GC Method Translation in Adsorption Gas Chromatography (PLOT columns)

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Introduction

Method translators are extremely helpful tools when modifying / developing a gas chromatographic (GC) method. Changes to GC method parameters like; inlet/outlet pressure, flow/carrier gas type or even capillary column dimensions will result in different retention times for our analytes and will affect resolution. Method translators calculate new analysis conditions by keeping the analytes elution temperatures the same, thus preserving elution order. Using this tool, the analysis method can be translated to a different column dimension, carrier gas type, linear velocity, for example, with very little time spent on the method development. Method translation works well for the columns with liquid stationary phases. The purpose of this work is to present feasibility and accuracy of the method translators for the porous layer open tubular (PLOT) columns.

There are two reasons we thought it would not be accurate for PLOT columns:

- Inaccurate flow control due to flow restriction through the column. Thick layers of particles are difficult to deposit in an even layer. Uneven coating thickness could affect the column internal diameter/flow
- PLOT column chromatography or gas/solid chromatography is based on adsorption/desorption principles – a surface process. Do the same rules work in gas-solid as in gas-liquid chromatography?

Analysis of gases using Alumina Column

Translation to Alternative Carrier Gases

To prove this concept, we translated the original method from helium carrier gas to nitrogen and hydrogen using a “Translate” function (Figure 1). The column length was determined by counting the number of column loops on the cage. A faster technique for determining length is to measure the column hold-up time using an unretain compound. This approach will not work with Alumina columns because even the lightest analytes, like methane, show some retention. Since we were using the FID, there aren’t many other options for unretained compounds.

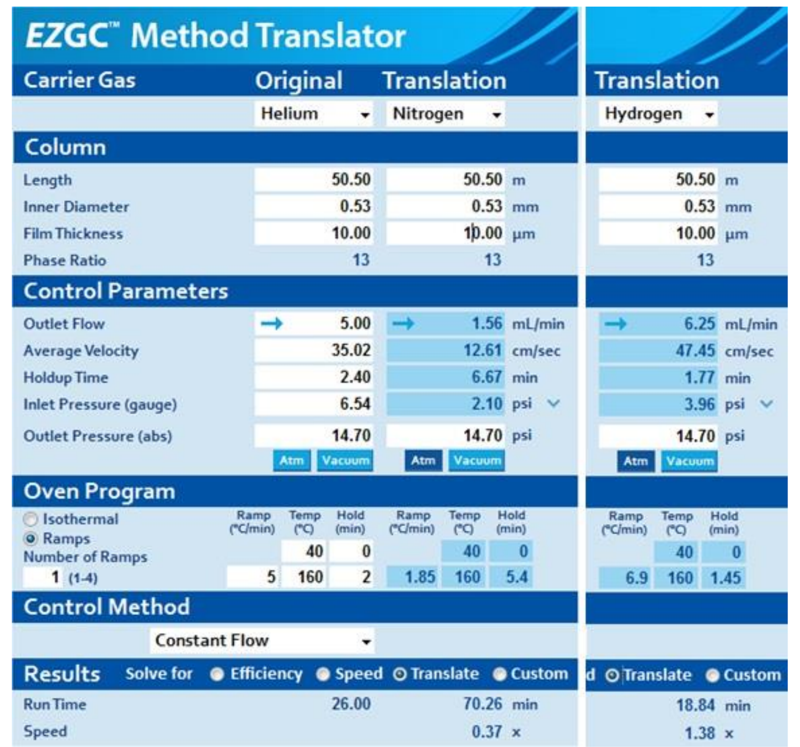
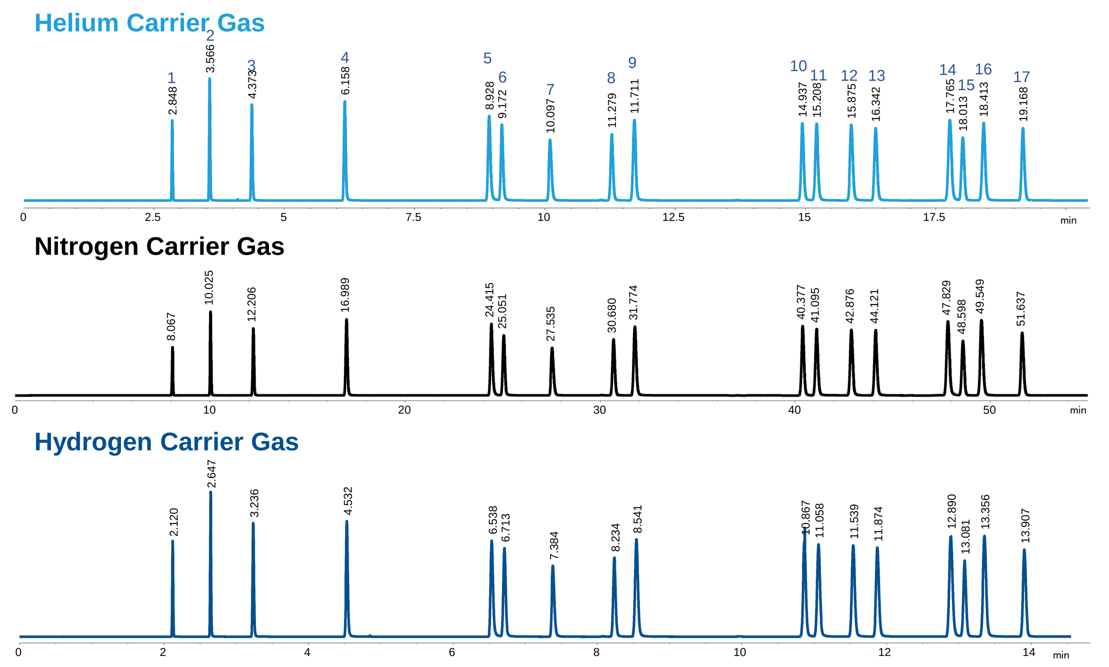


Figure 1: Translation with the EZGC Method Translator using Alumina/KCl BOND 50m x 0.53mm x 10µm column and helium carrier gas to hydrogen and nitrogen.



#	Compound
1	Methane
2	Ethane
3	Ethylene
4	Propane
5	Cyclopropane
6	Propylene
7	Acetylene
8	Propadiene
9	Butane
10	Trans-2-butene
11	1-butene
12	Isobutene
13	Cis-2-butene
14	Isopentane
15	Methyl acetylene
16	Pentane
17	1,3-butadiene

Figure 2: Chromatograms using all three carrier gases and translated analysis conditions, respectively showing similar elution pattern.

Compound	Helium Carrier Gas RT (min)	Helium Carrier Gas Elution T (°C)	Nitrogen Carrier Gas RT (min)	Nitrogen Carrier Gas Elution T (°C)	Hydrogen Carrier Gas RT (min)	Hydrogen Carrier Gas Elution T (°C)	Stdev El. T
Methane	2.85	54.24	8.07	54.92	2.12	54.63	**0.34**
Ethane	3.57	57.83	10.03	58.55	2.65	58.26	**0.36**
Ethylene	4.37	61.87	12.21	62.58	3.24	62.33	**0.36**
Propane	6.16	70.79	16.99	71.43	4.53	71.27	**0.33**
Cyclopropane	8.93	84.64	24.42	85.17	6.54	85.11	**0.29**
Propylene	9.17	85.86	25.05	86.34	6.71	86.32	**0.27**
Acetylene	10.10	90.49	27.54	90.94	7.38	90.95	**0.27**
Propadiene	11.28	96.40	30.68	96.76	8.23	96.81	**0.23**
Butane	11.71	98.56	31.77	98.78	8.54	98.93	**0.19**
Trans-2-butane	14.94	114.69	40.38	114.70	10.87	114.98	**0.17**
1-butane	15.21	116.04	41.10	116.03	11.06	116.30	**0.15**
Isobutene	15.88	119.38	42.88	119.32	11.54	119.62	**0.16**
Cis-2-butane	16.34	121.71	44.12	121.62	11.87	121.93	**0.16**
Isopentane	17.77	128.83	47.83	128.48	12.89	128.94	**0.24**
Methyl acetylene	18.01	130.07	48.60	129.91	13.08	130.26	**0.18**
Pentane	18.41	132.07	49.55	131.67	13.36	132.16	**0.26**
1,3-butadiene	19.17	135.84	51.64	135.53	13.91	135.96	**0.22**

We used the retention times and oven temperature profile to calculate the analytes’ elution temperatures for all three carrier gases. Since the main principle of the translation is to preserve the elution temperature from one analysis to the other, we should expect minimal deviation between the calculated elution temperatures. Both carrier gas show minor deviations which could be attributed to the estimated column length.

The second parameter investigated was resolution. Despite the considerable differences between the analytes retention times, we noticed little change in the resolution with slightly better numbers when using a nitrogen carrier gas. We plotted the resolution numbers below (Figure 4). Closely eluting compounds, where we strive to maintain resolution, showed a very narrow standard deviation window.

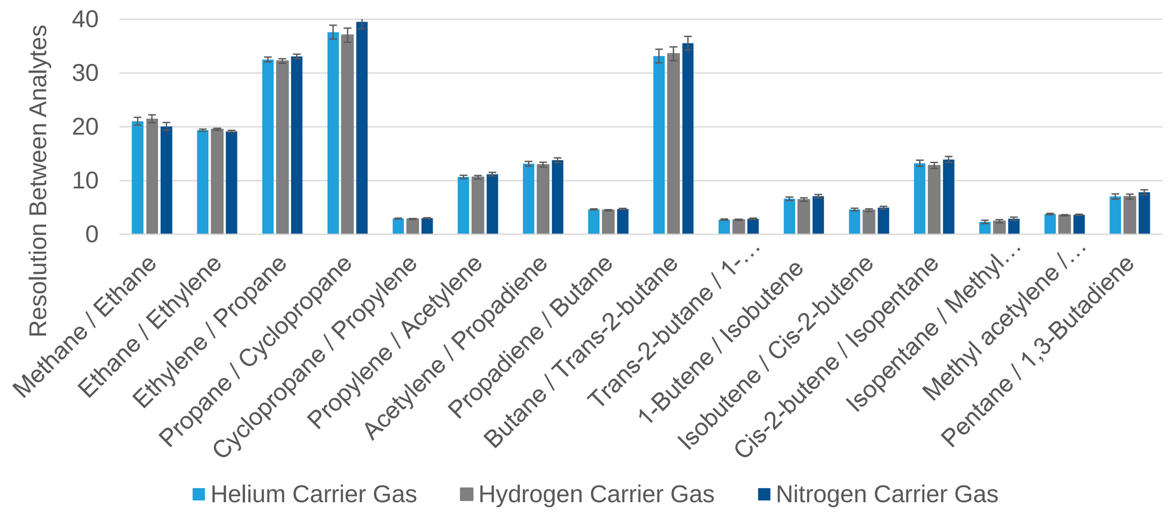


Figure 4: Comparison of resolution numbers obtained using all three carrier gases

Analysis of solvents using porous polymer column

Translation to nitrogen carrier gas using the same velocity

Nitrogen is the slowest of all the carrier gasses and for this reason is often avoided. To give it some appeal, we have translated the original method using helium carrier gas to a nitrogen carrier gas by trying to preserve the analytes' retention times between both methods. We used a Translator to match the nitrogen linear velocity with my original linear velocity from a helium run and then kept the GC oven program the same.

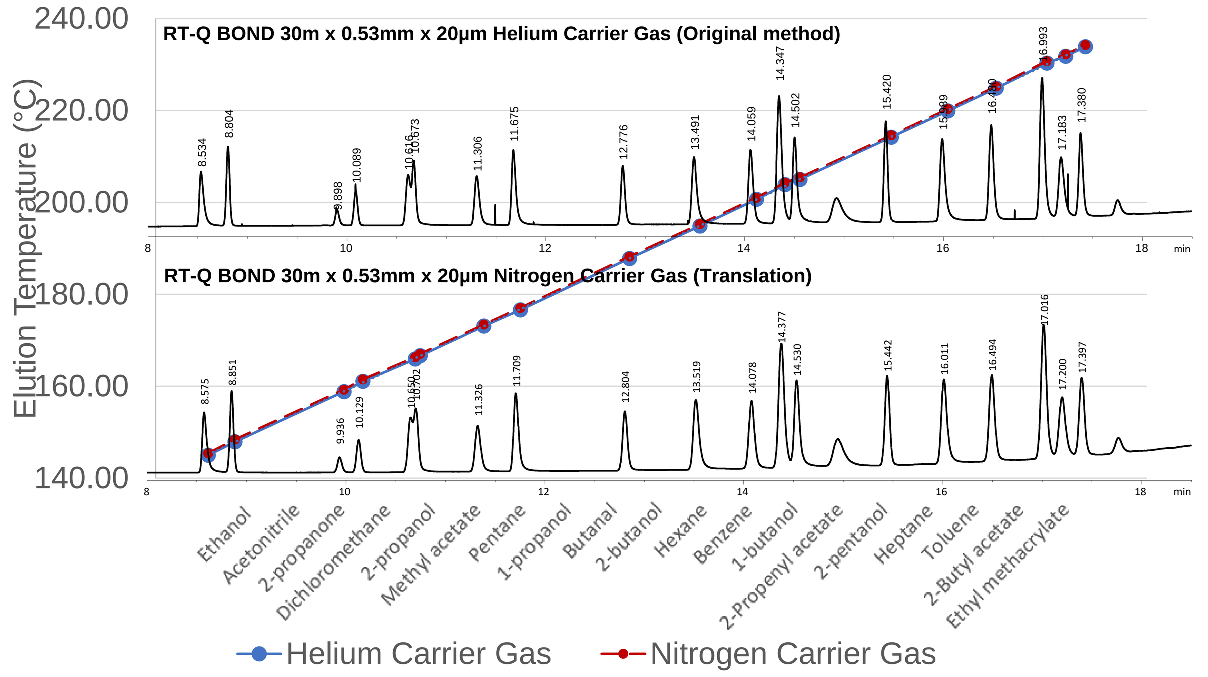


Figure 5: Chromatograms using helium and nitrogen carrier gases, same carrier gas velocity, and oven heating profile. Overlaid is a plot of the elution temperature of the analytes for both carrier gases respectively.

Using nitrogen outside the optimal carrier gas velocity window resulted in a decrease in the resolution between the analytes (approx. 15%, Figure 6). More importantly, retention times between both runs were in a 3-second window (Figure 5), illustrating the effectiveness of the translation.

Pairs	Resolution He CG	Resolution N_2 CG	% Difference
Dichloromethane / 2-Propanol	6.89	6.09	11.61
2-Propanol / Methyl acetate	0.64	0.55	14.06
Pentane / 1-Propanol	4.28	3.83	10.51
Hexane / Benzene	3.15	2.76	12.38
Benzene / 1-Butanol	1.74	1.47	15.52
Toluene / 2-Butyl acetate	11.87	9.55	19.55
2-Butyl acetate / Ethyl methacrylate	1.94	1.61	17.01

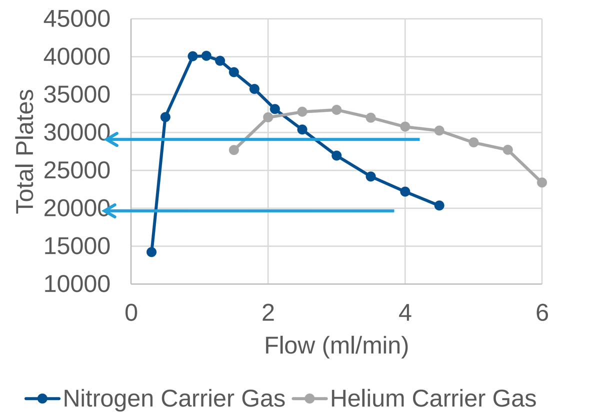


Figure 6: A table of critical resolutions from the chromatogram in Figure 6 (right). Relationship between Nitrogen and Helium carrier gas flow (ml/min) for a 30m x 0.53mm ID column. Since we used nitrogen carrier gas at the same velocity as helium we lost approximately 30% of the theoretical plates (left).

Translation to a shorter narrower bore column

A real test of the Method Translator is a translation to a shorter and narrower bore column. The translation from a 30m to 15m column, from a 0.53mm ID to a 0.25mm ID column, and even more crucial, from a 20µm to 8µm phase thickness as examples. Both columns have similar efficiency; the small difference is the phase ratio - beta of 7 for 30m column vs a beta of 8 for a 15m column.

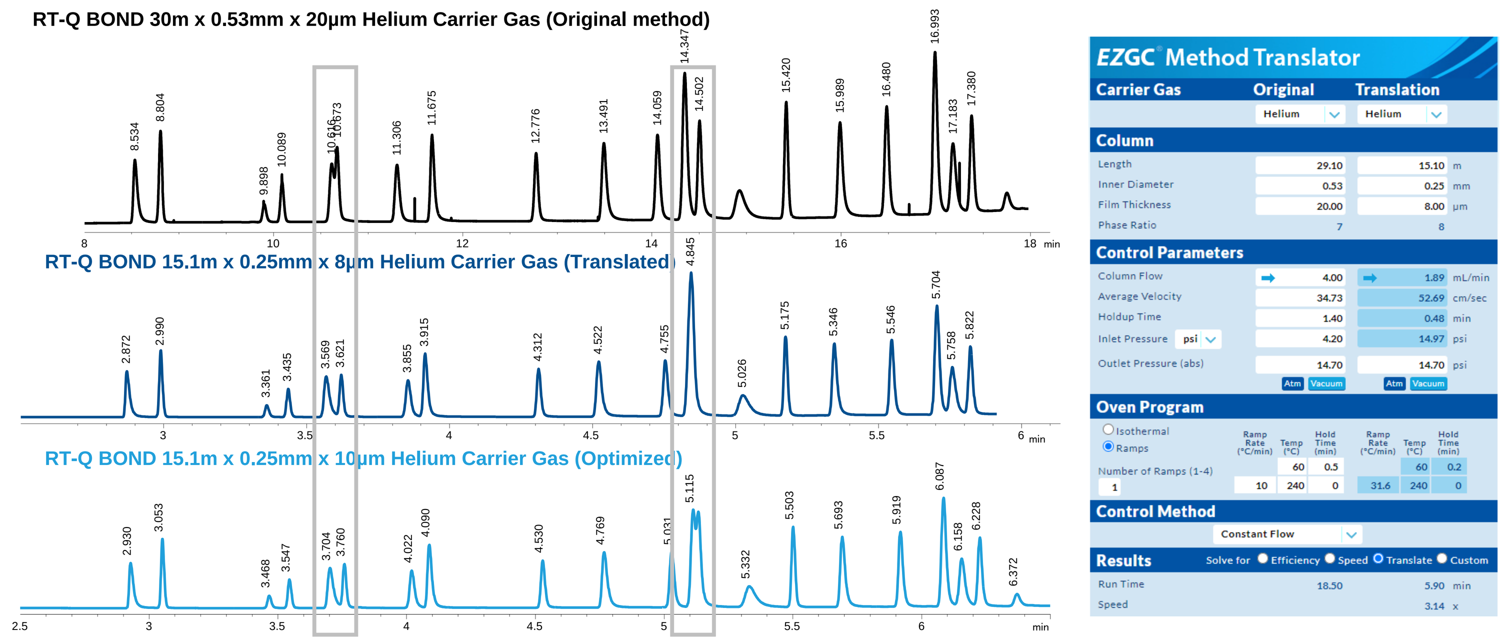


Figure 8: Top - Chromatogram using a 30m x 0.53mm x 20µm column and helium carrier gas, middle chromatogram – translated analysis to a shorter and narrower bore column 15m x 0.25mm x 8µm, bottom – optimized translated method – with reduced oven ramping rate, and increased flow to match the elution temperature in the original method. Reducing the oven heating rate or increasing column flow will lower the elution temperature of the analytes.

The translation was not 100% successful, however it offered a good starting point for method development. By modifying the original method to match the elution temperatures between both methods the resolution pattern resembles the original method. A few plausible explanations, why the translated method did not match the original method:

1. Error in determining the column dimensions
2. Beta plays a more important role than we have anticipated. Since the phase ratio between both columns is different, some compounds could have more retention than others.

Conclusion

Confirmed was that we can use a traditional GC method translator to translate the analysis method even when using PLOT columns. Analysis methods were successfully translated with a minimal method development to any alternative carrier gases, shorter/narrower bore columns, etc.