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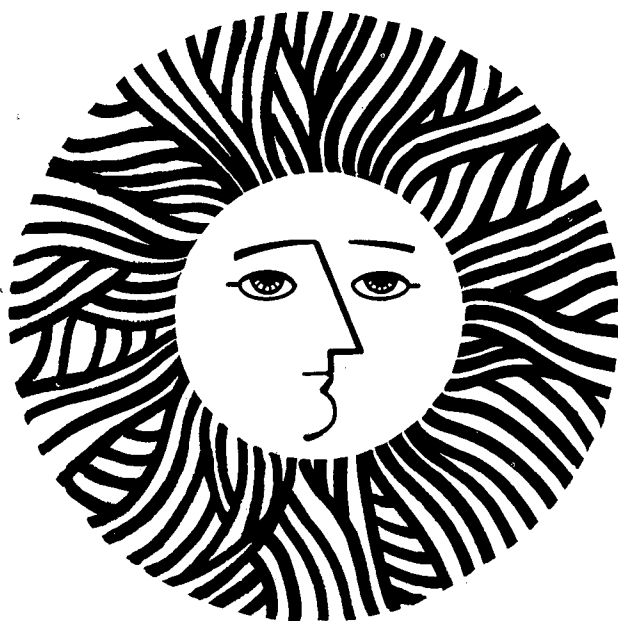
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Metal Coordination Chemistry: Removal and Recovery of Metals from Heavy Crude
and Shale Oils with multidentate Ligands

Quarterly Progress Report
for period

January 1 - April 1, 1981

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Introduction

The increased use of heavy crude oils and the future importance of synfuels, such as shale oil, makes it pertinent to identify the various inorganic and organometallic compounds that are contained in these fossil fuel products. The main reason for the speciation studies is to ascertain the inorganic or organometallic compounds that are potential candidates for the poisoning of hydroprocessing catalysts.

We have directed our program, which hopes to generate the technology to remove and possibly recover metal compounds from heavy crude and shale oils, this quarter towards the goals of: a) molecular characterization of the inorganic and organometallic compounds by high performance liquid chromatography in combination with graphite furnace atomic absorption detection; b) coordination chemistry of both arsenic and vanadium with substituted catechols, which are ligands capable of being placed in a polymeric backbone for future percolation column studies and; c) competition experiments where multidentate ligands and vanadyl tetraphenylporphyrin are reacted to establish equilibrium conditions under which, it is hoped, the vanadyl ion is more favorably disposed towards complexation with the multidentate ligand.

These areas will be discussed in this quarterly report.

Speciation Studies on Inorganic, Organometallic and Metallo-Organic Compounds Found in Shale Oil and Heavy Crude Oil.

We previously have successfully used a high performance liquid chromatograph in combination with a graphite furnace atomic absorption spectrometer (HPLC-GFAA), as an element specific detector, for speciation of inorganic arsenic and organoarsenic compounds in oil shale process waters¹. We have recently extended these studies, in collaboration with colleagues at the

National Bureau of Standards, to the shale oils and heavy crude oils we analyzed for total metal content and reported on in our first quarterly report ².

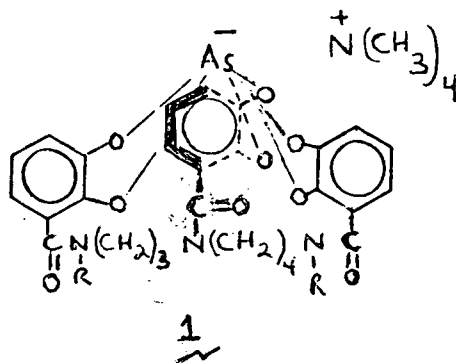
We used the technique of extracting the shale oils (Occidental, LETC and Parahoe shale oils) with a .02 M solution of ammonium carbonate and then analyzing the extracts for inorganic and organoarsenic compounds using a Dionex anion exchange column¹. In this manner, we tentatively identified arsenate (AsO_4^{3-}) from LETC shale oil, but are not positive about the presence of methyl and phenylarsonic acid as of this report. The Occidental and Parahoe samples also were examined and found to contain arsenate, but again, the identification of methyl and phenylarsonic acid is not clearly defined.

In the interest of trying to define the biogeochemical origin of the inorganic arsenic and organoarsenic compounds, we extracted a sample of oil shale kerogen, which came from Anvil Points, Colorado, with methanol. The methanol extract was analyzed by HPLC-GFAA, using the Dionex anion exchange column, and phenylarsonic acid was tentatively identified. We are in the process of a more unequivocal identification of this organoarsenic compound, but clearly this result is significant in that organoarsenic compounds, for the first time, have been identified in a fossil formation.

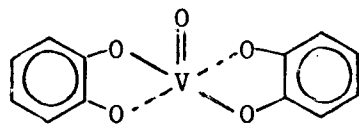
The heavy crude oil, Cerro Negro, from Venezuela was analyzed by HPLC-GFAA for vanadium compounds (318.4 nm) with chloroform as the mobile phase. These were preliminary experiments designed to get the appropriate conditions to separate the known vanadyl porphyrins and other vanadium compounds thought to be present in the crude oils. We have now assembled several vanadyl complexes of porphyrins and β -diketones and will determine their chromatographic properties to decide the identity of the unknown vanadium compounds found in the heavy crude oils.

Coordination Chemistry of Arsenic and Vanadium Compounds Found in Shale Oil and Heavy Crude Oil

We recently reported² on the synthesis of five coordinate arsenic complexes of methyl and phenylarsonic acid with substituted catechols. We have attempted to react arsenate (AsO_4^{3-}) with 3,4 LiCam, a substituted linear catecholamide. The reactions were run in a two-phase system to test the removal of arsenate from an aqueous solution. The arsenate did not, under conditions of phase transfer (tetramethylammonium hydroxide), react with 3,4-LiCam in the organic phase and we are in the process of reacting a water soluble linear catecholamide with arsenate to give a six coordinate arsenate anion complex, 1



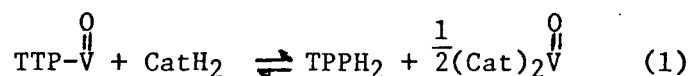
Similar coordination chemistry will be started the with vanadyl ion ($\text{V}=\text{O}^{2+}$) as the metal. Again, as with arsenic, five coordinate vanadyl complexes with catechols are expected, 2.



Competition Experiments Between Multidentate Ligands and Vanadyl

Tetraphenylporphyrin

The heavy crude oils, depending on origin, contain vanadium compounds in concentrations ranging from 200-6000 ppm. The only vanadium compounds that have been clearly identified are the vanadyl porphyrins³. While other ligands could complex the vanadyl ion, none have been identified. The Venezuelan heavy crudes contain approximately 30-50% vanadyl porphyrins from the total vanadium content. In view of these facts, we are presently attempting to compete vanadyl tetraphenylporphyrin, a model for the indigenous vanadyl porphyrins found in crude oils, with substituted catechols using visible spectroscopy to monitor the reactions (eq. 1).



We hope to gain insights into the stability of the catechol-vanadyl compounds, which will allow a more rational approach to removing vanadyl ions from porphyrins.

Future Work

The speciation studies of arsenic and vanadium compounds in shale and crude oils, respectively, by the HPLC-GFAA combination will be continued. The coordination chemistry and competition experiments will also be extended with both vanadium and arsenic.

Acknowledgments

We wish to thank members of Dr. Fred Brinckman's group at the National Bureau of Standards for performing the HPLC-GFAA analysis on the shale oil extracts and the heavy crude oils. The technical assistance of John Komlenic and Raja Tannous is gratefully appreciated.

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1. R. H. Fish, J. P. Fox, F. E. Brinckman and K. L. Jewett, submitted for publication (1981).
2. R. H. Fish and T. Vermeulen, LBID-318 quarterly report, Oct. 1 - Dec. 31, 1980 to BETC.
3. R. Bonnett and P. Brewer, Tetrahedron Letters, 2579 (1970).

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