AppNote 2/2006

Accelerating Single or Dual Column Environmental Methods using Low Thermal Mass Column Technology and Software-Controlled Independent Module Heating

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Keywords
Fast GC, Environmental, GC-MS

Abstract
Routine analytical methods employing mass spectral analysis on a gas chromatograph are often plagued with long run times in order to achieve acceptable separations. The Modular Accelerated Column Heater (MACH) System from GERSTEL is easily retrofitted to the Agilent 6890 GC with Mass Selective Detection. MACH is based on Low Thermal Mass (LTM) technology, that enables very fast temperature ramping and cooling, resulting in short cycle times and high sample throughput. Excellent linearity and precision in the analytical data is maintained, all performance gains are accomplished using conventional capillary columns, existing methods can be directly transferred and accelerated.

The MACH system is designed to allow two GC columns to be heated independently on the same GC, thus enabling independent optimization of temperature ramps for standard dual column confirmation applications. Furthermore, the system provides the flexibility needed to separate complex samples using inexpensive and efficient 2D heart cutting with different column phases on the one GC, as well as running two relative short columns, with different phases, independently heated in series to possibly allow very complicated chromatography to be run much faster.

Specific data will be reviewed illustrating performance when accelerating various environmental methods, with a focus on methods utilizing the Agilent 5975 MSD.

Introduction

Environmental contract laboratories are constantly faced with shrinking margins and the pressure to increase throughput without sacrificing data quality. Many techniques have been used in the past to reduce GC runtimes. Such techniques have employed high-voltage GC ovens, narrow bore columns, high pressure injections, supplemental oven heaters, and directly heated columns. While directly heating a narrow bore column has yielded excellent Fast GC results [1, 2], this technique has long been plagued with issues involving leaks, inability to use a pre-column, and reduced column lifetime. These issues are resolved in the GERSTEL MACH, providing separations normally associated with directly heated columns in a leak-free, user friendly package.

Figure 1 is a photograph of a two column MACH system installed on an Agilent 6890 with 5973 MSD. With this equipment, the columns reside in modules outside of the actual GC oven. Almost any brand or size of capillary GC column may be used. The columns are wound into a torus with a length of heater wire and sensor wire (Figure 2). The assembled torus can therefore be heated and cooled rapidly with very little electrical energy. Temperature heating rates in excess of 1000°C/min are possible, with cool down times of 30 seconds to three minutes, depending on the column length, are a vast improvement over standard GC ovens.

Figure 1. Dual column MACH connected to 6890 GC system.

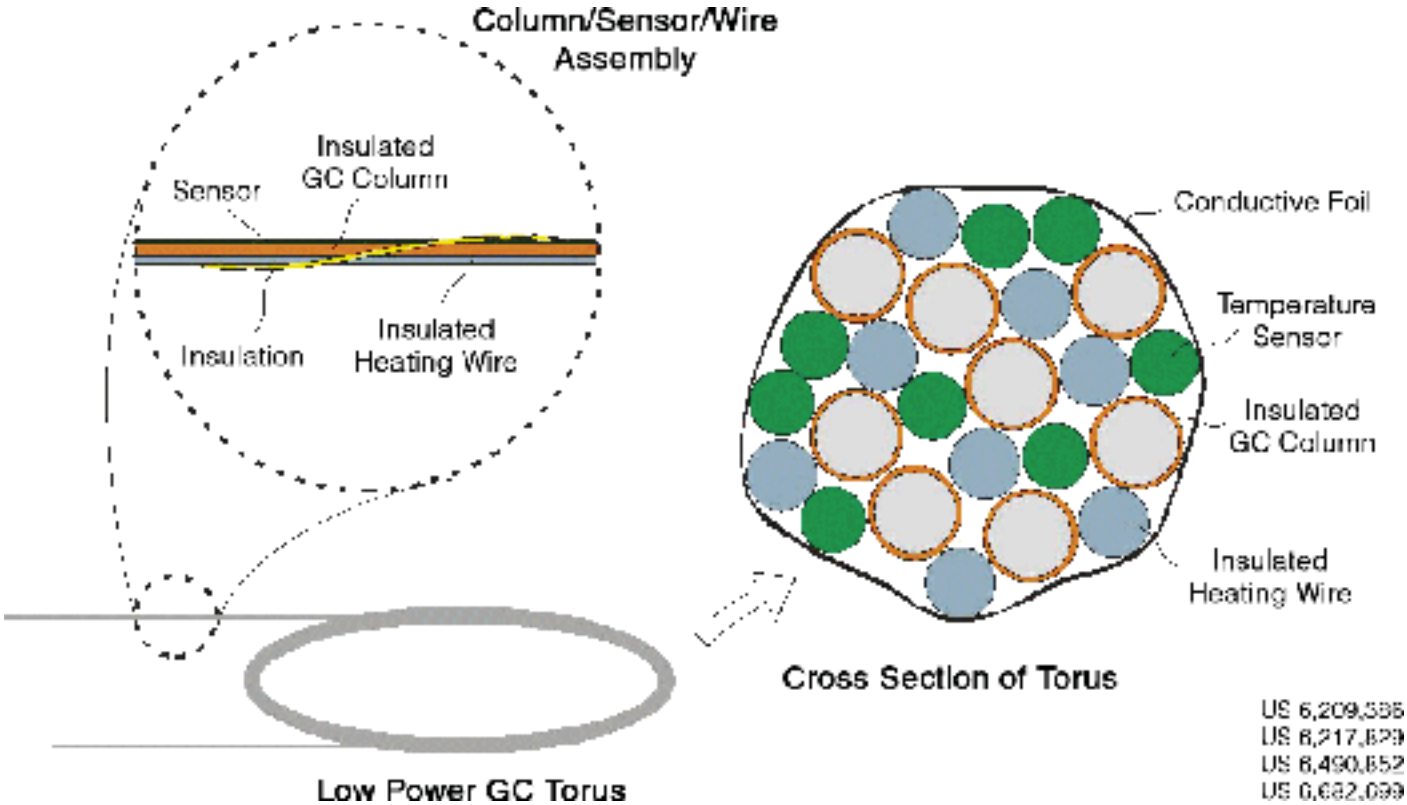

Figure 2. Low thermal mass column module diagram.

Column connections are made by attaching two lengths of fused silica capillary to the two columns ends, and connecting these to the injector and detector respectively using standard Valco and Agilent fittings.

Fast separations of two types of common environmental samples are illustrated below, Polynuclear Aromatic Hydrocarbons (EPA Method 610), and Semivolatile Organics (EPA Method 8270).

Experimental

Instrumentation. The Semivolatiles (8270) and PAH (610) separations were performed using the GERSTEL MACH system installed on an Agilent 6890N with 5975 Mass Selective Detector, a split/splitless inlet, and a GERSTEL MPS 2 autosampler.

Analysis conditions.

Injection:	1 µL, MPS 2
GC Inlet:	split 50:1; 280°C
GC Oven:	280°C, held for duration
MACH Module:	20 m Rtx®-5Sil-MS (Restek), MACH format d_i = 0.18 mm d_f = 0.18 µm He, P_i = 14.6 psi 35°C (0.5 min); 600°C/min; 120°C; 25°/min; 320°C (1.5 min)
MSD:	scan, 50-350 amu, 19.7 scans/s

Results and Discussion

Figure 3 is a chromatogram obtained using conventional GC conditions for the EPA Method 610 (courtesy of Restek Corp., Bellefonte, PA). Method parameters are listed in the figure. The method involves a fairly rapid ramp for a conventional oven, 25°C/min, with a slower 5°C/min ramp around the region of benzo[b]fluoranthene and benzo[k]fluoranthene elution. In addition, hydrogen was used as carrier gas to provide faster separation. The benzo[b]- and [k]fluoranthene pair represents one of the most difficult separations in this analysis. Peak separations of 50% or better are normally considered acceptable.

The MACH separation shown in Figure 4 compares favorably with the conventional separation in Figure 3. This analysis using the MACH system was begun at 35°C in order to achieve good solvent focusing and then ramped rapidly to 120°C to begin the separation. Using the enhanced ramp rates and flexibility of the MACH system, we were able to achieve comparible separation in less than 2/3 of the time, the fast cool-down of the system cut the total cycle time to about 50% of the standard cycle time.

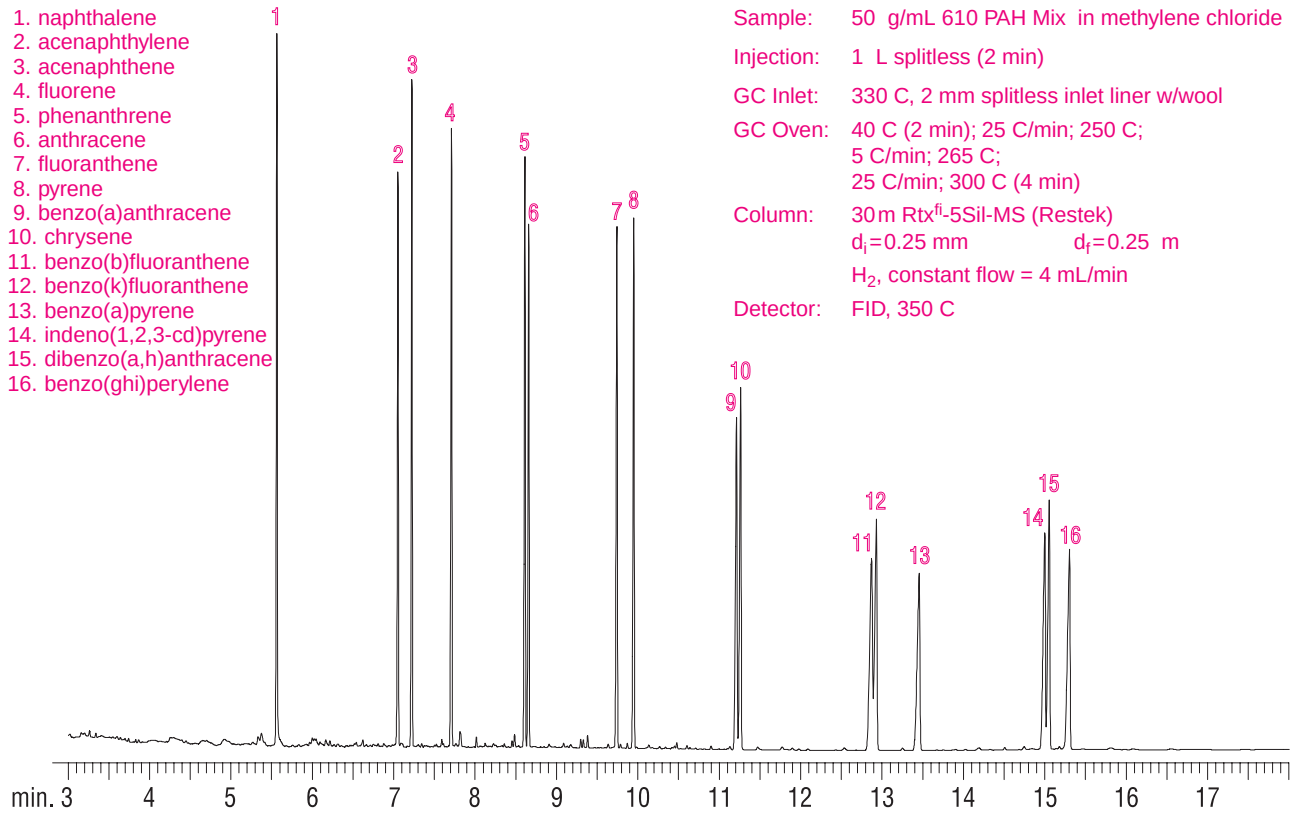

Figure 3. Conventional chromatogram for EPA method 610.

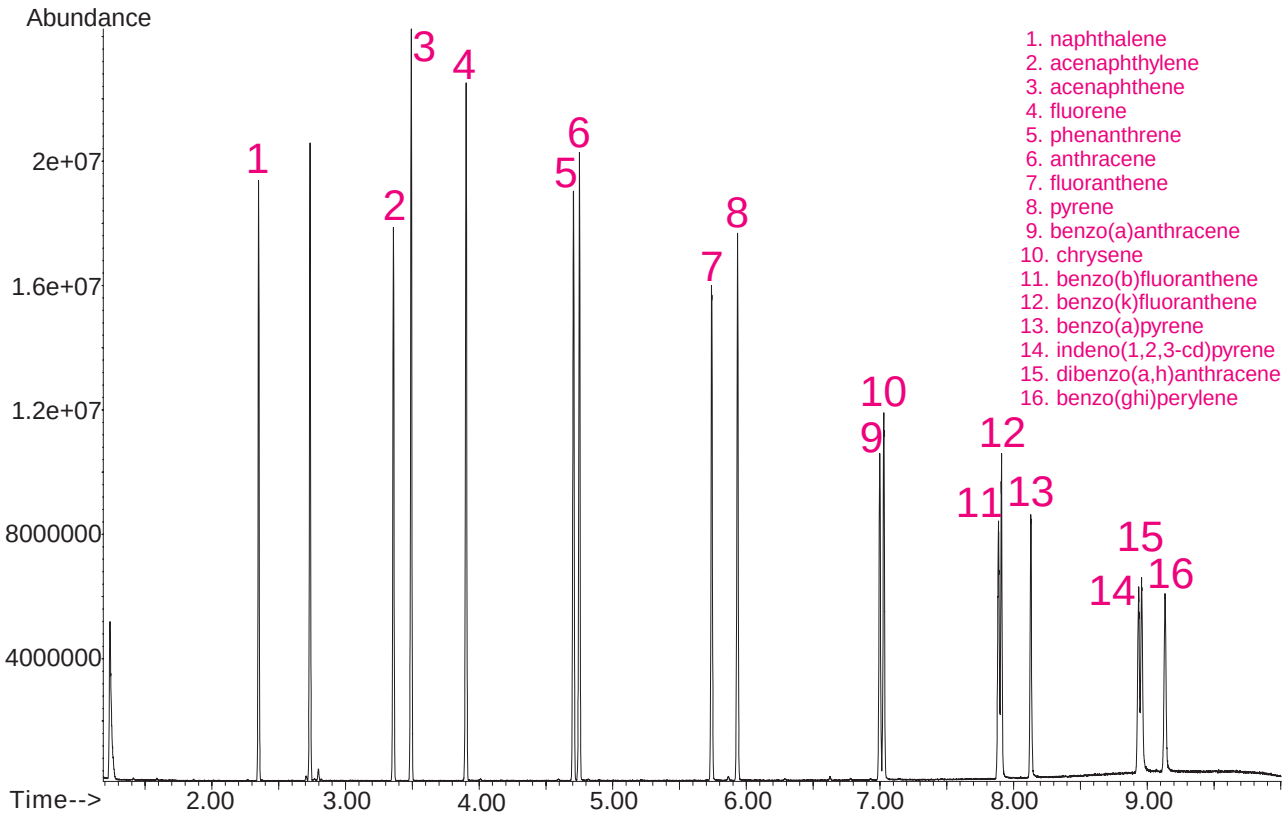

Figure 4. MACH chromatogram for EPA method 610.

Figure 5 is a chromatogram obtained using conventional GC conditions for EPA Method 8270 (Courtesy of Restek Corp., Bellefonte, PA). Method parameters are listed in the figure. This method also involves a fairly rapid ramp for a conventional oven, 20°C/min, with a slower 6°C/min around the region of benzo[b]fluoranthene and benzo[k]fluoranthene elution.

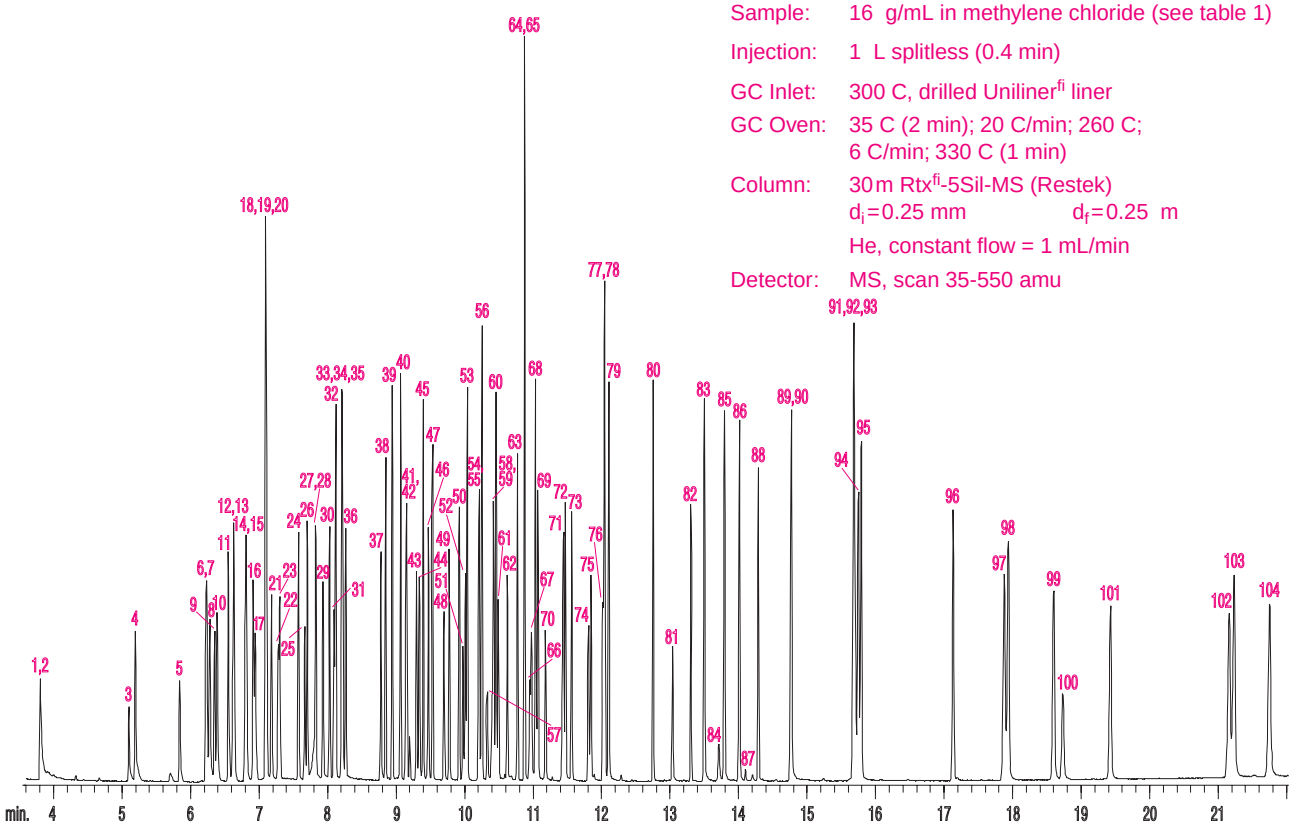

Figure 5. Conventional chromatogram for EPA method 8270.

1. N-nitrosodimethylamine
2. pyridine
3. methyl methanesulfonate
4. 2-fluorophenol
5. ethyl methanesulfonate
6. phenol-d6
7. phenol
8. aniline
9. bis(2-chloroethyl)ether
10. 2-chlorophenol
11. 1,3-dichlorobenzene
12. 1,4-dichlorobenzene-d4
13. 1,4-dichlorobenzene
14. 1,2-dichlorobenzene
15. benzyl alcohol
16. 2-methylphenol
17. bis(2-chloroisopropyl)ether
18. acetophenone
19a. 4-methylphenol
19b. 3-methylphenol
20. N-nitroso-di-*n*-propylamine
21. hexachloroethane
22. nitrobenzene-d5
23. nitrobenzene
24. isophorone
25. 2-nitrophenol
26. 2,4-dimethylphenol
27. bis(2-chloroethoxy)methane
28. benzoic acid
29. 2,4-dichlorophenol
30. 1,2,4-trichlorobenzene
31. naphthalene-d8
32. naphthalene
33. 2,6-dichlorophenol
34. 4-chloroaniline
35. hexachloropropene
36. hexachlorobutadiene
37. 4-chloro-3-methylphenol
38. isosafrole
39. 2-methylnaphthalene
40. 1-methylnaphthalene
41. hexachlorocyclopentadiene
42. 1,2,4,5-tetrachlorobenzene
43. 2,4,6-trichlorophenol
44. 2,4,5-trichlorophenol
45. 2-fluorobiphenyl
46. safrole
47. 2-chloronaphthalene
48. 2-nitroaniline
49. 1,4-naphthoquinone
50. dimethyl phthalate
51. 1,3-dinitrobenzene
52. 2,6-dinitrotoluene
53. acenaphthylene
54. acenaphthene-d10
55. 3-nitroaniline
56. acenaphthene
57. 2,4-dinitrophenol
58. pentachlorobenzene
59. 4-nitrophenol
60. dibenzofuran
61. 2,4-dinitrotoluene
62. 2,3,4,6-tetrachlorophenol
63. diethyl phthalate
64. fluorene
65. 4-chlorophenyl phenyl ether
66. 4-nitroaniline
67. 4,6-dinitro-2-methylphenol
68. diphenylamine
69. azobenzene
70. 2,4,6-tribromophenol
71. phenacetin
72. 4-bromophenyl phenyl ether
73. hexachlorobenzene
74. pentachlorophenol
75. pentachloronitrobenzene
76. phenanthrene-d10
77. dinoseb
78. phenanthrene
79. anthracene
80. di-*n*-butylphthalate
81. 4-nitroquinoline-1-oxide
82. isodrin
83. fluoranthene
84. benzidine
85. pyrene
86. *p*-terphenyl-d14
87. Aramite
88. chlorbenzilate
89. Kepone
90. butyl benzyl phthalate
91. benzo(a)anthracene
92. 3,3'-dichlorobenzidine
93. chrysene-d12
94. chrysene
95. bis(2-ethylhexyl)phthalate
96. di-*n*-octyl phthalate
97. benzo(b)fluoranthene
98. benzo(k)fluoranthene
99. benzo(a)pyrene
100. perylene-d12
101. 3-methylcholanthrene
102. indeno(1,2,3-cd)pyrene
103. dibenzo(a,h)anthracene
104. benzo(ghi)perylene

Table 1. Peak Identifications for Figure 5.

Comparing the conventional separation with the MACH separation for a 76-component subset of the key compounds shown in Figure 6, using the same temperature program developed for the PAH separation, enabled us to achieve a similar separation in less than half the time of the conventional analysis. Benzo[b]fluoranthene and benzo[k]fluoranthene are separated by at least 60%. (Figure 7B).

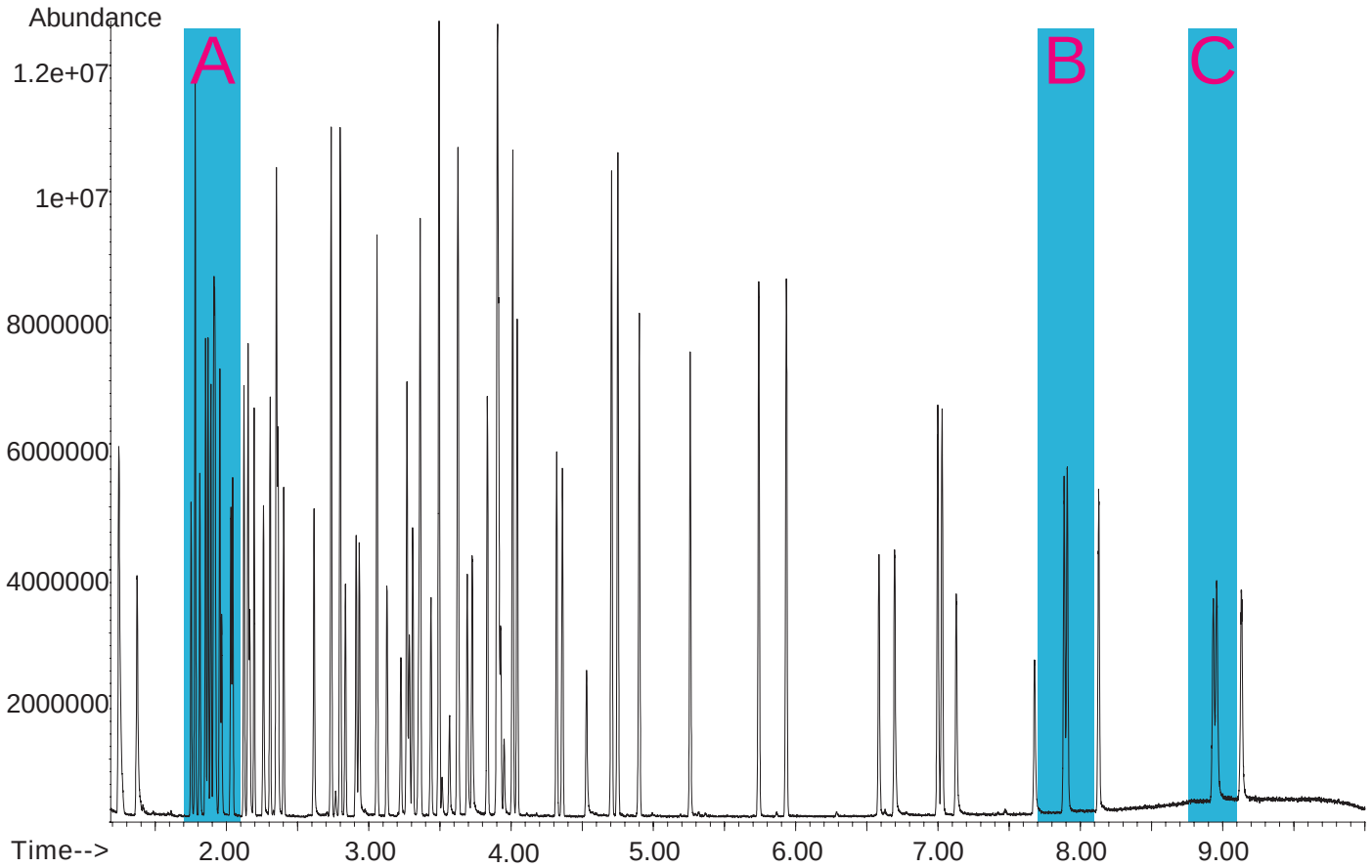

Figure 6. MACH chromatogram for EPA method 8270.

Additionally, as shown in Figure 7, other difficult regions in this separation, such as 1,3-dichlorobenzene, 1,4-dichlorobenzene, and 1,2-dichlorobenzene (7A) and indeno[1,2,3-cd]pyrene and dibenzo[a,h]anthracene (7C), are satisfactorily resolved. Resolving the aniline/bis(2-chloroethyl)ether pair will require some additional temperature program optimization.

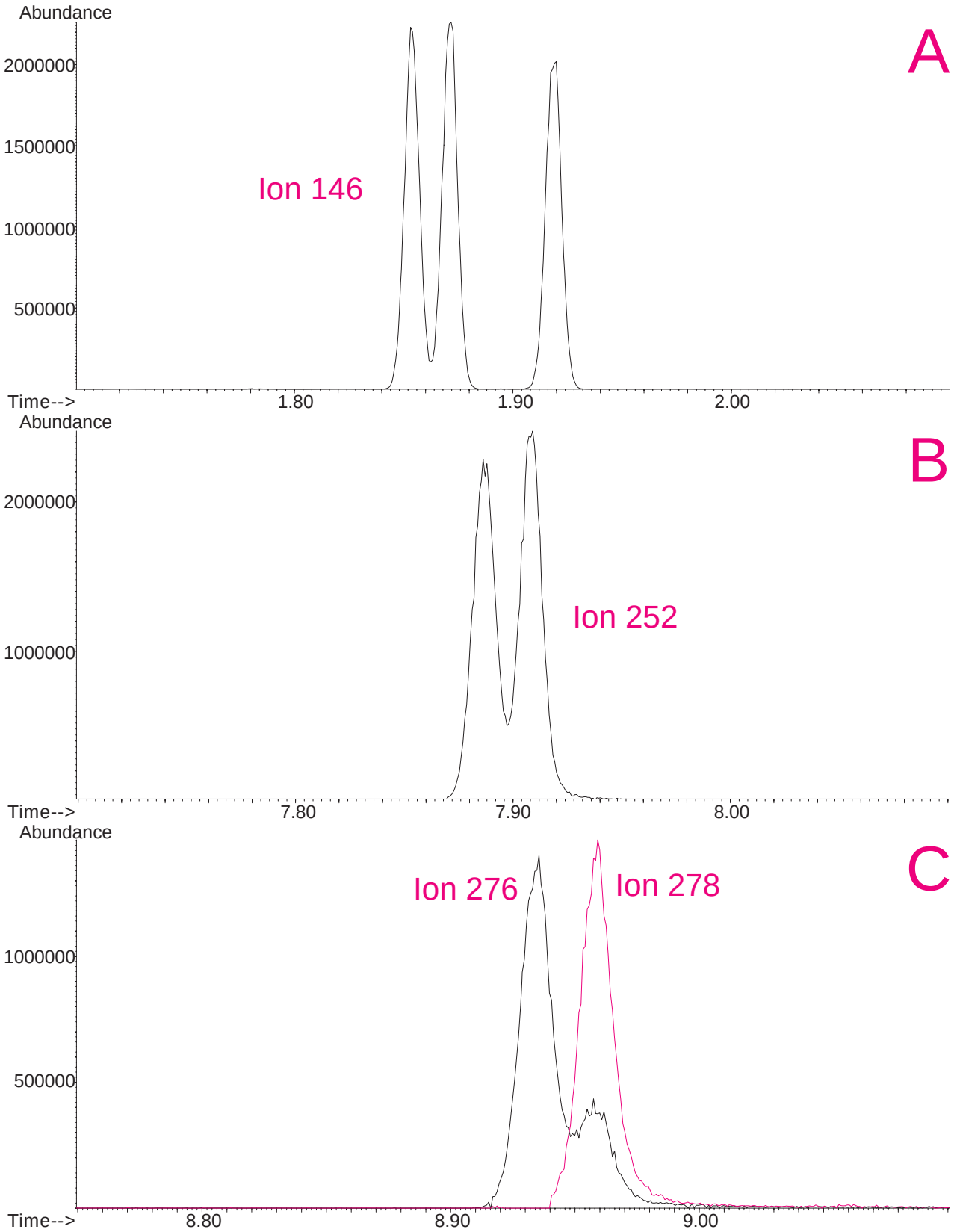

Figure 7. Highlighted regions from MACH 8270 chromatogram.

Conclusions

The enhanced capabilities of the MACH open a new door of opportunity in GC analysis. The ability to start at a low temperature, and then rapidly heat the column to a more suitable start temperature for rapid separation provides the analyst with the best of both worlds. Furthermore, precise control of temperature holds and negative ramps are available to help optimize fast separations.

We showed that by using the fast heating and cooling capabilities of the MACH we could accelerate conventional EPA methods 610 and 8270, cutting cycle time in half which can potentially double throughput on a single instrument.

Finally, the ability to use Fast GC techniques without worries of leakage, and the ability to use precolumns, makes this a simple and robust system to implement. By taking advantage of these abilities, commercial environmental labs can improve throughput without sacrificing data quality.

Acknowledgements

The authors would like to thank Dr. Frank Dorman and Jason Thomas of Restek Corp., Bellefonte, PA for their gracious assistance in this project.

References

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