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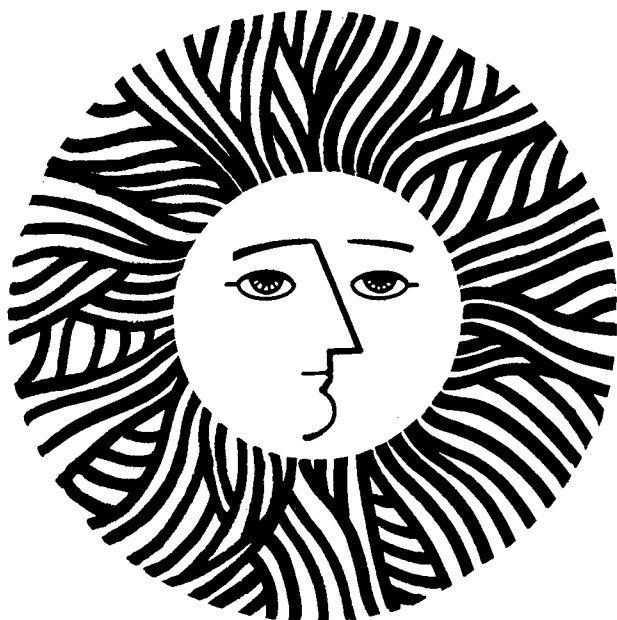
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Metal Coordination Chemistry: Removed and Recovery of Metal From Heavy Crude
and Shale Oils with Multidentate Ligands

Quarterly Progress Report
for period

July 1 - October 1, 1981

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Introduction

The identification of vanadyl porphyrin and non-porphyrin compounds in heavy crude oils is mandatory if methods for vanadium removal are to be implemented. The use of high performance liquid chromatography for the separation of the above-mentioned compounds and graphite furnace atomic absorption for detection (HPLC-GFAA) of vanadium (318.4 nm) compounds will be discussed.

The synthesis of linear catecholamides as possible ligands for removal of inorganic and organoarsenic compounds has been initiated and several new organoarsenic and inorganic arsenic have been prepared.

The removal of VO^{2+} ion from etioporphyrin, with multidentate ligands, represents a novel approach for the possible future utilization of polymeric multidentate ligands for removal and recovery of vanadium from heavy crude oils.

Speciation Studies of Vanadium Compounds in Heavy Crude Oils by High Performance Liquid Chromatography-Graphite Furnace Atomic Absorption Detection.

We have initiated speciation studies on Heavy Crude Oils (Cerro Negro, Wilmington, and Prudhoe Bay) via the HPLC-GFAA combination and have demonstrated the usefulness of this technique in identification of known vanadyl complexes and as a tool to fingerprint the oils.

Figure I demonstrates the potential nature of the HPLC-GFAA combination with known compounds (visible detector at 400 nm, GFAA detector at 318.4 nm for vanadium) using a solvent system chloroform, 30% in hexane to 70% chloroform in hexane, over 20 minutes and held at 70% chloroform -30% hexane for 10 minutes (flow rate 2.0 ml/min).

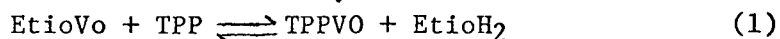
Figure II demonstrates the fingerprint of a pyridine extract of Cerro Negro heavy crude oil (Venezuelan) at 400 nm (visible detector) which was extracted to isolate the vanadyl porphyrins¹.

Competition Experiments Between Vanadyl Etioporphyrin and Multidentate

Ligands

We have continued our competition experiments by using HPLC-GFAA to analyze the equilibrium mixtures as well as multicomponent UV-VIS analysis with a microprocessor.

Figure III shows a competition experiment with the following equilibrium (eq.1):



as analyzed by HPLC-GFAA. The technique allows instantaneous analysis of vanadyl porphyrins and free bases, ie. EtioH₂ or EtioVo.

A multicomponent analysis of this above equilibrium with both a Cary 219-Apple II and H.P. 8550 UV-VIS instrument allows us to infer a definite shift to the right ie. TPPVO favored and are in the process of evaluating both methods for future competition experiments.

Future Work

It is hoped that the HPLC-GFAA combination will help facilitate both the speciation and identification work. We are continuing our vanadium chemistry and will shortly write-up the arsenic synthesis work.

Acknowledgements

I wish to thank John Komlenic and Raja Tannous for experimental help and the NBS group for high field mmr spectra.

References

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Presentations and Publications

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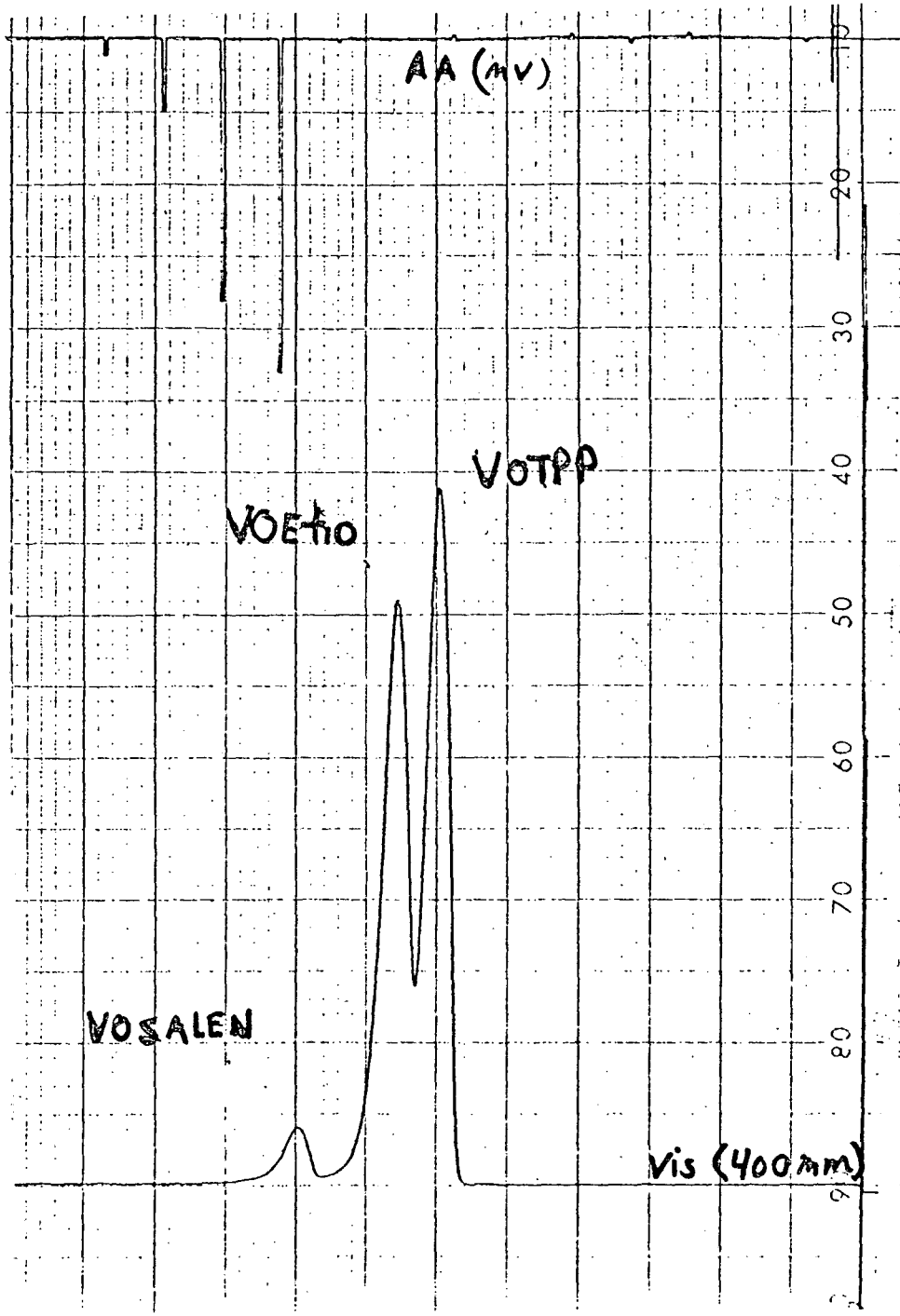


FIGURE I

<u>Mixture:</u> VO SALEN	<u>Column Cond.</u>
in VO TPP	30-70% CHCl ₃ in hexane
CHCl ₃ VO Etio	over 20 minutes
	70% CHCl ₃ in hexane
	10 minutes
<u>Fl. Rate</u> = 2.0 ml/min.	

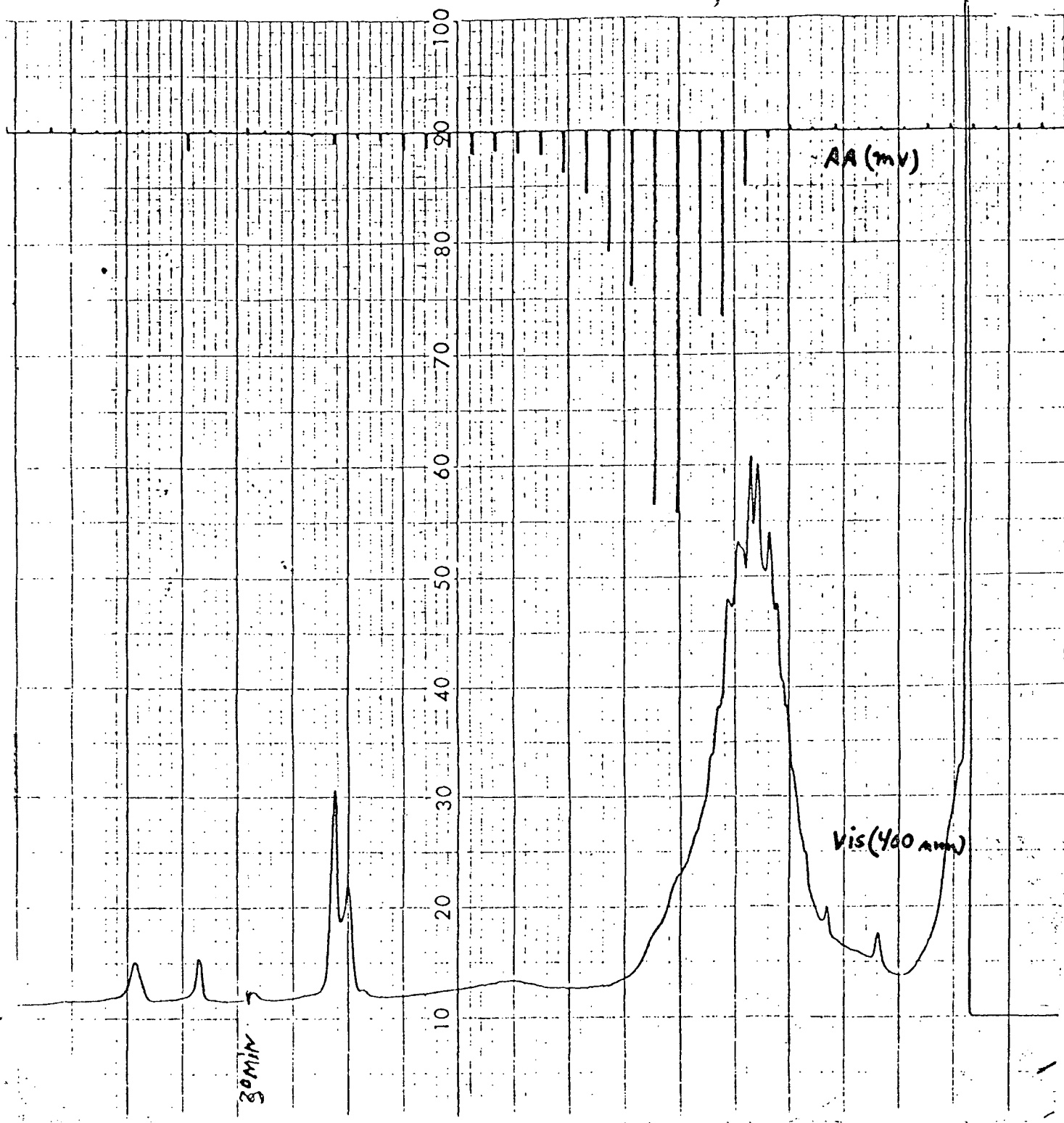


FIGURE II

Cerro Crude Oil
Pyridine Extract
Fl. Rate = 2.0 ml/min.

Column 0-100% CH₂Cl₂ in hexane over 30 min.
Cond. 100% CH₂Cl₂ 15 min.

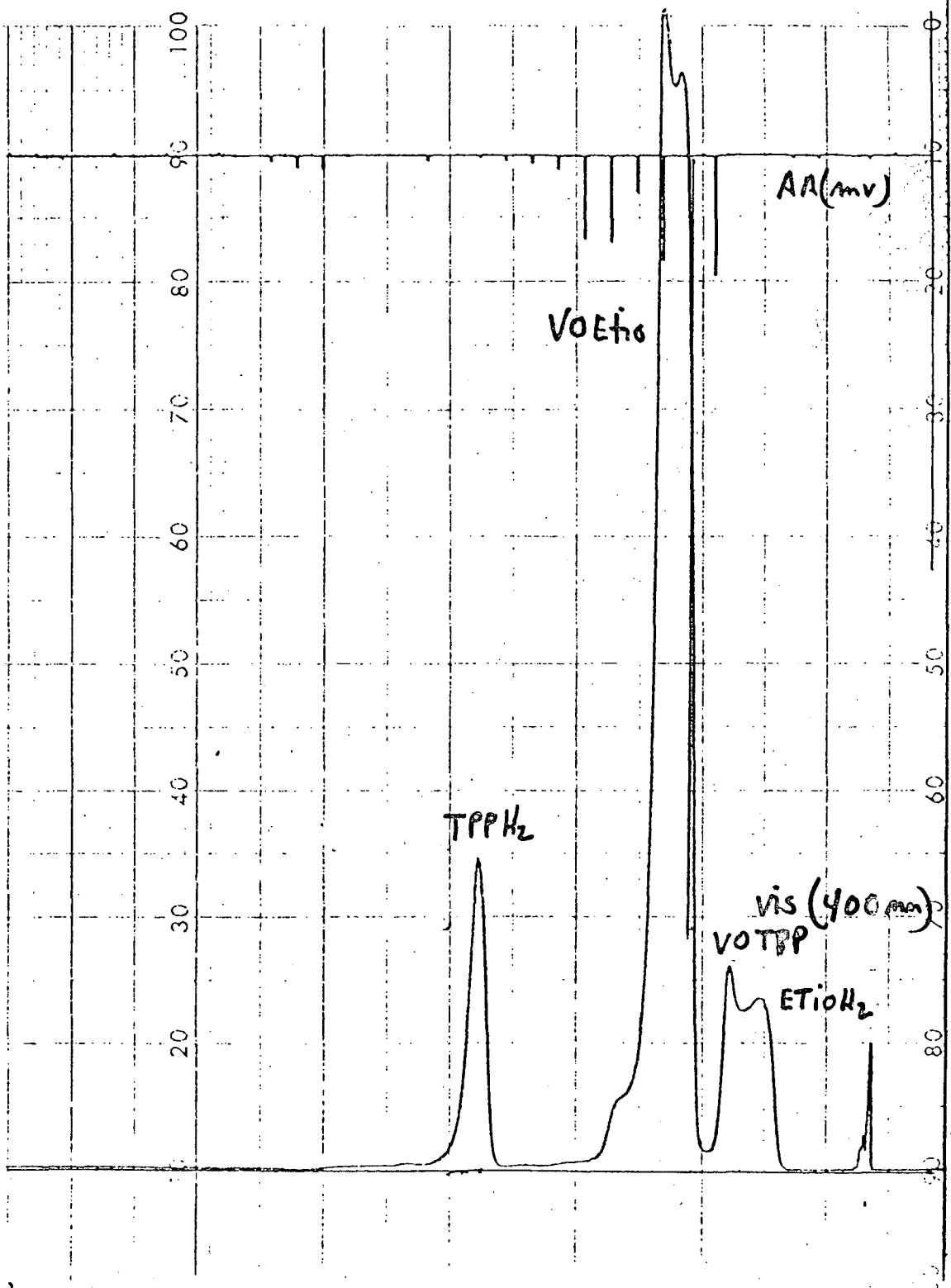


FIGURE III

Mixture: VOTPP, TPPH₂, VOEtio, EtioH₂

Col. Conditions

40-55% CH₂Cl₃
in hexane over
30 min.

Fl. Rate = 2.0ml/min.

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