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Symmetrical (double-speed) static coating for high-resolution gas chromatography column preparation

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Abstract

''Breakthrough'' during static coating could be avoided using a new coating strategy: while filling the capillary support with coating solution, a short mercury plug was placed at the middle of the support length. Mercury was frozen by a cold source and vacuum was applied to both open ends. In this way static coating became *symmetric* and so evaporation rate was doubled, on a time base, and more than doubled on a coated length base. Coating time at room temperature varied from ~20 min for 3-m columns to ~3 h for 15-m columns.

Keywords: Coating; Capillary columns; Instrumentation; Breakthrough

1. Introduction

GC capillary columns can be purchased or prepared in the laboratory [1] by dynamic or static coating procedures. Whenever accurate values of film thickness (d_f) are required, static coating (ST) should be selected since it provides columns with accurate d_f values [2].

Let us define the following: C_{coat} is stationary phase concentration into the coating solution, expressed in g of pure phase per 100 ml of solution; d_f is stationary phase film thickness (μm); d_c is internal diameter of the uncoated capillary support (mm); and δ_{st} is density of the stationary phase (g/cm^3).

C_{coat} might be expressed by a formula derived from geometrical and mass conservation concepts [3]:

$$C_{coat} = 100\delta_{st} \cdot \{1 - [(d_f/500d_c) - 1]^2\} \quad (1)$$

A simpler equation, although a bit more approximate, gives very similar results [2]:

$$C_{coat} = d_f/(2.5d_c) \quad (2)$$

After C_{coat} calculation (by Eqs. (1) or (2)) column makers must decide the type of end-closure [4] to use. End-closure (also called ''end-seal'') realization is indeed a critical step [5] even for trained operators. End seals can be prepared in a plethora of ways [4] which may differ as regards practicality and reliability of results. The main obstacle is the so-called ''breakthrough'' phenomenon (the sudden and unwanted outburst of coating solution due to uncontrolled evaporation at places other than the meniscus) which occurs while static coating is running.

Until now breakthrough has been the ubiquitous

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unforeseeable uncertainty of any static coating attempt, owing to one of the following reasons:

(1) imperfect end-seal execution,
(2) too high permeability of closure materials toward atmospheric gases (unsuitability of end-closure),
(3) presence of residual bubbles in the filled capillary support,
(4) excess of dissolved gases in the coating solution, and
(5) too high a coating temperature (sometimes kept above room temperature to speed solvent evaporation).

Breakthrough is essentially linked to end-closure realization (points 1 and 2, above). So, if breakthroughs are to be made negligible, one answer seems obvious: end-closure suppression.

However, if we try to put this into practice we might be very disappointed; in fact, when a suitable capillary support is filled with coating solution and vacuum is applied to both open ends, solvent will not evaporate equally from both arms due to some kind of slow liquid motion. After a brief time, a stationary phase plug develops in one of the support arms, and coating is spoiled.

If coating solution movement was hindered by a suitable reversible plug of mercury placed in the middle of the capillary support length, evaporation of coating solution solvent(s) from both capillary ends would be possible, in an identical manner. This new approach called *symmetrical static coating* is detailed in the following sections.

2. Materials and methods

2.1. Static coating set-up

The complete set-up is shown in Fig. 1, from 1 to 7.

A copper tube of ~15 cm×4 mm O.D.×2 mm I.D., was brazed (silver-alloy) with another short piece (~1.5 cm) of copper tube giving rise to an inverted metal ''T'' (Fig. 1, step 1→2), the base of which was cut longitudinally with a thin fretwork-saw (2→3). The copper halves (see the enlarged cross-section near 3) were pasted (hot-melt glue gun) inside the opposite jaws of a clothes-peg clamping head, made of wood and drilled (one side) to receive the copper stem inside (3→4). The stem was then threaded as much as possible through the bottom wall of a laboratory-made heavy-walled styrofoam ''Dewar'' (4→5); hot-melting glue was applied around the hole perimeter (Fig. 2, point ''B'') to avoid cryogen leakage and to mechanically fix the copper tube. The insulated container was filled with liquid nitrogen and then suspended over a thermostatic water bath kept at room temperature (7). Finally, the mercury section (~4–10 cm long) of the liquid-filled capillary support (first moved from the end to the middle of the capillary length; Section 2.2) was clamped between the jaws of the cooled clothes-peg. Briefly after clamping, mercury was rapidly solidified thus hindering any liquid movement. Vacuum [6] was symmetrically applied to *both* capillary ends *without* the risk of solvent breakthrough.

2.2. Mercury plug

About 10 μl of clean mercury was introduced into the filling tube [7] used to deliver the coating solution (Fig. 3) and was kept there until the capillary support was almost filled with coating solution. The filling tube was then lightly tilted to transfer the mercury toward the capillary support together with the rest of the coating solution. The mercury was suitable positioned halfway along the support length.

3. Results and discussion

The technique proposed in this work is interesting, because:

(1) end-closures are totally abolished,
(2) breakthrough risks, if any, are extremely low, and
(3) coating time is greatly reduced, due to solvent evaporation in both capillary arms.

The above advantages were obtained by just replacing the usual end-closures with a ''middle-closure'' made of frozen mercury. Such a new closure was reversible with ease and liquid Hg was discharged from the capillary support at the end of the coating procedure. In practice mercury was

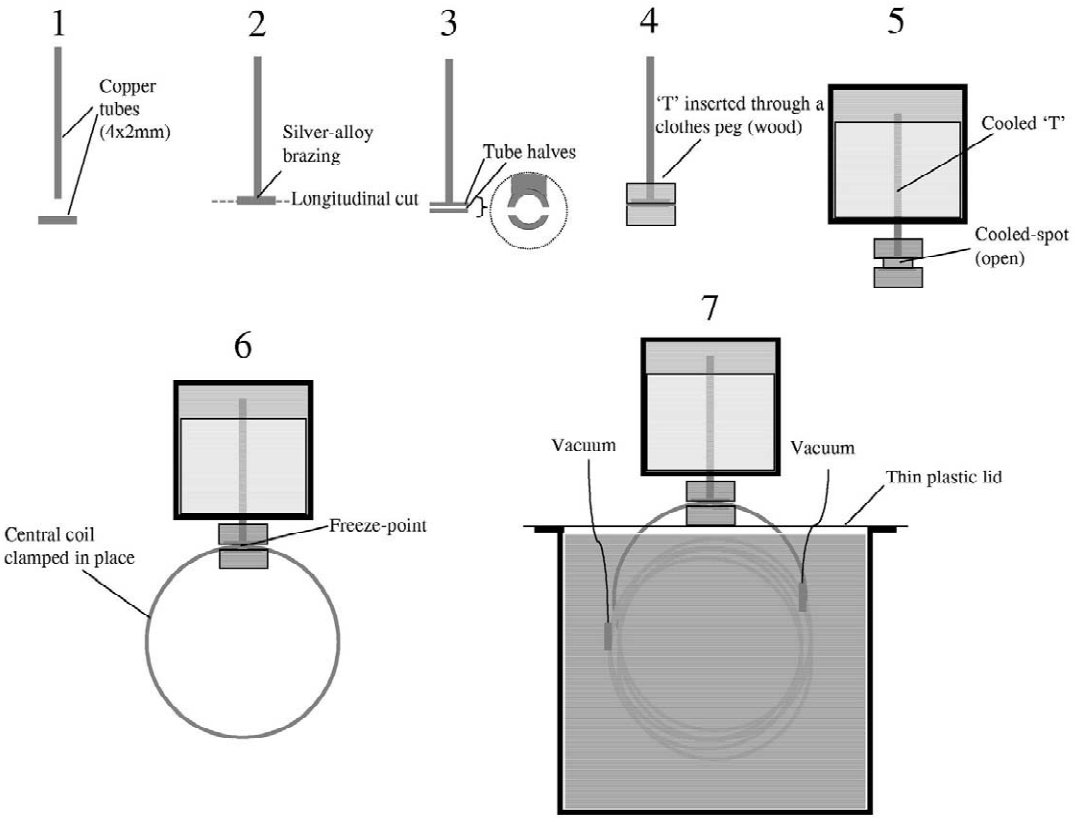

Fig. 1. Set-up of symmetrical static coating (see text for details). A colour copy of Fig. 1 can be requested from the author.

frozen by the cooling effect of boiling liquid nitrogen and the frozen metal was *not* allowed to melt until the end of the coating process. The cooled clothes-peg approach shown in Fig. 2 was used to freeze the mercury plug and and keep it frozen.

3.1. The mercury freezer

The clothes-peg head was cooled by heat absorption through the very heat conductive copper stem which was immersed into the liquid cryogen (Section 2.1). Heat exchange was also enhanced by a couple of 2-mm holes passing through the stem near its bottom (point A, Fig. 2). Liquid nitrogen flooded through these holes and reached the clothes-peg jaws, where it evaporated with heat absorption. The cooling effect was rather efficient, as highlighted by a continuous spurt of boiling nitrogen expelled through the upper open end of the copper stem. This way the clamped mercury was quickly frozen (melting point −38.8 °C) and remained solid while the cryogen was in the ''Dewar'' (a full charge of liquid nitrogen lasted for ~5 h).

3.2. Advantages of mercury

Mercury is well known by those column makers who perform dynamic coating procedures [8]. It generally does not react with stationary phases (with some exceptions, e.g. free fatty acid phase, FFAP), it is quite visible within a glass or fused silica capillary and it moves freely in its liquid state. Moreover, if we consider the rather low melting points of organic solvents usually used to prepare coating solutions (−130 °C *n*-pentane, −63 °C dichloromethane, −116 °C diethyl ether, −95 °C acetone, etc.) mercury, with its higher melting point, seems a suitable candidate to make middle-closures. With a mercury

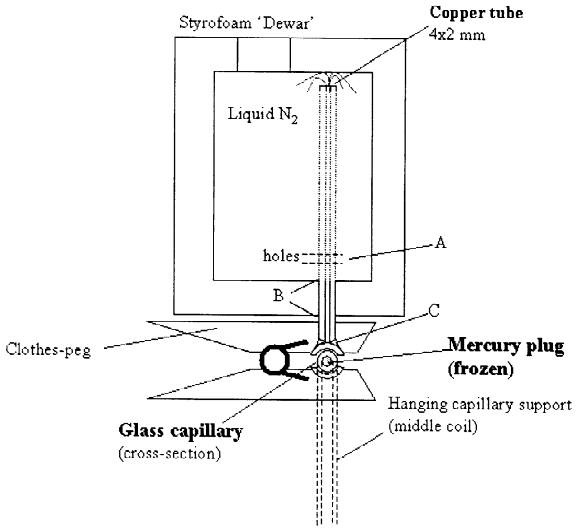

Fig. 2. Cooled clothes-peg assembly. The cross-section of the capillary sector containing the liquid Hg is shown clamped between the clothes-peg jaws, where mercury solidifies and remains frozen.

plug longer than 4 cm, mercury/coating solution menisci were near room temperature, so stationary phase polymers did not ''oil-out'' from the coating solution for (non-existent) cooling effects. The omission of any plug substance does not seem feasible; after support filling, the user might be able to solidify the neat coating solution (not an easy task, indeed), but a frozen solvent plug at the middle point of capillary support length could not be eliminated without re-melting it.

3.3. The pressurization step

Classical static coating procedures include a pressurization step [9] which is very useful to inhibit or recover breakthroughs. Pressurization does not seem so necessary when middle closures are used. However, if desired, the pressurization must be performed after Hg freezing.

3.4. Coating speed

Coating speeds reached by symmetrical static coatings were exactly two times faster than those of classically performed coatings. Fig. 4 reports results from a symmetrical coating experiment.

Data were acquired from the start to the end of the coating process. Initially coating speed was 10–12 cm/min. It decreased slowly to ~5 cm/min, after a lapse of <3 h and after production of 13 m of coated capillary.

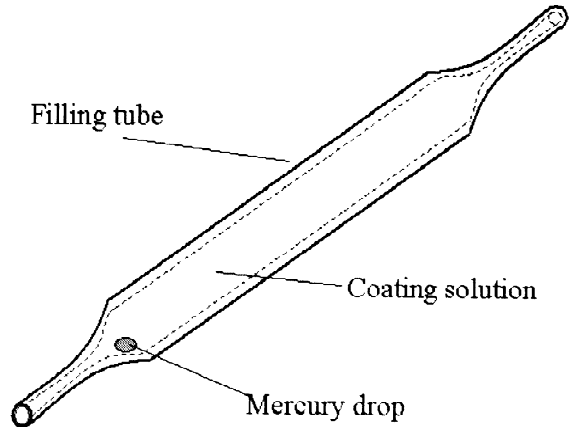

Fig. 3. Coating solution filling tube (connecting tubes omitted) containing the mercury drop. Mercury is delivered into the capillary support just rising up the glass tube, together with the coating solution.

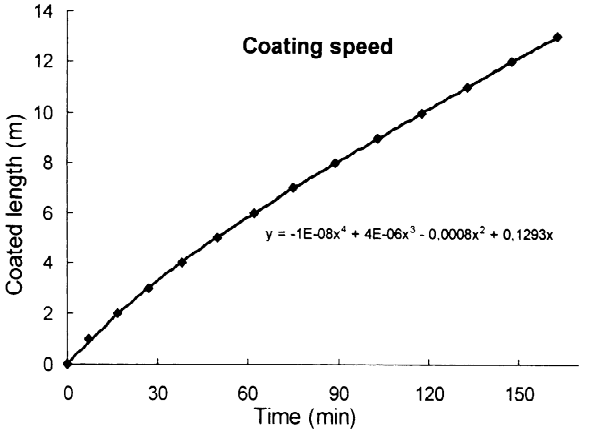

Fig. 4. Comprehensive coating speed on a 0.32-mm I.D. persilylated glass capillary. C_{coat} was 0.166% (w/v) (PS255 polydimethylsiloxane, dissolved in *n*-pentane-dichloromethane, 1:1). Note that breakthrough has not happened, notwithstanding omission of the pressurization step.

On a coated length base, symmetric coating would be even faster than twice the speed, owing to the decreasing value of coating speed with time. As for standard static coatings, coating speed was not too dependent on the internal diameter of the capillary support.

4. Conclusions

A novel static coating procedure without any end-closure use is presented, which allows the reliable application of vacuum to both capillary support ends (symmetrical static coating) and results in remarkable advantages over the classical static coating methods:

(1) coating speed (cm/min) is doubled, or more than doubled in terms of time required to obtain a certain coated length,
(2) no end-closures are necessary, and
(3) breakthrough risks linked to end-closures are overcome.

So far, the few columns coated symmetrically show the same performance as those coated by ''classic'' static coating. Subtle differences may become apparent when the number of columns produced symmetrically is statistically significant.

Acknowledgements

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