Journal of Chromatography, 178 (1979) 63–70
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CHROM. 11,941

PREPARATION OF SILYLATED CELITE BY A VAPOUR-PHASE METHOD

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(First received November 14th, 1978; revised manuscript received February 19th, 1979)

SUMMARY

Celite was silylated with hexamethyldisilazane (HMDS) vapour to produce gas chromatographic supports. The deactivated Celite supports obtained were of the highest quality. The process of preparation is simple, in that no post-treatment of silylated Celite is required, and neither harmful vapours nor waste solutions are produced.

It was confirmed that heating for a long period did not affect the quality of the product, in spite of the usual decrease in the concentration of surface hydroxyl groups. Reasons for this are proposed. Further, it was established that impurities in the HMDS, possibly amines, have no effect on silylation or on the quality of the Celite obtained.

INTRODUCTION

Advances in gas chromatography are approached from two directions, namely improvement in detector sensitivity and deactivation of the support material and the capillary column. In recent years, the former approach has been successful, but the latter has not. Several methods for the deactivation of diatomaceous earth support materials have been developed, including vapour-phase esterification with lower alcohols[1], silylation in dimethyldichlorosilane (DMCS) or hexamethyldisilazane (HMDS) solution[2] and thermal treatment with Carbowax 20M[3]. It is claimed that Celite of the highest quality can be obtained by pre-treating raw Celite with boiling concentrated hydrochloric acid prior to silylation[4,5]. Some workers have silylated Celite with DMCS in nitrogen carrier gas at room temperature[6], but this does not give high-quality material.

It is traditionally believed that DMCS is the most suitable reagent for either liquid-phase[7] or vapour-phase silylation. Furthermore, samples treated with DMCS contain a considerable amount of chloride on their surface, which must be removed by methoxylation with anhydrous methanol. The dehydration of methanol is very tedious. In the HMDS treatment, on the other hand, there is no need for such a difficult post-treatment[8–10]. To ensure complete silylation with HMDS, the treatment must be carried out at higher temperatures as HMDS has a low reactivity. This, however, introduces another problem. On heating the sample, physisorbed water molecules desorb at temperatures below about 120°, and above 150° the concentration of surface hydroxyl groups decreases without a major structural change[11–13]. If siloxane is formed, it does not react with silylating agents but has a high adsorption ability. Thus, the applicability of HMDS depends solely upon whether or not the unfavourable effect of siloxane can be avoided. With this in view, a test experiment was carried out with a 1-g sample, and we obtained an encouraging result.

In the present work, we investigated the following points to establish the applicability of HMDS:

(1) whether the HMDS method is applicable on a practical scale of production in which the dehydration process requires a long heating time;
(2) the required amount of HMDS applied;
(3) effects of impurities in HMDS; and
(4) the amount of HMDS consumed.

EXPERIMENTAL

Vapour-phase silylation apparatus

The apparatus for the vapour-phase silylation is shown schematically in Fig.1. The silylation reactor was a Pyrex glass tube of length 1000 mm and I.D. 70 mm and was arranged vertically. The lower part of the tube was packed with several glass Raschig rings of length 20 mm on which a glass-wool layer of depth 10 mm was placed. The reactor was put into an aluminium sheath 1020 mm in length and 0.5 mm thick. Cooling of the ends of the reactor was prevented by using additional heaters. HMDS vapour was supplied from a modified 1-l Claisen flask in an oil-bath maintained at a temperature in the range 135–140°.

The reactor was fitted at the top with a three-way stopcock (head) connected to the vapour source and nitrogen reservoir. Effluent of HMDS was introduced into a receiving flask. To check the uniformity of the temperature, five thermocouples were bound to the aluminium sheath with Ilon wire. An additional thermocouple was in direct contact with the glass surface. The main heater was PID controlled in the range 170–300°.

General procedure

Pre-treatment. Celite was treated successively with the following three solutions[10]: solution I, 1 part of concentrated hydrochloric acid was added to 50 parts of water; solution II, 35 of sodium hydroxide were dissolved in 1.5 l of water; solution III, solution I was diluted 1:1 with water.

About 1000 g of Celite 545 (60–80 mesh) were immersed in 3.5 l of solution I at room temperature for 24 h. After immersion, the Celite was washed with distilled water until the washings were neutral and filtered under vacuum. The residue was immersed in 1.5 l of solution III. After 1 min, the residue was washed with distilled water until the washings were neutral, rinsed three times with 1-l volumes of methanol, spread over a 100 × 120 cm polyethylene vat in a layer several millimetres thick and air-dried at room temperature for 2–4 h.

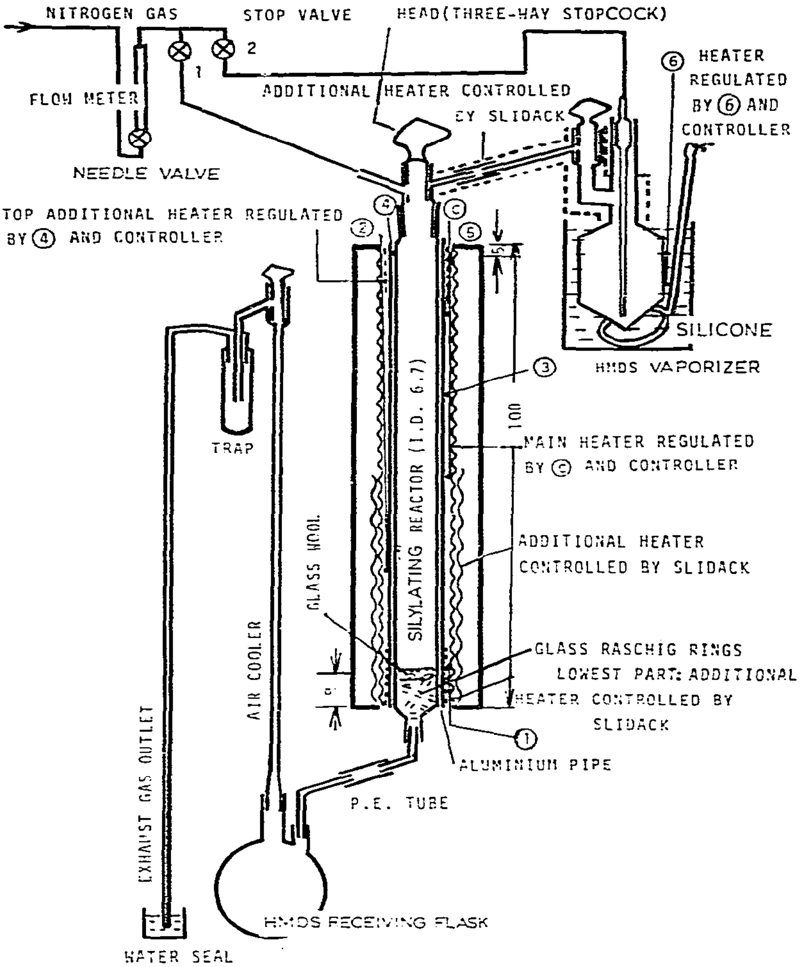

Fig. 1. Apparatus for silylating 1 kg of Celite. 1–6, Thermocouples connected to a temperature recorder; 4,6, connected to temperature regulators; (c), thermocouple connected to a regulator to control the reactor temperature. Dimensions in cm.

Silylation. Commercial HMDS was supplied by Kishida Chemical (Tokyo, Japan) and had a nominal purity of 99%. However, its true purity, checked by gas chromatography, was about 97.5%.

The pre-treated Celite was packed into the reactor tube up to the level of 87 cm high, its weight being about 840–900 g (dry).

It took about 1 h for the temperature of the reactor to increase from room temperature to 210°. During this period, dry nitrogen was passed through the reactor by opening the stop-valve 2, in order to remove adsorbed water and methanol from the Celite surface. Then the nitrogen flow was switched to the HMDS vaporizer. The temperature of the oil-bath around the vaporizer was increased quickly to a pre-set temperature of 134°. When the temperature reached 100°, the flow of nitrogen was stopped. During the supply of HMDS, the exposed head of the reactor was kept at a temperature above 150° in order to prevent the condensation of HMDS before it was caught in the receiver. A higher flow-rate of HMDS, say about 400 g/h, in the initial stage was preferable. An example of the temperature changes is shown in Fig. 2. After this treatment, the nitrogen flow was switched to the initial path and residual HMDS vapour in the reactor was purged. No further post-treatment was required, in contrast to the usual situation with DMCS. The HMDS collected in the recieving flask was re-used.

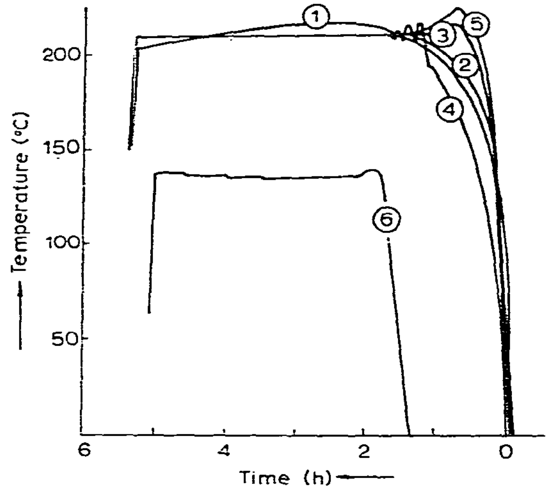

Fig. 2. Changes of temperature during silylating operation. 1–6, Thermocouples according to Fig. 1.

Evaluation of the quality of the silylated Celite

The evaluation was made with a Shimazu Model 3BT gas-chromatograph[14]. The column was a stainless-steel tube (500 × 3 mm I.D.) and the test gas was mixtures of air and methanol (the silylated Celite was packed in the column without any stationary liquid phase). The quality of Celite was classified as A, B, C and D in descending of quality. In class A, the peaks for air and methanol completely overlapped. In class B, a slight shoulder occurred; in class D, a clear separation of the peaks was observed; class C was intermediate between B and D.

RESULTS AND DISCUSSION

Effect of pre-heating the reactor

About 90 min were allowed from the start of heating of the reactor before the HMDS was introduced. This pre-heating period was considerably longer than that in the previous test experiment, when only 1 g of Celite was treated. In spite of this long treatment, the reaction conditions selected gave high-quality Celite, as checked by the above method. A further check of the quality was made by using the Celite as the support in a gas chromatographic column operating under the usual condition. The results are given in Fig. 3, which indicates that there is no difference between the qualities of the present and previous class A Celites, the ratio between the peak heights of cholestane and cholesterol being 0.343 in each instance. In contrast, class C Celite gave a peak with a long tail for cholesterol, and the

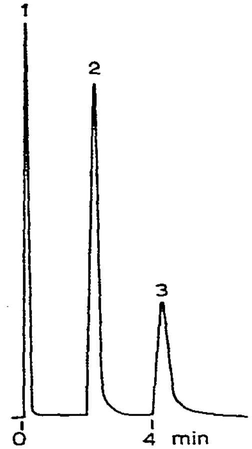

Fig. 3. Gas chromatogram of cholestane–cholesterol mixture. Support, Celite, pre-treated with hydrochloric acid as described, then silylated with HMDS vapour; liquid phase, 1.6% OV-1 on support; glass column, 2 m × 3 mm I.D.; oven temperature, 230° isothermal; injector temperature, 320°; nitrogen flow-rate, 70 ml/min. Peaks: 1 = solvent (chloroform); 2 = cholestane; 3 = cholesterol.

Celite produced by conventional liquid-phase silylation gave no observable peak for cholesterol.

It took 90 and 120 min for the reactor temperature to increase to 170° and 260°, respectively. The higher the temperature of and the more prolonged the heat treatment, the more silanol groups disappear. However, Celites pre-heated at 170°, 210° and 260° had the same quality. The reasons for this are discussed below.

Surface hydroxyl groups give IR absorption peaks at 3780 and 3200–3650 cm^{-1}. Usually the former is assigned to single hydroxyl groups, designated I, and the latter to hydrogen-bonded hydroxyl groups, II. Hydroxyl group II is easily cleaved and water is released on heating at 120–450°, while hydroxyl group I is converted into siloxane only at much higher temperatures[12,15]. Under the present heating conditions, hydroxyl group I survives and is easily silylated with HMDS. The methyl "umbrella" of the $-Si(CH_3)_3$ group on the surface completely covers the sites occupied by hydroxyl groups II. If the hydroxyl groups at the latter are changed to the original form I on contact with moisture, the regenerated hydroxyl groups I may not act as strong adsorption sites owing to steric hindrance by the methyl "umbrella". The geometrical arrangement is shown schematically in Fig. 4.

Amount of HMDS applied in silylation

In a previous paper[8] the ratio of the amount of HMDS fed to the amount of Celite was 30–40. On the basis of this ratio, production on a practical scale, *e.g.*, 1-kg batches, becomes difficult and uneconomical. In order to reduce the amount of HMDS required, one must increase the chance of contact between the HMDS molecules and the reaction sites as there is no consecutive reaction. This is achieved by using the column for as long a period as possible, and by eliminating residual gases from the pores of the Celite. With these requirements, in view, the present design of the column was adopted and no carrier gas was used.

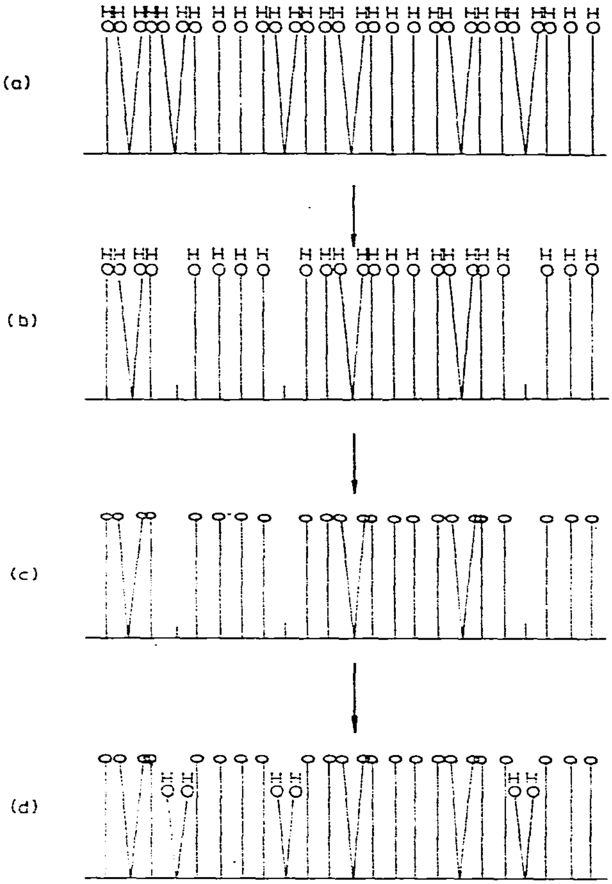

Fig. 4. Surface structure of Celite. (a) 120° dried (model proposed by Bather and Gray[12]); (b) 260° pre-heated; (c) 260° silylated; (d) one of the possible structures of silylated Celite after contact with moisture at room temperature (regenerated OH groups cannot come into direct contact with approaching molecules). The black short bars show posterity of surface hydrogen-bonded hydroxyl groups and the ovals the methyl "umbrella" of the trimethylsilyl group.

The minimal amount of HMDS required was determined as follows. Three samples of Celite were withdrawn from the upper, middle and lower parts of the column, and their qualities were compared. It was assumed that a sufficient amount of HMDS had been fed in if the three samples were of the same quality. The required amount of feed thus determined was 900 g of HMDS per 900 g of Celite in the present apparatus. This is a fairly favourable value from a practical point of view.

Effect of impurities in commercial HMDS

The purity of the HMDS used was 97.5%, in view of the process used for its synthesis[16] the main impurities may be diethyl ether and amines. Gas chromatographic analysis showed that there is no peak due to diethyl ether, but possibly one to amines, as slight tailing occurred as shown in Fig. 5. This impurity did not react with water and may be an amine.

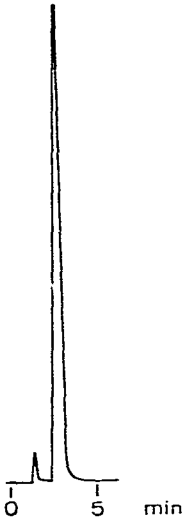

Fig. 5. Chromatogram of commercial HMDS. Liquid phase, 3% OV-1 on 60–80-mesh Celite treated by the proposed method. Stainless-steel column (2 m × 3 mm I.D.); oven temperature, 80° isothermal; injector temperature, 150°; nitrogen flow-rate, 20 ml/min; sample size, 0.4 μl. Peaks: unknown impurity; HMDS.

Further, the effect of impurities was studied by using HMDS reagent repeatedly. If the impurity reacts with Celite and has some influence on the quality of deactivated Celite, the quality may decrease with continued re-use of the HMDS. When the HMDS was re-used fourteen times, the impurity content increased to about 8%, but this reagent gave Celite of the same high quality. Hence the impurity appears to have no effect on the quality of the Celite obtained.

Amount of HMDS consumed in the silylation reaction

The amount of HMDS consumed was only 4–5 g, which corresponded to 0.5% (w/w) of the Celite treated. In the conventional method of silylation in the liquid phase, about ten times more HMDS is consumed.

CONCLUSION

It is usually considered that the gas-phase silylation process is superior to the liquid-phase process in terms of economy and ease of handling. Gas-phase silylation with HMDS, however, has not been used because of its low reactivity. It has been established in this work that the silylation with HMDS proceeds satisfactorily at a temperature between 170° and 260°.

The merits of the proposed method are as follows: (i) deactivated Celite of high quality is obtained without any special techniques; (ii) no post-treatment is required after the silylation; (iii) no solvent is wasted; and (iv) no harmful vapour is evolved.

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