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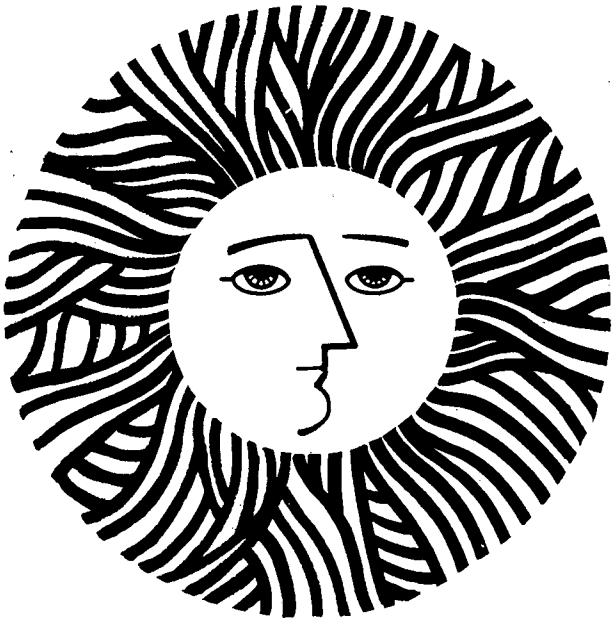

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LBID-523

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

Quarterly Progress Report for Period

January 1, 1982 - April 1, 1982

Prepared for the Bartlesville Energy Technology Center

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by

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April 1982

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Introduction

The identification of vanadyl porphryin and non-porphyrin compounds in heavy crude oils is important to study if methods for the removal of vanadyl ion ($v{=}o^{+2}$) from the heavy crude oils are to implemented in a logical manner. The initial speciation studies have been directed toward the separation of the vanadyl compounds in various heavy crude oils by size exclusion chromatography (SEC) and by use of solvent selective extraction techniques. Thus, the high, medium and lower molecular weight vanadyl compounds have been separated and fingerprinted for four heavy crude oils and the separation of vanadyl porphryins, extracted from the heavy crude oils with aqueous pyridine, has been analyzed with a polyamino-cyano (PAC) column. The competitive equilibrum studies, which are involved in understanding the structure-activity relationships for the speciated vanadyl porphryin and non-porphyrin compounds, were carried out with vanadyl octaethylporphryin and several multidentate ligands.

Both the fingerprinting and competitive equilibrum studies will be discussed in this quarterly.

FingerPrints of Heavy Crude Oils by HPLC-GFAA Analysis Using Both SEC and PAC Columns

Each of the heavy crude oils, i.e., Boscan, Cerro Negro, Wilmington and Prudhoe Bay, were treated similarly and this is shown in Chart 1.

The heavy crude oils, extracted oils (pyridne/water, 4:1), and the extracts, were analyzed by HPLC-GFAA using a 50 Å SEC column with element-specific vanadium detection at 318.4 nm. These separations of

vanadyl porphyrin and non-porphyrin compounds, by molecular weight (MW) provided a fingerprint of compounds of MW > 900; < 900, > 400; < 400 for each of the heavy crude oils studied. Figures 1-4 show the SEC results, and clearly, the vanadium histogramic fingerprints are distinctive for each oil. The visible detector at 408 nm represents a Soret for vanadyl porphryins. A calibration curve (mw vs. retention time) demonstrates that large molecules elute at the earlier retention times (10 min.) and the smaller molecules later (Figure 5). Table 1 summarizes the findings on concentration (ppm) of vanadyl compounds of > 900 mw; > 400, < 900; and < 400. It also defines the amount of vanadium extracted (%) for each of the oils.

Interestingly, we find that each heavy crude oil has lower molecular weight porphrin and non-prophyrin compounds initially complexed to the higher or asphaltene mw fractions and thus are extracted by the pyridine/water, ending up in the > 400, < 900 mw fractions.

Additionally, the amount (%) of vanadyl compounds extracted from each category of molecular weights is very similar for each oil, regardless of biogeochemical origin.

In order to better define the vanadyl porphryin and non-porphryin compounds that were extracted, we analyzed these fractions using a polyamino-cyano column, which separates compounds by their polarity properties (see Chart 1). The standards used are shown in Chart 2, while Figure 6 demonstrates the fingerprints and the visible detector results. Note, that by changing the wave-length various vanadyl porphrinic structures can be tentatively identified. Figures 7 and 8 compare the heavy crude oils and again shows a unique fingerprint for each oil. (Vis

detector at 408 nm, V at 318.4)

Clearly, the implications for identification of heavy crude oils of any origin are possible by element-specific HPLC-GFAA analysis.[1]

Competitive Equilibra Between Vanadyl Octaethylporphin and Several Multidentate Ligands Using Trifluoroacetic Acid as a Catalyst

In the continuation of trying to determine equilibrum constants for future removal of vanadyl ion from heavy crude oils with multidentate ligands, we have used uv-vis spectroscopy to ascertain these values with a model vanadyl porphryin and several multidentate ligands using acid catalysis. Equation 1 defines the conditions and Figure 9 the uv-vis results for VO octacthylporphin and tetraphenylporphryin using trifluoroacetic acid as a catalyst.

The use of acids, such as trifluoroacetic acid, seems to increase the rate of exchange. The K value we obtain via uv-vis spectroscopy is 6.2, and although this value is not acceptable for removal of vanadylion, it does represent a positive trend.

This aspect of our work will not be emphasized in the future until our speciation studies are more advanced and we are able to increase our supply of multidentate ligands and their corresponding vanadyl analogs. This aspect should be continued this summer with Dr. John Vollmer joining the group for these purposes and a graduate student, Brian Wines, advancing the speciation program.

Future Work

We will continue with our size exclusion chromatography work to further separate the various vanadyl compounds by molecular weight, i.e., > 900 and < 400. In addition, the non-porphryin compounds of high and low mw will be characterized by other spectroscopic techniques.

Acknowledgements

We wish to thank John Komlenic, Brian Wines and Raja Tannous for the experimental results reported in this quarterly report.

References

(1) W.A. Spencer, J.A. Galobardes, M.A. Curtis and L.B. Rogers. Chromatographic Studies of Vanadium Compounds from Boscan Crude Oils, DOE/ER/00854-32, August 1981. This report shows a complementary program at the Univ. of Georgia and we are indebted to Professor Rogers for a copy of his report. This is available from NTIS Springfield, VA 22161.

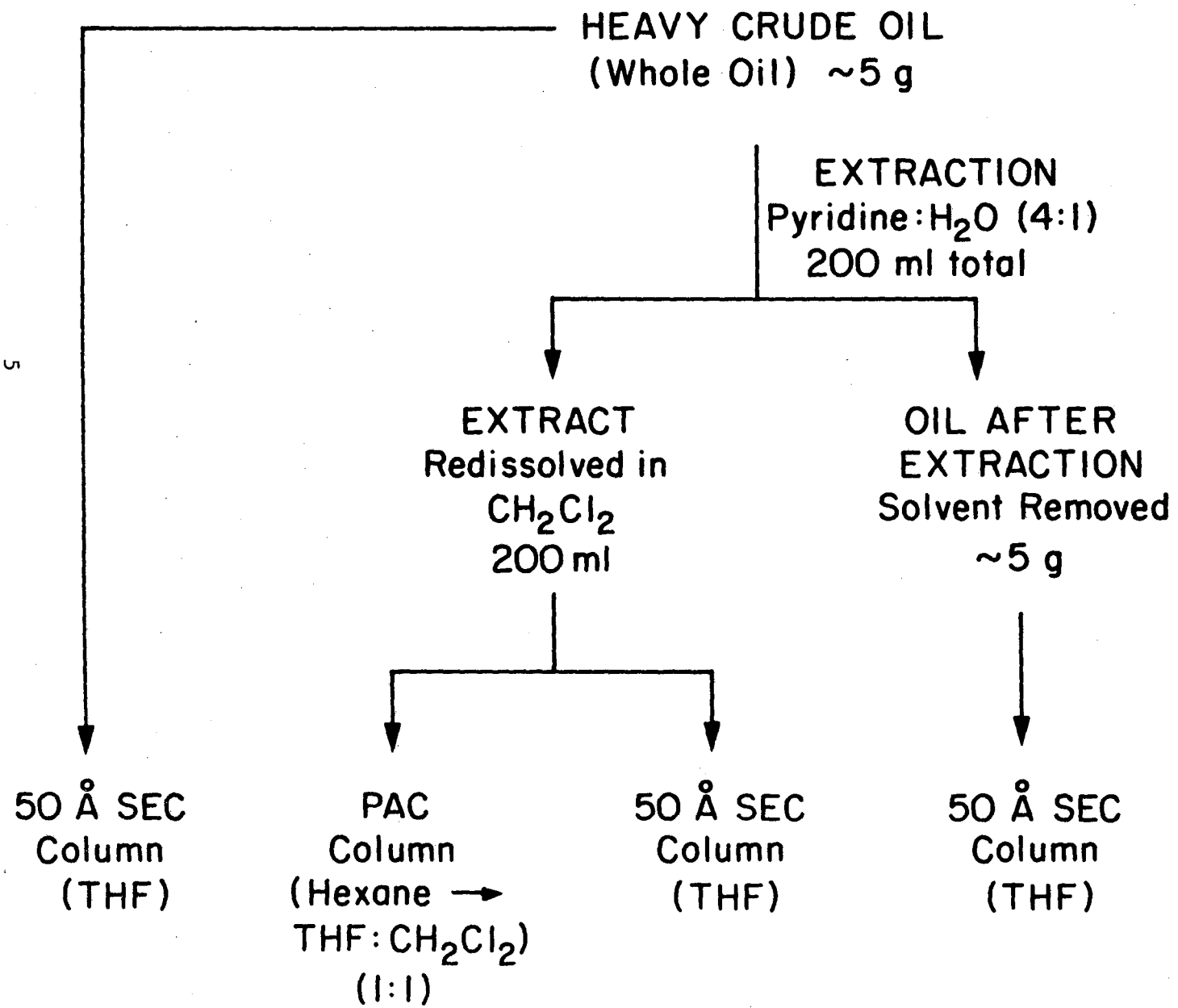
Presentations and Publications

J.J. Komlenic and R.H. Fish, 183rd National ACS Meeting Las Vegas, NV. March 29- April 3, 1982 Abstract Geoc 4. Fingerprinting and Speciation of Vanadyl (VO^{2+}) Compounds and Removal of Vanadyl Ions with Multidentate Ligands.

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

Chart 1

METHODS AND PROCEDURES



	V (ppm)
Boscan	1100
Cerro Negro	560
Wilmington	48
Prudhoe Bay	19

XBL 823-8656

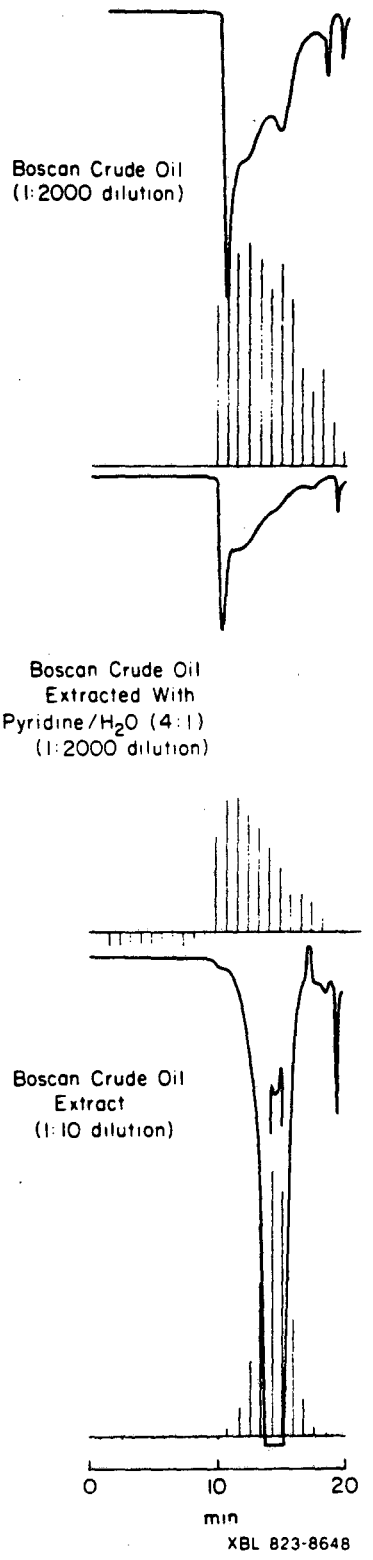

Boscan Crude Oil
(1:2000 dilution)
Boscan Crude Oil
Extracted With
Pyridine/H_2O (4:1)
(1:2000 dilution)
Boscan Crude Oil
Extract
(1:10 dilution)
0
10
20
min
XBL 823-8648

Figure 1

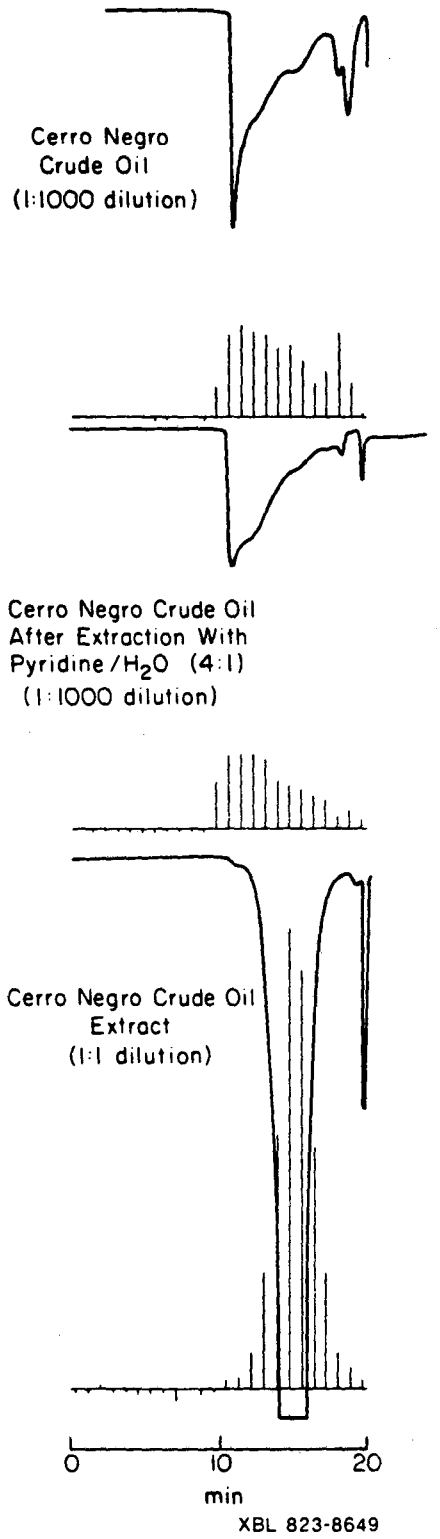

Cerro Negro
Crude Oil
(1:1000 dilution)
Cerro Negro Crude Oil
After Extraction With
Pyridine/H_2O (4:1)
(1:1000 dilution)
Cerro Negro Crude Oil
Extract
(1:1 dilution)
0
10
20
min
XBL 823-8649

Figure 2

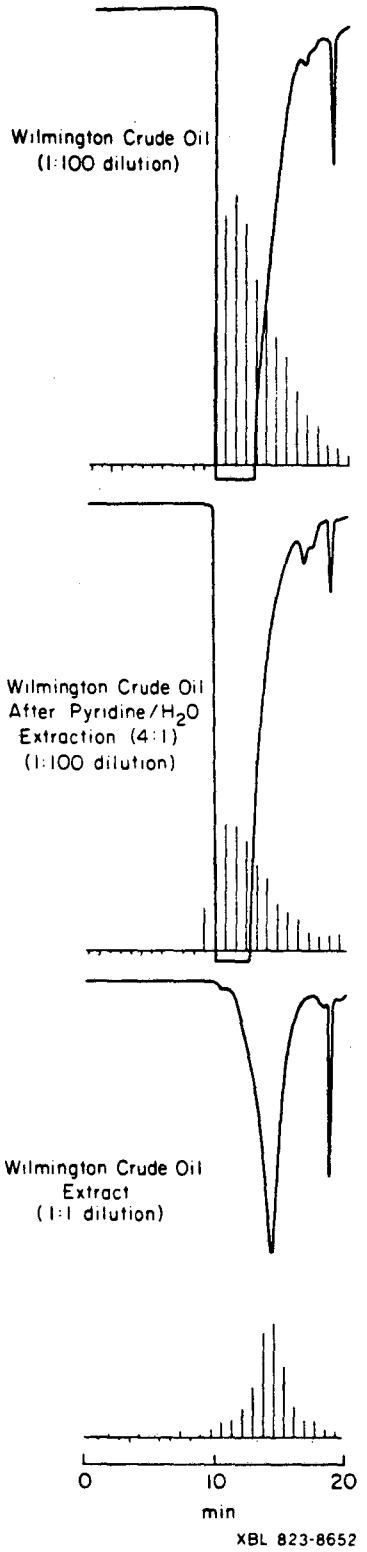

Wilmington Crude Oil
(1:100 dilution)
Wilmington Crude Oil
After Pyridine/H_2O
Extraction (4:1)
(1:100 dilution)
Wilmington Crude Oil
Extract
(1:1 dilution)
0
10
20
min
XBL 823-8652

Figure 3

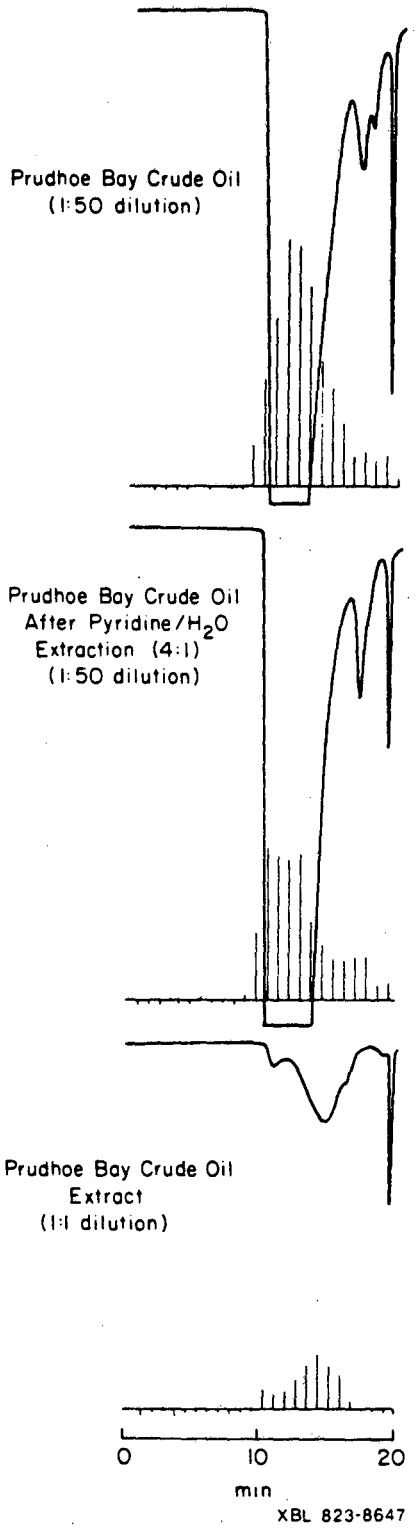

Prudhoe Bay Crude Oil
(1:50 dilution)
Prudhoe Bay Crude Oil
After Pyridine/H_2O
Extraction (4:1)
(1:50 dilution)
Prudhoe Bay Crude Oil
Extract
(1:1 dilution)
0
10
20
min
XBL 823-8647

Figure 4

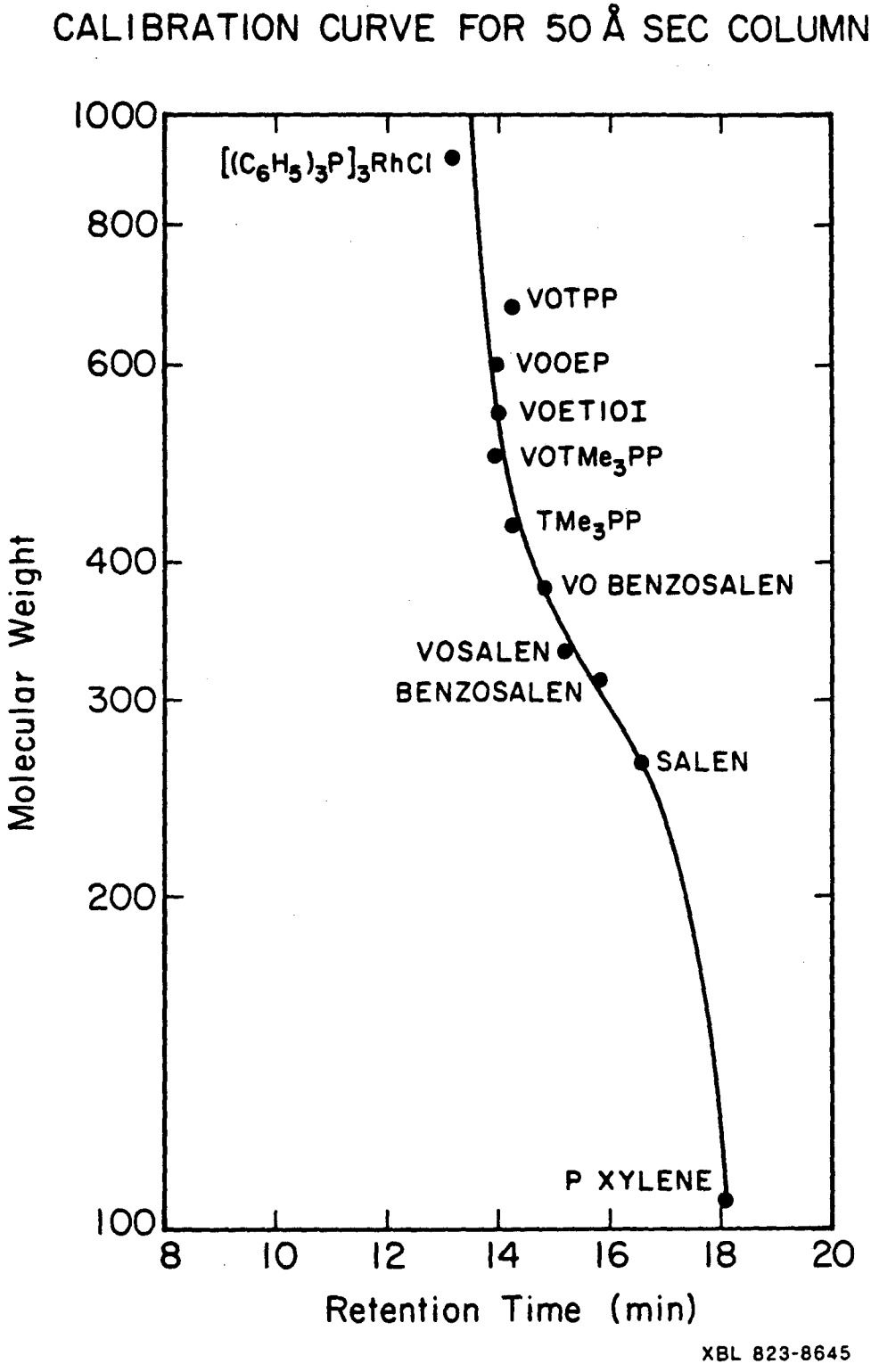

CALIBRATION CURVE FOR 50 Å SEC COLUMN
1000
800
600
400
300
200
100
Molecular Weight
[(C6H5)3P]3RhCl
VOTPP
VOOEP
VOETIOI
VOTMe3PP
TMe3PP
VO BENZOSALEN
VOSALEN
BENZOSALEN
SALEN
P XYLENE
8
10
12
14
16
18
20
Retention Time (min)
XBL 823-8645

Figure 5

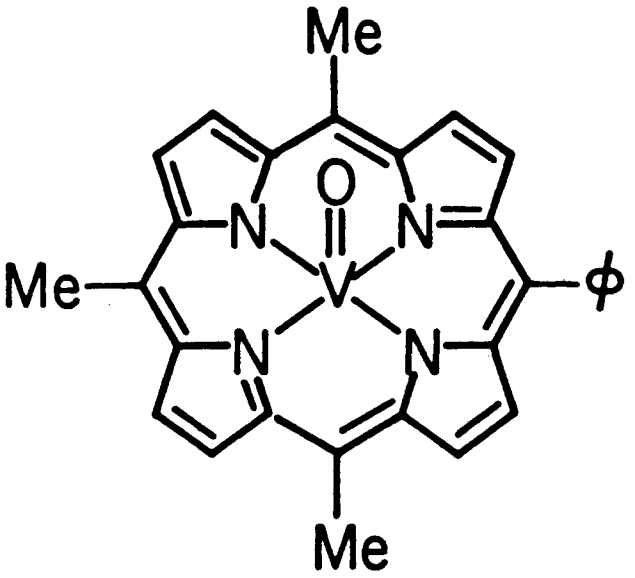
Table 1

	Boscan			Cerro Negro			Wilmington			Prudhoe Bay		
	NP[a] >900[c]	P[b] >400, <900	NP <400	NP >900	P >400, <900	NP <400	NP >900	P >400, <900	NP <400	NP >900	P >400, <900	NP <400
Whole Oil	560[d]	352	188	263	151	146	30.4	12.7	5.9	10.6	6.1	2.3
Oil After Extraction	302	173	65	137	87	56	7.7	3.5	1.8	5.5	2.0	1.5
Removed (By Difference)	258	179	123	126	64	90	22.7	9.2	4.1	5.1	4.1	0.8
%	46	51	65	48	40	61	75	72	70	48	67	35

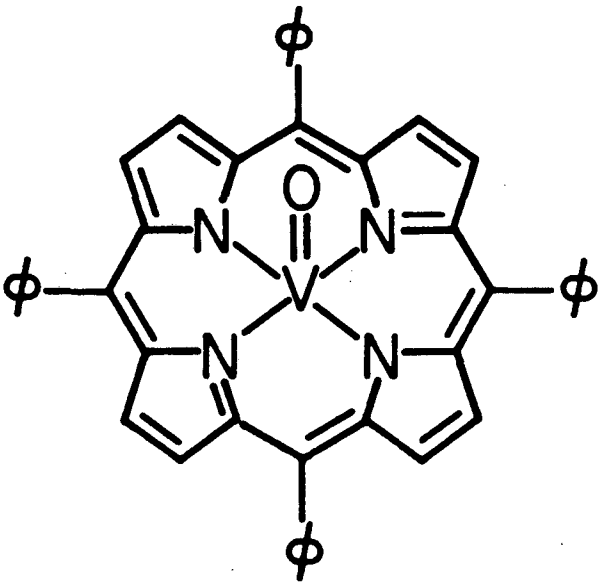
a) Non-Porphyrin
b) Porphyrin
c) Molecular Weight >900
d) PPM Vanadium

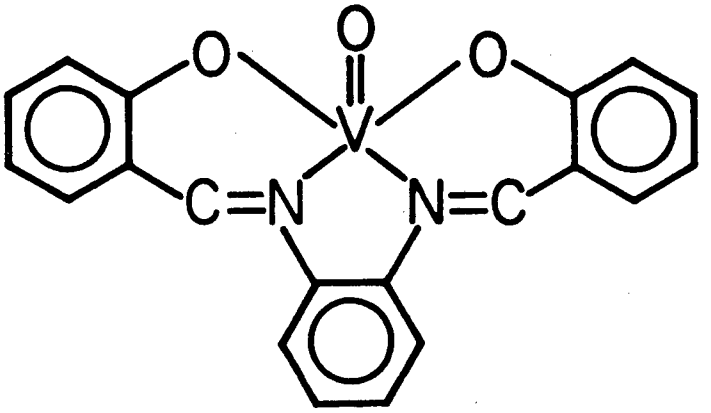
XBL 823-8694A

VOTMe$_3$PP

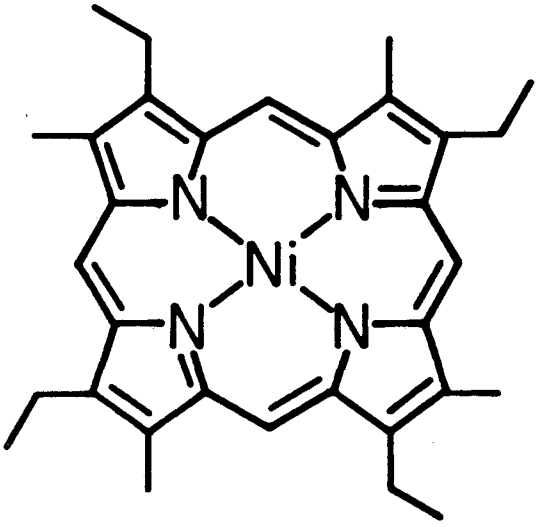


VOTPP

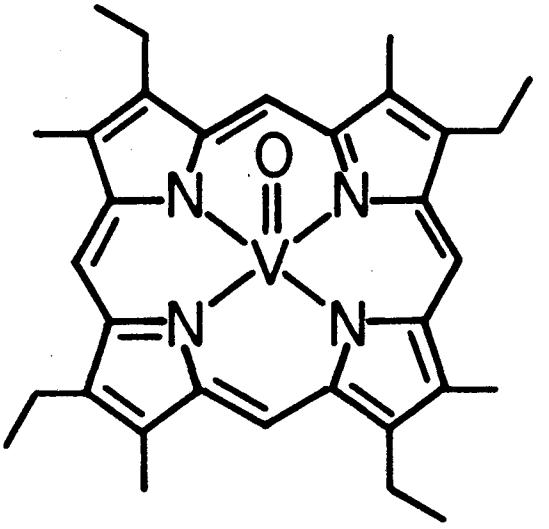




VOBENZOSALEN



NiETIOI



VOETIOI

XBL 823-8655

Chart 2

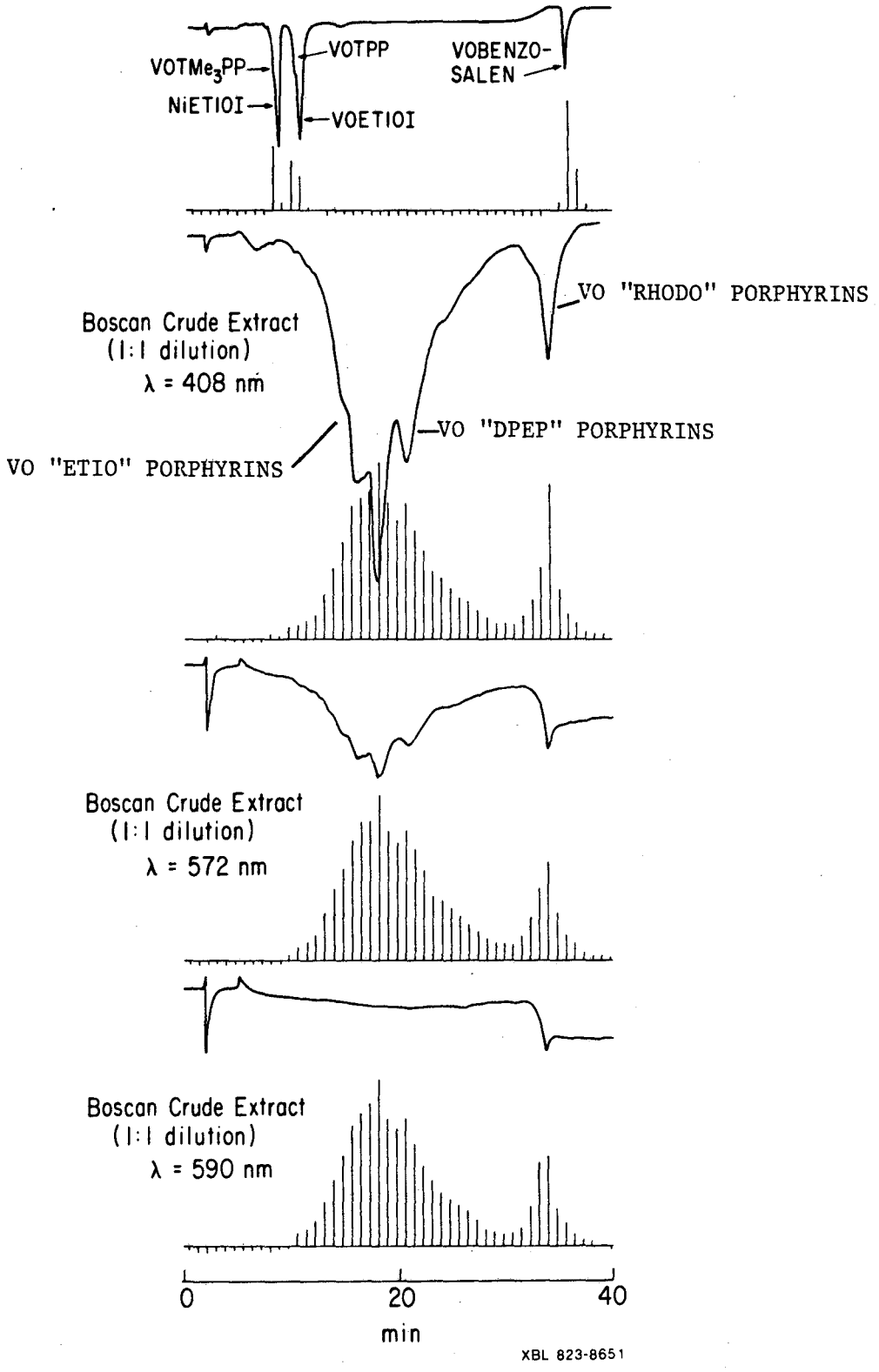

VOTMe3PP
NiETIOI
VOTPP
VOETIOI
VOBENZO-
SALEN
VO "RHODO" PORPHYRINS
Boscan Crude Extract
(1:1 dilution)
λ = 408 nm
VO "DPEP" PORPHYRINS
VO "ETIO" PORPHYRINS
Boscan Crude Extract
(1:1 dilution)
λ = 572 nm
Boscan Crude Extract
(1:1 dilution)
λ = 590 nm
0
20
40
min
XBL 823-8651

Figure 6

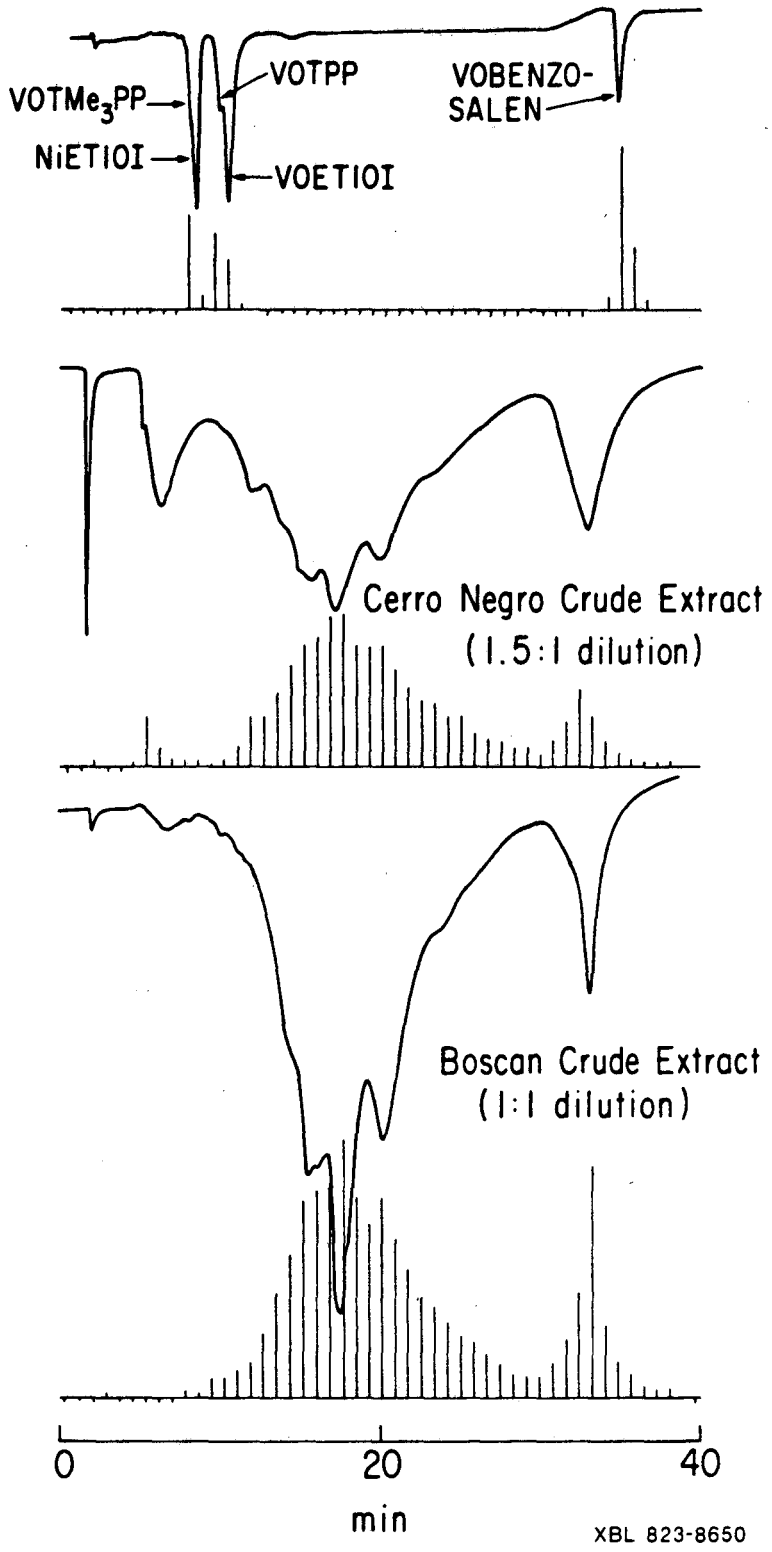

VOTMe3PP
NiETIOI
VOTPP
VOETIOI
VOBENZO-
SALEN
Cerro Negro Crude Extract
(1.5:1 dilution)
Boscan Crude Extract
(1:1 dilution)
0
20
40
min
XBL 823-8650

Figure 7

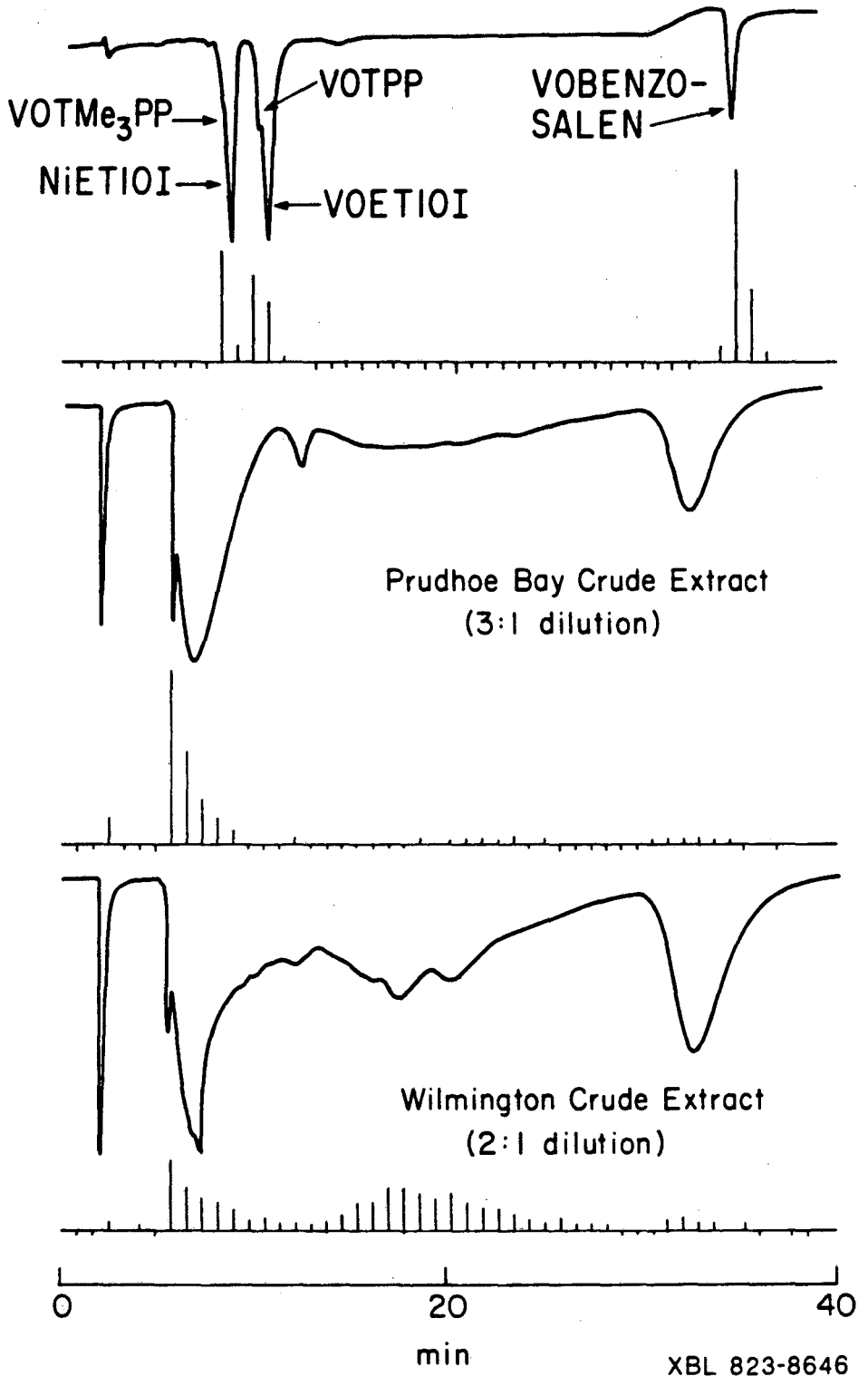

VOTMe3PP
NiETIOI
VOTPP
VOETIOI
VOBENZO-
SALEN
Prudhoe Bay Crude Extract
(3:1 dilution)
Wilmington Crude Extract
(2:1 dilution)
0
20
40
min
XBL 823-8646

Figure 8

Competition Experiments

$$\text{OEPVO} + \text{MLH}_2 \underset{}{\overset{H^+}{\rightleftharpoons}} \text{OEPH}_2 + \text{MLVO}$$

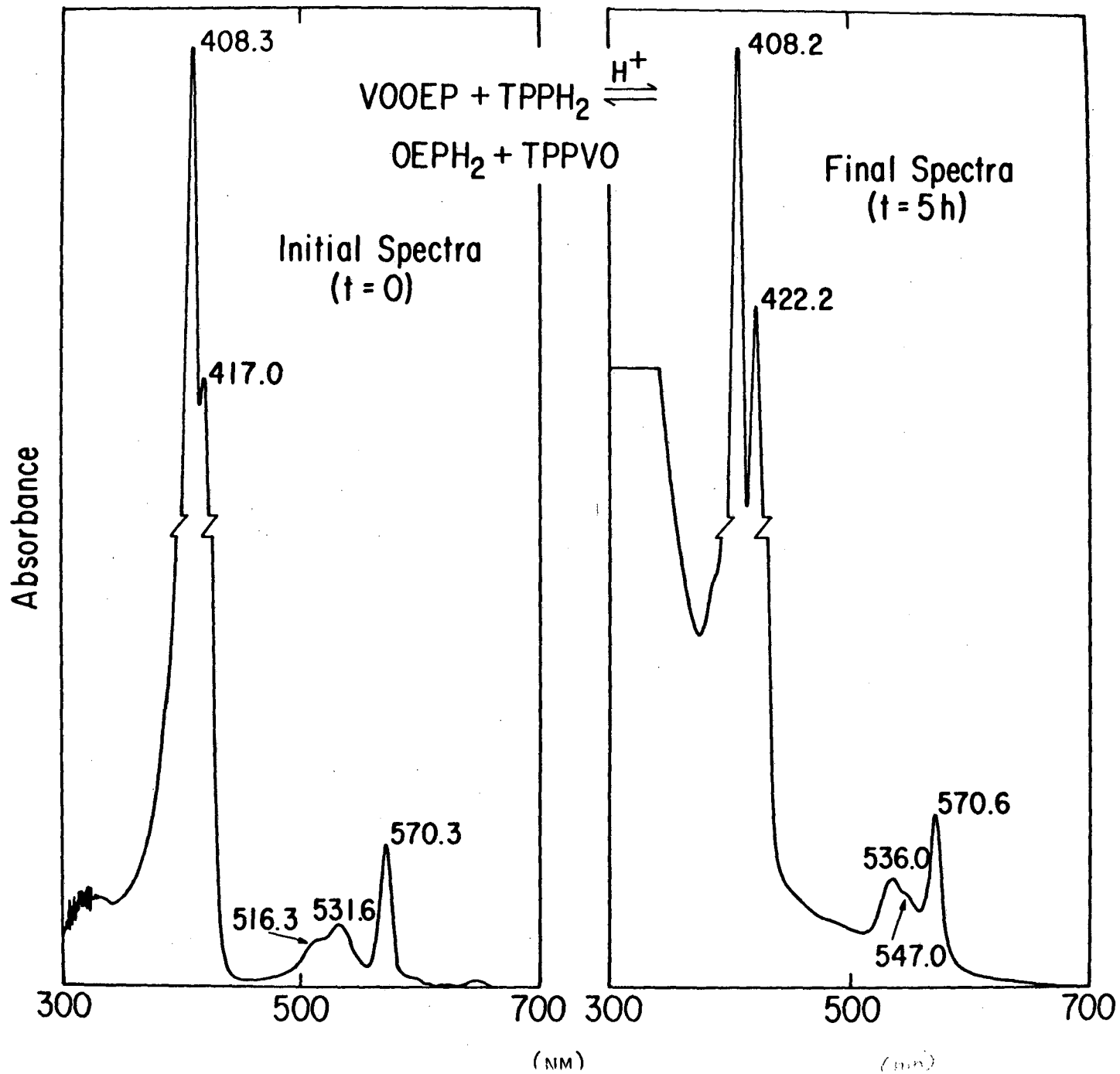
Conditions: 145°, N_2 atm
p-xylene
5 h
10% CF_3COOH

Equation 1

MLH_2 = TPPH_2, Benzosalen

XBL 823-8658

Figure 9


VOOEP + TPPH2 ⇌ OEPH2 + TPPVO
H+
Initial Spectra
(t = 0)
Final Spectra
(t = 5h)
Absorbance
408.3
417.0
516.3
531.6
570.3
408.2
422.2
536.0
547.0
570.6
300
500
700
300
500
700
(NM)

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