Journal of Chromatography, 148 (1978) 321–334

CHROM. 10,433

SIMPLE TECHNIQUES FOR TWO-DIMENSIONAL GAS CHROMATOGRAPHY

A. DUCASS, M.-F. GONNORD, P. ARPINO and G. GUIOCHON*

Laboratoire de Chimie Analytique Physique, Ecole polytechnique, Route de Saclay, 91128-Palaiseau Cedex (France)

(Received June 15th, 1977)

SUMMARY

The adaptation of the Deans system of double-column gas chromatography for use with a commercial chromatograph is described. Optimization of the carrier gas flow-rates through the two columns is achieved independently in each column. The importance of using an intermediate trap between the two columns is demonstrated. A system for automatic rejection of the major components of the analyzed mixture is described. Quantitative analysis of trace impurities has been performed using a suitable calibration.

INTRODUCTION

The use of glass capillary columns in chromatographic analysis is becoming more and more popular[1]. Yet most commercial gas chromatographs still require some change of the connections and the plumbing to fit such columns. As we shall show, it is not much more difficult to construct a complete system of valveless double column chromatography than a single split system. The in-series double column system is much more powerful and versatile. It allows the use of either classical or capillary columns with either single or double column chromatography. In each case, the different flow-rates through each column can be optimized independently which permits the achievement of difficult analyses. Once modified as described below, a conventional gas chromatograph can perform as well as very sophisticated multidimensional gas chromatographs[2–4], especially in the field of trace analysis, solvent removal or analysis of unresolved bands of compounds. We also describe a few applications of the two-column gas chromatograph to difficult analytical problems.

* To whom correspondence should be addressed.

EXPERIMENTAL

Description of the system

The valveless switching technique described by Deans[5] was selected. This technique offers the great advantage of removing all of the switching valves from the chromatographic gas flow so that they do not contribute to band broadening or tailing, and is now used on many multidimensional gas chromatographs[1–4]. Our system has been adapted for use with a Hewlett-Packard 5830 gas chromatograph (Hewlett-Packard, Avondale, Pa., U.S.A.). It could have been adapted for use with any dual-channel pressure-regulated gas chromatograph.

The flow connections are shown in Fig. 1, while Fig. 2 is a photograph of the actual equipment. The essential part of the system consists of a single short capillary jine 1 (C-D-E) which connects the inlet of the flame ionization detector FID A to the inlection port INJ B of the second column, and to the pressure manifold around the cross-connection (E). To E are connected a manometer (2) and two vent lines, one having a needle-valve (3) the other an electrovalve (4) and a needle-valve (5). In addition, very thin capillary tubing (F) of high pneumatic resistance separates the cross-connection D from the FID A. The gas which exits from column A is split into three streams whose flow-rates depend on the pneumatic resistance of the corresponding lines: one to the FID A, one to column B and one to the vent. The easy equilibration of these flow-rates permits the achievement of various types of analyses.

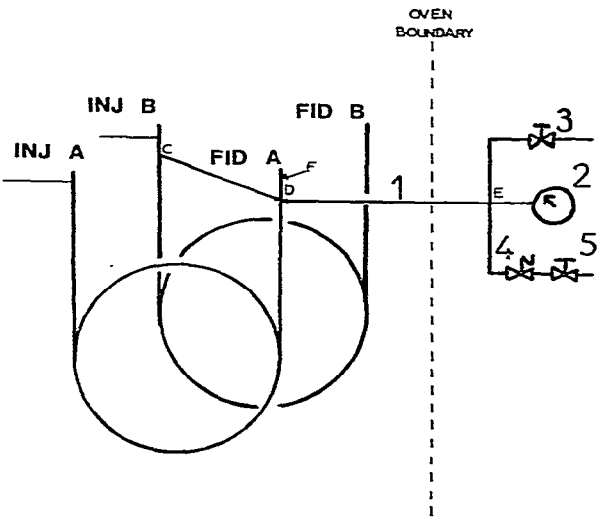

Fig. 1. Scheme of a double-column gas chromatograph: 1 = capillary line; 2 = manometer; 3 = needle-valve; 4 = electro-valve; 5 = needle-valve; C = T-connection; D and E = cross-connections; F = thin capillary restrictor.

Optimization of the carrier gas flow-rates

During the adjustment of the various valves, as described below, the flow-rates at injection ports A and B are read directly on the flow meters of the chromatograph. The use of digital mass-flow meters simplifies the adjustment of the flows. The flow-

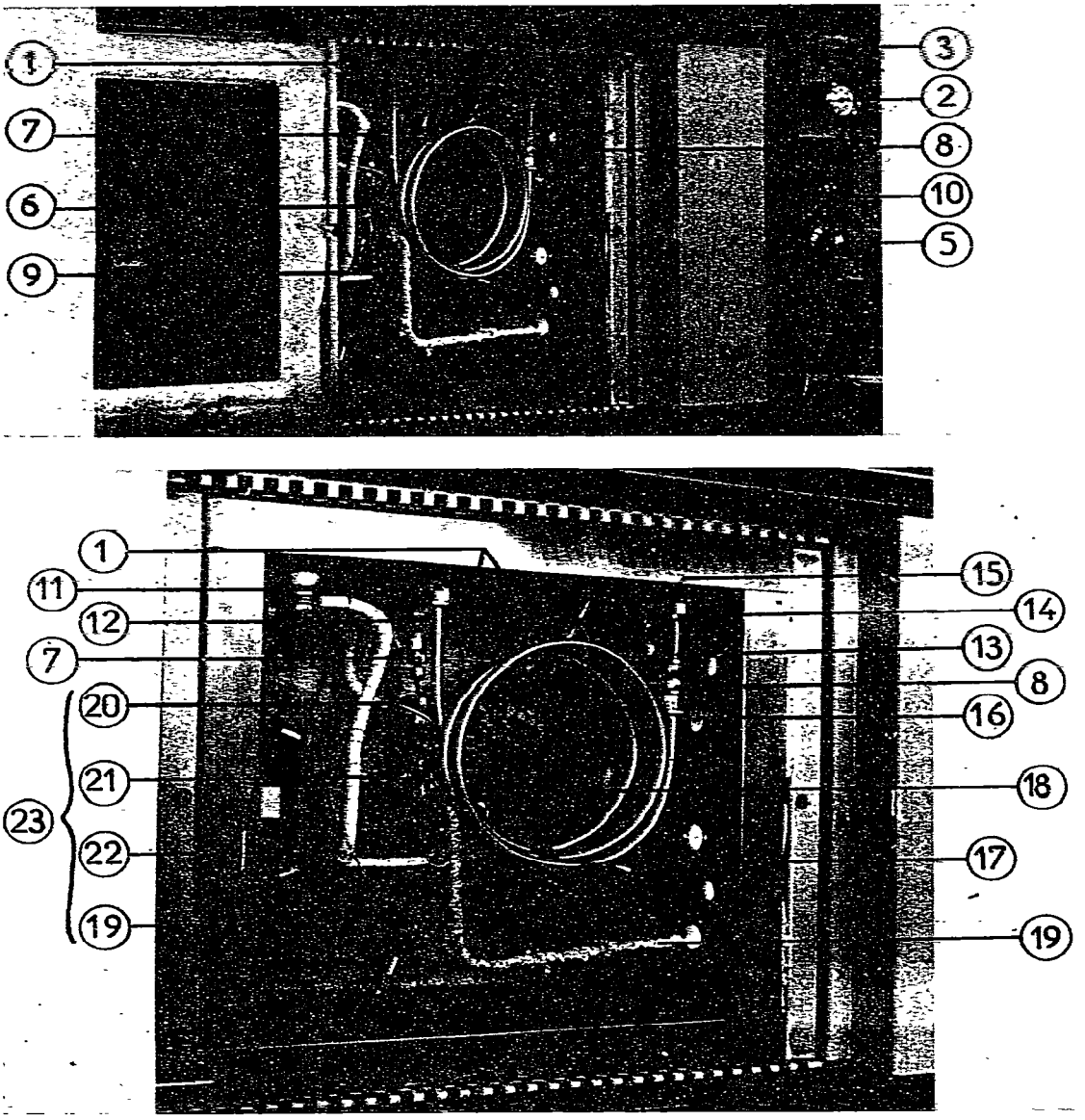

Fig. 2. Photograph of the double-column gas chromatograph. 1 = capillary line; 2 = manometer; 3 = needle-valve (split); 4 = electrovalve (not shown); 5 = needle-valve (vent); 6 = mantle tube; 7 = T-connection C: 8 = cross-connection D; 9 = beginning of column B (for details see Fig. 4); 10 = electronic command for automatic rejection of the major peaks; 11 = outlet of injection port A; 12 = outlet of injection port B; 13 = thin capillary restrictor F; 14 = inlet of FID A; 15 = inlet of FID B; 16 = capillary line leading toward the outside of the oven and cross-connection E (not shown); 17 = column A; 18 = column B; 19 = inlet of cold CO_2; 20 = outlet of cold CO_2; 21 = thermocouple to measure the temperature of the trap; 22 = power supply line; 23 = cold trap.

rates at the outlets of the FID burners A and B and at outlets of valves 3 and 5 are measured with a soap-bubble flow meter when required.

Normal use with two columns in series (see Fig. 1). Initially, there is no gas flow in either channels A or B. The pressure in injection port B is increased until the outlet rate of column B reaches the required optimum value. Some gas leaks from injection port B into the FID A, and manometer 2 reads a pressure intermediate between atmospheric pressure and the pressure in port B, because of the pressure drops in the tubing CD and F. The pressure in injection port A is then increased progressively until the manometer 2 reads a pressure equal to that in injection port B.

Thus, all the carrier gas which flows through the column B comes from the injection port A and through the precolumn A. No carrier gas coming from the pressure controller B enters injection port B since the pressure is equal at both ends of injection port B. The gas flowing out of column A is split between the FID A and column B. The ratio of the flow-rates to the FID A and column B is determined by the pneumatic resistance of the thin capillary restrictor (F) and of column B.

Split use with two columns in series (see Figs. 1 and 3a). In the case when A is a classical column and B a capillary column, the optimum flow-rate through A is much larger than through B. A split at D is required. The opening of valve 3 results in a decrease in pressure in C and D which is read on manometer 2. The original pressure at C and D is restored by increasing the pressure in injection port A. Valve 3 then acts as a split at the end of column A. The splitting ratio can be adjusted in order to obtain the optimum flow-rate through column A without any change of the flow-rate through column B which has been set first.

Use of a split with a single capillary column. When wording with a single capillary column (column B), the flow system is very similar to the one described above. The pressure in C and D, read at manometer 2, is set just below the pressure at injection port B, so that some carrier gas flows through both the column and the vent line. A mixture injected into injection port B will be split between valve 2 (venting) and column B, through which it is eluted. The splitting ratio can be adjusted to the required value as before. In this case the actual flow-rate through column A is not crucial. It is also possible to remove column A if the free end of cross-connection D is closed.

Rejection of unwanted products (see Figs. 1 and 3b). Opening of the electrovalve 4 results in a decrease in the pressure at D and C, the magnitude of which depends on the pneumatic resistance of the needle-valve 5 as compared to that of valve 3. Needle-valve 5 is set so that the flow through the corresponding line is larger than the flow through column A. Opening or closing of the electrovalve 4 results in a reversal of the flow in the C–D portion of the capillary tube. Thus electrovalve 4 commands the rejection and vent of the products eluted from column A.

System of intermediate trapping (see Fig. 4)

The device for intermediate trapping consists of a trap set into the circuit between the inlet of column B and the T connection C (Fig. 1). The trap used was GLT tubing (50 mm × 0.7 mm I.D.) (Scientific Glass, North Melbourne, Australia) filled with graphitized Sterling FTG carbon black. Cooling to 40° is achieved by circulating cold CO_2 in a tube (5 in Fig. 4) surrounding the trap. Heating to $> 400°$ is achieved in a few seconds by the Joule effect in the GLT itself by use of a large electrical current.

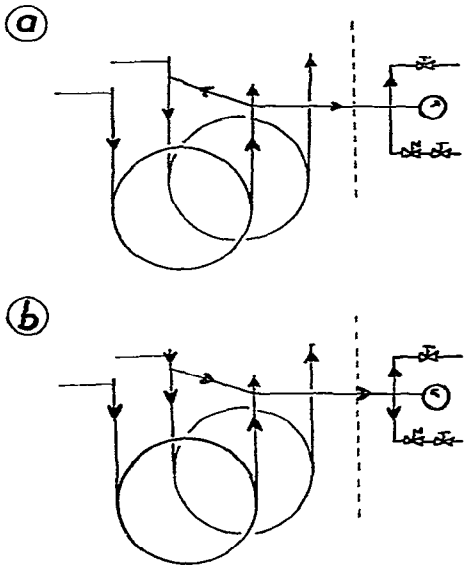

Fig. 3. Flow diagram of the double column gas chromatograph: (a) flow pattern during transfer from column A to column B with split and vent; (b) flow pattern during rejection of the eluent from column A.

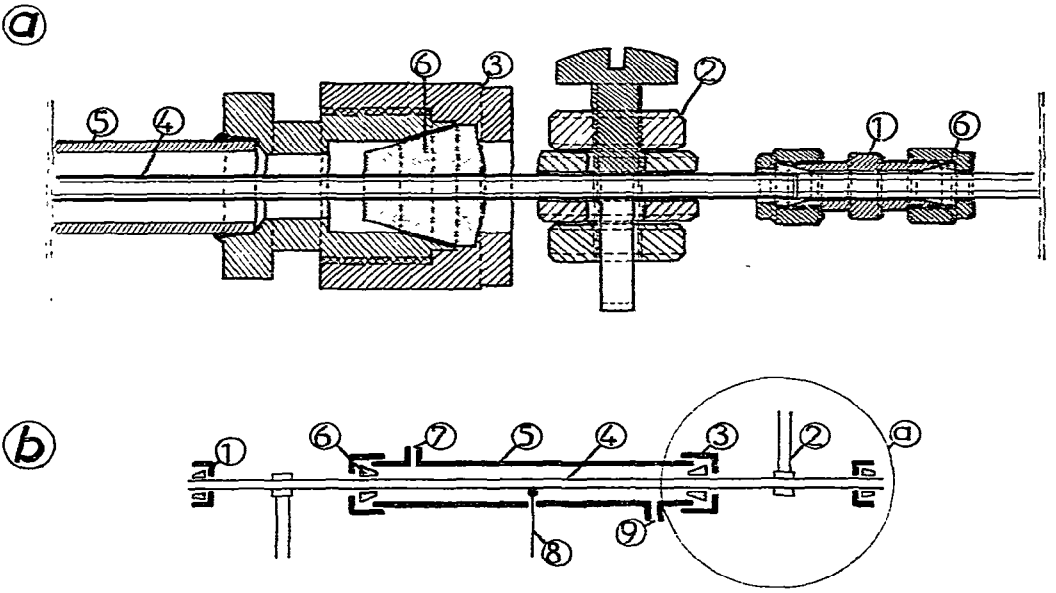

Fig. 4. Scheme of the cold trap: 1 = electrically isolated connection; 2 = electrical connection; 3 = electrically isolated connection with the mantle tube; 4 = GLT tubing; 5 = mantle tube; 6 = electrical insulating material; 7 = inlet of cold CO_2; 8 = thermocouple; 9 = outlet of cold CO_2; a = detail reported in Fig. 4a.

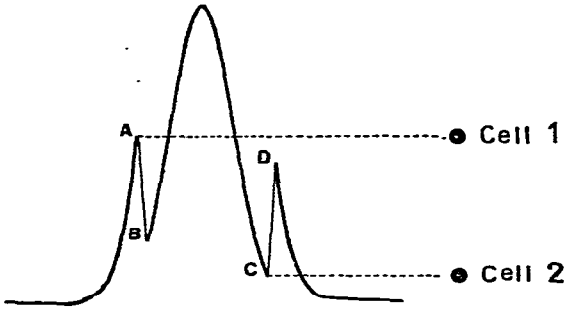

Fig. 5. FID response during the automatic rejection of one important product.

System of automatic rejection of major components

The automatic rejection of compounds present at large concentration in the analyzed mixture is controlled by using the chromatographic signal from FID A. If the chromatograph is controlled by a microprocessor, this operation can be achieved by software. We preferred to retrieve the information from the recorder by means of two photovoltaic cells, a small lamp and a mirror on the recorder pen. The cells (1 and 2 in Fig. 5) can detect the passage of the recorder pen and trigger the opening or closing of the vent according to the following scheme (see Fig. 5). During the elution of an important peak from the precolumn, the pen reaches the position of cell 1 in A. This cell then transmits a signal which opens the electrovalve 4 venting the eluent. Opening of electrovalve 4 results in a decrease in pressure at the cross-connections D and E; the gas flow to the FID A and hence the mass-flow rate of the solute to the detector decreases sharply and the signal decreases down to B, before increasing again as the elution of the component proceeds. After reaching a maximum, the signal again decreases until the pen reaches cell 2 in C. This cell closes electrovalve 4, and the original pressure at E and flow-rate to the FID A are re-established. The FID signal increases to D, the eluent being no longer vented but flowing again to the cold trap. The peak has been divided into two parts. Between A and D the product is rejected, the remainder of it being trapped for further analysis.

RESULTS AND DISCUSSION

Application to a synthetic mixture

Column A was a stainless-steel column (1 m × 4 mm I.D.) packed with 10% OV-101 on Chromosorb W 100–120 mesh. The column B was a PLOT column (12 m × 0.5 mm I.D.) coated with graphitized Sterling FTG thermal carbon black (6 mg/m) (refs. 6 and 7). The first column can partially separate *o*- from *m*- and *p*-xylene, while column B is able to separate *m*- from *p*- and *o*-xylene. The combination of the two columns allows an almost complete separation of the three xylene isomers (Fig. 6). The analysis of a mixture of aromatic compounds involves the following steps: injection, partial separation on column A and trapping of the interesting fraction (benzene, toluene, ethylbenzene or xylenes), heating of the trap and analysis on column B. The results and the effect of varying the conditions of trapping are discussed in the next section.

TABLE I

COMPOSITION OF THE AROMATIC SOLVENT MIXTURE (*cf.* Fig. 6)

Peak	*Product*	*Volume Fraction*
1	Benzene	1
2	Toluene	10^{-3}
3	Ethylbenzene	10^{-3}
4	*m*-Xylene	$1.5 \cdot 10^{-3}$
5	*p*-Xylene	$2 \cdot 10^{-3}$
6	*o*-Xylene	$2 \cdot 10^{-3}$

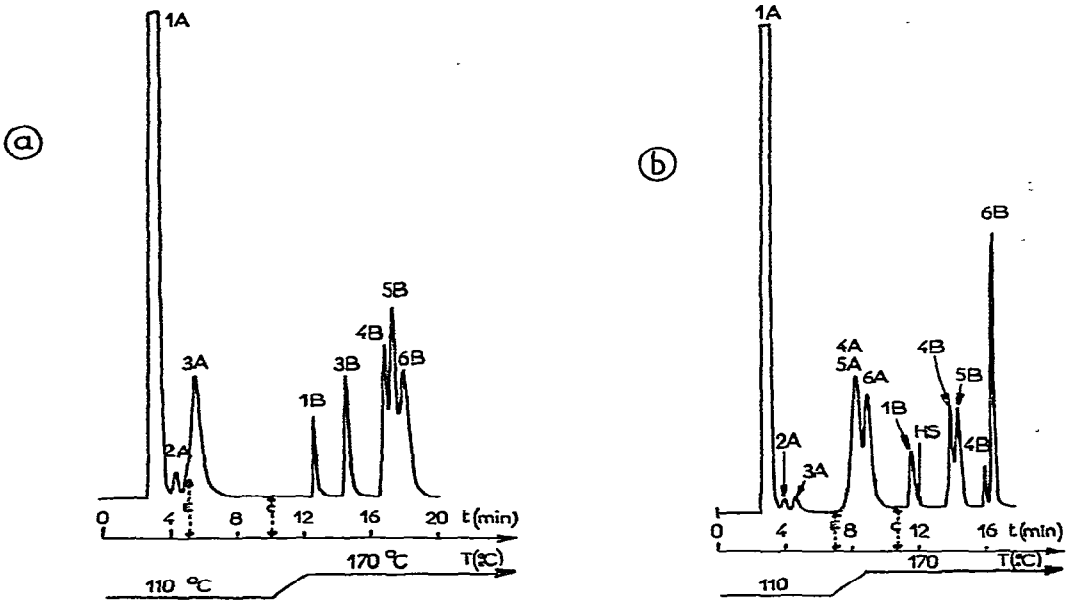

Fig. 6. Analysis by double column chromatography of a synthetic mixture of aromatic compounds. For key to the products see Table I. The letters A or B after the peak number mean that the corresponding peaks have been recorded from FID A or FID B respectively; E means the end of venting and beginning of the transfer to column B; C means a switch of the signal recorded from FID A to FID B. (a) No cool trap; the doublet [(*m*-xylene + *p*-xylene)/*o*-xylene)] is not seen on the chromatogram recorded from FID A because these products emerge from column A after C. (b) A cool trap is incorporated between columns A and B; the cooling of the trap is achieved just before the elution of *o*-xylene on column A. The flash heating of the trap is achieved after 11 min. The peak HS (heating signal) is the FID response of the flash heating.

Effect of intermediate trapping

In Fig. 6a it can be seen that the peak 3B is narrower than the peak 3A, although the analyses on each column are isothermal. This is due to the fact that the product emerging from column A at 110° is trapped at the beginning of column B

on graphitized carbon black at 110°. The analysis of such a product on column B gives the same chromatogram as if the mixture trapped at the inlet of column B had been injected directly in the injection port B, and column B is more efficient than A and about as fast. (Analysis on column B takes place at 170°.)

The situation is more complex for the xylenes, however, as they are eluted from column A during the heating period of column B. The peaks of *m*- and *p*-xylenes which are the first to enter the column B are narrowed by the temperature programming effect, but the peak of *o*-xylene which enters a hot column B is not. The partial separation between the *m*- and *p*-xylenes arises from the fact that they are first partially separated on column A. All cases are not as favourable as this one and a system of intermediate trapping is usually required in order to obtain a good separation. No influence of the separation on the first column then remains. In Fig. 6b is shown a chromatogram obtained from the same mixture as in Fig. 6a, using the same columns and temperatures but with the difference that peak 3A was vented and the system of intermediate trapping described was used during the elution of *o*-xylene.

The use of trapping is shown to have several advantages:

The sources of peak broadening and peak profile distortion occurring during the preseparation are eliminated. The peaks are as narrow and symmetrical as those resulting from a conventional injection on the analytical column (peak 6B).

The FID response to the flash heating (signal HS) is highly reproducible and gives an accurate time origin for the measurement of retention times on column B.

The total elimination of one peak from a compound band can be achieved (*e.g.*, *o*-xylene from *o*-, *m*- and *p*-xylenes). Since the xylenes were not totally resolved on the precolumn, some *m*- and *p*-xylene is trapped together with *o*-xylene (second peak 4B in Fig. 6b). It is also possible to trap exclusively pure *o*-xylene (but not while initiating the cooling of the trap after the complete elution of *m*- and *p*-xylene). Then peak 6B is completely separated and the non-trapped fraction of *o*-xylene gives a new peak 6B emerging just after the doublet of *m*- and *p*-xylenes (peaks 4B and 5B). Thus another advantage of intermediate trapping is the ability to isolate an individual compound from a complex band.

Automatic rejection of the major components

With natural mixtures a few components are often in large concentration while many other products are present in very small concentration. An analysis on a single column gives a number of major peaks and a forest of small peaks all over the chromatogram. In order to analyze these small peaks the injection of a large sample amount is often necessary. At this point, the major components give very large tailing peaks that can hide many smaller ones. We have solved this problem using two-dimensional chromatography in which the major products eluted on the first column are rejected and the remainder of the mixture is trapped and then analyzed on the second column without interference from the major products.

Such a system must be automatic in order to obtain reproducible analysis. In our case, the automation is performed by the two photovoltaic cells. We now describe the application of this system to a mixture of terpenes produced as previously[8] by chemical oxidation of nerol and geraniol using potassium dichromate–acetic acid as oxidizing reagent. One of the main difficulties encountered in the previous study was the identification of trace components by gas chromatography–mass spectrometry

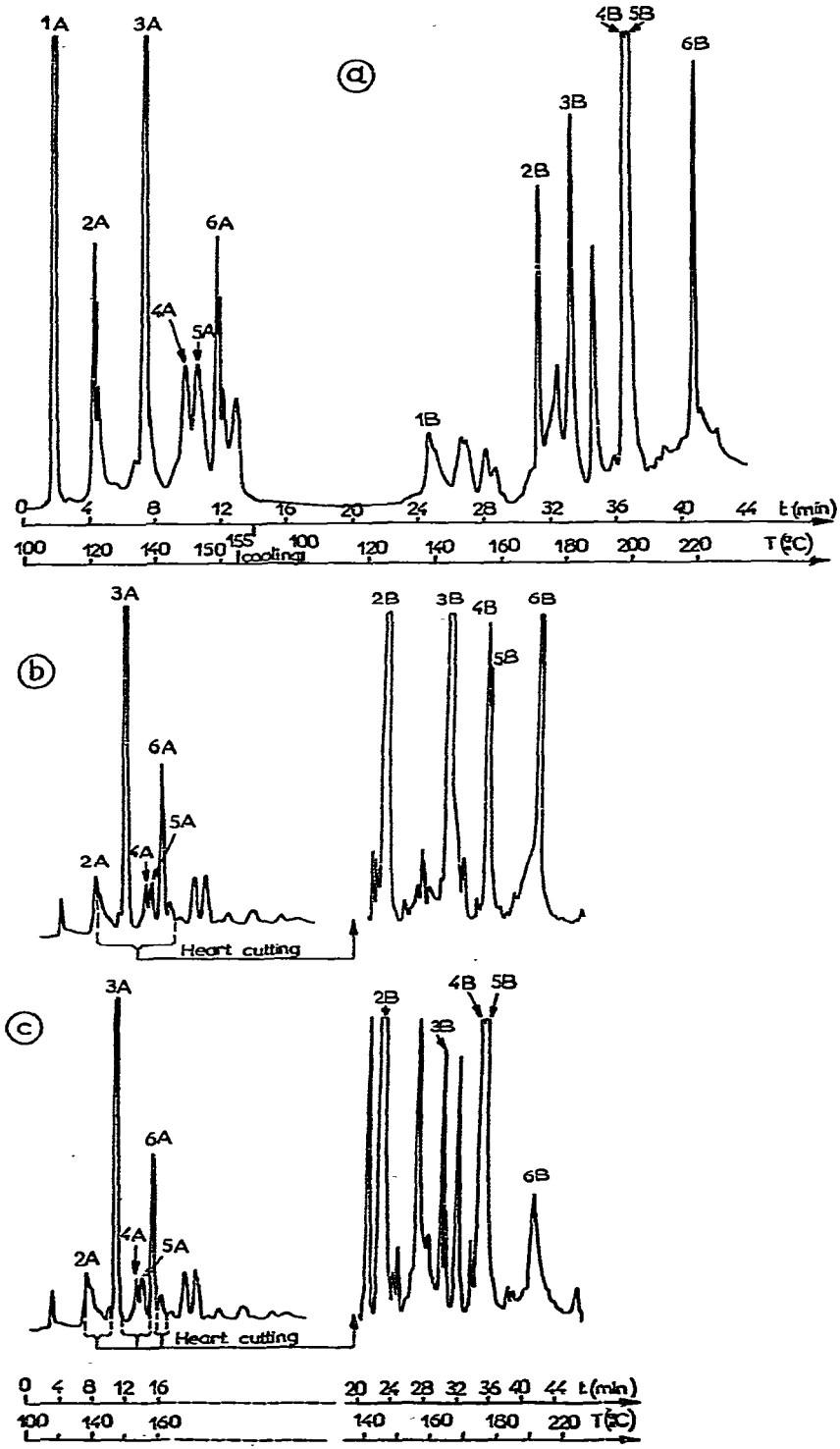

Fig. 7. Analysis of a terpene derivative mixture: column A, FFAP (1 m × 4 mm I.D.); column B, Sterling FTG graphitized carbon black (12 m × 0.5 mm I.D.). (a) Automatic rejection of the major peaks of the sample. (b) Simple heart cutting analysis. (c) Heart cutting analysis with rejection of the major peaks.

(GC–MS). Although the capacity of PLOT columns is large, many small peaks could not be identified since sufficient material could not be injected into the chromatograph.

The present analysis was performed upon the lighest compounds up to linalool. The precolumn was a conventional column (1 m × 4 mm I.D.) packed with Chromosorb W coated with 10% FFAP. Column 2 was the same as for the xylene analysis. The chromatogram in Fig. 7a shows, up to a time of 14 min, the elution on the precolumn A with linear temperature programming from 100 to 155°. Except for peak 1A which was rejected in the usual way, the major peaks are 2, 3 and 6. These peaks were rejected as described above. After 13 min the oven was allowed to cool to 100° and at 17 min the temperature programming was restarted at a constant rate of 5°/min up to 220°. Simultaneously, the cooling of the trap was switched off and it was left to warm up slowly. (This has little effect on peak broadening and avoids any risk of thermal degradation of the sensitive compounds analyzed here.) The second part of the chromatogram eluted on column B shows that the major peaks are the doublet of 2, 4 and 5. New peaks also appear on the chromatogram. From a quantitative point of view, the ratio of peaks 4 + 5 to peak 3 is 7:28 on the precolumn and 8:0.8 on the column B. Thus the concentration of the major compounds of the mixture has been reduced in the proportion of 40:1.

The chromatograms in Fig. 7b and 7c show the difference between a simple heart cutting[5] and the combination of heart cutting with rejection of the major peaks. For instance, the major peak (peak 3B in Fig. 7b) has a small shoulder on its tail. The same chromatogram in Fig. 7c shows the resolution of this doublet.

Quantitative trace analysis

Trace analysis is one of the most important fields of chromatography. Single column chromatography can achieve such analysis only when the trace impurities and the main products have very different capacity factors. Double column chromatography is required when it is desired to determine trace impurities that are eluted in the tail of a major component. In this case the first column is a classical one containing a large amount of liquid phase, in order to separate a large quantity of product. The main product is vented while the trace impurities known or believed to be present are trapped and reinjected into a second column on which they are separated.

We used this technique to separate the trace components present in a commercial solvent, cyclohexane (E. Merck, Darmstadt, G.F.R.), and examined the impurities which exhibited slightly greater retention (see Fig. 8). The first analyses carried out on column A gave a single peak (1A). The spike denoted 1'A results from the phenomenon shown in Fig. 5. The second analysis carried out on column B showed several impurities, the amounts of which were as large as the amount of the remaining solvent (see Tables II–IV); these impurities are mainly aliphatic hydrocarbons and unsaturated hydrocarbons such as cyclohexene or benzene and their light homologues. The measured concentrations are in agreement with those specified by Merck.

The determination of the concentrations of the impurities was performed in two steps: first, from chromatogram A, the weight fraction of the sample transferred to the trap and the second column is calculated; secondly, from chromatogram B, the relative concentration of each product transferred to column B is calculated. The second step is very easy since we assume that the FID has a linear response, and either

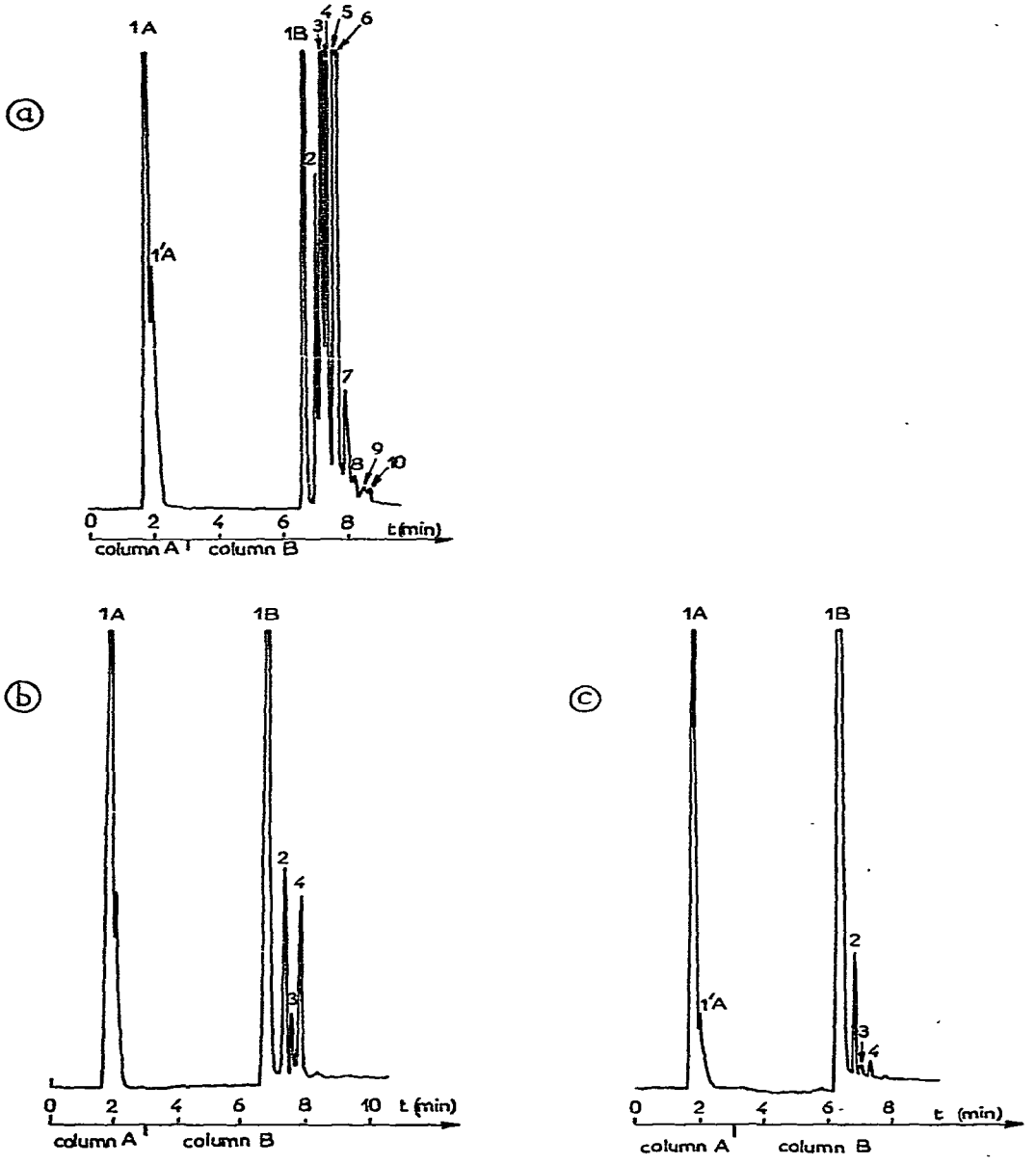

Fig. 8. Analysis by double-column gas chromatography of the impurities in some commercial cyclohexane solvents: (a) Merck pro analysis; (b) Merck Uvasol; (c) Merck pro analysis after distillation.

that this response is approximately the same for all of the components (unidentified impurities) or that a calibration is made.

It is more difficult to measure the concentration of the fraction of the eluent which is transferred to column B for two reasons: first, the FID response depends on the carrier gas flow-rate and this flow-rate is not the same during the two periods of

TABLE II

COMPOSITION OF CYCLOHEXANE SOLVENT (Merck pro analysis)

*Peak**	t_R *(min)*	*Area (%)*	*Concentration (ppm)*
1B	6.71	0.0216	220
2	7.09	0.0086	90
3	7.29	0.0456	480
4	7.43	0.0116	120
5	7.65	0.0136	140
6	7.69	0.0191	200
7	8.01	0.0055	60
8		—	
9	8.57	0.00020	2
10	8.75	0.00016	1.5

* *Cf.* Fig. 8a.

TABLE III

COMPOSITION OF CYCLOHEXANE SOLVENT (Merck Uvasol)

*Peak**	t_R *(min)*	*Area (%)*	*Concentration (ppm)*
1B	6.66	0.015	270
2	7.29	0.003	50
3	7.55	0.0004	10
4	7.82	0.002	40

* *Cf.* Fig. 8b.

TABLE IV

COMPOSITION OF CYCLOHEXANE SOLVENT (Merck pro analysis) AFTER DISTILLATION

*Peak**	t_R *(min)*	*Area (%)*	*Concentration (ppm)*
1B	6.23	0.0320	290
2	6.83	0.0022	20
3	7.06	0.00038	4
4	7.32	0.00025	2

* *Cf.* Fig. 8c.

venting and transfer; secondly, the fraction of the gas flow-rate eluted from column A which flows to FID A is not the same during the two periods of venting and transfer. In order to take these two phenomena into account we have to measure the increase, q, in the response of the FID A when changing from the venting period to the period of transfer. q is constant for a series of analyses when no modification is made in the flow system. We neglect its dependence on temperature. q can be determined experimentally from the chromatogram of a standard mixture. Thus, the knowledge of q and of the peak areas on the chromatogram provided by FID A allows the determination of the sample fraction transferred. This information is not available when the entire chromatogram A cannot or has not been recorded (*cf.* Fig. 6a) or when the peak area of the transferred fraction cannot be accurately measured (*cf.* Fig. 8).

In order to solve this problem we can assume that the ratio r remains constant

$$r = \frac{\text{[total area for the transferred fraction on FID B]}}{\text{[total area for the transferred fraction on FID A]}}$$

in a series of analyses if no modification is made to the flow system. r can be measured experimentally. In Fig. 6a, for example, we have:

$$\frac{\text{Concentration of } C_6H_6}{q \cdot (\text{area of peak 1A})} = \frac{\text{Concentration of } C_6H_5\text{–}C_2H_5}{(\text{area of peak 3A})}$$

hence:

$$q = \frac{0.4}{100} \cdot 10^3 = 4$$

while:

$$r = \frac{\text{area of peak 3B}}{\text{area of peak 3A}} = 0.3$$

Using these results, it is possible to obtain a quantitative analysis of the traces. In Fig. 8a, for example, we have:

$$(\text{Concentration of product 10}) = \frac{\text{area of peak 10}}{r[q \cdot (\text{area of peak 1A}) + (\text{area of peak 1'A})]}$$

This concentration in ppm is:

$$\frac{10^6 \cdot 153}{0.3(4 \cdot 69 \cdot 10^6 + 24 \cdot 10^6)} = 2.5 \text{ ppm}$$

An alternative method would be the use of an internal standard introduced in known amount and which could be entirely trapped and separated on column B from the compounds to be analyzed.

CONCLUSIONS

It has been shown that a commercial gas chromatograph can easily be transformed into a powerful two-dimensional chromatograph. The applications described here should be considered as imperfect illustrations of the method, since they have been performed on columns having a rather poor separating power and which could be considerably improved. Yet such examples forecast an important development of these techniques in the future. The availability of two-dimensional chromatography is fundamental in analytical chemistry since it permits the resolution of groups of compounds that cannot be separated by single column chromatography, or the isolation in the intermediate trap of an individual product from a mixture and subsequent chemical reactions or physical measurements for further identification. Our system for automatic rejection of the major components may play an important role in the industrial field since it allows a direct quantitative analysis of trace impurities in a complex mixture.

ACKNOWLEDGEMENTS

We thank Alain Debraine, Marc Godfrin and Guy Preau for technical assistance, and Jean-François Ferriot and Jean-Marie Schmitter for fruitful discussions.

REFERENCES

1 G. Schomburg, H. Husmann and F. Weeke, *J. Chromatogr.*, 112 (1975) 205.
2 Bulletin No. 1245, Packard, Downers Grove, Ill, 1977.
3 "Ventillose" Trennsäulen-Schalteinrichtung für Labor-Gas Chromatographen L 350 und L 402, Siemens, Karlsruhe, Bulletin PWK C 74000-B 5300-C 205-2 (1976).
4 Bulletin KI-125-01577, Perkin-Elmer, Beaconsfield.
5 D. R. Deans, *Chromatographia*, 1 (1968) 18.
6 C. Vidal-Madjar, J. Ganansia and G. Guiochon, in R. Stock (Editor), *Gas Chromatography 1970*, Institute of Petroleum, London, 1971, p. 20.
7 C. Vidal-Madjar, M.-F. Gonnord, S. Bekassy, P. Arpino and G. Guiochon, *Anal. Chem.*, 49 (1977) 768.
8 P. Arpino, C. Vidal-Madjar, S. Bekassy and G. Guiochon, *J. Chromatogr.*, 138 (1977) 173.