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A NEW, GENERALLY APPLICABLE PROCEDURE FOR THE PREPARATION OF GLASS CAPILLARY COLUMNS

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SUMMARY

A new procedure for the preparation of the inner surface of glass capillaries for subsequent coating with organic liquids is presented. This procedure is based on the production of a layer of barium carbonate crystals, grown from nuclei on the glass surface. In comparison with other methods it has the following merits: it greatly reduces dependence on glass type; it requires no difficult manipulations or materials; it gives high reproducibility and probability of success, producing almost neutral, thermostable columns with high resistance to rough usage, with wide applicability, and showing good, though not the highest, separation efficiency. This procedure is recommended in order to assist the numerous laboratories that wish to make their own glass capillary columns, without, however, needing to spend many months or even years in becoming specialized in this field. A simple, quick and almost universal method of preparation is needed to enable the bulk of their analytical problems to be handled.

A detailed description of the basic procedure alone is given. Various refinements are feasible, for example to increase separation efficiency or to include acidic columns by first transforming barium carbonate into barium sulphate.

INTRODUCTION

Laboratory-made versus commercial columns

As we have discussed this subject recently^{1,2}, it is intended to summarize here only the most important features, which concern the quality and the economic aspects of column making as well as an essentially psychological factor related to column handling.

Making glass capillary columns that fulfil high-quality requirements such as those described previously³, is still a difficult task, demanding a considerable degree of specialization. A better understanding of the processes involved may finally lead to simplification of the production methods; however, it remains doubtful whether a scientist interested in using, rather than in making, glass capillary columns should spend weeks, or even months, as is now necessary, in preparing high-quality columns.

Economically, it is reasonable for laboratories to make their own capillary columns only when the working hours involved are considered to be non-accountable.

On the other hand, a strong case can be made for the individual preparation of the columns. A non-specialized analyst considers a purchased glass capillary column to be an extremely friable and delicate object that should not be tampered with unless absolutely necessary. This unjustified fear of damaging the column leads to the use of an unsuitable application technique. It seems that the analyst who can rely on his own ability to replace a ruined column has far better pre-conditions for acquiring a correct technique.

It is the increasing importance we attribute to this last consideration that prompts us to assist those who wish to prepare their own columns, but does not, however, contradict our previous^{1,2} recommendation that a beginner should start by using one or more purchased columns of guaranteed quality.

Requirements for a general preparation procedure

Two of the above aspects (quality and economics) conflict with the third (the psychological factor). The solution to the problem must therefore be a compromise. The object is to introduce relatively simple preparation procedures that offer high probability of success after a few brief trials. The products may, on the other hand, be of good, if not the highest, quality in certain respects. The following fundamental requirements are considered in greater detail.

Lack of dependence on glass types. The controversy about the relative merits of published procedures, being successful in one laboratory and failing in another, is caused primarily by the high dependence on the raw material used. A procedure yielding excellent results may fail completely when glass with even minute structural variations is used.

Low sophistication. The procedure should not include very critical requirements, such as difficult manipulations, critical composition of reagents or sophisticated equipment design.

Wide application range. The product should be suitable for almost any kind of coating material and should, therefore, cover most analytical requirements. This universality includes polarity of liquid phases, temperature range, low adsorptive and catalytic activity, and controllable acid-base characteristics.

Interpretation of current experience

In recent years the importance of pre-treating the glass surface has become generally recognized⁴⁻⁸. Confusion has, however, arisen, about the use of terms such as "wettability", "deactivation" and "etching". Our interpretation of present knowledge and experience may be summarized as follows.

Two principles of wetting. Permanent spreading of a liquid over a solid surface may be brought about by two independent factors. A liquid film can be stabilized on a smooth (*i.e.*, degree of roughness far smaller than film thickness) surface by intermolecular forces that attract the liquid to the solid. This is the situation when untreated glass is coated with apolar polysiloxane phases. The second stabilizing factor is the so-called micro-roughness (degree of roughness of the same order of magnitude as film thickness). Both factors may operate to some extent in combination⁹. As has recently been confirmed⁷, the first wetting mechanism produces higher

separation efficiencies as a consequence of forming a more homogeneous liquid film. Thus for apolar coatings unnecessary roughening of the surface should be avoided.

In contrast, polar liquids spread almost exclusively on roughened surfaces only, whereby the necessary degree of roughening, together with a corresponding loss of film homogeneity, is a complex function of molecular structure, as partly described by polarity or surface tension.

While this interpretation may be widely accepted, confusion sometimes arises when deactivation is also to be included. The most efficient method of deactivation known is the heat treatment with polar phases according to the method of Aue *et al.*¹⁰, which leads to a paradoxical situation. Deactivation is most important for apolar coatings that are stable on smooth surfaces. However, the production of a coherent non-extractable layer of a polar phase before coating is feasible only on a roughened surface. Consequently, a perfectly deactivated apolar column requires a glass surface prepared for polar coating.

Evaluation of existing procedures

In considering mainly their suitability for general application, the procedures to be recommended consist of two groups. The procedures of the first group produce micro-roughness on the glass surface by etching or by effecting the growth of crystals or both. Those of the second group involve the introduction of extraneous small particles that act principally in the same way as a roughened surface.

The most promising procedure of the first group is etching with gaseous hydrogen chloride which, as Alexander and co-workers¹¹⁻¹³ have shown, simultaneously yields a layer of sodium chloride crystals. Without disregarding the elegance, simplicity, and the high merits of this method, as proved in many special applications⁴⁻⁶, a few limitations must be mentioned, which might affect its general applicability. Firstly, crystal growth seems to depend on the glass structure to such an extent that reproduction of an ideal degree of micro-roughness may present a problem. Secondly, the procedure is limited to soft glass, from which more or less only alkaline columns can be made. A further limitation is the solubility of the crystals in polar liquids.

The second group, introduced first by Kaiser¹⁴, had achieved prominence when Horning and co-workers^{15,16}, as well as Blumer¹⁷, Nikelly and Blumer¹⁸, and Schulte and Acker¹⁹, independently of each other, were successful in introducing fine silica particles in different ways. These procedures are virtually independent of the variety of glass used. They are, however, limited by the necessity of using relatively thick liquid films, which leads to lowered separation efficiency. Furthermore, it is our experience that the silica surface is catalytically active with certain liquid phases (*e.g.*, polyglycols) as well as with certain solutes. This activity proves to be a limiting factor for some high-temperature applications.

It is very difficult to judge from experience gained in our laboratory whether or not the procedure described in this paper shows fewer limitations for general use.

SELECTION OF ROUGHNESS-PRODUCING MATERIAL

Sodium chloride as an interlayer between the glass surface and the liquid film exhibits the following characteristics, thus favouring wide application: it is easily

produced with suitable density and size of particles; the crystals adhere firmly to the glass surface and they are chemically inert.

An ideal interlayer material should show in addition the following characteristics. It should be produced by reagents introduced externally, *i.e.*, glass should not be one of these reagents. The structure of the interlayer (the degree of roughening) should be predictable and reproducible. Finally, the material should be insoluble in water.

The most universal interlayer material we have found is barium carbonate. This water-insoluble substance can easily be formed by dynamically coating the glass surface with barium hydroxide solution. Carbon dioxide is used as the gas that pushes the plug of hydroxide solution. Simultaneously, it acts as the second reagent, producing barium carbonate before the liquid film starts to break up into droplets. This process can easily be conducted in such a way that the barium carbonate is formed exclusively on the glass surface, *i.e.*, without precipitation in the liquid phase, thus ensuring a perfectly even layer that is permanently bound to the glass surface. The density of this layer is easily controlled and reproduced by regulating the composition of the coating solution and the speed of coating. The process works on any kind of glass, although on borosilicate glass a micro-structure is obtained that is markedly different from that on soft glass. Variations usually observed within a selected type of glass, *e.g.*, Pyrex, can be neglected. As with HCl-treated columns, our capillaries are immediately coated with polar phases or deactivated before apolar coating. For every kind of coating the appropriate density of barium carbonate is selected empirically, over a range of approximately 100:1.

This brief survey establishes that treatment with barium carbonate possesses none of the weaknesses that are typical of the HCl treatment. Its only drawback is its lower chemical inertness. In the hydrated state, carbonate ions show moderate base strength, and the barium ion is a weak Lewis acid. Both effects are drastically reduced in the crystalline state, as both are basically involved in the formation of the very stable crystal. While we have not been able to detect any activity attributable to the barium ion, acids with a pK_s value lower than about 6, *i.e.*, most free fatty acids, have difficulty in passing over the carbonate surface. It should be emphasized, however, that barium carbonate treated Pyrex glass is much less basic than HCl-treated soft glass.

An aspect that requires further investigation should be mentioned here. We understand that the HCl treatment leaves the glass surface between the sodium chloride crystals uncovered. In contrast, we have obtained evidence indicating that barium carbonate covers the entire glass surface. Direct analytical proof is difficult to obtain because of the great difference between the barium-ion concentration in the well formed crystals and that in the very thin layer that is assumed to cover the glass between the crystals. One of our indirect arguments in favour of such a layer is the lack of dependence of the weak column basicity on the barium carbonate load in Pyrex columns. If the slightly acidic Pyrex glass surface between the basic crystals were bare, then a decreasing barium load should shift the column characteristics in the acidic direction. We interpret the fact that this shift cannot be observed by assuming that the barium carbonate treatment produces a coherent barium carbonate surface.

In order to eliminate the remaining base effect, and to prepare acidic columns,

barium carbonate has to be transformed *in situ* into barium sulphate, the crystals of which show complete chemical inertness. This step requires an additional treatment that is not dealt with in this paper.

We have, of course, examined numerous substances with respect to their suitability as an interlayer material. We were, however, not able to find any reasonable alternative to barium carbonate.

PROCEDURE

Crystallisation process

The formation of barium carbonate crystals very probably occurs as follows. Barium ions are adsorbed on the glass surface, where they act as crystallisation nuclei. Under favourable conditions, *e.g.*, thin liquid layer, high basicity and elevated temperature, crystallisation at these points proceeds so rapidly that not even traces of precipitation in the free liquid phase can be observed. The scanning electron micrographs (Fig. 1) show clearly that the crystals have been grown on the glass surface, to which they firmly adhere. According to Stumm and Hohl²², the crystallisation nuclei are understood to be complexes of barium ions bound to two silanol groups, their stability increasing with increasing basicity of the solution. The surface of freshly fused glass probably contains such complexes, formed by a variety of ions, in relatively high density. It is essential, therefore, to free the silanol groups from undesirable metal ions by rinsing with acid, which eliminates deposits of carbonates that would otherwise cause premature precipitation of barium carbonate.

Barium salt solution

Approximately 10 g of reagent-grade barium hydroxide [$\text{Ba}(\text{OH})_2 \cdot 8 \text{H}_2\text{O}$] are shaken with 100 ml of distilled water in a polyethylene or PTFE stoppered flask. After sedimentation, aliquots of the saturated barium hydroxide solution are pipetted out in order to prepare coating solutions.

All dilute barium salt solutions (the saturated solution is sufficiently alkaline) are made up with water and 1 *M* potassium hydroxide so as to be 0.2 *M* in potassium hydroxide. Besides creating conditions sufficient for stability of the complexes, this alkalinity ensures rapid uptake of gaseous carbon dioxide, as well as suppression of HCO_3^- ions in the HCO_3^- - CO_3^{2-} equilibrium.

To all barium salt solutions, 0.5% of a non-ionic detergent is added. We used Dehydrophen D (Dehydag GmbH, Düsseldorf, G.F.R.), which can, however, be replaced by an equivalent product. The concentration is not critical; we observed identical effects with 0.1–2%. Without detergent, however, the barium salt solution does not spread on the glass surface, thus causing irregular deposits of barium carbonate. When the solutions are prepared, minute precipitates are normally formed. To allow complete sedimentation we do not use a fresh solution before the next day.

Our standard barium salt solutions, with different barium hydroxide concentrations, are as follows: saturated and diluted 3, 10, 30 and 100 times, with the corresponding notation 1, 03, 01, 003 and 001, respectively.

Principles of the technique

Fig. 2 shows, schematically, the composition and functioning of the reaction

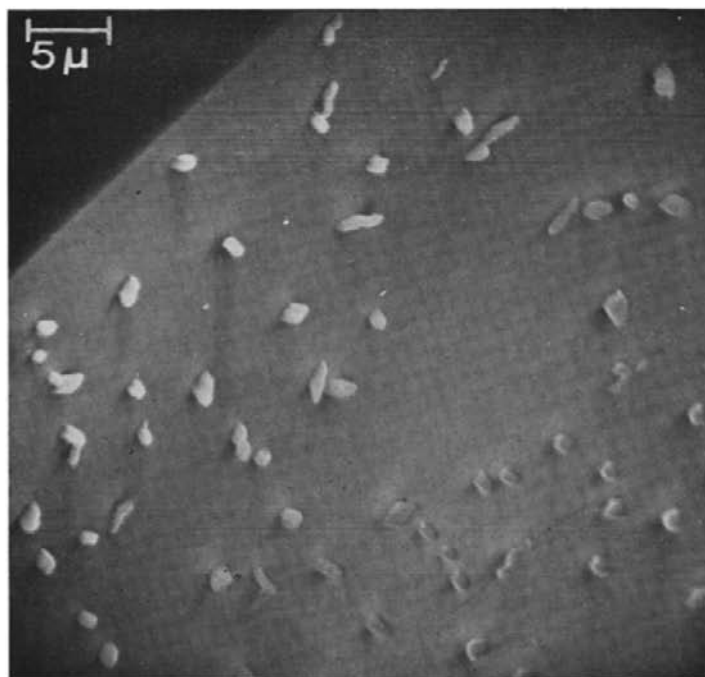
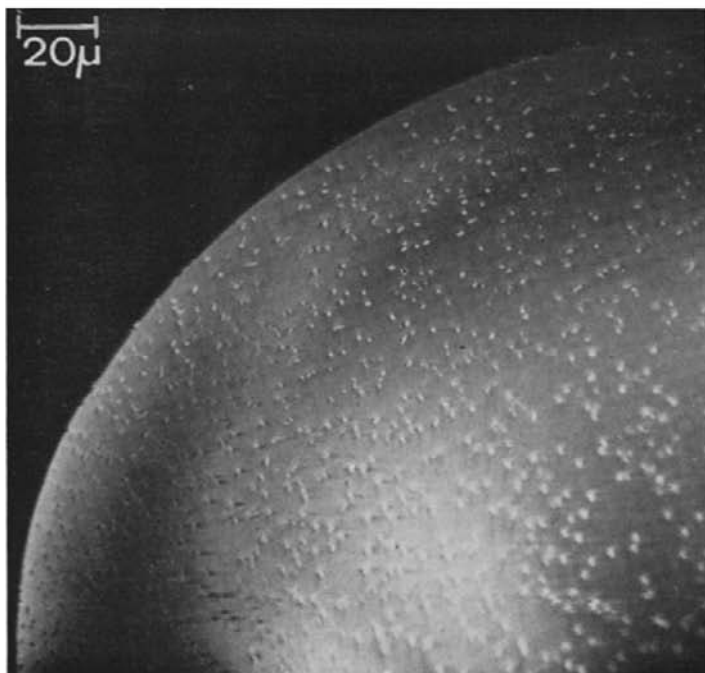


Fig. 1. Scanning electron micrographs of the inner wall of a Pyrex glass capillary after barium carbonate treatment 03, taken at an angle of 40° from the tube axis (Pretorius and co-workers^{20,21}). The crystals show the known shape of witherite (barium carbonate) and appear to have grown on the glass surface (micrographs by Department of Inorganic Chemistry, University of Zürich using a Cambridge Instruments Stereoscan 5 4).

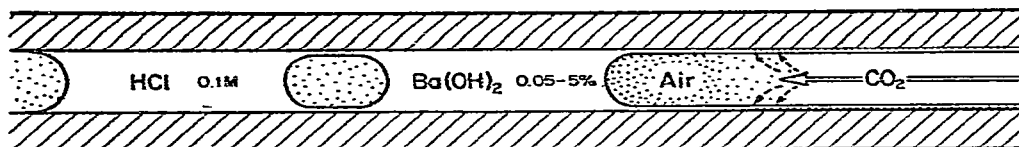


Fig. 2. Principles of the barium carbonate treatment. The glass surface is cleaned by washing with acid. Simultaneously free silanol groups are produced, which adsorb barium ions from the $\text{Ba}(\text{OH})_2$ solution. A short air plug ensures formation of a homogeneous aqueous film, the barium ions of which are then precipitated by carbon dioxide, which functions as a moving gas. Growth of barium carbonate crystals starts from the glass surface only.

zone, which, in one combined step, produces the permanently modified surface when it moves through the untreated glass capillary. As a rough rule we adjust the lengths of the single liquid plugs to about one tenth of the column length if the capillary has an approximately 0.3 mm I.D. For wider capillaries the relative plug lengths have to be increased to account for more efficient mixing of the two moving phases. For more narrow tubing the lengths can be reduced. The appropriate length is easily checked at the outlet of the column. At least two thirds of the second plug should still be strongly alkaline. The end of the second plug has to be separated from the carbon dioxide by a small zone of air, about 5 cm long for a capillary of, 0.3 mm I.D., independent of column length. Without this insulating zone, barium carbonate would be precipitated in large particles in the end of the liquid plug, yielding very irregular deposits on the column wall. The short air zone ensures the formation of an undisturbed liquid layer behind the liquid plug before the reaction with carbon dioxide starts. It may be surprising that, regardless of the intense diffusion between air and carbon dioxide, the short zone adequately fulfils this task. This is because the carbon dioxide that diffuses into the air plug is rapidly and totally absorbed by the alkaline coating. The suggested length of 5 cm is a compromise. A shorter air zone may not have sufficient insulating effect and a longer zone is undesirable because during the prolonged period between film formation and reaction the film may start to break up, in spite of the relatively high concentration of detergent. Again, the appropriate length is easy to check. The rear side of the moving hydroxide plug has to remain absolutely transparent the whole time. Inert impurities in the carbon dioxide will automatically accumulate in the air zone. Therefore, this zone always tends to increase, not decrease.

According to our experience, the regularity of the crystal layer increases with increasing reaction temperature. Empirically, we find the optimum temperature to be 80° . A higher temperature may cause difficulty for two independent reasons. Degassing of the liquids may disturb film formation because of the formation of foam plugs. In addition, excessive reaction of the liquids with glass may cause precipitation, especially within the alkaline plug. For soft glass with a particularly low chemical resistance, a reaction temperature below 80° may be advisable.

Practical directions

Straighten one end of the untreated glass capillary (length of end depending on oven geometry) to allow for easier application of solutions, and fill approximately one tenth of the column length with 0.1 M HCl through the straightened end (using

suction or pressure). After making a short air plug for visual control, introduce about the same length of the selected barium salt solution (concentration depending on proposed application). To avoid interference by ambient carbon dioxide, filling by suction is preferred. Disconnect the vacuum pump, and leave the straightened end immersed in the barium salt solution until the liquid stops moving. Withdraw the inlet end and immediately close it with a hermetically closing cap made from PTFE shrink tubing or equivalent material. Connect the outlet end to a buffer capillary with same I.D. and at least one fifth of the length. Place both capillaries in an oven with a glass door, whereby the straightened inlet end is pushed through a hole in the oven roof (Fig. 3). Adjust the temperature of the closed oven to 80°. Wait until liquid stops moving, which indicates pressure equalization between column and oven, and withdraw the cap from the column inlet. Wait until the plug end of the barium salt solution has fallen to the desired distance from the column end (3–10 cm, which is not critical). Then connect the column inlet to the carbon dioxide supply, ensuring that dead volumes of the carbon dioxide line (valves, manometer, etc.) have been flushed thoroughly before connecting, and adjust the desired moving rate to 1–2 cm/sec.

If no oven with a glass door is available, an alternative system, as indicated in Fig. 4, can be used. The flow-rate is determined by observing the movement of a short plug of, for example, toluene (a liquid with relatively low viscosity and volatility) in the buffer capillary. The longer the column, the longer the initial time during which exact determination is not possible. When the toluene plug reaches the end of the buffer capillary, disconnect the capillary and connect the opposite end. For repeated use an oven with a glass door is clearly preferable.

A few minutes after the barium salt solution has left the main column, open the door and disconnect the buffer capillary. If desired, push the liquids back and check that the remaining length gives an alkaline reaction with pH paper. Dry the

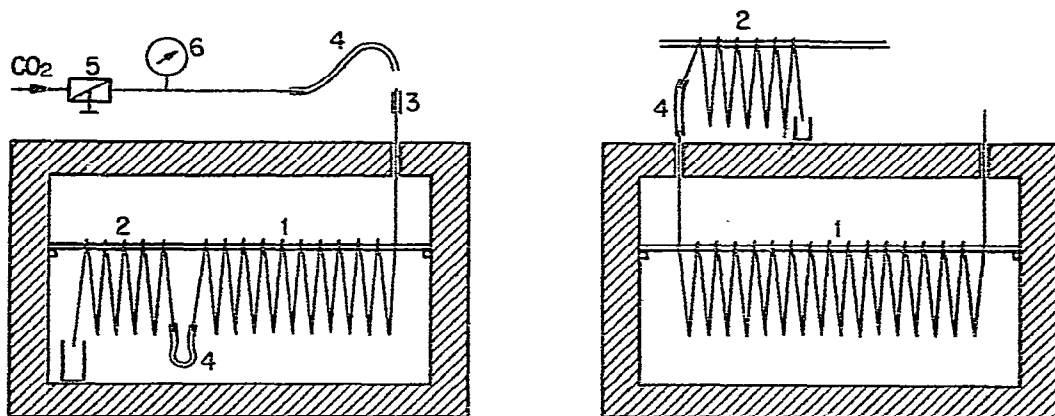


Fig. 3. Equipment for barium carbonate treatment including an oven with glass door. 1 = Glass capillary under treatment; 2 = buffer capillary; 3 = cap; 4 = elastic tubing; 5 = pressure regulator; 6 = manometer.

Fig. 4. Equipment including an oven without glass door. 1 = Glass capillary to be treated; 2 = buffer capillary containing a short plug of a liquid such as toluene; 4 = elastic tubing.

TABLE I
LIQUID PHASES AND THEIR PRE-TREATMENTS

Valuable for Pyrex glass, barium carbonate treatment at 80°, moving rate 1–2 cm/sec.

Liquid phase	Suitable pre-treatment		
Polyethylene glycol 20 000 (PG 20 M)	1	03	
Emulphor, Triton, Tergitol	1	03	01
OV-225, Silar 5CP, 7CP, 10C*	1	03	1 × PG**
OV-17, OS-124	03	01	1 × PG**
Ucon LB, Ucon HB	01	003	
SE-52, SE-54, OV-1, SE-30	01		2 × PG, 2 × E**
	003		1 × PG, 1 × E**

* The polar silicones, particularly Silar 10C, can be applied without PG pre-treatment.

** See under *Deactivation*.

treaded column by successively passing through it acetone and diethyl ether, each about one third of the column length. Evaporate off the ether with a flow of dry air. The column is now ready for immediate polar coating.

Liquid phase and suitable pre-treatment

Every organic liquid phase requires a certain degree of surface roughening for optimum film formation. Table I gives some information concerning this relationship for some liquid phases, selected to cover the entire range of polarity as well as the most common molecular structures. This information has been gained exclusively from experiments carried out in our laboratory. A simple rule is that more polar phases require a higher degree of roughening. In detail, however, the information becomes much more complex. For most liquid phases we find a wide range of suitable degrees of pre-treatment. It should not be concluded that the average degree is the most suitable, because by varying the pre-treatment it is possible to adapt the column characteristics for analytical purposes. As a further simple rule, it can be said that the highest degree of roughening is recommended in order to obtain the most durable column, *i.e.*, maximum thermostability and minimum sensitivity for heavy overloading, strong polarity, heavy sample by-products and high water content in the sample. The least amount of roughening, on the other hand, yields the best pre-conditions for high separation efficiency. This is a simplified rule; more detailed information can only be obtained from the individual phases.

The relationships given in Table I become even more relative when the following observations are included. It is possible to obtain perfectly stable columns, with excellent characteristics, outside the indicated range, as an example may show. A Pyrex capillary (Fig. 5) pre-treated with 30-fold diluted barium hydroxide solution (003) yields a very poor column after being coated with PG 20 M. This column, nevertheless, is conditioned during a few days at its normal temperature limit of *ca.* 250°. After rinsing and re-coating, it appears markedly improved, and the third coating may produce an excellent column. An analogous observation can be made when a Ucon phase is coated on a 03 or 1 pre-treated capillary. It is to be noted that silicone phases cannot be re-coated because of their autophobic behaviour.

It should be repeated that the above information has been obtained by using

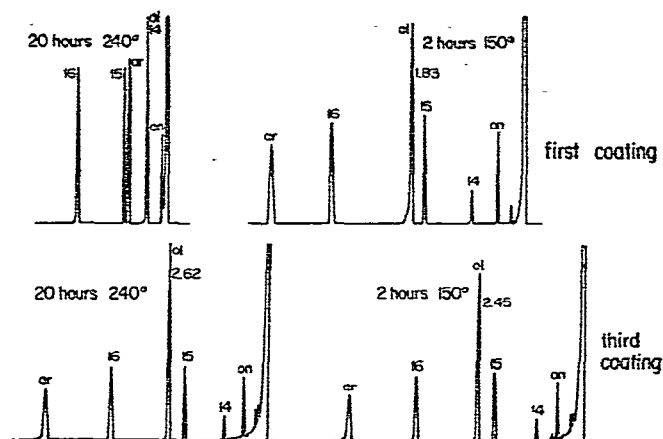


Fig. 5. Influence of repeated re-coating in the case of non-ideal surface pre-treatment. Pyrex capillary (18 m \times 0.34 mm I.D.) barium carbonate treated 003 (suitable treatment 1, 03). Isothermal runs at 100°; 2.2 ml H₂/min. Substances: cn = 5-nonanone; ol = 1-octanol; ar = naphthalene; 14–16 = *n*-tetradecane–*n*-hexadecane. Coating: 12% PG 20 M in dichloromethane, mercury plug, 0.3 cm/sec. Discussion see *Liquid phase and suitable pre-treatment*.

Pyrex glass. A change of glass type may markedly shift the indicated ranges. For instance, for soft glass considerably less roughening is needed.

Deactivation

The method used by Aue *et al.*¹⁰ to inactivate a solid surface by producing a non-extractable thin film of a highly polar polymer is widely accepted and has been applied to glass capillaries²³. The method we have used for several years is different in the following respects. It is our experience that a surface on which a polar liquid does not spread when applied in bulk amounts (*i.e.*, dynamic coating with a 1% or more concentrated solution), can ideally be covered by Aue *et al.*'s non-extractable film, when the deactivating agent is used in concentrations of 1‰ or less. The substance present in this dilute solution does not form a liquid layer after evaporation of the solvent. It is just sufficient to mask the most active sites. After heating it for 20–30 min, we repeat the treatment in order to cover remaining blanks. It seems that the film can be extended and completed in several steps, starting from the initially formed clusters. Extraction of non-adsorbed substance after heating is not necessary, as this is effected automatically during the subsequent coating.

Deactivation is only part of the above treatment. Wettability is also increased. Both effects are accomplished by the polyglycol treatment before coating with some polar phases, as indicated in Table I. A special case is the treatment we use before applying apolar coatings; in this treatment PG 20 M is used as an ideal deactivating agent, which greatly reduces adsorption of polar solutes on the column after apolar coating. However, the strongly polar PG is poorly wettable by apolar phases. Subsequent treatment with Emulphor (E in Table I) eliminates this problem, as this substance easily spreads on a PG layer due to the PG section of its molecule, while the hydrocarbon section, which is directed away from the solid surface, ensures

spreading of apolar liquids. In some instances treatment with Emulphor alone can yield sufficiently both effects.

The practical procedure is as follows. Solutions containing 0.1–1% of PG 20 M or Emulphor in methylene chloride (more concentrated solutions are used for more intense barium carbonate treatments) are passed through the capillary at normal coating rates of *ca.* 0.5–1 cm/sec. After quickly drying it by applying a vacuum to the outlet end, the column is mounted as usual in the oven of a gas chromatograph. It is flushed at room temperature for a few minutes with a high carrier gas flow. The flow is then reduced almost to zero and the oven is quickly heated and, with PG 20 M, is maintained for 20 min at 280°; the corresponding temperature for Emulphor is 240°. Before the heating is stopped, the carrier gas flow is increased again so as to prevent air from entering the column in the first moments of cooling. The cooled column is immediately ready for coating or for an additional PG or E treatment.

If a capillary is treated with barium carbonate with the intention of making a moderately polar or apolar column, then ether, which normally follows acetone the drying step, is replaced by a PG solution. In this event, a sufficient amount of acetone is introduced to ensure complete drying. (Ether has some drying effect, which is not true for methylene chloride).

As indicated in Table I (bottom), more PG and E treatments are required for a more roughened surface (*e.g.*, two PG and two E treatments on a 01 loaded surface). The additional work is however, worthwhile, as decreased adsorption and increased stability may be obtained.

Dynamic coating

Most liquid phases yield columns of almost identical quality after dynamic or static coating. As the dynamic procedure is time saving, we reserve static coating for those phases which, because of high viscosity, cannot be applied dynamically.

The mercury-drop method, developed by Schomburg *et al.*²⁴; effectively increases the reproducibility and safety of dynamic coating. It permits the use of about a two-fold concentration of the liquid phase, *i.e.*, only one half the amount of solvent has to be evaporated. This almost totally eliminates difficulties from plug formation, local accumulation of liquid phase, etc. We use low-viscosity phases, such as Emulphor, the Ucones, OS-124, etc., in concentrations of 16–20%, with dichloromethane as the preferred solvent. The coating rate is *ca.* 0.5 cm/min. PG 20 M, as an example of high viscosity, is applied in 12% solution at the rate of 0.3 cm/min. It has to be noted that rather thin films, only slightly more than 10^{-4} mm thick, are obtained in this way.

For columns with not less than 0.25 mm I.D., the practical procedure is simple. The coating solution is introduced by the suction method. When 6–8% of the column length is filled, the motion of the liquid is slowed down, so that it can barely be observed. This is effected by correspondingly reducing the vacuum applied at the column outlet. The inlet end is quickly withdrawn from the coating solution and dipped into a drop of mercury in a short, 2–3 mm wide glass tube. When a 2–3 cm long mercury plug has entered the column, normal dynamic coating is started. It is important that mercury that has been used for coating or been in contact with a coating solution should not be re-used before being carefully cleaned. Also air zones between mercury and coating solution that are longer than 10–15 mm should be

avoided. A longer air zone is too elastic and may therefore cause the mercury plug to jump.

Static coating

Viscous phases such as OV-1, SE-52, etc. are exclusively handled by static coating, as developed by Bouche and Verzele²⁵. For columns with 0.25–0.3 mm I.D., we use *ca.* 2‰ and for those with 0.3–0.4 mm I.D. *ca.* 1.5‰ solutions in methylene chloride. We still prefer to close one column end by sucking in *ca.* a 1-cm length of concentrated water glass and to start applying a vacuum at the opposite end after at least 6 h have elapsed.

The coating of the end sections, after dynamic or static coating, may be more or less irregular. We therefore rinse *ca.* 15 cm at each end with 0.5‰ PG 20 M (*i.e.*, a solution used for deactivation) in methylene chloride, connecting a 25- μ l syringe to one end by a short piece of flexible tubing, while applying a low pressure of inert gas to the other end.

Besides these major aspects, further information regarding specific manipulations, tools and aids should be described. We feel, however, that practical demonstration is more effective.

Testing and evaluation

After drying the freshly coated columns, they are flushed with 2–3 times the normal carrier gas flow in the closed oven, without heating (40–50°), for *ca.* 20 min. The oven temperature is increased within 1 h to 150°. After conditioning for 1 h at 150°, the routine tests for polarity/adsorption, acidity and separation efficiency are carried out, as described earlier²⁶. The results obtained indicate the characteristics of the column when it is fresh. Within a further 2–3 h the temperature is increased up to the limit (maximum temperature for continuous use) and this temperature is maintained overnight. With phases that are known to show moderate or high bleeding during initial conditioning, the column is disconnected from the detector. Before repeating the tests the next day, the outlet sections of these latter columns are again rinsed. Comparison of the two tests is in most instances strongly indicative of the column quality. The columns are then maintained at the upper temperature limit for 1–3 days in order to obtain information about long-term behaviour. This prolonged treatment is worthwhile only for columns showing reasonable results after the first night. After prolonged heating, valuable information is obtained from the bleeding test, carried out before cooling them down to test temperature.

Besides being dependent on the liquid phase, the temperature limit, as mentioned above, greatly depends on the character of the column surface. For Pyrex/barium carbonate columns we use the following temperature limits: OS-124, 200°; Ucon HB 5100 and Emulphor, 230°; PG 20 M and OV-17, 240°; OV-1 and SE-52, 250°. It must be emphasized that all types of column continuously withstand temperatures that are 20–30° higher without loss of separation efficiency. As stated earlier³, other, more critical, column characteristics can be determined, especially when long-term routine use is intended.

A few practical examples may elucidate these indications. Fig. 6 shows some results from the first conditioning period of an Emulphor column. Emulphor ON 870 (Applied Science Labs., State College, Pa., U.S.A.) is slightly acidic, probably due to oxidation processes. After 2 h of conditioning at 150°, this acidic character can still

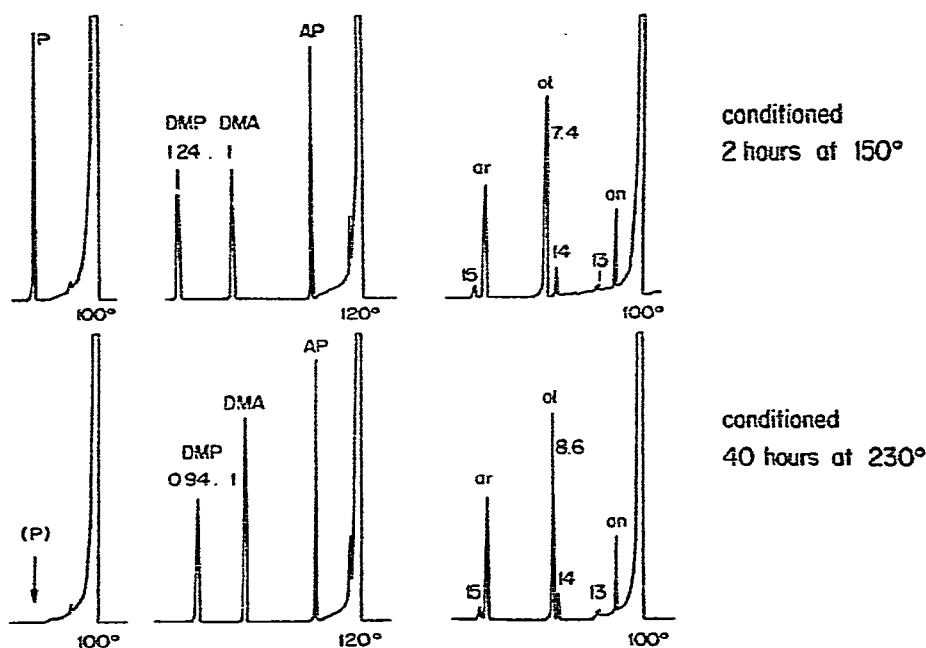


Fig. 6. Typical behaviour of a correctly prepared Emulphor column during conditioning. Pyrex capillary (20 m \times 0.34 mm I.D.) barium carbonate treated 01, coated with 16% Emulphor ON 870 in dichloromethane, mercury plug, 0.4 cm/sec. For substances, see Fig. 5, plus acetophenone (AP), 2,6-dimethylaniline (DMA), 2,6-dimethylphenol (DMP), propionic acid (P), and *n*-tridecane (13). For discussion, see *Testing and evaluation*.

be observed from the 2,6-dimethylphenol (DMP)–2,6-dimethylaniline (DMA) ratio 1.24:1. The same observation indicates that the basic character of the column surface is weak. After prolonged conditioning at 230°, the ratio becomes 0.94:1, showing a slightly basic character. As a consequence of this shift, propionic acid exhibits drastically changed behaviour. A less drastic but very typical change is seen in the polarity test. Chromatographically, the alcohols exhibit weakly basic characteristics. Therefore, octanol shows increased retention on the acidic column (see distance from tetradecane before and after heating). Naphthalene, as a slightly acidic substance, clearly shows the opposite tendency, being more retained on the basic column, that is, after heating. The improved ratio of octanol to tetradecane (8.6 after heating) may be a consequence of the same shift. Further, exact measurement showed a reduction in retention of 7% after heating.

Fig. 7 shows the effect of inefficient deactivation on the adsorption characteristics after prolonged heating. While the separation efficiency remains unchanged, the 1-octanol peak indicates strongly increased adsorption. When the 01 barium carbonate layer, deactivated with two PG 20 M treatments, is followed by two rinsings with E and heating to 240° (see under *Deactivation*), the octanol peak keeps its perfect shape after several weeks of continuous heating.

In order to be considered satisfactory, a column has to show the following results after being maintained for several days at the temperature limit. No significant

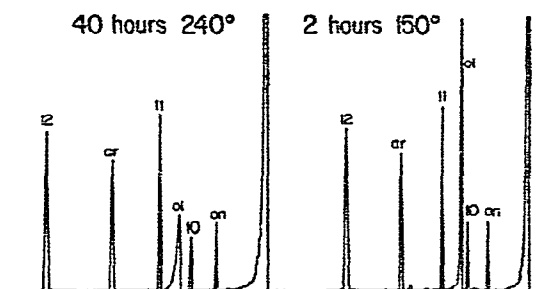


Fig. 7. Typical behaviour of an inefficiently deactivated column during conditioning. Pyrex capillary (20 m long, 0.34 mm I.D.) barium carbonate treated 01. Deactivation with 2.0% and 0.5% PG 20 M in methylene chloride, followed by maintaining at 280° for 30 min. Static coating with 1.5% SE-52 in methylene chloride. Isothermal runs at 75°. For substances, see Fig. 5, plus decane (10), undecane (11) and dodecane (12). For discussion, see *Testing and evaluation*.

increase in adsorption (no change in peak shape of 1-octanol, no change in peak-height ratio between 1-octanol and the next *n*-alkane); no significant change in polarity; no change in acid-base characteristics after the second day (a slight change during the first conditioning is normal); and no loss of retention after the second day (some column types show reduced retention after the first conditioning).

CONCLUDING RECOMMENDATIONS

When using the barium carbonate procedure for the first time, we recommend that a 30–50 m long and *ca.* 0.3 mm wide Pyrex capillary be treated with a 03 coating solution (a mixture of 10 ml of saturated barium hydroxide solution, 15 ml of distilled water, 5 ml of 1 *M* potassium hydroxide and 20 mg of non-ionic detergent), and coated, immediately after drying, with PG 20 M, Emulphor or Triton. This example requires minimum experience while yielding a column of wide applicability.

When some experience has been acquired, we recommend the use of apolar columns whenever it is clear that polar phases are not needed. Apolar columns, we specially recommend SE-52 and SE-54, exhibit a wider practical temperature range, less bleeding, less long-term polarity shift and longer life time, combined with higher separation efficiency. These conditions, however, hold only when adequate deactivation and wetting have been effected.

Although the barium carbonate treatment works on any kind of glass, we recommend the use of Pyrex or other borosilicate glass because it is more easily handled (drawing, straightening, etc.), more easily treated (no tendency for precipitation to occur and wider range of suitable treatments) and gives almost neutral columns.

In conclusion, it is necessary to emphasize again the essential role of the application technique, which is quite different from that suitable for packed columns, and which is less easily acquired than many analysts suppose. Weaknesses in the application technique will negate the effects of the best column.

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