
Chapter 10

Conclusions

A comprehensive two-dimensional supercritical fluid and fast temperature programmed gas chromatograph has been constructed. The chromatograms produced by the SFCxGC_{ftp} are comparable to that produced by GCxGC. However, less peak capacity can be produced than with GCxGC. On the other hand, more orthogonal separations are possible with SFCxGC_{ftp} because of the stronger group selectivity provided by SFC on silica gel.

In order to design and construct the SFCxGC_{ftp}, a fast resistive temperature programmed GC was developed. Further, group separation by SFC on silica gel was extended to include the class analysis of highly polar groups.

10.1 Group separation with SFC as a first separation dimension

It was demonstrated that the retention of highly polar compounds on silica gel columns could be much reduced by increasing the phase ratio (β -factor) of the column. Even alcohols and organic acids could be eluted from a silica gel PLOT column. Compounds of the same chemical class eluted together in a group and the co-elution between oxygenated and non-polar molecules were precluded. A competitive method for the analysis of oxygenates in petrochemical samples are provided when compared to other known procedures^{1,2}.

In supercritical fluids, the optimum flow rate (for maximum resolution) brings about very long retention times on account of slow mass transfer. However, because of excess resolution, flow

¹ *Annual Book of ASTM standards*, ASTM D4815-94a Volume 05.02 (1997)

² *Annual Book of ASTM standards*, ASTM D5599-95 Volume 05.02 (1997)

rates much above the optimum provided adequate separation of all groups in acceptable analysis times. This was true even for samples with wide boiling point ranges.

10.2 Fast resistive heating for boiling point distribution in SFCxGC_{ftp}

Various temperature measurement circuits were built and considered for use in fast gas chromatography. These generally operated reasonably well when no heating current was applied. However, when simultaneous heating and measurement was attempted many problems were encountered. The use of a micro thermocouple was successful for the measurement of temperatures during column heating. Micro-thermocouples were manufactured in-house and glued to the column using polyimide resin. Thermocouples provided reproducible results within a thermocouple placement. Unfortunately, thermocouples were found to be fragile and required frequent replacement. Different thermocouple placements influenced the thermocouple readings. Retention times of low boiling compounds compared well with those obtained from a conventional heated GC. However, at higher temperatures compounds tended to elute earlier on the resistive GC. This was due to the distance between the thermocouple and the column caused by the insulating glue.

The temperature programming rate was optimized to provide the highest peak capacity in the shortest time. This was obtained by maintaining a normalized ramp rate of 10°C/tm and changing flow rates and actual ramp rates. The highest peak capacity was obtained at a ramp rate of 450°C/min with a flow rate of 100 cm/sec. Under these conditions the 1 meter column delivered a peak capacity of n=60 in less than 30 seconds.

The influence of CO₂ as potential mobile phase for fast resistive GC was investigated. This was relevant due to the large amount of CO₂ gas produced when the SFC mobile decompresses at the restrictor. While the loss in efficiency can be recovered by decreasing the column diameter, best results will be obtained when H₂ together with a column with a small inner diameter is used.

10.3 The stopped flow pressure drop modulation interface

A novel interface was created to accomplish the comprehensive combination of SFC and temperature programmed GC. This interface uses stopped flow chromatography in the SFC separation axis. Stopped flow modulation caused a mild loss in peak capacity of the polar separation. However, adequate resolution between the studied groups was still obtained. Compounds eluting from the SFC were focussed in the interface due to loss of solvation when the supercritical mobile phase decompresses at the restrictor exit. This was augmented by the low starting temperature of the GC. The interface also allows for the exchange of carrier gas, providing the optimum separation speed during the GC separation. This interface is the subject of a provisional patent³.

10.4 Advantages to SFCxGC_{ftp}

There are numerous advantages to the technique relative to other multidimensional techniques. These are due to a low temperature 1st dimension, together with independent fast temperature programming in the 2nd dimension, exchange of the chemical composition of the mobile phase and de-coupling of the operating conditions of the two dimensions by connection through stop-flow modulation. Briefly the advantages are:

- A. Independent fast temperature programming in the 2nd dimension with a low temperature 1st dimension provides:**
1. Less correlation between the separation mechanisms of the 1st and 2nd dimensions. The two dimensions of the new SFCxGC apparatus is thus said to be potentially more orthogonal than GCxGC or existing SFCxGC instrumentation.
 2. Low temperature operation of the SFC dimension increases selectivity to chemical differences in sample components such as polarity, chirality or molecular shape, given a suitable stationary phase.
 3. Less critical injection times into the second 2nd dimension than for GCxGC or existing SFCxGC instrumentation. Temperature modulation in the SFCxGC interface is not

³ A.Venter, E.R.Rohwer, Chemical method of analysis, Patent number: SA2002/202

Assignee: University of Pretoria, March 2002,

required due to the focussing effect on the low temperature of the 2nd dimension column.

4. Efficient separation of volatile organic modifiers from analytes allowing the use of FID and Mass Spectrometric detection, despite the presence of modifiers in the 1st dimension mobile phase.
5. With this invention only the polydimethylsiloxane stationary phases, that can withstand high temperatures, are heated. The polar analysis is achieved at room temperature and does not rely on using polar phases such as the thermo labile polyethyleneglycol at elevated temperatures. This implies that samples with higher final boiling points can be analysed than with GCxGC instrumentation.
6. Thermally labile compounds are at high temperatures for a much shorter time and are therefore less likely to decompose than with GCxGC or existing SFCxGC instrumentation where both columns are operated at high oven temperatures for a prolonged time. This comprehensive combination of SFC and GC thus expands the scope of compounds to be analysed to include less stable ones.

B. Stop-Flow modulation

1. Provides flexibility in the operational parameters of each dimension allowing these to be optimised independently
2. A slower 2nd dimension allows easier interfacing with conventional Mass Spectrometry than GCxGC or existing SFCxGC instrumentation. GC peak widths are typically 40 to 500 ms wide.
3. Eliminates the need for complex thermal modulation of the interface.

C. Change in mobile phase composition

1. Allows the use of 1st dimension mobile phase that is incompatible with, or interferes strongly with detection in the 2nd dimension. Organic mobile phases or CO₂ with organic modifiers can be used with FID or MS detection.
2. Allows higher speed 2nd dimension separations thus improving total analysis time by reducing the 2nd dimension cycle time. This cycle is repeated many times during an analysis and thus contributes additively to the total run time.
3. Faster 2nd dimension analysis further implies that the 1st dimension can be run faster while still transferring ample cuts to the 2nd dimension. This helps to preserve the

resolution already obtained in the 1st dimension and the analysis to be completed in a shorter time. Peak capacity production per unit time is thus improved.

10.5 SFCxGC_{ftp} Applications

Two established ASTM methods could easily be combined with SFCxGC_{ftp}. The ASTM method ASTM D5186 for petrochemical group separation and ASTM D3710 for simulated distillation of gasoline samples together will provide ample information for petrochemical plant optimization or blending operations.

Because of the high degree of order attained with SFCxGC_{ftp}, the two-dimensional chromatograms may be very useful when combined with neural networks. These could be used for process control, to detect adulteration, or to identify the origin of a pollution incident.

This instrument will also be a valuable tool for the analysis of plant extracts, as was demonstrated for a lemon essential oil. Compound identification is eased for unknown mixtures by the independent presentation of sample dimensionalities.

The first results obtained with the comprehensive SFCxGC_{ftp} are very promising. This technique is sure to find its rightful place among the comprehensive chromatographic techniques. The potential to analyze a wide boiling point range of samples, the mild conditions compounds are subjected to, as well as the high selectivity of the low temperature first separation are bound to give SFCxGC_{ftp} an advantage over other available analysis techniques for some applications.