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TRACE ANALYSIS IN COUPLED SYSTEMS

TOTAL TRANSFER OF TRACES FROM PACKED TO CAPILLARY COLUMNS

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SUMMARY

The known advantages and disadvantages of packed and capillary columns prompted an attempt to combine the two types. Owing to the different carrier gas flows, this was only possible at the expense of sample, *i.e.*, a higher detection limit. The newly developed trap described is based on the "live principle" and enables components to be transferred from a packed to a capillary column without any loss. It can accommodate both the high flow-rates from the packed column and the low flow-rates supplying the capillary column.

INTRODUCTION

It has been shown in earlier papers[1–4] that the separation efficiency of a gas chromatographic (GC) system can be considerably improved by using column switching. "Live" column switching, as developed by us in conjunction with Schomburg and Weeke, has particular advantages over previous procedures. These advantages result from the following design features: (i) use of a coupling device with a very small volume; (ii) avoidance of any dead-volume; (iii) no valves in the separation passage or in the capillary tubes to the detectors; (iv) high switching speed without the baseline being affected by pressure jumps; (v) monitor-detector directly at the coupling of the separation columns to permit observation of the separation after the first column without delaying the analysis and also to permit fixing the switching time exactly; (vi) complete transfer of the injected sample to the main or monitor-detector to permit quantitative analyses; (vii) use of inert materials (glass, quartz, platinum) in the separation passages leaves the form of the peaks unaffected.

Fig. 1. shows the coupling of two capillary columns designed for the "live" column switching system, with which both backflush and cut can be performed. One of the problems in the use of capillary columns is the sample injection, which is performed in various ways[4,5], the most common being the split method.

There are several reasons for avoiding direct sample injection into the capillary column. This becomes particularly evident in trace analysis when sample volumes must be used, that are too large for direct injection or when a sample residue which

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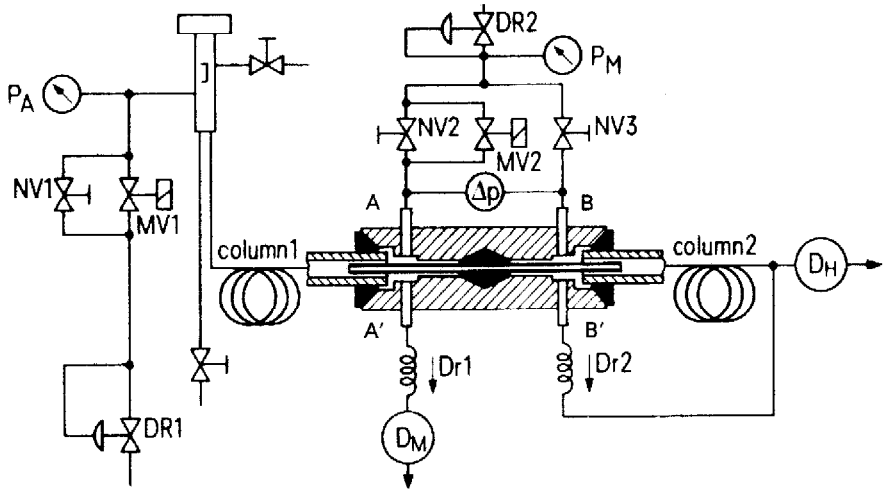


Fig. 1. "Live" column switching system; connection of two capillary columns. DR1, DR2 = pressure controller carrier gas; NV1,2,3 = needle valves; MV1,2 = solenoid valves; J = injector: P_A, P_M = pressure gauge; ΔP = differential pressure gauge; A, B = carrier gas inlet; A', B' = carrier gas outlet; Dr1,2 = capillary restriction; D_M = monitor detector; D_H = main detector.

does not evaporate impairs the separating qualities of the capillary. It is therefore necessary to couple packed columns with capillary columns[1-3]. When this is done, large volumes can be injected, and components which do not evaporate will not noticeably interfere. There is also the further advantage that the division of the flow takes place in the live coupling device, separate from the evaporation. This eliminates any discrimination during the division. It must, however, be noted that sample is lost in proportion to the flow in both columns.

The substances transferred must be focused at the beginning of the capillary column by means of a trap (Fig. 2). A better solution, particularly in trace analysis,

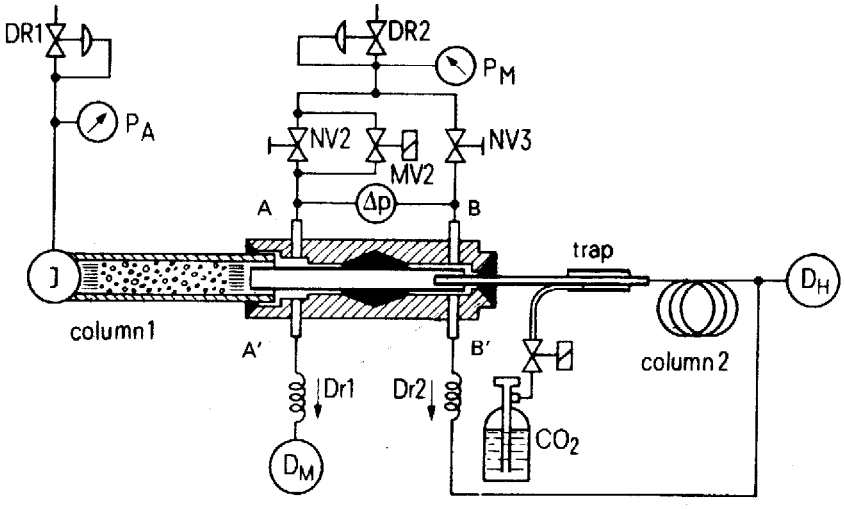


Fig. 2. Live column switching system; connection of packed and capillary columns with a split at the T-junction (partial sample transfer).

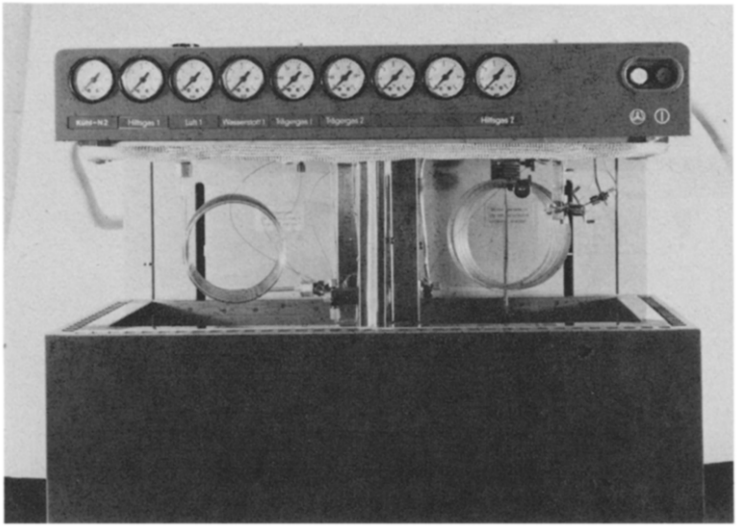


Fig. 3. SiCHROMAT-2 with total transfer trap.

is to transfer individual components or groups of components to the capillary column. The procedure necessary to achieve this is described in this paper.

EXPERIMENTAL

Apparatus

The experiments were carried out by the use of a Siemens SiCHROMAT-2 gas chromatograph with a double oven (Fig. 3). This permits the optimum adjustment of the separation temperatures for the packed and capillary columns.

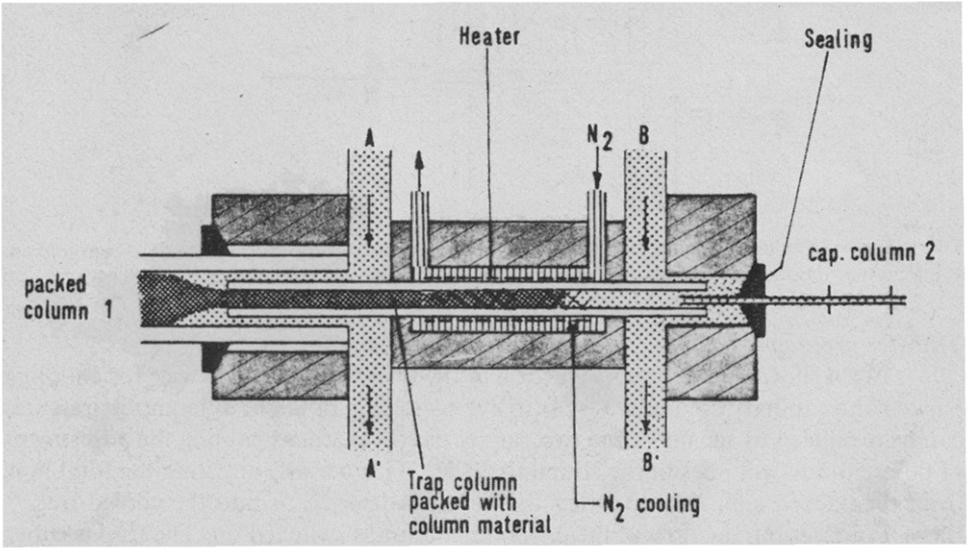


Fig. 4. Principle of total transfer trap. A, B = inlet auxiliary carrier gas; A' = outlet to monitor detector; B' = outlet to main detector.

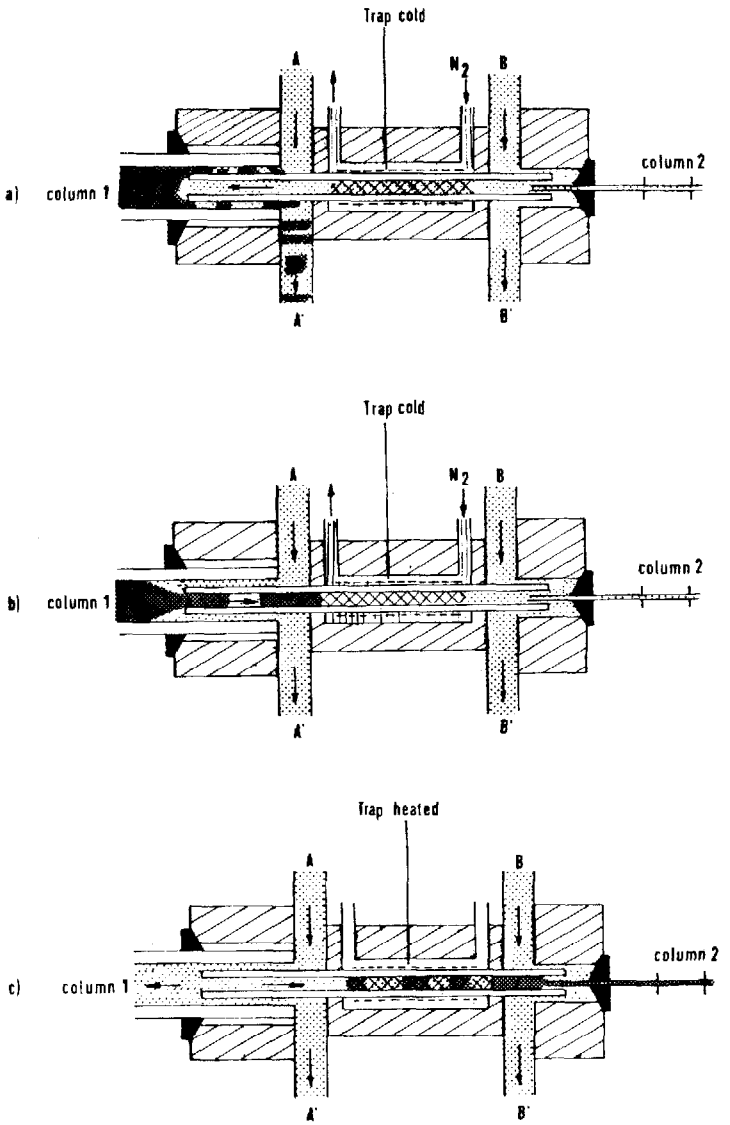


Fig. 5. Main functions of the total transfer trap. a, Sample to monitor-detector; b, sample to trap column; c, injection of the sample into column 2 and backflush of column 1.

Transfer procedure

Fig. 4 shows the basic construction of the transfer coupling device for coupling packed and capillary columns. Just as in live switching, different differential pressures can be produced by means of the two carrier gas flows, thus enabling the adjustment of different flow volumes in the coupling device. This permits directing the total flow from the packed column into either the monitor-detector or into the cooled trap.

For ejection, the flow of the capillary column is switched on. The trap is either temperature-programmed or ballistically heated by a fast electric heater and the sub-

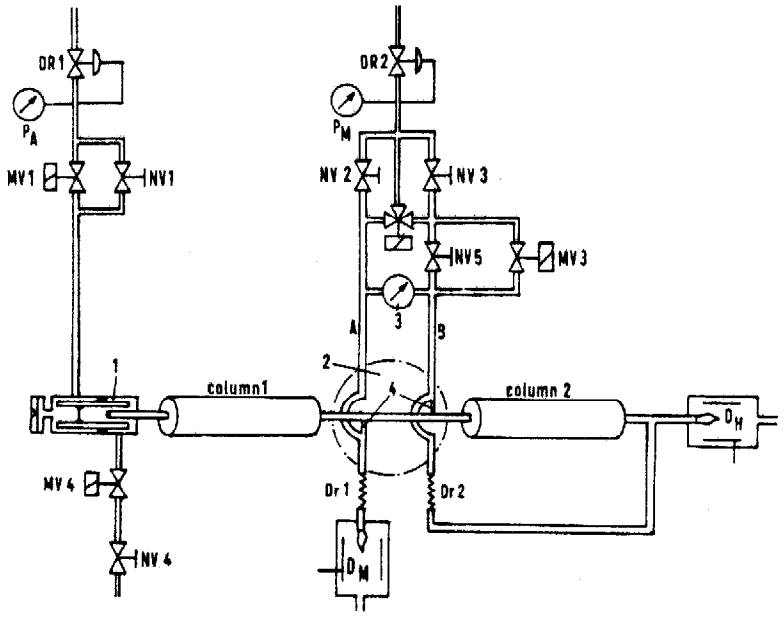


Fig. 6. Live column switching system: connection of packed and capillary column; total sample transfer. P_A, P_M = Pressure indicators; MV = solenoid valve; NV = needle valve; DR = pressure controller carrier gas; Dr = capillary restriction; 1 = injector; 2 = transfer coupling device; 3 = differential pressure gauge; 4 = connections. D_M = monitor-detector; D_H = main detector.

stances are desorbed. Thus, the total volume of the substance of interest can be injected onto the second column, the capillary column. The peak width can, if necessary, be improved by installing an additional trap ahead of column 2. This is best achieved by cooling the beginning of the capillary directly.

The function of the transfer coupling device is presented in Fig. 5a, b and c. In Fig. 5a the auxiliary gas pressure at point B is somewhat greater than at point A. As a result a small amount of auxiliary gas flows through the cold-trap from B to A. Everything coming from the column is then carried to the outlet A and to the monitor-detector with the auxiliary gas A. Column 2 is supplied by a part of auxiliary gas B. This permits the separation in column 1 to be observed at the monitor-detector. Fig. 5b shows the trapping of the sample of interest. Here, the auxiliary gas pressure at point A is considerably higher than at B, so that the entire gas flow coming from column 1 is transferred to the cold-trap and frozen out or adsorbed. Fig. 5c shows the transfer of the sample from the trap to column 2. Here, column 1 is simultane-

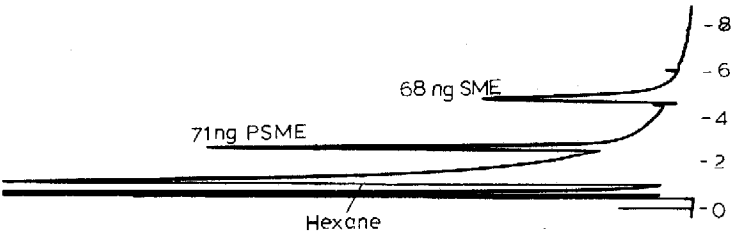


Fig. 7. Separation of palmitic acid methyl ester and stearic acid methyl ester on column 1, detected with monitor detector.

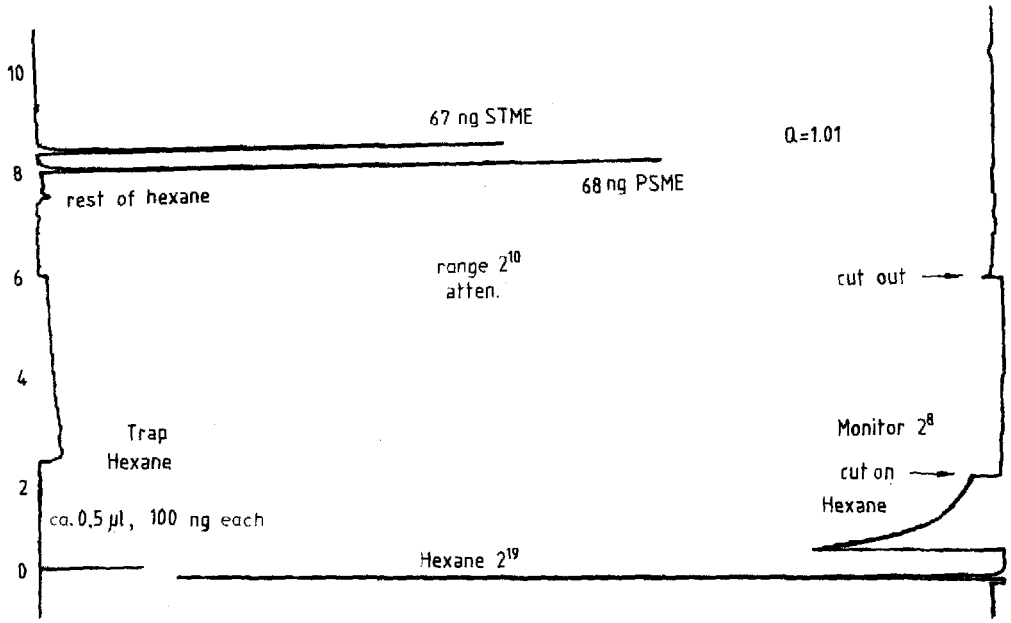


Fig. 8. Separation of PSME and StSME on a packed column (right side) and a capillary column (left side) by transferring the two esters to the capillary.

ously backflushed by the lowering the input pressure. This cleans the column for the next injection and prevents an unfocused component from being transferred to the capillary column during the desorption phase. The auxiliary gas pressure at A is somewhat higher than at B and, therefore, the trap is flushed out with the gas flow adjusted to the capillary column (column 2). Both, Duran glass and quartz tubing with an inner diameter up to 1.8 mm can be used for making the trap column. It can be packed with column materials, wall-coated or left empty.

Analytical system

Fig. 6 shows the construction of the separation system. The main difference between this system and the previously described live-switching system is not only in the heatable coupling tube but also in an additional solenoid valve, MV3, which permits the adjustment of the flow volume between the packed and the capillary column.

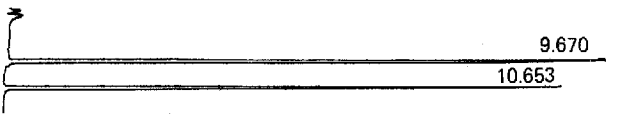
RESULTS AND DISCUSSION

The advantage of coupling packed and capillary columns is the relatively problem-free introduction of larger samples into packed columns. Only the components of interest enter the trap, and these are then injected into a highly efficient capillary and separated there. At the same time, switching permits the transfer of components of interest to the capillary column without any loss of separation efficiency or column life.

The analytical properties of the trap column are much more difficult to establish and must be closely examined in each individual case. In particular, the following must be noted: (i) trap temperature; (ii) temperature program for ejection; (iii) trap capacity, depending on the components of interest; (iv) type of trap column packing; and (v) recovery rate.

08.11.82 12.46 TRAP PRNR 1 LFNR 1
KANR 2 MTNR 3 RKNR 2 ZKNR 2 EICH 2 MISA 0 BERM E

NO.	NAME	CONC.	RET. TIME		AREA	FL/H	TR
1	PALMITAT	156.727	9.452	1	8.9916 E-02	0.054	BB
2	STEARAT	170.992	10.539	R1	9.2288 E-02	0.064	BB
		327.723	100.000		1.8220 E-02		
			REST		0.0000 E-00		



08.11.82 13.27 TRAP PRNR 1 LFNR 2
KANR 2 MTNR 3 RKNR 2 ZKNR 2 EICH 2 MISA 0 BERM E

NO.	NAME	CONC.	RET. TIME		AREA	FL/H	TR
1	PALMITAT	158.102	9.665	1	9.0703 E-02	)0.057	BB
2	STEARAT	172.773	10.645	R1	9.3248 E-02	0.062	BB
		330.878	101.000		1.8395 E-03		
			REST		0.0000 E-00		

08.11.82 14.16 TRAP PRNR 1 LFNR 3
KANR 2 MTNR 3 RKNR 2 ZKNR 2 EICH 2 MISA 0 BERM E

NO.	NAME	CONC.	RET. TIME		AREA	FL/H	TR
1	PALMITAT	157.504	9.665	1	9.0363 E-02	0.057	BB
2	STEARAT	171.797	10.645	R1	9.2720 E-02	0.062	BB
		329.306	101.000		1.8308 E-03		
			REST		0.0000 E-00		

Fig. 9. Repeatability of the total transfer trap unit. FL/H = Peak area to peak height ratio. TR indicator beginning and end of peak evaluation. BB = evaluation from one baseline point to another, T characterises a minimum between two peaks, etc.

No general statement can be made about these data. They must be ascertained by the user for each particular analytical application. One great advantage is that the trap column is only loaded with the components of interest. As a result, the capacity is not taken up by irrelevant components.

A simple example may be given to demonstrate the efficiency of complete transfer from a packed column to a capillary column.

Analytical data

Apparatus: Siemens SiCHROMAT-2.

Oven 1. Column: 2 m × 2 mm I.D. glass, 5% SE-30 on Chromosorb G. Carrier gas: nitrogen, 20 ml/min. Temperature: 200°C, isothermal.

Trap column. Effective trap: 10 mm × 1.8 mm I.D. 5% SE-30 on Chromosorb G. Carrier gas: nitrogen, 30 ml/min during trapping, 2.5 ml/min during heating.

Oven 2. Column: 20 m × 0.28 mm I.D. OV-1 glass capillary. Carrier gas: nitrogen, 2.8 ml/min. Temperature: 140–180°C, at 5°C/min. Sample: 200 ng palmitic acid methyl ester (PSME) and stearic acid methyl ester (StSME) in hexane.

Test procedure

The behaviour of the trap during adsorption and desorption was tested as follows:

(i) Mixtures of 2, 5, 10, 20, 50, 100 ng/μl

(ii) Sample volumes of 0.5, 1, 1.5 and 2 μl

(iii) Repeated injection with accumulation of the two esters.

It was observed that the peak area ratio in the range of from 2 to 100 ng fluctuated less than ±5%, and that the ratio of the volume injected to the amount determined was linear.

Fig. 7 shows the separation of the sample on the packed column, as recorded by the monitor-detector. In the measuring range 2^8, 71 ng PSME and 68 ng StSME are observed to be incompletely separated from the solvent. If the two esters are then trapped and transferred to the capillary column, as described above, the chromatograms shown in Fig. 8 result. To the right, the monitor-detector signal can be seen. Apart from the solvent (hexane) nothing else can be recognised at sensitivity 2^8, *i.e.*, both esters were completely transferred to the trap. To the left, the main detector signal can be seen. The first peak to appear is the hexane remaining with the two esters. It is as wide as the trap-time, because hexane is practically not adsorbed by the trap packing used. The hexane peak before the two esters corresponds to the amount of hexane taken up by the trap column. The two esters follow: they have been completely separated from the remaining hexane and are very narrow ($b_{1/2}$ less than 2 sec).

It is worth noting that this narrow half-peak width (measuring range 2^{10}) has increased the detection limit by a factor of 5. Another important attribute is the repeatability. Fig. 9a, b and c show, *e.g.*, three identical analyses with a repeat accuracy of *ca.* 0.5%.

CONCLUSION

The coupling of packed columns with capillary columns via a trap, which makes possible a total transfer, opens new possibilities for the trace analysis of samples with a troublesome residues by capillary GC. In the future, the properties of different packing materials for trapping materials with high boiling points and high polarity will be investigated. The accumulation of the traces in the trap column after repeated injections into the packed column will also be investigated.

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