



GC Ovens — A Hot Topic

John V. Hinshaw, ChromSource, Franklin, Tennessee, USA.

In this instalment of "GC Connections" John Hinshaw examines various means to heat gas chromatography columns. Conventional forced-air circulation ovens are most common, but a number of other ingenious heating methods have been used in the past and recent developments have brought innovations.

In the second Monday of October in Canada and on the last Thursday of November in the United States, many people celebrate Thanksgiving Day by partaking of a traditional turkey dinner with friends and family. The preparation of this large indigenous fowl is the topic of much debate regarding how to properly programme an oven to produce the best-tasting and safest result. Theories abound, ranging from isothermal heating at 160 °C for 10 min/kg to a negative temperature ramp descending ballistically from 230 °C to 180 °C that purportedly imbues a pleasant hue and texture. I'm sure it has occurred to many gas chromatographers that they have a vastly superior device for preparing baked meals in their laboratories, but how many have actually tried to do so?

I personally experienced one such attempt, although with something much smaller than a turkey. I once attended a holiday fête that took place adjacent to the gas chromatography (GC) laboratories where I worked, and employees were encouraged to bring a warm dish. One manager took this request unkindly and contributed one can of baked beans out of spite. He placed the unopened can in a GC oven and commenced a temperature programme from room temperature to 200 °C. After approximately 10 min, a muffled report echoed from the laboratory into the party. Afterwards, we always knew when that particular GC oven was being used by the accompanying aroma of burned beans. Of course, this use of laboratory equipment violates several safety rules as well as any decent laboratory results quality programme.

Naturally, GC ovens were not designed for cooking but rather to provide a suitable

thermal environment for GC peak elution. GC ovens have gone through an evolutionary development as have other GC components. Today, most GC ovens use rapidly circulating air to transfer heat to and from the column. Chromatographers have used other means to control the thermal environment surrounding a column, and some of these means have been quite ingenious. First, though, let's take a look at what kind of thermal conditions a column requires to deliver its best possible performance.

GC Oven Requirements

In GC, the relationship between peak retention and temperature is fundamental. Changes in temperature cause significant, exponential retention shifts. In a previous instalment of "GC Connections," I discussed the dependence of retention times upon column temperature as it relates to isothermal and temperature-programmed elution (1). In general, retention times decrease by a factor of two for every 15–20 °C increase in column temperature (T_c). This phenomenon allows chromatographers to control solute retention times by adjusting the column temperature. This same effect, however, causes small run-to-run shifts in the average column temperature to randomize peak retention times by a small amount from one run to the next. Slightly higher oven temperatures cause peaks to be eluted a little earlier, and lower temperatures shift retentions to slightly longer times. These long-term changes in average oven temperature are different from spatial fluctuations along the column caused by temperature gradients in the GC

oven, and they cannot account for short-term oven temperature fluctuations in time caused by normal electronic and software temperature-control processes. If large enough, these spatial and short-term changes will affect peak shapes and resolution: GC oven designers must consider all types of temperature variations.

Run-to-run temperature deviations: In general, I would like to keep run-to-run retention time deviations within a window of $\pm 10\%$ of the peak width at base. That way, there is little ambiguity concerning peak identification by absolute retention time. I can't assume that other, less stringent peak-identification schemes, such as identification by relative retention time, will be used, so I must consider the most difficult case. The narrowest practical peak widths will put the greatest demands on the oven temperature repeatability. Significantly retained peaks — those with retention factors of 2 or greater — are eluted from relatively short, 10 m \times 0.20 mm, thin-film capillary columns with base widths greater than or equal to 1.5 s. This figure assumes that the column operates at its optimum average linear helium carrier gas velocity of roughly 30 cm/s with the best theoretical efficiency. Chromatographers can obtain narrower peaks by operating columns at higher than optimum carrier-gas velocities or by choosing narrower or shorter columns — in other words by performing fast GC. But, in general, this method is as fast as peaks go for most GC systems in operation today. I'll take a look at one alternative heating system for fast GC later on in this "GC Connections" column.

The oven is not the only factor that contributes to run-to-run retention-time variations. The pneumatic system has a significant influence, and the data-handling system introduces other uncertainties, including determination of the exact run start time and the peak apex or centroid. I assembled a statistical analysis of these factors and the GC oven using typical values for modern GC instrumentation and columns, which resulted in too much material to reproduce in this column. Interested readers can refer to my website for this supplemental information (see <http://www.chromsource.com> and click on "GC Connections"). In this analysis, I assumed that the room temperature and GC line voltage supply are stable and do not influence the actual oven temperature and column pressure drop. This situation is not always the case, of course, and these problems fall into the category of instrument environmental difficulties that should be resolved before attempting to obtain the best retention-time reproducibilities.

"In GC, the relationship between peak retention and temperature is fundamental."

Isothermal elution: The analysis indicates that the average oven temperature must repeat from run-to-run to within less than $\pm 0.05^\circ\text{C}$ to hold retention times inside a window of $\pm 10\%$ of peak base widths for commonly encountered solutes. Lee, Yang and Bartle (2) cite a similar requirement in their 1984 book. These figures are for typical test mixture solutes separated at moderate isothermal temperatures on short narrow-bore, thin-film capillary columns, which represent the more difficult situation. Columns with thicker stationary films, longer columns, wide-bore columns and packed columns generate broader peaks and may tolerate a less stringent temperature environment and still deliver retention-time repeatability adequate for peak-identification purposes. Alternatively, fast GC separations generated on microbore columns with inner diameters smaller than 0.2 mm, on columns shorter than 10 m, or with elevated carrier-gas velocities greater than 100 cm/s may require better temperature control to contain retention times within $\pm 10\%$ of base-width window.

Pneumatic system: In general, modern pneumatic systems with electronic pressure controllers or high-precision mechanical regulators designed for capillary GC deliver

more than adequate carrier-gas control at pressures greater than 5 psig (35 kPa) with the best performance occurring at pressures of 20 psig (69 kPa) or greater. Random run-to-run pressure fluctuations are a less significant contributor to retention-time variability than normal oven temperature variations. At higher pressure drops, however, changes in atmospheric pressure can cause long-term retention time drift. In those instances, an electronic pneumatic system with atmospheric pressure sensing will compensate for these effects. High-output range electronic controllers that deliver pressures greater than or equal to 150 psig (1000 kPa) should be reserved for columns that require high pressure drops; they lack the resolution to deliver adequate low-pressure control. Pressure-controlled pneumatic systems can affect retention-time repeatability significantly when operated at pressures less than 3 psig (20 kPa), as may be required with wide-bore columns shorter than 20 m. In those instances, a flow-controlled system is desirable.

Temperature programming: With isothermal elution, peak base widths increase approximately in proportion to the retention time; however, with programmed-temperature elution, the base widths stay approximately constant across a GC run for peaks that are eluted during the temperature ramp. Most peaks are essentially immobilized at the initial column temperature; as the oven temperature increases, solutes begin to move along the column. Each analyte spends about the same time moving through the column (3), so the peaks have approximately the same widths as they are eluted. For temperature programming, oven temperature ramps must repeat the time-temperature curve with the same precision as required for isothermal elution. The oven heating system must have sufficient power to maintain a linear programme ramp from the start temperature to the final temperature. The maximum rate at which the oven temperature can increase linearly is related to the thermal mass of the oven cavity, including the column, the power that the heater can dissipate into the oven, the efficiency of the oven boundary insulation and the differential temperature between the inside of the oven and the external

environment. I'll take a look at some maximum heating rates for different kinds of ovens later in this column.

One principal difference between isothermal and programmed elution is the slight time lag between the actual column temperature and the set point temperature of the temperature ramp. As the oven temperature controller increases the set point temperature according to the demands of the programme ramp, the actual oven temperature lags behind by a small amount and the temperature inside the column lags a little more. The temperature lag is larger at higher programme rates. This temperature differential is a necessary by-product of both the nature of temperature-control algorithms and the physics of heat transfer from the heater to the column. For my purposes, it is the temperature in the column itself that counts.

Not only must the electronics and software repeat the same time-temperature profile across the run, but the thermal conditions in the oven must also be the same from the start to the end of the run. This condition is one reason temperature-programmed ovens require a temperature equilibration period after cooling down before a new run can commence. Shortly after the oven cools down, the oven temperature probe may indicate the initial oven temperature, but a significant amount of heat remains in the oven; the walls and the column can be significantly hotter than the indicated temperature. This situation is the reverse of the temperature lag encountered with oven heating, and good practice dictates that users allow sufficient time for the residual oven heat to dissipate and bring the column as close as possible to the initial oven temperature. An equilibration time of 2–4 min is typical for most air-bath GC ovens with temperature-programming capability. With isothermal elution, no equilibration time is necessary after the oven reaches its temperature for the first time, because the temperature is not changed during the run.

Oven gradients: A high degree of run-to-run average temperature repeatability ensures the best retention-time precision. GC ovens must also maintain a uniform and stable temperature profile across the column during elution. The process of solute partitioning and migration along the column averages out temperature gradients so that peaks are eluted as if they experienced the average column temperature along the length of the column. Minor temperature fluctuations of

less than 1 °C along the column do not affect retention times seriously, as long as these gradients are stable and repeatable. Unstable gradients that change from run to run, however, will impose additional uncertainty on retention times because they affect the average temperature that solutes experience.

Some temperature gradients are normal and necessary. The column inlet and outlet connect to the injector and detector, which are normally at elevated temperatures relative to the oven. Most modern capillary GC systems position the column ends inside the inlet and detector, which creates a negative temperature gradient from the inlet into the column and a positive gradient into the detector. The net effect on retention is negligible, because solutes will be retained weakly, if at all, in the short sections of heated column ends, which act more like connecting tubing. Gradients also exist close to the oven boundaries, because of heat losses or gains from cooler oven walls or warmer heated inlets and detectors. In a conventional air-bath oven, the column is normally positioned in the centre of the oven to immerse it in the most thermally uniform area. These kinds of stable temperature gradients do not affect performance seriously if they are stable during a run and from run to run in the long term.

Gradients that fluctuate from run to run will affect retention time stability, but gradients that fluctuate rapidly during a run will affect peak shapes. A poorly sealed air-bath oven can generate this type of gradient. A controlled amount of air is normally allowed to circulate through an air-bath oven to prevent the build up of explosive hydrogen gas. This circulation is performed in a way that prevents the generation of significant temperature gradients. But if the oven door or vent isn't sealed properly, significant amounts of cold air can enter and blow directly on the column to create a rapidly fluctuating localized temperature gradient. For fused-silica columns, with their thin walls and rapid thermal time constants, fluctuating gradients will alternately trap and release portions of solute bands as they pass by, which will distort the peak shapes and can even split peaks into apparent multiples.

Oven Heating Schemes

Over the years, GC researchers have envisioned and built a wide variety of column heating instruments. Early workers were well aware of the requirements imposed by the sensitivity of GC retention times to temperature changes and by the

problem of transient thermal gradients. They had it easier than present-day chromatographers, however, because they had to accommodate packed columns and metal or thick-walled glass capillary tubing, but not fused-silica tubing. Thin-walled, fused-silica tubing responds more rapidly to oven temperature changes and is more susceptible to the effects of rapidly changing oven gradients. The newest generation of GC ovens includes features designed to maximize performance with currently available columns.

I'll divide oven heating schemes into two broad categories: those that rely on a fluid to transfer heat to and from the column and those that use solid-state materials for heating purposes. Today, of course, air is the heat-transfer fluid of choice for most, but that was not always the situation. Chromatographers have experimented with various vapours and liquids as well. Solid-state ovens have been used for temperature programming with metal capillary columns, and small completely solid-state ovens are found primarily in portable instruments because of their low power requirements and good long-term stability. Columns installed inside resistively heated metal tubing that is suspended inside a conventional air-bath oven deliver very fast programming rates for high-speed GC.

Fluid ovens: The earliest report I could find of a fluid oven for GC dates back to 1952 and involves the suspension of the column inside a vapour bath over a boiling pure

substance (4). This technique of temperature regulation had been used in various related disciplines before gas-partition GC, and it was a natural step to use it for the then-new technique. Operators could change the temperature of the vapour bath by regulating the pressure inside a sealed oven container. *p*-Xylene, for example, boils at 138 °C at 1 atm, and temperatures approximately 30 °C lower were attainable at reduced pressures (5). Changing the oven temperature outside this limited range was inconvenient, because the pure substance had to be exchanged for another with a higher or lower boiling point. This arrangement produced a fairly stable thermal environment for the column, as long as the atmospheric pressure didn't change too much. Other problems arise with decomposition of the boiling substance at higher temperatures and the flammability of the vapours, and chromatographers abandoned this kind of system fairly early.

Oil baths were also used as oven thermostats (6). After the operating temperature was reached, a very uniform thermal environment was possible if the heating vessel was well insulated and efficiently stirred. Temperature control circuitry provided fairly good temperature stability. These baths could be temperature programmed but at a limited rate because of the large heat capacity of the oil. A main drawback of oil-bath ovens was the

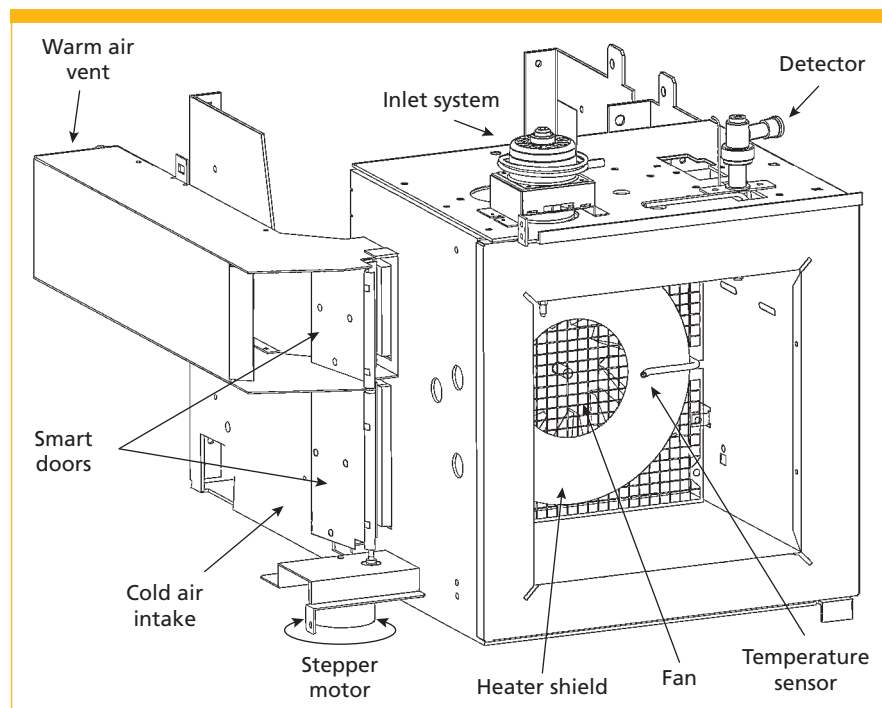


Figure 1: Modern GC oven schematic. (Courtesy of PerkinElmer Analytical Instruments, Norwalk, Connecticut, USA.)

"The development of GC ovens has helped foster the acceptance of new GC column technologies."

inconvenience of working with high molecular weight oils that would coat the column and connections. The slightest leak would permit the oil to enter and destroy the column or, at the least, drastically modify its retention characteristics. Changing the column was difficult and messy.

Air-bath ovens: GC researchers understood from the onset that an air-bath oven could be superior to liquid- or vapour-bath designs. The temperature in an air bath could be varied rapidly across a wide range without changing the working fluid, and it would be much easier to change columns. However, early air-bath oven designs from the 1950s suffered from large temperature gradients and a significant lag time between the oven set point and actual column temperatures. Special fans and better insulation helped to remedy the situation, and by the mid-1960s the air-bath oven was almost universally accepted. The subsequent introduction of microprocessor temperature control in the 1970s and the adoption of a number of other important features — including improvements made specifically for fused-silica columns — resulted in modern GC oven designs, such as the one shown in Figure 1.

The oven door (not shown) covers the front. The impeller fan at the rear of the oven creates a rapid, turbulent airflow that

minimizes gradients in the cylindrical column area in the oven centre. A heater shield prevents radiated heat from heating the column or the temperature sensor. A pair of smart doors opens under stepper-motor control according to the cooling demand of the oven programme. Cool air is forced into the lower door with a fan (not shown) and hot air exists through the upper door.

This type of oven can deliver retention time repeatabilities well within the criteria cited earlier in this column. Modern GC ovens are capable of linear temperature programming rates as high as 75 °C/min with a standard 2 kW heater, when the instrument software permits it. The maximum linear programme rate declines to approximately 20–30 °C/min at temperatures higher than 175 °C, because of increasing heat losses across the temperature gradient from the oven to the surrounding air. The more powerful optional heaters available with some instruments can yield programming rates as high as 120 °C/min that are suitable for high-speed GC separations.

The fastest GC total run times require not only fast heating but also rapid cooling to the initial oven temperature. The use of an extra fan — either separately or coaxially on the main fan motor shaft — that forces cooling air through the oven vents helps to speed cool-down time. Cryogenic cooling is another option that minimizes cool down, but it is not always convenient or available.

Solid-state ovens: GC experimenters also developed several solid-state column heating schemes over the years. An early design used heating wire that was simply wrapped around a packed column and

insulated with asbestos tape. Variable voltage provided rudimentary temperature control (7). Another approach connected a source of electrical current across the metal packed column itself, and at least one commercial gas chromatograph manufactured in the West used this method (8).

A current product line uses another approach to solid-state column heating by putting a column and a separate heater into a monolithic block. One or more metal capillary columns are wound with a heating element around a core, and the entire assembly is encased in thermoplastic resin. The column tubing terminates outside the oven assembly in adjacent valves, inlet systems, and detectors and the entire assemblage fits inside an insulated enclosure. This type of construction is attractive for portable isothermal gas chromatographs because once heated, it doesn't require much power to maintain temperature, and because it can be very small. However, changing the column requires a complete exchange of the inner oven assembly.

An alternative solid state-oven arrangement used a flat, helically coiled metal column sandwiched between two heated metal plates. This system was the Perkin-Elmer model 226 gas chromatograph (Norwalk, Connecticut, USA), which was marketed from 1962 to 1967. The instrument could perform 50 °C/min linear temperature-programming ramps that were quite fast compared with other instruments of the time, and it provided retention time and results reproducibilities comparable to those obtained using modern GC instrumentation (9). Figure 2 shows a photograph of this system's column oven assembly. The flat helical metal capillary column was sandwiched between two aluminium plates, with exit

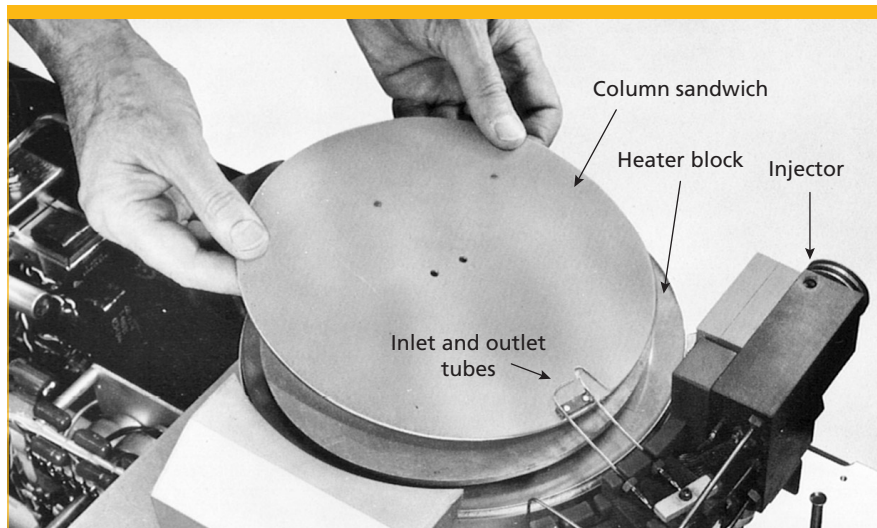


Figure 2: Perkin-Elmer model 226 column oven assembly. (Courtesy of PerkinElmer Analytical Instruments, Norwalk, Connecticut, USA.)

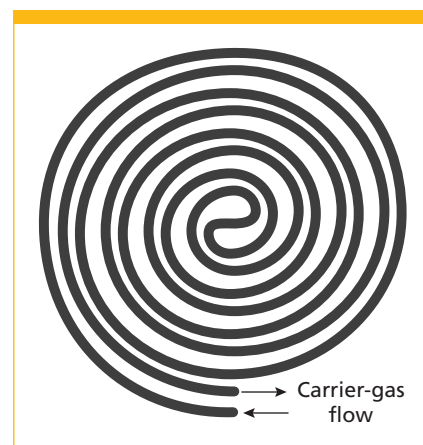


Figure 3: Metal column configuration for the PerkinElmer model 226 gas chromatograph.

holes for the column inlet and outlet. The sandwich was clamped between two flat heater blocks, and an insulated cover finished the assembly. Forced air or cryogenic fluid cooled the oven after temperature programming.

Figure 3 illustrates the column configuration itself. The column's outer diameter determined the number of column turns and, thus, the maximum length — longer columns with smaller diameters could be wound into the available space. The heater coils above and below the column were wound in a similar fashion. Columns were available with 0.010 in inner diameters and 300 ft lengths and with 0.020 in inner diameters and 200 ft lengths. Packed columns were available with 0.085 in inner diameters and 15 ft lengths.

More recently, researchers heated aluminium-coated, fused-silica columns directly by passing a current through the metallic outer layer (10,11). This device would have very fast heating and cooling rates, but this attractive concept was hindered by two principal difficulties. First, the outer metallic coating was uneven, which created unwanted temperature gradients, and second, each column coil had to be carefully insulated, thermally and electrically, from adjacent coils as well as from the column supports. Any contact created a large thermal gradient and shorted out the heater circuit.

A hybrid oven: A recent commercial system places a solid-state heating system inside a conventional air-bath oven. The EZ Flash GC system (ThermoOrion, Beverly, Massachusetts, USA) uses conventional 5 or 10 m fused-silica columns with inner diameters as large as 0.53 mm that are connected to standard inlet and detector ports with short lengths of deactivated fused-silica tubing. By using short columns with smaller inner diameters in combination with fast heating, this device can deliver the resolution of longer, larger-diameter columns in less time. Software

packages, such as the Agilent Technologies' Method Translation software (Wilmington, Delaware, USA), which is available free of charge at <http://www.chem.agilent.com/cag/servsup/usersoft/main.html>, can help determine appropriate column and elution condition adjustments.

The column runs coaxially inside a coiled, externally insulated, tubular, metallic heater that is suspended on a cage in an air-bath GC oven. The heater tube is insulated and is coiled to the same nominal diameter as conventional fused-silica columns. Inlet and detector covers over the heater and pneumatic connections insulate the column ends both electrically and thermally. An external controller senses the average heater temperature and regulates the electrical power accordingly. The device can achieve ramp rates as high as 1200 °C/min, a maximum temperature of 400 °C, and cool-down times of 1 min or less from 325 °C to 35 °C. Figure 4 shows the coaxial column-heater arrangement of this system. The heater insulation, the close contact between the column tubing and the heater, and its placement in a well-regulated air-bath oven minimize thermal gradients.

The EZ Flash GC system has an interesting history. It was first applied to explosives detection for airport security in the mid-1980s. A dual-column configuration delivered a combined sample preparation and analysis time of 18 s for explosives residues in a wide variety of gas, solid or liquid materials. In 1996, a multidimensional GC instrument based on the EZ Flash GC concept won the Pittcon Editor's Gold Award in recognition of the best new products. The current add-on single column system was introduced in 1998.

Conclusion

Gas chromatographers have invented and adapted various methodologies for controlling column temperature. Far from simple turkey baking requirements, the physics and chemistry of GC separation and elution determine the requirements for temperature control. The need for application flexibility or specificity determines what kind of heating system is appropriate. A broadly applicable system, such as the conventional air-bath oven provides the greatest flexibility at the expense of portability, power consumption, and space. Dedicated systems in which the column and heater are permanently mated yield low power consumption, portability and compactness. To a great extent, the development of GC ovens has helped foster the acceptance of new GC column technologies.

References

- (1) J.V. Hinshaw, *LC•GC*, **18**(10), 1040–1047 (2000).
- (2) M.L. Lee, F.J. Yang and K.D. Bartle, *Open Tubular Gas Chromatography: Theory and Practice* (John Wiley & Sons, Inc., New York, USA, 1984), 106.
- (3) J.C. Giddings, *J. Chem. Educ.*, **39**, 569 (1962).
- (4) A.T. James and A.J.P. Martin, *Biochem. J.*, **50**, 679–690 (1952).
- (5) A.I.M. Keulemans, *Gas Chromatography*, (Reinhold Publishing Corp., New York, USA, 1957), 59–61.
- (6) D.H. Desty and B.H.F. Whyman, *Anal. Chem.*, **29**, 320–329 (1957).
- (7) L.S. Ettre, *J. Chromatogr. Sci.*, **15**, 90–110 (1977).
- (8) L.S. Ettre, *Am. Lab.*, **31**(14), 30–33 (1999).
- (9) H.A. Gill and W. Averill, "Design Considerations and Performance of a Linear Programmed Temperature Gas-Liquid Chromatograph for Golay and Packed Columns," paper presented at the 1962 Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Pittsburgh, Pennsylvania, USA, 5 March 1962.
- (10) S.R. Lipsky and M.L. Duffy, *J. High Resolut. Chromatogr.*, **9**, 376–382 (1986).
- (11) S.R. Lipsky and M.L. Duffy, *J. High Resolut. Chromatogr.*, **9**, 725–730 (1986).

"GC Connections" editor John V. Hinshaw is president and principal scientist of ChromSource, Franklin, Tennessee, USA and a member of the Editorial Advisory Board of LC•GC Europe.

Direct correspondence about this column to "GC Connections," LC•GC Europe, Advanstar House, Park West, Sealand Road, Chester CH1 4RN, UK, e-mail: dhills@advanstar.com

For an ongoing discussion of GC issues with John Hinshaw and other chromatographers, visit the Chromatography Forum discussion group at <http://www.chromforum.com>.

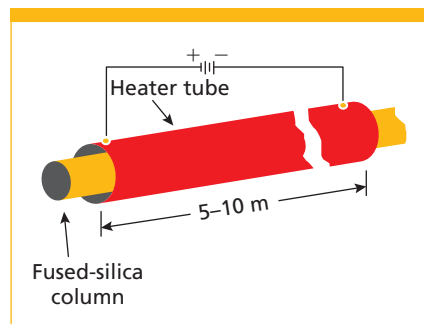


Figure 4: Heating schematic of the EZ Flash gas chromatograph. (Courtesy of Thermo Orion.)