Application Note No. 059

The Role of Selective Exclusion in the Analysis of Specific Hydrocarbons in n-Alkane Waxes

Diane Nicholas.

Introduction

The analysis of wax n-alkanes, between C_{10} and C_{70} +, in crude oil, condensates and wax deposit samples by high temperature split/splitless injection seems long and tedious if only a selection or one specific hydrocarbon needs to be focused on. The gas chromatograph oven conditions can be adjusted to only achieve separation around the peak(s) of interest, thereby reducing the analysis time, however, the total sample continues to be transferred onto the column, resulting in longer runs and much wasted time.

Selective exclusion can be used to only transfer those peaks of interest from the injector onto the column through the positive use of discrimination. The remaining sample may be vented through the split line and trapped, kept in the liner or in the case of Difficult Matrix Introduction (DMI) where the sample or sample extract is directly introduced into the injector, the DMI microvial, which may be replaced when necessary.

Principles

Selective exclusion is achieved using the Optic in expert mode, the split valve is opened and closed to transfer or exclude the sample components at various determined temperatures.

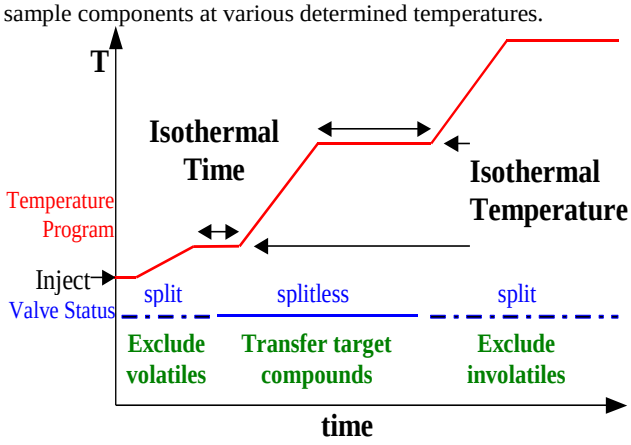

Figure 1: *Diagram of the Optic temperature program and valve state for selective exclusion*

1) The sample is injected with the injector at a cool temperature and the split valve open with a high flow. The temperature is then raised to a determined point for an isothermal time to eliminate the unwanted volatile components (this step may be discarded if the volatile components are of interest).
2) The split valve is then closed and the injector heated to a determined isothermal temperature for an isothermal time to transfer the components of interest.
3) The split valve is then opened again with a high flow and the injector temperature raised to the final temperature to vent the unwanted involatile components (this step may be discarded if the involatile components are of interest).

The injector temperatures used for exclusion of the volatile and involatile components and transfer of the target compounds are determined from a graph derived from data collected on the performance of the Optic injector, called the exclusion envelope.

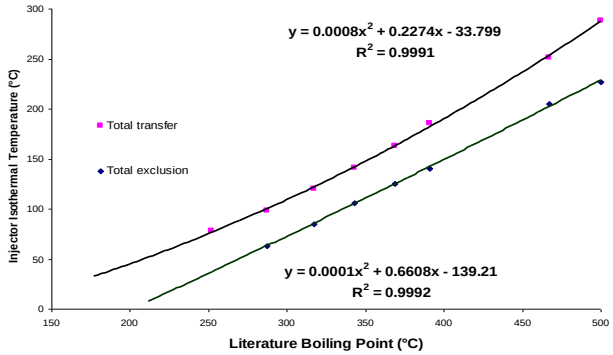

Figure 2: *The Exclusion Envelope*

The upper curve is used to determine the minimum injector temperature (y-axis) necessary for total transfer of a compound with a particular boiling point (x-axis). The lower curve is used to determine the maximum injector temperature possible with total exclusion of the compound. The isothermal temperature for each step is simply defined by putting the boiling points into the equations derived from these two curves. This desktop study is carried out and the conditions determined before trying out the analysis in the lab. Some optimisation of the precise isothermal temperature and time may be required.

There were three aims to this work:
1) To completely transfer all volatile compounds up to and including C_{20}, then exclude the involatiles
2) To completely transfer C_{40} and above, while excluding the volatiles
3) To transfer C_{30} only, while excluding the volatiles and involatiles

The method should be looked at in two stages. Firstly, the injector method is optimised, which is covered in this application note, then the oven temperature program may be adjusted to suit the separation and reduce the run time.

Instrumentation & Conditions

- ATAS Optic 2-200 programmable injector
- HP5890 with FID

Optic Conditions

Liner:	ATAS Fritted	
Mode:	Expert	
Gas Flows:	Split:	350 ml/min
	Vent:	50 ml/min
Initial temperature:	65 °C	
Ramp rate:	6 °C/s	
Final temperature:	500 °C	
Splitless time:	2 mins	
Transfer pressure:	14 psi	
Transfer time:	2 min	
Initial pressure:	6.5 psi	
Final pressure:	19.4 psi	

GC conditions:

Column: SGE HT-5 25 m x 0.32 mm i.d. x 0.1 um film

Initial Temperature:	50 °C
Initial Time:	3 mins
Ramp Rate:	10 °C/min
Final Temperature:	449 °C (10 mins)
FID temperature:	400 °C

Reference Chromatogram

GL Sciences B.V.
De Sleutel 9, 5652 AS, Eindhoven, The Netherlands
Tel. +31 (0)40 254 95 31 E-mail: info@glsciences.eu
Internet: www.glsciences.eu

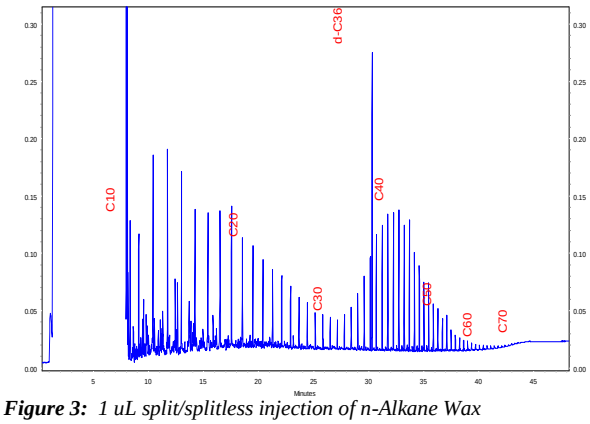

Figure 3: *1 uL split/splitless injection of n-Alkane Wax*

A splitless injection of the sample, using a splitless time of 2 minutes, a transfer pressure of 14 psi (the pressure used for modelling of the theory) and a final temperature of 500 °C, provided a reference chromatogram to ensure total transfer of the selected peaks when optimising the selective exclusion.

Transfer of the Volatiles

The boiling point of C_{20} is 344 °C, therefore for total transfer in splitless mode the injector must reach at least 139 °C.

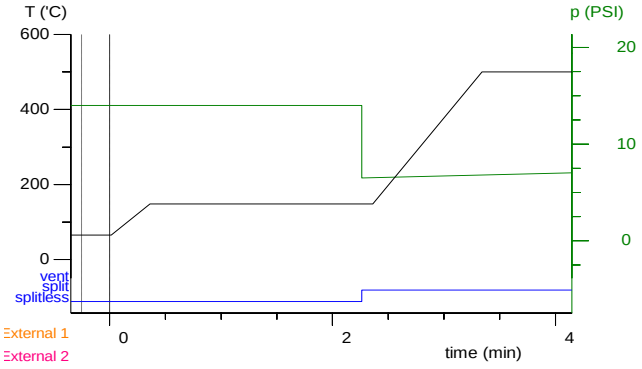

Figure 4: *Conditions used to selectively transfer up to C_{20}*

The *optimised* conditions, see Figure 4, were to inject the sample at a low temperature in splitless mode then, ramp the injector to an isothermal temperature of 148 °C for 2 minutes. At this point the split line was opened and the injector was ramped to its final temperature. This produced 100% transfer of C_{20} and below, and 1-2% transfer of the involatiles due to splitting.

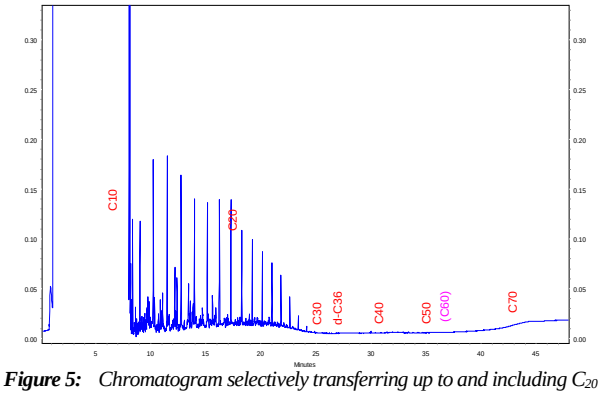

Figure 5: *Chromatogram selectively transferring up to and including C_{20}*

Transfer of the Involatiles

The boiling point of C_{40} is 525 °C. To totally exclude C_{40} the injector temperature must not reach 235 °C, as above this temperature it will begin to transfer. Therefore we can exclude all volatiles up to an injector temperature of 235 °C.

This time injection took place in split mode, see Figure 6, with a high split flow and the injector was ramped to an isothermal temperature of 235 °C for 5 seconds. At this point the split line was closed and the injector was ramped to its final

temperature. The split line was kept closed for 2 minutes before opening with a low split flow (using the vent valve). This produced 100% transfer of C_{40} and above, and a 1-2% transfer of the volatiles due to splitting, as was expected very little solvent was transferred onto the column, see Figure 7.

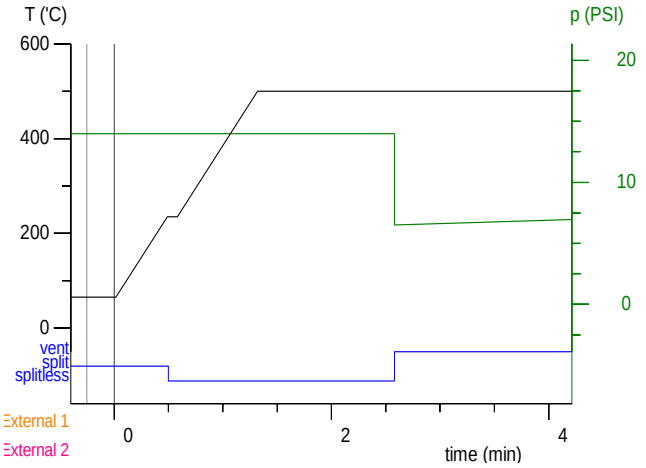

Figure 6: *Conditions used to selectively transfer above C_{40}*

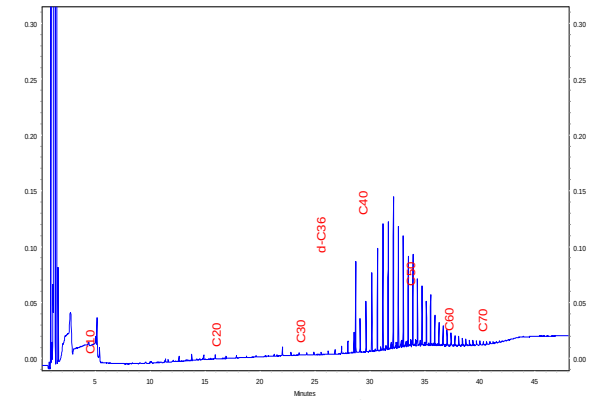

Figure 7: *Chromatogram selectively transferring C_{40} and above*

Transfer of C_{30}

The boiling point of C_{30} is 450 °C. To totally exclude C_{30} the injector temperature must not reach 178 °C, as above this temperature it will begin to transfer, total transfer occurs from 230 °C and above. Therefore we can exclude all volatiles up to 178 °C, transfer of C_{30} will take place at 230 °C, and exclusion of the involatiles will occur by then heating to the final temperature.

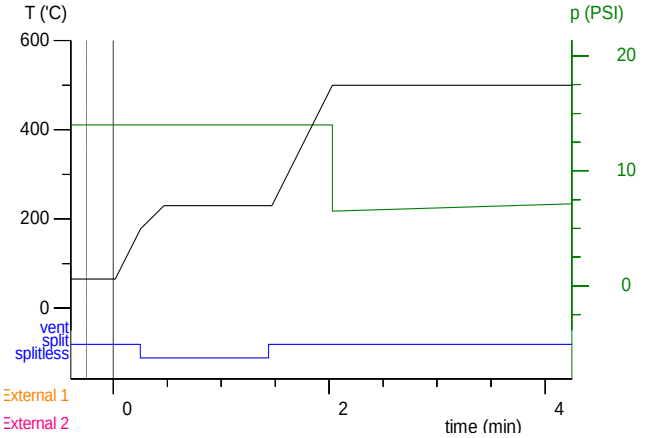

Figure 8: *Conditions used to selectively transfer C_{30}*

Injection took place in split mode with a high split flow and the injector was ramped to an isothermal temperature of 178 °C. At this point the split line was closed and the injector was ramped