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Speciation of Trace Organic Ligands
and Inorganic and Organometallic
Compounds in Oil Shale Process Waters

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ABSTRACT

The isolation and identification of organic ligands and inorganic and organometallic compounds in seven oil shale process waters has been carried out using a number of analytical techniques. Organic ligands, potentially associated with trace metals in the oil shale process waters, were either isolated, after methylene chloride extraction, by low pressure liquid chromatography or directly derivatized using lyophilized samples and then identified by capillary column gas chromatography in combination with electron impact mass spectrometry. Using these techniques, we were able to identify mono- and dicarboxylic acids, substituted phenols, substituted pyridines, aliphatic nitrogen heterocyclics, and substituted quinoline compounds.

The inorganic and organometallic compounds in these process waters were directly separated by high performance liquid chromatography and detected by graphite furnace atomic absorption spectroscopy (HPLC-GFAA). These initial studies resulted in tentative identification of several inorganic and organoarsenic compounds. A review of our analytical techniques and the identified compounds will be presented in this paper.

INTRODUCTION

Oil shale retorting produces a number of aqueous effluents that may reach the environment by accidental spills or discharge to surface and ground waters. These include retort water, gas condensate, and boiler blowdown. Retort water and gas condensate, the most voluminous and highly contaminated waters, are co-produced with the oil. They originate from combustion, mineral dehydration, steam and moisture in the input gas, and ground water seepage into in-situ retorts. The retort water is condensed at ambient or higher temperatures, while the gas condensate is condensed at lower temperatures, from 15 to -15°C. Blowdown is a concentrated underflow stream produced

in the boiler used to make process steam. These four types of water may contain a number of toxic trace metals, which may be associated with organic ligands as complexes, carbon-bonded organometallic compounds, or discrete inorganic compounds.

Considerable research has been directed towards the elucidation of organic compounds present in oil shale process waters (Yen et al., 1976; Pellizzari et al., 1979). However, studies linking organic ligands with trace metals have not been attempted. Additionally, the speciation or molecular characterization of inorganic and organometallic compounds in oil shale process waters has not been carried out. The studies under discussion are directed toward the isolation, identification, and fingerprinting of organic ligands and inorganic and organometallic compounds in seven oil shale process waters.

RESULTS

Samples

Organic ligands and inorganic and organometallic compounds were isolated and identified in seven oil shale process waters including retort water, gas condensate, and boiler blowdown. A summary of the waters that were investigated and their distinguishing characteristics is presented in Table 1. Simulated waters are produced in pilot-scale laboratory retorts designed and operated to simulate large-scale modified in-situ retorts. Two such waters were studied here--one from a steam-combustion run of Lawrence Livermore Laboratory's (LLL) 6000-kg retort (L-2) and the other from a combustion run of Laramie Energy Technology Center's (LETC) 136-tonne (150-ton) retort. Field in-situ process waters are produced during demonstration-scale field experiments conducted by industry and the Department of Energy to develop oil shale technology. Process waters from Geokinetics' horizontal true in-situ process, from LETC's Rock Springs Site 9 true in-situ experiment

Table 1. Water types and sources and retort operating conditions for samples used in characterization studies.

Water	Retort/ Process	Shale Source	Retorting Atmosphere	Retorting Temperature
SIMULATED IN-SITU RETORTS				
L-2 Retort Water	LLL 6000-kg/ modified in-situ	Anvil Points, Colorado	air/steam	887°C
136-tonne Retort Water (Run 13) (150-ton)	LETC 136-tonne/ (150-ton) modified in-situ	Anvil Points, Colorado	air	816°C
FIELD IN-SITU RETORTS				
Omega-9 Retort Water	LETC Site 9/ true in-situ	Rock Springs, Wyoming	air	(a)
Geokinetics Retort Water	Retort 16 true in-situ	Book Cliffs, Utah	air	(a)
Occidental Retort Water	Retort 6 modified in-situ	Logan Wash, Colorado	air/steam	(a)
Occidental Boiler Blowdown Water	Retort 6 modified in-situ	Logan Wash, Colorado	air/steam	(a)
Occidental Heater-Treater Water	Retort 6 modified in-situ	Logan Wash, Colorado	air/steam	(a)

(a) Field retorting temperatures are not accurately known due to corrosion problems with thermocouples. However, mineral analyses of spent shales from the Geokinetics and Occidental processes suggest temperatures may locally reach 1000°C.

(Omega-9), and three process waters from the Occidental Logan Wash modified in-situ process--retort water, boiler blowdown, and heater-treater water--were studied here.

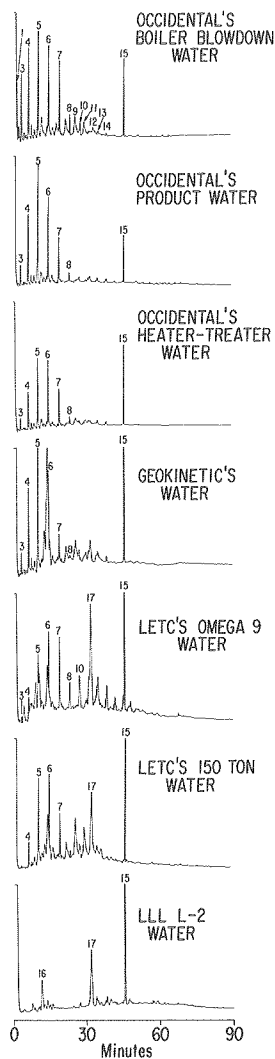
The processes investigated in this work do not represent commercial technology because additional work is required to resolve a number of technical problems, including rubblization and process control. This additional work may lead to the development of a process that is very different from those that generated the waters studied here. Therefore, the reader is cautioned that these results should not yet be extrapolated to a commercial oil shale industry.

Organic Ligands

The first class of organic ligands that were fingerprinted was the mono- and dicarboxylic acids. Since the esters of carboxylic acids are more volatile and, thus, more readily amenable to analysis by gas chromatography, we converted the carboxylic acids to their methyl esters. Each sample (20 ml) of process water was lyophilized and the residue placed in 20 ml of a 14% solution of

boron trifluoride in methanol and refluxed for 5 hours (Riley et al., 1979). After the usual workup, the benzene extracts were concentrated and analyzed by capillary column gas chromatography (10 m x 0.025 mm column wall coated with SP 2100 and programmed from 50 to 250°C, 3°C/min).

The chromatograms of the mono- and dicarboxylic acids for the seven process waters are presented in Figure 1, while selected compounds identified are found in Table 2. Other organic ligands were separated on low-pressure liquid chromatography columns using Florisil as the adsorbent. The dry Florisil column containing a concentrated methylene chloride extract of the designated oil shale process water was eluted under microprocessor-controlled gradient conditions using hexane, methylene chloride, and isopropyl alcohol. The various compounds that eluted from the Florisil column were examined at 254 nm and those that had absorptions at that ultraviolet line were analyzed further by capillary column gas chromatography (GC). After capillary GC analysis, the various classes of ligands were identified by capillary column GC in combination with electron impact mass spectrometry (GC-EIMS).



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Figure 1. Capillary gas chromatographic profiles of mono- and dicarboxylic acids found in the designated oil shale process waters.

The low pressure liquid chromatography (LPLC) method allowed separation of substituted phenols in Geokinetics' retort water (Table 3); aliphatic and aromatic nitrogen heterocycles (Occidental's heater-treater water; Figure 2, Table 4); and cyclic aliphatic ketones (Geokinetics' retort water; Table 5).

Our initial effort to understand the relationship between trace metals found in the process waters and the identified potential organic ligands resulted in our analysis of zinc in various fractions isolated from the 136-tonne (150-ton) retort

Table 2. Mono- and dicarboxylic acids identified in oil shale process waters by GC-MS

Compound	Identified by GC-MS
1	Methyl Pentanoate (n-C ₅)
2	Branched Methyl Ester (C ₅)
3	Methyl Hexanoate (n-C ₆)
4	Methyl Heptanoate (n-C ₇)
5	Methyl Octanoate (n-C ₈)
6	Methyl Nonanoate (n-C ₉)
7	Methyl Decanoate (n-C ₁₀)
8	Methyl Undecanoate (n-C ₁₁)
9	Mixed Methyl Esters
10	Methyl Dodecanoate + Dimethyl Azelate (n-C ₁₂)
11	Methyl Tridecanoate + Methyl Esters (n-C ₁₃)
12, 13, 14	Dicarboxylic Acids
15	n-C ₁₇ Internal Standard
16	Methyl Benzoate

water's methylene chloride extract. The total zinc concentration in the methylene chloride extract of 136-tonne (150-ton) retort water was found by graphite furnace atomic absorption spectroscopy (GFAA) to be approximately 1 ppm. Subsequent GFAA batch analysis of fractions collected via the LPLC column suggested that the zinc was associated with the nitrogen aliphatic and aromatic heterocyclic compounds (Sievers, 1980). These concentrations were approximately 1 ppm or less in the various samples containing these compounds.

Inorganic and Organometallic Compounds

In another approach to identifying inorganic and organometallic compounds, we used a new speciation technique which combines a high performance liquid chromatograph with an element specific graphite furnace atomic absorption detector (HPLC-GFAA) (Brinckman et al., 1977; Brinckman et al., 1980). We previously determined that arsenic was an important environmental metal to analyze by the HPLC-GFAA combination, since it was found in some process waters in concentrations as high as 20 ppm. The seven process waters previously described were filtered with a 0.45 μ m Millipore filter, diluted,

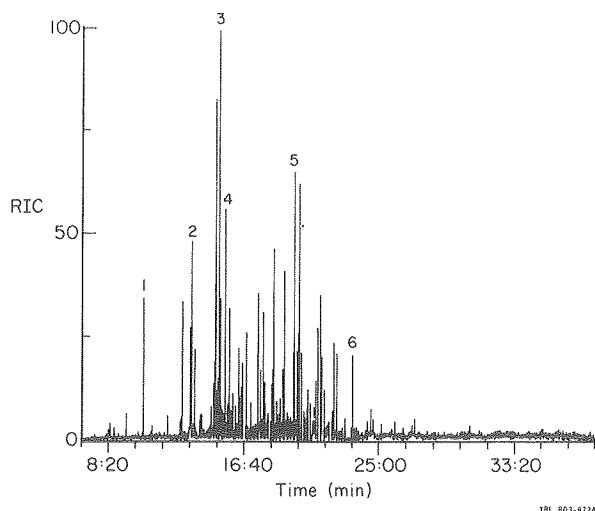


Figure 2. Capillary gas chromatographic profile of substituted aliphatic and aromatic nitrogen heterocyclic compounds found in Occidental's heater-treater water.

and analyzed directly by HPLC-GFAA at 193.7 nm.

A Dionex anion exchange column, 100% water-methanol (80/20) for 10 min followed by a gradient with 0.02 M ammonium carbonate (5%/min), was used to separate five known arsenic standards. These included arsenite (AsO_2^{1-}), dimethylarsinic acid ($\text{Me}_2\text{As}(\text{O})\text{OH}$), methylarsonic acid ($\text{MeAs}(\text{O})(\text{OH})_2$), phenylarsonic acid ($\text{PhAs}(\text{O})(\text{OH})_2$), and arsenate (AsO_4^{3-}). The pulsed output of the GFAA gives a series of histograms, which together represent the eluting HPLC peak. This is illustrated with the five arsenic standards (10 ng/peak) in Figure 3. The seven process waters were run in a similar manner and the retention times of the five standards were correlated with arsenic compounds observed in the samples. Table 6 summarizes the tentatively identified inorganic and organoarsenic compounds found in the seven process waters along with their retention times.

DISCUSSION

A profile or fingerprint for each series of identified compounds is used here to correlate the organic ligands and inorganic and organometallic compounds found in the various oil shale process waters with the specific retorting process.

The mono- and dicarboxylic acids are an example of organic ligands with definitive fingerprints. As expected, the Occidental process waters

Table 3. Substituted phenols from Geokinetics' retort water.

Compound	Identified by GC-MS ^a
1	Phenol
2	2-Methylphenol
3	3-Methylphenol
4	Dimethylphenol(isomer)
5	Dimethylphenol(isomer)
6	Dimethylphenol(isomer)
7	Trimethylphenol

^a30 M x 0.025 mm OV101 (40 - 250°C, 3°C/min).

Table 4. Substituted aliphatic and aromatic nitrogen heterocycles in Occidental's heater-treater water.

Compound	Identified by GC-MS ^a
1	2,3,5 trimethylpyridine
2	1-pent-1-one-pyridine
3	1-ethyl-2-methylpiperidine
4	3-methyl-1,2-diisopropyl-aziridine
5	2-methylquinoline
6	2,4-dimethylquinoline

^a30 M x 0.025 mm OV101 (40 - 250°C, 3°C/min).

Table 5. Aliphatic cyclic ketones from Geokinetics' retort water^a.

Compound	Identified by GC-MS ^a
1	Cyclopentanone
2	Cyclohexanone
3	3,3,5-trimethylcyclohexanone
4	2,3,4-trimethylcyclopent-2-en-1-one
5	3,4,5-trimethylcyclopent-2-en-1-one
6	3,5,5-trimethylcyclohex-2-en-1-one

^a30 M x 0.025 mm OV101 (40 - 250°C, 3°C/min).

^bSeparated on a Florisil column with isopropyl alcohol.

all have similar profiles, while the other process water samples had their own distinctive profiles. The concentration difference of the samples should be noted with the Occidental and Geokinetics' process waters concentrated to a similar extent

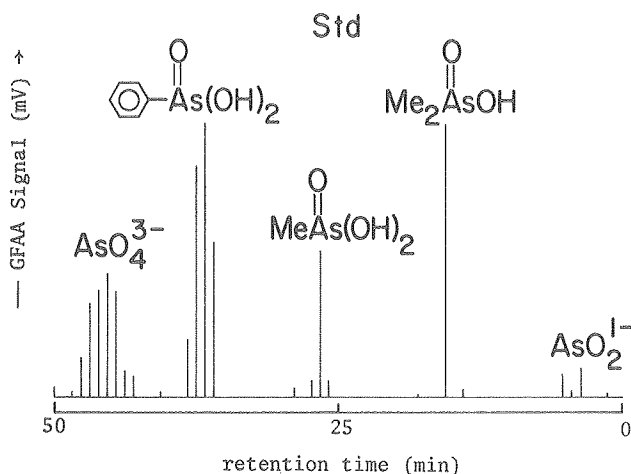


Figure 3. GFAA pulsed output of the standards (std) sodium arsenite, dimethylarsinic acid, methylarsinic acid, phenylarsinic acid, and sodium arsenate separated on a HPLC Dionex anion exchange column. Each peak represents 10 ng.

(30X). The L-2 and Omega-9 retort waters were twice as concentrated (60X) and the 136-tonne (150-ton) retort water was three times more concentrated (100X).

Significant differences between the process waters were not reflected in the monocarboxylic acids, which ranged from C_4 to C_{13} , but were more important with the identified dicarboxylic acids. For example, the identified dicarboxylic acids ranged from C_2 to C_{12} with all the Occidental process waters containing only C_8 to C_{12} dicarboxylic acids. The Omega-9 retort water contained all the identified dicarboxylic acids, while the L-2 sample contained none. Retort water from run L-2 may not be representative, because the run was incomplete (Burnham, 1980). Both the 136-tonne (150-ton) sample and the Geokinetics retort waters had slight differences, with the 136-tonne (150-ton) sample containing C_2 to C_5 and C_8 to C_9 dicarboxylic acids, while the Geokinetics sample had C_2 to C_4 and C_8 to C_{11} dicarboxylic acids. There were also several branched and cyclic aliphatic monocarboxylic acids present in all the samples as well as substituted benzoic acids.

Fingerprinting of other organic ligands has not been completed at this time; however, some preliminary results are presented in Figure 2 and Tables 3 to 5 for Geokinetics and Occidental waters.

Table 6. Identification of inorganic and organoarsenic compounds by HPLC-GFAA in various oil shale process waters^a.

Sample	NaAsO ₂ Sodium Arsenite	(CH ₃) ₂ As(O)(OH) Dimethylarsinic Acid	CH ₃ As(O)(OH) ₂ Methylarsinic Acid	Ø-As(O)(OH) ₂ Phenylarsinic Acid	Na ₃ AsO ₄ Sodium Arsenate	Unknown
Calibration	2.11 ± 0.43	16.28 ± 1.84	25.37 ± 0.44	35.7 ± 0.43	44.81 ± 1.1	--
SIMULATED IN-SITU RETORTS						
L-2 Retort Water	--	--	25.19 (+)	35.64 (+)	42.89 (+)	1.04
136-tonne Retort Water (150-ton)	--	--	23.79 (+)	--	43.91 (+)	0.46
FIELD IN-SITU RETORTS						
Omega-9 Retort Water	--	--	25.19 (+)	34.88 (+)	43.71 (+)	1.37 20.37
Geokinetics Retort Water	--	--	26.01 (+)	33.25 (+)	44.51 (+)	1.08 20.38
Occidental Heater-Treater Water	--	--	25.11 (+)	36.36 (+)	46.82 (+)	0.96 14.64
Occidental Boiler Blowdown Water	--	--	24.90 (+)	34.55 (+)	44.20 (+)	0.75
Occidental Retort Water	--	--	24.63 (+)	35.88 (+)	44.75 (+)	0.51 14.99

^a A dash (--) signifies that the species was not detected. A plus (+) signifies that the species was tentatively identified. The numerical values are the retention times at which the species or unknown peaks were detected.

These results indicate that oil shale process waters contain substituted pyridines, quinolines, aliphatic nitrogen compounds, substituted phenols, and aliphatic cyclic ketones.

The low-pressure liquid chromatographic separations of Geokinetics, 136-tonne (150-ton), and Occidental retort waters produced fractions whose identity was established by GC-MS. The profiles for these classes of compounds have not all been compared. However, a priori, they have similar classes of organic ligands differing only in concentration. It is hoped that future analyses will elucidate similarities and differences in a more definitive manner. More importantly, the metal-organic ligand correlations will be expanded to appropriate environmentally significant metallo-organic complexes other than the zinc-nitrogen heterocyclic complexes.

The HPLC-GFAA combination was used to fingerprint the inorganic and organoarsenic compounds in the seven oil shale process waters. These speciation studies, using the HPLC-GFAA combination, provided a technique to separate and identify single molecular inorganic and organometallic compounds. This will allow a rational approach to identifying specific toxic inorganic and organometallic compounds with known toxicological effects on both terrestrial and aquatic species (Fowler, 1978).

Table 6 indicates that the seven process waters contain substantially similar inorganic and organoarsenic compounds. They do differ, interestingly, in their individual concentrations. All the process waters contained detectable amounts of methylarsonic acid. Phenylarsonic acid appears to be present in all the samples studied, with the 136-tonne (150-ton) sample an exception. The predominant arsenical, both in concentration and presence in all samples studied, is arsenate (AsO_4^{3-}). All the process waters also contained a neutral arsenical, which we believe is a trialkylarsine oxide. No arsenite (AsO_2^{1-}) or dimethylarsinic acid ($\text{Me}_2\text{As}(\text{O})(\text{OH})$) was detected in any of the process waters studied. A complete analysis of these findings will be reported subsequently (Fish et al., 1980).

The differences between these process waters may be a reflection of operating conditions in the pyrolysis reaction and should be studied more thoroughly. Another significant question is the origin of the identified inorganic and organo-

arsenic compounds. The three possibilities, i.e., synthesis during pyrolysis; release during pyrolysis; or formation by bacterial biomethylation and conversion to the arsenic acids under the condition of high temperature and pH, will have to be studied in greater detail before the origin of these compounds can be determined.

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