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OILPRINT™

Forensic Geochemistry/Hydrocarbon Fingerprint Analysis

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OILPRINT™

DISCUSSION

OILPRINT™ is a chromatographic analysis for product characterization covering the molecular range of C_2 through C_{34} utilizing a programmed temperature chromatography procedure with a fused silica capillary open tube (column). This can yield a chromatogram with as many as 500 peaks, depending on the subject fluid. This qualitative analysis using biomarkers as well as easily identifiable peaks, such as normal paraffins and branched isoparaffins, and a peak digitizing process, allows identification and particularly, comparative interpretation possible.

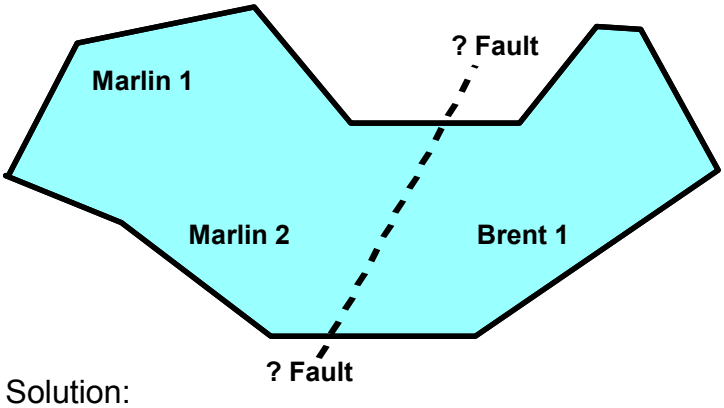
Polar plots are used as visual aids to the interpretive process. Dependent on the particular nature of the fluid to be analyzed, 50-100 peaks are selected for digitation for clustering, partitioning and discrimination. Ratios of approximately six to twelve selected peak pairs are plotted on the polar plot and overlaid with either a comparative standard or another fluid of interest as a graphical aid to the written interpretation.

Digitizing consists of the converting of the analog signal to a digital form followed by converting the chromatograph peaks to numbers. The preparation of the chromatogram for the data processing consists of drawing base lines, numbering the selected peaks for peak height determination, and the recording of the heights. This is done utilizing the OILPRINT™ chromatography digitizing system.

PTS Laboratories, Inc.

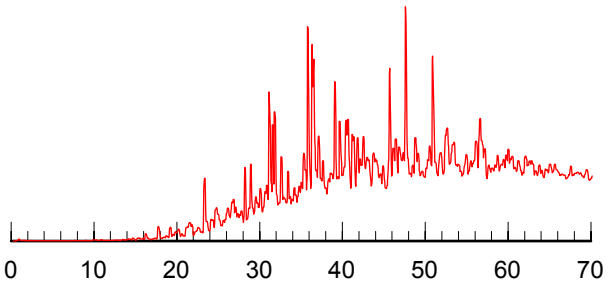
8100 Secura Way Santa Fe Springs, CA 90670

OILPRINT -- Forensic Geochemistry Provides Solutions



Reservoir Problem:

"Is there lateral/vertical continuity between Marlin 1, Marlin 2 and Brent 1?"

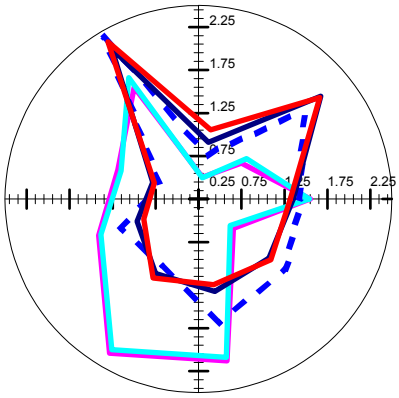


Solution:

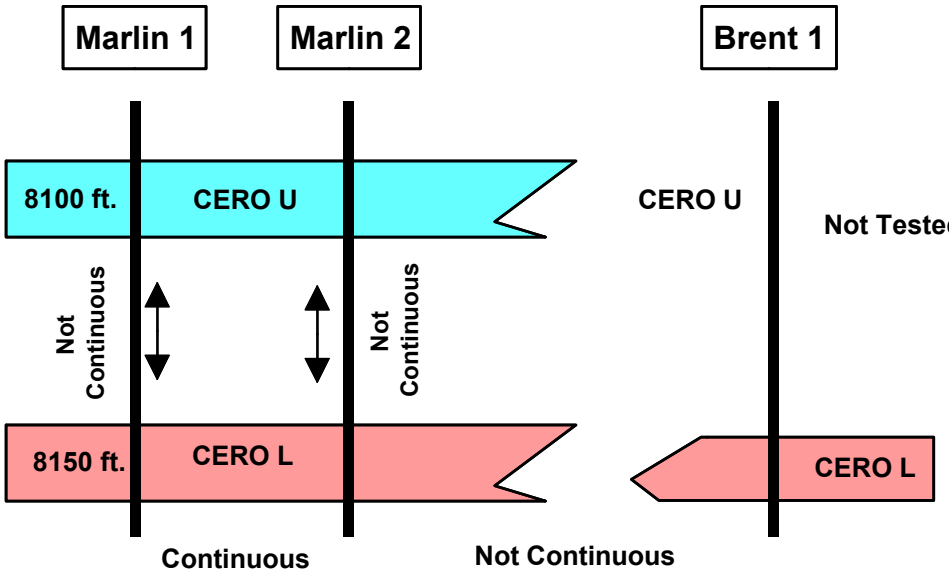
1. Analyze oils by OILPRINT chromatography

	Formation	Depth, ft	41/43	59/60	62/66	97/99	115/117	124/125	138/139	155/156	172/173	259/261	334/340
Marlin 1	Cero U	8100	0.82	1.07	1.32	0.93	2.36	1.26	1.31	2.09	1.37	0.80	1.35
Marlin 2	Cero U	8100	0.85	0.92	1.35	1.01	2.27	1.34	1.25	2.11	1.33	0.82	1.32
Brent 1	**Cero L**	**8170**	**0.79**	**0.77**	**1.41**	**1.22**	**2.43**	**1.70**	**1.12**	**1.81**	**1.21**	**0.71**	**1.54**
Marlin 1	Cero L	8150	0.62	0.50	1.54	1.46	1.88	2.21	2.27	0.98	0.92	1.21	0.73
Marlin 2	Cero L	8150	0.56	0.51	1.55	1.49	1.75	2.16	2.32	0.90	0.91	1.25	0.78

2. Calculate peak ratios



3. Plot peak ratios



Not Tested

Marlin 1; Cero U 8100'
Marlin 2; Cero U 8100'
Brent 1; Cero L 8170'
Marlin 1; Cero L 8150'
Marlin 2; Cero L 8150'

Reservoir Answer

Telephone (562) 907-3607 FAX (562) 907-3610 E-mail: ptsgeolabs@ptsgeolabs.com

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EXAMPLE REPORT

F I N A L R E P O R T

Phase Separated Hydrocarbon Characterization

Introduction

Subsequent to our preliminary report of June 14, 2000 that presented the results of analysis on sample PS1, we received two end member samples: a gasoline and a diesel. These were indicated to be the source of the hydrocarbon mix collected from PS1. At that time, our estimates of the percentage of various boiling point fractions were based on molecular weight ranges normally associated with gasoline and diesel fractions. It was also suggested at that time that there might be a third fraction present, which we called kerosene. Without the actual reference samples of gasoline and diesel it was only possible to present a range of values for the fractions.

With the end members available, laboratory mixes were generated and used to determine more precise values for the fractions present.

Conclusions

The end member gasoline chromatogram suggests that there is no kerosene fraction. There are, however, more heavier molecular weight components (C-10 to C-12) present than would normally be expected in most gasolines. These may represent a mixing of the gasoline at some previous time (in the storage tank) with small amounts of a slightly heavier fraction. The presence of these constituents should not make any difference in determining remedial processes.

Calculations based on the laboratory mixes provide a value of 31% gasoline and 69% diesel plus or minus 5%, for the PS1 sample.

Analyses and Discussion

Mixes of the end member gasoline and diesel were made in percentages of 25/75; 50/50; and 75/25. These along with the end members were analyzed by the OILPRINT^{TM} method for comparison with the data on PS1.

Ratios of hydrocarbon peaks in the C-10 to C-12 fraction were determined and are presented in Table 1. This is the area of overlap for the gasoline and diesel where neither fraction is overly dominant. That is, the molecular weight range is relatively small for both the diesel and gasoline when considering their total molecular weight distribution. These ratios are plotted in Figure 1 and the values for the PS1 sample are included. It can be seen that the PS1 plots in a narrow range between about 27% to 33%. An average for the four hydrocarbon peak number ratios is 31% gasoline and 69% diesel.

It will be seen that the plots for each ratio are not straight lines, which is to be expected. Peak heights do not normally respond in a linear fashion for mixes because peaks represent more than one compound in this molecular weight range. Figure 2 is a chromatogram of the end member gasoline and the small normal paraffin peaks C-8 through C-13 are identified. Small asterisks above some peaks indicate those which are larger than normal. Figure 3 represents the diesel end member and depicts the normal range of about C-11 to C-20 components with a few more heavier compounds out to about C-26. It also contains lighter components all the way to light gasoline (C-2 to C-5). Again, the amount of these lower boiling point compounds is somewhat higher than found in the average diesel.

Loren W. Slentz Ph.D.

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Example FSCOT Report
PTS File No.: 33999
July 10, 2000

TABLE 1
HYDROCARBON COMPOSITION
BY FRACTIONS OF SAMPLE FROM CITY WELL PS1

RUN No.	SAMPLE IDENTIFICATION	HYDROCARBON RATIOS BY PEAK NUMBERS			
		81/ 79	78/ 88	107/ 106	120/ 121
4054	DIESEL END MEMBER	5.77	4.51	4.90	0.78
4056	MIX 25% GASOLINE / 75% DIESEL	2.23	3.20	2.97	1.61
4060	MIX 50% GASOLINE / 50% DIESEL	3.58	2.45	2.32	2.09
4059	MIX 75% GASOLINE / 25% DIESEL	5.23	2.13	1.37	2.79
4061	GASOLINE END MEMBER	6.72	1.60	0.84	3.78
4052	PS1 LIQUID	2.71	3.15	2.82	1.75

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Figure 1
Percentage Composition of Diesel / Gasoline

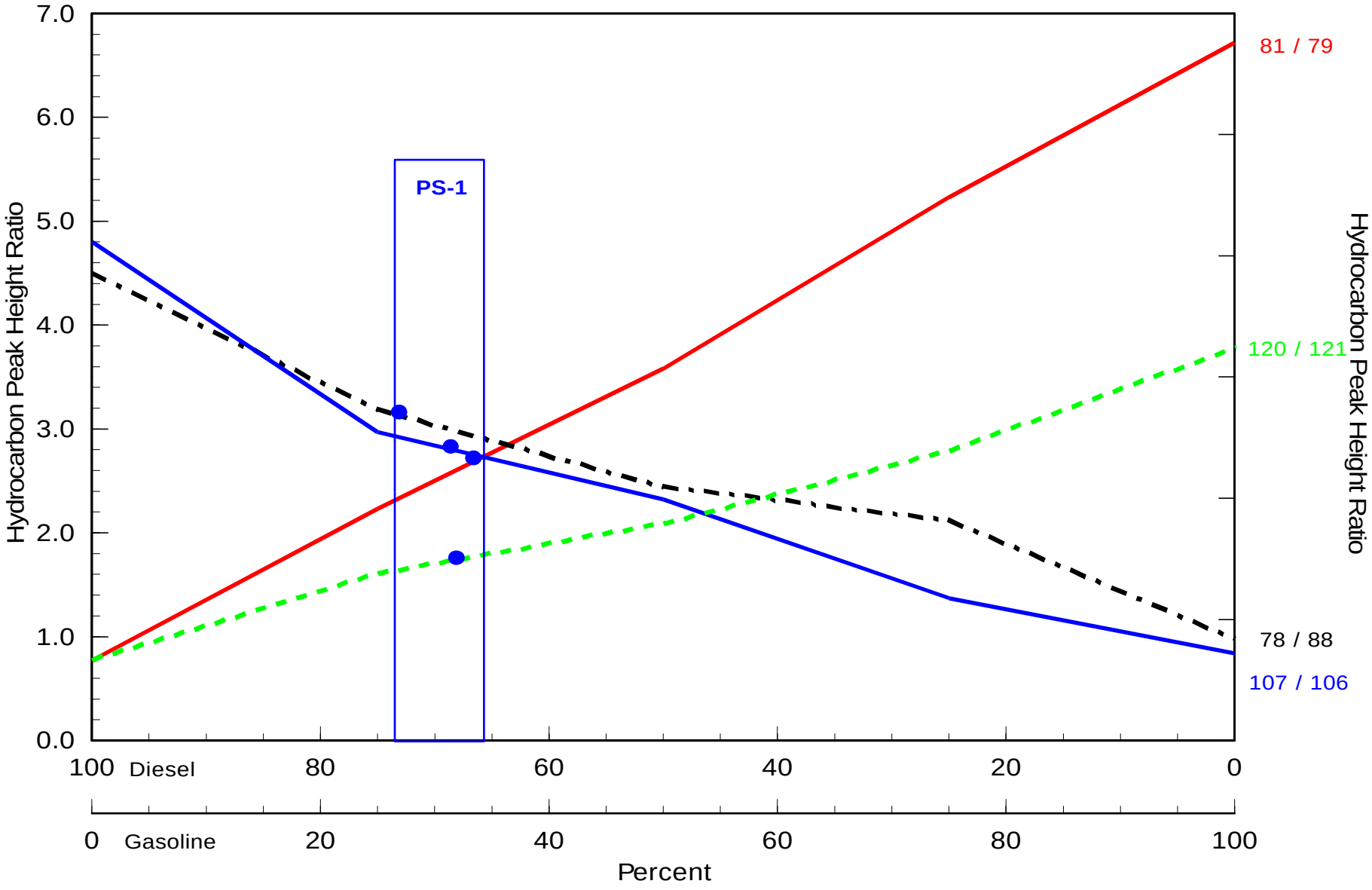


Figure 3
Phase Separated Hydrocarbon Characterization

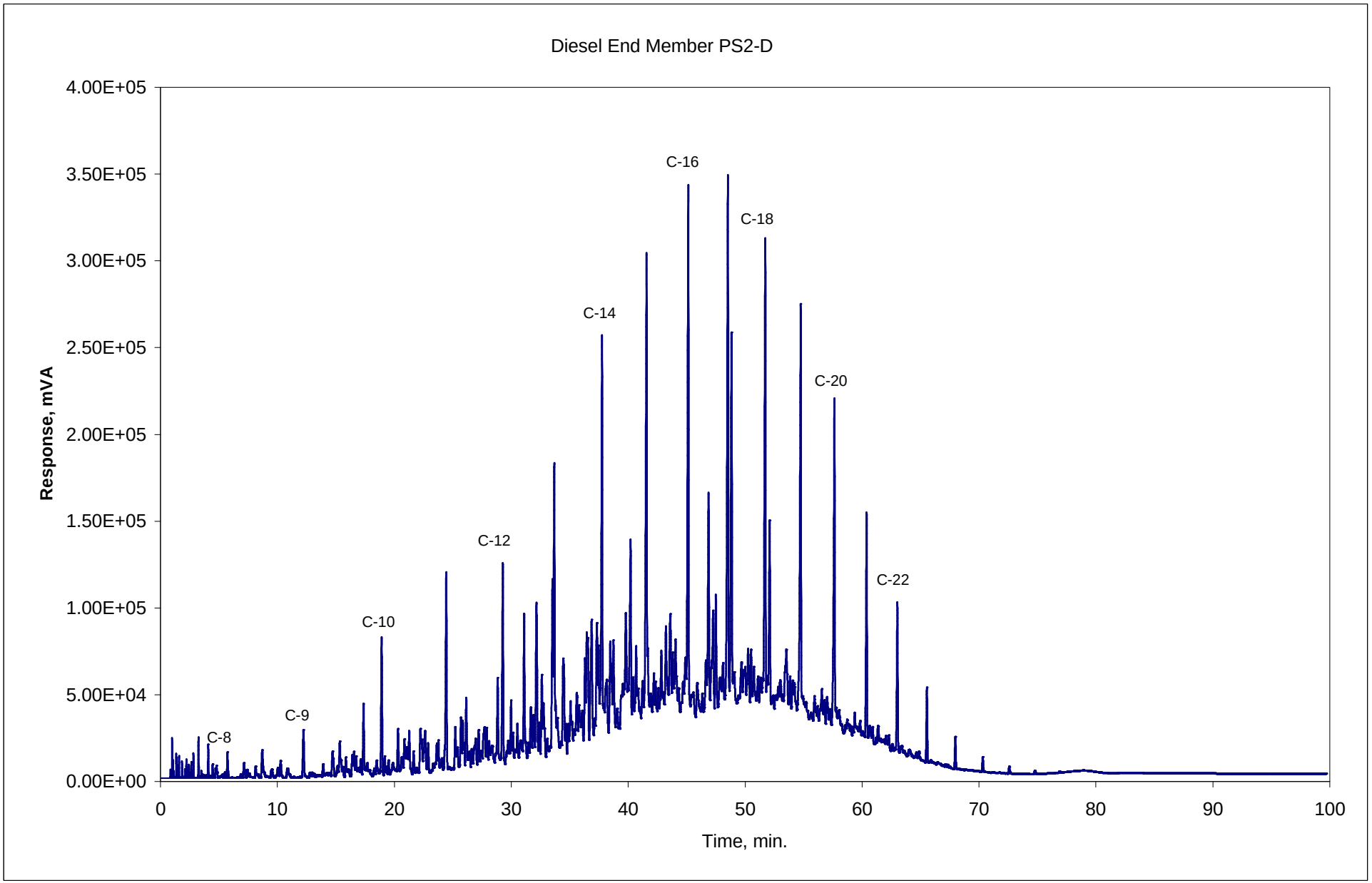
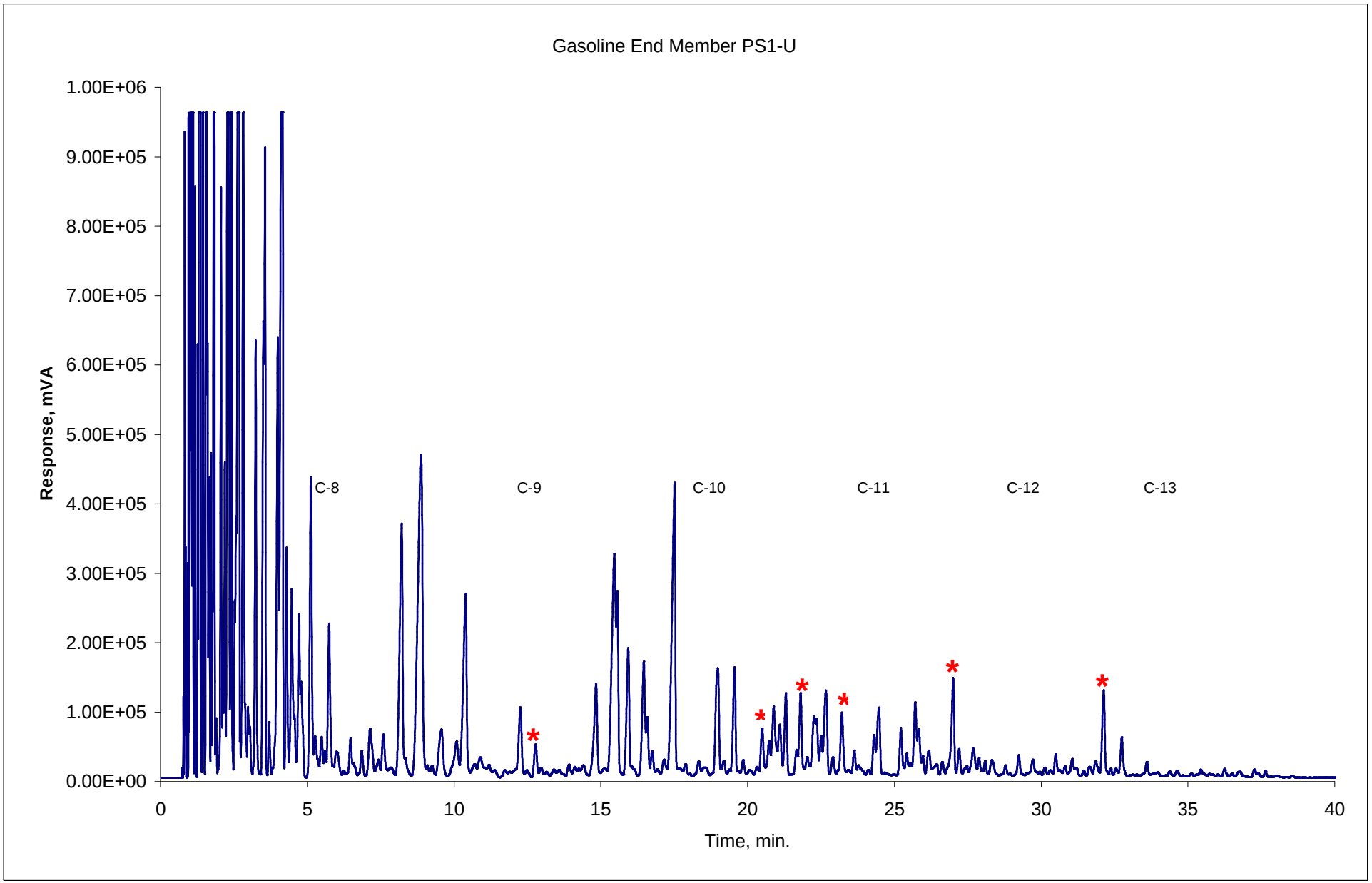


Figure 2
Phase Separated Hydrocarbon Characterization



P R E L I M I N A R Y R E P O R T

Phase Separated Hydrocarbon Characterization

Introduction

A fluid sample (PS1) from the subject boring/well was received for determination of the relative amounts of gasoline and diesel present in the mix. Analysis performed to provide the basis for this data also allows general observations about the overall hydrocarbon character.

Conclusions

The sample is a mixture of gasoline and diesel plus a small but significant third component consisting of a kerosene-like fraction.

There is little evidence of alteration of these products. That is, there has been little or no weathering – loss of light gasoline fraction, no water washing – loss of light aromatics such as benzene, toluene and xylenes, and no bacterial degradation – loss of normal paraffins. The presence of fresh gasoline as evidenced by the lack of weathering, suggests that this component is the result of an ongoing or recent (less than 6 months) release.

The percentage composition of the mix is as follows:

Light gasoline	C-2 to C-8	=	26.0%
Heavy gasoline	C-8 to C-9	=	9.1%
Kerosene	C-9 to C-11	=	18.2%
Diesel	C-11 to C24	=	46.7%

These values suggest a gasoline content (C-2 to C-8) of 25-30%. A kerosene content (C-8 to C11) of 20-25%. A diesel content (C-11 to C-24) of 45-50%. Possible overlap of the three fractions precludes any more precise determinations.

Analyses and Discussion

The sample was analyzed by OILPRINT^{TM} (using an F-SCOT chromatographic column) which provides information on the detailed hydrocarbon composition of the C-2 to C-34 fraction. The chromatogram is presented as Figure 1.

Data for the percentage composition calculations were obtained by using peak areas on the chromatogram. The values are not exact because there will be some overlap of various fractions. Without a reference sample it is not possible to determine the exact fraction coverage for the gasoline. Some gasolines contain very little C-8 to C-9 components while others may have 10 - 15%. The kerosene-like fraction probably extends into both the heavy gasoline and diesel fractions. And the diesel fraction may also extend into these fractions as well as have a trace of even light gasoline. Again, a reference sample of the diesel would allow more precise determination of the percentages.

Loren W. Slentz, Ph.D.