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# SPECIATION OF INORGANIC ARSENIC AND ORGANOARSENIC COMPOUNDS IN FOSSIL FUEL PRECURSORS AND PRODUCTS

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## INTRODUCTION

### Occurrence of Metals and Metalloids in Fossil Deposits

Transformations and bioaccumulation of trace metals and metalloids, especially arsenic, are well known to occur in modern microorganisms, including the bacteria[1,2] molds[3], and marine plankton or algae[4,5]. Such microflora demonstrate capacities for uptake of both inorganic and organic forms of elements, and in some instances, are shown to involve biomethylation of inorganic substrates which result in cellular incorporation of organometal(loid)s, e.g., methylarsonic acid or dimethylarsonic acid ions[5]. Arsenic is known to bioaccumulate in higher marine organisms to a substantial degree[6,7], where it resides in some shellfish tissues as arsenobetaine[8].

Similar considerations for ancient metal(loid) uptake or transformations appear quite reasonable for primordial microflora, especially the algae which account for the present ubiquitous distribution of kerogen in shale rocks[9,10]. In general, the fossil deposition record suggests that substantial metal(loid) accumulation also occurred in higher plants which underwent diagenesis to form

modern petroleum and coal deposits[11,12]. In many instances, various present-day species of plants are known to both selectively and extensively hyperaccumulate various metal(loid)s to such a degree that geochemical prospection is feasible by correlating metal concentration profiles with local flora[13]. It is not unexpected, therefore, to discern characteristic concentration patterns for trace elements in various fossil deposits - whether we regard these as essential or toxic to life - and to expect that gross differences in the profiles between the three main types: coal, kerogen, and petroleum, as summarized in Table I.

Similarly expected, though far more subtle, we might anticipate that element distributions for these three main fossil sources also depend upon specific sites, and reflect their terrestrial or marine origins, subsequent geochemical history, and maturation[19,20,21].

Molecular Nature of Metals and Metalloids in Fossil Deposits

The molecular forms of trace metal(loid)s in fossil deposits is doubtless complex, probably consisting of varying propositions of inorganic, metallo-organic (no covalent element-carbon bonds), and true organometallic chemical species residing in unspecified sites within the carbonaceous matrix. Over the years a very substantial solvent differentiation methodology has emerged,[22-24] which greatly aids the analyst in assessing the broad matrix categories of fossil materials, and produces reproducible information concerning possible ligation, elements present, and approximate molecular size (weight) of the soluble components.

For modern industrial processing requirements, all of which ultimately rely upon thermal "cracking" of the fossil organic host matrix, a much more refined understanding of both the original form of the selected element, its

relationship to other matrix elements, and the pathway(s) by which thermolysis can slightly or radically alter the elements original molecular form is crucial. Both from the standpoint of environmental impacts of such organometal(loid)s formed or released by processing[25], as well as the acute industrial problem of many of these trace elements poisoning effective "cracking" or upgrading catalysts[26], an urgent need exists to speciate trace elements in fossil precursors and products.

## THE PRESENT STATUS OF TRACE ELEMENT SPECIATION IN FOSSIL MATERIALS

### Underlying Analytical Requirements

The determination of the molecular forms of trace metal(loid)s in fossil materials ideally requires a technique with extreme selectivity, lack of interferences, sensitivity to the sub-ppm level, and the ability to deal with heterogeneous samples. The state-of-the-art analytical methods which are capable of meeting these criteria to varying degrees, without extensive sample preparation, are quite limited and have only recently been applied to limited types of fossil samples. These methods include SEM-EDX,[27,28] EXAFS,[29,30] Mossbauer spectrometry,[31] and ESR.[32]

Prior sample preparation has traditionally allowed the use of numerous methods, e.g. the determination of porphyrins using UV-visible spectroscopy in the Soret region. The methods used to pretreat samples range from solvent extraction to open column liquid chromatographic separations, and more recently high performance liquid chromatography, (HPLC).

The coupling of chemical separations, which provide selectivity and reduce interferences, with instrumental techniques, which are capable of providing further selectivity and the necessary sensitivity, has been an active

area of analytical research, being performed in both off-line and on-line modes. The recent emergence of a number of on-line "hyphenated" techniques,[33] GC-MS, MS-MS, LC-ESD (including variable- and scanning UV, IR, NMR, GFAA, FAA and electrochemical detectors) appears to be the most effective and versatile method to quantitate organic, inorganic, organometallic and metallo-organic compounds in complex matrices. Among these, automated coupling of high performance liquid chromatography (HPLC) in normal, reverse phase, ion exchange, or size exclusion modes with element-selective detectors appears most promising for the characterization of metal(loid) containing molecules in complex matrices.[34]

## Detection of Naturally-Occurring and Process-Formed Metall(loid) Molecules in Fossil Materials

The two most general classes that metal(loid) molecules may occur in are organic forms (organometallic or metallo-organic), and in mineral forms. The determination of mineral forms in coal using X-ray diffraction has provided information about the major and minor materials present[35]. The application of high temperature and low temperature ashing and a variety of wet chemical separations has provided more detailed characterization of elements occurring at trace levels. Recently the use of SEM-EDX has provided the identification of accessory minerals in coal and the location of certain elements in host minerals, such as arsenic in pyrite.[27,28] This technique is also capable of locating elements which are associated with the macerals found in coal indicating organic associations of certain elements during the coalification process. The subsequent mineralization, during the geochemical history, of metallo-organic compounds would yield submicron size mineral grains which are still difficult to characterize.

The use of Mossbauer spectroscopy to probe the environment that iron is found in coal has been reported[32]. Different oxidation states for iron have been detected and upon heating the formation of pyrite and non-stochiometric types of pyrrhotite have been identified.

The identification and investigation of metalloporphyrins in petroleum dates back to the 1930's[36] and has been amply reviewed[12]. More recently the extraction of gallium porphyrins from coal has been reported.[37] The isolation of nickel porphyrins from shale oil has also been reported using a liquid chromatographic separation.[38]

Electron spin resonance has also been used to study various nuclides in carbonaceous material.[32] In some instances sensitivity has been a problem but the doping of the matrix with the compound of interest serves as a chemical probe helping to determine sites capable of ligation.

The characterization of non-mineral, non-porphyrin metal(loid)s in fossil materials has been a difficult task because of the variable stoichiometry of metallo-organic ligands.[21] The use of sink float fractions has provided information on the inorganic and organic affinities of a number of elements in coals.[39] The organic affinities of these elements have been related to various physiochemical properties such as charge to radius ratio and various measures of complex formation (or stability). The application of liquid chromatographic separations of solvent extracts of a variety of fossil fuels and conversion products has followed the logic of the float sink procedure of obtaining different fractions to be analyzed for a variety of trace elements. The liquid chromatographic procedures generate fractions of differing polarity, functionality, and molecular size. The off-line procedure of analyzing liquid chromatographic fractions for a number of trace elements in

petroleum[40], coal liquids,[41,42,43] and shale oil[38] have been reported.

Reports of on-line, element-selective detection of chromatograhic effluents of fossil materials have appeared more recently and offer the advantages of increased resolution and easier chromatographic optimization because of the real time acquisition of elemental distributions during the chromatographic run. Brinckman et al.[44] have coupled a graphite furnace atomic absorption (GFAA) spectrometer to a high performance liquid chromatograph, which has been applied to the analysis of arsenic compounds in process waters and oils generated during oil shale retorting.[25,45] Hausler et al.[46] have interfaced an inductively coupled plasma emission spectrometer to a size exclusion chromatographic column to investigate coal derived materials. Olsen et al.[38] have used a directly coupled plasma emission spectrometer to analyze liquid chromatographic fractions of shale oil in an off-line mode, which led to the detection of nickel porphyrins.

More discrete chemical bonding information is obtainable by using extended x-ray absorbance fine structure measurements. The application of EXAFS to the analysis of titanium in solvent refined coals I and II as well as the unprocessed coal has been reported.[30] The EXAFS features indicate a conversion of mineral forms of titanium to organometallic forms during the liquefaction process. The analysis of vanadium in coal using the EXAFS procedure has elucidated vanadium to oxygen bonding rather than nitrogen (indicative of porphyrin types) or sulfur bonds.[29] This study also indicated that the form(s) of vanadium present in the coal were reduced to the 3+ oxidation state during the liquefaction process.

## Speciation of Arsenic Compounds in Shale Oil, Oil Shale Retort Waters and Oil Shale Kerogen

### A) Background

Shale oil is recovered from oil shale kerogen by a controlled pyrolysis at 500°C using surface and *in situ* technologies. These produce, along with the shale oil, considerable amounts of process waters which originate from mineral dehydration, combustion, groundwater seepage, and steam and moisture in the input gas. Since the waters are in intimate contact with raw and partially retorted retorted shale and shale oils, they constitute a leachate of these products.[47,48]

Several possible environmental problems are recognized in the formation and disposal of these retort process products. Firstly, the shale oils and retort waters contain a host of trace organic compounds[48,49] as well as a large array of trace metals and metalloids that are potentially toxic in certain forms to aquatic biota and man.[50-52] Secondly, in order to evaluate the latter contaminants for their environmental impacts, the key inorganic and organometallic forms associated with these toxic metals or metalloids (e.g., arsenic, cadmium, mercury, selenium, etc.) must ultimately be identified and their molecular features characterized or speciated.[53]

Even though the presence of arsenic in shale oil has necessitated the development of dearsenation processes to protect hydrotreating catalysts during shale oil processing, the molecular speciation of arsenic in shale oil has not been reported. Curtin et al.[54] found that arsenic was present throughout various boiling range fractions including a fraction obtained below 205°C. The development of methods for the molecular speciation of arsenic in shale oil would be invaluable to further optimize dearsenation processes as well as

process monitoring in support of dearsenation catalysts.

The HPLC-GFAA combinations provided an effective tool that allows direct separation and identification of these types of compounds in oil shale process products.[55-60] We recently reported on the successful use of two HPLC-GFAA units, in our respective laboratories, to separate and identify inorganic and organic arsenic compounds occurring in oil shale retort and process waters representing current experimental technology[25] as well as the shale oils.[61]

Arsenic was selected for study because of its widely acknowledged toxicity in groundwaters[62] and because previous work indicated[50] that total arsenic concentrations in oil shale process waters range from 5 to 15 g $mL^{-1}$ (ppm) and 20 ppm in the shale oils.[18]

## EXPERIMENTAL

### Procedures for Speciation of Arsenic Compound in Oil Shale Retort Waters and Process Waters, Shale Oil and Oil Shale Kerogen

Two Perkin-Elmer graphite furnace atomic absorption spectrometers, Models 4000 and 460, were used as arsenic-specific detectors for high performance liquid chromatographs (Altex Model 100A), in the respective laboratories. Additionally, each setup has an Altex 153 ultraviolet detector, which was used at 254 nm to monitor the organic matrix and to measure solvent fronts ($t_o$). Experimental parameters for coupling the HPLC to the GFAA detector, and optimization of arsenic speciation, have been previously described[55-58].

The size exclusion chromatographic separations were performed on both rigid and non-rigid polystyrene divinyl benzene packings using THF as the mobile phase. The rigid μ-Styragel columns [2(1000Å) and 1(100Å) columns] are capable of separating compounds of differing molecular size, by comparison

with polystyrene calibration standards, from less than 600 to greater that 19,000 daltons.

Oil Shale Retort Water Samples and Shale Oils Studied

Seven important *in situ* oil shale retort and process water samples were examined, including three waters from Occidental's Logan Wash modified *in situ* process[63] (retort, boiler blowdown, and heater treated waters); Geokinetic's horizontal, true *in situ* retort water[64]; Laramie Energy Technology Center's Rock Springs Site 9 true *in situ* experiment Omega-9 retort water;[65] and two large-scale simulated, modified *in situ* retort waters: one run, L-2 from Lawrence Livermore Laboratory's 6,000 kg retort,[66] and one from Laramie Energy Technology Center's 150-ton retort.[67] These materials were warmed to room temperature, filtered (0.45 m, Millipore), appropriately diluted with deionize water, and directly injected (100-250 L) into the HPLC-GFAA systems.

The shale oils investigated during this study were: Paraho shale oil, National Bureau of Standards SRM 1580, and Crude Shale Oil A and Centrifuged Shale Oil number 4101 (Fossil Fuels Research Materials Facility, Oak Ridge National Laboratory). The oils were diluted with THF to concentrations near ten percent, centrifuged where necessary and filtered through a 0.45 μm filter prior to injection into the HPLC-GFAA system.

Peak Identification for the Retort and Process Waters Studied by HPLC-GFAA

Figure 1 compares the arsenic-specific GFAA chromatograms obtained for the Occidental retort and process waters. Conventional chromatograms, taken with an ultraviolet (254 nm) detector in series with the GFAA detector, are shown superimposed (solid traces) on the arsenic-selective outputs; these clearly reveal the intensity and complexity of the organic matrix, and the

analytical limitations of non-selective detectors. Each time we ran a sample, we also ran five authentic arsenic standards (as 10 ng As in each peak) combined into one solution. These included sodium arsenite, dimethylarsinic acid, methylarsonic acid, phenylarsonic acid and sodium arsenate. We regarded each GFAA chromatographic peak as "positively" identified if its retention volume matched that of the mean value of the calibration peak for each arsenic species within two standard deviations of RSD < 5 percent $t_R$,[55,56,60]. "Tentative" assignments were given to those peaks outlying $2\sigma$, although spiking the field samples with authentic arsenic compounds yielded the same (increased) single chromatographic peak for both positively and tentatively, identified species.

Quantitation of Identified Arsenic Species in Oil Shale Retort and Process Waters

The representative figure and others[25] clearly demonstrate that each retort or process water has a distinctive "fingerprint" and that substantial but variable quantities or arsenate, methylarsonic acid and phenylarsonic acid are present, while arsenite and dimethylarsinic acid are probably absent, or at best, marginally detected. Estimated detection limits and sensitivities for each arsenic species were found to vary, mainly a consequence of the alkaline organic matrix and the fixed GFAA atomization program.[56,60] Consequently, we compared each sample chromatogram against that of a standard solution of authentic arsenicals in distilled water. Reliable retention times discussed above were obtained this way, as were approximate concentrations of arsenic species (Figure 2).

Comparisons Between the Retort and Process Waters

Arsenate is by far the major (0.6-10 ppm) arsenical component identified in all of the samples studied, but the variable concentrations of the other

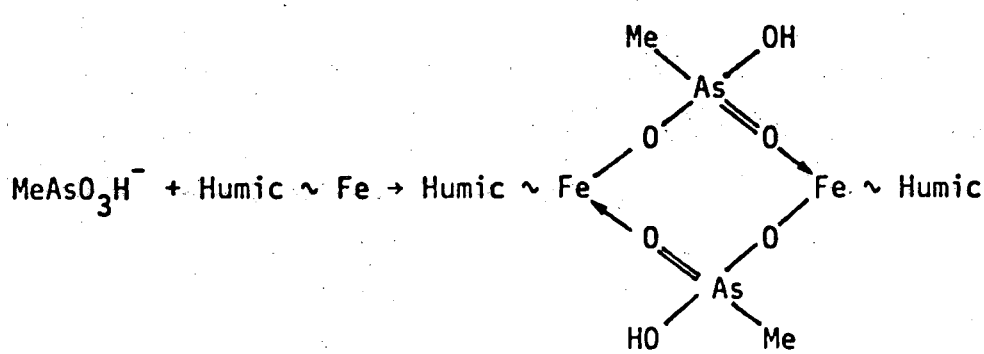
species suggest quantitative diagnostics for monitoring widely different production sites. It is interesting to note that Occidental's retort and process waters (Fig. 1) all contain methylarsonic acid, phenylarsonic acid, arsenate, and one or several neutral or weakly ionized arsenicals, possibly in the molecular $R_3As$ or $R_3AsO$ classes. Generally, neutral or weakly ionized molecules elute with the solvent front (at $t_o$ min) or with only slight retention (at $t_R$ min) in well-behaved ion exchange columns where k' ~1/ ; k' = $(t_R-t_o)/t_o$ and u = ionic strength[68].

The two true <u>in situ</u> retort waters, Geokinetic and Omega-9, also display early peaks and contain methyl and phenylarsonic acids, arsenate, and another unknown ionic arsenic species eluting at 20.4 min. Important in a different way, both simulated <u>in situ</u> process waters, 150-Ton and L-2 were distinguished by a significant diagnostic feature involving, respectively, absence of detectable [ 0.002 ppm] phenylarsonic acid in the 150-Ton sample, whereas L-2 water contains 0.3 ppm of this species. Beyond this, both 150-Ton and L-2 samples contained methylarsonic acid, arsenate, and the neutral component which suggested their similarity to Omega-9. These distinguishable fingerprints may reflect different operating parameters used in the controlled pyrolysis reaction possible with the 150-Ton and L-2 facilities. The similarities last noted may well indicate that basic chemical phenomena are the same in certain laboratory and field retorts, and imply that HPLC-GFAA fingerprinting may serve as a monitoring tool for correlating such operations.

The analysis of NBS shale oil SRM 1580, certified for organics only, is presented in Figure 3 and exemplifies the dual element selective chromatographic detection. The arsenic is eluted with a retention volume corresponding to a molecular species of close to 2,000 daltons, as is the iron. The

arsenic also appears to be distributed among species of various molecular weight. In the NBS oil, the arsenic and iron compounds coelute with a molecular species having an apparent molecular weight greater than 2,000 daltons. In the ORNL centrifuged oil, the arsenic was distributed towards lower molecular weights and the iron has a bimodal distribution with elution volumes corresponding to about 12,000 and 2,000 daltons.

The primary difficulty in trying to speciate metals in oils is in finding appropriate standards for macromolecular compounds. This is evidenced by the reporting of the distributions of metals without the necessary standards for chemical speciation.[42,29] Our experimental approach was to spike the Paraho shale oil with methylarsonic acid. The methylarsonic acid was ligated by the molecular weight compounds of 2,000 daltons, again coeluting with iron. We postulate that this association of arsenic with iron in macromolecules is analogous to the association of orthophosphate and metals such as chromium and iron via oxygen bonding in polymers. We envision iron complexes of humic acids, the precursors of many fossil fuels, ligating the anionic forms of arsonic acids via Fe-O-As bonding by the reaction:



This may indicate the competitive chemistry occurring in iron oxide guard beds used for the commercial dearsenation of shale oil. Our continuing arsenic speciation studies can provide information for innovative methods of removal of arsenate, methyl and phenylarsonic acids from shale oils. For example, one method we are studying involves reaction of alkyl and arylarsonic acids with polymer-bond catechols. Recent model compound reactions suggest that this method has exciting possibilities.[69]

Biogeochemical or Process Origins of Organoarsenicals

The origin of these observed organoarsenic compounds, at this time, is not understood. Kerogen, generally regarded as biogeochemical creation, largely from lipid fractions of ancient algae[48], forms the ubiquitous oil source matrix in shales. Thus, it is conceivable that these methyl- and phenylarsonic acids occur naturally following original biosynthesis or bioaccumulation[52,69] and subsequent mineralization in oil shale and are released with little decomposition upon pyrolysis, ending up as leachates in the process water after intimate contact with the shale oil. Ample evidence is available for both terrestrial and marine biomethylation of inorganic arsenic(V) by modern micro-organisms[52,70] and marine algae[52,69] to produce both dimethylarsinate and methylarsonate species; no analogous biophenylation is reported as far as we know. The negligible amounts of dimethylarsinate or arsenite in our sample waters may result, from oxidative loss of the latter in aged sample[71], or from oxidative pyrolysis of both species in aerobic retorts,[51,71] selective rates of formation during original biogenesis, or an alternative purely adiotic synthesis forming methyl- or phenylarsenic bonds in the hot reaction zone of the retort. This last pathway seems quite reasonable for the methylarsonic acid observed, since it parallels the long-known Meyer

reaction[72] between alklyl halides and arsenite salts. In boiling aqueous solution both alkylarsonic and dialkylarsinic acids can form, but arylarsonic acids are not similarly obtained,[73] thereby suggesting that the phenylarsonic acid observed may arise from other sources.

In order to shed light on the biogeochemical origin of the methyl and phenylarsonic acids, we recently extracted a Green River oil shale sample (NBS standard reference material) with methanol. By using our catechol-organoarsonic acid derivitization reactions, we have identified, in an unequivocal fashion, both methyl and phenylarsonic acids by capillary column gas chromatography - mass spectrometry analysis.[74] This, we believe, is the first positive identification of organoarsenic compounds in a fossil sample and represents a new area of research we have coined "organometallic geochemistry".

## CONCLUSIONS

The significant environmental implications are that potentially toxic inorganic arsenic and organoarsenic compounds in varied mixtures at appreciable concentrations are either released or synthesized during oil shale retorting processes representing present-day technology. The methods applied by us presage similar efforts with other toxic elements. The possibility of their bioaccumulation in soils, water, and edible biota at appreciable distances from the retorting site *via* disposal of retort leachate waters containing bioactive forms may represent potential health hazzards for humans as well as a threat to aquatic species. Suggested bioleaching of petroliferous shales[75,76] as an energy-conserving alternative to pyrolysis, must now be regarded with new concerns for re-release or biotransformation of arsenicals entrapped in kerogen, and this should guide research on other metals as

well.[70] A more immediate consequence of low-level exposure of workers in these future retort process plants to such inorganic and organoarsenic compounds will require monitoring, since there is not presently a complete understanding of *in vivo* mechanisms of arsenic and other heavy metal toxicity.[52]

We believe our studies have provided the first positive molecular characterization of any trace inorganic or organometallic substances in such fossil fuel precursors or recovery products. Since the HPLC-GFAA technique is shown to be broadly applicable to a wide variety of elements in many molecular classes, with great freedom from usual matrix interferences,[55-60] we envision similar utility for speciating other toxic metal-containing molecules in oil shale products. Among these prospects, mercury, selenium and lead are important because of their known biotransformations[70] and presence in kerogen pyrolysates.[51,75,76]

The definitive molecular speciation of arsenic is possible in some cases; however, macromolecular arsenic-containing species, evident in size exclusion chromatograms of various shale oils, must be evaluated in terms of: heteroatom content, correlations among a variety of elements, the extent and nature of the complexing capacity of the matrix for arsenic and the stability of these arsenic containing compounds. The conclusions drawn during this study are: (1) HPLC-GFAA permits the chemical speciation of arsenic in process fluids from oil shale retorting; (2) the association of arsenic with iron provides a preliminary chemical basis for understanding the presence of metals and metalloids in the macromolecular components of fossil fuels; (3) the anionic nature of arsenic may explain its unique behavior with respect to other elements' cationic behavior; (4) studies based on the uptake of alkyl- and arylarsonic acids by the macromolecular compounds in shale oil may provide

beneficial insights for optimizing the removal of arsenic from shale oil; and (5) the establishment of the biogeochemical origin of arsenate, methyl and phenylarsonic acids in oil shale kerogen has provided new insight in organometallic geochemistry.

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REFERENCES

1. R.C. Mc Bride and R.S. Wolfe, Biosynthesis of Dimethylarsine by Methanobacterium, Biochem., 10, 4312-4317 (1971).

2. C.N. Cheng and D.D. Focht, "Production of Arsine and Methylarsines in Soil and in Culture," Appl. Environ. Microbiol., 38, 494-498 (1979).

3. W.R. Cullen, B.C. McBride, and A.N. Pickett, "The Transformation of Arsenicols by Candida humicola, Can. J. Microbiol., 25, 1201-1205 (1979).

4. Bottino, N.R., Cos, E.R., Irgolic, K.J., Maeda, S., McShane, W.J., Stockton, R.A., Zingaro, R.A., "Arsenic uptake and metabolism by the alga Tetraselmis Chui, in Organometals and Organometaloids Occurrence and Fate in the Environment, F.E. Brinckman and J.M. Bellama, eds, pp. 116-129 (American Chemical Society Symposium Series 82, Washington, D.C., 1978).

5. M.O. Andrae and D. Klumpp, "Biosynthesis and Release of Organoarsenic Compounds by Marine Algae," Environ. Sci. Technol., 13, 738-741 (1979).

6. W.A. Maher, "Determination of Inorganic and Methylated Arsenic Species in Marine Organisms and Sediments," Anal. Chem. Acta., 126, 157-165 (1981).

7. A.A. Benson and R.E. Summons, "Arsenic Accumulation in Great Barrier Reef Invertebrates," Science, 211, 482-483, (1981).

8. T.S. Edmonds and K.A. Francesconi, "Isolation and Indentification of Arsenobetaine from the American Lobster Humarus americanus," Chemosphere, 10, 1041-1044 (1981).

9. R.F. Cane, "The Origin and Formation of Oil Shale," in Oil Shale, T.F. Yen, ed., Elsevier, Amsterdam (1976), pp. 27-60.

10. P.H. Abelson, "Conversion of Biochemicals to Kerogen and n. Paraffins," in Researcher in Geochemistry, Vol. II, P.H. Abelson, Ed., Wiley, New York (1967), pp. 63-86.

11. S.M. Manskaya and T.V. Diozdova, Geochemistry of Organic Substrates, Pergamon Press, Oxford (1968).

12. T.F. Yen, "Chemical Aspects of Metals in Native Petroleum," in The Role of Trace Metals in Petroleum, T.F. Yen, ed., Ann Arbor Sci., Michigan (1975), pp. 1-30.

13. J.A. Erdman and G.H. Harrach, "Uranium in Big Saga Brush from Western U.S. and Evidence of Possible Mineralization in the Owyhee Mountains of Idaho," J. Geo. Chem. Explor. 14, 83 (1981).

14. Hitchon, B., Filby, R.H., Shah, K.R., "Geochemistry of Trace Elements in Crude Oils", Alberta, Canada in The Role of Trace Metals in Petroleum.

Yen, T.F., ed., (Ann Arbor Science Publishers, Inc., Ann Arbor, 1975).

15. Shah, K.R., Filby, R.H., Haller, W.A., "Determination of trace elements in petroleum by neutron activation analysis, Part I", J. Radioanal. Chem., 6:185:192, 1970.

16. Shah, K.R., Filby, R.H., Haller, W.A., "Determination of trace elements in petroleum by neutron activation analysis, Part II," J. Radioanal. Chem., 6:413-422, 1970.

17. U.S. National Committee for Geochemistry, "Trace-element geochemistry of coal resource development related to environmental quality and health", National Academy Press, Washington, D.C., 1980.

18. Fruchter, J.S., Wilkerson, C.L., Evans, J.C., Sanders, R.W., "Elemental partitioning in an aboveground oil shale retort pilot plant", Environ. Sci. & Tech., 14:1374-1381, 1980.

19. D.W. Van Krevelen and J. Schuyer, "Coal Science, Aspects of Coal Constitution," Elsevlor: Amsterdam, 1957, pp. 96-103 and pp. 211-220.

20. T.F. Yen and G.U. Chilingarian, eds, Oil Shale, Elsevier Scientific Publishing Co., New York, 1976.

21. T.F. Yen, "The Role of Metal-Heteroatom Complexes in Fossil Fuel Production," in (NBS-DOE SP 618).

22. J.D. Saxby, "Chemical Separation and Characterization of Kerogen From Oil Shale", in Oil Shale, T.F. Yen and G.U. Chilingarian, eds., Elsevier Scientific Publishing Co., New York, 1976.

23. M.J. Mima, H. Schultz, and W.E. McKinstry, "Methods for the Determination of Benzene Insolubles, Alsphaltenes and Oils in Coal-Derived Liquids,"

in: Analytical Methods for Coal and Coal Products, Vol. 1, Clarence Karr, Jr., ed., Academic Press, New York, 1978, Chapter 19.

24. R.H. Filby, "The Nature of Metals in Petroleum," in The Role of Trace Metals in Petroleum, T.F. Yen, Ed., Ann Arbor Science, Michigan (1975), pp. 31-58.

25. R.H. Fish, E.E. Brinckman, and K.L. Jewett, "Fingerprinting Inorganic Arsenic and Organoarsenic Compounds in in situ Oil Shale Retort and Process Waters Using a Liquid Chromatograph Coupled with an Atomic Absorption Spectrometer as a Detector," Environ Sci. Technol., 16, 174-179 (1982).

26. National Research Council (U.S.) Panel on R&D Needs in Refining of Coal and Shale Liquids, "Refining Synthetic Liquid From Coal and Shale," National Academy Press, Washington, D.C. (1980), pp. 105-108.

27. R.B. Finkelman and R.W. Stanton, "Identification and Significance of Accessory Minerals from a Bituminous Coal," Fuel, 57:737-742, December 1978.

28. Finkelman, R.B., "Modes of occurrence of trace elements in coal", Dissertation, University of Maryland, 1980.

29. Maylotte, D.H. Doug, J., St. Peters, R.L., Lytle, F.W., and Greegor, R.B., Science, 214, 554 (1981).

30. Sandstrom, D.R., Filby, R.H., Lytle, F.W., and Greegor, R.B., Fuel, 61, 195, 1982.

31. Smith, G.V., Liu, J.-H., Saparoschenko, M., and Shiley, R., Fuel, 57, 41 (1978).

32. Shibata, K. Kakiyama, H. Sanada, Y., and Sohma, J., Fuel, 58, 888 (1979).

33. T. Hirschfeld, "The Hyphenated Methods," Anal. Chem., 52, 297A-312A (1980).

34. K.L. Jewett and F.E. Brinckman, "The Use of Element Specific Detectors Coupld with High-Performance Liquid Chromatographs," in Detectors in Liquid Chromatography, T.M. Vickery, Ed., Marcell Dekker, New York, in press.

35. H.J. Gluskoter, "Mineral Matter and Trace Elements in Coal," in: Trace Elements in Fuel, S.P. Baba, ed., American Chemical Society, Washington, D.C., 1975, pp. 1-22.

36. A. Treibs, "Chlorophyll- and Hamin-derivate in Bituminosen Gesteinen, Erdlen, Erdwachsen and Asphalten," Ann. der Chem. 510, 42, 1934.

37. R. Bonnett and F. Czechooski, "Metals and metal complexes in coal," Phil. Trans. R. Soc. Land. A., 300, p. 51-63 (1981).

38. K.B. Olsen, C.L. Wilkerson, A.P. Toste, and D.J. Hayes, "Isolation of Metallic Complexes in Shale Oil and Shale Oil Retort Waters," NBS SP 618.

39. P. Zubovic, "Physiochemical Properties of Certain Minor Elements as Controlling Factors in Their Distribution in Coal," in Coal, P.H. Given, ed., pp. 221-246, American Chemical Society, Washington, D.C., (1966).

40. R.H. Filby, Dissertation, Washington State University, 1971.

41. I. Schwager and T.F. Yen, Fuel, 57, p. 100, 1978.

42. C.S. Weiss, Dissertation, Washington State University, 1980.

43. D.W. Hausler, W. Hellgeth, L.T. Taylor, J. Borst and W.B. Cooley, "Trace Metal Distribution in Fractions of Solvent Refined Coal by ICP-OES and

Implications Regarding Metal Speciation," Fuel 60, 1981, pp. 40-46.

44. Brinckman, F.E., Blair, W.R., Jewett, K.L., Iverson, W.P., "Application of a liquid chromatograph coupled with a flameless atomic absorption detector for speciation of trace organometallic compounds, J. Chrom. Sci, 15:493-503, 1977.

45. Weiss, C.S., Brinckman, F.E., Parks, E.J., "Incorporation of arsenic in metal-containing macromolecules in shale oils as determined by multielement-specific size exclusion chromatography, 183rd National American Chemical Society Meeting, Las Vegas, NV. March 29-April 3, 1982.

46. D.W. Hausler and L.T. Taylor, "Size Exclusion Chromatography of Organically Bound Metals and Coal-Derived Materials with Inductively Coupled Plasma Atomic Emission Spectrometric Detection," Anal. Chem. 53, 1337-1231, 1981.

47. Anon., "Synfuels Uncertain and Costly Fuel Option," Chem. Eng. News, 57, 20 (1979).

48. Yen, T.F., Chilingarian, G.V., eds., Developments in Petroleum Science, 1975, 5, Oil Shale, Elsevier Scientific Publishing Co., Amsterdam.

49. Wen, C.S., Cheng, T.F., Knight, J.B., Poulson, R.E., Amer. Chem. Soc., Div. Fuel Chem. Preprints 1976, 21, 290.

50. Fruchter, J.S., Wilkerson, C.L., Evans, J.C., and Sanders, R.W., Environmental Sci. Technol. 1980, 14, 1374.

51. Shendrikor, A.D., Faudel, G.B., Environ. Sci. Technol., 1978, 12, 332.

52. International Conference on Environmental Arsenic, For Lauderdale, Florida, 1975, Proceedings in Environ. Health Perspect., 1977, 19, 1.

53. Ridley, W.P., Dizikes, L.J., Wood, J.M., Science, 1977, 197, 329.

54. Curtin, D.J., Dearth, J.D., Everett, G.L., Grosboll, M.P., Myers, G.A., Prepr. Pap. Am. Chem. Soc. Div. Fuel Chem., 23, 18(1978).

55. Brinckman, F.E., Blair, W.R., Jewett, K.L. Iverson, W.P., J. Chromatogr. Sci., 1977, 15, 493.

56. Brinckman, F.E., Jewett, K.L., Iverson, W.P., Irgolic, K.J., Ehrhardt, K.C., and Stockton, R.A., J. Chromatogr., 1980, 191, 31.

57. Stockton, R.A., Irgolic, K.J., Int. J. Environ. Anal. Chem., 1979, 6, 313.

58. Vickrey, T.M., Howell, H.E., Paradise, M.T., Anal. Chem., 1979, 51, 1880.

59. Van Loon, J.C., Anal. Chem., 1979, 51, 1189A, provides an overview of metal-specific chromatography. Parks, E.J., Brinckman, F.E. Blair, W.R, J. Chromatogr. 1979, 185, 563, discuss element-specific separations of metal-containing macromolecules.

60. Woolson, E.A. and Aharonson, N., J. Assoc. Off. Anal. Chem., 1980, 63, 523.

61. C.S. Weiss, E.J. Parks and F.E. Brinckman, "Arsenic; Industrial, Biomedical and Environmental Prospective," W.H. Lederer and R.J. Fensterheim ed., Van Nostrum Reinhold: New York, 1982.

62. Fowler, B.A., Ishinishi, N., Tsuchiya, K., Vahter, M., in Handbook on the Toxicology of Metals, Friber, L. et al., eds., Elsevier/North Holland Biomedical Press, Amsterdam, 1979.

63. Loucks, A.A., Occidental Vertical Modified Process for Recovery of Oil Shale, Nov. 1976-Oct. 1977, Phase 1, Summary Report, Volume 1.

64. Lekas, M.A., Proc. 12th Oil Shale Sympos., Colorado School of Mines, CO, 1979, 228.

65. Fox, J.P., Farrier, D.S., Poulson, R.E., Laramie Energy Technology Report, 1978, LETC/RI-78/7.

66. Sandholtz, W.A., Ackerman, F.J., Lawrence Livermore Laboratory Report, 1978, LETC/RI-78/7.

67. Harak, A.E., et al., "Report of Investigations", U.S. Bureau of Mines, 1974, N. 7995.

68. Snyder, L.R., Kirkland, J.R., Introduction to Modern Liquid Chromatography, 2nd ed., John Wiley & Sons, 1979, New York.

69 R.H. Fish and R.S. Tannous, "Synthesis, Structural Elucidation and Stereochemistry of Five-Coordinate Organoarsenic Catecholates," Organometallics (1982) [in press].

70. Brinckman, F.E., Bellama, J.M., eds., Organometals and Organometalloids: Occurence and Fate in the Environment, Amer. Chem. Soc. Sympos. Ser. 82, Washington, D.C., 1978.

71. Tallman, D.E., Shaikh, A.U., Anal. Chem., 1980, 52, 196.

72. Meyer, G., Ber., 1883, 16, 1439.

73. Doak, G.O., Freedman, L.E., Organometalic Compounds of Arsenic, Antimony and Bismuth, Wiley-Interscience, New York, 1970, p. 23.

74. R.H. Fish, R.S. Tannous, C.S. Weiss and F.E. Brinckman (1982) [in preparation for Organometallics].

75. Meyer, W.C., Yen, T.F., Amer. Chem. Soc., Div. Fuel. Chem. Preprints, 1974, 19, 94.

76. Murr, L.E., Torma, A.E., Brierly, J.A., eds., Metallurgical Applications of Bacterial Leaching and Related Microbiological Phenomena, Academic Press, New York, 1978.

## Figure Captions

(1) Element-specific chromatograms obtained by HPLC-GFAA (bottom of each sample set) and associated UV detector chromatograms (continuous trace shown at top of each set, inverted) are compared against authentic arsenic standards for three water samples taken at different stages of the Occidental Modified *In-Situ* Process, Retort 6, Logan Wash, Colorado. The chromatogram of the aqueous calibration solution shown at top identifies each of the five arsenicals present at a concentration of 10 mg $mL^{-L}$ (as As).

(2) Plots of chromatographic peak areas versus standard additions of individual arsenicals to diluted (1:10) Occidental Retort Water showing relative concentrations.

(3) Dual Element-Selective Detection for iron and arsenic of the size exclusion chromatogram for NBS Shale Oil SRM1580.

Table 1.

Comparison of Selected Elemental Concentrations[a] in Petroleum, Coal, and Oil Shale

| Element | Petroleum[b] | Petroleum[c] | Coal[d] | Oil Shale[e] |
|---|---|---|---|---|
| As | 0.111 | 0.263 | 15 | 44.3 |
| Be | -- | -- | 2.0 | -- |
| Cd | -- | -- | 1.3 | 0.64 |
| Cr | 0.093 | 0.008 | 15 | 34.2 |
| Fe | 10.8 | 40.7 | 1.6% | 2.07% |
| Ge | -- | -- | 0.71 | -- |
| Hg | 0.051 | 3.236 | 0.18 | 0.089 |
| Ni | 9.38 | 165.8 | 15 | 27.5 |
| S | 0.83% | 1.31% | 2.0% | 0.573% |
| Se | 0.052 | 0.530 | 4.1 | 2.03 |
| Si | -- | -- | 2.6% | 15% |
| U | -- | 0.060 | 1.6 | 4.5 |
| V | 13.6 | 87.7 | 20 | 94.2 |

[a]Concentrations in ppm except as noted.

[b]From Ref. [14], the average of 88 crude oils.

[c]From Ref. [15,16], the average of 10 crude oils.

[d]From Ref. [17], the average of 799 coals of varying ranks.

[3]From Ref. [18].

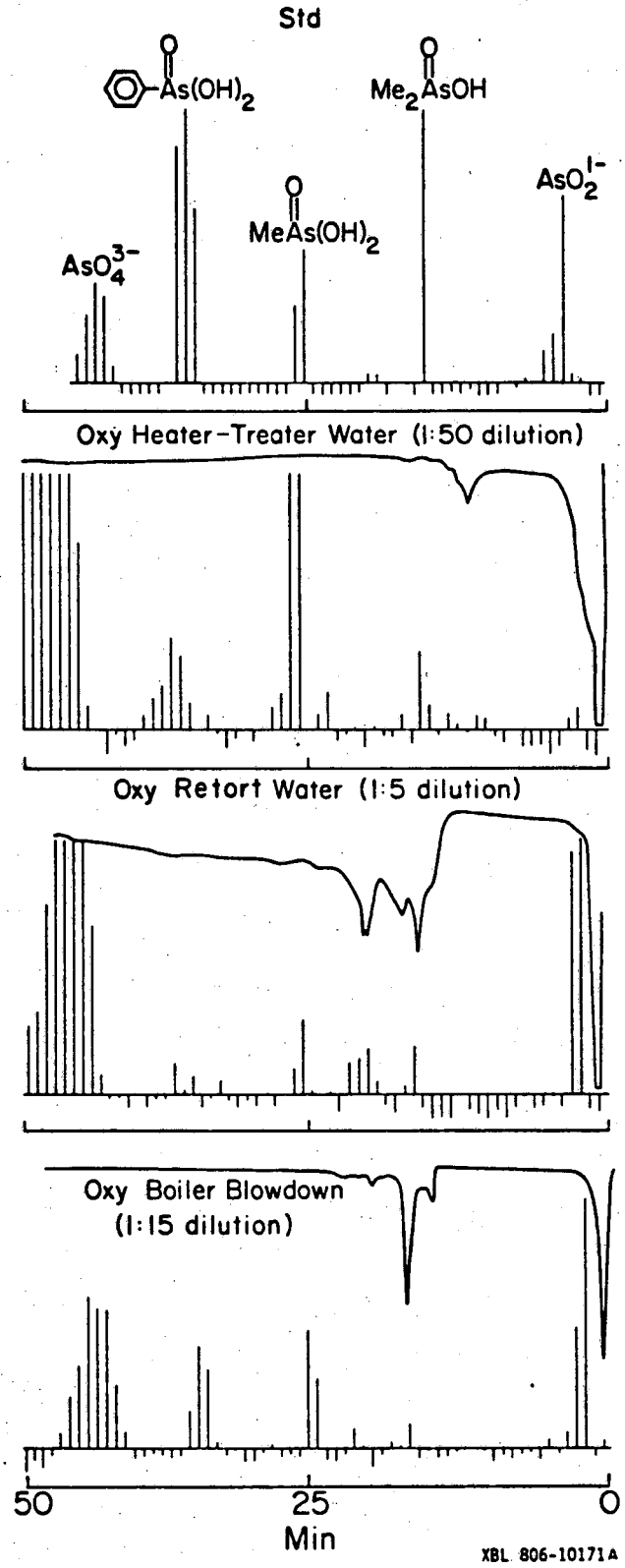
Std
As(OH)2
Me2AsOH
AsO2 1-
MeAs(OH)2
AsO4 3-
Oxy Heater-Treater Water (1:50 dilution)
Oxy Retort Water (1:5 dilution)
Oxy Boiler Blowdown
(1:15 dilution)
50
25
0
Min
XBL 806-10171A

Figure 1

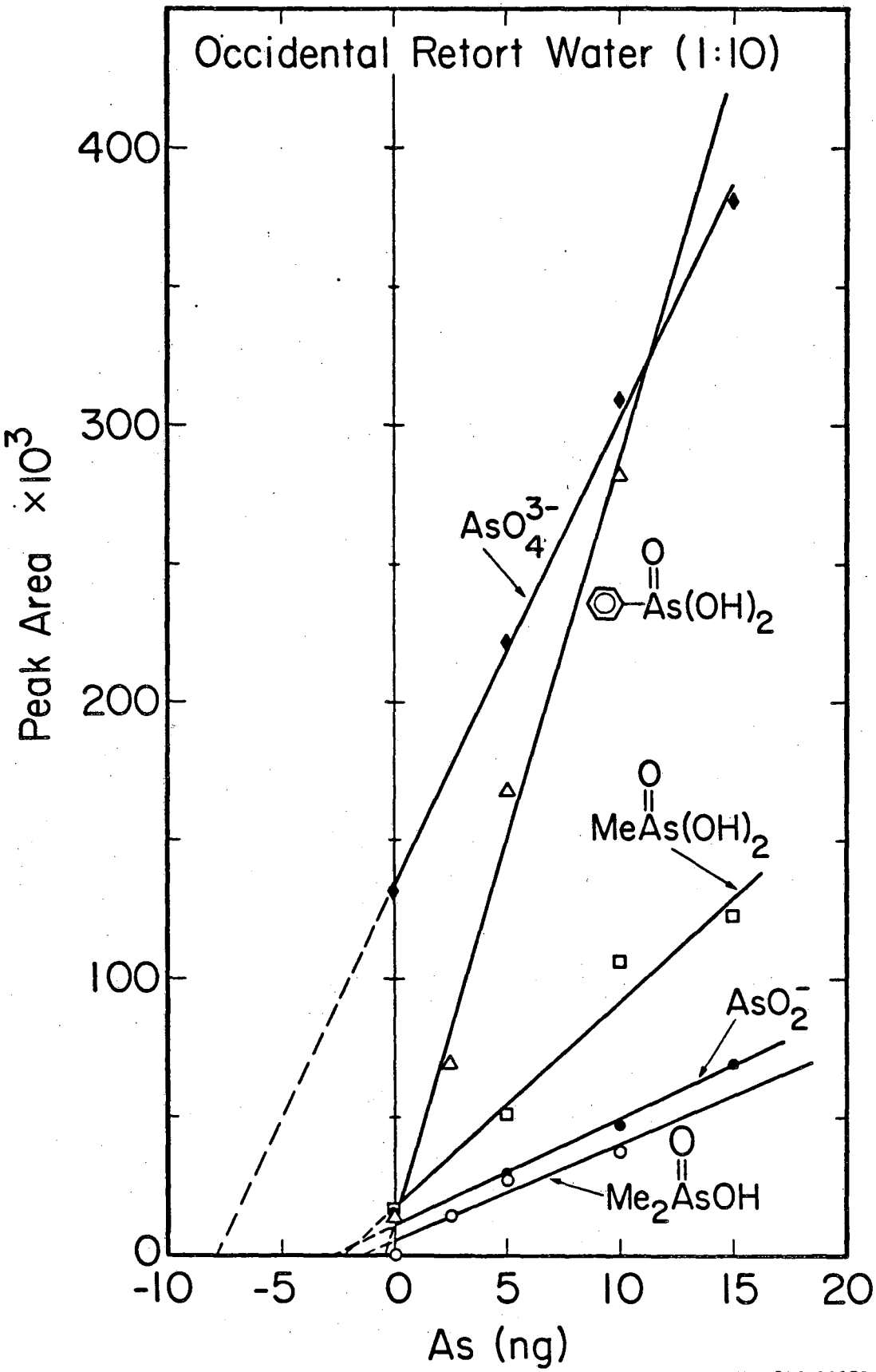
Occidental Retort Water (1:10)
Peak Area ×10^3
400
300
200
100
0
-10
-5
0
5
10
15
20
As (ng)
AsO4 3-
O
As(OH)2
O
MeAs(OH)2
AsO2 -
O
Me2AsOH
XBL 816-10279

Figure 2

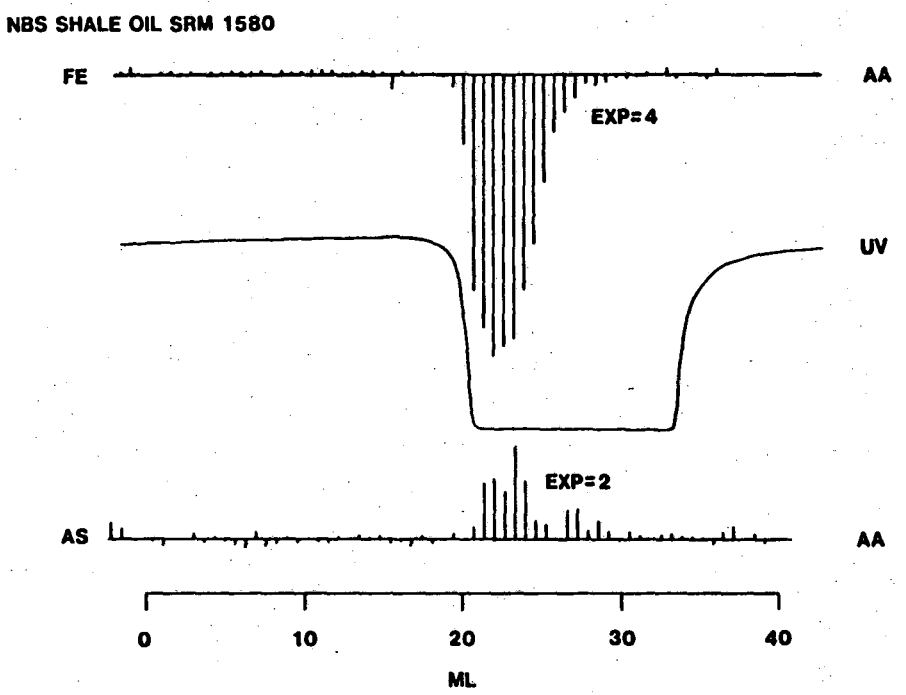


Figure 3

This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

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