Application Note No. 018

# Modelling an OPTIC 2 as an Alternative to Multidimensional Chromatography

*Diane Nicholas*

## *Introduction*

Multidimensional chromatography has been used since the mid-1950s as a method of selecting which components of a sample mixture enter the column. In particular, it can be used for solvent elimination or to selectively remove major components for the examination of trace components, therefore preventing the trace components from being eluted on solvent or major component tails. The detection limit and resolution around a certain peak can also be increased in this way. The life of the column is improved and the detector, especially mass selective detectors, are protected from dirtying by removing heavy, in volatile compounds or the major components before they enter the main chromatographic column, therefore also enhancing the sensitivity.

## *The OPTIC 2 Programmable Injector*

Most multidimensional systems are difficult to set-up, require specialist equipment and technical experience and have high running costs. For example, heart cutting transfers selected groups of peaks from the outlet of a first column to the inlet of a second, hence sacrificing the first, which requires frequent replacement. Using OPTIC as an alternative to multidimensional chromatography is cost effective, simplifies the technique of selectively introducing components into the column and protects the column and detector.

The OPTIC 2 was used on a gas chromatograph to produce a model for the analysis of volatile trace components in highly concentrated samples. This was achieved by the positive use of discrimination against the less volatile major component. Discrimination is a result of injection technique or temperature, the column phase, etc. has no impact on the transfer or exclusion of components, as the effects are achieved in the liner. Here, the difference in the volatilities of the trace and major components is used to specifically exclude the less volatile major component, hence removing up to 98% of it from the system, thereby improving the sensitivity for the analysis of the trace analyte through the ability to use highly concentrated samples and the detector sensitivity, as only a fraction of the sample is detected.

When using the OPTIC in Expert mode there are a number of parameters to consider, as shown in Figure 1, each of which was investigated to verify which strongly influenced the resultant discrimination. Other parameters include the split flow, the injection volume and the choice of liner. The parameters of major importance when using this method for selective discrimination were determined to be the isothermal temperature (parameter 5) and time (parameter 6) for the transfer of volatile components on to the column. The remaining parameters were optimised.

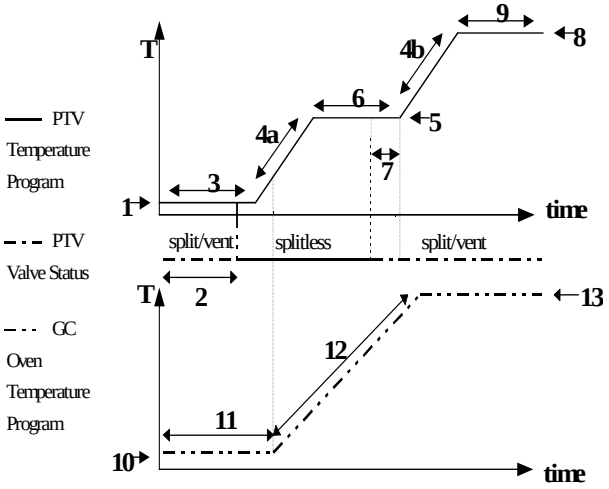


Figure 1: Diagram of the various parameters for the OPTIC Temperature Program and Valve Status in expert mode, and the GC Oven Temperature Program

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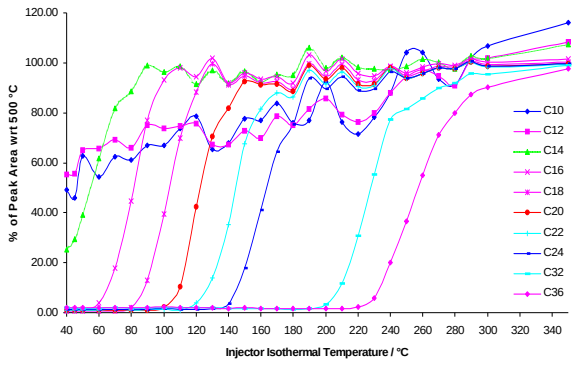
1. Initial Isothermal Temp. for Solvent Elimination
2. Split/Vent valve open time for Solvent Elimination
3. Isothermal Time for Solvent Removal
4. Ramp Rate 1 (**a**) and 2 (**b**)
5. Isothermal Temperature for Splitless State
6. Isothermal Time
7. Time between Valve Switching and Temp. Ramp
8. Final Temperature
9. Final Temperature Holding Time
10. Oven Initial Temperature
11. Oven Initial Temperature Holding Time
12. Oven Ramp Rate
13. Oven Final Temperature

The use of the isothermal temperature (parameter 5 in Figure 1) to achieve selective discrimination was investigated using a mixture of eleven Alkanes, comprising of between $C_8$ and $C_{36}$ in hexane, with OPTIC in expert mode. The isothermal temperature was then varied by 10 °C between the temperatures of 40 and 350 °C. This created an injector temperature profile. From this, a predictive model was produced to ascertain if a trace analyte is separable from a major component, by determining the minimum difference in the volatility of two compounds to achieve total selectivity. An exclusion envelope relating the literature boiling point to the injector isothermal temperature is presented as a technique of establishing the isothermal temperature to achieve selective discrimination. A procedure to predict the boiling point of unknown compounds in real samples is also presented. The isothermal time was investigated by varying it between 10 and 240 seconds.

## *Instrumentation*

Experimental work was carried out on an HP-6890 series gas chromatograph, equipped with an auto-sampler and FID, and an ATAS OPTIC 2-200 programmable injector. The column used was a CP Sil 8CB fused silica column with a length of 25 meters, internal diameter of 0.25 mm and a 0.25 micron film thickness. The detector temperature was 325 °C and the GC oven was programmed from 35 °C (with a 2 minute hold) to 350 °C at a rate of 40 °C, with an end time of 6 minutes. The OPTIC had an initial temperature of 40 °C (with a hold time 45 seconds) then was programmed to a specified temperature at a rate of 12 °C/s (hold time 60 seconds) before reaching its final temperature of 350 °C at a rate of 12 °C/s. A fritted liner was used and the split flow was 200 ml/min. The initial and final pressures were 14 PSI. The initial valve state was split, changed to splitless after 2 seconds then back to split, the time depending on the isothermal temperature. Due to the large quantities of sample excluded through the split line, it was re-routed via a T-piece from the bottom of the injector through the oven and out through a Tenax trap in the oven roof, to prevent condensation of sample and subsequent blockage of the split line. A small flow was kept through the original split line, connected to the purge line, to eliminate dead volume effects.

The volatilities of compounds were determined on an HP-5890 series gas chromatograph equipped with an auto-sampler, injector and FID. The column used was a CP Sil 5CB fused silica column with a length of 25 m, internal diameter of 0.32 mm and a 0.13 micron film thickness. The detector temperature was 325 °C, the injector temperature 300 °C and the GC oven was programmed from 80 °C to 300 °C at a rate of 10 °C with an end time of 5 min. The carrier gas flow was 1.0 $cm^3$/min.

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## *Effect of Isothermal Time on the Exclusion of Higher Alkanes*

The length of time that the injector is at the isothermal temperature has an effect on the exclusion of the higher alkanes, as shown by the example in Figure 2 at the isothermal temperature of 150 °C.

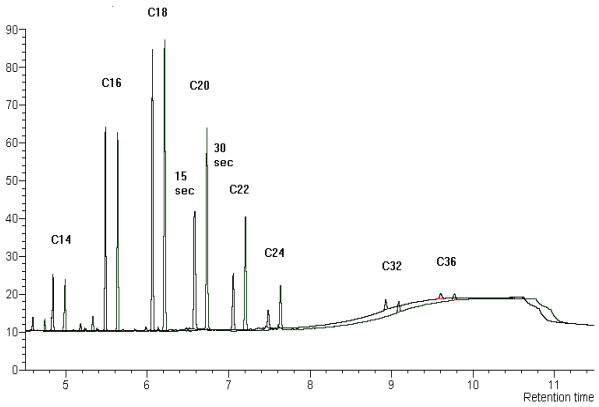


Figure 2: Effect of isothermal time on the exclusion of higher alkanes at isothermal temperature 150 °C

Clearly, the longer the temperature remains isothermal in the splitless state the larger quantities of both volatile and less volatile components are transferred on to the column. Therefore it is necessary to establish a balance, making the isothermal time long enough to ensure that all the volatile components of interest are transferred onto the column, but at the same time keeping it as short as possible to minimise the transfer of the remaining less volatile components during the splitless time under the conditions used. The best time was found to be approximately one minute for this application, and this can be optimised with a few injections.

## *Relationship between Effective and Literature Boiling Points*

The variation of injector isothermal temperature had a strong effect on the response of each of the hydrocarbons as can be seen in Figure 3.

Figure 3: Modelling the Exclusion of Alkanes by Variation of the Injector Isothermal Temperature

It became evident that there was total transfer from the injector to the column at a temperature far below the literature boiling point of the hydrocarbon. Therefore, the effective boiling point is defined as the injector temperature at which 50 % of a compound evaporates from the column under these conditions. A comparison of the effective boiling point (injector isothermal temperature) and the literature boiling point for each hydrocarbon is shown in Figure 4.

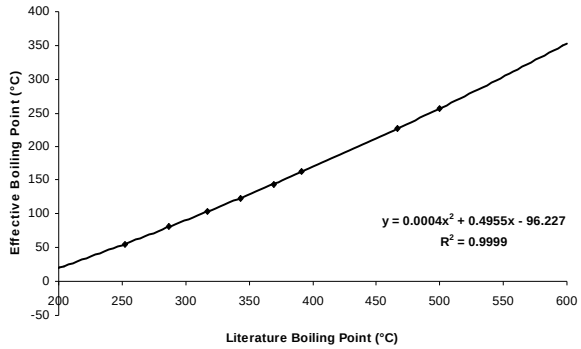


Figure 4: Relationship between effective and literature boiling points

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## *Use of the Isothermal Temperature to Achieve Selective Discrimination*

The importance of the isothermal temperature on discrimination is evident, as shown in Figure 3. Solvent elimination discriminates against or causes the loss of $C_8$ to $C_{12}$ as they are too close in volatility to the solvent. From $C_{14}$ and above the steep gradient of the curves when changing the isothermal temperature shows that discrimination occurs rapidly. Changing the isothermal temperature by only 50 °C has a major effect on the discrimination of a particular hydrocarbon and can decide whether it is transferred onto the column or not. It is evident that it is possible to selectively choose the components that enter the column by using the isothermal temperature. Just how close two components can be in volatility to selectively choose one while excluding the other is shown in Figure 5 by looking at the literature boiling points of each.

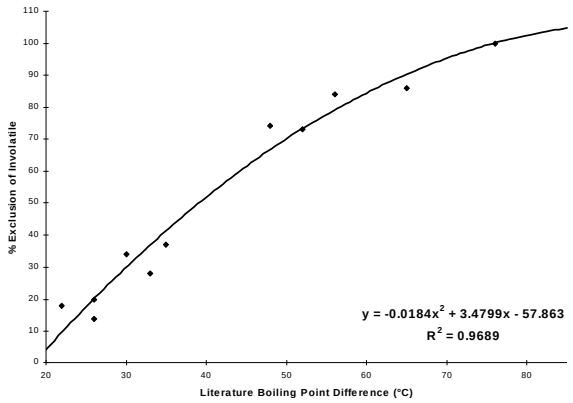


Figure 5: Derived from Figure 3 showing the relationship between the difference in literature boiling points of two components and exclusion of the in volatile for total transfer of the volatile*

A difference of 77 °C or above between two components can completely separate them. This chart can also be used to determine the extent of selectivity that can be achieved between two components if their boiling points or effective boiling points are less than this amount. However, their boiling points must be known to determine this.

## *Estimation of Literature Boiling Points*

A CP-Sil 5CB column is non-polar in nature and therefore retention times depend on the volatility of a compound, this is then linked to its boiling point. When 57 typical compounds comprising of alkanes, ethers, esters, etc. were run through such a column under a specific set of conditions a trend was exhibited linking their retention time (related to the effective boiling point) with their literature boiling points, as shown in Figure 6.

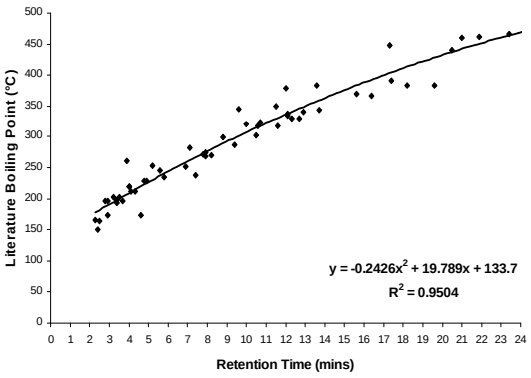


Figure 6: Relationship between literature boiling point and retention time*

Therefore, a simple method of approximating the literature boiling point of an unknown compound, to use when estimating the

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isothermal temperature, is to determine its retention time when it is injected into this system using the same conditions, then correlate this to its effective boiling point using the above graph.

## *Determination of the Injector Isothermal Temperature for Selective Discrimination*

When the boiling point, or effective boiling points, of two compounds are known the injector isothermal temperature can be predicted using the exclusion envelope in Figure 7. The upper curve is utilised to determine the lowest isothermal temperature feasible to ensure 100% of the more volatile component is transferred onto the column. The lower curve is used to determine the highest injector isothermal temperature possible for 100% exclusion of the less volatile component. The ideal isothermal temperature will lie between these two boundaries and with a few injections this can be determined exactly.

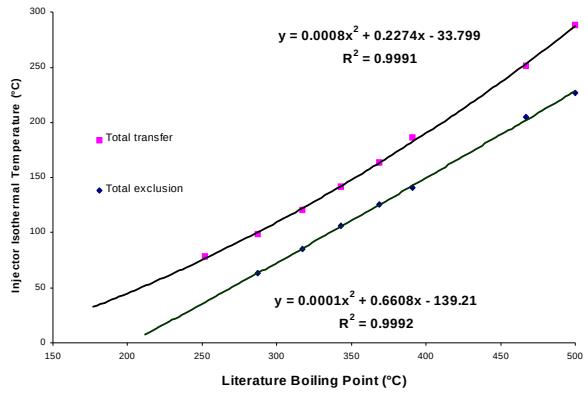


Figure 7: Exclusion envelope, predicting the injector isothermal temperature for selective exclusion*

## *Conclusions*

The OPTIC 2 is a very versatile programmable injector, and the analysis of trace components in highly concentrated samples is a further application of this instrument. By applying selective discrimination this ensures that the majority of a highly concentrated solution is removed before being swept on to the column, therefore the detection limits of the trace components are primarily limited by the solubility of the sample in the solvent used and the injection volume. This protects the column and the detector from heavy, in volatile components or large volumes of a solvent or unwanted compound and hence improves the sensitivity of the system. It is a simpler, more cost effective system than conventional multidimensional techniques and with only two main parameters to optimise; this can be accomplished in a few injections. This model can be applied to a large variety of compounds with known or unknown volatilities.

## *Acknowledgements*

Huw Crowther and Bryan White.

## *References*

IAMBEC MSc project by Diane Nicholas, University of Warwick 1999.

* These charts can be seen in more detail on the ATAS Website along with a procedure for this work titled ‘Procedure of Using OPTIC 2 for Selective Exclusion’.

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*Chromatography Technical Notes No 18A*

# Procedure of Using the OPTIC 2 for Selective Exclusion

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## *Introduction*

***Following on from the ATAS Chromatography Technical Notes No 18 here is a short procedure of how to estimate the injector isothermal temperature and time and optimise these conditions to selectively discriminate between two compounds in the liner. There are six steps:***

1. ***Approximate the boiling points, if they are not known***
2. ***Determine the extent of selectivity possible***
3. ***Predict the lowest injector temperature for total transfer of the volatile***
4. ***Predict the highest injector temperature for total exclusion of the involatile***
5. ***Optimise the injector isothermal temperature***
6. ***Optimise the injector isothermal time***

***Please note that other OPTIC and GC parameters require optimisation for each application, but the most important two for selective exclusion are described here.***

## *Approximation of Boiling Point*

***The boiling points of the two compounds to be selectively discriminated between can be predicted by determining their retention times when analysed using the following conditions:***

- Column: CP Sil 5CB fused silica 25 m x 0.32 mm x 0.13 µm film
- Oven: Initial Temperature: 80 °C
  Ramp Rate: 10 °C/min
  Final Temperature: 300 °C
  Final Time: 5 minutes
- Carrier gas: Helium
  Flow rate: 1.0 $cm^3$/min
- Detector: FID
  Temperature: 325 °C

The retention time is put into the equation from Figure 1, $y = -0.25x^2 + 19.79x + 133.7$, to calculate the approximate boiling points.

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### Determination of Extent of Selectivity Possible

A difference in boiling point of 77 °C or greater means that total discrimination is achievable, with only the minimal amount of the in volatile transferring on to the column due to splitting. By putting the boiling point difference into the equation from Figure 2, $y = -0.02x^2 + 3.48 – 57.86$, the percentage exclusion of the in volatile is determined for total transfer of the volatile.

### Prediction of Injector Isothermal temperature

Total transfer of the volatile compound is required, therefore its boiling point is put into the equation from the upper curve of Figure 3, $y = 0.0008x2 + 0.2274x – 33.799$, to determine the lowest injector temperature at which it is possible to totally transfer all of the compound on to the column. Whereas, total exclusion of the in volatile compound is required, therefore its boiling point is put into the lower curve in Figure 3, $y = 0.0001x2 + 0.6608x –139.21$, to establish the highest injector temperature possible before the involatile compound begins to evaporate moving on to the column. The ideal isothermal temperature lies between these boundaries.

## *Optimisation of Injector Isothermal Temperature and Time*

Carry out five to eight injections varying the injector isothermal temperature by 10 – 15 °C each time between the upper and lower limits predicted above. Compare the peak areas of the volatile and in volatile compounds to those obtained when a splitless injection is carried out and plot a curve, as shown in Figure 4. A balance can then be established between total transfer of the volatile compound and total exclusion of the in volatile compound. A similar procedure determines the best isothermal time by varying it by 15 – 30 seconds between the times of 30 seconds and 2 minutes.

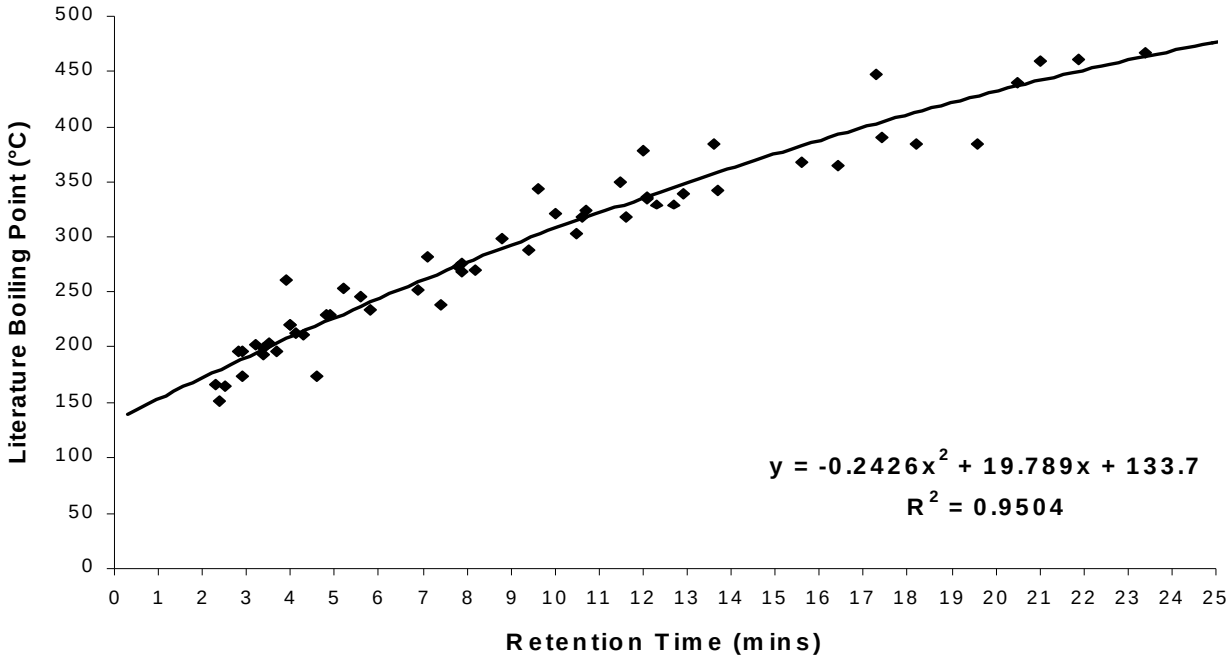


Figure 1: Relationship between literature boiling point and retention time


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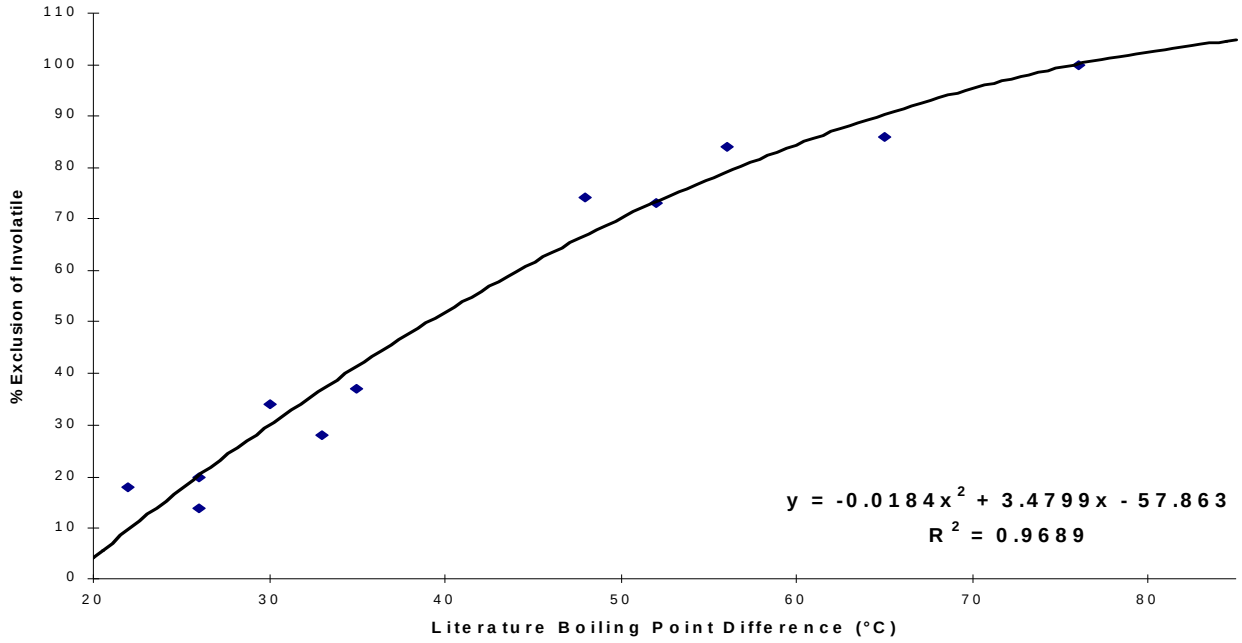


Figure 2: Relationship between the difference in boiling point of two components and percentage exclusion of the involatile for total transfer of the volatile

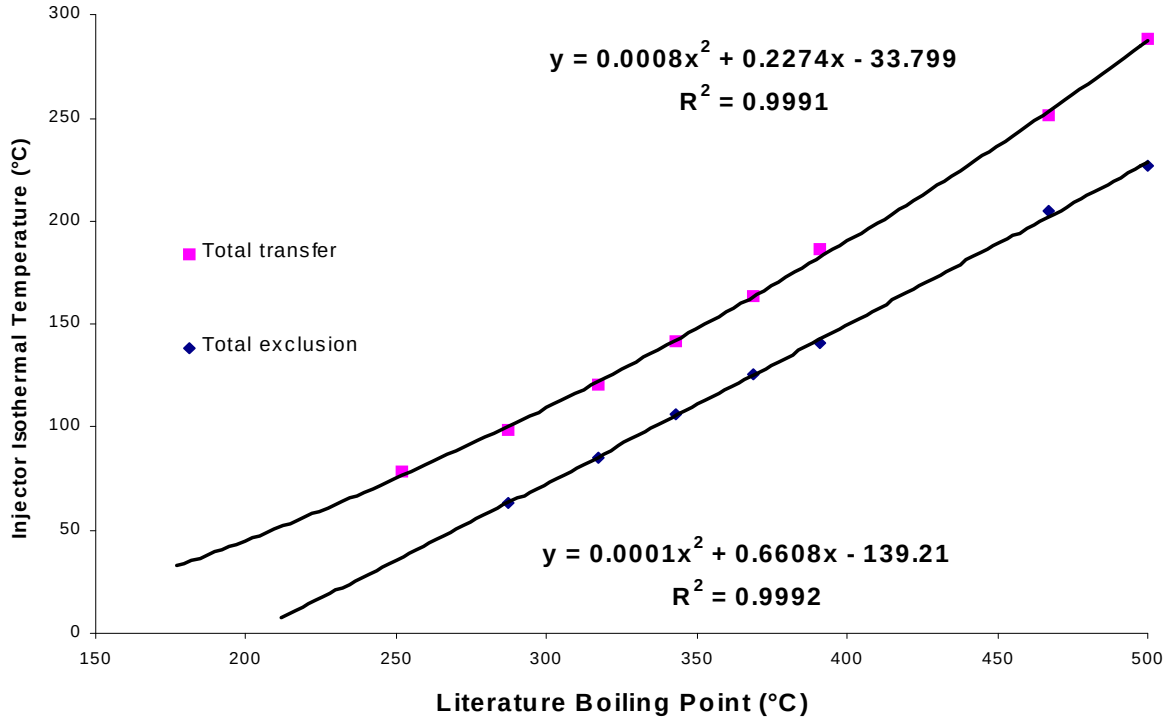


Figure 3: Exclusion envelope, predicting the injector isothermal temperature for selective exclusion

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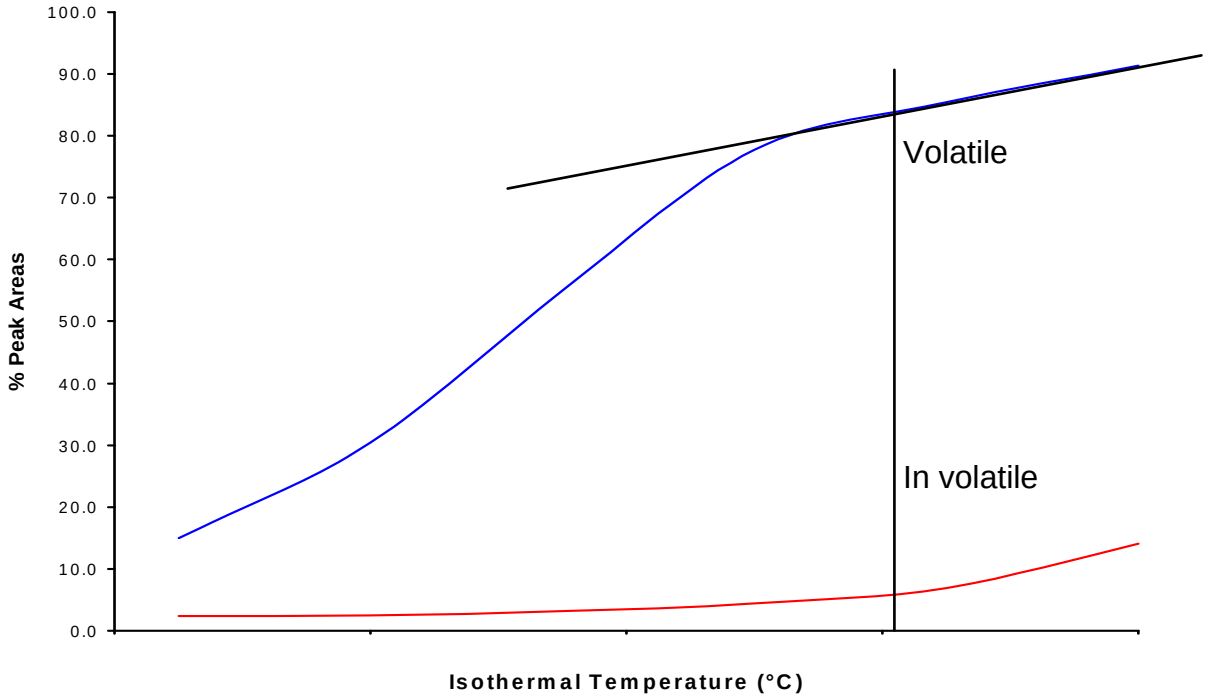


Figure 4: Comparison of peak areas in splitless mode to when at various isothermal temperatures in expert mode

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