

More Speed, Better Precision, Higher Sensitivity: Why Buy a New Gas Chromatograph?

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This article is adapted from one published in the November 2003 issue of *Nachrichten aus der Chemie*, the monthly news magazine of the German Chemical Society.¹ It discusses how gas chromatography (GC) instrumentation, columns and techniques have improved during the past 10–15 years, making even relatively new equipment obsolete for many applications. This article was translated from German by L.S. Ettre.

Let us assume that you would like to purchase a new gas chromatograph. However, your laboratory manager feels that the present instrument, bought 10 years ago, still works very well and nothing really has changed in the technology. Therefore, he does not want to allocate money for the purchase.

It is true that gas chromatography (GC) instrumentation has gone through many generations. Early on in the development of the technique, every year brought something new, but such a meteoric rise cannot last for long. Improvements have to slow down. However, this does not mean that the evolution stagnates: there are still plenty of new developments. Thus, while your old instrument works perfectly well according to the status of the technique 10 years ago, it will not permit you to utilize the innovations developed during the past decade. There are three fields in particular where your old instrument would hold you back: fast GC, better trace analysis and comprehensive multidimensional GC. Let us examine these three developments of the past decade.

Fast GC

A major trend in GC is to reduce the time of analysis. This can be achieved in several ways. The most important possibilities are reducing the diameter and length of the capillary column, increasing its heating rate or combining these two features.

The performance of a column is related directly to its

diameter: reduction of the diameter results in a concomitant reduction in the plate height — that is, an increase in the plate number per unit length. Theoretically, this would mean that a long column with very small diameter would have an enormous efficiency. However, such a column would need a very high carrier gas inlet pressure. This is one of the reasons that in practice, we have settled with 0.25–0.32 mm i.d. columns of 20–30 m in length. Nevertheless, if we further reduce the diameter, a much shorter column would still provide the same performance. At the same time, column length is related directly to the retention time: a 10 m × 0.12 mm column will have the same separation power as a 20 m × 0.25 mm column but will do the separation in half the time. The problem of inlet pressures that are too high can be overcome by using hydrogen instead of helium because its viscosity is only 45% of helium's. Another advantage of hydrogen is that its optimum velocity is about two to three times that of helium, further reducing the analysis time.

However, as always in life, there is no free lunch. Reduction in column diameter and length involves a reduction in sample capacity, peak width and carrier gas flow-rate (even with higher velocities). Instruments for such operation need more precise pneumatic regulators and inlet systems that can handle the small sample volumes. In addition, the reduction in the peak width induces special requirements for the detector and data

system: we need highly sensitive detectors with small time constants and fast data system sample handling rates. Without these, significant distortion in the peak shape, a shift in peak maximum (that is, a shift in the retention time), and false quantitative results will occur. These questions have been discussed in detail in a three-part article series by Hinshaw.²⁻⁴ Older instruments usually lack these possibilities; they work well with conventional columns and sample sizes but are not capable of functioning properly under the required new conditions.

The second way to speed up an analysis is to increase the temperature programme rate. With conventional capillary columns, we are generally accustomed to using relatively low programme rates (about 1–20 °C/min), and such rates provide good results. However, when using short, narrow-bore columns at higher carrier gas velocities, optimum performance provides higher rates.⁵ In addition, it has been shown that in many instances, even faster programme rates can be used without serious reduction in the column separation power: in the recent literature, one can find data on the use of programme rates as high as 20 °C/s (1200 °C/min). Such high programme rates cannot be achieved with conventional oven heating (air thermostat) systems, but require special techniques using resistive heating.⁶⁻⁹ Most recently, accessories permitting such use became available, but these cannot be installed in older instruments.

The recent literature usually distinguishes between conventional GC (CGC), fast GC (FGC) and very fast GC (VFGC). The general criterion in the classification is the peak width. Table 1 compares the analytical conditions and results obtained using these three versions of capillary GC.

Improved Trace Analysis

Since its beginning, GC has been used to determine small amounts of compounds present in an excess of large matrices. For example, determination of trace amounts of environmentally harmful impurities in soil, water and air became possible only with GC using highly sensitive and highly selective detectors.

During the past decade, a number of improvements have been introduced in instrument and system design that further enhance the possibilities of trace analysis. We should mention here, in particular, advances in sample introduction, in combined GC–mass spectrometry (GC–MS), and in column design.

Sample introduction: One of the fields where instrument construction has changed in the past 10–15 years is sample introduction. The newer GC systems permit the injection of large sample volumes, as much as hundreds of microlitres. Such large-volume injection devices are now part of the new GC instruments. The question here is not simply the replacement of the injectors: the evaporation of large volumes requires different heating profiles and ways to assure that excess solvent vapour that could be detrimental to the column and the detector exits separately.^{10,11} Other innovations in sample handling are headspace sampling,¹² solid-phase microextraction,^{13,14} and stir-bar extraction;^{15,16} these also require different instrument construction that is not available in older instruments.

GC–MS: Combined GC–MS systems have been available since the second part of the 1960s. The change that we have witnessed in the past decade is the use of the mass spectrometer

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as the standard detector for the gas chromatograph, fully utilizing its superior sensitivity. We do not speak anymore about “hyphenated systems,” as the mass spectrometer is considered an integral part of the unified system.^{17,18}

Present-day MS detectors usually have quadrupole construction with electron ionization. Modern quadrupole instruments reach the sensitivity of ion-trap systems and have very high scan rates that permit their combination with fast GC analysis. The newer instruments can be used easily in the chemical ionization mode, and it is also possible to automatically alternate chemical ionization from scan to scan with positive and negative ions. Triple-quadrupole instruments are also available for direct GC connection and permit the subsequent fragmentation of quasi-molecules formed in so-called soft ionization techniques. With the proper software, fast time-of-flight (TOF) mass spectrometers (with > 100 full-scale spectra) can provide both qualitative and quantitative results, even in the situation of overlapping peaks.

All these innovations occurred in the past 10–15 years and older instruments, even if they are capable of being combined with a mass spectrometer, lack the flexibility and ease of operation of the newer GC–MS systems, which have much improved software as well.

Capillary columns: In recent years, capillary columns have been further improved. When speaking about fast GC, we already mentioned the short columns with small (0.10–0.15 mm) internal diameters, and this miniaturization of the columns represents one of the major new innovations of the past decade. As mentioned earlier, the use of such columns requires improved GC systems with short connections, lower dead volumes, special inlet systems and highly sensitive detectors that are not available with older instruments.

Another innovation in capillary columns is related to the stationary phase. By properly tailoring the phase, its temperature stability is further improved, resulting in much lower phase bleeding and higher working temperatures.^{19,20} The low bleed rate is important particularly when such columns are used in GC–MS systems.

Comprehensive Multidimensional GC

Capillary columns permit the resolution of more than 100 sample components in a single run. Still, in the instance of very complex sample mixtures, the separation power of one column often is not enough. A partial solution to this problem was the so-called heart-cut technique, which utilizes two columns, and in which a difficult-to-separate fraction is transferred from the first column into the second column coated with a stationary phase of different polarity. In this way, a better resolution of the peaks in this region can be obtained. The disadvantage of a system such as this is that only a limited number of cuts can be transferred to the second column in a single run.

Essentially, comprehensive chromatography is based upon the same principles. However, now each peak from the first (usually non-polar) column, representing incomplete

separations of a number of overlapping peaks, is transferred to the second (polar) column for complete separation of the individual sample components. In this way, three-dimensional (3-D) chromatograms are obtained: the first two dimensions present the separation on the first and second columns, while the third dimension (the peak heights) gives quantitative information. The trick in the system is the way of transferring analytes from the first to the second column: the eluent from the first column is divided into small segments, which are trapped in a so-called modulator — essentially a cryogenic trap — which focuses each individual fraction and then, after rapid heating, injects it into the second column as a narrow band, starting its movement along the column. The second column is short and separates the individual fractions within a few seconds. The whole process must be performed very quickly because trapping and release of a fraction must be finished before the next peak reaches the modulator.

Comprehensive GC provides enormous separation power, and the resulting 3-D chromatogram might contain hundreds of peaks. For identification, the system must be connected directly to a TOF mass spectrometer. The amount of data generated by such GC × GC–MS systems is truly large, and the data handling puts very high demands on the data system.

This brief summary of the principles of comprehensive GC gives an indication of the complexity of the system, and those who are interested in its potential should study the growing literature.^{21–24} Today, accessories to the newer gas chromatographs are becoming available, permitting their modifications for such use. Obviously, older instruments cannot cope with this technique.

Instrumental Improvements

All the new developments discussed in this article represent new demands on instrumentation. These demands have been considered in the design of the newer gas chromatographs, from the injector to the detector and data system. Our discussion outlined some of these changes; a number of additional improvements help to obtain better accuracy and precision in routine applications. Here, only advanced electronic flow and pressure controls should be mentioned because they permit constant pressure or flow conditions, pressure programming and retention time locking and

automatic leak testing — just to mention a few capabilities. In addition, the newer instruments have improved software for both parameter control and data handling. None of these features is available with the older instruments.

We believe that there are enough reasons to replace older gas chromatographs with new, improved models. However, a word of caution: new instruments alone still do not guarantee correct analysis. The high methodical and design potential of the new instruments can be utilized fully only if users keep abreast of new developments.

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Table 1: Analytical conditions and results in gas chromatography*.

	CGC	FGC	VFGC
Column length (m)	20–30	10	5
Column i.d. (mm)	0.25	0.15	0.10
Carrier gas	helium	hydrogen	hydrogen
Average gas velocity (cm/s)	25–30	50–60	60–70
Pressure drop (Δp , <i>psig</i>)	10–20	15–17	20–25
Flow-rate (mL/min)	1–2	0.5–1	0.4–0.6
Heating rate ($^{\circ}\text{C}/\text{min}$)	1–20†	20–60†	60–1200‡
Peak width (s)	≥ 2	0.5–2	0.1–0.5
Analysis time (min)	≥ 10	5–10	1–5

* CGC = conventional GC; FGC = fast GC; VFGC = very fast GC

† oven heating

‡ resistive heating