Analysis of alkane, alkene, aromatic and oxygenated groups in petrochemical mixtures by supercritical fluid chromatography on silica gel

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Abstract

Pre-separation into chemical class by chromatographic methods is a powerful aid to analysis by capillary gas chromatography and provides valuable information in itself, since fuel properties are to a large extent dependent on the chemical group composition. Normal-phase supercritical fluid chromatography on silica gel has become the established method for the separation of the aromatic and aliphatic groups in petrochemical samples. This method was extended to include the analysis of alkane, alkene and oxygenate groups in gasoline range samples without significantly increasing the complexity of instrumentation. A systematic study of chromatographic parameters demonstrated that alkane–alkene group selectivity increases at high pressures. A flow splitter was built into the system and a new restrictor interface was designed to allow off-line transfer of separated groups to the GC or GC–MS for detailed characterization. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Gasoline; Petrochemical analysis; Diesel fuel; Alkanes; Alkenes

1. Introduction

No single separation method exists to date that provides a complete analysis of petrochemical samples. Extensive sample pre-treatment is necessary for preliminary separation of these mixtures. Pre-separation into chemical class by chromatographic methods is a powerful aid to analysis by capillary gas chromatography (GC) and provides valuable information in itself, since fuel properties are to a large extent dependent on the chemical group composition.

Normal-phase supercritical fluid chromatography (SFC) on silica gel with CO_2 as mobile phase has become the established method for the separation of the aromatic and aliphatic groups in petrochemical samples [1].

Norris and Rawdon [2] adopted the silver column from high-performance liquid chromatography (HPLC) [3] to further separate the aliphatic compound class into alkane and alkene groups. Silver columns are costly and unstable. The silver impregnated silica gel column requires replacement every 6–8 weeks [4]. Despite increased stability of silver impregnated cation-exchange columns, these systems are still complex, requiring backflushing to recover the alkenes and reproducible retention and switching times to prevent aromatics from entering and being irreversibly adsorbed by the silver column.

Sulphur hexafluoride (SF_6) was investigated as an alternative mobile phase for group separation [5]. SF_6 is a very weak solvent, less polarizable than

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CO_2. Separation of alkane and alkene groups without the use of a silver column was observed for samples in the gasoline boiling range [6]. By changing the polarity or identity of the mobile phase, the selectivity term of the resolution equation term is affected.

$$R = \frac{\sqrt{N}}{4} \cdot \frac{k}{k+1} \cdot \frac{\alpha - 1}{\alpha} \qquad (1)$$

The solubility parameter (δ) was first introduced by Hildebrand and Scott as a relative scale for solvent strengths. δ is a function of the cohesive energy density c:

$$\delta = c^{1/2} = (\Delta u^{\text{evp}}/v)^{1/2} \qquad (2)$$

where Δu^{evp} is the vaporization energy and v is the molar volume. Since the molar volume is indirectly proportional to the density of the fluid, the solvent parameter will vary as the density varies. The density is controlled by changes in pressure. By changing the pressure, the solvent strength (δ) is changed and this influences the retention factor term $k/(k+1)$ in Eq. 1 with a resultant change in resolution. Changing the pressure could, however also change the selectivity.

This paper investigates the dependency of alkane–alkene group resolution on pressure by independent investigation of the selectivity and the retention factor term of the resolution equation. Should increased resolution between alkane and alkene groups be attained when CO_2 is used at a low pressure (lower than the 150 atm suggested as optimum for the aliphatic aromatic separation [7]; 1 atm = 101 325 Pa) then this approach can be used as an alternative to the silver column which is unstable, costly and increases the complexity of the separation system.

Molecules containing oxygen and sulphur atoms are strongly retained by silica gel columns. Some researchers have used cyano columns as a cleanup step to remove oxygenates from the sample in fear of permanent damage to the activity of the silica gel column. When aromatics are recovered from the silica gel column by backflush as was initially done by Suatoni and Swab [8] to decrease analysis time, oxygenates will co-elute with the aromatics and be integrated as such. With the aromatics eluting in the forward mode before the backflush, oxygenates in

the sample can be quantified since they alone are now present in the backflush. This was demonstrated by Dark who quantified aromatics in the forward direction and oxygenated aromatics and polars by backflushing from an amino modified column using hexane as mobile phase [9]. Backflushing of polars from a cyano column with CO_2 was also demonstrated for SFC [10]. Since CO_2 is more polarizable than hexane [11,12] it was thought to investigate the possibility of recovering oxygenates directly from silica gel using this mobile phase. Oxygenates show reduced carbon response factors in flame ionization detection (FID) and correction before quantification is necessary. Most oxygenates present in gasoline samples at detectable concentrations are additives, added in areas where a cheap source of alcohol is available, possibly as by-products in synthetic fuel plants. The compound-specific response factors are often obtainable from tables available in textbooks such as Poole and Poole [13].

Other additives like MTBE (methyl *tert.*-butyl ether) and TAME (*tert.*-amyl methyl ether) used in lead-free petrol as alternative to TEL (tetraethyllead) are added because of their high anti-knock character. Although present at low concentrations, their retention behavior is of importance as they may show up in subsequent GC–MS analysis. In this paper backflushing of ethers and alcohols will be demonstrated.

Hyphenation of SFC eluents to other instruments is relatively easy compared to HPLC. CO_2 evaporates when it is depressurised at the column exit. No off-line reconcentration is therefore required and residual CO_2 does not interfere with GC–mass spectrometry (MS).

On-line heart cutting [14,15], off-line and comprehensive [16] hyphenation techniques have been used to couple supercritical fluid chromatographs with other SFC instruments, to gas chromatographs and to mass spectrometers [17,18].

One way to create the time space necessary for the lengthy boiling point analysis of separated groups by conventional GC is to store trapped fractions until the GC is ready to accept the next injection. This approach is called off-line hyphenation and requires the eluent to be trapped by solvent or adsorbent traps [19].

2. Experimental

2.1. Instrumentation

A supercritical fluid pump (Lee Scientific 501SFC, Salt Lake City, UT, USA) was used to deliver the supercritical CO_2 (SFC grade, Air Products, Sandown, South Africa), without helium head pressure, to the 250×2.1 mm, silica gel (5 μm particle size, 60 Å pore size) packed column (SFC group separation column, Hewlett-Packard). Fixed restrictors were used at the column exit to maintain the supercritical pressure conditions. 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. Integral restrictors were manufactured according to the process described by Guthrie and Swartz [20]. The column was connected to a six-port rotating valve (Vici CW6-K, Valco) to allow back-flushing to the detector and trap. The isothermal column conditions were maintained by a Pye-Unicam GCD gas chromatograph with two built-in FID systems. One FID system was disconnected from the gas supply and used as an interface for heating the second restrictor used for trapping of column eluents for off-line analysis.

To improve retention time reproducibility and to prevent plugging of the restrictor a new restrictor interface was designed. This interface allows direct contact between the heated block and the restrictor tip. Provision is made for connecting of traps of 4 mm and 8 mm O.D. to the restrictor interface. The interface consists of a copper body that rests on the GC heating block, connected to the inside of the oven by a 1/4 in. brass tube with 1/4 in. to 1/16 in. reducing connection (1 in. $=2.54$ cm). A filed needle is used as a wedge from above to press the restrictor firmly against the heated interface ensuring good thermal conduction (see Fig. 1).

The FID system, used for group quantitation, was designed for packed column GC and needed no alteration for SFC operation. The FID system and trapping interface were kept at 200°C. Chromperfect software (Justice Innovations, CA, USA) was used for data acquisition. An electrically actuated internal
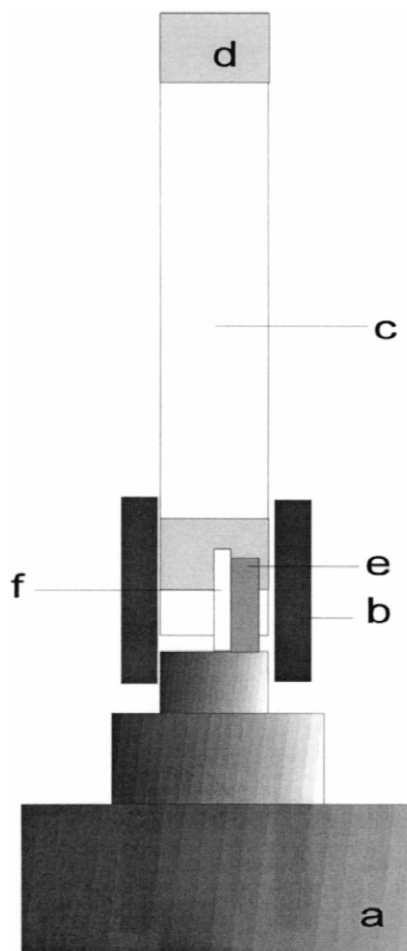

Fig. 1. Heated interface and traps for trapping of SFC eluent. (a) Heated interface, (b) heat shrink PTFE, (c) adsorbent material, (d) glass wool, (e) solid insert, (f) restrictor.

loop injector (Vici C14-W, Valco) with a 0.2-μl internal loop was used for sample injection. All connections were made of 1/16 in. O.D. $\times 120$ μm I.D. stainless steel (SS) tubing with electropolished ends and connected with SS ferrules and connectors.

2.2. Procedures and materials

For SFC dead time determination butane (Extra pure butane lighter fluid, Rizla, UK) and methane were injected by directing flow from the pressurised canisters directly through the injection valve and

simultaneously switching the valve to the inject position. Butane and methane were also bubbled through a solution of toluene (20 μl) in CS_2 (200 μl) and injected for analysis.

A standard solution containing docosane, hexene and toluene in CS_2 was injected into the SFC system at a pressure of 200 atm and temperatures of 20°C and 28°C. The flow-rate at 28°C and 200 atm was measured at the pump as 0.2 ml/min.

Stable temperatures below 28°C were obtained by submerging the column in a water bath, cooled down to 20°C with ice.

A standard was prepared that contained every second member of a homologous series of alkanes from hexane to docosane. A similar sample was prepared for alkenes from hexene through to hexadecene.

The samples were injected at pressures ranging from 90 to 130 atm and a temperature of 28°C.

For investigation into the relationship between pressure and resolution due to unsaturation a sample was prepared that contained decane, decene and toluene. Pressures ranged from 100 to 140 atm at 28°C.

Group separation was investigated by use of a standard containing hexadecane and 3-hexene. Based on the results of the previous two experiments the pressures investigated were 140 atm to 220 atm at 28°C.

All standards were of analytical grade and in all cases CS_2 was used as solvent.

Real petrol and diesel samples were sourced from a petrol station.

A standard solution containing 10% MTBE and 10% toluene in CS_2 was prepared. 0.2 μl of the standard was injected at 200 atm and 28°C and the flow-rate was 0.18 ml/min. The column was back-flushed after 10 min.

A petrol alcohol mixture (PAM) was prepared by adding 10% (m/m) butanol to a commercial petrol sample.

3. Results and discussion

3.1. Restrictor interface

Retention time irreproducibility is caused by temporal freezing of the restrictor opening as the pressurised CO_2 expands. This cools the restrictor tip and also causes the deposition of less volatile sample components leading to plugging of restrictors.

Very reproducible retention times (see Table 1) are obtained by the solid insert interface and the solid insert (filed needle) does not interfere with the trapping procedure.

3.2. Dead time determination

For the determination of k and α, accurate calculation of the column dead time or hold up time is necessary.

Problems with injection reproducibility are encountered when gases were used as probes for dead time determination. Solutions tend to become over saturated causing bubbles in the injector sample loop. This problem is especially severe for the more volatile methane. Solubility of methane in the toluene–CS_2 test solution was also very low, posing problems of detection for the unretained solute.

According to Table 2 there should be little difference between the retention factor values obtained from butane instead of methane as unretained markers for most combinations of temperatures and pressures to be studied in this investigation. CS_2

Table 1
Retention time reproducibility

	1 (min)	2 (min)	3 (min)	Average	Average deviation
Butane	2.489	2.496	2.493	2.493	$2.444 \cdot 10^{-3}$
Docosane	2.619	2.633	2.631	2.628	$5.778 \cdot 10^{-3}$
CS_2	2.850	2.857	2.854	2.854	$2.444 \cdot 10^{-3}$
Toluene	3.819	3.832	3.828	3.826	$4.889 \cdot 10^{-3}$

Table 2
Finding a suitable unretained marker

	t_R (methane) (min)	t_R (butane) (min)	k (butane)
120 atm, 28°C	6.80	7.27	0.07
40°C	5.60	6.45	0.15
200 atm, 28°C	3.99	4.00	0.003
40°C	3.66	3.79	0.04

could not be used as unretained marker with retention times similar to alkenes.

3.3. The influence of temperature on group separation

In order to obtain group selectivity the non-specific type interactions between the stationary phase and the saturated carbon chain must be negligible but the specific induction interactions between the double bonds (or other functional groups) and the stationary phase need to be as strong as possible.

Tagaki and Suzuki [21] investigated the influence of temperature on alkane–alkene separation and found that the best selectivity (α) and resolution (R_s) of homologs differing only in number of carbon atoms were nearly independent of temperature whereas the α and R_s of homologs differing in number of double bonds increased as the temperature was reduced. They concluded that separation by carbon number is controlled by entropy differences, whereas separation by double bonds is based on enthalpy contributions. This explains why the best group resolution were reported at sub-critical temperatures [7,9].

The pressure of 200 atm used during this investigation is based on experimental results obtained in Section 3.4. As all the alkanes elute unretained as a group at these conditions, no retention factor (k) values of the alkanes could be obtained for this group and the selectivity between the alkanes and the other groups could not be calculated. The k values of the other groups were calculated by taking docosane as unretained (t_m). This assumption is valid under these conditions where the alkanes elute as a narrow peak.

The increase in selectivity at temperatures below 28°C is relatively small compared to the increase in instrumental complexity required to maintain stable temperature conditions below 28°C. Table 3 shows the influence of temperature on the retention of docosane, hexene and toluene.

3.4. The influence of pressure on the alkane–alkene group separation

At first glance it would seem sensible to start the run at lower pressures for the alkane–alkene separation in order to improve the resolution, two factors have to be considered as a function of pressure: (1) the selectivity due to unsaturation (number of double bonds); (2) the selectivity due to carbon number (boiling point).

For increased resolution between the alkane and alkene groups at lower pressures the selectivity due to number of double bonds should increase and the selectivity due to boiling point should be weakly expressed.

3.4.1. Selectivity due to carbon number

From Fig. 2 it is clear that at low pressures, severe selectivity due to carbon number takes place. Alkanes are followed by alkenes of the same chain length. Separation both by boiling point and by number of unsaturated bonds is observed. Since two separation mechanisms are simultaneously operating, a chromatogram of a sample containing alkanes and alkenes of various chain lengths will not be ordered according to unsaturation. It is clear that the boiling point separation mechanism is expressed stronger

Table 3
The influence of temperature on retention factors

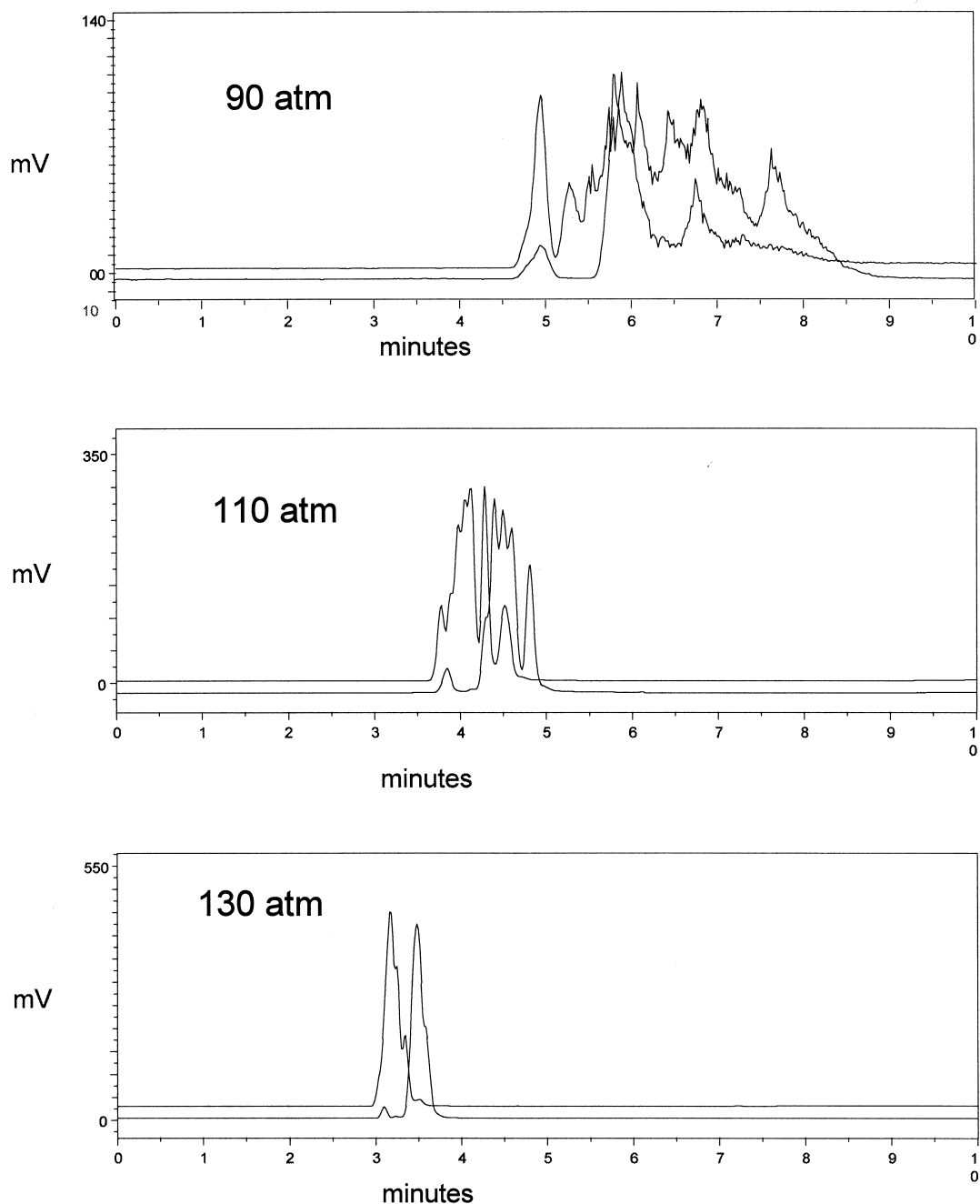|	28°C	20°C
Docosane (t_m)	0	0
Hexene	0.10	0.12
Toluene	0.44	0.45

Fig. 2. The influence of pressure on the separation of the alkane (C_6–C_{22}) and alkene (C_6–C_{16}) homologous series. Top trace: alkanes; bottom trace: alkenes.

than group selectivity at low pressures. The situation improves when pressure is increased and at 130 atm the two homologous series are ordered according to

unsaturation i.e., the group selectivity is strongly expressed and sample components are starting to elute as separate groups. At 130 atm hexadecane

appears to be separated from hexene, the first member of the alkene group but docosane still co-elutes with the alkene group. Thus group selectivity between alkanes and alkenes improves when pressure is increased.

It appears as if a certain minimum CO_2 density is required for dispersion forces between the fluid and analytes to be of the same order than those provided by the surface. When all molecules of a homologous series experience effectively no dispersion interaction with the stationary phase and dipole-induced dipole interactions alone dictate retention behaviour, true group separation can be obtained. Less polar fluids will show less interaction with the double bond and the double bond containing molecules will favor the adsorbed state. A theoretical maximum in the carbon number of alkanes that can be separated from the alkene group is expected and this maximum depends on the relative contribution of a double bond compared to the contribution of a methylene group to the phase distribution. This is a function of the relative polarity of the mobile phase and depends on the fluid identity.

Increasing the density can only serve to change the total number of interactions and not the relative contribution of the various types of possible interactions between the fluid and solutes. From Fig. 2 with CO_2 at 130 atm, 28°C where hexene is separated from hexadecane, one double bond appears to be equal to about 10 methylene groups in contribution to retention.

3.4.2. Selectivity due to level of unsaturation

Decane and decene (Fig. 3) were chosen as probe molecules for the investigation into selectivity (α) by number of unsaturated bonds with the same carbon
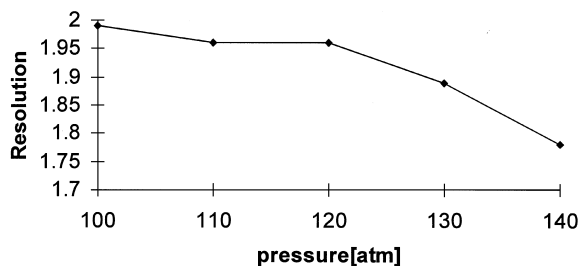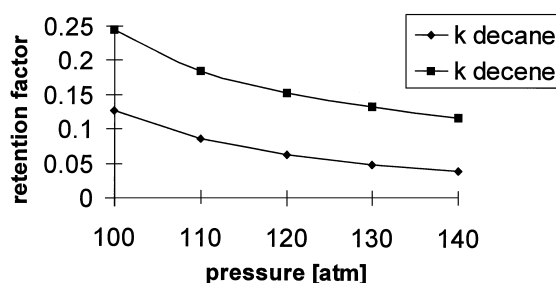

Fig. 4. Retention factors of decane and decene as a function of pressure.

number because they have an intermediate chain length to molecules in gasoline and diesel range samples.

The resolution of a single alkane–alkene pair is improved as the pressure is reduced.

Figs. 4 and 5 demonstrate that this improvement in resolution is due to an increase in the k values of both decane and decene at low pressures despite a decrease in α when the pressure is reduced giving rise to larger $k/k+1$ values in the resolution equation (Eq. 1). As the pressure is reduced, the total retention of solutes are increasingly dependent on factors that the two molecules have in common (the 10-carbon atom strong carbon chain) and the double bond contributes a smaller percentage to the total solute retention with a subsequent decrease in selectivity.

Changing the pressure from 90 to 140 atm does not change the plate number (N) appreciably. At 110 atm $N=8500$ and at 140 atm $N=8900$ indicating that α and k dominate the change in R_s (Eq. 1).

Group separation is thus likely to be reduced at

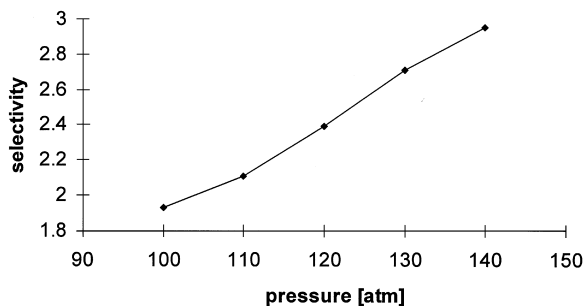Fig. 3. Resolution (R_s) of decane and decene as a function of pressure.

Fig. 5. Selectivity between decane and decene as a function of pressure.
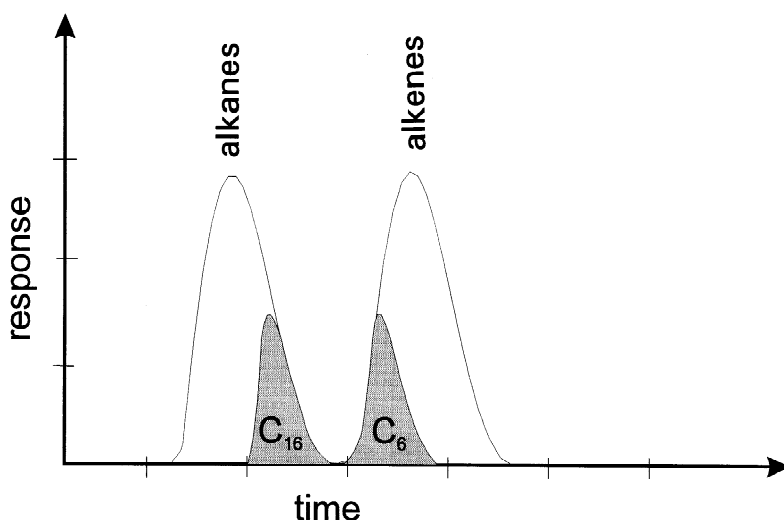
Fig. 6. Probes for the alkane–alkene group separation.

low pressures despite the increase in resolution between a single alkane–alkene pair.

3.4.3. The effect of pressure on group selectivity

In order to study the retention behaviour of the alkane–alkene group separation, hexadecane was chosen as the last eluting member of the alkane group and hexene as the shortest member of the alkene group found at appreciable levels in gasoline samples (see Fig. 6). In this way the maximum contribution to retention by methylene groups could be compared to the retention by an alkene with little retention due to its carbon chain. This separation pair

reflects on a true sample containing a broad volatility range but allows determination of k values of individual solutes, a calculation that would not be possible for more complex mixtures.

As it was already clear from the previous two experiments that group separation improves at high pressures, only pressures equal to and higher than the maximum pressure of the previous two experiments were investigated.

Resolution between the alkane group (hexadecane) and alkene group (hexene) (see Fig. 7) initially increases linearly with pressure at constant temperature but reaches a maximum at 200 atm. Resolution
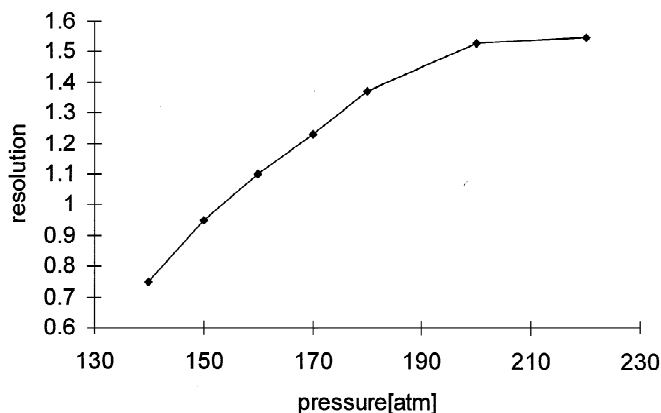

Fig. 7. Resolution between hexadecane and hexene as a function of pressure.
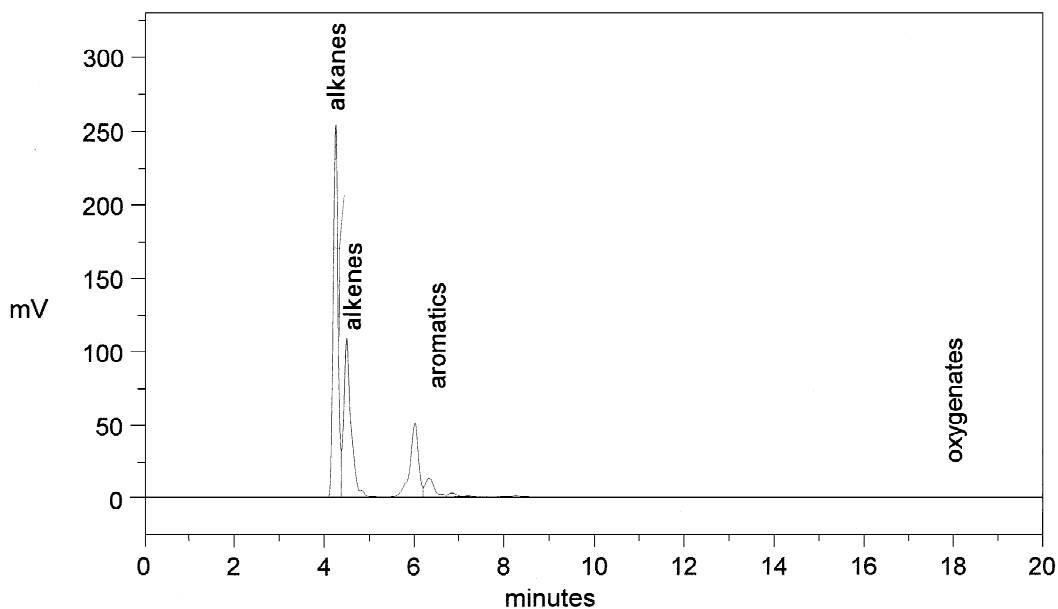
Fig. 8. Group separation by SFC of a commercial petrol sample.

improves only slightly with a further increase in pressure since the solvent strength of the mobile phase, at this pressure, is already approaching the interaction strength of the dispersion forces of the heavier alkanes with the stationary phase. In practical terms this means that the heavier alkanes already move through the column unretained at this pressure. At 28°C CO_2 is in the liquid state. The fact that an increase in resolution at near-critical temperature between 130 and 200 atm is observed at all, seems to indicate that the liquid compressibility influences k and α.

The plate numbers remain roughly constant at about $N = 6000$ (calculated for hexene) at all pressures studied. The k values become smaller at

high pressures with the alkanes eluting almost unretained at 200 atm. The resolution is increased because the α effects dominate the k effects in the resolution equation (Eq. 1).

3.5. Analysis of petrol and diesel samples

The SFC group quantitation (Fig. 8) results were compared to that of a multidimensional PIONA GC analyzer using stopflow conditions and column switching to analyze gasoline range samples into alkanes (P), isoalkanes (I), alkenes (O), naphthenes (N) and aromatics (A) (Table 4) [22].

There is a marked difference between the relative percentages of alkane and alkene concentration

Table 4
Comparison of SFC group quantification results with the PIONA analysis

	PIONA	SFC	SFC corrected for naphthenes
Cycloalkanes	2.44	–	
Isoalkanes	36.70	–	
Total alkanes	49.64	46.20	48.94
Alkenes	27.39	30.30	27.86
Aromatics	22.35	24.14	
Oxygenates	Not detected	Not detected	
Total aliphatic	77.03	76.50	

Table 5
Integration results of alkanes and alkenes of original petrol sample and that spiked with 1,2-dimethylcyclohexane

	Shell 93	Shell 93 spiked with cycloalkane
Alkanes	0.59	0.50
Alkenes	0.41	0.50

obtained by SFC and PIONA analysis for both samples. The percentages obtained for the total aliphatic group (alkanes + alkenes) appear to correlate well. The PIONA analysis also contains information on the relative percentages of branched and cycloalkanes but detailed information of this kind is not obtainable from the SFC chromatograms.

When the relative percentage of cycloalkanes (obtained from PIONA analysis) is subtracted from the SFC alkene value and added to the SFC alkane value, very good correlation for both the alkene and alkane values by the two methods is obtained. From this it seems probable that the naphthenes are co-eluting with the alkene group.

The relative concentration of alkenes did also increase when a naphthene was added to the petrol sample thus it can be concluded that naphthenes

co-elute with the alkenes and are integrated as such (Table 5). Confident claims of alkane and alkene contribution to the aliphatic group can only be made if naphthene contribution to sample composition is negligible or can be determined by some complimentary method.

The chromatogram of the diesel sample does not show a clear distinction between alkanic and alkenic groups (Fig. 9). This is due to the much larger span of carbon chain lengths present in diesel samples.

3.6. Oxygenates

Both MTBE and TAME are present in the backflush (Fig. 10).

Taking into account the reduction of the carbon response by oxygen atoms in the flame of -0.5 carbon atoms per primary alcohol [11] the oxygenate group is expected to integrate for 8.75% of the total but only integrates for 6.2%. The difference is probably due to flame conditions that are significantly different from the flame used to obtain the published response factors of oxygenates. This is most likely due to the high flow-rates of the expanded CO_2 mobile phase through the detector.
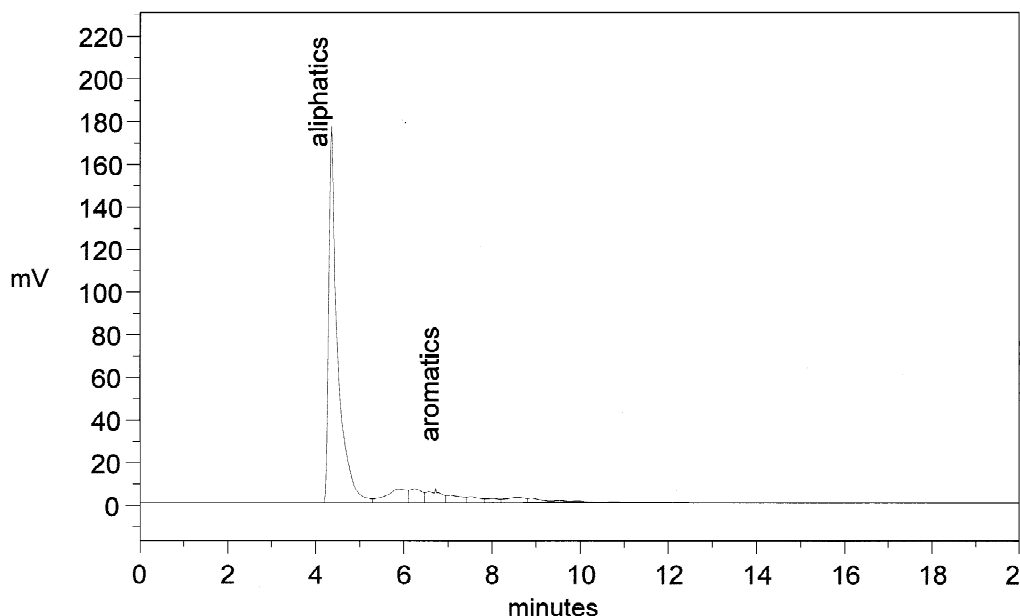

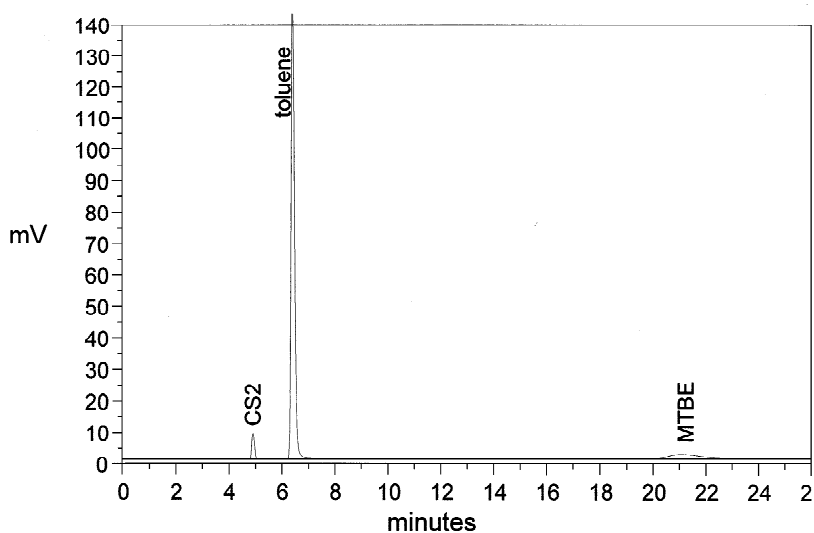Fig. 9. Group separation of a commercial diesel sample.

Fig. 10. MTBE is present in the backflush.

Improved response factors could be obtained experimentally. On the other hand the difference could be due to excessive tailing of the MTBE recovered by backflush.

Fig. 11 illustrates a PAM analyzed without pressure ramping on the backflush. Pressure ramping on the backflush does improve the peak shape of the oxygenate group. Integration benefits marginally from this procedure. The integration of the oxygenate group increases only to 6.4% when the pressure is ramped to 250 atm on the backflush (Fig. 12). It is

therefore believed that flame response factors are the major concern here.

4. Conclusions

A systematic study of the chromatographic parameters revealed that group selectivity (α) increases at high pressures resulting in better group separation despite a general decrease in retention factor (k) values. As the pressure is increased the k values of
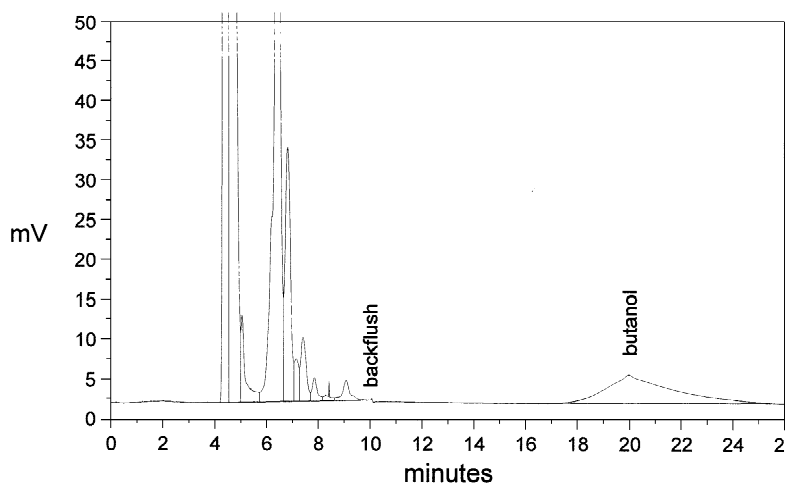

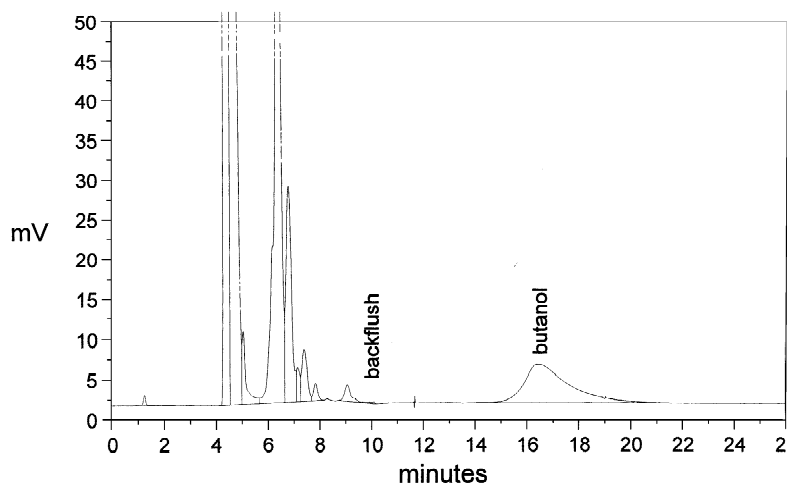Fig. 11. PAM analyzed without pressure ramp on backflush.

Fig. 12. PAM analyzed with pressure ramp on backflush. The pressure is ramped from 200 atm to 250 atm at 50 atm/min.

the alkanes decrease faster than that of the alkenes and this leads to increased selectivity. The best resolution between the alkane and alkene groups was obtained at 200 atm. A further increase in pressure did not significantly improve resolution. At a pressure of 200 atm and a temperature of 28°C, hexene could be separated from hexadecane ($R_s = 1.5$). Thus, in gasoline range samples, alkanes can be separated from alkenes. Unfortunately the cycloalkanes still co-elute with the alkene group. Either alkenes or naphthenes should not be present in samples or will have to be removed or quantified by alternative methods if the relative contribution of alkanes and alkenes to the aliphatic group are to be determined.

The optimum pressure for the alkane–alkene separation is higher than the 150 atm reported in the literature as optimum for the aliphatic–aromatic separation. Even so, excellent resolution was obtained between docosane and toluene at 200 atm. Oxygenates, including additives such as TAME and MTBE, are recovered by backflushing the column. A pressure ramp on the backflush slightly improves quantitation by improving peak shape.

Reduction of the temperature from the near-critical 28°C to 20°C yields a small increase in group resolution but this does not justify the added complexity of the cryogenics required to cool the column down to below room temperature. The improvement is more pronounced for the alkane–alkene separation

pair than for the aliphatic–aromatic separation and this might warrant future investigation.

The SFC design incorporates a post column split to improve detector stability and to facilitate group transfer for detailed GC–MS analysis. The solid insert interface allows direct heating of the restrictor tip, yielding very reproducible retention times. Group transfer by off-line collection on solid adsorbent traps will be demonstrated in a forthcoming article.

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