Journal of Chromatography, 477 (1989) 59–62
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

CHROM. 21 547

Note

Practical aspects of recycle gas chromatography with capillary columns

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Extracolumn dispersion and active surfaces are the most serious limitations to capillary column recycle gas chromatography (GC) with mechanical valves[1,2]. As the solute is switched from column to column, it must pass through a valve. The valve may act as an element of dispersion as well as a source of sites that offer specific interactions to the solutes to be chromatographed. Since the same column segments are to be used over and over, these factors must be rigorously controlled. The quality of column connections to the valve must be very high to prevent peak distortion due to unswept volumes. The exponentially modified Gaussian function can be used to evaluate peak distortion[1,3]. Methods of column activity testing[4] can be set up to determine the contribution of the valve materials toward adsorption, and perhaps catalysis of selected test compounds[5]. In this note, we address the cutting of fused-silica capillary columnns and assess the critical steps in making high-quality connections.

EXPERIMENTAL

A capillary column recycle gas chromatograph, based on an HP 5890A gas chromatograph and a microvalve (No. 4N6WT, VICI, Houston, TX, U.S.A.) was used as previously described[1]. A 30 m × 0.25 mm I.D. fused-silica column, coated with a 0.25-μm film of dimethylpolysiloxane (DB-1, J & W, Folsom, CA, U.S.A.) was cut in half so that two segments of equal length could be connected. Columns were cut with scribes by scratching the fused-silica surface perpendicular to the direction of the fiber axis, followed by pulling while the column is slightly bent[6]. Column ends were polished to a fine finish by using 6000-grit sand paper (Scientific Instrument Services, Ringoes, NJ, U.S.A.). The test method described by Grob[4] was used to evaluate column and valve activity under a variety of conditions. A commercially available standard (Fluka, Ronkonkona, NY, U.S.A.) was diluted 1:10 and 1:100 with hexane. The gas chromatograph was programmed from 40 to 65°C at 10°C/min, followed by a 1-min delay, and then from 65 to 140°C at 2°C/min.

RESULTS AND DISCUSSION

The importance of proper column cutting techniques has been stressed[7], and an

0021-9673/89/$03.50

entire paper by Roeraade[6] was devoted to the cutting of fused silica. It was pointed out that fused-silica tubing with thin walls is difficult to cut cleanly, and careful inspection of the surface may reveal a jagged or chipped surface. Difficulties may arise from two sources: unswept volumes and adsorptive surfaces. Bulk column material that finds its way into the column end during the cutting process should be removed. If a chipped surface results in the cut, the column flow is subjected to the fused-silica surface and in some cases the polyimide coating. In recycle GC, the effect of valve surfaces must also be considered. Materials used in valve construction are metals and synthetic/composite polymers. The effluent passes through a channel in the rotor and is therefore exposed to both types of surfaces. Some choice in the nature of the metal and rotor material is possible, *i.e.* the user can specify rotor and valve body materials.

Fig. 1 shows the effect of column connection techniques on chromatographic performance. Chromatogram A was obtained by connecting the 0.25-mm I.D. columns with a tapered glass union constructed in our laboratory. The union allowed the column ends to be butted together, and formed a tight seal with the fused-silica column by pressure against the polyimide layer. The column ends were inspected prior to connection to insure that reasonably good cuts were obtained. Chromatogram B was obtained after sanding the column ends and reconnection. Small particles of fused silica and polyimide were collected in the colum ends. Tailing is observed on the acid and free-base peaks. However, the effect is relatively minor. These particles can be removed by filling the column with a non-wetting solvent before grinding (*i.e.* hexane), followed by forceful expulsion. Fig. 2a–c shows scanning electron microscope photographs of the column material after (a) cutting, (b) sanding, and (c) particle removal. The jagged surface has been smoothed, and it is possible to obtain a perpendicular surface at the column end. The fused silica should be held at a 90° angle

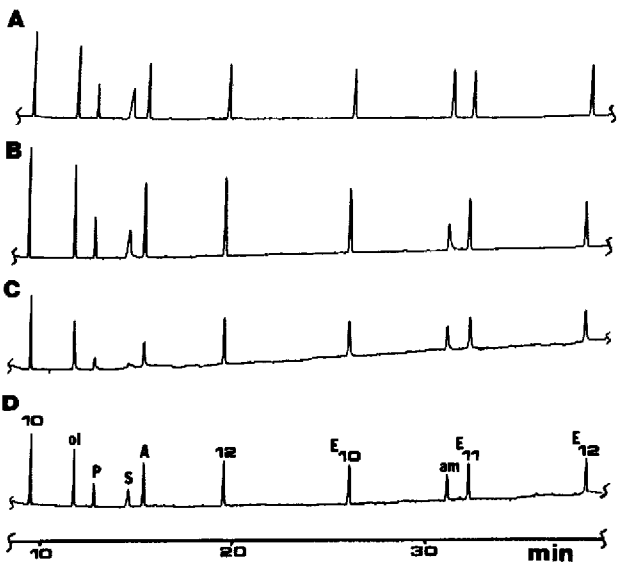

Fig. 1. Chromatograms of the test mix. (A) No extraneous material in the columns; (B) columns connected after sanding; (C) poor column-to-valve connections; (D) valve connections with polished ends.

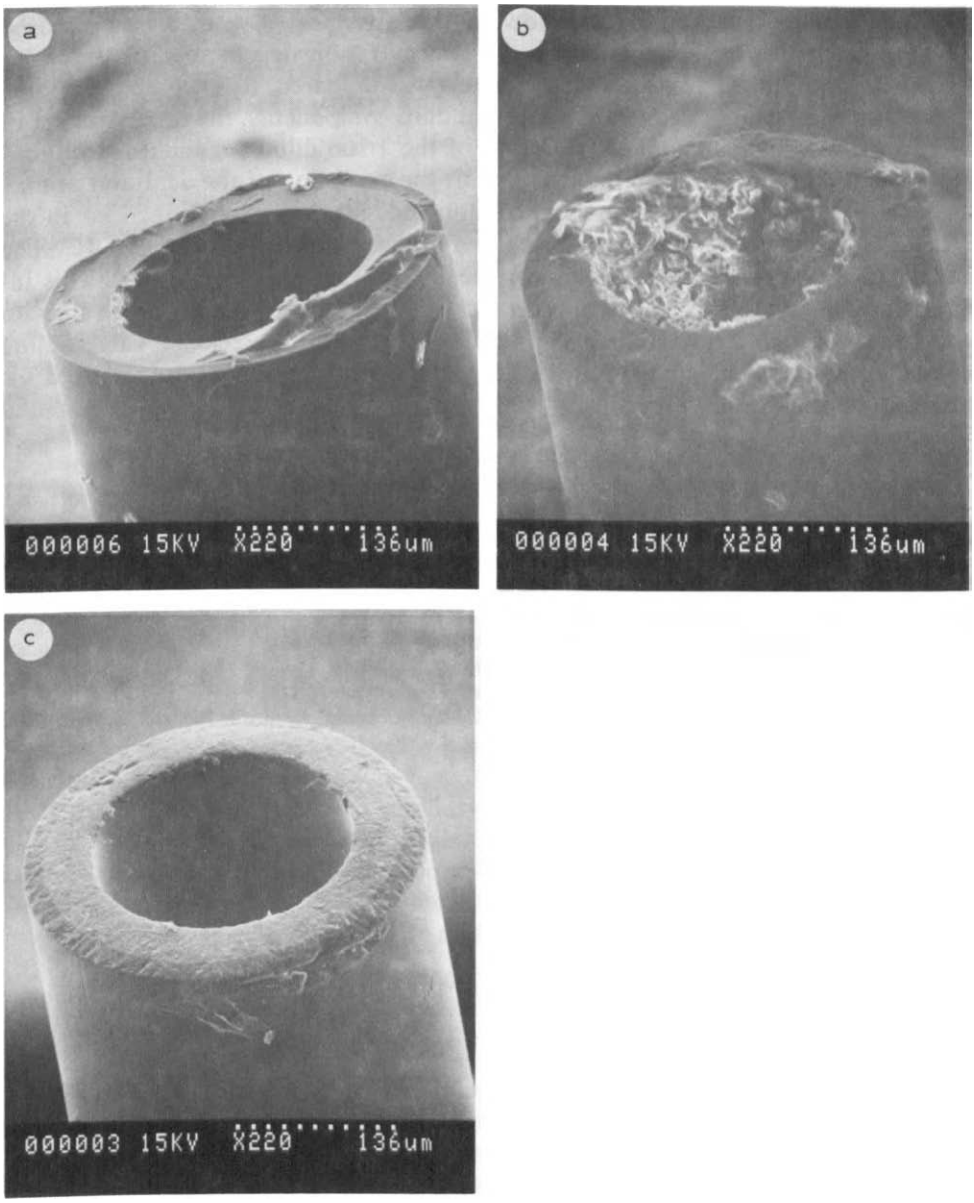

Fig. 2. SEM photographs of column end (a) after cutting, (b) after sanding, and (c) after washing.

in reference to the sanding material, and kept from bending when pressure is applied. This can be accomplished by insertion of the fused-silica end into a rigid structure that maintains a straight posture during sanding.

Exposure of the test sample to the materials of the valve during a single passage produces a slight reduction in the peak height of the amine, as shown in the chromatogram in Fig. 1D. No noticeable tailing from unswept volume was noticed. This is

expected since previous studies have shown that relative peak asymmetry is decreased at high capacity ratios[1]. To ascertain the concentration dependance of the valve activity, a more dilute solution of the standard was prepared. By chromatographing the minimum detectable quantities of the standard components, the relative effect of the adsorptive sites is magnified. Injection of the 1:100 diluted standard produced detectable peaks for all the components, with the exception of the acid and amine. Connections made with less than ideal column ends produce a small increase in the tailing of some of the components, as shown in the chromatogram in Fig. 1C. The alcohol, phenol, acid, aniline, and amine peaks show pronounced tailing. This indicates that the quality of the column connection to the valve is critical, and a smooth surface on the end of the column is essential to prevent unnecessary valve–solute contact. Although small changes are noticed, several valve passages are required for meaningful evaluations. Practical application of capillary recycle GC wil be presented in the near future[8].

REFERENCES

1 D. Roberts and W. Bertsch, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 11 (1988) 783.
2 W. Bertsch, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 1 (1978) 187.
3 D. Roberts, *Dissertation*, University of Alabama, 1989.
4 K. Grob, Jr., G. Grob and K. Grob, *J. Chromatogr.*, 156 (1978) 1.
5 S. T. Adam, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 11 (1988) 85.
6 J. Roeraade, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 6 (1983) 140.
7 W. G. Jennings, *Gas Chromatography with Glass Capillary Columns*, Academic Press, New York, 2nd. ed., 1980, p. 90.
8 D. Roberts and W. Bertsch, in preparation.