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ASPECTS OF DOUBLE-COLUMN GAS CHROMATOGRAPHY WITH GLASS CAPILLARIES INVOLVING INTERMEDIATE TRAPPING

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SUMMARY

The versatility of semi- and fully automated double-column systems containing one or two glass capillaries is improved considerably by the incorporation of intermediate trapping devices for the analysis of complex mixtures, including very dilute and aqueous solutions. For the main separation, glass capillaries are used exclusively in order to achieve optimum resolution of all interesting species as well as narrow peak profiles for low detection limits of trace components.

A length of 10–50 mm of the glass capillary acts as the trap; cooling and heating is executed by using a simple stainless-steel mantle tube with two separate entrances for either blowing cool nitrogen generated from liquid nitrogen or blowing hot nitrogen generated by electrical heating. There are four advantages in the use of trapping techniques in double column systems:

(1) Broad or distorted peak profiles generated at the pre-separation or during the elution from the pre-column and the transfer to the main column are eliminated; ideal plug injection of the on-column type is attained by this procedure.

(2) Repetitive pre-separation and cumulative trapping allow enrichment of trace components.

(3) The main separation can be performed with an isothermal mode of operation for retention index identification with high reproducibility.

(4) Two sets of independent retention index data are obtained when stationary liquids of different polarity are used in the two columns of the system and the re-injection procedure is adopted.

INTRODUCTION

In previous papers[1–4] we have described double-column systems in which glass or stainless-steel capillary columns were used for the main separation whereas the pre-separation was performed in packed columns. A dual-column, dual-oven system with a packed pre-column and a capillary as the main column with an electron capture detector for the sensitive detection of, for example, Δ^9-tetrahydrocannabiol in the main separation was described by Fenimore *et al.*[5]. The system also allows temperature programming in the pre-separation but uses heated valves for flow switching. Polydimensional gas chromatography (GC), also utilizing trapping and flow switching

with valves, was described in detail by Boer[6]. For certain cases, *e.g.* in the analysis of aqueous solutions[4], a special system was described that contains an additional injection port between the pre-column and the main column and that allows for reversible directions of flow of carrier gas in the pre-column during pre-separation with transfer of the cuts to the trap.

In all of the systems we have described previously, the "valveless" Deans[7] switching technique in which the interesting components never pass heated valves was used. Recently, we reported on a system in which two capillary columns were coupled without deterioration of resolution[7] and tailing behaviour[8], even without using intermediate trapping.

According to our experience, capillary columns (preferably made of glass) can be used with advantage as main columns in two-dimensional GC of complex mixtures for the following reasons:

(1) The separation efficiency in terms of effective plate numbers per metre and/or the total effective plate numbers that can be achieved in long columns as well as the tailing behaviour is superior in comparison with packed columns[4,8].

(2) Glass capillaries with high separation efficiency, defined polarity and excellent temperature stability can nowadays be prepared without difficulties[4,8-12].

(3) Compounds of low chromatographic volatility can be eluted at low column temperatures with moderate retentions and without decomposition because only small amounts of stationary liquids are contained in long columns[8].

(4) Capillary columns have very low pressure drops at high separation efficiency. High carrier gas flow-rates for rapid analyses can be used[8].

(5) Trace analyses can also be performed in capillary columns because trace components of a mixture can be introduced by different techniques of selective sampling without appreciable loss, or at least with tolerable loss, of material. In many instances, the amounts of trace components available in sample volumes of up to 5 μl are suitable for direct sampling without splitting or with only minor splitting. This method of sampling, which we call "selective", can be realized, with some limitations, by the splitless injection technique of Grob[10] or in double-column systems in the manner described in this paper.

DOUBLE-COLUMN SYSTEMS WITH PACKED PRE-COLUMNS

Some of the typical problems that arise in the analysis of complex mixtures that contain components with wide ranges of concentrations, volatilities and polarities can be overcome more effectively by using double-column systems with packed precolumns:

(1) The sampling and enrichment of trace amounts of substances contained in very dilute solutions of solvents with varying polarities can be performed advantageously with packed pre-columns because of their high sample capacity and because maximum resolution is not required in these pre-separations. The separation of the interesting species that may also be present in trace amounts is performed in the main (capillary) column, which is coupled with the packed pre-column. Large amounts of solvents, excess of derivatization reagents and uninteresting main components can be excluded from the chromatographic main separation by means of flow switching after pre-separation[3,4]. Deterioration of the capillary column with regard to separation

efficiency, polarity, catalytic activity and tailing behaviour is prevented. The size of the injected sample depends on the concentration of the trace components to be detected and on the capacity of the pre-column for the major components that are to be removed. If necessary, repetitive pre-separation with the aim of enrichment of trace components can be carried out.

(2) The removal of solvents or reagents may also improve the performance of sensitive specific detectors —electron capture, nitrogen flame ionization detectors (FID) and mass spectrometers[5,13].

(3) Components with very high retentions that are not of interest in the analysis can be removed either by venting between the pre-column and the main column or by back-flushing from the pre-column and venting before the injection port (see the left injection port in Fig. 1).

(4) Special column packings such as Porapak, Tenax or graphitized carbon black can be used for the rapid removal of water and similar, very polar solvents or components. The polarity of the stationary phase in the pre-column, of course, must be selected according to the type of compounds to be separated and removed.

(5) With intermediate trapping, an isothermal mode of operation in the main separation can be adopted for retention index identification. In the trap, enrichment of trace components by repetitive pre-separation is achieved before the main separation is initiated. Peak broadening or even peak distortion (tailing or leading), which occurs during pre-separation or in the connecting tubing is eliminated by the re-injection procedure, the application of which is necessary for subsequent separation at high resolution. Trapping is also very important for quantitative trace analysis when low detection limits are required. High signal-to-noise ratios are obtained only with narrow peaks, which are created by instantaneous vaporization from the trap, which is a piece of the high-resolution main column.

(6) The system described in more detail below gives useful possibilities for the analysis of aqueous solutions. It contains an additional injection port between the pre-column and the main column[4].

Instrumental

Application examples are given of the technically re-designed version[3] of a totally automated all-glass double-column system on the basis of a dual-channel FID gas chromatograph (Siemens L402) using a pre-programmable flow-switching unit with electronic timers. The automated and pre-programmable operation of such systems, including cooling and heating of the trap, is necessary for two reasons: series of routine analyses can be measured under constant conditions with regard to sampling, flow-rates, temperatures or residence times of the solutes in the two columns, and the timing of the various flow-switching operations can be performed with high precision without human interaction. Practical applications illustrate the performance of the improved set-up, a scheme of which is shown in Fig. 1. As described previously, two injection ports are part of the system, one before and one behind the pre-column(3). Two detectors permit the control of the pre-separation and the main separation, sample introduction and back-flushing. A photograph of the total set-up is shown in Fig. 2. The connection part between the two columns is made of glass and platinum, *i.e.*, without stainless-steel surfaces. The trapping device is a simple mantling tube made of stainless steel (5 mm I.D.) with two inlets for cool and heated nitrogen. In

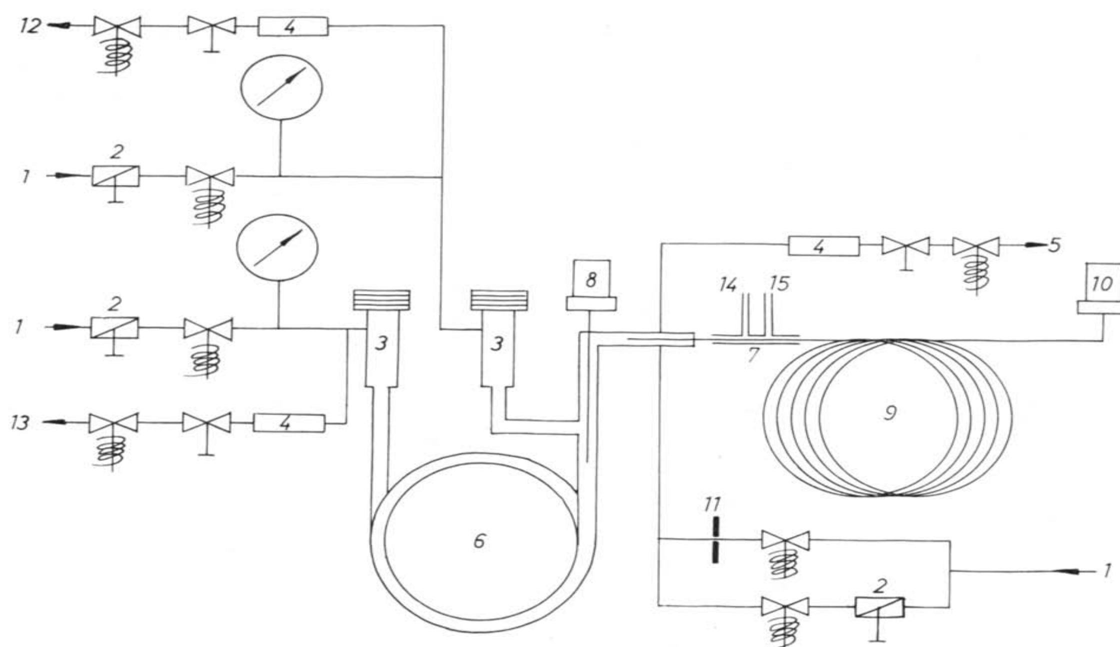

Fig. 1. Double-column gas chromatography with packed pre-column and trapping. 1 = Carrier gas; 2 = pressure controllers; 3 = injection ports; 4 = filter; 5 = split; 6 = packed pre-column; 7 = trap; 8 = control FID; 9 = glass capillary main column; 10 = FID; 11 = leak for make-up gas inlet; 12 = outlet for venting after pre-separation; 13 = outlet for back-flushed components from pre-column; 14 = inlet for heated nitrogen; 15 = inlet for cooled nitrogen.

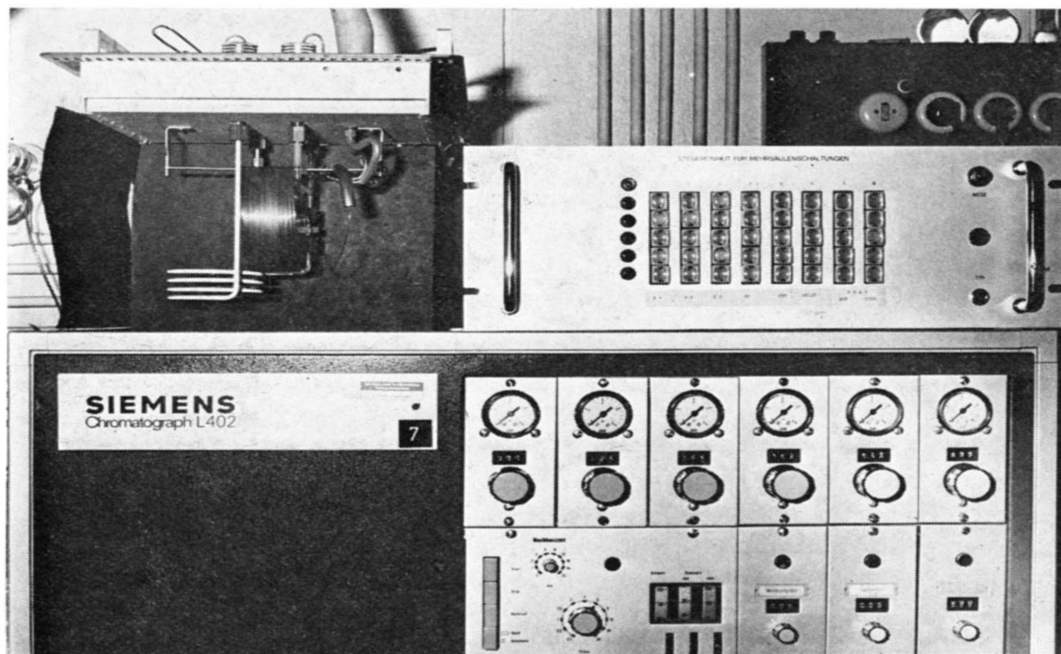

Fig. 2. Double-column system with packed pre-column, glass capillary main column and intermediate trapping.

the pre-programming unit, all relays and timers for operating the solenoid valves are integrated.

Applications

Removal of solvents from an artificial solution of two xylenes, toluene and butyl acetate. Chromatogram 1 in Fig. 3 shows the glass capillary chromatogram of the original sample that was injected into the port between the columns of the system. Chromatogram 2 shows the capillary chromatogram of the same sample after pre-separation on a packed column (Tenax). The concentration profile of the input signal recorded directly after sample injection and the profile of the back-flushed components, which was also measured at the control FID (8) just before trapping, are shown together with chromatogram 2, which was recorded after trapping and re-injection of the back-flushed material. The large amounts of solvents were removed from the pre-column by venting through the left injection port (see Fig. 1). This technique is also applicable to mixtures that give chromatograms with trace peaks on the tail of a solvent. The heart-cutting technique then has to be used (see below).

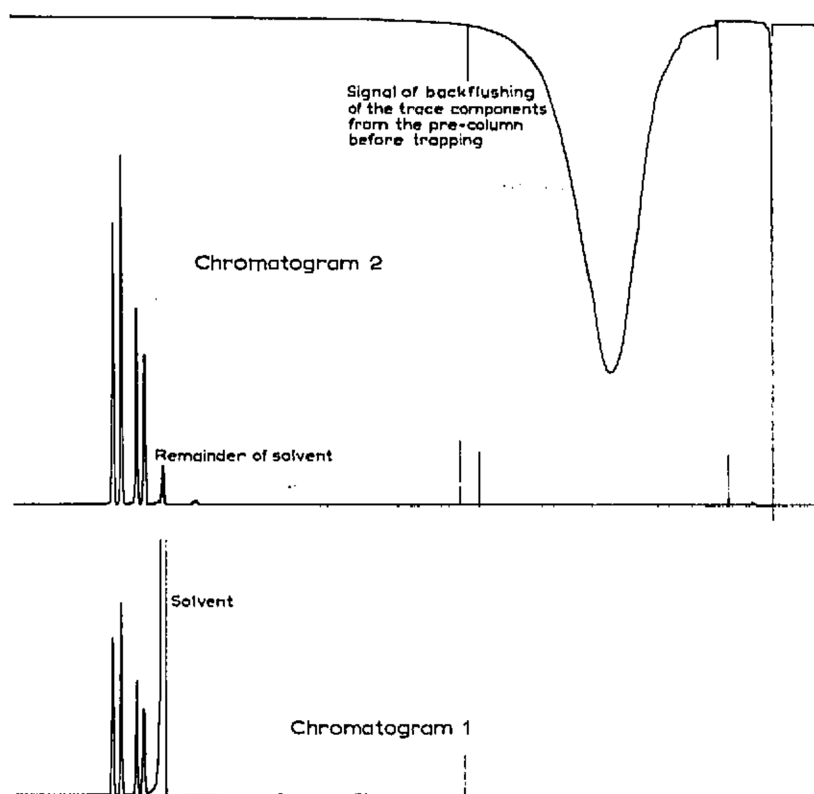

Fig. 3. Removal of polar solvents with non-polar pre-column. Pre-column: 1 m Tenax, 60–80 mesh; main-column: 110 m Dexsil 300 GC, 120°. Chromatogram 1: original sample measured in main column; chromatogram 2: cut after trapping and re-injection.

Determination of phenols in the wash water of a coke plant. In the same manner as in the previous application, wash water used in the extraction of phenols from coke gas was analyzed before and after de-phenolization. The identification of the phenols was carried out by means of a test mixture, the chromatogram (3) of which is given in Fig. 4. Chromatogram 1 shows the wash water before and chromatogram 2 after de-phenolization. The approximate concentration of phenols in the sample was about 0.1 % before and 0.01 % after de-phenolization. A 3-μl volume of the sample was injected into the right port and the procedure of automated two-dimensional analysis was the same as in the previous application.

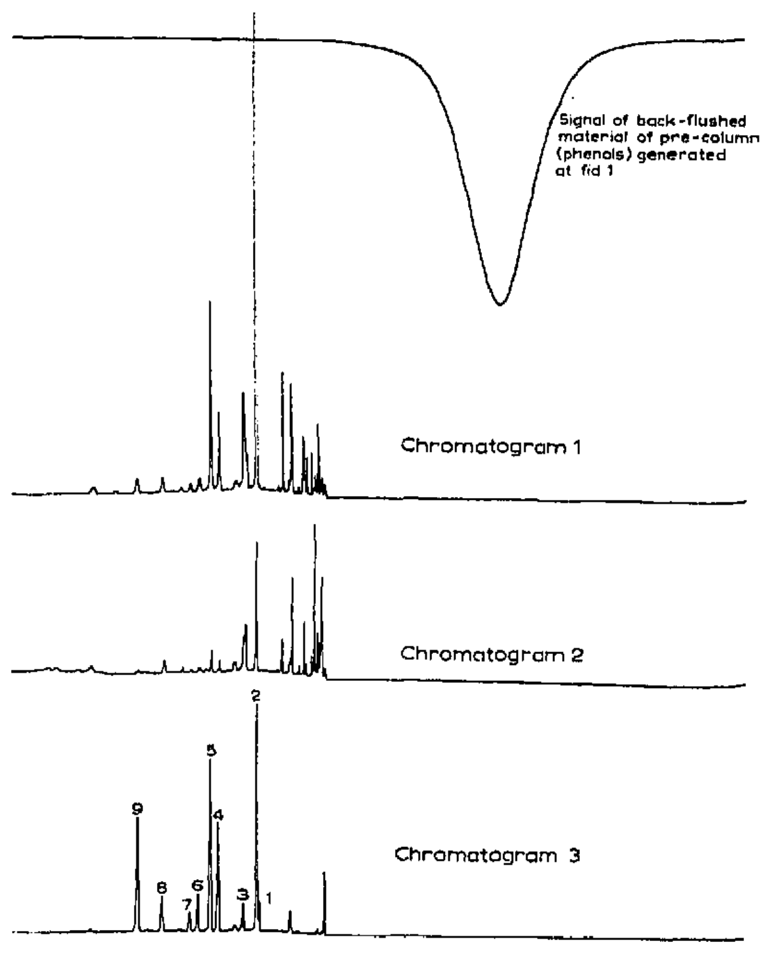

Fig. 4. Determination of phenols in dilute aqueous solutions. Pre-column: Tenax, 1 m, 80–100 mesh, 130°. Main column: tricresyl phosphate, 19 m, 0.25 mm I.D., 130°. Chromatogram 1: sample, 3 μl (split 1:30) waste water of coking plant before de-phenolization. Chromatogram 2: sample, 3 μl (split 1:30) after de-phenolization. Chromatogram 3: sample, 3 μl (split 1:30) test mixture. Peak 1 = 2,6-dimethylphenol; 2 = phenol; 3 = *o*-cresol; 4 = *p*-cresol; 5 = *m*-cresol; 6 = 2,4-dimethylphenol; 7 = 2,5-dimethylphenol; 8 = 2,3-dimethylphenol; 9 = 3,5-dimethylphenol.

Enrichment of trace components with repetitive pre-separation and subsequent re-injection for the main separation. The identification and determination of trace components in very dilute samples, for example by means of the combined application of retention data and mass spectra, in many instances suffers from a lack of mass spectrometric sensitivity when "good", *i.e.*, intense, mass spectra for pattern recognition or identification are required. With the complex mixtures that are encountered in our laboratories, for example in the radiation chemistry of biochemical material at low conversions, very often groups of isomeric compounds have to be separated in capillary columns with high resolution[3,4].

From the eluate from a packed column pre-separation with a high sample loading, a cut in the selected region of component retentions is taken and the trace components contained in this fraction of the eluate are trapped in the part of the main column that acts as the trap. This procedure is repeated as often as necessary in the same trap for enrichment.

The cumulated material is subsequently separated by the capillary column and can be detected with an increased signal-to-noise ratio with an FID, nitrogen FID or mass spectrometer. In Fig. 5, trace components of a mixture of silylated sugars have been enriched for better detection and mass spectrometric identification. Chromatograms are shown that illustrate the application of the enrichment technique. Chromatogram 1 was obtained with the original sample, chromatogram 2 is a capillary chromatogram of a mixture of silylated sugars after removal of solvents and components of high retention (cut 1). Chromatogram 3 was obtained after enrichment with a 13-μl sample separated with three succesive measurements ($6 + 6 + 1$ μl). In chromatogram 3, all components between peaks 3 and 4 have been enriched in comparison with peaks 1 and 2 (cut 2).

AUTOMATED GC SYSTEM WITH TWO COUPLED CAPILLARY COLUMNS

With many multicomponent mixtures, it is difficult to take a suitable cut from the eluate from the pre-separation for subsequent separation at high resolution. The resolution of a packed column may be insufficient and the chromatogram may not give enough information about all of the components present. The pre-separation must then also be carried out with a capillary column at high resolution (see Fig. 6).

The performance of the double-capillary column system described earlier[8] is improved by the introduction of a similar trapping device as used in the system in Fig. 1 for the packed column coupling. When using two capillary columns, the application of the trapping procedure is not so important, because enrichment of trace components or compensation for extensive peak spreading or distortion originating from the pre-separation may not be necessary. The latter effects on resolution can also be avoided by appropriate design of the coupling devices[8]. The main reason for trapping and re-injection is, in our opinion, the determination of the retention indices of the components of the complex mixtures when using stationary liquids with different polarities in the two columns and an isothermal mode of operation in one or both columns. Only then are the indices measured in the second column independent of the polarity of the stationary liquid in the pre-column and the residence time of the compounds in it[14]. Both columns may advantageously have identical or not very different separation efficiencies, as pointed out before.

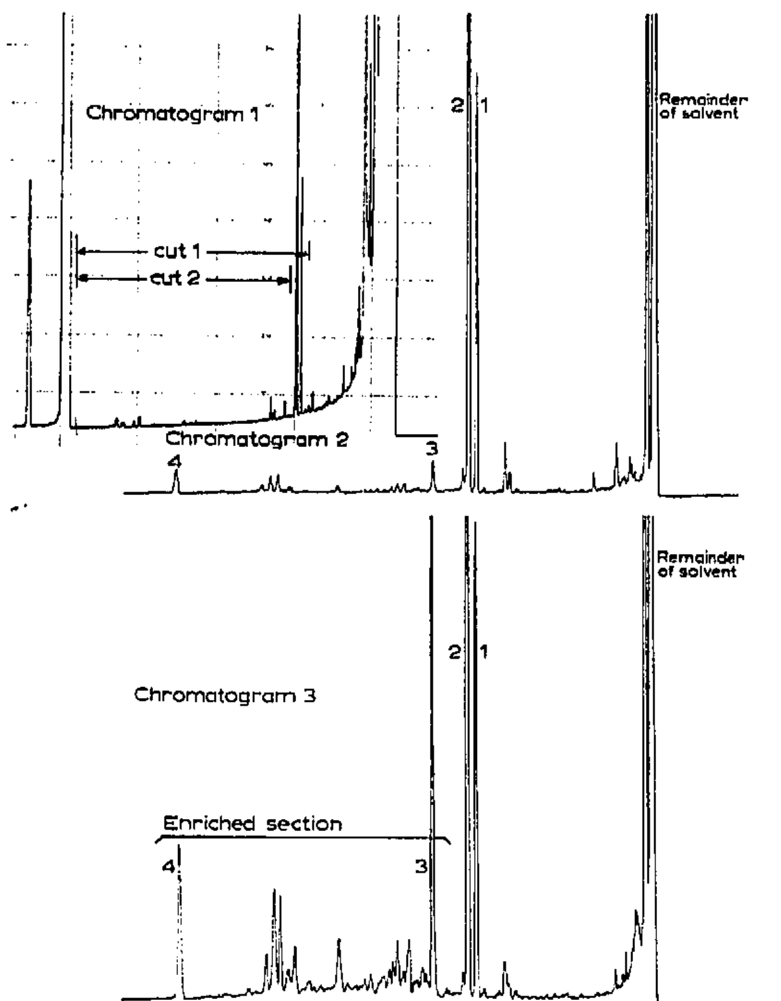

Fig. 5. Dual-stage gas chromatography with packed pre-column. Cutting and back-flushing of solvents and uninteresting components. Enrichment and re-injection of selected species. Chromatogram 1: Interesting part of original chromatogram. Chromatogram 2: Main separation with cutting and back-flushing (cut 1). Chromatogram 3: Main separation with cutting, back-flushing and enrichment (cut 2). Pre-column: 2 m SE-52 (5% on Chromosorb G), 170°. Main column: 50 m × 0.25 mm I.D. OV-101, 170°. Carrier gas: helium. Sample: 2-keto-gluconic acid lactone, methoximated and silylated.

Most of the important species of the mixture have to be resolved in the first column in order to obtain reliable retention indices for the stationary liquid of this column. Further, the selection of interesting species from the eluate from the separation in the first column is facilitated when the subsequent measurement is to be carried out with a stationary liquid of different polarity in the second column with the purpose of obtaining more reliable peak correlation in overlapping chromatograms. Even single peaks from the first-stage separation can be transferred precisely to the second-stage separation by the trapping technique. The manipulation of single peaks or of selected groups of peaks is especially important for peak correlation when severe

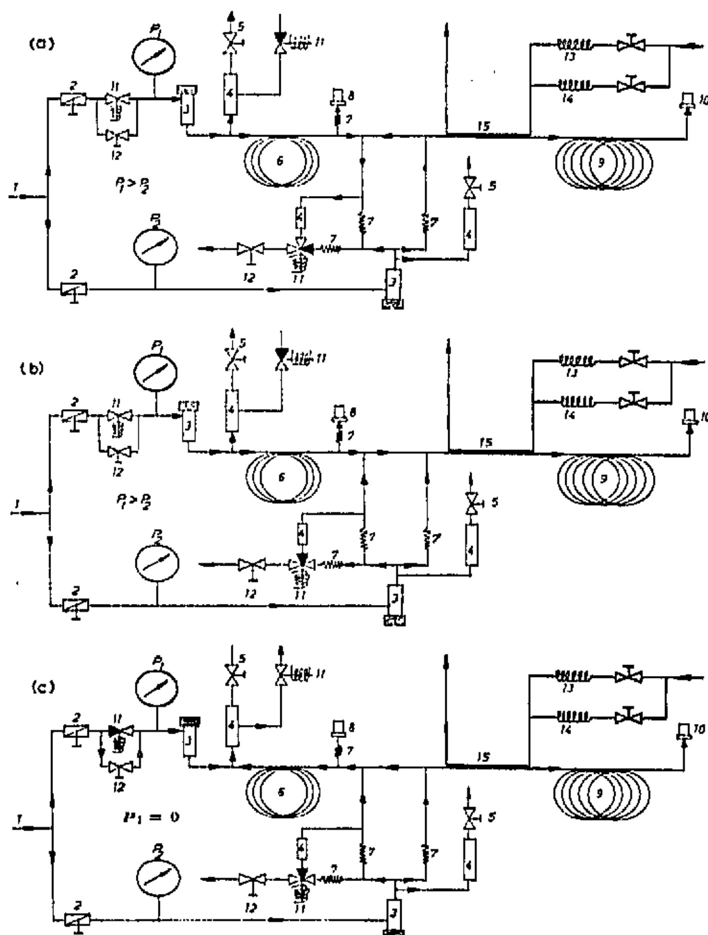

Fig. 6. Automated gas chromatographic system with two coupled capillary columns and intermediate trapping. 1 = Carrier gas; 2 = pressure controller; 3 = injector; 4 = filter; 5 = split; 6 = glass capillary pre-column; 7 = throttles; 8 = control FID; 9 = glass capillary main column; 10 = FID; 11 = solenoid valves; 12 = needle valves; 13 = cooled coil; 14 = heated coil; 15 = trap. System status: (a) eluate of pre-column vented; (b) eluate of pre-column transferred to trapping; (c) back-flushing of high-retention components from pre-column.

changes in retentions and new peak overlapping arise as a consequence of changes in the column polarities in the separation of mixtures that contain numerous compounds with various functional groups.

If intermediate trapping and subsequent re-injection are not applied, the retentions obtained in the chromatogram (recorded on FID (10) in Fig. 6) depend on the corresponding residence times of a certain species in the two columns of different polarities. Only when both columns have the same polarity can retention indices obtained with FID (10) be used for identification by comparison with tabulated retention data measured in the same stationary liquid. In the case of a change in polarity, a defined starting point for retention measurement in the second column is obtained only

by the re-injection procedure. Standard alkanes and methane for dead volume evaluation are introduced twice into the system. For the determination of retention indices in the first column, the *n*-alkanes are added to the original sample. After trapping of a selected group of peaks, suitable *n*-alkanes for the determination of retention indices in the second column are introduced into the injection port between the two columns and are trapped together with the compounds of the cut. Naturally, these *n*-alkanes must have carbon numbers that are different from those required for the first separation corresponding to the polarities of trapped solutes and the stationary liquids used. For each component that has been detected and characterized by its retention index I in both chromatograms via peak areas or by manipulation of single peaks in repetitive test measurements, a ΔI value can be calculated that may be characteristic of the functional groups contained in the molecule.

Instrumental

The system shown in Fig. 6 does not contain a pre-programming relay and timer unit, a simple three-position switch being operated in order to set the three different modes of operatoin: "sample transfer", "venting" and "back-flushing". The connecting tubing between the two capillary columns is about 50 mm × 0.3 mm I.D. and has a double-T construction for the introduction of scavenger gas. It is made of stainless steel, the inner walls of which are coated with glass. The sample does not come into contact with stainless-steel surfaces. For trapping, a device similar to that described above is used.

Applications

Analysis of perfume oil: Identification or characterization of components by determination of Kováts indices. The separation of a common perfume oil containing compounds with various functional groups was carried out by using a system with a non-polar OV-101 and a polar OS-138 (polyphenyl ether) glass capillary (see Fig. 7). The components of the marked cut in the OV-101 chromatogram were trapped and re-injected into the OS-138 column. For the determination of retention indices, C_8, C_{12} and C_{15} *n*-alkanes were added to the original sample. After trapping of the selected peak group, C_{13}–C_{18} *n*-alkanes were injected into the port between the columns in suitable amounts and trapped together with the sample components. Then the measurement of the chromatogram in the second column, which was performed at the same temperature as the first-stage separation, was initiated by setting of the switch for the simultaneous injection of methane. All separations were carried out isothermally in order to achieve maximum repeatibility and reproducibility of retention indices. By computer evaluation[15], retention indices and ΔI values were obtained, which were compared with tabulated data measured in the same stationary liquids or even in the same columns by using a GC single-column standard system. The results are given in Table I. Peaks 2, 7 and 8, for example, show much higher I values and they are considerably shifted relative to the *n*-alkanes in the stationary liquid with the higher polarity. They contain several polar functional groups. All types of cuts can be taken and enrichment of trace components can also be achieved.

Heart-cutting in a dual-capillary system: Separation of UV photolysis products of methyl isopropyl ether. In chromatogram 1 in Fig. 8a, the reaction mixture was pre-separated in a 20-m polypropylene glycol column and the marked cut was taken from

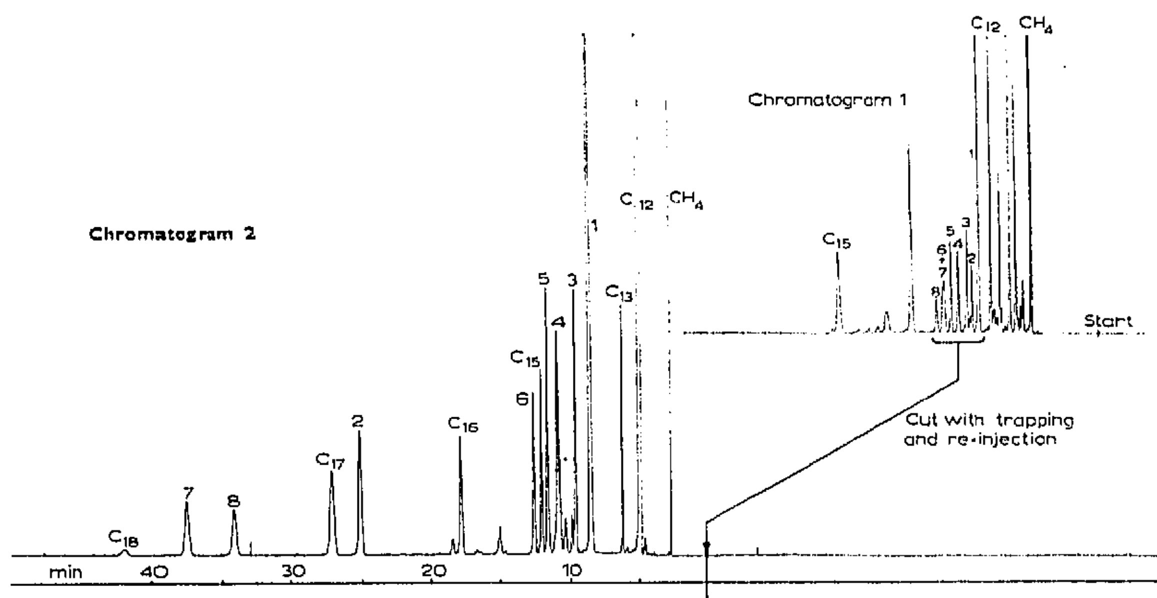

Fig. 7. Isothermal dual capillary column chromatography for identification of selected components of a perfume oil by I_{apolar}, I_{polar} and ΔI data. Chromatogram 1: column, 20 m × 0.25 mm I.D. OV-101, 160°, 0.3 bar N_2; sample, perfume oil + CH_4 + C_8 + C_{12} + C_{15}. Chromatogram 2: Column, 35 m × 0.25 mm I.D. OS-138, 160°, 1.0 bar N_2; sample, cut of chromatogram 1 after trapping and re-injection + $C_{12,13,15,16,17,18}$ + CH_4.

TABLE I

IDENTIFICATION OF SELECTED PEAKS OF PERFUME OIL BY I AND ΔI DATA USING A DUAL COLUMN SYSTEM WITH A NON-POLAR PRE-COLUMN AND A POLAR MAIN COLUNN

Peak No.	$I^{OV\text{-}101}_{160°}$	$I^{OS\text{-}138}_{160°}$	$\Delta I^{OS\text{-}138-OV\text{-}101}_{160°}$
1	1244	1403	159
2	1266	1684	418
3	1281	1440	159
4	1301	1471	170
5	1317	1489	172
6	1330	1512	182
7	1332	1776	444
8	1346	1754	408

the eluate by valveless flow switching. After trapping and re-injection, chromatogram 2 was obtained with a 100-m Marlophen main column.

For comparison the same cut was taken but no trapping was applied (see Fig. 8b). Comparison of chromatogram 2 with that of the same cut in Fig. 8a showes the effectiveness of the trapping and re-injection procedure.

The shape of the solvent peak that originates from the tail of the pre-separation solvent peak becomes "ideal" following the re-injection procedure and no longer overlaps with peaks of higher retentions. The amount of trapped material and there-

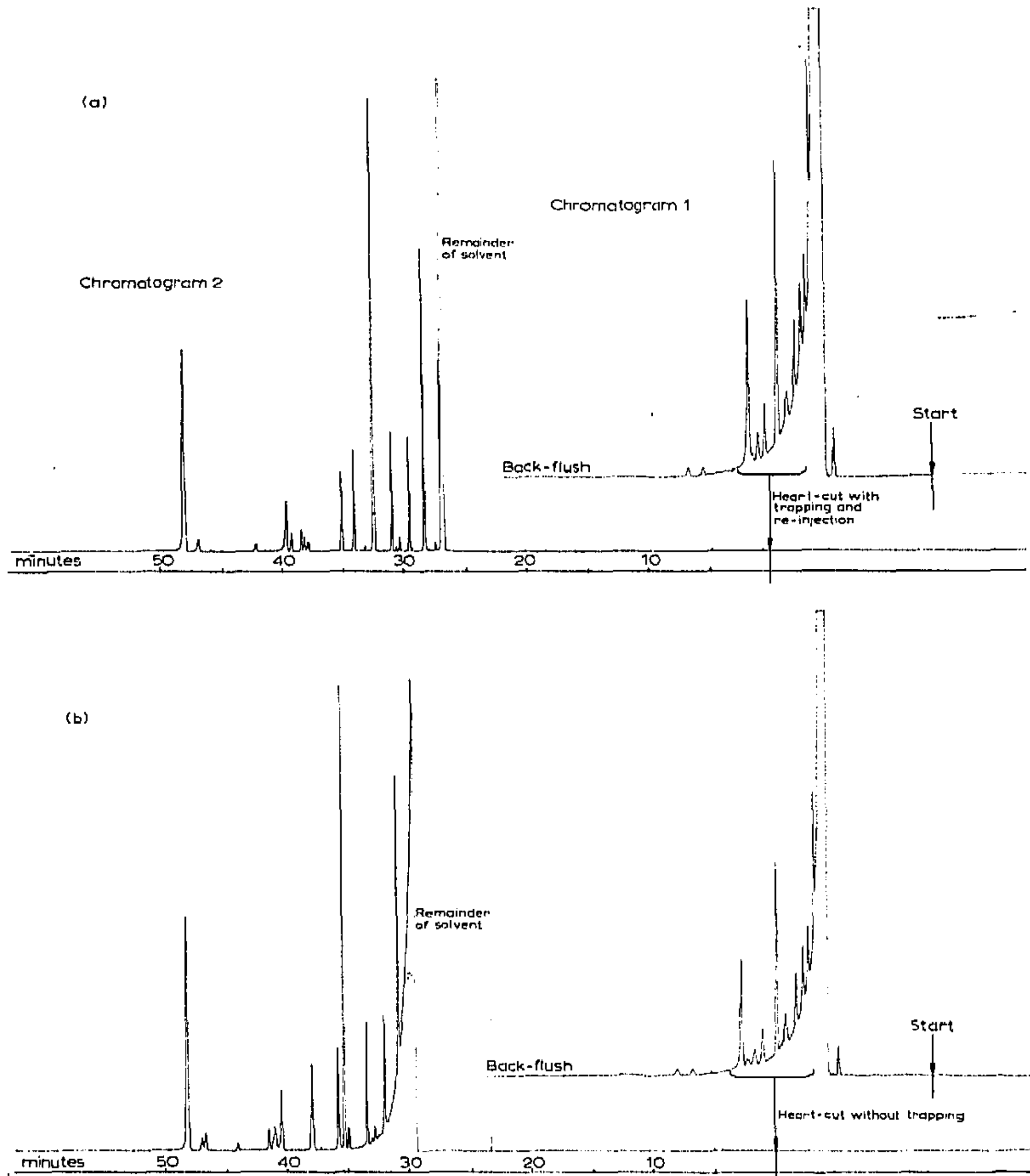

Fig. 8. Isothermal dual capillary column chromatography for separation of UV photolysis products of methyl isopropyl ether. (a), Heart-cut and back-flushing at pre-separation. Chromatogram 1: pre-column, 20 m × 0.25 mm I.D. PPG, 55°, 0.2 bar N_2, 3 μl. Chromatogram 2: main column, 100 m × 0.25 mm I.D. Marlophen, 1.5 bar N_2; sample, heart-cut from chromatogram 1. (b), Same but without trapping of heart-cut.

fore the detectability in trace analysis can be increased considerably by splitless injection in the pre-separation. The quality of the pre-separation chromatogram decreases because of stronger tailing and overlapping of the solvent peak. By cutting and trapping, however, well resolved chromatograms are still attained at much higher peak intensities for the trace components.

CONCLUSION

In this paper, we have tried to show that by double-column GC with glass capillaries as main columns, many of the difficult problems of qualitative and quantitative analysis can be solved, especially when intermediate trapping between the two columns is utilized.

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