

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

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### Introduction

The analysis of wax n-alkanes, between C<sub>10</sub> and C<sub>70</sub> +, 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.

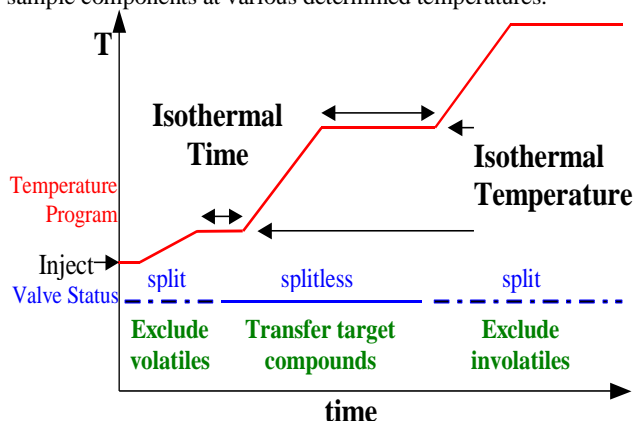
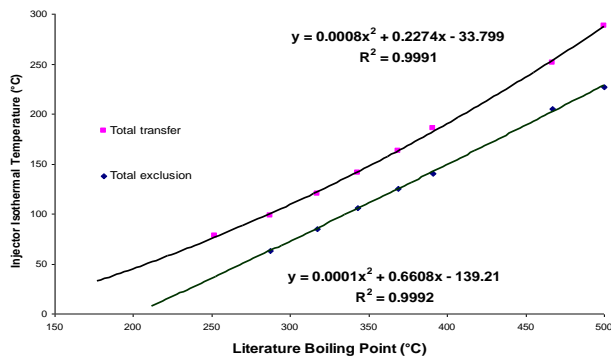


Figure 1: Diagram of the Optic temperature program and valve state for selective exclusion

- 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<sub>20</sub>, then exclude the involatiles
- 2) To completely transfer C<sub>40</sub> and above, while excluding the volatiles
- 3) To transfer C<sub>30</sub> 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***

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- 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

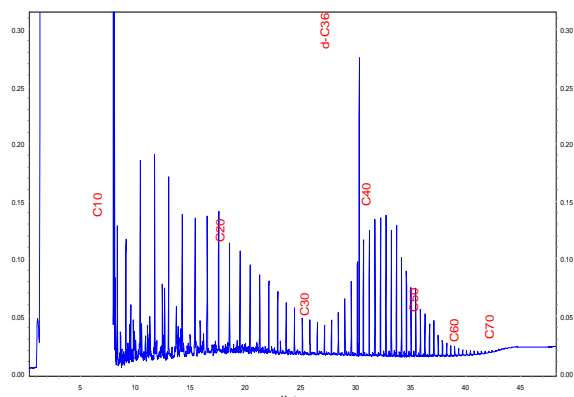
Initial temperature: 65 °C  
 Ramp rate: 6 °C/s  
 Final temperature: 500 °C  
 Splitless time: 2 mins  
 Transfer pressure: 14 psi  
 Transfer time: 2 min  
 Initial pressure: 6.5 psi  
 Final pressure: 19.4 psi

### **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***

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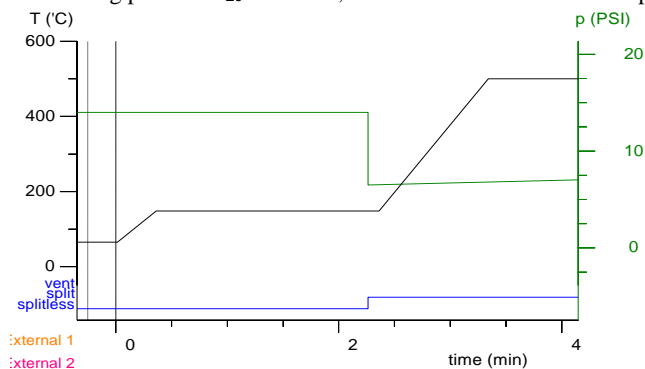


**Figure 3:** 1  $\mu$ L split/splitless injection of n-Alkane Wax

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.

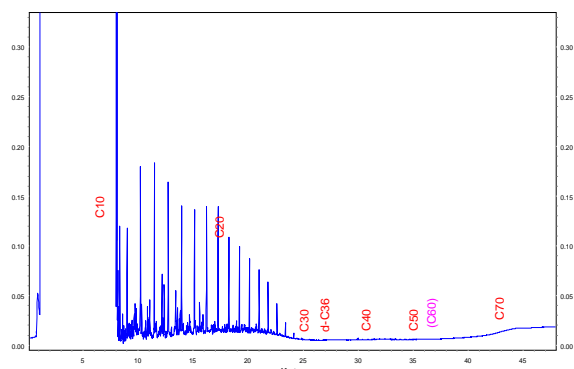
### Transfer of the Volatiles

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.



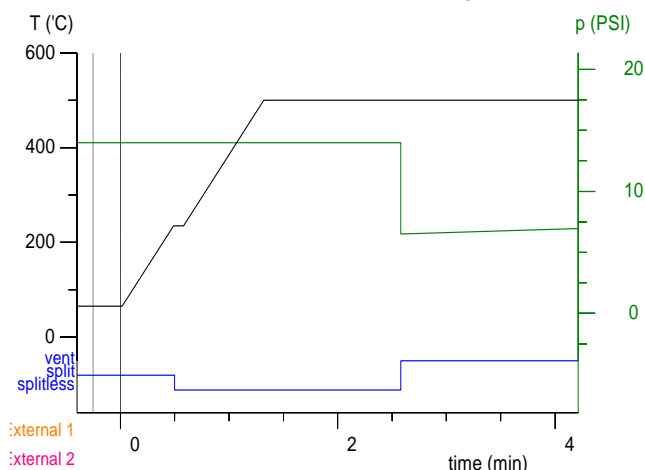
**Figure 5:** Chromatogram selectively transferring up to and including  $C_{20}$

### Transfer of the Involatiles

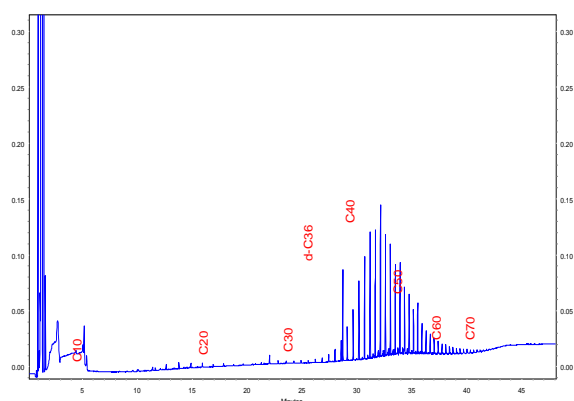
The boiling point of  $C_{40}$  is 525 °C. To totally exclude  $C_{40}$  the injector temperature must not reach 235 °C, as above this temperature it will begin to transfer. Therefore we can exclude all volatiles up to an injector temperature of 235 °C.

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<sub>40</sub> 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.



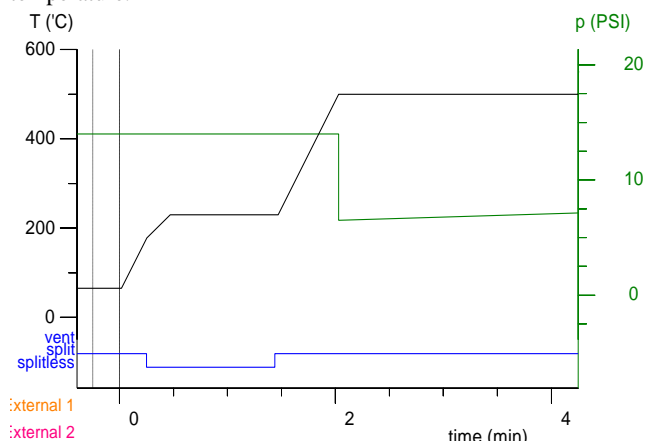
**Figure 6:** Conditions used to selectively transfer above C<sub>40</sub>



**Figure 7:** Chromatogram selectively transferring C<sub>40</sub> and above

## Transfer of C<sub>30</sub>

The boiling point of C<sub>30</sub> is 450 °C. To totally exclude C<sub>30</sub> 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<sub>30</sub> 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<sub>30</sub>

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