Exploration of High-Temperature Petroleum Analysis Using Comprehensive Two-Dimensional Gas Chromatography and Time-of-Flight Mass Spectrometry

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Introduction

The shift toward increasing use of heavy crude oils in the petroleum industry makes it necessary for the capabilities of instrumental analysis to follow suit. Determination of the range of hydrocarbons that can be examined is crucial for advanced techniques like two-dimensional gas chromatography coupled to time-of-flight mass spectrometry (GCxGC-TOFMS). The ability of the thermal modulator to provide crucial focusing and reinjection onto the second dimension of separation, which significantly increases the chromatographic space and peak capacity of the system, is evaluated using n-alkane and Polywax standards to test the upper limits of high-temperature analysis.

Principles of Thermal Modulation

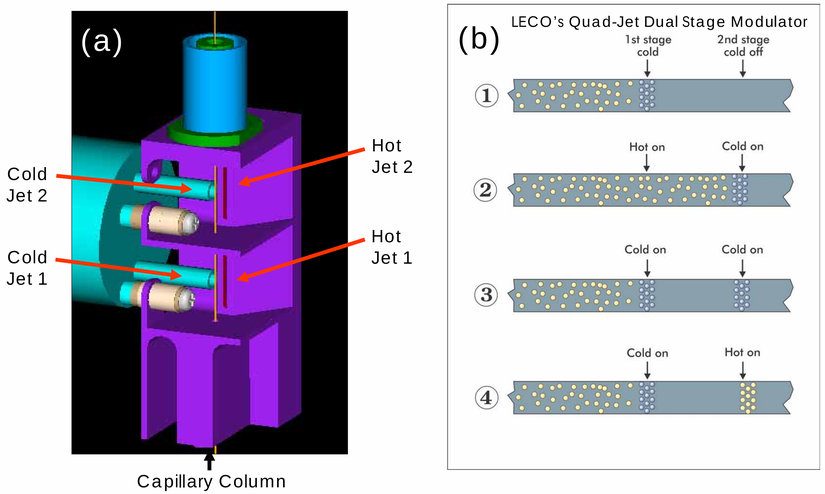

Figure 1: (a) A schematic model of LECO's Dual Stage Thermal Modulator is shown with (b) an illustrated representation of the principles of thermal modulation. The cold jet cyrofocuses analytes on the column, trapping them in a narrow band, while the hot jet releases them, "reinjecting" onto the second column.

Methods

Gas Chromatograph	Agilent 7890 with Gerstel Rail Autosampler
Injection	1μL, Split 20:1 or Splitless @ 380 °C
Carrier Gas	He @ 2.0 mL/min, Corrected Constant Flow
Column	Primary: ZB-35HT, 30 m x 0.25 mm i.d. x 0.25 μm Secondary: ZB-5HT 0.6 m x 0.25 mm i.d. x 0.10 μm
Temperature Program	1 min at 50 °C, ramped 10 °C/min to 400 °C, held 200 min Secondary oven +5 °C relative to Primary oven, Modulator +15 °C relative to Secondary oven
Modulation	MP=1s @ 0-2100s, MP=3s @ 2100-3300s, MP=6s @ 3300-5046s, MP=12s @ 5046-End
Mass Spectrometer	**LECO Pegasus 4D-C**
Transfer Line	380 °C
Ion Source Temperature	300 °C
Mass Range (m/z)	35 to 650
Acquisition Rate	1D: 10 spectra/s; GCxGC: 200 spectra/s

Chromatographic Results

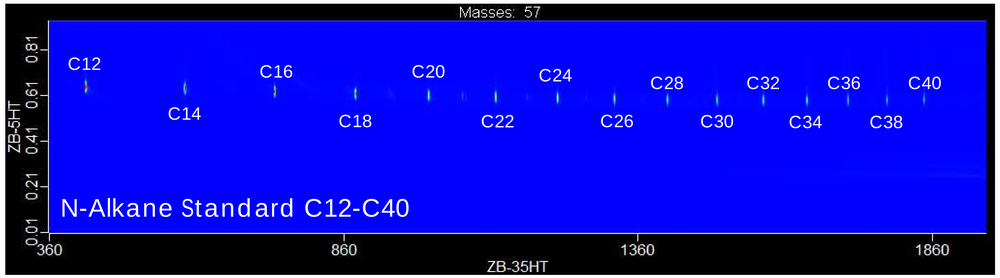

Figure 2: Contour plot showing GCxGC Acquisition of N-Alkane Standard with even-numbered carbon chain lengths from C12 to C40.

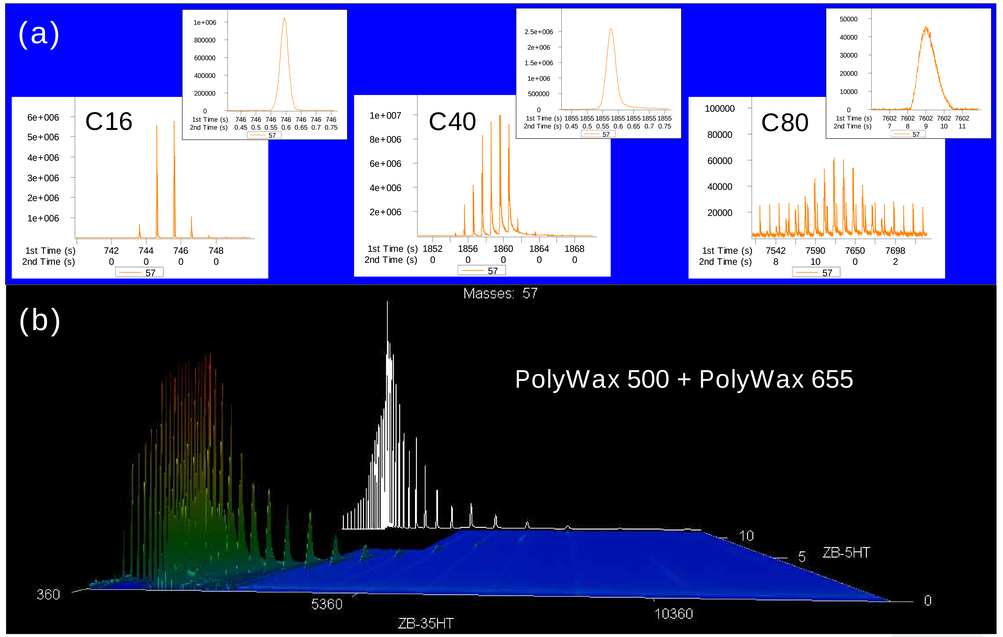

Figure 3: (a) Sections of the GCxGC chromatogram are shown for the C16, C40, and C80 peaks, with a zoom into one modulated slice of each peak. (b) 3D View showing GCxGC Acquisition of 1:1 mix of Polywax 500:PolyWax 655 standards in toluene with reconstructed 1D trace shown in white.

Counting Carbon Number

Carbon #	1st Dim. R.T. (s)	2nd Dim R.T. (s)
C12	422	0.605
C16	745	0.600
C20	1007	0.595
C24	1227	0.585
C28	1418	0.585
C32	1581	0.575
C36	1726	0.550
C40	1863	0.565
C44	1977	0.610
C48	2085	0.655
C52	2184	0.750
C56	2307	0.935
C60	2499	1.265
C64	2811	1.790
C68	3312	2.650
C72	4134	5.585
C76	5441	5.876
C80	7602	8.950
C82	9174	11.135
C84	11142	1.310*
C86	13614	5.150*

Table 1: The table above shows the 1st and 2nd dimension retention times (R.T.) of selected n-alkane compounds throughout the chromatogram, which can be used in future work as retention indices. *Note: longer retention on the secondary column caused wrap-around effects for these peaks which could not be avoided due to the upper temperature limits of the GC columns.

Conclusions

The LECO Dual Stage Quad Jet Thermal modulator is capable of trapping and refocusing n-alkanes up to at least C86, with limitations set by the maximum column temperature of 400°C. Because performance was consistent with both early and late-eluting compounds, with proportionally thin second-dimension peaks seen for both, GCxGC-TOFMS proves to be a system suitable for high-temperature petroleum analysis for C84 and beyond. Further work remains for the evaluation of other high-temperature column sets and different classes of high-temperature compounds within complex matrices.

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