METHOD FOR TESTING UNCOATED SUPPORTS AND GLASS CAPILLARIES

Yuzi TAKAYAMA

Materials Science, Toyohashi University of Technology, Toyohashi

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Using methane as a marker gas, a methanol peak with FID gas chromatograph was measured to evaluate uncoated supports and capillaries. The amount of methanol injected was finely controlled, and quantitative results were obtained as to characters of supports and capillaries. The present method was compared with Grob's testing one for capillaries and it was concluded that the both gave the same results.

1 Introduction

Deactivation for supports or capillaries is a necessary process to obtain acceptable peak profiles of samples containing highly polar compounds in gas chromatography and also sufficient temperature stability of the stationary liquid, depending on the catalytic properties of the supports surfaces or the capillaries inner surfaces. A method for testing inertness levels of the supports had been proposed.^{1,2)} But the previous method was rather qualitative. Then, a study was carried out to improve the method in quantitative view point and to make clear the reliability of the present method in comparison with the Grob's testing one.^{3,4)}

2 Experimental

2.1 Apparatus for preparing methane and methanol mixed vapour

In characterization of supports or capillaries, the amount of injected methanol must be finely controlled, since it is well known that adsorption effect gives rise to rapid increase in retention and tailing of the peak as the sample size is reduced. The control of the amount of methanol was achieved with an apparatus shown in Fig. 1. The cylindrical gas reservoir a in the

figure, was held at an atmospheric pressure by using a mercury reservoir. A mixture of air and methane was introduced into the reservoir a, contacted with a layer of methanol liquid on mercury, and saturated with methanol vapour. Thus, the concentration of methanol was well controlled, 23.3% by volume (1.31mg/ml) at 25°C. The concentration of methane was about 7% by volume but not carefully controlled, since methane is not adsorbed and its peak position is not affected by the amount injected. With a FID gas chromatograph, air is not detected, and methane can be used as a marker gas.

2.2 Mesurment of chromatogram

The amount of gas mixture injected was 50-1200 μ l for columns packed with supports, and 1.7-900 μ l for glass

capillaries. Uncoated supports were studied with a Perkin Elmer 1540 FID gas chromatograph operated at the following conditions. Supports were packed in a U-shape Pyrex glass column (105cm x 3.5 mm I.D.) held at 28°C. The flow rate of nitrogen carrier gas was 20ml/min, and the chart speed was 10mm/min.

The character of capillary (Pyrex, 10m x 0.15mm I.D.) was studied with Shimazu GC 6A gas chromatograph equiped with FID. The capillary temperature was held at 40°C, the linear velocity of nitrogen carrier gas was 16.7cm/sec, the split ratio was 130, and the chart speed was 40mm/min.

Fig. 1 Apparatus for preparing methane and methanol mixed vapour. a=cylindrical gas reservoir, inner diameter 40mm, capacity 75ml, b=spherical mercury reservoir, inner diameter 60mm, c=two way stop cock, d=gas sampling port with a septum, e=connecting flexible pipe, f=mercury, q=layer of methanol liquid.

3 Results and discussion

3.1 Capacity ratio k'_{MeOH} for supports and capillaries

The capacity ratio of methanol, k'_{MeOH} *, was measured as a function of the amount of methanol loaded onto the column, results being in Fig. 2 and 3.

Fig. 2 Surface tests of uncoated supports. Curve number 1-6 are supports number, respectively. 1=Chromosorb HP 80-100 mesh, 2=Chromosorb AW DMCS 80-100 mesh, 3=after drying followed by pretreatment, silylated Celite by HMDS vapour phase method, 100-120 mesh, 4=same as 3 except 5 days interruption was allowed between drying and silylation. 5=conventional silylated support by HMDS, 30-100 mesh, 6=Celite 80-100 mesh.

Support No. 1 is Chromosorb HP, and No. 2 Chromosorb AW DMCS. These support gave good results as expected. Support No. 3 and 4 were developed by the present author.^{5,6} They were prepared from Celite by a dynamic vapour phase silylation with hexamethyl disilazane (HMDS). The difference in

* k'_{MeOH} is evaluated for methanol by the relation.

$$k'_{\text{MeOH}} = \frac{t_{\text{R MeOH}} - t_{\text{R M}}}{t_{\text{R M}}}$$

$t_{\text{R MeOH}}$: retention time of methanol
peak

$t_{\text{R M}}$: retention time of methane peak

chromatographic characteristic between No. 3 and 4 originates from a slight difference during the preparation process. The preparation processes, *i.e.*, the pretreatment, drying and silylation, were carried out without interruption was in support No. 3, while in support No. 4 five days interruption was allowed between drying and silylation. The results are in good agreement with the previous one.⁷⁾ Support No. 5 is a commercial one silylated by HMDS. It is considered that some difference in preparation processes produced such a large difference in the characters of No. 3, 4, and 5. Support No. 6 refers to raw material Celite.

Fig. 3 Surface tests of uncoated glass capillaries. Curve No.7-10 are capillaries number, respectively. 7=untreated, 8=HMDS vapour phase dynamic silylated without any treatment, 350°C 8hrs, 9=pretreatments: 20% HCl 95% filling in capillary, 150°C 12hrs, silylation:same as 8, 10 =pretreatment:conc. HCl pass through capillary, 150°C 12hrs, silylation:same as 8.

In Fig. 3, one can see effects of surface treatments of glass capillary. Capillary No. 7 has a unfavourable character (curve 7). Curve 8 is obtained when the capillary is dynamically silylated with HMDS at 350°C for 8hrs. Fig.

4 shows an example of gas chromatogram with these capillaries. Curve 9 and 10 were obtained with capillary carefully treated as follows;

Capillary No. 9: 20% HCl was introduced into the capillary, up to 95% filling, then capillary was sealed. After heating the capillary at 150°C for 12hrs,⁴⁾ the capillary was washed with acetone until PH value of the elute became 7. After drying by nitrogen gas, immediately, it was silylated at 350°C for 8hrs. Capillary No. 10: Concentrated HCl was pass through the capillary held at 150°C for 12hrs. Then the capillary was treated by the same procedure as the above.

The difference in the character between No. 9 and 10 suggests the importance of pretreatments of the glass surface.

3.2 Comparison present method with Grob's one

To check the reliability of the present test method, test diagram was compared with Grob's one.⁴⁾ With above four capillaries, Grob's diagrams shown in Fig. 5 were obtained. The correspondence between Fig. 3 and 5 is excellent. It is thus concluded that Grob's test method can satisfactorily be replaced by the present one which is very simple.

Generally speaking, the solid surface has acid or base site. The former adsorbs electron donors such as alcohols and amines, while the latter acids. The curves in Fig. 3 suggest the presence of acid sites on the supports but may not base sites. However, there is a parallelism between the trend of these curves and the increase of tailing of acid in Fig. 5. The reason for this is unknown as yet, but it is said empirically⁹⁾ that methanol can be used

Fig. 4 Chromatograms of methane and methanol vapour mixture to measure k'_{MeOH} . Detail of capillaries: see Fig. 3. Peaks: 1=methane, 2= methanol. Condition: capillaries 10m x 0.15mm I.D., 40°C, nitrogen $u=16.7\text{cm/sec}$, injected volume 78 μl for No.7, 12 μl for No.8, split ratio 130.

Fig. 5 Grob's test diagrams. 13, 14, 17:n-alkanes, diol:2,3-butandiol, A:2,6-dimethyl aniline, P:2,6-dimethylphenol, ol:1-decanol, acid:butyric acid, each solute 10mg/25ml benzene, precolumn:Carbowax 20M coated,⁸⁾ $d_f = 0.039\mu\text{m}$, conditions:uncoated capillaries 5m x 0.15mm, temp. programmed $2^\circ\text{C}/\text{min}$ from 90°C , $u=15\text{cm}/\text{sec}$, detail of capillaries:see Fig. 3.

as a prob gas to check properties of the supports and the capillaries.

3.3 Adsorbing phenomenon for n-alkanes

Grob proposed the following model to explain a tailing of n-alkanes peak observed.⁴⁾ In the course of silylation with HMDS, produced NH_3 attacks glass surface, and a sponge-like structure is produced. Lee suggested¹⁰⁾ that such a sponge-like structure may not be produced if the silylation is carried out in

a dynamic flow system, since an accumulation of NH_3 is avoided. Curve No. 9 in Fig. 5 denies their expectation.

Unfavorable properties of this so-called sponge-like structure can easily be killed by coating the surface with a thin layer of SE-30. Results are shown in Fig. 6.

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Fig. 6 Chromatogram of n-alkanes. Capillary: SE-30 $d_f = 0.039 \mu\text{m}$ on capillary No. 9, cf. uncoated No. 9 shown in Fig. 5. $u = 13 \text{ cm/sec}$, solvent benzene.

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