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PREPARATION OF HIGH-CAPACITY HIGH-RESOLUTION OPEN-TUBULAR COLUMNS

FRANCIS W. KARASEK*, RICHARD J. SMYTHE, and RICHARD J. LAUB
Department of Chemistry, University of Waterloo, Waterloo, Ontario N2L 3G1 (Canada)
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SUMMARY

The preparation and use of large-bore open-tubular (LBOT) and porous-layer open-tubular (PLOT) columns are described. A simple yet versatile coiling apparatus has been devised that is useful for capillary as well as 1/8-in. tubing of any length. Several types of frames for long LBOT columns can be employed. A rigorous cleaning method for stainless-steel tubing is also detailed, and an apparatus for reproducibly coating LBOT or PLOT columns is presented. These two types of columns yield comparable efficiencies, but the LBOT columns could be prepared more easily and reproducibly.

INTRODUCTION

Gas chromatographic–mass spectrometric investigations of complex organic mixtures, such as engine-exhaust analysis, require high resolution from the initial gas chromatographic separation step[1,2]. To obtain mass spectra capable of providing component identification it is also desirable to use as large a sample injection as possible. The required resolution with maximum sample size can be achieved with long lengths of large-bore open-tubular (LBOT) or porous-layer open-tubular (PLOT) columns[3–12]. The preparation and properties of these columns have been summarized by Mon[4], Guiochon[13], and Nikelly[8].

High-resolution LBOT or PLOT columns of 0.03-in. I.D. may be as long as several thousand feet. Manipulation of such long lengths of tubing can be facilitated by tightly coiling the columns to fit into the oven of the gas chromatograph at hand. However, in the coiling process care must be taken to allow for adequate air circulation in and around the column coils. Nikelly[8] has shown that temperature gradients as high as 58° can result from uneven heating of different sections of the same gas chromatographic (GC) column. He achieved uniform heating by winding the tubing in tiers that were separated by coping-saw blades silver-soldered to threaded rods. The frame to which the rods were attached was built up as the column was coiled. Varia-

* To whom all correspondence should be addressed.

tions of Nikelly's method have been described by Warden and Schoenig[14], and Boogaerts *et al.*[15].

Once the column has been coiled, the interior surface of the tubing must be rigorously cleaned prior to coating. Several methods have been proposed[4,11,16], all of which involve passing plugs of solvents through the column under pressure. After thorough drying, the tubing is ready for coating. The dynamic method has been shown to be more effective than static methods[15], and the technique is simpler to carry out for LBOT columns. Dynamic methods also appear to be quite satisfactory for PLOT column types[7,8,11,12].

The techniques cited above are somewhat tedious or unnecessarily complicated, however, and so we designed uniquely simple devices for coiling, cleaning and coating long lengths of LBOT, PLOT, or $^1/_8$-in. columns. The coiling apparatus does not use a central sleeve or threaded racks but can be used with such frames if so desired. Cleaning and coating operations are carried out with a single stainless-steel reservoir, which was found to be adequate for column lengths of up to 500 ft.

EXPERIMENTAL

Coiling apparatus

The coiling device consists of a knock-apart drum fashioned from aluminum, brass and wood, and is shown in Fig. 1. The slots in the sides of the winding drum plates permit either a wire-tube or metal-strip frame to be used as the column is coiled. These two frame techniques are illustrated in Fig. 2. Fig. 2A depicts a frame of $^1/_4$-in.-wide strips of thin-gauge aluminum being assembled as the tubing is coiled. The strips were cut on a shear from scrap; each spacer strip supporting a tier is punched and bolted to radial strips. When the desired length of tubing is wound onto the frame, the drum is dismantled. The ends of the tier and radial supports are then trimmed, and the column is ready for cleaning and coating. Fig. 2B shows a very compact form of coiling, in which $^1/_8$-in. O.D. spacer tubes are used instead of strips.

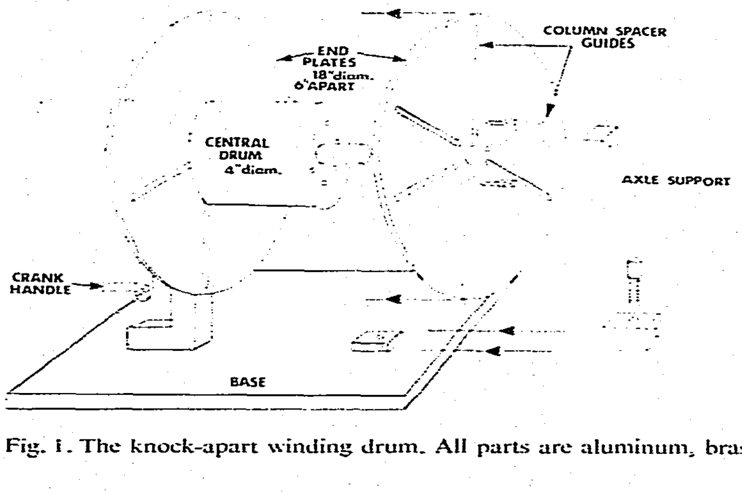

Fig. 1. The knock-apart winding drum. All parts are aluminum, brass or wood.

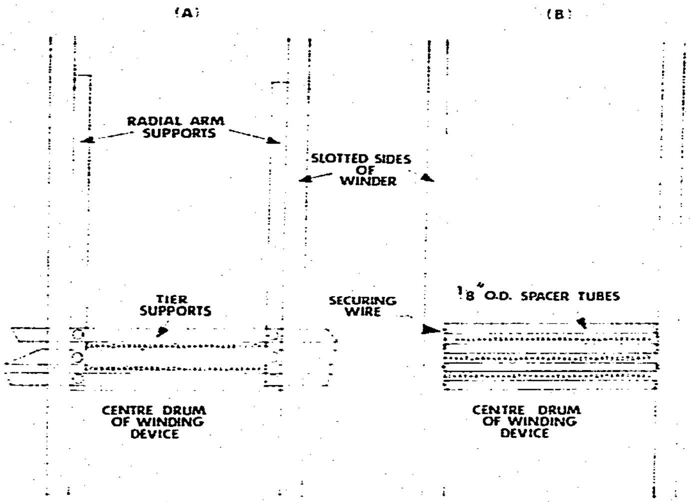

Fig. 2. Two methods for spacing coiled capillary columns. (A) Vertical (radial) and horizontal 1/4-in. aluminum spacer strips are used. (B) 1/8-in. tubes are used as spacers. The tubes are secured to each other with wire as shown.

Wire is threaded through the tubes and around the tiers to the next spacer tube, eventually securing the final coil of column tubing. This latter type of structure is essentially "frameless", and offers one of the more compact arrangements. Several thousand feet of $^1/_{16}$-in. tubing may be coiled in this manner with our device: its use can equally be extended to coiling $^1/_8$-in. columns.

Cleaning and coating apparatus

Fig. 3A shows the apparatus that is used to clean the inner surface of tubing and deposit the desired stationary phase or support. Fig. 3B illustrates the assembled cleaning and coating apparatus. The "O" ring-sealed reservoir is mach inedfrom a 2-in. diameter by 10-in. stainless-steel rod and is capable of holding approximately 75 ml of solution under 500 p.s.i.g. pressure. Connections to the pressure regulator are made with $^1/_8$-in. stainless-steel Swagelok tube fittings. The bottom of the reservoir is connected to the coiled capillary with a $^1/_8$-in. stainless-steel N.P.T. (National Pipe Thread) to $^1/_{16}$-in. tubing adaptor (Crawford Fitting, Salon, Ohio, U.S.A.: Cat. No. 100-1-2). The pipe thread end of the connector must not protrude above the bottom of the reservoir since the total volume of the plug used to prepare PLOT columns is only 1 to 2 ml. A protruding ridge will decrease the size of the plug entering the tubing, resulting in incomplete coating of the column. The pipe to tubing adaptor seal consists of a washer of PTFE instead of PTFE tape as is normally employed. The use of PTFE tape as a seal for the pipe threads produces very fine hair-like strips of PTFE as the adaptor is tightened. These strips of PTFE will eventually work their way into the tubing causing it to plug.

Cleaning procedure

We found the following cleaning procedure very effective for lengths of 500-ft. × 0.02-in. or 0.03-in. I.D. stainless-steel tubing. The reservoir apparatus,

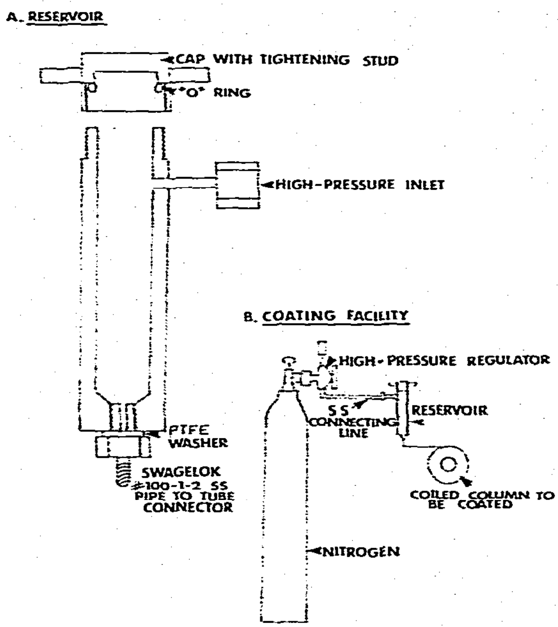

Fig. 3. Reservoir and associated apparatus for cleaning and coating capillary tubing.

nitrogen tank and column are assembled as shown in Fig. 3B. Five 25-ml portions of each of the following solvents are passed through the column at 500 p.s.i.g.: chloroform, acetone, water, concentrated nitric acid, water (to pH 7), concentrated ammonia, water (to pH 7), acetone and chloroform. The nitrogen flow is maintained for several hours after the last solvent plug, to thoroughly dry the inner surface of the tubing, which is then ready for coating.

Coating procedure

LBOT columns. The stationary phase/solvent mixture was typically 10.0 g of stationary phase (*e.g.* SF-96), 0.5 g of Igepal Co-880 (to reduce tailing), and 89.5 g of solvent (ether–acetone 50:50). The coating mixture was added to the reservoir, the reservoir cap replaced, and 20 p.s.i.g. applied from the nitrogen tank. A 250-ml erlenmeyer flask was used to collect excess solution that emerged from the column. After the coating plug was forced through, the nitrogen flow was maintained for 1 h. The collected coating solution was then returned to the reservoir, and the process repeated. In all, five coating steps were used, after which nitrogen was left flowing through the column overnight at 20 p.s.i.g. The column was then conditioned at 50 p.s.i.g. for 24 h at 25° below the maximum recommended operating temperature of the stationary phase.

PLOT columns. We found the method given by Nikelly[7] to be satisfactory. Several grams of untreated Chromosorb W are pulverized and sieved. A suspension of 0.5 g of support and 1.5 g of 5% stationary phase in chloroform is then prepared. This is added to the coating reservoir, to which is attached 50 ft. of 0.03-in. I.D. tubing, and nitrogen is applied at 20 p.s.i.g. The gas flow is continued at 5 p.s.i.g. for

30 sec after the coating suspension emerges from the column. Longer PLOT columns are prepared by coupling together coated 50-ft. lengths of column with $^1/_{16}$-in. male Swagelok unions.

RESULTS AND DISCUSSION

Many variations are possible with the knock-apart drum. The use of $^1/_8$-in. as opposed to $^1/_4$-in. spacers produces very compact column configurations. The more tightly wound columns assembled from $^1/_8$-in. spacers do not show any observable loss in performance when compared with identical columns wound with $^1/_4$-in. aluminum strips separating individual coils. The large thermal mass afforded by 1000 ft. of $^1/_{16}$-in. O.D. (0.030-in. I.D.) stainless-steel tubing and the long gas hold-up times also render high rates of programming (*i.e.* over 4°/min) unnecessary; a slow rate of programming further aids the establishment of thermal equilibrium between the various tiers. Our observations indicate that only sufficient space for adequate air circulation is required. The choice of spacers and frames or frame-free fabrication will therefore depend on the size of the GC oven to be used. Columns consisting of 1000 ft. of $^1/_{16}$-in. O.D. stainless-steel tubing have been wound in this laboratory to form cylinders 6-in. by 8-in. or 12-in. in diameter, both of which fit into Perkin-Elmer 900 or Hewlett-Packard 7600 Series gas chromatographs.

Fig. 4 shows a chromatogram of a commercial diesel fuel with a 500-ft. LBOT column containing OV-101. Fig. 5 illustrates the separation of phenol (b.p. 182°), *m*-cresol (b.p. 203°), and *o*-ethyl phenol (b.p. 206°) using a 200-ft. PLOT column. Resolution ($R_{1,2}$) of the latter two compounds is approximately 5 (calculated from

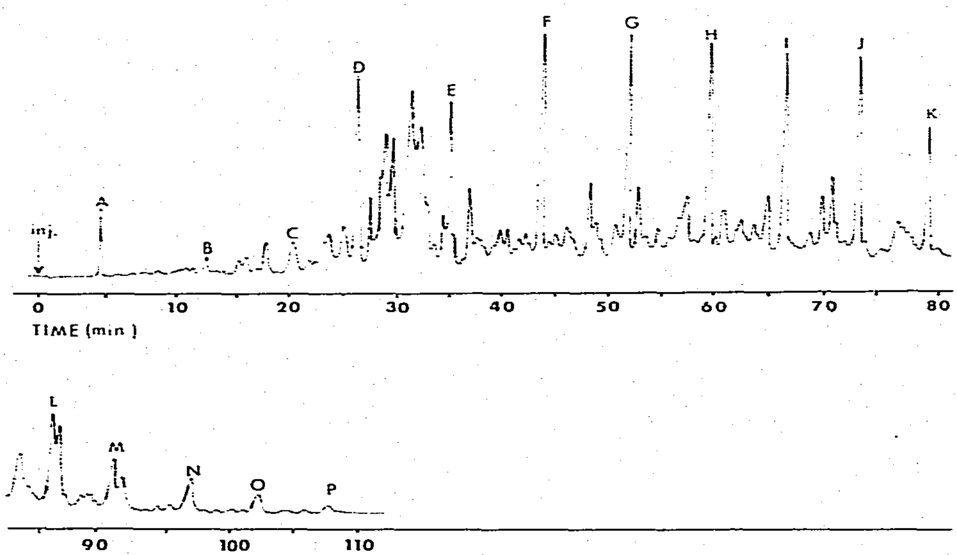

Fig. 4. Chromatogram of a commercial diesel fuel. Column, 500 ft. × 0.03 in. I.D. LBOT coated with OV-101 and Igepal Co-880. Perkin-Elmer 900 gas chromatograph: detector, flame ionization detector; range, × 10; attenuation, 64; column temperature, 40–220° at 2°/min; injector, 290°; detector, 275°; carrier gas, helium at a flow-rate of 30 ml/min; injection, 0.5 μl neat. Peaks: A, air; B–P are normal alkanes, from *n*-heptane to *n*-uneicosane.

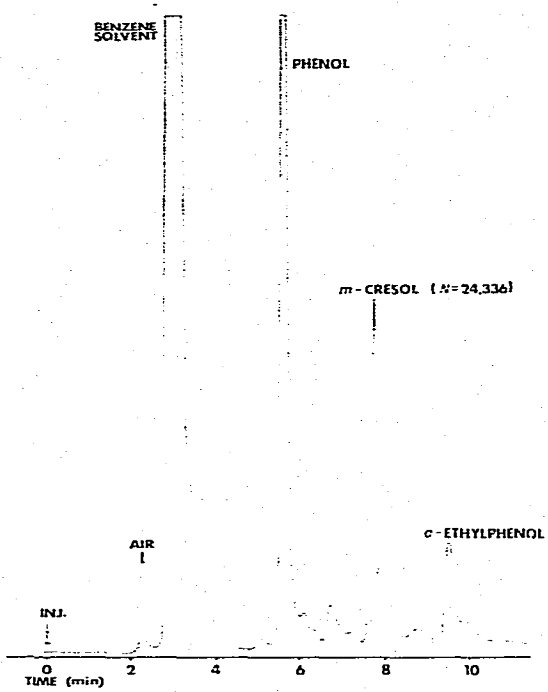

Fig. 5. Chromatogram of phenols. PLOT column: 200 ft. × 0.03-in. I.D. SF-96 on Chromosorb W; carrier gas, helium at a flow-rate of 6 ml/min; column temperature, 125° isothermal; sample size, 0.1 μl; other conditions are the same as Fig. 4.

$R_{1,2} = 2(t_{R2}-t_{R1})/(w_1 + w_2)$), which is particularly good since the analysis showed 25,000 theoretical plates, and was complete in less than 10 min. Chromatograms of the same mixture on a 500-ft. LBOT column containing the same stationary phase at the same conditions yielded similar results. The LBOT columns are preferred in analyses, however, since they are easier to prepare.

These results indicate that the preparation of high-speed high-resolution LBOT or PLOT columns lies well within the capability of most laboratories. Our apparatus consists of only readily-available materials and requires a minimum expenditure of time and effort. Resolution comparable to LBOT or PLOT columns can only be obtained with glass-bead-packed columns, but these are difficult to prepare reproducibly and have low sample capacity[13].

LBOT columns are preferred to PLOT columns since they are easier to prepare. However, in some instances, difficulties are encountered in getting the stationary phase to adhere to the walls of the tubing. To overcome this problem, addition of a surfactant such as benzyltriphenylphosphonium chloride has been suggested[17]. Alternatively PLOT columns may be used where the stationary phase is impregnated in the solid support rather than coated onto the tubing interior surface. Materials are now becoming available that prove to be superior to Chromosorb W for PLOT columns, one example being Silanox[9–11].

In summary: where speed and resolution are of prime concern to the chromatographer, there is no longer any reason not to prepare and use LBOT or PLOT columns.

Simple inexpensive devices for coiling, cleaning and coating such columns have been described here, which we hope will be of use in the optimization of gas chromatographic separations.

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