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DOUBLE-COLUMN GAS CHROMATOGRAPHY USING PACKED PRE-COLUMNS AND GLASS CAPILLARY MAIN COLUMNS

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SUMMARY

Methods of column switching are described that make possible back-flushing, heart cutting and trapping. Conventional packed columns are employed as pre-columns for their high sample capacity, and glass capillary columns are used as the main columns for their high separation efficiency.

Some typical examples of the application of double-column gas chromatography are presented: (1) solvent cutting for identification and exact quantitative determination of a phosphorus ester impurity in a sample of wheat flour (including trapping); (2) separation of trace amounts of methyl esters of fatty acids by means of back-flushing and trapping; (3) enrichment technique using trapping of trace elements in the front section of the capillary (plus solvent cutting, multiple injection and back-flushing); and (4) coupling a nitrogen-selective detector to the capillary main column to gain additional information. To illustrate the trapping effect, the separation number was determined with and without trapping.

INTRODUCTION

Techniques for switching separating columns were introduced into gas chromatography (GC) by Deans[1,2], Column-switching techniques have been used successfully in process gas chromatography for several years[3], but they have found only reluctant acceptance in routine analytical laboratories. The reason for the latter is that in the past manufacturers of equipment did not offer such systems and many analysts were discouraged from constructing them in-house because they lacked the technical know-how required.

The work of Schomburg and co-workers[4–7] resulted in a wide appreciation of two-dimensional gas chromatography and as a result such systems have since been introduced into the routine laboratory[8].

Two systems of switching separating columns are presented here that can be built in-house into almost all gas chromatographs using commercially available components and in which conventional packed columns are combined with glass capillary separating columns to produce a two-dimensional chromatographic system.

EXPERIMENTAL AND RESULTS

Procedure

When packed columns are coupled with glass capillary columns, the high capacity of the former and the high efficiency of the latter are simultaneously exploited. Packed columns are better suited as pre-columns for separating interesting trace components from solvents, major components or, for example, excess of derivitization reagents than are capillary columns, especially when wide differences exist in concentration, polarity and/or volatility. The polarity of the packed pre-column should accordingly be adjusted to the compound or compound group of interest.

The interesting compounds in the chromatogram are transferred from the pre-column to the main column and are separated there. After pre-separation, either the uninteresting compounds, still on the pre-column, can be back-flushed or, when interesting trace components are obscured by major components or solvents, the complete chromatogram can be obtained by heart cutting. The inlet section of the capillary column should be surrounded by a chilling device with which the interesting groups of peaks can be "frozen out" (trapped) and held there. Two results can be accomplished with the trapping method:

(1) Enrichment of trace components: in combination with back-flushing or heart cutting, there is the additional possibility of preventing high-boiling components and solvents from entering the capillary.

(2) Without the freeze trap, the sample feed from the packed pre-column to the capillary would be too broad; with trapping equipment, a "re-injection effect" at the front of the column is obtained for all practical purposes.

The various types of programme with the corresponding settings (open–shut) of the solenoid valves are presented in Table I and the apparatus is illustrated in Fig. 1.

Either splitless or split injection is possible. For splitless injection, the solenoid valves (SV) and the needle valves (NV) are set as follows: SV_1, open; $SV_{2,3,4}$ and NV_3, shut. For split injection, which is the normal arrangement, the following valve settings are selected: SV_1, open; $SV_{2,3,4}$, shut; NV_3, adjusted so that 0.5–1.5 ml/min of carrier gas flows through the capillary; at a carrier gas flow of *ca.* 30 ml/min, this NV_3 setting gives a splitting ratio of *ca.* 1:30.

The septum flushing of I_2 (*ca.* 0.5 ml/min) is regulated with NV_4. Moreover,

TABLE I

ADJUSTMENT OF THE SOLENOID VALVES FOR THE VARIOUS PROCEDURES

Procedure	*Solenoid valves (SV)*	
	Open	*Shut*
Heart cutting	1, 3, 4	2
Back-flushing	2, 4	1, 3
Trapping	1	2, 3, 4
Separation using capillary column only*	2, 4	1, 3
Separation using pre-column only**	1	2, 3, 4

* I_2 used for sample injection.
** Use only the D_1 chromatogram.

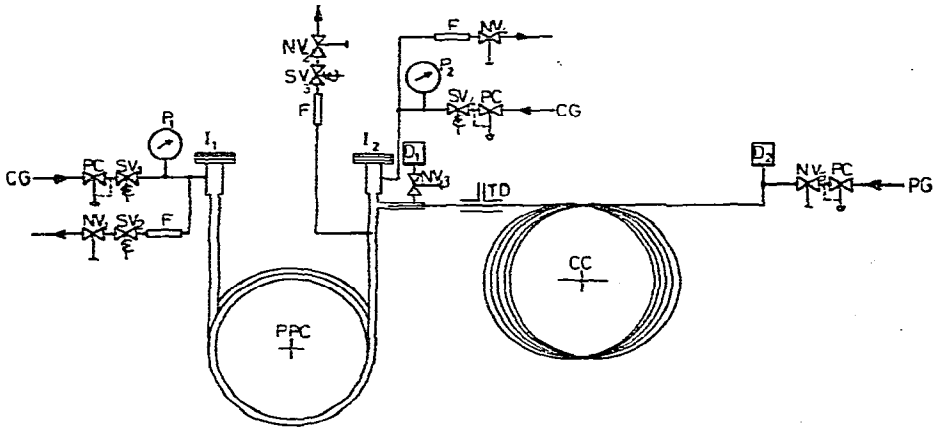


Fig. 1. Two-column system for gas chromatography using a conventional packed pre-column coupled with a glass capillary main column with a trapping device between the two columns. CC = capillary column; CG = carrier gas; D_1/D_2 = detectors; F = filter; I_1/I_2 = injection blocks; NV = needle valve; P_1/P_2 = pressure gauges; PC = pressure controller; PG = purge (make-up) gas; PPC = packed pre-column; SV = solenoid valve; TD = trapping device.

this flushing prevents the occurrence of unswept volumes from which substances might gradually vaporize into the chromatographic system.

The filters of NV_4 and SV_2/NV_1 are filled with activated charcoal–quartz-wool and adsorb substances flushed from the system and protect the valves.

Apparatus

Precise switching times are a necessary pre-condition for obtaining good reproducibility of the measurements. Flow switching is controlled by a timer.

The re-fitting shown in Fig. 1 was carried out on a Packard Type 419 (previously Becker, Delft, The Netherlands.) The equipment is supplied with two injection blocks and two flame-ionization detectors (FIDs); the latter can be replaced with nitrogen- or phosphorus-selective FIDs as desired. A flame-photometric detector (FPD) can also be adapted.

As can be seen from Fig. 1, there are two injection blocks, I_1 and I_2, one at the front of the pre-column and one at the end. One-dimensional chromatography using the capillary column only is possible by injecting the sample at I_2 (see Table I). Two detectors (D_1 and D_2) permit the operator to monitor the pre-separation and main separation and also the back-flushing and heart-cutting operations. A glass T-piece connects the two columns. Only detector D_1 is coupled to the system by a short stainless-steel capillary (I.D. 0.2 mm); no other metallic surfaces are employed.

A copper tube (length 40 mm; I.D. 10 mm; wall thickness 1 mm) is used for the freeze trap. The coolant passes through a 1/8-in. union at the centre of this tube and blows from there over the capillary. The coolant is liquid air obtained by passing air from a compressed air cylinder through a copper spiral cooled by the liquid nitrogen in which it is immersed. When the eluate from the pre-column is frozen out at the front of the capillary column, a temperature of *ca.* −150° prevails in the trap. At the end of the trapping procedure, the coolant feed is suddenly interrupted by an on–off valve. The capacity of the column oven heating system is sufficient under these con-

ditions for typical chromatograms of the separation in the capillary column to be obtained. It was not necessary to blow hot air or hot nitrogen into the freeze trap section of the capillary inlet.

Examples of application

Solvent cutting for positive identification and exact quantitative determination of triethyl phosphate in a sample of wheat flour (plus trapping). The four chromatograms in Fig. 2 (A–D) illustrate the effect of solvent cutting. The acetone extract of a flour sample was injected into injection block I_1 (see Fig. 1). After the solvent cut, the eluate from the pre-column was frozen out in the front section of the capillary main column before the actual chromatography. The major portion of the solvent was vented through SV_3/NV_2 (see Fig. 1).

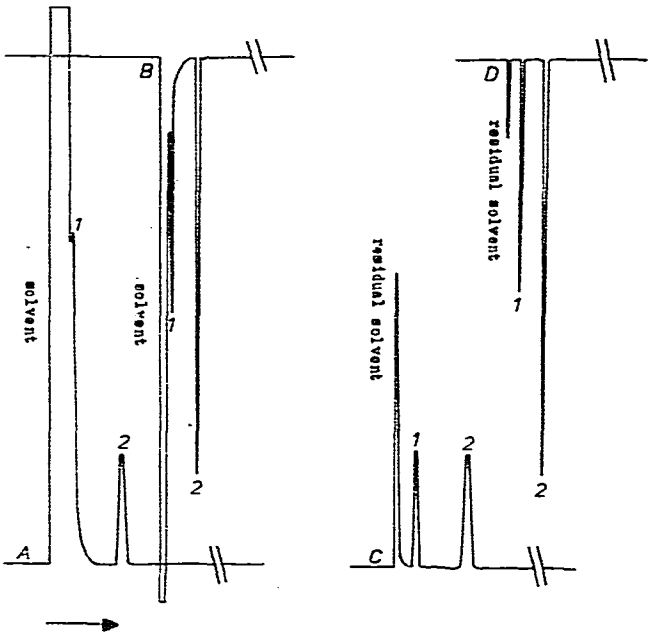


Fig. 2. Solvent cutting for the exact qualitative and quantitative determination of triethyl phosphate in flour. A, Chromatogram for the packed pre-column; B, chromatogram for the capillary main column; C, chromatogram for the packed pre-column after solvent cutting; D, chromatogram of the capillary main column after solvent cutting. Peaks: 1 = triethyl phosphate; 2 = triethyl dithiophosphate. Pre-column: length 1 m; I.D. 3 mm; glass; 10% SE-30 on Chromosorb W HP, 100–120 mesh. Capillary: length 15 m; I.D. 0.29 mm; glass; FFAP. Programming of column oven: 110–180° 8-min initial isothermal phase; heating rate 5°/min. Detectors (D_1/D_2): 2 FID, 270°. Injection blocks: 220°. Carrier gas, pre-column: He 25 ml, min. Capillary column inlet pressure: 0.6 bar. Splitting ratio: 1:30. Back-flush: 8 min after injection. Recorder: 1 mV full-scale, chart speed 5 mm/min.

Separation of trace amounts of methyl esters of fatty acids by means of back-flushing and trapping. Only the identification of oleic acid, linoleic acid and linolenic acid was of interest in the measurement illustrated in Fig. 3. The uninteresting major component (stearic acid) was back-flushed (see Fig. 3b). To save analytical time, the

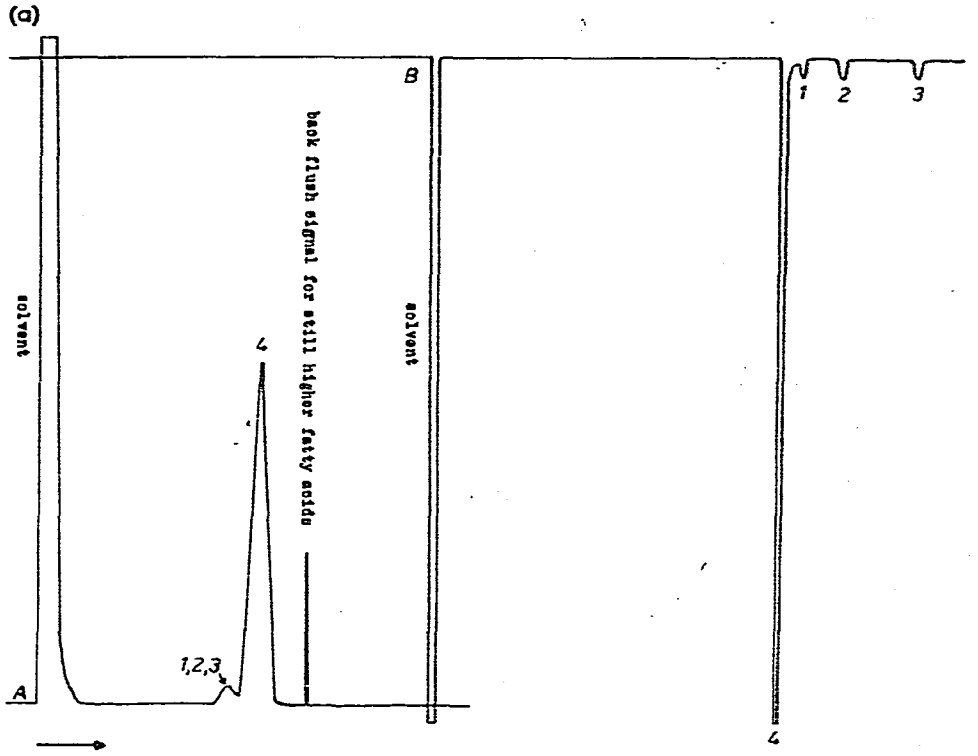


Fig. 3.

(Continued on p. 72)

still higher fatty acids in this example were also back-flushed out of the packed pre-column. For back-flushing, SV_4 and SV_2 were opened and, simultaneously, SV_1 and SV_3 were closed (*cf.*, Table I and Fig. 1). An interesting aspect of this example is the difference in the retention behaviour of methyl stearate on the packed pre-column (SE-30) and on the capillary main column (OV-225). Stearic acid comes through *before* the three unsaturated acids on the latter column but *after* them on the pre-column (Fig. 3a). This is an example of the use of separating columns of different polarities in two-dimensional GC in order to ensure the accuracy of an analytical result.

Enrichment technique using trapping of trace elements in the front section of the capillary (plus solvent cutting, multiple injection and back-flushing). Fig. 4 is an example of the use of the enrichment technique. Waste water containing 250 ppm (0.025%) of Sulfotepp was injected directly into the chromatograph four times, 1.0 μl each time, at 30-sec intervals. Valve system SV_3/NV_2 was opened for 4.5 min to remove the water and the components that are eluted prior to Sulfotepp from the chromatographic system, then SV_3 was closed again. Four peaks appeared at detector D_1 (see Fig. 1) corresponding to the individual injections. As soon as D_1 had returned to the baseline, valves SV_4 and SV_2 were opened and SV_1 simultaneously shut to back-flush the high-boiling components still on the pre-column. Thus, solvent cutting, trapping and back-flushing are combined in this example.

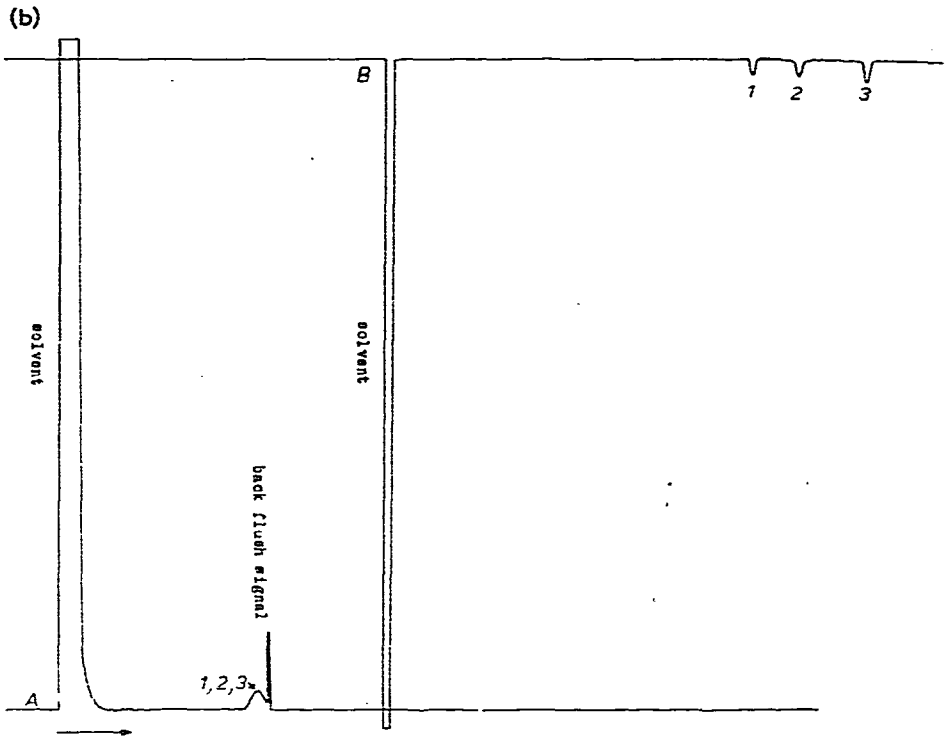


Fig. 3. (a) Separation of trace amounts of fatty acid esters. A, Chromatogram for the packed pre-column; B, chromatogram for the capillary main column. Peaks: 1 = oleic acid; 2 = linoleic acid; 3 = linolenic acid; 4 = stearic acid as major component. Pre-column as in Fig. 2. (b) Separation of trace amounts of fatty acid esters with back-flushing of the major component (stearic acid). A, Chromatogram for the packed pre-column; B, chromatogram of the capillary main column. Peaks: 1 = oleic acid; 2 = linoleic acid; 3 = linolenic acid. Capillary: length 28 m; I.D. 0.25 mm; glass; OV-225. Column oven temperature: 190°, isothermal. Detectors: 2 FID, 250°. Injection blocks: 200°. Carrier gas, pre-column: He, 25 ml/min. Capillary column inlet pressure: 0.6 bar. Splitting ratio: 1:25. Recorder: 1 mV full-scale, chart speed 5 mm/min.

Determination of separation number with and without trapping to illustrate the trapping effect. A comparison of separation numbers obtained for C_{14}/C_{15} *n*-alkanes with and without trapping (see Fig. 5) indicates the necessity of trapping the eluate from the pre-column in the front section of the capillary.

A separation number of 34.5 was found when trapping was used and 14 without trapping. Thus, only when trapping is used is it possible to exploit the high efficiency of the capillary column in a two-column switching system consisting of a packed pre-column and a capillary main column. The peak width (b_0) without trapping would be too large because of "sampling" of the capillary by the packed pre-column being too broad. Switching itself cannot influence the chromatography because switching of the valves is effected before chromatography on the capillary column and during trapping. Trapping results in a kind of "re-injection" effect[5] and is a sampling technique which can be called "ideal", as possible dead volumes are eliminated.

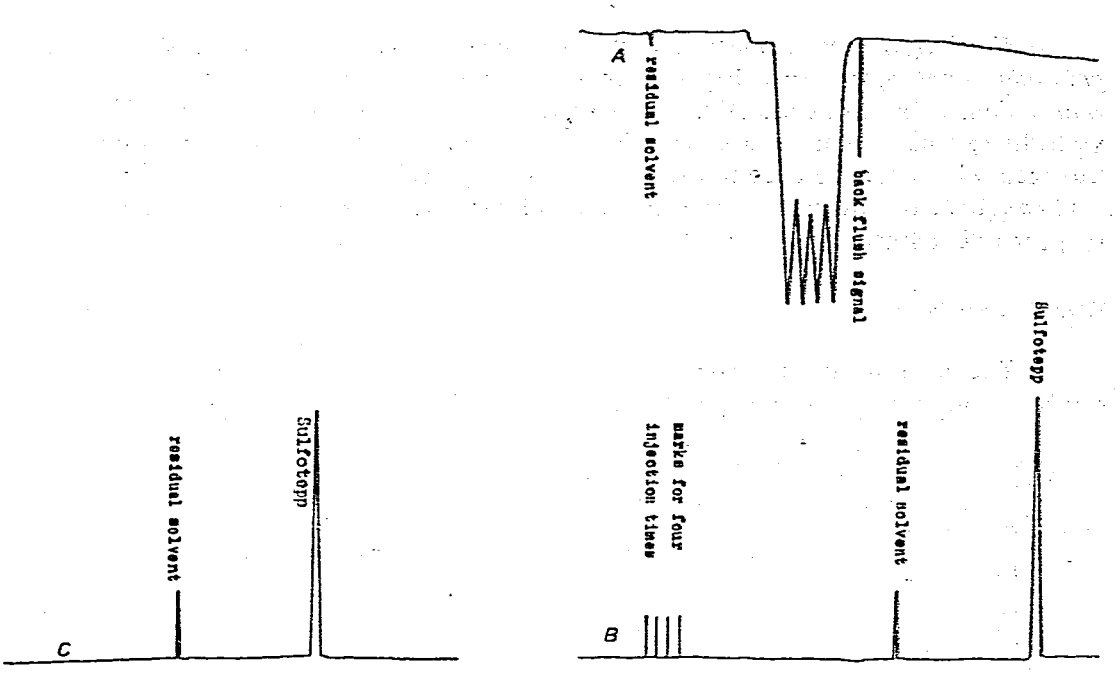


Fig. 4. Sulfotepp in waste water. Application of the enrichment technique using trapping at the front section of the capillary. Sulfotepp was injected four times, 250 ng each time, at intervals of 30 sec. A, Pre-column chromatogram; B, capillary column chromatogram; C, 1 μg of Sulfotepp injected in a single injection. Pre-column: as in Fig. 2. Capillary: length 15 m; I.D. 0.29 mm; glass; FFAP. Programming of column oven: 150–200°; 9-min initial isothermal phase; heating rate 5°/min. Detectors: 2 FID, 270°. Injection blocks: 220°. Carrier gas, pre-column: He, 25 ml/min. Capillary column inlet pressure: 0.6 bar. Splitting ratio: 1:16. Valve: SV_3 open for 4.5 min. Recorder: 1 mV full-scale, chart speed 5 mm/min.

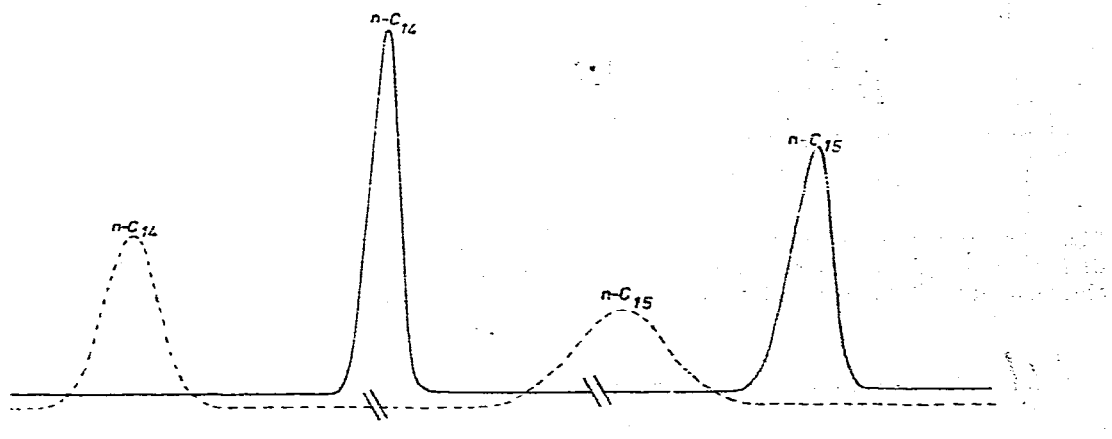


Fig. 5. Determination of the separation number for C_{14}/C_{15} *n*-alkanes in the two-dimensional system with trapping (solid line) and without trapping (broken line). Separation number with trapping, 34.5; without trapping, 14. Chart speed: 60 mm/min. Pre-column: as in Fig. 2. Capillary: length 40 m; I.D. 0.25 mm; glass; OV-101.Column oven temperature: 110°, isothermal. Detectors: 2 FID, 250°. Injection blocks: 220°. Carrier gas, pre-column: He, 25 ml/min. Capillary column inlet pressure: 1.0 bar. Splitting ratio: 1:20. Recorder: 1 mV full-scale, chart speed 60 mm/min.

Coupling nitrogen-selective detector (NFID) to the capillary main column to gain additional information. Fig. 6 is an *example of how additional analytical information is obtained* by using selective detectors in two-column systems. The NFID coupled with the capillary main column in this example indicates those substances containing nitrogen which can be chromatographed with high selectivity. Components that are FID-sensitive but do not contain nitrogen either give no signal or a negative signal (*e.g.*, residual solvent).

CONCLUSION

The purpose of this paper is to present an overview of the possibilities of double-column gas chromatography with a packed pre-column and a capillary main

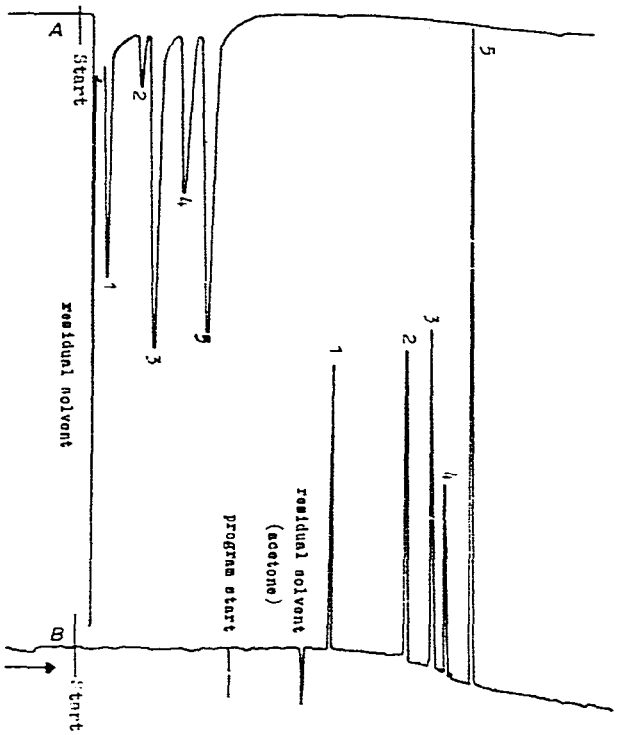
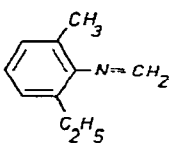


Fig. 6. Separation of reaction products and reactants as a criterion for process improvement decision-making; azomethine synthesis (intermediates for a herbicide synthesis). A, Pre-column chromatogram; B, capillary column chromatogram. Solvent cutting for 30 sec after injection. Peaks:

1 = aniline; 2 = unknown; 3 = 2,6-dimethylaniline; 4 = Schiff's base  ; 5 = 2-ethyl-6-methylaniline. Pre-column: as in Fig. 2. Capillary: length 40 m; I.D. 0.25 mm; glass; OV-101. Programming of column oven: 430 sec initial isothermal phase at 80°; then at heating rate of 5°/min to 150°. Detectors: 1 FID (for D_1, see Fig. 1) and 1 NFID (for D_2), temperature 250°. Injection blocks: 200°. Carrier gas, pre-column: He, 25ml/min. Capillary column inlet pressure: 0.8 bar. Splitting ratio: 1:20. Recorder: 1 mV full-scale, chart speed 5 mm/min.

column. It has been shown that by using automatic switching satisfactorily reproducible results can be obtained.

The coefficient of variation of the retention times is $<3\%$, even under the least favourable conditions, and $<1\%$ under normal circumstances. This guarantees a positive identification of substances based on their retention data.

The examples of applications show that column switching techniques can possibly eliminate the necessity for extractions and clean-up of extracts.

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