

# Multidimensional Tandem Capillary Gas Chromatography System for the Analysis of Real Complex Samples. Part I: Development of a Fully Automated Tandem Gas Chromatography System

Luigi Mondello\*, Maurizio Catalfamo, and Giovanni Dugo

Dipartimento Farmaco-Chimico, Facoltà di Farmacia, Università degli Studi di Messina, Viale Annunziata, 98168 Messina, Italy

Paola Dugo

Dipartimento di Chimica Organica e Biologica, Facoltà di Scienze, Università degli Studi di Messina, Salita Sperone, 98166 Messina, Italy

## Abstract

A fully-automated, tandem high-resolution gas chromatography (HRGC–HRGC) system is developed for multitransfer operations. The system allows quantitative transfers from the precolumn to the main column without time restriction and makes it possible to perform multiple transfers using different temperature programs for the two GC ovens and columns, which may have different diameters and different stationary phase film thicknesses. When the multidimensional system is not in use, the two GC systems may be used independently without changing the hardware. As an example of the system's efficacy, a chiral separation of some lemon essential oil components is reported.

## Introduction

It is known that in highly efficient capillary gas chromatography (GC) systems, the complete resolution of all the volatile components of complex real samples (e.g., foods and flavors) cannot be achieved. To overcome this problem, it is possible to use longer columns to obtain a higher plate number. However, the use of longer columns usually implies longer analysis time and a decreased sensitivity, and resolution does not increase much because it is proportional to only the square root of the plate number. A different approach would be to change the polarity of the stationary phase to increase selectivity, but this would not be sufficient to separate all the compounds. The best means of increasing both selectivity and capacity is provided by two-dimensional techniques. The purpose of a typical multidimensional GC (MDGC) as a chromatographic system is to transfer some portion of the sample components from a primary

column to a secondary column that is usually of different polarity.

MDGC has been used for many years in many different ways. According to Bertsch (1), the techniques that combine two separately controlled GC separation systems can be defined as, "two-dimensional gas chromatographic techniques." From this point of view, a multidimensional system, depending on its complexity, may be used in a combination of operational modes such as the following:

### Solvent-flushing

Solvent eluted from the first column (precursor) is vented to waste so that diluted samples containing water, chlorinated solvents, polar solvents, and derivatization agents that are not compatible with columns or detectors can be analyzed.

### Backflushing

Backflushing is widely used when the sample to be analyzed contains components that are eluted after the compounds of interest. The advantages are the reduction of the analysis time and the protection of both the detector and the second column from contamination with undesirable compounds.

### Heart-cutting

The transfer of one or more selected groups of compounds eluted from a gas chromatographic column onto a second column is usually referred to as "heart-cutting." The main application of heart-cutting is the optimization of chromatographic resolution, in which unresolved sample components eluted from the first column are selectively diverted to a second column of higher efficiency or better selectivity. At the same time, it is possible to collect information on the retention time in two different stationary phases, which facilitates the identification of the compounds.

\* Author to whom correspondence should be addressed.

A review of the literature indicates that GC–GC heart-cutting has been used since the mid-1950s in process chromatography, either with two packed columns, a packed column and a capillary column, or two capillary columns. A combination of two packed columns was introduced by Simmons and Snyder in 1958 (2) in such a manner that a preliminary cut from the first column could be charged directly to one or more secondary columns. Years later, Deans et al. (3) used the same system of columns in analytical process chromatography with a flow-switching device. The introduction of a precolumn into preparative scale chromatography has been described by Kaiser (4) using Deans's method. Two years later, Schomburg et al. (5) modified a commercially available cyclic preparative-scale GC for the application of cutting and backflushing using pneumatic switching devices, as described by Deans. In 1981, Deans (6) described the technique used for heart-cutting between packed columns and concluded that two packed columns in series with different stationary phases had demonstrably greater separation power than a single capillary column.

In 1963, Martin and Winters (7) introduced the combination of a packed column and a capillary column. The columns were situated in separate ovens, and a cold trap was positioned in the inlet of the capillary column for refocusing bands broadened in the packed column. In 1968, Deans (8) introduced a system that eliminated the use of mechanical valves in the oven and could be applied for the heart-cutting from a packed column to a capillary column. In the following years, the application of heart-cutting from a packed column to a capillary column was studied in depth. It is possible to find papers that mainly used a variant of Deans's switch, and some of them used mass spectrometric detection (6,9–14).

In 1964, McEwen (15) introduced the first MDGC system with a double capillary column system. In the early years, MDGC systems regularly employed a rotary switching valve. Installation and operation of a mechanical valve seemed easy, but dead volume and adsorption effects, limited maximum operating temperature, potential gas leakage or flow path plugging, and limited flexibility were the disadvantages of these systems. The use of off-line solenoid valves to alternate the line pressure at various times to direct or change the carrier gas flow direction overcame the drawbacks of multiport valves.

In 1968, Deans (8) reported a valveless switching system that allowed no valves or moving parts to be in either the sample flow path or the higher temperature zone. This technique was based on a pressure balance between the two columns (6,16–21), which is made possible by in-line restrictors and the use of additional makeup gas. An improvement of this system was presented by Schomburg et al. (22), in which the original valveless column connection of Deans's system was replaced with a "live" switching system containing a special coupling unit. The two capillary columns were inserted over a thin platinum capillary, which was the central component of the coupling piece. Supplementary carrier gas was added through two control lines and adjusted with needle valves.

A decade after the introduction of the switching technique proposed by Deans (3), a commercial instrument enabling solvent-flushing, heart-cutting, and backflushing was developed by Siemens. Many papers reporting the use of this instrument can

be found in the literature (22–88). In some of these papers, mass spectrometry (29,47–49,56,69,72) and FTIR (46,64) were used as detectors. Other commercial instruments were introduced by SGE (89–92), IBM (89–93), Chrompack (94–96), Perkin-Elmer (97), and Gerstel (98).

Mechanical valve-switching was described again by Jennings (99) and reviewed by Gordon et al. (89). In the literature, it is also possible to find various other applications of tandem capillary heart-cutting using a switching device with a mechanical valve (89,100–103).

In this paper, an MDGC system is described for multitransfer purposes based on a high-temperature valve to heart-cut fractions from the first capillary column to a second capillary column with a hot transfer line and a system to maintain a constant flow during the transfer. In the next parts of this series, we will use this MD system to solve analytical problems, regarding mainly the chemistry of the essential oils.

## Experimental

The MD system used in this study was a developmental model that consisted of two Shimadzu 17A GCs equipped (see Figures 1 and 2) with the following:

### GC 1

The first GC was equipped with two split-splitless injectors at 250°C with two manual flow controllers (injectors 1 and 2) and a flame-ionization detector (FID) at 250°C (FID 1); an SE-52 capillary column (30 m × 0.32-mm i.d., 0.45- $\mu$ m film thickness, Mega, Legnano, Italy). The temperature program was set at 45°C for 6 min, then programmed to 240°C at 2.0°C/min. The carrier gas was helium. A Valco six-port ( $1/16$ " ) two-position UW-type valve (valve 1) with a right-angle drive (A3RAD6WT) (Valco Europe, Schenkon, Switzerland) and a digital valve interface (DVI-220) (Valco Europe) connected to Event 91 on GC 1 were used. To connect the valve to the fused-silica tubing,  $1/16$ -in. removable fused-silica adapters (FS1R.5-5 and FS1R.4-5) (Valco Europe) were used. A solenoid valve (valve 2) was used to change the carrier pressure (P1, 110 kPa) (standby position, column 2) to a higher pressure (P2, 200 kPa) (cut position, columns 1 and 2) and was connected to Event 91 on GC 1. A solenoid valve (valve 3) was also used to change the carrier pressure (P3, 90 kPa) (standby position, column 1) to a lower pressure (P4, 2.5 kPa) (cut position, injector 1 and FID 1) and was connected to Event 91 on GC 1. A solenoid valve (valve 4) that allows the use of two splitter valves (A and B) with different ratios in injector 1 was connected to Event 91 on GC 1. An integrator Shimadzu model C-R3A (Milan, Italy) was connected to "start out" the signal on GC 1 and to start immediately with the GC. The GC started with an electrical signal that was generated with a microswitch mounted on injector 1 and connected to the "start in" on GC 1.

### Transfer line

An aluminium thermoregulated block (200°C) equipped with a heater assay and a thermocouple assay was connected to the temperature auxiliary exit (AUX2) exit on GC 1.

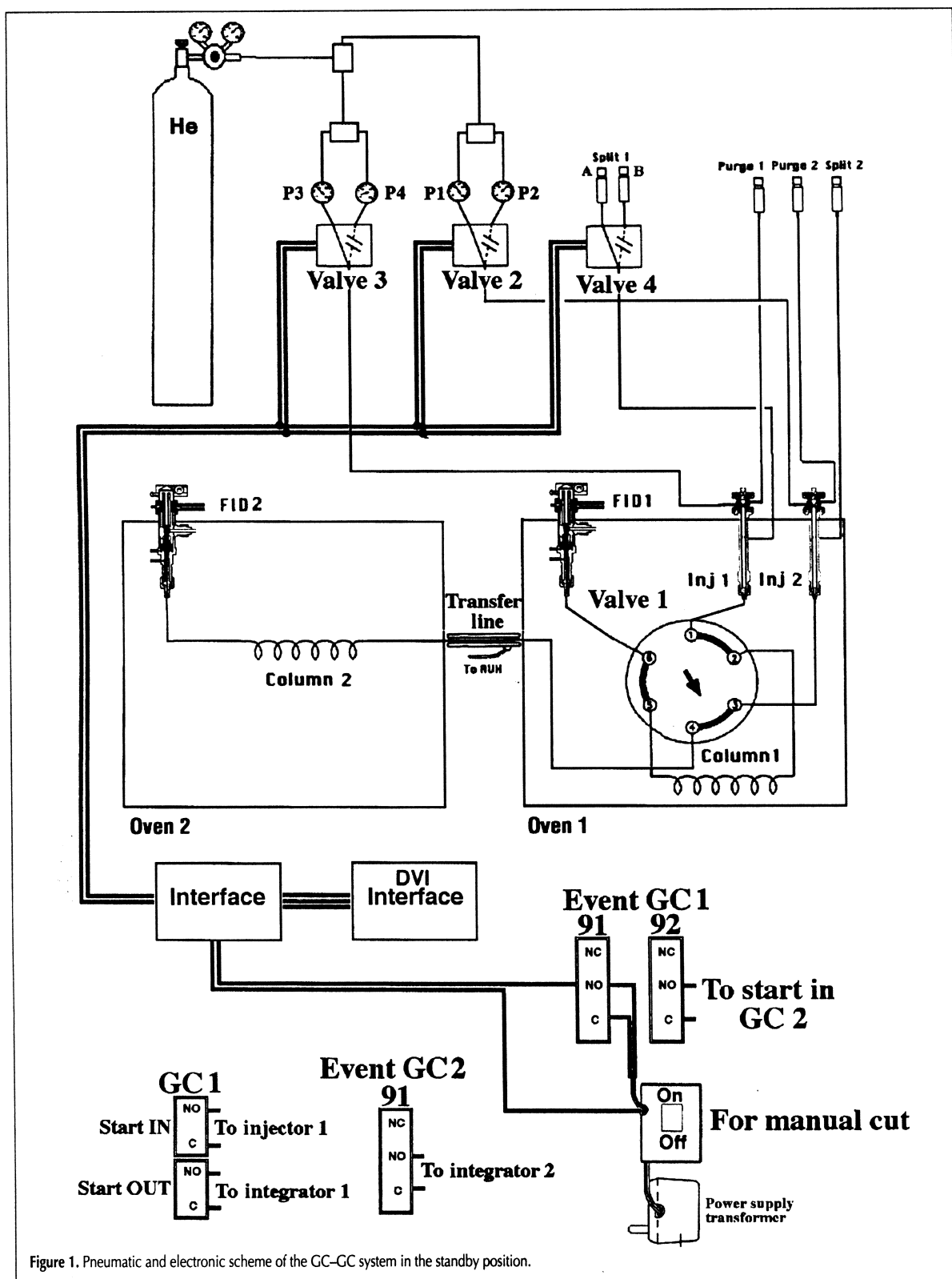


Figure 1. Pneumatic and electronic scheme of the GC-GC system in the standby position.

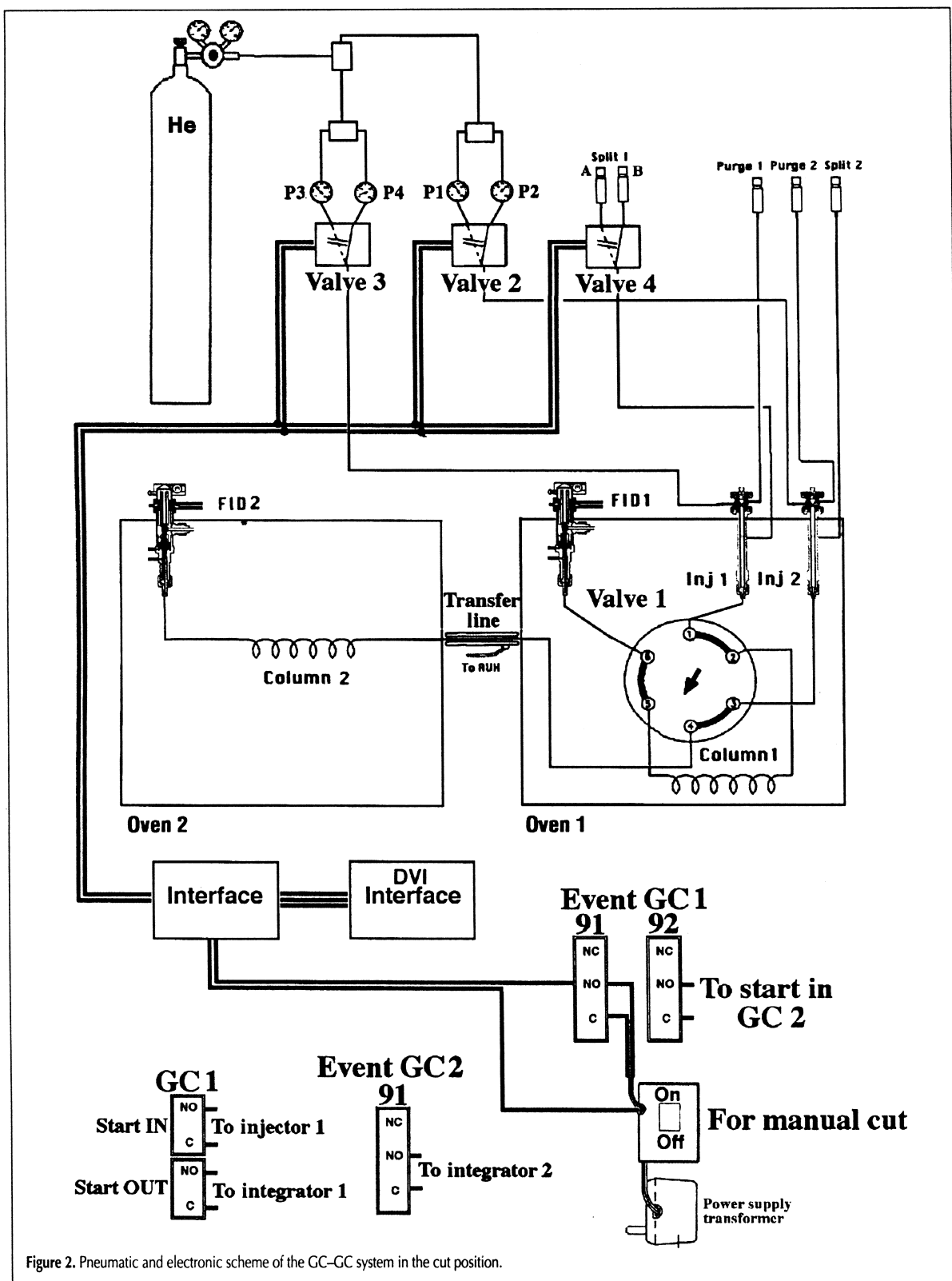


Figure 2. Pneumatic and electronic scheme of the GC-GC system in the cut position.

## GC 2

A MEGADEXDETTBS $\beta$  (diethyltert-butylsilyl- $\beta$ -cyclodextrin) column (25 m  $\times$  0.25-mm i.d., 0.25- $\mu$ m film thickness) (Mega) was used. The temperature was programmed at 45°C for 6 min, then programmed to 180°C at 2.0°C/min. The carrier gas was helium. An FID was used at 250°C (FID 2); the GC started with the first cut. A Shimadzu model C-R3A integrator was connected to "start out" the signal (Event 91) on GC 2, which, in this case, started with the GC. The GC started with an electrical signal generated by the external events on GC 1 (Event 92).

## Results and Discussion

The main disadvantages of using in-line rotary valves are possible dead volume, gas leaks, and incomplete chemical inertness. Technological advances in valve design have miniaturized connectors and eliminated unswept volumes. The six-port valve used here was a Valco 1/16-in. two-position A3RADC6WT-type valve. The valve has a rotor made of fluorocarbon-filled crosslinked polyimide and a port diameter of 0.40 mm and can be operated at up to 350°C. This valve is designed for use with fused-silica columns using a special adapter (Valco FSR.5-5) consisting of a liner that slides over the fused-silica tubing and a ferrule that tightens on the liner. The polyimide liner has an enlarged diameter at one end that is captured by the nut, ensuring that the liner and the tube within it are removed as the nut is unscrewed from the valve. As the sample proceeds through the valve switching passage, it is exposed to both stainless steel and elastomer sample-contacting surfaces.

Figures 1 and 2 show a scheme of the MDGC system used in this study in the standby and cut positions, respectively. When the six-port valve (valve 1) was in standby position (Figure 1), the flow paths were from injector 1 to column 1 to FID 1 and from injector 2 through the hot transfer line to column 2 to FID 2. In this configuration, it was possible to carry out analyses independently on the two columns without changing the hardware. When valve 1 was switched to the cut position (Figure 2) the flow path was from injector 2 to column 1 through the hot transfer line to column 2 to FID 2, and at the same time, solenoid valve 2 was switched on to increase the carrier pressure (from P1 [110 kPa] to P2 [200 kPa]); this permitted column 1 to obtain the same retention times, even for those compounds eluted after more than one transfer, for either of the analyses carried out in the standby and cut positions. The ability to increase this pressure is particularly important when a multitransfer is requested. In fact, when the same pressure as in the standby position was maintained in the cut position,

the flow rate decreased in the cut position when the precolumn (column 1) was added to the main column (column 2). The flow rate drop caused a shift in the retention times of the components eluted after each transfer, and this did not permit the automated transfer of more than one fraction during the same analysis.

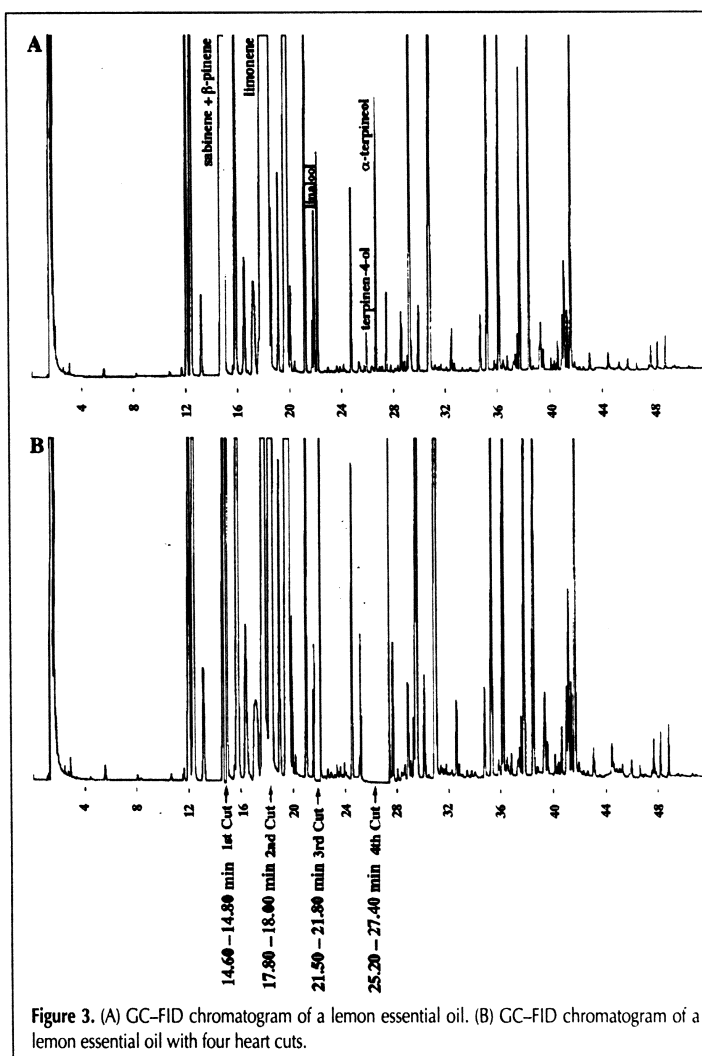


Figure 3. (A) GC-FID chromatogram of a lemon essential oil. (B) GC-FID chromatogram of a lemon essential oil with four heart cuts.

Table I. Relative Percentage and Transfer Windows of the Analyzed Components in Lemon Essential Oil

Component	Relative amount (%)	Transfer window (min)
Sabinene*	1.1–2.8	14.60–14.80*
$\beta$ -Pinene*	9.5–17.8	14.60–14.80*
Limonene	59.6–71.1	17.80–18.00
Linalool	13.2–18.5	21.50–21.80
Terpinen-4-ol†	0.01–0.08	25.20–27.40†
$\alpha$ -Terpineol†	0.06–0.28	25.20–27.40†

\* Coeluted.

† One heart cut.

When valve 1 was switched in the cut position, the flow surge also blew out the detector flame (FID 1). To overcome this problem, a second solenoid valve (valve 3) was added to decrease carrier pressure P3 (90 kPa) to pressure P4 (2.5 kPa) in order to maintain a constant flow in FID 1 and to protect the detector from a flow surge due to the absence of column 1 in the flow path. To allow a constant flow at FID 1, a solenoid valve (valve 4) was added. This valve permitted utilization of splitter 1A in the standby position (split ratio for the sample introduction) and splitter 1B in the cut position (high split ratio to allow the fast establishment of pressure P4). When this MDGC system oper-

ated in the standby position, the two columns worked independently, so split 1A and split 2 could be adjusted to optimize the more convenient split ratio, whereas splitter 1B was excluded. When the MDGC system was used, the split of injector 2 was adjusted so that the increased carrier could escape from the splitter when valve 1 was switched back to the standby position and the original pressure (P1) was re-established.

As shown in Figures 1 and 2, the system was completely automated by the use of the GC's external events. In fact, the time at which the valve should be switched to begin the cuts could be determined from a preliminary analysis. After this, a fully automated analysis was possible by programming the valve events.

The reproducibility of retention times in the pre-column was achieved by supplying, during the transfer, a pressure to the column inlet (injector 2) to balance the pressure drop due to the insertion in series of the main column (see Figures 1 and 2).

Figure 3A shows the chromatogram of a lemon essential oil obtained with the SE-52 column. In Figure 3B, the chromatogram of the same oil is reported with the indication of the four consequent transfers carried out. The transferred components and the transfer windows are shown in Table I. The content percentage of the transferred components in lemon oil are also reported in the same table.

Figure 4 shows the chiral chromatogram of the components present in the transferred fractions. Table II shows the results carried out for the enantiomeric distribution of  $\beta$ -pinene, sabinene, limonene, terpinen-4-ol and  $\alpha$ -terpineol.

Comparing chromatograms 3A and 3B, it is clear that retention times were also the same after the transfers. For this reason, considering the retention times obtained on the pre-column, it was possible to program the transfer windows for each fraction.

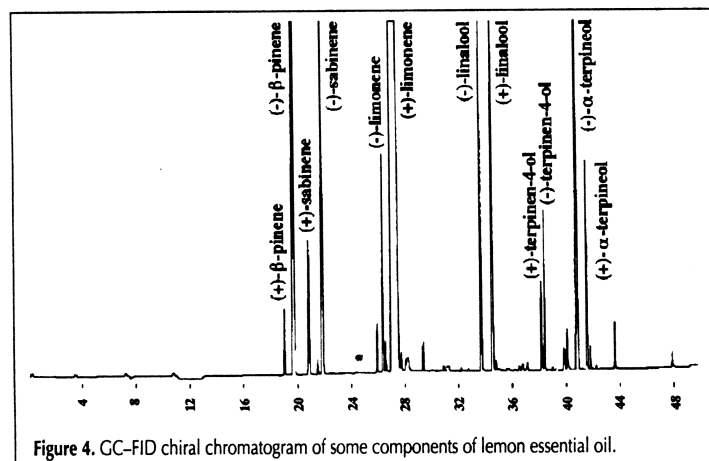


Figure 4. GC-FID chiral chromatogram of some components of lemon essential oil.

Table II. Enantiomeric Distribution of Some Components of the Lemon Essential Oil

$\beta$ -Pinene (+)/(–)	Sabinene (+)/(–)	Limonene (–)/(+)	Linalool (–)/(+)	Terpinen-4-ol (+)/(–)	$\alpha$ -Terpineol (–)/(+)
6.3/93.7	14.9/85.1	1.6/98.4	58.0/42.0	24.7/75.3	75.2/24.8

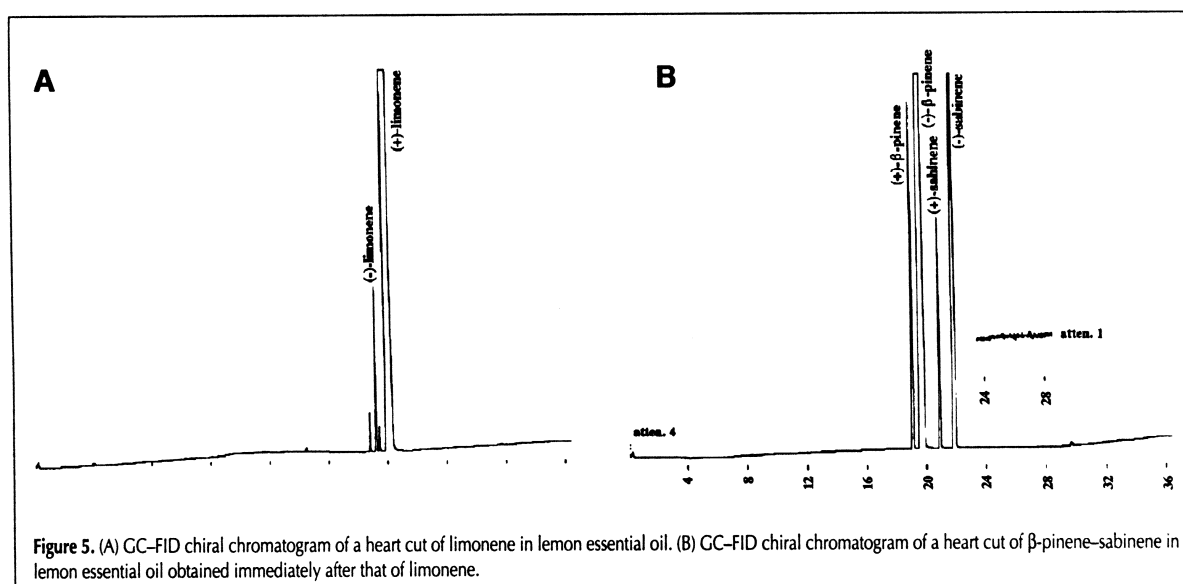


Figure 5. (A) GC-FID chiral chromatogram of a heart cut of limonene in lemon essential oil. (B) GC-FID chiral chromatogram of a heart cut of  $\beta$ -pinene-sabinene in lemon essential oil obtained immediately after that of limonene.

As shown in Figure 3 and Table I, sabinene- $\beta$ -pinene and limonene were partially transferred, whereas terpinen-4-ol and  $\alpha$ -terpineol were completely transferred.

Figure 5A shows the chiral chromatogram of the heart-cut of limonene, and Figure 5B shows the chiral chromatogram of the heart-cut of sabinene- $\beta$ -pinene obtained during an analysis carried out immediately after that of limonene. As can be seen by comparing the two chromatograms, no memory effect is apparent. Moreover, a standard mixture of the components under analysis has been injected directly in the chiral column without any modification of the MDGC system. Retention times obtained for this analysis were identical to those obtained for the same analysis with the MDGC system.

## Conclusion

In conclusion, the system described in this paper allows quantitative transfers from the precolumn to the main column without time restrictions and makes it possible to perform multiple transfers using different temperature programs for the two GC ovens and columns with both different diameters and different stationary phase film thicknesses. However, when the MDGC system is not in use, the two GCs may be used independently without any change to the hardware.

## Acknowledgment

The authors would like to thank Shimadzu Italia for their cooperation during the development of this work and Professor Carlo Bicchi (Dip. Scienza e Tecnologia del Farmaco, Università di Torino, Italy) and Mr. Mario Galli (Mega, Legnano, Italy) for the preparation of the chiral column used in this work as well as some helpful discussions.

## References

- W. Bertsch. Methods in high resolution gas chromatography. I. Two dimensional techniques. *J. High Resolut. Chromatogr. Chromatogr. Commun.* **1**: 85-90 (1978).
- M.C. Simmons and L.R. Snyder. Two stage gas-liquid chromatography. *Anal. Chem.* **30**: 32-35 (1958).
- D.R. Deans, M.T. Huckle, and R.M. Peterson. A new system for isothermal gas chromatographic analysis of light gases ( $H_2$ ,  $O_2$ ,  $CO$ ,  $CH_4$ ,  $CO_2$ ,  $C_2H_4$ ,  $C_2H_6$ , and  $C_2H_2$ ) employing a column switch technique. *Chromatographia* **4**: 279-85 (1971).
- R. Kaiser. *Preparative Gas Chromatography*. A. Zlatkis and V. Pretorius, Eds. John Wiley & Sons, New York, NY, 1971, pp. 181-210.
- G. Schomburg, H. Kotter, and F. Hack. Improvement of performance and economical utilization of automated preparative scale gas chromatography systems by incorporation of cut and backflush devices. *Anal. Chem.* **45**: 1236-40 (1973).
- D.R. Deans. Use of heart cutting in gas chromatography: A review. *J. Chromatogr.* **203**: 19-28 (1981).
- R.L. Martin and J.C. Winters. Adsorption of solutes at the liquid-gas interface as measured by gas chromatography and Gibbs equation. *Anal. Chem.* **35**: 116-17 (1963).
- D.R. Deans. A new technique for heart cutting in gas chromatography. *Chromatographia* **1**: 19-22 (1968).
- W.V. Ligon, Jr. and R.J. May. Quantity optimized two-dimensional gas chromatography for mass spectrometry. *Anal. Chem.* **52**: 901-905 (1980).
- R.J. Phillips, K. A. Knauss, and R.R. Freeman. Applications of heart cutting from packed to capillary columns. *J. High Resolut. Chromatogr. Chromatogr. Commun.* **5**: 546-52 (1982).
- M. Oréans, F. Muller, and D. Leonhardt. Trace-analysis in coupled systems; total transfer of traces from packed to capillary columns. *Proceedings of the 5th International Symposium on Capillary Chromatography*, Riva del Garda, 1983, pp. 461-73.
- W.V. Ligon, Jr. and R.J. May. Target compound analysis by two-dimensional gas chromatography-mass spectrometry. *J. Chromatogr.* **294**: 77-86 (1984).
- W.V. Ligon, Jr. and R.J. May. Isomer specific analysis of selected chlorodibenzofurans. *J. Chromatogr.* **294**: 87-98 (1984).
- W.V. Ligon, Jr. and R.J. May. Some experiences with two-dimensional gas chromatography/mass spectrometry. *J. Chromatogr. Sci.* **24**: 2-6 (1986).
- D.J. McEwen. Backflushing and two-stage operation of capillary columns in gas chromatography. *Anal. Chem.* **36**: 279 (1964).
- D.R. Deans and I. Scott. Gas chromatographic columns with adjustable separation characteristic. *Anal. Chem.* **45**: 1137-41 (1973).
- J.A. Rijks, J.H.M. Van Den Berg, and J.P. Diependaal. Characterization of hydrocarbons in complex mixtures by two-dimensional precision gas chromatography. *J. Chromatogr.* **91**: 603-12 (1974).
- W. Bertsch, E. Anderson, and G. Holzer. Two-dimensional high resolution GLC environmental analysis, preliminary results. *Chromatographia* **10**: 449-54 (1977).
- W.G. Jennings, S.G. Wyllie, and S. Alves. WCOT glass capillary columns in flavour chemistry. *Chromatographia* **10**: 426-29 (1977).
- E.L. Anderson, M.M. Thomason, H.T. Mayfield, and W. Bertsch. Advances in two-dimensional GC with glass capillary columns. *J. High Resolut. Chromatogr.* **2**: 335-42 (1979).
- H. Brotell, G. Rietz, S. Sandqvist, M. Berg, and H. Ehrsson. Two-dimensional capillary gas chromatography without intermediate trapping. Electron capture detector quantitation of an amino alcohol (KABI2128) in serum after trifluoroacetylation. *J. High Resolut. Chromatogr. Chromatogr. Commun.* **5**: 596-603 (1982).
- G. Schomburg, F. Weeke, F. Muller, and M. Oréans. Multi-dimensional gas chromatography (MDC) in capillary columns using double oven instruments and a newly designed coupling piece for monitoring detection after pre-separation. *Chromatographia* **16**: 87-91 (1982).
- W. Chinghai, H. Frank, W. Guanghua, Z. Liangmo, E. Bayer, and L. Peichang. Determination of amino acid enantiomers by two-column gas chromatography with valveless column switching. *J. Chromatogr.* **262**: 352-59 (1983).
- G. Schomburg, H. Husmann, E. Hubinger, and W.A. König. Multidimensional capillary gas chromatography - Enantiomeric separations of selected cuts using a chiral second column. *J. High Resolut. Chromatogr.* **7**: 404-10 (1984).
- P.A. Rodriguez and C.L. Eddy. Use of a two-dimensional gas chromatograph in the organoleptic evaluation of an orange extract. *J. Chromatogr. Sci.* **24**: 18-21 (1986).
- A. Bernreuther, N. Christoph, and P. Schreier. Determination of the enantiomeric composition of  $\gamma$ -lactones in complex natural matrices using multidimensional capillary gas chromatography. *J. Chromatogr.* **481**: 363-67 (1989).
- A. Mosandl, U. Hener, U. Hagenauer-Hener, and A. Kustermann. Direct enantiomer separation of chiral  $\gamma$ -lactones from food and beverages by multidimensional gas chromatography. *J. High Resolut. Chromatogr.* **12**: 532-36 (1989).
- J.C. Duinker, D.E. Schulz, and G. Petrick. Selection of chlorinated

- biphenyl congeners for analysis in environmental samples. *Mar. Poll. Bull.* **19**: 19–25 (1988).
29. F.R. Guenther, S.N. Chesier, and R.E. Rebbert. The analysis of polychlorinated biphenyls by multidimensional gas chromatography. *J. High Resolut. Chromatogr.* **12**: 821–24 (1989).
  30. S. Nitz, H. Kollmannsberger, and F. Drawert. Determination of sensorial active trace compounds by multi-dimensional gas chromatography combined with different enrichment techniques. *J. Chromatogr.* **471**: 173–85 (1989).
  31. D.E. Schulz, G. Petrick, and J.C. Duinker. Complete characterization of polychlorinated biphenyl congeners in commercial Aroclor and Clophen mixtures by multidimensional gas chromatography - electron capture detection. *Environ. Sci. Technol.* **17**: 852–59 (1989).
  32. A. Mosandl, A. Kustermann, U. Hener, and U. Hagenauer-Hener. Analytische differenzierung natürlicher und naturidentischer  $\gamma$ -lactone in lebensmitteln. *Dtsch. Lebensm.-Rundsch.* **85**: 205–209 (1989).
  33. A. Mosandl, G. Bruche, C. Askari, and H.-G. Schmarr. Stereoisomeric flavor compounds XLIV: Enantioselective analysis of some important flavor molecules. *J. High Resolut. Chromatogr.* **13**: 660–62 (1990).
  34. E. Guichard, A. Kustermann, and A. Mosandl. Distribution of  $\gamma$ -lactone enantiomers and stereodifferentiation of dihydroactinidiolide using multi-dimensional gas chromatography. *J. Chromatogr.* **498**: 396–401 (1990).
  35. A. Bernreuther, V. Lander, M. Huffer, and P. Schreier. Enantioselective analysis of dec-2-en-5-olide (Massoialactone) from natural sources by multidimensional capillary gas chromatography. *Flav. Fragr. J.* **5**: 71–73 (1990).
  36. A. Mosandl, U. Hener, U. Hagenauer-Hener, and A. Kustermann. Stereoisomeric flavor compounds. 33. Multidimensional gas chromatography direct enantiomer separation of  $\gamma$ -lactones from fruits, foods, and beverages. *J. Agric. Food Chem.* **38**: 767–71 (1990).
  37. U. Hener, P. Kreis, and A. Mosandl. Enantiomeric distribution of  $\alpha$ -pinene,  $\beta$ -pinene and limonene in essential oils and extracts. Part 2. Oils, perfumes and cosmetics. *Flavour Fragr. J.* **5**: 201–204 (1990).
  38. A. Mosandl, U. Hener, P. Kreis, and H.-G. Schmarr. Enantiomeric distribution of  $\alpha$ -pinene,  $\beta$ -pinene and limonene in essential oils and extracts. Part 1. Rutaceae and Gramineae. *Flavour Fragr. J.* **5**: 193–99 (1990).
  39. U. Hener, A. Hollnagel, P. Kreis, B. Maas, H.-G. Schmarr, V. Schubert, K. Rettinger, B. Weber, and A. Mosandl. Direct enantiomer separation of chiral volatiles from complex matrices by multidimensional gas chromatography. *Flavour Sci. Technol., Weurman Symp.*, 6th 25–28 (1990).
  40. L.L. Lamparski, T.J. Nestrick, D. Janson, and G. Wilson. Development of an HRGC–HRGC–IRMS system: Instrument design and performance data. *Chemosphere* **20**: 635–45 (1990).
  41. M. Herraiz, G. Reglero, T. Herraiz, and E. Loyola. Analysis of wine distillates made from muscat grapes (Pisco) by multidimensional gas chromatography and mass spectrometry. *J. Agric. Food Chem.* **38**: 1540–43 (1990).
  42. A. Mosandl and V. Schubert. Stereoisomeric flavor compounds XXXVII: Enantiomer separation of 1-alken-3-yl esters and their chirality evaluation from essential oil using multidimensional gas chromatography (MDGC). *J. Essent. Oil Res.* **2**: 121–32 (1990).
  43. A. Mosandl, K. Fischer, U. Hener, P. Kreis, K. Rettinger, V. Schubert, and H.-G. Schmarr. Stereoisomeric flavor compounds. 48. Chirospecific analysis of natural flavors and essential oils using multidimensional gas chromatography. *J. Agric. Food Chem.* **39**: 1131–34 (1991).
  44. U. Hener, P. Kreis, and A. Mosandl. Enantiomeric distribution of  $\alpha$ -pinene,  $\beta$ -pinene and limonene in essential oils and extracts. Part 3. Oils for alcoholic beverages and seasonings. *Flavour Fragr. J.* **6**: 109–11 (1991).
  45. V. Karl, H.-G. Schmarr, and A. Mosandl. Simultaneous stereoanalysis of 2-alkyl-branched acids, esters and alcohols using a selectivity-adjusted column system in multi-dimensional gas chromatography. *J. Chromatogr.* **587**: 347–50 (1991).
  46. S. Nitz, H. Kollmannberger, B. Weinreich, and F. Drawert. Enantiomeric distribution and  $^{13}\text{C}/^{12}\text{C}$  isotope ratio determination of  $\gamma$ -lactones: Appropriate methods for the differentiation between natural and non-natural flavours? *J. Chromatogr.* **557**: 187–97 (1991).
  47. H.-U. Humpf and P. Schreier. Bound aroma compounds from the fruit and the leaves of blackberry (*Rubus laciniata* L.). *J. Agric. Food Chem.* **39**: 1830–32 (1991).
  48. A. Bernreuther, J. Bank, G. Krammer, and P. Schreier. Multidimensional gas chromatography/mass spectrometry: A powerful tool for the direct chiral evaluation of aroma compounds in plant tissues. I. 5-Alkanolides in fruits. *Phytochem. Anal.* **2**: 43–47 (1991).
  49. A. Bernreuther and P. Schreier. Multidimensional gas chromatography/mass spectrometry: A powerful tool for the direct chiral evaluation of aroma compounds in plant tissues. II. Linalool in essential oils and fruits. *Phytochem. Anal.* **2**: 167–70 (1991).
  50. K. Rettinger, V. Karl, H.-G. Schmarr, F. Dettmar, U. Hener, and A. Mosandl. Chirospecific analysis of 2-alkyl-branched alcohols, acids, and esters: Chirality evaluation of 2-methylbutanoates from apples and pineapples. *Phytochem. Anal.* **2**: 184–88 (1991).
  51. V. Schubert and A. Mosandl. Chiral compounds of essential oils. VIII: Stereodifferentiation of linalool using multidimensional gas chromatography. *Phytochem. Anal.* **2**: 171–74 (1991).
  52. D. Lehmann, C. Askari, D. Henn, F. Dettmar, U. Hener, and A. Mosandl. Simultane stereodifferenzierung chiraler  $\gamma$ - und  $\delta$ -lactone. *Dtsch. Lebensm.-Rundsch.* **87**: 75–77 (1991).
  53. V. Schubert, R. Diener, and A. Mosandl. Enantioselective multidimensional gas chromatography of some secondary alcohols and their acetates from banana. *Z. Naturforsch.* **46**: 33–36 (1991).
  54. J. de Boer and Q.T. Dao. Analysis of 7 chlorobiphenyl congeners by multidimensional gas chromatography. *Proceedings of the 13th International Symposium on Capillary Chromatography*, Riva del Garda, 1983, pp. 1367–76.
  55. C. Askari, U. Hener, H.-G. Schmarr, A. Rapp, and A. Mosandl. Stereodifferentiation of some chiral monoterpenes using multidimensional gas chromatography. *Fresenius J. Anal. Chem.* **340**: 768–72 (1991).
  56. N. Kannan, G. Petrick, D. Schulz, J. Duinker, J. Boon, E. van Amhem, and S. Jansen. A comparison between activated charcoals and multidimensional GC in the separation and determination of (non-ortho Cl substituted) toxic chlorobiphenyls. *Chemosphere* **23**: 1055–76 (1991).
  57. P. Kreis and A. Mosandl. Chiral compounds of essential oils. Part XIII. Simultaneous chirality evaluation of geranium oil constituents. *Flavour Fragr. J.* **8**: 161–68 (1993).
  58. W.A. König, B. Gehrcke, D. Icheln, P. Evers, J. Donneck, and W. Wang. New selectively substituted cyclodextrins as stationary phases for the analysis of chiral constituents of essential oils. *J. High Resolut. Chromatogr.* **15**: 367–72 (1992).
  59. P. Kreis and A. Mosandl. Chiral compounds of essential oils. Part XI. Simultaneous stereoanalysis of *Lavandula* oil constituents. *Flavour Fragr. J.* **7**: 187–93 (1992).
  60. P. Kreis and A. Mosandl. Chiral compounds of essential oils. Part XII. Authenticity control of rose oils, using enantioselective multidimensional gas chromatography. *Flavour Fragr. J.* **7**: 199–203 (1992).
  61. A. Mosandl, C. Askari, U. Hener, D. Juchelka, D. Lehmann, P. Kreis, C. Motz, U. Palm, and H.-G. Schmarr. Chirality evaluation in flavour and essential oil analysis. *Chirality* **4**: 50–55 (1992).
  62. V. Karl, K. Schumacher, and A. Mosandl. Enantiomeric 2-methylbutanoates: Sensory evaluation and chirospecific analysis. *Flavour Fragr. J.* **7**: 283–88 (1992).
  63. G. Schmidt, G. Full, P. Winterhalter, and P. Schreier. Synthesis and enantiodifferentiation of isomeric thespiranes. *J. Agric. Food Chem.* **40**: 1188–91 (1992).
  64. S. Nitz, B. Weinreich, and F. Drawert. Multidimensional Gas Chromatography - Isotope Ratio Mass Spectrometry (MDGC–IRMS). Part A: System description and technical requirements. *J. High Resolut. Chromatogr.* **15**: 387–91 (1992).



65. N. Kannan, D.E. Schulz-Bull, G. Petrick, and J.C. Duinker. High resolution PCB analysis of Kanechlor, Phenochlor and Sovol mixtures using multidimensional gas chromatography. *Intern. J. Environ. Anal. Chem.* **47**: 201–15 (1992).
66. J.C. Duinker, D.E. Schulz, and G. Petrick. Multidimensional gas chromatography with electron capture detection for the determination of toxic congeners in polychlorinated biphenyl mixtures. *Anal. Chem.* **60**: 478–82 (1988).
67. A. Mosandl. Echtheitskontrolle natürlicher Duft- und Aromastoffe. *Kontakte* **3**: 38–49 (1992).
68. M. Suárez, C. Duque, C. Bicchì, H. Wintoch, G. Full, and P. Schreier. Volatile constituents from the peelings of lulo (*Solanum vestissimum* D.) fruit. *Flavour Fragr. J.* **8**: 215–20 (1993).
69. G. Full, P. Winterhalter, G. Schmidt, P. Herion, and P. Schreier. MDGC-MS: A powerful tool for enantioselective flavor analysis. *J. High Resolut. Chromatogr.* **16**: 642–44 (1993).
70. K. Himberg, E. Sippola, F. David, and P. Sandra. Real-time control of column switching in multidimensional gas-chromatography. *J. High Resolut. Chromatogr.* **16**: 645–50 (1993).
71. P. Kreis and A. Mosandl. Chiral compounds of essential oils. Part XIII. Simultaneous chirality evaluation of geranium oil constituents. *Flavour Fragr. J.* **8**: 161–68 (1993).
72. G. Full, P. Winterhalter, G. Schmidt, P. Herion, and P. Schreier. MDGC-MS. A powerful tool for chiro-specific analysis in flavour chemistry. *Fifteenth International Symposium on Capillary Chromatography*, Riva del Garda, 1993, p. 822.
73. A. Steinborn, W. Engewald, and R. Reinhardt. The simultaneous use of different separation modes in multidimensional capillary gas chromatography. *Proceedings of the 13th International Symposium on Capillary Chromatography*, Riva del Garda, 1993, pp. 892–98.
74. P. Kreis and A. Mosandl. Chiral compounds of essential oils. Part XVII. Simultaneous stereoanalysis of Cymbopogon oil constituents. *Flavour Fragr. J.* **9**: 257–60 (1994).
75. P. Kreis and A. Mosandl. Chiral compounds of essential oils. Part XVI. Enantioselective multidimensional gas chromatography in authenticity control of Balm oil (*Melissa officinalis* L.). *Flavour Fragr. J.* **9**: 249–56 (1994).
76. B. Faber, A. Dietrich, and A. Mosandl. Chiral compounds of essential oils. XV. Stereodifferentiation of characteristic compounds of *Mentha* species by multi-dimensional gas chromatography. *J. Chromatogr. A* **666**: 161–65 (1994).
77. T. Kopke, A. Dietrich, and A. Mosandl. Chiral compounds of essential oils. XIV. Simultaneous stereoanalysis of Buchu leaf oil compounds. *Phytochem. Anal.* **5**: 61–67 (1994).
78. V. Karl, J. Gutser, A. Dietrich, B. Maas, and A. Mosandl. Stereoisomeric flavour compounds LXVIII. 2-, 3-, and 4-alkyl-branched acids, part 2: Chiro-specific analysis and sensory evaluation. *Chirality* **6**: 427–34 (1994).
79. A. Glausch, G. J. Nicholson, M. Fluck, and V. Schurig. Separation of the enantiomers of stable atropisomeric polychlorinated biphenyls (PCBs) by multidimensional gas chromatography on Chirasil-Dex. *J. High Resolut. Chromatogr.* **17**: 347–49 (1994).
80. A. Jayatilaka and C.F. Poole. Identification of petroleum distillates from fire debris using multidimensional gas chromatography. *Chromatographia* **39**: 200–209 (1994).
81. I.H. Hardt, A. Rieck, C. Fricke, and W. A. König. Enantiomeric composition of sesquiterpene hydrocarbons of the essential oil of *Cedrela odorata* L. *Flavour Fragr. J.* **10**: 165–71 (1995).
82. A. Mosandl. Enantioselective capillary gas chromatography and stable isotope ratio mass spectrometry in the authenticity control of flavours and essential oils. *Food Rev. Int.* **11**: 597–664 (1995).
83. B. Maas, A. Dietrich, D. Bartschat, and A. Mosandl. tert-Butyldimethylsilylated cyclodextrins: Versatile chiral stationary phases in capillary gas chromatography. *J. Chromatogr. Sci.* **33**: 223–28 (1995).
84. D. Bartschat, D. Lehmann, A. Dietrich, A. Mosandl, and R. Kaiser. Chiral compounds of essential oils XIX. 4-Methyl-5-decanolide: chiro-specific analysis, structure and properties of the stereoisomers. *Phytochem. Anal.* **6**: 130–34 (1995).
85. X. Wang, C. Jia, and H. Wan. The direct chiral separation of some optically active compounds in essential oils by multidimensional gas chromatography. *J. Chromatogr. Sci.* **33**: 22–25 (1995).
86. A. Kauzinger, F. Podebrad, R. Liske, B. Maas, A. Dietrich, and A. Mosandl. Stereochemical differentiation and simultaneous analysis of 3-, 4-, and 5-hydroxyalkanoic acids from biopolyesters by multidimensional gas chromatography. *J. High Resolut. Chromatogr.* **18**: 49–53 (1995).
87. E.A. Guichard. Determination of chiral lactones of wine and microbiological substrates by multidimensional gas chromatography. *Lab. 2000* **7**: 46–50 (1995).
88. J. de Boer, Q.T. Dao, P.G. Wester, S. Bowadt, and U.A.Th. Brinkman. Determination of mono-ortho substituted chlorobiphenyls by multidimensional gas chromatography and their contribution to TCDD equivalents. *Anal. Chim. Acta* **300**: 155–65 (1995).
89. B.M. Gordon, C.E. Rix, and M.F. Borgerding. Comparison of state-of-the-art column switching techniques in high resolution gas chromatography. *J. Chromatogr. Sci.* **23**: 1–10 (1985).
90. D.W. Wright, K.O. Mahler, and L.B. Ballard. The application of an expanded multidimensional GC system to complex fragrance evaluations. *J. Chromatogr. Sci.* **24**: 60–65 (1986).
91. D.W. Wright, K.O. Mahler, L.B. Ballard, and E. Dawes. The application of multidimensional techniques to the rapid pyrolysis-GC profiling of synthetic polymers. *J. Chromatogr. Sci.* **24**: 13–17 (1986).
92. E.L. Colling, B.H. Burda, and P.A. Kelley. Multidimensional pyrolysis-gas chromatography: Applications in petroleum geochemistry. *J. Chromatogr. Sci.* **24**: 7–12 (1986).
93. S.M. Sonchik. The analysis of PCBs in methylene chloride using column switching. *J. Chromatogr. Sci.* **24**: 22–25 (1986).
94. V.G. van Hese and D. Grant. Automatic multidimensional capillary GC. On-line pre-separation and sample pretreatment. *American Laboratory* **20**: 26–33 (1988).
95. C. Bicchì, A. D'Amato, C. Frattini, G.M. Nano, and A. Pisciotta. Some applications of multidimensional gas chromatography to the enrichment of minor components in essential oil analysis. *J. High Resolut. Chromatogr.* **12**: 705–708 (1989).
96. C. Bicchì and A. Pisciotta. Use of two-dimensional gas chromatography in the direct enantiomer separation of chiral essential oil components. *J. Chromatogr.* **508**: 341–48 (1990).
97. G. Johnson, C. Marmonier, and G. Garrabé. Introduction aux techniques multidimensionnelles pour la chromatographie en phase gazeuse. *Spectra 2000* **135**: 23–35 (1988).
98. A. Hoffmann, R. Bremer, and J.A. Rijks. Application of multi column switching capillary GC-MS in identification of trace impurities in industrial products. *Proceedings of the 15th International Symposium on Capillary Chromatography*, Riva del Garda, 1993, pp. 830–36.
99. W. Jennings. State-of-the-art gas chromatography: Instrumental design. *J. Chromatogr. Sci.* **22**: 129–35 (1984).
100. J.F. Elder, Jr., B.M. Gordon, and M.S. Uhrig. Complex mixture analysis by capillary-to-capillary column heartcutting GC/MS. *J. Chromatogr. Sci.* **24**: 26–33 (1986).
101. O. Gyllenhaal, B. Lamm, and J. Vessman. Enantiomer separation of tocinide and some of its analogues and derivatives on a chirasil-val capillary column. *J. Chromatogr.* **411**: 285–95 (1987).
102. K.A. Krock, N. Ragunathan, and C.L. Wilkins. Parallel cryogenic trapping multidimensional gas chromatography with directly linked infrared and mass spectral detection. *J. Chromatogr.* **645**: 153–59 (1993).
103. N. Ragunathan, T.A. Sasaki, K.A. Krock, and C.L. Wilkins. Multidimensional fast gas chromatography with matrix isolation infrared detection. *Anal. Chem.* **66**: 3751–56 (1994).