EFFECTIVENESS OF ELECTRONIC PRESSURE CONTROL

IN GAS CHROMATOGRAPHY

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Scientific instrument manufacturers continue to automate more of the processes involved in performing analytical experiments. These efforts improve laboratory productivity, allow the experiment to be performed unattended, and often accomplish better precision in the final results. Occasionally, these enhancements are promoted as panaceas for many experimental difficulties. But some elixirs induce other problems and limitations often not mentioned by the promoter.

Establishing a method in gas chromatography involves choosing settings for numerous parameters, including:

- Column Stationary Phase (*i.e.,* DB-1)
- Column Length
- Column Internal Diameter
- Film Thickness for Stationary Phase
- Column Temperature Program
- Carrier Gas (*i.e.,* He)
- Carrier Flow Rate

Their optimization is always limited by compromises between goals of:

- **SPEED**
- **RESOLUTION**
- **SAMPLE CAPACITY**

The final separation can be aimed toward any one of these goals, or balanced among any two, but all three goals can<u>not</u> be achieved at once. For example, for ultimate speed, the column should be short and with a thin film stationary phase, the column temperature program rate would be rapid, the carrier gas is hydrogen, and the carrier flow rate fast. However, for the best separation of two adjacent peaks, the column length would need to be much longer and with a narrower internal diameter, the initial column temperature low enough to allow analyte refocusing on the column, the column program rate and carrier gas flow lowered, and the carrier gas of choice is nitrogen.

Both speed and resolution can be achieved somewhat by selecting a medium length column with a thin film, a reasonably fast column temperature program rate and a reasonably fast flow rate - obviously a compromise! However, what is sacrificed is sample capacity. Heavy doses of analytes require thick film columns with slower temperature program rates to keep peaks from overloading and overlapping. These needs are not compatible with both speed and resolution.

Once the chromatographic goal or compromise is set, most of these parameters can be readily chosen and become fixed for the entire chromatographic run. Only two parameters[1] can be realistically varied within a run - column temperature programming and carrier flow rate.

Of the two, temperature programming has the much greater effect on the chromatogram. A common rule of thumb is that retention times are cut in half for every 20°C increase in column temperature. Thus, a temperature change from 100°C to 200°C would, following this premise, shorten the elution times by a factor of 32. Such a dramatic change to be generated by carrier flow would put flow radically away from its optimum and cause the column backpressure to be excessively high or even exceeding the available supply pressure. Generally, column flow is preset to the optimum value for the desired goal and the column temperature program is varied to achieve the desired separation of peaks.

Viscosity of the carrier gas is a function of temperature. (See Figure 1)[2]

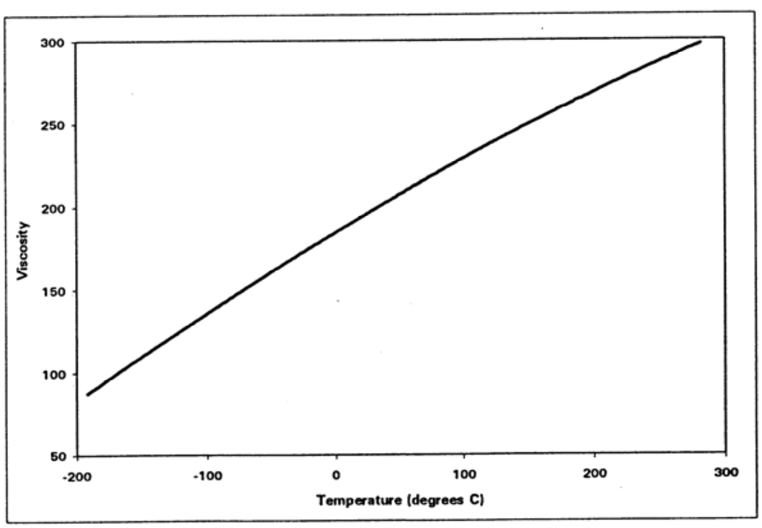

Figure 1. Viscosity versus Temperature for Helium

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[1] Column characteristics can be altered singularly by column switching with valving.

[2] Extrapolated from data in CRC Handbook of Chemistry and Physics, 1972.

During a temperature program, this change in viscosity causes an increase in column backpressure if flow is constant or a decrease in flow if the column backpressure is fixed throughout the run. If column flow is set near its optimum at the initial column temperature, then maintenance of this flow keeps it at the best flow throughout the chromatogram. A flow controller is employed to keep this flow constant and to vary the column backpressure as the column temperature varies. A typical backpressure versus column temperature plot at a fixed flow rate is shown in Figure 2. Flow controllers are the pneumatics of choice to keep flow at its optimum throughout the run.

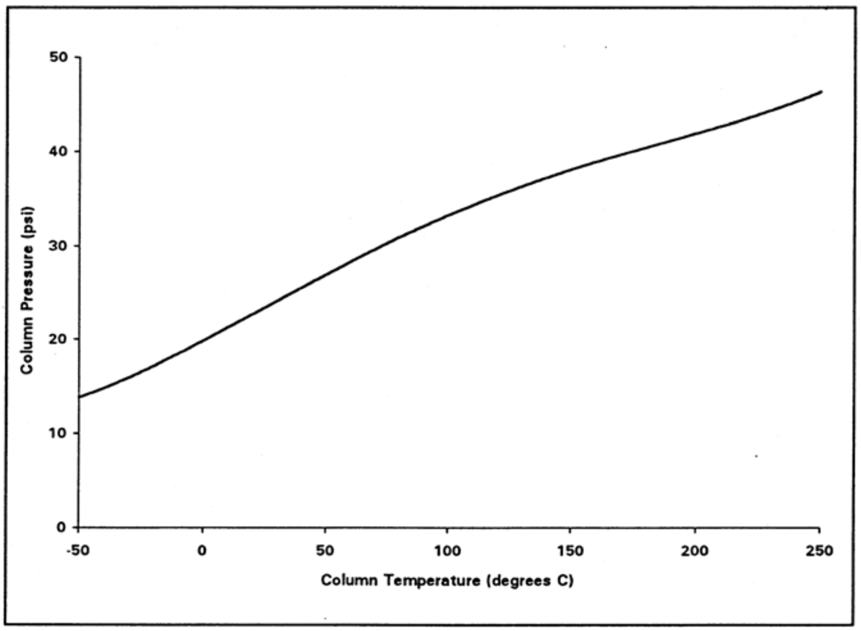

Figure 2. Typical Column Backpressure versus Temperature at Constant Flow (5.2 ml/min)

However, flow controllers cannot be properly used with split/splitless capillary injectors. When the splitter vent is closed, all flow is directed onto the column. When the splitter vent is opened, the vent has little or no restriction and all flow passes out to vent with no flow through the more restrictive column. To keep column flow consistent, whether the splitter vent is open or closed, the column must be maintained under constant head pressure. However, under constant pressure, flow varies with column temperature due to changes in carrier gas viscosity. Figure 3 illustrates a typical column flow versus column temperature plot for a fixed column pressure.

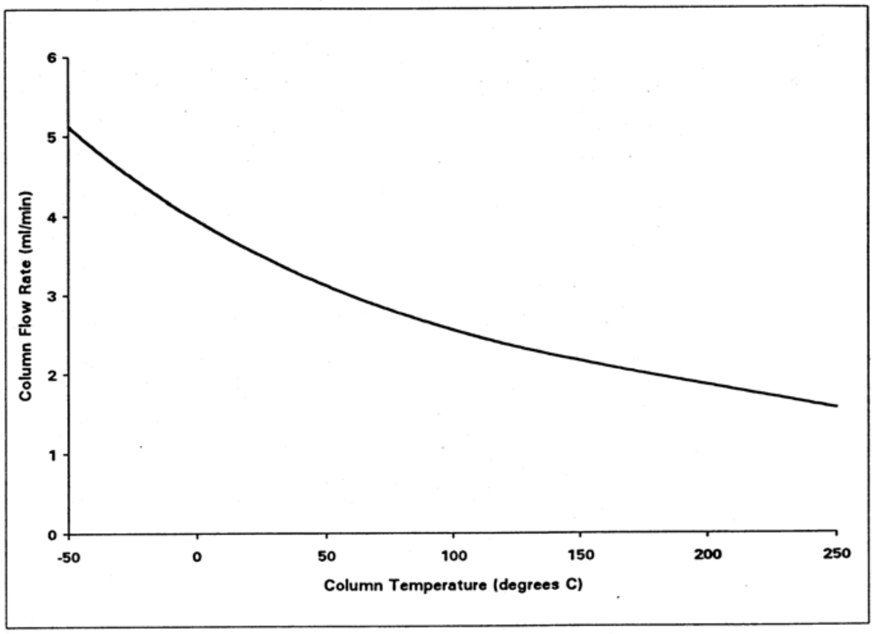

Figure 3. Typical Column Flow Rate versus Temperature at Constant Pressure (14.5 psi)

Programmable electronic pressure control (EPC) has been utilized to take advantage of features for both flow controllers and pressure regulators. It can operate in a constant pressure mode or in a programmed mode to simulate constant flow. In the "programmed" flow mode, the operator must specify the column length and internal diameter to allow computation of the pressure needed to achieve a given column flow rate.

EPC has been promoted as:

1. Allowing higher carrier gas flows at the column temperature limit.
2. Conserving supply gases by turning them off at run end.
3. Documenting and storing gas flow settings.
4. Reducing peak broadening and peak tailing of late-eluting peaks.
5. Shortening analysis time.
6. Increasing sample throughout.
7. Optimizing detector gases.
8. Reducing discrimination in splitless injections with pressure programming.
9. Improving stability and reproducibility in gas flows.
10. Improving retention time stability.
11. Enhancing peak area stability.
12. Reducing GC-to-GC variability.

"Advantages" 1 and 2 are indisputably valid. "Advantage" 3 is useful but documentation of carrier gas settings (column pressures, computed flows and computed linear velocities) is also available on Varian Star 3600CX and 3400CX GCs with optional Electronic Pressure Readout (EPR). "Advantages" 4, 5, and 6 can be more readily achieved with column temperature programming (as discussed earlier). Examples given for EPC illustrate a reduction in run time of only 2.5 minutes with a 31-minute chromatogram with flow programming, contrasted with constant pressure - not a significant savings for most laboratories. "Advantage" 7 is useful primarily for detector designers or for experimenters to verify recommended settings; usually detector gases are set to flows specified by the manufacturer and not varied. "Advantages" 8[3], 9[4], 10[4] and 11[4] are arguably achievable without EPC. "Advantage" 12 is a benefit only if one specific column is used in multiple instruments; variation in column dimensions can introduce major errors (up to 22%) in the computation of flow from pressure and up to a 56% shift in retention times with EPC (see Flaw A discussion).

However, EPC has several major flaws exposed in common chromatographic experiments:

EPC LIMITATIONS

A. Errors in Flow Calculation - Flow is related to pressure by, among other parameters, column internal diameter to the **FOURTH POWER**. Typically, column internal diameters have a dimension tolerance of ±4.8%.[5] Unless the accurate value is entered (not usually provided by the column supplier), an error of up to ±22% in flow rate can be realized just from EPC computing flow with a slightly inaccurate diameter. This error can provide a major departure from the expected flow without warning or indication and can cause a shift in expected retention times of up to 56% when compared with another column using isothermal conditions.[6] Flow controllers always maintain their flows without any computational errors.

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[3] "Advantage" 8 has been readily demonstrated by Varian (GC Advantage Note 1) without a need for EPC.

[4] Flow stability and precision become apparent with retention time and area reproducibilities. Retention time precision is readily achievable to much less than 0.1% RSD with most high performance GCs and Varian specifies their AutoSampler area precision as less than 1% RSD (<1.5% for split/splitless). Data generated with EPC in the "programmed" flow mode show equivalent results (HP Application Note 228-141, p. 4).

[5] Verbal information from J&W Scientific Technical Support.

[6] Column temperature programming reduces this error.

B. Dual-Column Chromatography - Peak confirmation is often conducted by simultaneously running samples on two different columns from a single injection. Expected shifts in retention times and peak area ratios assist in identifying peaks and verifying peak purities. When columns have different dimensions, computation of flows through EPC becomes invalid - which column parameters are entered? Either flow-controlled or pressure-controlled systems can work quite satisfactorily for this application.

C. Column Switching - A common practice in chromatography, especially in gas analyses, is to perform coarse separations into component groups on a precolumn and to direct early elutors to one column and then to switch columns in the middle of the run to place the late components onto a second column. The two columns may not necessarily have the same dimensions. Thus, flow computed by EPC for one column may not be maintained with the second. With a flow controller, flows are maintained constant whichever column is on-line.

D. Valve Applications - Custom valve utilizations offer specific optimizations of column selectivities or specialized flow patterns to accomplish unique separations. Any valve actuation that alters downstream resistance to flow, such as insertion of a column, can result in radical changes in column flow if pressure is held constant or even "flow-programmed" by EPC. Such applications[7] include column isolation, column addition, heart- or end-cutting to a second column, backflush to vent, two column interchange with backflush to detector, loop sampling with backflush of precolumn to vent, and loop sampling with foreflush to vent and same carrier to detector in both modes. Flow controllers maintain constant flows in all these valve configurations and are the appropriate pneumatics for most valve uses. EPC would not be suitable here.

E. Adjustment of Balancing Restrictors - Often, when columns are switched in and out of a valved system, balancing restrictors (usually adjustable needle valves) are employed to eliminate dramatic pressure/flow surges during the switch. With flow controllers, the restrictor setting is easily performed by noting the backpressure without the restrictor and adjusting it to the noted pressure with it in. Since EPC is pressure controlled, even in the "programmed" flow mode, a restrictor can only be adjusted by balancing flows with an external flow meter. If the restrictor is not set properly, EPC can yield much higher flow on one side compared with the other. The "pressure-programmed" mode would yield the same results; pressures needed to achieve constant flow cannot be predicted and pressure settings must be determined empirically with an external flow meter.

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[7] Valve configurations for the applications cited are illustrated in Valco Instrument Catalog, Houston, Texas, 1990.

F. Packed Columns - Although capillary columns are very prevalent now, packed columns are still in common usage, especially with gas analyses. EPC is designed specifically for capillaries and does not properly maintain constant flow for packed columns as the anticipated column restriction is not predictable from packed column dimensions. Flow controllers give constant flow for <u>both</u> packed and capillary columns, even with temperature programming.

G. Leak/Plug Diagnosis - A flow controller adjusts column backpressure to maintain constant flow. A pressure gauge (or electronic pressure readout - EPR) plumbed between the flow controller and sample injection point provides readings for this backpressure. With a given set of operating conditions, including a specific column, flow, and column temperature, a certain backpressure is attained. If any condition is different or if a leak or plug is generated, this backpressure will be altered. By noting the backpressure at the start of a run, the operator can compare it with previous runs. If a change is noted, the operator can presume conditions have changed, including a leak if pressure is lower or a plug if pressure is higher. Varian Star 3600CX and 3400CX GCs with optional EPR can document the initial column backpressure within the run log, available in the report generated by In-Board Data Handling (IBDH) or the Star Workstation. EPC has no such diagnostic feature; it remains a pressure-controlled system. Even with a small leak or plug, pressure is maintained and the actual flow increases with a leak or decreases with a plug. EPC anticipates a certain resistance to flow based on column dimensions; if that resistance changes unexpectedly, the desired flow is not maintained. EPC can only catch major leaks when the down-stream resistance drops precipitously; subtle leaks are not sensed.

Flow controllers do not provide proper solutions for every chromatographic configuration. They are not yet available, for a reasonable cost, in a programmable mode. Also, flow controllers are sensitive to changes in their environmental temperatures (Varian Star 3600CX and 3400CX GCs both have heated pneumatics compartments to eliminate any effect on flow from room temperature fluctuations[8]). And flow controllers are very slow to respond to downstream changes in flow resistance, such as switching to backflush a column. A pressure regulator can be installed in parallel with a flow controller. There it provides faster recovery from such disruptions and still allows maintenance of the good features of a flow controller.

Split/splitless injectors must employ pressure regulation to handle the opening of the splitter vent, as discussed earlier. However, with the Varian 1075 Split/Splitless Capillary Injector (but not with the Varian 1077-style injector), a flow controller can be plumbed in parallel with the mandated pressure regulator. Now, the pressure regulator provides the higher flows needed when the splitter is open and the flow controller takes over when the splitter is closed. Column flow is maintained constant throughout a temperature program.

Flow controllers, however, can:

- not yield computation flow errors due to column dimension inaccuracies,
- properly handle dual column chromatography,
- maintain constant flow when column switching,
- achieve consistent flow for numerous valving applications,
- allow balancing restrictors to be set with ease
- work with both packed and capillary columns without compromises, and
- provide easy diagnosis of leaks, plugs or incorrect chromatographic settings.

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[8] R. Bramston-Cook, "An Effect of Ambient Temperature Changes in Gas Chromatography", Lotus Consulting Monograph, 1994.

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