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A DEVICE WHICH PERMITS SELECTIVE PURGING OF THE SOLVENT AND OTHER COMPONENTS FROM A GAS–LIQUID CHROMATOGRAPHIC COLUMN

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SUMMARY

A gas–liquid chromatographic column configuration is described which utilizes two auxiliary ports located approximately one-third of the column length from the column inlet.

In the purge mode of operation, one port is pressurized while the other is open to vent. This permits selective purging of certain components of the sample mixture from the column. In the conventional mode of operation, both ports are effectively closed. The usefulness of this column configuration is demonstrated with the trimethylsilyl derivatives of 2- and 5-isosorbide mononitrates.

INTRODUCTION

The difficulties attendant upon the introduction of 1–5 μl of a solution into a gas–liquid chromatographic (GLC) column have been previously described[1]. These include: (1) flooding of the liquid phase with solvent and, in many cases, reagents; (2) filling the column gas volume with vapor which is eluted all too slowly from the column to produce a steeply declining baseline; (3) saturating a detector such as the flame ionization detector (FID), which is designed to detect submicrogram quantities, with milligrams of solvent and reagents; and (4) increasing maintenance problems due to build-up of combustion products (in the case of the FID) on detector components.

A number of techniques have been described to eliminate these difficulties. Transfer of the sample from a precolumn into the analytical column has been effected by selectively directing the gas flow by a system of valves[1–3] or by manual means[4,5] from the precolumn into the analytical column at the appropriate time. Late-eluting components which are not to be analyzed with the analytical column are removed from the precolumn by backflushing[1–3] or by continued elution[4,5]. Horning *et al.*[1] in studies concerned with the design of a biomedical instrument, backflush the sample from a primary column into the analytical column after the solvent and reagents have eluted from the primary column. Mellor[6] utilizes two columns — each of which is equipped with an FID — to effect cutting, holding, and backflushing through the use of valves and a trap which can intercept components as the effluent from one column passes to the other column. Many reports[7–11] have described multicolumn instruments for the selective transfer of effluent from one column to one or more additional columns within the instrument. Most of the instruments[1,6–8,10,11] require valves through which the sample must pass. This can lead to losses due to adsorption if the solute(s) is particularly labile or of relatively low volatility.

Deans[3] has described a novel backflushing technique which involves two columns in series. This method of flow control is unique because it is done by "outside" valves which do not come into contact with the sample. This basic technique was further utilized by Crossley[2] and Eppert[9] to provide backflush capability. The subject of this report is a novel GLC column configuration which permits selective purging (in contrast to backflushing) of solvent, reagents and late-eluting components, which are of no interest, after they have traversed approximately one-third of the column length. This is done with a single column instrument and without necessity of transferring the components-of-interest through a valve or into another column. Gas flow within the column is controlled by valves which are outside of the column. The usefulness of this device has exceeded our original expectations. The salient features are shown in Fig. 1.

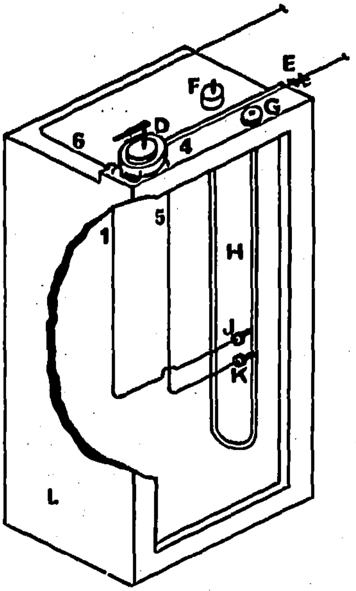

Fig. 1. A schematic representation of a selective-purge column installed in a gas chromatograph. (D) Valco valve; (E) flow controller (hand operated); (G) inlet and carrier gas; (F) detector; (H) glass column ($^1/_4$ in. O.D.); (J) upstream fitting; (K) downstream fitting; (L) oven; (1) upstream connection (1/16-in. O.D. tube); (4) vent-to-flow controller; (5) downstream connection (1/16-in. O.D. tube); (6) purge gas connection to flow control; (2) and (3) plugs (not illustrated).

A conventional GLC column is modified to include two auxiliary ports about 2 in. apart and approximately one-third of the column length from the column inlet. Through the use of a valve and an auxiliary source of carrier gas, the gas flow-rate and its direction in the column can be controlled. For conventional column operation, the valve is used in position B (Fig. 2); this effectively closes both of the auxiliary ports. In the purge mode, the downstream port, K, is pressurized with the auxiliary carrier gas, and the upstream port, J, is open to vent. Thus, the gas phase in the column between K and the injection port is purged to vent as it reaches J. The back pressure in the vent is adjusted with flow controller, E, to effect splitting of the carrier gas stream at K. This maintains the carrier gas flow in the column section between K and the detector. This prevents serious disruption of the detector signal when the valve is actuated.

Position A **Position B**

Fig. 2. The six-port Valco valve illustrated in the two operating modes: Position A, column purge; position B, column in conventional operation. Connections: (1) upstream connection; (2) and (3) plugs; (4) vent connection; (5) downstream connection; (6) purge gas connection.

EXPERIMENTAL

Instrumentation

A Varian Model 2100-20 gas chromatograph equipped with dual flame ionization detectors was used. The glass column was 6 ft. × $^1/_4$ in. O.D. with 2 mm I.D. with two auxiliary ports prepared from the same tubing stock. The packing consisted of 3% OV-210 on Chromosorb W (HP), 80–100 mesh (Pierce Chemical Co., Rockford, Ill.). The valve was a Valco Model VSV-6-HT (Valco Instruments, Houston, Texas). The capillary tubing was 0.06 in. O.D. × 0.02 in. I.D. 316 stainless, seamless, steel (Hardy and Harmon Tube Company, Norristown, Pa.). The glass to metal seals at the auxiliary ports utilized Swagelock® $^1/_4$-in. to $^1/_{16}$-in. reducing unions with $^1/_4$-in. O-rings. All other connections were made with the appropriate Swagelock® fittings. A Brooks (Brooks Instrument Co., Inc., Hatfield, Pa.) flow controller was placed in the vent line. The column was operated at 140°.

Reagents

The 1,4:3,6-dianhydro-D-glucitol 5-nitrate (5-ISMN) and 1,4:3,6-dianhydro-D-glucitol 2-nitrate (2-ISMN) were prepared by B. Palameta (Ayerst Research Laboratories, Montreal, Quebec). The trimethylsilylation was effected with a 1:3 (v/v) solution of N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA) and pyridine (Pierce Chemical Company, Rockford, Ill.). Approx. 1.0 ml of this trimethylsilylating solution was added to 1.0 mg each of 2-ISMN and 5-ISMN. After 15 min at room temperature, the solution was ready for analysis.

Operation of the instrument

The column parameters were optimized in the conventional manner with the valve in position B (Fig. 2). With a purge gas flow of *ca.* 60 ml/min, the valve was turned to position A. The flow controller in the vent line was then adjusted until actuation of the valve resulted in no significant change in the baseline.

The sample was injected with the valve in position A. After most of the solvent and reagents had been vented, but before the components-of-interest reached the upstream port, J, the valve was turned to position B. After the solutes had proceeded past port K, the valve was returned to position A to purge late-eluting components which were of no interest.

RESULTS AND DISCUSSION

The chromatograms illustrated in Fig. 3 demonstrate the effectiveness with which the BSTFA and pyridine are vented from the column. Ten replicate determinations of the response factors for the trimethylsilyl (TMS) derivative of 2-ISMN and 5-ISMN yielded standard deviations of 3.2 and 1.2% in conventional and

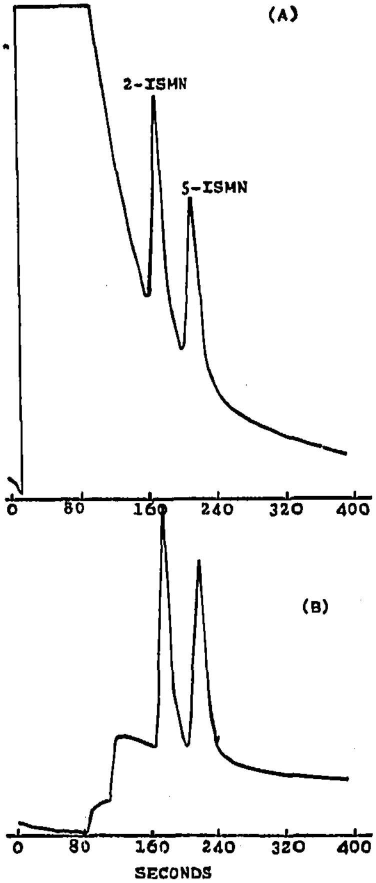

Fig. 3. Separation of the trimethylsilyl (TMS) derivatives of 2-ISMN and 5-ISMN with a 6-ft. column, 3% OV-210 on Chromosorb W (HP) at 140°. (A) Conventional operation with auxiliary ports closed. (B) An 80-sec purge after injection, followed by conventional operation.

purge operations, respectively. This is because the 80-sec purge after injection completely eliminates saturation of the detector and yields a much flatter baseline. This remarkable improvement is best understood if the assumption is made that the solvent vapors, which fill the gas phase, are flushed from the column in a manner analogous to that of an exponential dilution flask. The concentration, C, of the vapor at the detector is then given by the equation:

$$C \doteq C_0 \exp(-ut/v) \tag{1}$$

where u = carrier gas flow-rate (ml/min), t = time (min), v = volume of flask (ml) and C_0 = initial concentration of vapor in the gas phase of the column. The chromatographic processes which involve the solvent vapors are neglected, since this treatment is illustrative rather than rigorous.

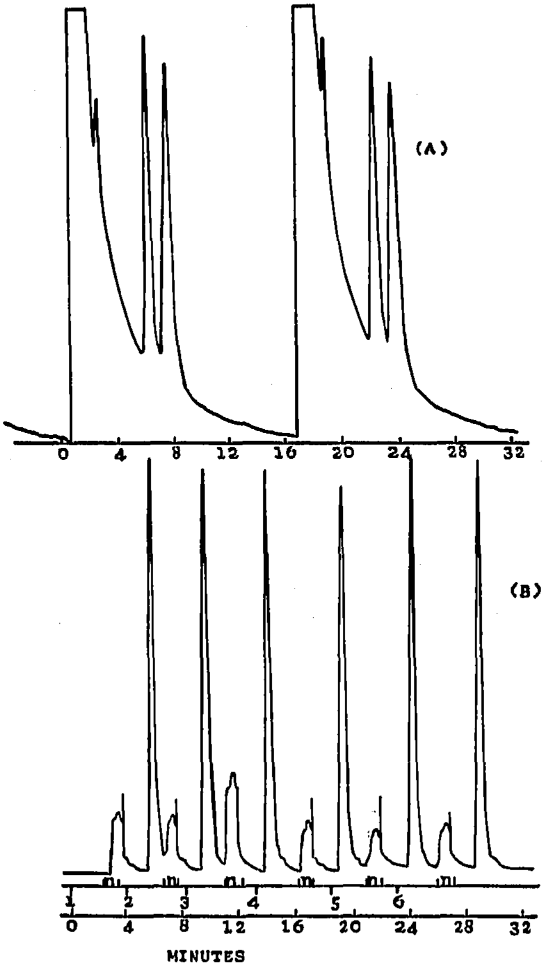

Fig. 4. GLC separation of the TMS derivatives of 2-ISMN and 5-ISMN. (A) Two injections with the column operated in the conventional mode. (B) The numerals 1–6 indicate injections. The periods during which the column was operated in the conventional mode are designated by n.

If the parameters for conventional column operation are C_0 and v, then the corresponding parameters for the same column in the purge mode are $3 \cdot C_0$ and $v/3$ because the vapors are vented after traversing one-third of the column length. The other parameters are essentially the same in both modes of operation. Substituting these values into eqn. 1 indicates that solvent concentration in the column gas phase decreases forty times faster in the purge mode than in the conventional mode.

The chromatograms shown in Fig. 4 illustrate the versatility of this column configuration. With injection at the beginning of an 80-sec purge period followed by a 40-sec conventional operation period before the valve was returned to purge mode, the venting of all components in the solution is permitted except the TMS-derivative of 2-ISMN. Thus, much more rapid analyses are possible if only one component is of interest.

Our experience with this column configuration has revealed a number of other advantages:

(1) The solvent vapors can be vented to the laboratory exhaust system; thus eliminating the need to place a fume hood over the detector.

(2) The purge mode when used with the flame photometric detector prevents the extinguishing of the flame.

(3) This column configuration would be ideal for use with a detector which is easily disequilibrated by large amounts of reagents, *e.g.*, an electron capture detector.

REFERENCES

1 E. C. Horning, C. D. Pfaffenberger and A. C. Moffat, *Anal. Chem.*, 44 (1972) 2.
2 J. Crossley, *Chem. Ind. (London)*, (1966) 1969.
3 D. R. Deans, *J. Chromatogr.*, 18 (1965) 477.
4 W. J. Kirsten and P. E. Mattsson, *Anal. Lett.*, 4 (1971) 235.
5 J. Novak, V. Vasak and J. Janak, *Anal. Chem.*, 37 (1965) 660.
6 N. Mellor, *Analyst (London)*, 96 (1971) 164.
7 M. C. Simmons and L. R. Snyder, *Anal. Chem.*, 30 (1958) 32.
8 K. J. Bombaugh, B. J. Hayes and W. R. Shaw, *J. Gas Chromatogr.*, 3 (1965) 373.
9 G. Eppert, *J. Gas Chromatogr.*, 6 (1968) 361; and references cited therein.
10 J. D. Rynbrandt, D. F. Ring and B. S. Rabinovitch, *J. Gas Chromatogr.*, 6 (1968) 531.
11 R. L. Burnett, *Anal. Chem.*, 41 (1969) 606.