THE USE OF MULTIDIMENSIONAL GC TECHNIQUES FOR THE ANALYSIS OF COMPLEX PETROCHEMICAL PRODUCTS

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Declaration

I, the undersigned, hereby declare that the work contained in this thesis is my original work and has not previously in its entirety or in part been submitted at any university for a degree.

Signature: Date:

R. van der Westhuizen

ABSTRACT

The composition of petrochemical products obtained from Fischer Tropsch (FT) technologies is of the highest complexity possible and may contain thousands of components. Chemicals produced from FT feedstocks often contain trace level contaminants that can poison catalysts or that affect product performance in down-line processes. Single dimension GC analysis of these mixtures provides incomplete information because of lack of separation power.

This study evaluates the separation power of heart-cut GC-GC, comprehensive GCxGC and sequential GC-GC for three selected challenging petrochemical applications. The fundamental theoretical aspects of the techniques are discussed.

Oxygenates are removed as far as possible in C_{10} – C_{13} alkylation feedstocks, used in the production of linear alkyl benzenes, because the oxygenates may have deactivating effects on some expensive alkylation catalysts. Residual oxygenates may still be present and can consist of hundreds of components. Detection of individual components at ng/g levels is required. Heart-cut GC-GC is used to illustrate the separation and enrichment power for oxygenates in an alkylation feedstock. The stationary phase in the first dimension column was selected to provide separation of the oxygenates from the hydrocarbons in a relatively narrow window. The oxygenate fraction is then enriched by repeated injections and collection on the cryotrap. After sufficient enrichment, the trap is heated and the oxygenates are analysed on the second dimension column.

Comprehensive GCxGC and Sequential GC-GC are compared for the separation and analysis of the oxygenated chemical component classes in the alkylation feedstock, before removal of oxygenates.

Cyclic alcohols can occur in detergent alcohols produced from FT feedstocks. These cyclics are regarded as impurities because they affect the physical properties of the detergents. The cyclic and noncyclic alcohols in a narrow C_{12} – C_{13} detergent alcohol distillation cut have similar boiling points and polarities, and separation of individual components is thus difficult to achieve. Comprehensive GCxGC and sequential GC-GC are evaluated for the separation of the alcohol component classes. The study shows that both approaches provide component

class separation but the high resolving power of the second column and the optimal chromatographic operating conditions of sequential GC-GC provide better separation of the individual components.

The study illustrates the immense power of the three multidimensional GC techniques namely heart-cut GC-GC, comprehensive GCxGC and sequential GC-GC. The three multidimensional GC techniques each have their own advantages, disadvantages and unique applications and should be used as complementary rather than as competitive analytical tools.

OPSOMMING

Fischer Tropsch (FT) petrochemiese produkte is van baie hoë kompleksiteit en kan uit duisende komponente bestaan. Chemikalië afkomstig van dié voerstrome bevat soms spoorhoeveelhede onsuiwerhede wat deaktiverend op kataliste kan inwerk of wat die werkverrrigting van finale produkte kan beïnvloed. Enkeldimensie GC analises van die komplekse mengsels is meesal onakkuraat as gevolg van geweldige piekoorvleueling.

Die studie evalueer die skeidingsvermoë van drie multidimensionele tegnieke, *Heart-cut GC-GC, Comprehensive GCxGC* en *Sequential GC-GC* vir geselekteerde petrochemiese toepassings. Die fundamentele teoretiese aspekte van die tegnieke word bespreek en drie analitiese toepassings word beskryf.

Oksigenate word so ver moontlik verwyder uit C_{10} – C_{13} paraffien-voerstrome, wat gebruik word in die vervaardiging van liniêre alkielbenzene, aangesien dit deaktiverend kan inwerk op alkileringskataliste. Die oorblywende oksigenate kan uit honderde komponente bestaan sodat analise van individuele komponente tot op lae ng/g vlakke nodig is. *Heart-cut GC-GC* word gebruik om die skeiding en verryking van die oksigenate in die alkileringsvoerstroom te illustreer. Die stationêre fase in die eerste-dimensie kolom is so gekies dat skeiding tussen oksigenate en koolwaterstowwe verkry word. Met herhaalde inspuitings verhoog die oksigenaat-konsentrasie op die cryo val en - na voldoende verryking - word die val verhit en die oksigenate geanaliseer op die tweede dimensie kolom.

Die skeiding en analises verkry met *Comprehensive GCxGC* en *Sequential GC-GC* word vergelyk vir die chemiese klasse-skeiding van die alkileringsvoer (voor verwydering van oksigenate).

Sikliese alkohole kan voorkom in detergent-alkohole vervaardig vanaf FT voerstrome. Dit word as onsuiwerhede beskou aangesien dit die fisiese eienskappe van die finale produkte beïnvloed. Die sikliese en nie-sikliese alkohole se kookpunte en polariteite is baie naby aanmekaar sodat skeiding van individuele komponente moeilik verkry word. *Comprehensive GCxGC* en *Sequential GC-GC* word evalueer vir die skeiding van die alkohol. Die studie toon aan dat albei die tegnieke skeiding gee van die chemiese komponent-klasse maar dat die

hoë-resolusie tweede-dimensie kolom en die optimisering van die experimentele kondisies van die *Sequential GC-GC* sisteem beter skeiding van individuele komponente gee.

Die uitsonderlike skeidingsvermoë van die drie multidimensionele tegnieke, *Heart-cut GC-GC, Comprehensive GCxGC* en *Sequential GC-GC* word geïllustreer in die studie. Elke tegniek het sy eie voordele, nadele en unieke toepassings en die drie tegnieke behoort as komplementêre eerder as kompeterende tegnieke gebruik te word.

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Table of Contents

1. INTRODUCTION AND AIM

Petroleum and petrochemical products are very complex mixtures consisting of thousands of components, continuously presenting challenges to the analytical chemist. Gas chromatography (GC) is most often the analytical technique of choice for these analyses because it provides better separation capabilities than any other analytical technique. Moreover, several universal, selective and spectroscopic detectors can be coupled to a GC column. Single column chromatographic methods, however, do not have sufficient separation power or peak capacity for complex petroleum mixtures. Even state-of-the-art capillary columns with peak capacities close to 1000 are unable to unravel this complexity.

Traditionally, petrochemical products are therefore made less complex by separating the mixture into a number of fractions (fractionation). Techniques commonly applied in petrochemical laboratories are column chromatography (CC) or its miniaturised format solid phase extraction (SPE), liquid-liquid extraction/distribution (LLE), derivatisation, distillation, etc. The selected technique depends on the problem at hand. Fractionation techniques aim to selectively isolate specific chemical classes as a concentrated group. Chemometrics are often used in connection with these techniques, as it offers the advantage of saving time and improving the correlation of different parameters [1, 2, 3]. Some typical fractionation techniques evaluated by the author in the Sasol laboratories are presented.

The excellent selectivity attainable with CC and/or SPE is frequently used in petrochemical applications to obtain chemical class separation of component classes, e.g. paraffins / olefins, aromatics and oxygenates (**Figure 1.1**). Glass CC columns are normally home-made, packed to uniform density with a slurry of the adsorbent (silica-gel in this case) in the solvent of choice, normally a non-polar solvent like hexane or pentane. The formation of air bubbles and channels leading to breakthrough should be prevented. More recently, pre-packed SPE columns became commercially available. They contain stationary phases related to those used in HPLC. Typical phases are silica gel, reversed phase material, Florisil^{TM} and ion exchange media. The pre-packed columns, however, have limited capacity and do not exhibit a high degree of resolution in terms of number of theoretical plates. Notwithstanding, pre-packed SPE columns are highly convenient to use because they are automated packed to uniform density, giving highly reproducible results.

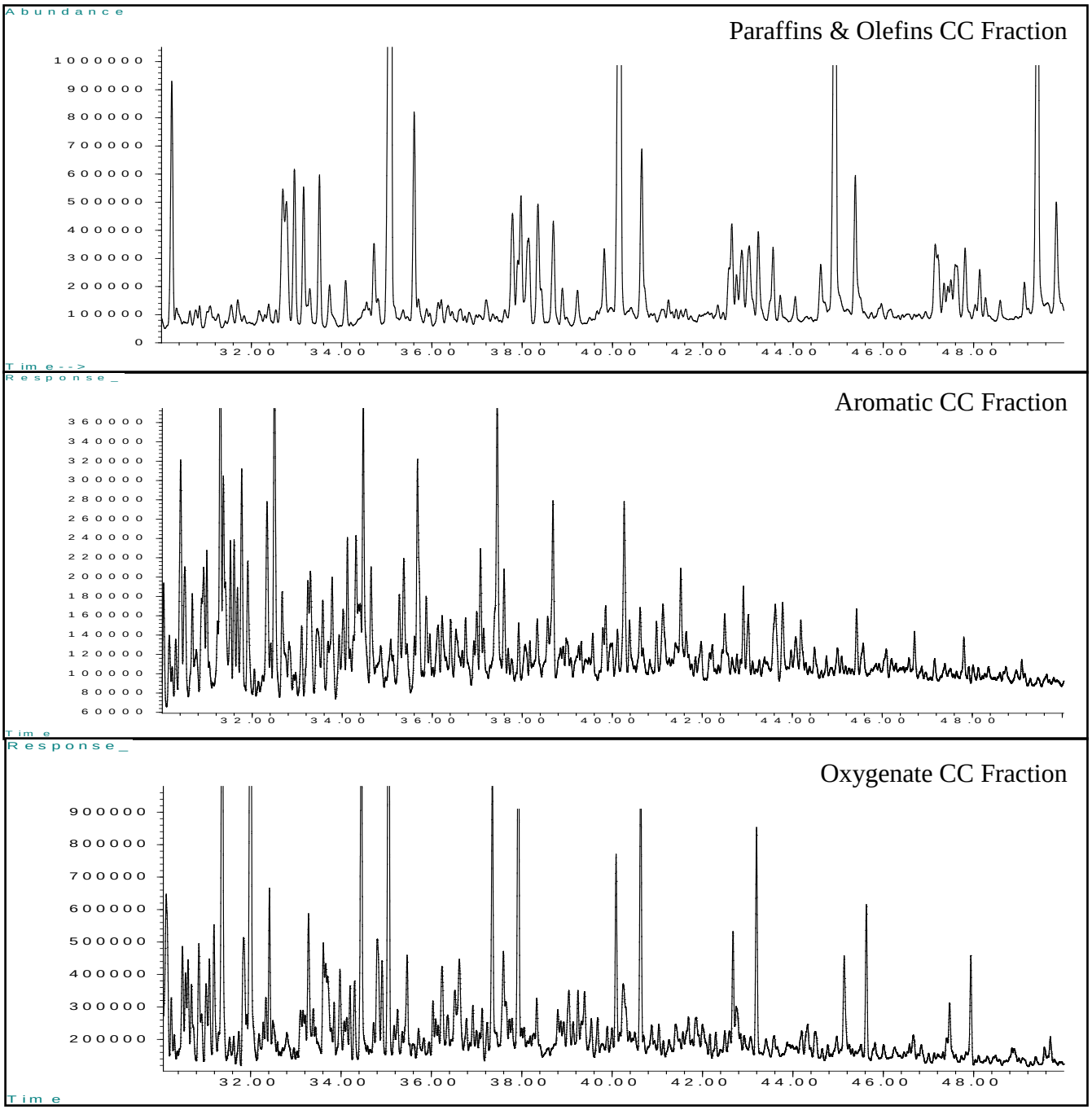


Figure 1.1. FID Chromatograms of paraffin and olefin, aromatic and oxygenate fractions after CC fractionation of a complex petrochemical feedstock.

The fractionation principle depends on the nature of the stationary phase and involves mechanisms of adsorption, partition or ion-exchange. The most important adsorbents for petroleum analysis are silica gel, alumina and zeolitic molecular sieves for fractionation according to polarity and octyl-, octadecyl- and phenyl derivatised silica gel for separation according to hydrophobicity [4]. Columns should be solvated prior to use if reproducible

results are to be obtained, especially with the more hydrophobic stationary phases. The important physical effect of solvation is to organise the organic moieties of the stationary phase in a regular array that is more accessible to solutes in the mobile phase. A number of solvents may be used as mobile phases. The flow rate may be enhanced by applying pressure from above or suction from below. Enhanced flow rate is often used for relatively simple applications but gravity flow is essential when the full resolving power of the sorbent is required [5].

For the fractionation of the petrochemical feedstock shown in Figure 1.1, the following CC conditions were applied:
Column: A 50 cm glass column, slurry-packed with 50 g of silica-gel 60 (0.063 – 0.02 mm diameter) in n-hexane.
Mobile phases: 200 ml each of n-hexane, dichloromethane and methanol was used to extract the paraffins and olefins, aromatics and oxygenates, respectively. All solvents were HiperSolv HPLC grade.

In the chromatograms in Figure1.1 (30 – 50 min zoomed in to illustrate the complexity of the samples), fractionation is clear but still a high degree of peak overlap occurred as was evidenced by GC/MS analysis.

For the isolation of olefins from a paraffin matrix, or dienes from an olefin matrix, silver ion chromatography is a powerful mechanism. Ion-exchange silica-based benzenesulfonic acid phases are converted to the silver form by eluting a silver nitrate solution through the column. Silica gel impregnated with silver nitrate may be used as well, but contamination of fractions with silver ions may occur. Saturated components (aliphatic and alicyclic) are eluted with a hydrocarbon solvent like hexane. Mono-unsaturated components are eluted with chlorinated solvents. For the elution of components with a higher degree of unsaturation, e.g. dienes, trienes, etc., the chlorinated solvent is mixed with methanol, acetonitrile or acetone [5]. As illustration, **Figure 1.2.** shows the separation of the diene peaks from 1-octene and C_8 cyclic olefins by using silver ion chromatography. A 1-octene sample was spiked with a number of diene and cyclic olefin standards; 1,7-octadiene, 4-methyl-1,4-heptadiene, 2-methyl-1,3-heptadiene, 1-methyl-1,4-cyclohexadiene, 3-methyl-1,5-heptadiene, 1,3-cyclo heptadiene and two C_8 cyclic olefins (ethylcyclohexene and 1,2,3-trimethylcyclohexene). The 1-octene and

cyclic olefins were eluted with dichloromethane and the dienes with a mixture of dichloromethane and methanol. The extracted ion fragments used in the chromatogram to differentiate between dienes and olefins are the following: m/z 110 is the molecular mass of C_8 dienes, m/z 83 is typical of olefins, m/z 81 and 95 are typical of dienes and cyclic olefins and, m/z 94 of cyclic dienes.

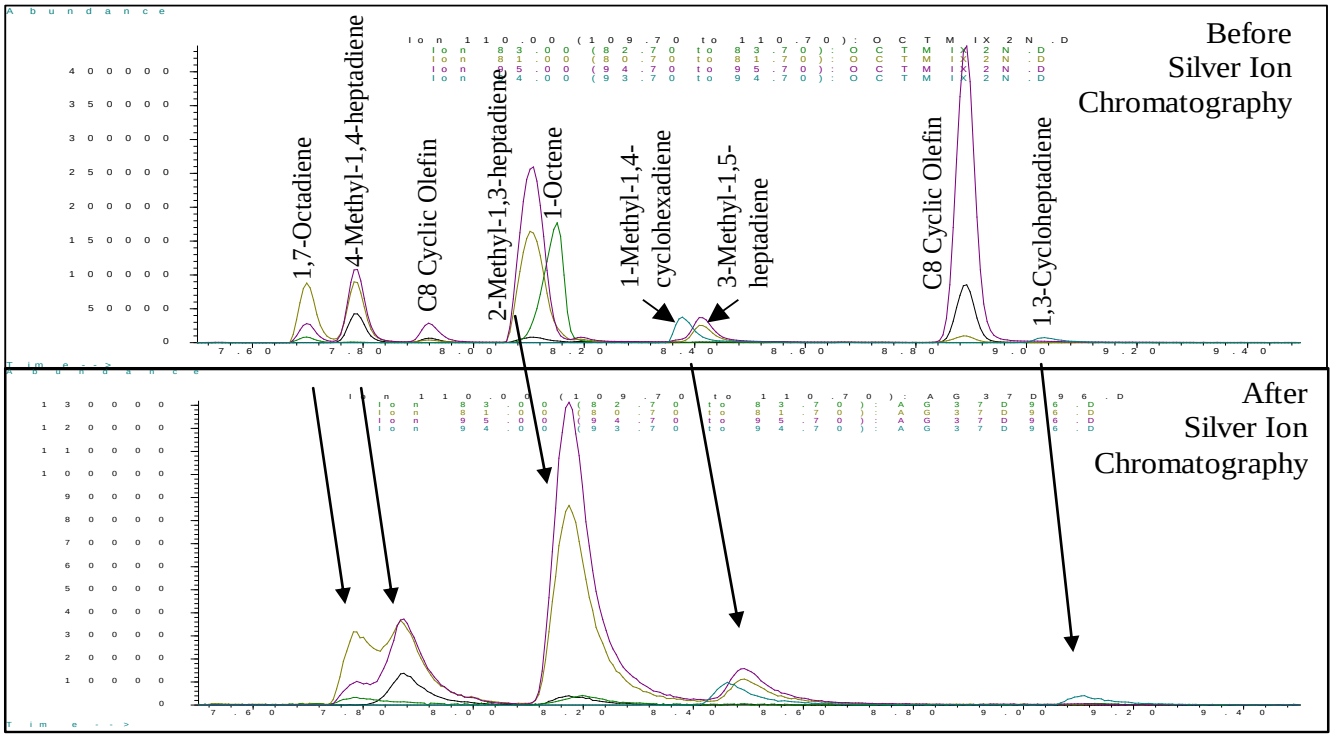


Figure 1.2. Extracted ion chromatograms at m/z 110, 83, 81, 95 and 94 indicating the separation of the dienes and cyclic dienes from the 1-octene and the C_8 cyclic olefins.

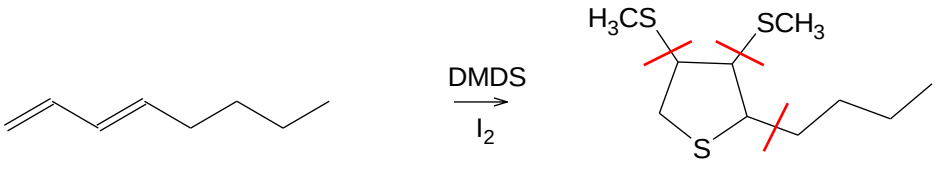
Even though LLE is still used extensively for petrochemical applications, the present tendency is to replace it with other techniques. This is mainly because expensive and high purity solvents are required for trace analysis and because there is a need to reduce the associated environmental and health risks [6]. Moreover, with some exceptions e.g. fractionation of hydrocarbons and polyaromatic hydrocarbons in the two-phase system cyclohexane/ nitromethane, fractionation is often far from complete.

The integrity of samples of high quality could be jeopardised if solvents of inferior quality are used. Expensive, high purity solvents are therefore obligatory for SPE and silver ion chromatography. The silver has the additional disadvantage that it is corrosive and potentially

harmful to the environment. Moreover, often solvents need to be evaporated after extraction to concentrate the analytes. If the analytes have relatively low boiling points, some of them may evaporate together with the solvents, leading to inaccurate results. These techniques can be very time-consuming and tedious, especially when columns need to be hand-packed and conditioned to ensure a sufficient separation.

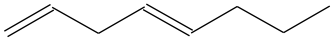
A large number of derivatisation methods are used to alter the retention behaviour of specific solutes, promoting them to be better separated from co-eluting compounds in complex mixtures [7]. As an example, the separation of dienes from cyclic olefins and olefins is described. The components have very similar boiling points and polarities and are therefore very difficult to separate, even with high resolution gas chromatography. Moreover, the mass spectra of dienes are very similar to those of cyclic olefins for the same carbon number, while the mass spectra of cyclic dienes are very similar to those of bicyclic olefins. Unsaturated components can react with dimethyldisulfide (DMDS) to form distinctive cyclic, bicyclic or linear S-compounds, while saturated components do not react with DMDS. The sulfide compounds are well separated from cyclic olefins and MS provides structural information about the dienes themselves [8, 9, 10]. The reactions with DMDS of some typical C_8 dienes are discussed.

Conjugated dienes produce 5-membered cyclic rings where the inner two carbons (previously attached to the double bonds) each contain a methylene sulfide group. The outer carbons will react to form a sulfide ring structure. The formed derivatives have distinctive fragmentation patterns and specific molecular masses, e.g. 236 g mole^{-1} for 1,3-octadiene.

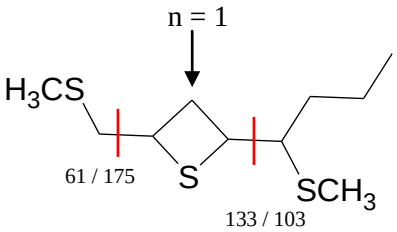


1,3-Octadiene M=236 g/mole (1.1)

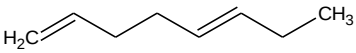
Derivatisation of non-conjugated dienes produces cyclic structures if the number of methylene groups (n), separating the double bonds of the diene, is less than four.



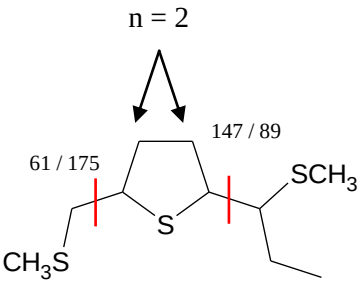
DMDS
I_2



1,4-Octadiene (n=1) M=236 g/mole (1.2)

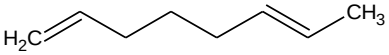


DMDS
I_2

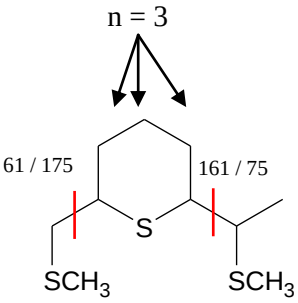


(1.3)

1,5-Octadiene (n=2) M=236 g/mole



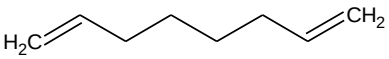
DMDS
I_2



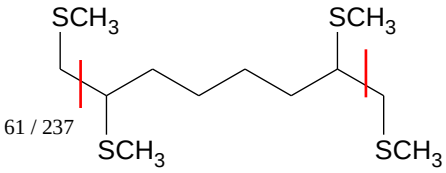
(1.4)

1,6-Octadiene (n=3) M=236 g/mole

If n = 4 or more, the structures will not be cyclic.



DMDS
I_2



(1.5)

1,7-Octadiene (n=4) M=298 g/mole

Cyclic and non-cyclic C_8 olefins only contain one double bond and can therefore only react with two sulphide molecules to form structures with molecular masses of 204 and 206 g/mole respectively. Derivatisation may be done in the GC inlet or in an off-line separate procedure. Interpretation of the mass spectra may be very complicated. The mass spectra of the derivatisation products are seldom in the mass spectral libraries and need to be interpreted using electron impact fragmentation rules. It is easy to make errors with the interpretation, especially when one starts to look at the derivatisation products of branched isomers. The mass spectral data of 1,3-octadiene and 1,6-octadiene are shown in **Figures 1.3A and 1.3B**, respectively.

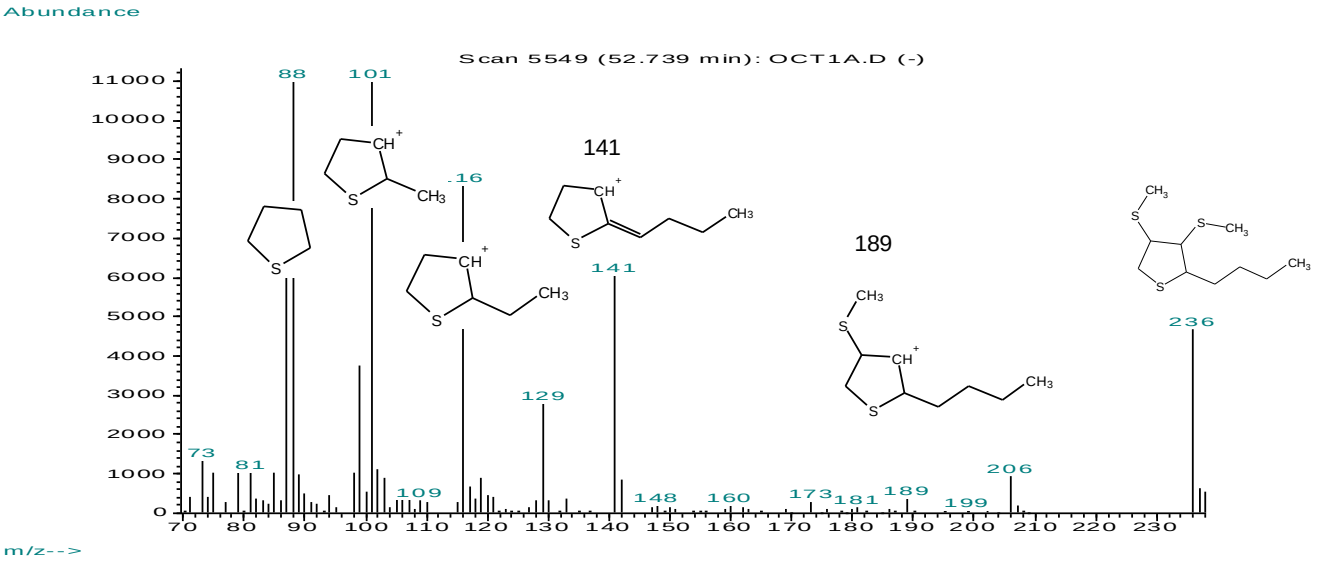


Figure 1.3A. Mass spectrum of the DMDS derivative of 1,3-octadiene

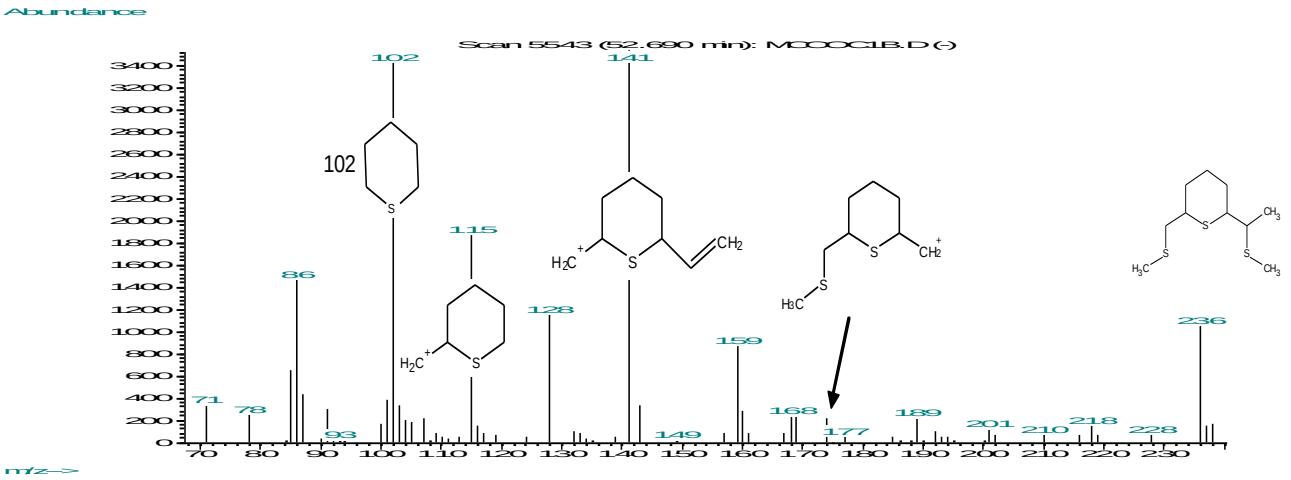


Figure 1.3B. Mass spectrum of the DMDS derivative of 1,6-octadiene

The above described fractionation techniques are commonly performed off-line and are very time-consuming and prone to artefacts. Instrumental methods that possess fractionation capabilities are therefore more than welcome as they are mostly automated which not only reduce the hands-on time for the chemist, but also produce much more reproducible results.

GC combined with spectroscopic detectors such as mass spectrometry (MS) and/or atomic emission detection (AED) has made identification of co-eluting components much easier. With MS, one can extract mass fragments that are distinctive for certain component classes as will be demonstrated by numerous examples in this study. With AED, element selectivity (O, S, etc.) is guaranteed. But for highly complex samples, the fractionation ability of MS and AED is still not enough.

Multidimensional techniques, mainly using packed columns, were introduced as a means to obtain better group-type separations of complex mixtures. The PIONA analyzer was developed in the seventies, with PIONA standing for paraffins, iso-paraffins, olefins, naphthenes and aromatics. It was first introduced as the PNA analyzer. Refiners used this method to control the reformer process. The ratio of naphthenes and aromatics from the reformer feed was used to predict the final octane number of the reformate, which was the basis for gasoline production. The instrument progressed to the nPiPNA, which extended the method to the analysis of iso-paraffins and later to the PIONA analyzer. This system exploited the unique separation of naphthenes and paraffins by carbon number on a column packed with zeolites of a specific pore size (molecular sieves 13X). In later years it was extended to include samples having boiling points up to 270 °C (C_{12} n-paraffin) and implemented in a commercial instrument. The PIONA method can be used to analyze hydrocarbon samples from C_3 to C_{12}. The upper limit of the procedure is set by the separation on the molecular sieve column. In order to elute higher boiling components, the temperatures have to be raised above 400°C and thermal degradation of the sample components may occur [11]. Additional environmental regulations required a reduction of olefins and aromatics in naphtha samples. To keep the octane number to an acceptable level, refiners blended isomerate, alkylate and oxygenates into the gasoline. To accommodate the oxygenate addition, the PIONA analyser was once again upgraded to the PIONA Plus Oxygenates analysis system known as the AC Reformulyzer ^{TM} [12].

Heart-cutting techniques using capillary columns were also developed in the seventies [13,14] but seldom applied in the petroleum industry because such systems lacked ruggedness. Fraction transfer was controlled by pressure balancing at a two-column midpoint and this was difficult to establish correctly with the pressure controllers available at that time.

In the early nineties, Phillips et al. described comprehensive GCxGC [15,16]. Over the last decade, this technique has established itself as a rugged method for high resolution GC as recently illustrated by Ong et al [17]. Its main benefits are superior resolution and enhanced sensitivity compared to conventional capillary GC. The most important outcome of GCxGC has been the great increase in peak capacity. For a complex sample, it is possible to locate a lot more peaks in a chromatogram, because of the expansion of the available separation space. Specific problem separations may now be resolved. GCxGC arises from the pulsing of solute emerging from one column (the pre-column) into a second column, with the time period of pulsing shorter than the primary column peak elution duration. This process is realized by the use of a modulator at the column junction. A number of modulators have been described and development work is still ongoing. The modulators operate under conservation of mass principals, such as thermal and cryogenic modulators. The dual-jet cryogenic modulator, which is most often used in commercially available GCxGC systems operates by pulsing the cryogenic jets on and off [17]. The choice of column phases is governed by the need to achieve maximum component separation for a particular sample. A typical combination is a non-polar pre-column, which separates according to boiling point, coupled onto a polar column (separation according to polarity). The GCxGC results can only be achieved if the second column analysis is very fast. Complete elution on this column is required within a few seconds. The main column is a short column ($\approx$ 1 – 1.5 m) with a narrow inner diameter ($\approx$ 0.1 mm) and a thin film thickness ($\approx$ 0.05 – 0.1 μm). Fast data acquisition (100 – 200 Hz) is critical for fast-eluting GC peaks. Only few detectors are able to detect at this high speed. FID is used most often, but ECD and AED applications have also been described. Time-of-flight MS (TOFMS) is the mass spectrometer of choice for GCxGC analysis as it permits data acquisition at thousands of spectra per second. The resulting data-files are very large (Mb-Gb range) making data manipulation and interpretation a lengthy procedure.

GCxGC has already shown to be very promising for chemical class separations of complex mixtures [18, 19]. The signal enhancement obtained with GCxGC is also well documented and a number of applications have reported low ng/g detection limits. For flavour components in the food industry, comprehensive GCxGC with time-of-flight detection MS (TOFMS) was demonstrated to drastically improve the separation with quantification down to the low (35 – 85) ng/g [20]. Other applications are in the perfume industry and in environmental analysis [21, 22]. A number of authors improved chemical class elucidation by the use of selective detectors. Hua *et al.* used a sulfur chemiluminescence detector coupled to GCxGC for the selective profiling of sulfur-containing compounds in diesel oils [23]. Van Stee *et al*. combined GCxGC with AED detection to provide valuable element selective information, identifying clusters of components containing chlorine, sulfur and nitrogen in pesticides [24].

In this work a variation of GCxGC was investigated, namely sequential GC-GC. Sequential heart-cutting lies in between heart-cut GC-GC or MDGC and GCXGC. Like in MDGC, chromatographic fractions that elute from the pre-column are transferred into a second capillary column. In contrast to GCXGC, the main column is a full length column and gives maximum separation power. Sequential runs are programmed in which one time fraction of 30 s to 1 min is heart-cut to the second column per run. For all runs, successive heart-cut windows are selected, for example ten analyses are programmed and a heart-cut window from 5 to 6 min is chosen for the first run. For the second run, the fraction between 6 and 7 min is transferred to the main column, etc. Fully automated sequences can be programmed for repetitive injection to the pre-column. For interpretation, all main run chromatograms are put together and a 3D plot (x=heartcut fraction, y= retention time in the main column, z=signal abundance) is constructed from these data.

With the advancement of multidimensional chromatographic techniques and the ability to analyse at the lower ppb levels, the real complexities of petrochemical products can more and more be unravelled.

The main aim of this study was to evaluate the features of the different multidimensional techniques (GC-GC, GCxGC and sequential GC-GC) and to demonstrate their separation power for petrochemical applications. In Chapter 2, the fundamental theoretical aspects of the techniques are discussed. Three challenging analyses have been selected and are

described in Chapter 3 to 5. Chapter 3 describes the use of heart-cut GC-GC for the analysis of ng/g levels of oxygenates in a C_{10} – C_{13} alkylation feedstock. Chapter 4 details the comparison of comprehensive GCxGC and sequential GC-GC for the separation and analysis of chemical component classes. Chapter 5 describes the separation and analysis of cyclic and bicyclic alcohols from non-cyclics in C_{12}-C_{13} detergent alcohols by using comprehensive GCxGC and sequential GC-GC.

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2 FUNDAMENTAL ASPECTS

2.1 Fundamental aspects of gas chromatography

Gas chromatography (GC) is a powerful separation technique with applications in numerous fields like in the petrochemical, pharmaceutical, fragrance, forensic, environmental to mention a few. It is one of the most important and most economical of all separation methods. The gaseous mobile phase transports the sample through an immiscible stationary phase, which is fixed in a column. The mobile and stationary phases are chosen to enable the sample components to distribute between these phases in varying degrees. The components that are strongly retained by the stationary phase move slowly with the flow of the mobile phase. The less strongly retained, the faster the components move. The result is the separation of the components into peaks that can be detected [1,2].

In the GC inlet system, the sample is vaporised and introduced onto the head of the GC column. Elution is done by the flow of the inert gaseous mobile phase. The mobile phase does not interact with molecules of the components; it only serves for the transport of solutes through the column axis.

Gas chromatography can be divided into two groups: gas liquid chromatography (GLC) and gas solid chromatography (GSC). GSC and GLC can be performed in packed columns and in capillary or open tubular columns. Capillary gas chromatography (CGC) is nowadays the most popular form of GC because it offers much more resolution power compared to packed column gas chromatography (PCGC) [3].

Gas solid chromatography is based upon a solid stationary phase in which retention of analytes is a result of physical adsorption. Gas solid chromatography has limited application owing to semi-permanent retention of active or polar molecules and severe tailing of elution peaks. GSC nowadays is used only for special separation problems, and GSC columns are, therefore, referred to as tailor-made columns

Gas liquid chromatography, on the other hand, has a widespread use in all fields of science. GLC is based upon the partition of the analyte between a gaseous mobile phase and a liquid phase immobilized on the surface of a capillary column or an an inert solid [3].

The heart of a GC system is the column responsible for the separation of components. The choice of column depends mainly on the complexity of the sample that needs to be analyzed. The effectiveness of a chromatographic column in separating two solutes depends upon the relative rates at which the peaks elute. These rates are determined by the magnitude of the equilibrium constants by which the solutes distribute themselves between the mobile and stationary phase. The equilibrium constant *K* is defined as

$$K = \frac{c_S}{c_M} = \frac{m_S / V_S}{m_M / V_M} = \frac{m_S}{m_M} x \frac{V_M}{V_S} \qquad (2.1)$$

where C_S is the molar concentration of solute in the stationary phase and C_M is the molar concentration of solute in the mobile phase; *m* is the mass and *V* is the volume of the stationary (S) and mobile (M) phases. Ideally *K* is constant over a wide range of solute concentrations. The average linear rate $\bar{v}$ of solute migration is:

$$\bar{v} = \frac{L}{t_R} \qquad (2.2)$$

where t_R is the retention time (time it takes for a solute from injection until its reaches the detector), *L* is the column length.

The resolution equation is the key equation to obtain optimal separation, where R is the resolution:

$$R = \frac{\sqrt{N}}{4}\left(\frac{a-1}{a}\right)\left(\frac{k}{1+k}\right) \qquad (2.3)$$

In CGC, the column length, the column diameter and the film thickness affect the column efficiency *N*. *N* can be defined by the following equation where *L* is the length of the column, and *H* is the length of one plate (length needed for one equilibrium).

$$N = \frac{L}{H} \qquad (2.4)$$

The stationary phase controls the column selectivity α for a given separation. Column selectivity describes the interaction of solutes with the stationary phase. It is expressed by the following equation where $t_{R'2}$ is the residence time of compound 2 in the stationary phase, $t_{R'1}$ is the residence time of compound 1 in the stationary phase and t_M is the time both solutes spend in the mobile phase:

$$\alpha = \frac{t_{R2} - t_M}{t_{R1} - t_M} = \frac{t_{R'2}}{t_{R'1}} \tag{2.5}$$

The retention factor *k* can be expressed as the time a solute spend in the stationary phase over the time it spends in the mobile phase:

$$k = \frac{t_R - t_M}{t_M} = \frac{t_{R'}}{t_M} \tag{2.6}$$

and therefore

$$\alpha = \frac{k_2}{k_1} \tag{2.7}$$

Figure 2.1 illustrates R_S = 1 for two closely eluting peaks.

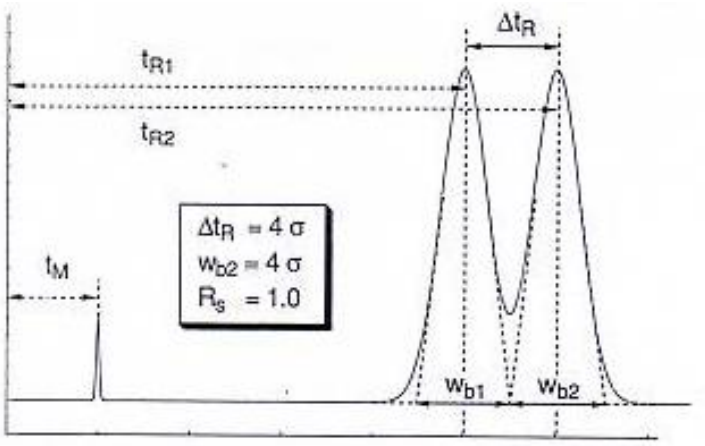


Figure 2.1. Illustration of resolution.

An increase in column efficiency *N*, separation factor α or retention factor *k* will enhance the separation power of the column. The effect of these parameters on R_s can be seen in ***Figure 2.2*** and ***Figure 2.3***. To increase column efficiency, a number of measures can be taken. The plate length can be decreased by working at optimal velocity and by decreasing the diameter of the column. Longer columns will lead to increased efficiency but with longer analysis times and lower sensitivity. By using thicker films, working at lower temperatures and selecting the best stationary phase for the application, *k* will increase, which again leads to better resolution.

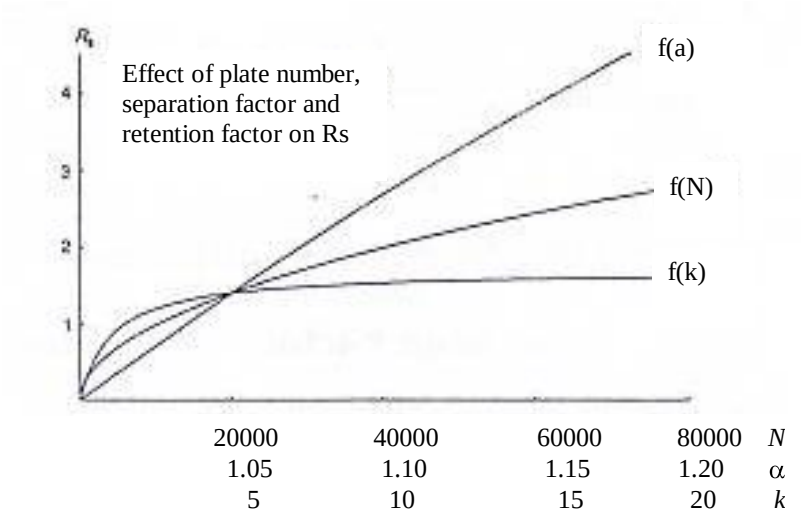


Figure 2.2. Effect of N, α and k on the resolution.

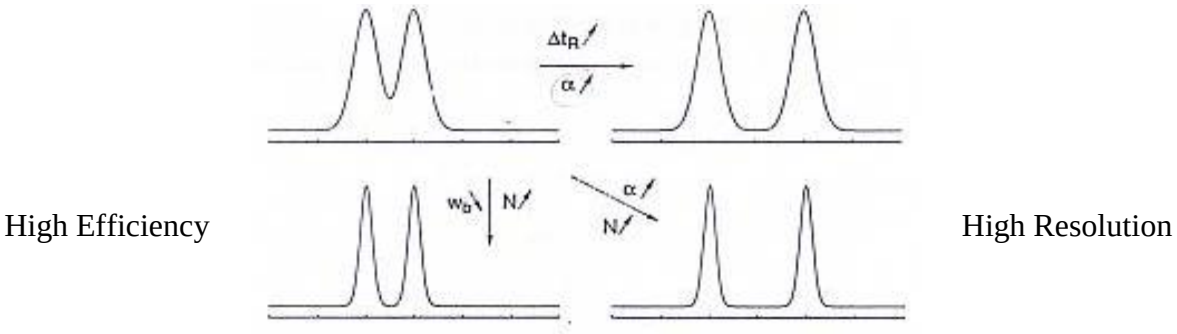


Figure 2.3. The effect of high selectivity vs. high efficiency on peak resolution.

Two basic GC column types can be distinguished; the packed column and the open tubular or capillary column.

Packed columns do not provide high resolution because they have low plate numbers. The low efficiency is compensated for by the high selectivity of hundreds of stationary phases. The high plate numbers of capillary columns make selectivity less important. Packed columns are short columns ($\approx$ 3m) with inner diameters of about 1.5 to 10 mm. The columns are packed with an inert support whose internal pore diameters range from 2 μm to about 9 μm. The support is deactivated and does not take part in the separation. The inert support is coated with a stationary phase. Packing materials are chosen for particular applications. Because of the packed bed, the resistance to the mobile gas flow is high. A total plate number of 10 000 is the maximum that can be reached with packed columns [3].

Initially all GC applications made use of packed columns in which the stationary phase was a thin film of liquid adsorbed on the surface of a finely divided inert solid support. From theoretical studies, it became evident that unpacked columns with smaller internal diameters provided better separation efficiency and speed [4,5]. The current trend is to replace packed columns with capillary columns whenever possible because the latter technique provides much higher resolution and more reliable results.

The development of capillary columns provided a major breakthrough in gas chromatography. Capillary columns have internal diameters ranging from 1 mm to 0.1 mm and are usually constructed of fused silica. A protective coating of polyimide is applied to the outer wall of the column to make it flexible and easy to handle. Capillary columns may be packed with solid particles (micropacked) or open tubular with an unrestricted flow path through the column. Open tubular columns are divided into wall-coated open tubular (WCOT) columns, support-coated open tubular (SCOT) and porous layer open tubular (PLOT) columns. The inner surface of the WCOT column is coated with the stationary liquid phase. Viscous polymers wet the surface of the column, with the result that a very thin, uniform coating is applied to the column walls. A variety of functional groups can be blended into the stationary phase to provide stationary phases of different polarity and/or selectivity. SCOT columns are generally less efficient than WCOT columns but significantly more than packed columns. The inner

surface of SCOT columns is lined with a thin film of support material. These columns hold much more solid phase material and have much higher sample capacity. SCOT columns are only applied for some specific applications.

Columns can be tailored for specific analysis, like for highly volatiles or for high boiling components. Thicker films (1 to 5 µm) permit analysis of highly volatile components while films ranging from 0.1 to 0.5 µm are valuable for analysing high molecular weight compounds within reasonable analysis times.

WCOT columns can be divided into three groups according to inner diameter. The *conventional capillary columns,* most often used for complex separations, have an *i.d.* of 0.18 to 0.32 mm. *Widebore* or *megabore* columns have an *i.d.* of 0.53 mm and are used as an alternative to packed columns for the analysis of less complex mixtures. *Narrowbore* columns with *i.d.*'s ranging from 0.15 to 0.05 mm provide very high efficiencies and short analysis times.

The carrier gases (mobile phases) commonly used are nitrogen, helium and hydrogen. The relation between column efficiency (*H*) and the mobile phase velocity (*u*) was derived for packed columns by Van Deemter, Zuiderweg, and Klinkenberg [4]. Golay, who is regarded as the inventor of capillary columns, applied this relationship to capillary columns [5]:

$$H = \frac{2D_M}{u} + \frac{1+6k'_0+11k'^{\,2}_0}{96(1+k'_0)^2}\frac{ud^2_p}{D_M}u + \frac{k'_0}{24(1+k'_0)^2}\frac{ud^2_f}{D_1} \qquad (2.8)$$

$$H = \frac{2D_L}{u} + 2\left(\frac{k'_0}{1+k'_0}\right)^2 \frac{u}{k'_0\ k_m} \qquad (2.9)$$

For nitrogen, the longitudinal diffusional spreading of the solutes is relatively small but the resistance to mass transfer in the mobile phase is high, in contrast to helium and hydrogen where it is just the opposite. This is due to the differences in the diffusivities of the gases. For columns with small amounts of stationary phase, the resistance to mass transfer in the stationary phase can be neglected, and the minimum plate height H_{min} is nearly independent of the nature of the carrier gas. The optimum mobile-phase velocity u_{opt} is proportional to the diffusion coefficient in the mobile phase $D_{\text{M.}}$ For nitrogen, the optimal velocity is 10 cm/s, for helium it is 25 cm/s and for hydrogen it is 40 cm/s when using 0.25 – 0.3 mm inner diameter

columns. By using hydrogen for thin-film columns, analysis times are four times shorter than when using nitrogen. However, helium is often preferred above hydrogen because of safety reasons and because of its superior performance in the combination CGC with mass spectrometry (MS).

In thick-film columns, the resistance to mass transfer is more significant due to the large contribution by the stationary phase. The selection of carrier gas depends on whether efficiency or speed is considered most important. For a given column, the selection of carrier gas and optimum flow rate is best determined experimentally by making *H* – *u* plots [3].

From the resolution equation (2.3), one can deduct that the selectivity factor α has a higher impact on resolution than the other factors. The interaction between solute and stationary phase is very complex and may include non-specific interactions (like dispersion), specific interactions (like dipole – dipole, induced dipole and hydrogen bonding) and chemical interactions (like acid – base, proton acceptor – proton donor, electron acceptor - electron donor and inclusion) [3].

The terms selectivity and polarity are commonly used to describe stationary phases. Because capillary columns have very high efficiency, fewer stationary phases are required than for packed columns. Stationary phases used most often are methylsilicones, methylphenylsilicones, methylcyanopropylsilicones, methyltrifluoropropylsilicones and polyethylene glycols. The functional groups of these stationary phases are the methyl, phenyl, cyano, trifluoro and hydroxyl-ether groups. Columns are often coupled to obtain selective tuning and functional groups are modified to provide specific interactions. Some phases, like chiral phases and liquid crystals, are tailor made to obtain specific separations.

An important concept in the framework of this thesis is the column peak capacity. The peak capacity of a capillary column is the maximum number of compounds that can be resolved by the chromatographic system. The peak capacity is described by:

$$n_p = \frac{\sqrt{N}}{4R_s} \ln\left[\frac{1+k_c}{1+k_1}\right] + 1 \qquad (2.10)$$

where k_c is the retention factor of the last peak, k_1 is the retention factor of the first peak and R_s is the required resolution. For capillary columns with high efficiency, the peak capacity ranges from about 500 to 1000 [3].

2.2 Multidimensional heart-cutting GC-GC

With state-of-the-art hardware, detectors and columns, capillary gas chromatography is a mature technique that provides high resolution. But even with capillary columns containing up to 200 000 – 300 000 plates, and with peak capacities of up to 1000, separation of all the components in highly complex mixtures is still not possible and a high degree of peak overlap still occurs. Because of co-elution with larger amounts of matrix components, compounds of interest at trace level are often difficult to isolate. From the resolution equation (2.3) it is seen that R_s depends on the square root of N. Increasing the column length to obtain the required resolution is not always effective. A large increase in column length is required for a small increase in resolution. By increasing the selectivity factor α slightly, a much larger increase in resolution is obtained. However, analysing a given sample on a second column i.e. a column with completely different selectivity will not always provide the answer as separated peaks on the first column will now overlap on the second column and vice-versa. The ideal situation is when two selectivities are combined in a multidimensional approach. The peak capacity will ideally be the product of the individual column peak capacities [3]. In conventional heart-cut GC-GC, only a selected fraction is heart-cut and analysed on the second column. The technique is useful for detailed analysis of target components as will be illustrated in Chapter 3.

If the heart-cut is cold trapped before analysis on the second column, the selectivities of the two columns are decoupled and separation on the second column is independent on the first column selectivity. The separation obtained on the first column is partly destroyed by the focussing effect of the trapping device. Only a small part of the first separation is used and the rest of the first column separation is disregarded. The technique is therefore regarded as non-comprehensive.

Initially, valve systems were employed to connect the two columns and for transfer of the fraction to the second column. These systems suffered from catalytic activity on the metal surfaces. The Deans switching system, introduced in 1968 [6], was valveless and used

pneumatic pressure balancing. Carrier gas flows were controlled at the injection port and at the column intersection port. Fractions were sent to the second column or vented to waste. Stabilising the carrier gas pressures in the injector and midpoint connector was challenging and considerable technical difficulties were experienced in achieving the necessary pressure equilibration for reproducibility of cutting and retention-time stability. With the invention of electronic mass flow controllers, used in the modern equipment today, the problems were solved.

Columns used for heart-cut GC-GC may be the same as the columns used for one dimension GC (^{1}D GC). As the columns in modern GC-GC instruments are housed in separate ovens and with independent temperature programming, there is not much restriction on the columns as long as the main aim, to obtain the required separation for the analytes or heart-cut fraction of the particular sample, is obtained. The column combination should be carefully selected to obtain maximum resolution of the target components.

The conventional detectors used for ^{1}D GC are also used for heart-cut GC-GC if the second dimension separation is not a fast analysis. For Fast GC analysis the requirements for detectors mentioned in paragraph 2.3 applies.

2.3 Comprehensive multidimensional GCxGC

“Comprehensive” in chromatography stands for complete development of a specific analysis on two different stationary phases. Comprehensive GCxGC arises from the pulsing of solutes eluting from one column (pre-column) into a second column at a frequency lower than the time it takes for a single peak to elute from the first column. The modulator at the column junction facilitates the transfer of solute from one column to the next at predetermined frequencies. The entire sample is analysed in both GC dimensions and the separation obtained in the first column is preserved.

By separating components on two columns of totally different selectivities, an orthogonal separation is obtained. The peak capacity is ideally the product of the individual column peak capacities. Theoretically, by combining two columns of different selectivity’s and with peak capacities of 500 each, the peak capacity of the system should be 250 000. Nowadays, the

peak capacity of the main second columns is ca. 20 resulting in peak capacities of 10 000 which is still a major increase compared to ^{1}D GC.

A number of modulators have been described. Modern instruments mostly make use of thermal or valve-based modulators [7, 8, 9]. Thermal modulators trap the analytes by using a cryogen like liquid nitrogen or CO_2 to produce local cold spots on a segment of the GC column. When cryo-trapping is stopped, by moving the cold spot to a different position on the column, by interrupting its delivery or by heating, the trap is brought back to oven temperature and analytes are introduced onto the second column. The entire sample is passed from the first column to the second, resulting in peak amplitude enhancement. The main drawback of thermal modulators, especially those using CO_2, is that they have difficulty in trapping very volatile analytes i.e. carbon numbers less than C_6.

Valve-based modulators offer a simple, rugged and less expensive alternative to thermal modulators. They use multi-port valves to transfer the eluent from one column to the other. No breakthrough of analytes, even highly volatile components, occurs. However, because a large portion of the sample does not go to the second column, no peak amplitude enhancement occurs, making this method less attractive for trace analysis. Problems may also be experienced with sorption of the higher-boiling analytes to the valves. A stand-alone pulse generator to power and control the valve has recently been described. Another major advancement is the extension of the working temperature of the valve to $\approx$ 250 °C [10].

Like with ^{1}D and heart-cut GC-GC, the choice of column phases is governed by the need to obtain maximum component separation for a particular sample. Using orthogonal columns, the differences in the column's separation mechanisms are maximised [11,12].

For GCxGC, the first column is a full length column (30-60 m), often with a non-polar stationary phase and the analysis gives a boiling point separation of the eluting components. The second column is much shorter and contains another stationary phase that gives a different selectivity. Separation on the second column can be based on polarity, molecular geometry, size, etc. Thus the separations strategies in the two dimensions can be completely different or orthogonal.

GCxGC results in fast analysis (3-6 s analysis times) in the second column. A short column with a narrow inner diameter and thin film thickness is therefore the logic choice. Harynuk et. al. reported the use of stop-flow GCxGC where the flow in the primary column is stopped periodically so that the second dimension separation may proceed for longer than the conventional modulation period [9].

The sampling or modulation speed for a GCxGC system should be short enough to modulate the components in the sample. Each peak is divided into several 'slices' by the modulator and each package is delivered to the second dimension column. The modulation time should also be long enough to elute all compounds from the second dimension column before a subsequent modulation is started. In other words, 'wrap around' should be avoided. Peak shapes and resolution in the first dimension should be preserved [10]. As different peaks of the same sample may differ in width and height, it is not possible to have the same number of modulations for each peak. The relative position of the modulation (phase of the modulation) may differ. The pulses of peaks seen in GCxGC may be anywhere from in-phase to 180° out-of-phase. It is therefore very important to synchronise the start of the chromatographic run and the modulator. Modern equipment can deal with this but minor changes in time shifts can also be corrected for by GCXGC software (GC Image).

For the fast eluting and extremely narrow peaks eluting from the second column, fast detection and data acquisition is essential. The detector cell should be as small as possible to not influence the peak width or shape. Flame ionization detection (FID) has been the detector of choice for most current GCxGC applications. The detection volume in an FID is limited to the flame volume and it contributes the least to band broadening [13]. The FID has data acquisition rates of 100 – 200 Hz. Ysacker [14] evaluated the electron capture detector (ECD) for fast GC. He concluded that the ECD make-up flow-rate is a key parameter when coupling narrow bore columns to ECD. The make-up flow should be sufficiently high to eliminate peak tailing caused by the large detection cell volume (450 μl). At very high make-up flows of 400 – 1100 $ml.min^{-1}$, the ECD exhibits a mass-flow sensitive response, instead of a concentration dependant signal.

The μ-ECD is more suitable to GCxGC analysis since the internal cell volume is about 10 times smaller than that of a conventional ECD. To avoid undue band broadening, it is still necessary to use high detector temperatures and very high make-up flows.

Van Stee et. al [15] investigated the use of AED detection for GCxGC and obtained valuable element-selective information. Minor adaptations were done to the transfer line dimensions and gas flow rates. The highest data acquisition rates (10 Hz) were used i.e. five to six data points per peak. Therefore correct quantitation can be questioned.

If one takes into account the thousands of peaks generated by GCxGC, it is essential to be able to identify the components. The only mass spectrometer able to provide spectra at 0.02 s or better is the time-of-flight (TOF) mass spectrometer. The TOF permits up to 500 full range mass spectra per second and can therefore be used for the very narrow peaks. The mass spectral information can display a mass unique to each analyte where co-elution still may exist. TOFMS has been combined with GCxGC for mass detection and quantification for a number of applications [10]. It was found to be a powerful separation and identification technique for unravelling the nature of complicated mixtures of compounds and the enhanced overall resolution also facilitates quantification. Data files are very large and data interpretation may take hours to complete.

2.4 Multidimensional sequential GC-GC

Sequential GC-GC uses the principle of heart-cutting but with a time-window instead of a selected part of the chromatogram. Using multiple injections, the heart-cut from each of the predetermined time-windows is sent to a cryo-trap that is kept at -70 °C (liquid nitrogen is used to cool down the trap). After the entire heart-cut has been trapped, the cryo-trap is heated and the heart-cut is released and analysed on the main column. Reproducible cutting and retention time stability are obtained by electronic mass flow controllers and proportional backpressure regulators with pressure sensing. Fully automated sequences can be programmed for repetitive injection to the pre-column. Once a method has been set up, the instrument can run continuously without intervention (i.e. over a weekend). Data manipulation is quick as each heart-cut is analysed separately, using the conventional GC software.

The two columns are housed in separate ovens for independent temperature programming. The first oven is fitted with a multidimensional column switching system (MCS) with computer controlled, fully automatic pressure equilibrium for high resolution capillary GC. The MCS allows peak selection and heart-cutting from the pre-column.

The column switching system consists of a mass flow controller (MFC) to control a counter-current flow in the interface, a digital pressure gauge to display the actual pressure between the pre- and main column, a proportional valve to balance the pressure between the pre- and main columns and the column switching device with five connections for the pre-column, main column, vent line for heart-cutting, control capillary and a line for the control flow.

When the heart-cutting mode is on (**Figure 2.4**) selected components are transferred from the precolumn to the main column; when the heart-cutting mode is off, the components are vented through the vent line (**Figure 2.5**) [16].

The time available for the analysis on the second dimension column is only limited by the time available for the first dimension analysis. Both columns can be conventional high resolution capillaries and experimental conditions can be manipulated to obtain optimal resolution for both columns.

Just like with normal heart-cutting GC-GC, it is not essential to have detectors with high data acquisition rates. The detectors normally used in ^{1}D GC are also suitable for sequential GC-GC. However, if fast GC is used in the second dimension, fast detection is also required.

The choice of time-window depends on the complexity of the sample and the resolution of analytes on the second column. Heart-cuts are typically 30 to 60 s.

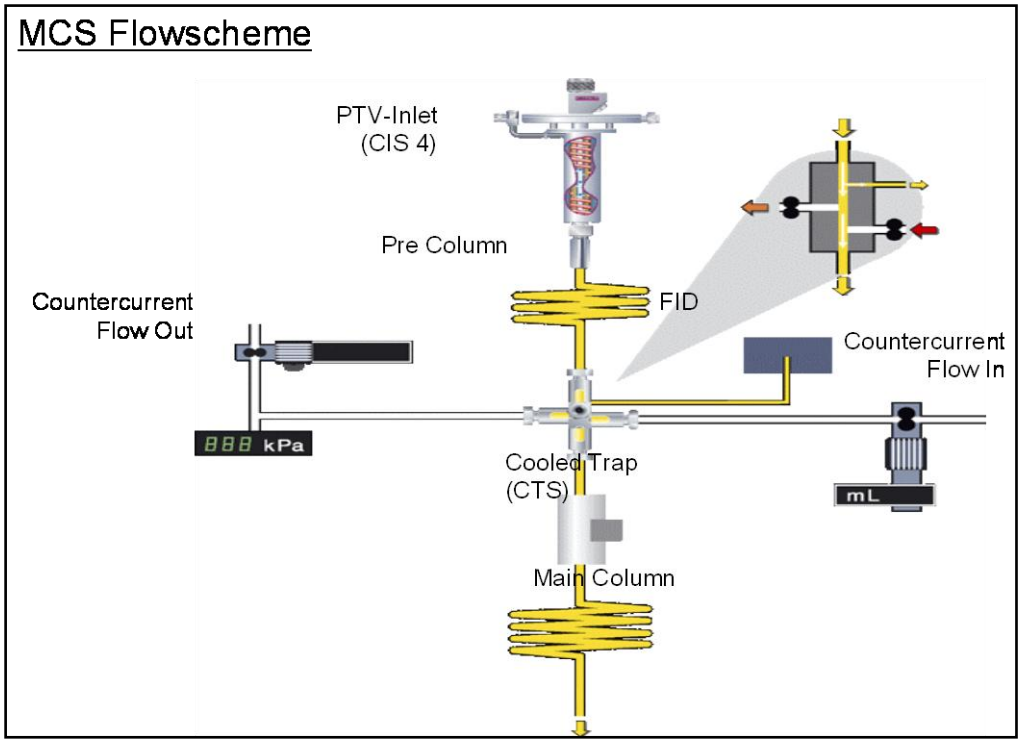


Figure 2.4. MCS in the heart-cut mode.

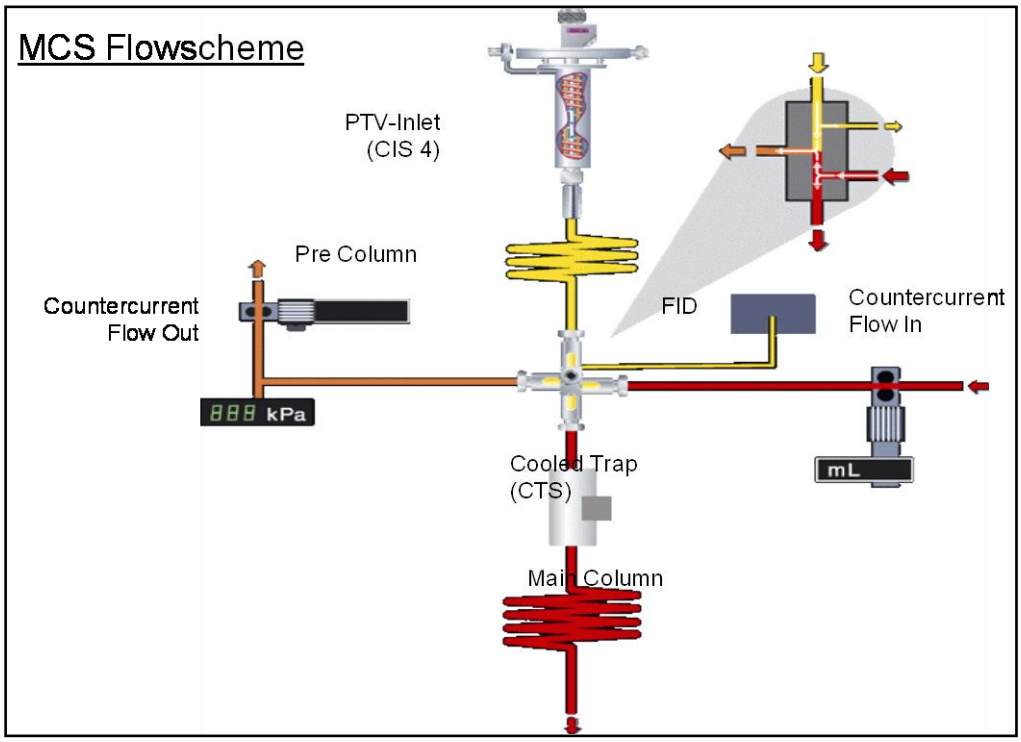


Figure 2.5. MCS in the vent mode.

2.5 Other selective tools

Mass spectrometry (MS) is the most powerful analytical technique available today and in its hyphenation with CGC a third dimension is added to the analysis. The MS is highly versatile and is widely used for identification of components in complex mixtures. It not only provides structural information about components, but also provides sensitive and selective quantification.

Several types of mass spectrometers are currently available. The principle of the two mass spectrometers used in this work are detailed.

The quadrupole is used extensively in capillary GC in petrochemical laboratories. This instrument is more compact, less expensive and more rugged than most other types of mass spectrometers. It has relatively high scan rates and an entire mass spectrum can be obtained in 100 ms. At the heart of the quadrupole instrument is the four parallel cylindrical/hyperbolic rods that serve as electrodes. Opposing rods are connected electrically, one pair to the positive terminal, the other to the negative terminal. In addition, variable radio frequency ac potentials, which are 180 ° out of phase, are applied to each rod. The sample molecules can be ionised by either chemical ionisation (CI) or electron ionisation (EI). Molecular and fragment ions are formed (depending on the ionisation technique) and are accelerated into the space between the rods by a potential of 5 to 10 V and separated from each other according to their m/z ratio. The ac and dc voltages on the rods are increased simultaneously while maintaining their ratio constant. The ions that are not within the selected m/z range, strike the rods and are neutralised. Only the ions within the specified m/z window reaches the transducer. The separated ions are then detected by an electron multiplier. The resulting mass spectrum is a line spectrum of intensity versus *m*/*z* ratio. To detect all ions, the voltage is varied in time, and all the selected ions are scanned (full-scan) [2,3].

During electron ionisation the sample molecules are bombarded with electrons of 70 eV. Fragmentation of the molecules occurs. The energy in the molecule is relatively large. Fragmentation can be so extensive that the molecular ion may not be observed. Chemical ionisation is a softer ionisation technique. It uses a reagent gas like methane. The reagent gas is ionised by the electrons and the ions formed then interact with the sample molecules.

These reactions have lower energy and less fragmentation occurs. The molecular ion is much more intense than with electron ionisation.

By plotting the total ion current against time, a chromatogram of the mass spectrometer is constructed. When identifying the sample components, the recorded mass spectra are recalled. A number of spectral libraries are available which aids with identification of components. For highly complex mixtures, where a high degree of peak overlapping occurs, ion extraction is a very useful selective tool. By extracting ion fragments typical of a specific component or class of components, valuable information can be obtained.

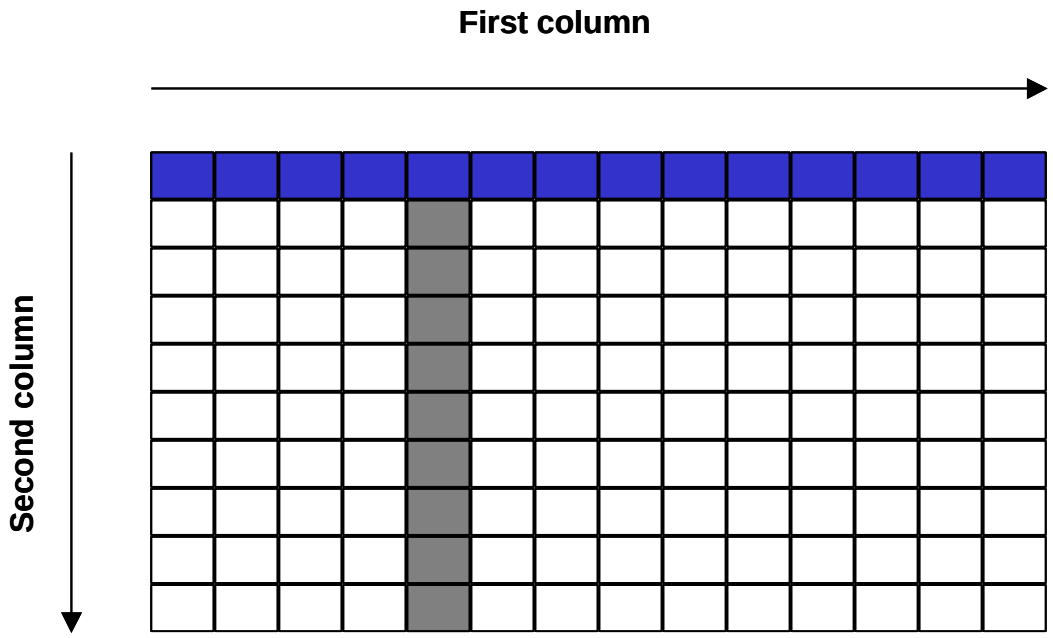
Selected ion monitoring (SIM) enables quantification of target compounds with high selectivity and sensitivity. In this mode, the voltages on the quadrupole rods are adjusted stepwise to detect only a few selected ions. The voltage times on the rods are longer than when a full scan is made. For normal ^{1}D GC and for heart-cut and sequential GC-GC where fast GC analysis is not used in the second dimension, the data acquisition rate of the quadrupole instrument is sufficient. When fast data acquisition is essential, like with comprehensive GCxGC, the TOFMS is the only MS with high enough data acquisition rates to detect the very narrow and fast eluting peaks.

In time-of-flight mass spectrometers (TOFMS), positive ions are produced by bombardment of the sample with brief pulses of electrons, secondary ions or laser generated photons. The ions produced are accelerated by an electrical field pulse into a field-free drift tube. Because all ions entering the tube ideally have the same kinetic energy, their velocities vary inversely with their masses. After acceleration in the ion source, small ions arrive earlier at the detector than heavy ones. The detectors are multi-channel arrays that are capable of resolving small differences in time. A reflector device in the linear flight tube enhances the resolution by focusing the ion beam on the detector. Faster ions penetrate more deeply into the reflector and therefore have a slightly longer flight path. The development of plasma and laser desorption made TOFMS the mass spectrometer of the future. TOF instruments have excellent sensitivities. Resolutions in the range of 5000 – 10 000 have been obtained and ions with m/z > 100 000 have been recorded. In this study, the TOFMS system was a high speed MS thereby reducing the resolution to the level of a simple quadrupole MS.

2.6 Summary

For clarity, a schematic overview of the different multidimensional techniques applied in this work is presented.

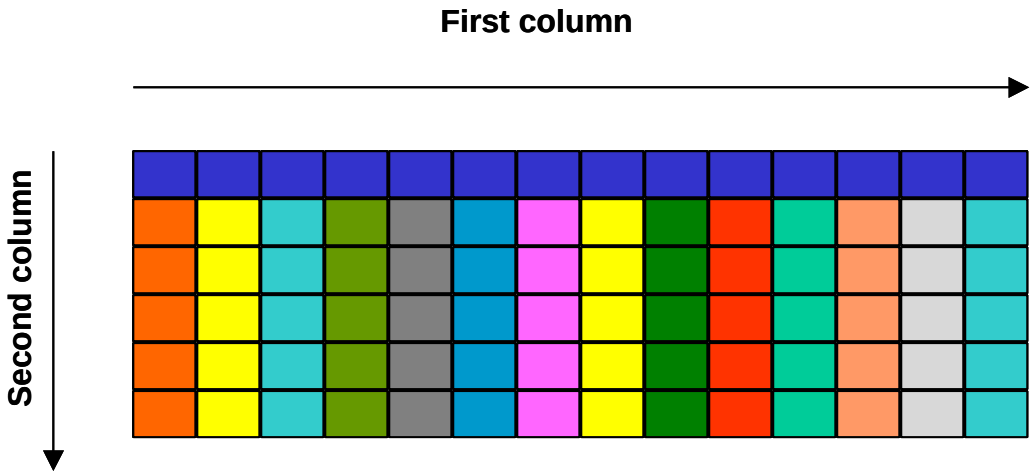
Heart-cutting GC-GC



Features:

- Two highly efficient columns are used
- A selected fraction is transferred to the second column
- Enrichment of the selected fraction in the cryo-trap can be done by multiple injections
- Hyphenation to a quadrupole MS is possible
- Data handling is easy and not time-consuming

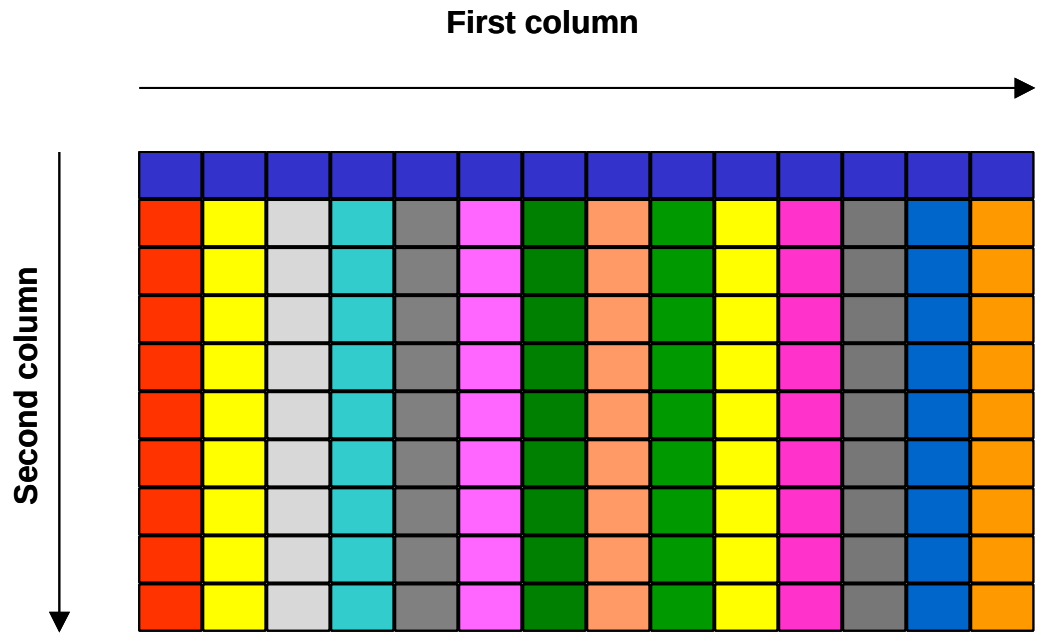
Comprehensive GCxGC



Features:

- A highly efficient and a poorly efficient fast column are combined
- Complete development in the second dimension
- Very high peak capacity ($n_p = n_{p1}$ x n_{p2})
- Hyphenation to a high speed TOFMS is mandatory
- Fast but data handling is very time-consuming

Sequential GC-GC



Features:

- Two highly efficient columns are used
- Multiple injections have to be carried out; thus time-consuming
- Complete development in the second dimension
- Very high peak capacity (n_p = *number of time windows* x n_{p2})
- Hyphenation to a quadrupole MS is possible
- Data handling is easy and not time-consuming

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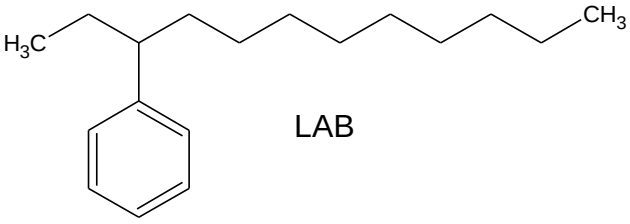
3 THE USE OF HEART-CUT GC-GC FOR THE ANALYSIS OF TRACE LEVELS OF OXYGENATES IN A C_{10} – C_{13} ALKYLATION FEEDSTOCK

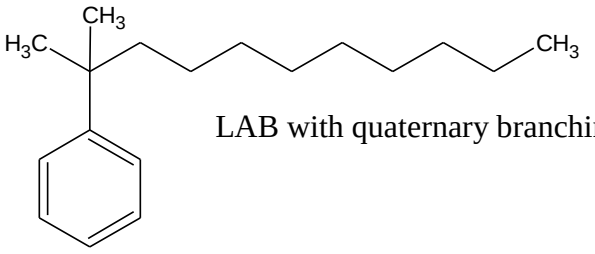
3.1 Introduction

Linear alkylbenzene sulfonates (LAS – R-$SO3^-$) are surfactants used in the production of detergents. LAS are synthesized by alkylation of benzene with linear alkanes (dehydrogenated to alkenes) in the C_{10} to C_{13} carbon number range, followed by sulfonation of the resulting linear alkylbenzenes (LAB). More than 70 % of the paraffins in the world market are used for LAB production.

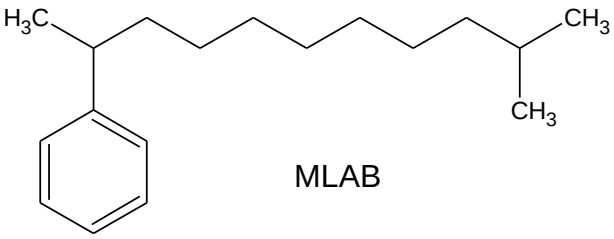
LAB's thus consist of a hydrocarbon chain with a benzene ring attached to it (**Figure 3.1**). A number of isomers are possible with the benzene ring on different positions of the alkyl chain. Special isomers are MLAB's (methyl branched LAB), which are desirable products. They have a benzene ring on the β-carbon (which improves surfactancy) and a methyl group somewhere along the chain (which enhances solubility). Quaternary branching (where the benzene ring and a methyl or higher branch is on the same carbon) is undesirable because these isomers possess low biodegradability.



LAB



LAB with quaternary branching



MLAB

Figure 3.1. Different linear alkylbenzenes (LAB)

Petrochemical products are often used as the paraffinic feedstock for LAB production. The *Alkylation Feedstock,* produced from Fischer Tropsch technology, has high linearity (≥ 97 %) and contains mostly paraffins, some olefins and oxygenates, but no aromatics. The oxygenates act as poisons for some alkylation catalysts, and should be removed down to low ppm levels by extraction, guard-bedding or selective hydrogenation.

It is important to be able to analyze and identify the remaining trace level oxygenates. The oxygenates may consist of a few hundred components and analysis of individual components at the low ng/g level is required. This is very challenging for any analytical technique and normally not possible with single dimension GC. Separation of the oxygenates from the hydrocarbon matrix and enrichment of the oxygenates prior to GC analysis is therefore essential. This is commonly done with column chromatography with silica gel as adsorbent. This method, however, requires large volumes of sample and solvents, is very tedious and time-consuming and prone to the formation of artefacts. Solvents need to be distilled off again afterwards to isolate the analytes. Highly volatile analytes often evaporate together with the solvents, leading to inaccurate results.

In this study, the features of single dimension GC and heart-cut GC-GC were compared for the analysis of oxygenates in an *Alkylation Feedstock*, the oxygenates of which were already removed down to the ppm level.

Heart-cut GC-GC is commonly used when co-eluting peaks necessitates better resolution. Heart-cut GC-GC columns are chosen to ensure optimal resolution on both columns. Both columns are full length, high efficiency columns and optimal separating conditions (temperature programs and flow rates) further ensure optimal resolution power for this system. This superior resolution power is, however, only applied to the heart-cut fraction.

A modern heart-cut GC-GC instrument (**Figure 3.2**) consists of two separate GC's with independent temperature control. The first GC houses a cooled injection system (CIS), the column switching device (CSD) and the monitor FID. The CIS eliminates the danger of inlet discrimination by temperature programming of the injector system and allows monitoring and control of both flow and pressure.

Figure 3.2. Modern heart-cut GC-GC instrument

The CSD (**Figure 3.3**) regulates peak collection or heart-cutting from the pre-column. Carrier gas is fed from the mass flow controller (MFC) to the control line inlet on the CSD. The MFC controls flow to the second column when a heart-cut is made or else to the vent lines. The vent and control lines are stainless steel capillaries. The vent line runs from the outlet on the column switching device (CSD) to the inlet on the proportional valve. The other connections on the CSD are the pre-column connection that is connected to the inlet system, the control capillary that connects the CSD to the monitor FID and the transfer capillary that runs through the cryotrap and is connected to the main column in the second GC. The GC‘s are connected via the cryotrap where heart-cut fractions are trapped at a temperature of -70º C, using liquid nitrogen as cooling gas.

The instrumental set-up of heart-cut GC-GC also allows to enrich important fractions present in low traces for in depth analysis. This principle was used for the separation, enrichment and identification of the trace levels of oxygenates in a complex C_{10} – C_{13} alkylation feedstock obtained from FT technologies. The separation process takes place on the pre-column and enrichment is done by using multiple injections, followed each time by accumulation of the

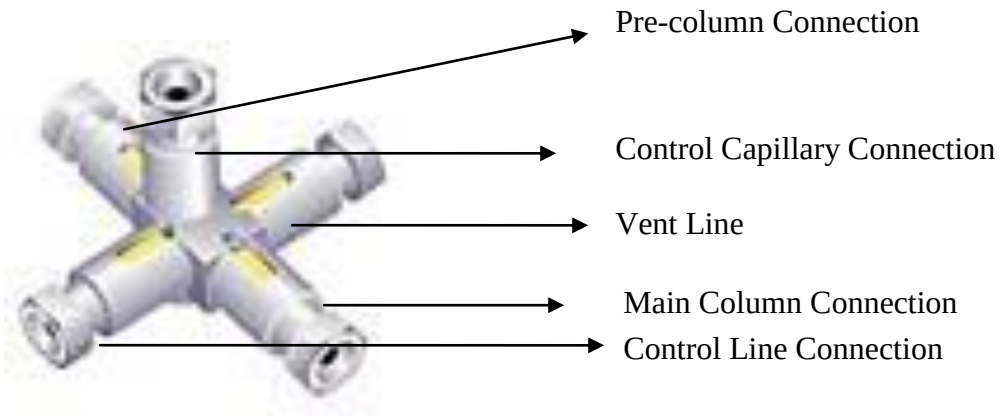


Figure 3.3. The column switching device regulates heart-cutting from the pre-column

oxygenate heart-cut on the cryo-trap. After sufficient enrichment, the accumulated fraction is sent to the main column.

Because the levels of oxygenates in the alkylation feedstock are very low, it is difficult to illustrate the separation of oxygenates from the hydrocarbons by this analytical approach. Therefore, the alkylation feedstock before and after removal of the oxygenates was analysed.

3.2 Experimental

Single dimension GC

Gas chromatograph: Agilent 6890 GC

Column 1: 60 m L x 0.25 mm I.D., 0.2 µm d_f, RT2340 (biscyanopropyl silicone)

Column 2: 60 m L x 0.25 mm I.D., 0.5 µm d_f DBWax (polyethylene glycol)

Column 3: 60 m L x 0.25 mm I.D., 0.4 µm d_f TCEP (1,2,3-tris-(cyanoethoxy)propane)

Oven temp: 60°C/1min – 4°C/min – 240°C/10 min (140°C for the TCEP column)

Carrier gas: helium

Pressure: constant pressure @ 108 kPa

Detectors: FID and Quadrupole Mass Spectrometer

Injection volume: 0.5 µL

Injector: Split at 250 °C

Split ratio: 100 :1

Heart-cut GC-GC

Gas chromatograph: 2 x Agilent 6890 GC
Multicolumn switching: Gerstel MCS – dual oven set-up – cryofocusing
Column 1: 60 m L x 0.25 mm I.D., 0.2 µm d_f, RT2340 (biscyanopropyl silicone)
Oven 1: 60°C/1min – 4°C/min – 240°C/10 min
Column 2: 30 m L x 0.25 mm I.D., 0.5 µm d_f DBWax (polyethylene glycol)
Oven 2: 60°C/36 min – 20°C/min – 240°C/10min
Carrier gas: helium
Pre-column: constant pressure @ 270 kPa
Analytical column: constant pressure @ 120 kPa
Detectors: FID and Leco Pegasus III time-of-flight mass spectrometer
Injection Volume: 1.0 µL
Injector: Programmable temperature vaporisation inlet
Injector Temp: 60°C/0.1 min – 600°C/min - 250° C
Split ratio: 100 :1

Internal standard

An internal standard of 1 µg/g of 3-nonanol was used for semi-quantification purposes. This component was not detected in the alkylation feedstock before oxygenate removal. FID response factors for the unknown oxygenates could not be determined because hundreds of oxygenated components exist in the C_{10} – C_{13} carbon number range and standards are not commercially available for all of these components.

3.3 Results and discussion

3.3.1. Single dimension GC to separate the oxygenates

Table 3.1 gives a list of carbon numbers of the component classes with boiling point ranges in the C_{10} to C_{13} distillation cut. The boiling points range from about 170°C to 235°C.

Table 3.1. Boiling point distribution for C_{10} to C_{13} hydrocarbons

n-Paraffins	Carbon Number	Boiling Range (°C)
	C10	174
	C11	
	C12	
	C13	235
Oxygenates		
Alcohols	C7 - C10	176 - 229
Ketones	C8 - C11	173 - 231
Aldehydes	C8 - C11	175 - 233
Esters	C9 - C12	172 - ?
Acids	C7 – C10	205 - ?
Ethers	C9 - C12	171 - 220

The prerequisite of the column (also the first column in a heart-cut GC-GC method) is that it should provide a selective separation of the oxygenates from the C_{10} – C_{13} hydrocarbon matrix. Oxygenates and hydrocarbons of a distillation cut elute together on non-polar columns because the separation is mainly according to boiling point. For separation of oxygenates to occur, the differences in polarity of the oxygenates and the hydrocarbons should be exploited.

Four polar capillary GC columns were evaluated for the separation of oxygenates from the hydrocarbon matrix. The most effective column should then be used as the pre-column in the GC-GC system. The evaluation of the columns was done on a single dimension GC because it is easier to change columns on this system than on the multicolumn switching system which is sensitive for leaks and which uses delicate and expensive graphpack ferrules.

The first selection is a DBWax column containing a polyethylene glycol as stationary phase. It has a relative high upper temperature limit and therefore a long lifetime. Because it

separates according to polarity, it is ideally suited to analyse narrow distillation cuts (where boiling point separation already occurred to a large degree).

For a column to give better separation than polyethylene glycol, it should be even more polar. A RT2340 column with a biscyanopropyl silicone stationary phase and a TCEP (1,2,3-tris-(cyanoethoxy)propane) column were therefore also evaluated.

The TCEP column has been demonstrated to successfully separate the lower boiling oxygenates (C_1 – C_5) and aromatics (C_6 – C_8) from gasoline [1]. This column is also used as the pre-separation column in the AC Oxygenate Analyzer in the ASTM method D4815 [2]. The column has, however, not been applied to higher boiling oxygenates (C_7 – C_{11}) in the C_{10} – C_{13} carbon number range.

We also had a look at a CP-Lowox column, a unique multi-layer column that exhibits extremely high polarity and column stability and has been shown to provide accurate analysis of oxygenate traces in the C_1 to C_{10} carbon number range [3, 4]. However, problems were experienced connecting the column to the multicolumn switching system because the external diameter was too high for the CSD in the GC-GC system.

The first column evaluation was performed by the analysis by GC-MS of the alkylation feedstock with high concentration of oxygenates i.e. before oxygenate removal. Based on the obtained chromatograms and spectral data, the programmed retention time indices were compared and are tabulated in **Table 3.2**. The DBWax column does not sufficiently separate the less polar oxygenates from the hydrocarbon matrix. These components represent about 0.1 % of the total oxygenates. The acids eluted from this column. The RT2340 column provided sufficient separation of the oxygenates from the C_{10} – C_{13} hydrocarbon matrix. The phase has a maximum temperature limit of 250°C allowing the elution of the highly polar acids. The TCEP column provided quite good separation of oxygenates from the hydrocarbons. The maximum temperature limit of this column, however, is much lower than for the other two columns (TCEP - 140°C, DBWax - 240°C, RT2340 – 250°C) and the C_9 and C_{10} acids did not elute from this column (final temp of 140°C/10 min).

Table 3. 2 Retention indices on the DBWax, RT2340 and TCEP columns

		DBWax		RT2340		TCEP	
Peak Nr.	**Component**	**Ret Time**	**Ret Index**	**Ret Time**	**Ret Index**	**Ret Time**	**Ret Index**
	Highest boiling hydrocarbon (C13 internal olf.)	26.4 (Min)	1361	16.5 (Min)	1363	10.8 (Min)	1359
1	C9 Ester (Lowest boiling oxygenate)	24.7	1329	18.3	1410	14.6	1456
2	C10 Acetal	26.2	1357	18.9	1424	11.8	1387
3	C10 Acetal	27.1	1373	19.2	1429	14.3	1451
4	C9 Ester	24.7	1328	19.73	1441	14.6	1456
5	C9 Ester	26.5	1362	20.2	1453	16.2	1491
6	C9 Ester	29.2	1408	21.6	1481	16.6	1499
7	C10 Ester	30.9	1435	21.7	1484	20.0	1559
8	C9 Aldehyde	27.4	1378	21.9	1489	17.5	1515
9	C11 Acetal	30.0	1422	22.3	1495	18.2	1529
10	C9 Ketone	27.2	1375	22.5	1499	17.7	1520
11	C9 Ketone	28.2	1392	23.0	1508	18.6	1537
12	C10 Ester	29.2	1408	23.1	1511	21.5	1583
13	C10 Ester	31.6	1446	23.6	1520	23.0	1605
14	C9 Alcohol	32.7	1462	23.9	1526	23.8	1617
15	C8 Alcohol	34.4	1486	25.3	1551	22.3	1595
16	C10 Aldehyde	31.9	1450	25.6	1555	21.0	1575
17	C10 Ketone	31.7	1447	26.0	1563	25.6	1641
18	C9 Alcohol	35.8	1506	26.3	1567	21.2	1579
19	C9 Alcohol	36.6	1515	26.8	1576	23.8	1617
20	C9 Alcohol	38.5	1540	28.7	1606	25.7	1642
21	C11 Aldehyde	36.2	1510	28.9	1609	24.4	1625
22	C11 Ketone	36.0	1508	29.4	1616	28. 6	1681
24	C10 Alcohol	40.3	1562	30.0	1625	27.8	1667
25	C11 Alcohol	40.5	1565	30.3	1629	29.1	1682
26	C10 Alcohol	42.3	1585	31.9	1652	28.9	1681
28	C11 Alcohol	43.9	1603	33.0	1666	30.0	1693
29	C11 Alcohol	44.3	1605	33.0	1667	30.2	1695
30	C11 Alcohol	45.9	1624	34.7	1688	32.2	1716
32	C7 Acid	49.4	1659	47.5	1825	37.4	1765
34	C8 Acid	52.9	1691	49.5	1843	42.2	1805
36	C9 Acid	56.3	1721	53.6	1878	Did not elute	
38	C10 Acid	59.7	1750	59.6	1924	Did not elute	

The selection of the RT2340 over the DBWax column is further supported by the data discussed below. The total ion chromatogram on the DBWAX column and a zoom into the region between 23 – 35 min are shown in **Figure 3.3** and **Figure 3.4**, respectively. The

separation between the oxygenates and the hydrocarbon matrix seems to be complete.

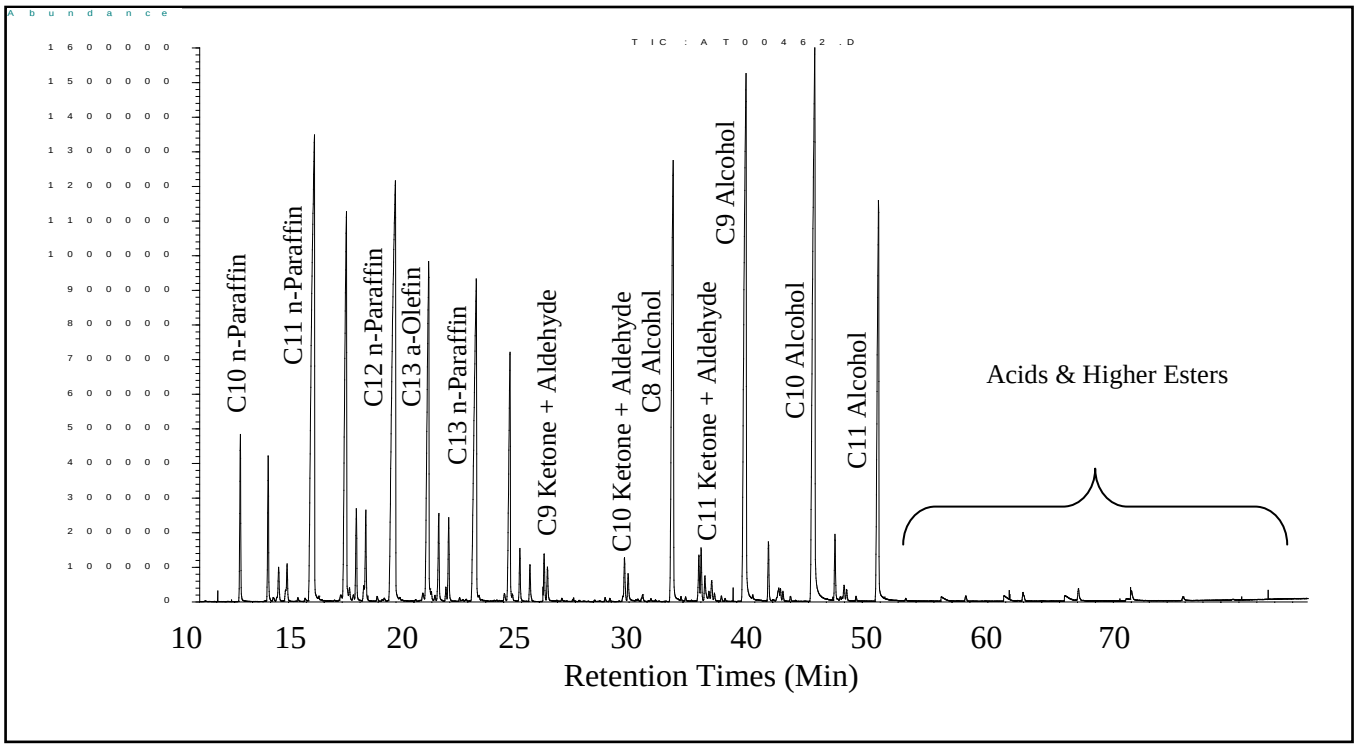


Fig. 3.3. Total ion chromatogram of the alkylation feedstock on the DBWAX column

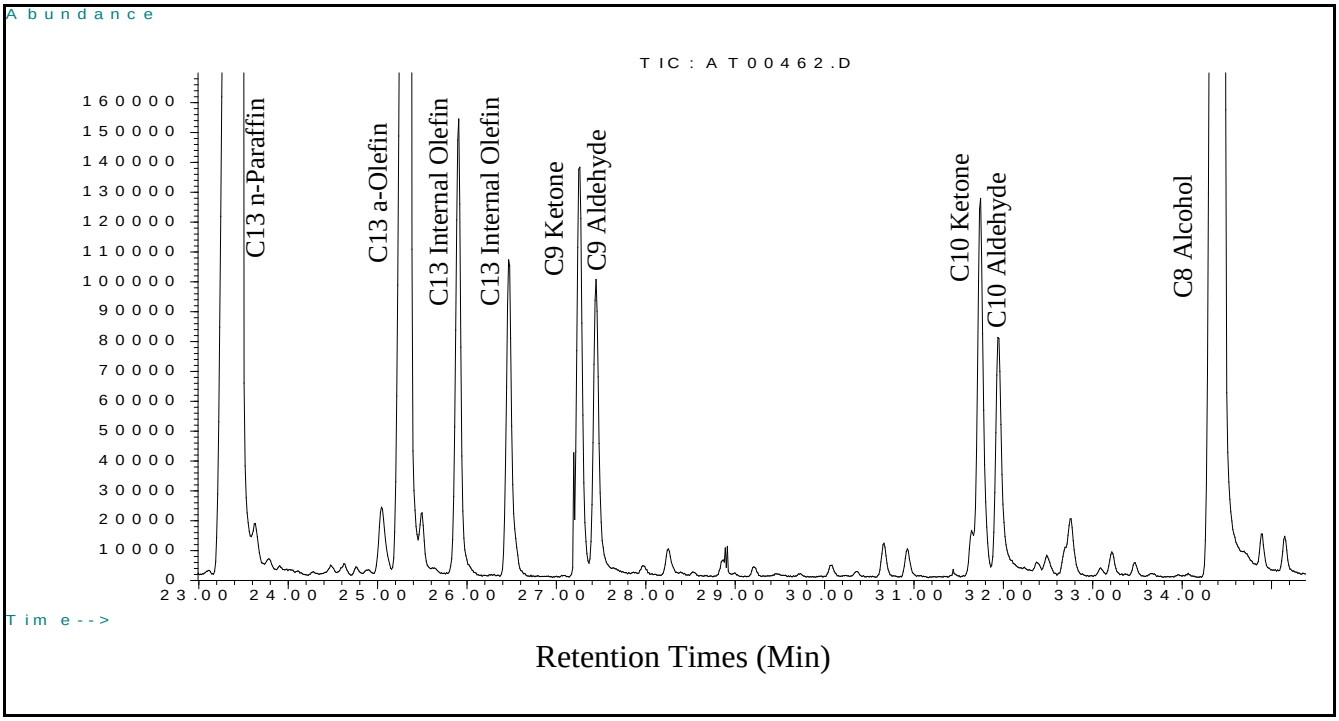


Fig. 3.4. Zoom of the TIC of the alkylation feedstock on the DBWAX column

However, some of the lower level, less polar oxygenates like the C_8 ethyl ester and acetate esters co-elute with the hydrocarbons. This is illustrated by the ion extracted chromatograms at m/z 61 ($CH_3COOH_2^+$ typical for acetate esters), 88 ($CH_2COHOC_2H_5^{+\circ}$ Mc Lafferty of ethylesters) and 182 (the molecular ion of a C_{13} internal olefin) in **Figure 3.5**.

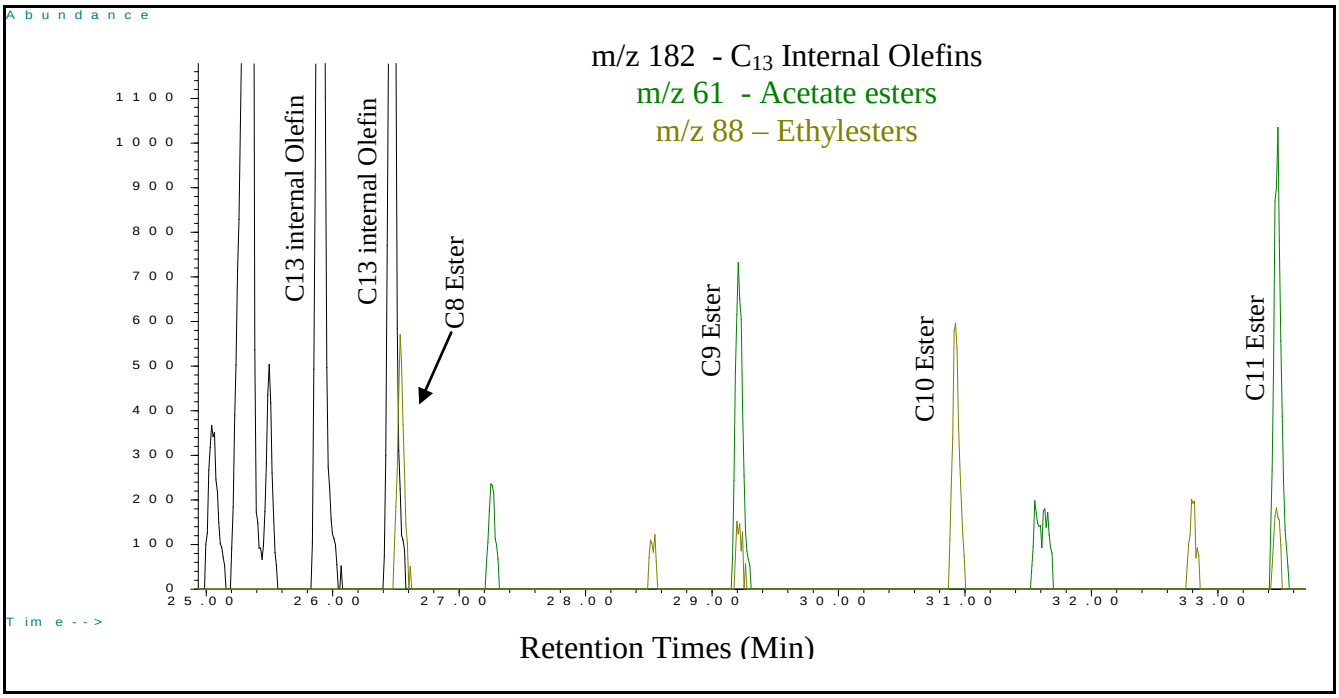


Figure 3.5. Extracted ion chromatograms of the alkylation feedstock, zoomed in between 25 - 34 min on the DBWax column.

On the RT2340 column much better separation of those oxygenates from the hydrocarbons occurs. The hydrocarbon (m/z = 182) and the ester peaks (m/z 61 and 88) were completely resolved on this column. The oxygenate peaks tend to group closer together on the biscyanopropyl column than on the polyethylene glycol column. This is illustrated in **Figure 3.6,** comparing the relevant part on the two columns. On RT2340, all oxygenates are better separated from the hydrocarbon matrix, while on the DBWax column the alcohols are better separated from the carbonyl compounds. The perfect combination for a heart-cut GC-GC experiment is thus the RT2340 as pre-column guaranteeing the best oxygenate/hydrocarbon separation and the DBWax as second column providing the best separation in the oxygenate fraction.

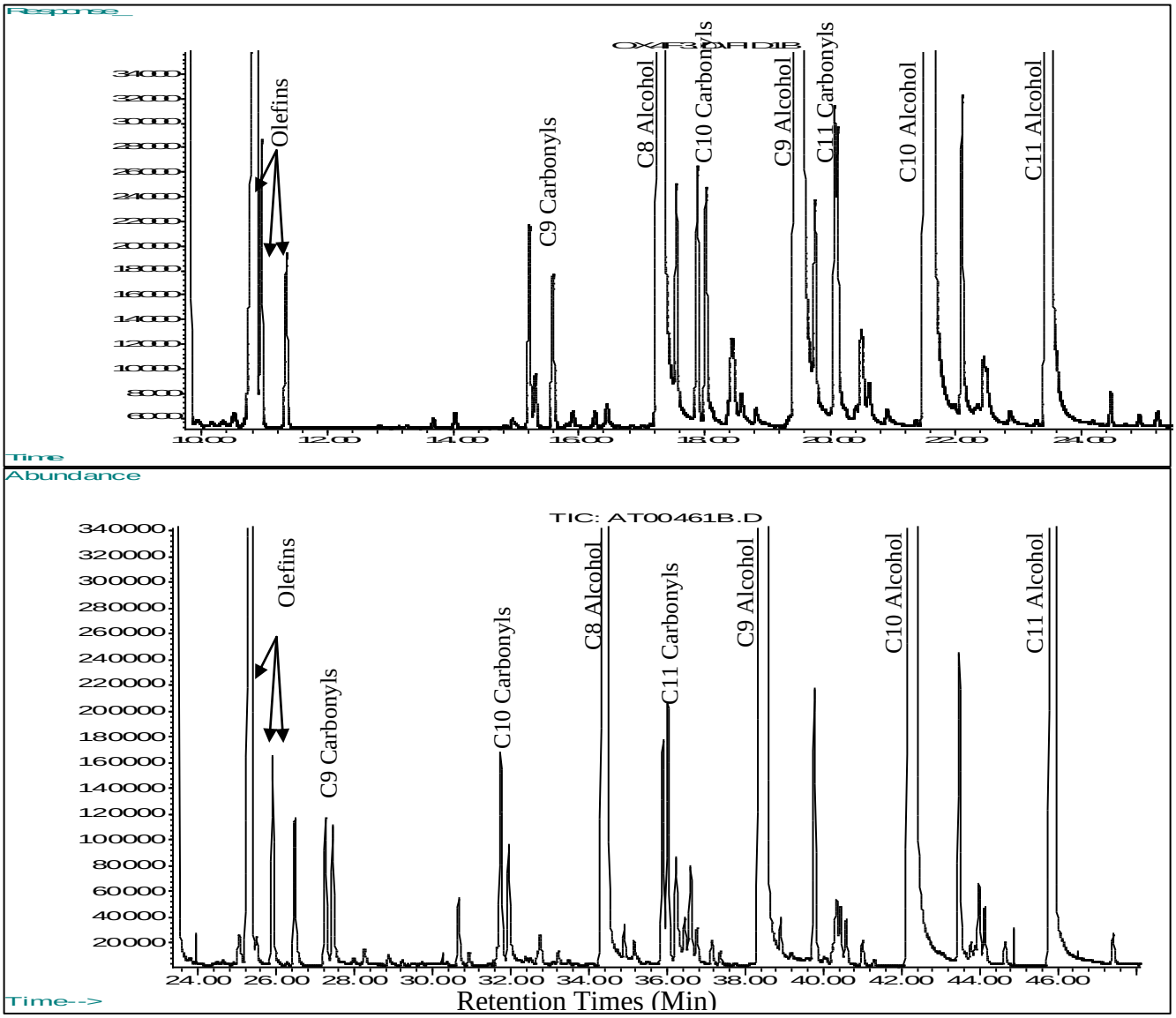


***Figure 3.6. Chromatograms* of the *alkylation feedstock* on the RT2340 column (top) and on the DBWAX column (bottom).**

3.3.2. Heart-cutting and enrichment

The heart-cut time window was determined by comparing the pre-column separation of both samples, the alkylation feedstock before and after removal of oxygenates (**Figure 3.7**). Oxygenate peaks eluted between 13 to 33 min and this time window was therefore selected as the heart-cut time window. For the heart-cut GC-GC analysis, the pre-column was slightly overloaded (1 μl injection) to ensure that all oxygenate peaks could be observed.

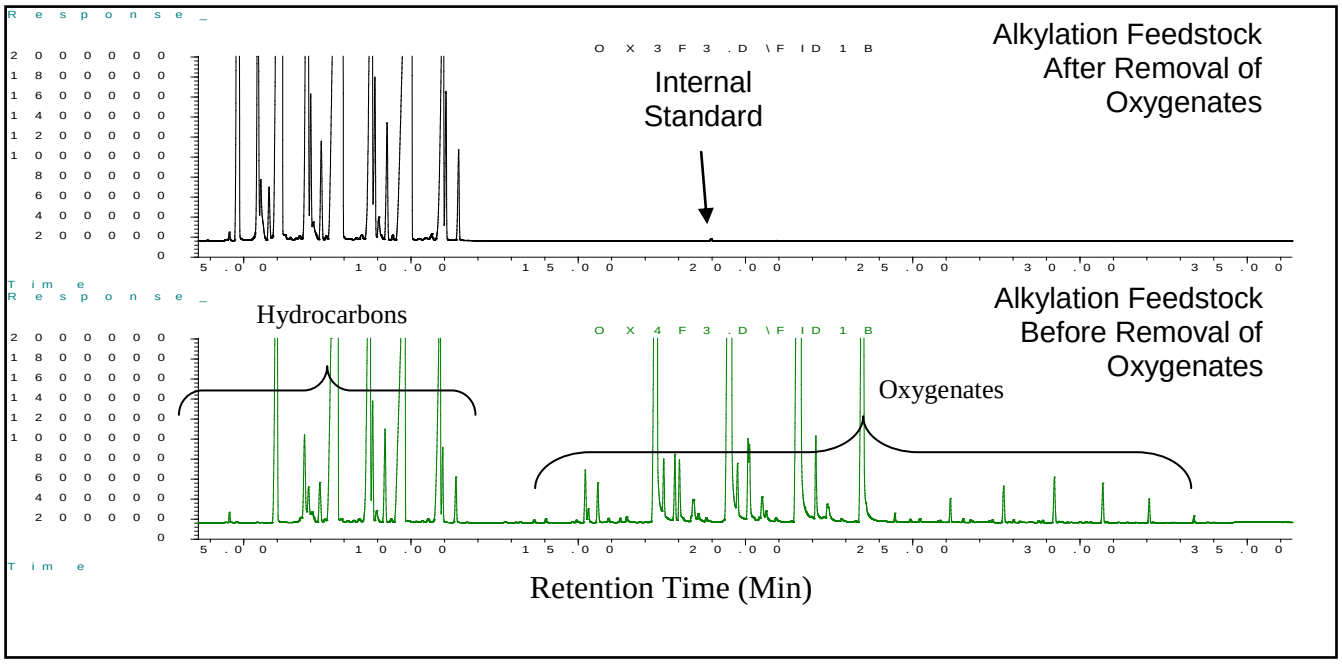


Figure 3.7. The first dimension (monitor) FID chromatograms of the C_{10} – C_{13} low oxygenate alkylation feedstock and the high alkylation feedstock.

Multiple injections were made and heart-cuts of the oxygenate region (13 – 33 min) were each time transferred to the cryotrap where the oxygenates accumulated at a temperature of -70 °C. After sufficient enrichment of the analytes (10 injections), the trap was heated and the accumulated oxygenates were desorbed onto the main column where separation and detection was done.

Figure 3.8 shows the second dimension chromatogram (main column) of the concentrated heart-cut fraction after 10 injections.

The method is only semi-quantitative because standards of all of the oxygenated components are not available and it is furthermore impractical to determine the FID response factors for the few hundred oxygenates. However, the FID response to the oxygen-containing internal standard, 3-nonanol, in the same carbon number range as the unknown oxygenates, should not differ too much from the FID response of the unknowns.

Oxygenates present at much less than 1 ng/g could be detected with this method. It is possible to further improve the sensitivity of the method by injecting more times, collecting more heart-cuts and therefore enriching the oxygenate heart-cut fraction even more.

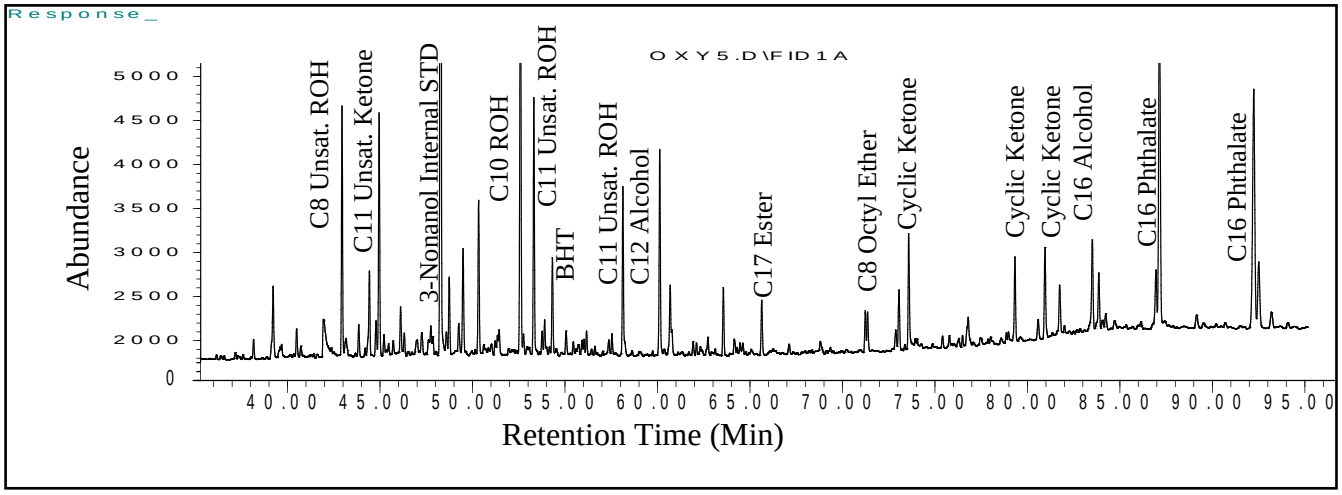


Figure 3.8. Second dimension chromatogram of the oxygenate heart-cut after enrichment.

More that 300 peaks at sub-ng/g level were observed. Most of these components are unsaturated or cyclic alcohols and carbonyls. The influence of some of these solutes on the performance of alkylation catalysts is presently investigated. The source of the phthalates is unknown but they are suspected to originate from contamination during the sampling procedure.

3.4 Summary

Heart-cut GC-GC has been successfully applied for the separation of oxygenates from a complex C_{10} – C_{13} hydrocarbon matrix. Heart-cut GC-GC is thus a very valuable multidimensional GC technique for the separation and enrichment of selected heart-cut fractions, which are not obtained on ^{1}D GC methods due to peak overlap or a too low concentration of targeted components. It has the advantage of increased peak capacity and resolution but this is only of benefit to the heart-cut fraction. Fortunately, in this application appropriate column selection allowed to concentrate all oxygenates in one fraction.

The biscyanopropyl column is the column of choice as the pre-column. It has been shown to outperform the other polar columns for the separation of oxygenates from the hydrocarbon matrix of the C_{10} – C_{13} alkylation feedstock. The best analytical column proved to be a polyethylene glycol column. Using multiple injections, heart-cutting the selected analytes and accumulating them on the cryotrap may seem like a tedious way of separating and enriching analytes. This is not true at all. A fully automated sequence running overnight was set up. The internal standard helped to obtain reproducible semi-quantitative data.

The features of heart-cut GC-GC have been compared with those of comprehensive GCxGC and sequential GC-GC (Chapter 4).

3.5 References

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4 COMPARISON OF COMPREHENSIVE GCXGC AND SEQUENTIAL GC-GC FOR THE ANALYSIS OF OXYGENATES IN A C_{10} – C_{13} ALKYLATION FEEDSTOCK

4.1 Introduction

Multidimensional GC techniques characterized by a highly improved separation power compared to ^{1}D GC, are more and more considered panaceas for the analysis of highly complex mixtures like those encountered in the petroleum industry.

The techniques of comprehensive GCxGC and sequential GC-GC have been evaluated and compared for the analysis of the oxygenates in a C_{10}-C_{13} alkylation feedstock. The main aim was to evaluate the features of both techniques for chemical class separation of components and to decide whether the time is ready to implement them in the Sasol laboratories. Whereas comprehensive GCxGC is claimed to be a mature technique, sequential GC-GC is new and is therefore highlighted in this work. In order to evaluate the technique in terms of robustness, two sequential GC-GC systems were used; one placed at the Research Institute for Chromatography, Kortrijk, Belgium and one at the Sasol laboratories.

Comprehensive GCxGC provides separation of the entire sample in both dimensions with a single injection, using short, fixed and pre-defined modulation times of a few seconds to transfer a slice of a single peak to the second dimension column. The modulator is at the interface of the two columns and is responsible for the quantitative transfer and compression of all solutes or a representative fraction thereof from one dimension to the next. Peaks eluting from the pre-column are trapped and focussed, usually by thermal means onto the second column. Each pulse becomes very narrow because of the focussing process. Because modulation is a mass conservation process, the peak height increases to accommodate the reduction in peak width. The increased height and narrowness of the peaks provides an increase in sensitivity [1].

In recent years, heart-cut GC-GC has very much been overshadowed by comprehensive GCxGC because the latter provides separation of the complete sample in both dimensions with only a single injection. Sequential GC-GC uses the heart-cutting principle but with a time-window instead of a selected part of the chromatogram. Multiple injections are done;

each time a new time-window is transferred to the cryotrap and released to the second column for analysis, until the entire sample is analysed on both columns. The method is fully automated by using an auto injector and setting up a sequence of methods. Sequential GC-GC heart-cut time windows are much longer than the modulations of GCxGC. They are fixed and can range from less than 30 s to 1 min or more. The technique lies in between heart-cut GC-GC and comprehensive GCxGC.

4.2 Experimental

The alkylation feedstock before oxygenate removal was analysed by both GCxGC and sequential GC-GC by using the following experimental conditions.

Comprehensive GCxGC

Gas chromatograph: Agilent 6890 GC – FID
Column set:
Column 1: 50 m L x 0.2 mm I.D., 0.5 µm d_f PONA (polydimethylsilicone)
Modulator loop: deactivated fused silica: 1 m L x 0.1 mm I.D.
Column 2: 2 m L x 0.1 mm I.D., 0.1 µm d_f Solgel Wax (polyethylene glycol)
Modulation: 5700 ms cold jet (focusing), 300 ms hot jet (injection)
Carrier gas: helium, constant pressure @ 500 kPa
Injection: 0.2 µL, split flow 744 mL/min
Oven program: 100°C (0 min) – 2°C/min – 180°C (10 min)
Detector: FID acquisition @ 100 Hz

Sequential GC-GC at RIC

Gas Chromatograph: 2 x Agilent 6890 GC – FID
Multicolumn switching: Gerstel MCS – dual oven set-up – cryofocusing
Column set:
Column 1: 50 m L x 0.25 mm I.D., 0.5 µm d_f HP5-MS (5%phenyl-95%methylsilicone)
Oven 1: 100°C – 1°C/min – 160°C
Column 2: 30 m L x 0.25 mm I.D., 0.25 µm d_f Solgel-wax (polyethylene glycol)
Oven 2: 80°C – 1°C/min – 140°C

Both oven programs started at the point of injection

Sequential heart-cut: 40 heart-cuts (1 min)

Carrier gas: helium

Pre-column:constant pressure @ 350 kPa

Analytical column: midpoint pressure @ 100 kPa (pressure controlled)

Detection: FID at 100Hz

Sequential GC-GC at Sasol

Gas Chromatograph: 2 x Agilent 6890 GC – FID

Multicolumn switching: Gerstel MCS – dual oven set-up – cryofocusing

Column set:

Column 1: 50 m L x 0.25 mm I.D., 0.5 µm d_f PONA (100% methylsilicone)

Oven 1: 60°C/1 min – 3°C/min – 240°C – 20°C/min – 320°C/27 min

Column 2: 30 m L x 0.25 mm I.D., 0.5 µm d_f DBwax (polyethylene glycol)

Oven 2: 60°C/40.5 min – 4°C/min – 240°C/4 min

The second oven started after the cryofocusing, independent from the first oven

Sequential heart-cut: 80 heart-cuts (30 s)

Carrier gas: helium

Pre-column:constant pressure @ 270 kPa

Detection: FID at 20 Hz, TOFMS at 20Hz

Data handling

GCXGC data are treated with dedicated software (GC Image™ Data from Zoex corporation) that divides the original 1-dimensional chromatogram into 'slices' that match with the modulation time (e.g. 6 s) and puts the data into a matrix. This matrix of signal abundances can be plotted as a ^{3}D or a contour plot, but also individual slices (i.e. 2nd dimension chromatograms) can be shown.

In sequential GC-GC, a different analysis is started for each heart-cut window. This results in 40 chromatograms (i.e. output of the second column) for 40 heart-cut windows. These chromatograms can be shown individually since they consist of different data files. At RIC, a program was written to bundle via Excel all chromatograms into one matrix. From this matrix, ^{3}D and contour plots can be drawn using the GC Image™software. New software for

sequential GC-GC is presently under development in RIC, Belgium to combine GC Image™ with retention time locked software and MS-deconvolution reporting software. In the Sasol laboratories, data were introduced in Excel, overlapping peaks in the windows were grouped and contour or cone plots were made via Matlab™.

4.3 Results and discussion

4.3.1. Comprehensive GCxGC

From the ^{3}D GCxGC contour plot of the alkylation feedstock in **Figure 4.1**, the separation of the oxygenate classes of ketones, aldehydes and alcohols from the hydrocarbons can be seen. The paraffins and olefins elute closely together on the polar Solgel column, used in the second dimension GC, as this stationary phase does not retain non polar hydrocarbons to a large extent. These components therefore elute first and very fast from the column. Other column combinations should be selected to unravel the hydrocarbon part completely. The peaks were elucidated by means of standard mixtures of the different classes.

It is important to note that comprehensive GCxGC is not as easy as commonly claimed. A large number of experiments had to be performed before the separation shown in Figure 4.1 was obtained. Connections, column length in the second dimension and data handling (manipulation) all contribute to the obtained data. As illustration, **Figure 4.2** shows the first separation obtained with only one meter second column and a modulation time of 4 s. It is obvious that the peak shape for the main components is far from perfect decreasing tremendously the peak capacity on the second dimension.

The peak capacities in comprehensive GCxGC will be discussed after presentation of the sequential GC-GC data. This will allow a good comparison between the two techniques.

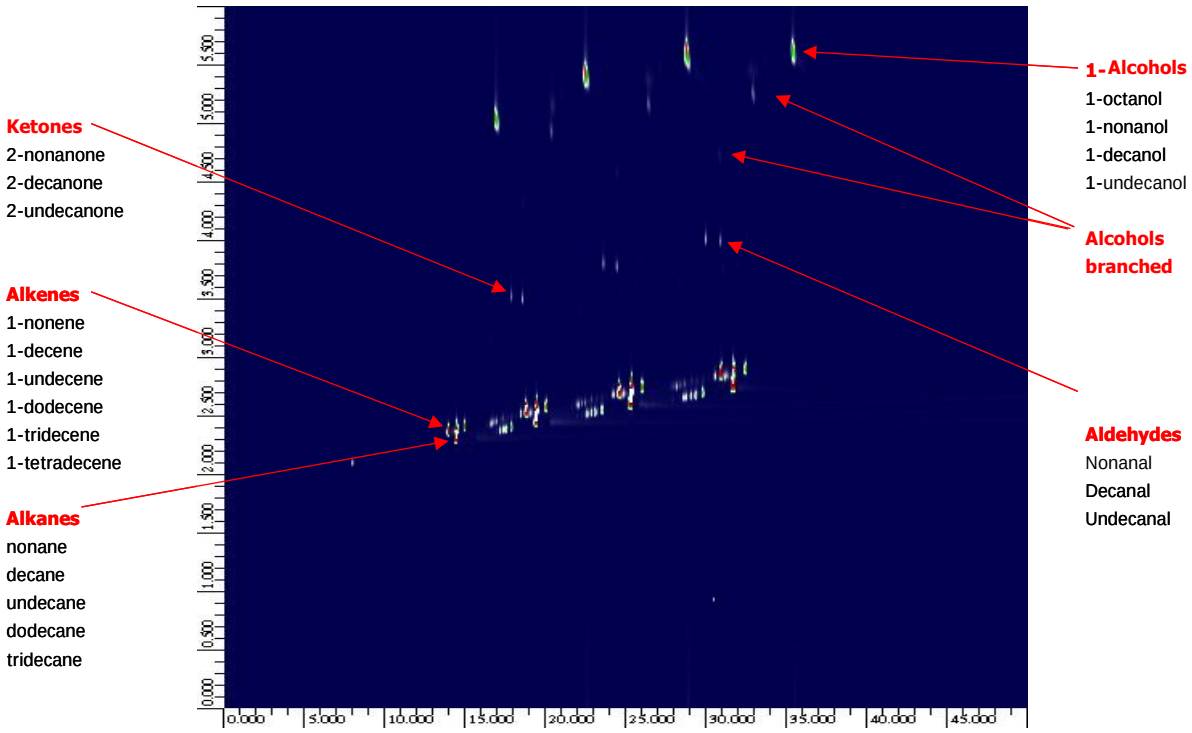


Figure 4.1. GCxGC ^{3}D contour plot of the alkylation feedstock

4.3.2. Sequential GC-GC

In sequential GCxGC, the first decision to be made is the selection of the time window. This is arbitrary and depends on the problem at hand and on the decision of the operator. The “RIC” chromatogram on the first dimension column is shown in **Figure 4.3**. In the first instance time slots can be selected according to the obtained separation. For example, a good fractionation in Figure 4.3 would be 10 min slots starting from 2 min (indicated by colours in the figure). Each fraction is well defined and no peak overlap occurs. Peak capacities, however, increase with the number of sequences and therefore slots are typically in the order of 30 s (Sasol sequential GC-GC analysis and Chapter 5) to 1 min (RIC sequential GC-GC analysis).

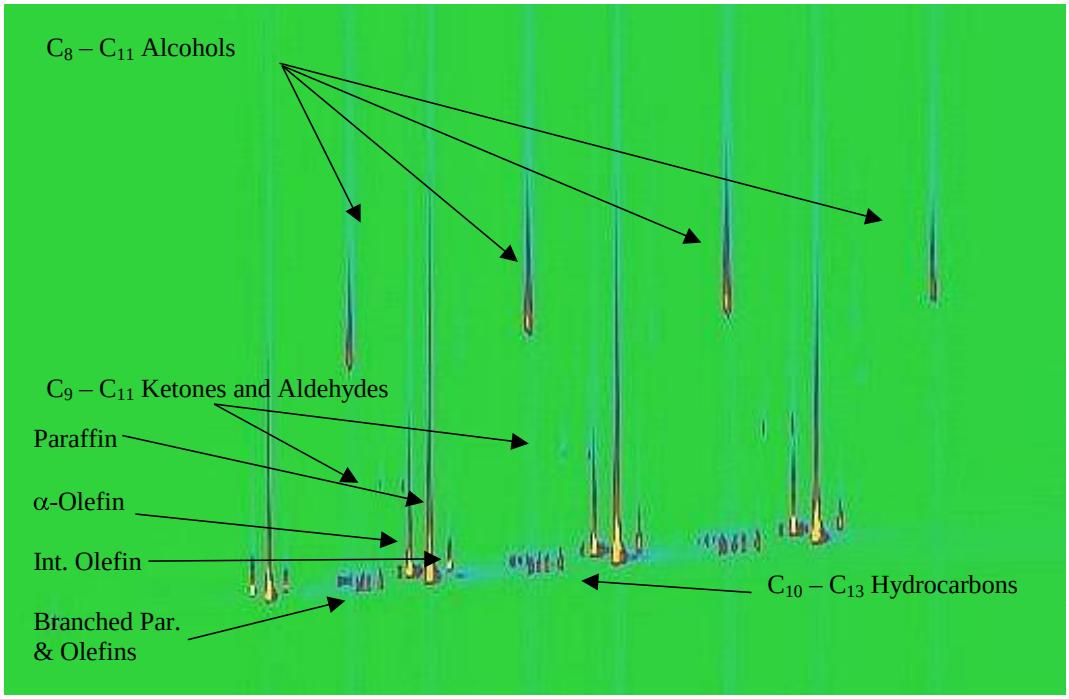


Figure 4.2. GCxGC [3]D contour plot of the alkylation feedstock with a 1 m column and a 4 s modulation time

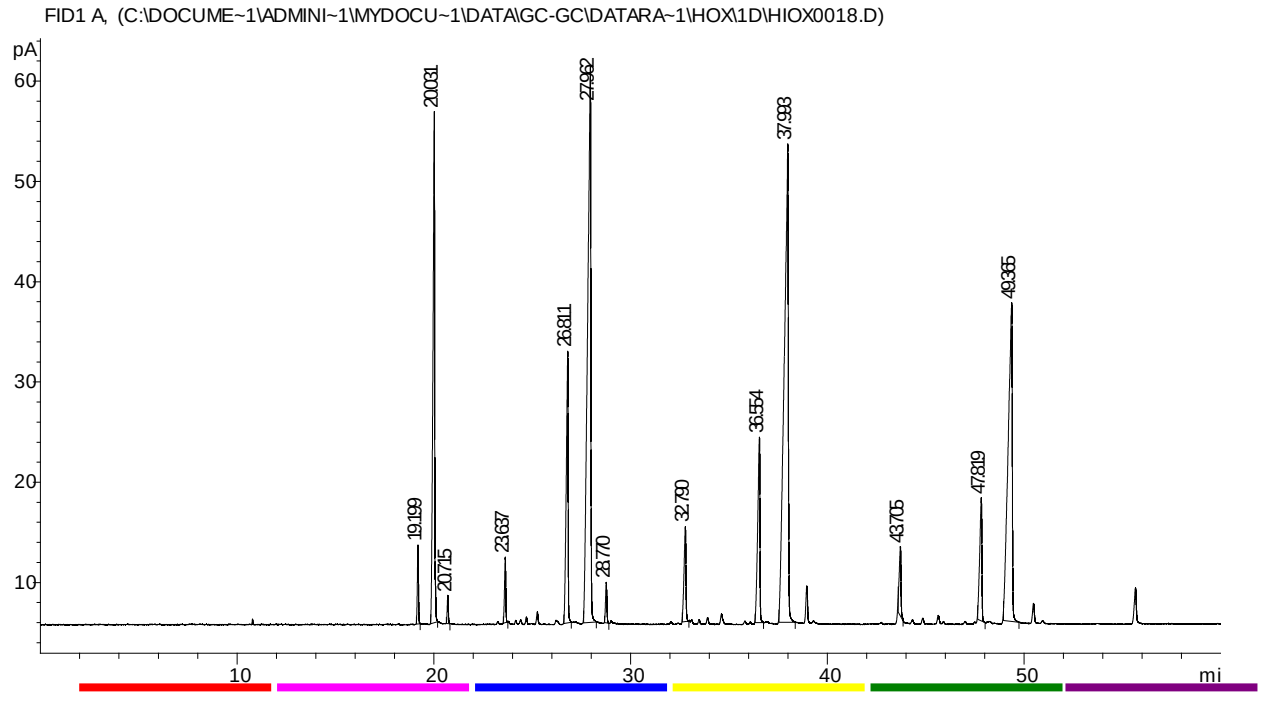


Figure 4.3. First dimension chromatogram in the RIC sequential GC-GC analysis

Figure 4.4 shows the chromatogram with 1 min slots. Some peak overlap can occur that should be corrected for by the software (as in comprehensive GCxGC) or by the operator. New software is presently under development using the principle of retention time locking (GC) and deconvolution reporting software (MS) [2]. For this application the same software was applied in both cases.

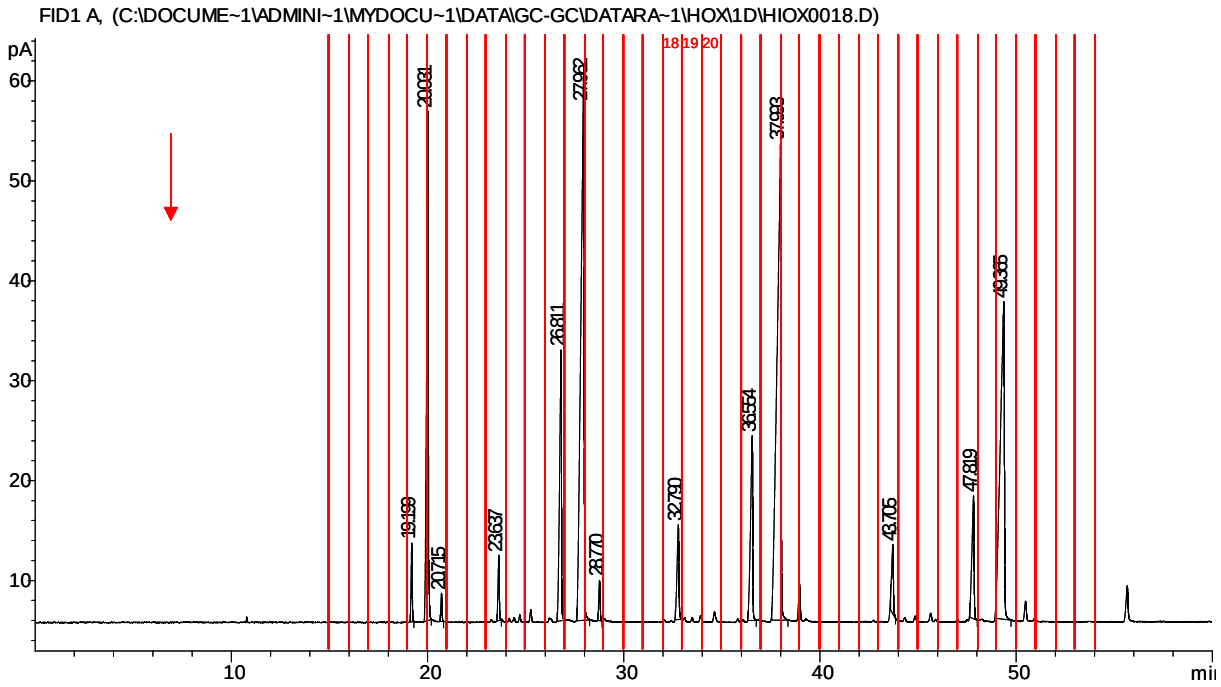


Figure 4.4. First dimension chromatogram in the RIC sequential GC-GC analysis with 1 min slots.

For sequential GC-GC, even a small shift in retention times between successive ^{1}D injections would lead to inaccurate results, especially when the window edge is on a first dimension peak. To minimize this effect, electronic pressure control (EPC), the use of auto injectors and a leak-free system are crucial to ensure reproducible and accurate results.

The separation of the components according to chemical classes is demonstrated in the ^{3}D contour plot (**Figure 4.5**). Zooming into the specific regions, several chemical classes can be distinguished. The oxygenates are indicated in the contour plot. The white cadre embraces the alcohols; the yellow one the carbonyls. Comparing the contour plots of Figure 4.2 and Figure 4.5, the same classes can be distinguished but the sequential GC-GC plot allows

easier elucidation of the classes. This is mainly due to the increased peak capacity. As example, the iso-alcohols (a+a', b+b') are clearly split into two peaks in the sequential GC-GC analysis whereas this is not obvious from the comprehensive GCxGC analysis. Moreover, some peaks appear only in the sequential analysis e.g. x and y. Another feature of sequential GC-GC is that distribution of the classes over the plot is more linear than in comprehensive GCxGC.

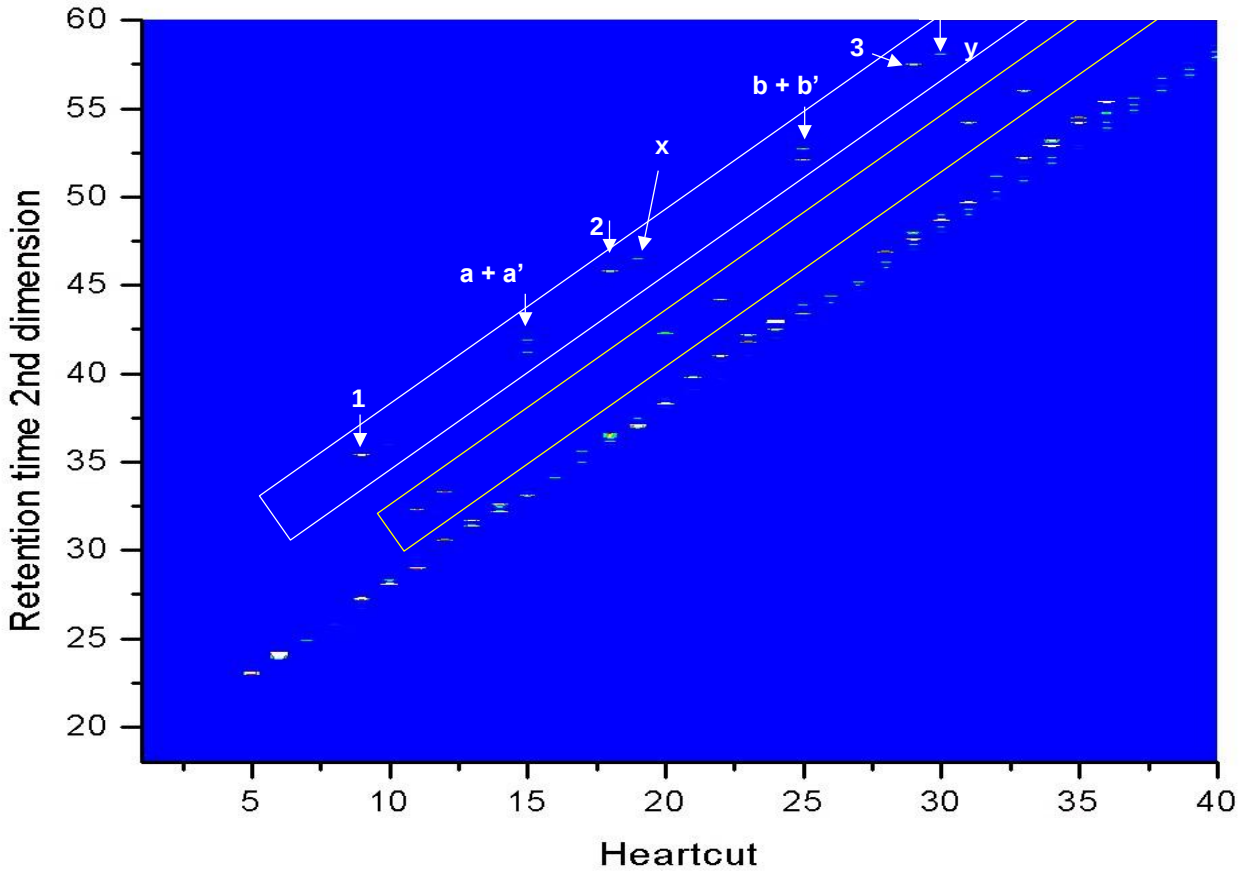


Figure 4.5. Sequential GC-GC ^{3}D contour plot of the alkylation feed

The total "Sasol" ^{3}D cone plot is shown in **Figure 4.6**, while **Figures 4.7 to 4.9** shows details on the hydrocarbons, the linear and branched alcohols and the ketones and aldehydes, respectively.

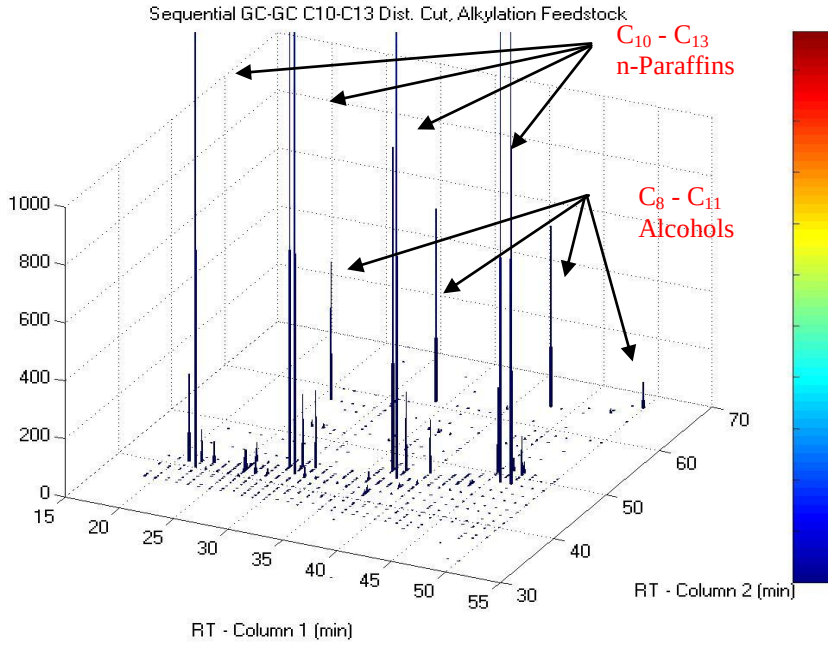


Figure 4.6. The ^{3}D cone plot of the sequential GC-GC analysis of the C_{10} – C_{13} alkylation feedstock

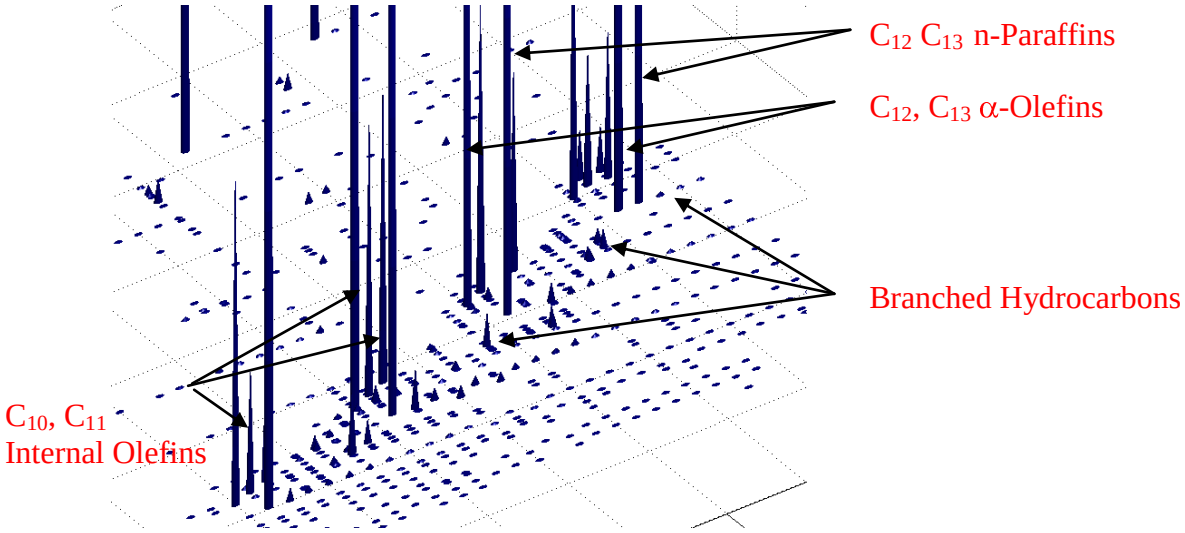


Figure 4.7 The paraffinic/olefinic region of the ^{3}D sequential GC-GC cone plot was rotated and zoomed in to show the separation of the n-paraffins, α-olefins, internal olefins and branched hydrocarbons

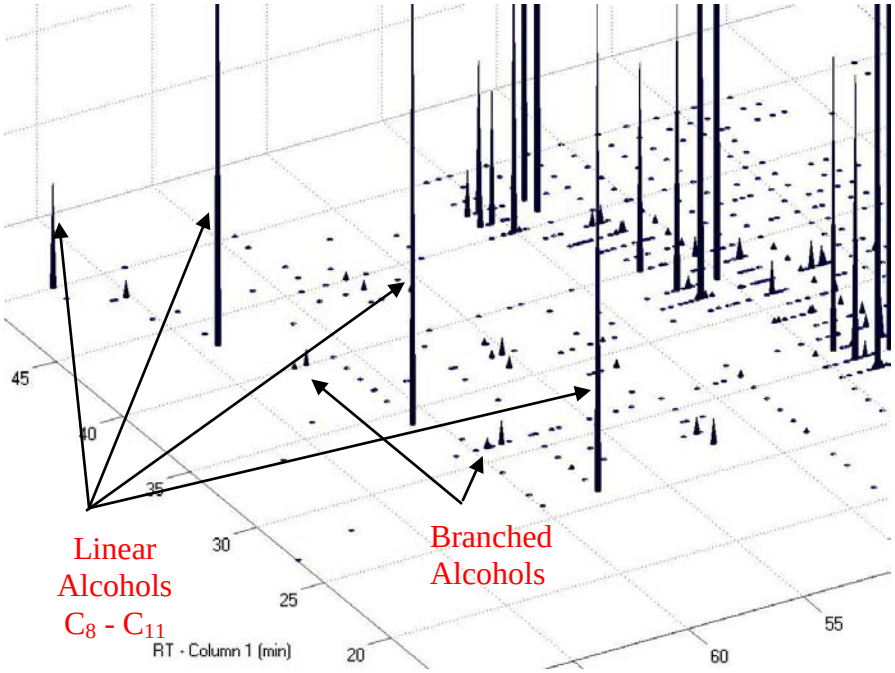


Figure 4.8. Sequential GC-GC ^{3}D cone plot was rotated and zoomed in to illustrate the separation between the linear and branched alcohols

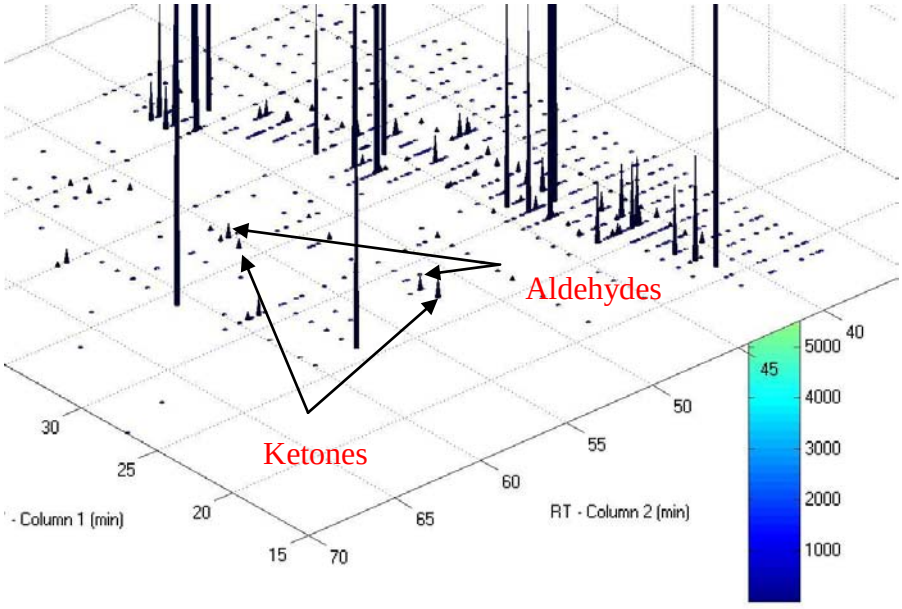


Figure 4.9. Ketones and aldehydes are separated by the sequential GC-GC as illustrated by the ^{3}D cone plot.

Some of the mass spectra, obtained by TOFMS are shown in **Figure 4.10**.

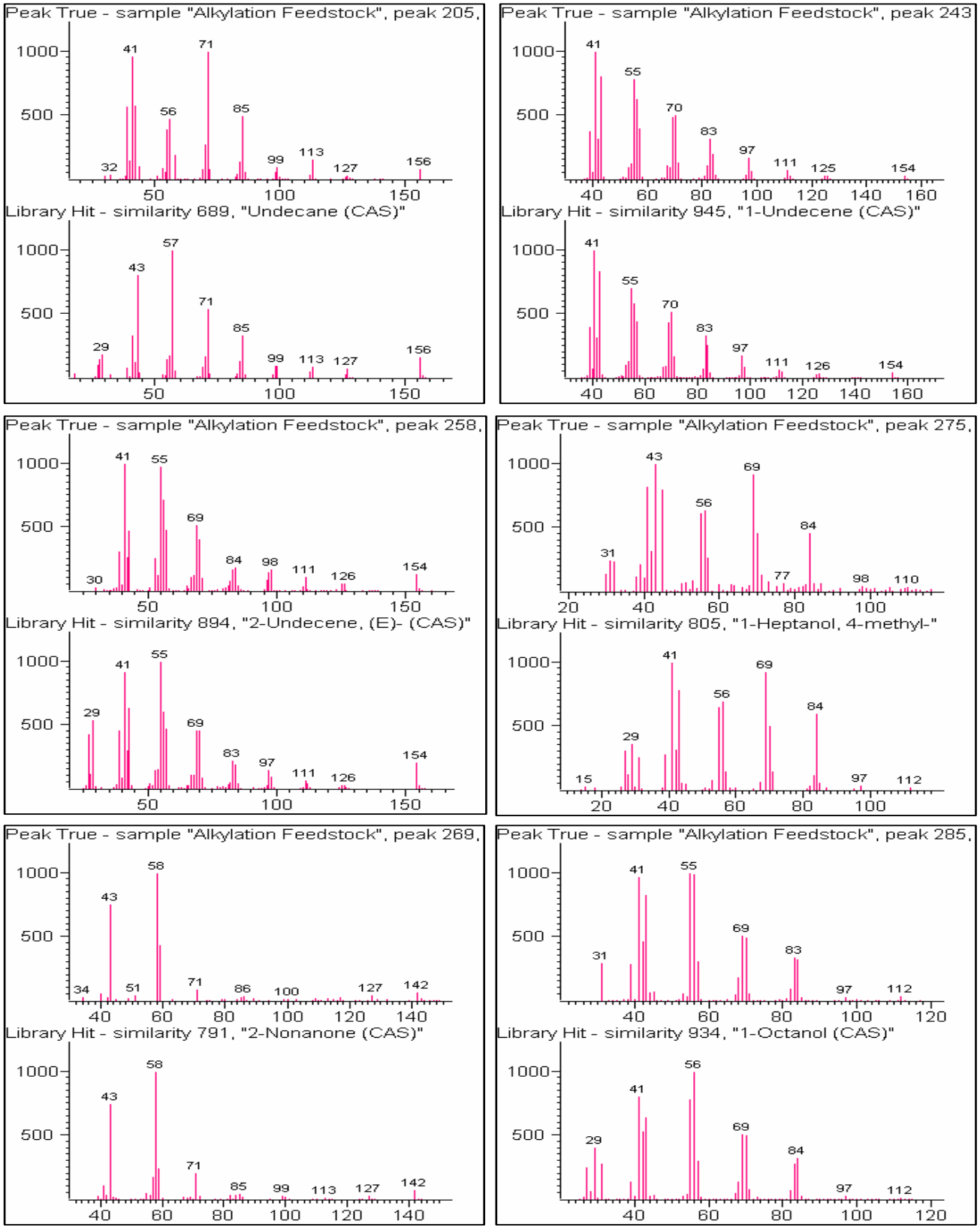


Figure 4.10. Some representative mass spectra of the alkylation feedstock

The performance of the two techniques can be evaluated from the 2nd-dimension chromatograms (i.e. the chromatograms of selected "slices" of the 2D separation).

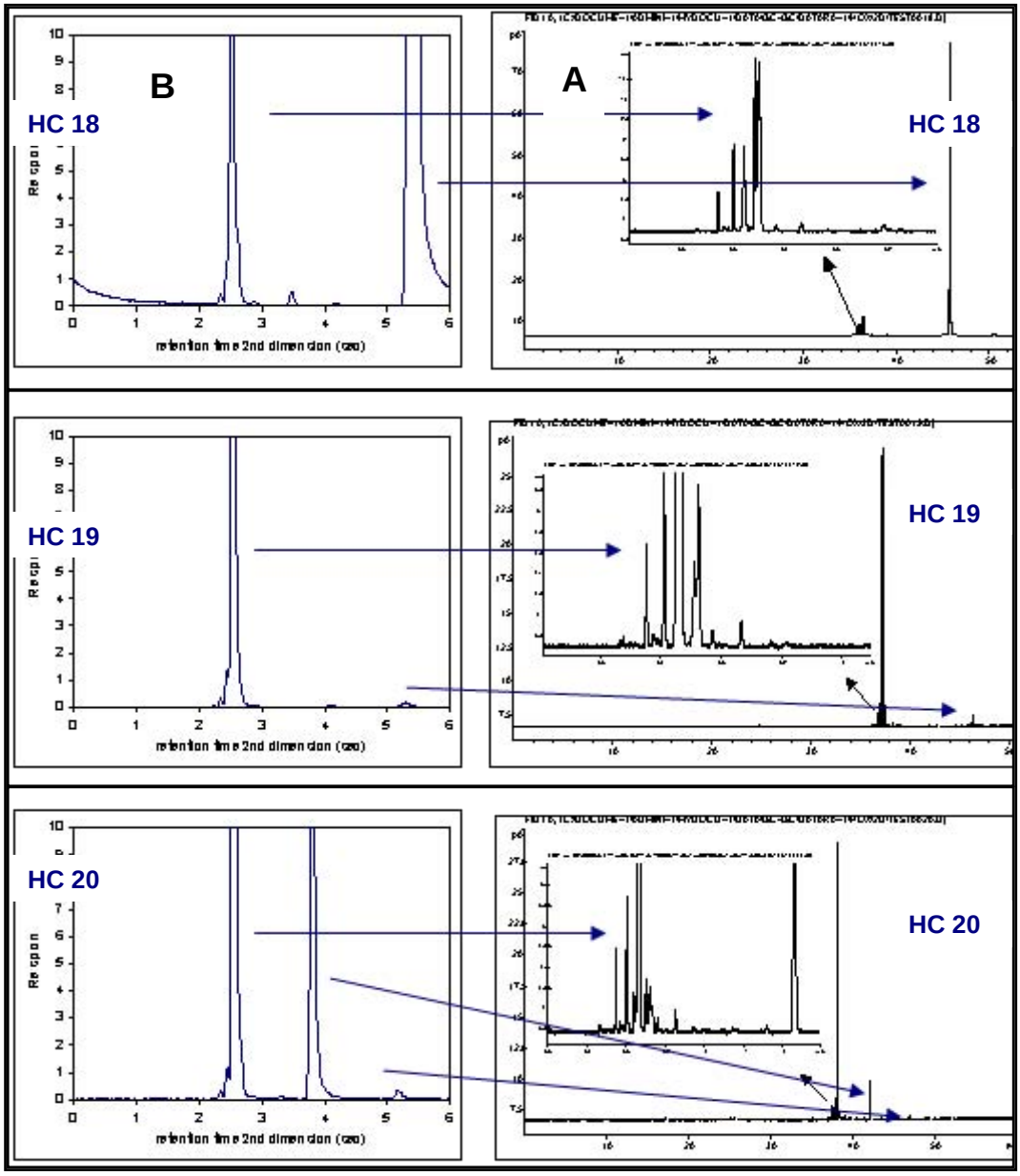


Figure 4.11. 2nd-dimension chromatograms of "heart-cut fractions" 18, 19 and 20 of the sequential GC-GC (A) and comprehensive GCxGC (B) analyses of an alkylation feedstock

Figure 4.11A shows the chromatograms of the second column for the compounds that elute from the pre-column in sequential GC-GC in the "heart-cuts" 18, 19 and 20. One can create

similar chromatograms for the GCxGC set-up. As shown in **Figure 4.11B**, three "modulated packages" (summation of the relative second dimension cuts to simulate the same, larger time cut of sequential GC-GC) are selected, representing the same compounds as the ones shown in the fractions 18, 19 and 20 of the sequential GC-GC approach. They are called "heart-cut 18", "19" and "20". Note that in **Figure 4.11A** and **Figure 4.11B**, the marked compound groups are the same.

Theoretically, the peak capacity in comprehensive GCxGC is:

$$n_{p\ \textit{total}} = n_{p\ \textit{first dimension}} \times n_{p\ \textit{second dimension}} \qquad (4.1)$$

For the temperature programmed window of the column in the first dimension, $n_{p\ \textit{first dimension}}$ is *ca.* 400 and the short 0.1 mm column in the second dimension provides roughly 10 n_p/m (the reference to the number of peaks / m is just for comparison with sequential GC-GC; peak capacity has a square root relationship with *N*, the number of plates and therefore with the length of column, as can be observed from eq. 2.10 on page 20). For the chromatogram shown in **Figure 4.1,** the total peak capacity can be estimated to be 8 000 (400 x 20).

Calculation of the peak capacity in sequential GC-GC is not straightforward! An approximation is:

$$n_{p\ \textit{total}} = n_{p\ \textit{first dimension}} \times \text{number of heart-cuts} \qquad (4.2)$$

Visual inspection of Figure 4.11 however indicates that this is an underestimation. A single first dimension heart-cut of 0.5 - 1 minute consists mostly of a single peak, at most it will contain three peaks (See Fig. 4.4). The same heart-cut separates into ten or more peaks in the second dimension. On the other hand, using equation 4.1 is an overestimation. The real peak capacity in sequential GC-GC is somewhere in between equations 4.1 and 4.2 and presently experimentally verified by means of standard compounds [3].

Nevertheless, using equation 4.2 the peak capacities are twofold in the RIC approach (40 heart-cuts) and fourfold in the Sasol approach in sequential GC-GC compared to comprehensive GCxGC.

4.4 Summary

Both comprehensive GCxGC and sequential GC-GC are very powerful and promising analytical tools for the characterization of complex samples. Each system has its pro's and con's.

The main advantage of comprehensive GCxGC is the fact that only a single injection is necessary for analysis of the entire sample. This results in much shorter instrument time. An analysis that can be done in ca. 2 h with GCxGC will take, depending on the heart-cuts, 1 to 3 days with GC-GC. By automating the GC-GC analysis method, the hands-on time is similar to GCxGC. We should note, however, that when MS is combined with both techniques, the situation is different. Sequential GC-GC can be coupled to slow scanning rate mass spectrometers i.e. a quadrupole or a TOFMS at 20-30 Hz. For comprehensive GCxGC, a TOFMS with scan rates of 100 to 500 Hz is mandatory, resulting in very long data handling times.

Sequential GC-GC compares very favourably with GCxGC for chemical class separation of complex mixtures. Better sensitivity and resolution are obtained because the experimental conditions of the second dimension can be optimised in terms of length, internal diameter and film thickness of the column. Temperature programming is possible and optimal gas flows can be used. This leads to high column efficiency in both GC dimensions and therefore high resolution and peak capacities. The resolution power shown in this chapter is the highest ever seen in the Sasol laboratories for the characterization of complex petroleum products.

References

[1] G. Seconnino. 2003. GCxGC, RMIT University Website, 06 November 2003. [Available on internet:] http://www.rmit.edu.au/browse;ID=ktg59442x0e6z [Date of Access: 29 March 2005].

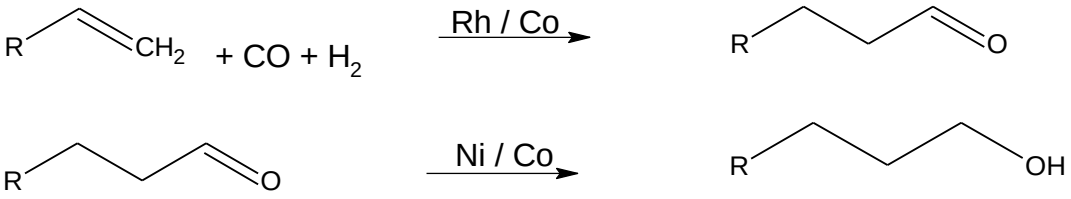
[2] P. Sandra, F. David, B. Tienpont, unpublished results, personal communication.

[3] P. Sandra, F. David, B. Tienpont, unpublished results, personal communication.

5 ANALYSIS OF CYCLIC, BICYCLIC AND NON-CYCLIC ALCOHOLS IN C_{12}-C_{13} "DETERGENT" ALCOHOLS BY COMPREHENSIVE GCXGC AND SEQUENTIAL GC-GC

5.1 Introduction

C_{12}-C_{13} alcohols are base chemicals for the production of detergents. These "detergent" alcohols are synthesized by hydroformylation of C_{11} – C_{12} alkenes with cobalt or rhodium as catalyst. The aldehydes formed are then hydrogenated to alcohols with a nickel or cobalt catalyst.



The "alkenenic" feed is obtained through Fischer Tropsch technology and the synthesized alcohols, mainly linear, may contain some iso-alcohol impurities with cyclic, branched and/or branched/cyclic structures [1].

Detergent manufacturers do not appreciate the presence of cyclic alcohols in C_{12}-C_{13} "detergent" alcohols and a limitation on the content of these components has been introduced. The cyclic alcohols indeed may affect the properties and performance of the detergents produced downstream. To study their effects on detergent performance and also for mass balance purposes, it is essential to have a good analytical method to separate the cyclic, bicyclic and non-cyclic alcohols from each other.

This challenging analytical problem has been tackled with ^{1}D GC-MS analysis and with the multidimensional techniques comprehensive GCxGC and sequential GC-GC both coupled to TOFMS. We have to note that the comprehensive GCxGC profiles were recorded by the LECO company and that, in our opinion, the best column combination was not selected. The obtained data, however, allows for making a fair comparison with sequential GC-GC.

5.2 Experimental

^{1}D GC-MS

Gas chromatograph: Agilent 6890-5973 MSD
Column: 30 m L x 0.25 mm I.D., 0.5 µm d_f DBWax (polyethylene glycol)
Oven: 60°C/1min – 3°C / min – 240°C
Pressure: 164 kPa
Injection: 0.5 µl, split ratio 100:1
Carrier gas: Helium,
Detector: Quadrupole MS, 10 Hz
Scanning range: m/z 30 - 300

Comprehensive GCxGC

Instrument Pegasus ^{4}D GCxGC-TOFMS.
Column 1: 30 m L x 0.25 mm I.D., 0.25 µm d_f DB5 (5% phenyl 95% methyl silicone)
Column 2: 2 m L x 0.1mm I.D., 0.1 µm DB17 (50% phenyl 50% methyl silicone)
Modulation frequency: 6
TOFMS Data acquisition rate:125 spectra/s
The Nist mass spectral library was used to enable identification.

Sequential GC-GC

Gas Chromatograph: 2 x Agilent 6890 GC – FID
Multicolumn switching: Gerstel MCS – dual oven set-up – cryofocusing
Column set:
Column 1: 50 m L x 0.25 mm I.D., 0.5 µm d_f PONA (100% methylsilicone)
Oven 1: 60°C/1 min – 3°C/min – 240°C – 20°C/min – 300°C/27 min
Column 2: 30 m L x 0.25 mm I.D., 0.5 µm d_f DBwax (polyethylene glycol)
Oven 2: 60°C/40.5 min – 4°C/min – 250°C/2 min
The second oven started after the cryofocusing, independent from the first oven
Sequential heart-cut: 25 heart-cuts (30 s)

Carrier gas: helium

Pre-column:constant pressure @ 270 kPa

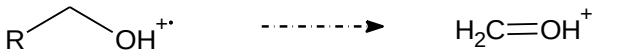
Detection: FID at 20 Hz, TOFMS at 20Hz

5.3. Results and discussion

5.3.1. ^{1}D GC-MS analysis

^{1}D GC analyses of the C_{12}/C_{13} detergent alcohols produce extensive co-elution of cyclic and non-cyclic alcohol components on non-polar GC columns. The boiling points of the components in this relatively narrow distillation cut are very similar and almost no separation of the cyclic from the non-cyclic alcohols occurs. For alcohols, a polyethylene glycol column is by far the best selection through specific hydrogen bridge interaction, but extensive co-elution still prevents identification and quantification. Fortunately, by applying mass spectrometric detection and operation either in the ion extraction or monitoring mode, specific ions can be selected to partly unravel the complexity.

For long chain alcohols, there are three important mass fragmentation types: loss of hydrogen, loss of water and hydrocarbon fragmentation [2]. The first process that an alcohol undergoes upon electron bombardment is the removal of one of the non-bonded electrons on the oxygen atom. The ion radical decomposes further, and one of the energetically most favoured paths is the α-cleavage to obtain a stable oxonium ion.



Alcohol Oxonium m/z = 31

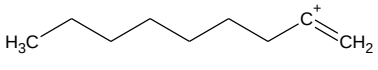
This oxonium ion is m/z 31 for primary alcohols.

Mass spectra of primary linear alcohols look very similar to those of alkenes. The molecular ion is seldom present and a M -18 fragment (loss of water) is observed but at a lower intensity than for the corresponding alkenes. This is illustrated in **Figure 5.1** showing the similarity of the mass spectra of 1-dodecene (C_{12} α-olefin) and 1-dodecanol (C_{12} linear alcohol, non-

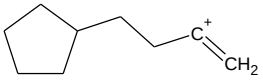
cyclic). The molecular masses of these components differ by 18 mass units. The main differences between the two spectra are the intensities of ion m/z 168 and the presence of the oxonium ion m/z 31 in the alcohol spectrum. In both spectra, the hydrocarbon homologous series ions are m/z 41, 55, 69, 83, 97, 111 and 125. As typical for linear chains, the intensities of these ions decrease in function of increasing mass. Mono-cyclic primary alcohols, on the other hand, should give an ion at m/z 31 and the homologous series – 2 amu. This is indeed the case as shown in Figure 5.1 for a C_{12} cyclic alcohol recorded during the analysis. Reason for this is that standards of the cyclic alcohols are not available and real sample analysis has to be used. Compared to the linear alcohol, the ions of the homologous series m/z 81, 95, 109, 123 are much more intense. This is important because mono-cyclic alcohols can be characterized through the general picture of the spectrum namely a Gaussian shape of the homologous ion series. The last spectrum in Figure 5.1 concerns a recorded bicyclic alcohol with carbon number 10. The last ion m/z 136 is (M-H_20) which corresponds, for comparison, with a m/z 164 ion for the C_{12} bicyclic molecule. This is – 4 amu compared to the linear ion and – 2 amu compared to the mono-cyclic ion. The expected homologous series should thus also be – 2 compared to the mono-cyclic alcohols. This is true as ion m/z 121 is the main ion. However, other homologous series ions are hardly detected because of the stability of the bi cyclic ion m/z 121.

Note that in the real recorded spectra in Figure 5.1, ion m/z 31 is highly intensive illustrating that the alcohols are primary in nature.

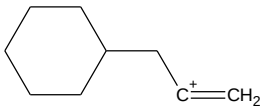
Several ions can be selected for differentiation of the alcohols but m/z 125 (because of its low intensity for the high concentrations of the linear alcohols in the sample), ion m/z 123 and ion m/z 121 are good selectors.



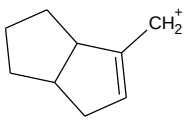
m / z = 125



m/z = 123



m/z = 123



m/z = 121

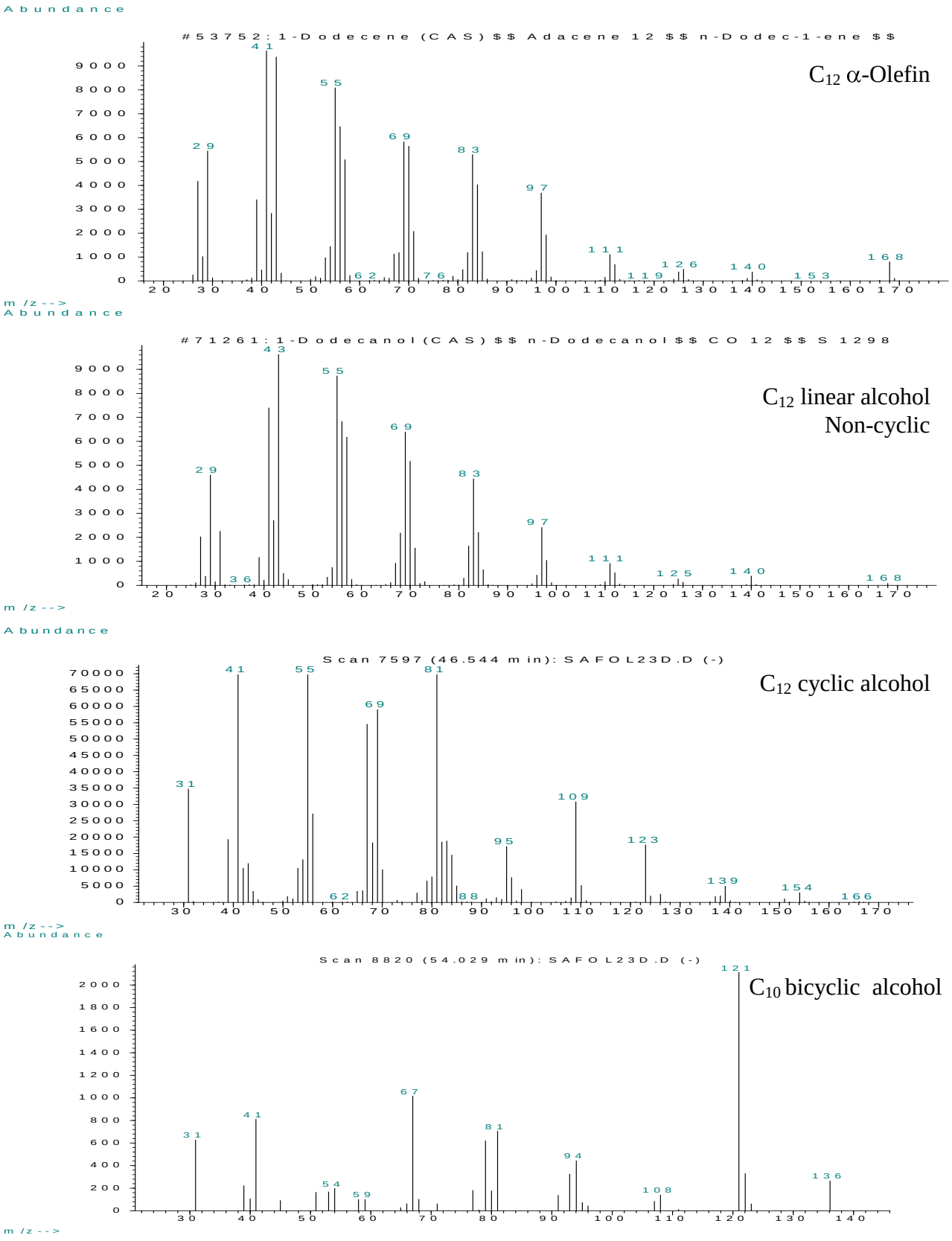


Figure 5.2. Mass spectra of 1-dodecene, 1-dodecanol, a C_{12} cyclic - and a C_{10} bicyclic alcohol

Figure 5.2 shows the extracted ion chromatograms of the C_{12}/C_{13} detergent alcohol sample. Extensive co-elution of the non-cyclic (m/z = 125) and the cyclic (m/z = 123) alcohols is noted while the bicyclic alcohols (m/z = 121) have a longer elution time. A rough idea on the complexity of the sample is obtained by single column GC-MS but quantification cannot be performed because of lack of an universal signal and/or standard compounds.

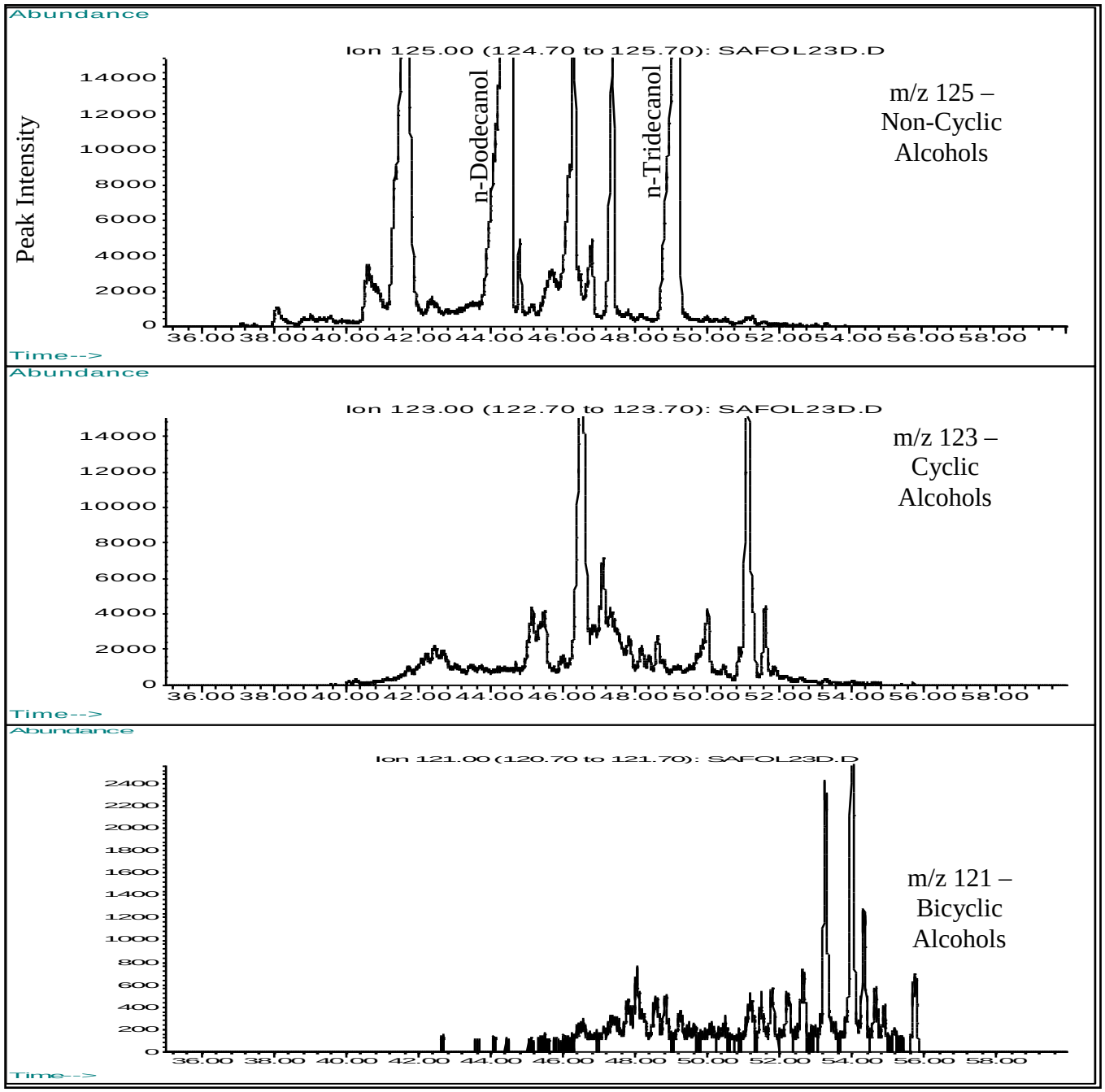


Figure 5.2. Extracted ion chromatograms of a C_{12}/C_{13} detergent alcohol product showing extensive peak co-elution

5.3.2 Comprehensive GCxGC

The chromatographic data obtained with the Leco instrument are shown in **Figure 5.3** (Contour plot) and **Figure 5.4** (surface plot).

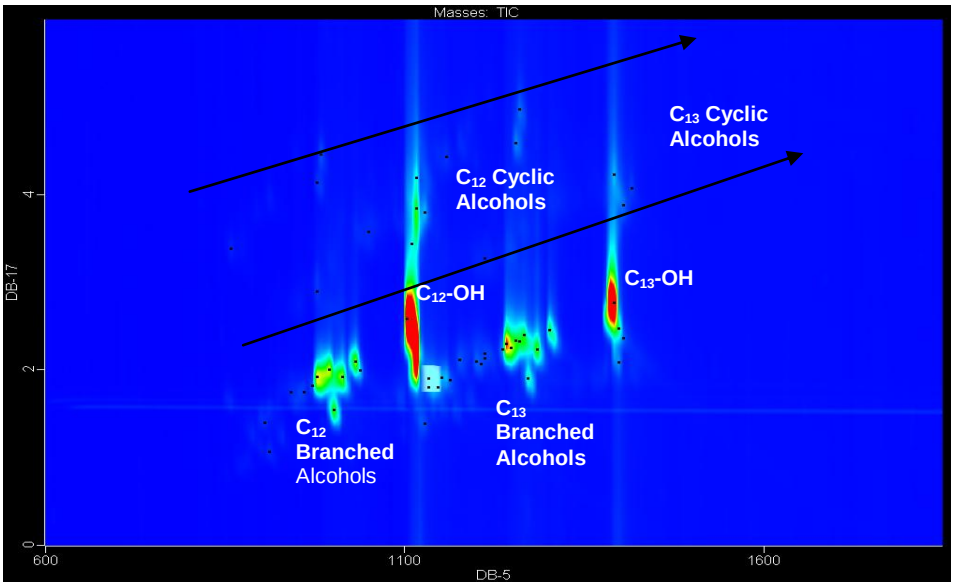


Figure 5.3. GCxGC-TOFMS contour plot indicating the separation of the cyclic alcohols from the non-cyclic alcohols

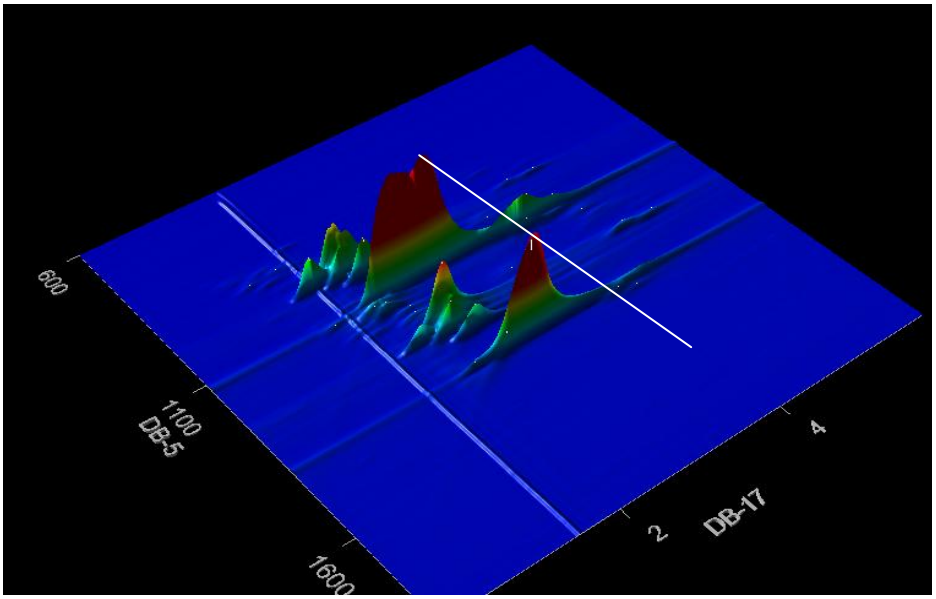


Figure 5.4. Comprehensive GCxGC-TOFMS surface plot providing a ^{3}D view of the separation of the cyclic from non-cyclic alcohols in the C_{12} – C_{13} alcohol sample

The data is a little bit disappointing because a DB-5 (5% phenyl methyl silicone) column was used in the first GC dimension and a DB-17 (50% phenyl 50% methyl silicone) column in the second dimension. Multidimensional GC techniques have increased peak capacities and resolution if columns of totally different selectivities or orthogonality are used in the separate GC dimensions [3]. This is not the case here. Nevertheless, the dots in the contour plot show the deconvoluted mass spectra indicating that at least 50 products could be elucidated.

Considering the interesting data obtained with sequential GC-GC in the previous chapter and the novel character of this technique, it was decided to tackle this problem immediately with sequential GC-GC rather than optimising the columns in comprehensive GCxGC.

5.3.3 Sequential GC-GC

Sequential GC-GC was performed on a 50 m PONA (dimethyl silicone) column as the pre-column and on a 30 m DBWax (polyethylene glycol) column in the second dimension. The first dimension columns separate the components mainly according to boiling point while the second dimension columns separate according to polarity. Orthogonality is hereby guaranteed.

For sequential GC-GC, the monitor FID chromatogram (first dimension separation, non-polar column) was divided into 30 s heart-cut time-windows. A fully automated sequence was programmed for repeated injections in the pre-column and heart-cutting, cold-trapping and analysis on the second main column. Twenty-six injections were done altogether and with each injection, a single heart-cut was analysed as described above. FID and TOFMS detectors were used to enable quantification and identification of the components. The data was processed and the two sets of retention times and peak areas were used to produce ^{3}D cone plots. **Figure 5.5** shows the 30 s divided FID chromatogram.

Data handling was done by putting the data in an Excel file, grouping similar peaks in the time-windows and making plots using in-house developed software based on Matlab 6.1.

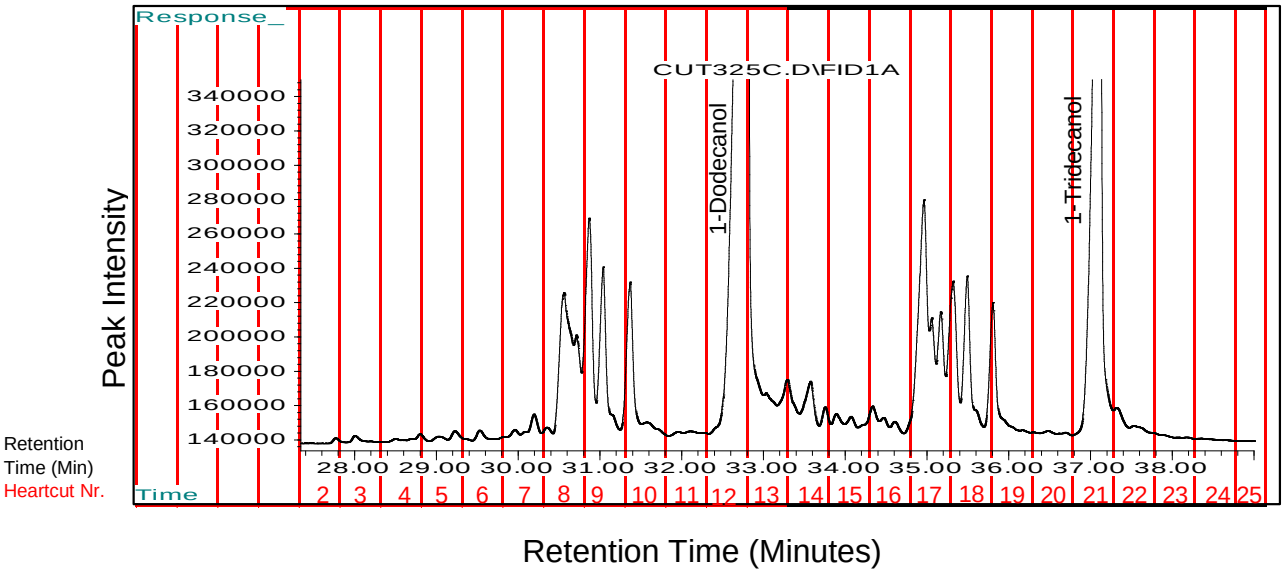


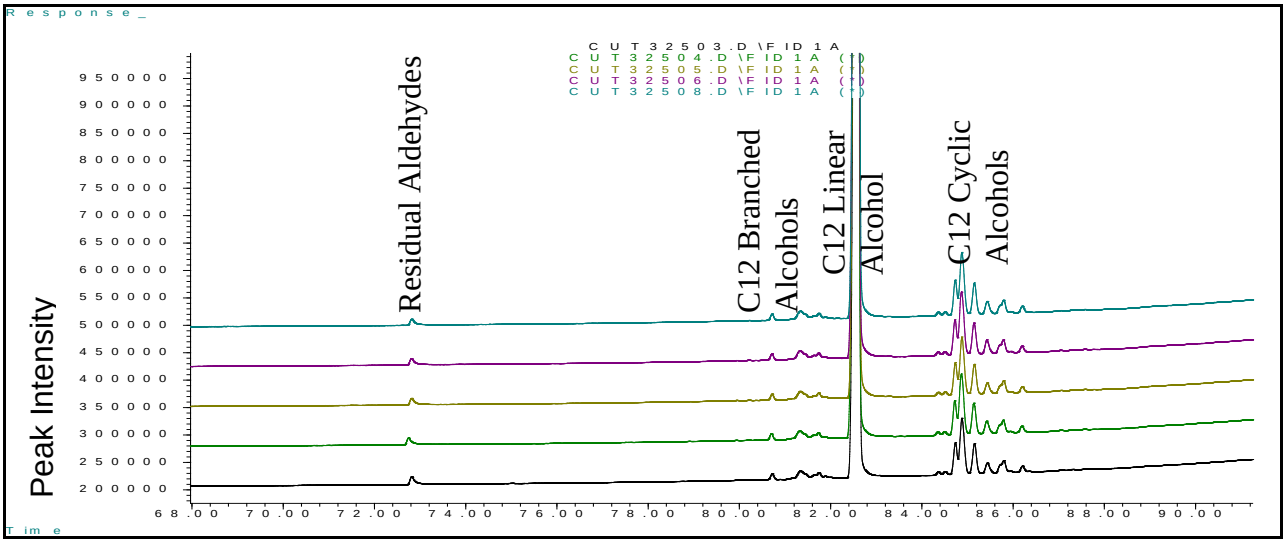
Figure 5.5. The ^{1}D monitor FID chromatogram divided into 30 s heart-cut time-windows

With sequential GC-GC more than 600 peaks were observed for this narrow distillation cut. Cyclic, bicyclic and non-cyclic alcohols were separated completely from each other. Traces of the aldehydes (hydroformylation intermediate products that did not hydrogenate fully to the alcohols) were observed as well. These components were not observed in either the ^{1}D GC-MS or the GCxGC-TOFMS analysis.

An important aspect of sequential GC-GC is repeatability of the heart-cuts. Nowadays with electronic pneumatic control and full automatic operation, this should be very good. Repeatability is illustrated in **Figure 5.6**, showing the FID chromatograms of five consecutive cuts of heart-cut 12. An average random uncertainty (deviation from the mean value) of less than 3 % was obtained for the main peak (C_{12} linear alcohol, 1-dodecanol).

In Figure 5.5, heart-cut 12 seems to be a very pure fraction consisting only of the C_{12} linear alcohol. Actually heart-cut 12 in the second dimension contains more than 15 peaks which, except for the linear alcohol and residual aldehyde, are mainly cyclic alcohols and some branched alcohols.

In sequential GC-GC, the second column can easily be coupled to an FID, a TOFMS or parallel FID/TOFMS via a T-split at the end of the second column.



Retention Time (Minutes)

Figure 5.6. Repeatability illustration of sequential GC-GC. Second dimension FID chromatograms of five repeated injections of heart-cut 12

This allows good quantification via the universal FID detector and excellent identification through TOFMS with its deconvolution capabilities. We have to note, however, that most of the iso-alcohols are not in MS libraries. Notwithstanding this, to which class compounds belong, can easily be elucidated.

Figure 5.7 shows the total ion chromatogram (TIC), attenuated 10 times, of heart-cut 12. Compared to Figure 5.6, qualitatively the profile is the same but peak intensities differ because of the ionisation and fragmentation process. Selecting fragment m/z 31 (the oxonium ion of primary alcohols) shows that all compounds, be they linear, branched, cyclic or bicyclic alcohols are primary alcohols ($R\text{-}CH_2\text{-}OH$).

Some representative mass spectra for heart-cut 12 obtained by TOFMS are shown in **Figure 5.8**. Presently not all compounds have been identified but important information to fine-tune the synthesis is already available.

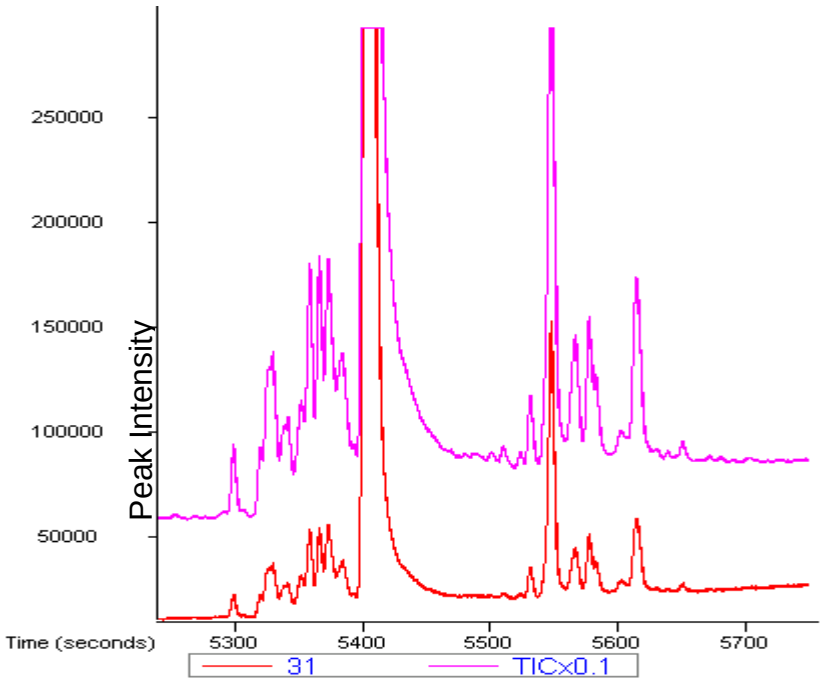


Figure 5.7. TOFMS total ion and extracted ion m/z 31 chromatograms of heart-cut 12

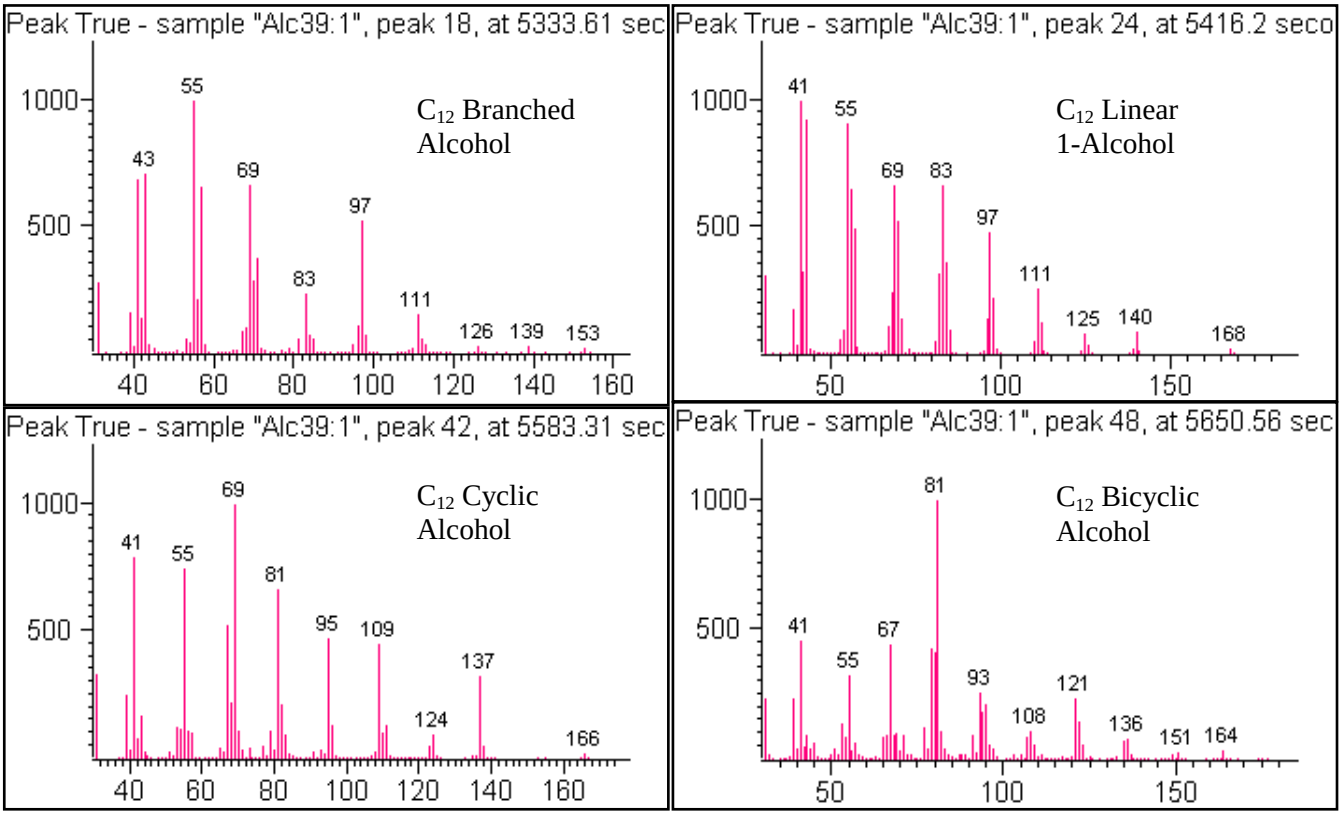


Figure 5.8. Some representative mass spectra of heart-cut 12

The sequential GC-GC-TOFMS approach also allows to "repeat" what has been done in ^{1}D-GC-MS. The separation of the chemical component classes of non-cyclic, cyclic and bicyclic alcohols, by selecting ions m/z 125, 123 and 121, is shown in **Figure 5.9** for heart-cuts 13 to 21.

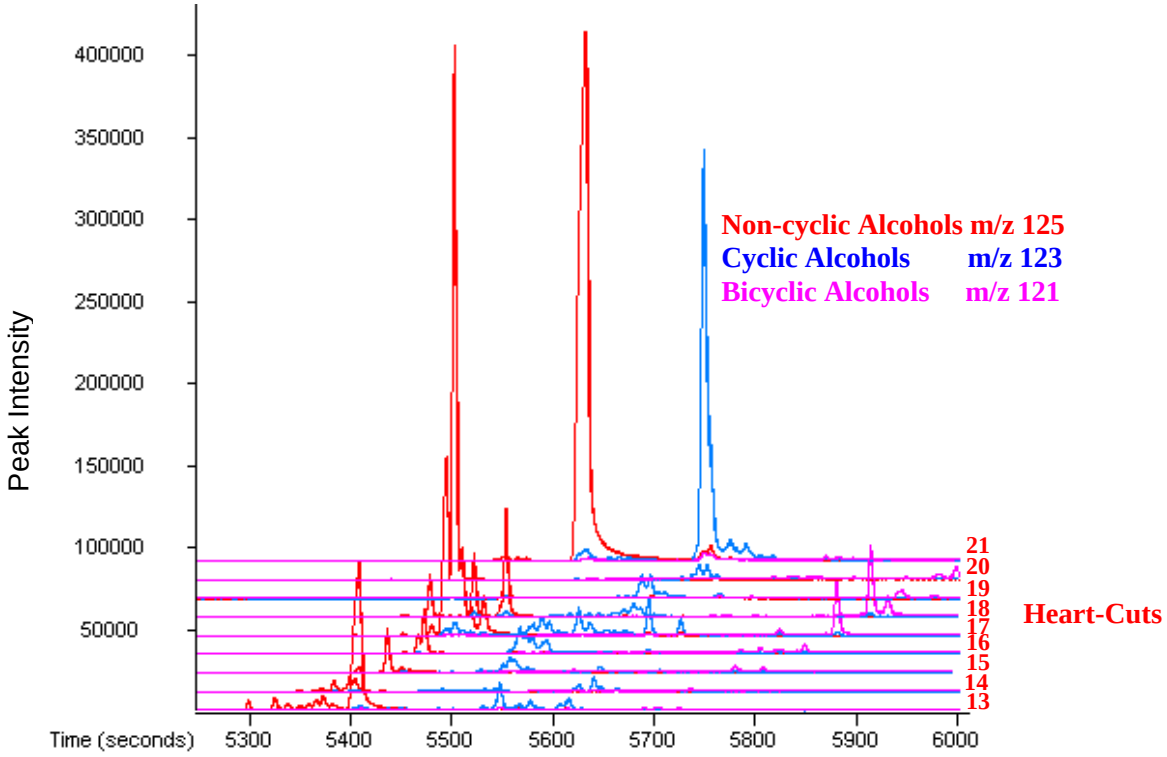


Figure 5.9. The m/z 125, 123 and 121 extracted ion chromatograms representing the non-cyclic, cyclic and bicyclic alcohols, respectively, in heart-cuts 13 to 21

Based on all the information obtained by sequential GC-GC and TOFMS, more than 600 peaks (products) were recorded.

Figure 5.10 shows a ^{3}D cone plot of the pre- and main column retention times, as well as the FID peak areas. The C_{12} and C_{13} linear alcohols are the two main peaks. The methyl- and higher degree of branched alcohols elute first, followed by the linear alcohol and lastly the cyclic and bicyclic alcohols. By zooming in and rotating the cone plot, Figure 5.10 results in **Figure 5.11** where the class separation of the aldehydes (unreacted feed product), the linear and branched alcohols, the cyclic alcohols and the bicyclic alcohols is indicated.

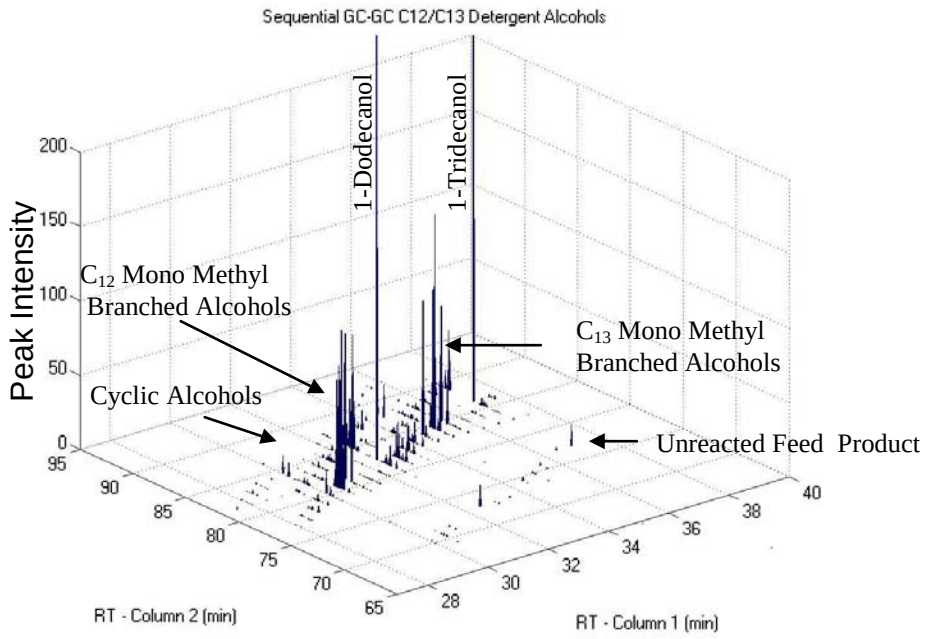


Figure 5.10. Sequential GC-GC ^{3}D plot of the C_{12}-C_{13} detergent alcohol product

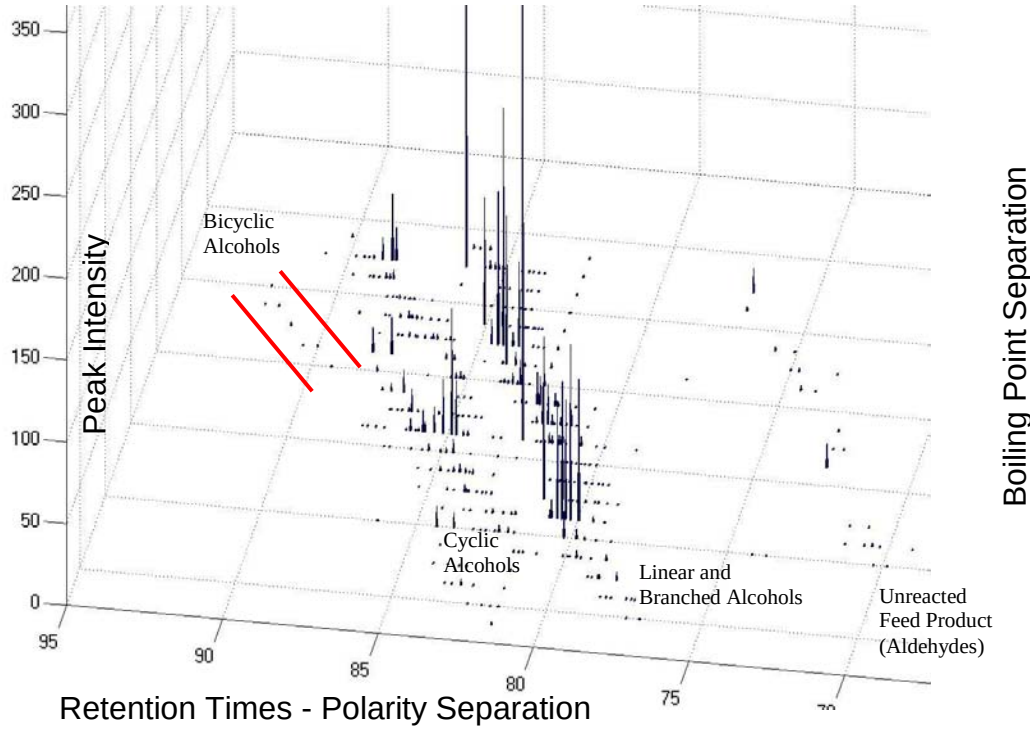


Figure 5.11. Sequential GC-GC ^{3}D cone plot illustrating the chemical class separation

5.4 Summary

For very complex mixtures like the C_{12}-C_{13} “detergent” alcohol product, normal GC analysis seldom provides the separation that is required. Hyphenation with MS definitely increases the quality of the obtained data but too much overlap hinders complete characterization of the sample.

Multidimensional GC techniques offer increased resolution and peak capacity if two correctly selected orthogonal columns are used.

The comprehensive GCxGC conditions used for this application are a good illustration of a wrong selection of the two dimensions. This is often the case in recent literature where the power of comprehensive GCxGC is illustrated with a bad selection of a ^{1}D GC analysis column. Nevertheless, separation of the cyclic from the noncyclic alcohols was noted albeit the resolution of the components within a group was not very high. Further work was not carried out considering the superior performance of sequential GC-GC.

Modern Sequential GC-GC uses fully automated methods and sequences for repeated injections in the pre-column and heart-cutting, trapping and analysis on the second main column. Repeated injections are necessary to analyse the complete sample in both dimensions. This makes the technique laborious but considering the wealth of information obtained, sequential GC-GC outperforms all other GC techniques. The complete separation of the chemical component classes as well as of the different isomers was represented in a ^{3}D surf plot. Moreover, by using FID and TOFMS, both quantitative and qualitative characterization are feasible.

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6. FINAL CONCLUSION AND FUTURE PERSPECTIVES

Petrochemical products are of the highest complexity of all products and there are strict specifications on the composition of most products in the chemical industry. Trace (from ppm to ppt) level components can poison catalysts in downstream processes or affect product performance. Trace components are often buried deep underneath the complex matrix and one only becomes aware of their existence when complaints are received of catalysts being poisoned or of products not conforming to product specifications.

A number of feedstocks for the production of detergents are obtained from petrochemical products. A “paraffinic” feed is dehydrogenated to olefins and reacted with benzene to produce linear alkylbenzenes. “Detergent” alcohols are produced by hydroformylation / reduction of olefins. The paraffins and olefins used in these processes are mostly obtained from narrow distillation cuts of petrochemical feedstocks originating from Fischer Tropsch technology.

Capillary gas chromatography is by far the best analytical technique to unravel the complexity of these feedstocks. The resolution power of a single column is, however, often too small for complete separation of all solutes and especially for elucidation of trace compounds in a complex matrix.

Multidimensional GC techniques provide unparalleled separation and identification power for the analysis of complex mixtures. The highly increased separation power, compared to ^{1}D GC analysis, is mainly due to the huge increase in selectivity and peak capacity that results from the use of two columns with different selectivities. The larger the difference between the two phases is, the higher is the orthogonality and thus peak capacity.

In this study heart-cut GC-GC, comprehensive GCxGC and the novel developed sequential GC-GC were evaluated for some very challenging applications.

Heart-cut GC-GC is a well-known technique often used for separation, enrichment and detailed analysis of selected fractions of a sample. It is not a comprehensive technique because only the selected heart-cut fraction is analysed on both highly efficient columns

and not the complete sample. For the analysis of ppb levels of oxygenates in a "Low Oxygenate Alkylation Feedstock", this technique provided excellent separation of the components classes of oxygenates and hydrocarbons (**Chapter 3**). Sufficient enrichment of the oxygenate fraction was obtained by multi-injections and multi-heart-cutting / cryofocusing to reach those low levels. Trace components could be identified by MS and are presently investigated as "possible catalytic poisons".

Comprehensive GCxGC provides separation and analysis of the entire sample on both GC columns with a single injection. The first column is a high-resolution capillary column that typically contains a stationary phase that separates components according to boiling point. The temperature program is normally slow and in the order of 1 – 4 °C.min^{-1}. The modulator is operated at a fixed frequency to deliver several slices of each ^{1}D peak to the ^{2}D column. Each fraction is re-focussed before injection on the ^{2}D column. The latter column is a very short and narrow column with a thin layer of stationary phase to provide ultra fast separation in a few seconds. It is normally run under isothermal conditions. The ^{2}D column is chosen to be of opposite selectivity compared to the ^{1}D column and separation normally is based on polarity or size. The fast separation on the second column results in very narrow peak widths in the order of 100 – 600 ms and, because mass is conserved, increased peak heights. Few detectors (FID, TOFMS) have sufficiently high scanning and recording rates to detect these very narrow peaks. Comprehensive GCxGC provides excellent separation of components classes in complex mixtures as illustrated in this work for the analyses of oxygenates in a C_{10}-C_{13} alkylation feedstock (**Chapter 4**) and of cyclic and bicyclic alcohols in C_{12}-C_{13} "detergent" alcohols (**Chapter 5**).

The same samples were analysed by sequential GC-GC, a novel technique lying in between heart-cut GC-GC and comprehensive GCxGC. The technique provides separation and analysis of the entire sample on two GC columns but with multiple injections. Both columns as well as experimental conditions like temperature and flow are chosen to provide optimal separation power in both dimensions. The multiple injections are automated by programming a sequence of methods that run continuously. Even though quite a lot of instrument time (it could take days to run a long sequence) is used with this technique, the hands-on time is low. No intervention is necessary while the

sequence is running. Sequential GC-GC provides better separation of components on the second dimension column than GCxGC because the column dimensions, gas flow rates and temperature programs are optimised. Sufficient analysis time is available for the ^{2}D analysis in contrast with GCxGC where the time is limited by the frequency of the modulation. The analysis by sequential GC-GC of cyclic, bicyclic and non-cyclic alcohols in C_{10} – C_{13} detergent alcohol products provided a wealth of information that could not be obtained with the other multidimensional techniques (Chapter 5). As both FID and TOFMS detectors can be applied (also in parallel) the qualitative and quantitative information is unique.

The three multidimensional GC techniques, discussed in this study, are definitely very valuable tools for the analysis of highly complex mixtures. Each technique has its own specific applications and advantages and should therefore be regarded as "complementary" rather than as "competitive" tools.

Heart-cut GC-GC and comprehensive GCxGC are ready to be implemented, in the near future, in petroleum QA-QC laboratories. Sequential GC-GC, on the other hand, still has to mature in R&D laboratories. However, developments are going very fast and a prototype to speed up sequential GC-GC has already been constructed in the laboratories of Prof. Sandra (Research Institute for Chromatography, Kortrijk, Belgium).

By using modulator accelerated column heater (MACH) systems, allowing heating-up rates of 1000°C/min and cooling-down in a few seconds and containing 10 m L x 0.1 mm i.d. columns, the analysis on the second column can be reduced to 1 min but still with 100.000 plates (**Figure 6.1**). By using two such columns and a pressure balanced system, each cut can be analysed in time with the first dimension selected time window (**Figure 6.2**).

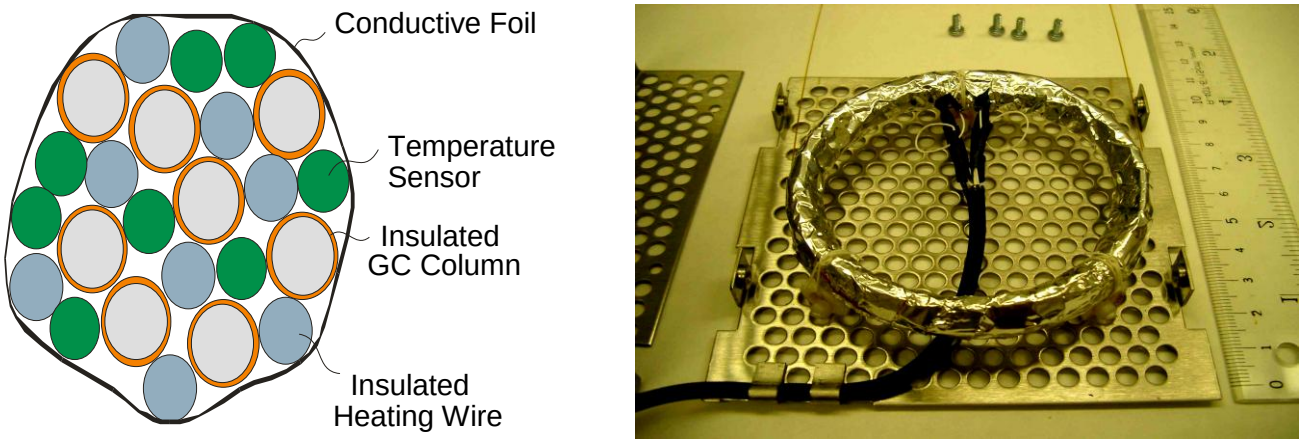

Figure 6.1. Construction of a MACH column

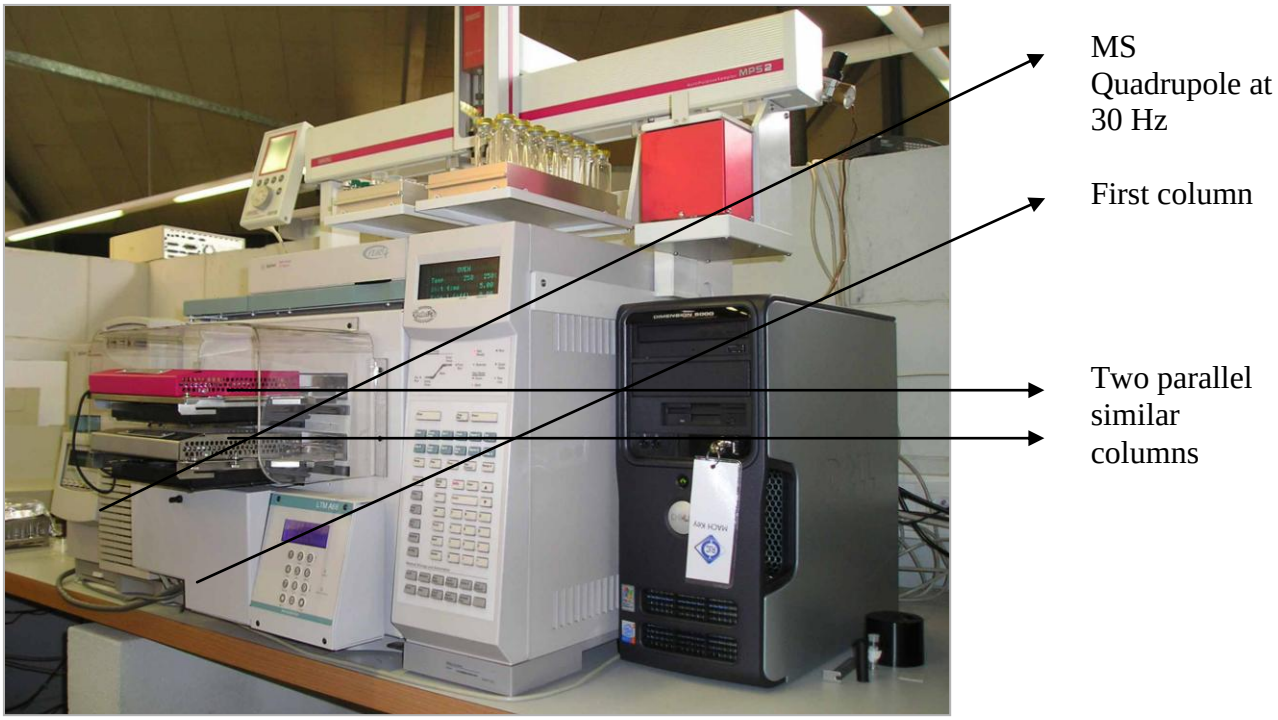

Figure 6.2. Set-up of sequential GC-GC with two parallel high speed columns