

Gas Chromatography Ovens

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The transit of peaks through a gas chromatography (GC) column depends strongly on the thermal profile they encounter on the way. Gas chromatographers primarily rely on the classic hot-air-bath type of oven, but several alternatives are also in use. This instalment examines ovens for GC in several forms plus how oven thermals affect peak retention behaviour.

Gas chromatography (GC) ovens were not developed for cooking purposes, but rather to provide a suitable thermal environment for the elution of chromatographic peaks from GC columns. That being said, I have seen a number of inappropriate applications for GC ovens including reheating of cold pizza for lunch and the warming of casseroles for company potluck dinners. Some of us have even been known to trick out the oven door switch and use an idle GC system as a room heater on cold days.

GC ovens have gone through an evolutionary development just like other GC components have. Today, the majority of GC ovens use rapidly circulating air inside an insulated enclosure to transfer heat to and from the column, much like the convection ovens found in many high-end kitchen ranges. Some readers may be familiar with other means that chromatographers use to control the thermal environment surrounding a column; some of these are quite ingenious. First, though, let's take a look at what kind of thermal conditions a column needs to deliver excellent separation performance.

GC Oven Requirements

In gas chromatography, the relationship between peak retention and column temperature is fundamental. Changes in temperature cause significant exponential retention shifts, so GC instruments control solute retention times by carefully managing the column temperature along with the column pressure drop. In general,

retention times decrease by a factor of two for every 15–20 °C increase in column temperature (T_c). Peak retention depends differently on column temperature with isothermal versus temperature-programmed elution, but in both cases tight control of the temperature is paramount. This same temperature dependency also causes minor temperature shifts to randomize peak retention times by a small amount from one run to the next. Slightly

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higher overall oven temperatures cause peaks to be eluted a little earlier, and lower temperatures shift retentions to longer times. In addition to changes in the average oven temperature from one run to the next, other important temperature variabilities include spatial fluctuations along the column because of temperature gradients in the GC oven and dynamic short-term oven temperature fluctuations because of electronic and software temperature-control processes. If large enough, such spatial and short-term changes will affect peak shapes and resolution.

Run-to-Run Average Temperature Deviations

In general, run-to-run retention time deviations should stay within a window of about $\pm 10\%$ of the peak width at base. That way there is little ambiguity concerning peak identification by absolute retention time, including for partially separated peaks. The narrowest practical peak widths will put the most demands on the oven temperature repeatability. Relatively short, 10-m long, 0.20-mm i.d., thin-film capillary columns elute significantly retained peaks — those with retention factors of two or greater — with base widths of about 1.5 s minimum. This figure assumes that the column operates at an optimum average linear helium carrier gas velocity of about 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 going to “fast” GC. But in general this is about as fast as peaks go for the vast majority of GC systems in operation today.

The oven is not the only factor that contributes to run-to-run retention time variations. The pneumatic system also influences retention times significantly, and the data handling system introduces other uncertainties including its 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.

Interested readers can refer to a website for this supplemental information (1). In this analysis, the room temperature and GC line voltage supply are assumed to be stable and to not influence the actual oven temperature and column pressure drop. This is not always the case, of course, and such problems fall into the category of instrument "environmental" difficulties that should be resolved before attempting to obtain the best retention time reproducibilities.

Isothermal Elution: According to this analysis, the average oven temperature needs to repeat from run to run within less than ± 0.05 °C to hold retention times inside a window of $\pm 10\%$ of peak base widths, for commonly encountered solutes. Lee, Yang, and Bartle cite a similar requirement in their 1984 book (2). 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 cases.

Columns with thicker stationary films, columns that are longer, wide-bore columns, and, of course, packed columns generate broader peaks and may tolerate a less stringent temperature environment while still delivering retention time repeatability that is adequate for peak identification purposes. On the other hand, fast GC separations performed on microbore columns with inner diameters under 0.2 mm, on short columns under 10 m, or with elevated carrier-gas velocities over 100 cm/s, may require better temperature control to contain retention times within a $\pm 10\%$ of base-width window.

Temperature Programming: With isothermal elution, peak base widths increase approximately in proportion to the retention time, but with single-ramp 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 upon injection at the initial column

temperature; as the oven temperature increases, solutes begin to move along the column. Each spends about the same time moving through the column (3), which results in the peaks having approximately the same widths as they are eluted. For temperature programming, oven temperature ramps need to repeat the time and 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.

One principal difference between isothermal and programmed elution is the slight time lag between the

actual column temperature and the setpoint temperature of the temperature ramp. As the oven temperature controller increases the setpoint 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 our purposes, it is the temperature in the column itself that counts.

The electronics and software must repeat not only the same time and temperature profile across the run, but also the thermal conditions in the oven must be consistent. This is one reason why 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 there is still a significant amount of heat remaining in the oven; the walls and the column can be significantly hotter than the indicated temperature. This is the reverse of the temperature lag encountered with oven heating, and good practice dictates that sufficient time be allowed to dissipate the residual oven heat 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 required 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 also must 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. Where GC column ends are positioned inside the inlet and detector, a negative temperature gradient exists from the inlet into the column and a positive gradient out into the detector. The net effect on retention is negligible, since solutes will be weakly retained, if at all, in the short sections of heated column ends, which act more like connecting tubing. Gradients also exist close to the oven walls 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 stable temperature gradients do not seriously affect performance if they are stable both during a run and in the long term from run to run.

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 normally circulates through an air-bath oven, to prevent the buildup of explosive hydrogen gas. This is done in such a way that significant temperature gradients are not generated. But if the oven door or vent isn't sealed properly, significant amounts of cold air can enter and blow directly on the column and create a rapidly fluctuating localized temperature gradient. For fused-silica columns in particular, 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 may even split peaks up into apparent multiples.

GC operators play an important role in ensuring the minimum possible gradients, by installing columns correctly. As much as possible, columns should be centred within the column oven, with no length of the column closer than about 1 in. (2.5 cm) from the oven walls, except of course for the inlet and detector connections. Column mounting brackets provided by the manufacturer are the best way to provide secure and centred column mounting.

Oven Heating Schemes

Over the years, GC researchers have envisioned and built a wide variety of column heating schemes. 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 all columns.

Oven heating schemes fall 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 of us, but that was not always the case. Chromatographers have experimented with various vapours and liquids, as well. Solid-state ovens have been applied to temperature programming 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 or directly heated

column tubing, 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 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 even before partition GC came into its prime in the 1950s, and it was a natural step to use it for the then-new technique. The operator could change the temperature of the vapour bath up or down by regulating the pressure inside a sealed oven container. For example, *p*-xylene boils at 138 °C at 1 atmosphere and temperatures down to about 30 °C lower were attainable at reduced pressures (5). Changing the oven temperature outside this limited range was not very convenient because the pure substance had to be exchanged for another with a higher or lower boiling point. This

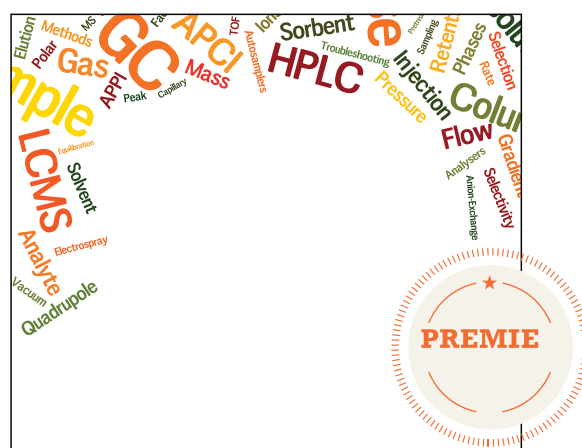
arrangement produced a fairly stable thermal environment for the column, as long as the atmospheric pressure didn't change too much. There were also problems with decomposition of the boiling substance at higher temperatures, as well as the flammability of the vapours, and chromatographers abandoned this heating system fairly early.

Oil baths were also used as oven thermostats (6). After the operating temperature was reached, if the heating vessel was well insulated and efficiently stirred, a very uniform thermal environment was possible. Temperature control circuitry provided fairly good temperature stability. Such 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 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 very least, drastically modify its retention characteristics. Changing the column was difficult and messy. A water bath was also used, but with a limited temperature range.

Air-Bath Ovens: GC researchers understood at the onset that an air-bath oven was potentially superior to liquid or vapour bath designs. The temperature in an air bath could be varied rapidly over 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 setpoint and actual column temperatures. Improved 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

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features — including improvements made specifically for fused-silica columns — resulted in modern GC oven designs that are ubiquitous today. GC air-bath ovens are available in both cylindrical and cubic forms.

Common features among air-bath ovens include high-speed fans for turbulent mixing that minimizes internal gradients. The columns and temperature sensor are shielded from direct thermal radiation emitted by the oven heating element. Incrementally positioned oven vents supply regulated amounts of cooling air for improved control at temperatures close to ambient and open fully for maximum cool-down rates.

These ovens can routinely deliver retention time repeatability well within the criteria cited earlier in this article. Today, GC ovens are capable of linear temperature programming rates up to at least 75 °C/min with a standard heating element. However, the maximum linear programme rate declines to around 20–30 °C/min at temperatures above about 175 °C because of increasing heat losses through the temperature gradient, through the oven insulation, and out to the surrounding environment. More powerful oven heaters available with some instruments can yield higher programming rates up to 120 °C/min that are suitable for higher speed GC separations. When the columns occupy only a fraction of the full oven volume, even faster heating and cooling are obtainable by reducing the oven air volume with an internal insulating blanket.

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

Solid State Ovens: GC experimenters also developed a number of different solid-state column heating schemes over the years. An early design used heating wire that was simply wrapped around a straight or U-shaped packed column and insulated with

asbestos tape. A variable voltage gave rudimentary temperature control (7). Another approach connected a source of electrical current across the metal packed column itself, and at least one commercial GC used this method (8). This approach has also been applied to metallic open-tubular columns and metal-coated fused-silica columns (9).

A different solid-state column heating design packages the 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 then encased in thermoplastic resin. The column tubing terminates outside the oven assembly in adjacent valves, inlet systems, and detectors, and the entire assemblage is placed inside an insulated enclosure. This type of construction is attractive for portable isothermal GC systems because once heated, it doesn't require a lot of power to maintain temperature and it can be very small in size. Changing the column requires a complete exchange of the inner oven assembly, however.

Micro GC: GC systems that use nonconventional micromachined inlet, column, and detector modules have experienced significant development in the past decade. Such devices may use columns etched into a planar substrate with integral or attached heating elements. Small both in size and power consumption, these GC systems are finding a niche in field portable applications.

Hybrid Ovens: Some of the most recent high-speed GC arrangements for benchtop instruments use a hybrid combination of an air-bath that surrounds solid-state heated columns. By using short columns with smaller internal diameters in combination with fast heating, such a device can deliver the resolution of longer, larger diameter columns in less time. In one arrangement, the column runs coaxially inside a coiled, externally insulated metallic tubular heater that is suspended on a cage in the air-bath GC oven. Such devices can achieve ramp rates up to 1200 °C/min, although at such rates the oven temperature

separation, but this is certainly an impressive capability. This type of hybrid arrangement is available as a special oven door with integrated electronics and controller.

Conclusion

Gas chromatographers have invented and adapted various methodologies for controlling column temperature. Far removed from simple cake 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 the kind of heating system that is appropriate. A broadly applicable system such as the conventional air-bath oven gives 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. Interest in high-speed and high-resolution GC will continue to spur developments in column heating technologies.

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