PRIMER ON TEMPERATURE CONTROL AND MONITORING IN GAS CHROMATOGRAPHY

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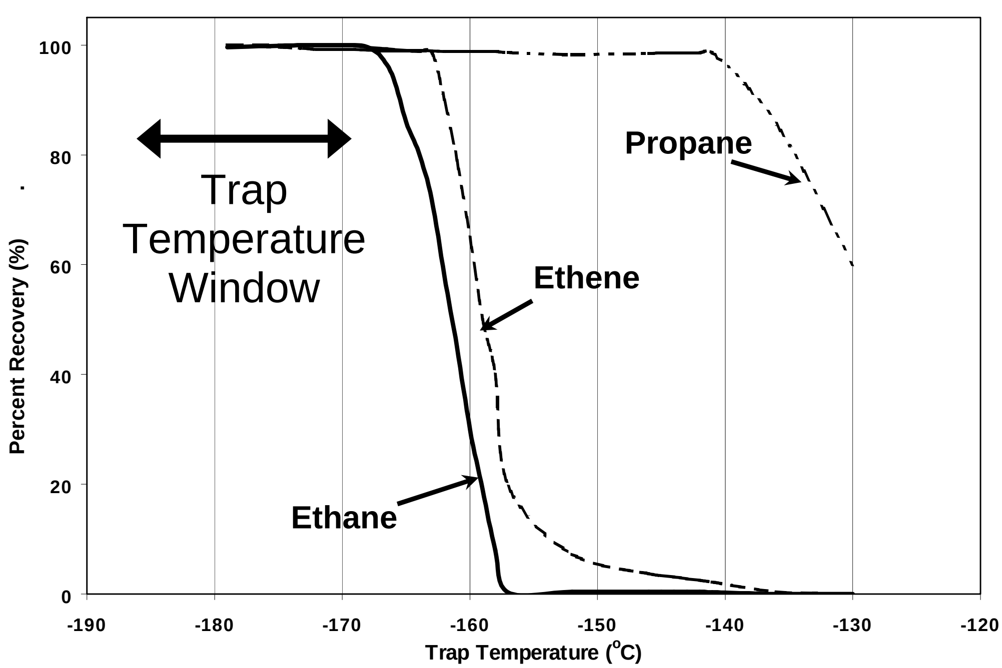
Temperature is the primary driving force in generating a chromatogram by gas chromatography. Carrier gas flow and the column material also play a role in the separation process, but column temperature yields the greatest impact in speeding up or slowing the elution of analytes through a column. Chromatographic separation is achieved by the analyte partitioning – "dissolving" – into the column material surface or by adsorption onto the surface and then the subsequent analyte release back into the carrier flow. The speed of this equilibration process is dramatically altered by a change, even a subtle change, in the column temperature. Precise control of the column temperature is mandated to achieve reproducible retention times.

Trace levels of analytes can be concentrated through use of cryogenic trapping prior to injection into the column. Temperature control and accuracy for the sample concentrator are critical in the determination of trace non-methane hydrocarbons in ambient air or vehicle exhaust. Methane is not usually quantitated, and in fact, can become a chromatographic interference with the measurement of other light hydrocarbons. Although the trapping temperature for methane is very near the temperature needed to ensnare ethane, judicious selection of a proper trap temperature can exclude methane, oxygen and carbon monoxide, while still fully trapping ethane and all other hydrocarbons. The temperature window for this selection is very narrow – less than 16 ^{o}C (see Figure 1). Small variations in temperature can trap methane and oxygen if too cold (< -184 ^{o}C) or release ethane (and others) if too warm (> -168 ^{o}C). Careful setting and control of this initial trapping temperature are mandated to yield full accounting of all non-methane hydrocarbons and exclusion of methane and oxygen.

Figure 1. Recovery of Selected Hydrocarbons versus Cryogenic Trap Temperature

Temperature of a cryogenic trap must be maintained within the narrow window shown to provide full recovery of light hydrocarbons and to reject methane and oxygen. Methane and oxygen are not plotted here as oxygen extinguishes the detector flame and prohibits the monitoring of methane.

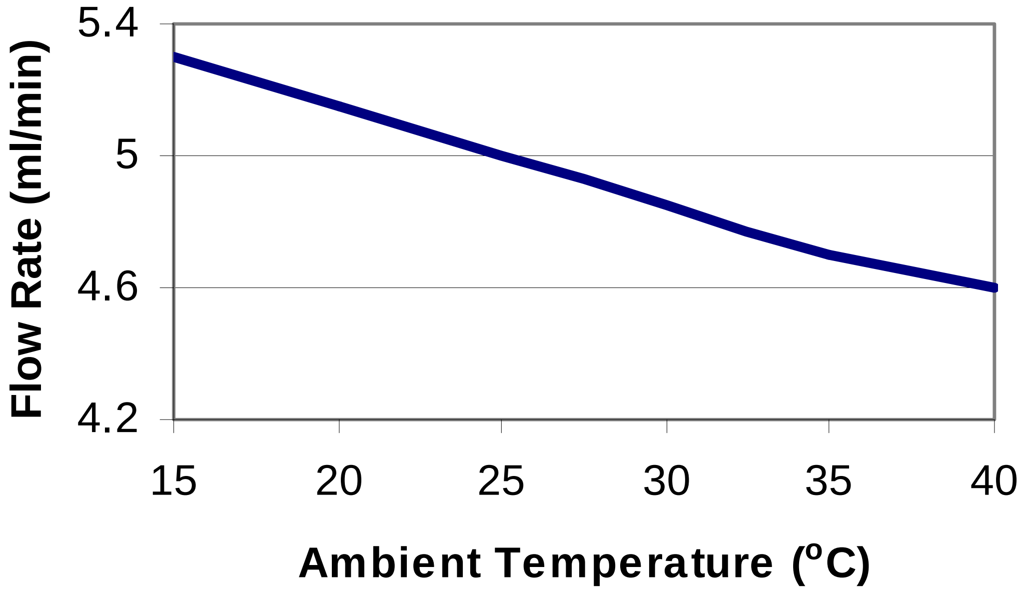


Temperature also plays an important role in keeping sample analytes vaporized before and after the column. Injectors and detectors must be warm enough to keep any sample components from condensing within these zones.

Another interesting application of temperature control in gas chromatography is the maintenance of carrier gas flow with varying ambient temperatures.[1] Gas viscosity increases with temperature – hence the increased column backpressure during temperature programming. As their temperature environment rises, most flow controllers yield a lower output flow due to the change in gas viscosity (Figure 2). For example, an ambient temperature change of 5 °C can result in a significant flow change of 3%. By maintaining the controller at a fixed, above ambient temperature, its output flow is maintained despite common variations in room temperature. And retention times become more reproducible over a longer interval due to the more consistent flow rate.

Figure 2. Typical Flow Rates Measured at Various Flow Controller Temperatures for 0-10 ml/min Flow Controller (Varian P/N 03-917146-01)

Output of a flow controller varies with the temperature environment for the controller. For example, a change in temperature from 20 °C to 25 °C will yield a change in flow from 5.2 ml/min to 5.0 ml/min. If the controller is not maintained at a constant temperature, this swing in ambient temperature can result in significant changes in retention times due a change in room temperature.



[1] "An Effect of Ambient Temperatures Changes in Gas Chromatography", R. Bramston-Cook, Lotus Consulting, 1995.

TEMPERATURE CONTROL -

Control of temperature can be accomplished through very simple circuitry or very sophisticated digital algorithms (see Table I). The simplest controller is a rheostat – style that throttles the voltage applied to a heater. The desired temperature is reached by adjusting the applied voltage and then maintaining that voltage with this simple controller. The thermal environment of that heat zone is greatly affected by a change in temperature, as the applied voltage is not altered as the zone's surroundings change in temperature.

Table I. Different Approaches to Temperature Control

Type of Control	Heating Method	Features	Analogous Use	Identification	Temperature Programming
Rheostat	Constant voltage supplied to heater	Very simple hardware, but set temperature changes with thermal environment	Home wall heater	Setting 0-100% of full power, no temperature setting	Very difficult
Simple 0n/off with Feedback	Feedback through thermal probe. Voltage turned on/off to maintain setting	Simple circuitry, but temperature overshoots/undershoots and/or slow heating	Thermostat on home furnace	Temperature entry, but cycles noticeably away from set point	Yes, but significant overshoot at end
Proportional with Feedback	Feedback through thermal probe. Applied voltage varies with deviation from setpoint	Faster heat-up and better stability at set point	Digital controller on home climate system	Actual temperature close to setpoint	Yes –small overshoot/under shoot
Proportional/ Integral/Derivative (PID)	Automatically sets proportional bandwidth and adjusts offset to setpoint	Faster heat-up and cool-down and better stability		Set temperature maintained under all conditions	Yes – minimal overshoot/under shoot

Providing feedback from a temperature probe to the controller corrects this problem. As the temperature of the zone deviates away from the setpoint, the controller alters the applied power to the heater to maintain a constant value. A simple version of this controller can provide an average temperature at the setpoint, but can oscillate over and under the desired value. When the circuit senses that temperature is below the setpoint, power is applied to the heater. After the temperature reaches the setpoint, power is turned off. Unfortunately, residual heat in the heater causes the temperature to overshoot. Power remains off until the zone cools back to the setpoint. The circuit is reenergized when the temperature drops below this point. However, since the heat transfer from the heater is not instantaneous, temperature then undershoots the desired value, and the whole process cycles again.

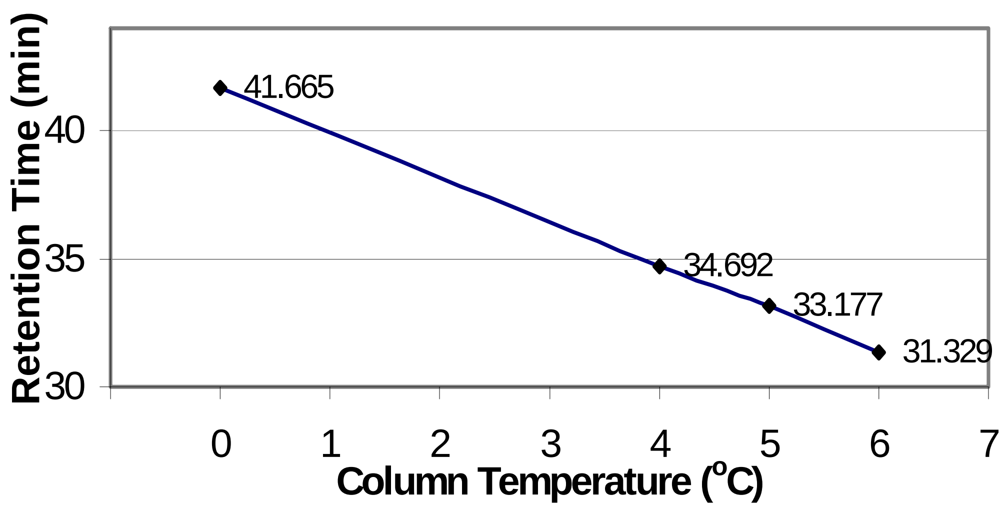
This temperature variation is not critical for most zones unrelated to the chromatographic process. For example, most injectors and many detectors do not rely on consistent temperatures; they only need to be warm enough to maintain the sample in the vapor state. However, one detector - the thermal conductivity detector - is critically dependent on a very consistent temperature for optimal performance. This detector utilizes the temperature difference between its filaments and the surrounding block as the means to detect a thermal conductivity response. A cycling block temperature readily yields an oscillating baseline and degrades this detector's performance dramatically.

Temperature cycling in the column oven can lead to significant deterioration in retention time reproducibility for analytes. This error is not always predictable, but one example of the impact is illustrated in Figure 3. To minimize temperature effects on retention times (see reproducibility study in Figure 7), column temperature needs to be maintained well within ± 0.02 °C of the setpoint.

Figure 3. Effect of Column Temperature on Retention of Propane

Lower column temperatures will retain analytes longer on the column. Even a subtle change in column temperature of 1 °C can effect a time shift of ~1.7 minutes on the retention of propane. Column temperature must be maintained to less than 0.02 °C to achieve retention reproducibility of under 0.03 minutes.

Column – Varian Chrompak Alumina-KCl PLOT, 0.32 mm ID, 50 m.; column flow – 4.0 ml/min.
Temperature program: isothermal hold until propane elutes then ramp at 10 °C/min to 200 °C.



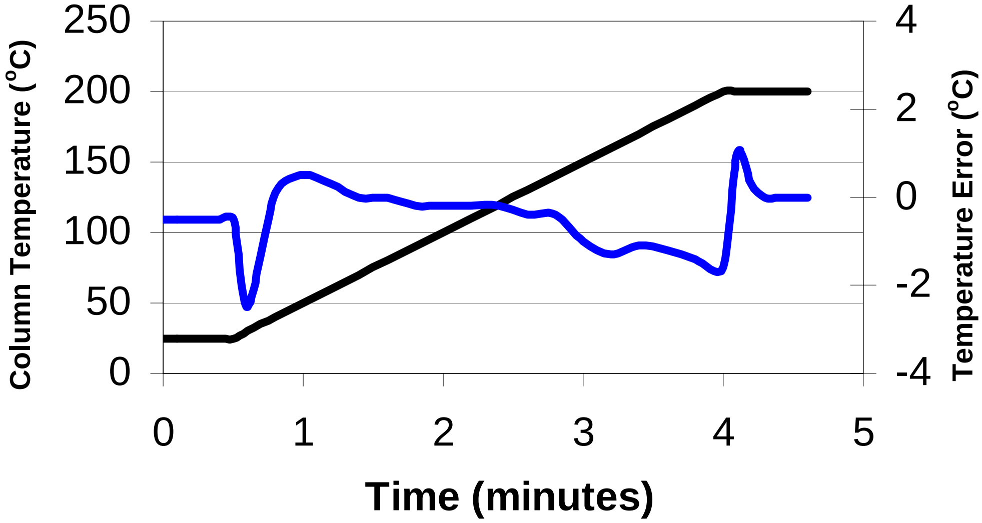
A solution to minimize this temperature oscillation is to employ a proportional controller. This device throttles back power to the heater when temperature approaches the setpoint and then maintains just enough power to maintain that setting. When a large temperature change is needed, the circuit allows full power to be applied for a rapid heat-up, but then zeroes into the setpoint as the desired temperature is neared. Overshoot and undershoot are minimized.

Another type of controller combines proportional control with two additional adjustments, which help to compensate for changes in the temperature environment. These adjustments are labeled "integral" and "derivative", and the controller is then called "Proportional/Integral/Derivative" or PID. The proportional, integral and derivative terms in the control logic must be adjusted to a particular heat zone based on its thermal mass and expected heating rates. For the integral term, the difference between the setpoint and actual temperatures is integrated and the result then adjusts the heating power to bring the actual temperature to the setpoint. The derivative function of the difference between the setpoint and actual temperatures adjusts the heating power proportionally to the rate of temperature change. The advantages of PID control are the faster temperature ramping with faithful tracking of the setpoints, very minimal overshoot/undershoot at the final temperature, and very accurate maintenance of the temperature. Figure 4 provides an example of temperature deviations with column oven ramping utilizing a PID controller.

Figure 4. Temperature Deviations of Column Oven Ramp from 25 °C to 200 °C with Proportional/Integral/Derivative Controller on the Varian 3800

Proportional/Integral/Derivative (PID) controlling of the heater circuit for the column oven of the Varian 3800 permits faithful tracking of the temperature ramp of 50 °C/min from 25 °C to 200 °C. As the temperature approaches the endpoint, the heater is automatically throttled back to minimize gross overshooting the final temperature.

Ambient temperature: +21 °C; no coolant used.



TEMPERATURE MONITORING -

Temperature zones can be monitored with several commercially available probe styles. Two common probes in gas chromatography are thermocouples and platinum resistive probes. Both are small, can operate within most temperature ranges of gas chromatographs and can be utilized with any of the controllers discussed above. However, each has distinctive advantages.[(2)]

Thermocouples are based on voltage generated from the contact of two dissimilar metals. This voltage is a function of temperature. By monitoring this voltage, the thermocouple's response can be converted to temperature. Thermocouples are relatively inexpensive, simple, rugged and available in a variety of temperature ranges. However, they are notably very nonlinear without corrections, especially over a wide temperature range (see Figure 5). In addition, they have very poor sensitivity (Type K: 40 μV/°C). These probes are distinguishable by characteristic color coding of the polarized connecting wires and usually by a special yellow connector to the controller. Table II lists several common thermocouples and their coding.

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(2) *Omega Complete Temperature Measurement Handbook and Encyclopedia, Volume MM*, Omega Engineering, Stamford, Ct 1998.

Figure 5. Temperature Errors with Type K Thermocouple[3] (yellow / red leads) without Corrections

Thermocouples have limited linear ranges and can deviate significantly away from the true temperatures outside these ranges. For example, a Type K thermocouple reads "–145 ^oC" for –196 ^oC (liquid nitrogen), "–76" for –99 ^oC, "+266.6" for +270 ^oC and "+449.6" for +450 ^oC.

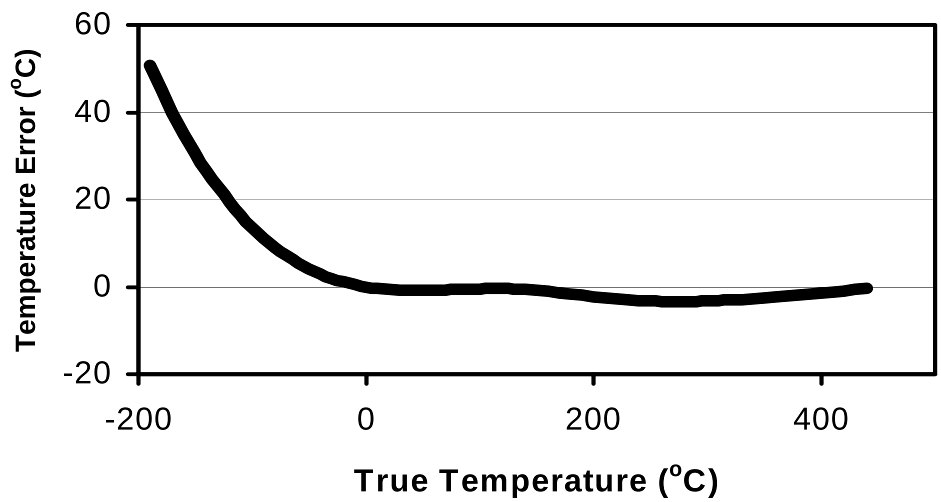

Table II. Characteristics of Several Common Thermocouples

Type	Color Coding (+ / -)	Contact Metals	Linear Temperature Range[4]	Reference Junction
K	Yellow / Red	Nickel-Chromium / Nickel-Aluminum	-20 ^oC to +1000 ^oC	0 ^oC
J	White / Red	Iron / Constantan	0 ^oC to 500 ^oC	0 ^oC
R / S	Black / Red	Platinum-Rhodium / Platinum	+500 ^oC to 1500 ^oC	0 ^oC
E	Purple / Red	Nickel-Chromium / Constantan	+250 ^oC to 800 ^oC	0 ^oC

Without special circuitry sensing for open probes, thermocouples are very prone to yield thermal runaways if the interconnecting wiring is broken or shorted. Usually, conversion from voltage to temperature is set such that 0 voltage is 0°C. If the setpoint on the controller is, say 200 °C, and the thermal couple wiring is broken the controller will improperly sense the temperature zone as "too cool" (in fact, 0 °C) and will apply heat. As the zone is not being monitored correctly, the zone will suffer from thermal runaway with disastrous consequences, including potential meltdowns.

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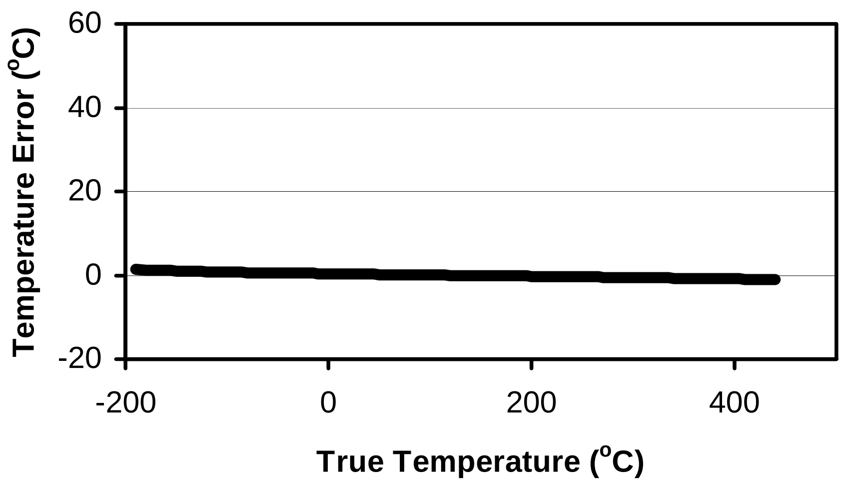
(3) *Omega Complete Temperature Measurement Handbook and Encyclopedia, Volume MM*, Omega Engineering, Stamford, CT 1998.

(4) Linear ranges are indicated without corrections. For example, Type K could be linearized with a ninth-order (*sic*) polynomial, but the correction is not usually possible through most GC controllers.

Resistive probes (often called RTD - resistance temperature detector) sense temperature as a change in resistance. Platinum is the most useful material, as it possesses one of the highest resistivity per foot of wire. The length of platinum wire in probes is usually set to make 100 Ω equal to 0 °C. A higher probe temperature will generate a higher resistance. The platinum probe is very linear over a very wide temperature range (see Figure 6), is the most accurate of all available sensors[5], and is very stable under a variety of environments. Sensitivity is reasonable with a 1 °C change yielding a very readable resistance change of +0.385 Ω. Moreover, if the probe suffers a broken interconnecting wire, the temperature is always sensed as too high (∞ resistance) and the temperature controller turns off applied heat. If one wire shorts to the instrument case or to its other leg, the controller can be programmed to sense the fault, generate an error and turn off the heater. Platinum probes are usually identifiable by a ceramic covering over the probe and interchangeable connecting wires.

Figure 6. Temperature Errors with Platinum Resistive Probe[6]

Platinum probes are very linear over a very wide range without corrections. For example, this probe reads "–194.7" for –196 °C, reads "-98.2" for –99 °C, and reads "+449.0" for +450 °C. Note – the scaling here matches Figure 5 for direct comparisons.



Platinum probes are more expensive than thermocouples, require a current source to measure resistance, and can suffer from self-heating. Passing a current through a resistor causes Joule heating ($I^2 R$) that can yield a higher temperature at the probe than expected. By keeping the probe in good contact with the thermal zone to be measured or by maintaining an active airflow around it, this self-heating is greatly minimized. Also, very long connecting wires can add an effective resistance to the probe; connecting wires should not be excessively long or, with some monitors, a third compensating wire can be added to negate contributions from these connecting wires.

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(5) Temperature readout of a probe can be verified by dipping the probe into liquid nitrogen (-196 °C), ice water (0 °C) and boiling water (+100 °C).

(6) *Omega Complete Temperature Measurement Handbook and Encyclopedia, Volume MM*, Omega Engineering, Stamford, CT 1998.

VARIAN GAS CHROMATOGRAPHS

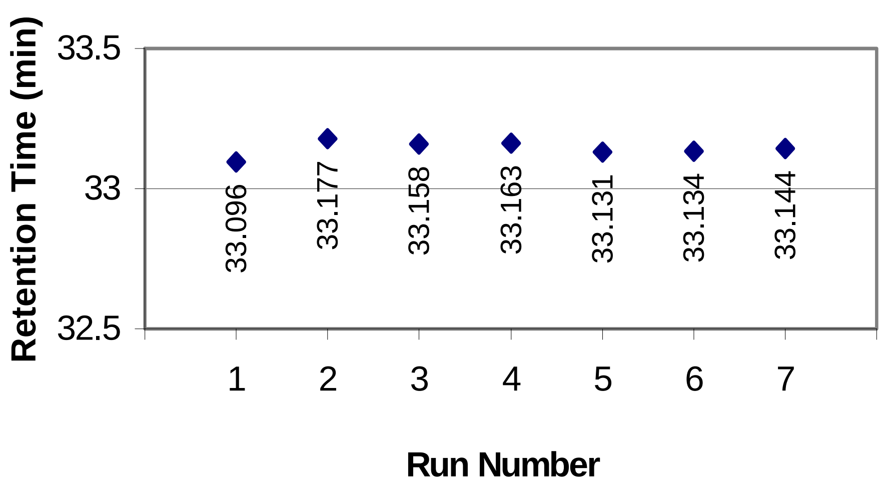
From the Varian 3700, to the Vista 6000/4600, Varian 3000 Series (including 3300, 3350, 3400, 3410, 3500 and 3600) and now to the Varian Model 3800/3380, Varian has always utilized fully proportional/integral/derivative (PID) heating circuits for all temperature zones, including column, injector, auxiliary, and detector ovens. Zones heat up very rapidly, zero into the setting nicely and maintain the set temperature with little or no variation. Subambient temperatures can be programmed for the column oven and for any of three injector zones on the Varian 3800.

Temperature is controlled by varying the time that voltage is applied to a heater. If the temperature is far from the setpoint, the frequency of the applied voltage is high. As the temperature approaches the setpoint, the frequency is reduced until the desired temperature is maintained. Figure 7 illustrates typical thermal stability of the Varian 3800 through a study of retention time reproducibilities. Heat-up is rapid with minimal overshoot and the actual temperature faithfully follows the set point (see Figure 4).

Figure 7. Retention Time Reproducibility of Propane (over an 18 hour period).

A standard deviation of 0.026 min. demonstrates thermal stability of the column of < 0.02 ^{o}C for the starting temperature, even after temperature cycling to 200 ^{o}C.

Column – Varian Chrompak Alumina KCl, 0.32 mm ID. 50 m.; column flow – 4.0 ml/min. Temperature program: 5 ^{o}C isothermal hold until propane elutes, then ramp at 10 ^{o}C/min to 200 ^{o}C.

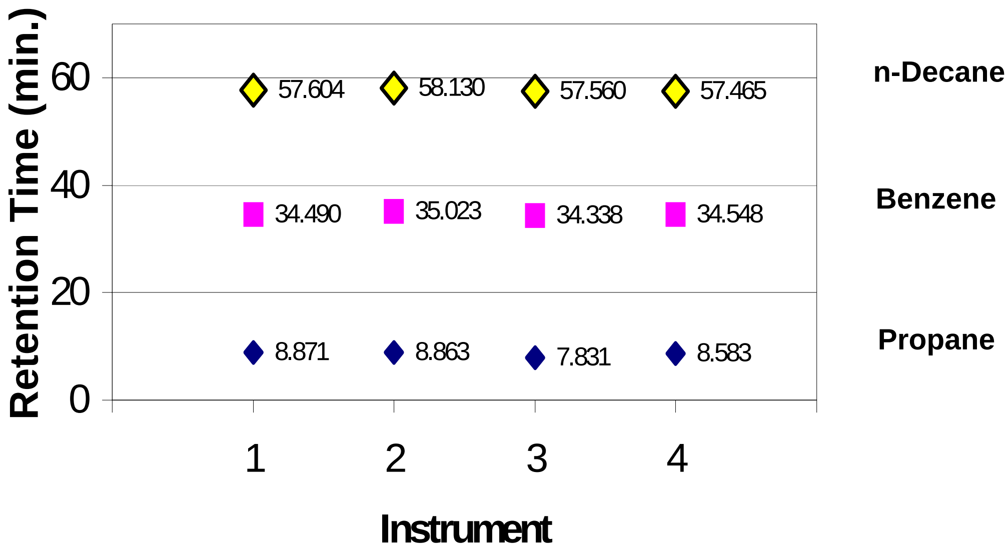


For monitoring temperatures, Varian has long employed the higher performance platinum resistive probes in all thermal zones. Temperature accuracy with platinum probes is < ±1 °C over the complete temperature range of the conventional Varian instrument (-99 °C to +450 °C). These performance yields better consistencies in chromatograms when transferring methodologies to other Varian chromatographs. Figure 8 shows retention times for several hydrocarbons on four different Varian chromatographs. Even with subtle differences in columns and column flows, these retention times are remarkably close because column temperatures are identical with use of platinum probes.

Figure 8. Retention Time Consistencies for Selected Hydrocarbons with Four Different Varian Gas Chromatographs

Temperature accuracy plays a major role in enabling retention times to be consistent among several gas chromatographs. Subtle differences in column flow and length are overwhelmed by the impact of temperature.

Column temperature program: -45 °C, hold 0.1 min., ramp to +180 °C at 3 °C/min, ramp to +250 °C at 50 °C/min.; Column: J&W DB-1, 0.32 mm, 1 µ film, ID, 60 m, Column flows: #1 –1.9 ml/min, #2 –1.85 ml/min, #3 – 2.2 ml/min, #4 – 2.0 min/min.



The allowable heating rates are dependent on the expected thermal mass of the heated zone. For example, thermal conductivity detector ovens are purposefully massive to provide the required thermal stability. Sample concentrators, on the other hand, have low thermal mass to permit rapid heating and cooling. When a type of zone is specified in the Varian 3800 setup, an anticipated heating rate is defined. If a zone heats more rapidly or more slowly than expected, error messages are triggered and the zone is turned off. This checking prevents thermal runaways and detects faulty heater cartridges. Table II lists the possible thermal zones in the 3800 in order of expected heating rates.

Table II. Order of Expected Heating Rates for Varian 3800 Heated Zones

Fastest ↓ Slowest

Sample Preconcentrator Trap (SPT)
1079 Temperature Programmable Injector
Column Oven
1041 Syringe Injector
FID/ECD/TSD/PFPD Ionization Detectors
Valve Oven
Methanizer
Thermal Conductivity Detector (TCD)

Possible error messages on the Model 3800 relating to thermal zones are listed below. Most of these failures will cause all zones to be disabled, and the problem must be corrected before the instrument becomes functional again. Improper assignment of heat zones during instrument set-up can yield several of these errors, as the zone may not be able to attain the expected heating rate.

- "Zone X[7] temp probe response is too slow" – Zone is not heating up as expected – heater cartridge is likely to have failed.
- "Zone X temp probe response is too fast" – Zone is heating faster than expected and is likely to have suffered a thermal runaway.
- "Zone X is out of ready band" – Actual temperature is away from setpoint by a zone-specific tolerance.
- "Zone X temp probe is open" – Wiring to the probe has possibly broken; the probe should be replaced.
- "Zone X temp probe is shorted" – Wiring to the probe has undoubtedly shorted; the probe should be replaced.
- "Zone X thermal runaway" – Zone is heating far too quickly and is shut down to reduce potential damage.
- "Zone X maximum temp has been exceeded" – Zone is above maximum permitted temperature and is shut down to reduce potential damage.
- "Zone X lower than minimum temp" – Zone is cooler than expected and the heater cartridge has probably failed.
- "Zone X max setup temperature exceeded" – Zone is above maximum temperature specified in "instrument setup" and is shut down to reduce potential damage.

The Electronic Flow Controllers (EFC) in the 3800 possess built-in heating to control their temperatures to +45 °C. Consequently, any change in ambient temperature will have no effect on performance accuracy of the flow controller. For manual flow controllers, a non-standard heating pad can be mounted on the pneumatics panel and controlled through an available heat zone of the Model 3800.

Top performance for a gas chromatograph mandates careful control of nearly all temperature zones within the instrument. Stable temperature settings for the column oven and for column flow controllers enhances retention time reproducibility. Accurate temperature monitoring and control improve method transfers to different instruments. Moreover, employment of platinum resistive probes provides more protection from disastrous thermal runaways. Full proportional/integral/derivative control of all thermal zones minimizes potentially devastating effects of temperature overshoot and undershoot.

[7] Zone X can be any of the six available injector/detector heating zones or the column oven on the Varian 3800.

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