High Throughput and Rapid Response Gas Chromatography

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Have Large Cumbersome Air Blown Gas Chromatography Ovens Had Their Day?

Since the late 50's, conventional gas chromatographs (GC) have been designed in much the same way, with a heated circulating air oven for the column and block heater ovens for the injector and detector. Evolutionary development of the column oven has been influenced by the improvement in column technology from the original large diameter packed columns to todays small bore wall coated capillary columns with their impressive separation capabilities. Current GC column ovens have large stirring fans, high power heaters, multiple skin chambers, forced air cooling and sophisticated electronics to control the heating and cooling cycles.

The last ten years has seen the commercial development of Fast GC systems which dispense with the traditional air blown column oven altogether and heat the column either directly or with very closely coupled heaters along the length of the column. Fast GC can be described as any GC, which performs the same analysis as conventional GC in a reduced time whilst retaining the required resolution. This not only includes the actual sample analysis, but also the cool-down, hence total cycle time. Typically Fast GC enables a 5 to 10 fold reduction of analysis time, with similar enhancements for the cool-down.

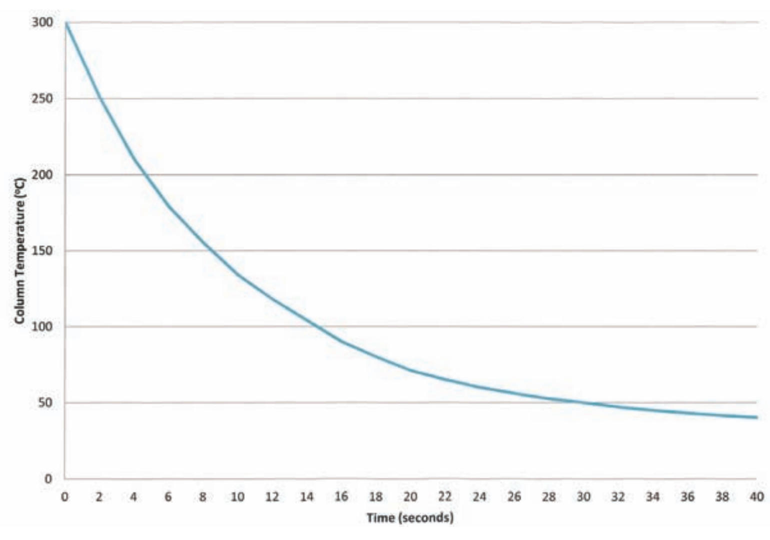

Figure 1. Cooling curve of Ellutia 300 Series Fast GC from 300°C to 40°C in 40 seconds.

These low thermal mass Fast GC systems heat close to the minimum mass possible and therefore can heat and cool the column at rates way beyond the capabilities of conventional GC ovens. The improved heating and cooling rates *(Figure 1)* achieve vastly reduced cycle times using much less energy, increasing the throughput of a GC, hence, reducing the cost and energy consumed per sample.

What is this New Technology?

Currently a plethora of technologies are available for low mass Fast GC column heating systems, some of which are illustrated below:

- Columns etched onto silicon wafers with built in heating. These have been found to be mainly suitable for low boiling point components and gas samples *(Figure 2)*.
- Resistive heater wire bundled with the coils of a fused silica capillary column.
- Resistive heater wire arranged in parallel and close to a fused silica capillary column.
- The fused silica column placed inside a steel tube which is resistively heated *(Figure 3)*.
- Direct resistive heating of inert coated steel capillary columns *(Figure 4)*. These systems heat the minimum mass possible.

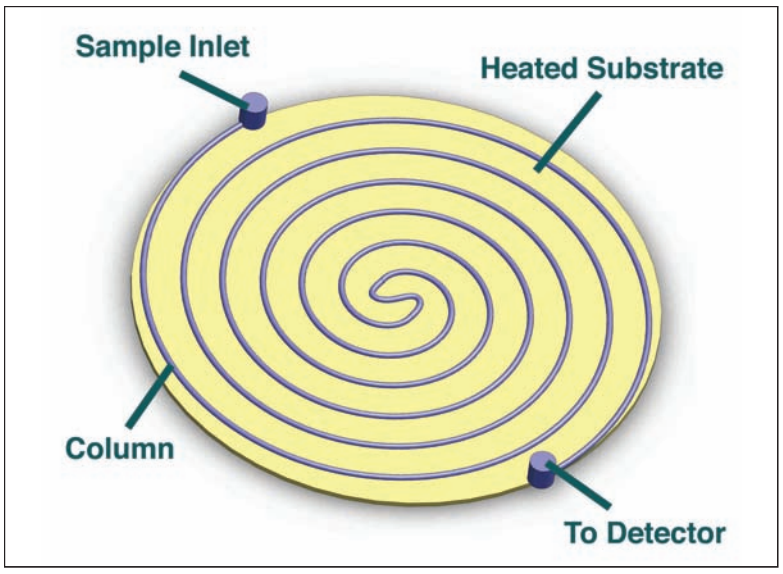

Figure 2. Example of low mass silicon wafer GC column heater.

Some of these low mass technologies are available as accessories to retro-fit onto conventional GC systems, allowing the use of existing injectors, detectors and data collection/manipulation software.

Currently, standalone systems are increasing in popularity, as these provide the benefits of the retro-fit Fast GC accessories, but are optimised towards low mass heating and cooling, therefore producing a further increase in performance, and generally requiring less power.

With such low masses being heated, a small amount of power can give a very rapid change in temperature causing instability in the system.

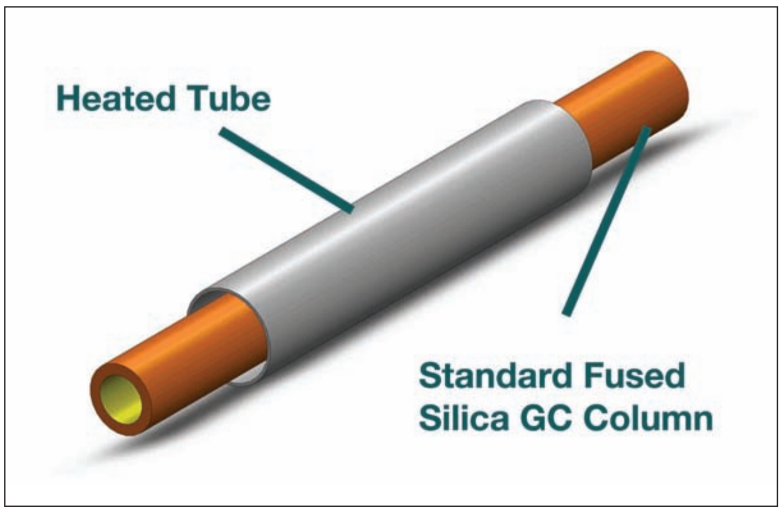

Figure 3. Diagram showing a fused silica GC column in a steel resistively heated tube.

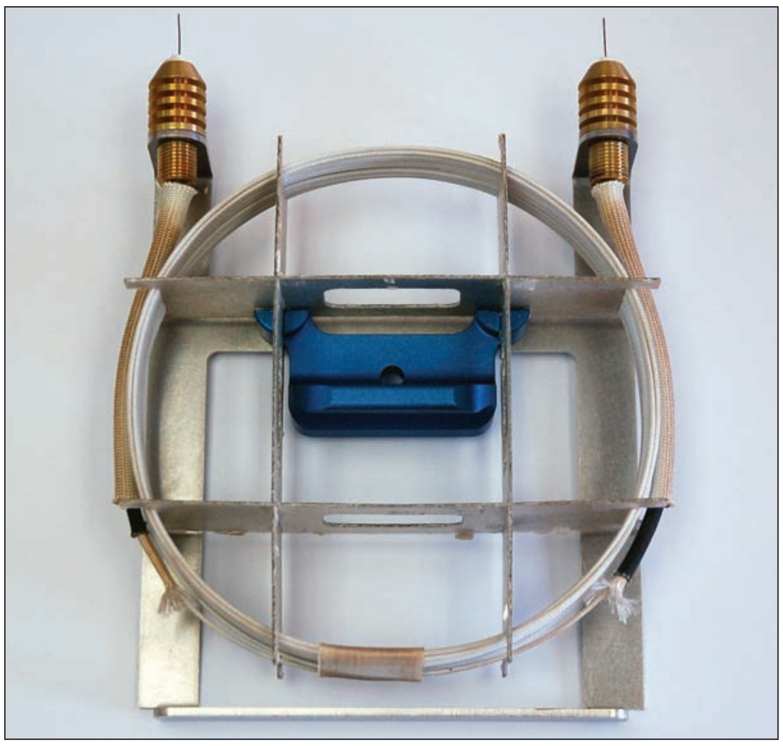

Figure 4. Steel column used in direct resistively heated systems.

Specialised control systems have to be employed to accurately control the temperature of the column. Some systems use a temperature sensor to measure the column temperature but these have problems due to their lag. Therefore, the actual temperature of the column can be several degrees above or below the sensors reading.

Systems that employ heating of stainless steel columns or sheaths can utilise the physical properties of the alloy. As the steel changes temperature, the resistivity alters and therefore its resistance varies. Electronic circuitry is designed to measure this resistance whilst applying power to the column. By using the dimensions of the column or by calibrating at a known temperature, the actual temperature can be calculated.

Due to the lack of an air blown oven surrounding the column, the elimination of cold spots is of vital importance. Cold spots along the column can cause a number of adverse effects to the chromatography. Problems such as thermal peak splitting (also known as Christmas-tree peaks), severe peak tailing or discrimination of high boiling compounds, can all be attributed to cold spots in the column. In general the temperature of the main coil of most systems is very consistent, the problem is commonly associated with the limbs used to connect to the injector and detector. Most systems employ extended heated zones in this area, specifically to eliminate cold spots. Other accessory systems use the whole conventional GC oven as an interface oven between the column and the injector/detector. Due to running the oven at elevated temperatures for prolonged periods of time, a reduction in lifetime of the oven is likely and a vast amount of energy is wasted, negating the saving in energy of low mass heating systems.

Control of column temperature in low mass systems is now as good as conventional GC systems and in certain cases performance is far better as the faster chromatography demands more accurate regulation. *Table 1* indicates the reproducibility of a low mass Fast GC systems for the retention time, peak area, height and width.

	C10				C25			
	RT (S)	Peak Area	Peak Height	Peak Width (S)	RT (S)	Peak Area	Peak Height	Peak Width (S)
Mean	14.58	17402	68943	0.245	56.7	20126	62289	0.3036
S.D.	0.0264	289	1585	0.0088	0.02562	569	2072	0.005838
RSD	0.181	1.66	2.3	3.58	0.045	2.83	3.33	1.92

Table 1. EZ Flash reproducibility data C10 and C25 alkanes after 50 injections.

Capabilities of Low Mass Fast GC Systems

Figure 5 displays a chromatogram containing C8 – C40 alkanes employing a linear heating ramp (red line). As expected the latter peaks (higher boiling compounds) are broader due to longer retention in the column. This has caused a large decease in size and lowered the separation of these peaks, although the whole sample is still eluted in less than 4.5 minutes.

Generally in conventional GC without additional attachments, heating ramps are restricted to ~40°C/min especially at upper temperatures of the column. This is attributed to the vast amount of power required to raise the temperature of the column and the oven at elevated temperatures. One of the main advantages of low mass Fast GC is the ability to use ramps typically ranging from 100 – 200°C/min all the way to the upper temperature of the column. As the amount of power required to elevate the temperature is low, the ability to perform increasing ramps towards the end of the run, enables sharper peaks and a reduction in time for the longer retention time components. The effect of increasing the ramp towards the end of the run is shown in *Figure 6*.

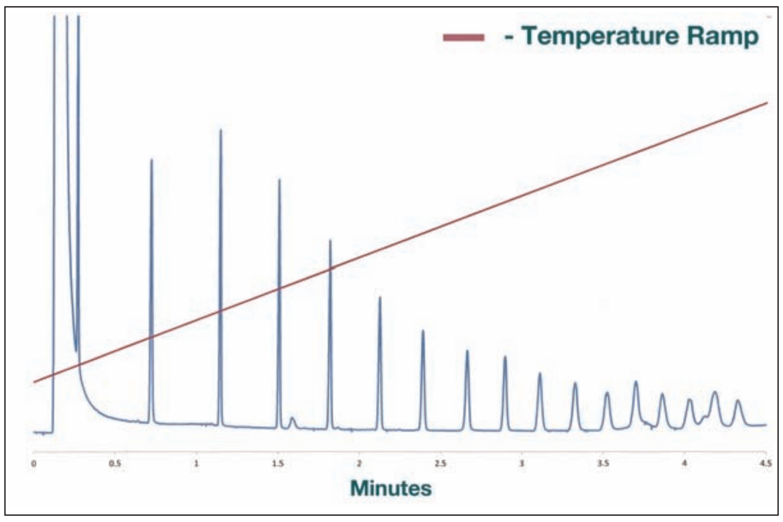

Figure 5. C8 – C40 using a linear temperature ramp.

The final 7 peaks have been subjected to elution during a more rapid temperature ramp, causing them to become sharper and eluted faster whilst retaining baseline separation. *Figure 7* displays the effect of employing a faster ramp on the lower boiling point components. Therefore the whole time for the chromatogram is reduced to ~3 minutes whilst retaining total separation of all components.

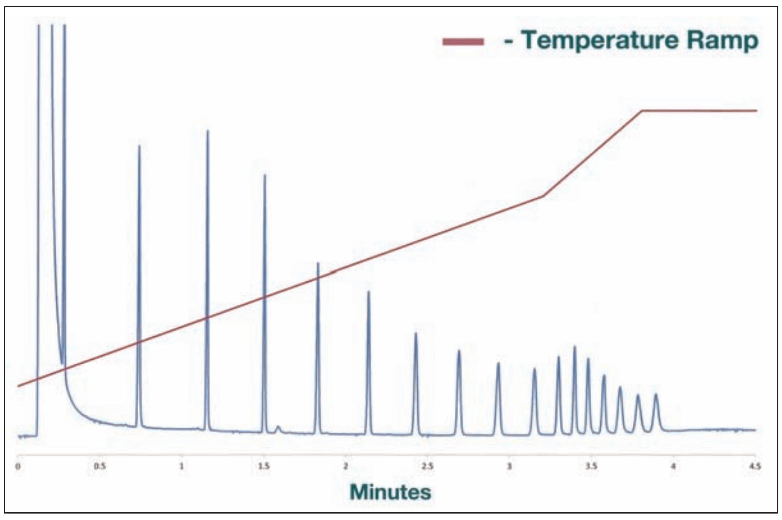

Figure 6. C8 – C40 with increased temperature ramp towards the end of the run.

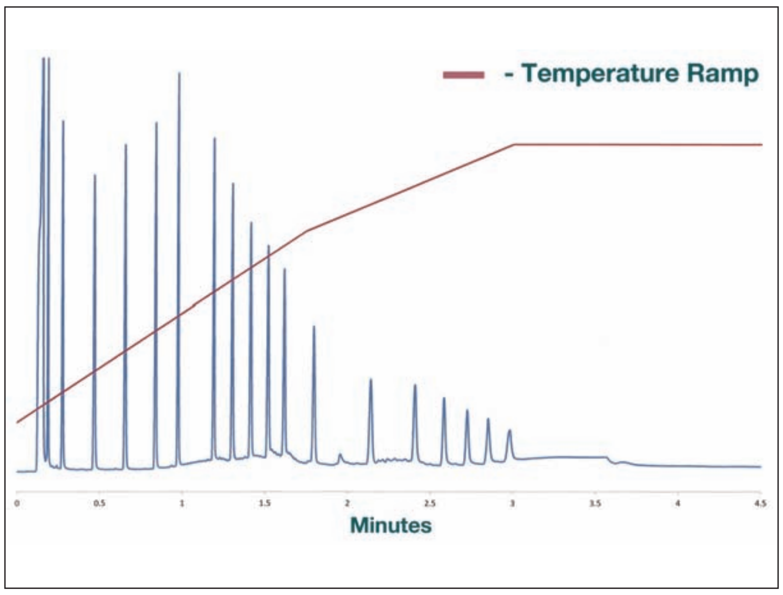

Figure 7. C8 – C40 with initial fast temperature ramp.

Getting the Best Results from a Low Mass Fast GC

One of the most important secrets of low mass Fast GC is eluting peaks during a rapid temperature ramp. This forces the back half of the peak from the column at a higher temperature than the front, producing a narrower peak and improving resolution. In order to elute on a rapid temperature ramp, all of the peaks of interest must be removed from the column before the maximum temperature is reached. This is advantageous for systems employing steel columns as opposed to the conventional fused silica, due to their extended temperature capabilities.

Another key influence of gaining separation in low mass Fast GC is increasing the ramp rate to separate peaks. Generally slower temperature ramps during the unresolved peaks elution is commonplace, although the opposite has been observed with low mass Fast GC. By employing faster ramps to produce sharper peaks, often resolution is achieved whilst gaining the benefit of reduced time.

To enable peaks to be eluted quicker, the implementation of shorter columns (typically 3-7 m) with thinner film thicknesses (typically 0.1-0.25 micron) are employed. As well as the increase in speed, employing shorter lengths has the advantage of reducing peak broadening and tailing effects, whilst reducing analysis time. By decreasing the column internal diameter, an increase in efficiency is obtained, as the number of theoretical plates per meter is greater. The use of thinner films enable faster interactions between the compounds and the stationary phase, decreasing the broadening of peaks although the trade off with resolution is of vital importance.

As with conventional GC, the use of H2 is preferred over He and N2 as carrier gas to maintain resolution whilst reducing column dimensions. Hydrogen can be used at higher linear velocities without severe detrimental effects to the efficiency, which can be observed at higher velocities with He and worse with N2. Improved performance with H2 as carrier gas has been observed at velocities even higher than the Van Deemter curve would predict (typically 100-120 cm/s). Although higher velocities are employed, with the combination of smaller diameter columns and reduced time for analysis and cool-down, a vast saving per sample of carrier gas is obtained, leading to monetary and environmental savings.

With the implementation of low mass Fast GC systems the environmental impacts are drastically reduced compared to systems containing conventional GC column ovens. As well as the vast reduction in power needed to elevate the temperature of the column, the energy required by the cooling systems is also far less. Generally to cool the conventional GC column oven, the hot air is directed from the rear of the instrument into the laboratory environment. This may gradually raise the ambient temperature during each cool-down cycle, especially if numerous systems are in use. To overcome these rises, expensive air conditioning units are commonly installed to maintain constant ambient temperature throughout the analytical laboratories. This means a great deal of energy is wasted unnecessarily both by the instruments on heating/cool-down and the air conditioning units. Conventional GC systems, especially those with increased powered fans for rapid cool-down, also produce a vast amount of noise compared to the near silent low mass Fast GCs.

Types of system available

- Portable gas analysis systems *(Figure 8)*
- Accessories that fit onto or inside conventional ovens *(Figure 9)*
- Dedicated fast direct heated column systems *(Figure 10)*

Figure 8. Ellutia semi-portable low mass fast GC.

Figure 9. Ellutia EZ Flash retro-fit low mass fast GC accessory.

Figure 10. Ellutia 300 Series low mass fast GC system.

Application Areas Which Successfully Use Low Mass Fast GC Systems Rapid Results

Process control, industrial clean-up operations and forensic science, do not often require analysis of large number of samples, but generally require information about sample composition instantly, as down time or slow response can result in lost revenue or even lives.

In each of these cases, Fast GC can give the user a unique advantage over conventional analysis.

In many industries, chemical reactions are used in the formulation of target compounds. The knowledge about the reaction process in pseudo-realtime can be very important due to the formulation of intermediate compounds. Fast GC allows the user to record a greater number of data points throughout a reaction, compared to conventional GC or liquid chromatography (LC).

High Throughput

As legislation becomes ever tighter for environmental, food and health samples, an increasing number of analyses need to be performed. Gas chromatography is a widely used technique for these types of samples. Therefore efficiency in this field will inevitably be required and Fast GC provides one of the valuable tools to enable this to happen.

A vast array of samples run in application laboratories now require full identification using sophisticated multi-dimensional and multi-channel detection systems. These systems are in general, very expensive and can only run a limited number of samples per day. Many of the samples analysed by these instruments are found to contain below the permissible limits for the analytes of interest.

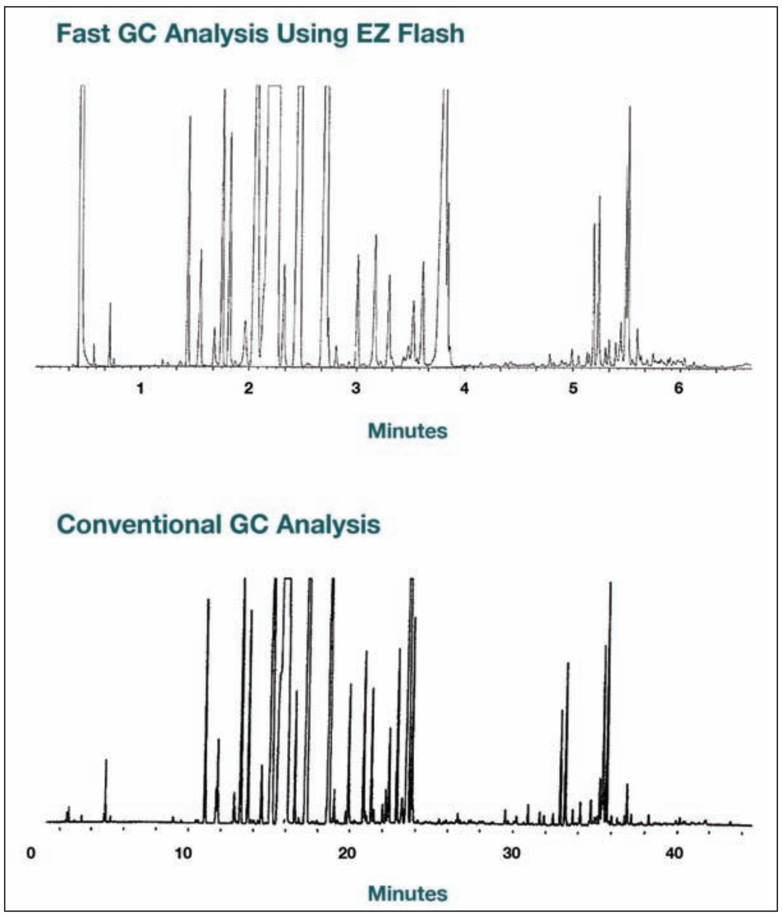

Figure 11. Lime oil analysis performed by conventional GC and EZ Flash fast GC accessory.

Screening with Fast GC enables only the positive samples (those above the permissible limits) to be fully examined on the bottleneck instruments, improving lab efficiency and throughput. Chromatograms of a distilled lime oil sample obtained from a conventional GC and a low mass Fast GC accessory is displayed in *Figure 11*, showing the rapid increase in time for analysis.

Fast Column Clean-up Without Back-Flushing

Some applications only require identification of volatile compounds amongst a less volatile matrix. Conventionally this could be achieved by sophisticated back-flushing systems. However with Fast GC higher temperatures on the column can be achieved within a few seconds hence allowing the less volatile matrix to be eluted giving a clean system ready for the next run to be carried out.

Semi-Portable Systems

Direct heated Fast GC systems require significantly less power and therefore lend themselves more readily to portable or semi-portable instrumentation, allowing on-site analysis.

Conclusions

In recent decades, tremendous progress has been made in gas chromatographic trace analysis, in terms of selectivity and detection limits. The obstacle which now faces most Chromatographers is the analysing of large numbers of samples in as little time as possible. One of the most cost effective methods is to dramatically reducing the analysis and cool-down times of the GC.

The new technique of low mass resistive heating systems combined with current GC sample introduction and detector technologies appear to be the answer. A very large number of applications can be greatly accelerated by way of extremely fast heating rates and short cool-down periods. In routine analysis, in particular, this means dramatic time saving as a result of greater sample throughput, and thus increased efficiency for the laboratory.

The lower power and gas requirements of the new techniques means greener instruments, less heat expelled into the laboratory and with a higher throughput producing a lower cost per sample, compared to conventional GC systems.

New Column Formats for Faster and High Resolution Separations

Dionex is pleased to announce the release of three new MAbPac™ SCX-10 column formats for faster MAb analysis, pH gradients, and LC/MS use. The MAbPac SCX-10 is designed specifically for high-resolution analysis and characterisation of MAb variants.

The new formats include: 4 × 150mm for fast MAb separations; 4 × 50mm column for pH gradients; and 2 × 150mm for upstream separations in LC/MS applications.

The MAbPac SCX-10 column’s unique nonporous pellicular resin provides exceptionally high resolving power, permitting the separation of MAb variants with high resolution. Hydrophobic interactions with the resin are essentially eliminated resulting in highly resolved peaks.

The column, complementing the MAb Characterisation platforms, is designed to address the regulatory requirements for biopharmaceutical characterisation, providing unmatched column-to-column and lot-to-lot reproducibility.

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Ellutia 300 Series High Throughput GC

The 300 series High Throughput GC from Ellutia is a new type of gas chromatograph using directly heated columns for rapid heating and cool down. It is truly a “FAST” GC with cycle times that are measured in seconds and not minutes. The system does not have an oven as in conventional GC products because direct heating of the column eliminates the need for one.

The 300 series fast GC is equipped with a split/splitless injector, EFC (Electronic Flow Control), 4-channel EPPC (Electronic Programmable Pressure Control), various detector options and boasts a small footprint of just 320mm x 370mm that makes it a valuable space saver.

A major bonus feature of the system is ACI (automatic column installation) allowing for easy push button exchange of columns. Simply place the column cartridge in position, press the column install button and let the install mechanism align and seal the column.

For more information on the 300 Series GC please visit www.ellutia.com/300series.html

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