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Chemical Characterization of Organic Compounds in Leachates from Surface-Retorted Oil Shale Generated by Gas Combustion and Indirect Pyrolysis

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Chemical characterization of leachates from surface-retorted oil shale generated by gas combustion (Paraho process) and indirectly-heated pyrolysis (TOSCO II process) revealed the presence of several classes of organic acids. Paraho leachates contained various oxygenated species, such as aliphatic monocarboxylic acids (C_5-C_8), dicarboxylic acids (C_8-C_{11}), and arenecarboxylic acids, with benzoic acid as the major component. A series of methyl-substituted arenecarboxylic acids were identified in the TOSCO leachate, with 3,5-dimethylbenzoic acid as the major component. Differences in chemical composition of the two leachates can be explained in terms of the different processes used to generate the two types of spent shale. Arenecarboxylic acids in both leachates were quantitatively determined. The potential exists for leaching of these oxygenated species from spent shale.

KEY WORDS: Gas chromatography-mass spectrometry, arenecarboxylic acids, oil shale.

INTRODUCTION

Current energy shortages brought about by dwindling world

petroleum supplies, coupled with higher fuel costs, have provided impetus for development of an oil shale industry. About 80 percent of the potential oil shale resource of the Green River Formation, containing an equivalent of about 1.2 trillion bbl of oil, lies in the Piceance Creek Basin of Colorado.¹ Recently, commercial development of this natural resource has become a reality.

Retorting of oil shale results in the production of oil, process gases, process water, and a carbonaceous residue known as spent shale. Current retorting technology is conducted either above ground in surface retorts, or underground by modified-in-situ (MIS) processes. Spent shale generated by either process contains, in addition to elemental carbon, various organic compounds, many of which are leachable by water as evidenced from total organic carbon measurements.^{2,3} Organic carbon concentrations in leachates from MIS spent shales range from 152 to 2,455 mg/L, while those from surface-retorted spent shale vary from 94 to 205 mg/L.³ A major disadvantage of the MIS process is the potential for chronic ground-water contamination caused by leachable organic compounds.

Surface retorting of oil shale, on the other hand, results in production of large quantities of spent shale. It is estimated that approximately 312 million tons per year of spent shale will be generated by 1987.⁴ Several surface-retorting facilities, such as the Exxon-TOSCO Colony Project and Union Oil Parachute Creek Project, are in the construction phase, with plans for commercial production within the next few years. Paraho Development Corporation has operated an existing experimental retort at the Anvil Points Oil Shale facility near Rifle, Colo., for several years. It is expected that millions of tons of spent shale will be generated by these facilities in the near future. Disposal plans include redistribution of large quantities of spent material into nearby canyons and valleys. Most surface-retorting oil shale facilities are being designed for zero discharge to the region's surface waters. However, because of the proximity of these facilities to the Colorado River, the potential exists for degradation of water quality by oil spills, process effluents, and spent shale leachates.

Although surface-retorted oil shale has been reported to contain numerous organic compounds,^{5,6} as well as hazardous and carcinogenic substances,^{4,7} very little information is available on the leaching potential of organic compounds associated with spent shale.

Drainage of water from a spoil pile, either by surface runoff or infiltration through the pile, could be significant after a storm or snowmelt, resulting in degradation of the region's surface- and ground-water quality by organic contaminants.

A laboratory study was undertaken to characterize organic contaminants in surface-retorted spent shale leachates, to identify potential environmental problems associated with leachates from spent shale piles. Spent shale samples from two surface-retorting processes were chosen for this study. One sample was generated by the Paraho process, which is a gas combustion process conducted in an oxidizing atmosphere. The other sample was derived from the TOSCO II process, an indirectly-heated pyrolytic process, in which retorting takes place in a reducing atmosphere. The objective for this study was to determine if any differences existed between the organic contaminants in leachates derived from spent shale generated by these two processes. Following definitive chemical characterization, a method was developed for determination of major selected organic contaminants in spent shale leachates. This report describes the results of our experiments.

EXPERIMENTAL

Sample collection and preparation

Two samples of spent shale were used in the studies. One sample, generated by the Paraho process, was supplied by the Laramie Energy Technology Center (LETC), Laramie, Wyo. The other sample generated by the TOSCO II process was supplied by The Oil Shale Corporation (TOSCO) Research Center, Golden, Colo. The Paraho sample was ground in a porcelain mortar to a fine powder (approximately No. 200 mesh) and stored in airtight glass jars. The TOSCO sample, which was received as a fine powder (No. 200 mesh) was stored as received in teflon bottles.

Total Organic Carbon (TOC)

TOC analyses were made on an Oceanographic International Carbon Analyzer.† The sample was pipeted into a carbon-free

†The use of brand names in this report is for identification purposes only and does not imply endorsement by the U.S. Geological Survey.

precombusted ampoule, acidified, oxidant added, and purged with O_2 to remove inorganic forms of carbon. The ampoules were then sealed and heated in a pressure vessel to oxidize the organic carbon to CO_2 . The digested ampoules were broken in a closed-purge system, purged with N_2 . The resultant CO_2 was measured by nondispersive IR. Organic carbon concentrations were determined by correlation to a working standards curve.

Leaching of spent shale

Spent shale samples were leached with "Baker Analyzed" reagent HPLC water by a static and dynamic method.

Static method

One hundred grams each of Paraho and TOSCO spent shale samples were placed in 500 mL erlenmeyer flasks. Two hundred milliliters of organic-free water were slowly added to each flask. The flasks were stoppered and stored in the dark for 22 days. The flasks were periodically shaken. A water blank was subjected to the same conditions. The water in each flask was decanted off, and the pH of the leachate measured. After adjusting the pH to 12 with 5% KOH solution, the leachates were each extracted with methylene chloride (2×50 mL) and ether (1×50 mL). The combined organic extracts were dried over anhydrous Na_2SO_4 and concentrated in a Kuderna-Danish apparatus to a volume of approximately 5 mL. The solution was further concentrated to a volume of approximately 100 μ L under a stream of N_2 . Following the addition of d_{10} -biphenyl as the internal standard, the extract was analyzed by gas chromatography-mass spectrometry (GC-MS) for base-neutral organic compounds. The aqueous solution was adjusted to pH 1 with 10% H_2SO_4 solution and extracted with methylene chloride (2×50 mL) and ether (1×50 mL). The combined organic extracts were concentrated in a similar manner as the base-neutral extract. The acid extract was methylated with diazomethane. After the addition of d_{10} -biphenyl as the internal standard, the methylated-acid fraction was analyzed by GC-MS.

Dynamic method

One hundred grams each of TOSCO and Paraho spent shale were

packed in borosilicate glass columns 40 cm long and 2.5 cm ID. Five hundred milliliters of water were added to each column. Fractions of the eluate were collected for pH and TOC determinations. The pH of the leachate obtained by the static method was 8.1 for the TOSCO leachate, and 11.5 for the Paraho leachate. By the dynamic method, the pH of the TOSCO leachate ranged from 6.7 to 8.3, while the pH of the Paraho leachate ranged from 11.3 to 11.8.

Instrumentation

Instrumental analyses were performed on a Finnigan OWA 20 computerized capillary gas chromatography-quadrupole mass spectrometry system (GC-MS-COM). The GC was equipped with a wall-coated open tubular (WCOT) fused-silica capillary column 30 m long by 0.26 mm ID, coated with SE-54. The linear velocity of He through the column was 26 cm/s; injections were made using the splitless-injection technique. The GC oven was held at 50°C for 4 min and programmed at 6°C per min to 300°C. One microliter of each sample extract was injected at 50°C. The vent valve was automatically opened at 45 s, and the filament and multiplier were automatically turned on at 240 s. Data acquisition began simultaneously with injection of the sample. The mass spectrometer was operated in the electron impact mode using an ionizing voltage of 70 eV and an ionization current of 250 μ A. The instrument was repetitively scanned from 40 to 450 amu in 0.9 s.

Determination of arenecarboxylic acids

Twenty-five grams each of TOSCO and Paraho spent shale samples were equilibrated with 50 mL of "Baker Analyzed" reagent water in stoppered erlenmeyer flasks for 22 days. The leachates were decanted into separatory funnels, and the pH adjusted to pH 1 with 10% H_2SO_4 . Each sample was extracted with dichloromethane (2×20 mL) and ether (1×20 mL). The combined organic extracts were dried over anhydrous Na_2SO_4 and concentrated in a Kuderna-Danish apparatus to a volume of 0.5 mL. Each extract was methylated with a methanolic solution of ethereal diazomethane. After removal of excess diazomethane under a stream of dry N_2 , a known amount of d_{10} -biphenyl (internal standard for quantitation) in isoctane was added. The extracts were evaporated in a stream of

dry N_2 to a volume of $100 \mu\text{L}$. The concentration of the internal standard in each extract was $80 \text{ ng}/\mu\text{L}$.

A standard solution containing 12 arenecarboxylic acids in methanol was methylated with ethereal diazomethane. After removal of excess diazomethane, and addition of d_{10} -biphenyl (internal standard) in iso-octane, the solution was made up to a volume of 5 mL . Each μL of the standard solution contained 80 ng of each component and 80 ng of d_{10} -biphenyl. A reconstructed ion chromatogram (RIC) of a standard mixture of arenecarboxylic acid methylesters is shown in Figure 1. The relative retention times (RRT) as well as characteristic ions in the mass spectra of these compounds is shown in Table I.

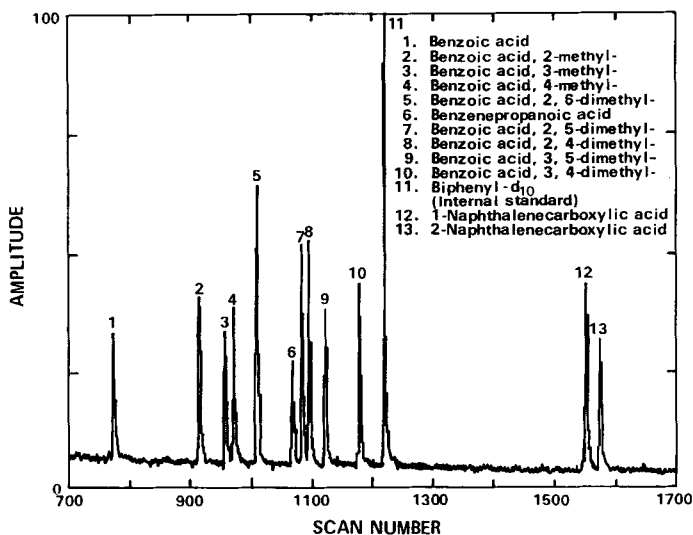


FIGURE 1. Reconstructed ion chromatogram (RIC) of a standard mixture of arenecarboxylic acid methylesters.

The standard solution for GC-MS was analyzed at a concentration of $80 \text{ ng}/\mu\text{L}$ of each component. A library of mass spectra of standard arenecarboxylic acids was created, making the internal standard d_{10} -biphenyl the first entry in the library. The library was edited; and for each library entry, a response factor, a

TABLE I
Gas chromatography-mass spectrometry data of standard arenecarboxylic acid methyl esters

Compound name	Molecular formula (molecular weight)	Relative retention time (RRT)	Characteristic ions (relative intensity) m/z	Ion used for quantitation m/z
1. <i>d</i> ₁₀ -Biphenyl (Internal Standard)	C ₁₂ D ₁₀ (164)	1.00	164(100); 162(48); 160(26)	164
2. Benzoic acid, methyl ester	C ₈ H ₈ O ₂ (136)	0.63	77(90); 105(100); 136(34)	105
3. Benzoic acid, 2-methyl-, methyl ester	C ₉ H ₁₀ O ₂ (150)	0.75	91(83); 119(100); 150(61)	119
4. Benzoic acid, 3-methyl-, methyl ester	C ₉ H ₁₀ O ₂ (150)	0.79	91(72); 119(100); 150(45)	119
5. Benzoic acid, 4-methyl-, methyl ester	C ₉ H ₁₀ O ₂ (150)	0.80	91(59); 119(100); 150(42)	119
6. Benzoic acid, 2,6-dimethyl-, methyl ester	C ₁₀ H ₁₂ O ₂ (164)	0.83	105(56); 132(100); 164(62)	132
7. ^a Benzenepranoic acid, methyl ester	C ₁₀ H ₁₂ O ₂ (164)	0.88	91(69); 104(100); 164(31)	104
8. Benzoic acid, 2,5-dimethyl-, methyl ester	C ₁₀ H ₁₂ O ₂ (164)	0.89	105(74); 132(100); 164(68)	132
9. Benzoic acid, 2,4-dimethyl-, methyl ester	C ₁₀ H ₁₂ O ₂ (164)	0.90	105(50); 133(100); 164(55)	133
10. Benzoic acid, 3,5-dimethyl-, methyl ester	C ₁₀ H ₁₂ O ₂ (164)	0.92	105(46); 133(100); 164(52)	133
11. Benzoic acid, 3,4-dimethyl-, methyl ester	C ₁₀ H ₁₂ O ₂ (164)	0.97	105(37); 133(100); 164(40)	133
12. 1-Naphthalenecarboxylic acid, methyl ester	C ₁₂ H ₁₀ O ₂ (186)	1.27	127(81); 155(100); 186(75)	155
13. 2-Naphthalenecarboxylic acid, methyl ester	C ₁₂ H ₁₀ O ₂ (186)	1.29	127(76); 155(100); 186(71)	155

^aBenzenepropanoic acid is not an arenecarboxylic acid.

specific ion used for quantitation (Table I), and the standard amount of the compounds were entered. The quantitation procedure processed a data file by locating the internal standard d_{10} -biphenyl within a fixed retention time window. After successful location of the internal standard, the mass spectrum of each compound of interest was selected from the library and compared against each mass spectrum in the sample run, within a fixed relative retention time window, using a reverse-library search routine. If the compound was located, the area of a specific preselected ion was measured and stored. The procedure generated a quantitation and identification report for each file processed. The identification report provided a "fit" value, which is a measure of how well the library spectrum matched the unknown. A value of 0 to 1,000 was assigned to each compound, with a value of 1,000 being a perfect fit.

Computer calculations to quantitate each component are expressed by the following equations:

$$\text{Response Factor} = \frac{\text{Area} \times \text{Standard Amount}}{\text{Standard Area} \times \text{Amount}} \quad (1)$$

and

$$\text{Amount} = \frac{\text{Area} \times \text{Standard Amount}}{\text{Standard Area} \times \text{Response Factor}} \quad (2)$$

Where Amount and Area refer to the quantity and integrated area of a specific ion of the compound of interest; Standard Amount and Standard Area refer to the quantity and integrated area of a specific ion of the internal standard, d_{10} -biphenyl.

RESULTS AND DISCUSSION

Elemental analyses of two samples of surface-retorted spent shale are shown in Table II. Examination of the data shows that spent shale generated by the TOSCO II process contains more organic carbon than spent shale from the Paraho process. This finding is consistent with indirectly-heated pyrolysis of the TOSCO process, where the net retorting temperature is approximately 480°C.⁸ In the Paraho process, temperatures in the combustion zone may reach 760°C to

Table II
Elemental analyses in percent of TOSCO II and Paraho spent shale

	TOSCO II	Paraho
Carbon (total)	10.21	6.83
Carbon (mineral)	5.74	3.87
Carbon (organic)	4.47	2.96
Hydrogen	0.45	0.19
Nitrogen	0.42	0.27
Oxygen	17.49	12.14
Sulfur	0.85	0.81
Ash	73.95	84.76

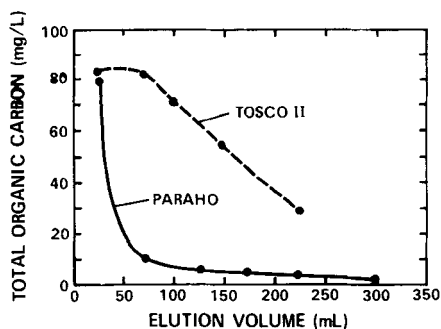


FIGURE 2. TOC elution profiles of TOSCO and Paraho spent shales.

815°C,¹ resulting in lower amounts of organic carbon associated with the residual spent shale.

TOC elution profiles of TOSCO and Paraho spent shales are shown in Figure 2. These profiles indicate that both types of spent materials contain water soluble organic compounds that are leachable by distilled water. In addition, the TOC profiles indicate that TOSCO material contains more leachable constituents than Paraho material. The shape of the profiles also indicates that Paraho spent shale contains largely hydrophilic organic constituents, while the TOSCO material contains more hydrophobic organic compounds. In order to fully assess the environmental impacts of oil shale retorting, it is essential to chemically characterize leachates by

techniques more definitive than TOC measurements. Leachates generated by the static method were chemically fractionated into base-neutral and acid fractions, and analyzed by capillary GC-MS. A preliminary analysis indicated the base-neutral fraction did not contain any detectable organic compounds. This finding is consistent with a recent publication⁹ which reports that alkylpyridines, which are unique to shale oil, were found in water which had been in contact with shale oil, but were not detected in aqueous extracts of raw shale or retorted shale. A series of arenecarboxylic acids were identified in the acid fraction of leachates from TOSCO and Paraho spent shales.

Acid fraction of Paraho leachate

An RIC of a methylated extract of the acid fraction with a list of compounds identified is shown in Figure 3A. A series of aliphatic

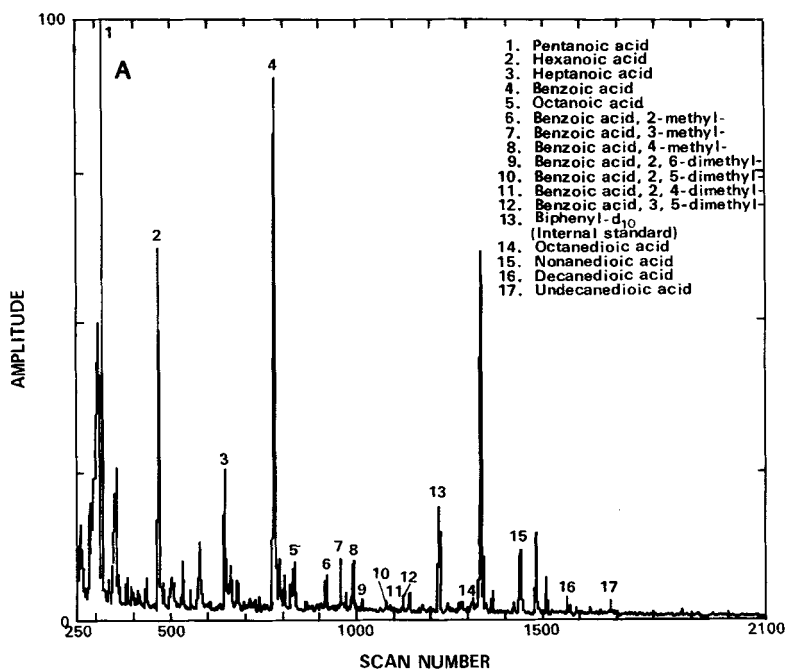


FIGURE 3A. Reconstructed ion chromatogram (RIC) of methylated extract of acid fraction of Paraho leachate.

monocarboxylic acids (C_5 - C_8) were identified. Lower members of this series (C_2 - C_4) were not found, presumably, because of losses encountered during sample preparation and volatility of the methyl esters. Dicarboxylic acids (C_8 - C_{11}) also were present in this fraction. Aliphatic monocarboxylic acids (C_7 - C_{10}) and dicarboxylic acids (C_4 - C_{11}) have been previously reported in Paraho retort water,¹⁰ and aliphatic monocarboxylic acids (C_2 - C_{10}) have been identified in product water from simulated in situ oil shale retorting.¹¹ Several arenecarboxylic acids were also identified in this fraction; benzoic acid was the major component and methyl-substituted benzoic acids were minor components.

Acid fraction of TOSCO II leachate

An RIC of a methylated extract of the acid fraction and a list of identified compounds is shown in Figure 3B. No aliphatic

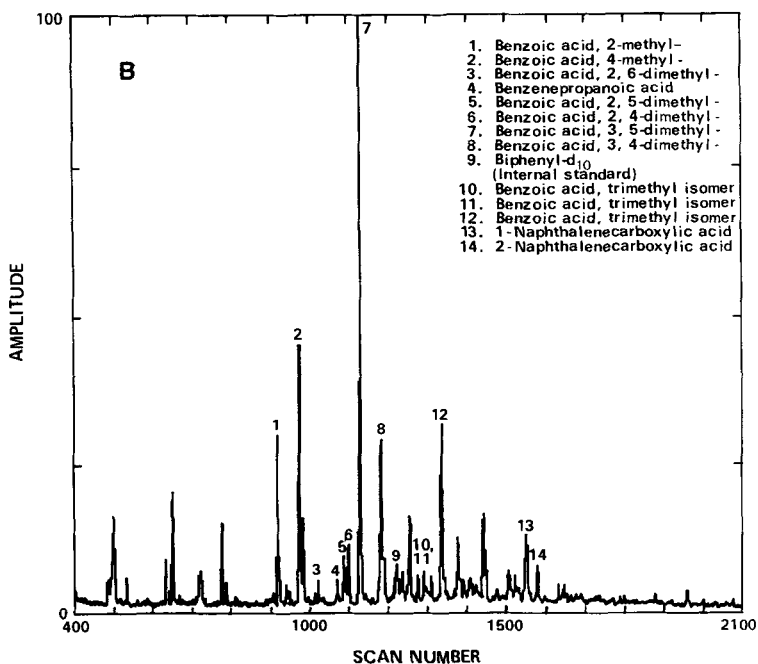


FIGURE 3B. Reconstructed ion chromatogram (RIC) of methylated extract of acid fraction of TOSCO leachate.

monocarboxylic acids, dicarboxylic acids, or benzoic acid were identified in this fraction. A series of methyl-substituted benzoic acids were identified; 3,5-dimethylbenzoic acid was the major component. In addition, several trimethyl-substituted benzoic acids and two naphthalene carboxylic acid isomers were identified in this fraction.

Arenecarboxylic acids in spent shale leachates

Concentrations of arenecarboxylic acids in both types of spent shale and leachates are shown in Table III. The data indicate the Paraho leachate contains benzoic acid as the major component (448 $\mu\text{g/L}$); whereas, the TOSCO leachate contains 3,5-dimethylbenzoic acid as the major component (539 $\mu\text{g/L}$). In addition, the TOSCO leachate contains higher concentrations of methyl-substituted benzoic acids than the Paraho leachate. These differences can be explained in terms of the process used to generate the two types of spent shale. In the Paraho process, which is conducted under oxidizing conditions, alkyl-substituted aromatic compounds are oxidized mainly to benzoic acid, with only minor amounts of methyl-substituted benzoic acids. The TOSCO process, which is conducted in a reducing atmosphere, presumably preserves the alkyl-substituents, resulting mainly in the formation of methyl-substituted benzoic acids. It has been reported that photo-oxidation of No. 2 fuel oils results in the formation of oxygenated compounds including alkylated benzoic acids and naphthoic acids having antimicrobial activity.¹² Benzoic acid and methyl-substituted benzoic acids also have been identified in water produced during in situ combustion experiments for the recovery of tar sands.¹³ The arenecarboxylic acids identified in these spent shale leachates are reported for the first time.

Aliphatic mono and dicarboxylic acids in spent shale leachates

Aliphatic mono- and dicarboxylic acids (Figure 3A) were found only in the Paraho spent shale leachate and not in the TOSCO leachate. These compounds are presumably formed by oxidation of kerogen during the retorting process. It has been reported that oxidative degradation of kerogen from Green River shale results in the formation of aliphatic monocarboxylic, dicarboxylic, and aromatic acids.¹⁴⁻¹⁶ The reducing atmosphere of the TOSCO process could

TABLE III
Arenecarboxylic acid concentrations in spent shale and leachates

Number	Compound	TOSCO II		TOSCO II	
		($\mu\text{g}/\text{kg}$ spent shale)	Paraho	($\mu\text{g}/\text{L}$ leachate)	Paraho
1.	Benzoic acid	ND	896.0	ND	448.0
2.	Benzoic acid, 2-methyl-	491.0	43.0	245.0	21.5
3.	Benzoic acid, 3-methyl-	2.0	78.4	1.0	39.2
4.	Benzoic acid, 4-methyl-	7.3	28.2	3.6	14.1
5.	Benzoic acid, 2,6-dimethyl-	23.0	ND	11.5	ND
6.	Benzenepropanoic acid	4.3	ND	2.2	ND
7.	Benzoic acid, 2,5-dimethyl-	136.0	5.8	68.0	2.9
8.	Benzoic acid, 2,4-dimethyl-	116.0	5.5	58.2	2.8
9.	Benzoic acid, 3,5-dimethyl-	1,079.0	14.0	539.0	7.0
10.	Benzoic acid, 3,4-dimethyl-	5.3	ND	2.7	ND
11.	1-Naphthalenecarboxylic acid	D	ND	D	ND
12.	2-Naphthalenecarboxylic acid	41.0	ND	20.5	ND

ND Not detected.

D Detected, not quantified.

account for the absence of aliphatic monocarboxylic and dicarboxylic acids in these leachates.

CONCLUSIONS

A series of arenecarboxylic acids were identified and quantified in surface-retorted oil shale leachates, generated under laboratory conditions, using gas chromatography-mass spectrometry-computer techniques. Leachates from the Paraho material contained lower-molecular-weight aliphatic monocarboxylic, dicarboxylic, and arenecarboxylic acids, with benzoic acid as the major component. These oxygenated compounds are presumably formed under the oxidizing conditions of the Paraho retorting process. The TOSCO leachates did not contain detectable amounts of aliphatic monocarboxylic or dicarboxylic acids. A series of methyl-substituted arenecarboxylic acids were identified in the TOSCO leachate, with 3,5-dimethylbenzoic acid as the major component. Reducing conditions of the TOSCO process apparently precluded further oxidation of methyl-substituted benzoic acids to benzoic acid.

Although spent shale is known to contain aliphatic, alicyclic, aromatic, and polycyclic aromatic hydrocarbons,^{5,6} these compounds are not measurably leached by distilled water under the laboratory conditions used. Mechanisms of sorption/desorption, chemical alteration, and biological degradation of organic compounds associated with spent shale, as well as movement of these compounds through hydrologic systems, are not known. Incorporation of oxygen into hydrocarbons by processes such as photo-oxidation or biological degradation will greatly increase their water solubility and subsequent mobility in the hydrologic environment. Although data obtained from laboratory leaching experiments cannot be extrapolated to or simulate actual field conditions; nevertheless, the potential exists for leaching of these oxygenated species from spent shale. While the method described in this report is used for the determination of arenecarboxylic acids in aqueous leachates of surface retorted oil shale, it is suggested that these analytical techniques can be applied to other environmental samples such as surface and ground waters in the vicinity of oil shale retorting operations.

Further studies on leachates generated from raw and spent shale in the field will determine whether arenecarboxylic acids have any utility as indicators of contamination derived from oil shale development.

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