

Determination of Liquid and Solid Phase Composition in Partially
Frozen Middle Distillate Fuels

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INTRODUCTION

One of the tasks of the United States Navy Mobility Fuels program at the Naval Research Laboratory is to determine the effect of composition on the freezing properties of liquid fuels (1,2). The combination of requirements for ship and jet aircraft fuels of a low freezing point (to permit cold temperature operations around the world) and a flash point minimum (to reduce the hazard of storage and transport of liquid fuels on board ship) leads to opposing compositional needs. This is because many components of a fuel that tend to lower the freezing point (small hydrocarbons with higher vapor pressures) will also reduce the flash point. Because of these constraints, it is not always practical to produce fuels meeting these requirements from available crudes. This limits the amount of crudes and hence the amount of JP-5, the Navy fuel for carrier based aircraft, which can be produced from "a barrel of crude." With increased knowledge and understanding of the components that first crystallize out of a cold fuel, it may be possible to modify refining techniques to increase the yield of Navy liquid fuels per barrel of crude without compromising either the freezing point or the flash point restrictions.

Part of this task was a study of partially frozen fuels, in particular, to isolate and characterize the "precipitate" (solid crystals plus entrapped liquid) which can cause aircraft fuel-tank holdup, filter plugging, and related jet aircraft engine problems at low temperature operation. In order to accomplish this, the liquid "filtrate" had to be separated from the precipitate and a quantitative analysis made of several components (especially the normal alkanes) in the original fuel and in both fractions. The importance of the saturated hydrocarbon fraction, particularly the higher normal alkanes, in raising the freezing points of hydrocarbon fuels had been suggested by Dimitroff et al. (3-5); Petrovic and Vitorovic (6); Solash et al. (2); and others.

This paper deals with the method used to separate the liquid filtrate from the precipitate in fuels cooled to predetermined temperatures below their freezing points, the method of analyzing the fuel and fuel fractions, and the results obtained from a study of one particular jet fuel.

The fuel used to test the method was a shale-derived fuel (NRL No. J-22) from the Shale-II refining process conducted by the Standard Oil Company of Ohio (SOHIO) at their refinery at Toledo, Ohio (7-9). This fuel met the military specification requirements for Navy JP-5 jet turbine fuel (10); its actual freezing point of -48°C (11) was below the specification maximum requirement (10) of -46°C . This fuel, referred to hereafter as J-22, was chosen because the normal alkane concentrations in shale-derived fuels are considerably greater than those in petroleum-derived fuels (8). Table 1 lists the concentrations of the n-alkanes present in measurable amounts in the J-22 fuel.

TABLE 1. n-Alkane Concentrations in Filtrate of Fuel J-22
JP-5 Shale II, as a Function of Temperature

		Normalized Concentrations (X_F')*						
		°C						
Fuel		Sample, X_0						
°C		-57.5	-55.3	-53.6	-51.4	-48.5	-48**	
<u>n-Alkane</u>								
C ₁₀	4.50	1.04	1.03	1.01	1.00	0.98	0.97	
C ₁₁	8.55	0.94	0.96	0.97	0.98	0.97	0.98	
C ₁₂	7.10	0.71	0.77	0.83	0.91	0.95	0.99	
C ₁₃	4.41	0.47	0.56	0.67	0.83	0.92	1.00	
C ₁₄	1.36	0.42	0.51	0.57	0.70	0.91	0.94	
C ₁₅	0.35	0.43	0.54	0.66	0.83	0.97	0.97	

*Normalized data = concentration divided by concentration in original sample

**Data extrapolated to freezing point (-48°C)

ISOLATION OF PRECIPITATE FROM FILTRATE

A glass apparatus constructed for the isolation of the partially frozen precipitate is shown in Figure 1. The design was based on the fractional crystallization device used by Pitzer and Scott (12) and is similar to that of Dimitroff et al (5), at the U. S. Army Fuels and Lubricants Laboratory. It is referred to as a "Liquid-Solid separator" (LSS), as it was called by Dimitroff.

The LSS consisted of four components, A, B, C, and D, which were attached together by means of O-ring joints with clamps. Glass-metal joints connected the LSS to copper coils immersed in the bath, which carried dried nitrogen gas from the flow meters. The assembled LSS was immersed in a refrigerated and stirred methanol bath in a large clear-glass Dewar flask. Dry ice was added to the methanol to help cool the system rapidly to the freezing point of the fuel, at which time the fuel was added. A weighed sample of fuel (about 8 grams) was introduced through the open stopcock J by a hypodermic syringe with a long needle. A temperature controller then cooled the system to the desired temperature and maintained it to within $\pm 0.1^\circ\text{C}$ during crystallization and filtration. A very slow stream of nitrogen flowing through stopcock K (stopcocks I and L being closed), bubbling up through the fritted glass disc H and out through stopcock J prevented any liquid fuel from flowing down through the disc before and during crystallization. Approximately 20 minutes were allowed at the desired temperature for crystallization to be completed.

Stopcocks J and K were then closed, and L and I opened to allow a slow stream of nitrogen under pressure (up to 15 psig) through L to force the liquid filtrate through the fritted glass disc, and down the funnel M and into the preweighed filtrate cup D. Entrapped liquid was forced out of the precipitate by stirring and tamping. To carry this out, dome B was removed and the gelatinous precipitate stirred and pressed with a glass rod having a flattened end. The rod was either kept in the apparatus during the entire freezing process or cooled in dry ice just prior to insertion. In this way the precipitate was spread more evenly over the fritted glass disc, eliminating channels through which the nitrogen could pass. Attempts to compress the precipitate by the rod and thus force the liquid through the disc were unsuccessful. After stirring, dome B was replaced by a plain dome without a stopcock, B', and further filtering allowed to take place under nitrogen pressure. The plain dome eliminated nitrogen leakage through stopcock J. This

stirring process was repeated several times if necessary. Although the J-22 fuel separated quite easily without stirring and tamping, other fuels, especially diesel, proved quite difficult to separate, and much stirring was needed.

After the filtration was completed, the nitrogen flow was stopped. The Dewar flask was lowered until the glass-metal connectors to the nitrogen tubes were just out of the bath. The copper coils were disconnected, and the entire LSS removed from the bath. The filtrate cup was quickly detached, and a weighed glass vial placed under the glass funnel M before any melted precipitate appeared in the funnel.

The filtrate in the cup was weighed, and a sample taken for analysis. As the LSS warmed to room temperature most of the precipitate melted and flowed down into the vial. Nitrogen under low pressure helped force the flow. The residues on the fritted disc and stirring rod were washed down with n-pentane into another weighed vial. After removing the pentane by bubbling nitrogen through the solution at ambient temperature and pressure, the residue was weighed and combined with the precipitate in the first vial, which had also been weighed. After thorough mixing, a sample was taken for analysis. Careful tests showed that the higher n-alkanes (and other material) present in this residue were not swept out with the nitrogen sparging at a slow rate through the pentane solution. Since the amount of pentane present in the sample was readily determined, the composition of the precipitate was converted to a pentane-free basis.

SAMPLE ANALYSIS BY GAS CHROMATOGRAPHY

The concentrations of the n-alkanes in the original fuel samples, filtrates and precipitates were determined using an OV-101 fused silica capillary column, 0.2 mm i.d. x 50 m long, in a Hewlett-Packard Model 5880 gas chromatograph (GC). The inlet split ratio was 60:1; the column oven was temperature programmed from 50° to 200°C and the inlet and detector outlet temperatures were both 300°C. Iso-octane was used as the internal standard. Moreover, the concentrations of quantitatively prepared solutions of pure n-alkanes were accurately determined using iso-octane as the one internal standard.

Additional data were obtained when necessary by combined GC/MS (EI mode). The GC/MS unit consisted of a Hewlett Packard Model 5710 GC, a H-P Model 5980A mass spectrometer and a Ribermag SADR GC/MS data system. An all-glass GC inlet system was used in conjunction with a 0.31 mm x 50 m SP2100 (similar to OV-101) fused silica capillary column.

The gas chromatograms for the original fuel, the filtrates and precipitates are very similar, with differences noticeable only in the relative heights of the major n-alkane peaks. The chromatogram for J-22 fuel, shown in Figure 2, is relatively simple. The components are bounded by normal nonane, n-C₉, on the light end and by normal hexadecane, n-C₁₆, on the heavy end. The normal alkanes dominate the chromatogram, accounting for 26% by weight of the fuel (Table 1). There are a few other sharp, prominent peaks, some of which are labelled on the chromatogram for reasons discussed below.

CONCENTRATIONS OF n-ALKANES IN LIQUID AND SOLID PHASES

Filtrate

Normalized filtrate composition data as a function of temperature are listed in Table 1. For each n-alkane going from left to right these data approach unity at the freezing point of -48°C . Since this temperature (actually the melting point) is the point at which the last trace of solid material melts, or redissolves, the composition of the filtrate at this point should be the same as that of the liquid fuel. The descending columns in Table 1 show decreasing concentrations as the carbon number of the n-alkanes increases, showing that the higher the n-alkane the more readily it crystallizes, or freezes, out of solution. These data, when plotted as the logarithm of the n-alkane concentration in the filtrate vs. the reciprocal of the absolute temperature, form straight lines for all the n-alkanes, as would be expected for a Van't Hoff solubility plot.

Precipitate

Since the precipitate, a waxy crystal matrix, entrapped significant amounts of filtrate, the concentrations of the n-alkanes in the precipitate varied unpredictably depending on handling and treatment and were not used in this study directly. The interest lies rather in the n-alkane concentrations in the actual crystalline solids formed. Because the amount of entrapped liquid in the precipitate was large, only by indirect methods was it possible to estimate the amount of true solids present and the composition of those solids.

Estimating n-Alkane Concentration in Solids Fraction of Precipitate

Since the precipitate contains some solid crystals and some entrapped liquid, let Z equal the weight fraction of liquid entrapped in the precipitate:

$$W_L = ZW_P, \quad (1)$$

Based on mass balance considerations, and assuming that the liquid portion of the precipitate is entrapped filtrate, it can be shown (17) that

$$X_S = (X_P - ZX_F)/(1 - Z) \quad (2)$$

where X_S , X_P , and X_F are the concentrations of a given component in the solid fraction, precipitate, and filtrate respectively. Equation 2 expresses the concentration of any component A in the solid fraction of the precipitate as a function of its concentration in the filtrate (X_F) and precipitate (X_P), and the fraction of liquid in the precipitate (Z). We have determined X_F and X_P , and the problem is to estimate Z.

Estimation of Z

If there is a species k in the precipitate which has a very low freezing point and does not freeze (form crystals) under the conditions of the experiment, it would therefore be present only in the liquid fraction of the precipitate ($X_S = 0$). It is thus possible to estimate Z by making use of this information and applying Equation 2. Solving Equation 2 for Z, gives

$$Z = X_P/X_F \quad (3)$$

The Z obtained from Equation 3 for component k is also applicable to the solid A components since it is the result of the same dilution of the precipitate by liquid filtrate. Hence, we can estimate Z by means of the ratio of component k in the precipitate to that in the filtrate.

Estimating the Fraction of Solids in the Sample

From the weights of total material in the sample (W_0), filtrate (W_F), precipitate (W_P), the fractions of filtrate (F), precipitate (P), and solids (S) it can be shown (17) that:

$$F = W_F/W_0 \quad 4)$$

$$P = W_P/W_0 \quad 5)$$

$$S = W_S/W_0 = (1 - Z)P \quad 6)$$

Thus, by means of Equations 4, 5, and 6 and knowing Z, we can calculate F, P, and S.

Estimating Percent of n-Alkanes in Fuel Found in the Solid Phase

Not only is the concentration of each n-alkane in the crystalline solid of interest, but of even greater interest is the percent of each n-alkane or other frozen component present in the fuel that is found in the solid phase. If we define X_S as the percent of a given component present in the fuel that is found in the solid phase, then it can be shown (17) that

$$X_S = P(X_P - ZX_F)/X_0 \quad 7)$$

Thus X_S depends on directly determined experimental data and on the value of Z, which can be determined indirectly as explained previously.

Choice of Noncrystal-Forming Components for Estimating Z

After careful examination of the gas chromatograms for the jet fuel J-22, two k compounds were selected, labelled a and b in Fig. 2, which do not form solid crystals. The retention time of a was between that of C_{10} and C_{11} , and that of b between C_{12} and C_{13} . They were identified by GC/mass spectrometry as 4-methyl decane and 2-methyl dodecane. The freezing point (T_m) of 4-methyl decane is -92.9°C , (13), well below the temperatures of these experiments. The drastic difference in freezing points effected by branching is typical of branched isomers vs straight-chain alkanes ($n-C_{11}$, $T_m = 25.6^\circ\text{C}$). These two compounds were selected because they exhibited sharp, distinct GC peaks, and because their concentrations in the filtrate and precipitate were essentially constant with temperature in both the filtrate and precipitate. The average normalized concentration data (relative to concentrations in the original sample) were slightly greater than unity (about 1.06) in the filtrate, and slightly below unity (about 0.91) in the precipitate. This would be expected for compounds which do not crystallize out, since their concentrations (relative to that in the sample) in the filtrate would rise as other materials precipitate out. Conversely, their concentrations in the precipitate (since they appear only in the liquid fraction of the precipitate) would decrease as the alkanes concentrate in the precipitate.

n-Alkane Concentrations in the Solids

By means of the concentrations of the k components a and b , Z values were calculated using Equation 3. Using Equation 2, and knowing Z , the concentrations of each alkane in the solids (X_S) were calculated. Normalized concentrations of each n-alkane in the solids are listed in Table 2. Average values of Z are shown later in Table 4.

Table 2. n-Alkane Concentrations in Solid Phase of Fuel J-22 JP-5 Shale II, as a Function of Temperature

Normalized Concentrations (X_S')*					
$^{\circ}\text{C}$	-57.5	-55.3	-53.6	-51.4	-48.5**
<u>n-Alkane</u>					
C ₁₀	0.42	0.44	0.33	0.31	0.08
C ₁₁	1.61	1.49	1.46	1.16	0.29
C ₁₂	4.26	3.90	4.42	3.68	0.96
C ₁₃	6.55	5.76	7.53	6.64	1.91
C ₁₄	8.01	7.57	9.85	9.48	2.76
C ₁₅	8.63	8.00	10.29	9.74	2.66

*Normalized data—concentration divided by concentration in original sample.

**Data listed here because they are useful later on. The value of Z at this temperature was very inaccurate.

It is apparent that the larger the n-alkane the greater is its concentration in the solid phase. The concentrations of the smaller n-alkanes generally show an increase in concentration in the solids as the temperature decreases. This is expected as more crystals freeze out of the liquid and form part of the solid phase. On the other hand, it can be seen that the reverse is true for the heavier n-alkanes in the solid phase. At the higher temperatures they will form most of the solid crystalline phase. As the temperature decreases and more of the lighter n-alkanes appear in the solid phase, the absolute proportion of the heavier n-alkanes must get smaller, and so the concentration decreases with decreasing temperature.

The values of the normalized n-alkane concentrations in the solid phase, X_S' , were calculated by dividing the values of X_S obtained from Equation 2 by the concentration in the fuel, X_0 , for each n-alkane. The sensitivity of X_S' to the accuracy of the value of Z can be readily seen: an error of 5% in the value of Z when $Z = 0.85$ causes an error of 25% in the value of X_S' , whereas an error of 5% in Z when $Z = 0.70$ causes an error of 11% in X_S' . Thus one of the more important and difficult tasks was obtaining accurate values of Z . The values of S , X_S and X_S' all depend on the factor $(1 - Z)$, the uncertainty of which increases as Z approaches unity. In general, however, the values of X_S' as a function of temperature show the expected relationship for a component freezing or crystallizing out of a liquid solution.

Percent of n-Alkanes in Fuel Found in the Solid Phase

Table 3 shows the variation of X_S' , the percent of the n-alkanes present in the original fuel that are found in the solid phase, using Equation 7 with the average value of Z. It is seen that the increase in the percent found in the solid phase increases with the carbon number and varies inversely with temperature for each n-alkane.

Table 3. Percent of Total Fuel n-Alkanes Found in Solid Phase as a Function of Temperature
Fuel: J-22, JP-5 Shale II

Percent of Total Fuel n-Alkanes: $X_S'' = X_S' \cdot S$					
°C	-57.5	-55.3	-53.6	-51.4	-48.5
n-Alkane					
C ₁₀	3.4	3.2	1.5	0.90	0.22
C ₁₁	13.2	10.9	6.6	3.4	0.78
C ₁₂	34.9	28.5	19.9	10.7	2.6
C ₁₃	53.7	42.0	33.9	19.3	5.2
C ₁₄	65.7	55.3	44.3	27.5	7.4
C ₁₅	70.8	58.4	46.3	28.2	7.2

Freezing point extrapolated for $X_S'' = 0$: range -48.7° to -47.2°
(average -47.9°C)

MATERIAL BALANCES

Overall Balance

By means of Equations 4, 5 and 6 the total overall material balances were estimated and the results listed in Table 4. The percent recovery, defined as 100 times the ratio of the weight of the filtrate plus precipitate to the weight of the original fuel, varied between 98.8 and 99.7%

Table 4. Total Material Balances-Fuel: J-22, JP-5 Shale II

°C	-57.5	-55.3	-53.6	-51.4	-48.5**
% Filtrate	44.7	67.8	79.6	90.1	83.9
% Precipitate	54.9	31.4	19.9	8.7	16.1
% Recovery	99.7	99.2	99.5	98.8	-
% Solids***	8.2	7.3	4.5	2.9	2.7
Z*	0.85	0.76	0.77	0.67	0.83

*Fraction liquid (filtrate) in precipitate, P
**Not accurate-some information lacking in these early runs
***Freezing point extrapolated for S = 0 is -48°C

n-Alkane Balance

Perhaps the most important check for self-consistency for the type of data gathered in this study is a material balance for each of the compounds present. For every run, a material balance for each of the n-alkanes and k compounds was carried out. Material balances are shown for all the n-alkanes present for one specific run at -53.6°C in Table 5.

Table 5. n-Alkane Balance, (mgs.) - Fuel: JP-5, J-22, -53.5°C, Z = 0.767

n-Alkane	Filtrate F	Precipitate (P)			Total Liq. F + L	Recovery F + P	Fuel Sample	Percent Recovery
		Liquid L	Solids S	Total L + S				
C ₁₀	282	55	6	61	337	343	357	96.1
C ₁₁	510	100	45	145	610	655	678	96.6
C ₁₂	362	71	111	182	433	544	563	96.6
C ₁₃	191	38	113	151	229	342	350	97.7
C ₁₄	47	9	48	57	56	104	108	96.3
C ₁₅	14	3	13	16	17	30	32	93.8
TOTAL	1406	276	336	612	1682	2018	2088	96.8
TOTAL FUEL	6292	1233	375	1608	7525	7900	7934*	99.6
Percent n-Alkane in Total	22.4	22.4	89.6	38.1	22.4	25.5	26.3	-

* Starting weight of sample used in Run No. 30

Only in one case was the discrepancy between the "input" (fuel) and the "output" (filtrate plus precipitate) greater than 4%. This occurred with C₁₅ where the concentrations were extremely low. The method of analysis by gas chromatography used in this study clearly gave consistently good results.

Determination of Z by Liquid Chromatography

Because the value of Z is of the greatest importance in this study, two other methods for determining it were investigated as a check on the accuracy of the method used, which we call the "k-component method." One of these methods was high performance liquid chromatography (HPLC) (14,15). Samples of fuel, filtrate, and precipitate for a particular run were analyzed for three classes of compounds: saturated, monocyclic, and dicyclic aromatic hydrocarbons. The fuel sample contained no internal standard, but the filtrate and precipitate each had an internal standard, iso-octane, added to it. Since iso-octane is a saturated hydrocarbon and was present to about 9% by weight, the percentages of the three fractions determined by HPLC had to be adjusted for no iso-octane present.

Table 6 gives the results of the HPLC analyses. Both the percentages obtained by HPLC analyses of the precipitate and filtrate containing iso-octane and the adjusted values are listed. As expected, the percent of saturated hydrocarbons is greater in the precipitate than in the filtrate, whereas the reverse is true for the monocyclic and dicyclic aromatic hydrocarbons. To calculate Z, we first assume that no dicyclic aromatic hydrocarbons freeze or crystallize out of the fuel. Then this fraction can be assumed to be a k compound. By Equation 3, $Z = 0.78/1.02 = 0.765$, total solids, $S = 4.8\%$ and saturated hydrocarbons making up 97.5% of S. By GC analysis, using components a and b as k compounds, Z for Run No. 30 was determined to be 0.766 and $S = 4.8\%$ with the normal alkanes comprising 89.6% of the solids.

Table 6. Hydrocarbon Fractions Determined by High-Pressure Liquid Chromatography - Fuel: J-22, JP-5 Shale II. Run No. 30: T = -53.6C

Hydrocarbon Fraction	Percent (w/w) in Fuel	Percent (w/w) in		Percent (w/w) in	
		Filtrate*	Precipitate*	Filtrate**	Precipitate**
Saturated	76.58	75.01	80.23	75.52	80.70
Monocyclic aromatics	22.45	23.99	19.00	23.46	18.51
Dicyclic aromatics	0.97	1.00	0.77	1.02	0.78

*iso-octane present as internal standard

**Adjusted for no iso-octane

If the assumption is made that neither monocyclic nor dicyclic aromatic compounds appear in the solid phase, the value of Z becomes 0.78, the average value taking both the monocyclic and dicyclic aromatic components as k compounds. The total solids S becomes 4.5% still in remarkably close agreement to the GC analysis.

The other confirmatory method involved the use of dye tracers to obtain the values of Z. This was suggested in a recent paper by Moynihan et al. (16). However, we were not able to use the dye method successfully for our purposes. Our work with the dye tracer method is reported elsewhere (17).

SUMMARY AND CONCLUSIONS

The liquid (filtrate) and the solid crystals containing a large portion of entrapped liquid (precipitate) from partially frozen samples of middle distillate fuels were separated from each other and collected by means of a liquid-solid separator (LSS) developed at NRL. This was done at several temperatures below the freezing point of the original fuel samples. The collected filtrates and precipitates along with original fuel samples were analyzed quantitatively for the normal alkanes and other specifically designated components (k-compounds) by gas chromatography.

The filtrate data were straightforward, and Van't Hoff plots of the n-alkane concentrations (log concentration vs. reciprocal temperature) formed straight lines. Their slopes demonstrated the importance of the higher n-alkane in fuel freezing, or crystallization, at low temperatures.

Since the precipitate consisted of a waxy crystal matrix in which significant amounts of liquid (filtrate) were entrapped, the data presented some problems of interpretation. Modifications in the method resulted in better separation, but it was still far from complete. An indirect method (using k-compounds) was derived to estimate the total solid fraction in the precipitate and also the individual n-alkane concentrations in the crystalline solids.

It was seen that the solid fraction increased with decreasing temperature, and that the fraction (or percent) of the n-alkanes in the original fuel that appeared in the solid phase increased with the carbon number and was inversely proportional to the temperature for an individual n-alkane.

Results of total material balances as well as of individual n-alkanes gave close agreement, within a few percent in nearly all cases. Tests using high pressure liquid chromatography further validated the method used.

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NOMENCLATURE

	Fuel Sample	Filtrate	Precipitate	Precipitate Solids	Precipitate Liquid
Total Material:					
Weight	W_s	W_f	W_p	W_s	W_l
Fraction of Sample		$F = W_f/W_s$	$P = W_p/W_s$	$S = W_s/W_s$	$L = W_l/W_s$
SPECIES A.W.S:					
Weight	w_i	w_j	w_k	w_i	w_k
Concentration (w/W)	$X_i = w_i/W_s$	$X_j = w_j/W_f$	$X_k = w_k/W_p$	$X_i = w_i/W_s$	$X_k = w_k/W_l$
$Z = W_i/W_s$					
c - Crystalline Species					
l - Monocrystalline Species					
Subscripts:			Superscripts:		
o - Original Sample				o - Normalized Data (Concentration divided by that of original sample)	
F - Filtrate					
P - Precipitate					o - Percent concentration of a species in the fuel found in the solid phase
S - Solids Fraction of Precipitate (Crystals)					
L - Liquid Fraction of Precipitate					
T - Total					

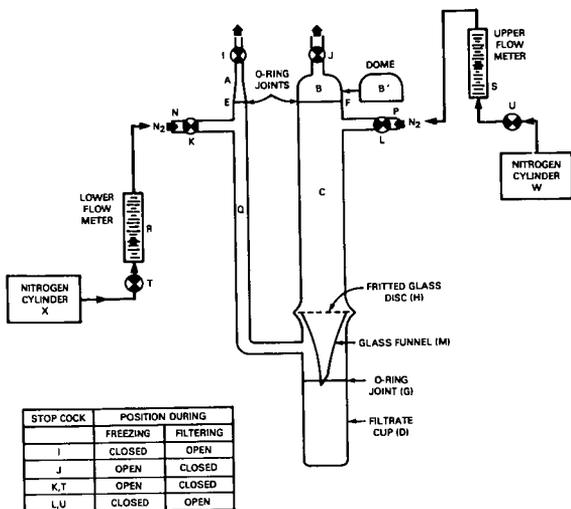


Fig. 1 - Liquid-Solid Separator

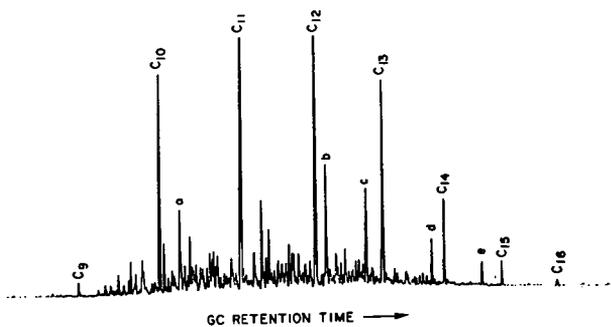


Fig. 2 - GC Trace
Fuel: J-22, JP-5 Shale II