

# Chapter 8

## The modulator:

### Design, construction and characterization

#### 8.1 Introduction

In normal GCxGC operation, an apolar column is used as the first separation step. Normally with GCxGC, both columns and the modulator are in the same oven, heated at the same rate. Boiling point separation is achieved as the oven temperature is ramped. Segments refocused from the first column contain compounds with very similar boiling points. A polar column is used as the second dimension but since analytes are of similar boiling point, separation takes place mainly due to differences in polarity. A small peak capacity is required for the relatively simple mixtures transferred to the second column.

With the proposed SFCxGC<sub>fp</sub> the polar separation precedes the boiling point separation. The modulator transfers groups of similar polarity but varying widely in boiling point to a second column. The temperature of the second column is subjected to a very fast ramp to effect the boiling point separation. Thus the modulator also needs to be able to handle a wide boiling point range. Peaks eluting from the SFC are much wider than those from capillary GC and this provides some relief as far as the modulation frequency is concerned relative to other systems. More time is allowed for the second separation, however a large peak capacity is required in the second column to elucidate all components. The

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modulator is in a different thermal zone from the two columns. The SFC is operated isothermally at 28°C and the GC is typically ramped from -50°C to 300°C and back down to starting temperature after each cycle.

A phase change from dense fluid in the supercritical fluid to the gaseous phase has to take place in the modulator. This is brought about by the restrictor that maintains high upstream pressure throughout the SFC column. Upon decompression after the restrictor, sample components fall out of solution and are collected inside the modulator through a reduction in pressure.

A large amount of gaseous CO<sub>2</sub> is produced when the fluid decompresses at the restrictor. As demonstrated in Chapter 3, CO<sub>2</sub> is unsuitable for fast GC operation. Thus, the modulator also needs to replace the CO<sub>2</sub> gas with a faster carrier gas, like H<sub>2</sub>.

With GCxGC the second dimension is isothermal for each subsequent transfer. Hence, very narrow input bandwidths are required for each cut transferred to the second dimension. The injection bandwidth is less critical for SFCxGC<sub>ftp</sub> because additional focusing is achieved before temperature programming of the GC column. Compounds are refocused on the GC column at the low starting temperature.

## **8.2 Suggested modulator designs**

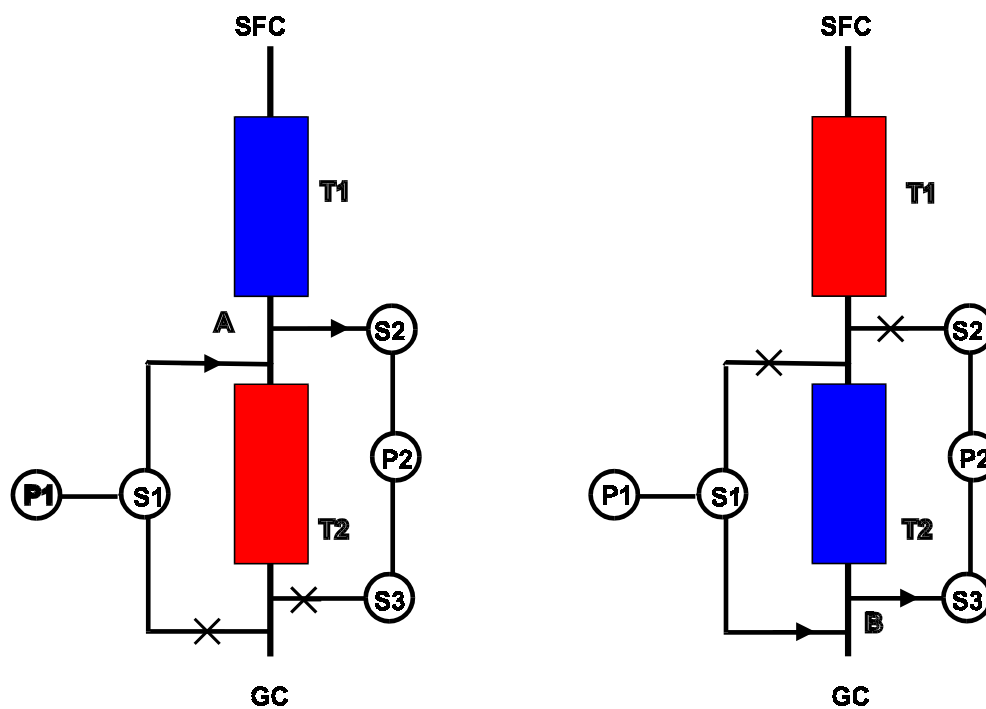
Modulators can arbitrarily be divided in two classes: Continuous and stop-flow modulators. The operation of two potential continuous flow-modulators and a stopped flow version are described in this section.

### 8.2.1 Two-stage continuous modulator with pressure modulation

This modulator design requires the use of two Deans switches (also called ‘live switching’ or valve-less switching’) connected in series. The device is schematically presented and the operation described in Figure 8-1.

The design illustrated in Figure 8-1 employs two areas that can be heated and cooled down sequentially. During one phase the area directly following the restrictor exit from the SFC T1 will be cold. During this phase, solenoid valve S2 is open and solenoid S1 directs hydrogen from P1 to position A. CO<sub>2</sub> from the SFC escapes through pressure relief valve P2 because of the directing effect at A by the slightly higher pressure provided by S1 while analytes are trapped by the cold zone. Analytes focused in T2 during a previous modulation cycle are desorbed into the GC by hydrogen flow from position A.

Figure 8-1: Gas exchange by Live Switching (Deans principle)



In the second phase T2 is cooled down. When T2 is cold T1 is instantaneously heated to desorption temperature while S2 is closed and S3 is opened. S1 directs hydrogen to position B and CO<sub>2</sub> from the SFC transfer trapped analytes in T1 to T2. The CO<sub>2</sub> then escapes through P2 because of the directing effect of the slightly higher pressure provided by S1 while the analytes are retained by T2. Alternatively modulation could also be effected with a single thermal zone and one valve-less pressure-switching step by leaving out T<sub>1</sub> in Figure 8-1. This is made possible by the focusing effect of the GC column at its low starting temperature. Operation is similar to that described above but with a single thermal zone. With reference to Figure 7-3, the skewed band of the single stage modulation will be refocused by low starting temperature of the GC column.

### **8.2.2 Stopped flow pressure modulation**

The SFC analysis was allowed to progress, typically for 5seconds, where after the flow was stopped by a high pressure, low volume valve placed between the SFC column and restrictor. The SFC restrictor pierced through the septum of a split/splitless injector and the eluent was focussed on the head of the 2<sup>nd</sup> dimension column at the sub-ambient GC starting temperature. The split valve was closed during the 5-second collection time of SFC eluent. This allowed total transfer of sample components. Prior to the GC analysis the split valve was opened to relieve the CO<sub>2</sub> pressure that built up in the injector and 2<sup>nd</sup> dimension column due to the expanding SFC mobile phase. This facilitated the exchange of CO<sub>2</sub> with H<sub>2</sub>. After concentration of analytes on the GC column, a five-second equilibration time was allowed for the pressure in the injector to normalize to the H<sub>2</sub> carrier head pressure setting of the GC.

The stopped flow modulator was built and used for all the SFCxGC<sub>ftp</sub> experiments presented in this thesis.

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## 8.3 Experimental

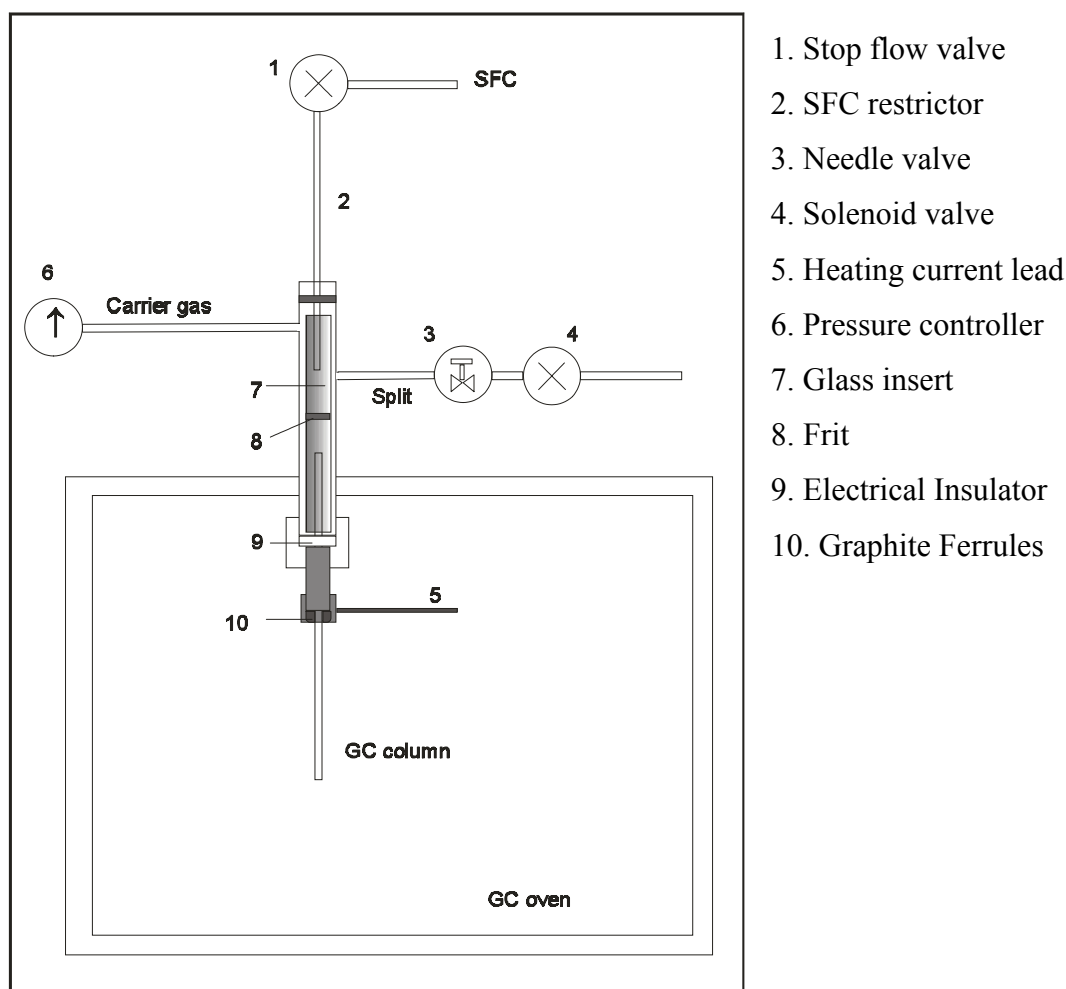
### 8.3.1 Hardware design

The SFC analysis was allowed to progress, typically for 5 seconds, where after the flow was stopped by actuating a six port valve (CW6-K, Vici, Switzerland) with all but two adjacent ports closed off. A simpler low dead volume valve would suffice. Valve switching was controlled with a TTL pulse from a multipurpose input/output board (PCI 6024E, National Instruments, Texas, USA). The valve was placed in between the splitter-restrictor assembly and the SFC column outlet (see Figure 8-2). The eluent was transferred to a split/splitless injector on the Varian 3300 through one of the SFC restrictors and focused on the head of the 2<sup>nd</sup> dimension column. The split valve was closed during the 5-second collection time of SFC eluent. The eluent cut was focused on the head of the capillary column at the sub ambient GC starting temperature. Prior to the GC analysis the split valve was opened to relieve the CO<sub>2</sub> pressure that builds up in the transfer interface and 2<sup>nd</sup> dimension column due to the expanded SFC mobile phase. The injector splitter was opened and closed with a solenoid valve controlled by TTL pulse from the computer. The entire column was cooled down to the ramp starting temperature with liquid CO<sub>2</sub> using the conventional sub-ambient temperature control of the Varian 3300. This allowed the oven fan and cryogenics to be switched on during sample collection and automatically switched off for the duration of the resistive GC analysis phase. External oven control was achieved through a small modification on the temperature control board of the GC as described in Chapter 4. After concentration of analytes on the GC column, a five-second-equilibration time was allowed for the pressure in the injector to normalize.

### 8.3.2 Demonstration of the interface

A packed silica gel column, similar to the one described in Chapter 4, was connected before the modulator. A standard solution, simulating a petrol sample, was injected. This solution contained the aliphatic group represented by the n-alkanes from octane to hexadecane, the mono-aromatic group represented by benzene, toluene and the chrysenes, and di-aromatics represented by naphthalene and methyl-naphthalene. Chromatograms of unmodulated and modulated runs were collected from the second FID. The comprehensive SFCxGC<sub>ftp</sub> chromatogram for this standard obtained after modulation and GC separation is presented in the next chapter.

**Figure 8-2: Schematic diagram of stop flow modulator.**



## **8.4 Results and Discussion**

### **8.4.1 Number of modulation stages**

The stop flow modulator is a two-stage modulator. The stop flow valve represents the first stage and prevents the elution of more sample components while the second dimension analyzes the previous fraction. Focussing is achieved by the second stage and this occurs due to the sudden pressure drop after the restrictor with concurrent loss in solvent strength of the SFC mobile phase. This is augmented by stationary phase focusing at the low starting point of the GC temperature program.

### **8.4.2 Run time of the modulated 1<sup>st</sup> dimension chromatogram**

For packed column separation, as described in Chapter 6, an unmodulated runtime of 20 minutes was normal. The first eluting SFC peaks were typically 1 minute wide. To obtain 10 samples per peak, a 6 seconds modulation time was required. A typical GC cycle time of 1 minute and a collection time of 5 seconds increased the runtime to 200 minutes. This number of cuts was adequate to conserve the information contained in the first chromatogram and allowed for reconstruction of the SFC chromatogram from GC data points. At a fixed frequency of sampling, determined by the GC cycle time, the longer the sampling time, the faster the average SFC mobile phase flow rate. This lead to narrower SFC peaks and shorter analysis times. The GC cycle time is the sum of the sampling and equilibration times, the duration of temperature ramp and the GC column cool down time. The ramp time of the fast GC was optimized in Chapter 4. A further increase in peak capacity production per unit time with the current fast GC design is impossible without reducing the column diameter. However, metal columns with smaller internal diameters are not currently available.

The GC cool down time was facilitated by the host oven fan together with active cryogenic cooling with liquid CO<sub>2</sub>. The capillary column typically cooled down to -50°C from 300°C in 25 seconds.

#### **8.4.3 The influence of modulation on SFC flow rates**

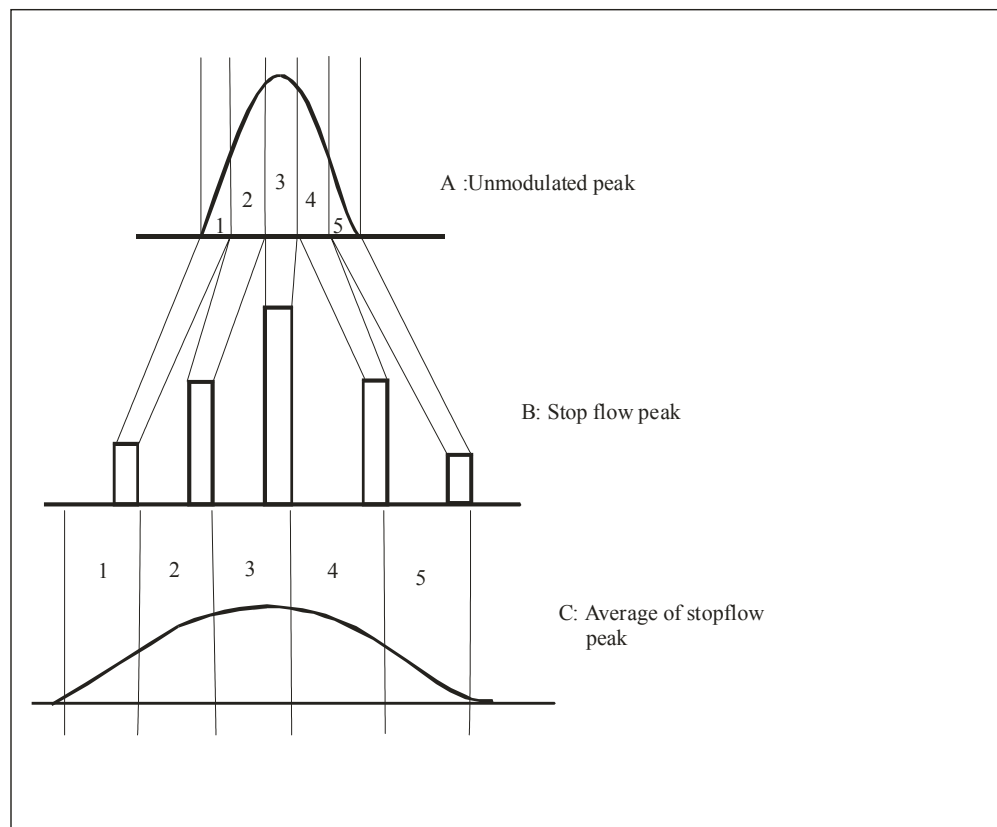
For stopped flow operation the linear flow rate in the SFC column was cycled between a fast value, maintained for 5 seconds and a no-flow period of up to one minute. A new 'virtual peak' can be calculated for the SFC analysis that is the average of the no-flow and the flow conditions. This is represented by peak C in Figure 8-3.

Chromatogram C is the peak that will be obtained by an instrument that uses continuous operation when a flow rate is chosen to produce a chromatogram of similar duration. The SFC flow rate for continuous operation can be adjusted, through use of the appropriate restrictor size, to be the same as the calculated average flow, obtained with repetitive stopped flow operation. This will produce the same runtime of 200 minutes and provide enough analysis time for the GC separation. The slower continuous flow rate will have a beneficial effect on the resolution when compared to stopped-flow operation. This can be explained at the hand of the Van Deemter equation:

The B term that describes longitudinal diffusion is the same for stopped flow and continuous operation because the total analysis times are of the same duration. The C-term decreases in direct proportion to the flow rate and will always produce a smaller plate height when a slower flow rate is used. With stopped flow operation, to achieve the average flow rate, the flow rate has to be faster when flow is allowed to compensate for the no-flow interval. Hence, flow rates are above optimum when the average flow rate is at the optimum. With continuous operation, a continual slower flow rate (equal to the average) is prevalent and can thus be chosen nearer to the optimum.

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**Figure 8-3: Unmodulated, stopped flow and the virtual peaks.**

#### 8.4.4 Advantages to the stopped flow interface

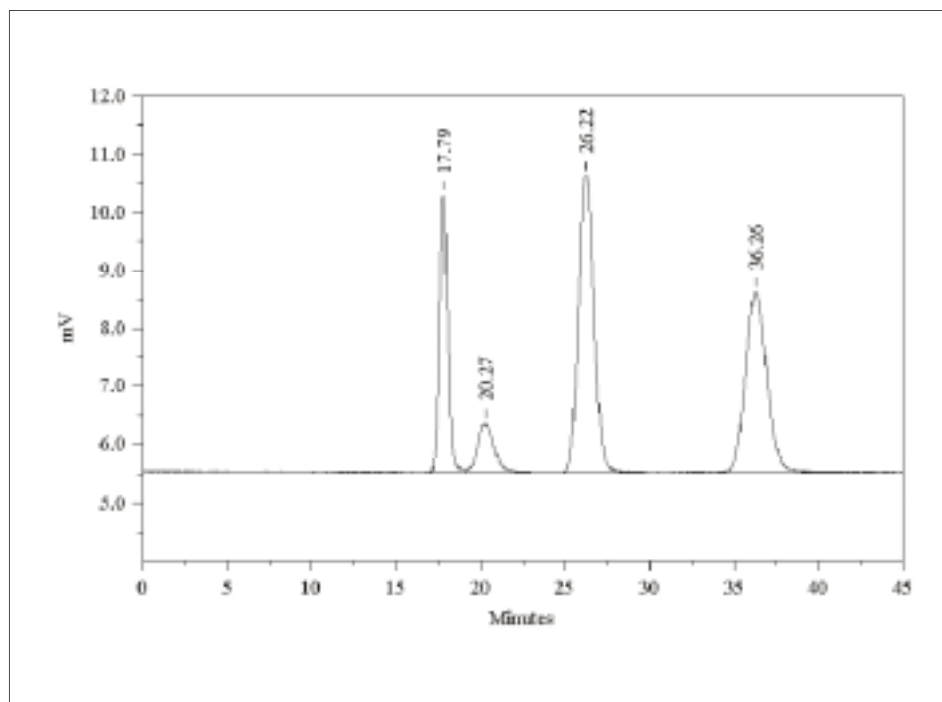
The use of a stop flow valve instead of continuous operation eliminates the need for thermal modulation in the interface. This simplifies construction and control. Removal of the excess CO<sub>2</sub> gas that forms when the SFC mobile phase decompresses is aided by separating the collection and second dimension analysis events. Also, the use of valve-less Dean's switches with a continuous interface requires cumbersome fine-tuning of the relative pressures for proper operation. This is not required for stopped flow operation. The stop flow valve also provides adequate and flexible separation space (time) for the second dimension to achieve high enough peak capacity and to satisfactorily elucidate the wide boiling point distribution of each cut.

Continuous operation will require that cut fractions be held in the thermal trap for up to a minute and may require unattainably effective trapping to prevent breakthrough.

#### 8.4.5 Influence of stopped-flow modulation on the SFC chromatogram

**Figure 8-4: Unmodulated SFC chromatogram.**

Conditoins: Pressure=150 atm; Temperature= 28°C; Flow rate=120 ml/min

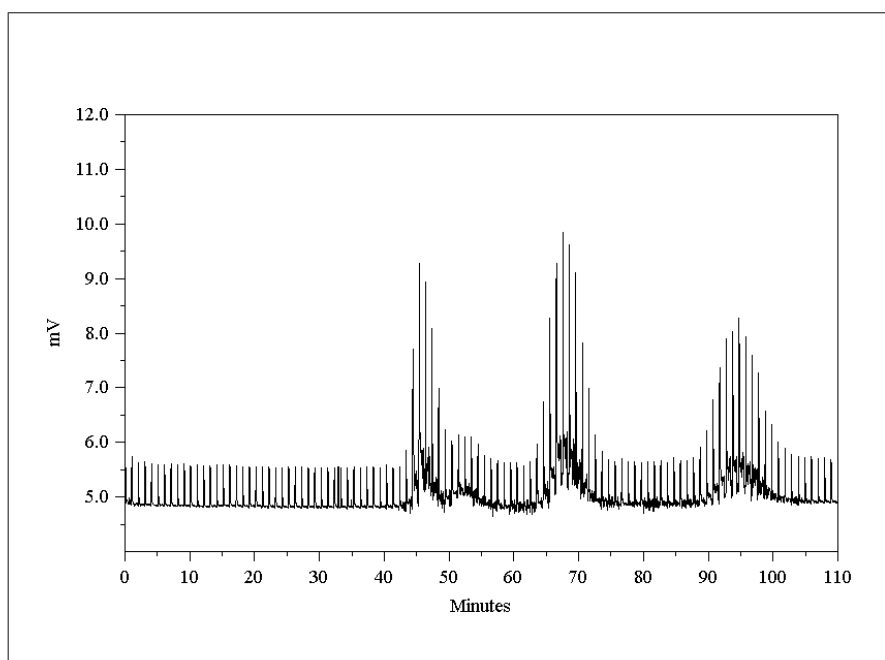


The peak capacity of comprehensive multidimensional techniques approaches the product of the individual peak capacities of the two separations<sup>1</sup>. When calculating the peak capacity of the total system the unmodulated peak capacity of the 1<sup>st</sup> dimension is no longer a true reflection of the attained peak capacity after modulation. With the stop flow conditions used for flow modulation, the peak capacity of the SFC separation is equal to the peak capacity of the 'new' chromatogram that is obtained after the average of flow and no-flow conditions have been obtained. Figure 8-4 shows an unmodulated chromatogram of the SFC separation. The peak capacity of the unmodulated chromatogram is  $n_c=12$ . Figure

8-5 shows the modulated chromatogram. The peak capacity of this chromatogram is reduced to  $n_c = 8$ . This is probably due to the increased residence time of the sample in the column leading to more longitudinal diffusion (B-term) and thus an increased plate height. In this case, faster restrictors were used for the modulated chromatogram. This may also adversely affect the Van Deemter C-term. However, the faster flow rate for the modulated chromatogram reduced the run time to 100 minutes, while still allowing ample samples across the SFC peak.

**Figure 8-5: Modulated SFC chromatogram.**

5 second collection time. GC cycle time: 60 seconds.



#### 8.4.6 Modulation programming

In SFC, pressure programming is often used to solve *the general elution problem* in the same way as temperature programming does for GC. Sometimes this can not be done due to factors such as the mechanical strength of the column walls in capillary SFC or when pressure-programming facilities are not available. It should

in principle be possible to combat the general elution problem with *programmed modulation*, which would be equivalent to flow programming. Here the collection time is increased from cut to cut in proportion to the peak broadening. The number of cuts per peak can be kept constant at the 6 required to recreate the first dimension chromatogram from the GC data points. A programmed effect will be obtained in the resultant three-dimensional chromatogram leading to savings in SFCxGC<sub>ftp</sub> analysis time and improved detection limits.

## 8.5 Conclusions

A modulator was constructed that uses stopped flow and pressure drop modulation to transfer cuts from the SFC to a fast temperature programmed GC for volatility analysis. The modulator also allows for the exchange of CO<sub>2</sub> with H<sub>2</sub> carrier gas for a more efficient high speed GC separation.

The modulator provides for easy and flexible interfacing between the two dimensions of the SFCxGC<sub>ftp</sub>. It is robust, as it does not require the use of thermal zones or moving parts other than the valve internals at room temperature.

The Peak capacity of the SFC analysis is slightly decreased by stopped flow operation. A peak capacity of 8 was achieved after stop flow modulation with the packed column. Together with the peak capacity of 60 for the GC<sub>ftp</sub> a total peak capacity for the of 500 can be projected for the SFCxGC<sub>ftp</sub>.

However, more than 220 000 theoretical plates have been reported for SFC separations when 11 SFC columns were connected in series and used together with methanol modifier<sup>1</sup>.

Thus, the peak capacity of SFCxGC<sub>ftp</sub> could approach that of GCxGC.

## Chapter 8

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<sup>1</sup> T.A.Berger, W.H.Wilson, Anal.Chem. 65 (1993) p1451

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