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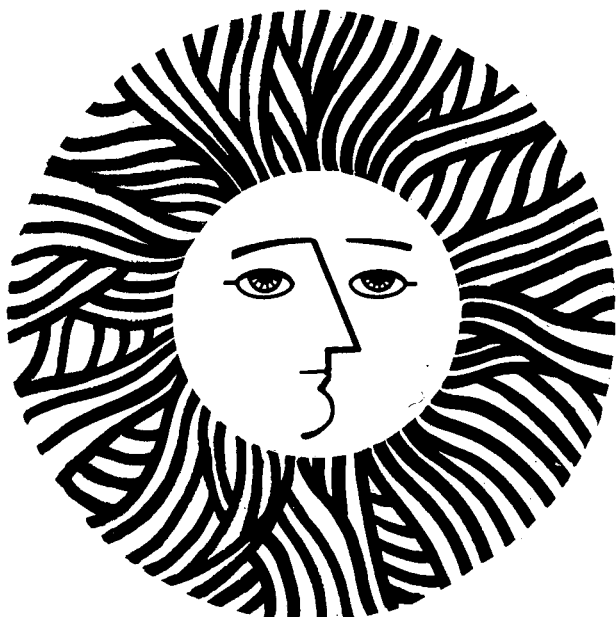


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Metal Coordination Chemistry: Removal and Recovery of Metals from Heavy Crude
and Shale Oils with Multidentate Ligands

Quarterly Progress Report
for period

April 1 - July 1, 1981

Prepared for the
Bartlesville Energy Technology Center
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Introduction

We have continued our speciation studies with the thought that identification of unknown arsenic compounds in shale oil, and in the future vanadium compounds in heavy crude oil, could be tentatively identified by their HPLC capacity factors (t_R) and correlated to substituent constants of known organoarsenic compounds. This has become a reality, i.e., being able to correlate $\log t_R$ with a substituent parameter to provide a linear relationship and this will be discussed in this report.

The arsenic coordination chemistry has developed to the point where the substituted catechols could be used to remove these compounds from shale oils if they could be incorporated into polymers, while the potential use of tetraazamacrocycles for vanadyl ion removal will be scrutinized.

The competitive equilibrium between model vanadyl porphyrins and multidentate ligands would provide insights into the role of multidentate ligands as candidates for removal of vanadyl ions from heavy crude oil and studies along these lines will be discussed in this quarterly report.

The isolation of inorganic and organoarsenic compounds from the biogeochemical precursor to shale oil that of Green River Formation Oil Shale Kerogen will be discussed.

Speciation Studies of Inorganic, Organometallic and Metalloorganic Compounds of Arsenic and Vanadium in Shale Oil and Heavy Crude Oil

An important aspect of any speciation studies of inorganic or organometallic compounds in the parts per million range ($\mu\text{g/ml}$) is the ability to identify, even tentatively, compounds that are unknown.

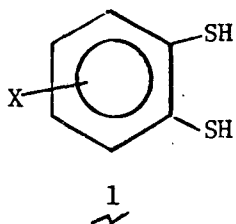
We have developed a technique that will allow a prediction of molecular structure from ion exchange chromatographic retention. Thus, by plotting the logarithm of the capacity factor for a number of known organoarsenicals with structural substituent parameters based on the ionization of organophosphoric acid, we find that a linear correlation exists^{1,2}.

This exciting result should allow us to tentatively identify any organoarsenic compound in fossil fuel products such as shale oil and retort waters. More importantly, we could extend these studies to unknown vanadyl compounds in heavy crude oils, which could greatly facilitate the identification of compounds other than the known vanadyl porphyrins.

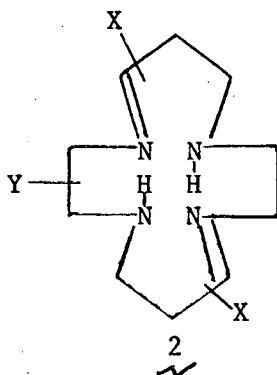
Coordination Chemistry of Arsenic and Vanadium Compounds Found in Either Shale Oil or Heavy Crude Oil

The coordination chemistry of organoarsenic and inorganic arsenic compounds with substituted catechols has shown that these reactions proceed in a facile manner to give either five coordinate arsenic catecholates (organoarsenic compounds) or octahedral coordinated arsenic compounds (arsenate). These compounds have been identified by high field nuclear magnetic resonance spectroscopy and electron impact mass spectrometry.

These studies are to be extended to benzenedithiol derivatives, 1, because of the more favorable coordination of sulfur to arsenic over oxygen-arsenic coordination.



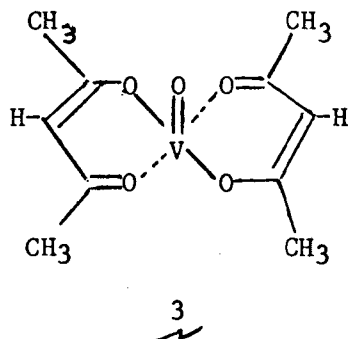
The vanadium coordination chemistry is focusing on a series of porphyrin models, i.e., the substituted tetraazamacrocycles, 2, (14 membered ring).



We are presently trying to synthesize the $V=O^{2+}$ complexes of these porphyrin models in order to better understand the chemical and physical properties of this yet unreported class of vanadyl compounds.

Competition Experiments Between Vanadyl Compounds and Multidentate Ligands

The previous experiments were designed to ascertain a reactivity order in the removal of vanadyl ion ($V=O^{2+}$) from vanadylacetylacetonate, 3.

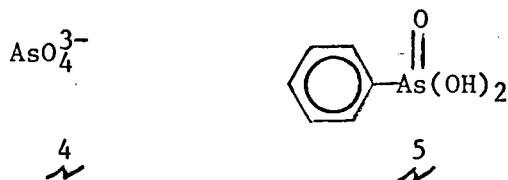


We found that the catechols, porphyrins and tetraazamacrocyclic ligands were able to remove $V=O^{2+}$ ion from 3. However, in order to better accentuate the vanadyl compounds known to be present in the heavy crude oils, we decided to use vanadyl etioporphyrin as the target compound for removal of vanadyl ion.

We are presently using ultraviolet and visible spectroscopy to study the competitive equilibrium between vanadyl etioporphyrin and multidentate ligands and will report these results in future reports and publications.

Isolation and Identification of Organoarsenic and Inorganic Arsenic Compounds Found in Oil Shale Kerogen

In order to more clearly define the biogeochemical source of the inorganic arsenic and organoarsenic compounds identified in shale oils and the retort waters, we extracted a green River Oil Shale Kerogen (NBS Standard reference material) from Anvils Point, Colorado and identified arsenate,⁴ and phenylarsonic acid,⁵



We are presently going to derivatize compound 5 with 3-methylcatechol to give a five coordinate phenylarsenic-methylcatecholate previously prepared for our arsenic removal studies. This compound will be subjected to GC-EIMS; thereby, providing unequivocal evidence for its structural identification.

We reported this finding at our DOE/NBS workshop², and will report this first identification of an inorganic and organometallic arsenic compound in a biogeochemical source, at the Xth International Conference on Organometallic Chemistry, Aug. 9-14, 1981 in Toronto, Canada at a special Environmental Symposium in which we are invited speakers¹.

Future Work

The speciation studies will be continued on both the shale oils and heavy crude oils. The coordination chemistry using benzenedithiols for the arsenic compounds and the tetraazamacrocycles for the vanadyl compounds will be continued. The synthesis of new multidentate ligands will also commence this summer and these compounds will be added to our list of competitors for the studies involved in the removal of $V=O^{2+}$ ions from petroporphyrins.

Acknowledgments

I would like to thank C. S. Weiss, K. L. Jewett, and F. E. Brinckman for collaborative studies on the isolation and identification of arsenic compounds in fossil fuel materials. The experimental help of John Komlenic and Raja Tannous is appreciated.

References

1. C. S. Weiss, F. E. Brinckman, and R. H. Fish, Occurrence of Organo-arsenic Compounds in Oil Shale Processing: Molecular Diagnostics for Their Chromatographic Speciation. To be presented at the Xth International Conference on Organometallic Chemistry, Toronto, Canada, August 9-14, 1981.
2. C. S. Weiss, K. L. Jewett, F. E. Brinckman, and R. H. Fish, DOE/NBS Workshop on Environmental Speciation and Monitoring Needs for Trace Metal-Containing Substances from Energy Related Processes, Gaithersburg, MD, May 18-20, 1981. A full account will be published in the Proceedings of the above-mentioned workshop.

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