Chapter 6

Supercritical Fluid Chromatography: Demonstration of group separation

6.1 Introduction

For many years group analysis of fuel samples were done with the laborious fluorescent indicator adsorption test (FIA)[1] or an equivalent thin layer chromatographic (TLC) method. These methods use fluorescent dyes to determine the paraffinic, olefinic and aromatic content of petrochemical samples. NMR[2] and MS[3] methods are sometimes used but these methods are expensive to operate and require specially trained operators. Gas chromatography is well established for analysis of petrochemical samples with boiling points below 200°C[4]. While normal phase HPLC shows excellent group separation capabilities, it is hampered by the lack of a suitable universal detector. The use of CO_2 in SFC combines the group separation power of HPLC with the detection capabilities of GC, especially since the universal and very linear flame ionization detector (FID) can be used. In recent years SFC has become the standard technique for group analysis in petrochemical samples[5].
This chapter demonstrates the use of the ASTM method D5186 of 1991 for PAH analysis and includes a comparison of data obtained with SFC and HPLC methods.

Although one-dimensional chromatographic methods have been proposed for oxygenate analysis, multidimensional methods are better suited for the complexity of petroleum samples[6]. In some instances, multiple columns are used. Here oxygenates are selectively retained in a polar column before being back-flushed into a non-polar column for alcohol and ether component separation[7]. Other methods apply multidimensional schemes through selective detection. Oxygen selective flame ionization (OFID)[8], atomic emission detection (AED)[9] and Fourier transform infrared (FTIR)[10] are examples. Recently, the use of comprehensive GCxGC was demonstrated for the separation of benzene, toluene, ethylbenzene and the xylenes (BTEX), alcohols and ethers[11]. MTBE and several alcohols were successfully separated form a petrol sample and quantified. However, the separation of other ethers was hampered by co-elution with non-polar components.

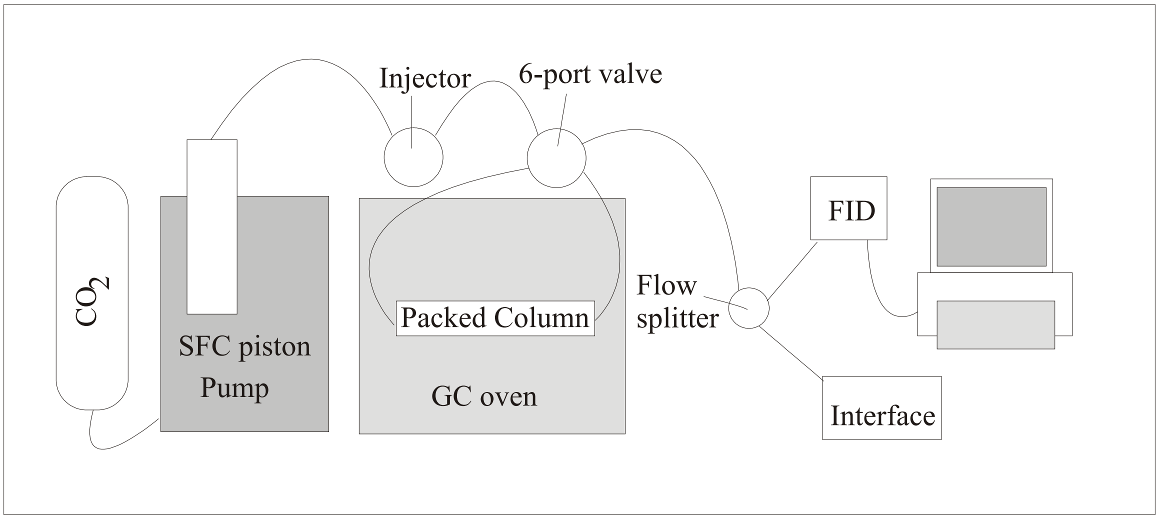
In this chapter the novel application of a silica gel PLOT column to facilitate oxygenate analysis is proposed. With this method oxygenates can be separated into various subgroups including acids and di-ols. Oxygenates are analyzed on silica gel and the FID, without the use of modifiers or back flushing techniques, by altering the phase ratio (β).

6.2 Experimental

6.2.1 Instrumentation for packed column PAH group separation

The instrumentation used in this section was developed during the authors M.Sc. studies[12].

Figure 3-1: The Supercritical Fluid Chromatograph.



A supercritical fluid chromatograph (Lee Scientific 501SFC, Utah,USA) was used to deliver supercritical CO_2 (SFC grade, Air Products, ZA) , without helium head pressure, to the 2.0mm X 250mm silica gel packed column (SFC group separation column, Hewlett Packard). Integral restrictors were used at the column exit to maintain the supercritical pressure conditions.

These were manufactured according to the process described by Guthrie and Swartz[13]. One end of a polyimide coated fused silica tube (50µm i.d. 350µm o.d.) (Polymicro Technologies, USA) was gently heated in a small high temperature glass blowers flame until it formed a conical closure. The restrictor is attached to the SFC and pressurized. The closure was gently sanded open with emery paper (no.500) until the desired flow rate was obtained.

Two restrictors were coupled to the column exit by means of a tee junction (Valco PN: ZT1C, Valco, Switzerland) to improve FID flame stability for group quantitation and to allow for off-line collection of separated groups. The column was connected to a six-port switching valve (Vici CW6-K, Valco, Switzerland) to allow back flushing to the detector. The isothermal column conditions were maintained by a PYE-Unicam GCD gas chromatograph with two FIDs. One FID was used for group quantitation while the other was only used to heat the second restrictor tip. These FIDs were designed for packed column GC and needed no alteration for SFC operation. The FIDs were maintained at 300°C. Chromperfect software (Justice Innovations, California) was used for data acquisition. An electrically actuated internal loop injector (Vici C14-W, Valco,Switzerland) with an 0.2µL internal loop was used for sample injection. All connections were made of 1/16” o.d. 120µm i.d. stainless steel (SS) tubing with electro-polished ends and connected with SS ferrules and connectors.

A pressure of 150atm at 28°C was used for all experiments[14].

6.2.2 Instrumentation for PLOT column separation

A Chrompack CPsil PLOT column was used for the analysis. The PLOT column was connected to a filter (Valco ZUFR1) by means of a two-piece removable fused silica adapter (Valco FS1.8-5). These adapters are made of graphite and were not very successful for the high-pressure work. PEEK adapters are also available and might work better for this application. The filter was connected to a low dead volume two-way split connector. Two restrictors were glued into two pieces of electrolytic cut SS tubing with Epoxy glue. This approach was also used for the PLOT column connections when the fused silica adapters failed. The SS tubing was connected to the two way split with PEEK ferrules and 1/16" SS Valco nuts to form stable low dead-volume connections. One restrictor was connected to the FID on the Pye-Unicam packed column gas chromatograph.

A Valco injector with 0.2µL internal loop was used for sample introduction. This was connected to the PLOT column with a 20cm piece of electrolytic cut SS tubing through a butt connector.

High pressure liquid CO_2 was delivered from a Lee Scientific 501 pump. SFC grade CO_2 (Air Products) was used as mobile phase.

Initial experiments were performed at 150atm and 28°C, using the entire 30m column.

6.3 Results and discussion

6.3.1 Demonstration of the group separation of petrochemical samples using a silica gel packed column

The SFC system was tested according to the recommendations of the ASTM method and resolution between docosane and toluene of $R = 7$ far exceeded the required minimum resolution of $R = 4$.

Table 6-1 lists a comparison between the SFC method following the guidelines of ASTM D5186-91 and an established HPLC method. Very good correlation between the two methods was obtained except in the case of the Natref LCO sample. Here no clear distinction between the mono and di-aromatics could be observed. This type of sample would benefit from a multidimensional approach where the differences in boiling point should aid separation within this continuum of distribution on the polar separation axis.

Table 6-1 A comparison of the SFC and HPLC analysis of 4 Diesel samples. Values are presented as mass %. (HPLC analyses by Sastech, Sasolburg, ZA)

Class	HT-SR		HX		Secunda DHT		Natref LCO	
	SFC	HPLC	SFC	HPLC	SFC	HPLC	SFC	HPLC
Aliphatic	99.93		99.86	98.61	69.65	70.19	22.57	25.37
Mono-aromatic	0.07	<1%	0.14	1.39	26.52	28.71	43.35	24.5
Di-aromatic					2.43	1.1	25.99	37.13
Poly-aromatic					1.4	0	7.14	13.0
Oxygenates							0.95	

The HPLC method could not analyze for oxygenates because in order to elute the very polar compounds, solvents of increasing solvent strength were added to the mobile phase. Typically methanol or acetonitrile is used and this masks the oxygenate peak. The results obtained with SFC shows that the Natref LCO sample was the only sample that contained an observable amount of oxygenates.

6.3.2 Investigations into the group separation achieved with the PLOT column

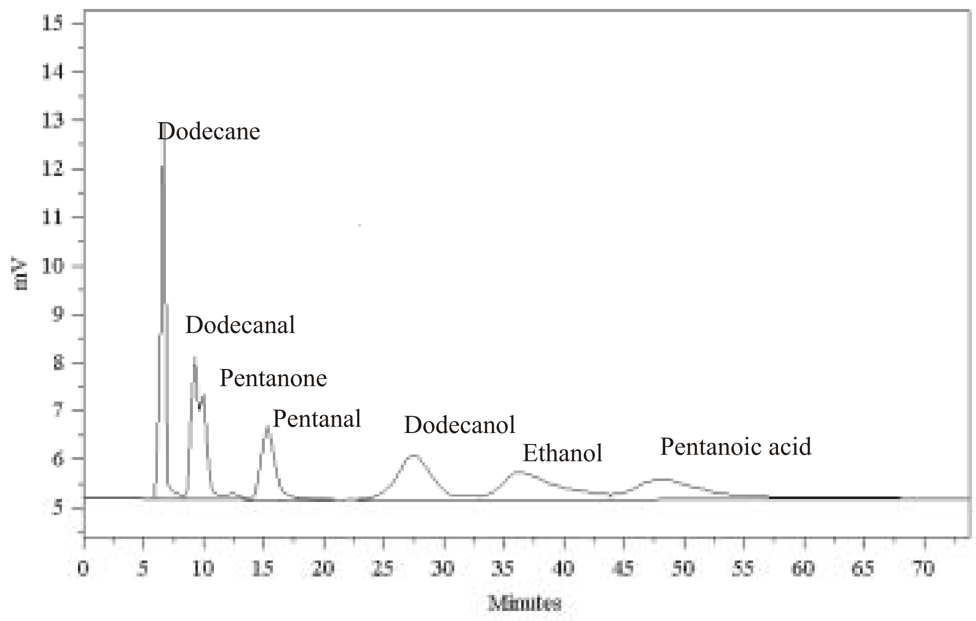
6.3.2.1 PLOT column oxygenate elution pattern

The inherent separation power of capillary columns prompted the investigation into the use of a silica gel PLOT column for petrochemical group separation. However, non-polar compounds showed almost no retention on this polar silica gel stationary phase. Even anthracene, with three benzene rings, was only marginally separated from the comparatively more volatile dodecane. (Figure 6-6). However the low retention of the PLOT column allowed for the elution of very polar oxygenated compounds.

From Figure 6-3 it can be seen that the silica gel PLOT column successfully segregated the oxygenated compounds from non-oxygenated compounds such as alkanes and poly-nuclear aromatics like anthracene (Figure 6-6). The oxygenate class was further separated into various groups e.g. aldehydes and ketones, followed by the alcohol group.

Carboxylic acids also eluted from the PLOT column. The tailing observed for the ethanol and the carboxylic acid was most likely produced by the strong hydrogen bonding interactions of the -OH moiety with active sites on the silica surface.

Figure 6-3: The elution order of some general groups with the Si-PLOT column and CO_2 at 150atm and 28°C.



6.3.2.2 The influence of temperature on group resolution

Homologues of the same functionality are spread over a large retention time window. Those with higher boiling points elute later. Thus, it was thought that an increase in temperature might serve to reduce this spreading and focus individual groups closer together.

Unfortunately higher temperatures reduced the selectivity between the different groups and this lead to a loss in group-resolution. This correlates with the theory explained in Chapter 5.4.3 . Similar to the interaction with π-bonds, the specific interactions between the oxygenated groups and the hydroxyl groups on the silica gel surface are enthalpy controlled, while the non-specific London forces, that increase with molar mass of the homologue, is entropy controlled. Thus, an increase in temperature decreased the strength of the polar interactions and increased the relative contribution of vapor pressure to the retention mechanism, thereby reducing selectivity.

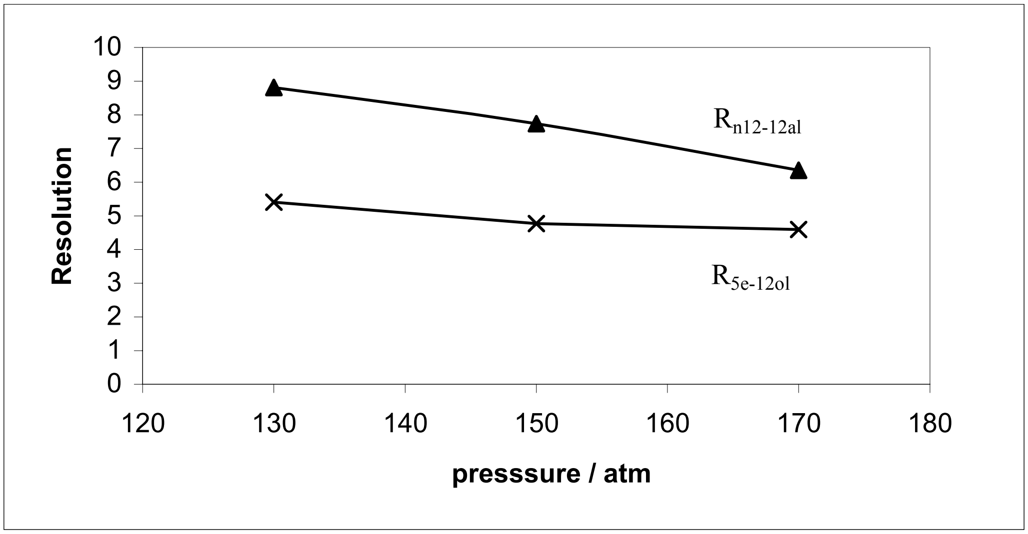
6.3.2.3 The influence of pressure on group resolution

Molecules of each group were chosen to represent a range of compounds that arbitrarily define a group. These molecules are called group boundary molecules. In Figure 6-4 dodecane (n-12) was chosen to represent the non-polar molecules.
Ethers, aldehydes and ketones elute in the same window and no pressure dependence on their group separation could be obtained. The resolution between dodecane and dodecanal (12al) was used as representatives for the non-polar and carbonyl separation. Methyl ethers elute later than ethers with long side chains on both sides. Thus, the separation between the alcohol group, here represented by the dodecanol (12ol) and the methyl ethers represented by MTBE (5e) was also demonstrated.

For both the ether-alcohol and ether alkane separation, group resolution seemed to decrease with an increase in pressure. This can be ascribed to the decrease in the capacity factor value as explained with the resolution equation in Chapter 3. The strong influence of pressure on the capacity factor and thus chromatographic resolution was surprising since the temperature of 28°C that was used is below the critical temperature for CO_2. This reminds us that near critical fluids also have some properties normally associated with supercritical fluids.

Figure 6-4: Group resolution of boundary molecules as a function of pressure

$R_{n12\text{-}12al}$ denotes resolution between the aliphatic and carbonyl groups.
$R_{5e\text{-}12ol}$ signifies resolution between the ether and alcohol groups.



6.3.2.4 Comments on flow rates and runtimes

Most of the chromatograms shown here were obtained in about 1 hour. This was achieved by using very fast linear flow rates. The flow rate, measured as decompressed CO2 gas at the column exit, was typically 480ml/min. This corresponds to a linear flow rate of 7.7 cm/sec.

According to theory[15] the optimal average flow rate u_{opt} in GC is expressed as:

$$u_{opt} = \frac{4D_G^0 j(1+k)}{r}\left(\frac{3}{1+6k'+11k^2}\right)^{1/2}$$

Where

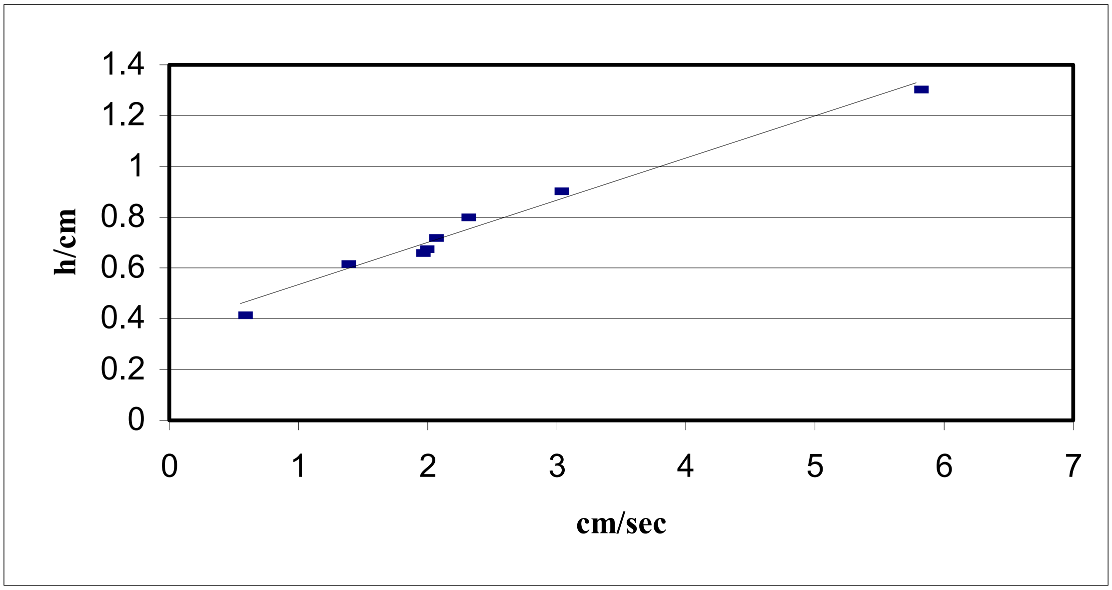
D^0_G = mobile phase diffusion coefficient at outlet pressure
j = compressibility factor
k = capacity factor
r = column radius

The contribution to band broadening by diffusion into the stationary phase was neglected.

Diffusion coefficients are much lower in supercritical fluids compared to GC, especially at the high pressures used here. Typical values for solute diffusion in CO_2 approaching the liquid state is 10^{-4} cm^2/s. Using this value for a compound with a capacity factor of k=2 it can be calculated that the optimum flow rate for this column should be as low as 1,6 x 10^{-4} cm/s.

It was attempted to obtain a Van Deemter curve. However even at analysis times of more than 9 hours, the minimum in plate height was not reached.

Figure 6-5: Van Deemter curve for a 0.3mm i.d. Silica gel PLOT column at 150atm



The application of mobile phase velocities, much above optimal is a general trend in capillary SFC[16]. The decrease in analysis time by the use of high mobile phase velocity can be justified by the large amount of excess resolution that was obtained. Compound specific resolution was not required since it was attempted to effect oxygenate group separation. This separation will be followed by a second boiling point analysis in the proposed $SFCxGC_{ftp}$.

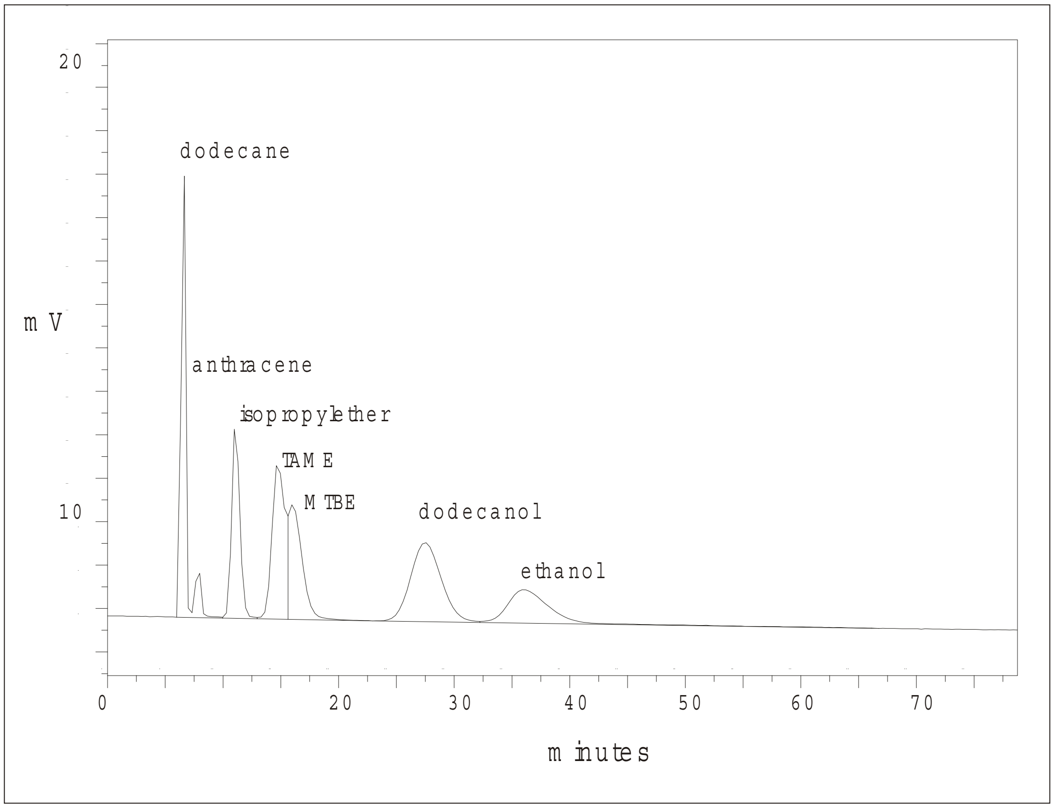
6.3.2.5 Applications of the Silica gel PLOT column

Figure 6-6 shows the retention of compounds relevant to the petrochemical industry. Ethers elute in the same retention time window as the carbonyl compounds.

The alcohols were very well separated from the ethers. Diisopropylether (DIPE) was separated from methyltert-butyl ether (MTBE)and tert-amylmethyl ether (TAME) but unfortunately TAME and MTBE were not well resolved at these pressures. Alcohols with near carbon numbers will also co-elute. A second separation, to analyze for the individual components of each group will be needed if compound specific analysis is required. Non-polar compounds were however unlikely to co-elute with ethers which is a major advantage over the previously described GCxGC[10] method.

Figure 6-6: Separation relevant to the petrochemical industry

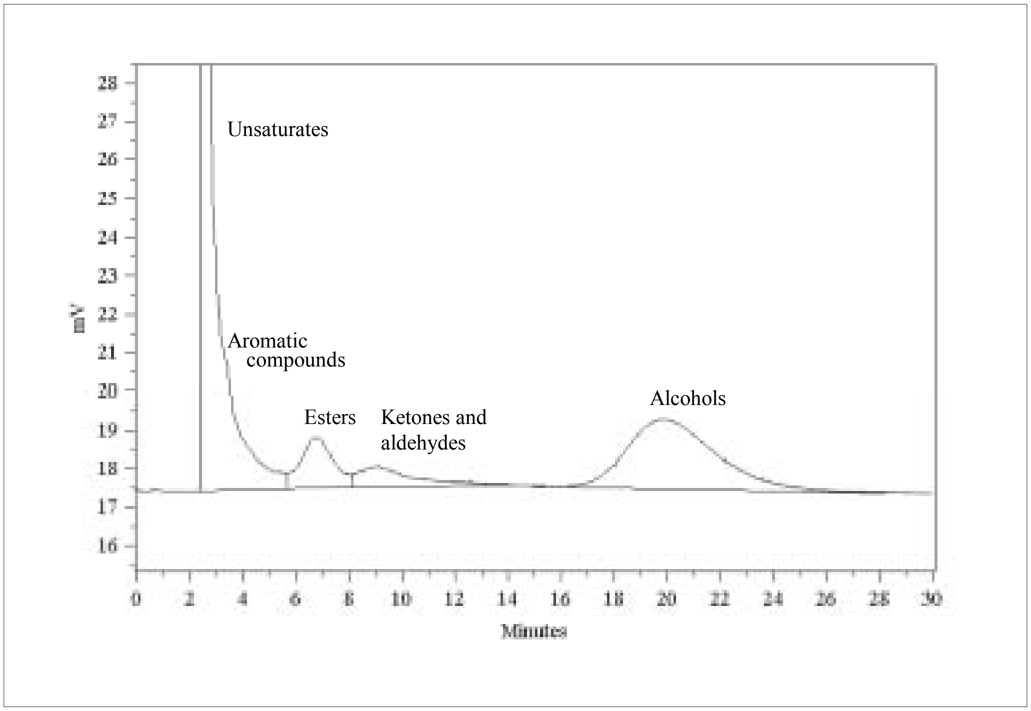
Conditions: 30m 0.35i.d. Si-PLOT column; Pressure 150 atm;
Temperature 28°C; Flow rate 7.7cm/sec.



A commercial lemon essential oil was also analyzed. Compounds were clearly separated into various groups identified as esters, aldehydes and ketones and the alcohols. The groups were not baseline resolved at these pressure conditions. This analysis may benefit from using a lower pressure. However, as will be demonstrated in Chapter 9 when this separation was combined with GC in the SFCxGC$_{ftp}$, a fast and efficient separation was obtained.

Figure 6-7: Analysis of a lemon essential oil

Conditions the same as for Figure 6-6.



6.4 Conclusions

The results obtained with the packed column SFC method correlated well with those obtained with HPLC. Moreover, unlike with the HPLC method, quantification of the oxygenate group was also possible after the column was back-flushed following the elution of the other groups.

It was also demonstrated that when a silica gel PLOT column was used, oxygenated molecules could be eluted without back-flushing of the column. Oxygenates were further separated into groups of increasing polarity. Thus, the ethers, ketones and aldehydes were separated from the alcohols and the alcohols were separated from the oxy-acids.

The analysis of compounds pertaining to the petrochemical industry was demonstrated. Here the separation of the ethers from the methyl ethers and alcohols, without any interference from the non-polar molecules, are very promising.
The PLOT column was also applied to the analysis of a lemon essential oil. The sample was fractionated into four distinct groups. The groups were identified as the aliphatic and aromatic class, the esters, the aldehydes and ketones and finally alcohols eluted.

Both the packed column and PLOT group type analyses separated compounds according to polarity. This type of analysis is largely independent of boiling point especially in the case of the packed column. These two columns will thus be very useful for comprehensive multidimensional separation schemes where the second separation is based on volatility. This will be demonstrated in Chapter 9.

Chapter 6

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