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THE PARTITIONING OF ARSENIC IN INDIGENOUS AND RETORTED OIL SHALE

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INTRODUCTION

The distribution of organometallic compounds in shale oils is somewhat variable, but typical analyses indicate the presence of elemental Cd, V, Hg, Sn, Se and As. Of these, the relatively high concentrations of arsenic have, in particular, presented problems for the processing and refining of oil shale into final oil products. Typically, approximately 30 ppm of arsenic compounds are present in Paraho-retorted (indirect mode) shale oils, with similar arsenic concentration ranges being found in shale oils obtained via other above-ground or *in situ* processing methods.

These arsenic concentration levels reduce the efficiency of current processing systems due to the rapid deactivation and/or poisoning of hydrogenation catalysts. The hydrodenitrogenation activity of a commercial nickel-molybdenum hydrotreating catalyst was found by Curtin, et al. (1), to decrease at a substantially slower rate when charging dearsenated shale oil. Thus, one factor in the development of an oil shale conversion/oil upgrading technology program is a detailed understanding of the arsenic chemistry.

The majority of the studies dealing with arsenic have been prompted by oil-upgrading considerations and have examined potential dearsenation methods which would be applicable prior to hydrotreating, e. g., reactive heat transfer solids, hydrovisbreaking, guard beds and caustic washing. From a processing standpoint, these methods have been moderately successful but various disadvantages remain. These efforts have been supplemented to a certain extent by studies directed at more fundamental questions of the arsenic chemistry in oil shale and shale oil. In this context, a topic of significant current interest is the identification and partitioning of these trace arsenic compounds.

The origin and identification of the arsenic components in shale oil have not been studied in detail; one exception is the recently reported work of Fish and Brinckman (2). Although various geochemical schemes have been advanced in the literature, certain analytical results (3) have suggested that arsenic exists in the indigenous oil shale primarily in inorganic forms. There have been numerous studies on the biogeochemical creation of kerogen and the role of ancient algae in this process. The uptake and metabolism of inorganic arsenic and other inorganic forms of elements by algae (5, 6) and other microflora (7) is well documented. It has been shown by Andrae and Klumpp (6) that the biomethylation of inorganic arsenic in the +5 oxidation state by marine algae produces both dimethylarsine and methylarsonate species. Concerning the origin of the arsenic compounds in shale oil, it has been suggested that (I) the arsenic is originally concentrated in the organic matter in the oil shale and is released with little decomposition during the pyrolysis process and (II) the inorganic arsenic compounds present as a fraction of the mineral matrix react with various hydrocarbons upon pyrolysis to form organoarsenic compounds.

The principal objective of this study was to characterize the arsenic distribution in both oil shale and shale oil. These obtained results can be used to develop a more complete description of the total As balance among products of a conversion process: shale oil, spent shale, gas and water products. For example, it has recently been shown by Fish, et al. (8) and Fox, et al. (9) that both inorganic and organic arsenic species are present in oil shale retort process waters. Results obtained by this study of the identification of specific arsenic compounds in Paraho shale oil are compared with the recent "fingerprinting" study of Fish and Brinckman (2). The details of the processes whereby arsenic compounds are formed in indigenous oil shale and retorted shale oil are beyond the scope of this study, but these data may provide added insight.

ARSENIC DISTRIBUTION IN OIL SHALE

Experimental

The oil shale samples used in this study were obtained from the Green River formation, C-a tract, Mahogany zone. Standard pulverizing and sieving procedures reduced these samples to

the -50 +325 mesh size range.

Two separation methods were investigated in an attempt to preferentially isolate and concentrate the arsenic constituents in these samples: heavy media liquids gravitational separation and isodynamic magnetic separation (Frantz, Model L-1). In the first method, heavy media separations at densities of ρ : >2.25, <2.25 and >1.65, <1.65 g cm⁻³ were utilized and oil shale fractions of the following three grades, as determined by Fischer Assay, 25, 31 and 44 GPT, were obtained.

Arsenic concentrations were determined by neutron activation analysis. Arsenic concentration measurements were performed for the original oil shale, bitumen-free oil shale and the bitumen fraction. The latter two fractions were obtained using the Soxhlet extraction method based on a 3:7 mixture of methanol:benzene. The mineral composition of the various samples was determined from X-ray diffraction data (Phillips, APD-3500).

Results and Discussion

Analysis of the three grades of oil shale indicated that the arsenic concentration is a function of oil shale richness and increases with increasing organic content. An increase of 102% in the arsenic content was determined between the 25 and 44 GPT samples, i. e., the arsenic concentration increased from 42 to 85 ppm. The major mineral constituents were identified to be ankerite, dolomite, aragonite, calcite, quartz, albite, analcime and illite. The mineral composition was essentially uniform among the three different shale grades and, therefore, no preferential of arsenic is expected on this basis.

The measurement of arsenic concentration as a function of the organic carbon content is not an absolute determination of the partitioning of arsenic between the organic and inorganic matter in oil shale. These results indicate an association between arsenic and the organic matter phase in Green River oil shale, but do not differentiate between indigenous organoarsenate compounds and inorganic As compounds which are intimately associated with the organic matter. Results are later presented which support the latter alternative.

The results of the Soxhlet extraction indicated that the bitumen accounted for a fairly constant fraction, approximately 20 wt %, of the total organic matter in these samples (see Table I). The arsenic concentration in the bitumen fractions was reasonably constant among the three different grades, although small, approximately 2 ppm. Thus, it appears that the arsenic fraction which may be organic in nature is intrinsically associated with the kerogen matrix and inseparable by simple, organic solvent extraction methods.

TABLE I

ARSENIC CONCENTRATION IN ORIGINAL AND TREATED OIL SHALE

Grade (GPT)	Fraction	Yield (Wt %)	[As] + δ^a (ppm)
25	Original	100	41.7 + 2.3
	Bitumen	3.2	1.7
	Bitumen free	96.8	39.3 + 5.3
	Low temp. ash	90.0	46.5 + 0.7
	Total organics	13.5	----
31	Original	100	49.7 + 0.9
	Bitumen	3.5	1.7
	Bitumen free	96.5	49.3 + 2.5
	Low temp. ash	86.8	55.0 + 4.2
	Total organics	16.2	----
44	Original	100	84.5 + 0.6
	Bitumen	3.9	2.3
	Bitumen free	96.1	84.6 + 5.0
	Low temp. ash	81.2	108.0 + 2.8
	Total organics	22.9	----

a. δ represents single standard deviation for several measurements.

The solid oil shale fractions insoluble in benzene (i. e., bitumen-free oil shale) were analyzed for both organic carbon and arsenic content and both sets of data increased with increasing oil richness (see Table I). For example, the organic carbon concentration increased by

approximately 20% between the 25 and 31 GPT oil shale samples and by about 41% from the 31 GPT to the 44 GPT sample. The corresponding values for the percent arsenic increase were 19% and 70%, respectively. Although the arsenic concentration is somewhat dependent on the organic carbon content of bitumen-free oil shale, it was determined that greater than 95% of the As is associated with either the kerogen or mineral matrix. This is based on the arsenic concentrations in the bitumen fractions and the original oil shale.

Since the arsenic distribution is largely concentrated in the naturally occurring mineral matrix which is closely associated with organic matter, the isodynamic magnetic separation procedure was applied to concentrate arsenic according to the magnetic properties of the oil shale for further characterization. The arsenic concentration was determined as a function of the transverse angle at which the fractions were collected, i. e., <10, 10, 15, 20 and >25 degrees, at a fixed longitudinal slope of 15° and a current of 1.2 A. The data obtained using this experimental configuration were directly related to the magnetic susceptibilities of each fraction. These results are summarized in Table II. The arsenic content was preferentially separated with respect to magnetic susceptibility and concentrated by about a factor of 2.5 relative to the original sample.

TABLE II

ISODYNAMIC MAGNETIC SEPARATION YIELDS AND [As], [C_{org}], [Fe] AND [S] DISTRIBUTIONS FOR GREEN RIVER OIL SHALE^a

Trans-verse Angle (degree)	25 GPT Oil Shale					44 GPT Oil Shale				
	Yield (Wt %)	[As] (ppm)	[C _{org}]	[Fe] (Wt %)	[S]	Yield (Wt %)	[As] (ppm)	[C _{org}]	[Fe] (Wt %)	[S]
Original	100	42	11.5	1.1	0.7 ^b	100	85	19.5	2.4	1.3 ^c
>25 (6.0)	1.4	144	11.4	2.4	0.9	19.3	136	18.6	3.5	1.4
25 to 20 (4.8)	19.2	47	10.5	1.7	0.8	14.4	100	20.5	2.6	1.3
20 to 15 (3.6)	27.4	37	11.1	1.2	0.6	20.8	84	21.2	2.2	1.2
15 to 10 (2.4)	38.2	37	11.0	0.8	0.6	22.0	78	20.9	2.1	1.2
<10 (1.2)	13.8	35	10.8	0.6	0.5	23.6	62	21.0	1.6	1.3

a. Mahogany zone, C-a tract, particle size: 100 x 200 mesh.

b. Pyritic sulfur, 0.40; organic sulfur, 0.12; sulfate sulfur, 0.14 wt %.

c. Pyritic sulfur, 0.97; organic sulfur, 0.31; sulfate sulfur, 0.02 wt %.

[As] determined by Instrumental Neutron Activation Analysis (INAA).

[Fe] and [S] measured by X-ray Fluorescence.

() estimated mass susceptibility, x 10⁻⁶ cgs.

The isodynamic magnetic separation results suggest an association between the arsenic content and iron containing sulfide minerals, e. g., Fe_{1-x}S, Fe(AsS)₂, etc., the principal magnetic materials in oil shale. This is consistent with the presence of a large arsenic fraction in the mineral matrix and the determination by derivative thermogravimetric analysis of a pyritic sulfur decomposition (10) temperature of about 510°C (see Figure 1). X-Ray diffraction results indicated that the more magnetic fractions contained relatively larger concentrations of ankerite, albite and analcime, whereas the predominantly nonmagnetic fractions contained more aragonite and calcite. The correlation of the arsenic concentration with constituents having a high magnetic susceptibility is probably the result of complex chemical interactions involving As, Fe and S containing species. This is indicated in Table II by the similar trends of the arsenic and iron concentrations as a function of the transverse angle. The sulfur concentration dependence is not as strong since the sulfur composition includes pyritic, organic and sulfate sulfur at various wt % in the 25 and 44 GPT samples. A previous study (11) has also suggested that the arsenic in oil shale is bound up with pyrite.

In addition to the herein reported results, scanning electron microscopy (SEM) data indicate that arsenic is mainly present in the form of inorganic compounds in indigenous oil shale. These data exhibited the same correlations with transverse angle as summarized in Table II. In view of the above suggested inorganic nature of the arsenic constituents and the strong correlation with organic carbon content, the arsenic distribution processes need to be examined in relation to the organic decomposition occurring during the pyrolysis of the oil shale and in the resulting products.

ARSENIC DISTRIBUTION IN SHALE OIL

The primary objective of these studies was to determine the arsenic distribution in shale oil distillates and residue according to boiling point ranges, molecular weight (size) ranges,

specific compounds and concentration ranges.

Experimental

A sample of Paraho shale oil was fractionally distilled into the following four cuts: (a) naphtha (B. P. IBP-191°C, 1.8 wt %), (b) furnace oil (B. P. 191-360°C, 35.7 wt %), (c) gas oil (B. P. 360-516°C, 46.6 wt %) and (d) residuum (B. P. >516°C, 15.9 wt %). These fractions, except for the naphtha cut and the original sample were passed through a GPC (Gel Permeation Chromatography) column with THF eluent to obtain molecular weight distributions. The residuum fraction was further separated using prep GPC into sixteen equal-volume oil-plus-eluent (CH_2Cl_2) fractions, since this fraction contained the highest arsenic concentration among the four separated samples.

High performance liquid chromatography (HPLC) was used to separate a sample of Paraho shale oil into five different classes of compounds: saturate, aromatic, polar, hexane insoluble and volatiles. In addition to the hexane-insoluble fraction, a hexane- and toluene-insoluble fraction was prepared. (See Table IV)

Semiquantitative product identification was obtained from X-ray photoelectron spectroscopy (XPS) data. XPS was employed to characterize the shale oil-insoluble fractions after extraction with hexane and hexane and toluene in order to identify the surface constituents in the hydrocarbon solvent-insoluble fractions. Spectra were obtained using a Perkin-Elmer PHI Model 550 ESCA/SAM/SIMS which operated at a base pressure of about 1×10^{-8} torr. The samples were irradiated with $\text{MgK}\alpha$ radiation at a power of 400 watts. All spectra were calibrated relative to the C(1s) line at 285.0 eV binding energy. The analysis method to determine relative concentrations in units of atomic percent is accurate to $\pm 20\%$ and precise to about one-tenth of the concentration.

Results and Discussion

Analysis of the four cuts obtained by fractional distillation indicated no significant correlation between the arsenic concentration and the boiling point range (see Table III). The arsenic levels in all the fractions were essentially constant, 25-33 ppm, except for the naphtha fraction which contained an arsenic concentration of ~ 2.7 ppm. Such a distribution suggests a fairly uniform mixture of organoarsenic compounds of varying structural complexity. The results in other studies (1, 12, 13) of shale oils indicate that the arsenic concentration profile may be dependent on the process used in recovering the oil. Paraho shale oil is obtained by an above-ground retorting technique, compared to other shale oils processed by *in situ* and other heat transfer methods.

TABLE III

ARSENIC DISTRIBUTION IN PARAHO SHALE OIL ACCORDING TO BOILING POINT RANGES

Fraction	Yield (Wt %)	[As] (ppm)
Whole shale oil	100	28
IBP - 191°C (naphtha)	1.8	2.7
191 - 360°C (furnace oil)	36	25
360 - 516°C (gas oil)	46	28
>516°C (residuum)	16	33

The GPC plots of wt % oil versus retention time of the furnace oil, gas oil and residuum fractions were displaced from one another according to the relationship retention time \propto (effective molecular size) $^{-1}$. Figure 2 shows the GPC curves of the three distillation fractions which are strongly overlapped and parallel the boiling point range results. The relative arsenic concentration was fairly constant among the three separated fractions, 25-33 ppm (see Table III). Therefore, no direct dependence was found between arsenic concentration and effective molecular size for the tested Paraho shale oil samples.

Due to the small displacement of the GPC curves in Figure 2, further separation of the residuum fraction using preparative GPC was done in order to obtain a more detailed characterization of the heavier molecular weight composition. The results of this separation were analogous to the previous data in that there was no direct dependence of relative arsenic concentration on molecular size with the exception of the first fraction (i.e., largest molecular size) which contained an unusually high concentration of arsenic, approximately 97 ppm. The remaining fractions centered around a mean of about 30 ppm. Thus, no direct correlation between the arsenic concentration and effective molecular size ranges was found, with the possible exception of very large molecular sizes which, in any case, amount to a small percentage of the total oil.

The HPLC physicochemical separation techniques were employed to obtain the following classes of compounds: saturate, aromatic, polar, hexane insoluble and volatiles. The hexane-insoluble fraction overwhelmingly contained the highest arsenic concentration, approximately 85

times more than the original sample. This fraction, however, accounted for only 0.7 wt % of the original sample. Based on these results, a hexane- and toluene-insoluble fraction was also obtained for comparison purposes.

The shale oil insolubles obtained by treatment with hexane, and hexane and toluene were analyzed using X-ray photoelectron spectroscopy to identify trace arsenic constituents. Spectra were scanned from 0 to 1000 eV binding energy and arsenic, magnesium, carbon, nitrogen, oxygen and sulfur were detected. Figure 3 shows the As(3d) and Mg(2p) spectra measured for the hexane- and toluene-insoluble oil shale fraction. An identical spectrum was obtained for the hexane-insoluble fraction. Arsenic was determined to be present on the surface at low concentrations of approximately 0.5% atomic. However, considering the toxicity of this element, these concentration levels are not insignificant.

Binding energies of reference arsenic compounds are available in the literature (14). Due to the low arsenic concentrations in the complex matrix structure on the surface of the shale oil insolubles, a definitive identification of specific arsenic compounds is difficult, but the data strongly suggest the presence of As_2O_5 and organic arsenic compounds, such as phenylarsonic acid. Fish and Brinckman (2) have recently identified methyl- and phenylarsonic acids and arsenate in methanol extracts of Green River oil shale using the HPLC-GFAA and GC-MS techniques. Since these authors used a much more rigorous experimental procedure, their results are considered to be more definitive than the XPS data of this study. Both sets of data, however, are consistent with each other and indicate organic as well as inorganic arsenic compounds in shale oil.

In order to further identify the major arsenic constituents in shale oil, a sample of the hexane and toluene extracted material was demineralized using an HCl/HF mixture. The XPS spectra detected aluminum, carbon, chlorine, magnesium, nitrogen, oxygen, sulfur and silicon. Arsenic was not detected after the HCl-HF treatment. Figure 3 shows the Mg(2p)-As(3d) region of the electron spectrum for the hydrocarbon insoluble fraction both before and after acid extraction and the absence of the arsenic peak is clearly evident in the demineralized sample. It is known that arsenic pentoxide is soluble in alcohol and both alkaline and acidic solutions, but it is not clear to what extent phenylarsonic acid is soluble or reactive in acidic solution.

CONCLUDING REMARKS

The trace metal composition of oil shale and its retort products is increasingly the subject of experimental investigation for reasons of: fundamental chemistry, processing and potential environmental effects. The relatively large concentration of arsenic in indigenous oil shale was found to be in the form of inorganic compounds, particularly in combination with other heteroatoms, such as O, Fe and S. In addition, its concentration in the oil shale was found to increase with organic carbon and higher magnetic susceptibility species, such as iron-containing compounds. The arsenic distribution in shale oil appears to be characterized by both organic and inorganic species, including arsenic pentoxide and phenylarsonic acid. The origin of the organoarsenic compounds is attributed to both organometallic addition and substitution reactions during the pyrolysis process.

In terms of arsenic removal, the results of this study indicate little possibility of significant arsenic reductions in the naturally occurring fossil fuel before the oil extraction (conversion step). The apparent intimate association of arsenic with the organic matter phase suggests that dissolution of arsenic by conventional chemical and/or physical separation methods is not feasible. The distribution of arsenic in the product oil is essentially uniform with respect to boiling point range and effective molecular size range. Conventional removal of arsenic compounds from the shale oil either before or during retorting/conversion remains the more promising approach.

TABLE IV
ARSENIC CONTENT OF PARAHO SHALE OIL HPLC FRACTIONS

	Yield (Wt %)	[As] (ppm)
Whole shale oil	100	33
Volatiles	18	---
Aromatics	34	5
Saturates	19	8
Polars	29	34
Hexane Insolubles	0.71	2800
Hexane/Toluene involubles	0.23	4600

[As] determined by INAA.

Figure 1
TG/DTG CURVES OF ISODYNAMIC MAGNETICALLY SEPARATED
GREEN RIVER OIL SHALE: a) > 25° TRANSVERSE ANGLE, b) 25-20°, c) < 10°

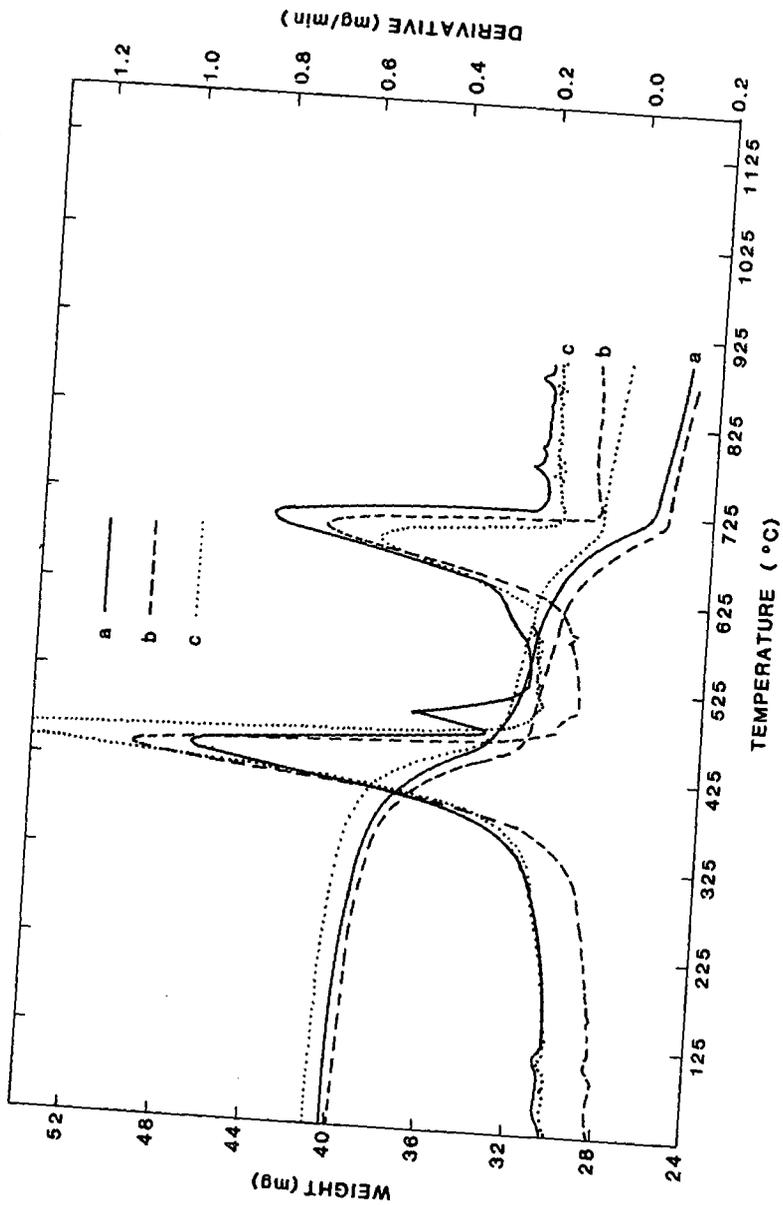


Figure 2

GPC PLOTS OF CONCENTRATION VS. RETENTION TIME
FOR PARAHO SHALE OIL AND DISTILLED FRACTIONS

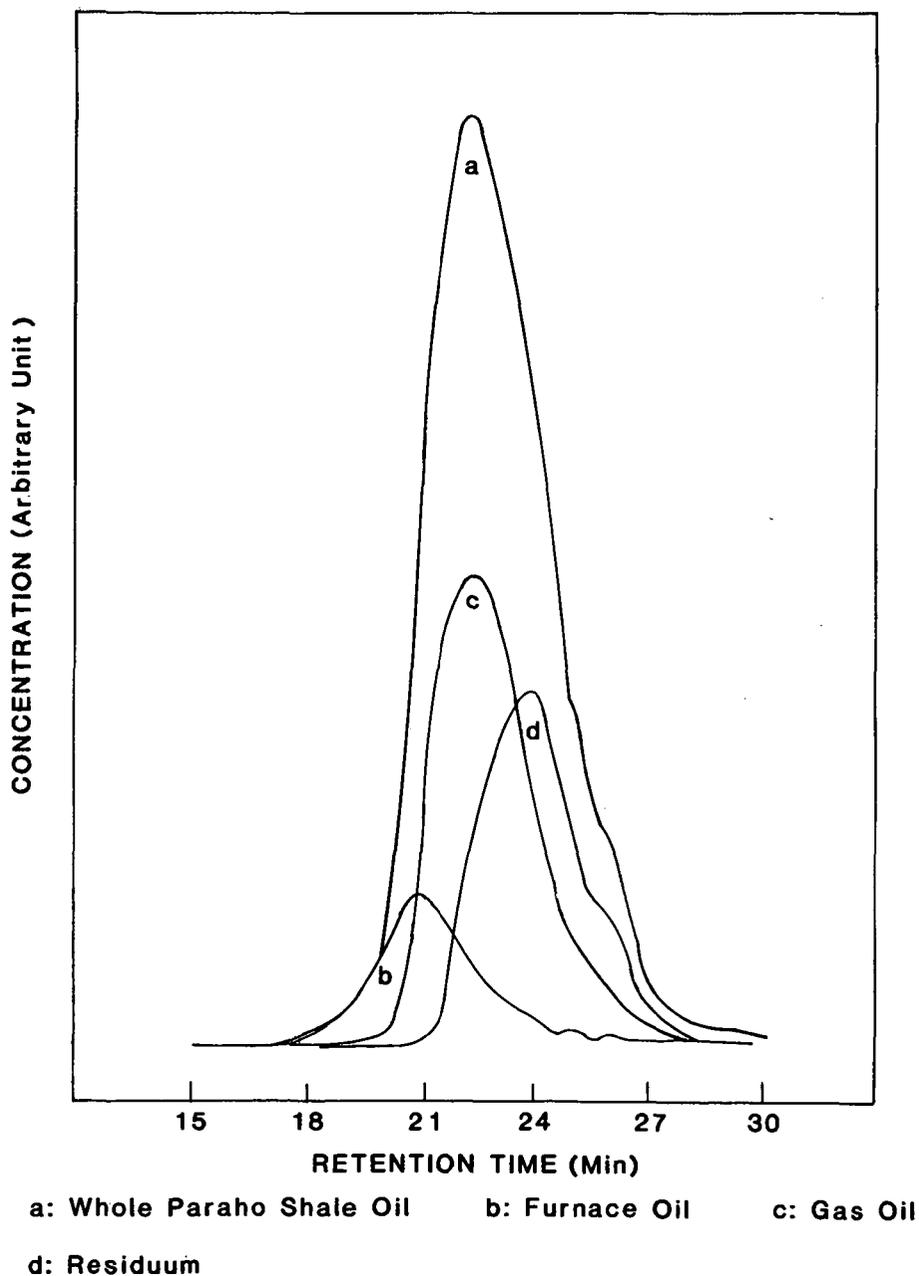
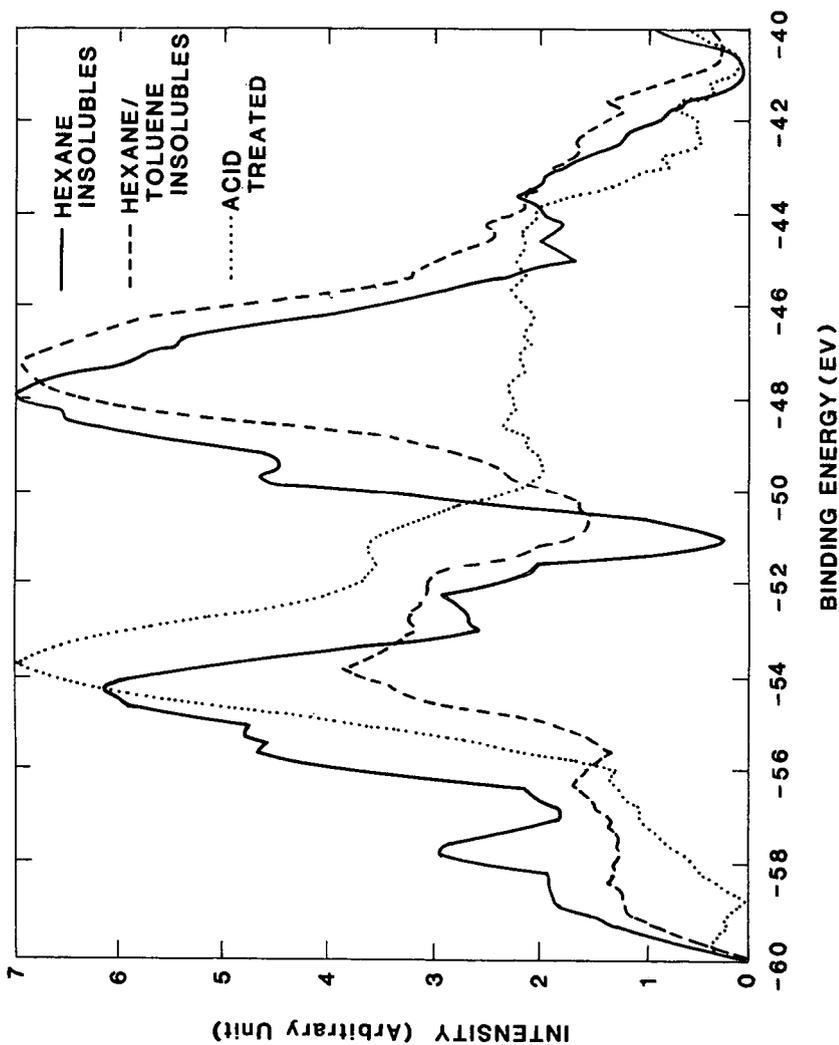


Figure 3

XPS SPECTRA OF HEXANE INSOLUBLES, HEXANE AND TOLUENE INSOLUBLES,
AND DEMINERALIZED FRACTIONS OF PARAHO SHALE OIL



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