Memorandum

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Brea, California

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TO: **Bob Boust**

FROM: **Robert Haddad**

GEOCHEMICAL COMPARISON OF FREE PRODUCT SAMPLE FROM MW-2 AND FRESH "SEAL KOTE", SERVICE STATION # 7376, PLEASANTON, CA

SUMMARY

A simple comparison of the two HRGC traces (Figs. 1A and 1B) clearly indicates that the MW-2 free product is not solely derived from the Seal Kote mixture. This conclusion is supported by the results of the simulated distillation which indicate a very narrow boiling point range for the Seal Kote product and a fairly wide range for the MW-2 free product.

Taken together, these results can be used to make the following conclusions:

(1) The MW-2 product **contains a wide range of weathered hydrocarbons**, including a minor amount of gasoline.
(2) These hydrocarbons are **not derived** from the Seal Kote product.
(3) The amount of Seal Kote product in the MW-2 free product (if any) is unknown.
(4) If desired, we can determine (1) if any Seal Kote is present (in addition to the other hydrocarbons in the MW-2 mixture) and (2) the relative amounts of any Seal Kote present in the MW-2 free product mixture.

INTRODUCTION

At your request, samples of a tar-like free product obtained from MW-2 at SS # 7376 and Seal Kote asphalt sealant where comparatively analyzed using high resolution gas chromatography (HRGC) and simulated distillation (ASTM 2887). Because the free product was found in MW-2 shortly following the application of the Seal Kote product at this station, these analyses were undertaken to test the hypothesis that the Seal Kote product had seeped into the monitoring well.

Based on the results presented and discussed below, it's clear that the MW-2 free product contains a broad range of petroleum hydrocarbons including those present in the Seal Kote

product. Given the hydrocarbon distribution presented in the gas chromatogram fingerprints, it is concluded that the free product has a composition consistent with that of a weathered crude oil and is not simply derived from the Seal Kote mixture.

RESULTS AND DISCUSSION

Samples of (1) free product collected from MW-2 and (2) an asphalt sealant product labeled "Seal Kote from vendors batch tank" were submitted to Unocal's Trace Organic Geochemistry Laboratory for analysis. Samples were analyzed for hydrocarbon distribution using high resolution gas chromatography (a technique used for whole oil analyses - Whole-oil HRGC) and simulated distillation (ASTM method 2887). The simulated distillation technique was developed to evaluate hydrocarbon mixtures based on boiling points of the compounds in the mixture.

The gas chromatograms from the whole-oil HRGC analyses are presented for comparative purposes in Figure 1A for the MW-2 free product and Figure 1B for the Seal Kote mixture. A casual evaluation of these two GC traces quickly illustrates that the two products are not identical. In fact, the most significant difference is that the Seal Kote had a very low extractable hydrocarbon content while the MW-2 had extractable hydrocarbons ranging from nC4 out to nC35.

MW-2 Free Product

The MW-2 free product (Fig. 1A) contains compounds ranging from butane (nC4) to nC38-nC40. A close evaluation of the hydrocarbon distribution in this figure illustrates the following:

(1) There is a minor gasoline range component (nC4-nC10) containing many of the hydrocarbon compounds found in refined gasoline. This fraction is dominated by branched and cyclic compounds and appears to contain 2, 2, 4-trimethylpentane (iso-octane). This compound is most often associated with a refined gasoline source and would appear to indicate the presence of refined gasoline in the MW-2 mixture. If desired, further analysis (specifically a high resolution finished gasoline analysis) of the free product could provide more definitive information regarding the origin of this fraction.

(2) The material in the diesel range (nC10-nC25) does not have the appearance of a typical diesel fuel product. Diesel fuel usually ranges from nC9 to approx. nC25 with a large unresolved complex mixture (UCM or "hump") exhibiting a mode or mid-point somewhere in the nC15-nC17 range. In fresh diesel fuel, normal alkanes and isoprenoids are usually present as discrete peaks above the hump. As biodegradation occurs, the normal alkanes are preferentially degraded leaving the isoprenoid peaks as the most significantly resolved peaks on the hump.

Unlike typical diesel fuel chromatograms, the MW-2 free product has a hump which extends from nC9 to about nC35 and, in general, has a maximum at about nC20. This represents an extreme shift in a normal diesel fuel hump. In addition, a close examination of the HRGC data (Fig. 2) indicates that the normal alkanes are not resolvable while the isoprenoids are still present. Taken together, the presence of the isoprenoids and the shift in the hump maxima suggest that this distribution is not simply derived from a weathered diesel fuel.

The minor secondary maxima located in the nC29 range is most likely due to the presence of complex, multi-ring hydrocarbons such as steranes and hopanes. These compounds are commonly called biomarkers and are not found in diesel fuels. They may be the result of heavier fuel oils in the mixture. While improbable, the distribution of the nC10-nC35 fraction of MW-2 is very similar to what one might see in a highly weathered crude oil.

Seal Kote Product

The HRGC analysis of the Seal Kote mixture (Fig. 1B) indicates that very little of this viscous material was extracted in the normal hydrocarbon extraction procedure used in our laboratory. The most likely explanation for this is the specific nature of the composition of the Seal Kote mixture. My guess is that the mixture is composed of hydrocarbons containing functionalized groups (such as alcohols, esters, and ethers) and that the increased polarity of the mixture prevents it from solubilizing in the non-polar solvents commonly used in hydrocarbon analyses.

Both samples were further analyzed using the ASTM 2887 Simulated Distillation procedure. In this GC analysis, the boiling point distribution of the mixture is determined and plotted as a function of the amount of material (in wt%) in the mixture which boils at a specific temperature. In addition to the boiling point distribution plot, a GC trace of the mixture is also available for evaluation. The GC trace for the Simulated Distillation of the MW-2 free product is presented in Figure 3A. A quick comparison of this GC trace with the HRGC trace discussed above (Fig. 1A) shows similar patterns. For example, the gasoline range components discussed above are evident in the front end of the Figure 3A GC trace. The nC10-nC35 distribution, including the bimodality, is also evident in this figure.

Because the Seal Kote mixture was not extractable by normal solvents, we used a more polar compound (Acetone) as a solvent. Figure 3B illustrates the Simulated Distillation GC trace for the acetone extractable component of the Seal Kote mixture. Compared to the MW-2 sample (Fig. 3A), the material in the Seal Kote mixture has a fairly narrow carbon chain distribution (mode about nC35-nC40).

Figure 4 is a plot of the distillation curve for both the MW-2 free product and the Seal Kote sample. As suggested by the GC analyses, there is a wide boiling point distribution for the MW-2 free product sample. In fact, based on the Simulated Distillation analysis, 80 wt% of the

mixture boils between 550 F and 917. As might be expected from the narrow distribution of product in Fig. 3B, the Seal Kote mixture has a much more narrow boiling point distribution. For this product, 80 wt% of the mixture boils between 849 F and 1059 F.

To some degree this is a comparison of apples and oranges. This is due to the fact that different solvents were used to extract the samples. Based on these results we can say that the MW-2 free product contains a wide range of hydrocarbons which are extractable in solvents commonly used in environmental analyses. Similarly, we can state that the Seal Kote product does not contain significant amounts of these compounds.

Because the MW-2 sample was not extracted with acetone, it is impossible to estimate the amount of Seal Kote (if any) present in the MW-2 free product mixture. If it decided that this is an important piece of information, we can perform this type of extraction and submit the extract for HRGC analysis. A comparison of the acetone extract should provide a qualitative estimate of the amount of Seal Kote (if any) in the MW-2 free product.

CONCLUSIONS

A simple comparison of the two HRGC traces (Figs. 1A and 1B) clearly indicates that the MW-2 free product is not solely derived from the Seal Kote mixture. This conclusion is supported by the results of the simulated distillation which indicate a very narrow boiling point range for the Seal Kote product and a fairly wide range for the MW-2 free product.

Taken together, these results can be used to make the following conclusions:

(1) The MW-2 product **contains a wide range of weathered hydrocarbons**, including a minor amount of gasoline.

(2) These hydrocarbons are **not derived** from the Seal Kote product.

(3) The amount of Seal Kote product in the MW-2 free product (if any) is unknown.

(4) If desired, we can determine (1) if any Seal Kote is present (in addition to the other hydrocarbons in the MW-2 mixture) and (2) the relative amounts of any Seal Kote present in the MW-2 free product mixture.

RIH/cs

xc: R. E. Bock
B. J. Kelly
G. T. Ririe
P. C. Stern

Fig 1A

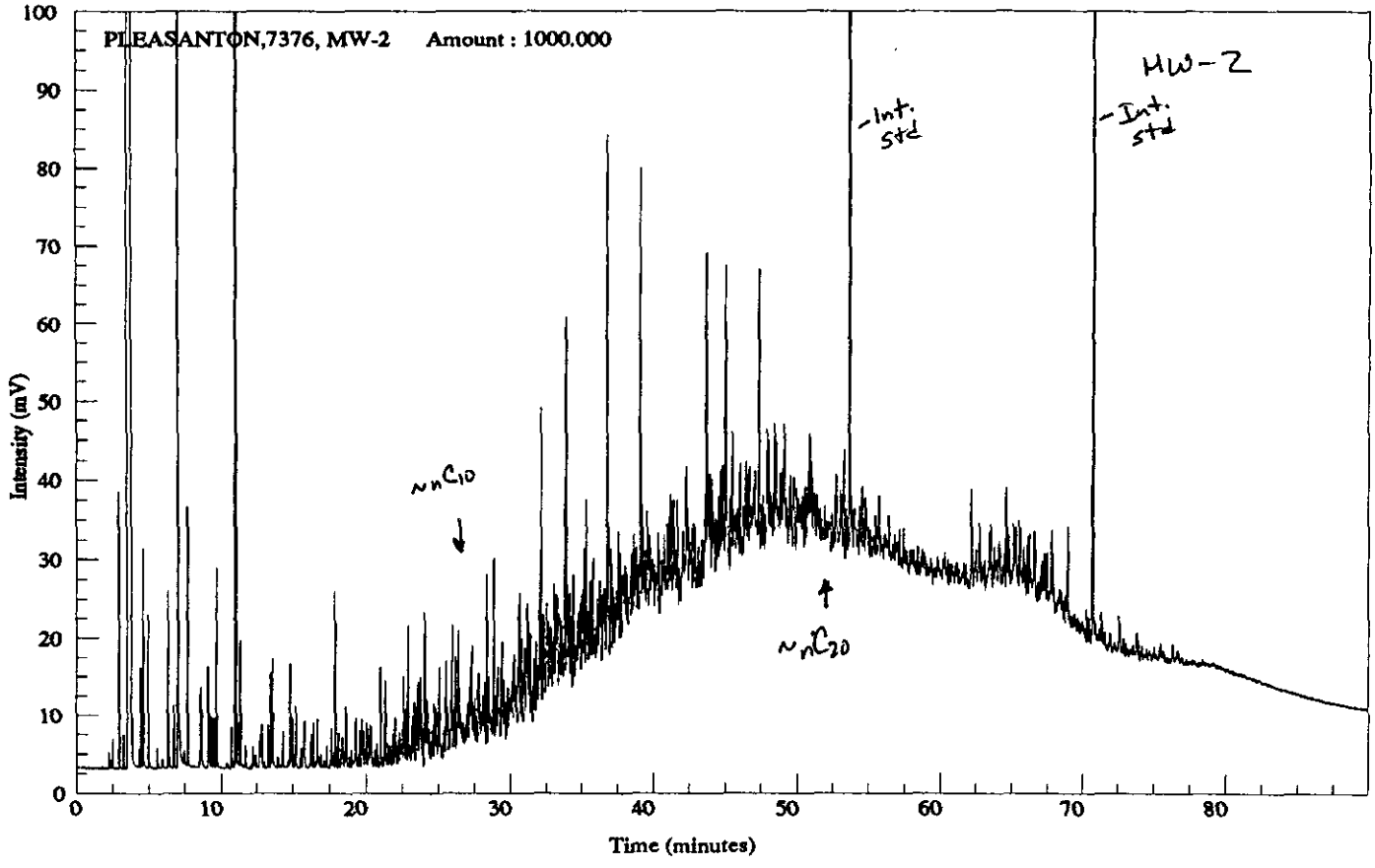

PLEASANTON,7376, MW-2 Amount : 1000.000
MW-2
-Int. std
-Int. std
~nC10
~nC30
Intensity (mV)
Time (minutes)

Fig. 1B

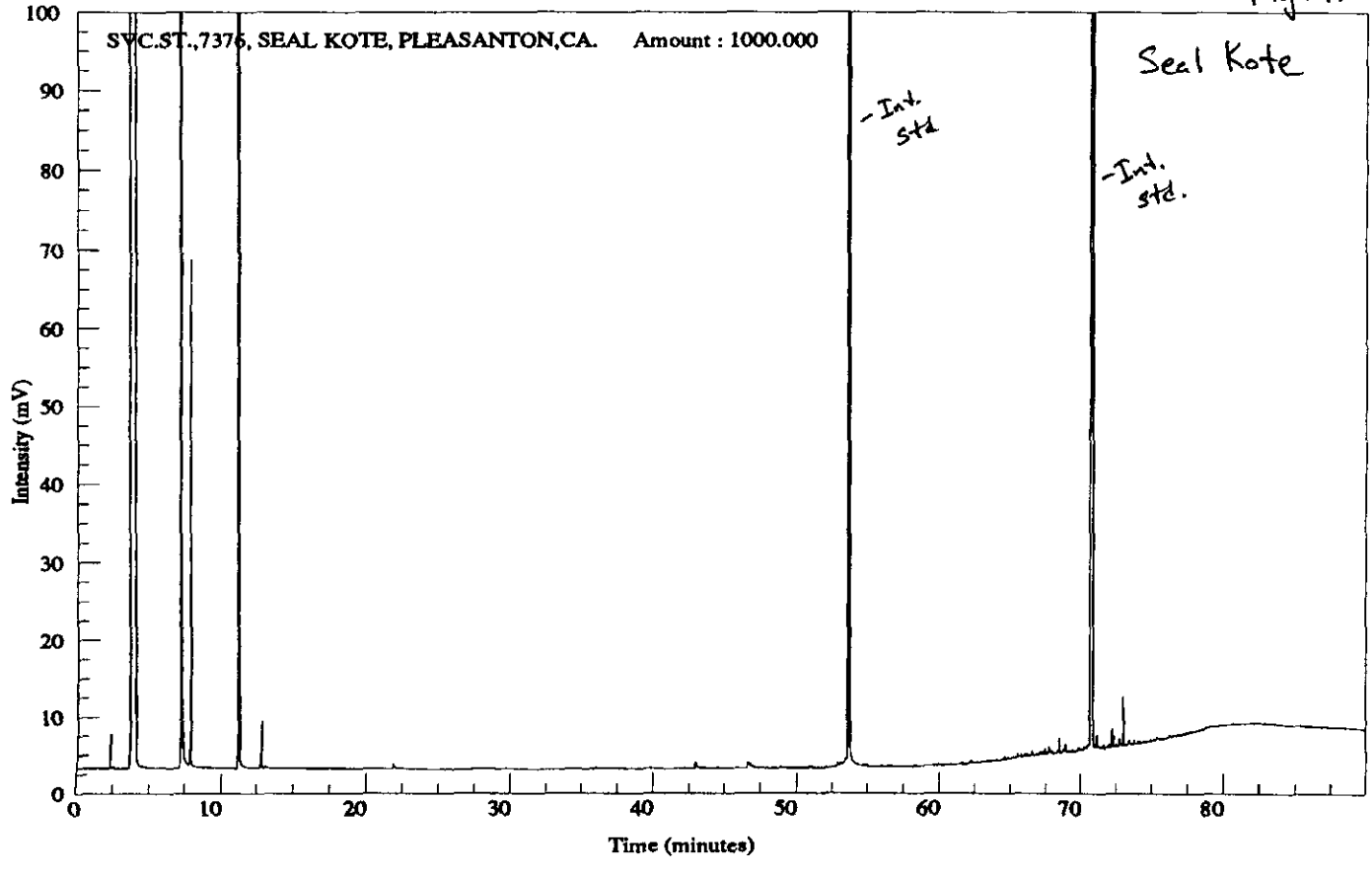

SVC.ST.,7376, SEAL KOTE, PLEASANTON,CA. Amount : 1000.000
Seal Kote
-Int. std
-Int. std.
Intensity (mV)
Time (minutes)

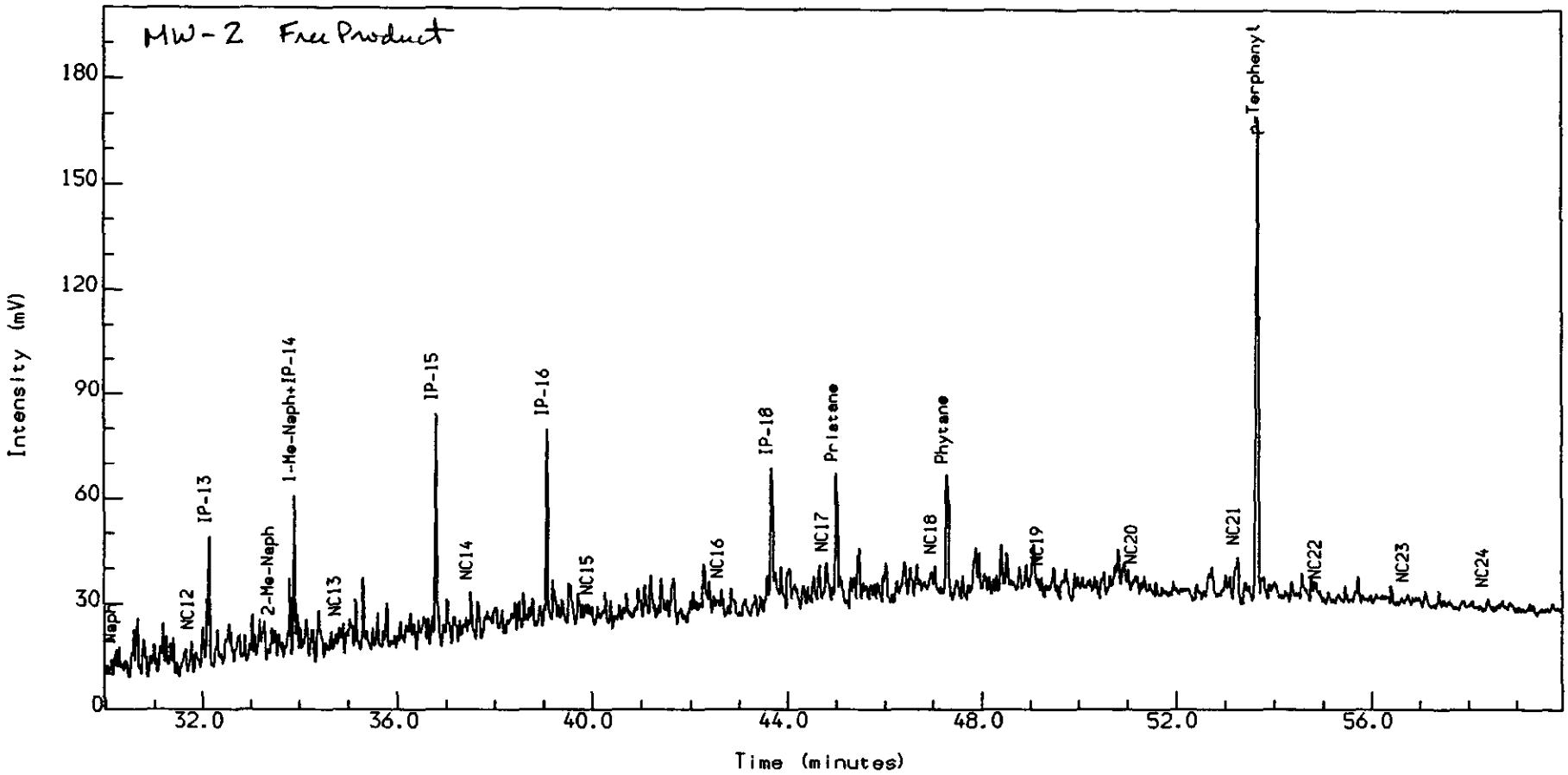
Fig. 2

Unocal Petroleum Geochemistry Group (SCSVAX)

Analysis Name : [METHDEV] 3 MW-2,1,1.

PLEASANTON,7376, MW-2 Amount : 1000.000

Multichrom



Instrument : HP5890

Channel Title : Whole Oil/Ext (FID)

Lims ID :

Acquired on 24-JAN-1995 at 10:24

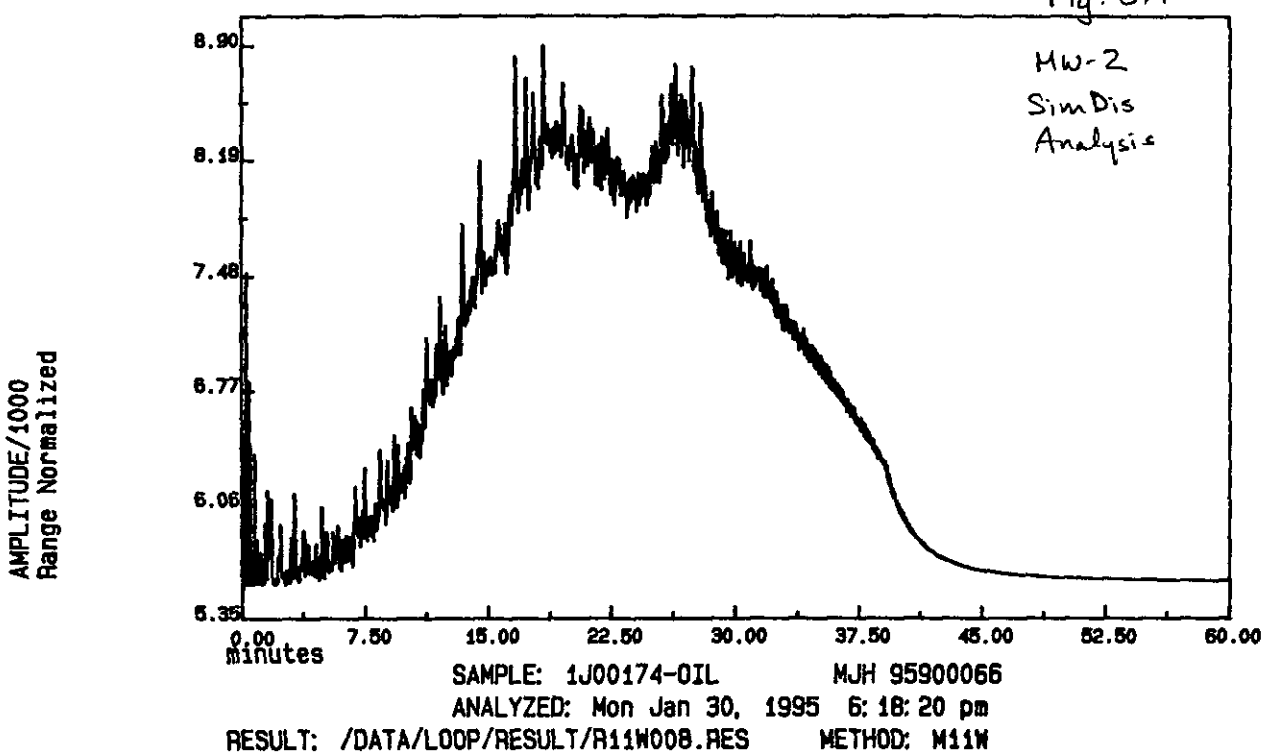
Reported on 24-JAN-1995 at 11:55

Method : OILVV

Calibration : 09DEC94

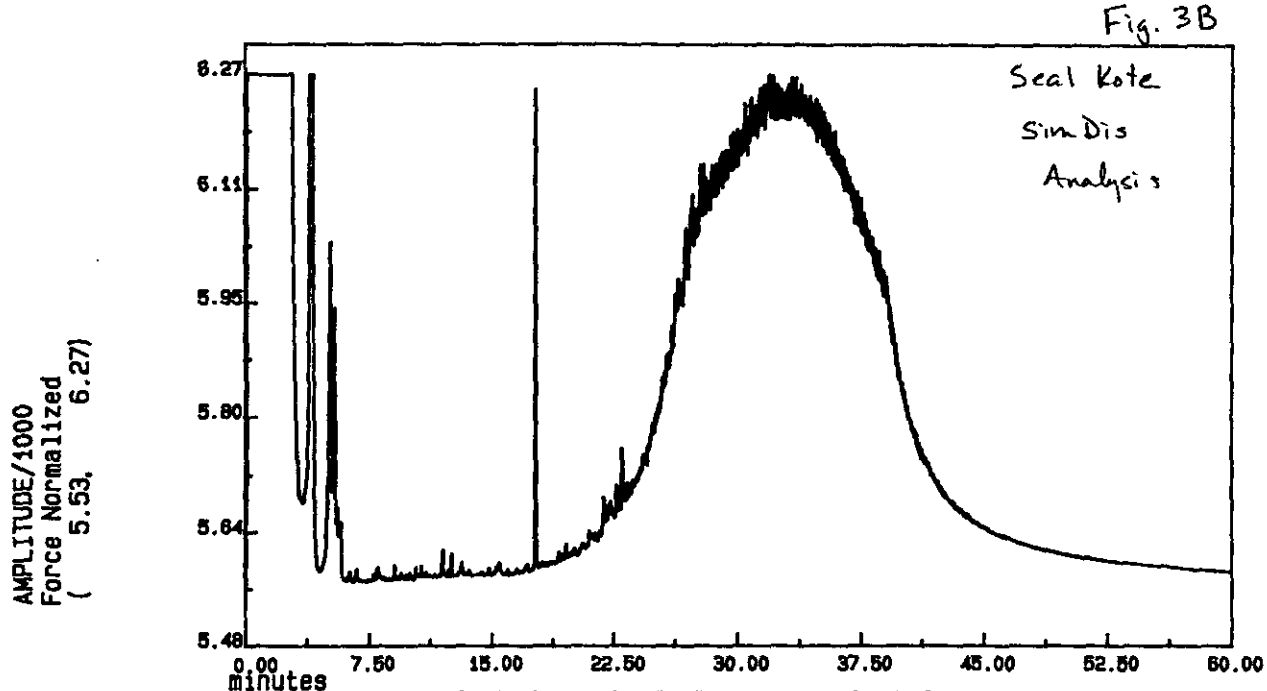
Run Sequence : OIL1

Fig. 3A



SAMPLE: 1J00174-OIL MJH 95900066
ANALYZED: Mon Jan 30, 1995 6:18:20 pm
RESULT: /DATA/LOOP/RESULT/R11W008.RES METHOD: M11W

Fig. 3B



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Simulated Distillation Results (ASTM 2887)

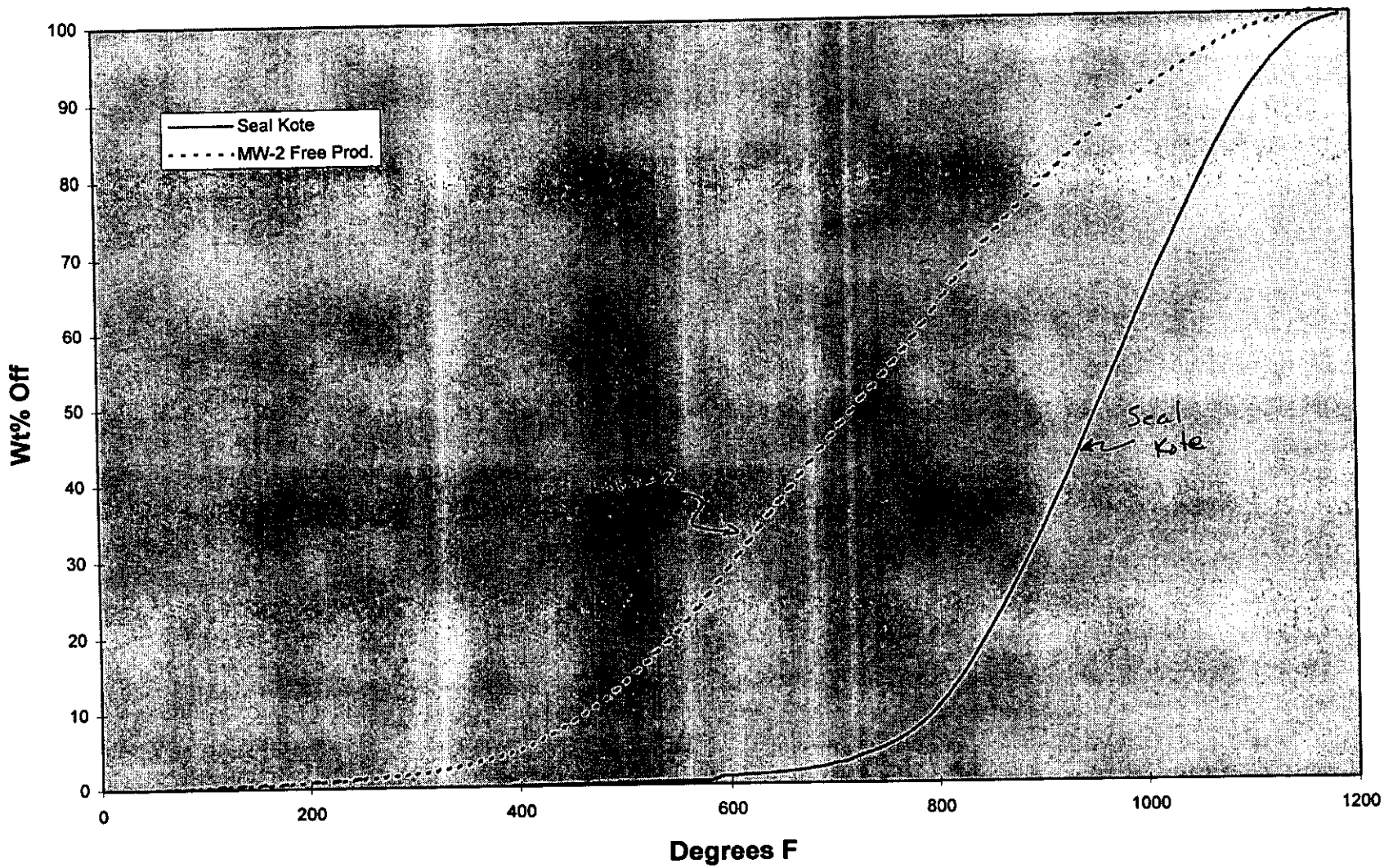

Figure 4

Fig. 4