obtained are between 800 and 1000 plates and the scale of production is between 20 and 200 tonnes per year.

Large scale GC can be used for the industrial production of ultrapure compounds or for the selective removal of impurities. For difficult separations, it is economically competitive with other techniques such as distillation. Whenever it is applicable, it is always competitive with preparative HPLC. Its applications are limited to compounds with normal boiling points under 250°C.

Preparative GC works well with a relatively simple technology; thus, over the last 10 years, technological improvements have been limited to automation in line with modern standards and to maintain simplicity. No major improvement is expected in future, except to adapt the process to specific cases (e.g. ultrapurification of gases for the electronics industry with an impurities level as low as 0.1 p.p.b. and simultaneous separation and reaction in a chromatographic column). The number of installations working throughout the world is limited to about 100, although the potential of the technique is much greater. The future is likely to see the development of some new very large scale applications.

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Multidimensional Gas Chromatography

P. Marriott, RMIT University, Melbourne, Victoria, Australia

Multidimensional Concepts

The multidimensional approach to solute separation involves the use of more than one column (almost always two columns) arranged in series, such that chosen components in a chromatogram, or selected sections of a chromatogram, are subjected to separation on each of the columns in the system.

Multidimensional methods may include interfacing of a chromatographic column with a multichannel detection system (mass spectrometry, atomic emission, Fourier transform infrared (FTIR), diode array detection and the like). This review will not extend into this area, focusing rather on multidimension gas chromatography (GC) separations. Within coupled separations, especially online and automated systems, simplification of the total sample analysis by incorporation of extraction steps such as solid-phase extraction, solid-phase microextraction, supercritical fluid extraction and other sampling approaches, combined with chromatographic separation, can be considered multidimensional analysis. These will also not be included here, and details on these methods should be sought elsewhere.

Why are multidimensional methods implemented for chromatographic analysis? The usual answer lies in the need for enhanced separation of closely eluting compounds – compounds with similar retention factor, k. Historically, chromatography has searched for better means to resolve compounds; as methods improve, we can separate compounds of closer chemical nature. Traditionally, chromatographers have improved column selectivity to provide a larger magnitude in differences of distribution constant, K (where $K = k\beta \propto t'_R$; therefore larger retention time differences results from increased K differences), or increased efficiency of the chromatographic process with narrower chromatographic bands giving better resolution. The former is achieved by using a stationary phase or separation mechanism with greater discrimination between the solutes to be separated, and the latter by employing narrower-bore columns, smaller particle packing sizes or other physical means to reduce peak dispersion. Very soon in the historical development of GC, it was recognized that one stationary phase would probably not resolve many compounds (hence the plethora of stationary phases that were produced), but also that a given mixture can contain a range of different classes of compounds that may best be separated on different phases. Thus, improved separation may require two columns for the one analysis. Two separate columns means that

the sample must be analysed twice, but when used in a coupled column arrangement the advantages of both columns can be utilized simultaneously. This is the genesis of multidimensional chromatography.

Effective implementation of multidimensional methods for improved solute separation depends on a number of critical parameters. Firstly, each dimension should separate according to different physical or chemical properties of the analytes and we look to specific selectivity differences towards a problem separation. Secondly, an efficient means of interfacing the (two) separation modes is also required. Switching valves or other methods will be needed to redirect the flow stream from one column to another. This may be combined with a method for peak compression or peak focusing between the two dimensions. Finally, the compatibility of the two separation modes must be taken into account. This will depend upon the carrier fluid (gas, liquid) that is used for each mode, and the mechanism by which solutes are retained on each dimension. For example, multidimensional high performance liquid chromatography (MDHPLC) combining strictly normal and reversed-phase modes will present a challenge because of the incompatibility of the mobile phases required by the two modes.

Basic Instrumental Requirements and Considerations

The main concern in implementing a multidimensional separation solution will be how to design the instrumental set-up. The greater the difference between the two dimensions, the greater the potential difficulty in their coupling, since there will be greater dissimilarity in the mechanisms of separation. The wide choice of column chromatography separation methods explains why the coupling or interfacing may present a challenge. If the two dimensions are of the same chromatographic type – GC–GC, HPLC–HPLC, supercritical fluid chromatography (SFC)–SFC etc. – the task is not so problematic. Where different carrier phases are required for the two dimensions, chromatographic integrity must be maintained. Transferring a solution phase from HPLC to capillary GC or SFC requires an interface that can effectively introduce analyte into the narrow-bore column without compromising band dispersion, and whether analytical scale or large volume solvent injection is to be used determines the interface complexity.

Table 1 presents a summary of the potential successful multidimensional column chromatography methods. Some options will be generally incompatible, such as IC coupled with GC, since exclusion of the electrolyte carrier fluid from the GC system will be difficult, and ionic analytes for which IC is usually used will not be suited to GC analysis. The suitability of HPLC–GC and GPC–GC for volatile organics is the reason why these liquid-phase first-dimension separations are useful for sample differentiation prior to the GC step. **Table 2** further outlines various procedural aspects of selected multidimensional methods.

For multidimensional GC (MDGC) analysis, it is not a difficult task when dealing with relatively low boiling mixtures to couple two columns together, and to have gas-sampling valves or a flow-switching device to allow transfer of effluent. The classical Deans switch relies on pressure differences to pass carrier flow in different directions. **Figure 1** presents a schematic diagram of a typical commercial MDGC system, comprising one oven, two columns, two detectors, a midpoint restrictor at which point the diversion of column flow to either the first detector or the second column occurs. A cold trap focuses heart-cut

Table 1 Possible multidimensional coupling of separation dimensions in column chromatography

		Second dimension						
		GC	*NPHPLC*	*RPHPLC*	*IC*	*GPC*	*SFC*	*CE*
First dimension								
	GC	✓					✓	
	NPHPLC	✓	✓	✓	✓	✓	✓	✓
	RPHPLC	✓	✓	✓	✓	✓	✓	✓
	IC		✓	✓	✓			✓
	GPC	✓	✓	✓	✓	✓	✓	✓
	SFC	✓					✓	
	CE	✓	✓	✓	✓			✓

GC, Gas chromatography; NPHPLC, normal-phase high performance liquid chromatography; RPHPLC, reversed-phase high performance liquid chromatography; IC, ion chromatography; GPC, gel permeation chromatography; SFC, supercritical fluid chromatography; CE, capillary electrophoresis.

Table 2 Selected multidimensional (MD) chromatography modes and application areas

Dimension 1	*Dimension 2*	*Interface*	*Method*
Packed GC	Capillary GC	Heart-cut valve	Trace enrichment
Packed/capillary GC	Packed/capillary GC	Direct coupling; pressure tuning	Multi-chromatography
Capillary GC	Capillary GC	Heart-cut valve, with options (see Table 1)	Conventional high resolution MDGC
Capillary GC	Capillary GC	Continuous transfer; peak compression	Comprehensive 2D gas chromatography
HPLC	Capillary GC	Large volume injection	Multidimensional HPLC-GC
HPLC-GPC	Capillary GC	Large volume injection	Prior class separation before GC step

fractions, and a solenoid-controlled shut-off valve closes the flow through to the monitor detector and effects the transfer of the flow of column 1 to column 2.

Direct coupling of two or more columns, with all the effluent from one column passing wholly into the second column without hindrance (see later for variations on this theme), is normally not considered a MDGC analysis because MDGC methods should lead to greater *peak capacity* for the total system. Capacity may be thought of as the total available or achievable peak separation on a column. In simple terms, this is the total retention space divided by an average peak width parameter defining acceptable neighbouring peak resolution, i.e. the maximum number of peaks, resolved to a given extent, which can be produced by the system. Consider temperature-programming analysis. Assuming that the total chromatographic adjusted retention time is 90 min, and each peak basewidth is 10 s (peak widths may be approximately constant across the whole analysis, depending on the temperature ramp rate chosen), then a maximum of 540 baseline separated peaks could be recorded on this column. In practice, the actual number would be much smaller since the peaks are not eluted uniformly over the total time of the analysis.

Expanding System Capacity

Statistical methods have been employed to determine the ability of a column to resolve a complex mixture of compounds, assuming their distribution within the column to be entirely random. This theoretical analysis is informative, but typical complex mixtures must be treated on a case-by-case basis. The chromatographer must define the information required from an analysis; there may be no need to resolve every peak in a mixture if the required target solutes are only a small fraction of the total components. An optimized separation need focus only on those components which must be analysed. For example, the analysis of benzene and toluene in gasoline fractions, where only the resolution and quantification of these compounds are required, means that the measurement of all other components is of less or even of no concern.

The capacity of the total system (or the restricted region about the target solutes) will be expanded in the multidimensional analysis. Specific regions of the effluent from the first column must be isolated and these small fractions transferred to the second column. These two columns may be referred to as the pre-column or first dimension, and the analytical column or second dimension.

Consider the above GC column with a capacity of 540 peaks. If this is coupled to a second column with capacity of, for example, 280 peaks, and if the two columns represent completely orthogonal separations, we would have a theoretical capacity of $540 \times 280 = 151\,200$ peaks. More generally:

$$n_{\text{tot}} = (\bar{n})^z$$

where n_{tot} is total peak capacity, $\bar{n}$ is the average capacity on each column and z is the number of coupled columns.

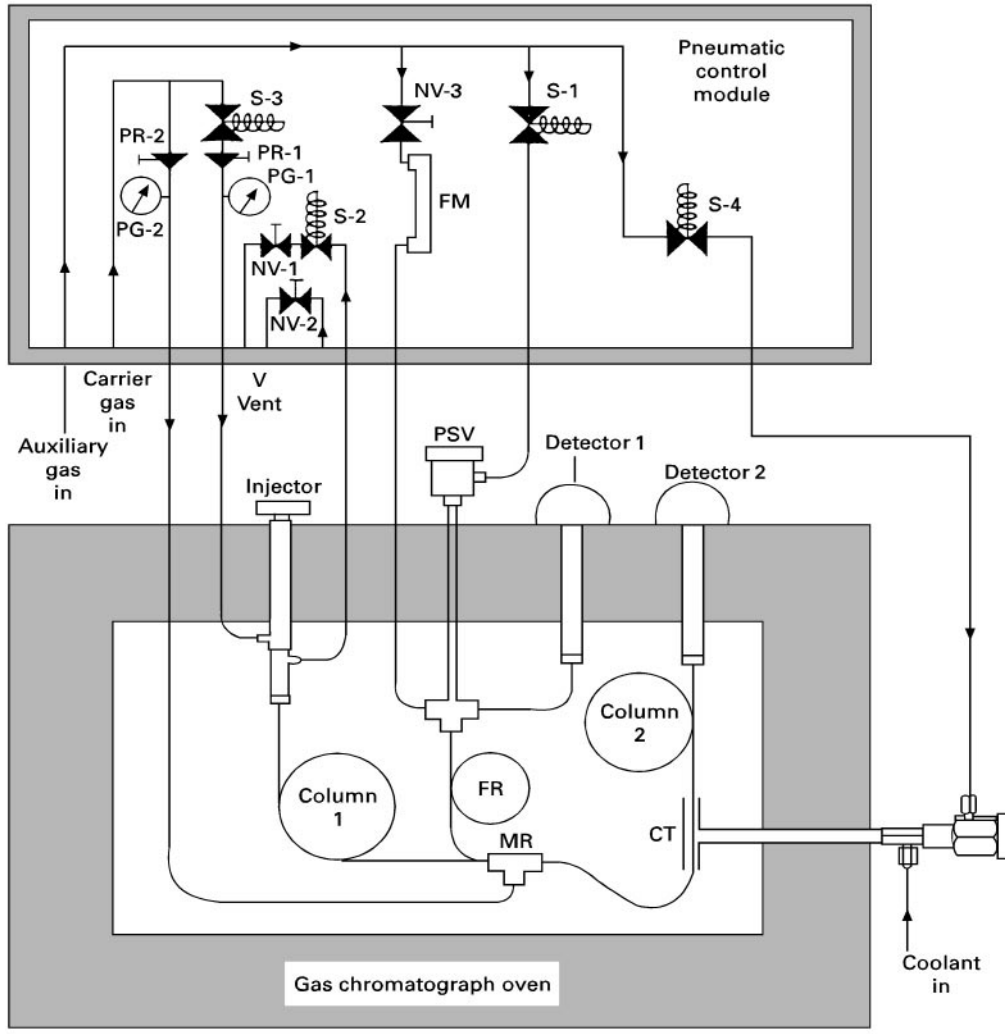
This can only be possible if the full capacity of each dimension can be achieved in the MDGC analysis. This is not normally so; it depends critically on the manner in which the column interfacing is performed, and how the transfer and subsequent second-dimension analysis is carried out. In fact, with selected heart-cut analysis, the total system capacity is better described as the summation, rather than the product, of the capacity of the two coupled columns:

$$n_{\text{tot}} = 2\bar{n}$$

or, more generally:

$$n_{\text{tot}} = \sum n_1 + n_2 + \ldots n_z$$

Consider a first column with a small unresolved group of, say, five peaks each of 10 s basewidth, eluting over a period of 35 s which is transferred to the second column. The peak capacity of the first column in the region of interest is only 3.5. If the second column has the ability to separate these peaks



Solenoid valves
S-1 Controls pneumatic shut-off valve
S-2 Controls injection splitter and back-flush operation
S-3 Controls pre-column carrier gas input
S-4 Controls CO_2 or optional liquid nitrogen cold trap

Pressure regulators
PR-1 Sets pre-column carrier gas input pressure
PR-2 Sets midpoint carrier gas pressure

Pressure gauges
PG-1 Monitors pre-column pressure
PG-2 Monitors midpoint pressure

Fixed restrictor
FR Deactivated transfer line from midpoint restrictor to monitor detector

Peripheral hardware
FM Flow meter
MR Midpoint restrictor
CT Cold trap
PSV Low dead volume pneumatically controlled shut-off valve

Needle valves
NV-1 Controls injector split flow
NV-2 Controls midpoint split flow for packed to capillary column operation
NV-3 Controls make-up gas flow rate

Figure 1 Multidimensional gas chromatography schematic diagram. Courtesy of SGE International.

just to basewidth, then its capacity towards the target solutes is 5. (If the peak separation is random, we will require a higher peak capacity in order to be assured that the five peaks will be separated.) In GC, solute boiling point plays a key part in the retention of compounds, and superposed on this primary retention parameter will be secondary properties such as polarity of the column and solutes, defining solute-specific interactions. Since each column's retention depends in the first instance on the overall volatility of each component, then the heart-cut or transferred solutes cannot be distributed over the total elution space of the second column. Rather, it is restricted to the range that the combined effect of boiling point and polarity imposes on the compounds. A non-polar first column means close eluting solutes have similar

boiling points. A polar second column will enhance solute polarity differences to achieve separation. **Figure 2** shows examples of heart-cutting poorly resolved sections of one column to another column. If the solutes subsequently elute relatively close together, much of the theoretical capacity of the second column is not employed.

In many MDGC systems, a cryofocusing step is used at the start of the second column to collect heart-cut fractions as a narrow band, as shown in Figure 2B centre. When the cryogenic fluid is turned off, the solutes recommence their travel on the second column, starting at the same initial position and time. If unresolved compounds from the first column are separated, the aim of the experiment is achieved. The use of a second oven, in which the second column is located, may require a cold trap since just keeping the second oven at a low temperature may not be sufficient to immobilize the solutes. If trapping is not required, the second oven may track the temperature of the first oven.

The need for a cryogenic trapping procedure requires further consideration. Since it will focus solutes at the start of the second column, it will also remix partially resolved compounds. Depending on whether the solutes reverse their relative retention on the two phases, the action of focusing the solutes may either improve or worsen the separation.

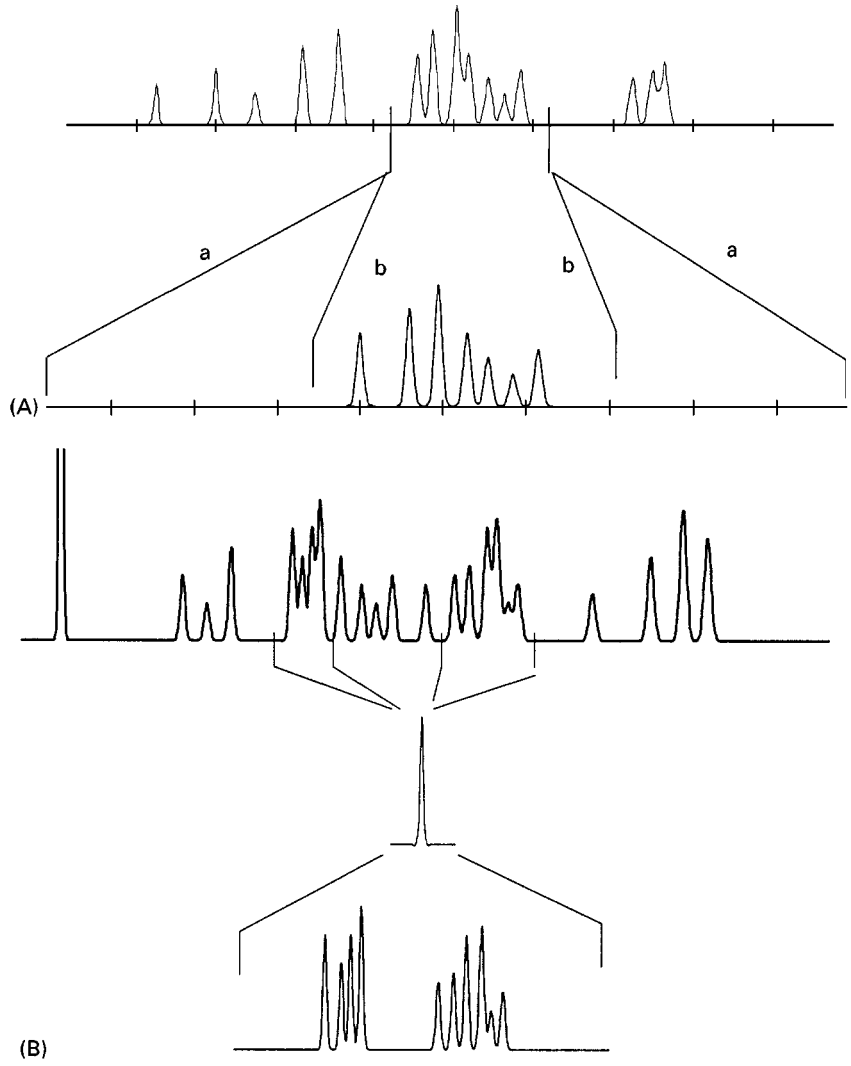


Figure 2 (A) Heart-cutting the poorly resolved section of the top column to the bottom column improves separation, but the full capacity of the second dimension may not be fully used. A second-dimension analysis, which only requires the space shown by lines labelled b, would be preferable to that shown by lines labelled a, where excess analysis time would result. (B) Two heart-cuts are performed on the first dimension (top). Both heart-cuts enter one cryogenic trap with all components recombined into one band (centre). The second-dimension analysis (bottom) is then used to provide greater selectivity difference for the range of solutes and enhanced separation of the components.

In summary, MDGC may be used in the following arrangements:

- single oven, with or without a cryotrap
- dual oven, with or without a cryotrap
- single or dual oven with multiple sorption/collection traps
- single oven with rapid second-dimension analysis and modulated transfer system – the so-called comprehensive 2D GC.

Figure 3 summarizes a number of different arrangements for performing multidimensional chromatography. Irrespective of the dimension types, the coupling must enable the flow stream to introduce solute into the second dimension. Direct coupling (or pressure tuning in GC) need only use a column connector, but other methods use multiple heart-cuts into one storage reservoir, as indicated by the circle shown in 3A (e.g. a single cryotrap in GC), or separate storage devices with discrete analysis of each, as shown in 3B, or a specially designed modulator to allow continual sampling/analysis of fractions from dimension 1, as in 3C (see later). In the case of method 3A, 2D will probably require a broad range of analysis conditions since collected fractions will have a wide volatility range. In 3B, each separate 2D analysis need only be performed over a limited range of conditions, selected according to volatility considerations.

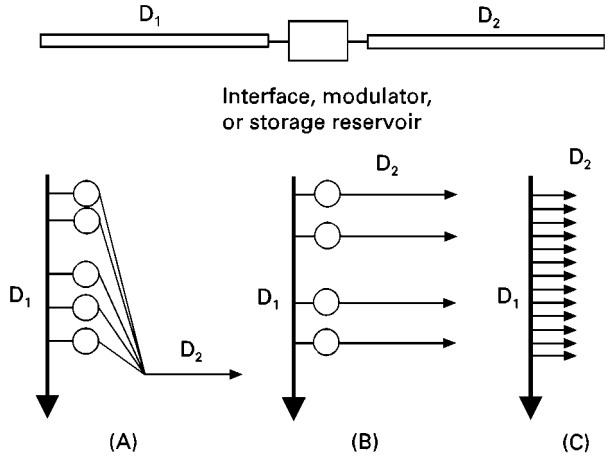


Figure 3 Coupling two dimensions, transferring selected bands and completing the second-dimension analysis can involve a range of procedures. (A) The second separation dimension can be a single chromatographic analysis, with selected dimension 1 (D_1) heart-cuts combined, e.g. in a cold trap, prior to dimension 2 (D_2). (B) A series of second-dimension analyses, each for an individual D_1 heart-cut, can be run with each heart-cut stored in a separate sample reservoir, e.g. sampling loops in HPLC or cold traps in GC. (C) By operating the second dimension in a rapid repetitive fashion, the comprehensive chromatograpy method is possible.

In regular MDGC, there will be a limited number of second-dimension analyses, or a limited number of heart-cut events. Conventionally, both dimensions will employ columns of reasonably normal types in respect of lengths, diameters and carrier gas flow rates.

In an offline system, or where fractions are collected in a storage section prior to introduction into the second dimension, such as a sampling loop in HPLC, the time between collection of heart-cut and second-dimension analysis might not strictly represent a continuous coupled analysis.

MDGC for Trace Enrichment

A capillary column has a limited sample capacity. Excessive amounts of sample lead to nonlinear conditions and broadened peaks are obtained. Such broadening can obscure small peaks of interest which elute with a similar retention factor to that of the large component, affecting quantification and identification of the trace solute. In MDGC, sample may be injected into a packed column which has a greater ability to maintain linear conditions at higher injected amounts. The zone of enriched trace component can then be heart-cut to a capillary column. Most of the major component will have to be excluded by the heart-cut event, and since now it does not overload the capillary column, there will be less probability that it overlaps the trace solute. Much more of the trace solute is passed to the capillary column than is otherwise possible. This application does not necessarily require different column phases on both the packed and capillary columns. The first column can be considered to be part of the sample introduction step into the second column.

Use of a Series of Parallel Heart-cut Reservoirs/Traps

Parallel traps are used to store successive heart-cut fractions prior to subsequent analysis. These might be liquid-phase loops (HPLC) or cryogenic traps (GC; Figure 3B). An array of packed cryogenically cooled traps may be used to collect selected fractions of heart-cut effluent from a capillary GC pre-column. The individual traps are then eluted into a second analytical capillary column, chosen for particular suitability to the required analysis. The effluent from the analytical column may then be split to different detectors, and the use of mass spectrometry/flame ionization detector and FTIR has been described, with FTIR receiving the larger flow due to its less favourable detection sensitivity. This procedure has been demonstrated with petroleum samples, where

FTIR is most advantageously used for isomers of compounds such as the xylenes. However, the complications arising from multiple trap management will reduce its attraction for many analysts.

Backflushing

In GC analyses where a sample consists of a wide boiling range of components, and where their prior separation is either difficult or troublesome, injection will introduce the low volatility components into the chromatographic column. If the target solutes are those that are eluted quickly, considerable time must be spent waiting for the high boiling point components to be eluted before the next analysis can be commenced. In MDGC, it is possible to reverse the flow in the pre-column (refer to column 1 in Figure 1) to back-flush the heavy constituents out of the column and vent them through the split vent line. This can be completed whilst the higher volatility components are being separated on the second column. This flow switching will be commenced when the desired solutes have passed the midpoint valve between the two columns (back-flushing is the oldest form of MDGC and has been employed since the earliest days of GC). Back-flushing can likewise be easily incorporated into other coupled separation systems such as MDHPLC.

Pressure Tuning

The technique of pressure tuning involves variation in the midpoint pressure between coupled columns to alter overall solute selectivity. This is not strictly an MDGC method, and has been given the term multichromatography in order to differentiate it from regular MDGC. However, pressure tuning is possible on regular MDGC systems, and some specific multidimensional results can be achieved on multichromatography pressure-tuned systems. The unified chromatography procedure, promoted by Bartle, alters the characteristics of the carrier phase during an analysis, for example progressing from GC to SFC conditions by applying a pressure programme to the carrier stream. Thus, one column is used, but different chromatography mechanisms are employed. This variation is again not strictly multidimensional. The pressure-tuning arrangement is shown in **Figure 4**.

Compounds are immediately presented to the second column as soon as they are eluted from the first column; their motion is not hindered by trapping or any other similar solute-focusing effect. Changing the midpoint pressure alters the relative flows in each column. Flow change by itself does not alter the capacity factor on either column (i.e. k is constant),

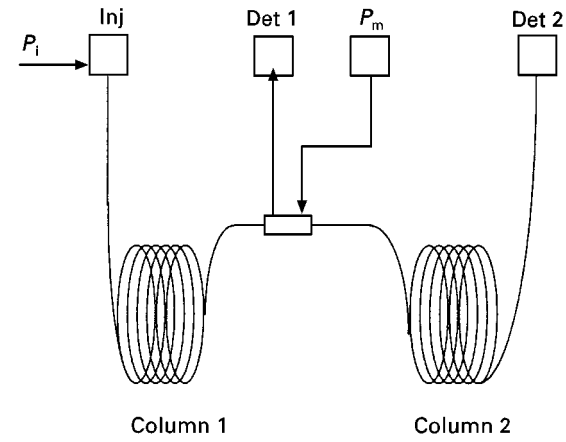


Figure 4 The pressure-tuning method involves a coupling between the two columns where additional pressure (P_m, midpoint pressure) can be applied above the natural pressure. P_i, inlet pressure; inj, injector; Det 1, Det 2, detectors 1 and 2.

although of course temperature change may affect relative k values. However, the overall k value may change dramatically with midpoint pressure changes. The contribution of each column in determining overall solute capacity on the system is varied, and so relative solute positions may change and best separation conditions may be determined. This procedure is essentially a continuously variable (at least over a given range) phase composition method, simulating column phases of selectable polarity based on the two phases comprising the coupled columns. It is possible to predict the effect of pressure on the overall separation, since individual retention factors on each column can be determined. The effect of carrier flow rate on each individual column's performance should still be considered. **Figure 5** represents results which may be obtained, with the unretained peak time giving retention factors on each column. Peak overlap and exchange of relative retention of components are precisely what may be seen experimentally.

For a given column length, the total separation space does not increase in this method.

Comprehensive Multidimensional Chromatography

Comprehensive multidimensional chromatography is closest to a true continuous multidimensional column method since it subjects every emerging peak in the first dimension to second-dimension separation in almost continual fashion. Figure 3C is a representation of this approach. The term comprehensive chromatography is attributed to Bushey and Jorgenson, who demonstrated the advantages of the technique for coupled HPLC dimensions. Two major

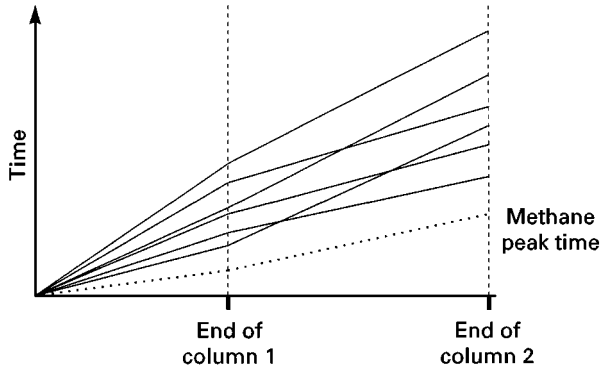


Figure 5 Pressure tuning allows retention factors to be determined on each separate column section provided t_Rs of compounds (solid lines) and t_M (dotted line) are known on each dimension. After the midpoint, various solutes may swap position, possibly leading to better overall separation. The effect of the pressure tuning can be predicted by moving the right-hand vertical line along the horizontal axis.

variations depend on whether all the column flow or only a portion from the first column is transferred to the second column. These require different technical implementation of column coupling.

The second column elution time must be very short with respect to that on the first dimension – less than the frequency at which the first column effluent is sampled. This ensures that each second-dimension elution is completed before the subsequent band is introduced into the second column. Result presentation is best if the second-dimension analysis is rapid with respect to bandwidths on the first column, for example, a second-dimension analysis time about one-fifth of the peak width time on the first column. Given this requirement, first column performance leading to broad peaks may be required. The two columns chosen should ensure orthogonality. Retention of compounds in dimensions one and two can be defined as ${}^1t_R$ and ${}^2t_R$ respectively.

The final chromatogram will be a two-dimensional array of retentions, with a third dimension of peak height, leading to a contour plot chromatogram. Data presentation protocols and concepts such as retention indices, quantitative analysis considerations and relationships between peak position and phase polarities are only just being explored. Much further work is needed to evaluate these systems fully. **Figure 6** demonstrates how the three-dimensional data are presented in terms of a contour plot. The peak contour comprises a series of slices in the second dimension which is reconstructed as a peak with dispersion in both dimensions. The original first-dimension separation is shown.

In the comprehensive gas chromatography ($C(GC)^2$) method, peak compression by a means of a focusing step between the two dimensions may be advantageous. This allows a very narrow band to be introduced to column 2 and allows the best peak capacity to be achieved on this column. Ideally, overlapping components in dimension 1 will be resolved on dimension 2. Peak compression of 20–50 times have been demonstrated, and this immediately translates into significant peak sensitivity enhancement with $C(GC)^2$.

In HPLC, the collected fraction of effluent would typically be analysed on a conventional column, so it would have a typical retention time in minutes.

Comprehensive Gas Chromatography

The $(GC)^2$ part of the abbreviation serves to indicate the multiplicative capacity of the system, and the term comprehensive reflects that the full suite of peaks from the first dimension is analysed.

The second dimension analysis time will be about 5 s or less, and the second dimension, comprising a short, high-phase ratio, narrow-bore open tubular column, might have a total peak capacity of only 10–20 peaks. $C(GC)^2$ uses first and second dimensions

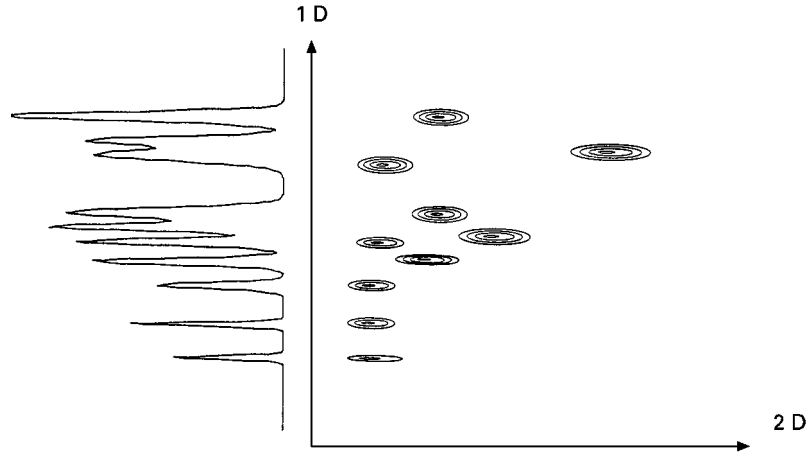


Figure 6 Peak contour representation of two-dimensional separation in comprehensive chromatography.

at the same oven temperature, allowing the second column effectively to resolve on the basis of polarity difference between the two columns. If adjusted properly, the full peak capacity on the second dimension should now be available for separation, and the total peak capacity should be the product of the first column capacity and the capacity available on the second column at any chosen operating temperature (the second column operates almost isothermally for each individual analysis).

Having a high peak capacity should not be too critical on the second column, but phase polarity or selectivity difference should be carefully chosen.

Peak compression, followed by fast second dimension analysis, results in improved sensitivity of detection; if a 5 s band of effluent from column 1 is compressed and leads to a detected peak width of 250 ms, a 20-fold sensitivity increase should result.

Technically, $C(GC)^2$ with compression in time requires novel procedures. Two systems have been described for $C(GC)^2$ employing band compression. One is based on a rotating elevated temperature modulator which passes closely over the junction between the two columns, incorporating a thick film accumulator section between the columns at the junction. An alternative device employs a longitudinal oscillating cryogenically cooled trap that can collect and focus solute from the first column, then pulse or remobilize the narrow band into the second column.

Given the need for very rapid analysis, rapidly recording detector systems are required.

Peak position in the two-dimension separation space will now be a complex function of volatility and polarity, determined by the individual mechanisms of the two columns chosen, and a full interpretation of the $C(GC)^2$ method is required in this respect. Possibilities for class separation demonstrate that the method has potential for multiresidue and screening applications, and characterization of petroleum products.

See also: **II/Chromatography: Gas:** Column Technology; Historical Development; Theory of Gas Chromatography. **III/Gas Analysis: Gas Chromatography.**

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Pyrolysis Gas Chromatography

C. E. R. Jones, Redhill, Surrey, UK

Introduction

The gas chromatographic process is wholly dependent upon solutes having significant vapour pressures at the upper limiting operating temperature of the chosen solvent so that the partition of those solutes between the mobile and stationary phases affords viable separation.

Such a limitation prohibits the analysis of any intractable samples (i.e. potential solutes) unless the means to modify them are invoked.