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THE PARTITIONING OF MAJOR, MINOR AND TRACE ELEMENTS DURING SIMULATED IN-SITU OIL SHALE RETORTING. DECEMBER MONTHLY PROGRESS REPORT

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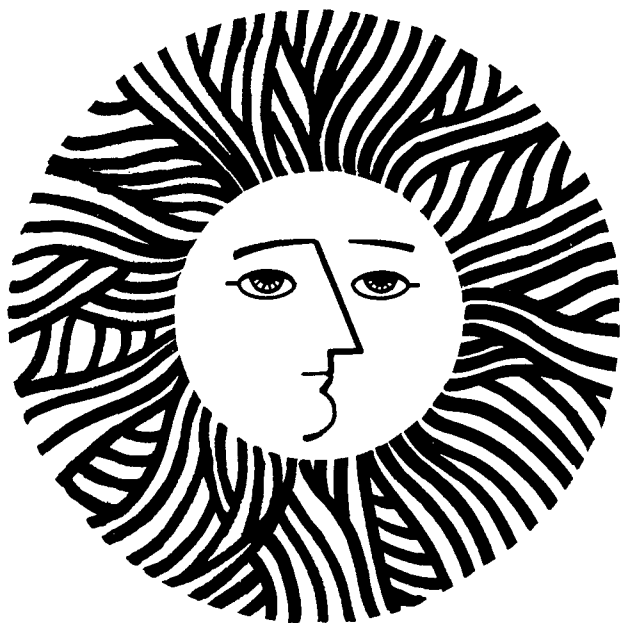
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January 10, 1980

TO: Art Hartstein

FROM: Richard Fish, Mathilde Kland, and Phyllis Fox

RE: December Monthly Progress Report
The Partitioning of Major, Minor and Trace Elements
during Simulated In-Situ Oil Shale Retorting
LBID-160

NAVY CORE PROJECT

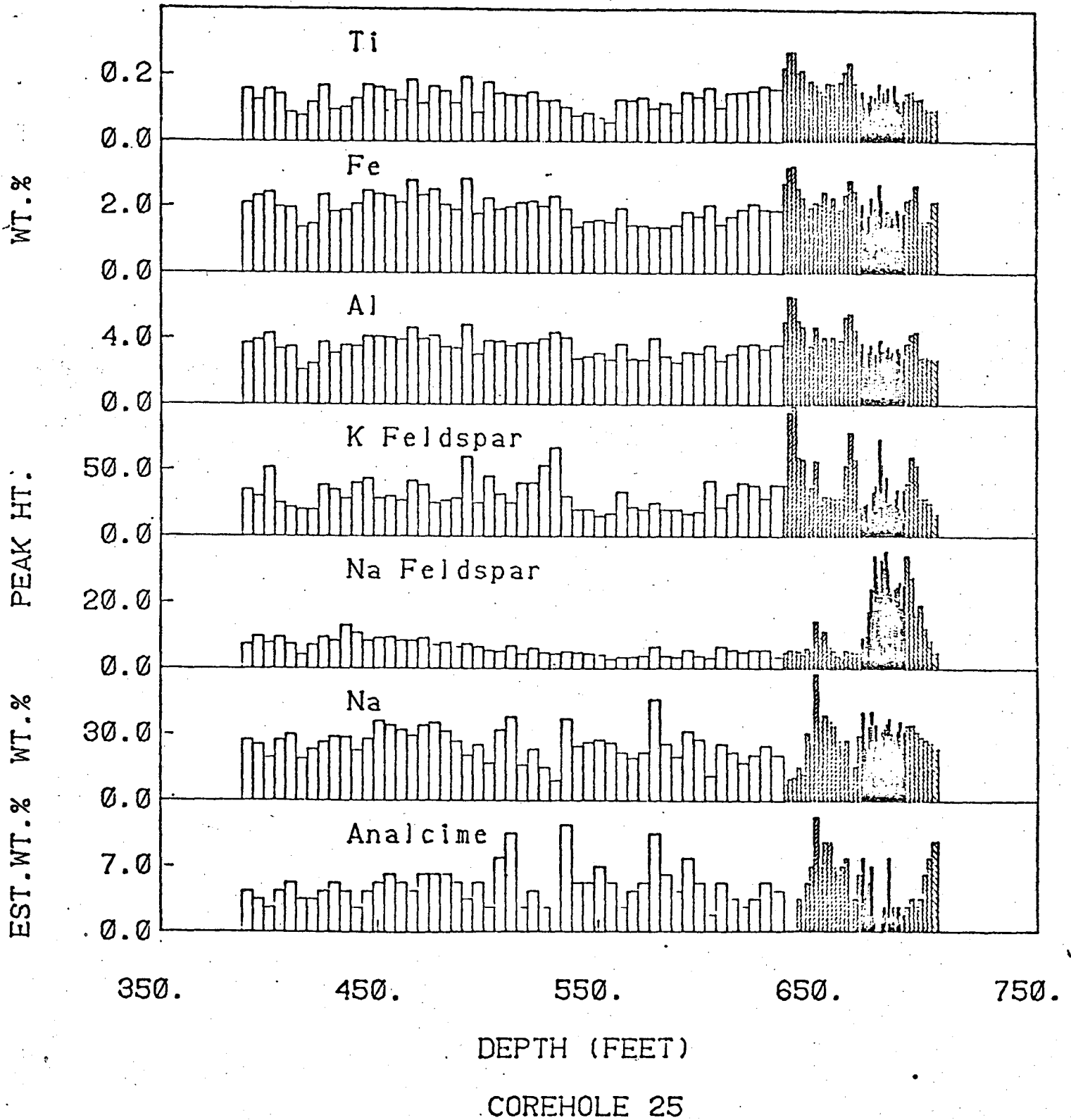
The computer plotting routine previously used to display mineralogical and elemental abundance data was modified to plot histograms rather than scatter diagrams, at Ward Smith's request. The new routine was used to investigate correlations between various mineral phases and trace elements in Core 25. A sample plot is shown as Figure 1.

The final report on this project was initiated, and the "Analytical Method" section was partially written. A literature survey of minerology and chemical composition of Green River oil shales was initiated. A modified Zeeman atomic absorption technique to measure Cd in raw oil shales was developed and work was started on the analysis of Cd in 280 samples from Core Holes 25 and 15/16.

β -DIKETONE - METAL COMPLEXES

We successfully separated the known Cu, Al, and Zn complexes of 1,1,1,2,2,3,3,-Heptafluoro-7,7-dimethyl-4,6-octanedione (HFOD) on a gas chromatograph equipped with a 30-m glass capillary column interfaced with a quadrupole mass spectrometer (GC-MS). This is the first time that these types of metal complexes have been separated by glass capillary columns (Figures 2 and 3). We were unable to chromatograph the corresponding Hg or Ni complexes and further work in this area will be done.

Figure 1. Histogram of three minerals and four elements determined for Core 25 composite sample collected from four stratigraphic zones.



Now that we can analyze the known $\text{Cu}(\text{FOD})_2$, $\text{Al}(\text{FOD})_3$, and $\text{Zn}(\text{FOD})_2$ complexes by GC-MS, we are studying the pH profile of these metals when extracted from aqueous media by HFOD. A model experiment with 0.025 molar zinc acetate dihydrate using HFOD as the chelating agent and tri-n-butyl phosphate (TBP) as a co-ligand was carried out in December. Addition of the co-ligand TBP to the HFOD/ C_6H_{12} system increased the fraction of the Zn^{2+} extracted threefold to 53% with a pH optimum of 5.3.

Our work on the pH profiles of various metals, known to be present in retort waters, will continue and plans for extracting known process waters by this method, in conjunction with GC-MS, are being formulated.

ORGANOARSENIC AND INORGANIC ARSENIC SPECIATION BY HIGH PERFORMANCE LIQUID CHROMATOGRAPHY-GRAPHITE FURNACE ATOMIC ABSORPTION DETECTION

The analysis of process waters from Occidental's process (Heater-Treater water, Product water, and Logan Wash Boiler Blowdown), LETC's 150-ton retort, LLL's 6000-Kg retort run L-2, Geokinetic's process, and LETC's true in-situ Site 9 experiment (Omega-9), for inorganic and organoarsenic compounds, was successfully accomplished by high performance liquid chromatography using graphite-furnace atomic absorption detection (HPLC-GFAA).

Five known arsenic compounds--arsenite (AsO_2^-), dimethylarsinic acid ($(\text{CH}_3)_2\text{As}(\text{O})\text{OH}$), methylarsonic acid ($\text{CH}_3\text{As}(\text{O})(\text{OH})_2$), phenylarsonic acid ($\text{C}_6\text{H}_5\text{As}(\text{O})(\text{OH})_2$), and arsenate (AsO_4^{3-}) were separated on a Dionex anion exchange column using a solvent combination of 0.02M ammonium carbonate in water/methanol (85:15, v/v) with water/methanol (80/20 v/v, 10%/min).

Subsequent analyses of the seven mentioned process waters, using similar chromatographic conditions with the HPLC-GFAA combination, allowed, for the first time, separation and tentative identification of several inorganic and organoarsenic compounds (Table 1). As one can see, arsenate, methylarsonic acid, and phenylarsonic acid are the predominate species

Table 1. Tentative identification of inorganic and organoarsenic compounds by HPLC-GFAA in various process waters.

Sample	Retention times ^a (min)					Unknown
	NaAsO ₂	(CH ₃) ₂ As(O)(OH)	CH ₃ As(O)(OH) ₂	∅-As(O)(OH) ₂	Na ₃ AsO ₄	
OXY Heater-Treater Water	--	--	29.35(+)	--	48.67(+)	1.8
OXY Boiler Water	--	--	28.02(+)	--	49.41(+)	1.47 33.01 35.16
OXY Product Water	--	--	27.76(+)	--	45.6(+)	2.13
L-2	--	--	26.13(+)	40.37(+)	--	1.26 33.37 53.15
150-ton water	--	--	28.81(+)	--	46.79(+)	1.82
Omega-9	--	--	27.88(+)	--	--	1.59 22.2 41.39
Geokinetics	--	--	26.39(+)	39.55(+)	--	2.16 22.25

^aA dash (--) signifies that the species was not detected. The numerical values are the retention times at which the specie or unknown peaks were detected.

tentatively identified. Interestingly, no arsenite or dimethylarsinic acid was present, while all the samples had a neutral organoarsenic compound that eluted with the solvent front.

This collaborative effort, with Drs. K. Jewett and F. Brinckman, of the National Bureau of Standards, will continue in order to identify, by other spectroscopic techniques, the remaining inorganic and organoarsenic compounds as well as to study other metals, such as Se, by HPLC-GFAA.

IDENTIFICATION AND QUANTIFICATION OF FATTY ACIDS AS LIGANDS OF METALS IN OIL SHALE WATERS

We have recently analyzed five process waters by capillary gas chromatography in order to obtain a profile of their fatty acid content. The initial analysis was done on the benzene extracts of the derivatized fatty acids (methyl esters) using a 10 m x .025 mm glass capillary column coated with SP2100.

Further confirmation with known fatty acid methyl esters and analysis by GC-EIMS have allowed the compounds in Table 2 to be identified in 150-ton retort water, OXY boiler blowdown, OXY product water, OXY heater-treater water, and L-3 retort water.

The quantification of each mono- or di-carboxylic acid identified and the significance of these results with regard to the profile of the fatty acids and the individual process will be discussed further in the next report.

Table 2. Identification of mono- and di-carboxylic fatty acids in retort process waters.

Chain Length ^a	Carboxylic Acid ^b
C ₄	isobutyric
C ₄	butyric
C ₅	isovaleric
C ₅	2-methylbutyric
C ₅	valeric
C ₆	2,3,-dimethylbutanoic
C ₆	branched C ₆ Acid (unidentified)
C ₆	2-ethylbutanoic
C ₆	2-methylpentanoic
C ₆	3-methylpentanoic
C ₆	4-methylpentanoic
C ₆	hexanoic
C ₆	unsaturated C ₆ Acid (unidentified)
C ₇	two C ₇ acids (unidentified)
C ₇	iso-heptanoic (5-methylhexanoic)
C ₇	heptanoic
C ₇	cyclohexanecarboxylic Acid

Table 2. (continued)

Chain Length ^a	Carboxylic Acid ^b
C ₈	four unbranched C ₈ acids (unidentified)
C ₇	benzoic acid
C ₈	octanoic
C ₉	branched C ₉ acids (unidentified)
C ₈	methylbenzoic
C ₁₀	decanoic
C ₁₁	undecanoic
C ₁₀ -C ₁₁	branched C ₁₀ -C ₁₁ acids (unidentified)
C ₈ (diacid)	octandioic
C ₁₂	dodecanoic
C ₉ (diacid)	monadioic
C ₁₃	tridecanoic
C ₁₀ (diacid)	decandioic
C ₁₄	tetradecanoic
C ₁₁ (diacid)	undecandioic
C ₁₅	pentadecanoic
C ₁₂ (diacid)	dodecandioic
C ₁₆	hexadecanoic

Table 2. (continued)

Chain Length ^a	Carboxylic Acid ^b
C ₁₃ (diacid)	tridecandioic
C ₁₄ (diacid)	tetradecandioic
C ₁₅ (diacid)	pentadecandioic

^a retention time increases from one acid to another, e.g.
C₄ < C₆.

^b analysis of methyl esters on a 10 M SP2100^(GC) or 30 M OV101 glass capillary column (GC-MS) at 70° - 250° C (3° per minute).

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