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Review

Fast gas chromatography and its use in trace analysis

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Abstract

There is revived interest in the development and implementation of methods of faster GC. The paper summarises the advantages of faster GC analysis, general approaches to faster GC method development and practical aspects of fast gas chromatography with the utilisation of open tubular capillary columns with the stress on trace analysis. There are a number of ways to take the advantage of the improved speed of analysis by faster GC. Numerous options exist for pushing the speed of capillary gas chromatography (CGC) analysis. The scope of this paper is also to give an overview of the present state of faster GC instrumentation which is already available for trace analysis. The practicality of fast CGC is a function of sample preparation and the matrix interferences and how they affect the resultant resolution that may be achieved. Researchers have demonstrated the applicability of fast GC to trace and ultratrace analysis of volatile and semivolatile compounds also with narrow bore columns and difficult sample matrices (such as food, and soil extract). The main development of faster GC methods has been observed in the field of environmental analysis. Practical applications are presented. Both optimised sample preparation and experimental conditions for faster GC are the future perspective of trace analysis.

Keywords: Reviews; Trace analysis; Fast gas chromatography; Instrumentation, fast GC

Contents

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1. Introduction

Since the first description of gas–liquid chromatography by James and Martin in 1952 [1], gas chromatography (GC) besides its own technical development and the development of separation methods as a science discipline has been used to solve a large number of significant problems in various branches of science. Additionally, GC has found an impressive number of industrial applications.

The most important breakthrough in GC was the introduction of open tubular columns by Golay [2]. Since that time tremendous developments in column fabrication and instrument design have made the open tubular column the standard for most analytical applications. Capillary gas chromatography (CGC) is the most efficient method for the analysis of volatile and semivolatile compounds; it is therefore, highly suitable for the analysis of multicomponent mixtures of volatile constituents. The present CGC system allows analysis of compounds up to those with volatility equivalent to a molecular mass of *n*-alkane with the carbon atom number 120 (M=1682), if stability permits. The present state of development of instrumentation and column technology of high-resolution GC (HRGC) offers:

(i) The availability of various injection systems which allows efficient sample injection of compounds with a broad range of volatilities and concentration levels with minimal peak broadening and a possibility of large volume injection (LVI), which for trace analysis makes the sample preparation step easier, faster and/or allows lower limits of detection (LODs).

(ii) Accurate oven temperature control and electronic pressure control of carrier gas.

(iii) Capillary columns of different lengths and internal diameters, with the possibility to select stationary phases of different polarity and selectivity, film thickness, defined thermal stability and guaranteed reproducibility of column chromatographic properties (retention index, efficiency, inertness, phase ratio); bleeding of stationary phases is a measure of analytical sensitivity and today there are commercially available low bleeding columns, which are important to the field of trace analysis.

(iv) A number of reliable sensitive, universal and selective detectors; positive compound identification, particularly in multicomponent mixtures, is easy to establish by coupling to spectrometric methods, predominantly mass spectrometry (MS).

The primary objective of chromatographic analysis is to achieve the desired resolution of compounds of a mixture, or the critical pair of compounds, in the shortest possible time. Most analyses that have been performed with conventional capillary GC (columns with internal diameter, I.D., 0.2–0.32 mm) provide analysis times in the range of 10–60 min, depending on the type of sample, the number of components to be analysed and the chosen experimental conditions. The total cost of these analyses may be reduced through a reduction in analysis time.

The interest in fast GC dates back to the period directly after the invention of capillary columns. In 1962 Desty et al. [3] demonstrated the potential of capillary columns with a reduced diameter for high speed separations. The introduction of fused capillary columns by Dandeneau and Zerenner in 1979 [4] coupled with GC instrument improvements and the development of consistent column preparation processes has greatly enhanced the transition from packed to capillary columns. Though the principles and theory of fast GC were already established in the 1960s, the road of method development of fast CGC to routine analysis was fairly long. Chromatographers often used columns which were much longer than really necessary. Their primary goal was not the analysis speed. It showed the necessity to solve the problem of complexity of samples. The general focus was on the problem of separation and identification of compounds in multicomponent mixtures. Other demands on the development of capillary GC were brought about by trace analysis [environment, food, (bio-) medical sciences]. So, the focus was sample preparation, but also deactivation procedures to provide a better column wall inertness to analyse a wide range of analytes (from non-polar to polar at low levels of concentration).

In the 1990s the significant increase of cost per analysis (with high-cost equipment), the growth of the number of samples required to be analysed and situations where the results of the analysis are needed in a shorter time (on-site, in-field analysis) have been the consistent pressure and interest to decrease the time of analysis. The use of faster GC has been long hindered by a lack of adequate instrumentation. Today, commercial instrumentation

dedicated to fast GC is available and it can be implemented for routine analysis. When considering the merits of developing and validating a routine GC method, the total time involved with analysing the sample must be considered [5]. The total analysis time is the sum of the time for sample preparation, sample introduction, separation and detection, cool down and reequilibration, and reporting. Any time that the other factors become equal to or greater than the separation itself, the benefits derived from speeding up the separation become less significant. Fast GC brings with it the promise of providing faster, more cost-effective analytical answers. The effort required to develop and/or to improve the current method speed can be minimised by understanding relationships involved. For the best separation/speed tradeoff different method parameters have to be optimized.

This paper summarises advantages of faster GC analysis, general approaches to faster GC method development [5–15] and practical aspects of fast gas chromatography with the utilisation of open tubular capillary columns [5,7,8,13,15,16]. The scope of this paper is also to give an overview of the present state of possibilities and limitations of faster GC instrumentation used for trace analysis.

Trace component determination has been considered according to the convention when the analyte concentration is in the range of 1 to 100 mg/kg (or 0.0001 to 0.1%, w/w) and ultratrace component determination when the analyte concentration is lower than 1 ppm ($<$1 mg/kg, or $<$0.0001%, w/w) [17]. HRGC and GC–MS of volatile and semivolatile compounds in simple, but predominantly in multicomponent mixtures at the trace level concentration has been the most convenient method compared to other analytical methods, to achieve reliable and precise analytical results. A great part of trace anthropogenic contaminants and biogenic compounds in the environment, which are the subject of monitoring, represent volatile and semivolatile compounds and they are amenable to GC analysis. A sample preparation step is used to convert the sample into a form suitable for the measurement step. It is mostly necessary to perform isolation of the determined analytes from a sample matrix, preconcentration of the searched compounds, and/or the removal of interfering constituents [18]. The main developments of methods of faster GC have been observed in the field of environmental analysis. Practicality of faster GC is a function of a sample preparation step and the matrix interferences. However, sample preparation is not directly included in this review.

2. Definitions of faster GC

The analysis time of a GC separation depends on the sample type, the number of components to be analysed and the chosen experimental conditions. For very complex samples containing several dozens of peaks, the minimum obtainable separation time will be typically in the minute range [15]. For simple mixtures separations in the millisecond range can be achieved. The terms ''fast GC'', ''very fast GC'', ''ultra fast GC'' are commonly used in the literature. Dagan and Amirav [19] defined a speed enhancement factor to divide analyses into the three fast categories. This factor is the increase in speed that can be obtained by using a shorter column and a higher carrier gas velocity in comparison to the same analysis on a conventional GC column under optimum gas velocity conditions.

Van Deursen et al. [20] suggested a classification based on the peak half width (2.354σ is half width) obtained and the total analysis time. Every reduction of analysis time results in an identical reduction of the chromatographic zone breadth due to the shorter residence time of the components in the column.

Classification of faster GC is then summarised in Table 1. The speed enhancement factor shows the gain in speed compared to conventional CGC [19]. Definitions based solely on run time miss the important aspects of peak separation and peak capacity [5]. In other words, a poor separation of three peaks in 1 min is inferior to the baseline separation of 15 peaks in the same minute. Although the analyses both end in 1 min, the second case provides more separation power per time. Therefore, it is important to use a definition that takes account of the degree of separation per time. Thus, a definition on peak width seems reasonable. Klee and Blumberg [5] calculated peak width as a function of column I.D. to illustrate the benefit of smaller diameter columns for faster GC. From comparison it is apparent that moving from a 530 to a 100 μm column can generate approximately nine-times narrower peaks with the

Table 1
Classification of faster capillary GC

Type of analysis	Analysis time range [15]	Peak width at half height [15]	SEF [19]	Efficiency (N)
Fast	Minutes	1–3 s	5–30	≥Comparable to conventional HRGC
Very fast	Seconds	30–200 ms	30–400	25 000
Ultra fast	Sub-seconds	5–30 ms	400–4000	7000

SEF—Speed enhancement factor compared to conventional HRGC; N—plate number.

same resolution and peak capacity. Classification based on a peak width is very useful also from the point of view of the major requirements for instrumentation [15]. As an example, the final peak width determines the injection requirements, the detector time constant, the required programming rate, etc. The usual value of a peak width in the half height is 0.2–3 s (in fast GC) to 5–30 ms (in ultra fast GC). Thanks to the same and in some case even higher separation efficiency compared to conventional CGC [19,21,22], Table 1, the use of fast GC is advantageous for routine analysis and can be typically obtained from columns with an inner diameter of 100 μm [21–27]. Fig. 1 compares conventional CGC and fast GC of polychlorinated biphenyl (PCB) analysis. Ultra fast GC offers very low efficiency (Table 1) and its applicability is almost negligible. Very fast GC (ca. 25 000 plates) is applied for routine analysis of simple mixtures, mainly in monitoring studies and can be obtained by using a short column of about 1–3 m with inner diameters ranging from 50 to 320 (530) μm. Typical analyses are shown in work of Dagan and Amirav [19] and Sacks and co-workers [28,29].

3. Advantages of faster GC

Interest in the development and implementation of faster GC methods continues to increase. There are a number of ways to take advantage of the improved speed of analysis by faster GC. The first and the most obvious is the increased laboratory throughput resulting in the reduced cost per analysis and the required time to get results. Often a GC separation is a small part of the total sample analysis. So, those applications, where the GC separation is the bottleneck, using fast GC techniques is indeed a significant advantage. The reduced operating costs of a GC analysis (e.g., lower carrier gas consumption) is always a benefit. The use of optimised sample preparation methods combined with fast GC bring both the high sample throughout and reduced costs per analysis. In the Belgian 1999 ''dioxin'' food crisis Sandra and David [21] optimised both sample preparation and CGC analysis that resulted in high-throughput CGC [more than 50 PCBs and fatty acid methyl ester (FAME) samples per day with the same robustness as conventional method]. Using the much faster PCB-monitoring analysis, some 50 000 analyses were performed and some 4000 samples of various food products were able to be released in a limited time.

One of the most important application of fast GC is in situations, where the results of the analysis are needed close to where the answer is needed (e.g., process control, on-site environmental and industrial hygiene applications), the shorter time required to get results is attractive (field-portable GC instruments).

Another advantage of fast GC is that a total system can be better described if more analytical data are available. Many more replicate analyses are performed in the same time that it would take to perform a single conventional GC analysis. This can also be associated with better analytical precision if more replicates can be done, as has been mentioned.

4. Approaches towards faster GC

The basic principles and the theory of fast GC were already established in the 1960s. Since that time many studies on the theoretical backgrounds of fast GC, the development of suitable instrumentation and applications of the technique were published. They were summarised by Korytár and Matisová

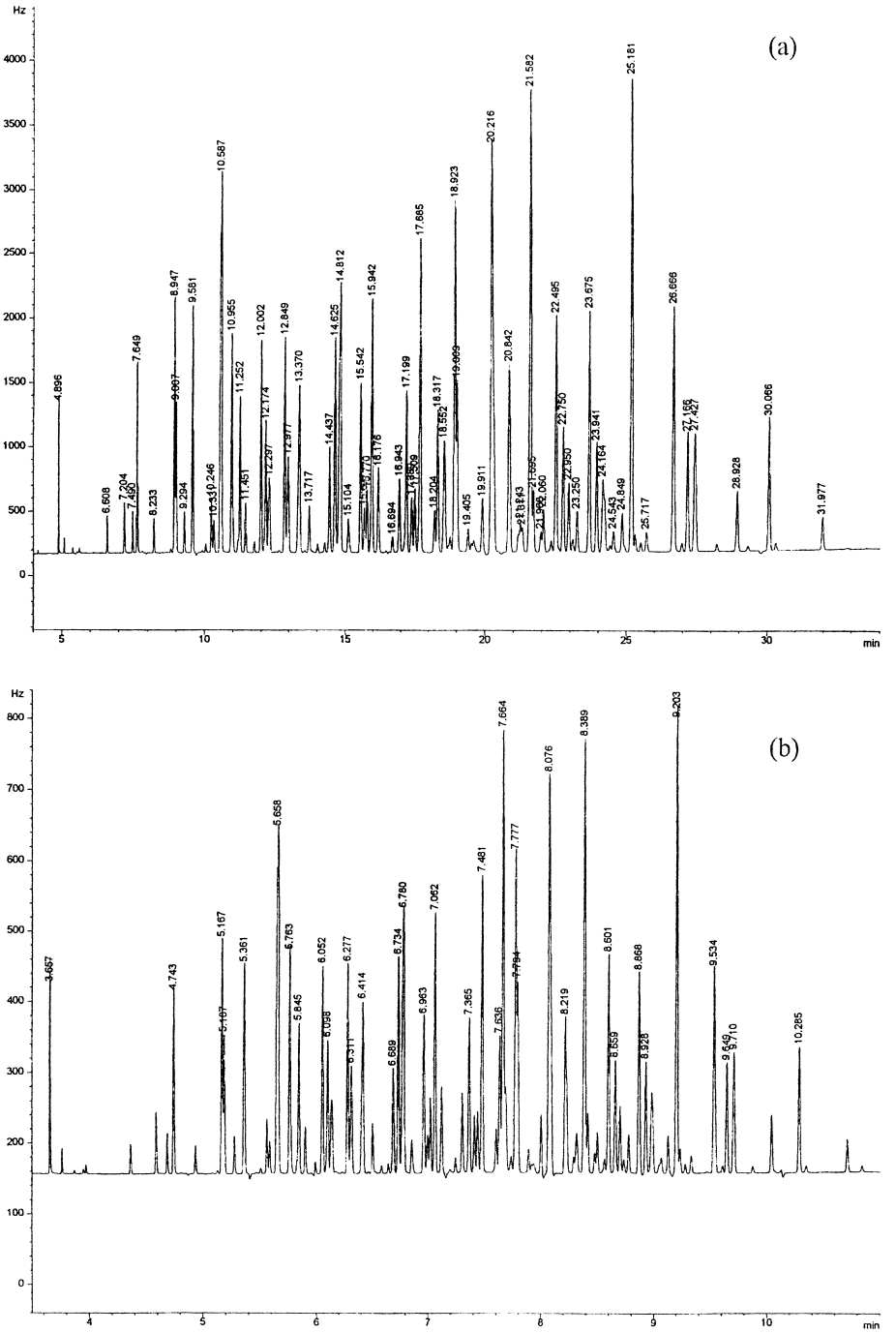


Fig. 1. Analysis of PCB mixture dissolved in *n*-hexane on a 30 m×0.25 mm I.D., 0.25 μm, column (a) and on a 10 m×0.1 mm I.D., 0.1 μm narrow bore 95% dimethyl–5% diphenyl polysiloxane column (b). Carrier gas: hydrogen, constant flow mode. Splitless injection volume, 1 μl; temperature, 250 °C. Detection: μECD. (a) Carrier flow, 1.2 ml/min; pressure, 51 kPa at 50 °C. Splitless time, 0.75 min. Oven temperature program: 50 °C (1 min), 40 °C/min, 150 °C, 4 °C/min, 270 °C (5 min). (b) Carrier flow, 0.5 ml/min; pressure, 177 kPa at 50 °C. Splitless time, 0.5 min. Oven temperature program: 50 °C (1 min), 40 °C/min, 150 °C, 14 °C/min, 270 °C (1.06 min) [22].

[12,13] and Korytár et al. [15]. Cramers and Leclercq [9], and Cramers et al. [10] in their review papers define limits and offer guidelines for optimisation of the technique. Numerous options exist for speeding up GC separations [15]. Which option to select depends strongly on the application under study. Here, a classification system containing 13 basic classes of chromatogram, with various options for speeding up, can be used to advantage [15].

The outcome of routes towards faster separation in CGC follows from the equations derived by Cramers and Leclercq [30,31] that express the analysis time as a function of various operational parameters of a GC system. The explicit relationships can be obtained only under extreme conditions of either a high or a very low ratio of inlet to outlet pressure conditions and a negligible influence of the stationary phase to chromatographic band broadening. Most of the applications of faster GC have been observed under high-pressure drop conditions.

From the theory [30,31] basically three general routes towards faster GC separation are evident and are explicitly shown and discussed in a our recent review paper [15]. Table 2 offers three distinct approaches with a number of options (within the given route) for faster separations. These are specifically:

(1) Minimisation of the resolution to a value just sufficient. In order to minimise the number of the required plates, N_{req}, and thus to minimise the analysis time, the resolution, R_s, should never be better than strictly necessary and only those peaks that are really important should be separated.

$R_s = 1.0$ might already be sufficient for quantification if a not too high degree of accuracy is needed.

$R_s = 1.5$ suffices for all analyses, even those requiring utmost accuracy.

Options summarised in Table 2 are devoted to over-resolved peak separations.

(2) Maximisation of the selectivity of the chromatographic system. Selectivity is the ability to distinguish between compounds. This can be done (once the method for sample preparation has been selected): (i) through separation; (ii) through specificity of detection towards certain compounds.

Altering selectivity of columns is often not of much advantage where the column capacity is exceeded by the sample complexity (number of components).

For faster GC there will be a revival of interest in tailoring stationary phase selectivity for target separations [32]. Improved column technology (e.g., sol–gel) will allow the production of a wider choice of selective open tubular columns. Fine tuning of selectivities can be obtained by electronically adjusting the mid point pressure between two serially connected columns—the selectivity of the ensemble can be adjusted within the limits imposed by the individual columns—with widely different selectivities [33,34]. In this way flexibility can be built in the one-dimensional column system and selectivity can be performed automatically (for some moderately complex mixtures) instead of tedious column replacement.

Two columns of different selectivity can be combined in series (tandem) with or without an intermediate trap [35]. When a trap is used a portion of the effluent from the first column containing one or more target compounds is focused in the trap and reinjected onto the second column. If sequential heart cuts are made for the entire effluent from the first column, and if the peak widths from the first column are sufficiently large that several cuts are made during the elution from the first column of a single peak, the trap serves to modulate the chemical signal from the first column. The result is comprehensive two-dimensional GC. This powerful technique results in very high peak capacity and has been applied to very complex mixtures. In the second dimension a very fast separation is obtained (on the order of seconds). Comprehensive GC×GC opens new futures for GC [36,37], also in the field of trace analysis—due to the potential of enhanced sensitivity as a result of analytes being zone-compressed by modulation at the end of a first-dimension column and using a very fast elution in the second-dimension column. GC×GC is often used in a normal temperature program experiment, but can be considered a fast method when the number of resolved peaks in a given time is considered. It should be noted that sensitivity enhancement is merely with respect to peak response height [38,39]. There is no improvement in peak areas, because the injected quantity of sample is only dependent on the injection mode. However, the time compression effect does mean that the narrow peaks have a response that gives a significant signal above the noise level, thus a peak that might not have been seen in conventional GC is

Table 2
Routes towards faster GC [15]

No.	Speeding up options	Gain in time and practical aspects
(I) Minimise resolution to value just sufficient		
1	Shorter column length	Time gain proportional to length reduction in isothermal GC (IGC). In temperature-programmed GC (TPGC) gain smaller if larger temperature range is covered, because run time is now determined by time taken for oven to reach temperature needed to elute last component. Shortening a column is irreversible. Recommended to start with option 2
2	Above optimum carrier gas velocity	Time gain proportional to velocity increase in IGC. Gain in TPGC small, especially if larger temperatures are covered. Maximum velocity restricted by pressure regulators
3A	Higher isothermal temperature (isothermal GC only)	Gain approx. twofold for each 15 °C temperature increase (IGC). Bear in mind maximum operating temperature
3B	Higher initial temperature	Gain in TPGC strongly depends on original and final programme. Typical gains only several minutes
3C	Higher final temperature	
4A	Faster temperature programming	Gain proportional to increase in rate (TPGC). Programming rates above approx. 20–40 °C/min require special instrumentation
4B	Convert isothermal GC to temperature-programmed GC	Substantial gains possible upon going from IGC to TPGC
5	Pressure/flow programming	Gain generally modest; requires electronic pressure/flow control
6	Lower film thickness	Gain proportional to reduction of film thickness (thin film columns); larger gains for thick film columns
(II) Maximise selectivity of chromatographic system		
7	Use more selective stationary phase or apply coupled columns	Significant gain in elution time is possible, but phase selection can be tedious
8	Use 2D GC*	Unresolved peaks can be transferred to second column for further separation on different stationary phase. Very large gain possible, but more complex instrumentation is required
9	Use selective detection	Significant gain possible because compounds of interest have to be separated only from each other. Separation from matrix compounds no longer necessary. Can also be used in combination with other options
10	Apply MS detection	Significant gain possible, especially in combination with spectral deconvolution techniques. Can also be used combined with other options
11	Apply backflush	Typical gain, 2–5-fold. Requires special instrumentation
(III) Implement method that reduces analysis time at constant resolution		
12	Reduce column inner diameter	Gain proportional to reduction of column I.D. (high pressure drops) or square of reduction (low pressure drops). Ruggedness can be a problem
13	Use hydrogen as carrier gas	Gain 60% vs. He or 100% vs. N_2; requires special safety precautions
14	Apply vacuum-outlet conditions	Up to sixfold gain for short, wide-bore columns. Gain for standard columns negligible. Only possible with MS detection
15	Apply turbulent-flow conditions	Not a viable option for daily practice

* 2D GC—Two-dimensional gas chromatography.

now measurable in GC×GC. It is probably recognized that one of the major goals of chromatography over the years has been improved sensitivity, and this is a significant additional outcome of GC×GC [37] (e.g., LODs of selected PCBs congeners in GC×GC–μECD, about 10 fg [40]). It is often stated that an increased signal response is obtained in GC×GC compared with the normal CGC [37].

Utilising selective detection only compounds of interest have to be separated from each other. Separation from matrix compounds is no longer necessary (or to some extent only), which makes the

sample preparation step easier. The importance of selective detection increases in trace analysis. GC–MS can rapidly and automatically detect and resolve overlapping peaks for compounds that have some differences in their mass spectra. This has been successfully utilised in the field of trace analysis of pesticides (in food) with vacuum-outlet conditions [41], when the entire column operates at a low pressure, which increases gas-phase diffusion coefficient. The column is operated under vacuum conditions, such as reported by van Deursen et al., with a restrictor at the column inlet and a wide bore column [42]. Vacuum-outlet techniques can significantly increase column efficiency for fast separation with short columns [43]. However, vacuum-outlet GC fails for congener-specific PCB work for a lack of separation power that results in coelution of isomers that cannot be differentiated on the basis of their mass spectra [23].

(3) Implementation of a method that reduces analysis time at constant resolution. Options that reduce the analysis time at constant resolution would be the only valid approach (or some increase in R_s, with more resolved components might constitute a faster analysis, Table 2).

Multicomponent samples (e.g., gasoline, naphtha constituents, PCBs in environmental matrices) would result in an unacceptable loss of resolution trying to chose options from the first general route, so the options which reduce analysis time at constant resolution would only be valid.

The order of routes represents a recommendation on how to start the exploration towards a shorter analysis time. There is no a single method that will result in a significant time reduction for all applications. Capillary GC is routinely applied to an extremely wide range of analytical problems. A closer look at the full range of applications shows that the various chromatograms can be categorised into a limited number of classes [15]. There are two most important degrees of freedom: (i) the number of peaks; (ii) the difference in boiling points between the first and the last eluting peak.

In a real chromatogram not all peaks are equally important, so the extent of their resolution is also not expected or required to be equal. Korytár et al. discuss selecting the optimum method for minimum time operation [15].

Klee and Blumberg [5] highlighted recently the most important theoretical concepts for the practical optimisation of speed of analysis of routine CGC methods:

(i) To increase the carrier gas flow-rate; for microbore columns, the relative loss in efficiency at higher carrier gas velocities is much smaller than with large-diameter columns; when the carrier gas velocity of a fast GC separation is 40% above the optimal value only an 8% faster analysis can be obtained [9,44].

(ii) To increase temperature-heating rates.

(iii) To use faster carrier gas (hydrogen).

(iv) To reduce the column length.

(v) To reduce the column internal diameter.

(vi) To reduce the thickness of the stationary phase.

(vii) To use a detector that operates at a lower outlet pressure.

These points are certainly not independent, so the optimisation can be a complex interplay of parameters. For practical CGC Klee and Blumberg [5] and Korytár et al. [15] consider the same most important parameters to increase the speed of analysis. An inappropriate combination of these options complicates the method development. Any fully optimised chromatographic method is a tuned compromise between speed, sample capacity, and resolution [5]. The ability to optimise any given separation is also constrained by instrumental limitations: solute detectability (limited by detector sensitivity and noise level), available inlet pressure, maximum oven temperature ramp rate, maximum detector sampling rate, and sample volume introduction. Recent GC designs have incorporated improvements allowing method developers to push analysis speeds much faster than were possible just a few years ago.

Klee and Blumberg [5] propose two general approaches to fast GC method development: start from scratch, or modify a current method taking into consideration the effects of individual changes that lead to faster analysis. The path that is taken depends on the status of the current method. Many theoretical and practical contributions helped to identify the influence of different parameters (such as column dimensions, carrier gas type and pneumatic conditions, stationary phase type and thickness, heating rate in a temperature program) on the separation/speed tradeoff. The discovery of GC method translation [45] and evaluation of translatable and non-

translatable changes [46] helped to eliminate uncertainties and provide a predictable means of evaluating method tradeoff. A version of method translation software is available free from the internet [47]. The transfer of standard validated operating procedure developed for conventional capillary columns into operating procedures for narrow bore columns was proved to be very helpful utilising method translation software [21,22,24]. Transferring a standard operating procedure for a conventional column (whatever its dimension and stationary phase film thickness) to an operating procedure for a narrow bore column (coated with the same stationary phase), all operational conditions for the new column were calculated in order to obtained the same resolution for various compound group analysis [22], in trace level concentration, e.g., for PCB analysis ([22], Fig. 1), PCBs in food [21], residues of pesticides in water [24]. The gain in analysis time is also predicted [21,22,46]. The use of method translation principles for the analysis of optimum chromatographic conditions helped to define both a generally optimal heating rate (approximately $10\,^{\circ}C/t_M$; t_M denotes a void time) [48] for temperature-programmed GC and a speed-optimized flow [44,49] for both isothermal and temperature-programmed GC. It is important to remember, that the relative retention (including elution order) of solutes depends on temperature [5]. Changes also arise from increasing the column flow-rate without changing the temperature ramp rate proportionally. The effort required to identify peaks after the relative retention has changed can be quite burdensome for methods applied to samples comprising many peaks. According to Klee and Blumberg [5], method translation ensures that relative retention remain constant.

5. Instrumentation and its utilisation in trace analysis

Instrumentation developed for faster GC and the practical consequences of implementation of various approaches to faster analysis with regard to instrumentation were discussed [5,7,8,11,13–15]. This paper will focus on instrumentation from the point of view of its applicability to trace analysis. Instrumentation may be in principle categorised into two classes: dedicated instrumentation (developed specially for faster GC, namely for very-fast and ultra-fast GC) and commercial instrumentation of a novel generation (suitable both for conventional and fast GC). A part of GC instrumentation developed for conventional CGC (those with suitable injectors, detectors, fast electronics) may be adapted for fast GC (with an external pressure regulator with the higher pressure range, very-fast heating systems). There are general requirements that apply for faster GC instrumentation (the choice of carrier gas, inlet pressure regulators, injection systems, columns, ovens, detectors) and some may be considered specific to trace analysis (injection systems, detectors).

Advances in manufacturing processes of field portable instruments, namely silicon micromachining techniques [7], have produced practical injectors and detectors suitable for use with microbore columns. Additionally, since these micromachined components require extensive control, the resulting analytical instrument has unprecedented precision in its functioning and time-controlled events.

In the field of trace analysis, methods of faster GC have been developed mostly with two categories of instrumentation:

(i) Commercial gas chromatographs for faster CGC analysis and/or conventional gas chromatographs (with or without additional options for faster CGC instrumentation).

(ii) Field portable GC systems.

5.1. Carrier gas and pressure regulators

The carrier gas choice can have a substantial influence on analysis speed. This influence depends on the column pressure drop (Dp) [44,50,51]. The speed of analysis is proportional to the molecular diffusivity of a solute in the gas. Hydrogen is obviously the best carrier gas for faster analysis [9,10] because of its large binary diffusion coefficient values. It has to be emphasised that comparing the relative speeds of helium (the second choice) and hydrogen it follows, that at a low Dp (short wide-bore columns) helium is approximately 20% slower than hydrogen, at a high Dp (narrow-bore columns) a 40% speed disadvantage of helium over hydrogen is produced.

With regard to safety concerns there are inherently safe instrument designs and a commercial availabili-

ty of means (e.g., safety interlocks, hydrogen generators with limited capacity) that have increased the use of hydrogen in method development [21–23,25–27] and in routine analysis [15].

In field portable instruments the most frequently used carrier gases have been helium [52–55] and hydrogen [56,57]. The elimination of on-board gas supplies would reduce instrument size and mass considerably but would require the use of air as the carrier gas. There are several drawbacks to this approach. In particular, with atmospheric-pressure detection, the air would have to be compressed, and binary diffusion coefficients in air are unfavourable for high-efficiency column operation when the relatively high flow-rates needed for high-speed separations are used. In addition, some stationary phases are degraded from exposure to oxygen, and air gives poor performance for most detectors [58]. But stationary phase materials capable of withstanding prolonged exposure to air at elevated temperatures without degradation have been identified [59].

Pressure can become a limiting factor for a number of options for faster GC [15]:

(i) The minimum inlet pressure required for stable operation of the carrier gas systems (with the use of shorter columns); the maximum inlet pressure with regard to column length and carrier gas nature (long narrow-bore columns with I.D.≤0.25 μm; for the same column I.D. helium requires much higher inlet pressure than hydrogen). Hydrogen's low viscosity results in lower inlet pressure requirements.

The new generation of chromatographs is equipped with electronic pressure/flow control units (EPC) with the inlet pressure limit up to 1000–1200 kPa. These pressures are compatible with most narrow-bore columns. As an example, a pressure of 1100 kPa is sufficient for columns of 50 μm I.D. up to a length of 15 m. Such a column would generate the same number of plates as a 100 m×320 μm I.D. column. EPC allows continuous change in the column head pressure with the modes of constant flow (also with temperature programming) and programmed flow (important for thermo labile compounds).

5.2. Injection systems

To avoid peak width broadening the injection system has to satisfy the required input band width. Any extra-column contribution to band broadening defeats the efficiency proffered by options for faster GC [15]. The simplest way to achieve the narrow initial band width is the utilisation of high split flows [6]. Under temperature-programmed conditions, operation at a much lower split flow is possible, because the input band width is refocused by thermal focusing at the initial temperature. These approaches have also been utilised in applications in trace analysis (Table 3).

A drawback of splitting techniques are the poor LODs. A variety of special injection techniques have been developed for successful operation of a high-speed capillary GC system (injection valves [60], cryofocusing inlets [8,61]) for the introduction of sample vapour. An interesting development of a rapid screening technique for organochlorine pesticides in water using a microsample preparation (solvent microextraction) combined with fast GC with cryofocusing inlet was described [62]. These injection methods offer narrow input bands, but only very small sample quantities are introduced onto a column, and/or most of the sample is split to vent. They require low volume injection, which negatively influences the minimum detectable concentration, C_{min}, ($C_{min}=Q_{min}/V_{inj}$, where Q_{min} denotes the minimum detectable amount for a mass sensitive or a concentration sensitive detector, V_{inj} is the sample volume introduced onto a column). Due to a low injection volume, the minimum detectable concentration is far too high for many practical applications. To improve the minimum detectable concentration, larger sample volumes have to be injected utilising non-splitting injection techniques.

Owing to the focusing effects, splitless and on-column injection, and the programmable temperature vapouriser (PTV) have been successfully combined with fast CGC. It needs, however, optimization of various experimental parameters. van Ysacker et al. [63] explored non-splitting injection techniques, and splitless injection in detail. Splitless injection requires a liner with a small inner diameter to obtain acceptable splitless time at the low flow of narrow-bore column. Splitless injection has been the most frequently utilised for applications in environmental analysis [21,22,24] (Table 4). Introduction of volumes up to 1 μl without any peak distortion was

Table 3
Methods of fast GC with split injection applied to trace analysis

Analytes (sample type)	Sample pretreatment (time)	Injection system, V_{inj}, p_i	Column and temperature conditions	Carrier gas, F (ml/min)	Detection method (DAR)	Analysis time (min)	RSD (%)	Ref.
19 drugs of abuse (toxiclean drug mixture) (10 ppm)	–	Split, 16:1 1 μl	6 m×0.32 mm I.D., 0.1 μm 100% dimethylpolysiloxane 85 °C, 2 °C/s, 215 °C, 0.75 °C/s, 245 °C (EZ Flash)	He 4.47	FID	1.5	<0.81	[68]
BHT, (chewing gum) (108 ppm)	MAE with hexane–isopropanol (90:10), 1 min	Split, 31:1 1 μl	5 m×0.32 mm, 0.25 μm 95% dimethyl–5% diphenyl polysiloxane 85 °C, 63 °C/min, 127 °C, 130 °C/min, 300 °C (1.5 min) (EZ Flash)		FID	<3	2.8	[69]
15 solvents used in pharmaceuticals (DME) (0.1–10 ppm)	Static headspace 10 min	Split, 20:1 1000 kPa	30 m×0.20 mm I.D., 1.10 μm 6% cyanoprophenyl–94% dimethylpolysiloxane 40 °C, 11.2 °C/min, 240 °C	He 0.96	EI-Q-MS	<9	<10	[86]
20 organochlorine pesticides (in hexane–toluene, 1:1) (100 ppm)	–	Split, 5:1, 1 μl, 305 kPa	Dual-column ensemble 7 m×0.18 mm I.D., 0.18 μm Column 1: (trifluoropropyl)methyl polysiloxane; column 2: 5% phenyl–95% dimethyl polysiloxane 175 °C, 50 °C/min, 300 °C	H_2	TOF-MS (25 spectra/s) FID[a]	<2	–	[87]

V_{inj}—Injection volume; p_i—inlet pressure; F—flow-rate; DAR—date acquisition rate; RSD—relative standard deviation; FID—flame ionization detection; BHT—2,6-di-*tert*.-butyl-*p*-cresol; MAE—microwave-assisted extraction; DME—1,3-dimethyl-2-imidazolidinone; EI—electron impact; Q-MS—quadrupole mass spectrometry; TOF-MS—time-of-flight mass spectrometry; FID[a]—in junction point to monitor eluent from the column 1.

observed with the column I.D. of 100 μm ([22], Fig. 1).

On-column injection is one of the most suitable injection modes for fast GC applications in the field of trace analysis. Besides offering the possibility of injecting larger sample volumes, it eliminates the discrimination of high boiling analytes. With on-column injection the liquid sample is introduced directly into the column without an intermediate vaporisation step [25,26]. The other approach is the technique utilising a solvent vapour exit outlet introduced by Magni [64].

The disadvantage of utilisation of on-column injection in fast GC is the limitation factor, which is the thickness of a syringe needle. Smaller bore columns (<200 μm) have to be connected with a pre-column retention gap of a larger diameter. If peak broadening inside the retention gap can be only partly compensated by the solvent effect and/or trapping at the commencement of the analytical column, a large the difference between the diameter of the retention gap and the column should not be used. For a narrow-bore column a few microlitres should be considered as large volumes. Usual volumes for fast GC when using narrow-bore (e.g., 100 μm I.D.) analytical columns are ca. 0.1 μl. Our recent publications [25,26] presented configuration (a normal-bore retention gap (5 m×0.32 mm I.D.) was coupled to a narrow-bore analytical column (5 m× 0.1 mm I.D.); with a standard glass press-fit connector) that allows introduction of 40–80-fold larger sample volumes without any distortion of peak shapes compared to ''usual'' fast GC set-ups using narrow-bore columns (Fig. 2). Fig. 3 illustrates the influence of various factors on the measured peak width. Compounds with different boiling points behaved differently. Focusing effects depend on compound volatility, pre-column length, volumes injected, inlet pressure, column temperature during the period of sample flow (injection temperature) [25,26]. There is a limitation of on-column injection analysing very polar compounds with regards to a retention gap inertness [65]. Analysis of real-life samples might lead to problems with the tolerance of

Table 4
Non-splitting injection techniques combined with fast GC applied to trace and ultra trace analysis

Analytes (sample type)	Sample pre-treatment, (time)	Injection system, V_{inj}, p_i	Column and temperature conditions	Carrier gas, F (ml/min)	Detection method (DAR)	Analysis time (min)	RSD (%) (LOD)	Ref.
Thiosulfinates (onion juice)	Organic solvent partition with diethyl ether	Splitless 1 μl	10 m×0.32 mm I.D., 4 μm methylsilicone 70 °C, 5 °C/min, 200 °C	He, 3.5	EI-MS	<14	–	[88]
100 PCBs (reference sediment) (1.4–120 ng/g)	Ultrasonic extraction in hexane; then SPE	Splitless 0.25 μl 590–960 kPa	40 m×0.10 mm I.D., 0.10 μm proprietary phase 75 °C (0.5 min), 50 °C/min, 125 °C, 305 °C	H_2, 0.7	EI-TOF-MS (20 spectra/s)	–	(1.1–16.0 pg/μl)	[23]
PCBs (in hexane) (100 ppb)	–	Splitless/ cryotrap 1 μl	3 m×0.25 mm I.D., 0.25 μm 100% polydimethylsiloxane 100 °C, 12.5 °C/min, 150 °C	H_2, 6.1	ECD 40 Hz	<6	9–21	[73]
PCBs (egg yolk, animal feed, fat, meat products) (~100–2000 ppm)	Ultrasonic extraction with light petroleum (30 min), then MSPD with acidic silica gel (10 s)	Splitless 1 μl	10 m×0.1 mm I.D., 0.1 μm 95% dimethyl–5% diphenylpolysiloxane 70 °C (0.45 min), 110 °C/min, 150 °C, 13.2 °C/min, 200 °C, 35.2 °C/min, 300 °C (0.4 min)	H_2, 67.2	μECD	8.2	<10 (0.03 pg)	[21]
15 organophosphorus pesticides (in ethyl acetate extract of residue free wheat grains) (2×10^{-3}–4.8 ppm)	–	Splitless 1 μl	5 m×0.25 mm, 0.25 μm PLOT 60 °C (0.5 min), 360 °C/min, 90 °C, 63.5 °C/min, 180 °C, 82.9 °C/min, 325 °C (1.25 min) (EZ Flash)	–	FPD	3.7	0.027–0.057	[70]
Aromatic, aliphatic hydrocarbons (in pentane) (1–2 ppm)	–	Splitless/ cryofocusing 1 μl	5 m×0.10 mm I.D., 0.45 μm 95% dimethyl–5% diphenyl polysiloxane Precolumn: 0.2 m×0.32 mm I.D. 40 °C (1.5 min), 50 °C/min, 250 °C (1 min)	H_2, 0.6	FID	<0.4	–	[71]

17 pesticides (river water) (spiked at 100 pg/ml)	Extraction with dichloromethane, extract concentration	PTV in solvent vent mode 40 μl (8×5 μl) 480 kPa	10 m×0.1 mm I.D., 0.25 μm 100% methyl polysiloxane 80 °C (3.7 min), 100 °C/min, 150 °C, 30 °C/min, 250 °C (3 min)	He	QMS full scan mode (5 scan/s)	8.5	1.4–9.9 (1–100 pg/ml)	[24]
Toluene, trichlorethane, hexane, dichloromethane, acetone, ethanol (*water)	Hollow fibre membrane extraction, N_2 extraction gas	Microtrap injection 14 cm×0.52 mm I.D. Carbotrap C; TD	30 m×0.25 mm I.D., 1 μm 100% dimethylpolysiloxane isothermal 95 °C	–	FID	2	<1.4 (low ppb)	[72]
Cyclohexane, toluene, *o*-xylene, IPB (wastewater) (spiked at 10 ppb)	RASE	Injection loop/cryofocusing device; TD, 100 μl	5 m×0.25 mm I.D., 0.1 μm 100% dimethylpolysiloxane isothermal 40 °C	H_2, 6.2	FID	<20	–	[89]
H_2S, COS	0.23 m×0.53 mm I.D. polydivinylbenzene PLOT column; cryoconcentrator	TD	PLOT polydivinylbenzene 30 m×0.53 mm I.D. isothermal 50 °C	He	PID	3	 (10 ppb)	[90]
Chlorine and sulfur containing compounds [in soil (acetonitrile extract)] (1.0–24.5 ppm)	SFE (CO_2)	TDM	1.9 m×0.1 mm I.D., 0.25 μm 100% methyl polysiloxane isothermal 170 °C for Cl 2.5 m×50 μm I.D., 0.25 μm 30% phenyl polysiloxane isothermal 180 °C for S	CO_2, 0.86	RPD	<10	1.0 (24.8 pg/s for Cl) (9.2 pg/s for S)	[91]
Ammonia (atmosphere)	Collection tube 5% KOH coated Porasil B	TD	Isothermal 105 °C	He+1% CH_4	FTD	–	<5 (20 pptv)	[92]

LOD—limit of detection; EI-MS—electron impact mass spectrometry; PCBs—polychlorinated biphenyls; SPE—solid-phase extraction; ECD—electron-capture detection; MSPD—matrix solid-phase dispersion; μECD—micro-electron-capture detection; PLOT—porous layer open tubular column; FPD—flame photometric detection; PTV—programmable temperature vaporization injector; * continuous monitoring; TD—thermodesorption; IPB—isopropylbenzene; RASE—rapid aqueous sample extraction; COS—carbon oxysulfide; PID—photoionization detection; SFE—supercritical fluid extraction; TDM—thermal desorption modulator; RPD—radiofrequency plasma detection; FTD—flame thermionic detection; other abbreviations as in Table 3.

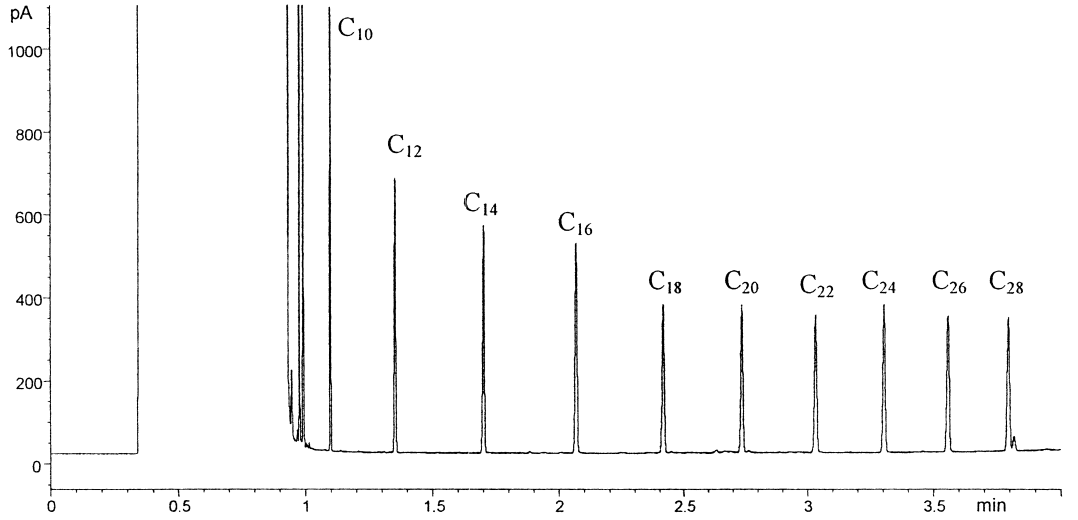


Fig. 2. Analysis of *n*-alkanes test mixture dissolved in *n*-pentane. Carrier gas: hydrogen. On-column injection: oven track mode; concentration, 1 ng/μl per component; injection volume, 8 μl; constant pressure, 413 kPa. Column: 5 m×0.10 mm I.D., 0.4 μm, 100% polydimethylsiloxane phase; 3 m×0.32 mm I.D. non-polar pre-column. Oven temperature program: 80 °C (0.65 min), 65 °C/min, 300 °C. Detection: FID; data acquisition rate 200 Hz; temperature, 350 °C [26].

the GC system to co-injected matrix components [66].

Combination of PTV (with solvent vent mode) with fast CGC with narrow-bore column (100 μm I.D.) allows even larger sample volume introduction, resulting in excellent LODs; e.g., analysing residual pesticides in water a large volume (20 μl [27], 40 μl [24]) was introduced by repeated injections of 5 μl and/or 10 μl without any peak distortion (Fig. 4). There might be problems with losses of some compounds due to liquid rinsing or flooding the liner and depression of adsorption in the PTV [24], and/or with thermolabile compounds decomposition [27]). Time elapsed for solvent evaporation and sample transfer step are relatively long compared to GC separation time.

Some specialised non-splitting techniques (with an on-column or pre-column focusing devices) to produce a narrow input band for very fast and ultra fast GC rely on cryofocusing and thermal desorption) [28,61]. The broad plug of vapour sample of volatile organic compounds (VOCs) (e.g., atmospheric pressure vapour samples [29]) is accumulated and refocused by cryogenic cooling. For reinjection of the sample the trap is rapidly heated. Detection limits for the direct air monitoring instrument are in the low parts-per-billion range for a sample size of about 1 ml.

An important group of injection techniques for very fast and ultra fast GC are the miniaturised mechanical switching valves. A portable high speed GC system using micro-machined valves and a sample loop on a silicon chip is commercially available. Its inlet system is optimised for use with short narrow-bore columns [67]. Using a simple experimental set-up [the technique of equilibrium (ab)sorption] equipped with an open-tubular enrichment column it is possible to produce a homogenously enriched sample plug, allowing reproducible injections of an enriched sample into the micro GC system [55] (Fig. 5). The enriched sample flow generated allows highly reproducible injections onto the narrow-bore column using the ''time-slice'' injection technique of silicon-micromachined injection valves.

A specially designed fast SPME injector with a microvolume stainless steel tube was used on the compact GC. This injector can be heated at a very fast rate (e.g., from 40 to 200 °C in milliseconds) by a capacitance discharge heating unit. For the field

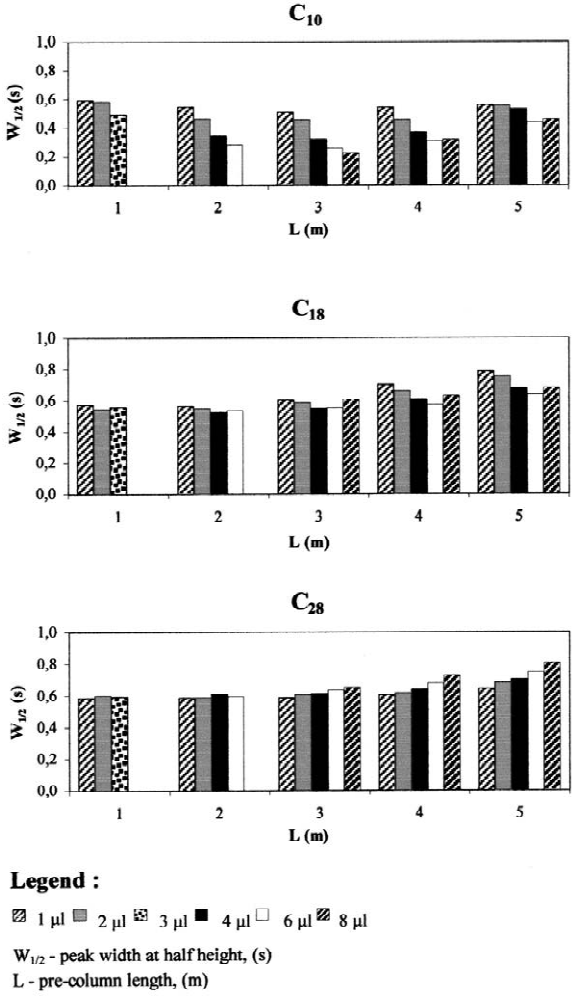


Fig. 3. Graph of the dependence of peak width at half height on sample volume injected (1, 2, 4, 6 and 8 μl, for 1 m long pre-column only 1, 2, 3 μl) and the pre-column length. Other conditions as in Fig. 2.

sampling, the desorption time for the SPME fibre was reduced to 30 s [57].

5.3. Columns and ovens

Column choice in faster GC depends on the application. Tables 3–5 list columns used for various applications in trace analysis.

Shorter columns of various diameter, or the use of high carrier gas flow-rates are beneficial for simple mixtures, where components differ sufficiently in physico–chemical properties [68–72]. Short columns are also frequently applied for rapid profiling of complex mixtures, such as PCBs [73], or pesticide extracts from water samples [74,75]. In this regard, it is worth mentioning a vacuum-outlet GC system with a 0.53 mm I.D. column that provides benefits of high speed analysis, increased sample capacity and very narrow peaks (e.g., of the order of 1.5 s at basewidth, when analysing Aroclors, column/pre-column dimensions see Fig. 6) [23]. The vacuum outlet condition is usually one where a significant portion of the column is under vacuum.

In open tubular columns the speed as well as the sample capacity are related to the column I.D. and also to film thickness (d_f) [9,10]. The use of columns with a reduced diameter is the most logical option for faster GC from the group of ''constant-resolution'' options [15]. By reducing I.D., a higher efficiency per length (L) is produced. Decrease of column diameter results in a proportionally decreased value of minimum plate height (H_{min}) [9,10]. Therefore, the column length can be decreased by the same factor in order to yield the same plate number. When the I.D. is reduced, optimal average linear velocity (u_{opt}) is also faster. Both results lead to a shorter void time (t_M) and a proportionally shorter analysis time at the same separation power [5]. For example, if the original method were developed on a 25 m×250 μm I.D. column, a 10 m×100 μm I.D. column would be chosen in order to get the same separation. The penalties to be paid are a much lower sample capacity and much higher carrier gas pressures required to perform a run [5,9,10]. With carrier gas inlet pressure the required value of hydrogen is significantly lower compared to helium. For a number of reasons (e.g., sample capacity, inlet pressure values required, temperature-programmed rates), 100 μm I.D. columns seem to represent the current limit for routine use [5].

The approach to overcome the limitation of narrow-bore columns with regard to sample capacity, was the introduction of multicapillary column (a parallel configuration of some 900 narrow-bore capillaries of 40 μm I.D.) [76]; currently it is only available with a length of 1 m and is therefore only suited for relatively simple mixtures requiring only low plate numbers.

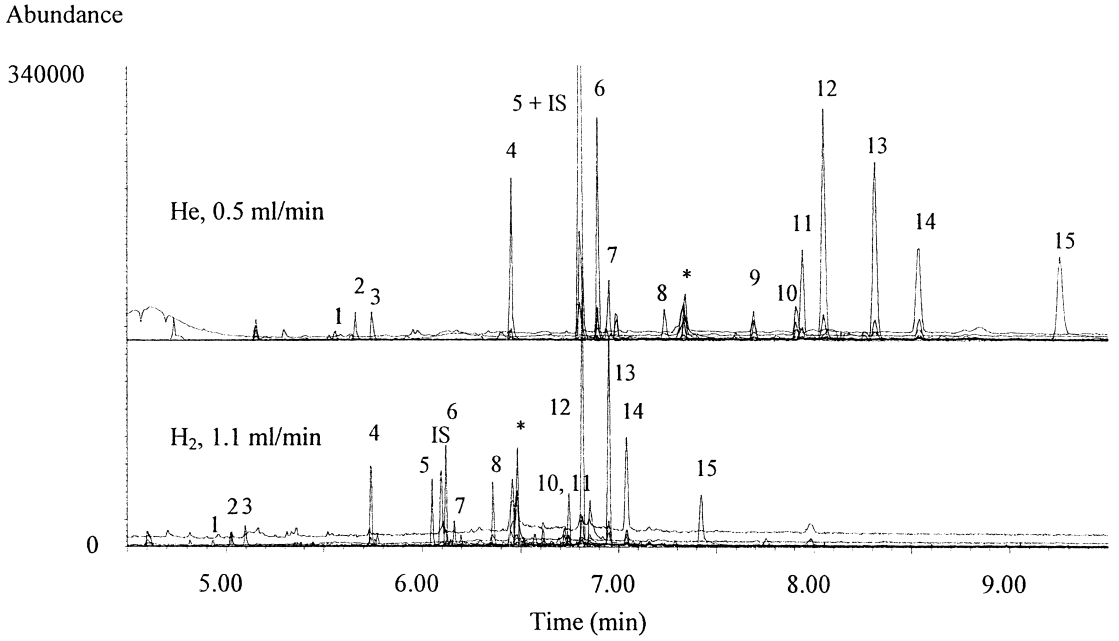


Fig. 4. GC–MS target ion chromatograms of 15 OCPs in tap water obtained at optimized conditions using (a) helium and (b) hydrogen as a carrier gas. Column: 15 m×0.1 mm, 0.4 μm, 100% polydimethylsiloxane phase. PTV injection: injection volume (2×10 μl); concentration, 0.5 μg/l per component; concentration of internal standard (I.S.) propazine; 0.2 μg/l. PTV temperature program: 50 °C (1 min), 720 °C/min to 300 °C (5 min); solvent vent 100 ml/min until 0.9 min. Oven temperature program: 45 °C (3.4 min), 120 °C/min to 280 °C (6 min). Peak labels: (1) 1,3,5-trichlorobenzene, (2) 1,2,4-trichlorobenzene, (3) 1,2,3-trichlorobenzene, (4) pentachlorobenzene, (5) α-HCH, (6) hexachlorobenzene, (7) γ-HCH, (8) pentachloronitrobenzene, (9) aldrin, (10) isodrin, (11) *cis*-heptachloroepoxide, (12) *o,p′*-DDE, (13) *p,p′*-DDE, (14) dieldrin, (15) methoxychlor [27].

For faster separations isothermal and temperature programmed operations have been used. Faster temperature programming is an attractive option for speeding up separations of samples that contain a limited number of peaks covering a wide range of boiling points [15]. There is a problem in resolving compounds with similar physico–chemical properties under faster GC conditions and high temperature programming rates [26,77]. For constant resolution situations (Table 2), the typical guideline is that the ratio (programming rate/void time) should be kept constant (the optimum ratio is in general ca. 10 °C/void time) [48].

The maximum allowable heating rate, and evidently also the cooling time, of the oven are hence important parameters. The latest generation of GC ovens allows maximum programming rates of 50–100 °C/min. Higher heating rates are difficult to obtain due to the higher thermal mass of standard ovens. An important aspect for routine analysis is the oven recycle time. Since the heating (and cooling) of the oven also depends on the oven dimensions, reducing the oven size allows faster ramping. Reducing the oven size by 50% [with an oven insert (pillow)] faster ramping and reduction of the total analysis time was obtained [22] with the same reproducibility of retention time compared to standard oven size. Application of method translation was found to be more accurate with the reduced oven size.

For faster heating, systems based on resistive heating were developed. So called ‘‘flash GC’’ is available nowadays as a stand-alone system (Flash-GC instrument) or as an upgrade kit (EZ Flash) which enables a conventional GC system to be converted to a flash GC system [78,79]. In the commercial EZ Flash system the capillary column is placed inside a resistively heated metal tube. It provides fast and reproducible heating rates up to 1200 °C/min and can cool from 300 to 50 °C in less

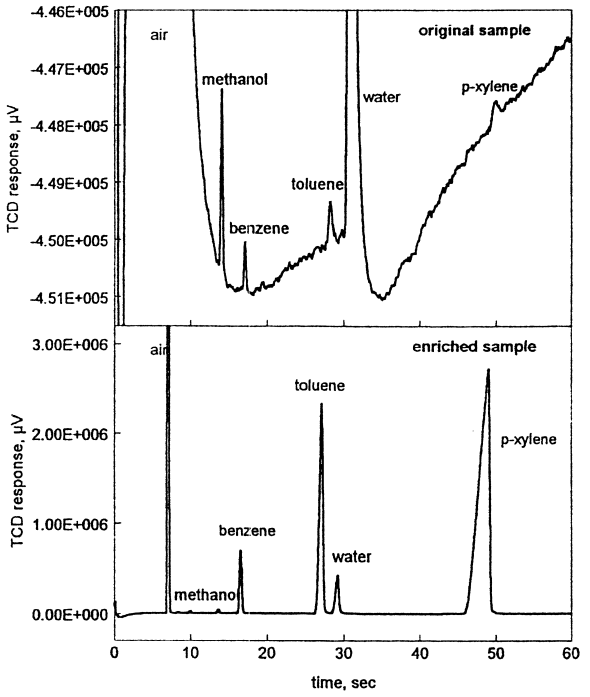


Fig. 5. Enrichment of a gaseous sample containing benzene, toluene and *p*-xylene in air using the equilibrium (ab)sorption method. Carrier gas: helium; pressure 200 kPa. Trapping column: 1 m×1 mm I.D., 5 μm Thermocap; sampling temperature, 30 °C; desorption temperature, 200 °C. Concentration, 1 ppm per component. Column: 6 m×0.15 mm I.D., 0.4 μm; nitroterephthalic acid modified polyethylene glycol phase. Oven temperature: isothermal 40 °C. Detection: TCD. Note the difference in the *y*-scale [55].

than 30 s [77,80]. The system is compatible with standard split/splitless injectors. A commercial system introduced recently by Thermo Finnigan GC system [81] is rather similar, but may have some advantages over the EZ Flash system. The possibility of rapid screening of, e.g., selected polycyclic aromatic hydrocarbons (PAHs), triazines and organophosphorous pesticides employing EZ Flash with FID has been tested (standards dissolved in neat solvents have been used for the experiments on a 5 m×0.25 mm I.D., 0.2 μm capillary operated at a programming rate 100 °C/min) (Fig. 7) [80]. There were significant resolution losses compared with a conventional column operated at heating rates 10–15 °C/min. Due to originally over-resolved peaks, with EZ Flash temperature programme the peaks of interest could still be separated. The narrow peaks obtained in the fast separation resulted in very low LODs of around 5 pg for PAHs and 10–30 pg for pesticides. This [80] and other study of organophosphorous pesticides in food crops [82] show dramatically improved detectability of analytes due to much narrower peak widths—compared to conventional CGC. In the case of flash GC significantly better retention time repeatability was observed compared to faster GC employing fast temperature programming with a conventional oven [82]. This demonstrates that rapid temperature programming has distinct potential for the rapid screening for microcontaminants. For detailed analysis of complex mixtures it is, however, not suited. A disadvantage of fast programming can be the substantially higher elution temperature of the peaks of interest [80] which could lead to a potential problem of thermal instability of analytes.

5.4. Detectors

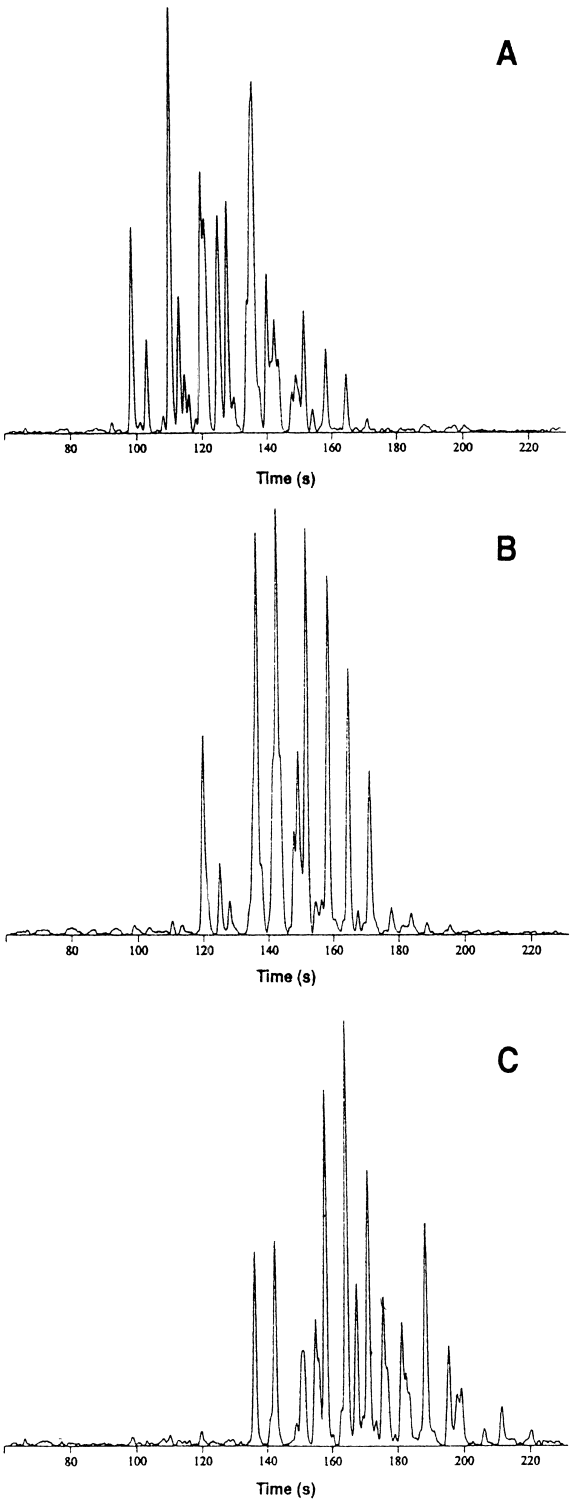
Peak broadening caused by the detector must be small enough to preserve the column efficiency. The sampling frequency of the detector must be high enough to provide some 15–20 data points across the peak for an accurate representation of the peak [83]. Current instruments typically use data sampling rates in the range 0.5 up to 500 Hz. Electrometer-amplifier time constants of about 5 ms are typical [8]. The list of mostly used detection methods for faster CGC with characteristic properties are summarised in Table 6. Flame ionisation detection (FID) and thermal conductivity detection (TCD) have been used most frequently for faster GC. In trace analysis selective detection has an advantage (e.g., method LODs of selected PCB congeners in food with μECD [21], signal-to-noise ratio >3, were 0.2 pg for conventional CGC, fast GC resulted in an increased sensitivity, LODs were 0.03 pg).

Micromachined TCD in field-portable GCs have cell volumes of only a few nanolitres [7]. Detection limits are in the 1 ppmv range [7]. FID when used with μGC, is a factor of approximately 2–10 more sensitive than μTCD with mass detection limits in the 10^{-12} g range. Very often for environmental analyses these detection limits are 2–3-orders of

Table 5
Trace and ultratrace analysis with field-portable GC systems

Analytes (sample type)	Sample pre-treatment (time)	Injection system, V_{inj}, p_i	Column and temperature conditions	Carrier gas, F (ml/min)	Detection method (DAR)	Analysis time (min)	LOD	Ref.
42 Hydrocarbons, chlorinated aliphatics and aromatics, oxygenated compounds, terpenes (test atmosphere) (15–18 ppm, v/v)	Dual-bed adsorbent preconcentrator	Cryofocusing inlet system 0.5 μl, 101.3 kPa	Pressure tunable column ensemble Column 1: 4.5 m×0.25 mm I.D., 0.25 μm dimethyl polysiloxane Column 2: 7.5 m×0.25 mm I.D., 0.25 μm trifluoropropylmethyl 30 °C (195 s), 30 °C/min, 60 °C (40 s), 50 °C/min, 120 °C	Air	PID	>6.7	–	[93]
Benzene, toluene, ethylbenzene, *o*-xylene (test atmosphere) (10 ppm, v/v)	–	Cryofocusing inlet system 0.5 μl, 101.3 kPa	6 m×0.25 mm I.D., 0.25 μm 95% dimethyl–5% diphenyl polysiloxane isothermal 50 °C	Air	PID	0.5	–	[58]
BTEX, hexane (residential house air) (15.3–257 ppb)	SPME (PDMS–DVB) 1 min	Specially designed fast SPME injector (30 s desorption time) – 345 kPa	50 m×0.2 mm, 0.5 μm 30 °C, 15 °C/min, 250 °C	Hydrogen, 4.0	In series PID, FID, DELCD	<15	1.3–8.6 ppb	[57]
43 various compounds (test atmosphere) (100 ppb)	Multiadsorbent module	1000 kPa	15 m×0.25 mm I.D., 0.25 μm 5% phenyl–95% dimethyl polysiloxane 35 °C (1.5 min), 20 °C/min, 140 °C	Ambient air	SAW, 10	26.5	100 ppt	[94]
BTEX (in methanol) (1000 ppm)	–	Splitless, 0.1 μl, 287 kPa	10 m×0.18 mm I.D., 1 μm 100% polydimethylsiloxane Isothermal 30–100 °C	Helium, 2.0	QIT-TOF-MS (60 spectra/s)	<1.5	10–100 ppb	[54]

BTEX—Benzene, toluene, ethylbenzene, *o*,*m*,*p*-xylene; SPME—solid-phase microextraction; PDMS–DVB—polydimethylsiloxane–divinylbenzene; DELCD—dry electrolytic conductivity detection; QIT-TOF-MS—quadrupole ion trap time-of-flight mass spectrometry; other abbreviations as in Tables 3 and 4.



magnitude too high. This relatively high detection limit for μGC instruments (for FID and μTCD) led to the development of portable sample preconcentration methods [7,57]. Photoionization detection (PID) is well suited for vacuum-outlet portable GC, but has relatively large cell volume (~ 100 μl) [84]. The combination of atmospheric pressure air as carrier gas, modest operating pressures, and polymer-coated surface acoustic wave (SAW) sensor detection is well-suited for field instrumentation. The SAW detector cell has an internal volume of <2 μl [84].

The important trends in GC are the ever increasing need for positive identification and the need for more flexible systems that allow the analysis of a wide variety of samples in one system [20]. These trends clearly result in a strong requirement for mass spectrometric detection. Important mass analysers are the ion trap, the sector instrument, quadrupole and time-of-flight mass spectrometry (TOF-MS). The resulting mass spectrometers show differences in terms of acquisition rates, detection limits, mass spectrometric resolution and quality of mass spectra obtained. The choice of the most suitable MS method is very much dependent on the composition of the sample, detection limit, mass spectrometric resolution, quality of the mass spectra obtained and speed of GC analysis. With MS detection target analytes can readily be identified in crowded chromatograms. By using extracted ion traces, non-separated peaks can even be quantified. In addition, the limits of detection decrease. Typical maximum acquisition rates of scanning mass spectrometers like ion trap, the quadrupole and the sector instrument, range from 10 to 20 spectra per second in the full scan mode. Therefore, only chromatographic peaks with a width of 0.5 s or more can be accurately represented, which is mostly sufficient for fast CGC.

Fig. 6. Reconstructed ion chromatograms of Aroclors analyzed using vacuum-outlet GC–TOF-MS: (A) Aroclor 1248, (B) Aroclor 1254 and (C) Aroclor 1260. Carrier gas: helium; flow-rate, 5 ml/min constant flow mode. Fast splitless injection: volume, 1 μl; temperature, 260 °C; splitless time, 15 s. Column: 5 m×0.53 mm I.D., 0.5 μm 95% dimethyl–5% phenyl polysiloxane phase, 3 m×0.18 mm I.D. pre-column. Oven temperature program: 60 °C (0.25 min), 120 °C/min, 120 °C, 40 °C/min, 260 °C. Detection: data acquisition rate, 15 spectra/s [23].

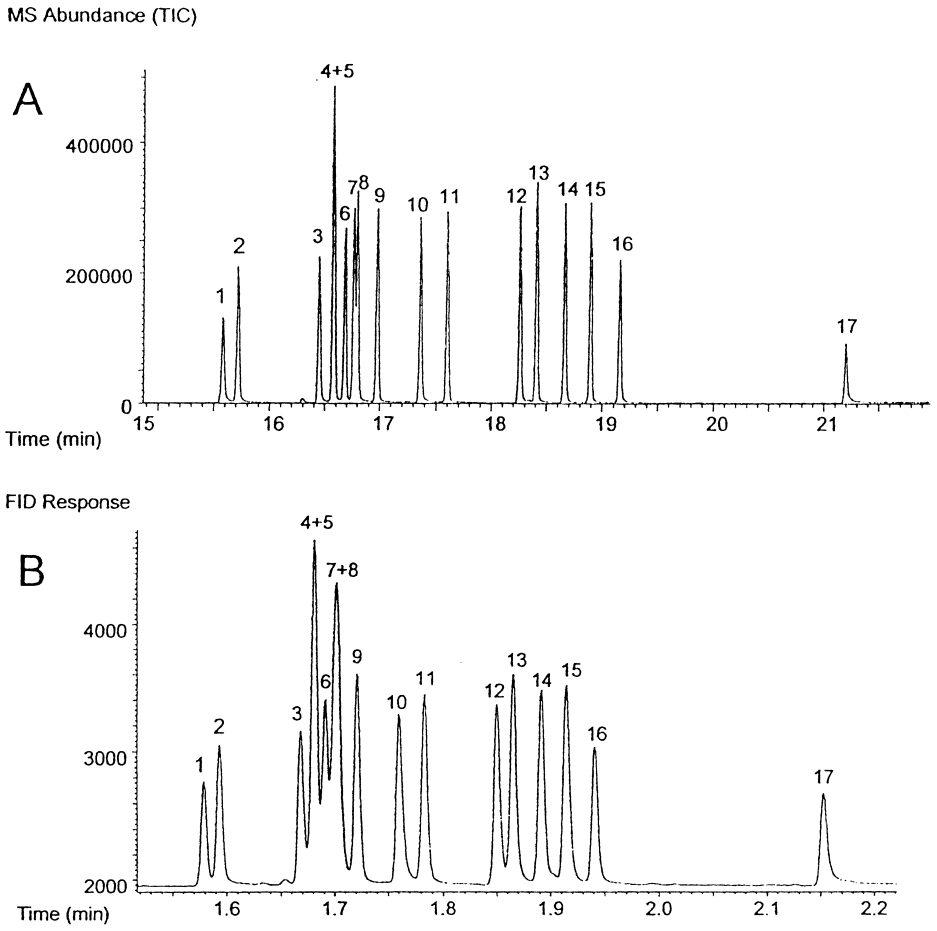


Fig. 7. GC chromatogram of a mixture of 17 triazines in methyl acetate. Carrier gas: helium. Column stationary phase: 95% dimethyl–5% diphenyl polysiloxane. (A) Conventional GC. Split injection: 1:10; concentration, 50 ng/μl per component, constant pressure, 50 kPa. Column: 23 m×0.25 mm I.D., 0.25 μm. Oven temperature program: 50 °C (2 min), 10 °C/min, 320 °C. (B) EZ Flash. Splitless injection: concentration, 1 ng/μl per component; injection volume, 1 μl. Column: 5 m×0.25 mm I.D., 0.2 μm. Temperature program: 50 °C (15 s), 100 °C/min, 300 °C. Peak labels: 1=desisopylatrazine, 2=desethylatrazine, 3=atraton, 4=prometon, 5=simazine, 6=atrazine, 7=propazine, 8=terbumeton, 9=terbutylazine, 10=secbumeton, 11=sebutylazine, 12=simetryn, 13=prometryn, 14=terbutryn, 15=dipropetryn, 16=cyanazine, 17=metamitron [80].

For very fast separations on short columns (the seconds, subseconds range) the spectral acquisition rate of scanning mass spectrometer is too low. TOF-MS can provide up to 500 full spectra per second. The quality of the recorded spectra and their similarity with library spectra is very high [20]. Deconvolution algorithms offer the possibility to identify overlapping peaks. For example, Cochran [23] has shown that a loss of separation power (utilising vacuum-outlet GC) is offset by deconvolution capabilities of TOF-MS for compounds that have at least some differences in their mass spectra. Automated peak-find accuracy has been shown to increase for close-eluting compounds when spectral acquisition speed is increased. The resulting deconvoluted mass spectra of environmental contaminants are library searchable. TOF-MS in combination with narrow-bore columns may offer the most efficient tool yet for trace-level analysis (e.g., estimated LODs, at an S/N of 3, are approximately in the pg range for full-mass range acquisition data for key PCBs, are excellent detection limits) [23].

Table 6
Detectors of a commercial instrumentation with digital electronics suited to faster CGC

Type of CGC analysis	FID	FPD	NPD	μECD	TCD	MS	
						Scanning	Non-scanning
Fast	+	+	+	+	+	±	+
Very fast	±	–	±	–	+	–	+
Cell volume/sensing volume	Close to 0	Close to 0	Close to 0	150 μl*	Low**		
Maximal sampling frequency (Hz)	200	50	200	50		10–20	500

+ Full applicability; – non-applicable; ± applicability depends on the peak width obtained; NPD—nitrogen–phosphorus detection; TCD—thermal conductivity detection; MS—mass spectrometry; other abbreviations as in Tables 3 and 4.
* Operated at a sufficiently high make-up gas flow (ca. 60 ml/min) it is compatible with fast GC.
** In field portable GC systems the detectors are made by micro-machining techniques and have cell volumes of only a few nanolitres [7].

Current developments in the technology of instruments with MS detection for the field-mobile instruments are improving the practice of field GC–MS. Ion mobility spectrometry (IMS) devices operate at atmospheric pressure and rely on separation of ions in a uniform electric field on the basis of differences in their mobility [52]. A quadrupole ion trap (QIT) TOF-MS system was designed for field portable use [54]. A photoionization source was used to ionize the effluent of the GC column.

6. Conclusion

There are various tools of faster CGC from the theoretical point of view and it is discussed how they relate to practical faster GC development. Faster CGC method development and validation can be simplified if key concepts are kept in mind (number of components to be analysed and their physico–chemical properties, selection of column and carrier gas, speed-optimised flow-rate, optimal temperature programme, sample capacity). The use of faster GC has long been hindered by a lack of instrumentation. Today, commercial instrumentation is available and faster GC can be implemented to routine analysis also in the field of trace analysis. Thanks to the same and in some cases even higher separation efficiency compared to conventional CGC the use of fast GC is advantageous for routine analysis. Ultra fast GC offers very low efficiency and its applicability is limited, if not negligible. Very fast GC is applied for routine analysis of simple mixtures, mainly in monitoring.

For faster CGC analysis hydrogen is the carrier gas of choice. Safety precautions allow safe use of hydrogen as carrier gas. Electronic pressure control units built in a new generation of gas chromatographs are available with inlet pressure up to ca. 1200 kPa. In open tubular columns the speed as well as the sample capacity are related to the inside column diameter. Sample capacity is thus drastically reduced ($\propto d_c^3$) for narrow bore columns. 100 μm columns represent the current limit for routine use. The peak widths are smaller on the narrow bore column and therefore, peaks are taller. Using the method translation software, an existing operating procedure for a standard capillary column can be translated into an operating procedure for a narrow bore column, resulting in a faster analysis with the same resolution. Both qualitative and quantitative data remain unaffected. Sample capacity could be a concern and is estimated to be in the low-nanogram range for individual components that are compatible with the stationary phase. It might be a problem with analytes having a low detector response, or mixtures having component(s) of interest that may vary over a wide range of concentrations. With regard to high sample capacity vacuum-outlet GC with wide bore columns was found to be a useful tool in environmental analysis, also for rapid profiling of complex mixtures.

For trace and ultratrace analysis non-splitting injection techniques have to be utilised. The most widely used injector in fast GC is splitless (with the injection volume up to 1 μl in combination with narrow bore columns—without peak distortion). On-column injection allow eight-times, PTV 40-times higher injection volumes. Another possible injection is splitless combined with cryofocusing, for volatile

compounds the utilisation of various traps combined with thermodesorption. Specialised injection techniques have been utilised in field portable instrumentation. Most commercial detection systems are compatible with fast GC requirements. For trace analysis selective detection is advantageous. TOF-MS is uniquely positioned to be the detection method of choice for faster CGC because of its high-speed acquisition rates and nonskewed spectra that allow for powerful peak-find and deconvolution algorithms. Scientists have recognised the unique power of GC×GC to resolve complex samples and also to improve analysis sensitivity which seems to be a promising potential or the alternative of either a more complicated sample preparation or having to analyse a sample with another complementary technique to obtain all the information the sample may hold [85].

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