

## 4. COMPOSITION ANALYSES OF FLUID SAMPLES

For oil and gas mixtures, the phase behavior and physical properties such as densities, viscosities, and enthalpies are uniquely determined by the state of the system, i.e., the temperature, pressure, and the composition. In simulating the phase behavior and physical properties of complex hydrocarbon mixtures accurately, it is necessary to have detailed and accurate compositional information for each mixture. [1]

### 4.1 GAS CHROMATOGRAPHY AND TBP DISTILLATION

Traditionally, compositional data in the oil industry have only been reported to C7+, the compositional information being mainly based on low temperature fractionate distillation data. This level could be inadequate for accurate modeling of the phase equilibrium and physical properties of the hydrocarbon mixtures. [2,3]

Methods have been developed for experimentally determining the composition of hydrocarbon mixtures with good reproducibility. [1] These methods yield more accurate and detailed description of the hydrocarbon systems and are described in this chapter.

Gas chromatography (capillary column chromatography) has enabled separation and quantification of individual components in a multicomponent reservoir fluid. [2] The compositional description of the reservoir fluid is done by analyzing separately samples of the gas and liquid phases, which when recombined in the correct gas to liquid ratio will yield the reservoir fluid composition.

The compositional description of the gas phase is carried out in one step: N<sub>2</sub>, CO<sub>2</sub>, C1-C10 by gas chromatography.

The liquid phase compositional description is carried out in two steps:

1. To C10+ using capillary column chromatography.
2. From C10 to C20+ using a mini distillation apparatus. [3]

### 4.2 Gas Chromatography (GC)

Gas chromatography (GC) is a common type of chromatography used in analytical chemistry for separating and analyzing compounds that can be vaporized without decomposition. Typical uses of GC include testing the purity of a particular substance or separating the different components of a mixture (the relative amounts of such components can also be determined). In some situations, GC may help in identifying a compound. In preparative chromatography, GC can be used to prepare pure compounds from a mixture.[1]

#### 4.2.1 Principle

In gas chromatography, the mobile phase (or "moving phase") is a carrier gas, usually an inert gas such as helium or an unreactive gas such as nitrogen. Helium remains the most commonly used carrier gas in about 90% of instruments although hydrogen is preferred for improved separations.[4] The stationary phase is a microscopic layer of liquid or polymer on an inert solid support, inside a piece of glass or metal tubing called a column (a homage to the fractionating column used in distillation). The instrument used to perform gas chromatography is called a gas chromatograph (or "aerograph", "gas separator").

The gaseous compounds being analyzed interact with the walls of the column, which is coated with a stationary phase. This causes each compound to elute at a different time, known as the retention time of the compound. The comparison of retention times is what gives GC its analytical usefulness.

The principle of a Gas chromatograph unit is seen in Fig. 4.1.

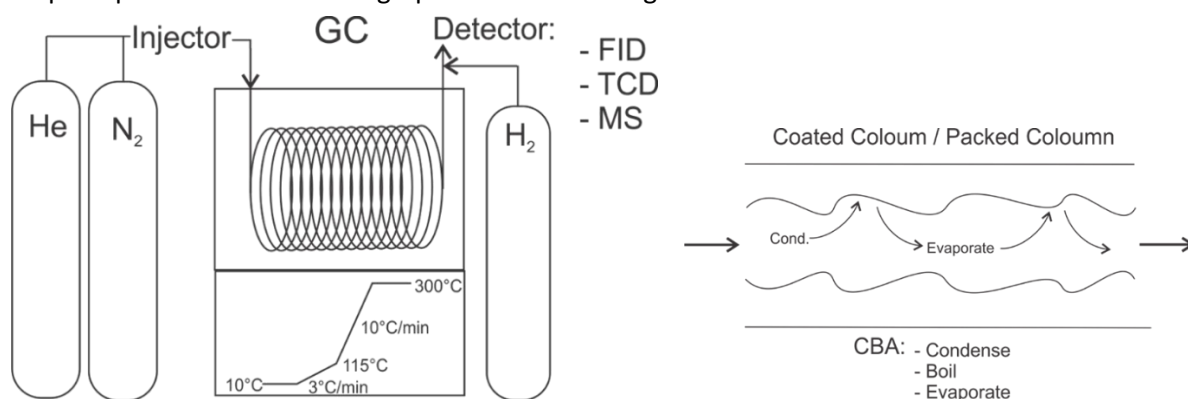


Fig. 4.1. Principle of the gas chromatograph unit (left) and the column separation (right).

The fluid sample is injected and evaporated in the injector port and the compounds are separated and transported through the temperature controlled GC-column by a carrier gas, normally He or N<sub>2</sub>.

The partitioning and speed between the individual compounds are mainly controlled by the boiling point and oven temperature, typically increasing from 10 -300°C during the analyses.

#### 4.2.2 Detector systems

The individual components and the relative amount are detected in the detector system.

Inorganic compounds like N<sub>2</sub>, CO<sub>2</sub>, and H<sub>2</sub>S are detected by a Thermal Conductivity Detector (TCD), [6] while for organic compounds we use a Flame Ionization Detector (FID) [7], Fig. 4.2.

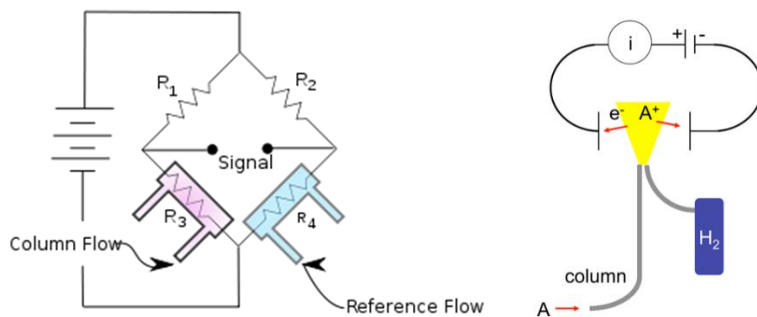


Fig. 4.2. Principle of the TCD (left) and FID (right) GC-detectors.

Most compounds have a thermal conductivity much less than that of the common carrier gases of helium or hydrogen. When an analyte elutes from the column the effluent thermal conductivity is reduced and a detectable signal is produced.

The operation of the FID is based on the detection of ions formed during combustion of organic compounds in a hydrogen flame. The generation of these ions is proportional to the mass of organic species in the sample gas stream.

The GC chromatogram gives separated peaks of the individual components, Fig. 4.3.

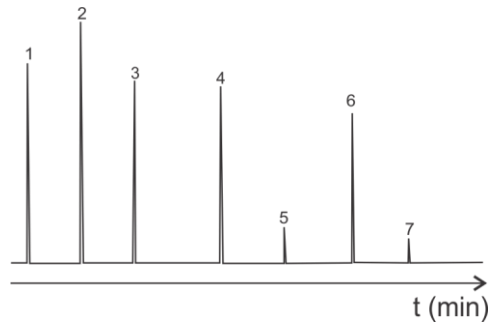


Fig. 4.3 Principle of GC Chromatogram

The peaks are identified as compounds based on the retention time verified by instrument calibration with known component mixtures. The relative peak area of the individual compounds ( $A_i$ ) are integrated and reported.

#### 4.2.3 Quantification of inorganic compounds by TCD

Gas samples with inorganic gasses  $N_2$ ,  $CO_2$  and  $H_2S$  are quantified in the TCD detector, and the relative peak Area for all components in the chromatogram is integrated.

The Area of the individual inorganic peaks ( $A_i$ ) could be quantified as a mass ( $m_i$ ) by analyzing an inorganic calibration gas with known composition and concentrations as standard ( $s$ ) at fixed instrument conditions, giving the retention times for individual gasses. The peak Area ( $A_s$ ) <sub>$i$</sub>  is a measure of mass of the individual inorganic compounds ( $m_s$ ) <sub>$i$</sub> , and a calibration constant for the individual inorganic compounds in the gas could be calculated:

$$R_i = \left( \frac{m_s}{A_s} \right)_i \quad (4.1)$$

When the Gas sample is analyzed on the same GC with the same setup, the individual inorganic gasses are detected by the retention time and the peak Areas for individual inorganic gasses, ( $A_i$ )<sub>sample</sub>.

The ( $m_i$ )<sub>sample</sub> could then be quantified by:

$$(m_i)_{sample} = (A_i)_{sample} \cdot R_i \quad (4.2)$$

#### 4.2.2 Quantification of organic compounds by FID

In GC analyses organic components are detected by the FID detector. The integrated peak Area for the individual components ( $A_i$ ) is proportional to the mass of the components ( $m_i$ );

$$A_i \propto m_i \quad (4.3)$$

##### 4.2.2.1 Gas samples

In natural gas samples, normally all HC components are less than C11, and the mass ( $m_i$ ) of the individual components could be expressed by:

$$m_i = \frac{A_i}{\sum A_i} \quad (4.4)$$

##### 4.2.2.2 STO samples

GC analyses of an oil sample (STO) with a large number and significant part of the HC components are above C9, the  $\sum A_i$  could not be found. By introducing an internal standard in the STO sample, isooctane, which is not occurring in natural oil and gas samples, a calibration factor could be made, Fig. 4.4.

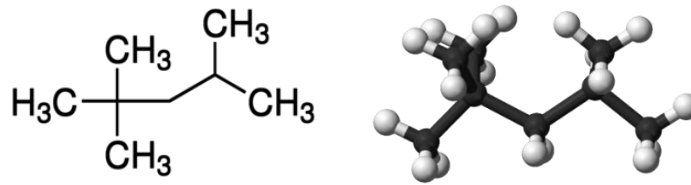


Fig. 4.4 Isooctane (2,2,4-Trimethylpentane) as internal standard in GC analyses of STO samples

Exact mass of Isooctane (~10%) is added to the STO sample. The Area respond ( $A_i$ ) for each component could be converted to mass using the calibration factor for the internal standard (iso-octane),  $R_s$ :

$$R_s = \frac{m_s}{A_s} \quad (4.5)$$

And expressed as mass (relative):

$$m_i = R_s \cdot A_i \quad (4.6)$$

The mass of oil could be expressed as :

$$m_{STO} = \sum_{C1}^{C9} m_i + m_{C10+} \quad (4.7)$$

The area respond for the pseudo-components ( $A_i$ ) are the sum of all peaks within a fraction as seen in fig. 4.5 of C6, C7, or C7+ .

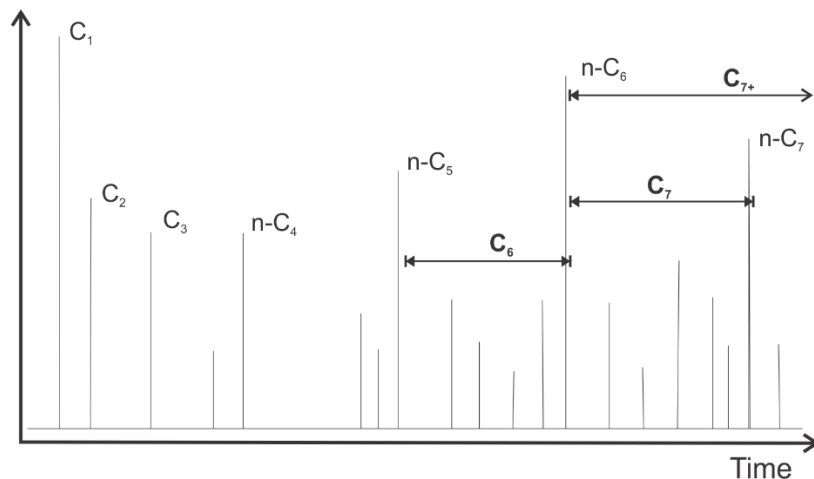


Fig. 4.5 HC pseudo components extract from an GC chromatogram

The largest peaks observed is normally the n-components (n-C5, n-C6, n-C7) and often with the longest retention time within the Cn fraction.

### 4.3 Mole fractions of Gas phase ( $y_i$ ) and STO ( $x_i$ )

All arriving fluid samples need to be stabilized to ambient conditions prior to the analyses, as samples of liberated gas ( $(V_g)_{sc}$ ) and Stabilized oil (STO) from the flash experiment, but also separator gas or dry gas samples.

From the GC analyses, the composition of Gas phase ( $y_i$ ) and STO ( $x_i$ ) could be determined. The analytical data from the gas chromatographic measurements and all of the data from the distillation are available in terms of mass fractions ( $m_i$ ) of the individual components. The molecular weights,  $M_i$ , therefore, play an important role in converting the mass fractions to mole fractions of STO ( $x_i$ ) or Gas phase ( $y_i$ ). The molecular weight of the residue  $M_{C^+}$  fraction (typically C7+, C10+, or C20+) is especially important.

$$x_i = \frac{m_i}{M_i} \quad (4.8)$$

where

$m_i$  is the mass of component or fraction  $i$

$M_i$  the molecular weight of component or fraction  $i$ .

The previous section indicates that the molecular weight measurement is difficult to perform. Often relatively large errors are associated with experimentally determined molecular weights.

Fortunately, when a distillation analysis has been performed, it is possible to check the reported weight fractions and associated molecular weights of components, hydrocarbon fractions, and residue, for consistency. Only an additional measurement of the molecular weight of the whole oil sample is required. For example, an analysis by distillation of an oil sample results in the information shown in Tbl. 4.1 and Tbl. 4.2.

Tbl. 4.1. Measured and calculated Molecule Weights (M) and densities ( $\rho$ ) from NS Gas Condensate

	M		
	Condensate	C10+	C20+
Measured M, (g/mole)	111	175	319
Calculated M using C10+ (g/mole)	111		
Calculated M using C20+, (g/mole)	111	175	
Measured $\rho$ , g/cm <sup>3</sup>	0.756	0.825	0.891
Calculated $\rho$ , using $\rho_{C10+}$ (g/cm <sup>3</sup> )	0.752		
Calculated $\rho$ , using $\rho_{C20+}$ (g/cm <sup>3</sup> )	0.752	0.826	

In order to check the consistency of the reported C20+ molecular weight, the average molecular weight ( $\bar{M}$ ) of the whole sample is calculated as follows:

Basis in 1 g STO

$$\bar{M} = \frac{m}{M} = \frac{1}{\sum_i \frac{m_i}{M_i}} \quad (4.9)$$

This value may be compared with a measured mean molecular weight for the whole oil sample. The analysis data are considered internally consistent if the two values of oil sample average molecular weights agree to within 2- 3 molecular weight units.

In addition, one may back-calculate the values of C10+ and C20+ molecular weights, which also must agree closely with the experimentally observed values for C10+ and C20+.

The average density of the oil sample,  $\bar{\rho}$ , can also be calculated from the data for the fraction given in Tbl. 4.1 as follows:

$$V = \frac{m}{\rho} \quad \text{and} \quad \rho = \frac{m}{V} \quad (4.10)$$

$$\bar{\rho} = \sum_i \frac{m_i}{\sum_i \frac{m_i}{\rho_i}} \quad (4.11)$$

where

$m_i$  is the mass of component or fraction i

$\rho_i$  is the density of component or fraction i.

Again, the calculated and measured average oil densities should agree closely.

Tbl. 4.2. Data for Computing Tbl. 4.1

	1	2	3	4	5	6
comp	Wt%	M	Mole%		$\rho$ (g/cm <sup>3</sup> )	
Gas	4.19	54.8	8.52	4.7	0.564	7.4
C5	6.78	72.2	10.45	7.5	0.628	10.8
C6	7.97	84.8	10.46	8.8	0.668	11.9
C7	15.18	91.5	18.46	16.8	0.738	20.6
C8	17.05	104.3	18.19	19.0	0.763	22.3
C9	9.81	119.0	9.18	10.9	0.783	12.5
(C10+)	(39.01)	(175)	(24.74)	(43.3)	(0.825)	(47.3)
C10	7.48	133	6.28	8.4	0.796	9.4
C11	5.82	145	4.46	6.5	0.796	7.3
C12	4.39	158	3.10	4.9	0.809	5.4
C13	4.21	171	2.74	4.6	0.820	5.1
C14	3.43	183	2.09	3.8	0.830	4.1
C15	2.73	197	1.54	3.0	0.837	3.3
C16	1.78	210	0.94	2.0	0.848	2.1
C17	1.92	226	0.95	2.1	0.845	2.3
C18	1.49	241	0.69	1.7	0.845	1.8
C19	1.36	250	0.61	1.5	0.854	1.6
C20+	4.42	319	1.54	4.9	0.891	5.0

Column 3 is obtained by: (column 1/column 2)/  $\sum$  (column 1/column 2)

Column 4 is obtained by: (column 2 x column 3)/100

Column 6 is obtained by: column 1/column 5

Calculated M using C10+ M = (4.7 + 7.5 + 8.8 + 16.8 + 19.0 + 10.9 + 43.3) = 111.0

Calculated M using C20+ M = 111.1 (see table)

Calculated M of the C10+ fraction using C20+  
 $M = 100(8.4 + 6.5 + 4.9 + 4.6 + 3.8 + 3.0 + 2.0 + 2.1 + 1.7 + 1.5 + 4.9)/24.74 = 175$

Calculated density using C10+ density =  $100/(7.4 + 10.8 + 11.9 + 20.6 + 22.3 + 12.5 + 47.3) = 0.752 \text{ g/cm}^3$

Calculated density using C20+ density =  $100/132.9 = 0.752 \text{ g/cm}^3$

## 4.4 Gas phase analyses

A chromatogram from a GC analysis of natural gas is shown in Fig. 4.6.

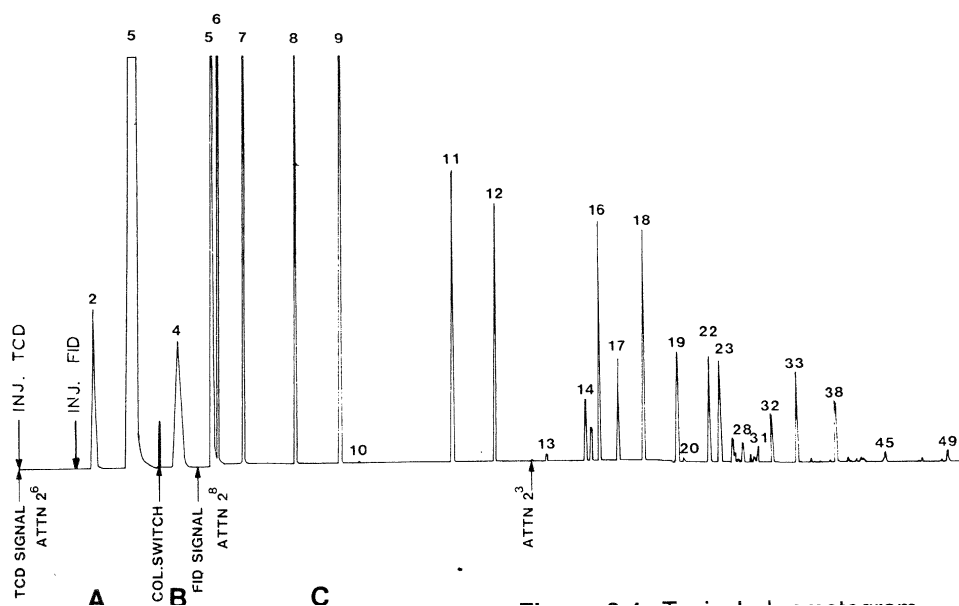


Fig. 4.6. Chromatogram for natural gas. Peak numbers correspond to Cal.no in Tbl. 4.3. [8].

The chromatographic separation of nitrogen, carbon dioxide, and hydrocarbons from C1 to C10+ was achieved by using a combination of packed and capillary columns. The sample was injected via two time-programmed loops into the column using thermal conductivity and flame-ionization detection. The hydrocarbons were analyzed by split injection using the capillary column, and temperature programming starting at 30°C, and the effluent gases were analyzed isothermally at 50°C. Approximately 60 hydrocarbons from C1 to C10+ detected together with two inorganic compound, Nitrogen and carbon dioxide. In the chromatogram, each peak is represented with an integrated Area, and in Tbl. 4.3 each component is represented as a mass %.

Tbl. 4.3. Composition of a Natural Gas Sample (Average of 8 Analyses).

Cal. no.	Comp	$m_i$ %	R.S.D. %	Cal. no.	Comp	$m_i$ %	R.S.D. %
2	Nitrogen	1.6542	0.5	25	2-Methyl Hexane	0.0145	5.5
4	Carbon Dioxide	2.3040	0.6	26	2,3-Dimethyl pentane	0.0045	5.6
5	Methane	60.5818	0.2	27	1,1-Dimethyl cyclopentane	0.0025	5.6
6	Ethane	15.5326	0.2	28	3-Methyl hexane	0.0125	5.1
7	Propane	12.3819	0.2	29	1,cis-3-Dimethyl cyclopentane	0.0060	5.5
8	Isobutane	2.0616	0.9	30	1,trans-3-Dimethyl cyclopentane	0.0060	5.5
9	n-Butane	3.2129	1.4	31	1,trans-2-Dimethyl cyclopentane	0.0094	5.0
10	2,2-Dimethyl propane	0.0074	2.0	32	n-Heptane	0.0290	3.8
11	Isopentane	0.7677	3.2	33	Methyl cyclohexane	0.0565	3.4
12	n-Pentane	0.6601	3.9	35	Ethyl cyclopentane	0.0035	3.8
13	2,2-Dimethyl butane	0.0059	5.4	36	1,trans-2,cis-4-Trimethyl cyclopentane	0.0004	185.2
14	Cyclopentane	0.0395	6.0	37	1,trans-2,cis-3-Trimethyl cyclopentane	0.0002	282.8
15	2,3-Dimethyl butane	0.0212	6.0	38	Toluene	0.0436	5.6
16	2-Methyl pentane	0.1404	6.0	39	2-Methylheptane	0.0039	6.6
17	3-Methyl pentane	0.0603	6.3	40	3-Methylheptane	0.0025	8.0
18	n-Hexane	0.1302	6.5	41	1,cis-3-Dimethyl cyclohexane	0.0044	7.6
2	Nitrogen	1.6542	0.5	42	1,trans-4-Dimethyl cyclohexane	0.0022	7.4
19	Methyl cyclopentane	0.0684	6.8	45	n-octane	0.0099	10.0
20	2,4-Dimethyl pentane	0.0032	6.8	47	m+p-Xylene	0.0029	15.7
21	2,2-Dimethyl pentane	0.0001	138.1	48	o-Xylene	0.0029	13.2
22	Benzene	0.0648	6.5	49	n-Nonane	0.0137	12.9
23	3,3-Dimethyl pentane	0.0005	9.5				
24	Cyclohexane	0.0624	6.2		Unidentified Decanes	0.0081	22.4

This information is usually too detailed for practical purposes, so the compositional information is regrouped into pseudo components. In the present sample, the regrouped gas phase analysis can be either that shown in Tbl. 4.4 or Tbl. 4.5. Both examples of regrouping will yield satisfactory descriptions of the gas phase composition.



Tbl. 4.4. Regrouped Composition of Separator Gas.

Component	$m_i$ %	$M_i$ g/mole	Mole $y_i$
Nitrogen	0.779	28.01	0.659
Carbon dioxide	10.499	44.01	5.652
Methane	46.577	16.04	68.795
Ethane	16.326	30.07	12.863
Propane	14.775	44.10	7.938
i-Butane	2.295	58.12	0.936
n-Butane	4.810	58.12	1.961
i-Pentane	1.050	72.15	0.345
n-Pentane	1.283	72.15	0.421
C6 Paraffins	0.728	86.18	0.200
C6 Naphthenes	0.065	70.14	0.022
C6 Total	0.793	84.59	0.222
C7 Paraffins	0.159	100.21	0.038
C7 Naphthenes	0.359	85.95	0.099
C7 Aromatics	0.055	78.11	0.017
C7 Total	0.573	88.59	0.153
C8 Paraffins	0.034	114.2	0.007
C8 Naphthenes	0.127	99.5	0.030
C8 Aromatics	0.049	92.1	0.013
C8 Total	0.210	99.7	0.050
C9 Paraffins	0.009	127.7	0.002
C9 Naphthenes	0.001	125.0	0.000
C9 Aromatics	0.006	106.2	0.001
C9 Total	0.016	118.5	0.003
DecanesPlus	0.012	140.0	0.002
$\Sigma$	100.000		100.000

Gas molecular weight,  $M_g = 23.69$

Gas gravity = 0.818

Tbl. 4.5. Regrouped Composition of Separator Gas  
(Corresponds to the Analysis in Tbl. 4.4)

Component	Mole % $y_i$
Nitrogen	0.66
CarbonDioxide	5.65
Methane	68.80
Ethane	12.86
Propane	7.94
i-Butane	0.94
n-Butane	1.96
i-Pentane	0.34
n-Pentane	0.42
Hexanes	0.22
Heptanes	0.15
Octanes	0.05
Nonanes	0.00
DecanesPlus	0.00
$\Sigma$	100.00
Molecular weight gas, $M_g$	23.69

#### 4.5 Liquid Phase analysis to C10+

The liquid hydrocarbon phase, i.e., the oil, is a much more complex mixture than the gas phase. Many more components appear in a typical gas chromatogram of a stabilized oil sample as shown in Fig. 4.7 [9]. Considerable overlapping of the peaks at the higher carbon numbers occurs, which makes good quantitative determination of the heavier components impossible from the gas chromatogram alone.

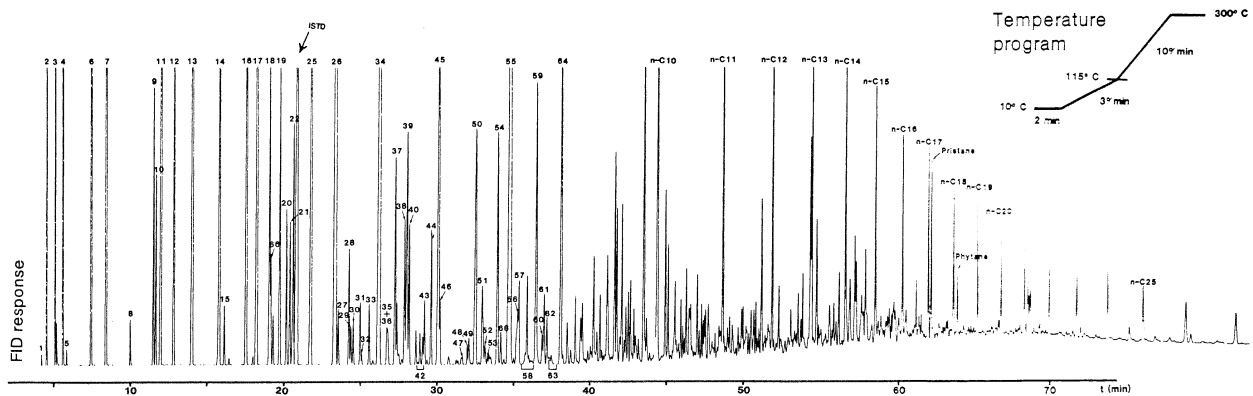


Fig. 4.7. Chromatogram of a condensate liquid sample. Peak numbers correspond to the crude oil sample in Tbl. 4.6 [9]. .

The gas chromatogram (Fig.4.7) of the oil is obtained by use of a chromatograph fitted with a fused silica capillary column. The analysis is temperature programmed from 10 to 300° C. The sample volume injected could be 10 microliter or even less, and with a split ratio of 1:100 before entering the column. The effluent detector is a flame ionization type (FID).

To properly quantify the individual components, an internal standard of known quantity is added to the sample. In this way one may compensate for column losses that are known to occur from carbon numbers of 15 and higher. The component used as the internal standard is iso-octane, which is normally not present in naturally occurring oils.

As for the gas sample analysis, a calibration program enables thorough identification and quantification of the components present between C2 and C9. Tbl. 4.6 shows a typical example of such an analysis.

Tbl. 4.6. Individual Component Report (Peak no. correspond with Chromatogram in Fig. 4.7) [9].

Peak	Comp i.	$m_i$ %	Mole %	Vol %	$M_i$	Liquid $\rho$ (g/cm <sup>3</sup> )
1	C2	0.007	0.058	0.017	30.070	0.3580
2	C3	0.072	0.412	0.122	44.097	0.5076
3	i-C4	0.051	0.222	0.078	58.124	0.5633
4	n-C4	0.189	0.816	0.276	58.124	0.5847
5	2,2-DM-C3	0.000	0.000	0.000	72.151	0.5967
6	i-C5	0.188	0.653	0.257	72.151	0.6246
7	n-C5	0.285	0.991	0.386	72.151	0.6309
	Light End Total	0.792	3.152	1.137	63.092	0.5964
8	2,2-DM-C4	0.012	0.034	0.015	86.178	0.6539
9	Cy-C5	0.052	0.185	0.059	70.135	0.7502
10	2,3-DM-C4	0.028	0.081	0.036	86.178	0.6662
11	2-M-C5	0.165	0.480	0.214	86.178	0.6577
12	3-M-C5	0.102	0.298	0.131	86.178	0.6688
13	n-C6	0.341	0.993	0.440	86.178	0.6638
	Hexanes Total	0.699	2.071	0.895	84.745	0.6687

14	M-Cy-C5	0.231	0.689	0.262	84.162	0.7534
15	2,4-DM-C5	0.015	0.038	0.019	100.205	0.6771
16	Benzene	0.355	1.140	0.343	78.114	0.8842
17	Cy-C6	0.483	1.440	0.528	84.162	0.7831
18	2-M-C6	0.000	0.000	0.000	100.205	0.6829
66	1,1-DM-Cy-Cs	0.116	0.298	0.131	98.189	0.7590
19	3-M-C6	0.122	0.307	0.152	100.205	0.6915
20	1,c/s-3-DM-Cy-C5	0.000	0.000	0.000	98.189	0.7493
21	1,tra/7S-3-DM-Cy-C5	0.052	0.133	0.059	98.189	0.7532
22	1,frans-2-DM-Cy-C5	0.048	0.122	0.054	98.189	0.7559
25	n-C7	0.405	1.014	0.504	100.205	0.6880
	Unspecified C7	0.171	0.427	0.215	100.205	0.6800
	Heptanes Total	1.997	5.609	2.267	89.426	0.7542
26	M-Cy-C6	0.918	2.348	1.016	98.189	0.7737
27	1,1,3-TM-Cy-C5	0.027	0.061	0.031	112.216	0.7526
28	E-Cy-C5	0.000	0.000	0.000	98.189	0.7708
29	2,2,3-TM-Cy-C5	0.042	0.093	0.050	114.232	0.7200
30	2,5-DM-C6	0.018	0.039	0.022	114.232	0.6977
31	2,4-DM-C6	0.000	0.000	0.000	114.232	0.7045
32	3,3-DM-C6	0.026	0.057	0.031	114.232	0.7141
33	1,trans-2,cis-3-TMCy-C5	0.025	0.056	0.028	112.216	0.7579
34	Toluene	0.958	2.610	0.941	92.143	0.8714
35	1,1,2-TM-Cy-C5	0.000	0.000	0.000	112.216	0.7769
36	2,3-DM-C6	0.033	0.073	0.040	114.232	0.7163
37	2-M-C7	0.137	0.300	0.167	114.232	0.7019
38	3-M-C7	0.094	0.206	0.113	114.232	0.7099
39	1,cis-3-DM-Cy-C6	0.190	0.425	0.211	112.216	0.7701
40	1,trans-4-DM-Cy-C6	0.072	0.162	0.081	112.216	0.7668
42	Unspecified naphthenes	0.028	0.062	0.031	112.216	0.7700
42	Unspecified naphthene	0.013	0.028	0.014	112.216	0.7700
42	Unspecified naphthene	0.011	0.025	0.012	112.216	0.7700
43	DM-Cy-C6	0.031	0.069	0.034	112.216	0.7700
44	1,trans-2-DM-Cy-C6	0.089	0.199	0.098	112.216	0.7799
45	n-C8	0.434	0.954	0.526	114.232	0.7065
	Unspecified C8	0.086	0.190	0.105	114.232	0.7000
	Octanes Total	3.231	7.957	3.551	101.978	0.7791
46	Unspecified naphthene	0.047	0.094	0.051	126.243	0.7900
47	2,2-DM-C7	0.009	0.018	0.011	128.259	0.7144
48	2,4-DM-C7	0.017	0.033	0.020	128.259	0.7192
49	1,cis-2-DM-Cy-C6	0.024	0.054	0.026	112.216	0.8003
50	E-Cy-C6 + 1,1,3-TM-Cy-C6	0.281	0.599	0.305	118.000	0.7900
51	Unspecified naphthene	0.047	0.093	0.051	126.243	0.7900
52	3,5-DM-C7	0.017	0.034	0.020	128.259	0.7262
53	2,5-DM-C7	0.003	0.006	0.004	128.259	0.7208
54	Ethylbenzene	0.114	0.270	0.112	106.168	0.8714
68	Unspecified naphthene	0.027	0.054	0.029	126.243	0.7900
55	m+p-xylene	0.697	1.649	0.687	106.168	0.86,83
56	4-M-C8	0.020	0.039	0.024	128.259	0.7242
57	2-M-C8	0.054	0.106	0.064	128.259	0.7173
58	Unspecified naphthene	0.009	0.018	0.010	126.243	0.7900
58	Unspecified naphthene	0.082	0.163	0.089	126.243	0.7900
58	Unspecified naphthene	0.007	0.014	0.008	126.243	0.7900
59	Ortho-xylene	0.230	0.545	0.223	106.168	0.8844
60	3-M-C8	0.023	0.045	0.027	128.259	0.7242
61	1-M,3-E-Cy-C6	0.078	0.155	0.083	126.243	0.8000
62	1-M,4-E-Cy-C6	0.034	0.068	0.037	126.243	0.7900
63	Unspecified naphthene	0.006	0.013	0.007	126.243	0.7900
63	Unspecified naphthene	0.004	0.007	0.004	126.243	0.7900
64	n-C9	0.471	0.923	0.559	128.259	0.7214
	Unspecified C9	0.124	0.243	0.148	128.259	0.7200
	Nonanes Total	2.427	5.241	2.598	116.277	0.7995

This detailed analysis up to C10+ is normally not needed in practice. Therefore, a regrouping of components into hydrocarbon fractions (pseudo components) may be carried out as shown in Tbl. 4.7.

Tbl. 4.7. Gas Components and Boiling Point Groups up to C10+ from Capillary GC-Analysis [9].

Comp.	Wt%	Mole%	Vol%	M	Liquid $\rho$ (g/cm <sup>3</sup> )
C1	0.000	0.000	0.000	16.0	0.260
C2	0.007	0.058	0.017	30.1	0.358
C3	0.072	0.412	0.122	44.1	0.508
i-C4	0.051	0.222	0.078	58.1	0.563
n-C4	0.189	0.816	0.276	58.1	0.585
2,2-DM-C3	0.000	0.000	0.000	72.2	0.597
i-C5	0.188	0.653	0.257	72.2	0.625
n-C5	0.285	0.991	0.386	72.2	0.631
Hexanes Total	0.699	2.071	0.895	84.7	0.669
Heptanes Total	1.997	5.609	2.267	89.4	0.754
Octanes Total	3.231	7.957	3.551	102.0	0.779
Nonanes Total	2.427	5.241	2.598	116.3	0.799
Decanes Plus	90.853	75.971	89.553	300.3	0.868

In addition to the weight fractions of the collective groups such as the C7, one may from such a detailed starting point calculate average molecular weights, average density, critical properties, and PNA distributions for each of the groups up to C10+. See Tbl. 4.8 and Tbl. 4.9.

Identification of the components in the range C10 to C20 based on the chromatogram in Fig. 4.7 is seen to be impractical. Hence the liquid phase analysis is extended beyond C10+ by a distillation technique.

Tbl. 4.8. Distribution of Weight, Mole, and Volume % of HC fractions in a Crude Oil Sample, from Capillary GC-Analysis [8].

Comp.	Wt%	Mole%	Vol%	M	Liquid $\rho$ (g/cm <sup>3</sup> )
Gas Components	0.792	3.152	1.137	63.1	0.596
Hexane Group	0.699	2.071	0.895	84.7	0.669
Heptane Group	1.998	5.612	2.263	89.4	0.756
Octane Group	3.231	7.957	3.551	102.0	0.779
Nonane Group	2.427	5.241	2.598	116.3	0.799
Decane Group	2.483	4.666	2.654	133.6	0.801
Undecane Group	2.239	3.799	2.388	148.0	0.803
Dodecane Group	2.569	3.994	2.709	161.5	0.812
Tridecane Group	3.127	4.479	3.238	175.3	0.827
Tetradecane Group	3.153	4.172	3.214	189.8	0.840
Pentadecane Group	3.988	4.890	4.041	204.8	0.845
Hexadecane Group	3.417	3.937	3.438	217.9	0.851
Heptadecane Group	4.286	4.577	4.355	235.1	0.842
Octadecane Group	3.060	3.076	3.099	249.8	0.845
Nonadecane Group	3.749	3.604	3.756	261.2	0.854
Eicosane Plus (C20+)	58.781	34.772	56.664	424.5	0.888

Tbl. 4.9. PNA Report, Paraffinic, Naphthenic, and Aromatic Contents of the Boiling Point Groups up to n-C9. [9]

Comp.	Wt%	Mole%	Vol%	M	Liquid $\rho$ (g/cm <sup>3</sup> )
Hexane group paraffins	0.647	1.886	0.836	86.2	0.663
Hexane group naphthenes	0.052	0.185	0.059	70.1	0.750
Heptane group paraffins	0.713	1.787	0.889	100.2	0.686
Heptane group naphthenes	0.930	2.682	1.034	87.1	0.769
Heptane group aromatics	0.355	1.140	0.343	78.1	0.884
Octane group paraffins	0.870	1.912	1.054	114.2	0.707
Octane group naphthenes	1.404	3.435	1.556	102.6	0.772
Octane group aromatics	0.958	2.610	0.941	92.1	0.871
Nonane group paraffins	0.739	1.446	0.877	128.3	0.721
Nonane group naphthenes	0.646	1.331	0.699	122.0	0.792
Nonane group aromatics	1.042	2.464	1.022	106.2	0.872

#### 4.6 Liquid Phase Analysis by TBP distillation

Distillation is the process of separating the components or substances from a liquid mixture by using selective boiling and condensation. Distillation may result in essentially complete separation (nearly pure components), or it may be a partial separation that increases the concentration of selected components in the mixture. In either case, the process exploits differences in the relative volatility of the mixture's components. In industrial chemistry, distillation is a unit operation of practically universal importance, but it is a physical separation process, not a chemical reaction.

The principle of a vacuum distillation unit is seen in Fig. 4.8. Typical required sample volume is about 100 ml. The distillation procedure used is a modification of the ASTM D-2892 procedure for true boiling point (TBP) distillation.

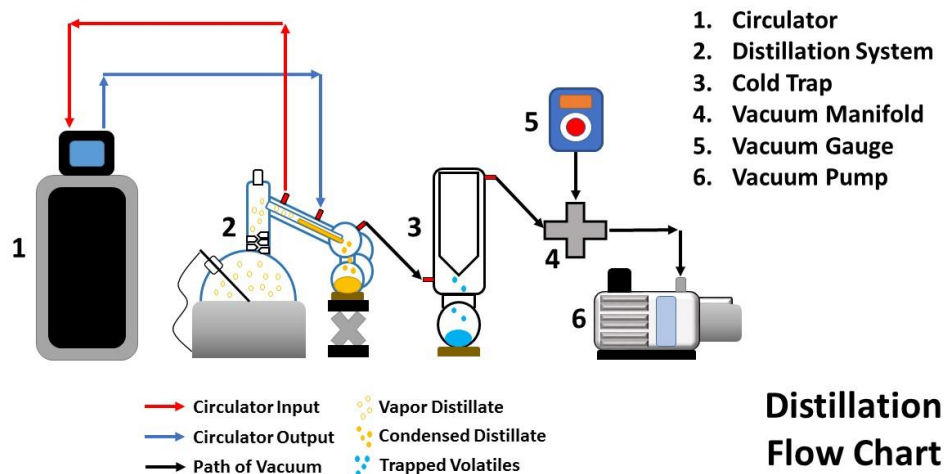


Fig. 4.8. Principle of a vacuum distillation unit.

#### 4.6.1 Liquid Phase Analysis from C10 to C20+

The results from a distillation analysis is shown in Tbl. 4.10. The distillation up to C10 was carried out at atmospheric pressure. From C10 to C20+, the distillation is carried out at a vacuum of 27 millibar (20 mm Hg) to reduce the temperature in the distillation system and avoid thermal cracking of the hydrocarbon components.

Tbl. 4.10. Data from TBP Distillation of a Stabilized Condensate. [9]

Frac.	Cut T °C 1Bar	Act.H temp °C	m%	Σm%	M	Mole%	ΣMole%	ρ g/cm <sup>3</sup>	Vol%	ΣVol%
Gas	-	-	4.19	4.19	54.8	8.52	8.52	0.564	5.60	5.60
C5	36.5	36.5	6.78	10.97	72.2	10.45	18.98	0.628	8.12	13.71
C6	69.2	69.2	7.97	18.94	84.8	10.46	29.43	0.668	8.97	22.69
C7	98.9	98.9	15.18	34.12	91.5	18.46	47.89	0.738	15.47	38.16
C8	126.1	126.1	17.05	51.17	104.3	18.19	66.08	0.763	16.81	54.97
C9	151.3	151.3	9.81	60.99	119.0	9.18	75.26	0.783	9.43	64.40
C10+	>151.3		39.01	100.00	175	24.74	100.00	0.825	35.60	100.00
C10	174.6	70.7	7.48	68.47	133	6.28	81.54	0.796	7.07	71.48
C11	196.4	88.6	5.82	74.29	145	4.46	86.00	0.796	5.50	76.98
C12	217.2	105.3	4.39	78.67	158	3.10	89.10	0.809	4.08	81.06
C13	235.9	121.5	4.21	82.88	171	2.74	91.84	0.820	3.86	84.92
C14	253.9	136.7	3.43	86.31	183	2.09	93.93	0.830	3.11	88.02
C15	271.1	151.1	2.73	89.04	197	1.54	95.47	0.837	2.45	90.47
C16	287.3	163.9	1.78	90.81	210	0.94	96.41	0.848	1.58	92.05
C17	303.0	177.8	1.92	92.73	226	0.95	97.35	0.845	1.71	93.76
C18	317.0	190.3	1.49	94.22	241	0.69	98.04	0.845	1.33	95.08
C19	331.0	202.2	1.36	95.58	250	0.61	98.65	0.854	1.20	96.28
C20+	>331.0	>202.2	4.42	100.00	319	1.54	100.19	0.891	3.73	100.01

Tbl. 4.11 compares compositional data obtained by gas chromatography and by distillation. There is generally satisfactory agreement. One advantage of the analysis by distillation is, however, that it produces a physical sample of each hydrocarbon fraction present in the oil sample.

Tbl. 4.11. Comparison of TBP Distillation and a Capillary GC-Analysis results (Average of Six). [9]

Frac.	Distillation			GC-analyses			
	m%	M	ρ, g/cm <sup>3</sup>	m%	M	ρ, g/cm <sup>3</sup>	RSD, %
C5	0.886	65	0.621	0.792	63.1	0.597	0.28
C6	0.737	82	0.695	0.699	84.8	0.669	0.26
C7	2.371	91	0.751	2.000	89.4	0.754	0.14
C8	2.825	103	0.778	3.237	102.0	0.779	0.21
C9	2.539	116	0.793	2.429	116.3	0.799	0.39
C10+	90.642	306	0.869	90.846	300.3	0.868	0.002
C10	2.479	132	0.798	2.437	133.6	0.801	0.49
C11	1.916	147	0.803	2.191	148.0	0.803	0.40
C12	2.352	163	0.817	2.523	161.5	0.812	0.33
C13	2.091	175	0.836	3.106	175.3	0.827	1.06
C14	3.667	190	0.843	3.124	189.8	0.840	1.13
Ci5	3.722	205	0.849	3.984	204.8	0.845	1.60
C16	2.034	215	0.853	3.383	217.9	0.851	6.05
C17	4.135	237	0.844	4.244	235.1	0.842	3.82
C18	3.772	251	0.846	3.201	249.8	0.845	12.12
C19	3.407	262	0.857	3.523	261.2	0.854	5.07
C20+	61.057	426	0.885	59.130	421.6	0.888	1.31

#### 4.6.2 EXPERIMENTAL EXTENSION BEYOND C20+

In some cases (e.g., dew-point calculations) quantitative extension beyond C20+ could be advantageous.

Breakdown of the C20+ fraction may be obtained by distillation, either at high temperatures (up to 550°C) or at lower vacuum pressures, typically 2.7 mBar (2 mm Hg). This is a time-consuming analyses and could be demanding because the process conditions are not easily controlled. Results from a vacuum distillation analysis at 2.7 mBar is given in Tbl. 4.12.

Tbl. 4.12. Extended composition data for a North Sea Gas Condensate

Comp	Mole%	$\rho$ (g/cm <sup>3</sup> ) 1atm, 15°C	M	PNA distribution (Mole%)		
				Paraffins	Naphthenes	Aromatics
N2	0.64					
CO2	9.16					
C1	68.8					
C2	8.43					
C3	5.11					
i-C4	0.81					
n-C4	1.45					
i-C5	0.52					
n-C5	0.53					
C6	0.63					
C7	0.83	0.741	96	0.50	0.42	0.08
C8	0.95	0.780	107	0.45	0.38	0.17
C9	0.52	0.807	121	0.48	0.27	0.25
C10	0.26	0.819	134	0.47	0.30	0.23
C11	0.20	0.810	147	0.56	0.27	0.17
C12	0.17	0.828	161	0.55	0.24	0.21
C13	0.16	0.849	175	0.54	0.22	0.24
C14	0.15	0.857	190	0.49	0.27	0.24
C15	0.11	0.868	206	0.52	0.20	0.28
C16	0.086	0.872	222	0.55	0.19	0.26
C17	0.078	0.859	237	0.57	0.20	0.23
C18	0.068	0.854	251	0.70 (C18+)	0.11	0.19
C19	0.050	0.866	263			
C20	0.046	0.873	339 (C20+)			
C21	0.035	0.876				
C22	0.025	0.876				
C23	0.034	0.875				
C24	0.023	0.877				
C25	0.017	0.876				
C26	0.018	0.878				
C27	0.014	0.882				
C28	0.012	0.886				
C29	0.013	0.889				
C30+	0.047	0.908				

The analysis time was 2-3 days. By this distillation, it is possible to extend the experimental composition analysis to C30+.

There is an empirical method developed for extrapolating the experimental C20+ analysis. This method performs well for most purposes and thus saves the time-consuming C20 to C30+ analysis.

## 4.7 PROPERTIES OF HYDROCARBON FRACTIONS

For the hydrocarbon fractions (such as  $C_n$ ), and the residue (e.g.,  $C_{20+}$ ), it is important not only to know their weight fraction, but also their physical properties such as densities, molecular weights, and PNA distributions. These properties will be different for each oil and may thus help to distinguish an oil of one reservoir from that of another reservoir.

Fig. 4.9 and Fig. 4.10 show plots of the density vs. carbon number for several North Sea oil samples. There are significant differences in the density vs. carbon number profiles, corresponding to different PNA distributions. This is in agreement with observations by Yarborough et al. [10].

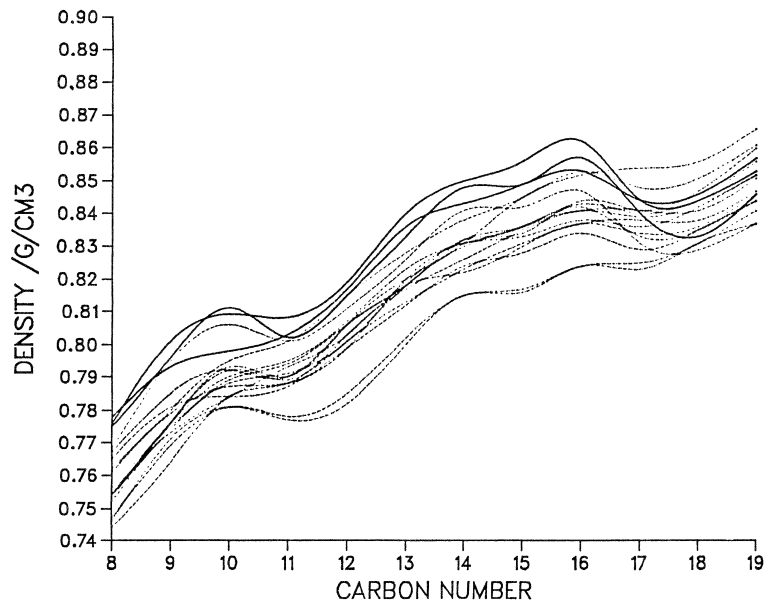


Fig. 4.9. Density of distillation fractions from paraffinic North Sea crude oils and condensates.

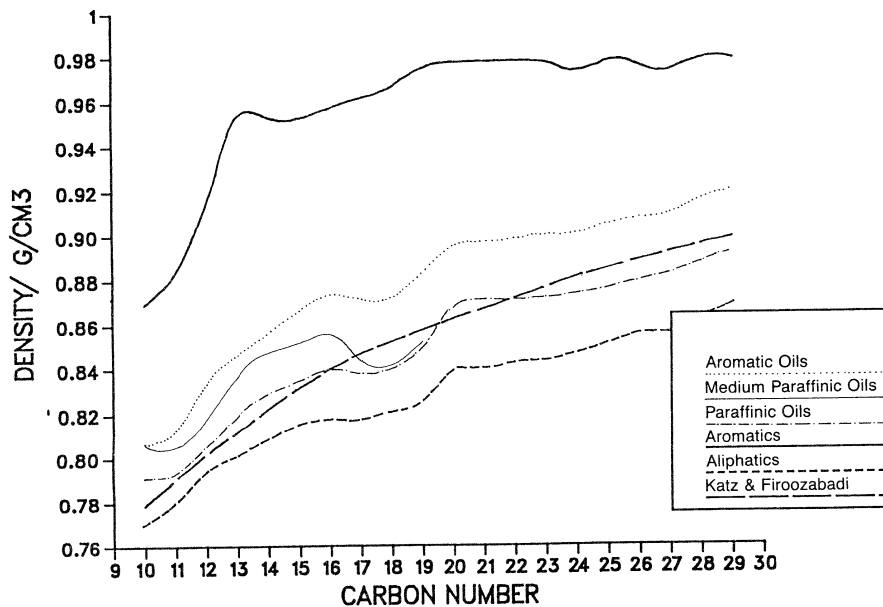


Fig. 4.10. Density profiles of North Sea oils and condensates

Similarly, Fig. 4.11 shows the molecular weight vs. carbon number for several different oil samples.



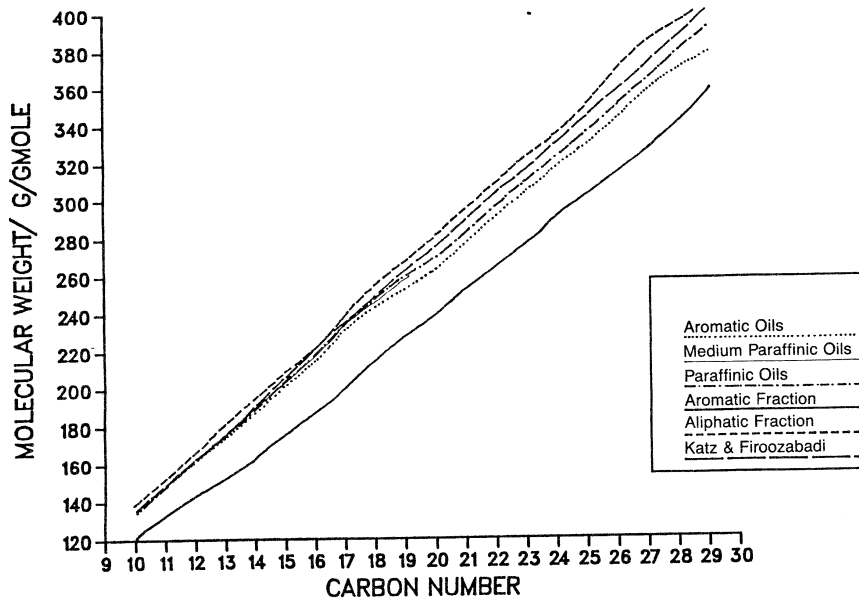


Fig. 4.11. Molecular weight profiles of North Sea oils and condensates

As observed by Katz and Firoozabadi [11], the average molecular weights of the hydrocarbon fractions are not significantly different for the different oils. This can be explained by the fact that even though the individual molecular structures within each hydrocarbon fraction may vary considerably, from n-paraffins to isomers to cyclic structures, their molecular weights will not be very much different. Different structures within a given hydrocarbon fraction have very similar ratios of hydrogen atoms to carbon atoms, and hence the molecular weights are also similar.

It is thus feasible to use general, average molecular weights for the fractions from C9 to C19. The average values of the molecular weights of Fig. 4.11 and the average densities of Fig. 4.10 are shown in Tbl. 4.13.

Tbl. 4.13. Average Densities and Molecular Weights of 11 Paraffinic North Sea Crude Oils and Condensates. [9]

Fraction	M (g/mol)	$\rho$ (g/cm <sup>3</sup> )
C9	118.6	0.778
C10	133.6	0.790
C11	148.0	0.792
C12	161.5	0.801
C13	175.3	0.816
C14	189.8	0.829
C15	204.8	0.834
C16	217.9	0.840
C17	235.1	0.837
C18	249.8	0.840
C19	261.2	0.849

Unlike Katz and Firoozabadi [11], general, average density values for each fraction are not used. As shown in Fig. 4.10, the density varies considerably with the structure (PNA distribution) of the hydrocarbon fraction.

## 4.8 Density measurement

Density measurements of the hydrocarbon fractions and residues are readily carried out using either a pycnometer or a Mettler/Parar densitometer.

The latter method [12, 13] is based on density-dependent frequency changes of an oscillating glass U-tube. The principle of the Anton/Parar instruments is shown in Fig. 4.12.

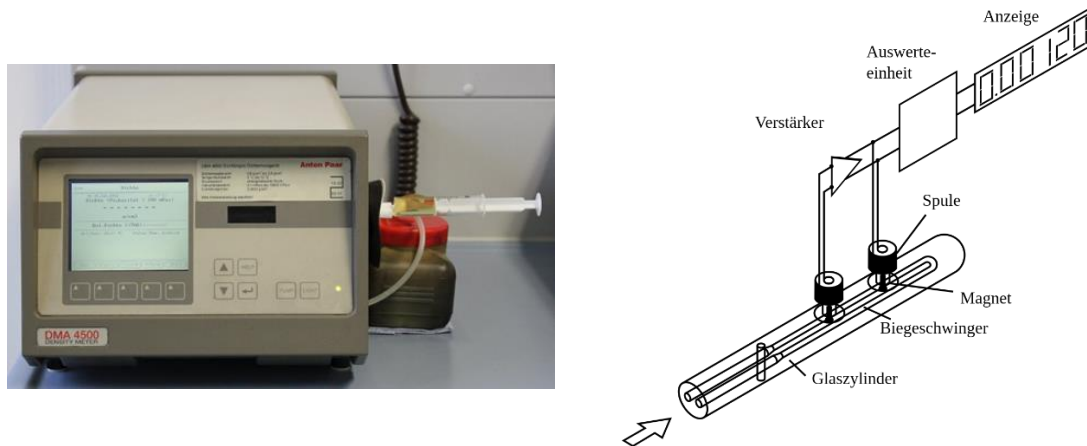


Fig. 4.12 The principle of the Anton/Parar instruments Density-dependent frequency changes of an oscillating glass U-tube

The instrument is calibrated against air and water at each test temperature. With the two calibration points, the unknown density is readily obtained from the measured frequency of the U-tube.

## 4.9 Molecular Weight Measurement

Several techniques have been proposed for determining average molecular weights of hydrocarbon fractions and residues. The techniques are based on boiling point elevation, freezing point depression, vapor phase osmosis, gel permeation chromatography, and other factors. All methods have limited ranges of accuracy and should be applied to specific ranges of molecular weights.

Most oils, oil fractions, and residues have molecular weights in the range of 100-500. This covers the hydrocarbons from C7 to C35. The method most suitable for determining molecular weights within this range is that based on freezing point depression. The principle, of this method is that the freezing point of a pure solvent (e.g., benzene or nitrobenzene) is lowered when the solvent is contaminated with a small amount of oil. Fig. 4.13 shows a typical temperature vs. time curve when a solvent is cooled.

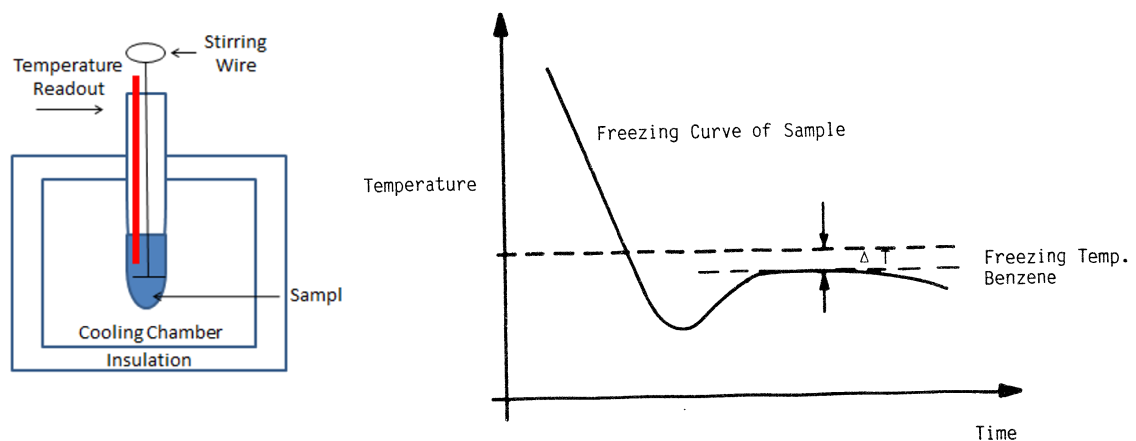


Fig. 4.13. Measuring principle and Freezing point depression diagram

The horizontal line corresponds to the melting point of the pure solvent,  $T_m$ . The temperature-line curve for the oil contaminated solvent will after a certain interval reach a constant value lower than  $T_m$ . The temperature difference,  $\Delta T$ , is a measure of the molecular weight per mole of a sample of the oil. If the apparatus is calibrated using substances of known molecular weight, the observed value of  $\Delta T$  may yield the average molecular weight of the oil sample. The method is very sensitive and, therefore, difficult to use, and must be carefully calibrated.

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