

Chapter 7

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Conclusion

In this dissertation the goal was to provide a guideline for the optimisation of GC x GC, as such a process is a lot more complex than in normal gas chromatography. The path taken to achieve this optimisation led to some interesting and previously ignored parameters that play an integral role in GC x GC performance. These included the careless use of “rules of thumb” to optimise linear flow rates, and the blind use of calculations done by the instrumentation without knowing the margin of error or even the formulas used!

It was also shown that GC x GC can be applied very successfully to the analysis of complex mixtures such as diesel petroleum samples. The applications on the diesel samples range from fingerprinting to quantitative component analysis.

7.1 Optimisation of GC x GC

The optimisation of a comprehensively coupled system proved to be a very complex procedure. Frequently used “rules of thumb” for the optimisation of one-dimensional systems involve approximations that are not obvious without careful understanding of the original optimisation studies. The one common error is to use the generally specified linear flow rate for a given column

inner diameter and the type of carrier gas. The optimum linear flow rate specified for columns with different diameters is good under conventional, atmospheric pressure conditions but is based on carrier gas diffusivities at atmospheric pressures, that do not apply directly to high pressure exit conditions. In GC x GC such high pressures exist since the second dimension acts as a restrictor at the end of the first column and diffusion in the carrier gas slows down appreciably. This change in the diffusion can be clearly seen in the calculations done to determine the optimum linear flow rates. The van Deemter optimum flow rate for hydrogen in a 0.25 mm internal diameter column is in the order of 40 to 50 cm/s, but we determined that our system has a optimum linear flow rate in its first dimension of 30 to 35 cm/s which corresponds almost to the optimum linear flow rate of helium under normal pressure conditions in a similar column. As a synergistic effect, the lower values of the first-dimension linear flow rate also result in much improved second-dimension resolution due to the lower linear flow rates and a yet unknown modulator effect.

When the second-dimension Van Deemter plot was drawn, some interesting results were obtained. It has to be reminded that a Van Deemter plot of this dimension is reasonable since it is run under isothermal conditions. The last part of the curve usually dictated by the Cu-term was a lot steeper than plots of similar column dimensions. This is believed to be the result of a less than perfect modulator that gives a measurable contribution to the second-dimension bandwidth.

The simplified flow optimisation method is justified and is recommended for any similar optimisation studies where different columns need to be coupled in GC x GC (verified for test compounds with second-dimension retention factors larger than three ($k > 3$)). The final suggested

inlet pressure (110 kPa) which is slightly too low for the first-dimensions and slightly too high for the second gives extremely improved results to the chromatogram (Figure 18) where a “rule of thumb” linear flow rate (of 50 cm/s) is used. The use of a wide boiling point range test sample such as diesel seems justified, as the modulator optimisation is strongly dependent on column oven temperatures and therefore needs to be checked over a wide temperature range.

In summary we propose an overall GC x GC optimisation guideline that involves the following steps:

- 1 Column selection (first- and second-dimension column length, internal diameter and film thickness) and carrier gas selection.
- 2 Stationary phase selection (based on dimensionality considerations, the polarity range of the compounds within the sample and thermal stability of the column phases)
- 3 Temperature programming of the first-dimension and modulation period chosen to maintain the recommended four second-dimension analyses per first-dimension peak. These parameters would depend on the type of analysis and consideration of the speed vs resolution trade-off.
- 4 Verification of modulator performance over the full column temperature range anticipated for the sample.
- 5 Flow optimisation (resolution calculations of selected test compounds at different system inlet pressures). This is required once a new set of column dimensions is selected, that has not previously been optimised with the selected carrier gas. Test compounds should be well retained in both dimensions ($k > 3$). A new set of column dimensions should be selected, if

the first- and the second-dimension linear flow optima are not compatible.

- 5 Second-dimension offset temperature should finally be adjusted so that the polarity range of the sample utilizes the full space of the two-dimensional separation plane without any “wrap-around”

7.2 The analysis of diesel petrochemical samples

This study confirmed the recent literature reports that GC x GC is a powerful technique for the analysis of petrochemical samples. In this method development study, different diesel samples were analysed and in their respective one-dimensional plots, clear differences can be seen regarding, for example, n-alkane patterns. These differences, however, are not clear enough to speculate on the differences in the total composition of the samples with different lubrication and combustion properties. In one-dimensional analysis, too many compounds co-elute and many are thus not identifiable. When involving two-dimensional separations, these smaller differences can be investigated. Under visual inspection differences can be easily spotted, which is a clear indication that this method can be used for fingerprinting purposes.