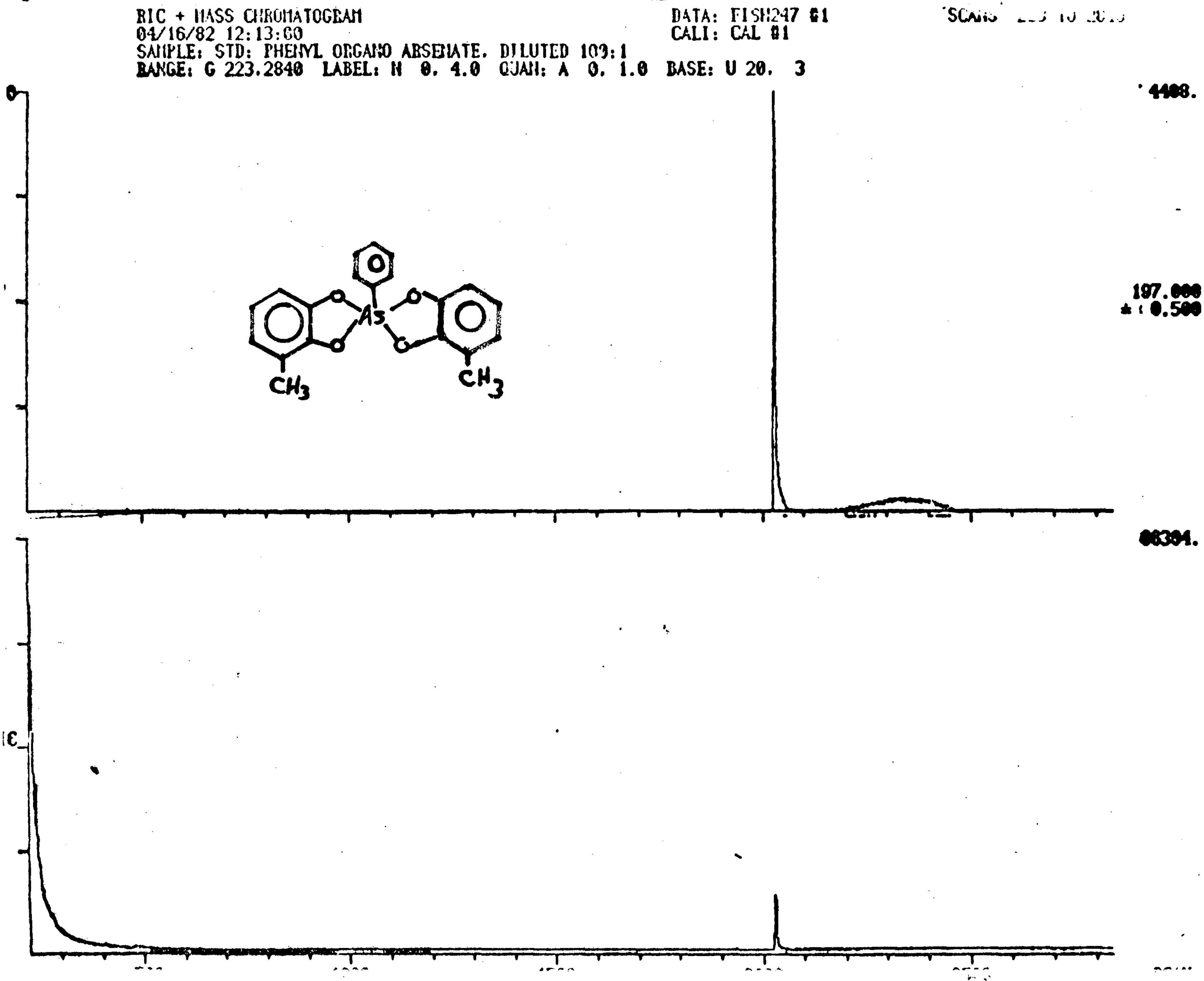
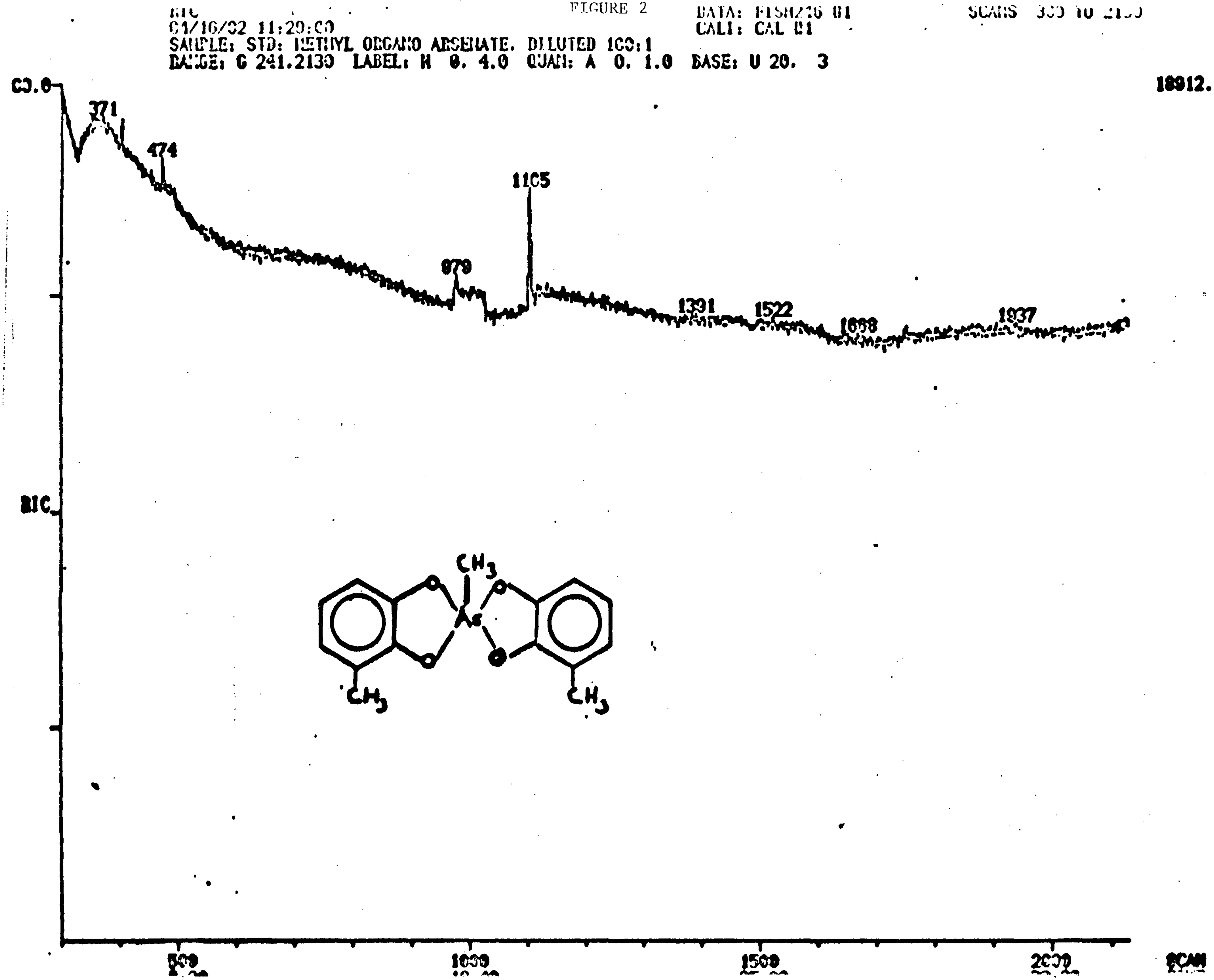

RIC + MASS CHROMATOGRAM
04/16/82 12:13:00
SAMPLE: STD: PHENYL ORGANO ARSENATE, DILUTED 100:1
RANGE: G 223.2840 LABEL: N 0, 4.0 QUAN: A 0, 1.0 BASE: U 20, 3
DATA: FISH247 #1
CALI: CAL #1
4408.
197.000
± 0.500
08304.
As
CH3
CH3

FIGURE 2



RIC
01/16/82 11:20:00
SAMPLE: STD: METHYL ORGANO ARSENATE. DILUTED 100:1
RANGE: G 241.2130 LABEL: N 0. 4.0 QUAN: A 0. 1.0 BASE: U 20. 3
DATA: FISH216 01
CALI: CAL 01
SCANS 300 TO 2130
100.0
18912.
RIC
371
474
979
1105
1391
1522
1698
1937
CH3
As
CH3
CH3
500
1000
1500
2000
SCAN

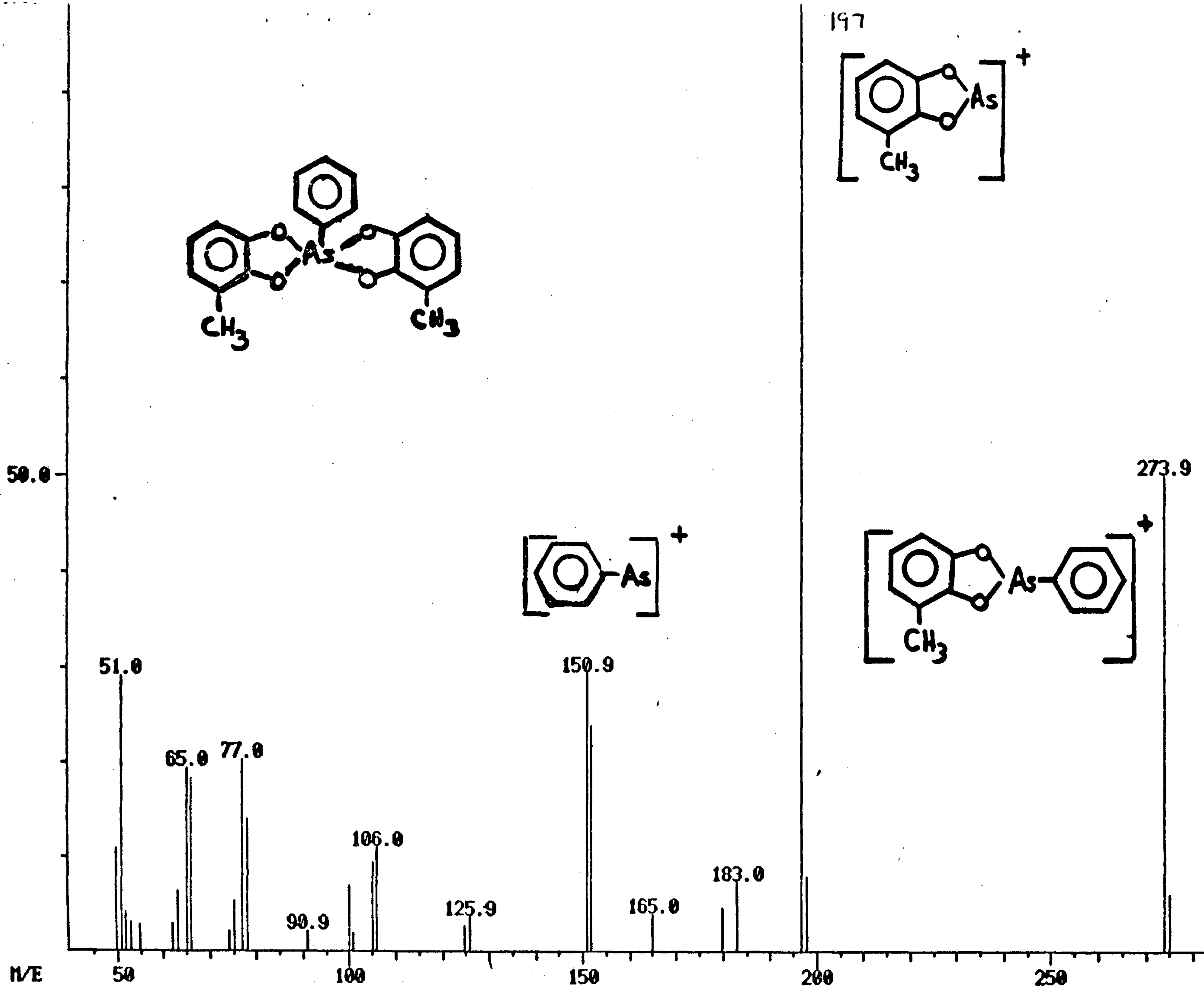


Figure 3 . GC-EIMS of the phenylarsonic acid·3-methylcatecholate.

FIGURE 4

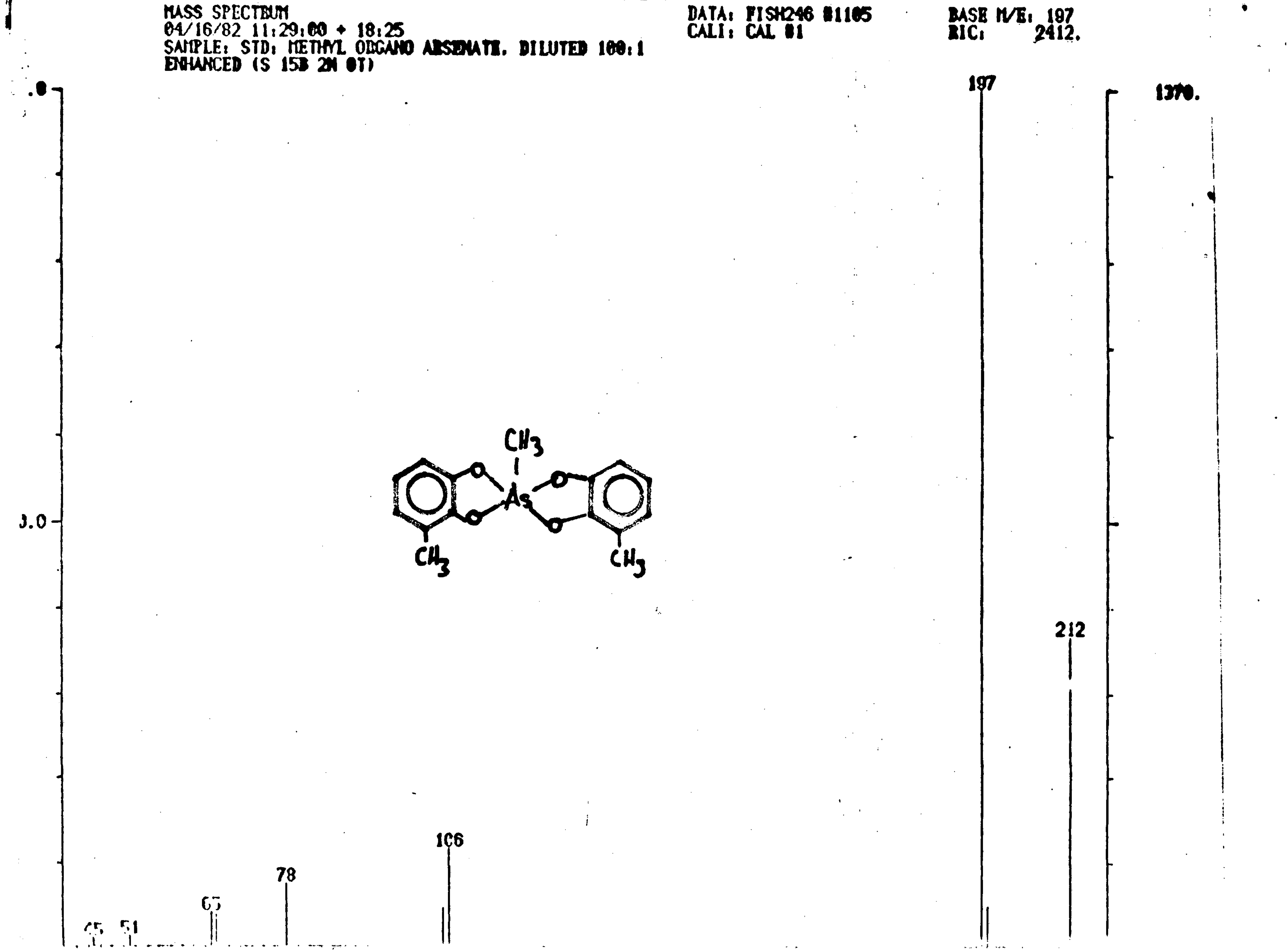

MASS SPECTRUM
04/16/82 11:29:00 + 18:25
SAMPLE: STD: METHYL ODGANO ARSENATE. DILUTED 100:1
ENHANCED (S 15B 2N 0T)
DATA: FISH246 #1105
CALI: CAL #1
BASE M/E: 197
RIC: 2412.
197
1370.
212
106
78
65
51
3.0
CH3
As
O
CH3
CH3

FIGURE 5

SAMPLE: HPLC MEOH EXTRACT 31-35.5 RT-1-83B, DILUTED 100:1
RANGE: G 250.4000 LABEL: N 0. 4.0 QUAN: A 0. 1.0 BASE: U 20. 3

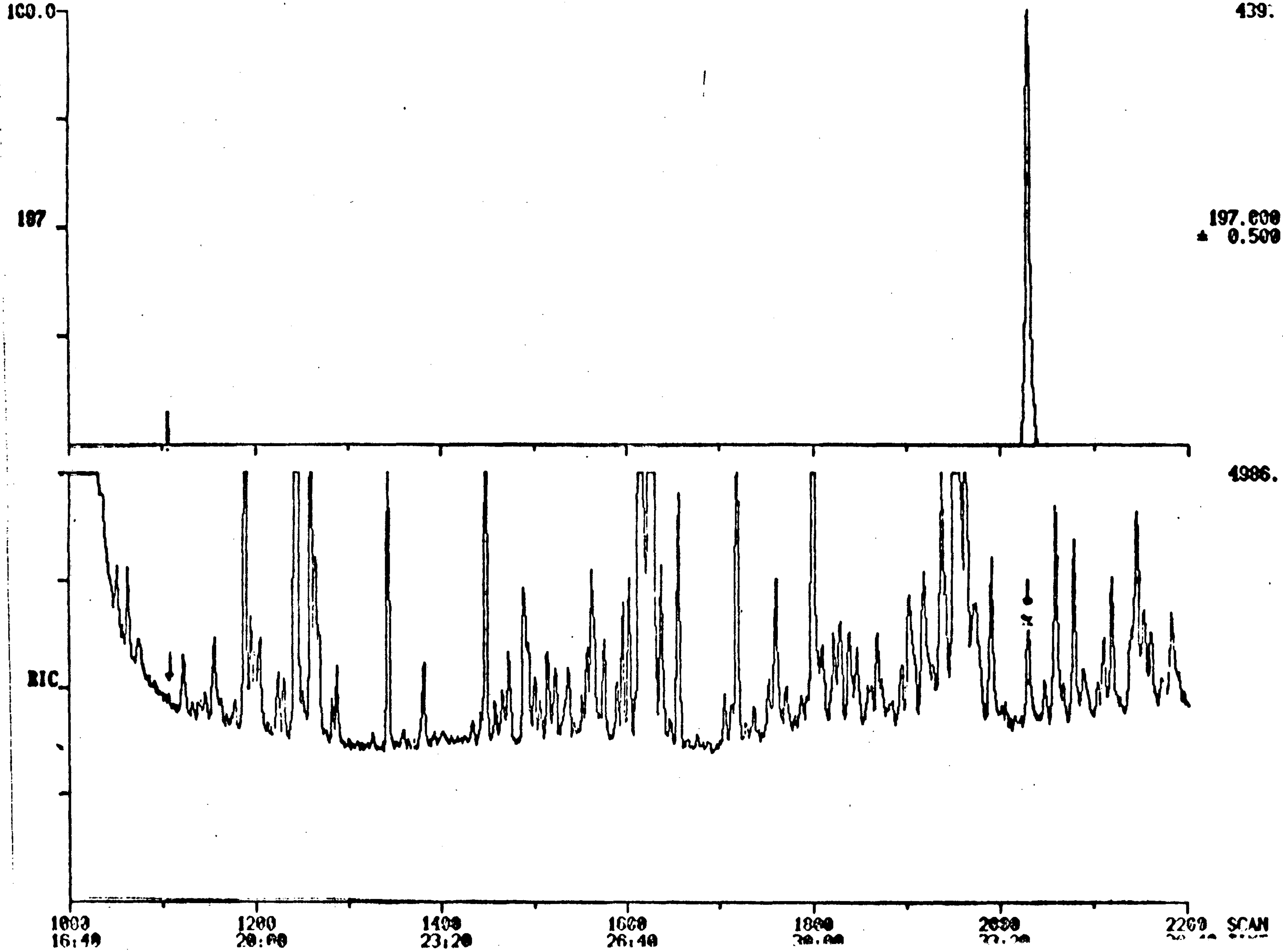
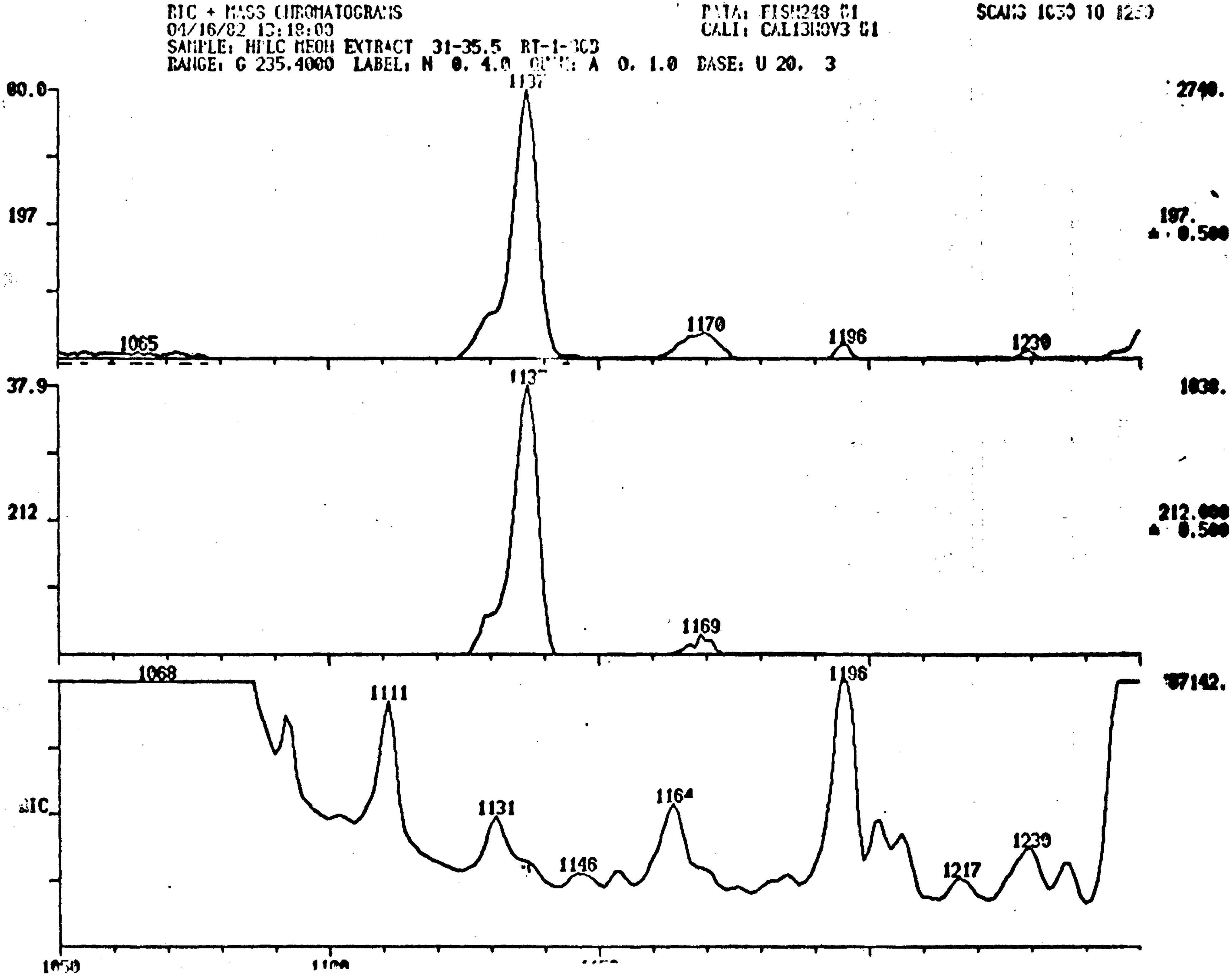


FIGURE 6



RIC + MASS CHROMATOGRAMS
04/16/82 13:18:00
SAMPLE: HPLC MEOH EXTRACT 31-35.5 RT-1-30B
RANGE: G 235.4000 LABEL: N 0. 4.0 QUAN: A 0. 1.0 BASE: U 20. 3
DATA: FISH248 01
CALI: CAL13NOV3 01
SCANS 1050 TO 1250
80.0
197
1137
1065
1170
1196
1230
2740.
197.
± 0.500
37.9
212
1169
1030.
212.000
± 0.500
RIC
1068
1111
1131
1146
1164
1196
1217
1239
1050
1100

FIGURE 7

RIC + MASS CHROMATOGRAMS
01/16/82 16:11:00
SAMPLE: HPLC MEOH EXTRACT 31-35.5 BT-1-80B, DILUTED 100:1
RANGE: G 250.4000 LABEL: N 0, 4.0 QUAN: A 0, 1.0 BASE: U 20, 3

DATA: FISH250 #1
CALI: CAL13NOV3 #1

SCANS 2000 TO 2100

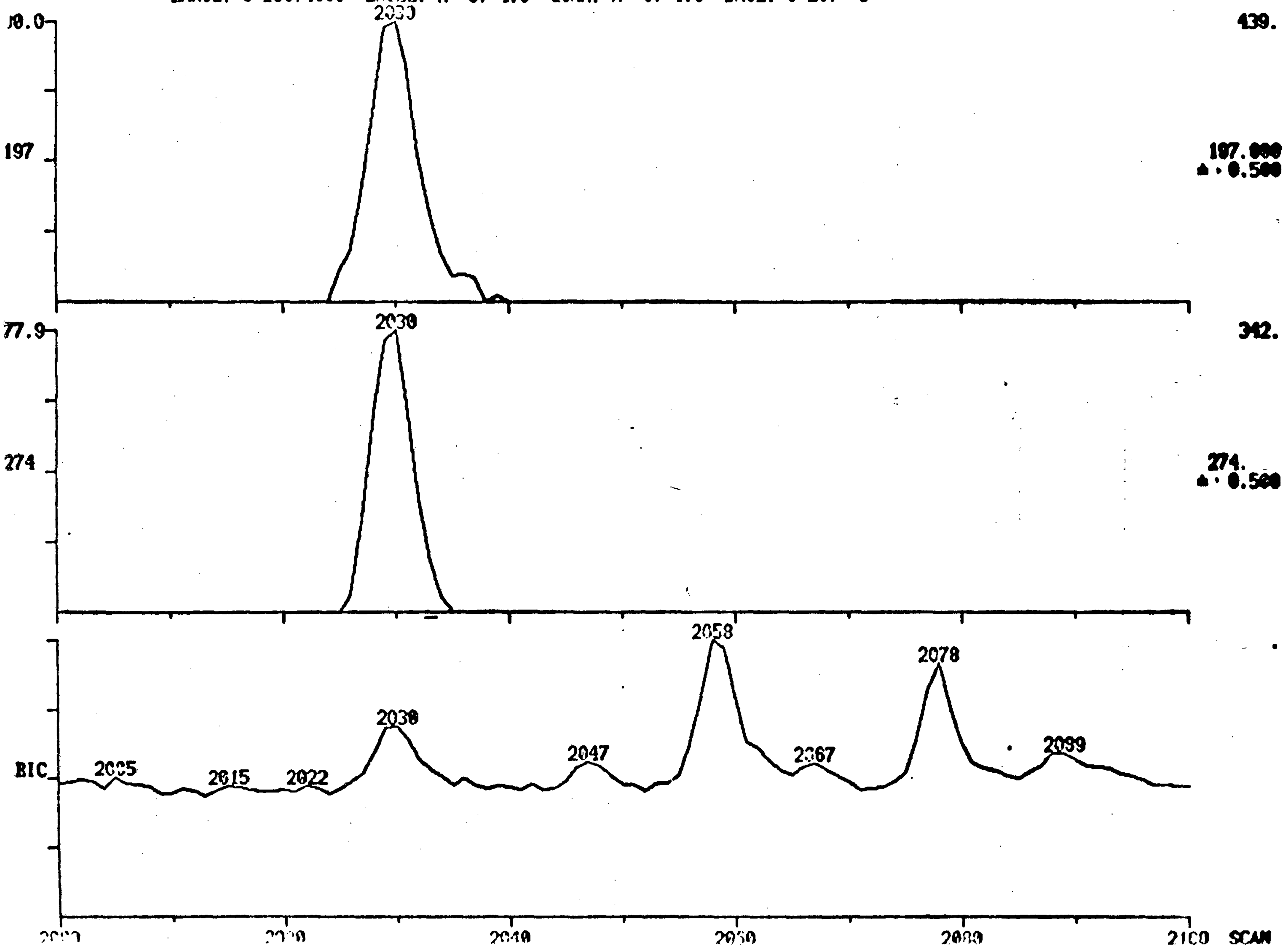


FIGURE 8

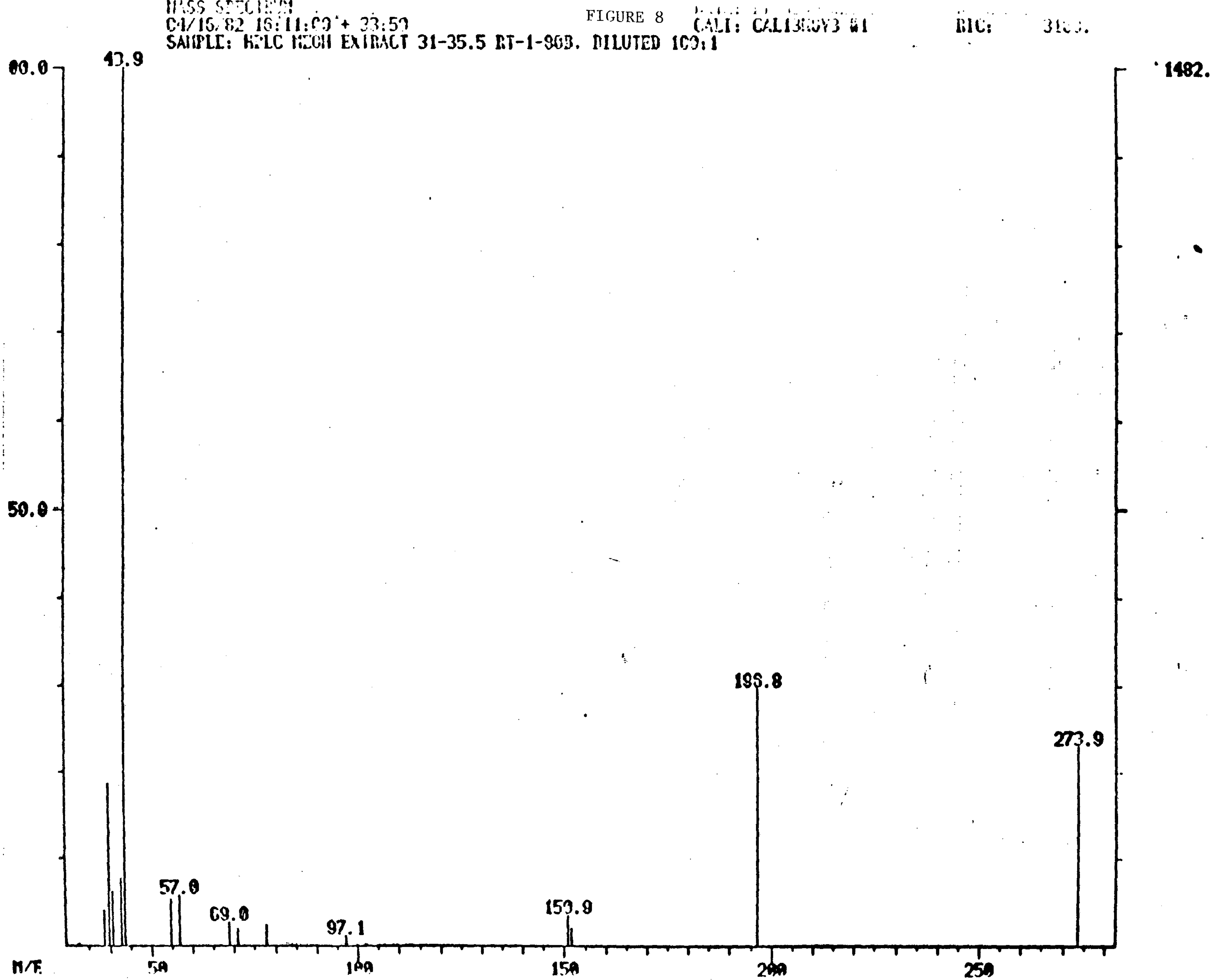

MASS SPECTRUM
04/16/82 16:11:00 + 33:59
SAMPLE: HPLC MEOH EXTRACT 31-35.5 RT-1-90B. DILUTED 100:1
CALI: CALI380Y3 #1
RIC:
1482.
100.0
50.0
43.9
57.0
69.0
97.1
150.9
195.8
273.9
M/E
50
100
150
200
250

FIGURE 9

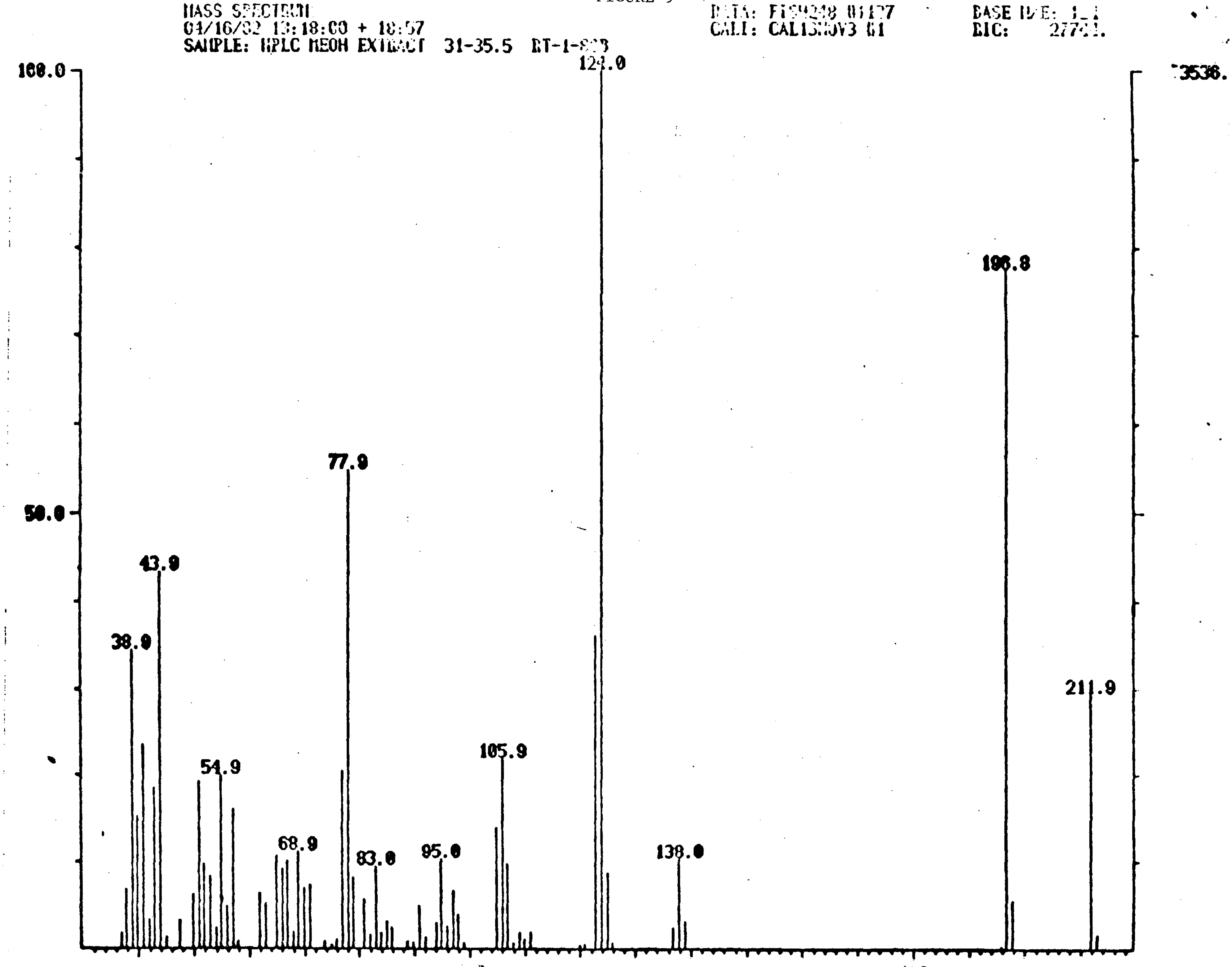
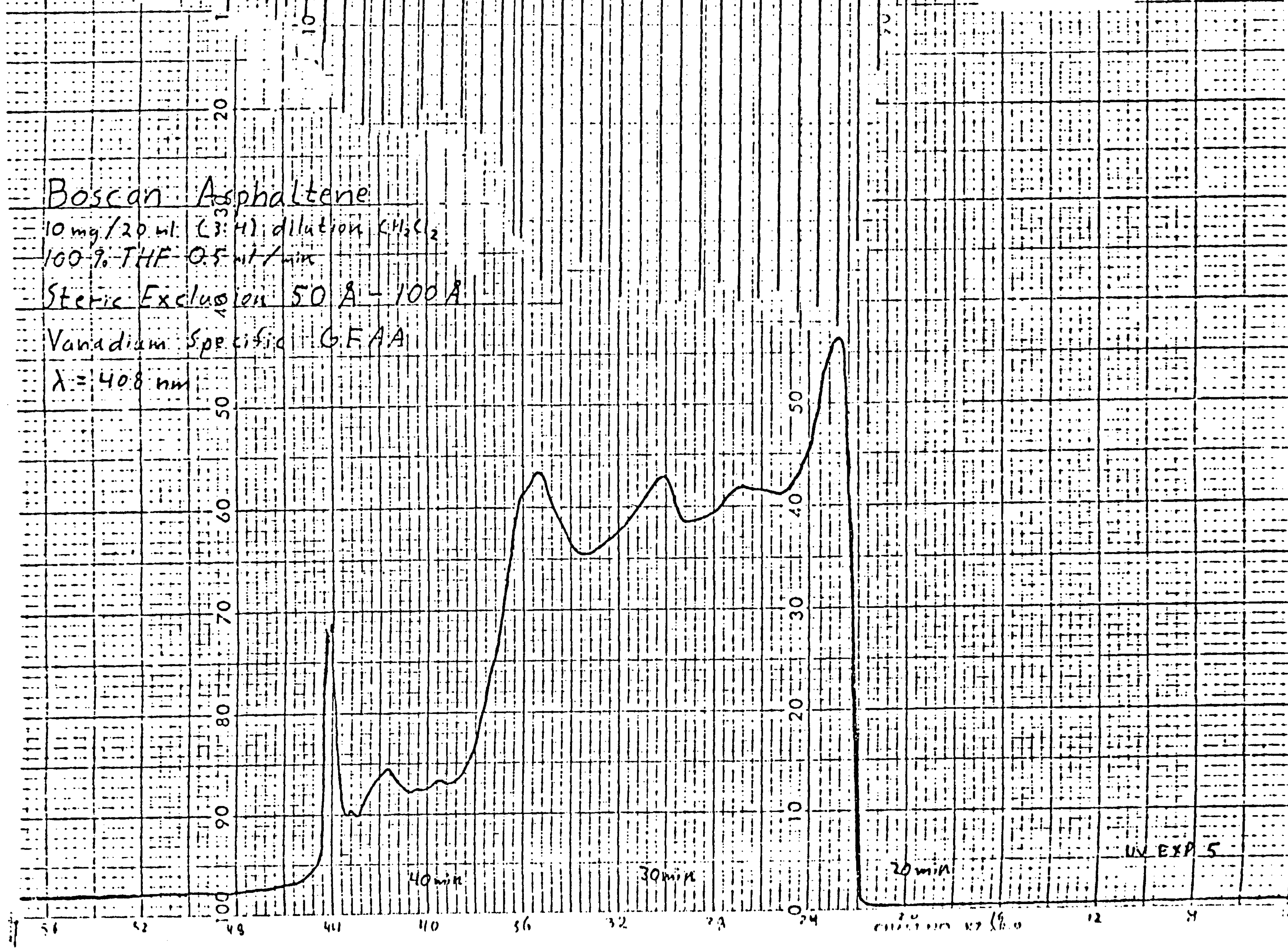
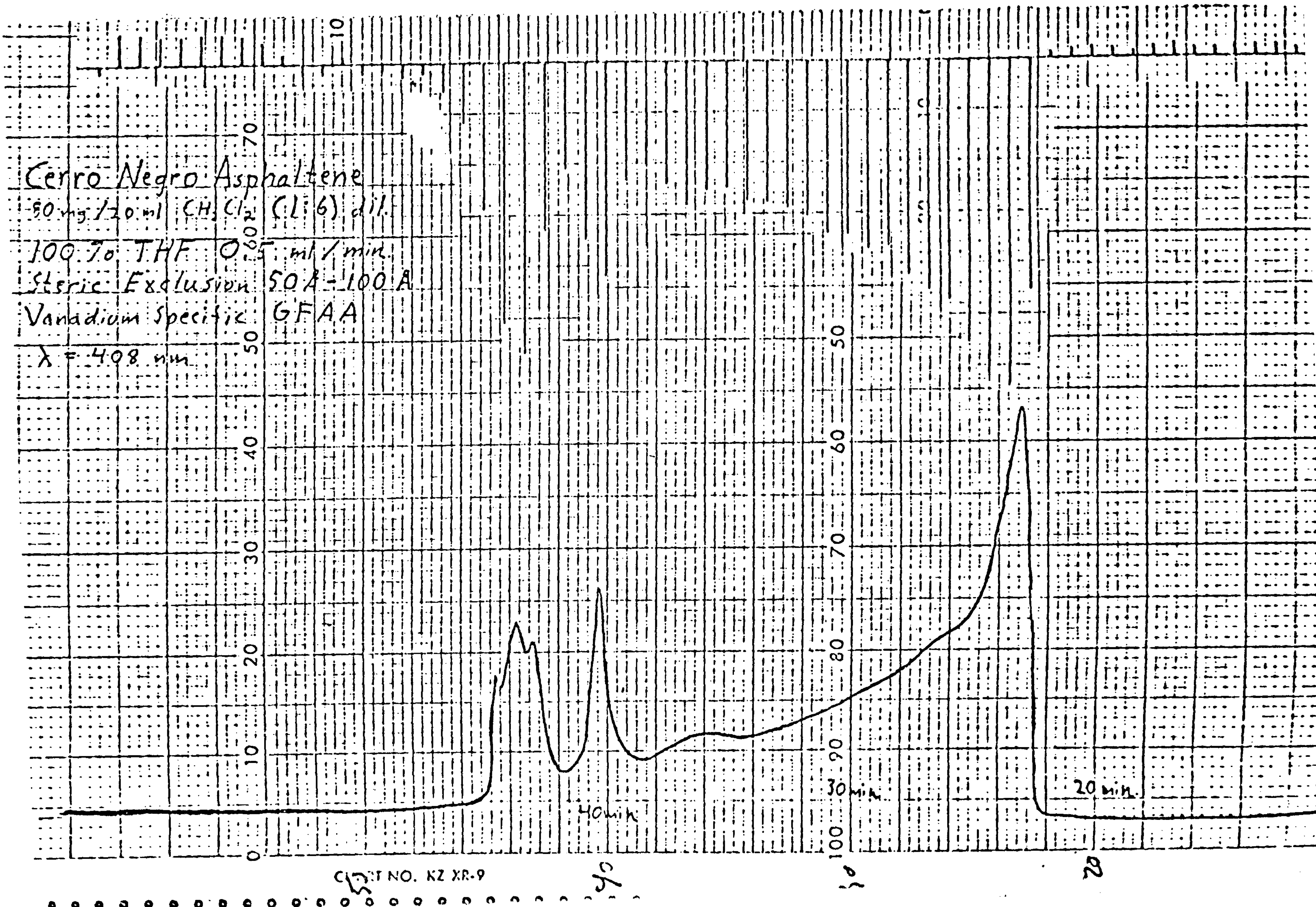

MASS SPECTRUM
04/16/82 13:18:00 + 18:57
SAMPLE: HPLC MEOH EXTRACT 31-35.5
DATA:
CALI:
BASE M/E:
RIC:
100.0
50.0
3536.
124.0
196.8
77.9
43.9
38.9
211.9
54.9
105.9
68.9
83.0
95.0
138.0

FIGURE 10



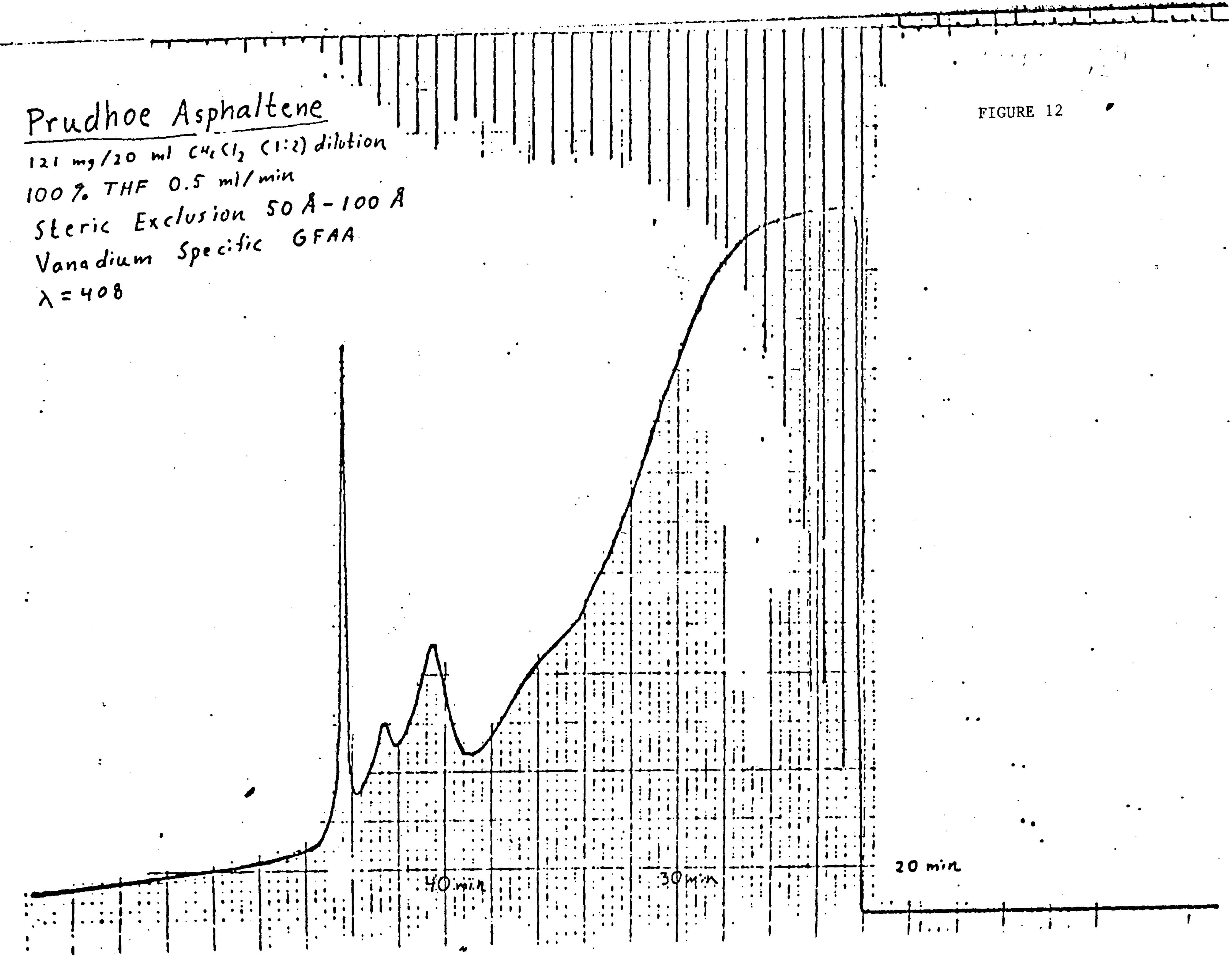
Boscan Asphaltene
10 mg/20 ml (3:H) dilution CH_2Cl_2
100 % THF 0.5 ml/min
Steric Exclusion 50 Å - 100 Å
Vanadium Specific GFAA
λ = 408 nm
40 min
30 min
20 min
UV EXP 5

FIGURE 11



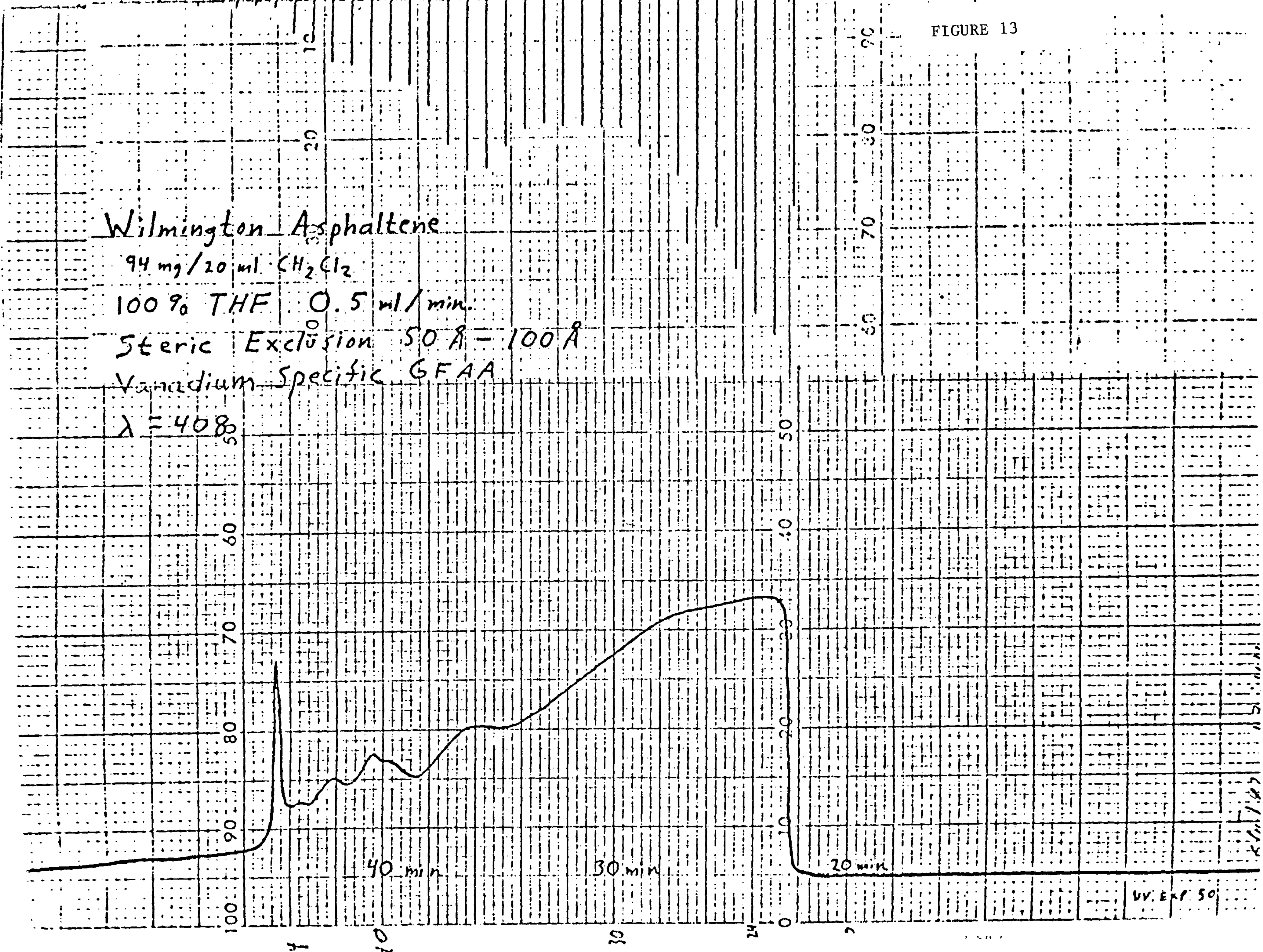
Cerro Negro Asphaltene
50 mg / 20 ml CH_2Cl_2 (1:6) dil.
100 % THF 0.5 ml / min.
Steric Exclusion 50 Å - 100 Å
Vanadium Specific GFAA
λ = 408 nm
20 min.
30 min.
40 min
CHART NO. KZ XR-9

FIGURE 12



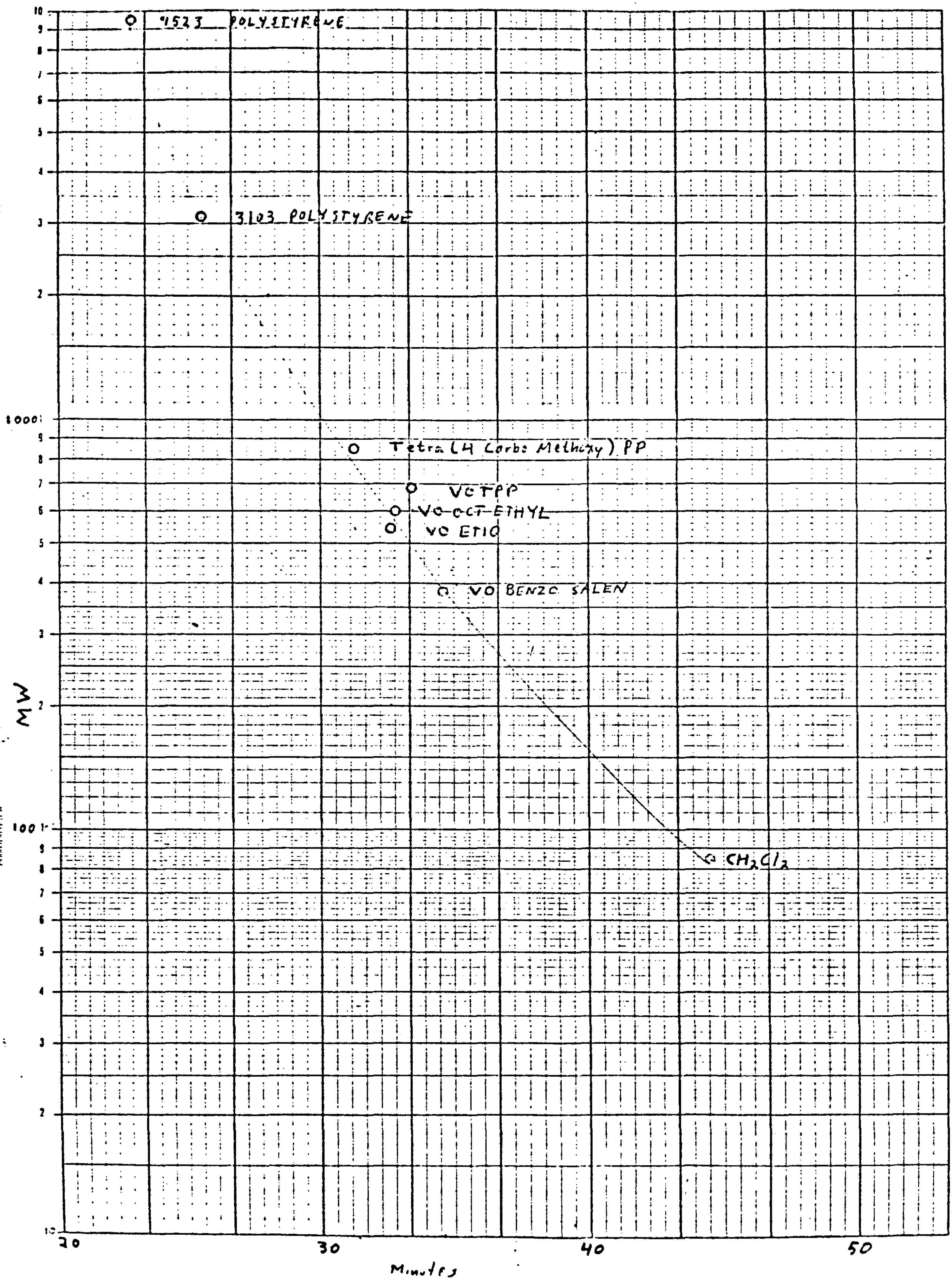
Prudhoe Asphaltene
121 mg/20 ml CH_2Cl_2 (1:2) dilution
100% THF 0.5 ml/min
Steric Exclusion 50 Å - 100 Å
Vanadium Specific GFAA
λ = 408
20 min
30 min
40 min

FIGURE 13



Wilmington Asphaltene
94 mg/20 ml CH2Cl2
100% THF 0.5 ml/min.
Steric Exclusion 50 Å - 100 Å
Vanadium Specific GFAA
λ = 408
40 min
30 min
20 min
UV. Exp 50

FIGURE 14



4523 POLYSTYRENE
3103 POLYSTYRENE
Tetra (4 Carbo Methoxy) PP
VOTPP
VO OCT ETHYL
VO ETIO
VO BENZO SALEN
CH_2Cl_2
MW
Minutes
1000
100
10
20
30
40
50

Table 1

	PPM V in Crude oil	PPM V in Asphaltene	Wt. % of Asphaltene in Crude	% of Total V in Asphaltene
Boscan	1100	4310	23.3	91.3
Cerro Negro	560	1680	25.7	77.1
Wilmington	49	422	7.05	60.7
Prudhoe Bay	19	327	2.75	47.3

Table 2. Vanadium Distribution in Heavy Crude Oils and Ashphaltenes

	Boscan			Cerro Negro			Wilmington			Prudhoe Bay		
	>900[a]	>400 <900	<400	>900	>400 <900	<400	>900	>400 <900	<400	>900	>400 <900	<400
Heavy Crude Oil	527[b] 47.9%[c]	251 23.4%	315 28.7%	298 53.2%	114 20.4%	148 26.4%	25.2 51.4%	9.4 19.1%	14.5 29.5%	11.3 59.7%	4.4 22.9%	3.3 17.4%
Asphaltene	2064[b] 47.9%[c] 91.2%[d]	777 18.0% 70.4%	1468 34.1% 109%	739 44% 63.7%	235 14% 53.0%	706 42% 123%	235 55.6% 70%	60 14.2% 47.9%	127 30.2% 65.7%	228 69.7% 55.5%	32 9.8% 20%	67 20.5% 55%

a) Molecular Weight 900

b) PPM Vanadium

c) Percent of Total Vanadium in Fraction

d) Normalized to the Heavy Crude Oils

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