High Speed PONA Analysis For Detailed Hydrocarbon Analysis Extended (DHAX) Using Hydrogen Carrier Gas For The Determination of Individual Components In Spark Ignition Fuels

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Abstract:

ASTM method D-6730-01 is specifically designed for the determination of the individual hydrocarbons present in spark ignition fuels, as well as fuel blends containing oxygenates such as MTBE, ETBE, t butanol, ethanol etc.

To maximize the resolution of these complex mixtures of spark ignition fuels, ASTM recommends a 100 meter x .0.25 mm id x 0.5um capillary column containing a deposition of 100% dimethyl polysiloxane liquid phase for the main analytical column. To control the selectivity of the aromatic compounds a short (typically 2-3 meters) tuning column containing a deposition of 5% diphenyl 95% dimethyl polysiloxane is connected to the inlet of the primary analytical column. To meet the demanding resolution and retention criteria in ASTM method D-6730-01, and in Canadian General Standards Board (CGSB) methodology for detailed hydrocarbon analysis (DHA), Restek Innovation chemists have reformulated our Rtx-1PONA column.

Project Goal

ASTM method D-6730-01 suggests using helium as the carrier gas, at a linear velocity of 24cm/sec. (approximately 2.3 ml/min). The tridecane (C13) retention time this combination yields, approximately 146 minutes, greatly limits sample throughput per day. Restek's enhanced Rtx-1PONA column meets or exceeds all criteria in the method, but does so in 30% less time: retention time for C13 is 97 minutes, using helium as the carrier gas.

In most applications hydrogen is a better alternative to helium as the carrier gas, because it can be used at much higher linear velocities without compromising critical resolutions. A revision to ASTM D 6730-01 proposed by Neil Johansen Inc. (Aztec, New Mexico), in association with Envantage Analytical Software Inc. (Cleveland Ohio), has established optimal DHAX (detailed hydrocarbon analysis-extended) parameters, including specifying hydrogen as the carrier gas. Using these conditions analysis time is reduced to within 71 minutes (C13) – a 53% reduction versus using helium as the carrier gas. The method is also extended to include middle distillates having final boiling points up to 509 C / 948 F. (n-38).

Introduction

Restek provided Neil Johansen Inc. with an enhanced Rtx 1 PONA column (100m x 0.25mm id x .5um df) and an Rtx 5 PONA tuning column for DHAX method development. Three (3) meters of the Rtx 5 tuning column was connected to the main analytical column, (Rtx 1 PONA) through a Universal Angled Press-tight Connector and was installed in a PerkinElmer Autosystem XL GC equipped with a flame ionization detector and programmable pneumatic control. The data system used was ChromPerfect Spirit (Justice Laboratory Software, Denville, NJ). The individual hydrocarbons were identified by using Dragon-DHA software, developed by Envantage Analytical Software Inc. in association with Neil Johansen Inc., which uses algorithms to process high-resolution chromatographic data.

The proposed DHAX method was optimized with hydrogen carrier gas at a rate of 3.62 mls/minute, constant flow, producing a linear velocity of 55 cm/sec. The column was briefly conditioned for 30 minutes at 300 C. The temperature was then lowered to 35 C. The dead time was adjusted to elute methane in 3.05 minutes $\pm$ 0.05 minutes, then a DHA Oxygenate setup blend was injected to determine the column's suitability for the method.

Figure # 1 illustrates the front end slice of the 30 component oxy set-up blend analysis. Key measurements such as: column efficiency, peak skewness, resolution and K' are calculated from this data. The calculated values shown here indicate the analytical column easily conforms to the ASTM D-6730-01 criteria.

Once established that the Rtx 1 PONA met method criteria, GC oven program parameters were entered and trial injections of the DHA/Oxy setup blend were begun. The analysis is permitted to run until the elution of C13 (tridecane). Based on the resolution of five critical pairs: t butanol / 2 methylbutene 2, 1 methylcyclopentene / benzene, 2,3,3 trimethylpentane / toluene, p xylene / 2,3 dimethylheptane, and 1 methylnaphthalene / C13, the tuning column length is incrementally reduced until the method criteria are met. In this example, the final tuning column length is 2.36 meters. Figure # 2 illustrates the complete 30 component Oxy set-up blend analysis. All critical pairs are sufficiently resolved, and meet method criteria. Tridecane (C13) retention time is less than 71 minutes. A 53% reduction in analysis time using hydrogen carrier gas, as compared to using helium.

Figures # 3-6 illustrate the analysis of the PONA VI reference standard processed by Dragon DHA software. Note: The analysis of the 400-plus component PONA VI reference standard, plus a complete analytical report generated by Dragon-DHA software, can also be viewed on the Restek website: www.restek.com/PONA

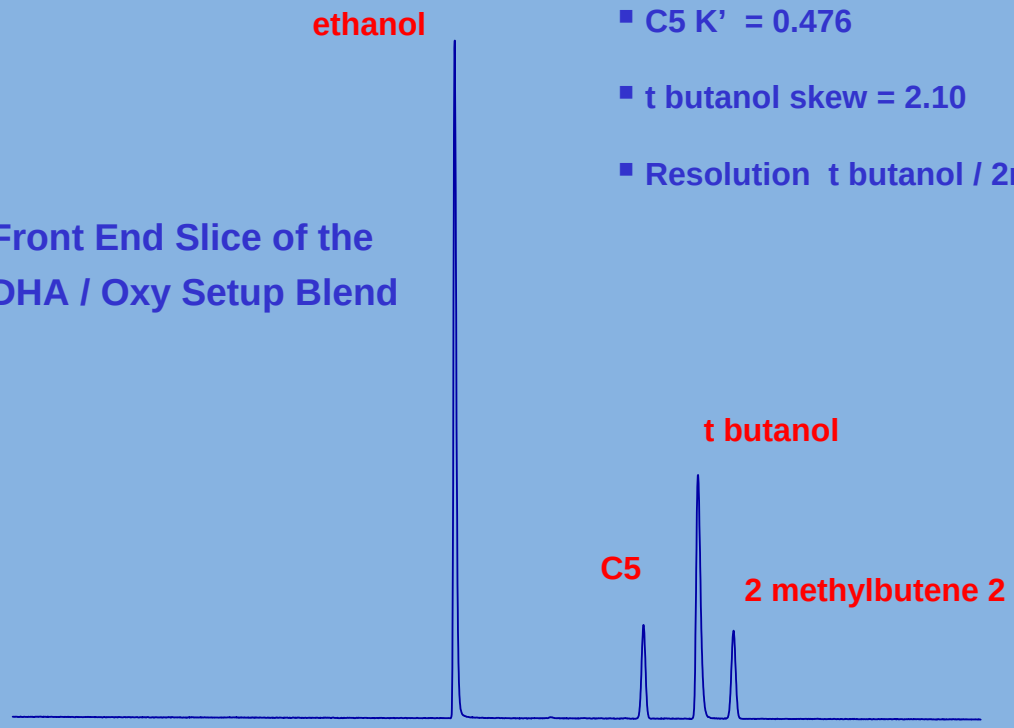
Fig. 1

Rtx 1 PONA 100 meter x .25mm x .5um

Oven temperature 35 C Isothermal
Constant Flow H2 @ 3.62 mls / min. (55 cm/sec.)

- **C5 efficiency = 586,825 total theoretical plates**
- **C5 K' = 0.476**
- **t butanol skew = 2.10**
- **Resolution t butanol / 2methylbutene 2 = 5.39**

Front End Slice of the DHA / Oxy Setup Blend

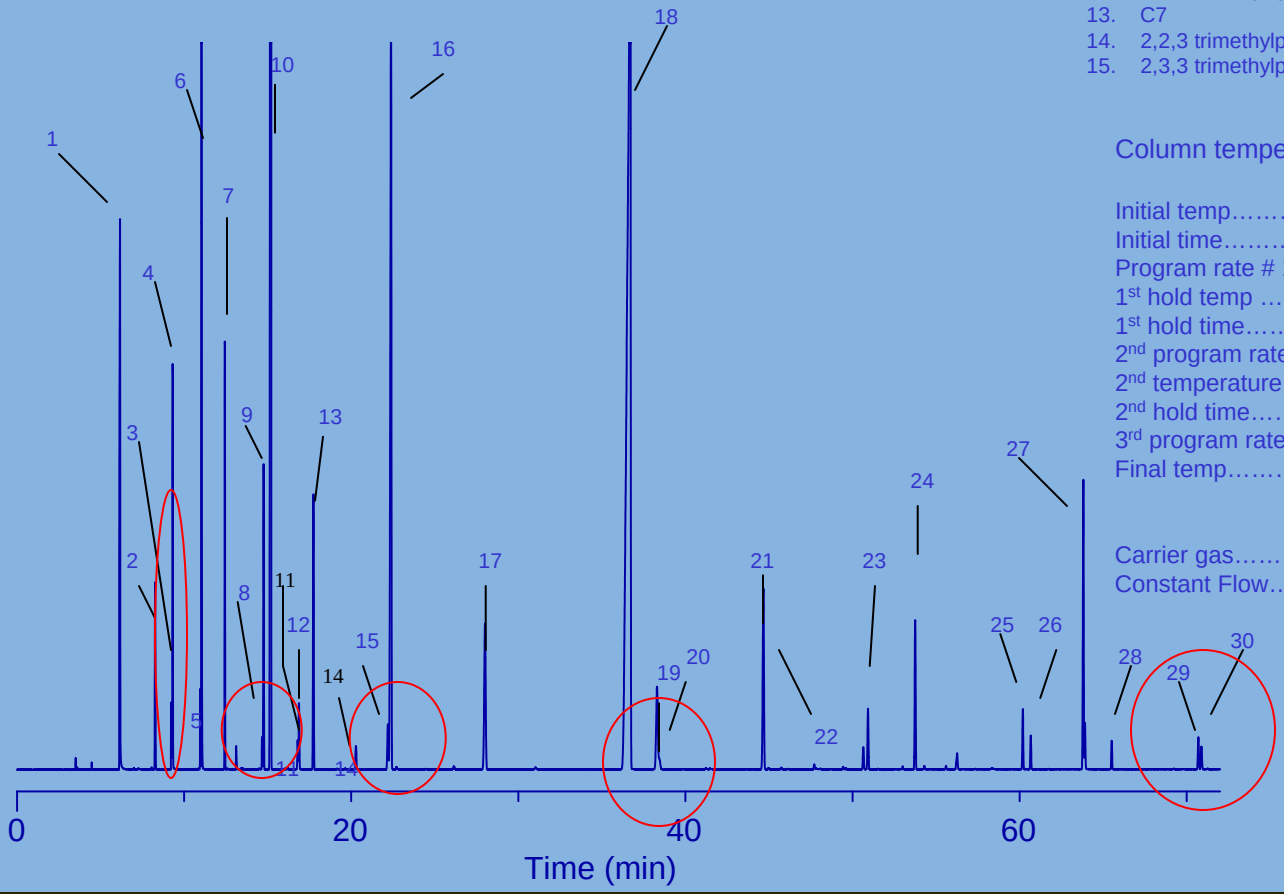


Data courtesy of Neil Johansen in association with Envantage Analytical Software, Inc.

Fig. 2

Rtx 1 PONA 100 meters x 0.25mm x .5um
Tuning column; Rtx 5 2.36 meters x 0.25mm x 1um

Data courtesy of Neil Johansen in association with
Envantage Analytical Software, Inc.

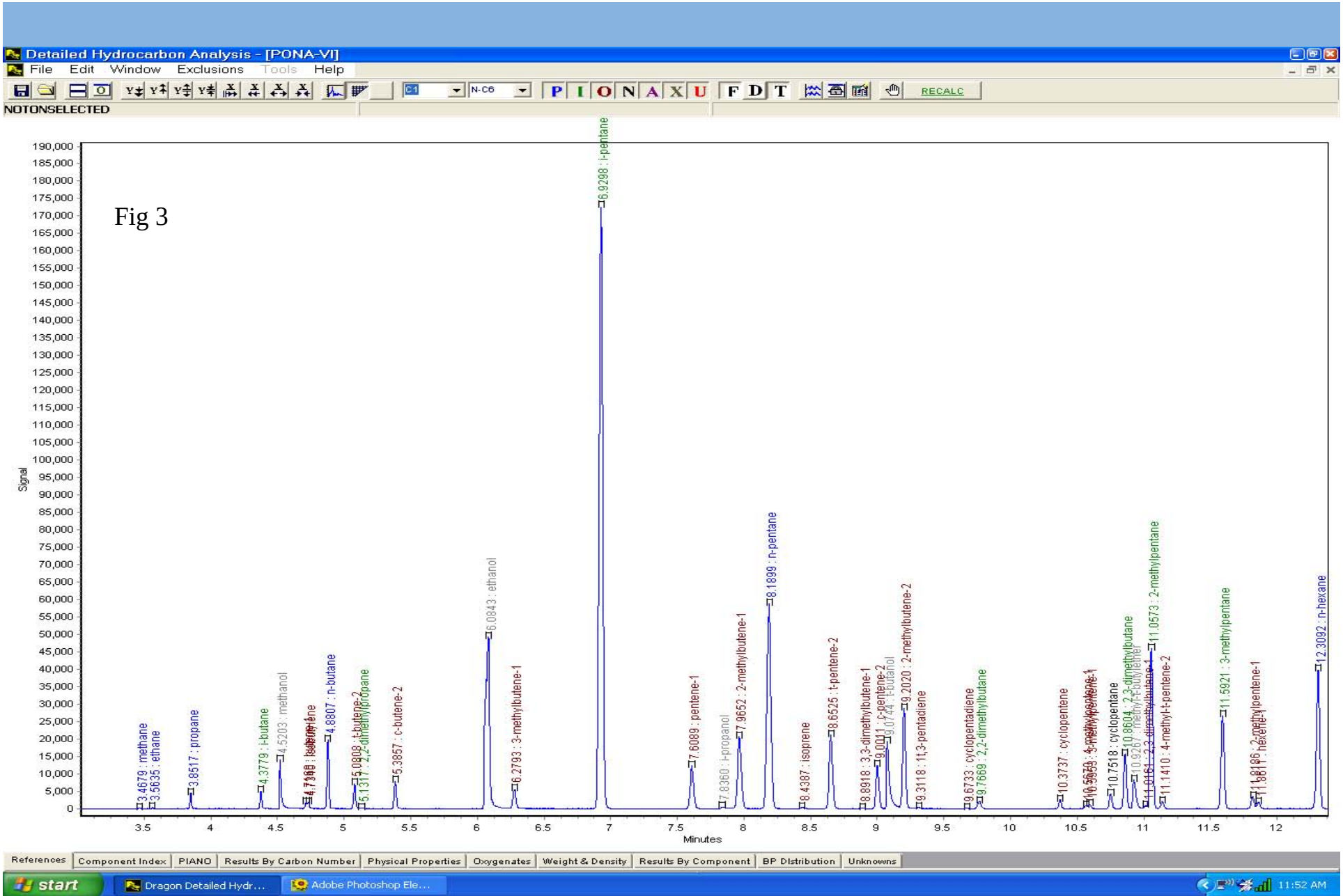


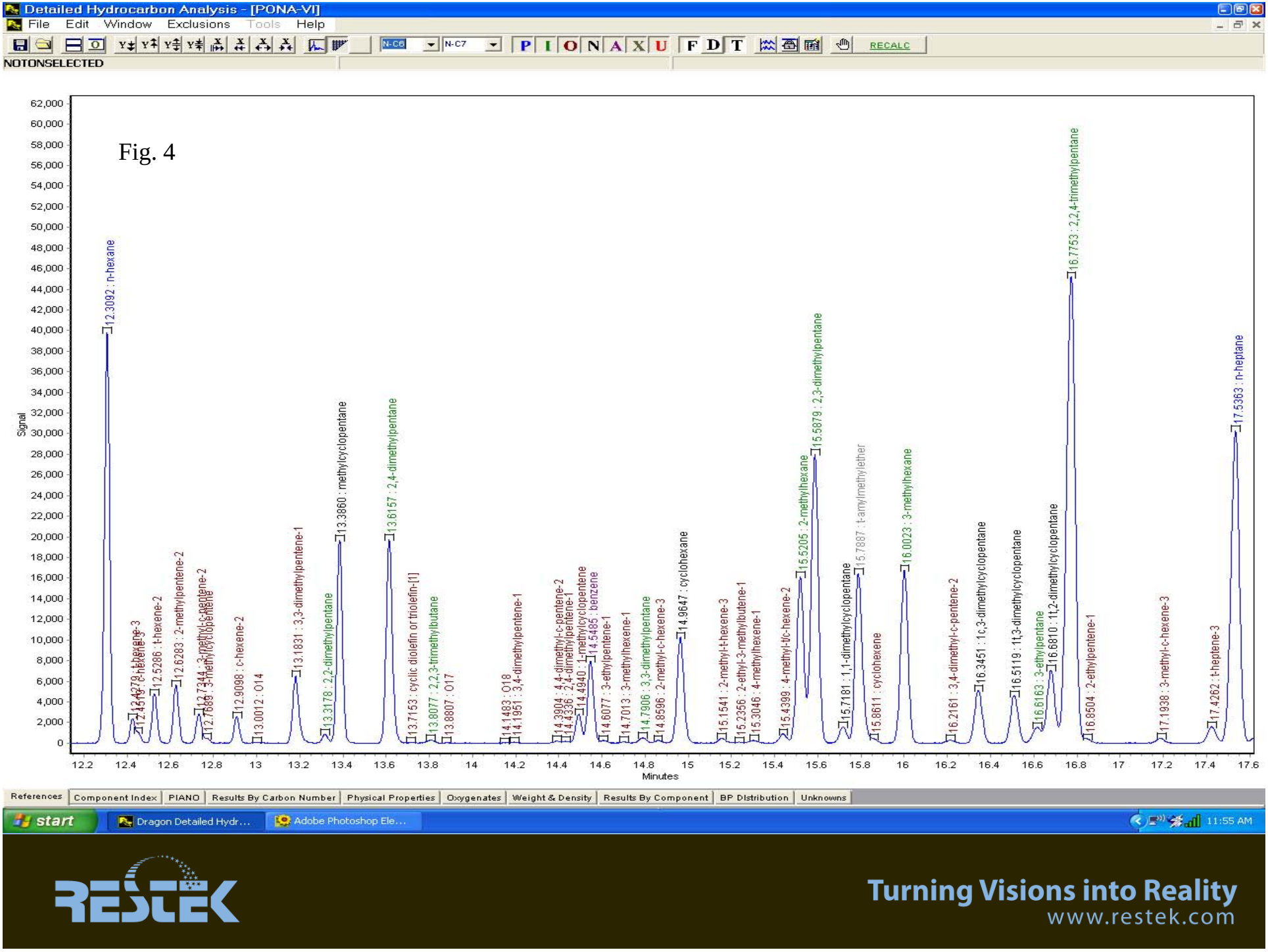
Peak #
1. ethanol
2. C5
3. t butanol
4. 2 methylbutene 2
5. 2,3 dimethylbutane
6. MTBE
7. C6
8. 1 methylcyclopentene
9. Benzene
10. cyclohexane
11. 3 ethylpentane
12. 1 t 2 dimethylcyclopentane
13. C7
14. 2,2,3 trimethylpentane
15. 2,3,3 trimethylpentane
16. Toluene
17. C8
18. Ethylbenzene
19. P xylene
20. 2,3 DMH
21. C9
22. 5 methylnonane
23. 1,2 methylethylbenzene
24. C10
25. C11
26. 1,2,3,5,tetramethylbenzene
27. Naphthalene
28. C12
29. 1 methylnaphthalene
30. C13

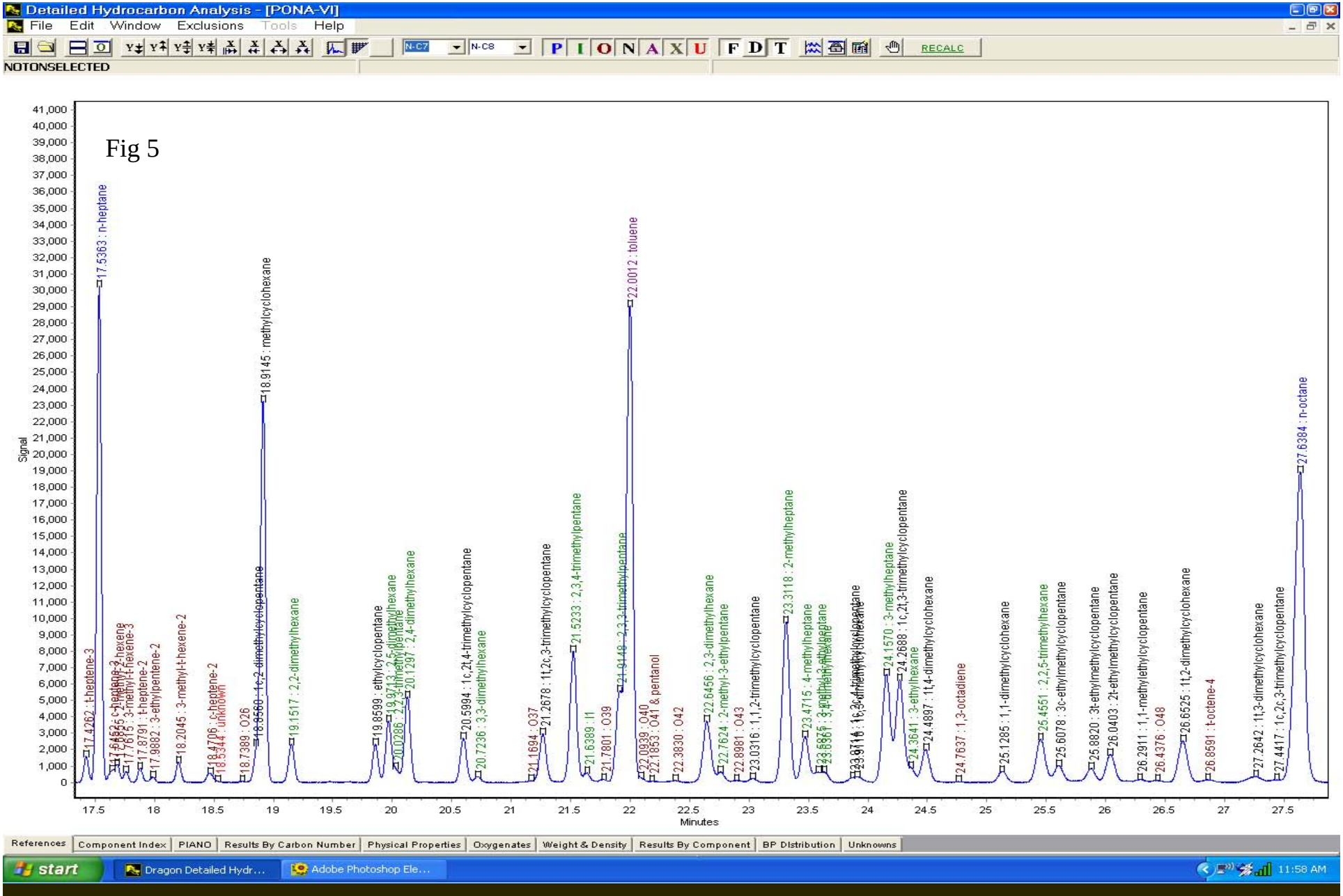
Column temperatrue program

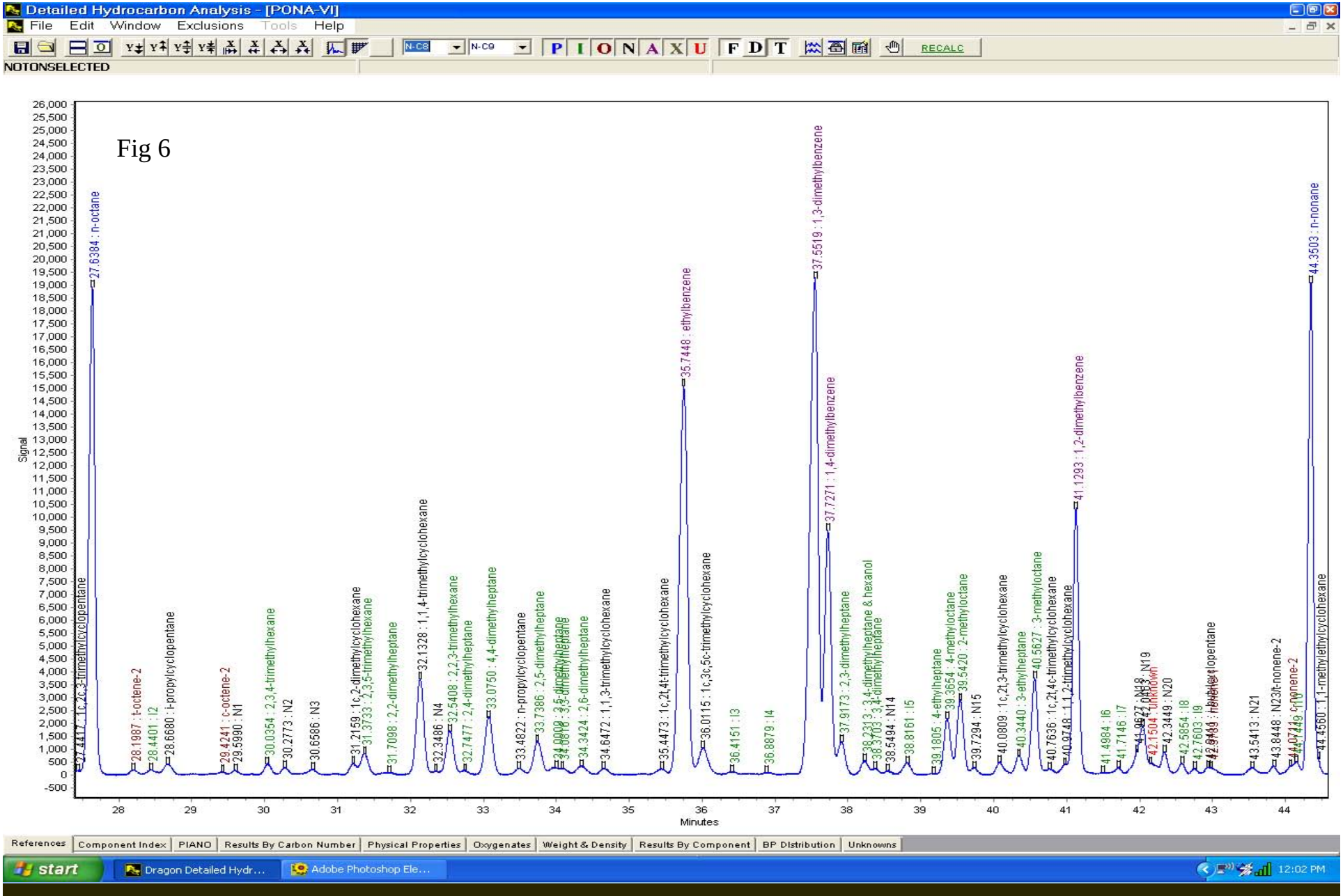
Initial temp……. 5C
Initial time…….. 8.32 min (elution time of C5)
Program rate # 1…22 C / min.
1st hold temp ……..48 C
1st hold time…….26.32 min. (elution of ethylbenzene)
2nd program rate….3.20 C / min.
2nd temperature…..141 C (elution of dodecane)
2nd hold time…….. 0 min.
3rd program rate… .1 C / min.
Final temp……300 C.

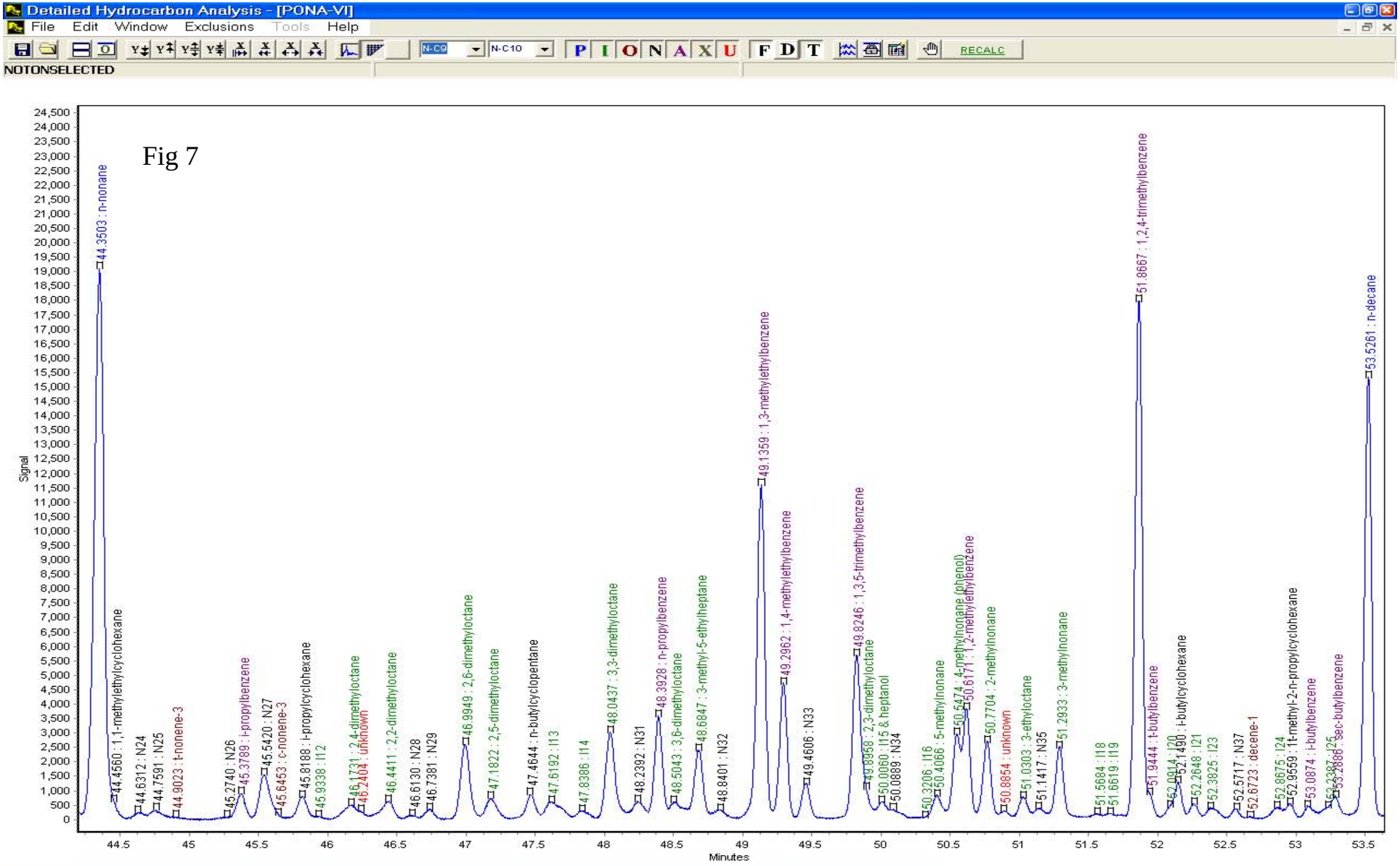
Carrier gas……..H2
Constant Flow……3.62 cc/min. (55 cm / sec)

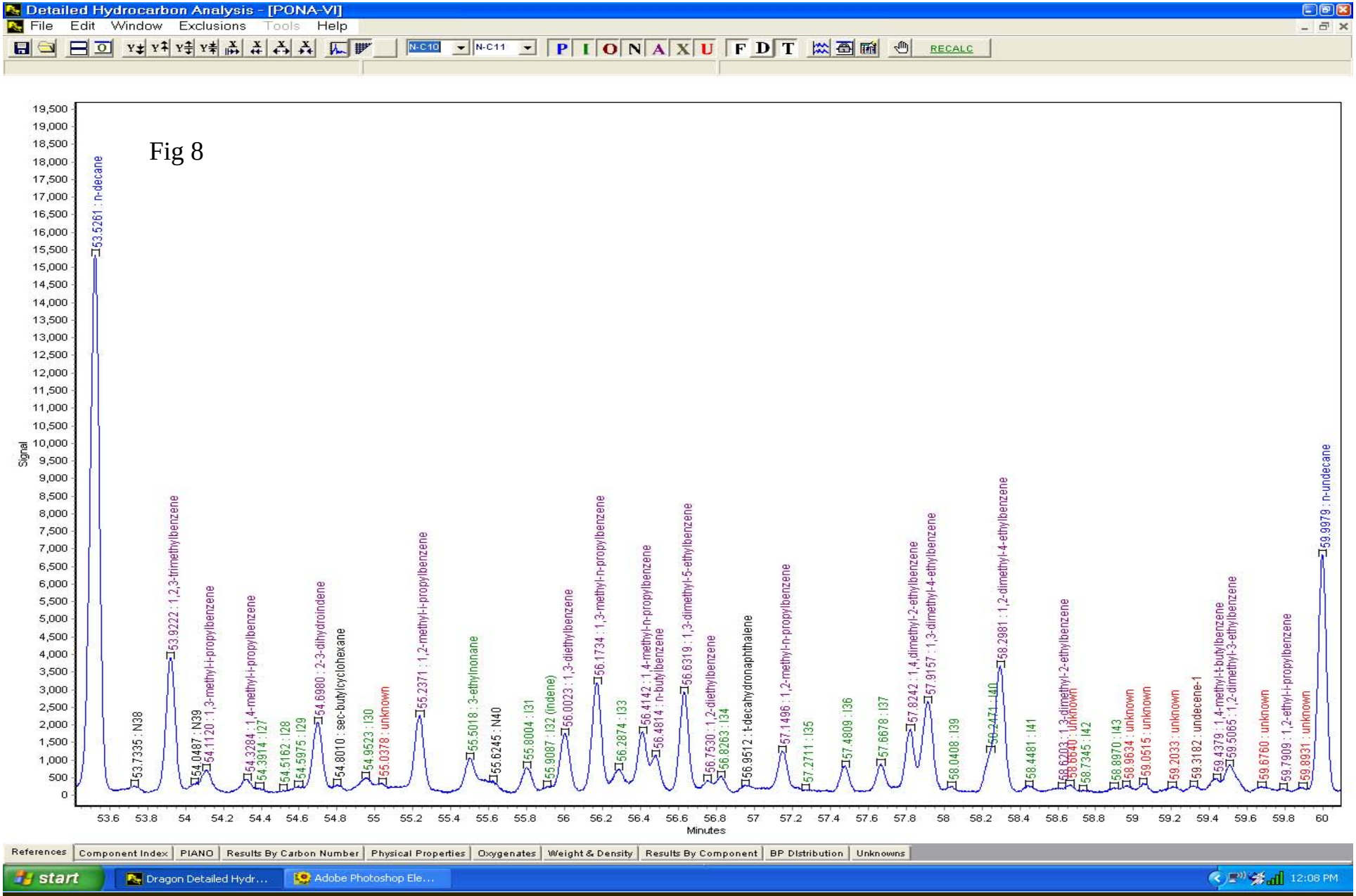


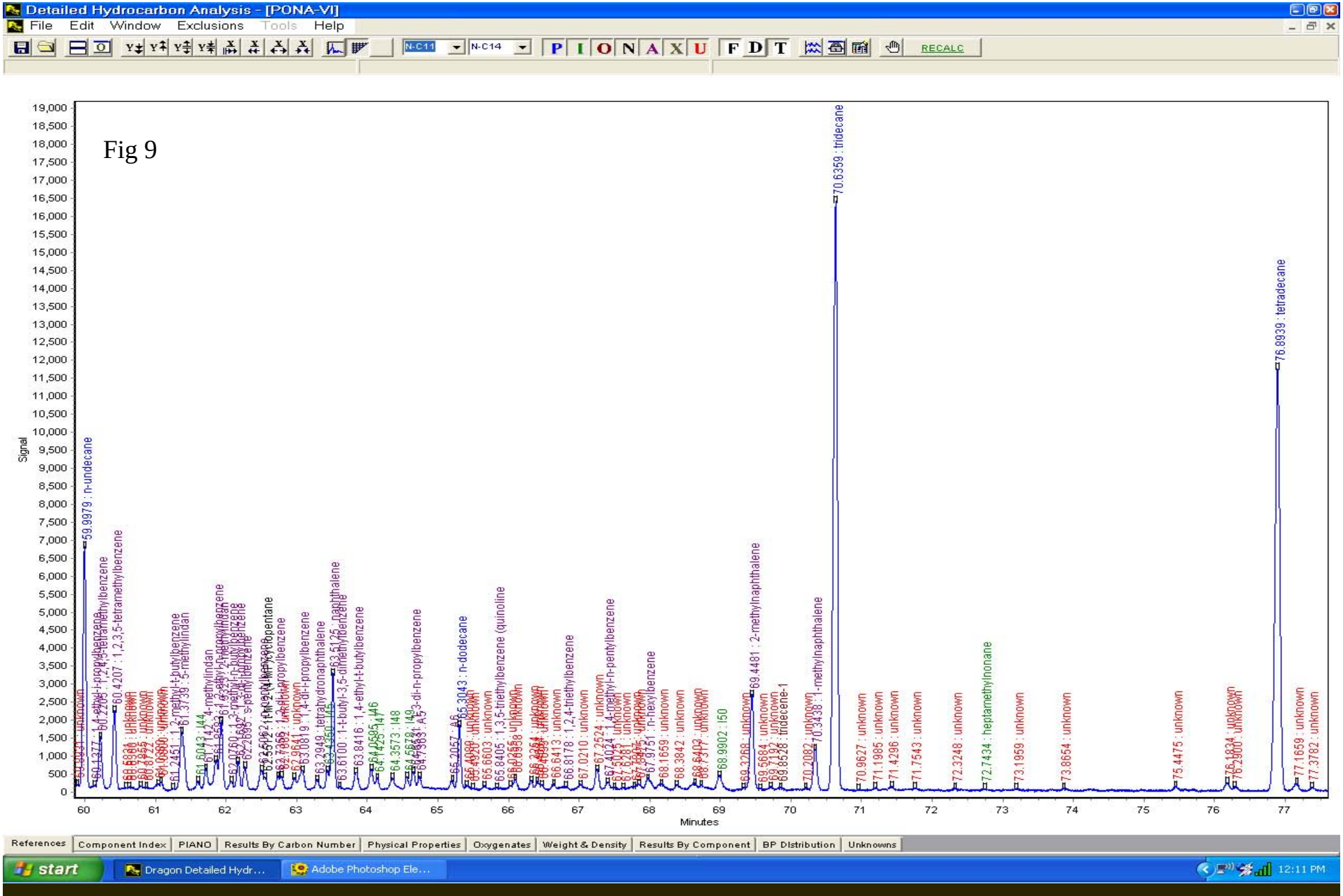












Conclusion:

The benefits of hydrogen carrier gas are obvious: all critical components are resolved, per method D-6730-01, in the greatly reduced time of 70.5 minutes (C13), verses 146 minutes or 97 minutes using helium carrier gas. Relative to the results anticipated in the method, we virtually doubled sample throughput.

To assure that all Rtx 1 PONA columns will perform as demonstrated, each column is evaluated for film thickness, column efficiency, peak skewness, selectivity, resolution, and bleed to guarantee performance and reproducibility.