

SYMPOSIUM ON CHARACTERIZATION AND CHEMISTRY OF OIL SHALES  
PRESENTED BEFORE THE DIVISIONS OF FUEL CHEMISTRY AND  
PETROLEUM CHEMISTRY, INC.  
AMERICAN CHEMICAL SOCIETY  
ST. LOUIS MEETING, APRIL 8 - 10, 1984

SOURCES AND KINETICS OF SULFUR SPECIES IN OIL SHALE PYROLYSIS GAS  
BY TRIPLE QUADRUPOLE MASS SPECTROMETRY

By

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INTRODUCTION

Understanding the chemistry of oil shale during a variety of retort processes has been a major goal of the Oil Shale Project at Lawrence Livermore National Laboratory. This understanding is critical to assure efficient recovery of good quality oil and to reduce the environmental impact of the retort operation. The gaseous sulfur species released in the process are of special interest because of their contribution to environmental pollution.

A fully computer-automated triple quadrupole mass spectrometer (1) was used to determine 10 sulfur containing gases from oil shale pyrolysis. The gases were present in concentrations ranging from tens of percent to less than 0.1 ppm. The TQMS was found to be the only instrument available with the required speed (10 gases determined in 600 ms), dynamic range ( $10^7$ ) and ability to analyze for a wide range in concentration with only a single standard (2).

We have published the results of studies on raw shales and shales treated with acid to remove carbonates, sulfates and pyrite (3). These shales were taken from a variety of depths at three geographical sites, two in Colorado and one in Utah. The major findings from this work were: (A) the relative ratios of concentration of the various sulfur gases were extremely constant over all samples analyzed; (B) the fraction of total sulfur in the shale that was released as sulfur-containing gases was extremely variable; and (C) we were able to differentiate between organic and pyritic sources for the sulfur gases.

This paper describes additional work done with organic and inorganic spikes added to raw shales and to acid-treated shales. The sulfur-containing organic spikes were chosen based on their sulfur group functionality to see if they would aid us in determining which sulfur functional groups in the oil shale kerogen produce various sulfur gases. The inorganic spikes were selected from those minerals found in burned shale to help in the delineation and prediction of sulfur scavenging in burned-shale recycle retorts.

EXPERIMENTAL

We had previously demonstrated the difficulty of using grab samples for trace sulfur species (2). Many of these gases are adsorbed or react with the sample bottle wall in a matter of hours. In addition, studies on major gases released in the retorting process using normal mass spectrometry (4) proved the need for kinetic data in order to more fully understand reaction mechanisms. We, therefore, developed two "on-line" methods for studying sulfur gas formation described in detail elsewhere (3). Briefly, these were a bulb type pyrolysis apparatus, used to give quantitative results for the composite gases formed under Fischer Assay-like conditions (Figure 1); and a Chemical Data Systems, Inc. Pyroprobe inserted directly into the source of the TQMS to pyrolyze samples and monitor gas evolution vs. temperature.

In the bulb apparatus, one gram of shale was placed in 1/2 atmosphere of nitrogen and heated at 11°C/minute to 500°C and held for an additional 16 minutes. The gaseous products were introduced into the TQMS and analyzed for 10 different gases by looking at specific daughters of selected parent ions. The gases analyzed for were hydrogen sulfide, methanethiol, ethanethiol, propanethiol, carbonyl sulfide, carbon disulfide, dimethylsulfide, dimethyldisulfide, thiophene and methylthiophene.

In the Pyroprobe, the samples were heated at 16°C/minute to 600°C while the same 10 gases were monitored continuously. A complete scan of all 10 gases, averaging 10000 points at each daughter, was done every 7 seconds. The two techniques were found to give very complementary data.

The oil shale used with the organic and sulfur-containing inorganic spikes came from a

Geokinetics test core at the 56-57' depth. This shale has a grade of 25 gal/ton and is very low in sulfur (0.11% total in the raw shale). The shale used with the remaining inorganic spikes came from the Tract C-a mine shaft at the 560' depth. This shale has a grade of 18 gal/ton and has 1.69% total sulfur in the raw shale. The shale used was treated with HCl to remove carbonates and sulfates. Both shales were ground to a talcum powder-like fineness.

Four sets of spiking experiments were carried out; (a) a variety of organic salts mixed with raw shale, (b) the same organic salts mixed with pure quartz sand, (c) sulfur-containing minerals mixed with raw shale, and (d) non-sulfur containing, but potentially sulfur-scavenging minerals mixed with HCl-treated shale. Spikes were ground with the oil shale in a "Wiggle-Bug" to ensure a fine and intimate mixture.

The organic salts selected as spikes were chosen because they were non-volatile and had a variety of sulfur functional groups. The compounds chosen were the Na<sup>+</sup> salts of thiodipropionic acid, thienylacrylic acid, ethylthiobenzoic acid, thioglycolic acid, 2,2'dithiodibenzoic acid, as well as L-cystine. The sulfur-containing minerals were CaSO<sub>4</sub>, MgSO<sub>4</sub> and pyrite (FeS<sub>2</sub>). The potential sulfur scavenging minerals were Dolomite, Ankerite, CaCO<sub>3</sub>, CaO, Siderite (FeCO<sub>3</sub>), Fe<sub>3</sub>O<sub>4</sub> and Fe<sub>2</sub>O<sub>3</sub>.

## DISCUSSION

The results from pyrolysis of oil shale mixed with the organic sulfur-containing spikes are shown in Table I. Under Fischer Assay-like conditions, the organic sulfur spikes did not give sulfur gases characteristic of the original functional group except for ethylthiobenzoic acid (ethanethiol) and thiodipropionic acid (thiophenes). In addition, thioglycolic acid produced a surprisingly large amount of CS<sub>2</sub>. The same spikes pyrolyzed with quartz sand instead of oil shale gave very similar results to those seen in Table I with the exception of thienylacrylic acid which formed large amounts of ethanethiol.

TABLE I  
SULFUR GASES FROM PYROLYSIS OF OIL SHALE SPIKED WITH  
ORGANIC SULFUR CONTAINING COMPOUNDS<sup>a</sup>

	Thiodi- propionic Acid	Thienyl- acrylic Acid	Ethylthio- benzoic Acid	L-Cystine	Thio- glycolic Acid	Dithiodi- benzoic Acid	Ave. Shale
Hydrogen sulfide	97.4	31.3	69.8	94.7	90.0	97.7	97.6
Methanethiol	.8	1.2	1.5	.5	1.3	1.0	1.3
Ethanethiol	1.0	.6	27.3	2.8	.7	.7	.4
Propanethiol	.03	-	.06	.05	.06	-	.08
Dimethyl sulfide	.2	-	1.0	-	-	-	.05
Dimethyl desulfide	-	-	-	.003	.01	.02	.005
Carbonyl sulfide	.4	.5	.4	.7	.7	.3	.3
Carbon disulfide	.1	-	-	.6	6.9	-	.09
Thiophene	.05	34.5	.02	.6	.3	.3	.05
Methyl thiophene	-	32.0	-	.05	.2	-	.11
% Conversion of sulfur to sulfur gases	42.5	4.7	20.9	41.7	38.5	6.8	7.6

a. Results are given as excess gaseous sulfur species formed, as percents of total excess sulfur gases.

In additional pyrolysis experiments, pyrite, MgSO<sub>4</sub> and CaSO<sub>4</sub> were added to raw shale samples. Pyrite occurs naturally in oil shale and the sulfates occur in weathered oil shale and burned shale that is used to heat raw shale in certain kinds of processing. As seen in Table II, both the pyrite and MgSO<sub>4</sub> gave a spectrum of sulfur gases similar to those found from raw shale. These results are consistent with our previous conclusion that the sulfur gas composition is strongly influenced by equilibrium forces. The CaSO<sub>4</sub> gave no gaseous sulfur species, probably because the stable reduction product in a pyrolysis gas atmosphere is CaS, not the oxide as would be the case for Mg, as is shown in Figure 2. (The equations used in Figure 2 have been simplified to increase readability.) The Y axis in Figure 2 is the Gibbs free energy change (G) in the following equation:

$$\frac{[C][D]}{[A][B]} = K = e^{-\Delta G/RT} \quad \text{for reaction } A + B \rightarrow C + D$$

Reactions with a negative free energy are thermodynamically favorable and reactions with a free energy change of -70 kJ/mole can remove gaseous reactants to part-per-million levels.

TABLE II  
SULFUR GASES FROM PYROLYSIS OF OIL SHALE SPIKED WITH  
INORGANIC SULFUR-CONTAINING COMPOUNDS<sup>a</sup>

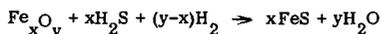
	<u>Pyrite</u>	<u>MgSO<sub>4</sub></u>	<u>Ave. Shale</u>
Hydrogen sulfide	98.4	97.0	97.6
Methanethiol	.6	1.5	1.3
Ethanethiol	.3	.5	.4
Propanethiol	.04	-	.08
Dimethyl sulfide	-	-	.05
Dimethyl disulfide	.01	-	.005
Carbonyl sulfide	.6	.3	.3
Carbon disulfide	.1	-	.09
Thiophene	.02	.1	.05
Methyl thiophene	.02	-	.11
Sulfur dioxide		.1	
% Conversion of sulfur to sulfur gases	13.8	.3	7.6

a. Results are given as excess gaseous sulfur species formed, as percents of total excess sulfur gases.

Note: No detectable sulfur gases formed from CaSO<sub>4</sub>.

Several aliquots of HCl-treated shale (carbonates and sulfates removed) were spiked with various minerals that were candidates for sulfur scavenging. As seen in Table III, Dolomite, CaCO<sub>3</sub> and Ankerite had little effect on the sulfur gas production. CaO caused sulfur gas production by factors of from 30 to 100.

Both forms of iron oxide presumably react with the H<sub>2</sub>S to form iron sulfide:



Thermogravimetric analysis of the FeCO<sub>3</sub> indicated that it decomposed to Fe<sub>3</sub>O<sub>4</sub> + CO<sub>2</sub> + CO between 400 and 500°C. This suggests that the reaction of FeCO<sub>3</sub> with H<sub>2</sub>S to form FeS may take place in two steps; the decomposition to the oxide followed by the formation of iron sulfide. However, it is possible that a direct displacement reaction takes place.

The changes in the Gibbs free energy of these H<sub>2</sub>S scavenging reactions are also given in Figure 2. The free energy change of the reaction of H<sub>2</sub>S with Fe<sub>3</sub>O<sub>4</sub> is similar to that with Fe<sub>2</sub>O<sub>3</sub>. In theory, the thermodynamics of H<sub>2</sub>S reacting with CaO are just as favorable as for iron oxides; However, in practice, CaO is less effective. The most probable explanation is that CaO is converted to CaCO<sub>3</sub> by reaction with the CO<sub>2</sub> produced during the early stages of kerogen pyrolysis. These results confirm our previous prediction (5) that iron oxides in the burned shale are responsible for the decreased H<sub>2</sub>S production observed from the Lurgi L-R process (6).

Trace sulfur species are not scavenged as effectively as H<sub>2</sub>S and account for about 20% of gaseous sulfur when iron oxides are present. The thiophenes are not removed by the minerals tested. Of the trace sulfur gases, COS is scavenged by iron oxides best, probably because it is the most sensitive to equilibrium forces.

#### ACKNOWLEDGMENTS

We wish to thank Arthur E. Lewis, Oil Shale Project Leader and Charles F. Bender, Chemistry and Materials Science Department Head for their continued encouragement and support. Work performed at Lawrence Livermore National Laboratory under the auspices of the U. S.

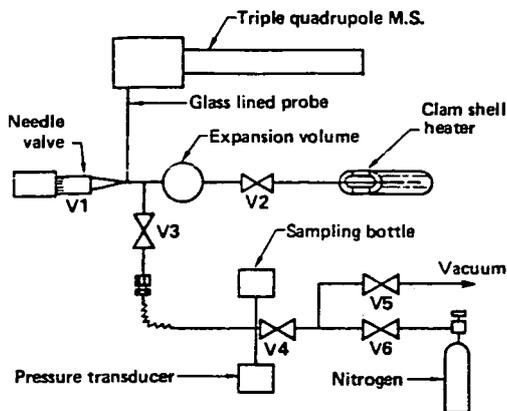


Figure 1. Schematic of bulb type pyrolysis system

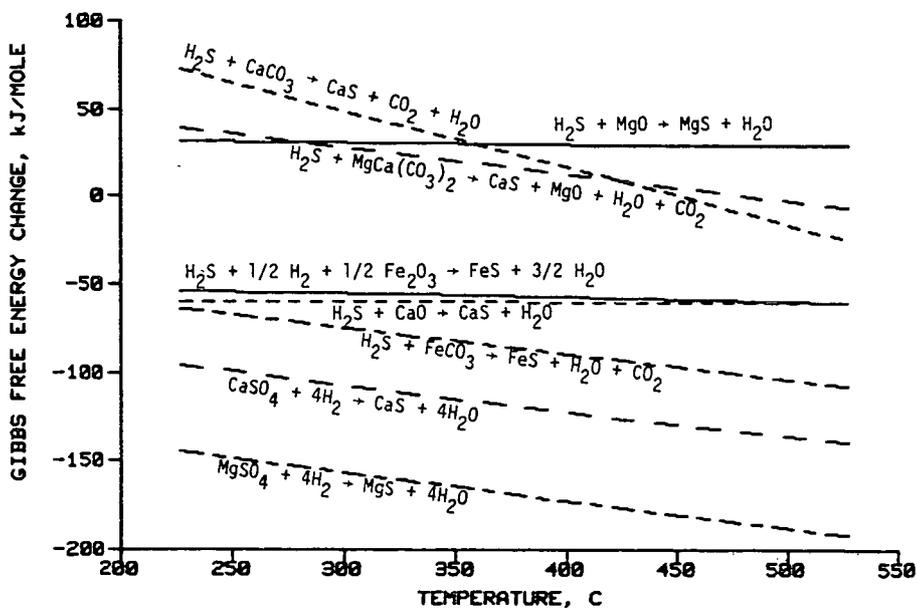


Figure 2. Thermodynamics of sulfur reactions.

TABLE III

SULFUR GASES FROM PYROLYSIS OF OIL SHALE SPIKED WITH MINERALS  
TO TEST THEIR SCAVENGING ABILITY<sup>a</sup>

	Raw Shale	HCl Treated	33% Dolomite	33% CaCO <sub>3</sub>	33% Ankerite	5.0% CaO	34% Siderite	5% Fe <sub>3</sub> O <sub>4</sub>	5% Fe <sub>2</sub> O <sub>3</sub>
Hydrogen sulfide	3364	4044	3803	3396	3203	1176	107	54	44
Methanethiol	26.9	11.9	17.0	15.2	13.6	16.4	5.5	4.7	4.9
Ethanethiol	10.4	6.7	9.6	8.8	7.2	7.7	.8	.8	1.1
Propanethiol	2.5	1.1	2.4	2.2	1.9	1.4	.2	.2	.2
Dimethyl sulfide	.5	-	-	-	-	-	-	-	-
Dimethyl disulfide	.05	.13	-	-	-	.10	.02	-	-
Carbonyl sulfide	10.4	38.9	20.7	17.6	16.4	3.8	3.2	2.3	1.9
Carbon disulfide	3.6	4.8	3.0	2.9	2.4	1.9	.8	.6	.5
Thiophene	1.8	.9	1.4	1.4	1.3	1.2	.8	.7	.7
Methyl thiophene	4.4	3.8	7.9	6.9	7.7	4.4	6.8	4.4	3.8
% Conversion of sulfur to sulfur gas	20.2	29.1	27.4	24.5	23.1	8.6	.9	.5	.4

a. Results are expressed as ugS per 1.0g equivalent raw shale. The oil shale used in all spiked samples was an 18 gal/ton sample from the 560' depth of Tract C-a and had been treated with HCl.

Dolomite = CaCO<sub>3</sub>·MgCO<sub>3</sub>

Ankerite = 2CaCO<sub>3</sub>·MgCO<sub>3</sub>·FeCO<sub>3</sub>

Siderite = FeCO<sub>3</sub>

## LITERATURE CITED

- (1) Wong, C. M., Crawford, R. W., Barton, V. C., Brand, H. R., Neufeld, K. W. and Bowman, J. E., Rev. Sci. Instr., 54, 996 (1983).
- (2) Wong, C. M., Crawford, R. W. and Yost, R. A., "An Evaluation of Triple Quadrupole MS/MS for on-Line Gas Analysis of Trace Sulfur Compounds from Oil Shale Processing", presented at the 30th Annual Conf. on Mass Spectrometry and Allied Topics, Honolulu, Hawaii, June 6-11, 1982, Special Publication Amer. Soc. of Testing and Materials, in press.
- (3) Wong, C. M., Crawford, R. W. and Burnham, A. K., "Quantitative Analysis and Kinetics of Trace Sulfur Gas Species from Oil Shale Pyrolysis by Triple Quadrupole Mass Spectrometry", Submitted to Analytical Chemistry (1983).
- (4) Huss, E. B. and Burnham, A. K., Fuel, 61, 1188 (1982).
- (5) Burnham, A. K. and Taylor, R. W., 15th Oil Shale Symp. Proceedings, Colorado School of Mines Press, Golden, CO, p. 299 (1982).
- (6) Weiss, H. J., Energy, p. 17 (winter, 1983).