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Note

Dynamic coating of glass capillaries with polar phases and Silanox*

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The potential benefits of glass capillary columns in gas chromatography have not been widely exploited, presumably because of technological problems and irreproducibility associated with their production. The nonuniformity and instability of liquid films, especially polar liquid films, when coated on smooth glass surfaces constitute a major limitation to high chromatographic efficiency[1]. To overcome these difficulties, many procedures have been developed for surface modification of the glass prior to coating. These include deposition of a layer of carbon[2] or of a polymer[3], gas phase etching[4], surface deactivation[5], and the formation of selective monomolecular layers[6].

German and Horning[7] have reported a simple two-step dynamic method of coating glass capillary columns using Silanox, a silanized silica powder. Their columns coated with SE-30 exhibited excellent thermostability and efficiency. Their method has been reported unsatisfactory, however, for the preparation of polar phase columns[8,9], as has also been our experience. Blakesley and Torline[9] have successfully produced polar columns by a modification of German and Horning's method[7], by coating Silanox on glass with a surface-active material. The use of surfactants, however, will change the retention and possibly the order of elution of compounds[10]. We wish to report the preparation of efficient polar-phase glass capillaries by a modification in the solvent system used in the German–Horning dynamic two-step coating procedure.

EXPERIMENTAL

Duran 50 tubing was cleaned prior to extrusion by immersion for 2 h in 4% aqueous NaOH saturated with potassium permanganate. The tubing was drained and successively rinsed with water, conc. HCl, water, and abs. methanol. After drying, the tubing was drawn with a Hupe-Busch 1045A glass drawing and coiling machine. From a 1.50-m Duran tube (7.0 mm O.D. × 5.0 mm I.D.), a 135-m capillary (1.0 mm O.D. × 0.62 mm I.D.) was obtained. Capillaries were coiled with a 12-cm diameter.

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The coiled capillary tubing was evenly spaced and affixed to a support cylinder (1.25 m × 12 cm O.D.). With the cylinder erect, the top of the column was connected to a 30-ml reservoir and the bottom to a flow restrictor consisting of a 10-m length of tubing identical to that being coated. Connections were made with standard 1/16-in. unions. Strips of teflon tape were wound around the capillary tubing between the back ferrule and nut. When the nut was tightened, compression caused the teflon to flatten into a washer which sealed the connection.

Capillaries were coated by a dynamic two-step process. The solvent used in both steps of the coating process was chloroform–acetone (10:1). In the first step, 0.10 g stationary phase was dissolved in 10.0 ml solvent, 0.25 g Silanox (Grade 101) was added, and the suspension was sonicated for 2 min. A plug of this suspension (20% of column length), preceded by a plug of solvent (5% of column length), was passed through the tubing at 18 cm/sec. After the liquid had been expelled, the coating was dried with carrier gas flow for 10–12 h. In the second step, additional liquid phase was dynamically coated on the Silanox bed utilizing the same apparatus as in the first step. A plug (20% of column length) of a solution of 0.25 g stationary phase in 10.0 ml solvent was passed through the tubing at 12 cm/sec. When the main plug of liquid had been expelled, the gas pressure was reduced in stages to promote smooth flow of the viscous secondary plugs formed by solution draining from the column walls. After the last plugs of solution had been expelled, the column was dried with gas flow for 10–12 h.

The column was conditioned in the chromatographic oven by purging with carrier gas at a temperature programmed from 20 to 250° at 2°/min and maintained at 250° for 12 h. The column was then silylated at 200° with four injections of 2.5 μl Silyl-8 at 5-min intervals and maintained at 200° for an additional hour.

DISCUSSION

The chloroform–acetone solvent combination had adequate density to stabilize the Silanox suspension and sufficient polarity to prevent the formation of a thixotropic gel[11] during the coating process. Irregularities in the thickness of the deposited Silanox bed could be seen after the first coating step; these irregularities, however, were eliminated during the second coating step. The localized patches of excess Silanox were apparently washed away, leaving a uniform thin layer of Silanox, which was estimated by scanning electron microscopy to be 2.5 μm thick.

Columns prepared by this technique with the polar liquid phases Silar-5CP, OV-225, OV-210, and Carbowax 20M TPA, have shown excellent efficiency and thermostability. A 135-m Silar-5CP column (0.62 mm I.D.) yielded 151,000 theoretical plates and 122,000 effective plates, as tested with methyl linolenate at 175° column temperature and 4.0 ml/min helium gas flow. Only minimal column bleed was evident during gas chromatographic–mass spectrometric application. Columns have displayed high durability, having tolerated splitless injection of flavour volatiles and fatty acid methyl esters for 6 months before appreciable losses in efficiency have occurred. The same coating procedure has been used with success using the apolar liquid phase OV-101.

The solvent mixture reported in this work has extended the German–Horning procedure[7] for dynamic two-step coating of glass capillary columns to include the

use of polar liquid phases. Whether all polar phases can be used may depend on their solubility in the employed solvent mixture.

Caution: Chloroform–acetone mixtures may be explosive. In the presence of basic substances, a catalytic, highly exothermic, condensation reaction takes place[12].

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