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SWITCHING VALVE FOR GLASS CAPILLARY GAS CHROMATOGRAPHY

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SUMMARY

Although valves are used in high-performance liquid chromatography and process gas chromatography (GC) on packed columns, valves were not appropriate for use in capillary GC because of excessive internal volumes and the dead volume in the connections. A new valve suitable for use with narrow-bore open-tubular columns was tested for inertness by means of the Grob test. Dead volume was investigated by peak symmetry measurement. As an application, the valve was used for a backflush experiment. The applicability as injection valve was tested by a reproducibility test.

INTRODUCTION

The use of valves for injection and column switching is common practice in high-performance liquid chromatography (HPLC) and gas chromatography (GC) with packed columns. Valve switching is much easier to instal and operate than flow switching ("Deans switching")[1]. However, valves are not suitable for use with narrow-bore capillary columns, because of the risk of band broadening due to large internal volumes and relatively large dead volumes associated with connections.

Recently, Valco Instruments (Houston, TX, U.S.A.) introduced a six-port valve, designed for use with 0.3–0.8 mm O.D. small-bore (0.25 mm) open-tubular columns (type N6WT-FSR). The valve has a 6.25-mm diameter rotor, made of fluorcarbon-filled cross-linked polyimide resin. The gas path volume between two connected ports is less than 0.2 μl. The residence time within the valve at typical flowrates (1–4 ml/min) is approximately 12 msec. A special Vespel ferrule system with 1/32-in fittings is used to eliminate unswept volumes from the connections. The valve can be operated remotely by means of an air actuator, which permits electronic controlled switching. With this valve, a wealth of switching systems becomes possible for narrow-bore open-tubular columns. Among these are backflush, stripping, the use of more than one type of column in one gas chromatograph, selection of injectors and detectors and heart cutting. It would also be possible to reduce the analysis time by multiple short-pass chromatography[2,5].

INERTNESS

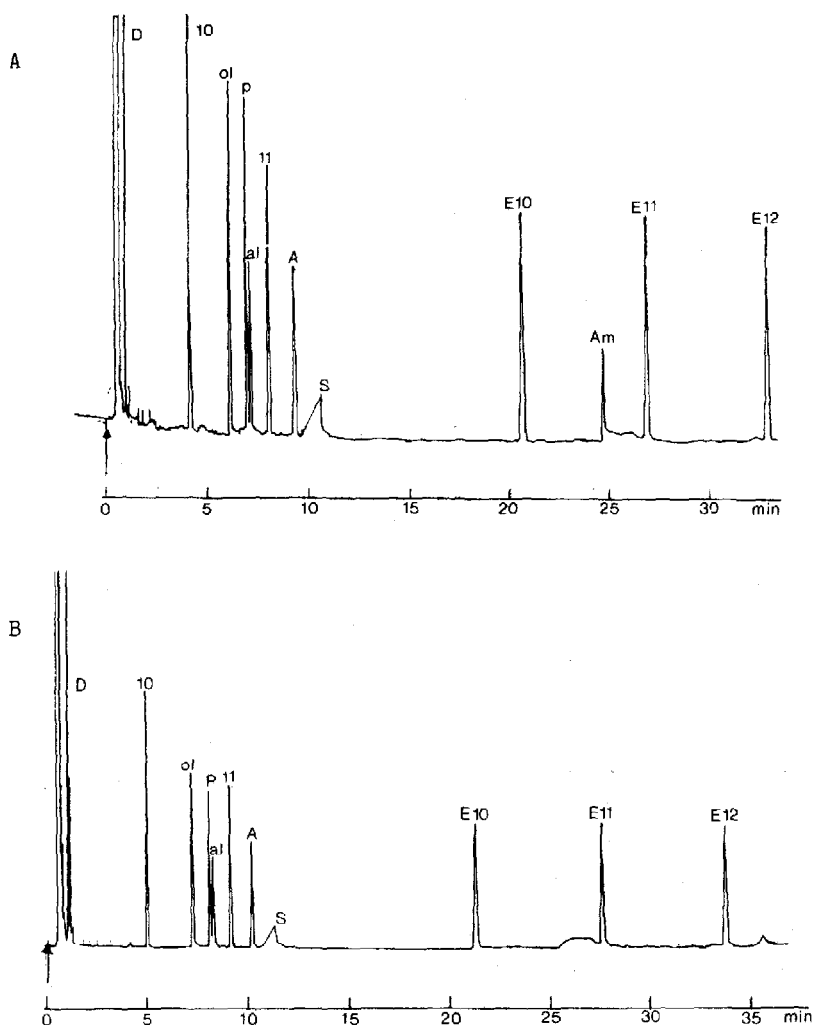An important feature of a valve is inertness. As the valve is part of the flow

Fig. 1. Grob test on 25 m × 0.22 mm I.D. CP™ Sil 5 CB fused-silica WCOT column (film thickness 0.15 μm). Gas chromatograph, Intersmat 120; carrier gas, hydrogen, 2.2 kg/cm²; oven temperature, programmed from 40 to 200°C at 2°C/min; flame ionization detector, 8 · 10⁻¹⁰ A f.s.; injection volume, 0.3 μl; injection mode, split, 100 ml/min; (A) without valve; (B) with valve. Peaks: 10 = decane; 11 = undecane; al = nonanal; ol = 1-octanol; D = 2,3-butanediol; A = 2,6-dimethylaniline; P = 2,6-dimethylphenol; am = dicyclohexylamine; S = 2-ethylhexanoic acid; E10–E12 = methyl esters of C_{10}, C_{11} and C_{12} acids.

path, the valve is likely to have some influence on the chromatogram. The Grob test[6,7] is designed to test columns for adsorptive sites. Of course, it can also be used to test other parts of the flow path of the gas, for instance a valve.

Fig. 1A shows the chromatogram of a Grob test mixture on a 25 m × 0.22 mm I.D. Fused-silica wall-coated open-tubular (WCOT) column, coated with 0.15 μm CP Sil 5 CB (Chrompack). After this chromatogram had been recorded, the column was broken at 45 cm upstream from the detector and the valve was incorporated. After injection of the Grob test mixture, we obtained the chromatogram

TABLE I

GROB TEST OF CAPILLARY COLUMN WITHOUT AND WITH VALVE: COMPARISON OF PEAK HEIGHTS

Compound	Peak height	
	Without valve	With valve
2,3-Butanediol	—	—
1-Octanol	1.00	0.90
2,6-Dimethylphenol	1.00	0.87
Nonanal	0.50	0.49
2,6-Dimethylaniline	0.64	0.63
2-Ethylhexanoic acid	0.16	0.14
Dicyclohexylamine	0.43	0

shown in Fig. 1B. The heights of the peaks, relative to the alkanes and esters, are compared in Table I. For 2,3-butanediol no exact value can be given, because this peak is outside of the range of the alkanes. Concerning the other components, some adsorption is observed for 2,6-dimethylphenol. Only dicyclohexylamine has completely disappeared. According to Stearns[8], this can be overcome by silylating the rotor of the valve.

For the following experiments, the valve was built into a Hewlett-Packard 5792 gas chromatograph, equipped with a flame-ionization detector. The valve was operated by means of an air actuator, Type AH 60 (Valco Instruments). Chromatograms were recorded on a flat-bed recorder (Type BD40 04/06; Kipp & Zonen, The Netherlands). Quantitative data were collected by means of a Hewlett-Packard 3390A integrator.

DEAD VOLUME

An ideal valve should have no dead volume. Dead volume causes tailing of the peaks and, as a consequence, gives inaccurate quantitative results. The effect of the valve on peak shape was checked by calculating the peak asymmetry of the propane peak in natural gas. For this test, the flow system and porous-layer open-tubular (PLOT) column shown in Fig. 2 and described below under Backflush experiment was used. The injection volume was 0.25 ml (natural gas), oven temperature 195°C,
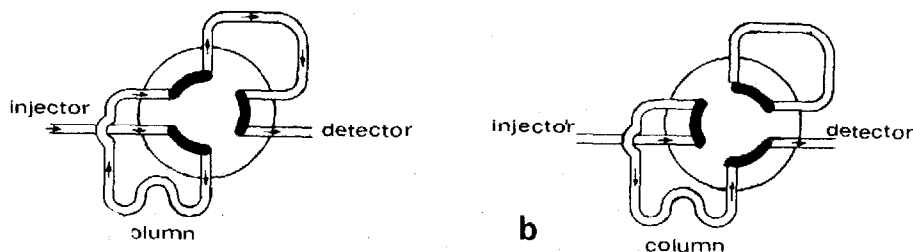

Fig. 2. Flow scheme for backflush experiment. a, Before switching; b, after switching (backflush).
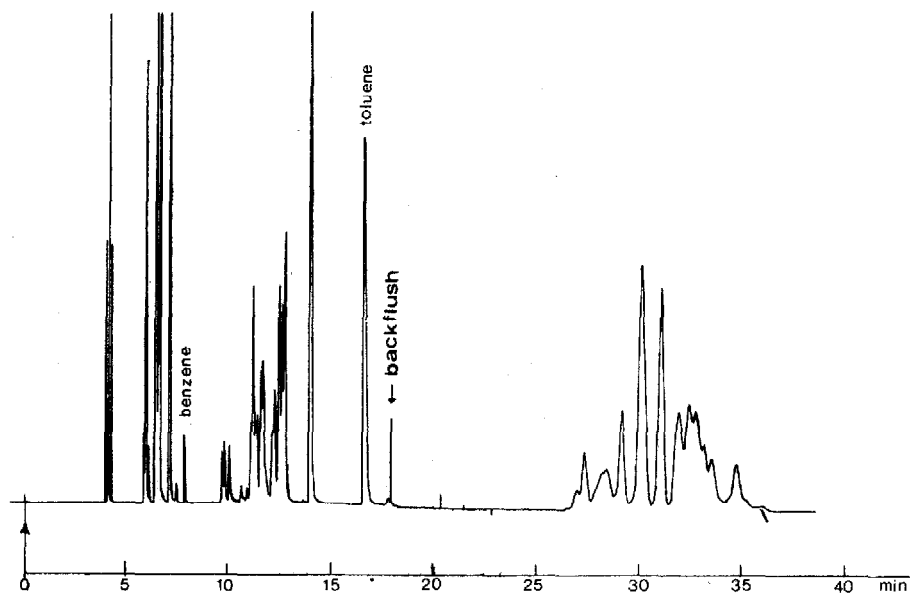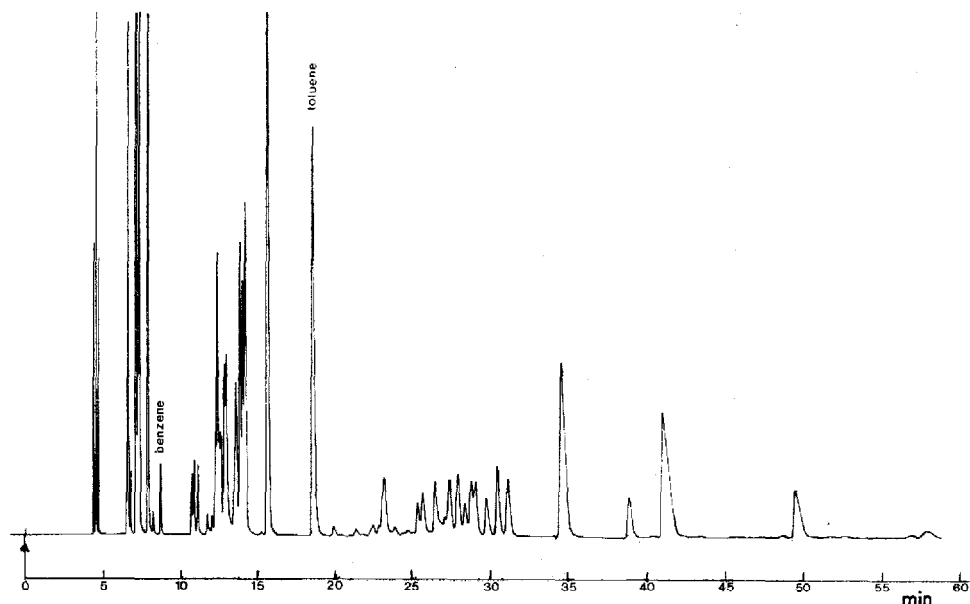
Fig. 3 (A) Analysis of naphtha on a 50 m × 0.32 mm I.D. alumina PLOT column. Oven temperature, 195°C; carrier gas, helium at 36 cm/sec; inlet pressure, 2.1 bar; split injection; injection volume, 0.1 μl; flame ionization detector, 10⁻¹¹ A f.s. (B) Analysis with backflushing. Conditions as in (A).

split flow 110 ml/min and gas (helium) velocity 36 cm/sec. In this configuration the gas flows through all six connections of the valve. Peak asymmetry (defined as peak width at 10% of the peak height behind the perpendicular through the top, divided through the peak width at 10% in front of the perpendicular) proved to be 1.08, an acceptable deviation from the ideal 1.00 for a symmetrical peak.

BACKFLUSH EXPERIMENT

As a test of the applicability of column switching, a backflush experiment was chosen. Backflushing of a complete column was preferred to backflushing of a pre-column (stripping) because of simplicity of construction. For stripping, an extra carrier gas supply and some flow restrictions are necessary. The flow scheme of this experiment is shown in Fig. 2. The valve is connected to the normal injector and to the GC detector by means of 20 cm of 0.32 mm I.D. fused silica. The column used was a 50 m × 0.32 mm I.D. fused-silica alumina PLOT column (Chrompack). This column is specially suitable for the analysis of lower alkanes. (A detailed description, preparation method and examples of applications were given by De Nijs and De Zeeuw[9]). This means that it takes a long time before a high-boiling sample is completely eluted. If one is interested only in the first part of the chromatogram (*i.e.*, the lower-boiling components), one can reverse the flow through the column after the last peak of interest has been eluted. High-boiling components that are in the first part of the column are then backflushed and washed out of the column. During backflush, they travel the same distance as during preflush, and in approximately the same time. The total analysis time will be about twice the preflush time. This can result in a great reduction in the analysis time. Another advantage is that there is no build-up of high-boiling components in the column, with effects on polarity and retention time. The column is completely clean after the backflushed components have been eluted, and ready for a new injection.

As all the components still in the column at the moment of switching are eluted through the detector, this part can also be integrated.

Fig. 3. shows the chromatogram of a backflush experiment with naphtha. Fig. 3A is the complete chromatogram. It takes more than 60 min until the last significant peak is eluted. In Fig. 3B, the flow is reversed after toluene has been eluted. Switching gives a spike on the chromatogram, because the high-pressure inlet part of the column is connected to the low-pressure detector and the gas is blown out quickly. After 37 min, the backflushed components are eluted through the detector. After this group of peaks, the baseline is completely straight, an indication that the column is clean. It might be expected that the backflush peak would be Gaussian in shape. This is not so owing to differences in the chromatographic conditions before and after switching. Before switching, the slow components are in the first part of the column,
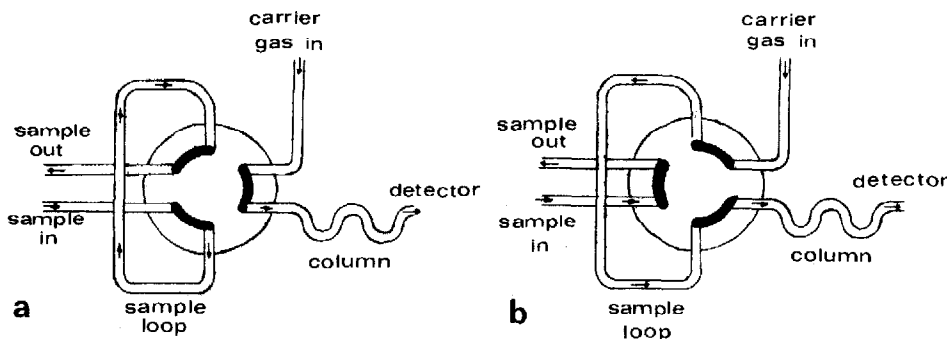

Fig. 4. Flow scheme for valve injection. a, Valve in load position; b, valve in inject position.
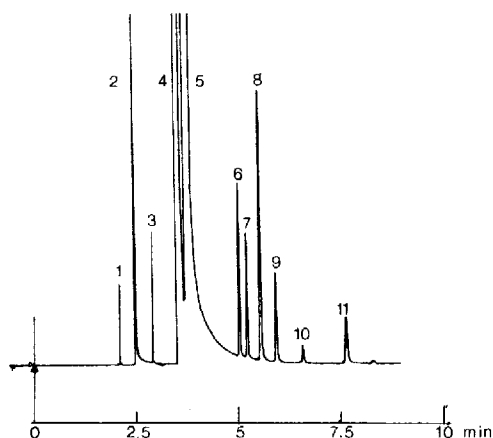
Fig. 5. Analysis of commercial butane on alumina PLOT column. Valve injection; oven temperature, 110°C; carrier gas, helium at 36 cm/sec; inlet pressure, 2.1 kg/cm²; flame ionization detector, 8 · 10⁻¹² A f.s. Peaks (area, %, in parentheses): 1 = ethane (0.041); 2 = propane (4.110); 3 = propene (0.092); 4 = isobutane (34.218); 5 = butane (60.402); 6 = *trans*-2-butene (0.238); 7 = 1-butene (0.181); 8 = isobutene (0.425); 9 = *cis*-2-butene (0.148); 10 = isopentane (0.033); 11 = pentane (0.111).

under high pressure. After switching, they are in the last part, under low pressure. This causes differences in retention time in the preflush compared to the backflush mode.

VALVE INJECTION

Another application is the use of the valve for injection into narrow-bore columns. Of special interest is the combination of the valve and the alumina PLOT column. Reproducibility of analysis of minor components in commercial butane for hobby-burners (Bunsen burner gas torch) was tested with the configuration shown in Fig. 4. Carrier gas (helium) was supplied to the valve by means of 0.32 mm I.D.

TABLE II

REPRODUCIBILITY OF VALVE INJECTION

Total area of all peaks on chromatogram: mean value, 1,382,240; standard deviation 13,518.1; relative standard deviation, 0.98%.

Compound	Peak area			% of total area		
	Mean value	Standard deviation	Relative standard deviation (%)	Mean value	Standard deviation	Relative standard deviation (%)
Ethane	568	5.1	0.90	0.9411	$0.29 \cdot 10^{-3}$	0.69
Propene	1268	13.4	1.06	0.0918	$0.42 \cdot 10^{-3}$	0.46
trans-2-Butene	3289	33.6	1.02	0.2378	$0.79 \cdot 10^{-3}$	0.33
1-Butene	2509	25.7	1.02	0.1815	$0.53 \cdot 10^{-3}$	0.29
Isobutene	5888	56.1	0.95	0.4256	$1.12 \cdot 10^{-3}$	0.28
cis-Butene	2033	22.2	1.04	0.1470	$1.15 \cdot 10^{-3}$	0.79

fused-silica tubing, connected with the injection port of the gas chromatograph. The sample loop was a piece of 14 cm × 0.22 mm I.D. fused silica, with an internal volume of 6.7 μl. With the valve in the load position, the gas to be analysed was flushed via a pressure regulator and a flow controller through the sample loop at a rate of 5 ml/min. After switching over to the load position, the contents of the sample loop were taken along with the carrier gas through the column. With this valve, ten injections were made (Fig. 5) and the peak areas were measured. Averages and standard deviations were calculated for peak areas and percentage of total peak area (Table II). Averages and standard deviations of the total area were within 1%, *i.e.*, the amount of sample injected was accurate to within 1%. The volume injected (the volume of the sample loop) is constant, but because gas is a compressible medium, a slight deviation in pressure in the sample loop causes the same deviation in the amount of sample injected. In the experiment performed, the pressure proved to be constant enough to give accurate results. Because a relatively large volume of gas is injected, without splitting, this configuration is especially suitable for the analysis of trace components.

The injection volume may be increased by lengthening the sample loop. However, if the loop is too long, the peak shape will be affected. On the other hand, the length of the injection plug is reduced, because of the pressure difference between sample loop and carrier gas.

The length of sample loop used is approximately the minimum possible with a six-port valve. Reduction of the sample loop volume may be attained by using fused silica of smaller inner diameter, but this will cause a large pressure drop in the sample loop. The outside diameter must be about 0.4 mm, to fit with the ferrules.

CONCLUSION

The six-port valve for narrow-bore open-tubular columns proved to have good inertness (except for dicyclohexylamine) and low dead volume. It is very appropriate for column switching. The combination of the valve and an alumina PLOT column has great possibilities for on-line gas analysis.

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