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Lawrence Livermore National Laboratory

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MEASUREMENTS OF POTENTIAL ATMOSPHERIC POLLUTANTS IN OFF-GASES FROM THE LLNL 6-TONNE RETORT, EXPERIMENT L-3

ABSTRACT

We measured total sulfur, hydrogen sulfide, hydrocarbons, and nitrogen in the off-gases from the Lawrence Livermore National Laboratory's 6-tonne/day Rubble In Situ Extraction Simulation facility with a series of on-line, gas-monitoring instruments and gas indicator tubes. In addition, using instrumental neutron activation analysis after collection in adsorbent traps or in filter and impactor samplers, we determined the concentrations of several trace elements in the off-gas vapors and in aerosol mists. The concentrations of hydrocarbons in the vapor and in the product oil were determined either by on-line gas chromatography and off-line gas chromatography, or off-line gas chromatography coupled with mass spectroscopy. The assembled data are used to estimate production factors for potential pollutants for use in developing emission control options and assessment of air quality.

INTRODUCTION

Oil reserves in the Colorado Piceance Creek Basin recoverable by in situ methods are estimated to be more than 200 billion tonnes.[1] Concurrent with the extraction of this oil by in situ and surface retorting is the possible release to the atmosphere of particles, inorganic compounds, organic compounds containing sulfur and nitrogen, toxic trace elements, and naturally-occurring radionuclides. To ensure industrial development of these reserves in a timely, cost-effective manner and in compliance with emission and air quality standards, the need for development and implementation of pollution control strategies must be assessed.

Oil shale retorting is being studied at the Lawrence Livermore National Laboratory (LLNL) and is applicable to the in situ process being evaluated by the Rio Blanco Oil Shale Corporation at tract C-a. The Oil Shale Group (OSG) of LLNL has operated a 6-tonne/day surface retort vessel which simulates some aspects of an in situ retort. These well-controlled retort experiments provide an excellent opportunity to collect information about the formation and distribution of off-gas constituents that will be useful in estimating the releases of potential atmospheric pollutants from in situ processing of oil shale.

In this document we report the measurements of potential atmospheric pollutants produced from Colorado tract C-a oil shale in LLNL's 6-tonne/day retort, Experiment L-3. This report includes aerosol particle and off-gas data that have not previously been reported. These data, including the pertinent production data reported in Campbell,[2] are used to estimate production factors, i.e., production rate of potential atmospheric pollutants per unit volume of oil and gas produced.

THE LAWRENCE LIVERMORE NATIONAL LABORATORY 6-TONNE/DAY RETORT FACILITY

The LLNL is conducting experiments with an insulated and electrically heated stainless steel retort vessel, 90 x 610 cm, with a 6-tonne oil shale capacity.[2] In a retort experiment, oil shale at the top of the vessel is first heated with nitrogen. When the desired temperature is achieved, air or an air-steam mixture is introduced, the combustible material is ignited, and the flame front moves through the shale bed, decomposing kerogen into oil, char, and gases. During the course of the burn, the shale oil is continuously eluted from the vessel by the off-gas stream. Oil collectors, condensors, and demisters, shown schematically in Fig. 1, separate the oil from the off-gas. This collection system is followed by an absolute (HEPA) filter to insure complete removal of the oil mist. Portions of the off-gas can then be either recycled or vented through a flare-stack. Temperatures, pressures, and flow rates are measured at all key locations and stored by an on-line computerized data acquisition system. Major inorganic and hydrocarbon components of the off-gas are monitored continuously with on-line gas chromatographs or an on-line infrared spectrophotometer.

During May 7-12, 1979, retort run L-3 was conducted in the 6-tonne retort. In this experiment the retort vessel was charged with two different grades of oil shale to simulate the effects of a step change in shale grade during retorting; the top half contained shale of oil content 73 l/tonne, and the bottom half contained shale of oil content 152 l/tonne. The major characteristics of the shale and operating conditions of the Experiment L-3 are summarized in Tables 1-3. A complete description of the L-3 burn, including detailed summaries of the on-line GC and IR off-gas analyses, are in Campbell.[2]

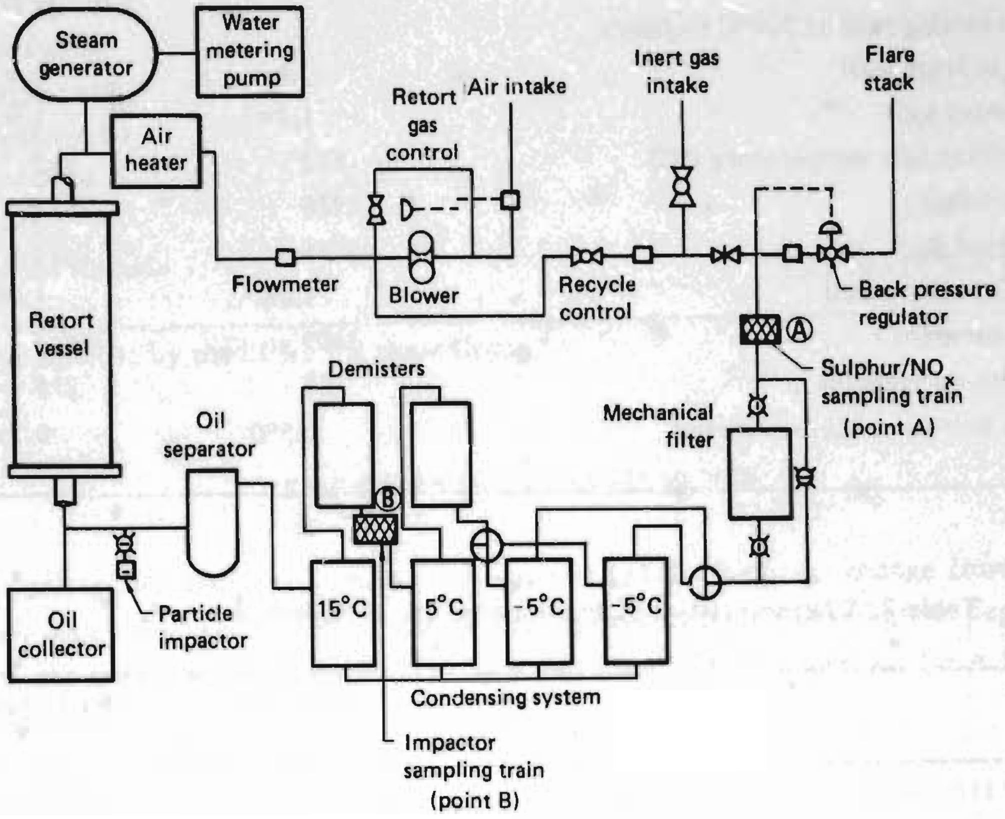

Figure 1. The LLNL Oil Shale Group's 6-tonne vessel for simulating modified <u>in situ</u> retorting.

Table 1. Characteristics of Experiment L-3.

	Lean shale	Rich shale
Average steam flow rate (l/s)	3.74	3.74
Average air flow rate (l/2)	3.68	3.24
Void fraction	0.28	0.30
Average retorting rate at 500°C (m/day):		
5.0 cm from wall	1.4	1.2
at center axis	1.1	1.9
Average center line temperature (°C)	842	945
Shale loaded (kg)	2976	2687
Shale retorted (kg)	2976	2172
Oil yield (U.S. petro bbl)	1.06	1.89
Off-gas volume (m^3)	1409	1015
Approximate oil yield (l)	180	274
U.S. petro. bbl/tonne shale retorted	0.380	0.794

Table 2. Characteristics of the shale burned in Experiment L-3.

	Lean shale	Rich shale
Oil content (l/tonne)	73	152
Depth of bed (m)	2.96	2.96
Particle size (cm)	0.001 to 30.5	0.001 to 30.5
Heat value (kcal/g)	1.003	1.893
Water content (ml/kg)	5.4	19.2
Total carbon (wt%)	14.1	21.4
Organic carbon (wt%)	8.8	17.1
Kerogen (wt%)	11.1	21.3
Total hydrogen (wt%)	1.5	2.5
Total nitrogen (wt%)	0.63	0.84
Total sulfur (wt%)	1.69	1.05
Ash (wt%)	70.2	61.8

Table 3. Characteristics of the oil produced in Experiment L-3.[a]

Total oil produced (l)	454.3
Total oil produced (kg)	433.9
Dewatered oil (kg)	406.4
C_5 and higher-molecular-weight hydrocarbons (kg)	406.4
Density (g/cm^3)	0.9015
Carbon (wt%)	84.95
Hydrogen (wt%)	12.11
Nitrogen (wt%)	1.66
Sulfur (wt%)	1.08
Ash (wt%)	0.003
Empirical formula	$CH_{1.71}N_{0.017}S_{0.0048}$

[a] Data provided by the LLNL Oil Shale Group.[2]

EXPERIMENTAL MEASUREMENTS

Ignition occurred at 25.6 h, and shutdown at 125 h. The grade change from the lean to rich shale occurred at 78.75 h. Steam was injected at a rate of 180 g/min beginning at 28.2 h and ending at about 125 h. Nitrogen was substituted for inlet air for a 1-h period starting at 50 h.

MEASUREMENTS OF CONSTITUENTS L-3 OFF-GASES

Analyses for N_2, O_2, H_2, hydrocarbons, CO, and CO_2 were made by the on-line gas chromatographs or an infrared spectrophotometer. The concentration of COS was monitored by microwave rotational spectroscopy (MRS). These measurements were taken every 20 min for HC, CO, and CO_2 and hourly for methane through C_9 hydrocarbons. The total off-gas flow was recorded every 15 min. In addition, a portion of the off-gas stream was aspirated into a separate gas monitoring system. As shown in Fig. 2, filtered off-gas was pumped into a mass-flow-controlled dilution system with a stainless steel bellows pump. Sulfur dioxide was monitored without dilution with a Thermo Electron Corporation Model 40 pulsed fluorescence analyzer (TECO-40). Nitrogen oxides were

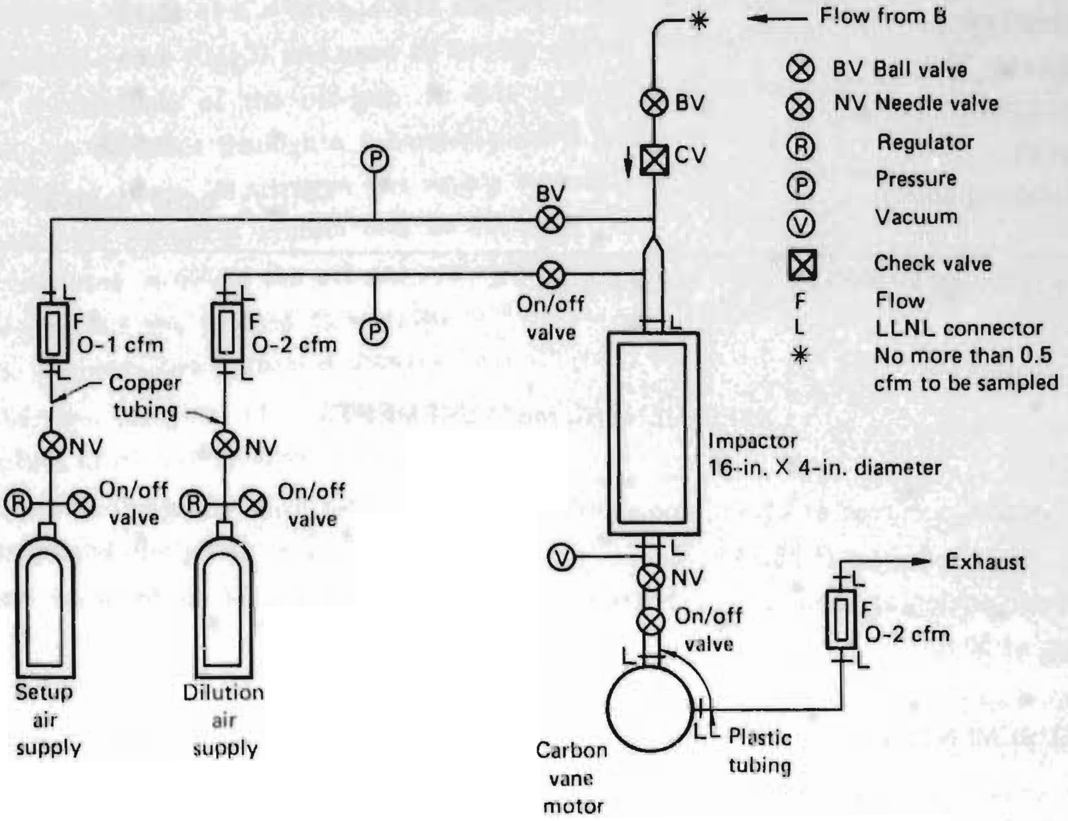

Figure 2. Schematic of the Environmental Sciences Division's aerosol sampling system.

measured by chemiluminescence with a Thermo Electron Corporation Model 14D analyzer (TECO-14D); H_2S was analyzed by pulsed UV fluorescence with a Thermo Electron Corporation Model 43 analyzer (TECO-43) preceded by a sulfur oxide scrubber; and total S was measured with a Meloy flame ionization monitor. Gastec and Drager gas indicator tubes were used periodically to measure H_2S, SO_2, NH_3, NO, NO_2, and NO_x. These measurements are summarized in Table 4.

A third portion of the off-gas was aspirated from a sampling port behind the first mist eliminator (see Fig. 3) and used to sample aerosol droplets and trace inorganic and organic constituents of the off-gas. In this system, aerosol particles and gases were drawn out of the duct through a 1.3-cm-diameter probe and fed to a sampling manifold located 4.6 m away. A nitrogen gas supply was used to equalize pressure between the retort and the sampling system and to set flow rates. A separate pure nitrogen gas supply was used to dilute the off-gas samples. This arrangement permitted operation of the samplers at the desired flow rates without drawing more than 3% of the off-gas stream. The sampling system is shown schematically in Fig. 4.

Aerosol samples were collected on either 47-mm Whatman #41, 0.4-μm pore Nuclepore, or on quartz fiber filters in a stainless steel holder fitted with Teflon O-rings, or in an MRI model 1502 7-stage, multicircular-jet, inertial cascade impactor with an integral back-up filter. Impaction substrates were either stainless steel pans or Whatman 41 filter material. The filter and impactor samplers were operated at 15 l/min. The aerosol samples were analyzed for trace elements by instrumental neutron activation analysis (INAA).

Organic vapors were collected by adsorption onto Tenax GC or XAD-2 resins contained in 3.2 mm-id glass tubes packed with about 0.1 g of Tenax. The adsorbant samplers were preceded by filter holders containing two glass fiber filters. These were operated for 2 to 10 min at flow rates of about 0.05 l/min and were used primarily to trap low molecular weight compounds. Analyses were done by GC and GC-MS after solvent extraction as described below. A series of larger, 9-mm-id stainless steel tubes, packed with about 1.0 g of XAD-2 resin were used to sample trace organic components, such as polynuclear aromatic hydrocarbons. These tubes, along with precleaned quartz prefilters, used to prevent aerosol droplets from entering the traps, were extracted with a 3:1 mixture of methanol and toluene, and analyzed by gas chromatography-mass spectrometry. Precleaned coconut charcoal, suspended in 9-mm-id glass tubes, was used to adsorb trace inorganic vapors, such as As and Se (or their compounds). These samplers were operated at flow rates of 3 l/min for 19 to 60 min. Elemental analyses were done by instrumental neutron activation analysis.

Table 4. Constituents monitored in off-gases from Experiment L-3.

Constituent	Measurement technique	Number of measurements	Sampling location[a]
H_2S	On-line pulsed fluorescence analyzer (OL-PFA) with gas preconditioner	6	A
	Gas indicator tubes	31	A
SO_2	On-line pulsed fluorescence	10	A
	Gas indicator tubes		A
COS	Microwave rotational Spectroscopy	12	A
Totals	On-line flame ionization detector	8	A
NH_3	Gas indicator tubes	5	A
NO, NO_2, NO_x	Chemiluminescence	3, 20, 7	A
	Gas indicator tubes		A
CO, CO_2	On-line infrared spectrometer Nondispersive infrared adsorption		A A
H_2, O_2, N_2, CH_4, C_2, H_2 C_2H_2, C_3H_6 C_4-C_9 hydrocarbons	On-line gas chromatograph		A
Hg	On-line Zeeman atomic absorption spectrometer		--[b]
Trace elements in off-gas vapors	Charcoal vapor trap/ instrumental neutron activation analysis	3	B
Trace elements in aerosol particles	Filter and impactor samplers/instrumental neutron activation analysis	11	B

[a] Samples were collected at two locations, designated A and B. The locations are shown in Figure 1.

[b] Measurements were made by Lawrence Berkeley Laboratory

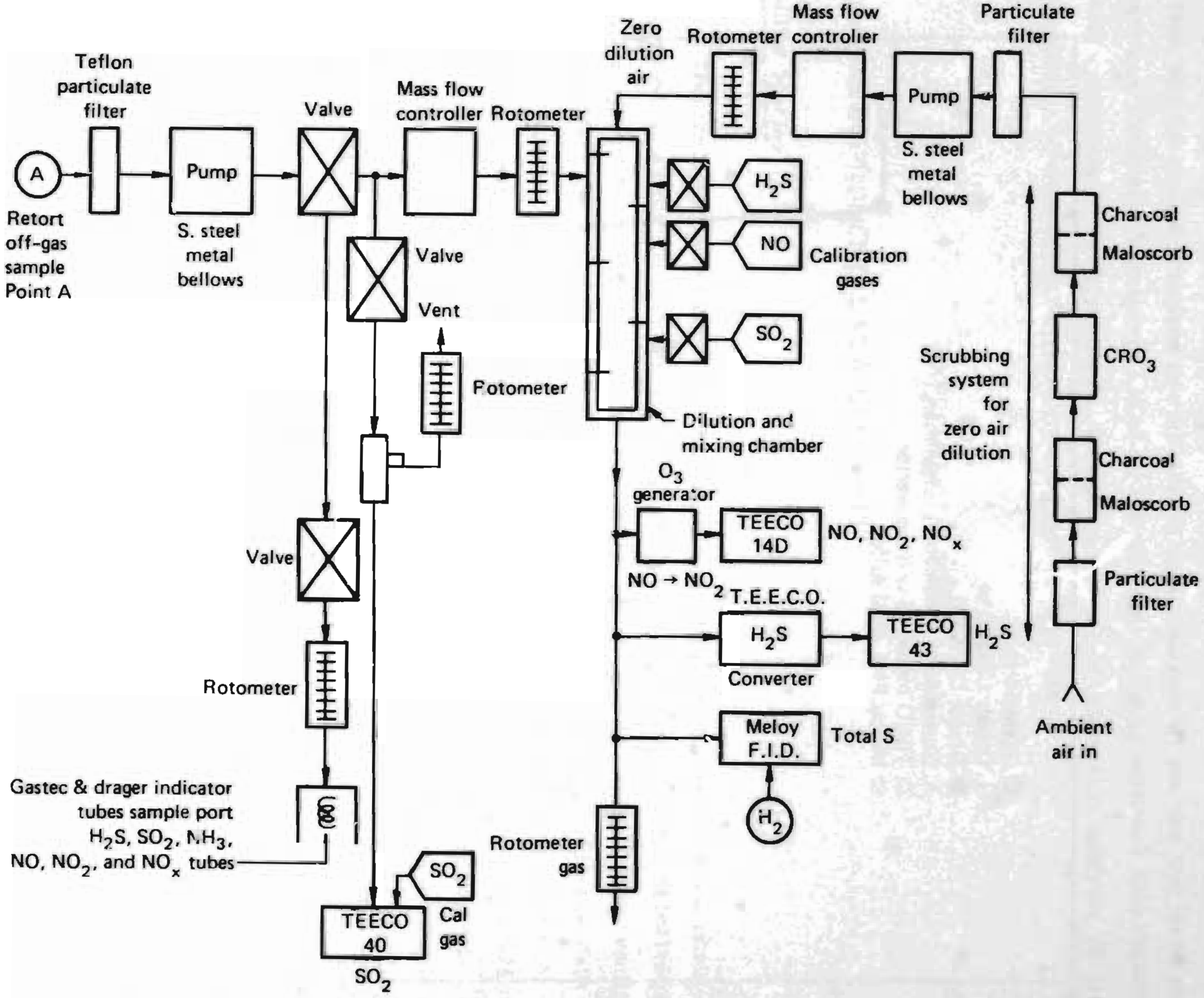

Figure 3. Schematic of the Environmental Sciences Division's off-gas monitoring system.

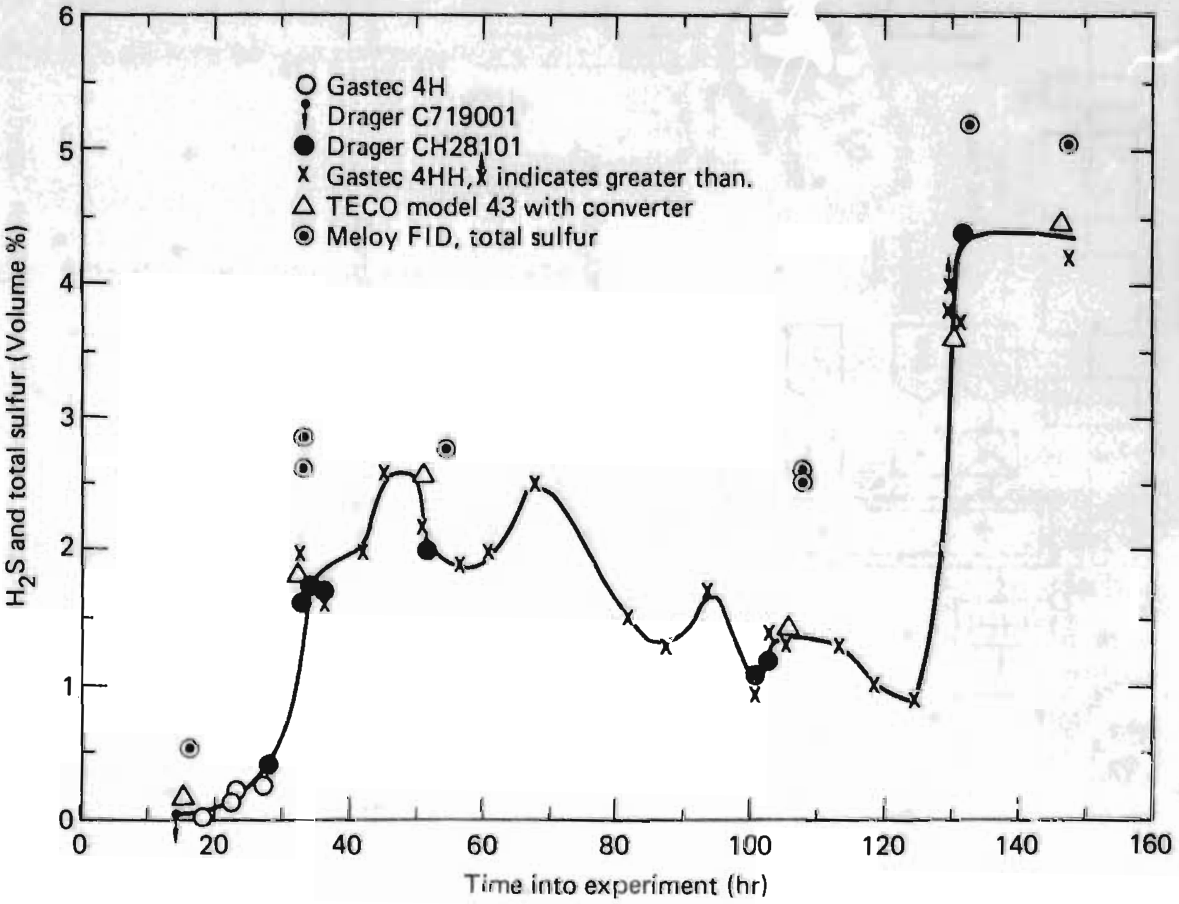

Figure 4. Concentration of H_2S and total sulfur during the L-3 retort.

In addition to the aerosol and gas measurements, aliquots of bulk oil and water produced in the retort were collected periodically, composited, and analyzed by INAA, wavelength dispersive x-ray fluorescence (XRF), and inductively coupled plasma-optical emission spectroscopy (ICP-OES). The samples for INAA and XRF were run directly, without treatment. Oil samples for ICP-OES were ashed under reflux for four days in a mixture of fuming sulfuric acid and nitric acid, and then treated with perchloric acid, dried, and the residue dissolved in dilute nitric acid. Samples of the raw and spent shale were also obtained. A complete list of all the samples, including pertinent data regarding their collection, is in Appendix A. Instrumental neutron activation analyses of trace elements in aqueous off-gas condensate are listed in Appendix B.

EXPERIMENTAL RESULTS

ON-LINE INSTRUMENTAL MEASUREMENTS

Sulfur Species

The concentrations of total sulfur (including all forms of sulfur in the gas phase and expressed as atomic sulfur) and H_2S, the most abundant sulfur species detected, are plotted against time-into-the-experiment (TIE) in Fig. 4. Data plotted include results of the Meloy FPD sulfur monitor (ENV), and of two sets of indicator tubes. The raw data are listed in Appendix B. Overall agreement between the different H_2S measurements was quite good, especially between the Drager indicator tube data taken at the two different sampling locations. One of the two measurements of H_2S with Gastec indicator tubes was lower than the other data by a factor of two. The H_2S concentrations measured with the Meloy analyzer appear to be about 10% greater than those measured with the Gastec indicator tubes used at the OSG sampling port. The highest concentrations of H_2S occurred when the lean shale was retorted, i.e., within the first 78 h. The high concentrations of H_2S after 130 h TIE reflect the much lower input gas flow rates after the run was terminated.

Total gaseous sulfur, including organosulfur compounds, are compared with the ENV H_2S measurements in Table 5 and in Fig. 4. In this experiment, the amount of sulfur emitted as H_2S was typically about 80% of the total sulfur, indicating that other forms of sulfur were present. The amount of large organosulfur compounds, and hence total sulfur present in the gas phase, will depend on the condensor temperature.

Table 5. Comparison of concentrations of total S and H_2S in discrete time intervals during Experiment L-3.

Time into experiment (h)	Concentration (%)		Ratio of sulfur in H_2S to total sulfur	Analytical method[a]
	S	H_2S		
32.1	--	1.83		PFD
32.6	--	1.60		GIT
32.9	2.64	--		FPD
33.0	2.85	--		FPD
34.0	--	1.70		GIT
36.3	--	1.68		GIT
Ave	2.76 ± 0.11	1.70 ± 1.12	0.58	
5.67	--	2.56		PFD
51.8	--	2.10		GIT
52.2	2.76	--		FPD
Ave	2.7	2.3 ± 0.23	0.79	
100.9	--	1.03		GIT
103.5	--	1.30		GIT
106.2	--	1.445		PFD
107.7	2.52	--		FPD
107.9	2.63	--		FPD
Ave	2.58 ± 0.06	1.26 ± 0.42	0.46	
129.5	--	3.9		GIT
130.4	--	3.63		PFD
131.2	--	4.4		GIT
132.3	5.2	--		FPD
Ave	5.2	3.98 ± 0.72	0.81	
146.7	--	4.48		PFD
147.3	--	4.20		GIT
	5.05	--		FPD
Ave	5.05	4.34 ± 0.14	0.81	

[a] Pulsed fluorscence detector (PFD), gas indicator tube (GIT), or flame photometric detector (FPD).

As shown in Table 6, the quantities of SO_2 detected in the off-gas were quite low, ranging from 7 to 22 volume ppm. The measurements of COS provided by Raley and Ward[3] ranged from 27 to 76 ppm, accounting for from 16 to 40 ppm of sulfur. The GC-MS analyses (discussed below) of gas phase sulfur compounds collected in a single Tenax sampler account for about 250 ppm of sulfur in the form of thiophenes of molecular weight greater than 113 (dimethylthiophene). The remaining sulfur may include lower-molecular-weight thiophenes, mercaptans, or possibly other organosulfur compounds.

Nitrogen Species

The concentrations of inorganic nitrogen species in the off-gas are listed in Table 7. Ammonia was the most abundant heteromolecular nitrogen compound detected; its concentration (30 - 190 ppm) was an order of magnitude higher than that of the oxides of nitrogen. Because of its solubility, most of the NH_3 was removed with the off-gas water. The largest NH_3 concentrations occurred after 75 h into the retort, when the rich shale was retorted.

CO, CO_2, H_2 and Hydrocarbon Analyses

Individual gas analyses for CO and CO_2 with the on-line infrared spectrometer, and for H_2, O_2, N_2, and C through C_9 hydrocarbons with the on-line GCs were performed at intervals of 1 h or less by the LLNL Chemistry Department. Detailed plots of the volume concentrations and cumulative moles of each of these species are available.[2,4] In Table 8 are listed the average concentrations for these species when lean and rich shale was retorted.

VAPOR PHASE TRACE ELEMENTS

Only three measurements were made of the concentrations of trace element vapors in the off-gas using the charcoal tubes; one at about 59 h when lean shale was retorted, and the other two at about 101 and 125 h when rich shale was retorted. In these measurements, up to six elements were determined (by INAA) above blank. These data are reported in Table 9. However, comparable quantities of the elements were often measured in each of the two sections of the charcoal traps, indicating that breakthrough had occurred. In that case, the values reported underestimate the true levels. Arsenic and Se were successfully measured earlier in the experiment, but broke through in the latter two measurements made near the end of the run, apparently because of higher

Table 6. Concentrations of sulfur dioxide in off-gas from Experiment L-3.

Time into experiment (h)	TECO-40[a] (ppm SO_2)	Indicator tubes (ppm SO_2)	Tube identification[b]
27.6	<0.5	<5	Gastec 5L
37.4	7		
46.8	22		
99.7	19.5	<5	Gastec 5L
		<1	Drager 6727101
104.5	14	<1	Gastec 5La
129.5	19.5		
130.2		<1	Gastec 5La
130.3		<1	Gastec 5L
131.2	15.5		
147.3	16.6	<1	Gastec 5La

[a] Discussion with Themro Electronic Corporation factory indicates that TECO-40 shows no response to large quantitites of H_2S or hydrocarbons when present simultaneously with SO_2. The difference then between the TECO-40 and indicator tubes is unexplained.

[b] Indicator tubes 5L, 5La, and 6727101 do not indicate H_2S; i.e., H_2S is not an interferent at any concentration.

Table 7. Concentrations of nitrogen species measured in off-gas from the Experiment L-3.

Time into experiment (h)	Concentration (ppm)[a]			
	NH_3	NO[b]	NO_2[b]	NO_x[b]
27.6	<1[c] <5[d]	--	<0.5	<2 <0.5
46.6	50[c] 80[d]	--	<0.4	<0.5
99.3	30[e] 40[e] 55[e]	--	--	--
100.4	--	<2	<1	--
129.5	180[e] 190[e] 180[d]	--	--	--
131.2	--	<2	<1 <0.4 <0.5 <0.5	--
147.3	150[e] 135[e]	--	--	--
149.7	--	<2	<1 <0.4	<0.5

[a] A succeeding measure at any TIE is entered below the previous measure.

[b] NO, NO_2, and NO_x were measured with a Thermo Electron Corporation Model 14DS Chemical Detection System, or with Gastec or Drager Indicator Tubes, Nos. 5 9L, 10, CH 30001, CH 29401, CH 31001, or 671901.

[c] Gastec indicator tube 3L

[d] Drager indicator tube 20501

[e] Gastec indicator tube 3M.

Table 8. Averages of the concentrations of gas-phase components measured in the L-3 off-gas by on-line GC, IR, or MRS (volume ppm).

	Concentration range[a]	
Species	Lean shale	Rich shale
CO	8 000	32 200
COS	65	35
CO_2	336 000	318 000
H_2	67 100	154 700
CH_4	11 400	20 200
C_2H_4	1 300	1 090
C_2H_6	2 800	4 200
C_3H_6	1 060	1 200
C_3H_8	1 200	1 800
C_4	1 620	2 200
C_5	820	1 150
C_6	760	930
C_7	630	790
C_8	380	500
C_9	150	100

[a] Data reported in Ref. 2.

vapor concentrations. This behavior may reflect differences in the composition of the two grades of shale. Alternatively, as suggested by Kland and Fox,[4] portions of the quantities of trace elements that are volatilized in the combustion region may have condensed or been adsorbed in cooler regions of the retort vessel, ahead of the flame front, escaping more readily as the flame front moved nearer the end of the vessel. In any event, the vapor concentrations of trace elements listed in Table 9 should not be regarded as highly reliable.

Table 9. Concentrations of vapor-phase trace elements in off-gas from Experiment L-3 (µg/m^3).

Trace element	TIE (h)		
	59	101	125
As	5.5 ± 1.8	16 ± 2[a]	17 ± 1[a]
Br	25 ± 17[a]	25 ± 19[a]	11 ± 7[a]
Cl	950 ± 250[a]	980 ± 280[a]	450 ± 98[a]
Cr	114 ± 14	<70	94 ± 36
Mo	4.2 ± 1.8	2.4 ± 1.4[b]	<1.5
Se	8.9 ± 1.0	18 ± 1[a]	14 ± 0.4[a]
Ba	<80	<64	<44
Co	<2.5	<3.6	<0.6
Fe	<5100	<5100	<1900
Ga	--	--	<4.3
Mn	<52	<37	<12
Sb	<3.9	<4	<1.5
U	<1.5	<1.6	<0.6
W	<1.5	--	<110
Zn	<41	<33	<44

[a] Comparable quantities were measured on both of the two trap sections; the value reported is a minimum.

[b] Largest quantity of the element was detected on the quartz wool plug. The value reported probably includes some aerosol.

[c] Average and standard deviation of values determined for prefilters.

[d] The value is based on a weighted average and reflects the largest individual measurement.

ANALYSIS OF THE TENAX TRAPS

Four of the Tenax traps (Nos. 3, 4, 6, and 8) and a fifth blank trap were selected for analysis. The Tenax traps were eluted with 10 ml of high-purity normal pentane and the eluents were reduced to a total volume of 100 µl by rotary evaporation and by evaporation under a stream of cold, pure nitrogen. Two-µl aliquots were analyzed by GC-FID with a

Varian model 3700 GC, with a 25-m, SE-52 WCOT column. Peak analysis was done with an automatic integrator. A 2-µl aliquot of the extract from Tenax trap #3 was also analyzed by GC-MS (Hewlett Packard model 5985B) also using a SE-52 WCOT column, yielding tentative identifications for 47 compounds. Nine hydrocarbons were identified by comparing their GC retention times and mass spectra with those of known compounds. Their corresponding vapor concentrations as well as the total hydrocarbon concentrations were estimated from the peak areas using the calibrated FID response factors, sample gas volumes, and solvent dilution factors. The solvent extraction efficiencies were assumed to be 100% in all cases. These data are summarized in Table 10. As indicated in Table 10, agreement was quite good between samples 6 and 8, in which only 5.5 and 6.2 cm^3 of retort gas were sampled. The concentrations determined from traps 3 and 4, however, were from 5 to 50 times lower than indicated by 6 and 8, suggesting that their break-through volumes had been exceeded. The total hydrocarbons detected in the blank (1.2 µg) was typically less than 1% of the sample.

To better resolve the components, the remaining extract of sample 8 was fractionated into an aliphatic and aromatic fraction by silica gel chromatography using n-hexane and CH_2Cl_2 eluents. Both fractions were analyzed by GC-FID and by GC-MS, both using 25-m, SP 2100 columns. Chromatograms of the aliphatic and aromatic fractions are reproduced in Fig. 5 and 6, respectively. The ordinates in the figures are scaled identically so that the peak heights may be compared directly. Estimates of the concentrations of aliphatic and aromatic hydrocarbons identified by GC-MS are listed in Tables 11 and 12, respectively. A total of 43 out of 133 peaks were identified in the aromatic fraction.

The concentrations of individual organosulfur compounds identified in the Tenax sample are listed in Table 13. No sulfur compounds were detected in the aliphatic fraction. The quantities of all of the organic compounds detected by class are presented in Table 14.

TRACE ELEMENTS IN OFF-GAS AEROSOL AND IN PRODUCT OIL

The series of filter samples was collected primarily to determine if chemical constituents of the off-gas aerosol, mostly oil mist, are fractionated with respect to size or bulk oil. Significant quantitites of the oil mist often penetrated the filters, despite the use of multiple filters. The problem was exacerbated in part by the highly variable aerosol concentration, which made it difficult to choose appropriate sampling times. Additional problems were encountered in handling and storing the oil-laden filters.

Table 10. Estimates of concentrations of selected hydrocarbons based on GC-FID analyses of Tenax porous polymer traps (mg/m^3).

	Tenax 8	Tenax 6	Tenax 4	Tenax 3
nonene	399	35	47	0.02
nonane	594	27	49	0.01
1-decene	623	436	105	0.39
n-decane	907	587	158	0.37
1-undecene	636	636	76	0.48
n-undecane	988	1070	133	0.79
1-dodecene	346	376	20	0.52
n-dodecane	573	619	28	0.62
C_{14} isoprenoid	77	82	2.1	0.10
1-Tridecene	102	124	1.6	0.27
n-Tridecane	154	184	2.0	0.34
Sample volume (cm^3)	6.2	5.5	27	7200
Total carbon (g/m^3)	18.7	20.5	82.9	144.6
TIE[a] (h)	104.5	90.0	87.9	57.3

[a] Time into the experiment

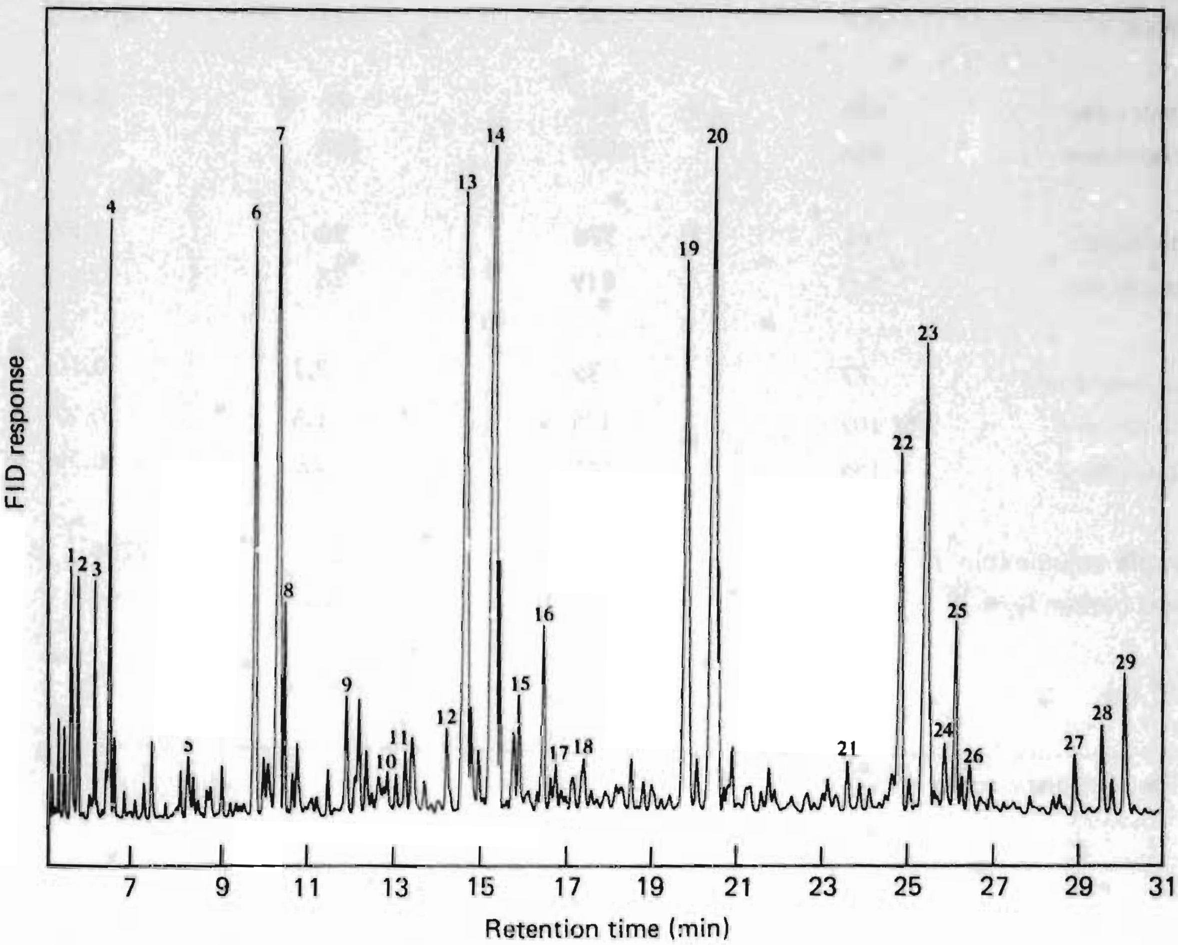

Figure 5. Gas chromatogram of vapor phase aliphatic compounds collected on a Tenax sample number 8.

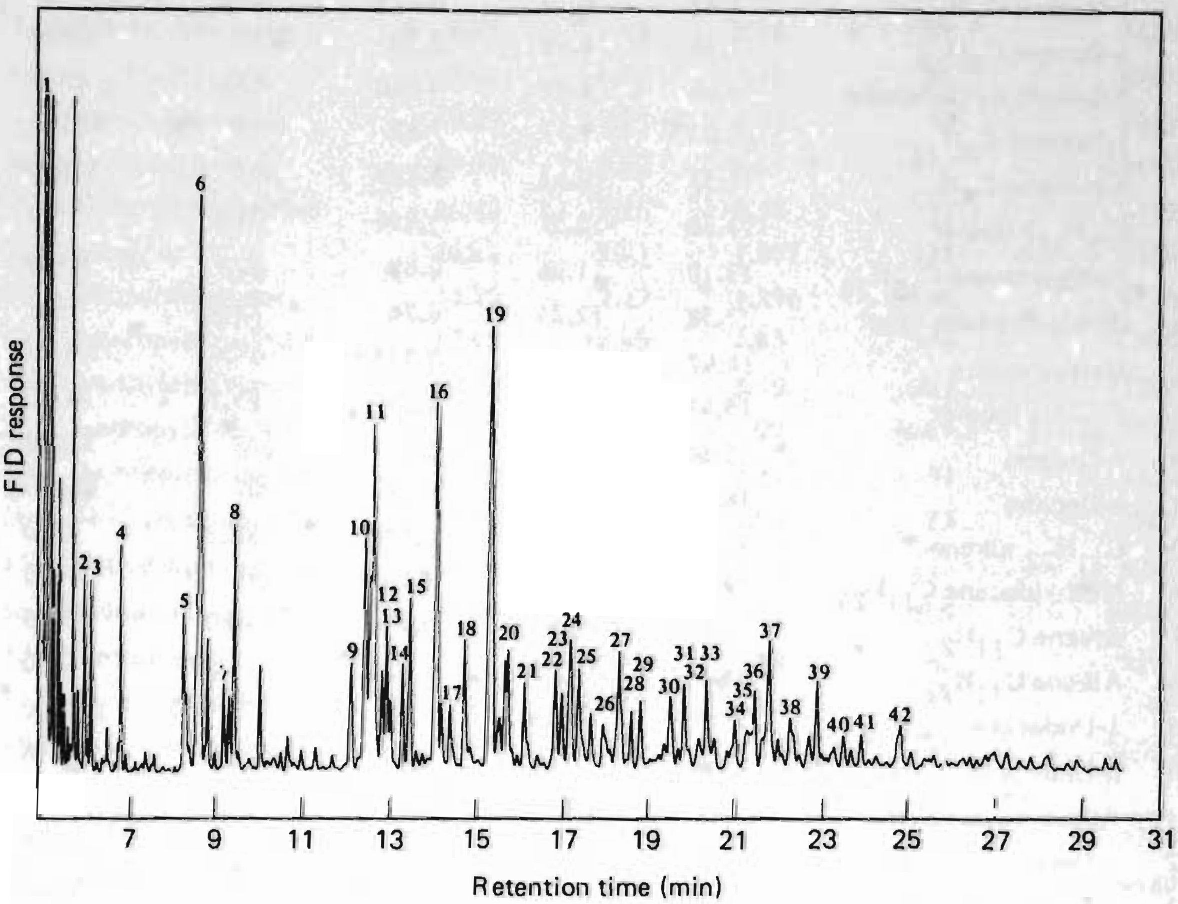

Figure 6. Gas chromatogram of vapor phase aromatic compounds collected on a Tenax sample number 8.

Table 11. Estimates of gas-phase concentrations of aliphatic and olefinic compounds identified in the hexane fraction of Tenax sample #8.

Peak no.	Compound	Retention time (min)		FID area[a]	Gas concentration	Specific concentration
		GCMS	FID	(%)	(mg/m^3)	($\mu g/g^b$)
1	C_8 Alkene	6.67	5.58	1.12	116	6190
2	C_8 Alkane	6.82	5.74	0.91	94.6	5045
3	1-Octene C_8H_{16}	7.27	6.14	0.811	84.0	4480
4	n-Octane C_8H_{18}	7.58	6.49	2.30	239	12700
5	Trimethylcyclohexene	9.48	8.29	0.440	45.6	2430
6	1-Nonene C_9H_{18}	11.00	9.87	3.85	399	21300
7	n-Nonane C_9H_{20}	11.57	10.43	5.725	594	31680
8	(C_9H_{18}) isomer	11.70	10.53	0.934	96.8	5160
9	Methylnonane $C_{10}H_{22}$	13.10	11.96	0.89	92.7	4940
10	(Propylheptane type)	13.38	12.25	0.76	79.3	4230
11	Methylnonane	14.47	13.33	0.555	57.6	3070
12	$C_{10}H_{18}$ isomer	15.42	14.30	0.849	85.7	4570
13	1-Decene	15.80	14.77	5.99	623	33230
14	n-Decane	16.43	15.43	8.69	907	48370
15	$C_{11}H_{22}$ alkene	16.98	15.95	0.860	88.1	4700
16	Methyldecane $C_{11}H_{24}$	17.55	16.53	1.40	144	7680
17	Alkene $C_{11}H_{22}$	17.83	16.82	0.426	43.0	2290
18	Alkene $C_{11}H_{22}$	18.50	17.48	0.724	73.0	3890
19	1-Undecene $C_{11}H_{22}$	20.92	19.94	6.12	636	33900
20	n-Undecane $C_{11}H_{24}$	21.60	20.60	9.48	988	52,690
21	Alkane type $C_{12}H_{26}$	24.73	23.67	0.550	54.7	2920
22	1-Dodecene $C_{12}H_{24}$	25.95	24.95	3.33	346	18450
23	n-Dodecane $C_{12}H_{26}$	26.55	25.57	5.50	573	30560
24	Alkene $C_{13}H_{26}$	27.03	25.96	0.818	83.3	4400
25	Alkane $C_{13}H_{28}$	27.25	26.24	1.55	160	8530
26	Alkene $C_{13}H_{26}$	27.60	26.55	0.656	66.4	3540
27	Alkane $C_{14}H_{30}$ (isoprenoid)	30.08	29.03	0.758	77.4	4130
28	1-Tridecene $C_{13}H_{26}$	30.72	29.67	0.993	102	5440
29	n-Tidecane $C_{13}H_{28}$	31.75	30.22	1.485	154	8210

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[a] Percentage of area identified was 68.85%.

[b] Total spectral peak area corresponded to 117 µg.

Table 12. Estimates of gas-phase concentrations of aromatic compounds identified in the methylene chloride fraction of Tenax sample #8.

Peak no.	Compound	Retention time (min)		FID area[a] (%)	Gas concentration (mg/m^3)	Specific concentration[b] (μg/g)
		GCMS	FID			
1	Toluene	6.38	5.68	2.45	170	9059
2	C_8 Aliphatic	6.70	5.93	1.19	83	4400
3	2-Ethylthiophene	6.85	6.08	0.98	68	3624
4	C_8 Aliphatic	7.62	6.77	1.17	81	4334
5	Ethylbenzene	9.23	8.23	1.33	92	4919
6	m + p-xylene	9.52	8.62	6.80	472	25150
7	Dimethylthiophene	10.18	9.16	0.74	51.3	2730
8	o-xylene	10.42	9.41	1.805	125	6670
9	Propylthiophene	13.20	12.12	1.296	90	4790
10	Isopropylthiophene	13.45	12.46	2.83	196	10480
11	Methylethylbenzene	13.63	12.66	3.19	221	11800
12	Isopropylthiophene	13.87	12.83	1.00	69.7	3714
13	Trimethylbenzene	13.97	12.95	1.31	91	4850
14	Methylethylbenzene	14.35	13.30	1.05	73	3900
15	Trimethylthiophene	14.50	13.48	1.69	117	6240
16	Trimethylbenzene	15.05	14.10	4.33	300	16010
17	Tetramethylhexadiene	15.42	14.40	0.89	62	3290
18	C_4-thiophene	15.77	14.75	1.40	97	5160
19	Trimethylbenzene + C_4-thiophene	16.32	15.40	7.05	489	26070
20	Indan + C_4-benzene	16.73	15.77	2.09	145	7710
21	Indene	17.18	16.14	1.21	84	4480
22	Methyl-Propylthiophene + Diethylthiophene	17.88	16.85	1.35	94	5010
23	Butylbenzene +	18.00	17.00	0.885	61	3270
24	Diethylbenzene + Diethylthiophene	18.20	17.21	1.90	132	7040
25	Dimethylethylbenzene + Diethylthiophene	18.38	17.40	1.57	109	5790

Table 12. (Continued)

Peak no.	Compound	Retention time (min)		FID area[a] (%)	Gas concentration (mg/m^3)	Specific concentration[b] (µg/g)
		GCMS	FID			
26	Diethylthiophene	19.05	17.96	0.869	60	3210
27	Methylindan + C_4-benzene	19.37	18.34	1.91	133	7080
28	Dimethylethylbenzene	19.70	18.62	0.78	54	2870
29	Dimethylethylbenzene	19.88	18.84	0.915	63	3380
30	C_4-benzene	20.58	19.53	1.11	77	4100
31	C_5-thiophene	20.87	19.84	1.35	93	4970
32	C_4-benzene + C_4-thiophene	21.28	20.18	0.632	44	2330
33	Tetramethylbenzene + methylindan	21.38	20.36	1.19	82	4380
34	Methylindan	22.12	21.02 (21.31)	0.887	61.5	3280
35	Isopropyldimethylbenzene	22.30	21.31	0.816	56.6	3020
36	Methylindene + methylindan	22.50	21.48	1.19	82.2	4390
37	Tetramethylbenzene	22.85	21.82	2.51	174	9270
38	Pentylbenzene	23.38	22.30	1.09	76	4040
39	Napthalene	23.87	22.92	1.06	73.5	3920
40	Dimethylindan	24.65	23.53 (23.70)	0.54	37.5 (25)	2000 (1360)
41	Dimethylindan	25.07	23.93	0.545	38	2015
42	C_5-benzene + Butylthiophene + Dioctylphthalate	25.93	24.84	1.13	78	4160

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[a] Percentage of area identified was 70.03%.

[b] Total spectral peak area corresponded to 117 µg.

Table 13. Concentrations of organosulfur compounds determined in the aromatic extract of Tenax sample no. 8.

Compound	Concentration (mg/m^3)	Sulfur concentration (volume ppm)
2-ethylthiophene	68	15
Dimethylthiophene	51	11
Propylthiophene	90	18
Iospropylthiophene	266	53
Trimethylthiophene	117	23
C_4-thiophene	∿360	∿65
Diethylthiophene	∿230	∿41
C_5-thiophene	93	15
Butylthiophene	39	7
Total		248

Results of the activation analyses of filter samples are listed in Table 15. The concentrations of many elements have large uncertainties because of the relatively low levels collected as compared to those in the blank filters. Because of the high degree of uncertainty in the data, only the ranges of the specific trace element concentrations are reported.

Results of the elemental analyses of the composite product oil samples by INAA, XRF, and ICP-OES are also included in Table 15. The concentrations of many of the elements were higher in the earlier retorted lean shale. The concentration of As and Se were comparable in lean and rich samples, and concentrations of Br and Cl were much greater in the oil derived from rich shale. The somewhat different behavior of As, Se, Br, and Cl might be related to their relatively high volatilities.

With the possible exceptions of As, Se, and Co, the concentrations of the remaining elements in the oil mist were greater than or equal to their concentrations in the bulk oil. However, this difference may be an artifact: some of the oil mist collected on the filters may have evaporated or been mechanically removed before the filters were sealed

Table 14. Concentrations of organic compounds extracted from Tenax sample #8, by class.

	Wt%[a]	mg/m^3	Mass per 1015 m^3 (kg)
Hydrocarbons:			
Aliphatic:			
C_8	2.64	498	0.50
C_9	3.93	736	0.75
C_{10}	6.52	1222	1.24
C_{11}	6.04	1132	1.15
C_{12}	3.35	628	0.64
C_{13}	1.67	314	0.32
C_{14}	0.413	77.4	0.079
Total	24.6	4607	4.68
Olefinic:			
C_8	1.07	200	0.203
C_9	2.46	461	0.468
C_{10}	3.32	623	0.632
C_{11}	4.48	840	0.853
C_{12}	1.845	346	0.351
C_{13}	1.34	252	0.256
Total	14.1	2722	2.76
Aromatic:[b]			
Benzenes[c]	$\sim$14	$\sim$2700	2.74
Naphthalene	0.39	73.5	0.075
Indans/Indenes	$\sim$2.6	$\sim$480	0.487
Thiophenes[b]	$\sim$7.2	$\sim$1350	1.37

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[a] Mass of compound divided by the total extractable mass of 117 μg. Total compounds accounted for was 92.4%.

[b] Includes alkylated forms.

[c] Includes estimated contributions from unresolved peaks.

for analysis. To help alleviate the problems in comparing the specific concentrations, we compute an enrichment factor that compares the ratio of elements calculated for the oil mist and for the bulk product oil. This enrichment factor, defined as the ratio of the concentration of an element in the oil mist to the concentration of Sc in the oil mist, all divided by the analogous ratio of concentrations in the bulk oil, is listed in Table 16.

Table 15. Concentrations of trace elements in aerosolized oil droplets and in product oil from Experiment L-3 (μ/g).

Element	Range in aerosol[a]	Product oil[a,b]	
		Lean	Rich
Al	--	4.1 ±0.1	
As	0.3-2.4	2.24 ±0.016, 3[d]	2.37 ±0.02, 3[d]
Ba	12-78	0.10 ±0.04	0.13 ±0.02
Be	--	(0.0025, 0.005[c])	
Br	0.12-5.1	0.028 ±0.004	0.087 ±0.0008
Cd	2.7		
Ce	--		
Cl	40-3000	4.8 ±0.1	25.9 ±0.3
Co	0.046-0.17	0.43 ±0.02	0.156 ±0.002
Cr	1.5-13.6	0.61 ±0.01	0.138 ±0.007
Cu	--	0.36 ±0.11	1.8 ±0.2
Dy	--	0.00087 ±0.00014	0.00038 ±0.00011
Fe	21-280	54 ±1,45[d]	11.6 ±0.6, 15[d]
Ga	--	0.30 ±0.01	0.054 ±0.005
Gd	0.76-9.9	--	--
Hf	0.18-0.66	--	--
Hg	--		
I	--	0.026 ±0.0023	0.0042 ±0.0015
In	0.0040-0.012	--	--
K	52	2.2 ±0.6	--
La	1.5-2.5	0.0027 ±0.0015	--
Lu	1.2-22	--	--
Mg	--	3.7 ±0.6	--
Mo	1.2-22	0.93 ±0.04	0.048 ±0.026
Mn	1.3-2.5	0.24 ±0.001	0.126 ±0.002
Na	640	24 ±2	0.112 ±0.003
Ni	2.1-3.7	(1.0, 5.4)[c]	
Pb	--	0.055[c]	≤ 1[d]
Sb	0.1-4.0	0.011 ±0.0018	--

Table 15. (Continued).

Element	Range in aerosol[a]	Product oil[a,b]	
		Lean	Rich
Sc	0.007-0.055	0.0011 ±0.0001	--
Se	0.1-2.5	0.65 ±0.01, 1[d]	0.62 ±0.01, <1[d]
Sm	0.035-0.059	0.00059 ±0.00012	--
Sr	5.0	--	--
Ta	0.012-0.071	--	--
Tb	0.012-0.051	--	--
Th	0.31-0.98	--	--
Ti	--	0.67 ±0.17	--
U	0.10	0.0070 ±0.0014	--
V	--	0.69 ±0.03	0.163 ±0.005, (0.17, 0.15)[c]
Yb	0.02-0.18	--	--
Zn	2.4-13	0.75 ±0.06	0.21 ±0.04

[a] Data are results of INAA of a single sample unless otherwise indicated.

[b] Analyses of two composite oil samples.

[c] Results of analyses by ICP-OES of a single composite sample containing oil formed from lean and rich shale.

[d] Analysis of a single composite sample by wavelength dispersive XRF.

Note that the filter samples provide data for only a very short portion of the retort. The bulk oil samples were composited and, hence, reflect much longer periods of operation. Therefore, small departures of the EF from unity should not be considered significant. Surprisingly, Ba, K, La, and Sm show some enrichment. However, with the exception of Ba, the EFs of these elements are less than 10 and, as suggested, they may be artifacts of the sampling, or they may be distributed by the use of values that are not truly the average. Arsenic, Se, and Co appear to be significantly depleted in the oil mist. Both As

Table 16. Enrichment of the concentrations of elements in oil aerosol relative to the bulk product oil.

Element	Enrichment Factor[a]
Ba	18
K	3.7
La	8.7
Sn	9.3
Br	0.7
Cl	1.3
Cr	0.45
Fe	0.48
Mg	0.2
Mn	0.85
Na	0.42
Sb	1.4
U	2.2
Zn	0.5
As	0.02
Co	0.02
Se	0.02

[a] Enrichment factor defined as the ratio of the concentration of the element in the oil aerosol to the concentration of Sc in the oil aerosol, divided by the corresponding ratio of elements for the bulk oils.

and Se form species that are volatile at the temperatures of the retort, and it is possible that the enormously greater surface area of the oil mist phase may permit some of these elements to escape into the vapor phase.

PRODUCTION FACTORS

To facilitate comparison of the L-3 data with data from other retorts, and to permit estimation of the emissions from commercial scale retorts, we elected to normalize the pollutant masses to the quantity of oil produced, obtaining a production factor. Only total oil recovered (including the contribution from both lean and rich shales) was measured by the oil shale group. However, the quantities of oil produced from lean and rich shale were estimated from the production efficiency (Fisher yield), the oil content (Fisher assay) of each shale grade, and the estimates of the amount of each type of shale retorted (see Table 1-3). The concentrations of constituents of the off-gas were measured periodically over time intervals relatively short with respect to the duration of the experiment. Further, both pollutant concentrations and flow rates varied during the course of the retort. The concentration of H_2S, for example, peaked at about 45 and 70 h (see Fig. 5). To accomplish the integration, pairs of successively measured pollutant concentrations (volume of pollutant per unit volume of off-gas) were averaged and then multiplied by the volume of off-gas flowing during the measurement interval. The concentrations of off-gas constituents measured by the on-line GC/IR instruments were recorded at intervals of one hour or less; hence, errors in the integration are minimal, and the major uncertainty in the cumulative value is that of the chemical analysis. As indicated in Table 4, the concentrations of H_2S, oxides of sulfur and nitrogen, NH_3, and total S were monitored far less frequently. Thus, cumulative values computed for these species are less certain. Integral values (kg) of each of the species measured were computed separately for the periods in which the lean and rich shale were retorted; e.g., from approximately 0 to 78 h and 78 to 125 h into the experiment, repectively, and are listed in Tables 17 and 18. Experimental measurements made beyond the shutdown at 125 h were included in the analysis, but in general did not account for major portions of the cumulative value. Also listed in Tables 17 and 18 are the cumulative emissions (kg) per U.S. petroleum barrel. Note that the quantities of oil retorted from the lean and rich shale, i.e. 1.06 and 1.89 U.S. petro bbl., respectively, are estimates based on the respective oil contents of the raw shale, (i.e., 73 and 152 l/tonne, see Table 2) the amount of shale retorted (2976 and 2172 kg), and the yield factors for lean and rich shale, 0.777 and 0.931, respectively.

Only three measurements were made of the concentrations of trace element vapors in the off-gas; one at about 59 h when lean shale was retorted, and the other two at about 101 and 125 h, when rich shale was retorted. Cumulative trace element vapor emissions (mg), and the normalized emissions (mg/U.S. petro bbl.) are listed in Table 18. Given that

Table 17. Cumulative quantities of off-gas constituents produced in Experiment L-3.

Species	Lean shale[a]		Rich shale[b]	
	kg	kg/U.S. petro. bbl.	kg	kg/U.S. petro. bbl.
H_2S	24.3	22.9	22.3	11.8
SO_2	0.042	0.040	0.048	0.025
COS	0.22	0.21	0.090	0.048
Thiophenes[c]	--	--	1.57	0.83
Total S[d]	42.0	39.6	39.2	20.7
NH_3	0.031	0.029	0.038	0.020
NO	<0.0037	<0.0035	<0.0027	<0.0014
NO_2	<0.0010	<0.00094	<0.00085	<0.00045
NO_x[d]	<0.00145	<0.0014	<0.0010	<0.00053
CO	9.73	9.18	38.0	20.1
CO_2	645	608	591	313
H_2	5.86	5.53	13.0	6.88
CH_4	8.0	7.5	13.6	7.20
C_2H_2	1.34	1.26	1.28	0.68
C_2H_4	3.63	3.42	5.36	2.84
C_3H_6	1.94	1.83	2.21	1.17
C_3H_8	2.31	2.18	3.37	1.78
C_4[g]	4.11	3.88	5.37	2.84
C_5[g]	2.57	2.42	3.49	1.85

Table 17. (Continued).

Species	Lean shale[a]		Rich shale[b]	
	kg	kg/U.S. petro. bbl.	kg	kg/U.S. petro. bbl.
C_6[g]	2.83	2.67	3.38	1.79
C_7[g]	2.77	2.61	3.34	1.77
C_8[g]	1.88	1.77	2.40,2.01[e]	1.27, 1.06[f]
C_9[g]	0.81	0.76	0.53, 3.20[e]	0.28, 1.69[f]
C_{10}	--	--	3.72[e]	1.97[e]
C_{11}	--	--	2.94[e]	1.56[e]
C_{12}	--	--	1.53[e]	0.81[e]
C_{13}	--	--	0.95[e]	0.50[e]
$>C_{13}$	--	--	0.21[e]	0.11[e]
Unidentified aromatics	--	--	2.0[e]	1.06[e]
Total[f] hydrocarbons	26.0	24.5	64.0	33.9

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[a] Values based on estimated lean shale yield of 1.06 U.S. petro bbl.

[b] Values based on estimated rich shale yield of 1.89 U.S. petro bbl.

[c] Value reported is the sum of the products of the concentrations of organosulfur compounds of molecular weight greater than 112 and the total off-gas volume eluted when rich shale was retorted (i.e., 1015 m^3).

[d] Based on measurement of total S by the on-line pulsed fluorescence monitor.

[e] Based on analysis of single Tenax adsorbant trap.

[f] Total hydrocarbons given by summing the individual values listed above.

[g] Conversion to kilograms assumes hydrocarbon is the simple alkane.

Table 18. Cumulative quantities of trace element vapors in off-gas from Experiment L-3.

Element	Lean shale[a]		Rich shale[b]			
		mg/U.S	mg		mg/U.S. petro. bbl	
	mg	petro. bbl.	101 h	121 h	101 h	121 h
As	7.7 ±2.6	7.3 ±2.5	16 ±1.7[c]	17 ±0.9[c]	8.5 ±0.9[c]	9.0 ±0.5[c]
Br	35 ±26[c]	33 ±24[c]	26 ±17[c]	11 ±6[c]	14 ±9[c]	5.8 ±2.0[c]
Cl	1400 ±300[c]	1300 ±280	1020 ±280[c]	460 ±100[c]	540 ±150[c]	240 ±53[c]
Cr	160 ±17	151 ±16	<71	94 ±34	<38	50 ±18
Mo	6.0 ±2.5	5.7 ±2.4	2.5 ±1.4[d]	<1.5	1.3 ±0.7[d]	<0.8
Se	13 ±1.4	12 ±1.3	18 ±0.8[c]	14 ±0.4[c]	9.5 ±0.4[c]	7.4 ±0.2[c]
Ba	<110	<104	<65	<45	<34	<24
Co	<3.4	<3.2	<3.7	<0.61	<2.0	<0.32
Fe	<7200	<6800	<5200	<1960	<2800	<1040
Ga	--	--	--	<4.3	--	<2.3
Mn	< 77	<73	<37	<12	<20	<6.4
Sb	<5.5	<5.2	<4.1	<1.5	<2.2	<0.80
U	<2.1	<2.0	<1.6	<0.6	<0.85	<0.32
W	<2.1	<2.0	--	<111	--	<59
Zn	<60	<57	<33	<45	<17	<24

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[a] Values based on a single measurement at 59 h TIE, and cumulative lean shale off-gas volume of 1409 m^3.

[b] Values reported correspond to two measurements (at 101 and 121 h TIE). Cumulative off-gas volume from high grade shale was 1015 m^3.

[c] Comparable quantities were measured on both of two trap sections; values reported are minimums.

[d] Value probably reflects aerosol droplets.

only three samplings are used in the analysis, and because of the breakthrough and blank-correction problems discussed above, the cumulative emissions of trace element vapors in Table 18 must be regarded as order-of magnitude estimates only.

We emphasize that the vapor phase quantities of hydrocarbons containing more than 5 carbon atoms will depend strongly on the condensor temperature. Further, sulfur content of the off-gas is more related to pyrite and organic sulfur content than to shale grade.

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DPH/adf

APPENDIX A

Table A-1	Sampling parameters for Experiment L-3 filter experiments.
Table A-2	Sampling parameters for Experiment L-3 organic vapor experiments.
Table A-3	Sampling parameters for Experiment L-3 inorganic vapor experiments.
Table A-4	Sampling parameters for Experiment L-3 impactor experiments.

Table A-1. Sampling parameters for L-3 retort filter experiments.[a]

Date	Time	Sample number	Filter type	Flow Rate[b] (l/min)	Sampling time (min)	Volume[b] (l)	Mass (mg)	Concentration (mg/m^3)
5/9	09:46[c]	RNF 001	NUC	4.81	9.0	43.3	--	--
	10:11	RNF 002	NUC	6.42	60.0	385.4	0.00	--
5/10	--	WHT 003	WHAT 41	9.45	10.0	94.5	19.39	205
5/11	10:20	WHT 005	WHAT 41	7.55	10.0	75.5	0.00	--
	14:35	WHT 007	WHAT 41	8.99	20.0	179.7	5.86	32.6
	15:02[d]	WHT 015	WHAT 41	8.99	5.0	44.9	0.47	<10.5
5/12	07:25	WHT 008	WHAT 41	13.54	15.0	203.1	8.38	41.3
		RNF 003	NUC		--		0.05	Filter Blank
		RNF 004	NUC		--		0.00	Filter Blank
		RNF 004	NUC		--		0.00	Filter Blank
		RNF 005	NUC		--		0.15	Filter Blank
		RNF 007	NUC		--		0.36	Filter Blank
		FP 002	QUARTZ		--			Filter Blank
		FP 003	QUARTZ		--			Filter Blank
		FP 004	QUARTZ		--			Filter Blank
		FP 005	QUARTZ		--			Filter Blank
		FP 006	QUARTZ		--			Filter Blank

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[a] Gas temperature in samples was 25°C.

[b] At 70°F, 1 atm.

[c] Unsuccessful run.

[d] Blank run on set-up nitrogen.

Table A-2. Sampling parameters for L-3 retort organic vapor experiments.[a]

Date	Time	Sample number	Filter type	Flow Rate[b] (l/min)	Sampling time (min)	Volume[b] (l)	Mass Concentration (mg)	(mg/m^3)
5/9	16:31	TENAX 001	Tenax Trap	0.350	10.0	3.50	--	--
	16:31	PF 001	Quartz Tilter	0.350	10.0	3.50	34.13	9750
5/9	16:50	TENAX 002	Tenax Trap	0.350	5.0	1.75	--	--
	16:50	PF 003	Quartz Filter	0.350	5.0	1.75	--	--
5/9	17:05	TENAX 003	Tenax Trap	0.362	20.0	7.24	--	--
	17:05	PF 005	Quartz Filter	0.362	20.0	7.24	--	--
5/10	13:38[c]	TENAX 004	Tenax Trap	0.00541	2.0	0.0270	--	--
	13:38	PF 017	Quartz Filter	0.00541	2.0	0.0270	--	--
5/10	--	TENAX 005	Tenax Trap	0.00198	2.0	0.00396	--	--
	--	PF 018	Quartz Filter	0.00198	2.0	0.00396	--	--
5/10	15:45	TENAX 006	Tenax Trap	0.00273	2.0	0.00546	--	--
		PF 025	Quartz Filter	0.00273	2.0	0.00546	--	--
5/11	13:56	TENAX 007	Tenax Trap	0.00400	2.0	0.00800	--	--
		PF 031	Quartz Filter	0.00400	2.0	0.00800	--	--
5/11	16:15	TENAX 008	Tenax Trap	0.00312	2.0	0.00624	--	--
		PF 032	Quartz Filter	0.00312	2.0	0.00624	--	--
5/12	08:40	TENAX 009	Tenax Trap	0.0034	2.0	0.00638	--	--
		PF 035	Quartz Filter	0.00314	2.0	0.00638	--	--
5/9	--[d]	XAD 001	XAD-2 Resin	3.75	60.0	225	--	--
		PF 002	Quartz Filter	3.75	60.0	225	344.54	1531
5/10	15:37	XAD 002	XAD-2 Resin	5.74	32.0	184	--	--
		PF 023,024 026,027	Quartz Filter	5.74	32.0	184	--	--
5/11	11:15	XAD 003	XAD-2 Resin	5.91	40.0	236	--	--
		FP 036,037	Quartz Filter	5.91	40.0	236	--	--
5/11	14:25[e]	XAD 004	XAD-2 Resin	6.28	5.0	31.4		
		PF 029,030	Quartz Filter	6.28	5.0	31.4		
5/12	08:30	XAD 005	XAD-2 Resin	6.68	60.0	401		
		PF 033,034	Quartz Filter	6.68	60.0	401		

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[a] Gas temperature in samples was 25°C. All samples run without dilution.
[b] At 70°F, 1 atm.
[c] Blank run on set-up nitrogen.
[d] Trap may be contaminated with aerosol.
[e] Blank run on set-up air.

Table A-3. Sampling parameters for Experiment L-3 inorganic vapor experiments.

Date	Time	Sample number	Sample type	Flow rate[a] (l/min)	Sampling time (min)	Volume (l)[a]	Mass (mg)	Concentration mg/m^3	Comments[b]
5/9	19:14	CHAR 001	Charcoal	3.50	60.0	210	--	--	Hose collapsed. Oil behind
		FP 001	Fluoropore	2.16	4.0	8.6	4.67	541	fluoropore changed to quartz
	19:40	PF 004	Quartz	3.49	16.0	55.8	265.08	4750	
	20:00	PF 006	Quartz	3.58	10.0	35.8	235.34	6574	
	20:10	PF 007	Quartz	3.63	5.0	18.1	139.57	7711	Yellow oil visible on quartz
	20:15	PF 008	Quartz	3.68	5.0	18.4	103.46	5623	wool
	20:20	PF 009	Quartz	3.68	5.0	18.4	110.99	6032	
	20:25	PF 010	Quartz	3.66	5.0	18.3	85.85	4691	
	20:30	PF 011	Quartz	3.66	5.0	18.3	93.95	5134	
	20:35	PF 012	Quartz	3.66	5.0	18.3	100.32	5482	
5/10	13:03	CHAR 002	Charcoal	3.60	50.5	182	--	--	
	13:03	WHT 002	What 41	3.52	3.5	12.3	142.76	11,610	Filter contaminated
	13:10	PF 013,014	Quartz	3.69	5.5	20.3	--	--	No pre weight
	13:20	PF 015, 016	Quartz	3.63	6.5	23.6	--	--	No pre weight
	13:40	PF 019,020	Quartz	3.66	15.5	56.7	--	--	No pre weight
	14:00	PF 021,022	Quartz	3.44	20.0	68.8	--	--	No pre weight
5/10	15:36	CHAR 003	Charcoal	5.93	19.0	(113)	--	--	No dilution
		WHT 009	What 41		19.0	(113)	--	--	System Leaked
		WHT 010	What 41		19.0	(113)	--	--	Volume in error
5/12	09:45	CHAR 004	Charcoal	8.50	60.0	510	--	--	Condensation noted in
		WHT 013	What 41		60.0	510	73.27	241	front of trap
		WHT 014	What 41		60.0	510	49.41	241	

[a] At 70°C, 1 atm.
[b] Gas temperature in samples was 25°C. All samples run without dilution.

Table A-4. Sampling parameters for Experiment L-3 impactor experiments.

Date	Time	Sample number	Sample type	Flow rate[a] (l/min)	Sampling time (min)	Volume (l)[a]	Mass (mg)	Concentration mg/m³	Comments[b]
5/10		IMP1-S1	What 541	17.1	60.25	413	1.76	4.26	Whatman 541 substrates.
	--	IMP1-S2	What 541	17.1	60.25	413	1.93	4.67	Dilution rate 10.29 l/min.
	--	IMP1-S3	What 541	17.1	60.25	413	13.44	32.5	Material lost from
	--	IMP1-S4	What 541	17.1	60.25	413	85.94	208	from stages 4 and 5.
	--	IMP1-S5	What 541	17.1	60.25	413	91.86	222	Total 566 mg/m³.
	--	IMP1-S6	What 541	17.1	60.25	413	34.34	83.2	47 mm Whatman 41 back-up filter.
	--	IMP1-S7	What 541	17.1	60.25	413	3.70	8.96	
	--	IMP1-S8	What 41	17.1	60.25	413	1.18	2.86	
5/11	09:38	IMP2-S1	What 541	0.59	15.0	8.8	1.3	148	Whatman 541 substrates.
		IMP2-S2	What 541	0.59	15.0	8.8	1.4	159	Dilution rate, 16.60 l/min.
		IMP2-S3	What 541	0.59	15.0	8.8	1.4	159	Total 2290 mg/m³.
		IMP2-S4	What 541	0.59	15.0	8.8	4.3	489	Substrate weights ±0.1.
		IMP2-S5	What 541	0.59	15.0	8.8	6.6	750	
		IMP2-S6	What 541	0.59	15.0	8.8	2.5	284	
		IMP2-S7	What 541	0.59	15.0	8.8	1.4	159	
		IMP2-WHT004		What 41	0.59	15.0	8.8	1.26 143	
5/11	13:25	IMP3-S1	Metal	1.4	40.0	56.0	0.07	1.2	Metal substrates.
		IMP3-S2	Metal	1.4	40.0	56.0	0.00	--	Total ~114 mg/m³.
		IMP3-S3	Metal	1.4	40.0	56.0	0.04	0.7	Dilution rate 15.22 l/min.
		IMP3-S4	Metal	1.4	40.0	56.0	0.96	17.0	47 mm quartz back-up filter.
		IMP3-S5	Metal	1.4	40.0	56.0	4.74	85.0	
		IMP3-S6	Metal	1.4	40.0	56.0	0.55	9.8	
		IMP3-S7	Metal	1.4	40.0	56.0	0.00	--	
		IMP3-PF028	Quartz	1.4	40.0	56.0	0.00	--	
5/12	07:45	IMP4-S1	What 541	16.7	34.0	567	5.88	10.4	Whatman 541 substrates.
		IMP4-S2	What 541	16.7	34.0	567	5.46	9.6	No dilution.
		IMP4-S3	What 541	16.7	34.0	567	8.14	14.4	47 mm Whatman 41 back-up filter.
		IMP4-S4	What 541	16.7	34.0	567	9.53	16.8	
		IMP4-S5	What 541	16.7	34.0	567	8.61	15.2	
		IMP4-S6	What 541	16.7	34.0	567	6.23	11.0	
		IMP4-S7	What 541	16.7	34.0	567	4.56	8.0	
		IMP4-WHT011		What 41	16.7	34.0	567	6.33 11.2	

[a] At 70°F, 1 atm.

[b] Gas temperature in samples was 25°C.

APPENDIX B

Table B-1	Concentrations of hydrogen sulfide in off-gas from Experiment L-3 (ppm).
Table B-2	Concentrations of total sulfur in off-gas from Experiment L-3 at different times into the experiment.
Table B-3	Concentrations of elements in condensed water vapor from Experiment L-3 (μg/g).

Table B-1. Concentrations of hydrogen sulfide in off-gas from Experiment L-3 (ppm).

Time into experiment, (n)	TECO-40 w/H_2S converter (ppm H_2S)	Indicator tubes (ppm H_2S)	Tube indentification
14.6	--	<1	Drager 6719001
15.3	1,650	--	
27.2	--	4,000	Drager CH28101
	--	2,200	Gastec 4H
32.1	18,300		
32.6	--	16,000	Drager CH28101
34	--	17,000	Drager CH28101
36.3	--	16,800	Drager CH28101
50.7	25,600		
51.8	--	20,000	Drager CH28101
	--	22,000	Gastec 4HH
100.9	--	11,200	Drager CH28101
	--	9,400	Gastec 4HH
103.5	--	14,000	Gastec 4HH
	--	12,000	Drager CH28101
106.2	14,450		
129.5	--	38,000	Gastec 4HH
	--	>40,000	Gastec 4HH
130.4	36,300		
131.2	--	44,000	Gastec 4HH (250 ml)
146.7	44,800		
147.3	--	42,000	Gastec 4HH (250 ml)

Table B-2. Concentrations[a] of total sulfur in off-gas from the Experiment L-3 at different times into the experiment.

Time into experiment (h)	Concentration (% vol./vol.)
16.2	0.522
32.9	2.64
33	2.85
52.2	2.76
107.7	2.52
107.9	2.63
132.3	5.20
147.5	5.05

[a] Measured with a Meloy sulfur oxide flame ionization detector.

Table B-3. Concentrations of elements in condensed water vapor from Experiment L-3.

Element	µg/g[a]	EF[b]
As	0.60 ± 0.006	3.2
Br	0.061 ± 0.003	27
Co	0.0049 ± 0.0003	0.14-0.4
Cr	0.041 ± 0.002	0.81
Eu	0.00031 ± 0.00024	--
K	5.9 ± 2.1	32
Mo	0.056 ± 0.017	0.73
Na	64 ± 2	32
Rb	0.018 ± 0.006	--
Sb	0.0145 ± 0.0005	16
Sc	0.000091 ± 0.000010	≅1.0
Se	0.106 ± 0.002	2.0
Sn	0.56 ± 0.14	--

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[a] Instrumental neutron activation analyses of a single sample.

[b] Enrichment factor calculated with respect to product oil.

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PAPER