Application of FTIR Remote Sensing Spectroscopy in Environmental Impact Assessments of Oil Fires

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Abstract

A series of laboratory measurements was conducted to determine the extent to which benzene and other aromatic components are destroyed when crude oil is burned on the open seas. The atmosphere above a pan containing Alaskan North Slope crude oil was monitored with a remote sensing FTIR spectrometer during both evaporation and burning. This data was used in conjunction with gas chromatographic analyses of the oil obtained before ignition and after the fire was extinguished (by covering the pan with a marinite slab) to estimate the C_6H_6 destruction efficiency of the oil fire. The results of these laboratory measurements are viewed in the context of data collected during mesoscale oil fires conducted at Little Sand Island in Mobile, Alabama.

Introduction

The possibility of using combustion to remediate oil spills on the open seas is being explored [1-4]. Gas chromatography (GC) and other point sampling techniques have been used to monitor pollutants released into the atmosphere during mesoscale oil fires in an effort to assess the environmental impact of this procedure. The potential to make continuous measurements along a line-of-sight could open a new dimension to this research. The capabilities of the present generation of FTIR remote sensing spectrometers, which include high resolution and fast scanning over extended optical paths, would seem to be well-suited to this application.

This hypothesis was examined in a series of oil burn experiments conducted in a 230 m^2 square pan located on Little Sand Island in Mobile, Alabama [4]. Spectra were measured over a 7 m path about 30 m downwind of the fire. The progression, beginning with a spectrum of the atmosphere before the oil was pumped (top) and ending with a spectrum taken shortly after the oil was ignited (bottom), is displayed in Figure 1. The absorbance centered at ~ 2900 cm^{-1} is indicative of the presence of non-aromatic hydrocarbons (NAHCs). Quantitative analyses of these spectra indicate that the atmospheric concentrations of these compounds exceeded 50 ppm (mole fraction) while the oil was being pumped from a barge into the pan, falling below the lower detection limits (LDL) of the instrument shortly after ignition. This suggests that the NAHCs present in the original crude oil were effectively destroyed in the fire. The fate of the C_6H_6, and other aromatic hydrocarbons which are either present in the original crude oil or produced as a result incomplete combustion, is of much greater concern. These compounds are more thermally stable and are considered to be a far greater threat to the environment than are the NAHCs. Unfortunately, C_6H_6 was not consistently detected in the spectra collected during the oil evaporation and burn tests conducted in Mobile. Presumably, this was because the atmospheric concentrations of C_6H_6 were below the instrument LDL. Consequently, no statement can be made concerning the fraction of C_6H_6 which is converted to CO_2 as compared to the amount which is merely dispersed into the atmosphere by the convective flow of the fire.

The objective of this study is to shed some light on this issue by observing what happens to C_6H_6 in small, well-controlled oil fires. In reviewing the results of these experiments, it is important to keep in mind that the motivation here, is not as it is in many other environmental studies, to measure trace quantities of hazardous chemicals. Significant releases of C_6 H$_6$ and other aromatic compounds are inevitable consequences of an oil spill. The central question addressed in this paper is whether less

C_6H_6 is released into the atmosphere as a result of burning the oil than would be the case if the oil was allowed to evaporate on the open seas.

Experimental

A circular pan (10 cm in diameter) was placed on a load-cell and filled with 540 g of Alaska North Slope crude oil. A GC analysis (Figure 2) of this oil indicated that it contained about 0.25% (by mass) C_6H_6. Unfortunately, the corresponding partial pressure was below the instrument LDL. This problem was solved by enriching the oil with an additional 20 g of C_6H_6. A spectrum of the vapor was collected and a sample of the liquid oil was extracted before igniting the oil. A second spectrum, this time of the atmosphere over the burning oil, was taken and the fire was extinguished by covering the pan with a marinite slab. This sequence, consisting of evaporation followed by burning, was repeated until the C_6H_6 and NAHCs could no longer be detected in the evaporation spectra. Spectra, which took approximately 5 minutes to acquire, were collected at each step and a sample of the liquid oil was extracted (for GC analyses) before each ignition. The line-of-site of the measurements, which was off-center and slightly above the flame, was fixed throughout the course of the experiment. About 100 g (18%) of the oil-benzene mixture were incinerated in 5 burns which lasted a total of 2000 s. The mass-loss curve over the full 4000 s (including both evaporation and burning) is displayed in Figure 3. The spikes, which occur at approximately 10 minute intervals, indicate when the fire was extinguished.

Absorbance spectra were obtained as signal averages over 1024 interferograms collected at 4 cm^{-1} resolution using a Midac[1] monostatic remote sensing FTIR. The concentrations of C_6H_6 were estimated from

$$x_a = \frac{A_a}{A_r}(\frac{l_r}{l_a})x_r ,$$ (1)

where A, l and x denote band integrated absorbance, optical path length through the sample, and mole fraction of the analyte (a) and reference (r). This strategy, consisting of oversampling the spectra and estimating concentrations from band averaged (rather than line) intensities was effective in reducing the level of random error. The precision of the reported concentrations was estimated by substituting

$$\Delta A_{ra} = \{\int [S_r(v) - x_a S_a(v)]^2 dv\}^{\frac{1}{2}}$$ (2)

for A_a in Eq.(1). Here S(v) denotes spectral absorbance and the integration is over the frequencies (r) which define the band. In the case of C_6H_6 , this procedure gave estimates ranging from about 2% (highest concentration) to 25% (lowest nonzero concentration) of the corresponding mole fraction. The contribution from systematic errors is more difficult to quantify. However, a total error of $\pm$ 25% of the reported value is consistent with previous experience in the quantitative analyses of similar compounds.

Aliquots of the oil samples were dissolved in CH_2Cl_2 and analyzed on a HP5730A GC equipped with a HP 3380A integrator and a flame ionization detector. An acceptable resolution of the lower molecular weight hydrocarbons was obtained using a 30 mL/min flow of He through a 3 m column packed with 10% SP 2100 on 100/120 mesh Supelcoport at 50 °C. Concentrations were determined from the ratio of the appropriate peak in the chromatogram of the sample to the corresponding peak in the chromatogram of the reference. The uncertainty in the amount of sample injected into the GC was

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[1]Certain commercial equipment, instruments, or materials are identified in this paper in order to specify the experimental procedure. Such identification does not imply that the material or equipment identified is necessarily the best available for the purpose.

the major source of error in these analyses. The syringe used to make the 0.5 μL injections was only calibrated to the nearest 0.1 μL so that the sample volume could not be determined to an accuracy better than $\pm$ 0.05 μL, or $\pm$ 10% of the reported concentration.

Results

The spectrum of the atmosphere above the pan prior to ignition is compared to a C_6H_6 reference spectrum [5] over the region corresponding to the stretching of aromatic C-H bonds in Figure 4. The integrated absorbance of this band corresponds to a partial pressure of about 150 $\pm$ 38 ppm (mole fraction) over the 10 cm path defined by the diameter of the pan. The intensity of this band, as well as the intensity of the adjacent band due to nonaromatic C-H stretching, falls below detectable limits during the period of time that the oil is burning (Figure 5). This indicates that these components are destroyed, rather than merely dispersed into the atmosphere, by the fire. Indeed, there appears to be almost complete conversion to CO_2 at the level of sensitivity of the measurement ($\sim$ 10 ppm). The peaks corresponding to CO, CH_4 and C_2H_2, which are prominent in the spectrum of the gases evolved during pyrolysis of the oil in N_2 (Figure 6), are not apparent in the spectrum of the atmosphere above the burning oil (top of Figure 5). The C_6H_6 destruction efficiency over all 5 burns was

$$DE = \frac{(X_i M_i - X_f M_f)}{X_i M_i} = 0.74, \tag{3}$$

where X is the mass fraction of the component under consideration (Table I) and M is the total mass of oil (Figure 3) before the first ignition (i) and after the last extinction (f). In contrast, the DEs for C_6H_{14} and C_7H_{16} were only 0.22 and 0.46, respectively. The anomalously high value obtained for C_6H_6 may be an indication that the added volume was never fully assimilated into the oil matrix.

The progression from the initial spectrum (top), taken before ignition, to the final spectrum (bottom), taken after the last extinction (Figure 7), indicate that the C_6H_6 and NAHC emisssions from the oil (at room temperature) were reduced below the instrument LDL after the oil had been burned for 2000 s. The GC data presented in Table I, however, indicate that the burned oil still contained significant amounts of these compounds. A further illustration of this effect is evident in Figure 8 which is a plot of the mole fraction of C_6H_6 in the vapor above the pan as a function of the mass fraction of C_6H_6 remaining in the liquid. The progression from the initial to the final evaporation is from right to left. The rapid fall-off in the slope of this curve after a mass fraction of 0.015 indicates that it is becoming increasingly difficult for the C_6H_6 molecules to escape the liquid. A likely explanation is that the increased viscosity which results from burning the more volatile fraction suppresses the further evaporation of the remaining low molecular weight compounds.

Conclusions

Although the results presented in this paper are of a preliminary nature, some clear trends have emerged. The destruction efficiency of benzene is high during the actual burning, at least in small laboratory oil fires such as the one considered in this investigation. The conversion to carbon dioxide was complete at the level of sensitivity of the FTIR and the spectra gave no indication of the presence of carbon monoxide or any other product of incomplete combustion. A significant fraction of the low molecular weight components, including benzene, are retained in the residue. The further volatilization of these compounds is apparently suppressed by viscosity effects which are more pronounced in the high molecular weight residue than in the original crude oil. A comparison of the spectra in Figures 5 and 7 clearly shows that there is less benzene above the pan during the burning and eventual evaporation of the residue than in the evaporation of the original oil. On this basis, it appears that combustion may be be effective in reducing the amount of benzene released into the atmosphere during oil spills.

The destruction efficiency of fires is known to depend on their size [6]. A logical next step in assessing environmental impact of oil spill combustion is to measure the destruction efficiency of benzene in oil fires as a function of this variable.

Acknowledgements
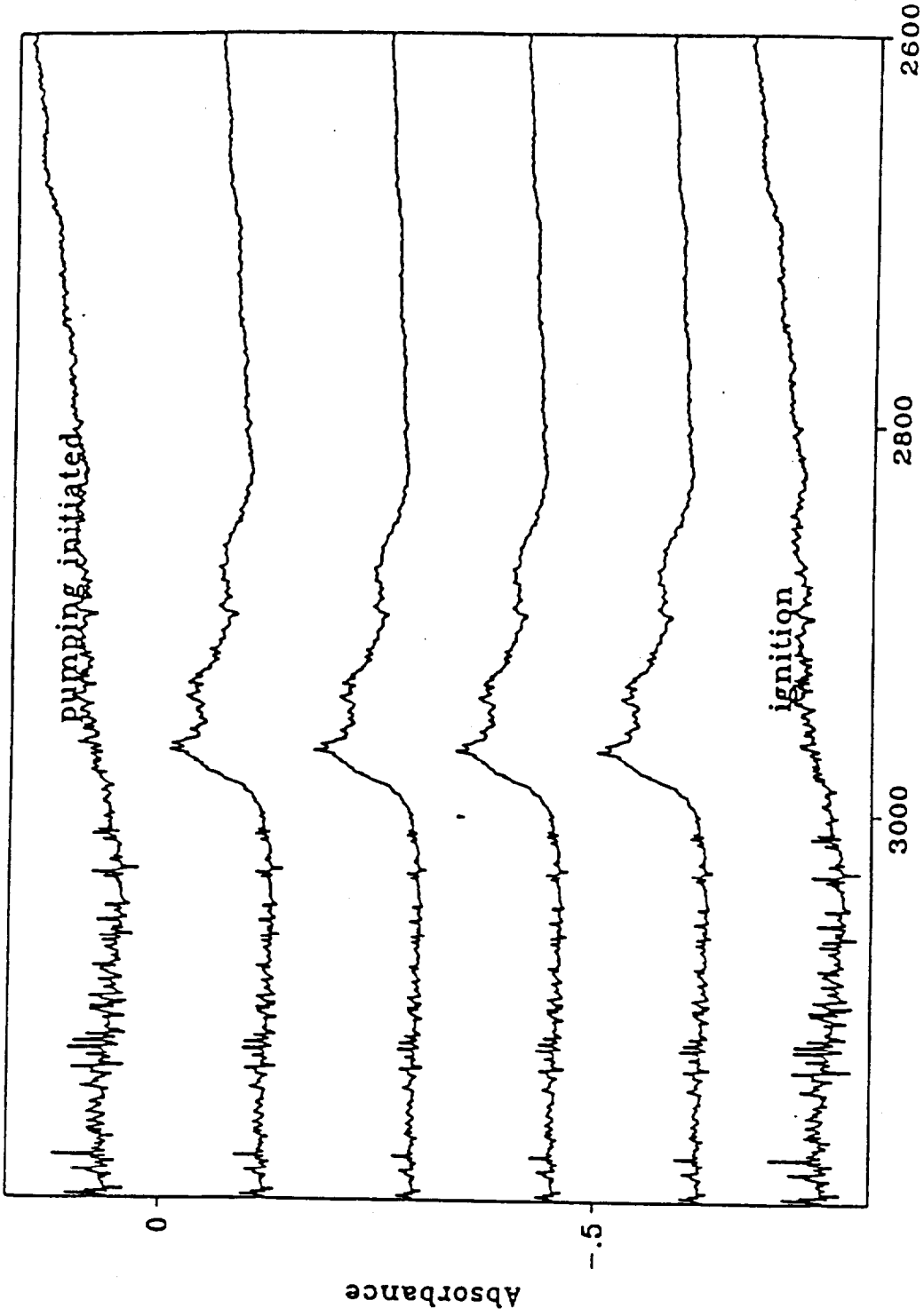
References

1.   Evans, D.D, Mulholland, G., Gross, D., Baum, H.R. and Saito, K.; "Environmental Effects of Oil Spill Combustion," NISTR 88-3822, National Institute of Standards and Technology; Gaithersburg, 1987.

2.   Evans, D.D, Walton, W.D., Baum, H.R. Lawson, J.R., Rehm, R., Harris, R., Ghoniem, A. and Holland, J.; "Measurement of Large Scale Oil Spill Burns," in "Proceedings of the Thirteenth Arctic and Marine Oil Spill Program Technical Seminar," Edmonton, 1990.

3.   Evans, D.D, Walton, W.D., Baum, H.R. Notarianni, K.A., Lawson, J.R., Tang, H.C., Keydel, K.R., Rehm, R., Madrzykowski, D. Zile, R.H., Koseki, H. and Tennyson, E.J.; "In-Situ Burning of Oil Spills: Mesoscale Experiments," in "Proceedings of the Fifteenth Arctic and Marine Oil Spill Program Technical Seminar," Edmonton, 1992.

4.   Walton, W.D., Evans, D.D., McGrattan, K.B., Baum, H.R. Twilley, W. H., Madrzykowski, Putorti, A.D., Rehm, R., Koseki, H. and Tennyson, E.J.; "In-Situ Burning of Oil Spills: Mesoscale Experiments and Analysis," in "Proceedings of the Sixteenth Arctic and Marine Oil Spill Program Technical Seminar," Calgary, 1993.

5.   Hanst, P.L. and Hanst, S.T.; "Quantitative Reference Spectra for Gas Analysis," Infrared Analysis, Inc.; Anaheim.

6.   Mulholland, G.W., Henzel, V. and Babrauskas, V.; "The Effects of Scale on Smoke Emissiom," in "Proceedings of the Second Symposium on Fire Safety Science, 1988.

Table 1. Composition of the Liquid Oil

Sample	Mass Fraction		
#	C_6H_6	C_6H_{14}	C_7H_{16}
1	0.035	0.0047	0.0064
2	0.026	0.0042	0.0058
3	0.014	0.0058	0.0055
4	0.012	0.0026	0.0038
5	0.011	0.0044	0.0042

Figure 1

Comparison of Spectra Measured During Fueling and Burning
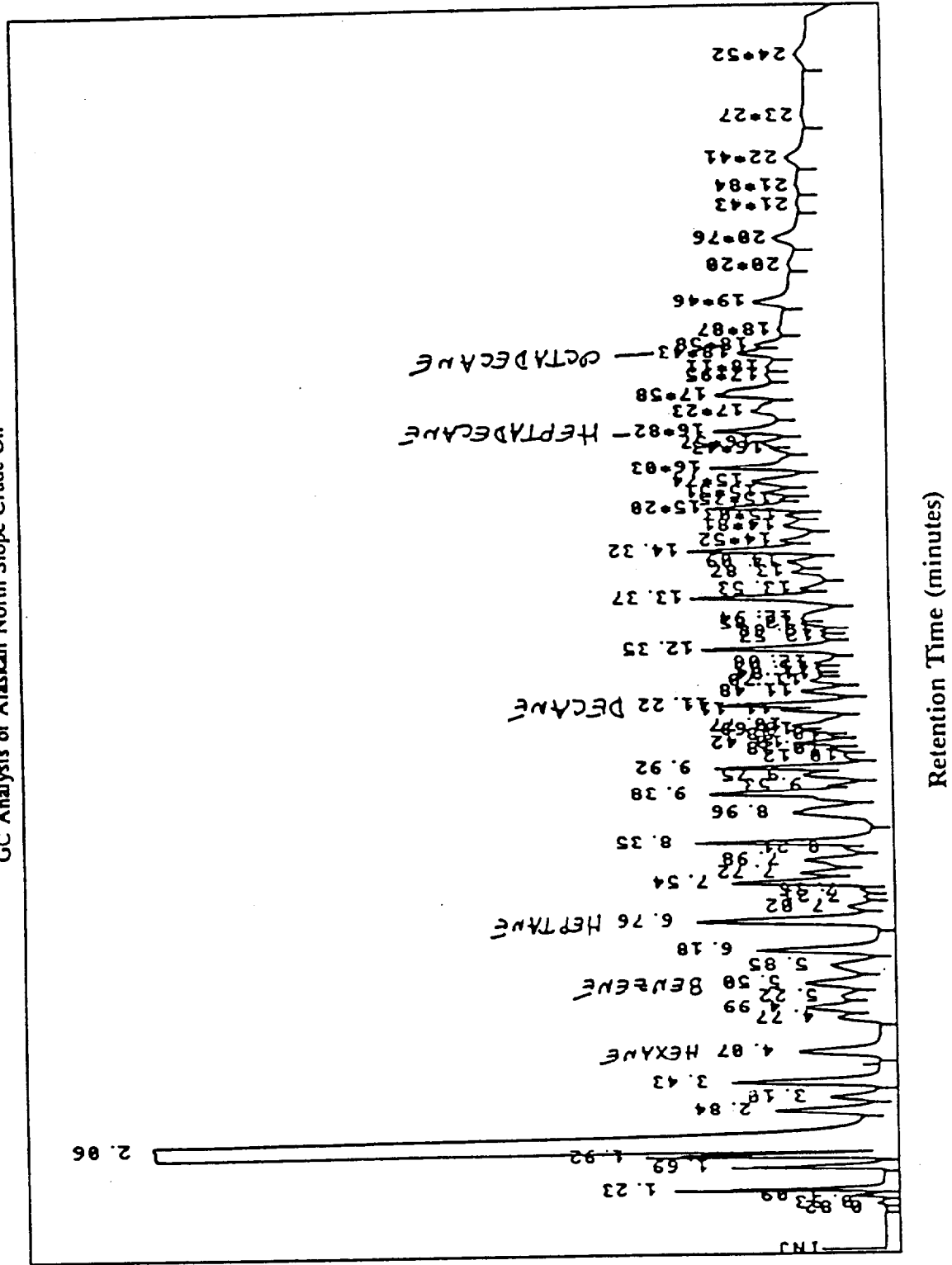
Figure 2

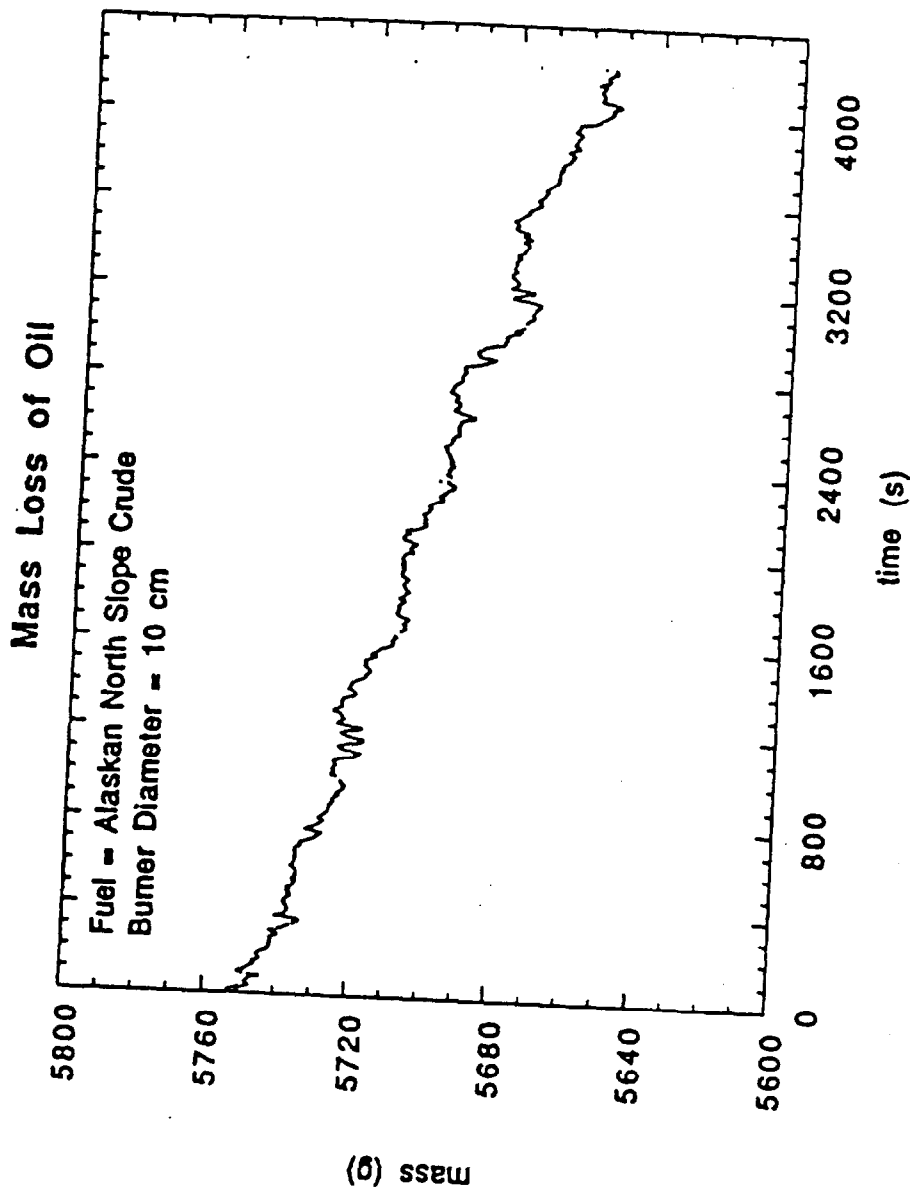GC Analysis of Alaskan North Slope Crude Oil

Retention Time (minutes)

INJ

0.83
0.93
0.69
1.23
1.69
1.92
2.06
2.84
3.18
3.43
4.07 HEXANE
4.77
5.30 BENZENE
5.32
5.85
6.18
6.76 HEPTANE
7.82
7.86
7.88
7.54
8.35
8.96
9.38
9.92
9.93
10.13
10.42
10.68
10.687
11.18
11.22 DECANE
11.88
12.00
12.35
12.68
12.88
12.94
13.33
13.37
13.82
14.32
14.52
14.81
15.28
15.31
15.55
15.74
16.03
16.42
16.82 — HEPTADECANE
17.23
17.28
17.95
18.11
18.43 — OCTADECANE
18.58
18.87
19.46
20.28
20.76
21.43
21.84
22.41
23.27
24.52

773

Figure 3

Mass Loss of Oil

Fuel = Alaskan North Slope Crude
Burner Diameter = 10 cm

774

Figure 4

Comparison of Sample and Benzene Reference Spectra

sample (4 cm−1)

reference (0.5 cm−1)

Absorbance

Wavenumbers (cm−1)

3100   3050

775
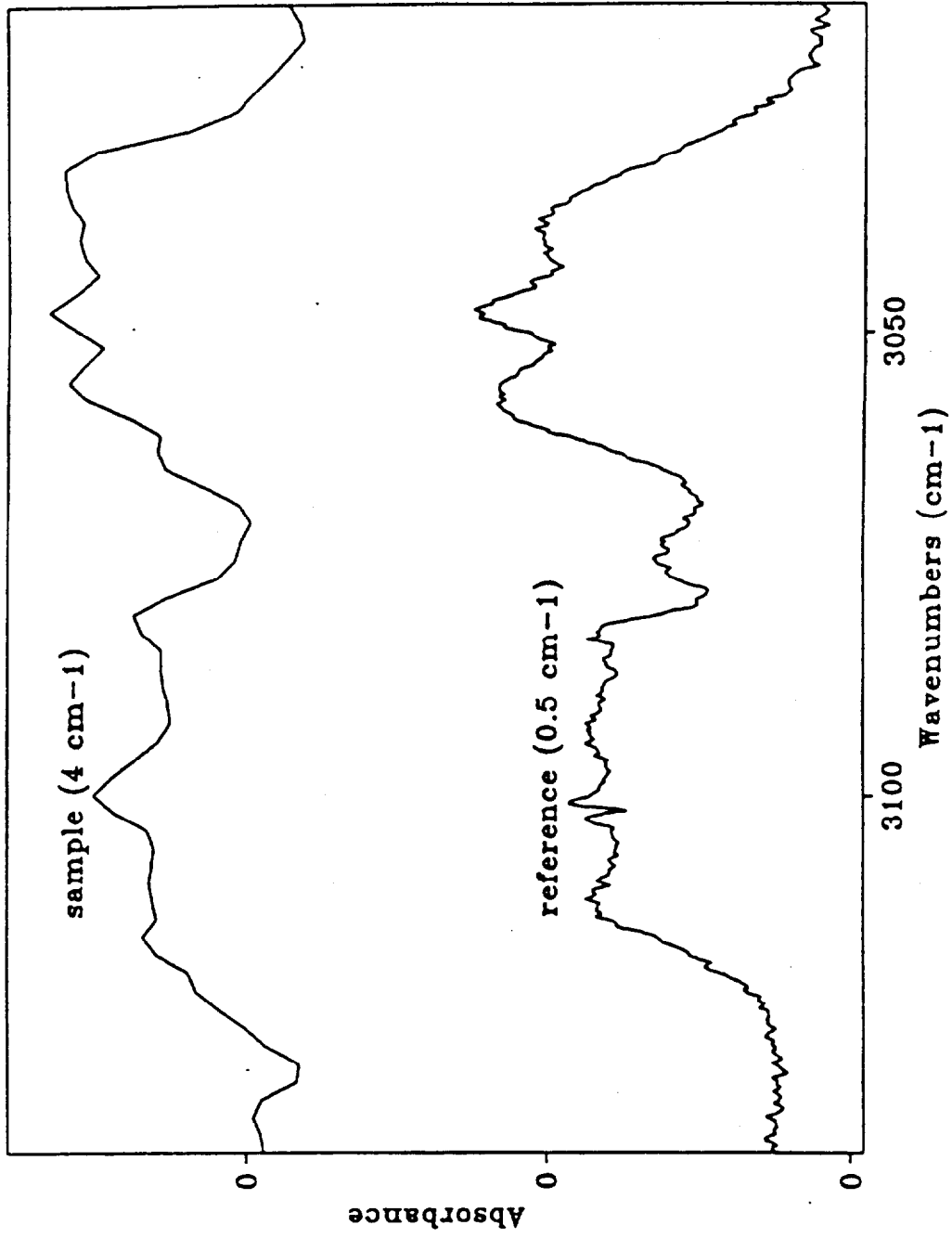
Figure 5

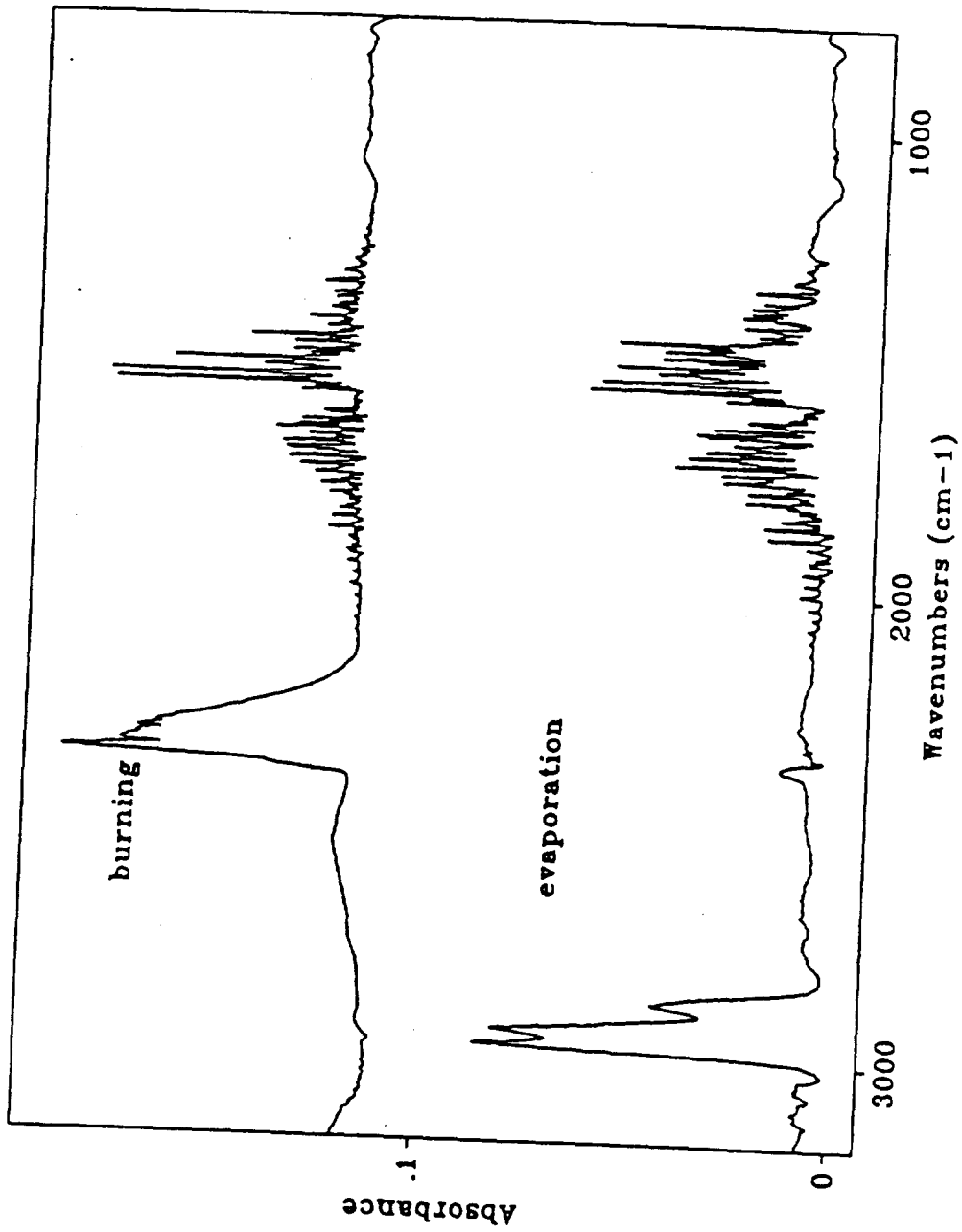Comparison of Spectra Taken During Evaporation and Burning

burning

evaporation

Wavenumbers (cm−1)

Absorbance

776

Figure 6

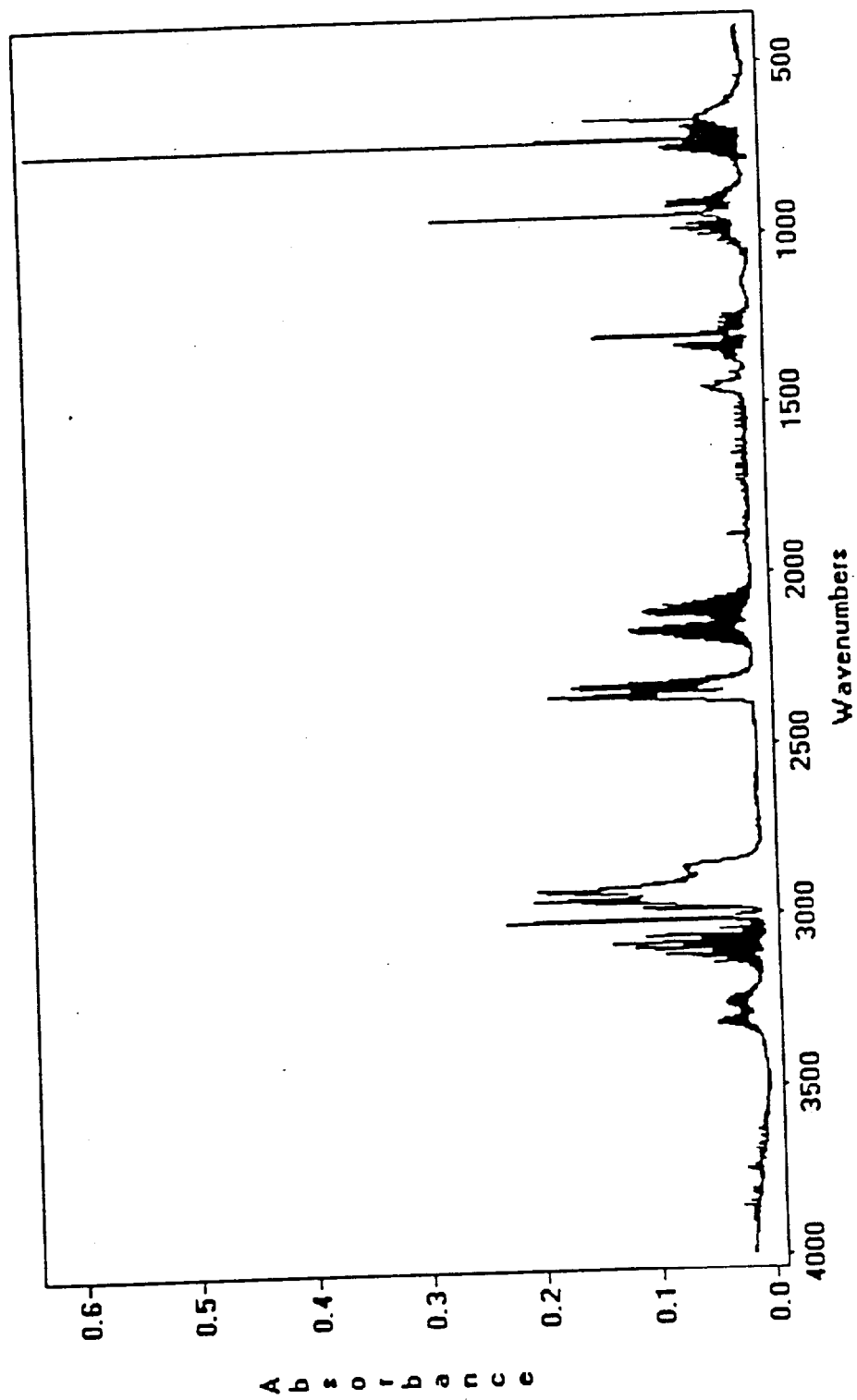Gases Evolved in the Pyrolysis of Alaskan North Slope Crude Oil
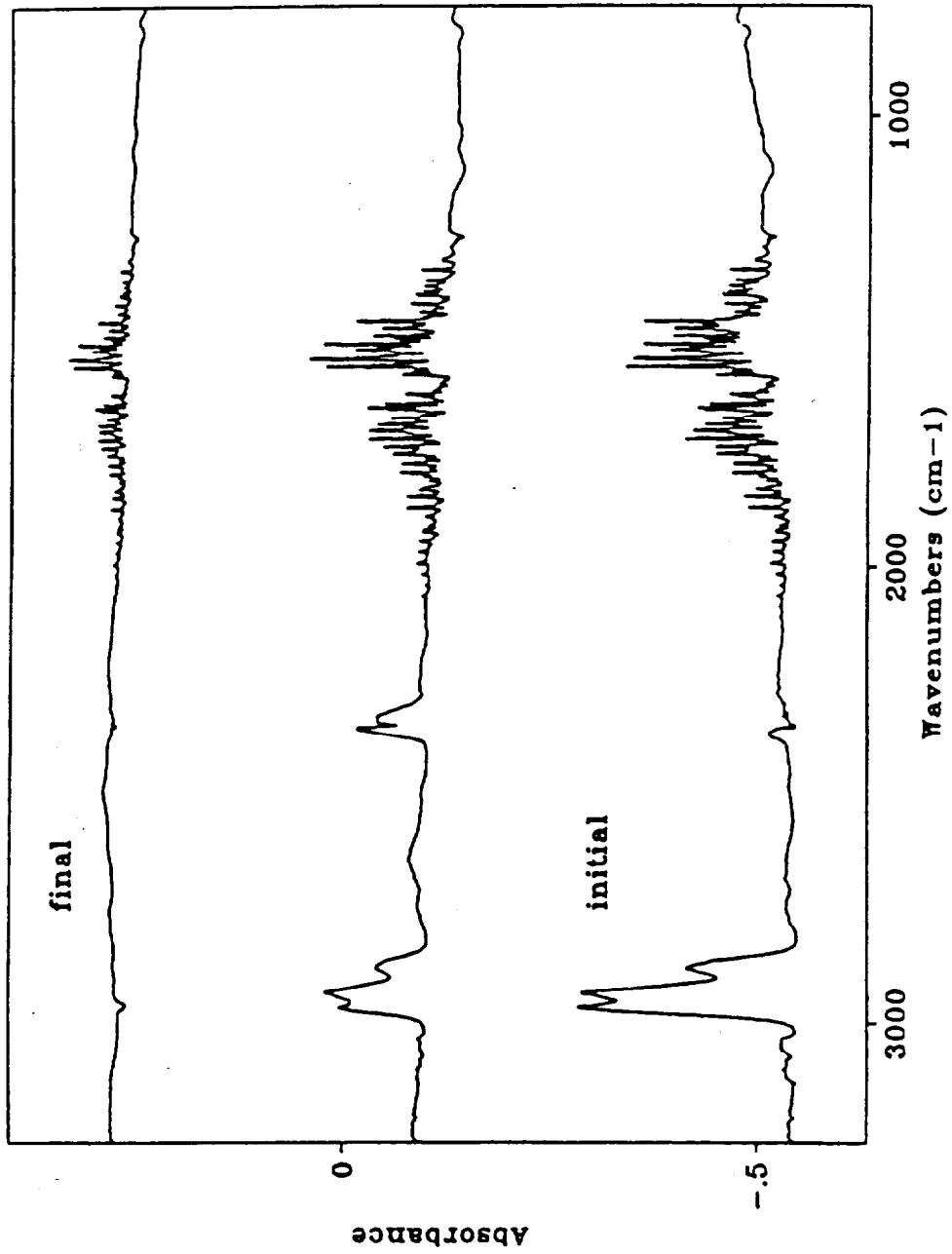
Comparison of Evaporation Spectra

Figure 7

Figure 8

Mole Fraction of C6H6 Vapor vs Mass Fraction of C6H6 in the Liquid

MASS FRACTION OF C6H6