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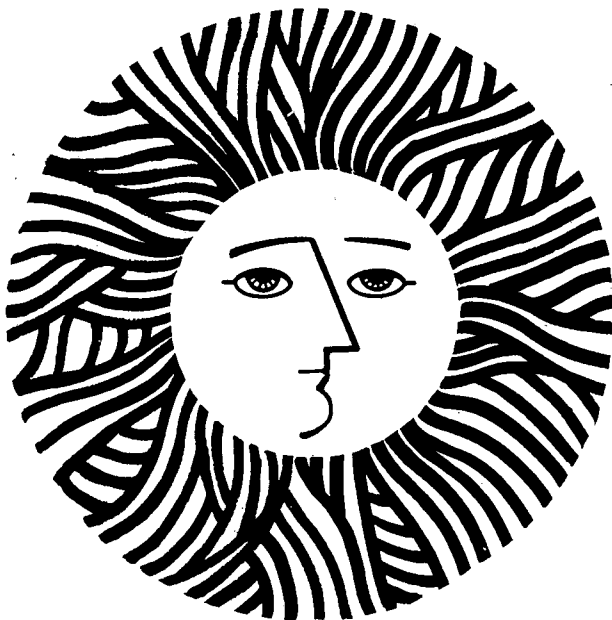
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Metal Coordination Chemistry: Removal and Recovery
of Metals from Heavy Crude and Shale Oils
with Multidentate Ligands

Quarterly Progress Report for Period
January 1, 1982 - April 1, 1982

Prepared for the Bartlesville Energy Technology Center

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Acct. No. 210D

Technical Project Manager: Dexter Sutterfield

by

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April 1982

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Introduction

The identification of vanadyl porphyrin 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 be 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 porphyrins, extracted from the heavy crude oils with aqueous pyridine, has been analyzed with a polyamino-cyano (PAC) column. The competitive equilibrium studies, which are involved in understanding the structure-activity relationships for the speciated vanadyl porphyrin and non-porphyrin compounds, were carried out with vanadyl octaethylporphyrin and several multidentate ligands.

Both the fingerprinting and competitive equilibrium 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 (pyridine/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 histogrammic fingerprints are distinctive for each oil. The visible detector at 408 nm represents a Soret for vanadyl porphyrins. 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 porphyrin and non-porphyrin 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 porphyrin and non-porphyrin 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 porphyrinic 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 equilibrium 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 porphyrin and several multidentate ligands using acid catalysis. Equation 1 defines the conditions and Figure 9 the uv-vis results for VO octaethylporphin and tetraphenylporphyrin 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-porphyrin 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

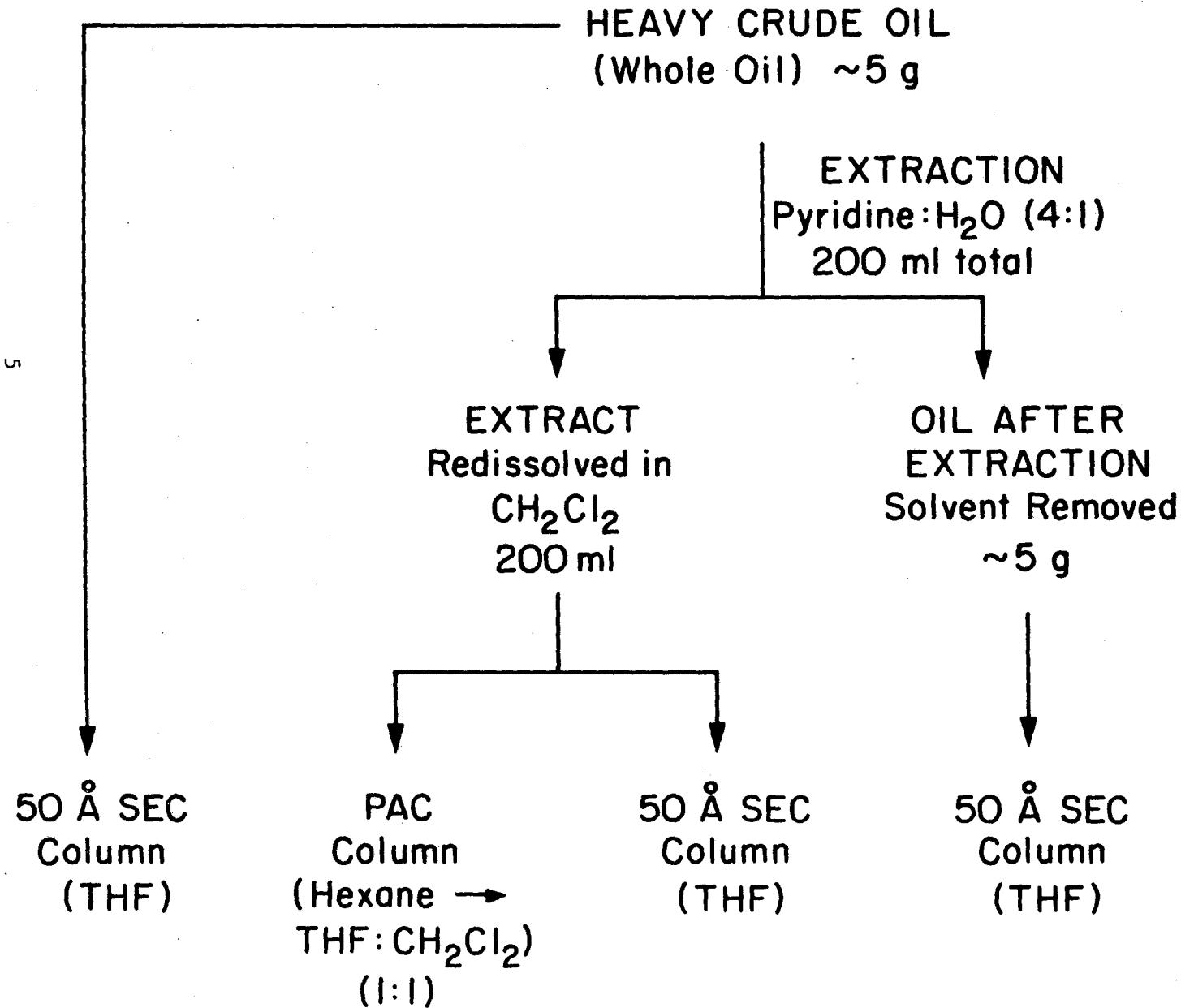
- (1) W.A. Spencer, J.A. Galobardes, M.A. Curtis and L.B. Rogers. Chromatographic Studies of Vanadium Compounds from Boscan Crude Oils, DOE/ER/00854-32, August 1981. This report shows a complementary program at the Univ. of Georgia and we are indebted to Professor Rogers for a copy of his report. This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

Presentations and Publications

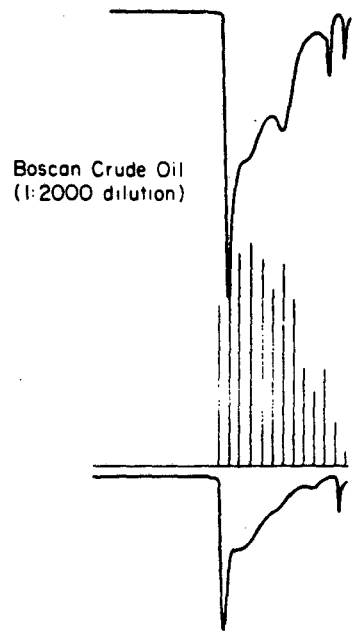
J.J. Komlenic and R.H. Fish, 183rd National ACS Meeting Las Vegas, NV. March 29- April 3, 1982 Abstract Geoc 4. Fingerprinting and Speciation of Vanadyl (VO^{2+}) Compounds and Removal of Vanadyl Ions with Multidentate Ligands.

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

METHODS AND PROCEDURES



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



Boscan Crude Oil
Extracted With
Pyridine/H₂O (4:1)
(1:2000 dilution)

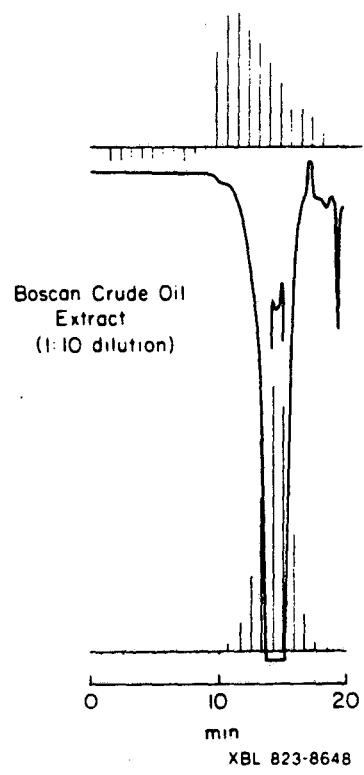


Figure 1
6

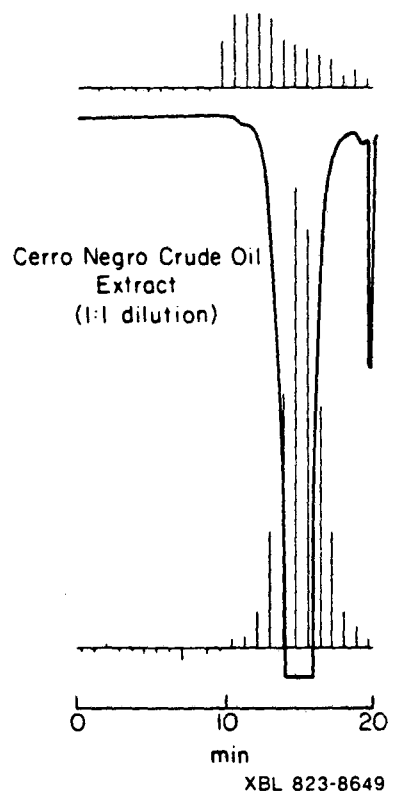
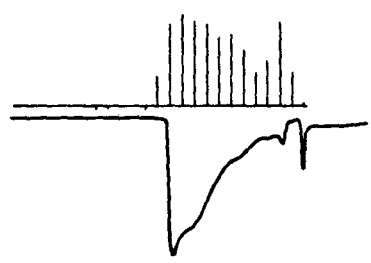
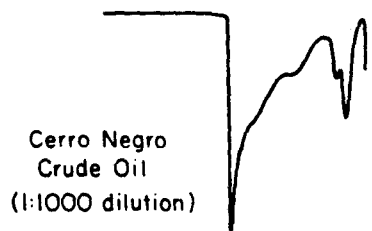


Figure 2
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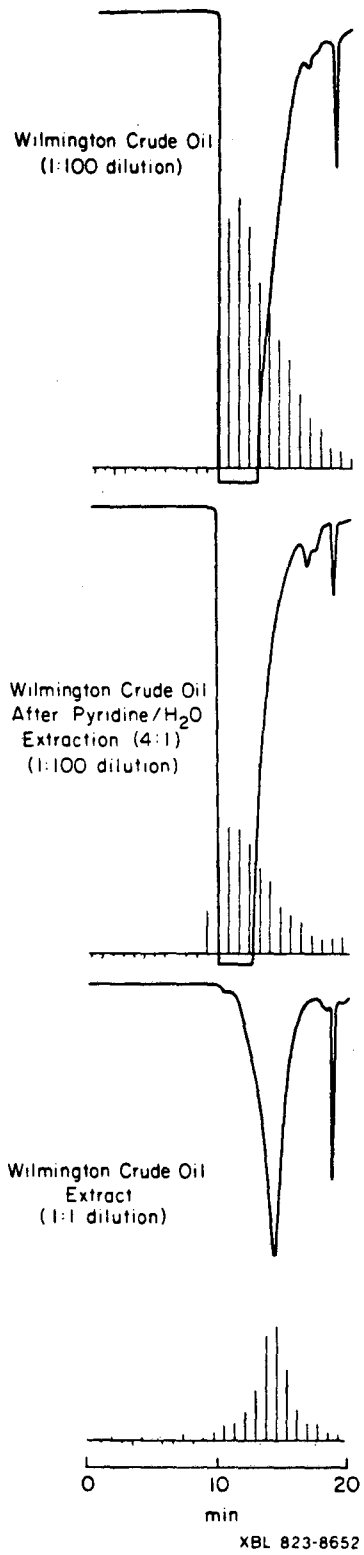


Figure 3

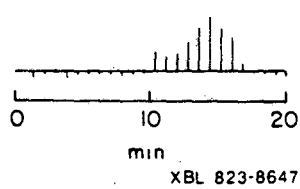
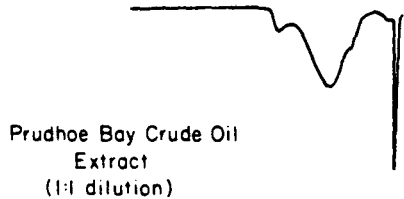
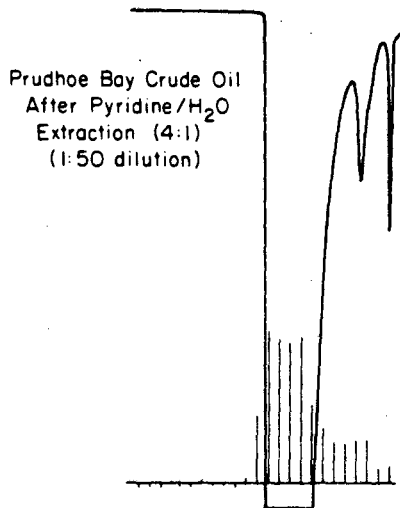
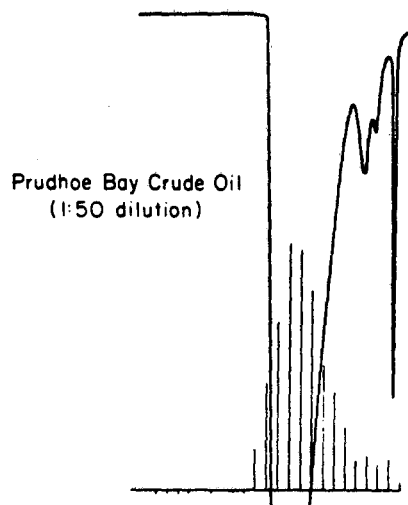
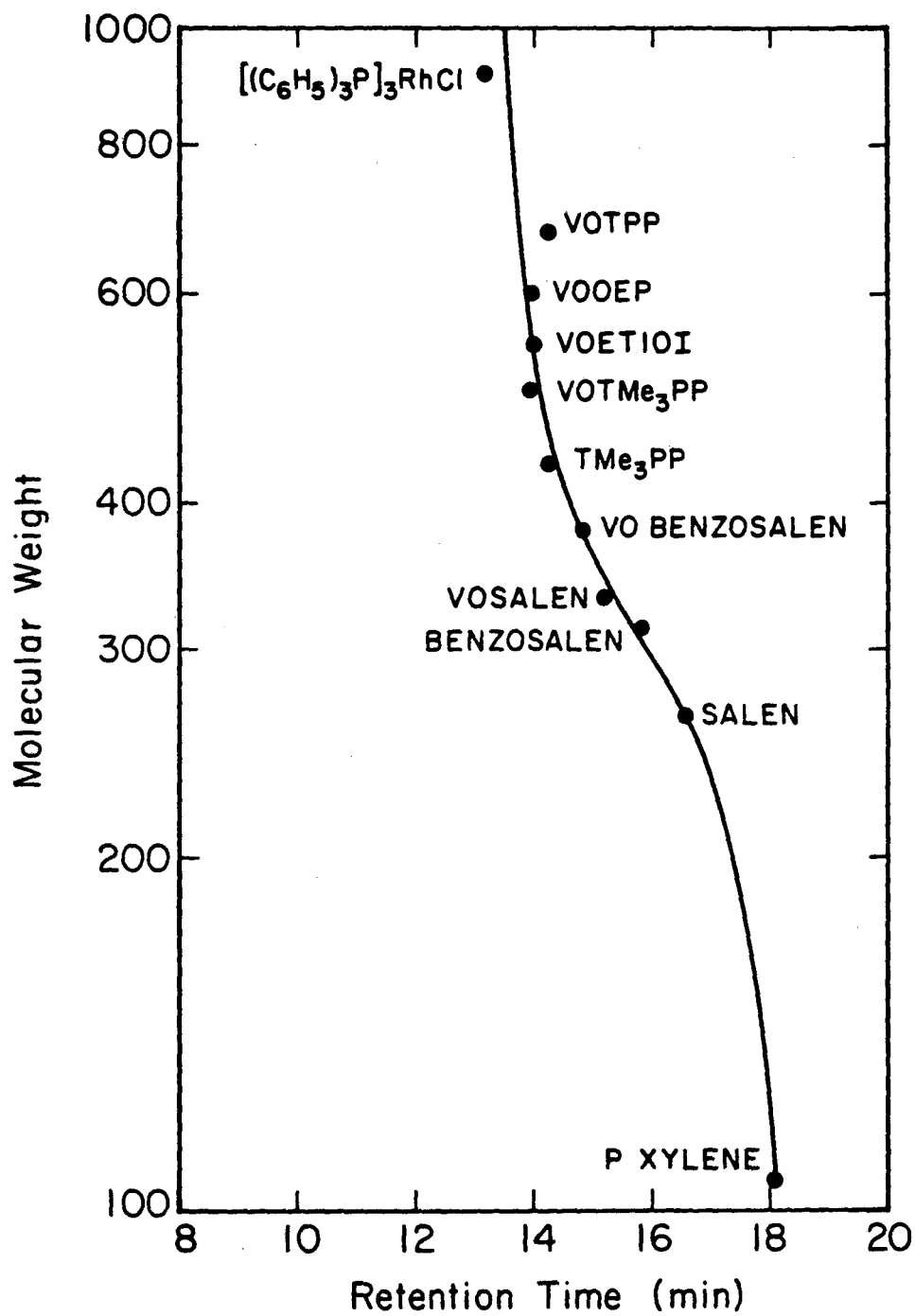


Figure 4

CALIBRATION CURVE FOR 50 Å SEC COLUMN



XBL 823-8645

Figure 5

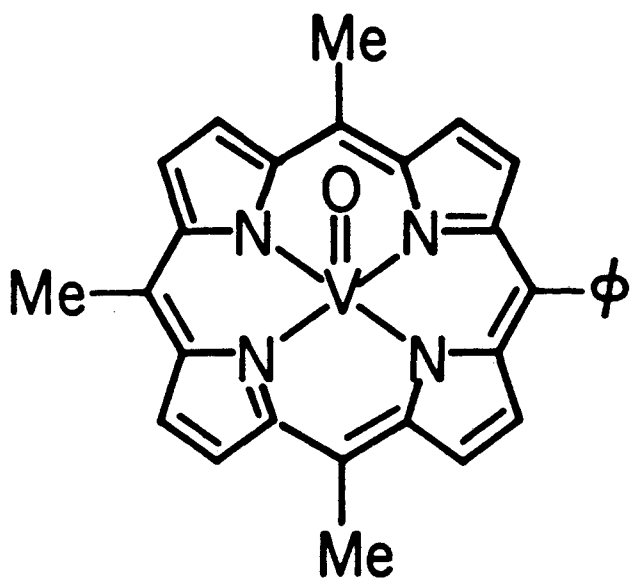
Table 1

| | 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 |

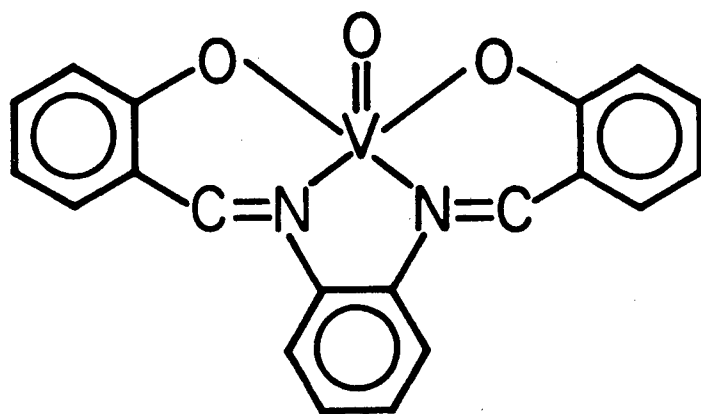
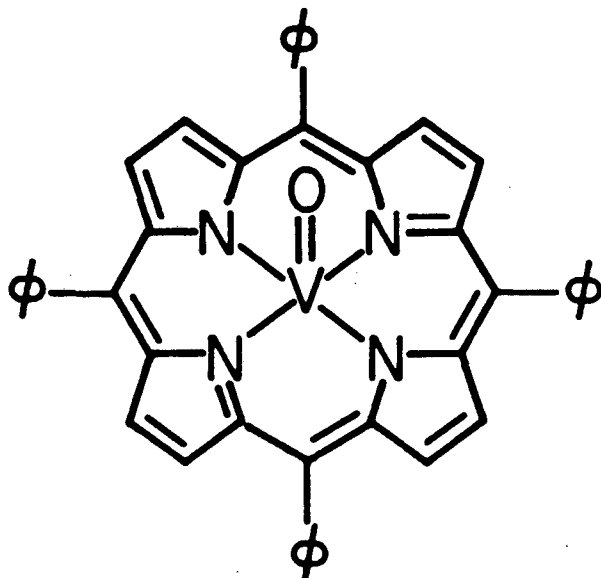
- a) Non-Porphyrin
b) Porphyrin
c) Molecular Weight >900
d) PPM Vanadium

XBL 823-8694A

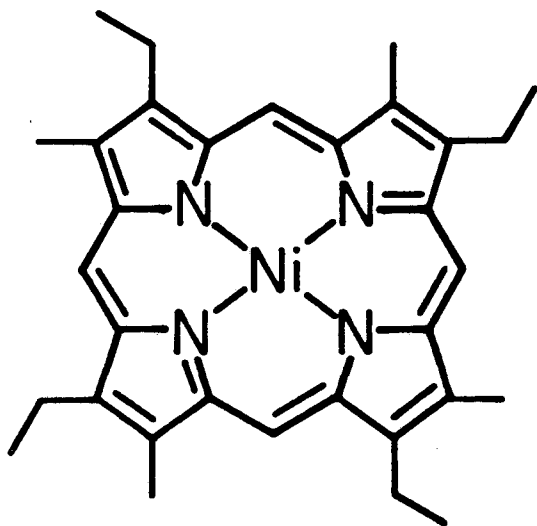
VOTMe₃PP



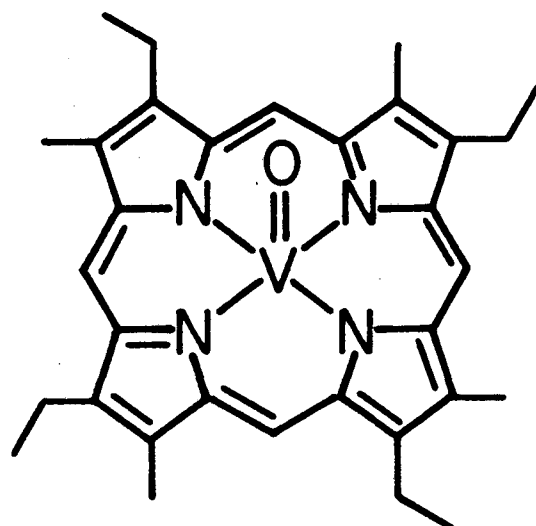
VOTPP



VOBENZOSALEN



NiETIOI



VOETIOI

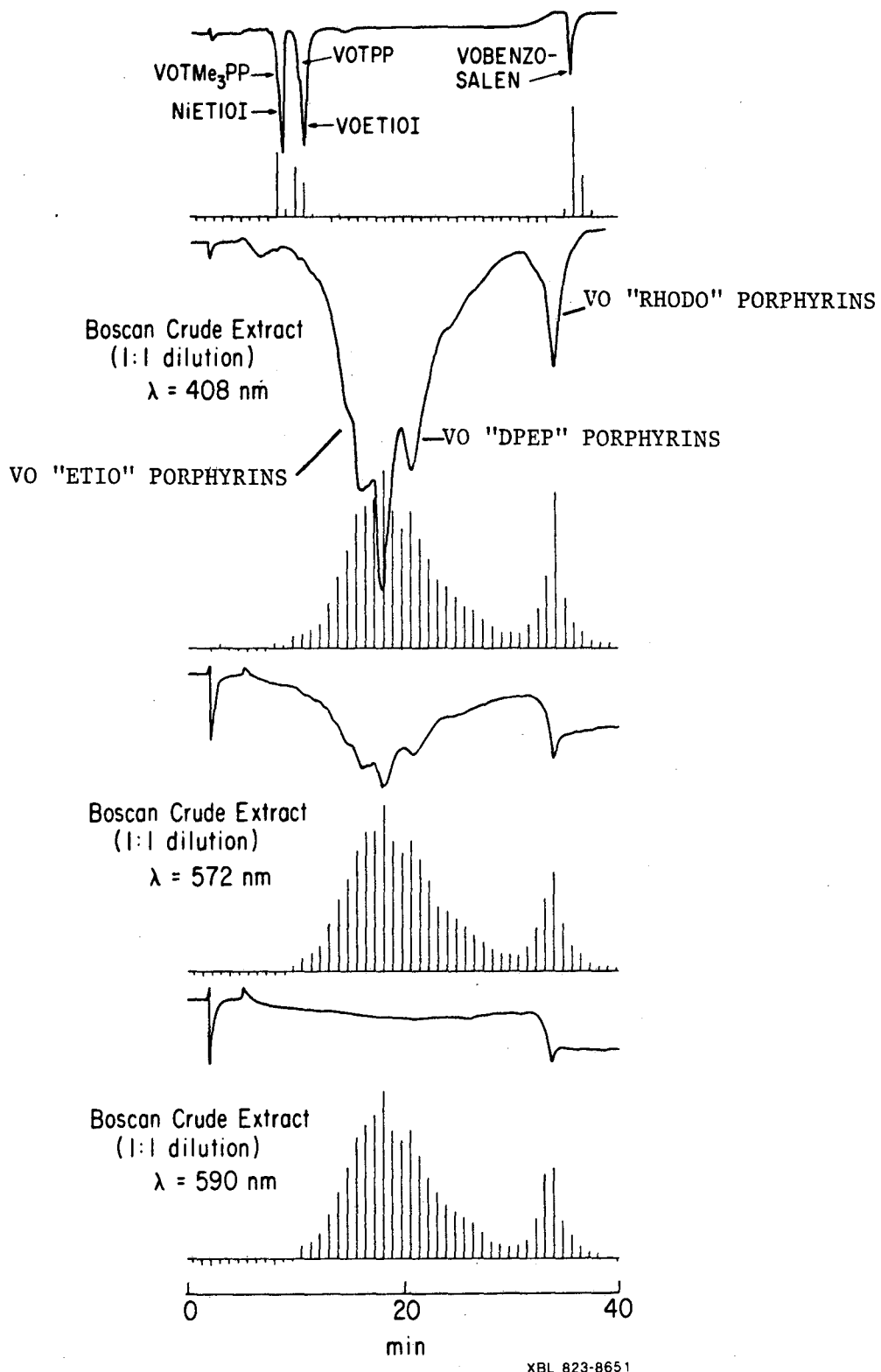


Figure 6

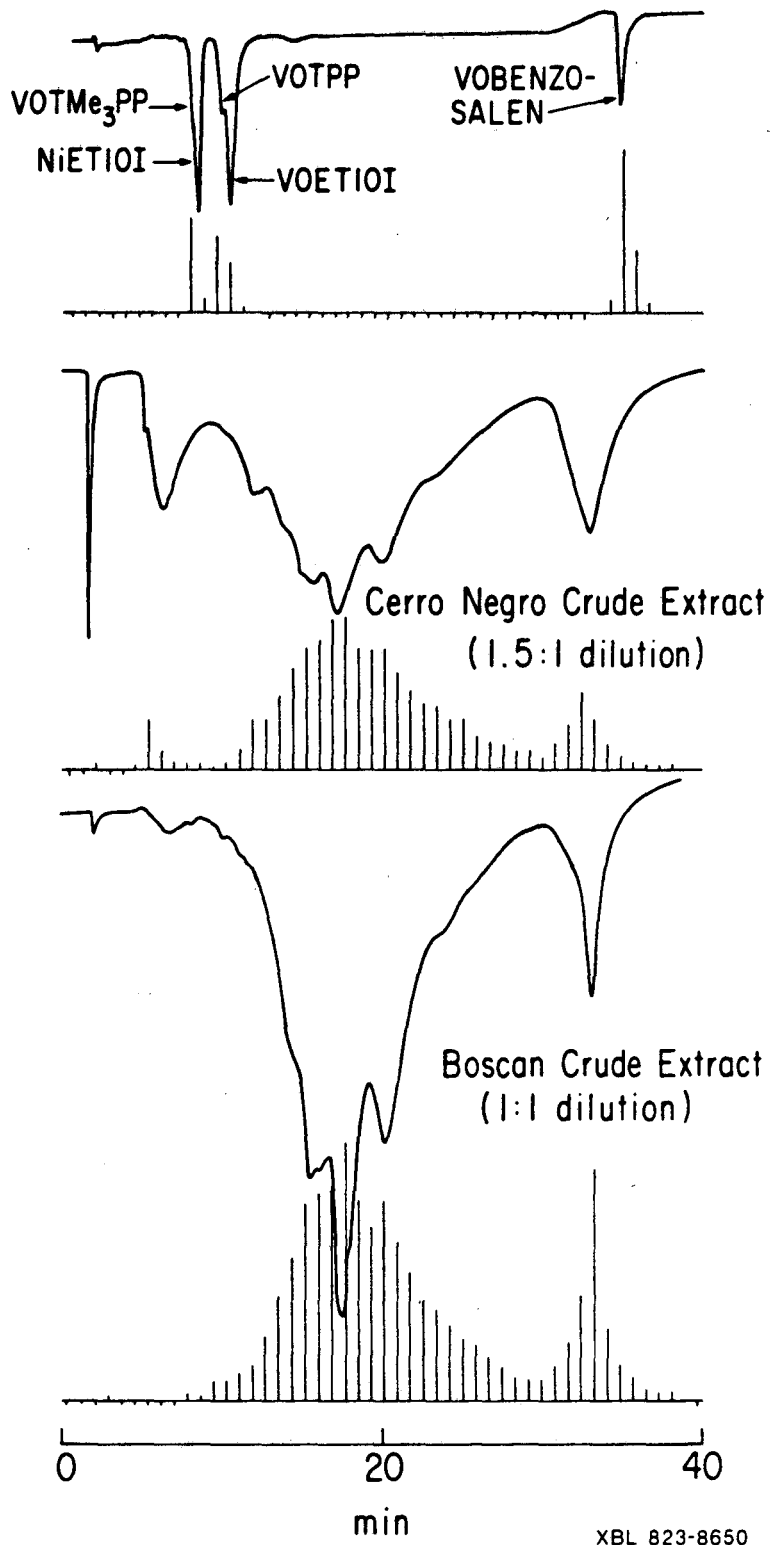


Figure 7

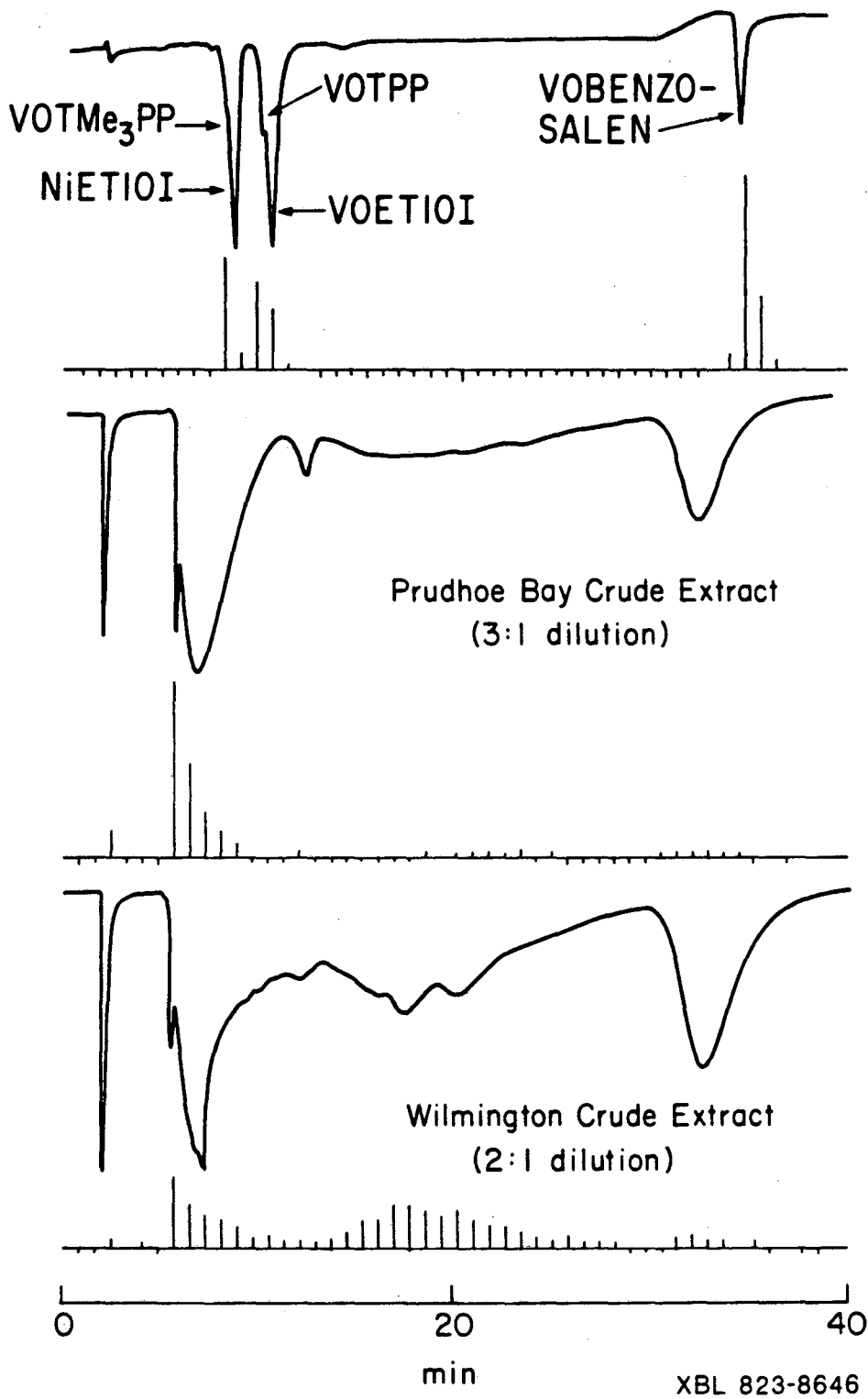
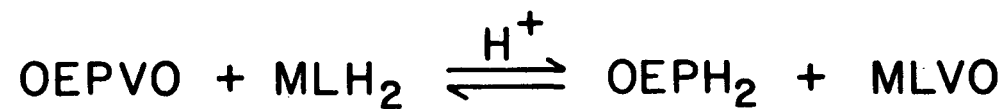


Figure 8

Competition Experiments



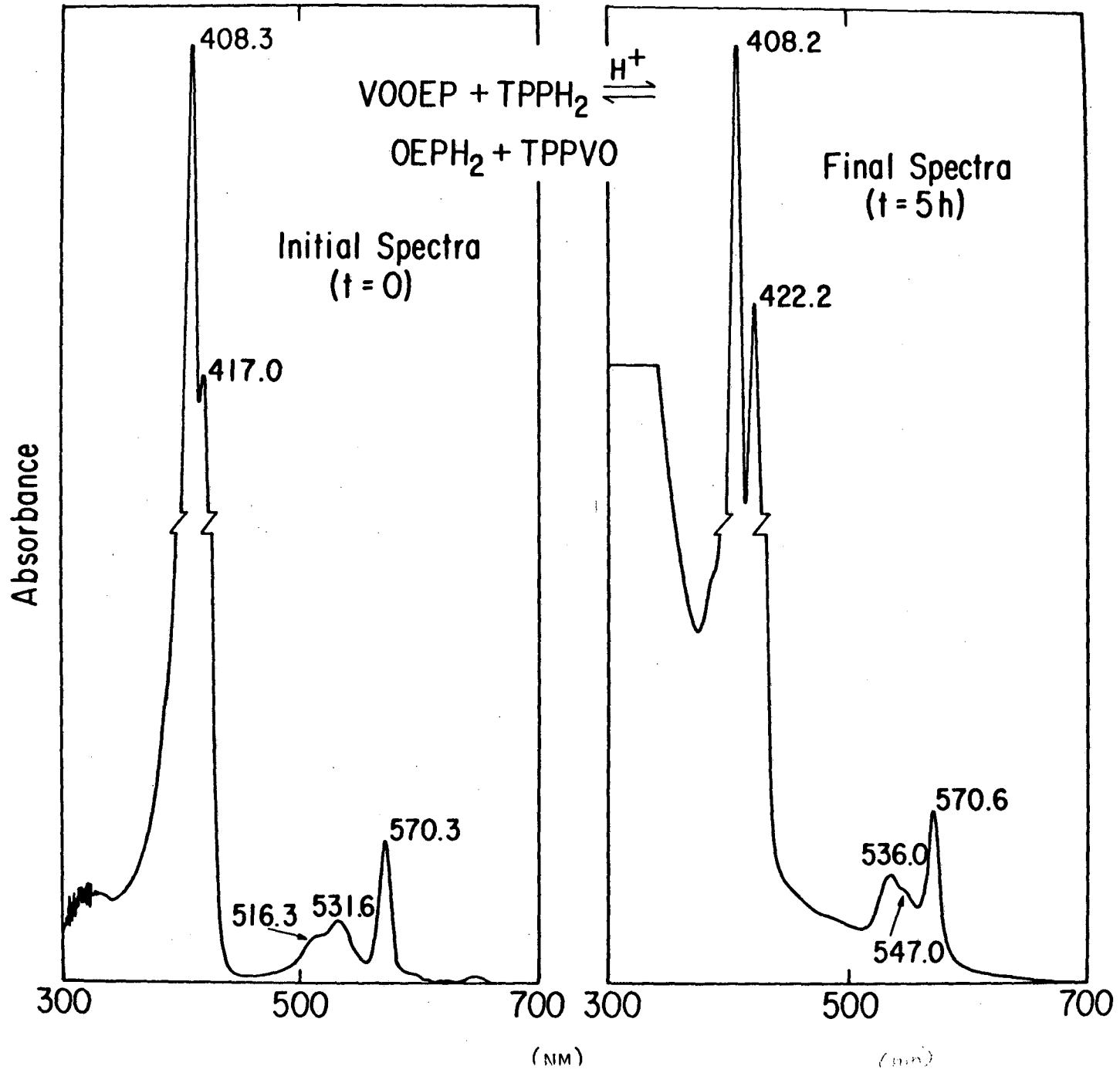
Conditions: 145°, N₂ atm
p-xylene
5 h
10% CF₃COOH

Equation 1

MLH₂ = TPPH₂, Benzosalen

XBL 823-8658

Figure 9



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