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

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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 (precolumn) 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.

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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-µm 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 (A3RADC6WT) (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.

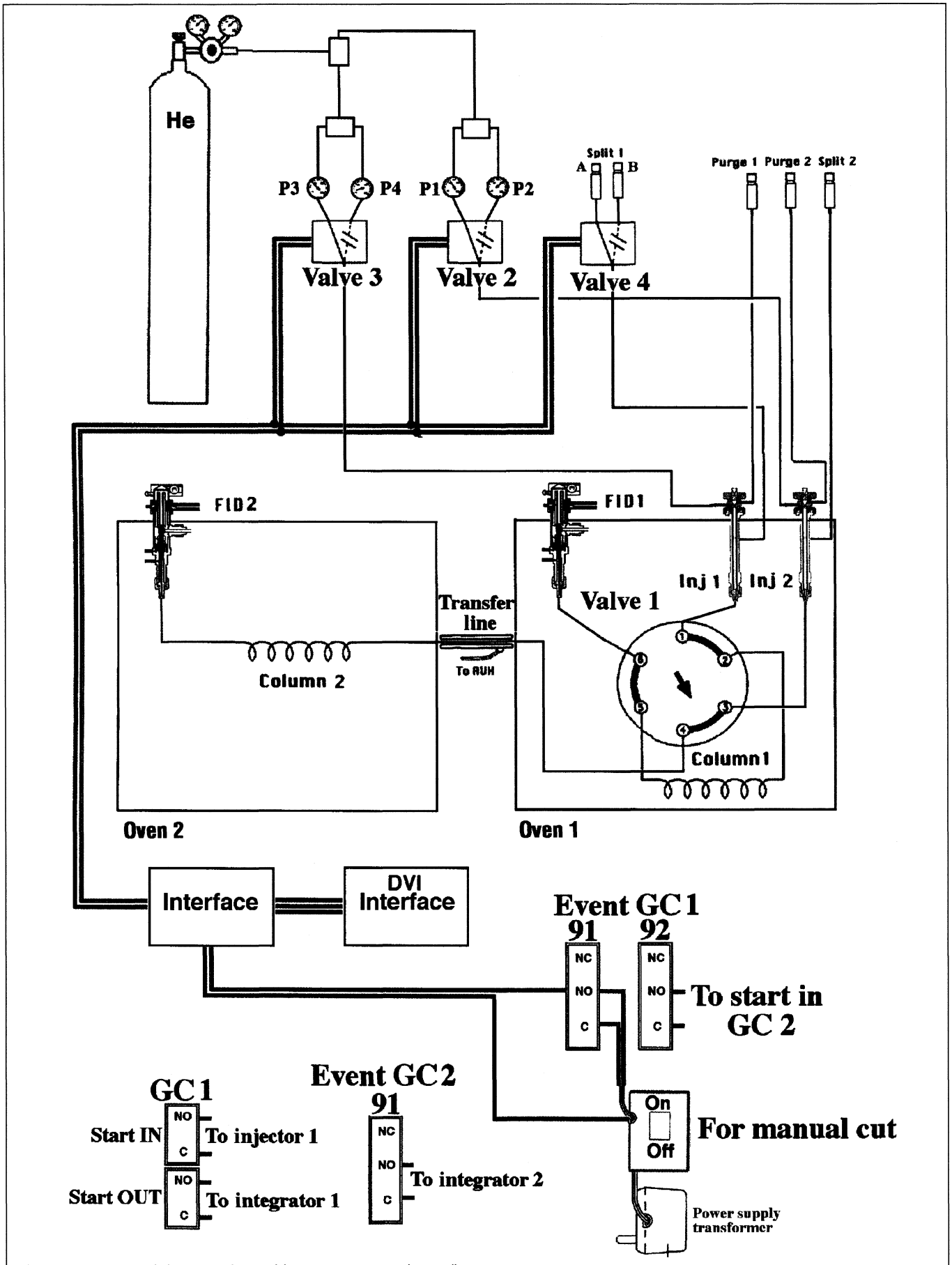

Figure 1. Pneumatic and electronic scheme of the GC–GC system in the standby position.

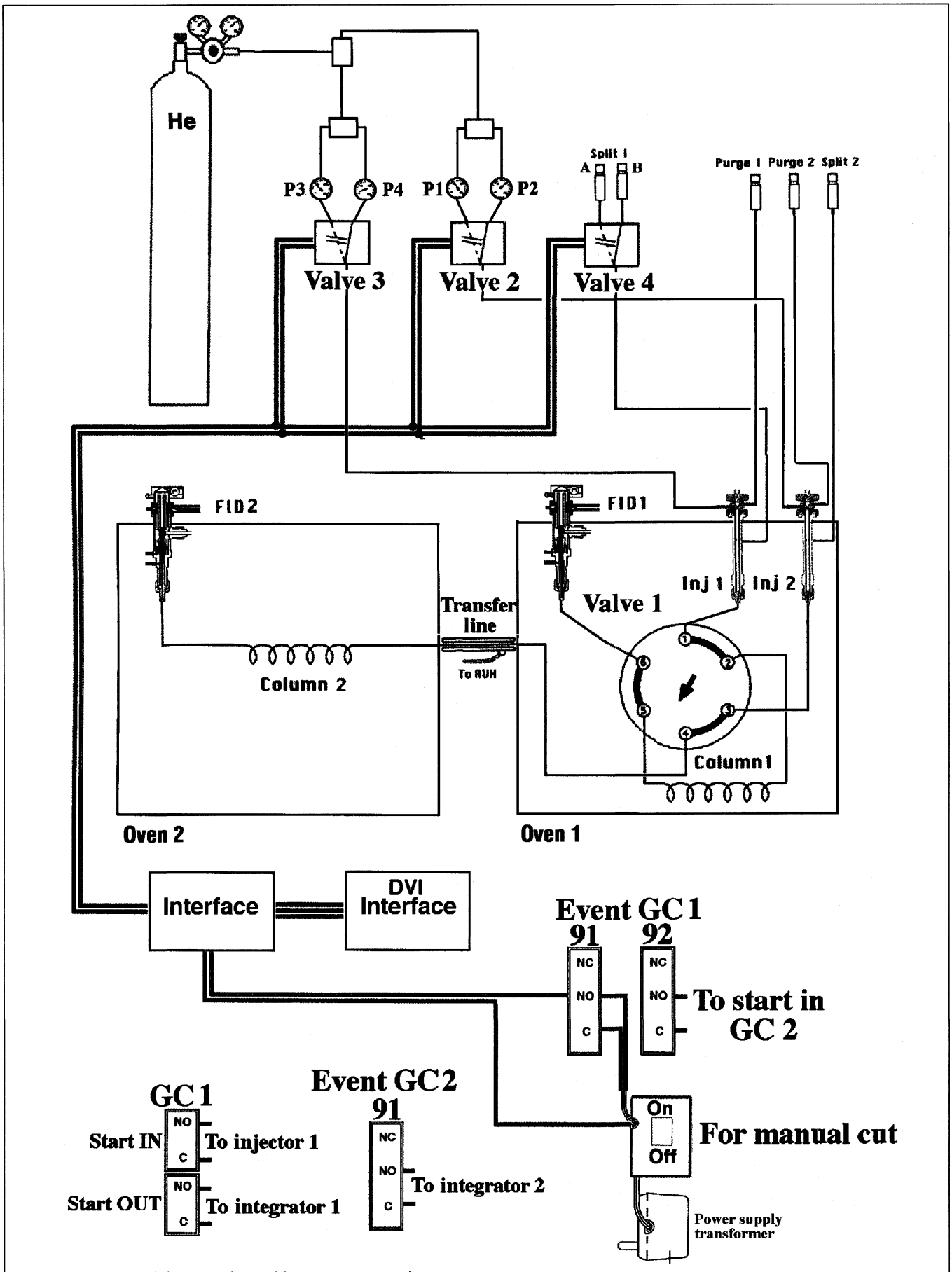

Figure 2. Pneumatic and electronic scheme of the GC–GC system in the cut position.

GC 2

A MEGADEXDETTBSβ (diethyltert-butylsilyl-β-cyclodextrin) column (25 m × 0.25-mm i.d., 0.25-µm 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.

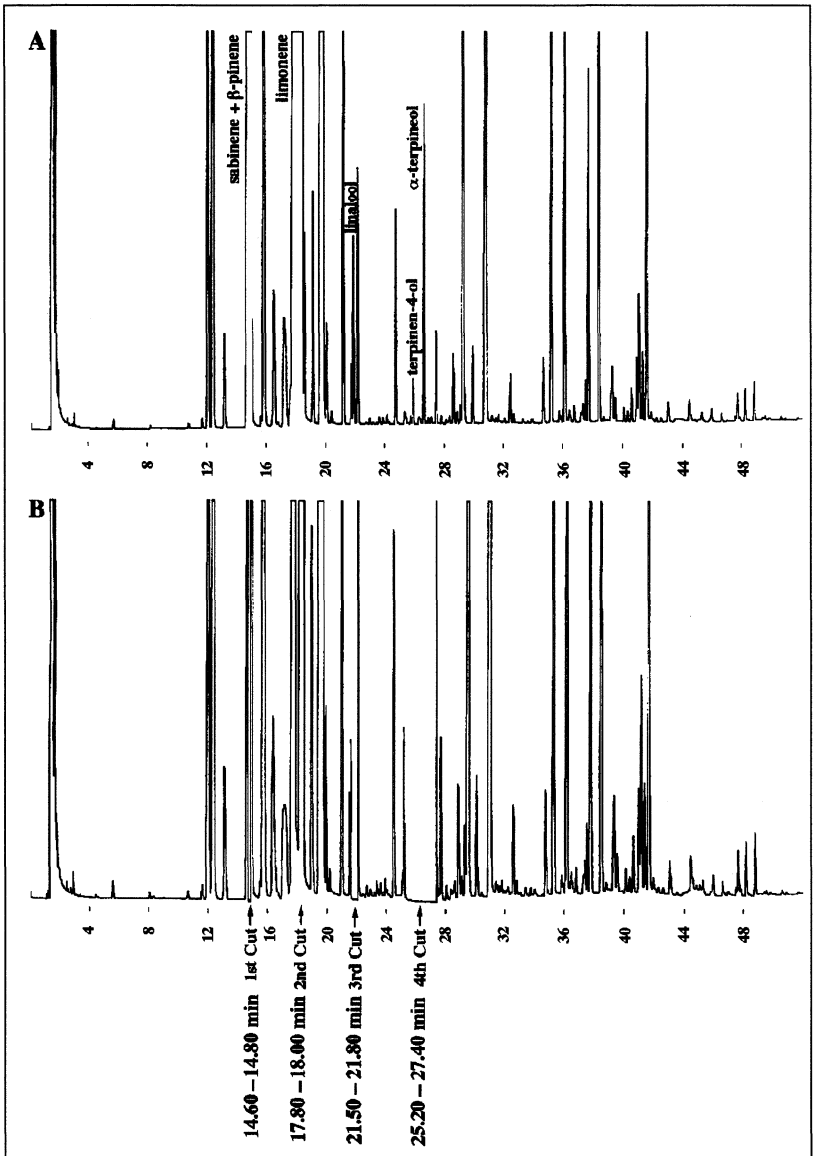

Figure 3. (A) GC–FID chromatogram of a lemon essential oil. (B) GC–FID chromatogram of a lemon essential oil with four heart cuts.

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*
β-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†
α-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 kP_a) to pressure P4 (2.5 kP_a) 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 operated 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 precolumn 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 β-pinene, sabinene, limonene, terpinen-4-ol and α-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 precolumn, it was possible to program the transfer windows for each fraction.

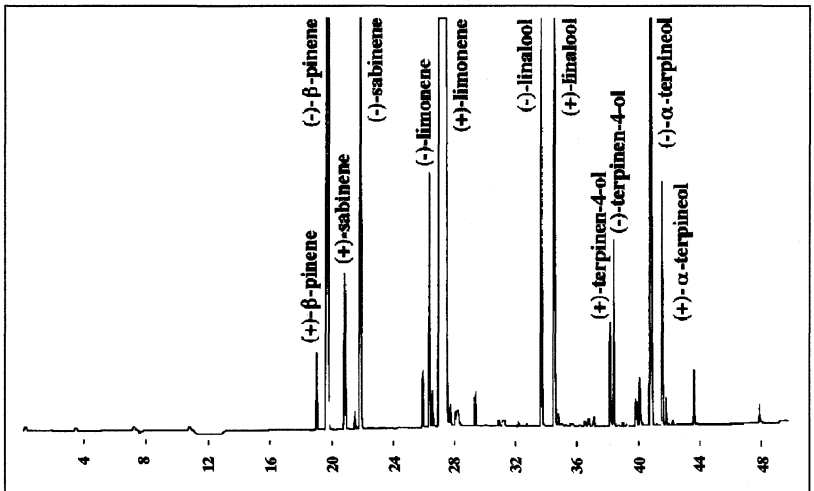

Figure 4. GC–FID chiral chromatogram of some components of lemon essential oil.

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

β-Pinene (+)/(–)	Sabinene (+)/(–)	Limonene (–)/(+)	Linalool (–)/(+)	Terpinen-4-ol (+)/(–)	α-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

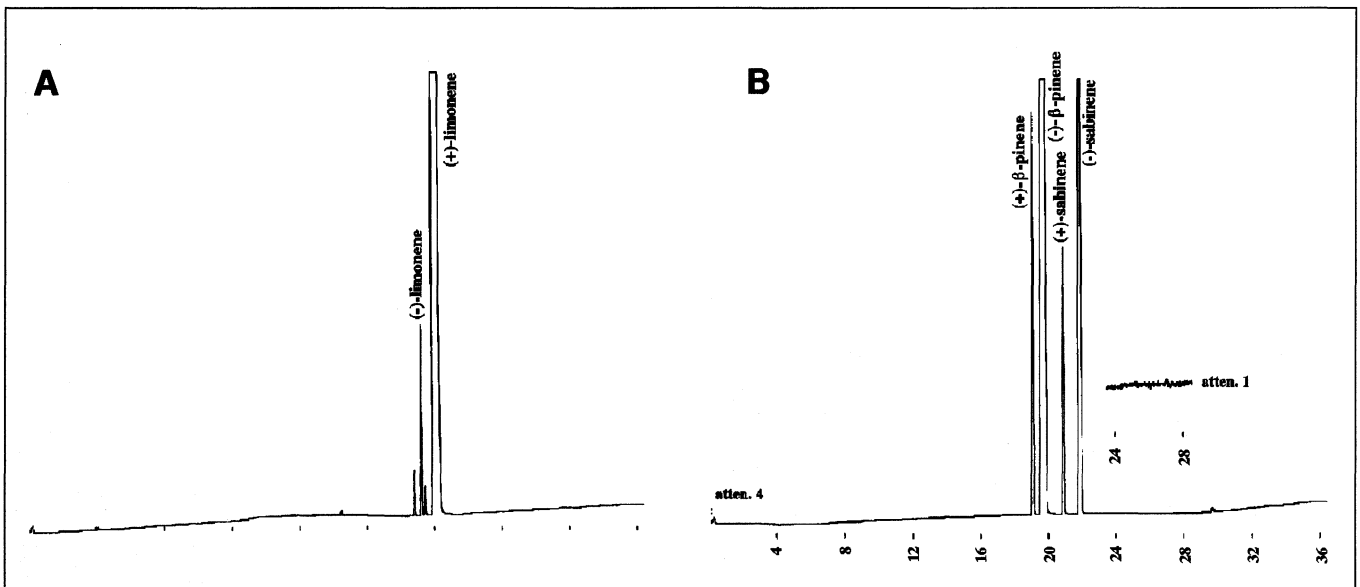

Figure 5. (A) GC–FID chiral chromatogram of a heart cut of limonene in lemon essential oil. (B) GC–FID chiral chromatogram of a heart cut of β-pinene–sabinene in lemon essential oil obtained immediately after that of limonene.

As shown in Figure 3 and Table I, sabinene–β-pinene and limonene were partially transferred, whereas terpinen-4-ol and α-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–β-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.

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