

Memorandum



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Alameda County  
Environmental Health

ERS  
Brea, California

August 23, 1996

FTS 96-223

TO: Dave DeWitt

FROM: Scott A. Stout, Ph.D., R.G. *SAS*

CHARACTERIZATION OF FREE PRODUCT  
FROM UNOCAL SS#5043, OAKLAND, CA

INTRODUCTION

At your request, the free product collected July 31, 1996 from a monitoring well (MW-6) at the Unocal service station (SS#5043) located in Oakland, California has been characterized. The sample was analyzed at Global Geochemistry Corp. (Canoga Park, CA) using; (1) high resolution gas chromatography (HRGC)<sup>1</sup>, (2) lead alkyls content and distribution and ethylene dibromide/ethylene dichloride analysis<sup>2</sup>, (3) oxygenate analysis using a GC via ASTM Method D4815, and (4) BTEX via EPA Method 8020. A split of the sample was also sent to Inchape Testing Services for determination of the sulfur content via ASTM D5453.

Approximately 3 feet of free product had accumulated in MW-6 at this site where there had been no previous product. Suspicions of a leaking UST system, in spite of new USTs and the station's use of a state-of-the-art TLS350 leak detection system, prompted immediate concern. The well was bailed free of product and a sample collected on July 31, 1996. No free product has returned to the well over the past three weeks. The lack of recurrence has now raised some suspicion that well tampering may have occurred.

The objective of the investigation was to describe the nature of the free product and to provide a basis for concluding whether or not it represented a recently released Unocal product(s).

<sup>1</sup>HRGC analyses were performed on an HP 6890 GC containing a 0.25 mm x 100 m capillary column coated with 0.25 micron thick SPB-1 stationary phase and equipped with a FID detector (det. temp. 320 °C). The oven program used was from 35°C (5 min) at 3 °C /min to 140 °C (0 min) and then 8 °C /min up to 315 °C (40 min). The pressure program use was from 28.4 psig (0 min) then 0.5 psi/min to 78 psig. A 1 ml autosampler injection (inj. temp. 320 °C) with a split of 400:1 and air flow of 300 ml/min was used. Compound identifications are based on retention time comparisons to known standards and were regulated by the presence of three internal calibration standards.

<sup>2</sup>EDB, EDC and the five Pb alkyls (TML, TMEL, DMEL, MTEL, and TEL) are determined by direct injection GC-ECD (electron capture detector) using a 0.25 mm x 60 m DB-5 stationary phase (0.25 micron thick coating) capillary column. The oven program used was from 90°C to 186°C at 8°C/min. A 5 ppm (ug/ml) detection limit is achieved.

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### RESULTS and DISCUSSION

#### Nature of the Free Product

The HRGC fingerprint for the free product is shown in Fig. 1. The free product is shown to contain hydrocarbons (HC) ranging from C4 to C14, i.e., its comprised almost exclusively of gasoline range organics (GRO; C3-C10). Most compounds within this range are identified and their relative weight% are listed in Table 1. For comparison, Table 1 also contains data relating to three 1993 Unocal gasolines refined at our San Francisco Refinery (SFR). Unfortunately, data relating to more recently-refined normal or the even newer reformulated gasolines (RFG) from SFR have not been analyzed by this method.

The identified compounds within the GRO are dominated by iso-paraffins (39.3 %wt) and aromatic HC (38.4 %wt; Table 1). The relatively high percentage of both of these octane-boosting compound classes indicates that **the GRO are undoubtedly derived from a blended gasoline.**

The iso-alkanes include over 10% of iso-pentane (2-methylbutane) and significant amounts of 2- and 3-methylpentane (Table 1). In total, the C5-C6 iso-paraffins account for 23.3 wt% of sample. This abundance of C5-C6 iso-paraffins indicates that the parent gasoline(s) was probably refined using a C5-C6 isomerization unit. SFR has had an isomerization unit since mid to late 1987. Therefore, this criteria cannot be used to dismiss the possibility of an SFR gasoline's presence.

There is also 0.61 wt% iso-octane (aka 2,2,4-trimethylpentane; Table 1) which suggests that the parent(s) also included an alkylate blend produced from an alkylation unit. This amount of iso-octane far exceeds the trace amounts expected in the 1993 SFR gasolines (0.1-0.3 wt%; Table 1). This would argue for the presence of a non-SFR gasoline component. However, SFR has been blending alkylate from LAR into the premium unleaded gasoline since Oct. 1995. Therefore, on this basis alone it cannot be determined that there is no SFR gasoline present.

The aromatic HC include the BTEX compounds (only minor B) and numerous C3-alkylbenzenes (e.g., 1,3,5- and 1,2,4-trimethylbenzenes). These are common components of most gasolines and generally appear in distributions similar to those observed in the MW-6 sample. The slightly reduced concentration of benzene is probably the result of weathering via water-washing (see below). Additional considerations regarding the BTEX compounds are discussed below. The presence of BTEX and C3-alkylbenzenes in this distribution is indicative of a reformat blended into the gasolines. Reformers are commonly in most refineries, therefore, this is not useful in a forensic sense. (In fact, SFR employs two reformers).

The presence of a small amount of olefins (1.40 wt%; Table 1) indicates that the parent gasoline(s) was probably refined using an catalytic or thermal cracking process (and not hydrocracking). SFR gasolines have historically not contained more than 0.5 wt% olefins (Table 1) because of the use of a Unicracker since the early 1970's. However, since Oct. 1995

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SFR has received a light CAT blending stock from LAR which has resulted in up to 5.0 wt% olefins in our unleaded gasolines. Therefore, on this basis alone it cannot be determined that there is no SFR gasoline present.

In summary, the molecular characteristics of the sample indicate that the parent gasoline's (or at least one component in a mixture of gasolines) blend included; (1) isomerase from a C5-C6 isomerization unit, (2) an alkylate from an alkylation unit, and (3) a catalytic blend from an FCC or thermal cracker. Given the refining history described in the preceding paragraphs it is not possible to determine that there is no SFR-refined (or blended) gasoline present in the sample. All that can be said is that **if the parent gasoline is entirely a Unocal SFR product then it must be no older than October 1995.**

### Aromatic Hydrocarbon Results

The results of the EPA Method 8020 analysis are given in Table 2. The separate BTEX analysis (EPA 8020) indicated that the free product contained 6280 ug/ml of benzene which corresponds

**Table 2: BTEX results for the MW-6 free product studied.**

$\mu\text{g/ml}$	Benzene	Toluene	Ethyl benzene	Xylenes	Total
MW-6	6290	49600	14500	73800	144190
MW-6 dupl.	6270	50000	15500	74200	145970
Average	6280	49800	15000	74000	145080
detection limit	5	5	5	5	

to 0.71 %vol benzene. Benzene content of reformulated gasoline (RFG) have been limited to <1.0 %vol since March 1995. Prior to this time there were no limits on the benzene content of gasolines sold in California (which typically ran 2-3 %vol). On this basis it cannot be determined for sure whether or not the free product is a pre- or post-RFG gasoline. The reason for this uncertainty is the potential for benzene to have been removed from the free product due to preferential weathering. (Of course, if the benzene content of the free product had been > 1 %vol then it could be safely concluded that a pre-RFG gasoline was present).

The ratio of B/T (0.13) is relatively low for most brands of fresh gasolines. However, SFR's high octane gasoline have typically been enriched in toluene due to the use of a significant reformate blending component to maintain octane. Therefore, the low B/T ratio in the free product could be indicating that (1) some benzene has been preferentially removed via water-washing or (2) the gasoline was refined with excess toluene (as was the case in pre-RFG SFR gasolines). Other BTEX-based ratios indicate other similarities with pre-RFG SFR gasolines. For example the T/BTEX (0.34) and T/X (0.67) ratios are consistent with previously studied 1993 (pre-RFG) SFR gasolines (Table 1). Therefore, **on the basis of the BTEX results there is no argument to be made against the free product being a pre-March 1995 SFR gasoline.**

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Oxygenate Analysis

Results of the ASTM D4815 analysis are given in Table 3. The sample was shown to contain no oxygenated compounds (alcohols and ethers) other than TAME (2-methyl-2-methoxybutane).

**Table 3: Results of the Oxygenate Analysis on MW-6 Free Product.**

µg/ml (ppm)	Methanol	Ethanol	tert-Butanol	MTBE	ETBE	TAME
<b>MW-6</b>	nd	nd	nd	nd	nd	915
<b>MW-6 duplicate</b>	nd	nd	nd	nd	nd	905
<b>detection limit</b>	200	200	200	200	200	200

MTBE - methyl tert-butyl ether

ETBE - ethyl tert-butyl ether

TAME - tert-amyl methyl ether; this result was double-checked by co-injection of a TAME standa

On average the sample contained 910.5 µg/ml of TAME.<sup>3</sup> This corresponds to about 0.12 wt% TAME, or only 0.019 wt% oxygen. RFG refined in California since March 1995 have been required to contain between 1.8 and 2.2 wt% oxygen. Therefore, this free product contains only about 1% of the required amount of oxygen for new reformulated gasolines. TAME is far less soluble in groundwater than MTBE (6000 vs. 43,000 mg/L @20°C) and therefore its concentration in the sample is not expected to have been significantly reduced due to water-washing. This suggests that the **TAME-containing gasoline component present in the sample is probably only a fraction (1% ?) of the total free product.**

TAME has never been intentionally added to gasolines refined at SFR; only perhaps as a contaminant in an MTBE blend. However, since MTBE is absent from this sample it is safe to assume that the **TAME-containing component of the free product was not an SFR gasoline.** Unfortunately, the small amount of TAME argues that this non-Unocal component is only a minor component of the free product. Because TAME has a lower blending ((R+M)/2) octane number (105 vs. 110) and a lower mass% oxygen (15.7% vs. 18.2%), it is far less commonly used than MTBE. This characteristic may help to identify a Bay Area source(s) of the TAME-containing component in the free product. Unfortunately, the available oxygenate unit construction records (Oil and Gas Journal's annual update) indicate that there are no West Coast refiners that are producing TAME.

Sulfur Analysis

Prior to RFG limits implemented in March 1995, the sulfur content of gasolines sold in California was limited to <300 ppm. Since March 1995 the maximum allowable S content was reduced to

<sup>3</sup>TAME is one of several oxygenates available to be added to gasolines (at volumes up to 20%) to boost octane while minimizing ozone-harmful emissions. It is produced from a C5 olefin stream reacted with ethanol (MTBE is produced from a C4 olefin stream reacted with ethanol). TAME's advantage is its lower vapor pressure (compared to MTBE) which allows more butane to be added and still maintain vapor pressure requirements.

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40 ppm. It was determined that the MW-6 free product sample contained 108 ppm sulfur. The high S content argues that the free product must (at least) contain a pre-March 1995 gasoline.

Gasolines refined at SFR had historically contained very low S (<1 ppm) due to use of the fixed-bed hydrotreater (which tends to remove sulfur as H<sub>2</sub>S and thereby protect the catalysts used in the Unicracker, two reformers and isomerization units). Since early 1995, the S content of SFR gasolines was increased to between 10-30 ppm S (average ~12.5 ppm) when a light CAT blending component was initially imported from LAR. (This light CAT contains higher S due to LAR's use of an FCC unit in which sulfur is not removed as effectively due to its fluid-bed nature). **The historically low values of S in SFR gasolines argues that the pre-March 1995 gasoline component in the free product (with its 108 ppm) is not an SFR gasoline.** Of course, the presence of a low sulfur SFR gasoline component cannot be dismissed since the possibility of mixing exist.

Lead Alkyl Results

The results of the lead alkyl analysis is given in Table 4. This table shows that the MW-6 free product contained all five Pb alkyls in an abundance totaling 0.679 grams Pb per gallon (glpg).

**Table 4: Results of the lead alkyl analysis of MW-6 free product.**

	wt. %	MW-6 (average)			% Standard Reacted Mixes			Other Mixes		Theoretical Mix
	lead	µg/mL	%	glpg	RM25	RM50	RM75	TEL only	PM80	10:25:55:10 RM25:TEL:PM80: RM50
TEL	0.640582	101.5	40.0	0.25	28.8	4.8	0.1	100	20	39.4
MTEL	0.669629	24.0	9.4	0.06	49.5	25.6	3.6	0	0	7.5
DEDML	0.701435	8.0	3.1	0.02	18.6	42.4	20.5	0	0	6.1
TMEL	0.736388	10.5	4.1	0.03	3.0	23.4	49.6	0	0	2.6
TML	0.775035	110.0	43.3	0.32	0.1	3.8	26.2	0	80	44.4
<b>TOTAL</b>		<b>254</b>	<b>100</b>	<b>0.679</b>						

This concentration of Pb is typical of leaded gasolines refined in the early to mid-1980's when the EPA mandated Pb maximum was reduced from 1.1 to 0.5 glpg. Since there is only a small amount of oxygenates (TAME) present, there is no reason to call upon a significant unleaded gasoline component to be present in this sample. Therefore, there is no reason to believe that there is a mixture of a leaded gasoline with an unleaded gasoline, resulting in the reported glpg value. **This supports an early-to-mid 1980's age for the free product's parent gasoline.**

Corporate records indicate that SFR had used specific Pb alkyl packages through time. Between 1975 and 1985 SFR used a reacted mix, RM50, in both the regular and premium leaded gasolines. As can be seen in Table 4, the mixture of lead alkyls in an RM50 lead

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package is very different from that found in the MW-6 free product. **This makes it highly unlikely that the free product was derived from a leaded gasoline refined at SFR in the early 1980's.**

In fact the Pb alkyl distribution in the free product does not resemble any single Pb package available for gasoline blending. Therefore, **a mixture of leaded gasolines each containing different lead packages must be present.** One can ask whether or not it is possible to derive the observed mixture in the free product from any of the lead packages used over time at SFR.<sup>4</sup> In theory, it would require a minimum of a 4-component blend to achieve a Pb alkyl distribution comparable to that observed in the free product. This is reflected in the theoretical mixture listed in Table 4. Such a mixture, if composed only of SFR gasolines, would require mixing of leaded gasolines over the minimum time period of 1975 to 1985. While this may be possible it appears to me as being extremely remote.

### Degree of Weathering

The free product contains an abundance of light (<C5) components. This indicates that the original release had probably occurred below ground thereby minimizing evaporative losses. The gasoline component does exhibit some indications of weathering due to water-washing. This is reflected in the low proportion of toluene relative to xylenes. Toluene is typically present in near equal abundance to xylenes in fresh regular gasolines (T/X~0.6-1.0). (In premium gasolines the T/X ratio can be as high as 4.8). However, because toluene is more water soluble than the xylenes, it is preferentially removed upon exposure to groundwater. This free product appears to have lost toluene due to water-washing (T/X ~ 0.4; Table 1). Benzene is even more soluble and the presence of a small amount of benzene (0.07 %vol of GRO; Table 1) indicates that water-washing is not complete. In my experience, **I would consider this gasoline to be moderately water-washed.**

The process of biodegradation typically accompanies water-washing. The most susceptible compounds to biodegradation are the n-alkanes and olefins. This sample contains only slightly reduced quantities of both of these compound classes as compared to fresh gasolines. This indicates that **the gasoline component of this free product is only slightly biodegraded.**

Given the limited data and the necessarily relative nature of the weathering 'data', it would be imprudent to try and assign an absolute age to the free product. Given my experience, however, **I would hesitate to call the gasoline component fresh** due to the slight to moderate weathering observed. I cannot be as definitive for the diesel fuel component since its nature is rather typical.

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<sup>4</sup>The other lead packages that have been used at various times at SFR include a physical mix of 80% TML and 20% TEL (1963-1975 premium gasolines), TEL-only (1963-1975 regular gasolines), and RM25 (1985-1986 premium gasoline; no regular leaded gasoline was produced at this time). After 1986 there was no leaded gasoline produced at SFR.

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### Origin of the Gasoline and Diesel Components

The prominence of 2,2,4-trimethylpentane or iso-octane (??? %vol of GRO) strongly suggests that an alkylate blending stock was among the blending components used in the parent gasoline. Unocal's San Francisco refinery (SFR) does not have an alkylation unit and therefore, our gasolines are typically reduced in isoparaffins (particularly, isopentane). However, beginning in October 1995 alkylate was piped to SFR from Unocal's Los Angeles refinery for blending with SFR gasolines. Therefore, the presence of iso-octane (and other isoparaffins) in this sample could indicate the presence of either (1) a non-Unocal gasoline or (2) a post-Oct. 1995 Unocal gasoline.

The presence of 1.65 %vol olefins in the gasoline range is more informative since SFR gasolines are typically reduced in olefins (< 0.5 %vol). This characteristic arises from the fact that we employ a hydrocracking unit (rather than an catalytic cracking unit). Hydrocracking produces an isomaxate gasoline blending component with little or no olefins. The presence of 1.65 %vol olefins argues strongly that **the gasoline component of this free product is not a Unocal refined gasoline.**

The nature of the diesel fuel is less descriptive as to its origin. The pristane/phytane (Pr/Ph) ratio of the diesel fuel (1.84; Table 1) should reflect that of its parent crude oil. SFR runs primarily Cook Inlet crudes for diesel fuel #2 production. Undegraded Cook Inlet crudes have Pr/Ph ratios between in the range 2.0 to 3.5 (B. Bromley, personal communication, 1994). The slightly lower Pr/Ph ratio of the free product's diesel fuel component suggests that the parent crude oil was probably not from the Cook Inlet. This conclusion is further substantiated by the high Pr/nC17, given the Ph/nC18 ratio.<sup>5</sup>

### CONCLUSIONS

The free product which accumulated in MW-6 at Unocal service station #5043 was analyzed by a variety of techniques. The primary objective of the study was to determine whether or not the sample consisted a recently-refined Unocal gasoline. The answer to this question is no; the free product is not a recently released gasoline refined at Unocal's San Francisco refinery. The basis for this conclusion is:

- (1) the free product contains a significant amount of lead and SFR has not produced leaded gasolines since 1986,
- (2) the free product contains sulfur well above the reformulated gasoline (RFG) maximum which SFR began producing in March 1995, and
- (3) the free product doesn't contain MTBE as would be expected in recently-refined SFR gasolines.

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<sup>5</sup>The basis for this statement is that Cook Inlet crude oils tend to fall along a single trend when the Ph/nC18 and Pr/nC17 ratios are cross-plotted. This trend line represents different degrees of biodegradation that had occurred in the original oil field reservoir. These ratios for the free product sample fall well off of the Cook Inlet trend indicating that the parent crude oil for this diesel fuel was probably not a Cook Inlet crude oil.

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These results clearly indicate that the free product is not a recently refined SFR gasoline. However, the MW-6 free product exhibits a diverse set of characteristics which, in my opinion, argues that it represents a mixture of gasolines. Thus the question shifts as to whether or not the MW-6 free product contains a recently-refined SFR gasoline as one of its components.

The presence of lead indicates that at least one of the components in the mixture must be a leaded gasoline. The peculiar lead alkyl distribution (Table 2) actually argues for a mixture of leaded gasolines being present. Therefore, while the lead content (0.679 glpg) argues for an early-to-mid 1980's age, the fact that the free product is a mixture means that all that can be said for sure is that there must be a leaded gasoline component that is from 1985 or earlier present. Based on the lead alkyl packages used at SFR in the 1970's and 80's, it would have been possible, though highly unlikely, to obtain mixture consistent with the MW-6 free product. This argues for the presence of someone else's leaded gasolines being present.

The presence of a small amount of TAME argues that there may be a more recent unleaded component also present in the mixture. Based on the low concentration of TAME (and absence of other oxygenates) this would seem to be a very small component (1% ?) in the mixture. Furthermore since SFR has never used TAME, it certainly could not be an SFR unleaded gasoline.

Based on the molecular characteristics at least one of the components included blends from; (1) a C5-C6 isomerization unit, (2) an alkylation unit, and (3) an FCC or thermal cracker. All three of these blending stocks have been available at SFR since Oct. 1995 (when the latter two stocks were first piped up from LAR). Since a mixture is known to exist, the refining characteristics alone do not argue against the potential for an SFR gasoline being among the components.

The high sulfur content (108 ppm) argued for a pre-March 1995 gasoline (see above). However, the historically low values of S in SFR gasolines argues that the pre-March 1995 gasoline component in the free product (with its 108 ppm) is not an SFR gasoline.

The gasoline mixture appears to be only moderately water-washed and slightly biodegraded. This alone would argue for it being a relatively 'fresh' gasoline, however, there is too much evidence that a significant portion of the product is historic (pre-1985). This discrepancy may be explained by the occurrence of a large pool in which the gasoline has not biodegraded over time. This seems highly unlikely given the non-recurrence of free product in the weeks following well purging.

Obviously, a definitive answer to the origin of the MW-6 product is elusive. It can be confidently stated that the product is not exclusively a recently-refined SFR gasoline. The origin remains unclear but is certainly worthy of considering the possibility of off-site (3rd party) sources and closely watching any additional appearances of free product in the area.

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If you have any questions concerning these conclusions please call me (at 714-577-1296 or at network 268-1296).

SAS/cs

xc: B. J. Kelly  
G. T. Ririe

Table 1: TABULATED HIGH RESOLUTION GAS CHROMATOGRAPHY DATA FOR MW-6  
FREE PRODUCT AND FRESH SFR GASOLINES

Retention Time	Compound Name/ Chemical Parameter	MW-6 Pk. Ht.	MW-6 wt%	SFR 87 1993	SFR 89 1993	SFR 92 1993
5.26	propane	0	0.00	0.00	0.00	0.01
5.427	2-MePropane	11119	0.22	0.08	0.10	1.07
5.515	isobutene+1-butene	969	0.02	0.02	0.02	0.02
5.555	n-butane	42259	0.83	0.84	1.02	4.86
5.602	t-2-butene	954	0.02	0.01	0.01	0.00
5.673	c-2-butene	559	0.01	0.00	0.00	0.00
5.875	3-Me-1-butene	561	0.01	0.00	0.00	0.00
6.011	2-MeButane	522492	10.29	7.77	8.76	7.38
6.15	1-pentene	1341	0.03	0.03	0.00	0.01
6.213	2-Me-1-butene	2829	0.06	0.05	0.02	0.01
6.257	n-pentane	154448	3.04	5.85	3.97	2.25
6.349	t-2-pentene	3551	0.07	0.05	0.02	0.00
6.442	c-2-pentene	1790	0.04	0.01	0.03	0.00
6.498	2-Me-2-butene	6038	0.12	0.03	0.03	0.02
6.713	2,2-diMeButane	10681	0.21	0.25	0.27	0.44
7.043	cyclopentane	722	0.01	0.76	0.60	0.42
7.2	2,3-diMeButane + MTBE	83384	1.64	9.01	8.94	8.38
7.271	2-MePentane	408589	8.04	4.74	4.70	3.49
7.561	3-MePentane	243205	4.79	2.87	2.79	2.17
7.95	n-Hexane	134129	2.64	3.93	2.59	1.56
8.089	t-3-Hexene	1986	0.04	0.00	0.00	0.00
8.136	3-MeCyclopentane	2810	0.06	0.02	0.02	0.01
8.33	3-Me-c-2-pentene	622	0.01	0.00	0.00	0.00
8.488	c-2-hexene	1643	0.03	0.00	0.00	0.00
8.593	3-Me-t-2-pentene	9505	0.19	0.17	0.15	0.14
8.663	methylcyclopentane	320857	6.32	2.99	3.07	2.23
8.766	2,4-diMePentane	56023	1.10	0.45	0.48	0.37
9.412	Benzene	40344	0.79	1.46	1.25	1.06
9.573	5-Me-1-Hexene	9857	0.19	0.00	0.00	0.00
9.704	Cyclohexane	72240	1.42	1.37	0.91	0.71
10.011	2-MeHexane	145300	2.86	2.23	2.31	1.97
10.076	2,3-diMePentane	72346	1.42	0.81	0.78	0.66
10.335	3-MeHexane	143878	2.83	2.55	2.43	2.12
10.802	2-Me-1-hexene	38026	0.75	0.22	0.20	0.18
10.855	2,2,4-triMePentane	43378	0.85	0.01	0.01	0.02
11.316	n-Heptane	101092	1.99	1.99	1.54	1.47
12.18	methylcyclohexane	70575	1.39	0.82	0.58	0.77
12.76	2,5-diMeHexane	17851	0.35	0.20	0.20	0.21
12.85	2,4-diMeHexane	26597	0.52	0.34	0.33	0.35
13.6	2,3,3- + 2,3,4-triMePentane	18422	0.36	0.03	0.04	0.03
13.81	Toluene	388438	7.65	7.77	8.69	9.31
14.143	2,3-diMeHexane	19943	0.39	0.22	0.23	0.22
14.448	2-MeHeptane	55144	1.09	0.74	0.74	0.73
14.526	4-MeHeptane	26600	0.52	0.36	0.36	0.35
14.606	3,4-diMeHexane	7109	0.14	0.13	0.15	0.13
14.83	3-Et-3-MePentane	65396	1.29	0.01	0.02	0.00
14.885	3-MeHeptane	18245	0.36	0.89	0.89	0.01
15.391	2-Me-1-Heptene	5426	0.11	0.01	0.01	0.02
16.228	n-Octane	43181	0.85	0.70	0.65	0.63

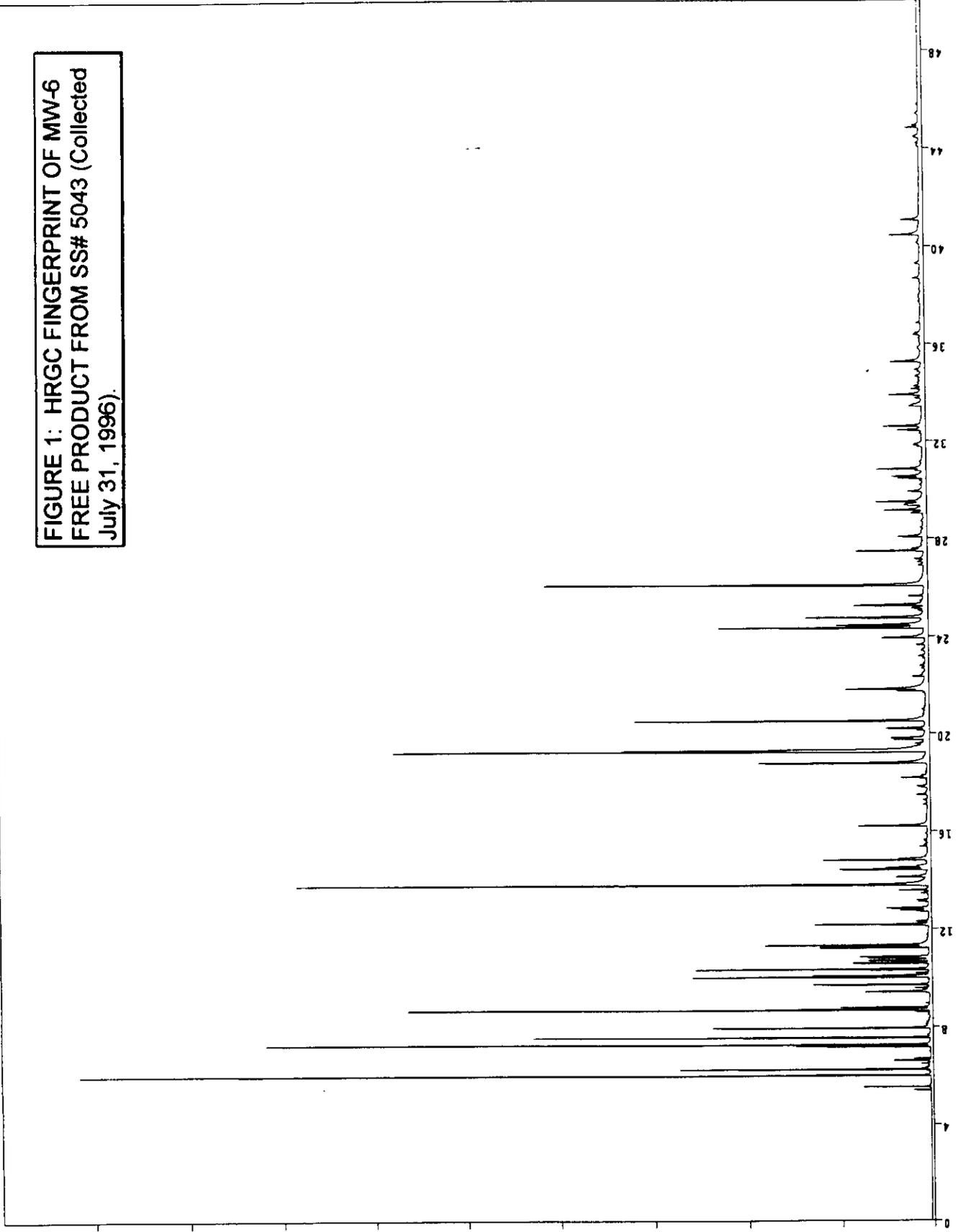
Table 1: TABULATED HIGH RESOLUTION GAS CHROMATOGRAPHY DATA FOR MW-6  
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Retention Time	Compound Name/ Chemical Parameter	MW-6 Pk. Ht.	MW-6 wt%	SFR 87 1993	SFR 89 1993	SFR 92 1993
17.095	2,2-DiMeHeptane	2717	0.05	0.01	0.01	0.00
17.504	2,4-DiMeHeptane	6678	0.13	0.03	0.03	0.02
17.813	EthylCyclohexane	3510	0.07	0.02	0.02	0.01
18.212	2,6-DiMeHeptane	16103	0.32	0.10	0.10	0.10
18.798	ethylbenzene	103728	2.04	2.00	2.15	2.51
19.281	m- + p- Xylene	326713	6.43	7.87	9.38	10.33
19.768	4-MeOctane	19864	0.39	0.23	0.21	0.00
19.825	2-MeOctane	21764	0.43	0.24	0.23	0.21
20.119	3-ethylHeptane	5464	0.11	0.29	0.28	0.21
20.194	3-MeOctane	24531	0.48	0.00	0.00	0.00
20.496	o-Xylene	177639	3.50	2.85	3.30	3.62
20.996	1-nonene	2085	0.04	0.00	0.00	0.00
21.736	n-nonane	17961	0.35	0.24	0.21	0.20
22.326	isopropylbenzne	7898	0.16	0.00	0.00	0.00
22.777	3,3,5-TriMeHeptane	3087	0.06	0.00	0.00	0.00
23.654	2,4,5-TriMeHeptane	5318	0.10	0.00	0.00	0.00
23.932	n-propylbenzene	27156	0.53	0.72	0.70	0.77
24.342	1-Me-3-ethylBenzene	126867	2.50	2.26	2.56	2.93
24.453	1-Me-4-ethylBenzene	55494	1.09	1.01	1.15	1.32
24.76	1,3,5-triMeBenzene	73816	1.45	1.23	1.38	1.45
25.153	3,3,4-triMeHeptane	8070	0.16	0.07	0.07	0.06
25.264	1-Me-2ethylBenzene	44024	0.87	0.75	0.85	0.98
25.862	3-MeNonane	1079	0.02	0.08	0.08	0.08
26.082	1,2,4-triMeBenzene	232474	4.58	3.66	4.09	4.42
26.372	Isobutylbenze	1686	0.03	0.09	0.09	0.10
26.78	sec-ButylBenzene	667	0.01	0.77	0.84	0.96
26.911	n-decane	3553	0.07	0.15	0.14	0.15
27.497	1,2,3-triMeBenzene	42441	0.84	0.00	0.00	0.00
28.07	indan	16370	0.32	0.41	0.45	0.54
29.148	1,3-diEthylBenzene	23446	0.46	0.22	0.23	0.25
29.352	1,4-diethylBenzene	10104	0.20	0.36	0.37	0.39
29.496	n-butylbenzene	28281	0.56	0.00	0.00	0.00
29.919	1,3-dimethyl-5-ethylbenzene	9013	0.18	0.05	0.05	0.06
30.448	1,4-dimethyl-2-ethylbenzene	15389	0.30	0.33	0.34	0.38
30.534	1,3-dimethyl-4-ethylbenzene	19324	0.38	0.55	0.58	0.65
30.839	1,2-dimethyl-4-ethylbenzene	28630	0.56	0.00	0.00	0.01
31.831	n-Undecane	5612	0.11	0.11	0.11	0.13
32.444	1,2,4,5-TetraMeBenzene	15399	0.30	0.31	0.32	0.32
32.607	1,2,3,5-TetraMeBenzene	23804	0.47	0.42	0.43	0.43
33.883	1,2,3,4-TetraMeBenzene	20215	0.40	0.25	0.26	0.30
35.276	Napthalene	19015	0.37	0.08	0.07	0.08
40.457	2-MeNapthalene	19100	0.38	0.02	0.00	0.00
41.086	1-MeNapthalene	11512	0.23	0.15	0.12	0.15

Table 1: TABULATED HIGH RESOLUTION GAS CHROMATOGRAPHY DATA FOR MW-6  
FREE PRODUCT AND FRESH SFR GASOLINES

Retention Time	Compound Name/ Chemical Parameter	MW-6 Pk. Ht.	MW-6 wt%	SFR 87 1993	SFR 89 1993	SFR 92 1993
<b>CMPD. CLASS TOTALS</b> (wt. % of ident. cmpds.)						
	% NORMAL ALKANES		9.89	15.22	11.23	12.52
	% ISO ALKANES		39.32	38.44	39.12	34.39
	% CYCLICS (SAT)		11.00	6.62	5.75	4.63
	% OLEFINS		1.40	0.49	0.38	0.28
	% AROMATICS		38.42	39.23	43.52	48.18
<b>REFINING CHARACTER</b>						
	Alkylation - wt. % iso-Octane		0.85	0.01	0.01	0.02
	Octane - iso-octane/MCH		0.61	0.01	0.02	0.03
	FCC v. Hydro. - wt % olefins		1.40	0.49	0.38	0.28
	Reformate - wt % aromatics		38.42	39.23	43.52	48.18
	Isomerase - wt % C5-C6 iso-		23.33	15.63	16.52	13.48
<b>EVAPORATION</b>						
	wt % < nC5		0.11	0.10	0.11	0.15
	n-pentane/n-heptane		0.01	2.94	2.58	1.53
	2-Mepentane/2-MeHeptane		7.41	6.41	6.35	4.78
<b>WATER WASHING</b>						
	benzene/cyclohexane		0.56	1.07	1.37	1.49
	toluene/methylcyclohexane		5.50	9.48	14.98	12.09
	total aroms/sat + iso + cyclics		0.62	0.65	0.78	0.93
	total aroms/cyclics		3.40	5.92	7.57	10.41
<b>BIODEGRADATION</b>						
	C4-C8 sat + iso/C4-C8 olefins		42.48	154.06	160.03	202.90
	3-MeHexane/n-Heptane		1.42	1.28	1.58	1.44
	MCH/n-Heptane		0.70	0.41	0.38	0.52
	iso + cyclics/iso+cyclic+sat		0.84	0.75	0.80	0.76
<b>BTEX CONTENT</b>						
	wt % Benzene		0.79	1.61	1.37	1.18
	wt % Toluene		7.65	8.56	9.54	10.35
	wt % EthylBenzene		2.04	2.20	2.36	2.79
	wt % Total Xylenes		9.93	11.82	13.92	15.52
	wt % TOTAL BTEX		20.41	24.20	27.19	29.84
<b>SELECTED RATIOS</b>						
	Benzene/Toluene		0.10	0.19	0.14	0.11
	Toluene/Xylenes		0.77	0.72	0.69	0.67
	Toluene/BTEX		0.37	0.35	0.35	0.35

FIGURE 1: HRGC FINGERPRINT OF MW-6  
FREE PRODUCT FROM SS# 5043 (Collected  
July 31, 1996).



9499

**Dewitt, David B.**

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**From:** Stout, Scott  
**To:** Dewitt, David B.  
**Subject:** 5043  
**Date:** Tuesday, August 27, 1996 2:34PM

Dave,  
Attached is a memo describing the MW-6 free product from SS5043. (Only Table 1 and the fingerprint are missing). The final memo should come your way in a few days.

<<File Attachment: MEMO1.DOC>>

I hope that this helps. This was a very complicated sample because of the mixed nature of it. We can definitively say, however, that the product does not contain any significant amount (and probably no) recently-refined SFR gasoline. This should answer the immediate objective of whether or not there's a problem with the USTs or piping system.

I am still a bit puzzled by the sample given the fact that product has not reappeared in the well. You may be on to something with the tampering theory, however, they'd of had to have poured a significant amount of leaded gasoline down there. Puzzling???

I would recommend keeping a close eye on things out there. If more product shows up there could be a problem. Let me know if this work results in any cost savings, e.g., no need to test the TLS350 system.

I am in Portland the rest of the week and in Rhode Island next week. I'll be checking my voice mail though if you have any questions.

Cheers,  
Scott

**Dewitt, David B.**

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**To:** Todd, Barbara F.  
**Cc:** Bock, Ronald E. -CERT; LaBeaux, Sandy X.; Cerovac, Scott  
**Subject:** Free product identification from SS #5043, Oakland

I have reviewed the memo from Dr. Scott Stoudt of FTS/ERS on his investigation of the free product recovered from monitor well MW-6 at this site. I have discussed the results with Dr. Scott and the following conclusions can be made:

1. The characteristics of the recovered fuel indicate that the fuel is not a recently refined Unocal gasoline (i.e., RFG). I also interpret this to indicate the TLS 350 did not "miss" a leak and the system is functional.
2. Based upon the compilation of a number of different points of evidence, there is apparently more than one source of gasoline and the characteristics of those gasolines are not from Unocal.
3. There is some evidence that some "old" gasoline is present and may be Unocal fuel; however, this ~~is~~ fuel was know to be there prior to the Reformat of the site.
4. Based upon the volume of recovered fuel from the well (slightly more than two gallons), the lack of recharge to the well and the relatively "fresh" nature of the fuel, I am convinced that most of this fuel is the result of vandalism of the well (i.e., dumping fuel in the well). This is not unheard of in our business.

Copies of Dr. Stoudt's memo are available if you need it.

August 23, 1996

4 gallons of SFR

To: Dave DeWitt

From: Scott A. Stout, Ph.D., R.G.

## CHARACTERIZATION OF FREE PRODUCT FROM UNOCAL SS#5043, OAKLAND, CA

### INTRODUCTION

At your request, the free product collected July 31, 1996 from a monitoring well (MW-6) at the Unocal service station (SS#5043) located in Oakland, California has been characterized. The sample was analyzed at Global Geochemistry Corp. (Canoga Park, CA) using; (1) high resolution gas chromatography (HRGC)<sup>1</sup>, (2) lead alkyls content and distribution and ethylene dibromide/ethylene dichloride analysis<sup>2</sup>, (3) oxygenate analysis using a GC via ASTM Method D4815, and (4) BTEX via EPA Method 8020. A split of the sample was also sent to Inchape Testing Services for determination of the sulfur content via ASTM D5453.

Approximately 3 feet of free product had accumulated in MW-6 at this site where there had been no previous product. Suspicions of a leaking UST system, in spite of new USTs and the station's use of a state-of-the-art TLS350 leak detection system, prompted immediate concern. The well was bailed free of product and a sample collected on July 31, 1996. No free product has returned to the well over the past three weeks. The lack of recurrence has now raised some suspicion that well tampering may have occurred.

The objective of the investigation was to describe the nature of the free product and to provide a basis for concluding whether or not it represented a recently released Unocal product(s).

### RESULTS and DISCUSSION

#### Nature of the Free Product

The HRGC fingerprint for the free product is shown in Fig. 1. The free product is shown to contain hydrocarbons (HC) ranging from C4 to C14, i.e., its comprised almost exclusively of gasoline range organics (GRO; C3-C10). Most compounds within this range are identified and their relative weight% are listed in Table 1. For comparison, Table 1 also contains data relating to three 1993

<sup>1</sup>HRGC analyses were performed on an HP 6890 GC containing a 0.25 mm x 100 m capillary column coated with 0.25 micron thick SPB-1 stationary phase and equipped with a FID detector (det. temp. 320 °C). The oven program used was from 35°C (5 min) at 3°C/min to 140°C (0 min) and then 8°C/min up to 315°C (40 min). The pressure program use was from 28.4 psig (0 min) then 0.5 psi/min to 78 psig. A 1 ml autosampler injection (inj. temp. 320 °C) with a split of 400:1 and air flow of 300 ml/min was used. Compound identifications are based on retention time comparisons to known standards and were regulated by the presence of three internal calibration standards.

<sup>2</sup>EDB, EDC and the five Pb alkyls (TML, TMEL, DMEL, MTEL, and TEL) are determined by direct injection GC-ECD (electron capture detector) using a 0.25 mm x 60 m DB-5 stationary phase (0.25 micron thick coating) capillary column. The oven program used was from 90°C to 186°C at 8°C/min. A 5 ppm (ug/ml) detection limit is achieved.

Unocal gasolines refined at our San Francisco Refinery (SFR). Unfortunately, data relating to more recently-refined normal or the even newer reformulated gasolines (RFG) from SFR have not been analyzed by this method.

The identified compounds within the GRO are dominated by iso-paraffins (39.3 %wt) and aromatic HC (38.4 %wt; Table 1). The relatively high percentage of both of these octane-boosting compound classes indicates that the GRO are undoubtedly derived from a blended gasoline.

The iso-alkanes include over 10% of iso-pentane (2-methylbutane) and significant amounts of 2- and 3-methylpentane (Table 1). In total, the C5-C6 iso-paraffins account for 23.3 wt% of sample. This abundance of C5-C6 iso-paraffins indicates that the parent gasoline(s) was probably refined using a C5-C6 isomerization unit. SFR has had an isomerization unit since mid to late 1987. Therefore, this criteria cannot be used to dismiss the possibility of an SFR gasoline's presence.

There is also 0.61 wt% iso-octane (aka 2,2,4-trimethylpentane; Table 1) which suggests that the parent(s) also included an alkylate blend produced from an alkylation unit. This amount of iso-octane far exceeds the trace amounts expected in the 1993 SFR gasolines (0.1-0.3 wt%; Table 1). This would argue for the presence of a non-SFR gasoline component. However, SFR has been blending alkylate from LAR into the premium unleaded gasoline since Oct. 1995. Therefore, on this basis alone it cannot be determined that there is no SFR gasoline present.

The aromatic HC include the BTEX compounds (only minor B) and numerous C3-alkylbenzenes (e.g., 1,3,5- and 1,2,4-trimethylbenzenes). These are common components of most gasolines and generally appear in distributions similar to those observed in the MW-6 sample. The slightly reduced concentration of benzene is probably the result of weathering via water-washing (see below). Additional considerations regarding the BTEX compounds are discussed below. The presence of BTEX and C3-alkylbenzenes in this distribution is indicative of a reformat blended into the gasolines. Reformers are commonly in most refineries, therefore, this is not useful in a forensic sense. (In fact, SFR employs two reformers).

The presence of a small amount of olefins (1.40 wt%; Table 1) indicates that the parent gasoline(s) was probably refined using an catalytic or thermal cracking process (and not hydrocracking). SFR gasolines have historically not contained more than 0.5 wt% olefins (Table 1) because of the use of a Unicracker since the early 1970's. However, since Oct. 1995 SFR has received a light CAT blending stock from LAR which has resulted in up to 5.0 wt% olefins in our unleaded gasolines. Therefore, on this basis alone it cannot be determined that there is no SFR gasoline present.

In summary, the molecular characteristics of the sample indicate that the parent gasoline's (or at least one component in a mixture of gasolines) blend included; (1) isomerate from a C5-C6 isomerization unit, (2) an alkylate from an alkylation unit, and (3) a catalytical blend from an FCC or thermal cracker. Given the refining history described in the proceeding paragraphs it is not possible to determine that there is no SFR-refined (or blended) gasoline present in the sample. All that can be said is that if the parent gasoline is entirely a Unocal SFR product then it must be no older than October 1995.

### Aromatic Hydrocarbon Results

The results of the EPA Method 8020 analysis are given in Table 2. The separate BTEX analysis (EPA 8020) indicated that the free product contained 6280 ug/ml of benzene which corresponds

**Table 2: BTEX results for the MW-6 free product studied.**

µg/ml	Benzene	Toluene	Ethyl benzene	Xylenes	Total
MW-6	6290	49600	14500	73800	144190
MW-6 dupl.	6270	50000	15500	74200	145970
Average	6280	49800	15000	74000	145080
detection limit	5	5	5	5	

to 0.71 %vol benzene. Benzene content of reformulated gasoline (RFG) have been limited to <1.0 %vol since March 1995. Prior to this time there were no limits on the benzene content of gasolines sold in California (which typically ran 2-3 %vol). On this basis it cannot be determined for sure whether or not the free product is a pre- or post-RFG gasoline. The reason for this uncertainty is the potential for benzene to have been removed from the free product due to preferential weathering. (Of course, if the benzene content of the free product had been > 1 %vol then it could be safely concluded that a pre-RFG gasoline was present).

The ratio of B/T (0.13) is relatively low for most brands of fresh gasolines. However, SFR's high octane gasoline have typically been enriched in toluene due to the use of a significant reformat blending component to maintain octane. Therefore, the low B/T ratio in the free product could be indicating that (1) some benzene has been preferentially removed via water-washing or (2) the gasoline was refined with excess toluene (as was the case in pre-RFG SFR gasolines). Other BTEX-based ratios indicate other similarities with pre-RFG SFR gasolines. For example the T/BTEX (0.34) and T/X (0.67) ratios are consistent with previously studied 1993 (pre-RFG) SFR gasolines (Table 1). Therefore, **on the basis of the BTEX results there is no argument to be made against the free product being a pre-March 1995 SFR gasoline.**

### Oxygenate Analysis

Results of the ASTM D4815 analysis are given in Table 3. The sample was shown to contain no oxygenated compounds (alcohols and ethers) other than TAME (2-methyl-2-methoxybutane).

**Table 3: Results of the Oxygenate Analysis on MW-6 Free Product.**

µg/ml (ppm)	Methanol	Ethanol	tert-Butanol	MTBE	ETBE	TAME
<b>MW-6</b>	nd	nd	nd	nd	nd	915
<b>MW-6 duplicate</b>	nd	nd	nd	nd	nd	905
<b>detection limit</b>	200	200	200	200	200	200

MTBE - methyl tert-butyl ether

ETBE - ethyl tert-butyl ether

TAME - tert-amyl methyl ether; this result was double-checked by co-injection of a TAME standa

On average the sample contained 910.5 µg/ml of TAME.<sup>3</sup> This corresponds to about 0.12 wt% TAME, or only 0.019 wt% oxygen. RFG refined in California since March 1995 have been required to contain between 1.8 and 2.2 wt% oxygen. Therefore, this free product contains only about 1% of the required amount of oxygen for new reformulated gasolines. TAME is far less soluble in groundwater than MTBE (6000 vs. 43,000 mg/L @20°C) and therefore its concentration in the sample is not expected to have been significantly reduced due to water-washing. This suggests that **the TAME-containing gasoline component present in the sample is probably only a fraction (1% ?) of the total free product.**

TAME has never been intentionally added to gasolines refined at SFR; only perhaps as a contaminant in an MTBE blend. However, since MTBE is absent from this sample it is safe to assume that **the TAME-containing component of the free product was not an SFR gasoline.** Unfortunately, the small amount of TAME argues that this non-Unocal component is only a minor component of the free product. Because TAME has a lower blending ((R+M)/2) octane number (105 vs. 110) and a lower mass% oxygen (15.7% vs. 18.2%), it is far less commonly used than MTBE. This characteristic may help to identify a Bay Area source(s) of the TAME-containing component in the free product. Unfortunately, the available oxygenate unit construction records (Oil and Gas Journal's annual update) indicate that there are no West Coast refiners that are producing TAME.

#### *Sulfur Analysis*

Prior to RFG limits implemented in March 1995, the sulfur content of gasolines sold in California was limited to <300 ppm. Since March 1995 the maximum allowable S content was reduced to 40 ppm. It was determined that the MW-6 free product sample contained 108 ppm sulfur. **The high S content argues that the free product must (at least) contain a pre-March 1995 gasoline.**

Gasolines refined at SFR had historically contained very low S (<1 ppm) due to use of the fixed-bed hydrotreater (which tends to remove sulfur as H<sub>2</sub>S and thereby protect the catalysts used in the Unicracker, two reformers and isomerization units). Since early 1995, the S content of SFR gasolines was increased to between 10-30 ppm S (average ~12.5 ppm) when a light CAT blending component was initially imported from LAR. (This light CAT contains higher S due to LAR's use of an FCC unit in which sulfur is not removed as effectively due to its fluid-bed nature). **The historically low values of S in SFR gasolines argues that the pre-March 1995 gasoline component in the free product (with its 108 ppm) is not an SFR gasoline.** Of course, the presence of a low sulfur SFR gasoline component cannot be dismissed since the possibility of mixing exist.

#### Lead Alkyl Results

The results of the lead alkyl analysis is given in Table 4. This table shows that the MW-6 free product contained all five Pb alkyls in an abundance totaling 0.679 grams Pb per gallon (gpg).

**Table 4: Results of the lead alkyl analysis of MW-6 free product.**

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<sup>3</sup>TAME is one of several oxygenates available to be added to gasolines (at volumes up to 20%) to boost octane while minimizing ozone-harmful emissions. It is produced from a C5 olefin stream reacted with ethanol (MTBE is produced from a C4 olefin stream reacted with ethanol). TAME's advantage is its lower vapor pressure (compared to MTBE) which allows more butane to be added and still maintain vapor pressure requirements.

	wt. %	MW-6 (average)			% Standard Reacted Mixes			Other Mixes		Theoretical Mix:
	lead	µg/mL	%	glpg	RM25	RM50	RM75	TEL only	PM80	10:25:55:10 RM25:TEL:PM80: RM50
TEL	0.640582	101.5	40.0	0.25	28.8	4.8	0.1	100	20	39.4
MTEL	0.669629	24.0	9.4	0.06	49.5	25.6	3.6	0	0	7.5
DEDML	0.701435	8.0	3.1	0.02	18.6	42.4	20.5	0	0	6.1
TMEL	0.736388	10.5	4.1	0.03	3.0	23.4	49.6	0	0	2.6
TML	0.775035	110.0	43.3	0.32	0.1	3.8	26.2	0	80	44.4
TOTAL		254	100	0.679						

This concentration of Pb is typical of leaded gasolines refined in the early to mid-1980's when the EPA mandated Pb maximum was reduced from 1.1 to 0.5 glpg. Since there is only a small amount of oxygenates (TAME) present, there is no reason to call upon a significant unleaded gasoline component to be present in this sample. Therefore, there is no reason to believe that there is a mixture of a leaded gasoline with an unleaded gasoline, resulting in the reported glpg value. **This supports an early-to-mid 1980's age for the free product's parent gasoline.**

Corporate records indicate that SFR had used specific Pb alkyl packages through time. Between 1975 and 1985 SFR used a reacted mix, RM50, in both the regular and premium leaded gasolines. As can be seen in Table 4, the mixture of lead alkyls in an RM50 lead package is very different from that found in the MW-6 free product. **This makes it highly unlikely that the free product was derived from a leaded gasoline refined at SFR in the early 1980's.**

In fact the Pb alkyl distribution in the free product does not resemble any single Pb package available for gasoline blending. Therefore, **a mixture of leaded gasolines each containing different lead packages must be present.** One can ask whether or not it is possible to derive the observed mixture in the free product from any of the lead packages used over time at SFR.<sup>4</sup> In theory, it would require a minimum of a 4-component blend to achieve a Pb alkyl distribution comparable to that observed in the free product. This is reflected in the theoretical mixture listed in Table 4. Such a mixture, if composed only of SFR gasolines, would require mixing of leaded gasolines over the minimum time period of 1975 to 1985. While this may be possible it appears to me as being extremely remote.

#### Degree of Weathering

The free product contains an abundance of light (<C5) components. This indicates that the original release had probably occurred below ground thereby minimizing evaporative losses. The gasoline component does exhibit some indications of weathering due to water-washing. This is reflected in the low proportion of toluene relative to xylenes. Toluene is typically present in near equal abundance to xylenes in fresh regular gasolines (T/X~0.6-1.0). (In premium gasolines the T/X ratio can be as high as 4.8). However, because toluene is more water soluble than the xylenes, it is preferentially removed upon exposure to groundwater. This free product appears to have lost toluene due to water-washing (T/X ~ 0.4; Table 1). Benzene is even more soluble and the presence of a small amount of benzene (0.07 %vol of GRO; Table 1) indicates that water-washing is not complete. In my experience, **I would consider this gasoline to be moderately water-washed.**

<sup>4</sup>The other lead packages that have been used at various times at SFR include a physical mix of 80% TML and 20% TEL (1963-1975 premium gasolines), TEL-only (1963-1975 regular gasolines), and RM25 (1985-1986 premium gasoline; no regular leaded gasoline was produced at this time). After 1986 there was no leaded gasoline produced at SFR.

The process of biodegradation typically accompanies water-washing. The most susceptible compounds to biodegradation are the n-alkanes and olefins. This sample contains only slightly reduced quantities of both of these compound classes as compared to fresh gasolines. This indicates that **the gasoline component of this free product is only slightly biodegraded.**

Given the limited data and the necessarily relative nature of the weathering 'data', it would be imprudent to try and assign an absolute age to the free product. Given my experience, however, I **would hesitate to call the gasoline component fresh** due to the slight to moderate weathering observed. I cannot be as definitive for the diesel fuel component since its nature is rather typical.

#### Origin of the Gasoline and Diesel Components

The prominence of 2,2,4-trimethylpentane or iso-octane (??? %vol of GRO) strongly suggests that an alkylate blending stock was among the blending components used in the parent gasoline. Unocal's San Francisco refinery (SFR) does not have an alkylation unit and therefore, our gasolines are typically reduced in isoparaffins (particularly, isopentane). However, beginning in October 1995 alkylate was piped to SFR from Unocal's Los Angeles refinery for blending with SFR gasolines. Therefore, the presence of iso-octane (and other isoparaffins) in this sample could indicate the presence of either (1) a non-Unocal gasoline or (2) a post-Oct. 1995 Unocal gasoline.

The presence of 1.65 %vol olefins in the gasoline range is more informative since SFR gasolines are typically reduced in olefins (< 0.5 %vol). This characteristic arises from the fact that we employ a hydrocracking unit (rather than an catalytic cracking unit). Hydrocracking produces an isomaxate gasoline blending component with little or no olefins. The presence of 1.65 %vol olefins argues strongly that **the gasoline component of this free product is not a Unocal refined gasoline.**

The nature of the diesel fuel is less descriptive as to its origin. The pristane/phytane (Pr/Ph) ratio of the diesel fuel (1.84; Table 1) should reflect that of its parent crude oil. SFR runs primarily Cook Inlet crudes for diesel fuel #2 production. Undegraded Cook Inlet crudes have Pr/Ph ratios between in the range 2.0 to 3.5 (B. Bromley, personal communication, 1994). The slightly lower Pr/Ph ratio of the free product's diesel fuel component suggests that the parent crude oil was probably not from the Cook Inlet. This conclusion is further substantiated by the high Pr/nC17, given the Ph/nC18 ratio.<sup>5</sup>

## **CONCLUSIONS**

The free product which accumulated in MW-6 at Unocal service station #5043 was analyzed by a variety of techniques. The primary objective of the study was to determine whether or not the sample consisted a recently-refined Unocal gasoline. The answer to this question is no; the free product is not a recently released gasoline refined at Unocal's San Francisco refinery. The basis for this conclusion is:

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<sup>5</sup>The basis for this statement is that Cook Inlet crude oils tend to fall along a single trend when the Ph/nC18 and Pr/nC17 ratios are cross-plotted. This trend line represents different degrees of biodegradation that had occurred in the original oil field reservoir. These ratios for the free product sample fall well off of the Cook Inlet trend indicating that the parent crude oil for this diesel fuel was probably not a Cook Inlet crude oil.

- (1) the free product contains a significant amount of lead and SFR has not produced leaded gasolines since 1986,
- (2) the free product contains sulfur well above the reformulated gasoline (RFG) maximum which SFR began producing in March 1995, and
- (3) the free product doesn't contain MTBE as would be expected in recently-refined SFR gasolines.

These results clearly indicate that the free product is not a recently refined SFR gasoline. However, the MW-6 free product exhibits a diverse set of characteristics which, in my opinion, argues that it represents a mixture of gasolines. Thus the question shifts as to whether or not the MW-6 free product contains a recently-refined SFR gasoline as one of its components.

The presence of lead indicates that at least one of the components in the mixture must be a leaded gasoline. The peculiar lead alkyl distribution (Table 2) actually argues for a mixture of leaded gasolines being present. Therefore, while the lead content (0.679 g/lpg) argues for an early-to-mid 1980's age, the fact that the free product is a mixture means that all that can be said for sure is that there must be a leaded gasoline component that is from 1985 or earlier present. Based on the lead alkyl packages used at SFR in the 1970's and 80's, it would have been possible, though highly unlikely, to obtain mixture consistent with the MW-6 free product. This argues for the presence of someone else's leaded gasolines being present.

The presence of a small amount of TAME argues that there may be a more recent unleaded component also present in the mixture. Based on the low concentration of TAME (and absence of other oxygenates) this would seem to be a very small component (1% ?) in the mixture. Furthermore since SFR has never used TAME, it certainly could not be an SFR unleaded gasoline.

Based on the molecular characteristics at least one of the components included blends from; (1) a C5-C6 isomerization unit, (2) an alkylation unit, and (3) an FCC or thermal cracker. All three of these blending stocks have been available at SFR since Oct. 1995 (when the latter two stocks were first piped up from LAR). Since a mixture is known to exist, the refining characteristics alone do not argue against the potential for an SFR gasoline being among the components.

The high sulfur content (108 ppm) argued for a pre-March 1995 gasoline (see above). However, the historically low values of S in SFR gasolines argues that the pre-March 1995 gasoline component in the free product (with its 108 ppm) is not an SFR gasoline.

The gasoline mixture appears to be only moderately water-washed and slightly biodegraded. This alone would argue for it being a relatively 'fresh' gasoline, however, there is too much evidence that a significant portion of the product is historic (pre-1985). This discrepancy may be explained by the occurrence of a large pool in which the gasoline has not biodegraded over time. This seems highly unlikely given the non-recurrence of free product in the weeks following well purging.

Obviously, a definitive answer to the origin of the MW-6 product is elusive. It can be confidently stated that the product is not exclusively a recently-refined SFR gasoline. The origin remains unclear but is certainly worthy of considering the possibility of off-site (3rd party) sources and closely watching any additional appearances of free product in the area.

If you have any questions concerning these conclusions please call me (at 714-577-1296 or at network 268-1296).

FIGURE 1: HRGC FINGERPRINT OF MW-6  
FREE PRODUCT FROM SS# 5043 (Collected  
July 31, 1996).