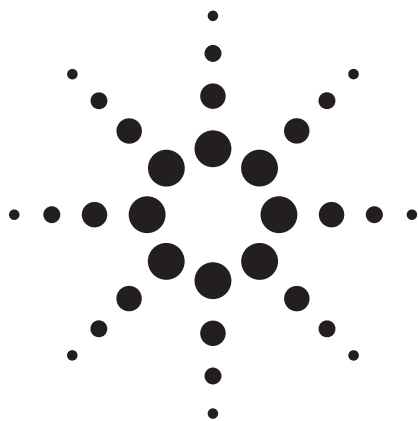# Low-Pressure Retention Time Locking with the 7890A GC

Application

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Abstract

Retention time locking was introduced over a decade ago with the Agilent 6890 gas chromatograph. The next generation of GC from Agilent – the 7890A – has enhanced and extended the functionality previously available, including a new electronic pneumatic control system capable of pressure control to the third decimal place. This application demonstrates the ability of the EPC system to be used for retention time locking at low pressures, in this case with a 320-µm column on a 5975 GC-MS.

Introduction

The introduction of retention time locking (RTL) with the 6890 GC gave users a new way of improving productivity by eliminating the need to constantly update compound retention time data whenever a column was trimmed or replaced. It also allowed the same methods to be run on multiple systems with the same retention times. The introduction of eMethods further enhanced the portability of these methods.

Most RTL-based methods were established on GC/MS systems, where a typical head pressure for a 30 m × 0.25 µm id column is > 10 psi. With setability to two decimal places, four-digit pressure setpoints for such columns (for example, 11.54 psig) result in excellent inter-instrument and intra-instrument RTL precision.

Amongst the many optimization tasks in GC method development is deciding on the best column dimension to select. This can realistically only be determined with full knowledge of the sample characteristics and analysis goals (that is, components of interest, complexity, detection limits required, and the matrix of the sample). Larger diameter columns have the advantages of ruggedness and sample capacity over smaller dimension columns. The larger the diameter of the column, the less pressure is needed to establish optimal flows. However, for the most precise RTL, one needs the ability to set pressure very precisely. With two-decimal-place precision at low pressures (for example, 1.28 psig), locking a system to a target retention time is less precise for column dimensions, such as 0.32-µm columns.

The 7890 GC's fifth generation EPC provides excellent low-pressure control, and with third-decimal-place control of the pressure, providing the precision demanded for RTL at low pressures. This application explores the suitability of the 7890 for RTL at low pressures with a 320-µm column and uses a translation of the method described in Agilent Technologies publication 5989-6569EN, "Reliable transfer of existing Agilent 6890/5973GC/MSD methods to the new 7890/5975 GC/MSD."

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Experimental

The method used for this example was translated using the Agilent Method Translator software to convert to a 250-µm id column method to a 320-µm method. A series of standards was run from 10 ppb to 5 ppm to illustrate the performance of the method, followed by trimming approximately 45 cm off the column and relocking the method.

Table 1.   Method Conditions

Column	HP-5 25 m × 0.32 µm × 0.52 µm p/n 19091J-112
Carrier gas	Helium, constant pressure mode – nominal 3.761 psi
RTL peak	Fluoranthene at 11.112 min
Split/splitless inlet	300 °C, pulsed splitless 7 psi for 0.3 in, 50 mL/min purge at 0.75 min
Oven	55 °C (1.1 min) to 320 °C (6.5 min) at 22.88 °C/min
Sample	1-µL injection, PAH 0.01 to 5 ppm concentration range
MSD	Scan 45–400 u Samples = 2^2 Autotune EM + 200V Source = 230 °C Quad = 150 °C Transfer line = 280 °C

Results and Discussion

The test sample with 16 polynuclear aromatic hydrocarbons (PAHs) was chosen for this example as it covers a wide range of physical properties and provides several challenging separations. This requires the retention time precision to be as tight as possible to ensure correct identification of the peaks of interest, and relocking must be effective or peak identification will fail on the different column.

Samples were injected in triplicate to measure the retention time precision of the locked method at different concentrations from 0.01 to 5 ppm. Table 2 shows the performance metrics for the retention time and also the correlation co-efficient for the analysis.

The initial retention times in Table 2 were achieved at a head pressure of 3.761 psig. This setpoint was determined from the retention time calibration and relocking process to be appropriate to achieve the target retention time of 11.112 min for the locking compound fluoranthene. Table 3 shows the calibration data from the RTL runs.

Table 3.   RTL Data

Run	Pressure (psi)*	Retention time (mins)	Deviation (seconds)
RTLOCK1.D	3.01	11.212	6.018
RTLOCK2.D	3.38	11.166	3.264
RTLOCK3.D	3.76	11.112	0.000
RTLOCK4.D	4.14	11.070	–2.508
RTLOCK5.D	4.51	11.020	–5.508
Maximum deviation		6.018 seconds	
Correlation co-efficient		0.999	

* Even though pressure setpoints used for RTL calibration need only be to be to two decimal places, the ability to precisely set locking pressures based on the calibration curve requires setability to the third decimal place.

Figure 1 shows the calibration curves corresponding to the linearity metrics summarized in Table 2.

Table 2.   Retention Time Precision of Low-Pressure RTL

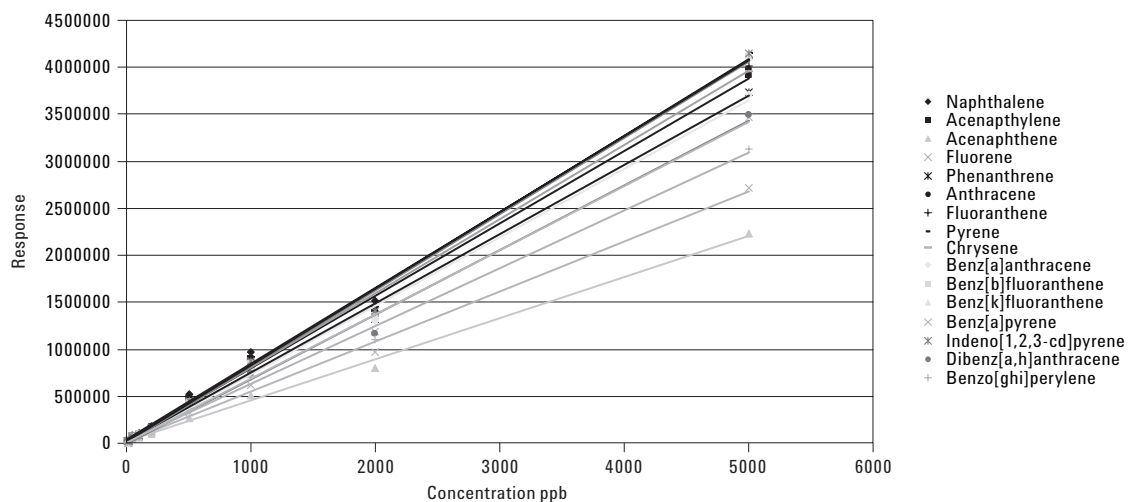|	Average retention time	RSD (%)	Calibration linearity (r^2)	RT before relocking	Relocked RT	ΔRT when relocked
Naphthalene	5.884	0.055	0.997	5.809	5.876	0.008
Acenapthylene	7.753	0.045	0.997	7.676	7.746	0.007
Acenaphthene	7.968	0.044	0.997	7.893	7.959	0.009
Fluorene	8.562	0.048	0.997	8.486	8.556	0.006
Phenanthrene	9.702	0.089	0.997	9.621	9.692	0.010
Anthracene	9.752	0.044	0.996	9.671	9.746	0.006
Fluoranthene	11.119	0.031	0.996	11.041	11.116	0.003
Pyrene	11.388	0.090	0.996	11.308	11.383	0.005
Chrysene	12.808	0.094	0.996	12.719	12.799	0.009
Benz[a]anthracene	12.855	0.046	0.997	12.774	12.849	0.006
Benz[b]fluoranthene	14.285	0.045	0.995	14.168	14.277	0.008
Benz[k]fluoranthene	14.314	0.069	0.995	14.201	14.306	0.008
Benz[a]pyrene	14.815	0.035	0.996	14.686	14.807	0.008
Indeno[1,2,3-cd]pyrene	17.088	0.051	0.996	16.890	17.074	0.014
Dibenz[a,h]anthracene	17.098	0.066	0.995	16.903	17.082	0.016
Benzo[ghi]perylene	17.725	0.089	0.997	17.508	17.709	0.016

Figure 1.   GCMS calibration curves for 16 PAHs using 320-µm id column with low-head pressure.

Figure 2 presents overlayed chromatograms for the replicate sample injections, showing the excellent precision of the replicate injections summarized in Table 2.
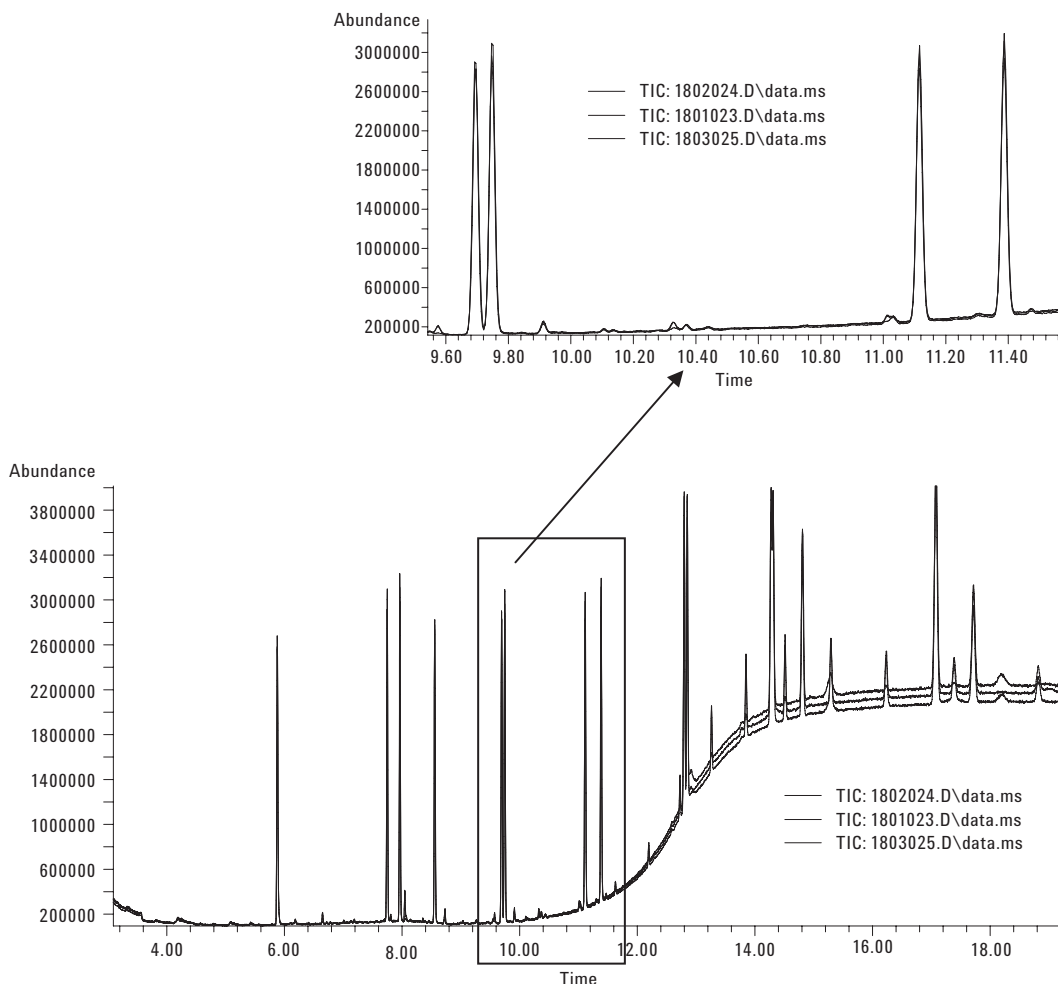

Figure 2.   Overlay of three replicate injections of 2 ppm standard prior to column maintenance and relocking, including a zoomed area of the four peaks from phenanthrene to pyrene.

A 45-cm length of column was removed from the column to simulate typical maintenance that may be performed on a column during routine use. The method was then relocked and the sample re-run to check the efficacy of relocking at low pressure. The relocked method had a resulting pressure of 3.168 psig. The change in locking pressure can, over time, provide guidance as to the extent at which column trimming can be undertaken without the need for full re-locking of the method.

Figure 3 shows an overlay of the before and after column trimming and the extent of the retention time change. Figure 4 presents an overlay of chromatograms, one of the originals and one after column trimming and relocking. The last two columns of Table 2 compare the relocked retention times of target compounds to the originals.
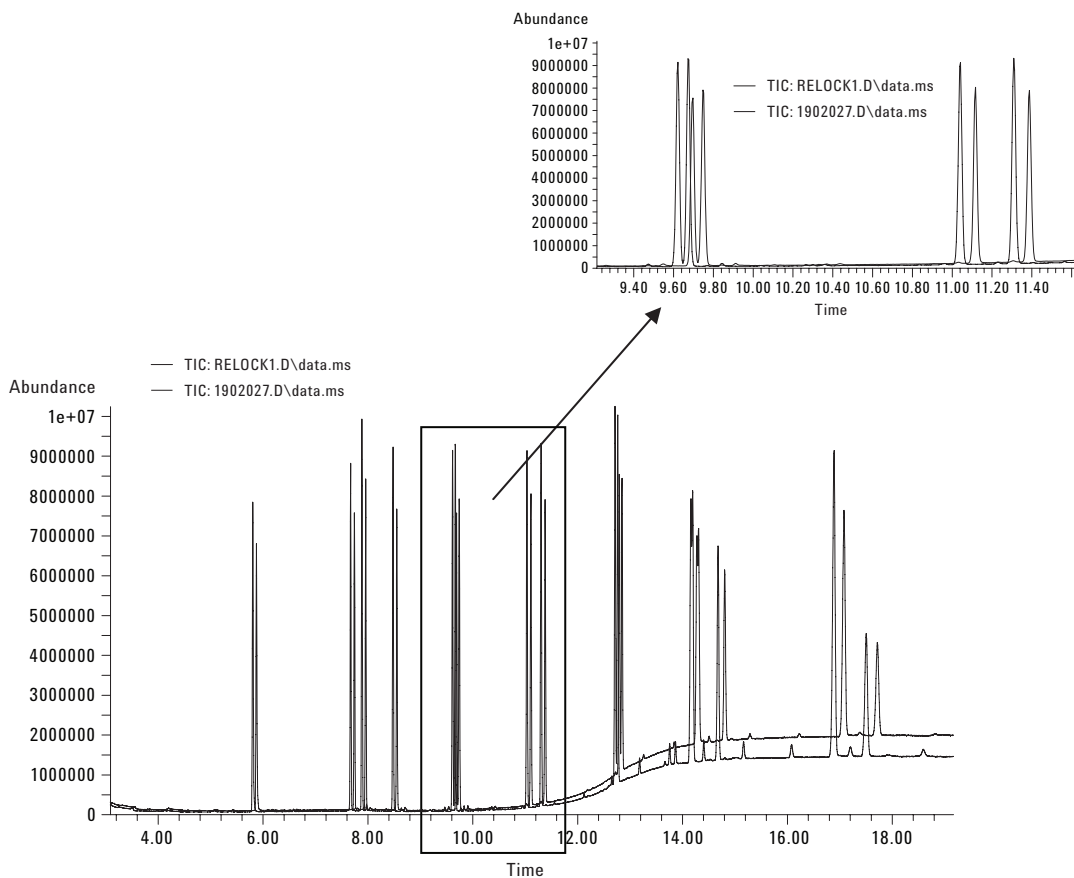

Figure 3. Overlay of injection before and after column maintenance showing the extent of retention time variation, including a zoomed area of the four peaks from phenanthrene to pyrene
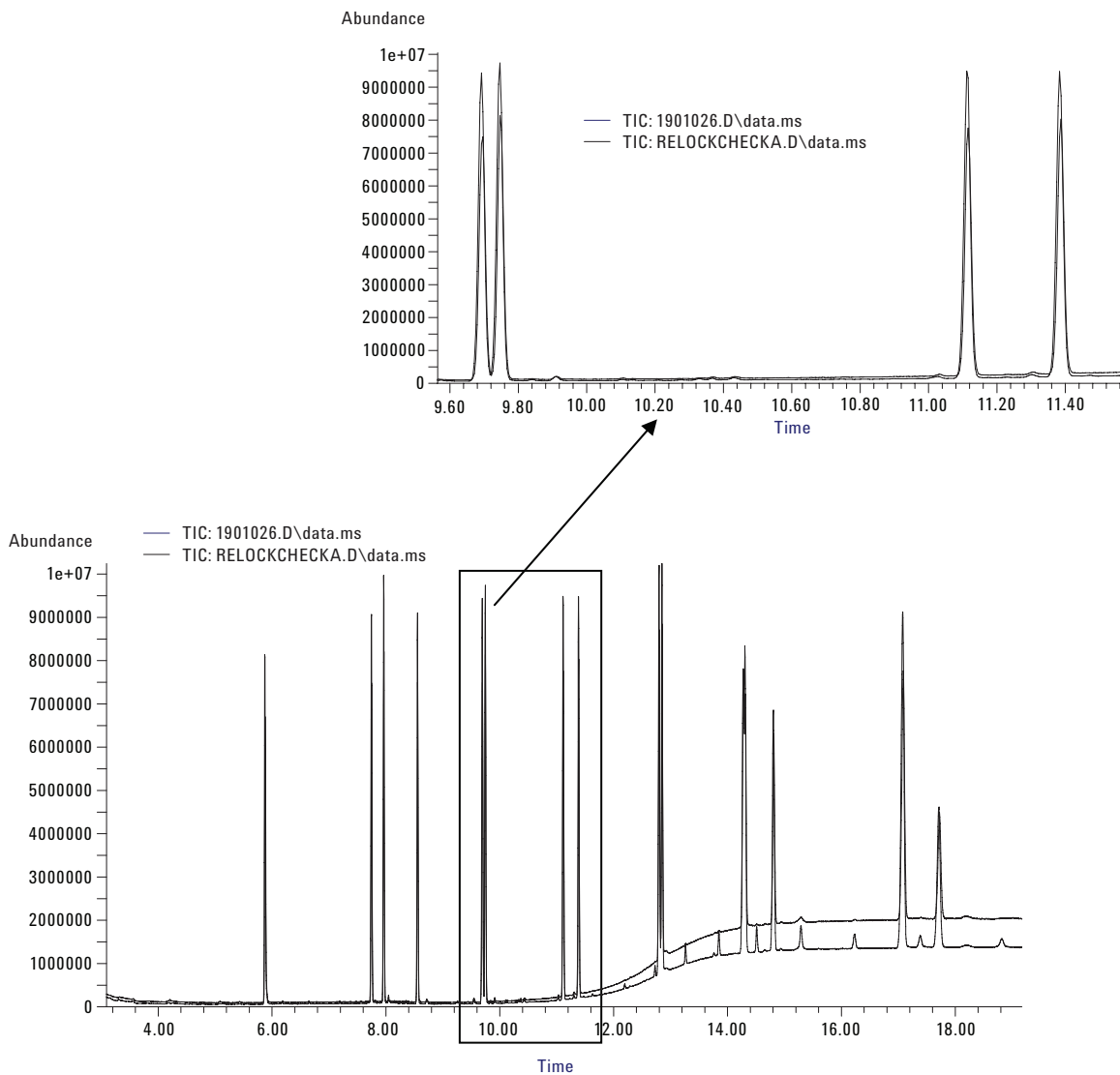
Figure 4. Overlay of injections before and after column maintenance and relocking, including a zoomed area of the four peaks from phenanthrene to pyrene.

Conclusions

This application demonstrates the ability of the 7890 GC system to perform RTL at low pressures (sub 5 psi), such as those experienced when using a 320-μm column in a GC-MS system. The average retention time variation before and after column maintenance for a 16-PAH mixture is less than 0.5 sec, providing high confidence in peak assignments, even with critical separations.

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