Title

METAL COORDINATION CHEMISTRY: REMOVAL AND RECOVERY OF METAL COMPOUND FROM HEAVY CRUDE AND SHALE OILS WITH MULTIDENTATE LIGANDS

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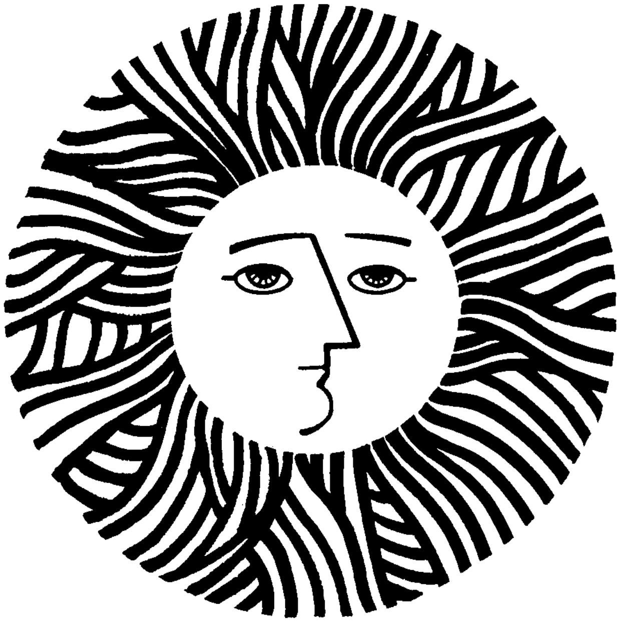
ENERGY & ENVIRONMENT DIVISION



LBID 629

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

Quarterly Progress Report for Period

July 1 - October 1, 1982

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Technical Project Manager: Dexter Sutterfield

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Table of Contents

Introduction 1

Identification of Arsenate in Green River Formation Oil Shale. 2

Synthesis of Vanadyl Non-Prophyrin Compounds as Model Compounds for Speciation Studies in Heavy Crude Oils 3

Analysis of Asphaltenes, Isolated from Heavy Crude Oils, via HPLC-SEC-GFAA for Vanadyl Compounds in the Molecular Weight Range Greater than 2,000 and Less than 400 4

Speciation of Vanadyl Non-Porphyrin in Heavy Crude Oils via HPLC-UV-VIS Fast Scan Analysis 8

Future Work. 9

Acknowledgements 9

References 10

Presentations and Publications 10

Publications 10

Introduction

The identification of organoarsonic acids found in Green River Formation oil shale has provided evidence for the biogeochemical origin of organoarsenic compounds in these fossil fuel precursors. In addition, we report on the identification of arsenate (AsO_4^{3-}), via gas chromatography-mass spectrometry analysis, found in the purified (HPLC) methanol extracts of Green River Formation oil shale. These speciation studies have opened the area of organometallic geochemistry a field hithertofore unexplored.

The identification of vanadyl non-porphyrin compounds in heavy crude oils is of importance to study, since they represent a considerably large percent (>50%) of the vanadium present in these oils.

In order to define these compounds, we needed to have an array of model vanadyl non-porphyrin compounds for comparison to those we separated via HPLC in the heavy crude oils. We thus report the synthesis of several series of vanadyl non-porphyrin that will help elucidate this important class of vanadyl compounds in heavy crude oils.

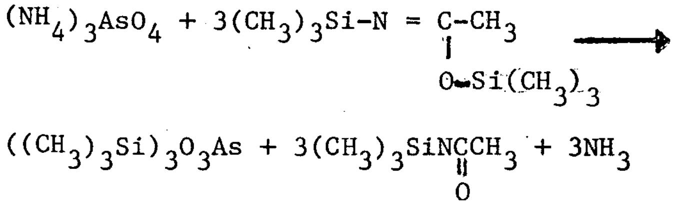
The asphaltenes in the heavy crude oils contain a significant percentage of the vanadium, and thus examination of their vanadyl compound content for porphyrin and non-porphyrin compounds by HPLC-SEC-GFAA analysis would be critical. Additionally, extraction of the asphaltenes with a pyridine/H_2O solution would be helpful in learning more about non-porphyrin vanadyl compounds complexed to the macro-molecular structure of the asphaltenic fraction.

Finally, we will introduce a new concept in speciation of vanadyl porphyrin and non-porphyrin compounds in heavy crude oils and that encompasses the utilization of HPLC separation and a new fast-scan uv-vis detector that provides uv-vis spectra (190-700 nm) on-line of constituents in the oils.

Identification of Arsenate in Green River Formation Oil Shale

In a previous report[1] and a subsequent publication that was recently submitted to Organometallics,[2] we provided unequivocal evidence for the speciation of methyl- and phenylarsonic acids in Green River Formation oil shale.

In order to provide similar data for arsenate (AsO_4^{3-}), we carried out derivatization experiments on an HPLC purified fraction of the total methanol extract. The HPLC purified methanol extract was evaporated, dissolved in water, and placed on a cation exchange column to convert the presumed sodium salt to the ammonium salt. The ammonium salt was lyophilized and reacted with (bistrimethylsilyl) acetamide (Eq. 1):

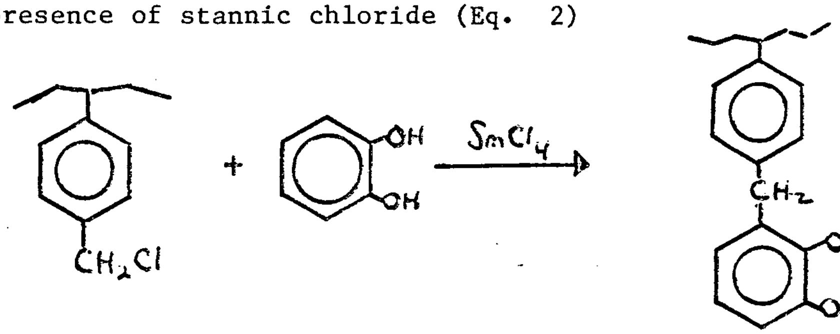


$$\mathrm{(NH_4)_3AsO_4 + 3(CH_3)_3Si{-}N = \underset{\substack{| \\ O{-}Si(CH_3)_3}}{C}{-}CH_3 \longrightarrow} \qquad (1)$$

$$\mathrm{((CH_3)_3Si)_3O_3As + 3(CH_3)_3SiN\underset{\substack{\| \\ O}}{C}CH_3 + 3NH_3}$$

The GC-EIMS analysis of the tris(trimethylsilyl) arsenate showed the reported ions at m/e 75, 147, 193, 207 and 269 (Figure 1) for this $((CH_3)_3SiO_3AsO)$ compound and clearly implicates arsenate as a natural product in Green River Formation oil shale.

In view of these very interesting and exciting results, we are now implementing another stage in our program to find innovative methods to remove the speciated organoarsenic and inorganic arsenic compounds from the shale oil and possibly from the retort waters. In an experiment to determine the feasibility of using polymer-bond catecholes for this purpose, we have initiated an experiment to determine whether 3-methylcatechol can remove methyl- and phenylarsonic acids from their association with Fe and ligands of molecular weight in the 2,000 dalton range[3] in Parahoe shale oil. The results of this experiment are not complete and we will report them in the next quarterly. In addition, synthesis of polymer-bond catechol has also been implemented for studies with authentic organoarsonic acids, i.e., methyl- and phenylarsonic acids. This synthetic method includes reaction of chloromethylated polystyrene-divinylbenzene polymer (20 oz. cross-linked) with catechol in the presence of stannic chloride (Eq. 2)



(2)

Synthesis of Vanadyl Non-Porphyrin compounds as Model Compounds for Speciation Studies in Heavy Crude Oils

The identification of Vanadyl non-porphyrin compounds, known to be present in heavy crude oils, is of the utmost importance if we are to use multidentate ligands to remove vanadyl ion from these oils. Additionally, these compounds may be responsible for the poisoning of catalysts used to upgrade these future fuel sources.

With this approach in mind, we needed to have a variety of vanadyl non-porphyrin compounds for the speciation studies. This quarter we initiated a synthesis program to generate these compounds and the following vanadyl non-porphyrin compounds were synthesized. (Chart 1)

These compounds are being tested to determine if they are constituents in the heavy crude oils Cerro Negro, Boscan, Wilmington and Prudhoe Bay via HPLC-UV-Vis Fast Scan analysis (see below).

Analysis of Asphaltenes, Isolated from Heavy Crude Oils, via HPLC-SEC-GFAA for Vanadyl Compounds in the Molecular Weight Range Greater than 2,000 and Less than 400.

During this quarter, work has continued with the asphaltenes of Boscan, Cerro Negro, Wilmington, and Prudhoe Bay heavy crude oils. Separation of the oils is achieved by agitating samples of oil in 10 volumes of pentane at about 300 motions per minute for 24 hours. Separations have also been made using heptane as the solvent, but these samples have not yet been analyzed. The asphaltenes are separated from the pentane solubles with a 0.45 micron millipore filter, washed with pentane and stored under nitrogen. X-ray fluorescence analysis for vanadium has been performed and compared with earlier results for whole crude oils (Table 1). A significant percentage of the vanadium in the oils is contained in the asphaltenes. The precentage of vanadium in the asphaltenes is not directly proportional to the amount of asphaltenes present in an oil and although the asphaltenes represent less than 3 percent of the weight of a crude they still account for almost half of the vanadium present.

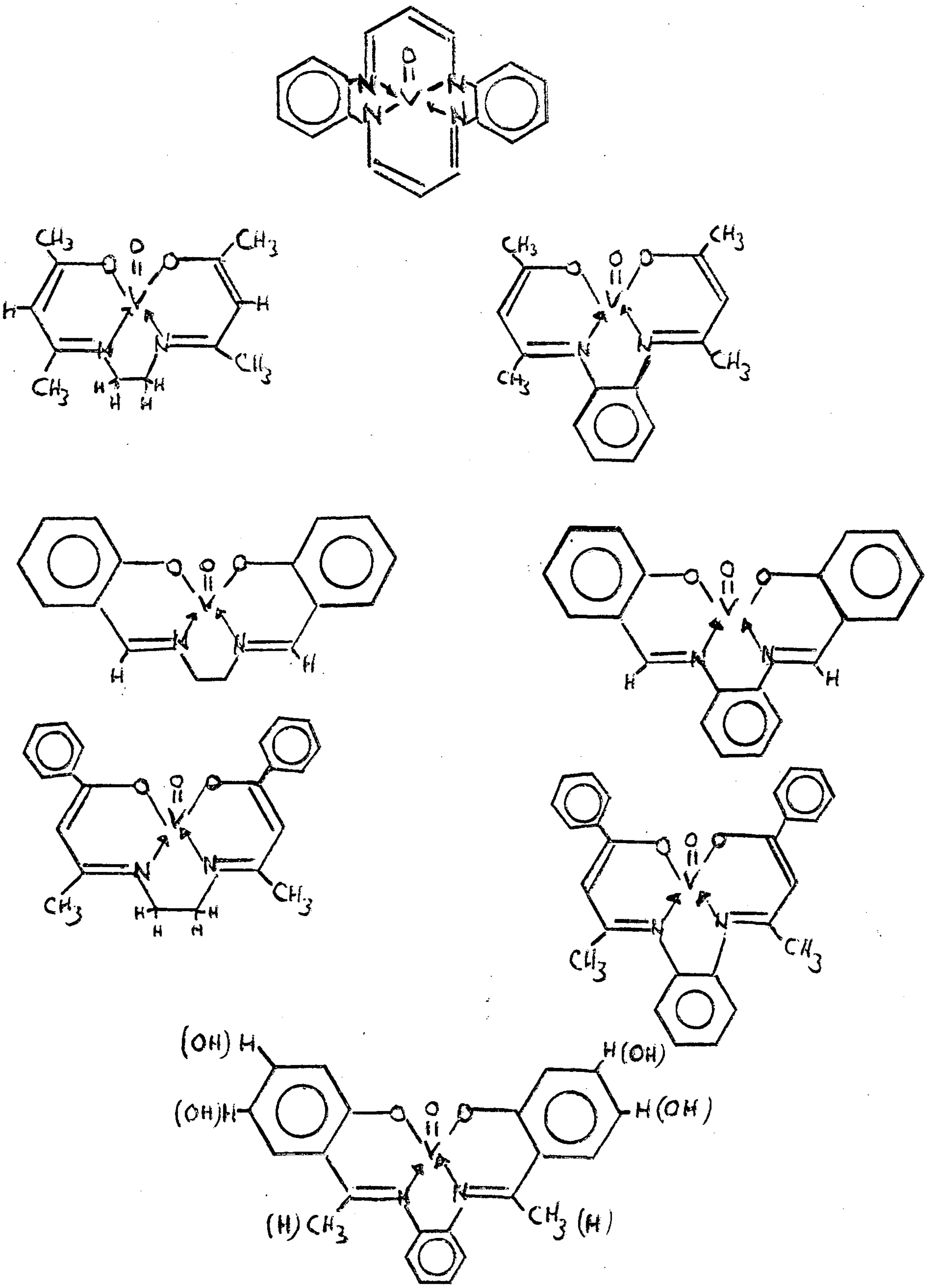


Chart 1: Vanadyl Non-Porphyrin Compounds Synthesized for Speciation Studies

Samples of the asphaltenes are redissolved in methylene chloride and analyzed by HPLC-SEC-GFAA using 50Å and 100Å SEC columns in series with element-specific vanadium detection at 318.4 nm. The visible detector was set at 408 nm to detect the soret bands of vanadyl porphyrins. The extraction and analysis procedure was repeated three times for each oil. Figures 2-5 show typical SEC results and Figure 6 is a calibration curve for the HPLC-GFAA. Following the usual procedure the asphaltenes were separated into four fractions by molecular weight: greater than 2000, less than 2000 but greater than 900, less than 900 but greater than 400, and less than 400. The third fraction is assumed to be rich in vanadyl porphyrins. Table 2 shows the asphaltenes compared with the whole heavy crude. It can be seen that the percentage of vanadium in the less than 900, greater than 400 molecular weight fraction is much lower for the asphaltenes. This does not mean that there are less porphyrins in the asphaltenes, but may indicate that the asphaltenic porphyrins are incorporated into larger complexes since there is intense visible absorption in the highest molecular weight fraction.

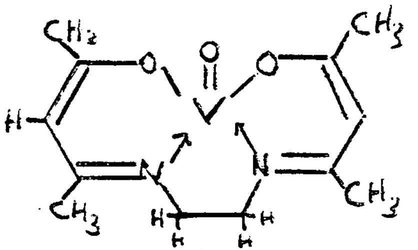
The pentane soluble, malthene, fractions of the oils were vacuum distilled to remove the pentane and then dissolved in methylene chloride for HPLC-SEC-GFAA analysis. The bottom line of Table 3 shows the molecular weight distribution of vanadium in the malthenes. Figures 7-10 show typical vanadium distributions for the malthenes of the four oils. By comparing the asphaltenes and malthenes with their whole oils, it can be observed, in general, that the asphaltenes are richer in the high molecular weight vanadium compounds and the malthenes are richer in vanadium in the two middle molecular weight ranges. The heavier vanadium concentrations in the very highest and very lowest molecular weight fractions of the asphaltenes conforms well with the concept of asphaltenes as large molecules with smaller molecules encapsulated within them. It is also interesting to note that Boscan crude, which has the highest asphaltenic vanadium concentration of the four oils studied, has an asphaltenic vanadium distribution which is very similar to the vanadium distribution of the whole crude oil. The four oils can also be divided into two groups: high asphaltene oils, including Boscan and Cerro Negro, and low asphaltene oils, including Wilmington and Prudhoe Bay. The high asphaltene oils have similar molecular weight distributions of vanadium in their asphaltenes and whole oils and have similar percentages of vanadium in the highest and lowest molecular weight ranges of the asphaltenes. The low asphaltene oils have more extreme variations in vanadium distribution between the asphaltenes and the whole oils and have significantly greater vanadium concentration in the greater than 2000 range than in the less than 400 range. The second feature is especially pronounced in the lowest asphaltene oil, Prudhoe Bay, which has 57 percent of its vanadium in the greater than 2000 range and only 17 percent in the less than 400 range.

Work has also been done on attempts to isolate vanadyl porphyrins from the asphaltenes. Following a procedure similar to that used by several other researchers, the asphaltenes were dissolved in xylene and extracted with a pyridine-water solution (Figures 11 and 12). The extracts have a strong absorbance at 408 nm, which is typical for vanadyl porphyrins. Of the four crude oils, only Boscan and Cerro Negro gave extracts with sufficiently large vanadium concentrations to make GFAA analysis possible. Analysis suing the HPLC-SEC-GFAA combination showed that a substantial portion of the vanadium compounds present in these two extracts were at a molecular weight too small for porphyrins (Table 3). Further analysis with a second HPLC system equipped with an amino-cyano column and a rapid scanning UV-VIS detector has established the presence of several vanadyl non-porphyrin compounds in the pyridine-water extract and future work will emphasize characterizing these vanadyl non-porphyrin compounds. When the Boscan extract was filtered to remove particles insoluble in pyridine and water, a large enough sample was recovered to allow HPLC-SEC-GFAA analysis. As can be seen from Table 3 and Figure 13 the non-pyridine-water soluble vanadium compounds are concentrated in the greater than 2000 molecular weight range.

Speciation of Vanadyl Non-Porphyrin in Heavy Crude Oils via HPLC-UV-VIS Fast Scan Analysis

A new detector has been acquired and has the potential of being able to help define the vanadyl non-porphyrin compounds thought to be present in large concentrations in most heavy crude oils. This detector, for our HPLC separated vanadyl compounds, is able to give UV-Vis spectra in the range of 190-700 nm for any compound or cluster of compounds eluting from an HPLC column.

We have used the fast scan detector to tentatively identify two vanadyl non-porphyrin compounds present in Prudhoe Bay and Boscan crude oils. By comparing the retention times of the authentic vanadyl non-porphyrin compounds, 1 and 2, with those in the crude oils and also comparing their respective UV-Vis spectra, we have been able to ascertain their possible presence in these heavy crude oils.



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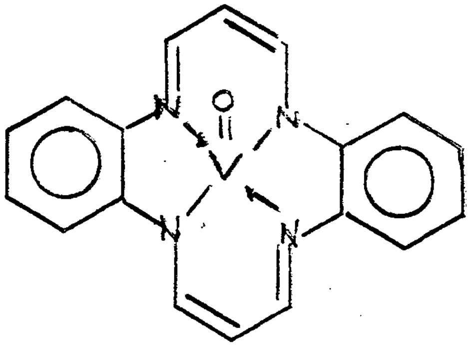


2

The obvious importance of this HPLC detector in future speciation studies can be seen in these preliminary results. In addition, we have connected the fast scan detector to the Apple II computer for on-line acquisition of the recorded UV-Vis spectra and will report on this in subsequent papers.

Future Work

We are concentrating on the polymer-bond catechols for initial studies with both methyl- and phenylarsonic acids. These studies will be eventually extended to removing these compounds from shale oils.

The speciation of vanadyl non-porphyrin compounds in asphaltenes from heavy crude oils and the oils themselves are continuing.

Acknowledgements

I would like to thank John Vollmer, Ann Strong, Angela Ausban, Maria Ferre, Raja Tannous, John Komlenic, Arne Thormodsen and Brian Wines for contributing experimental results for this quarterly report.

References

(1) R.H. Fish, LBID 566 Report to Bartlesville Energy Technology Centor April 1 - July 1, 1982.

(2) R.H. Fish, W.S. Walker, R.S. Tannous, C.S. Weiss and F.E. Brinckman, Organometallics (submitted for publication) 1982.

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

Presentations and Publications

The following presentations will be given at the Pacific Conference on Chemistry and Spectroscopy Oct. 27-29, 1982 in San Francisco, CA, in the Organometallic Chemistry Section chaired by R.H. Fish.

(1) Homogeneous Catalytic Hydrogenation of Polynuclear Heteroaromatic Nitrogen Compounds using Transition Metal Hydride, A.D. Thormodsen and R.H. Fish.

(2) The Synthesis of an Encapsulated Arsenic Anion by Reaction of Arsenate (AsO_4^{3-}) with a Linear Catechol Amide - 3,4-LICAM, R.S. Tannous and R.H. Fish

(3) Molecular Characterization of Vanadyl (VO^{2+}) Compounds in Heavy Crude Oil Asphaltenes, B.K. Wines, J.J. Komlenic and R.H. Fish.

Publications

R.H. Fish, R.S. Tannous, W.S. Walker, C.S. Weiss and F.E. Brinckman, Organometallic Geochemistry. 1. Isolation and Identification of

Organoarsenic Compounds from Green River Formation Oil Shale (submitted to Organometallics).

TABLE 1

	ppm V in Crude Oil	ppm V in Asphaltene	Wt. % of Asphaltene in Crude	% of Total V in Asphaltene
Boscan	1100	4310	25	98
Cerro Negro	560	1680	20	60
Wilmington	49	422	6.2	53
Prudhoe Bay	19	280	2.9	43

TABLE 2

Vanadium Distribution in Whole Crude Oils, Asphaltenes, and Malthenes
(by % of Vanadium in whole sample)

	BOSCAN				CERRO NEGRO				WILMINGTON				PRUDHOE BAY			
	>2000[a]	2000 900	900 400	<400	>2000	2000 900	900 400	<400	>2000	2000 900	900 400	<400	>2000	2000 900	900 400	<400
Whole Crude Oil	28	20	23	29	31	22	20	26	31	29	23	17	28	23	19	30
Asphaltene	33	19	19	29	34	16	26	34	37	16	27	30	56	15	12	17
Malthene	29	24	27	21	33	26	25	16	18	32	32	17	23	34	30	13

[a] molecular weight

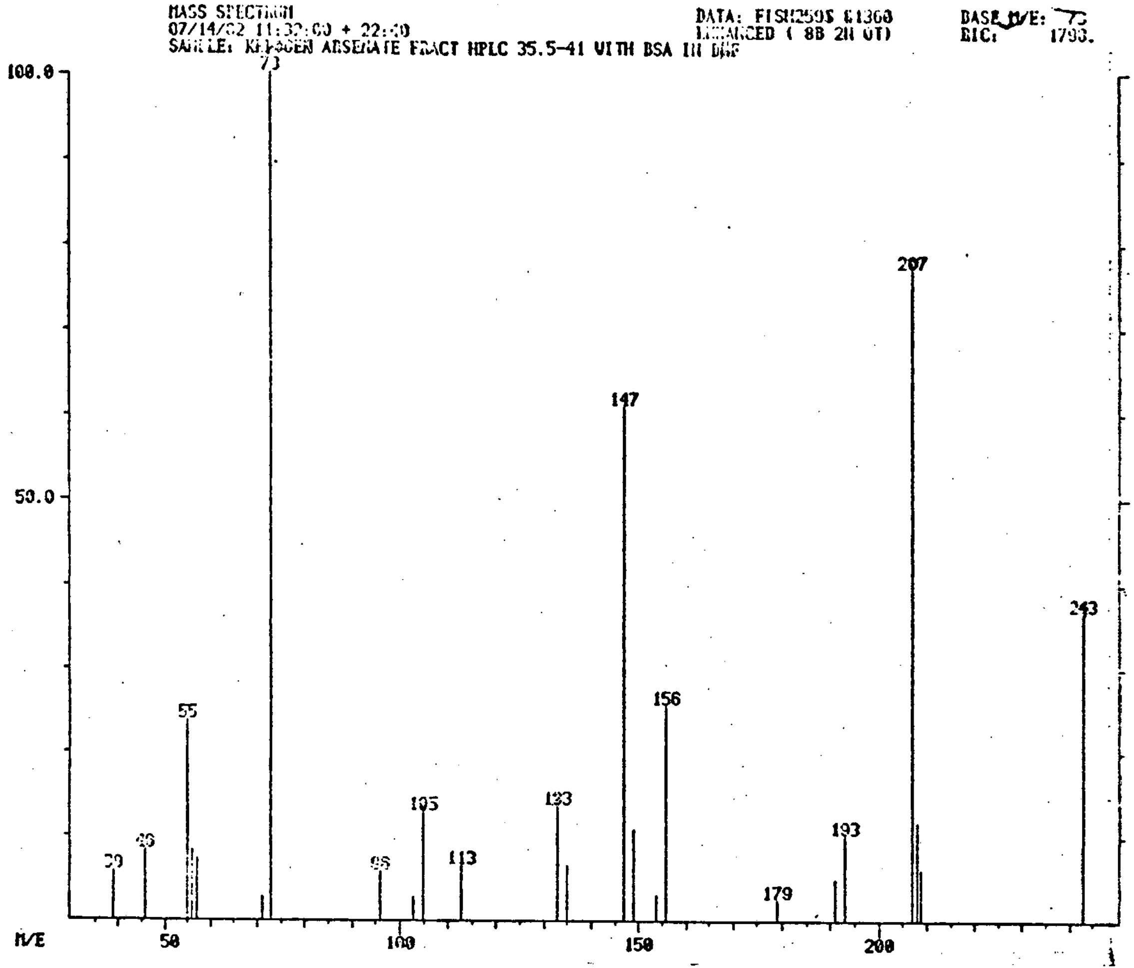
TABLE 3

Vanadium Distribution in Pyridine-Water Extracts of Asphaltenes

Vanadium distribution by MW (% of total V)

Sample	>2000	<2000 >900	<900 >400	<400
Boscan Extract	4	18	39	39
Cerro Negro Extract	4	20	36	40
Boscan Filtrate	54	24	12	10

Figure 1


MASS SPECTRUM
07/14/82 11:32:00 + 22:40
SAMPLE: KEROGEN ARSENATE FRACT HPLC 35.5-41 WITH BSA IN DMF
DATA: FISH259S G1360
ENHANCED (8B 2N 0T)
BASE M/E: 73
RIC: 1793.
100.0
50.0
M/E
50
100
150
200
39
46
55
73
96
105
113
133
147
156
179
193
207
243

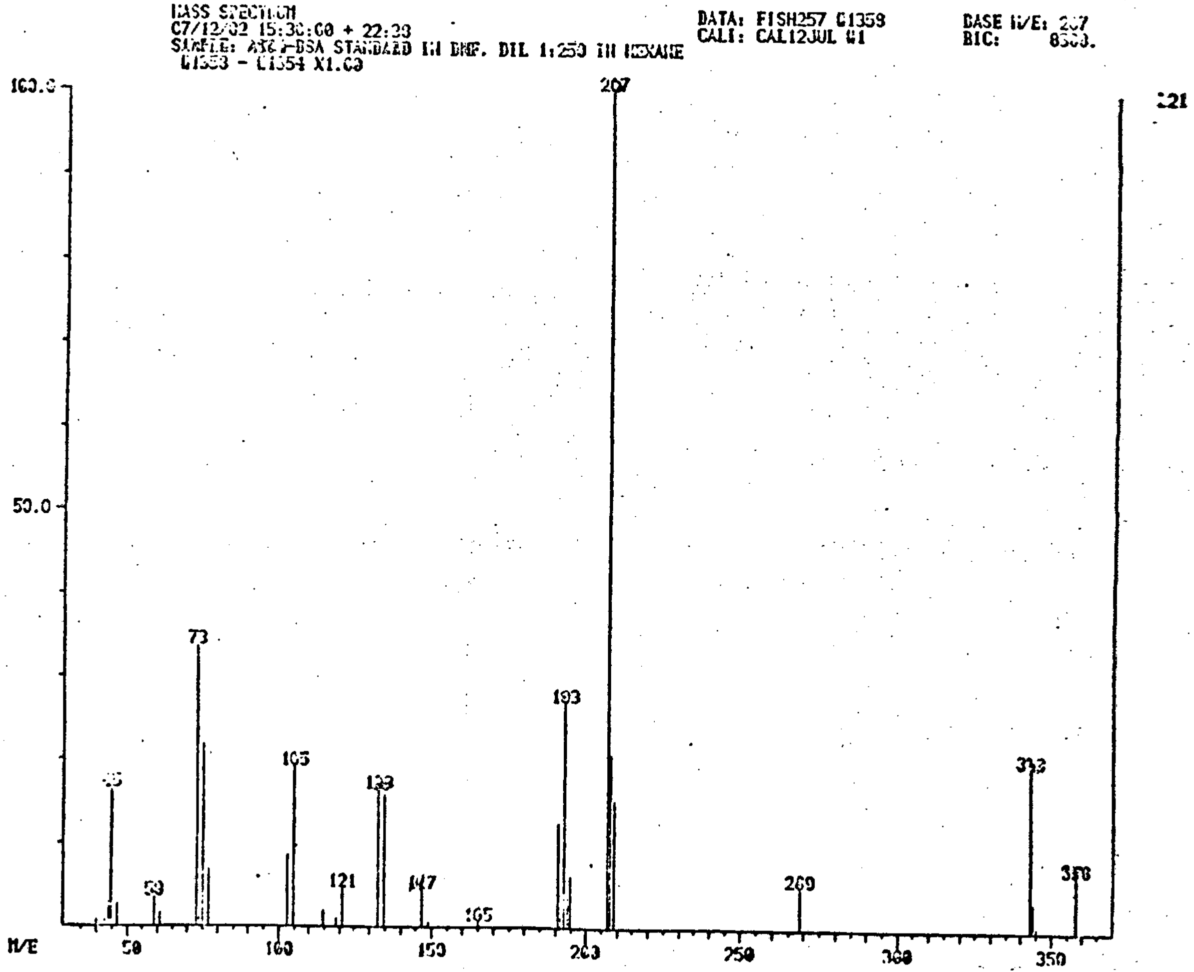

MASS SPECTRUM
07/12/82 15:30:00 + 22:30
SAMPLE: AS(?)-BSA STANDARD IN DMF. DIL 1:250 IN HEXANE
G1353 - G1354 X1.00
DATA: FISH257 G1359
CALI: CAL12JUL #1
BASE M/E: 207
RIC: 8500.
100.0
50.0
M/E
50
100
150
200
250
300
350
45
59
73
105
121
133
147
165
193
207
269
343
358
421

Figure 2

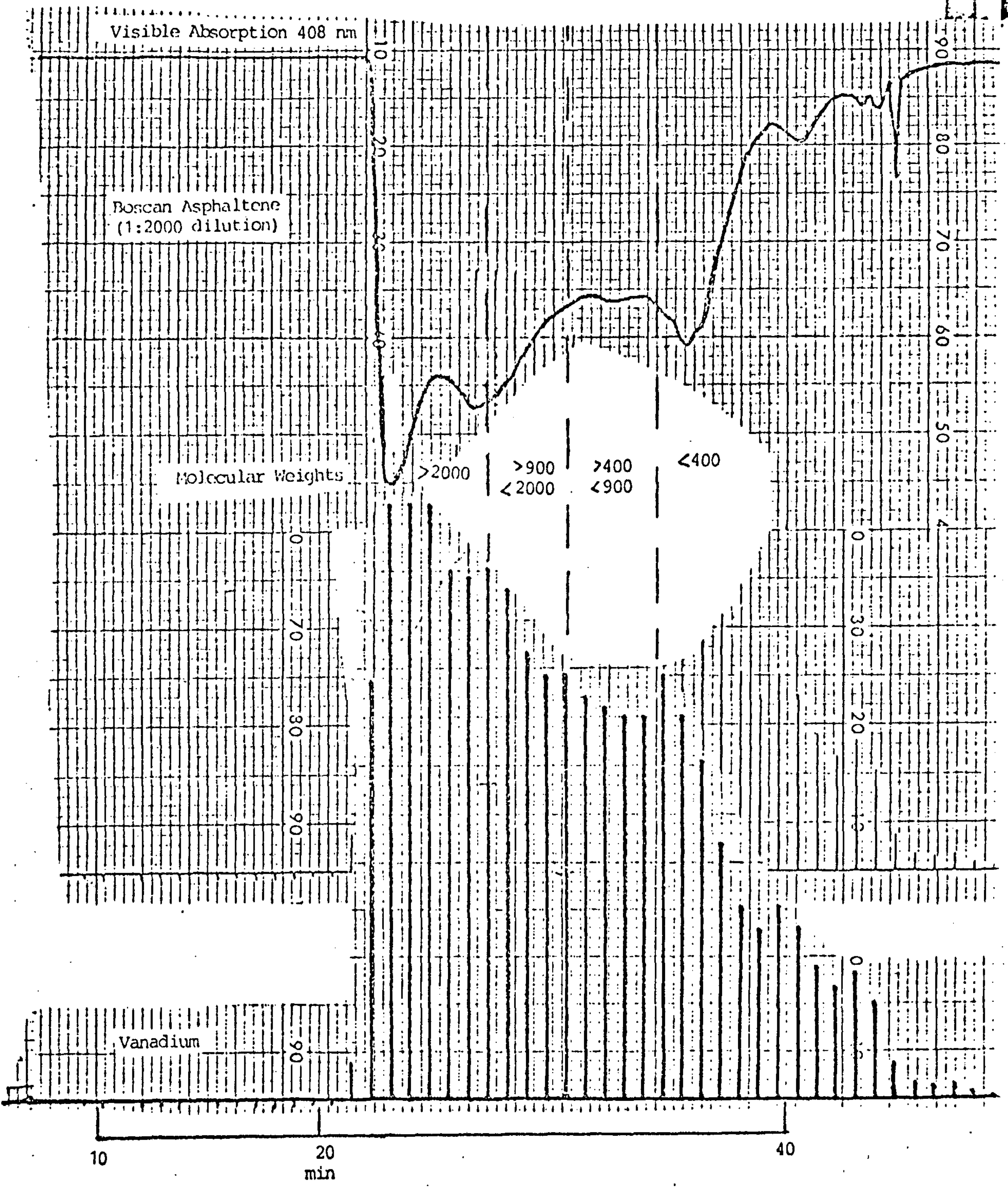

Visible Absorption 408 nm
Boscan Asphaltene
(1:2000 dilution)
Molecular Weights
>2000
>900
<2000
>400
<900
<400
Vanadium
10
20
30
40
50
60
70
80
90
0
70
30
90
0
30
20
10
0
90
10
20
40
min

Figure 3

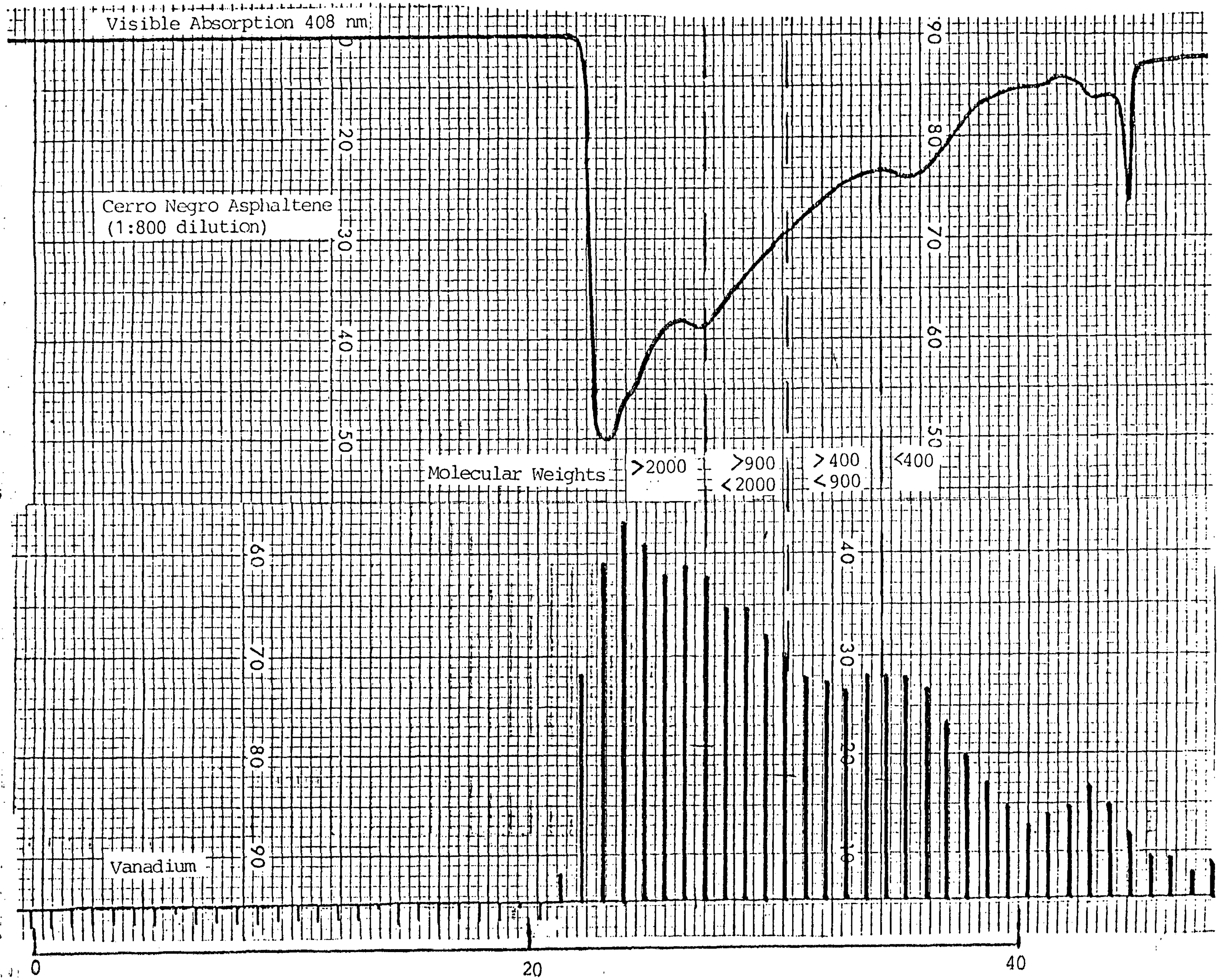
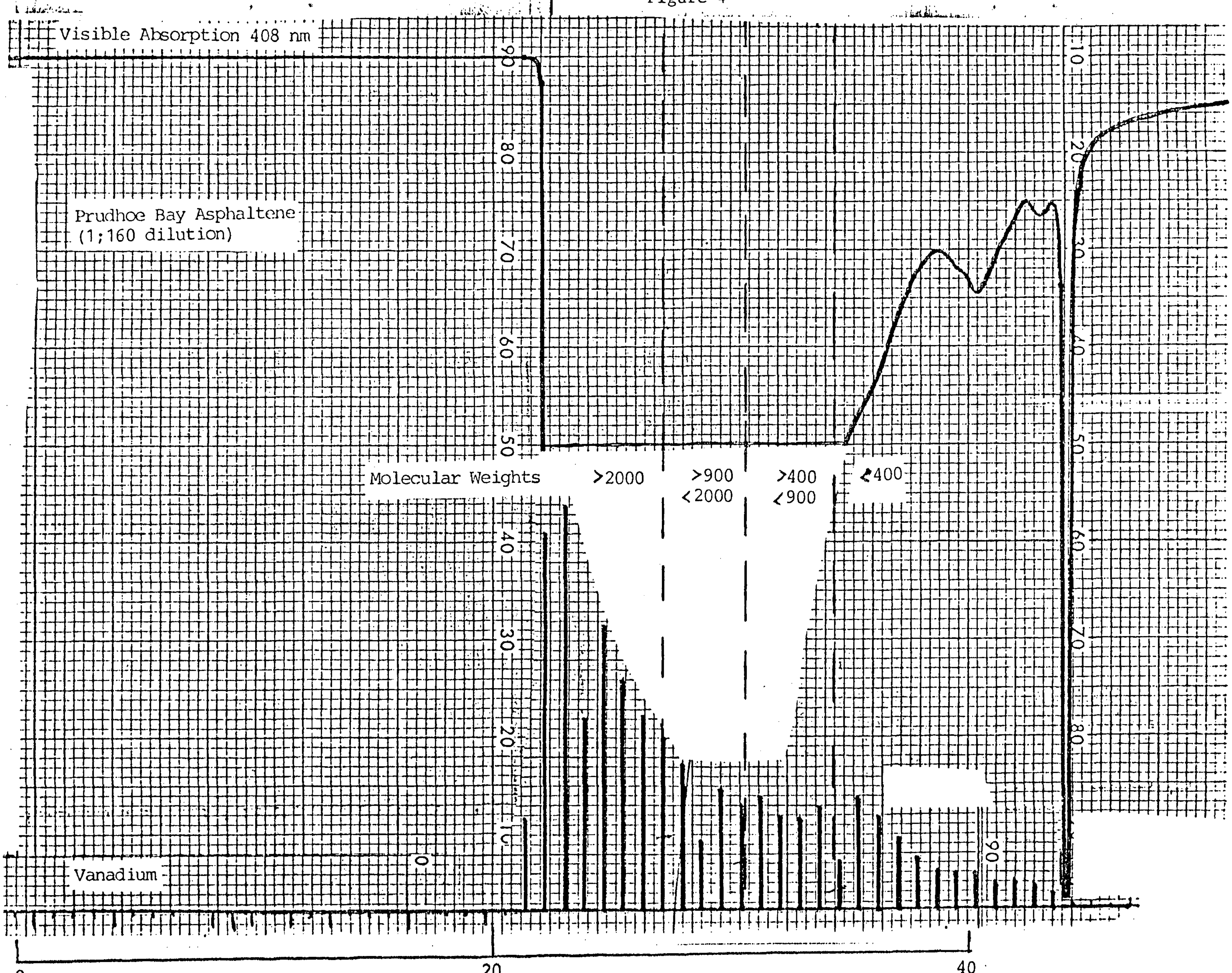

Visible Absorption 408 nm
Cerro Negro Asphaltene
(1:800 dilution)
Molecular Weights
>2000
>900
<2000
>400
<900
<400
Vanadium
0
20
30
40
50
90
80
70
60
50
60
70
80
90
40
30
20
10
0
20
40

Figure 4



Visible Absorption 408 nm
Prudhoe Bay Asphaltene
(1;160 dilution)
Molecular Weights
>2000
>900
<2000
>400
<900
<400
Vanadium
90
80
70
60
50
40
30
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90
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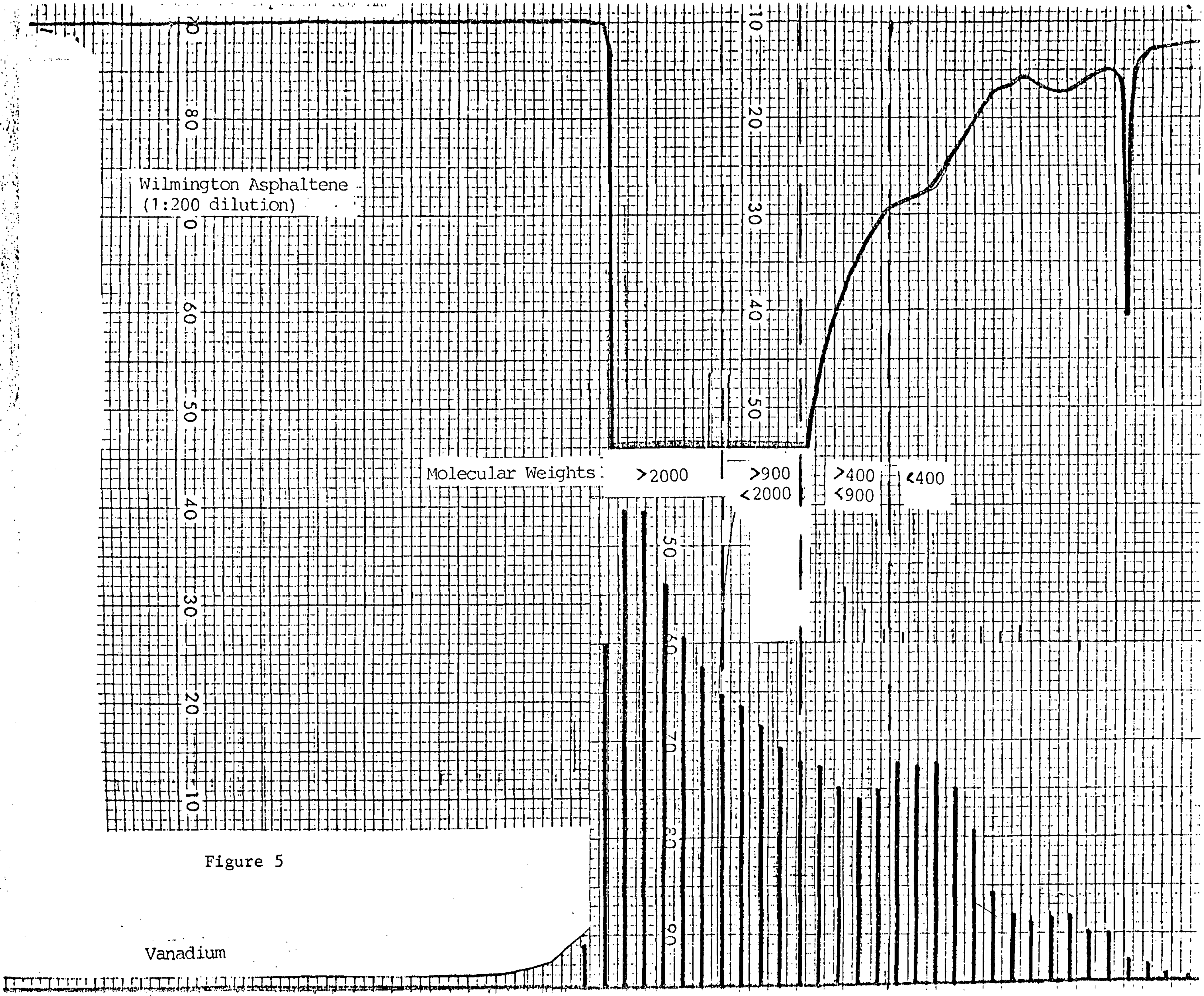
Wilmington Asphaltene
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Molecular Weights
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>900
<2000
>400
<900
<400
Vanadium
90
80
70
60
50
40
30
20
10
10
20
30
40
50
50
60
70
80
90

Figure 5

Figure 6

SEC CALIBRATION CURVE: 50 Å AND 100 Å COLUMNS IN SERIES

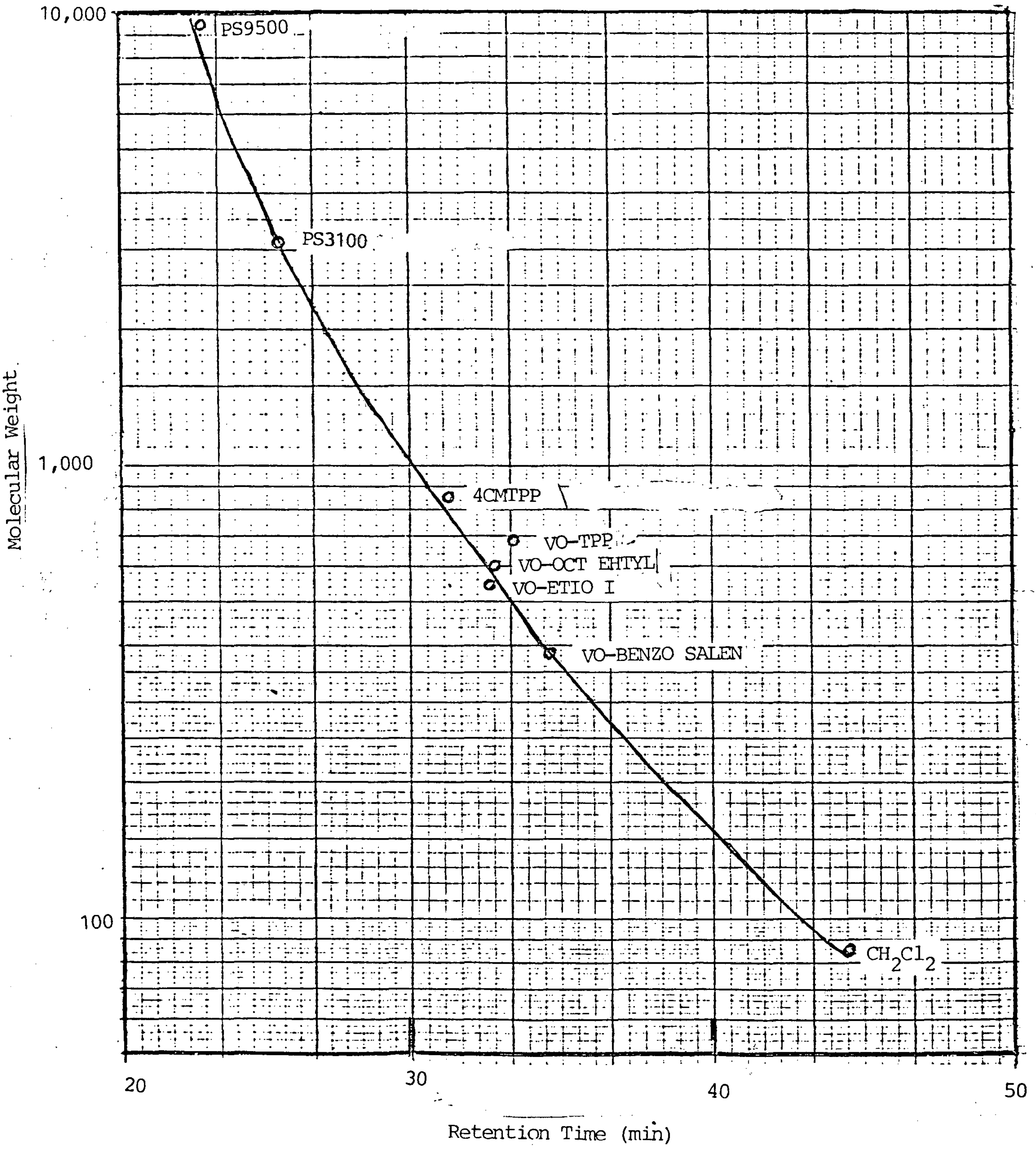
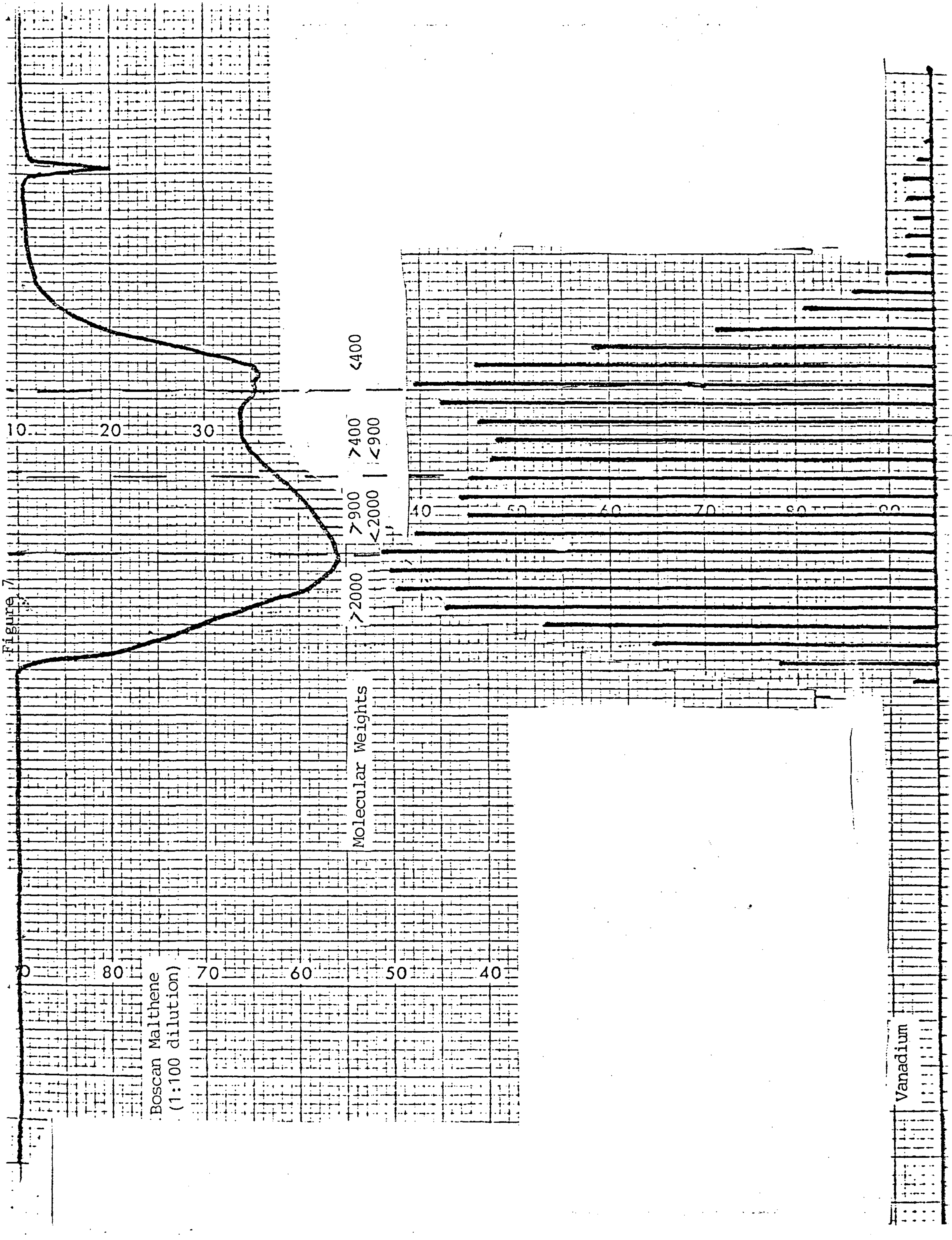


Figure 7


Boscan Malthene
(1:100 dilution)
Vanadium
Molecular Weights
<400
>400
<900
>900
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>2000
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30
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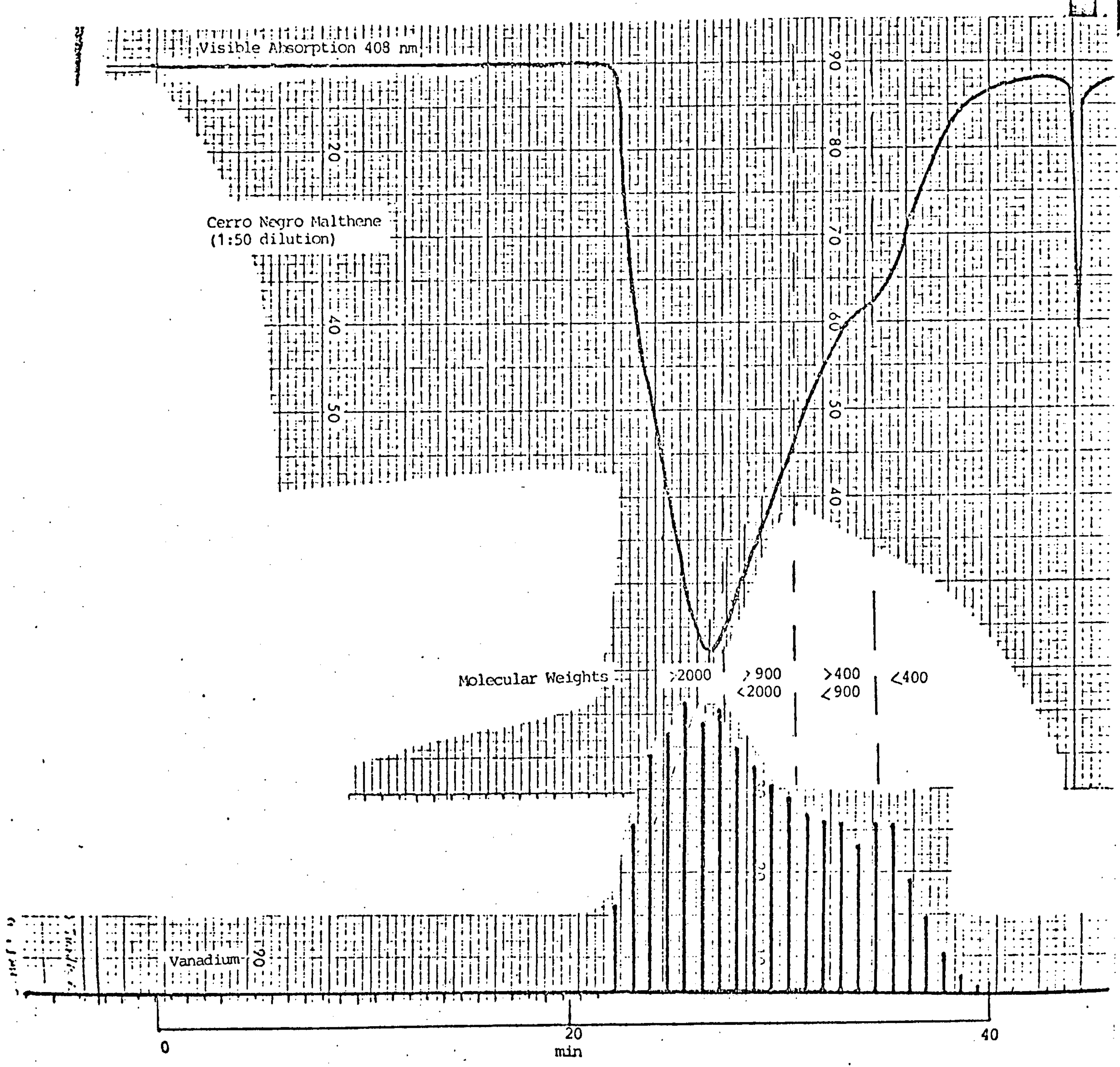
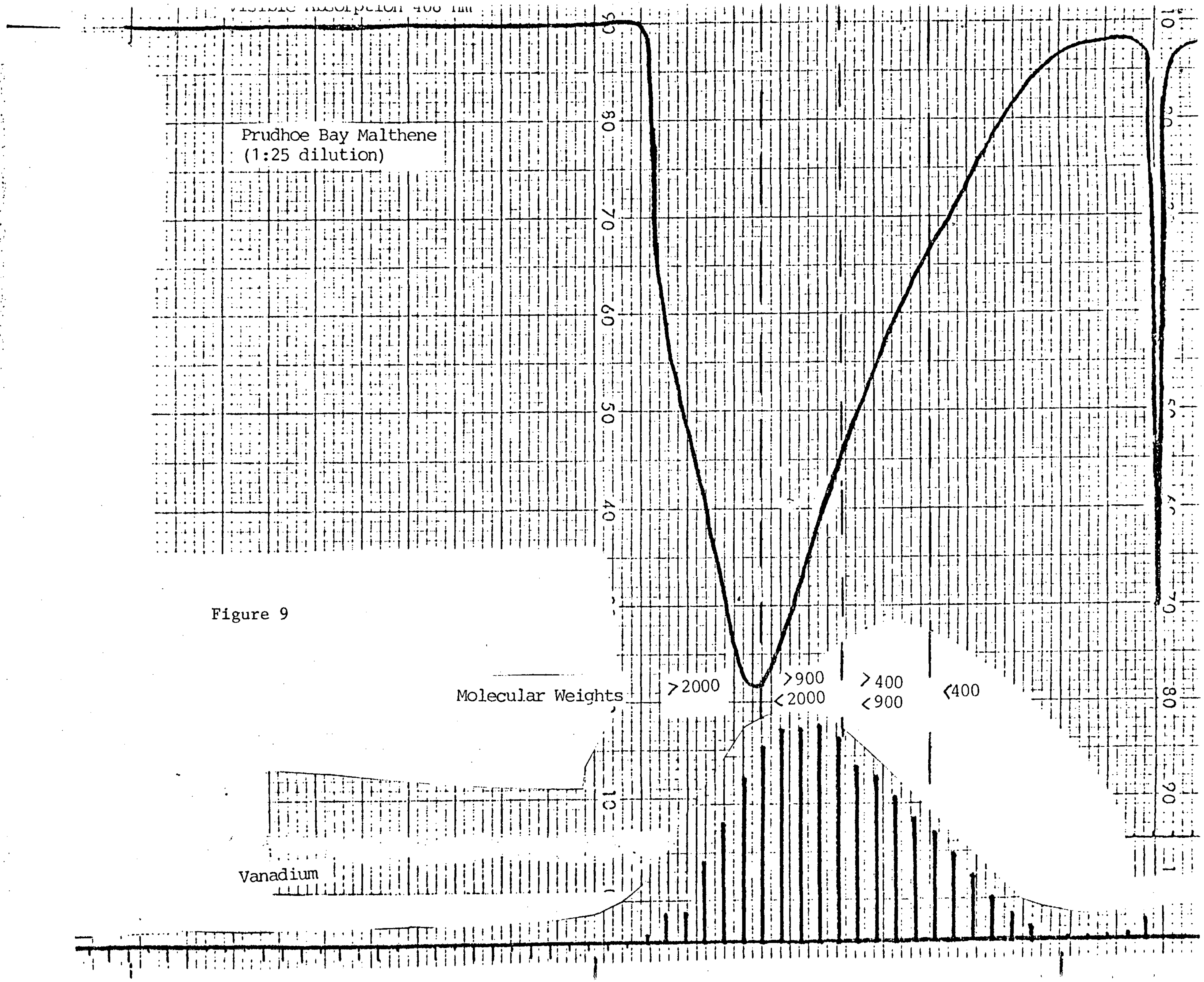
80
70
60
50
40

Figure 8


Visible Absorption 408 nm
Cerro Negro Malthene
(1:50 dilution)
Molecular Weights
>2000
>900
<2000
>400
<900
<400
Vanadium
0
20
40
min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Prudhoe Bay Malthene
(1:25 dilution)
Molecular Weights
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>900
<2000
>400
<900
<400
Vanadium
90
80
70
60
50
40
10
20
50
60
70
80
90

Figure 9

Figure 10

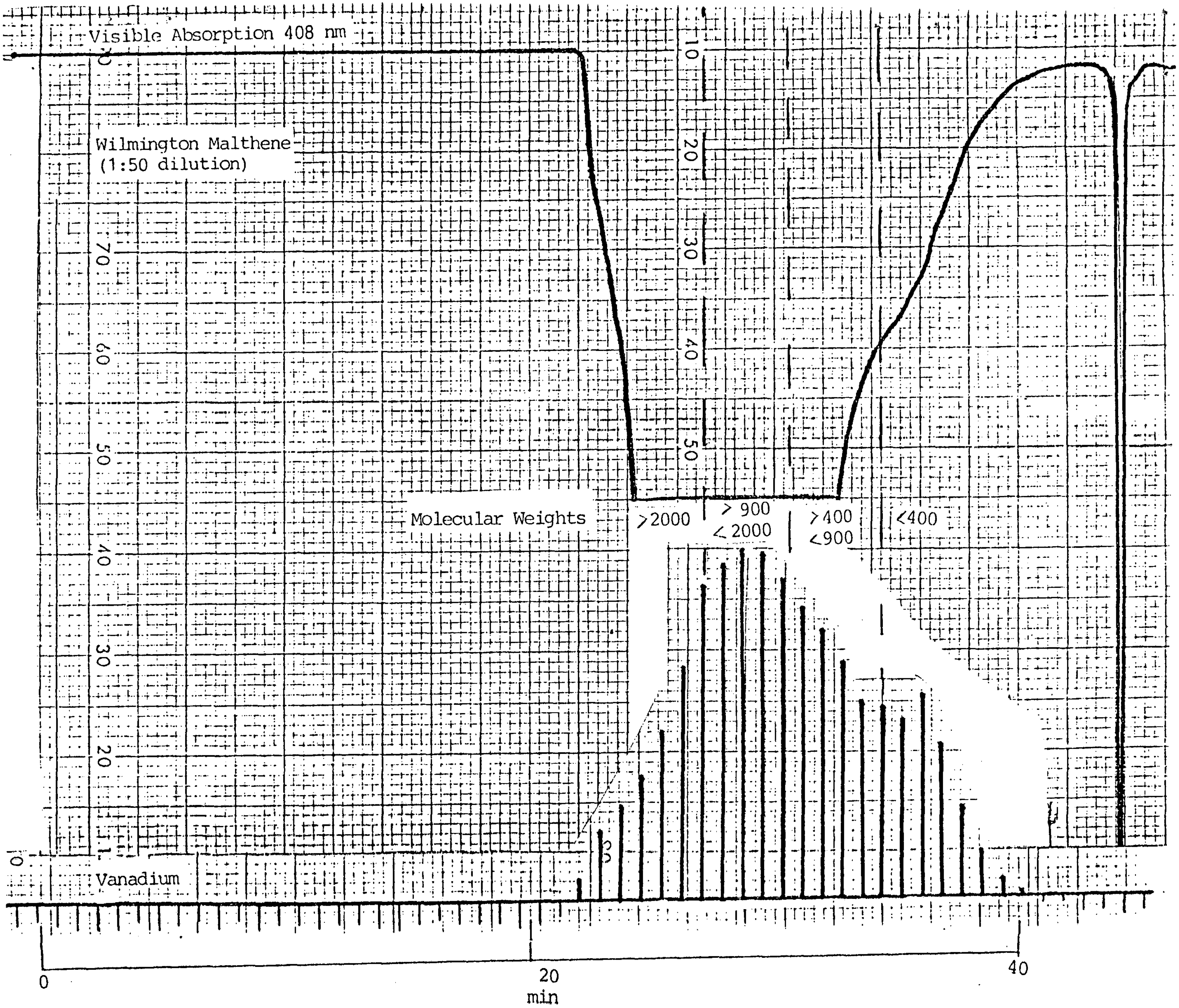

Visible Absorption 408 nm
Wilmington Malthene
(1:50 dilution)
Molecular Weights
>2000
> 900
< 2000
>400
<900
<400
Vanadium
70
60
50
40
30
20
0
10
20
30
40
50
0
20
40
min

Figure 11

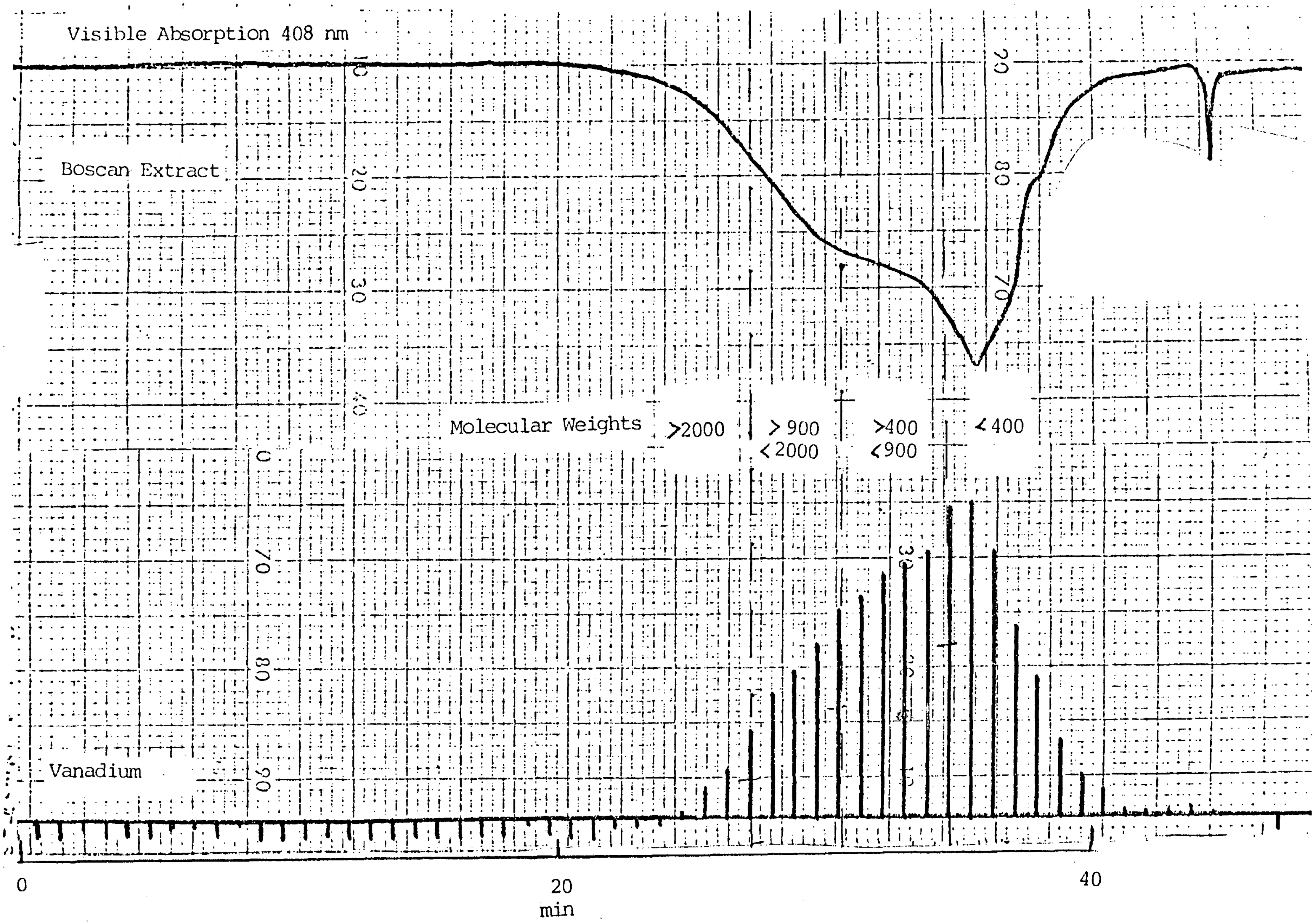
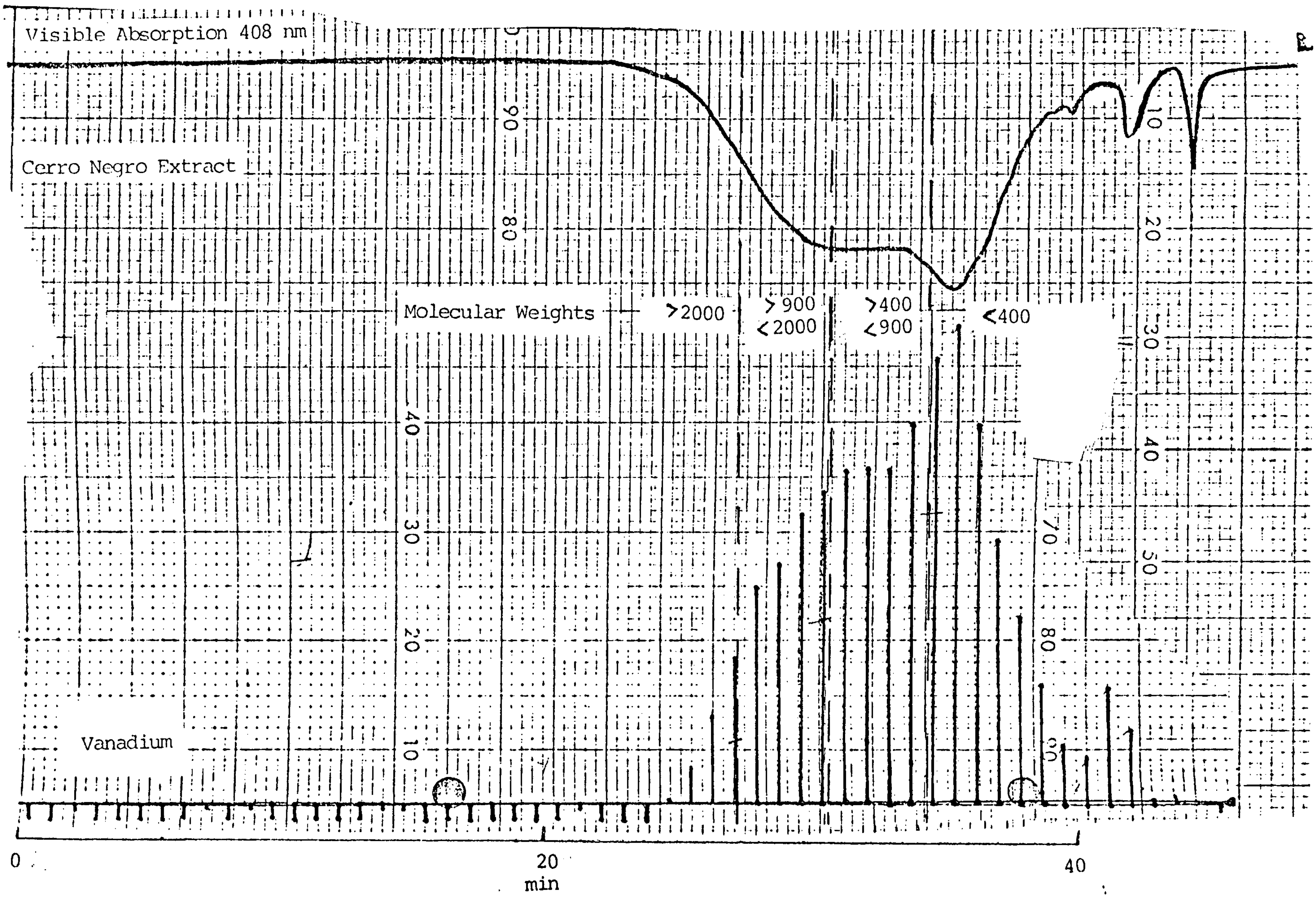

Visible Absorption 408 nm
Boscan Extract
Molecular Weights
>2000
>900
<2000
>400
<900
<400
Vanadium
0
20
40
min

Figure 12


Visible Absorption 408 nm
Cerro Negro Extract
Molecular Weights
>2000
>900
<2000
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<900
<400
Vanadium
90
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10
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30
40
50
70
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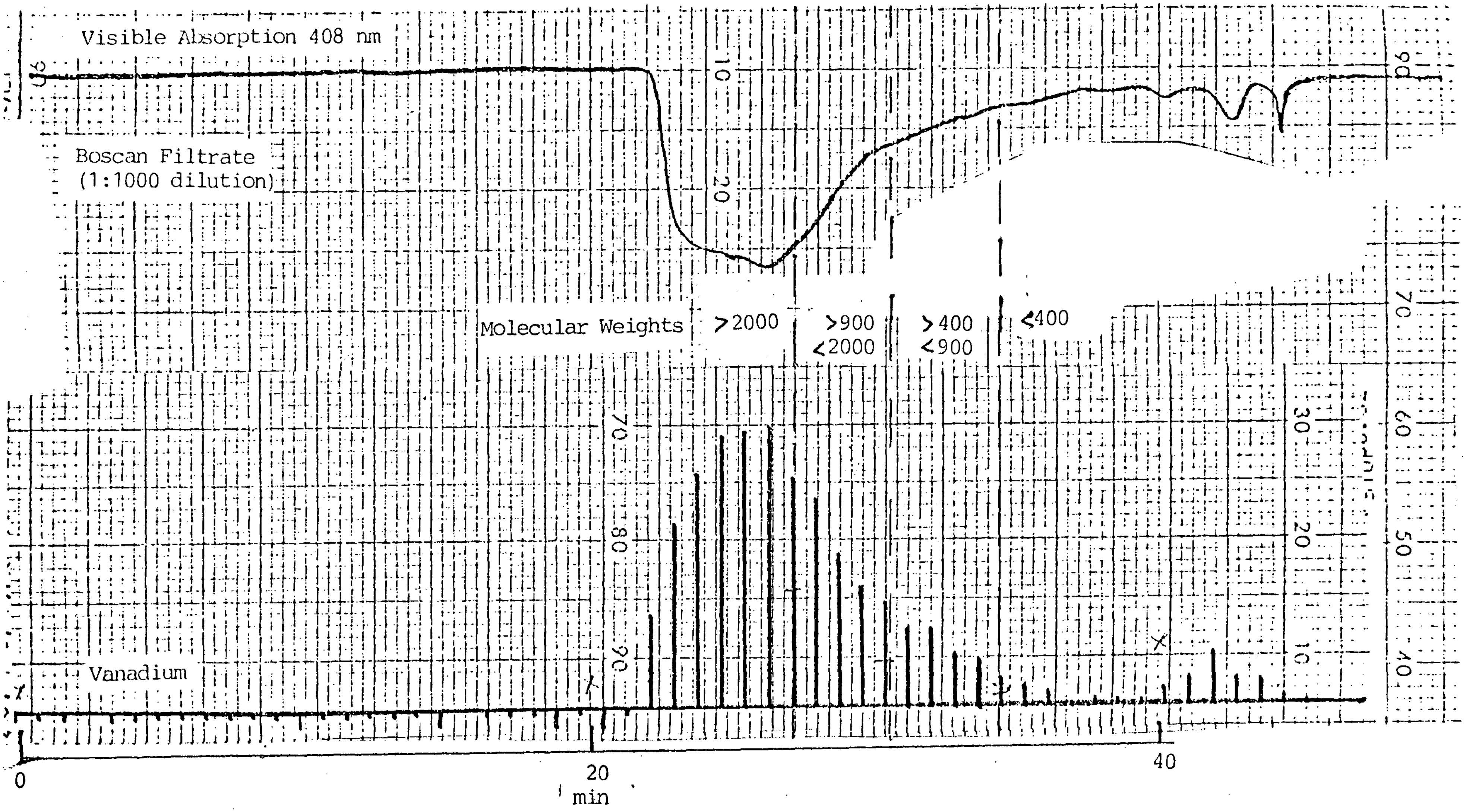
40
30
20
10
0
20
40
min

Figure 13


Visible Absorption 408 nm
Boscan Filtrate
(1:1000 dilution)
Molecular Weights
>2000
>900
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Vanadium
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min
40

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