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GAS-MODIFIED SOLID CHROMATOGRAPHY USING ORGANIC VAPOURS AS CARRIER GAS

II*. MECHANISM AND APPLICATION FOR AROMATIC AMINES

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SUMMARY

The modification of activated alumina by organic vapour and the physical adsorption of the vapour on activated alumina have been measured and their effect considered in relation to the retention volume of samples. It is suggested that in this type of chromatography the sample molecule on the adsorbent is displaced by a vapour molecule, called displacement effect. When ethylenediamine or cyclohexylamine is added to the carrier vapour, good chromatograms of aromatic amines can be obtained.

INTRODUCTION

The use of water[1–3], ammonia[4], carbon tetrachloride[5], benzene[6] or other vapours[5–9] as carrier gas in gas–liquid chromatography has been reported. Gas-modified solid chromatography using activated alumina or silica gel as adsorbent is useful for the separation of hydrocarbons, phenols, the isomers anthracene and phenanthrene, and the isomers α- and β-naphthols[7–9]. The function of the carrier vapour was suggested in terms of the formation of an adsorbed layer, which could make significantly smaller the adsorption energy of the adsorbent surface for the sample molecules[3,7–9].

The purpose of this paper is to examine this chromatographic mechanism and to describe the application of this system to the separation of amines.

EXPERIMENTAL

The operating procedure with the gas chromatograph, generating of organic vapour, condensing of organic vapour eluted from the column and detecting the sample component with an ultraviolet liquid cell at 254 or 280 nm were carried out

* For part I, see ref. 9.

as described earlier[7–9]. The temperature of the injection port of the gas chromatograph was set at 250°.

The columns were stainless-steel tubes, 50–150 cm long and 3 mm I.D. The solid adsorbents used were as follows: activated alumina for column chromatography, 200–300 mesh (Kishida Chemical Co., Osaka, Japan); silica gel K 923 for column chromatography, 100–200 mesh (Katayama Chemical Co., Osaka, Japan); Spherosil XOB 075, particle diameter 40–100 μm (Pechiney, Saint-Gobain, France, supplied from Gasukuro Kogyo, Tokyo, Japan). All chemicals used were of extra-pure grade.

Measurement of specific surface area

Fig. 1 shows the schematic diagram of the adsorption system and gas chromatograph. Activated alumina for column chromatography, 200–300 mesh (Kishida Chemical Co.), was used as the adsorbent, and, before the experiment, was dried at 200° for 5 h under a stream of nitrogen. About 100 mg of activated alumina were placed in the sample tube (E_1), quartz-wool being lightly packed at both ends of the tube. After inserting needle B into the injector (C_1), liquid ethanol was passed into the injector by microfeeder (A) for generating vapour.

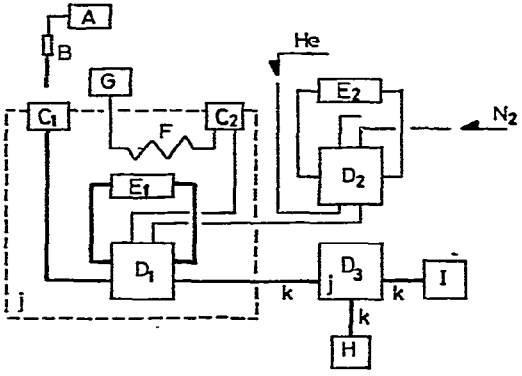

Fig. 1. Block diagram of apparatus for measurement of specific surface area. A, Microfeeder; B, needle; C, injector; D, six-way cock; E_1, sample tube, 3 mm I.D. and about 6-cm length; E_2, standard stainless-steel tube loop for the measurement of sample tubes volume; F, column; G, thermal conductivity detector, recorder and integrator; H, mercury manometer; I, vacuum pump; J, thermostating part and K, heating part.

Operational procedure. After evacuating the system, ethanol vapour was passed through the sample tube for several minutes. Next, by operating the six-way cock (D_3) to close the system, the system was filled with ethanol vapour until the inner pressure reached 60 cm Hg. Needle B was then withdrawn and the flow of ethanol stopped, the system being evacuated with a vacuum pump. This whole procedure was repeated three times.

Next, after filling the system with ethanol vapour, the inner pressure was set at an adequate level by operating the six-way cock (D_3) and vacuum pump (I).

From the manometer (H) reading it was possible to determine whether or not the gas–solid equilibrium was established. Usually this equilibrium was attained within 10 min. The other six-way cock (D_1) was then operated and the components

of the sample tube were passed into the gas chromatograph, which has a separation column, 35 cm long and 3 mm I.D., packed with Porapak T (Waters Assoc., Milford, Mass., U.S.A.), for analysis.

The amount of adsorbed ethanol was calculated as follows: (Total amount of ethanol detected by thermal conductivity detector) — (amount of ethanol in the gas phase).

The latter value was calculated by measuring the gas volume in the sample tube when it was filled with nitrogen. The responses of ethanol and nitrogen with the thermal conductivity detector were checked by injecting known amounts of each.

RESULTS AND DISCUSSION

Chemical modification of adsorbent

In the gas-modified solid chromatography using an organic vapour as carrier gas, the vapour was adsorbed physically and/or chemically on the surface of the support or adsorbent. The nature of the adsorbent used in our gas chromatographic system become different from that in its original condition because the adsorbent is modified by chemical adsorption of the vapour. The degree of modification was examined by measuring the relationship between retention volume (V_r), using helium carrier gas, and the length of time the ethanol vapour passed over the adsorbent (shown in Fig. 2).

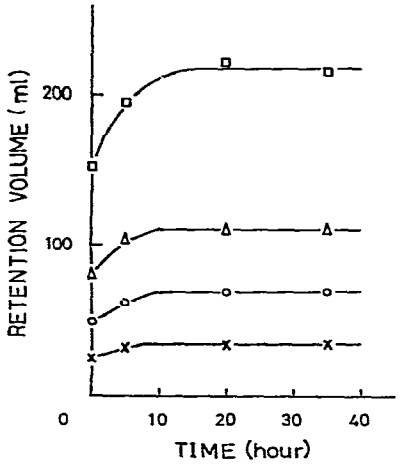

Fig. 2. Variation of retention volume (V_r) with time. Each V_r value is measured using helium carrier gas, and □, △, ○ and × are *n*-propylbenzene, ethylbenzene, toluene and benzene, respectively. Ethanol carrier vapour was passed over activated alumina for several hours. The time in hours is shown as abscissa. Column: stainless-steel tube, 50 cm long and 3 mm I.D., packed with activated alumina for column chromatography, 200–300 mesh; detector: thermal conductivity detector. Amount injected is 0.1–1 μl of each *n*-hexane solution containing about 1% of sample.

Fig. 2 was obtained as follows. First, retention volumes of samples were measured at the column freshly packed with new activated alumina, 200–300 mesh, using helium carrier gas. Then, after changing the carrier vapour from helium to ethanol vapour, the ethanol vapour was passed through the column at 200° for 5 or

15 h. The carrier vapour was then changed back from ethanol to helium, and the retention volume of the sample again measured. The above process was repeated several times.

Fig. 2 shows that the chemical modification of the adsorbent was almost complete within about 20 h and that the modified surface causes the retention volume to increase. It is therefore suggested that the chemical adsorption layer, which may have been built up by the reaction between ethanol molecules and active sites of the adsorbent, has a lipophobic character.

Physical adsorption layer on adsorbent

In gas-modified solid chromatography, the physical adsorption layer may have an important effect for the development of solute in the column, similar is that of the chemical adsorption layer, so this adsorption layer was examined in detail in gas chromatography using ethanol vapour and activated alumina. Although the specific surface area of an adsorbent is most commonly measured by using nitrogen, its value is dependent on the molecules adsorbed, such as H_2, N_2, CH_4, ethanol, etc.[10]. It is therefore more satisfactory to use ethanol molecules for the calculation of the specific surface area in this experiment.

We measured this value for activated alumina and the amount of ethanol molecules that adsorbed physically on its surface. The number of molecular layers was calculated by using the above two values and the area of molecular cross-section of ethanol, 24.7×10^{-16} cm^2 at 110°, calculated from the equation given in ref. 11.

The adsorption isotherm of ethanol vapour and activated alumina is shown in Fig. 3. X is the reduced pressure (P/P_0), that is, P is the pressure of vapour and P_0 the saturation pressure of vapour at the given temperature. V is the amount adsorbed

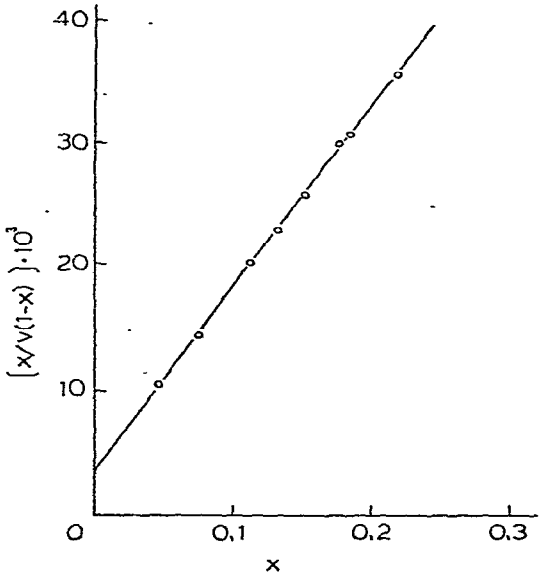

Fig. 3. Adsorption isotherm for ethanol vapour and activated alumina for column chromatography at 110°.

(cubic centimeters per gram of adsorbent at S.T.P.). The specific surface area of activated alumina was calculated from the intercept by the B.E.T. method[12]. The value obtained for ethanol vapour was 44 m^2/g.

The volume adsorbed on activated alumina at atmospheric pressure was also measured at several temperatures by using the same apparatus that was used for the measurement of specific surface area. The relationship between the number of molecular layers and temperature is shown in Fig. 4. It is suggested that there is only one physical adsorption layer of ethanol at temperatures above 110°.

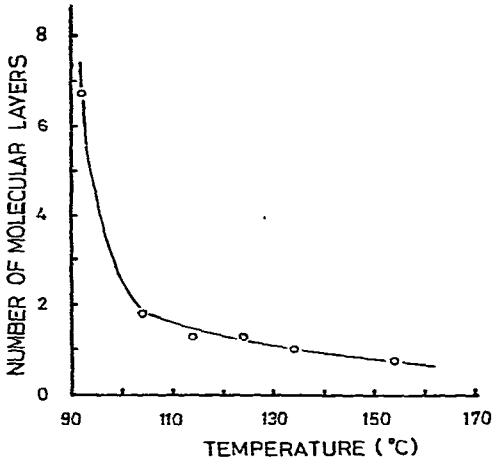

Fig. 4. Adsorption isobar for ethanol. Pressure, 760 mm Hg. Activated alumina for column chromatography was used as adsorbent.

Now it is clear that the adsorbent, activated alumina, has one physical adsorption layer when it is used in an environment of ethanol vapour at atmospheric pressure. It is possible to imagine that the molecule in the physical adsorption layer is always exchanged by another molecule, which is adsorbed on the surface from the vapour phase. Thus the solute molecule on the surface is also exchanged by a molecule of carrier vapour[13]. The retention volume of the solute may be affected by the above displacement mechanism, physical adsorption layer and chemical modification. These factors cause the ΔH value of the solute to decrease, as previously suggested[9]. The chemical adsorption layer, that is, the chemically modified surface of the adsorbent, and the physical adsorption layer, may act like the usual stationary phase in gas chromatography, but the displacement effect is a special effect that is not observed in ordinary gas chromatography. A remarkable example of this displacement effect is given later in Fig. 7.

Relationship between the composition of the vapour and that of the physical adsorption layer

In chromatography, the role of the solvent is very impressive, and the nature of a solvent mixture is sometimes very different from that expected from its composition. As it is difficult to determine the composition of the adsorbed molecules on

adsorbents, the nature of developing solvent is assessed from the data for some distribution factors[13]. It is, however, more satisfactory to determine the composition of the adsorbed molecules in order to examine the relationship between the role or strength of solvent and distribution factor.

According to earlier reports[7–9], mixed carrier vapours, in addition to pure organic vapours, are also used as carrier gases, and the composition of carrier vapour may not be identical with the composition of the adsorption layer. The mixed carrier vapour of *n*-hexane and ethanol is therefore examined as an example of a non-polar and polar vapour system, and the mixed carrier vapour of ethanol and methanol as an example of vapours that have almost the same characteristics. Analysis of the component of the adsorption layer was carried out by using the same apparatus as was used for the measurement of the specific surface area. The results obtained are shown in Fig. 5.

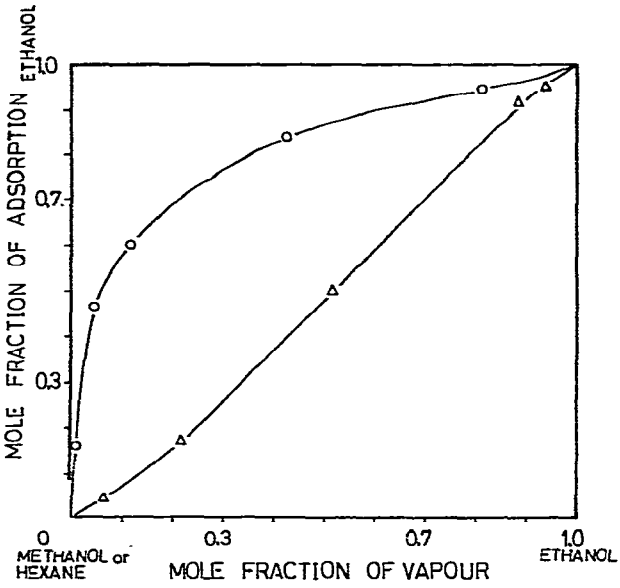

Fig. 5. Relationship between compositions of vapour and adsorption in two-Component system. ○ and △ indicate ethanol–*n*-hexane and ethanol–methanol systems, respectively. Adsorbent was activated alumina for column chromatography.

The relationship between the compositions of the carrier vapour and adsorbed layer in the system methanol–ethanol appears to be nearly ideal, but that in the system of *n*-hexane–ethanol non-ideal. Even though ethanol vapour is added in only a small amount to hexane vapour, the percentage of ethanol in the adsorption layer becomes very much higher. For this reason, the retention volume of isobutyl methyl ketone decreases remarkably at the first stage in the addition of ethanol to *n*-hexane, as shown in Fig. 6. The retention volume then gradually increases from 0.3 to 1.0 mole fraction of ethanol. It is suggested that this increase in retention volume may correspond to the increase in the amount of ethanol adsorbed.

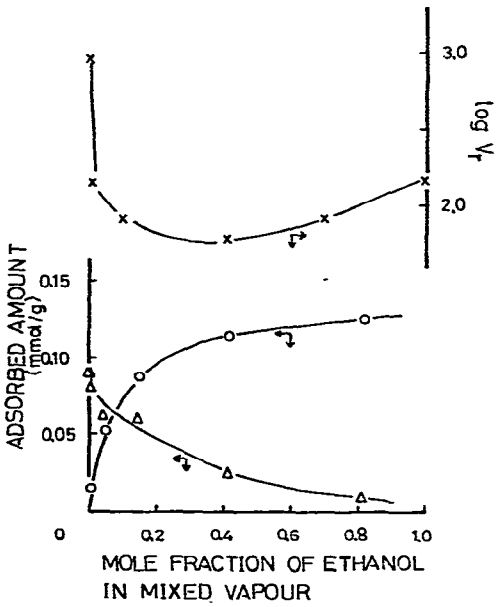

Fig. 6. Relationship between adsorbed amount and retention volume. The abscissa shows the mole fraction of ethanol in ethanol–*n*-hexane mixed carrier vapour. Activated alumina for column chromatography was used as adsorbent. ○ and △ indicate ethanol and *n*-hexane, respectively. × shows the retention volume of isobutyl methyl ketone in the gas chromatography using mixed carrier vapour and activated alumina[7].

When the mole fraction of ethanol in the methanol–ethanol system decreased from 0.1 to 0, the retention volume of dinitrobenzenes increased steeply[8], a phenomenon similar to that observed for isobutyl methyl ketone in the *n*-hexane–ethanol system. It is suggested that these phenomena are due to the molecular nature, molecular size and/or composition of the adsorption layer. With the *n*-hexane–ethanol system, the variation in retention volume may be explained by the difference in molecular nature, that is, in polarity, and, with the methanol–ethanol system, this phenomenon may be dependent on the molecular size rather than on the difference in their natures[8].

The latter explanation is confirmed by the following results. When isopropanol, ethanol, methanol and methanol that contains 1% of acetic acid are used as carrier vapour, the retention volumes of aromatics were almost identical except for pure methanol, in which retention volumes were doubled. It is possible that as each molecule of ethanol, isopropanol and acetic acid has straight carbon chains and a hydroxyl group, their molecular sizes may be similar when they adsorb on the surface of activated alumina.

It is of interest that the composition of the adsorption layer is different from that of carrier vapours, especially in the *n*-hexane–ethanol system. When a mixed carrier vapour is used, it is necessary to examine the composition of the adsorption layer in order to ascertain its effect on the retention volume.

These results can be applied in a study of liquid chromatography. Attention

must, however, also be paid to the composition of the adsorption layer on the adsorbent, which may be different from that of the eluent.

Effect of additions of amines into carrier vapour

o-, *m*- and *p*-Phenylenediamines, N-substituted amines, α- and β-naphthylamines, *o*-, *m*- and *p*-nitroanilines, N-phenyl-α- and N-phenyl-β-naphthylamines, etc. can be separated. Typical chromatograms are shown in Figs. 7–9. As the HETP of N-*n*-butylaniline is about 0.7 mm, this column has high efficiency for the separation

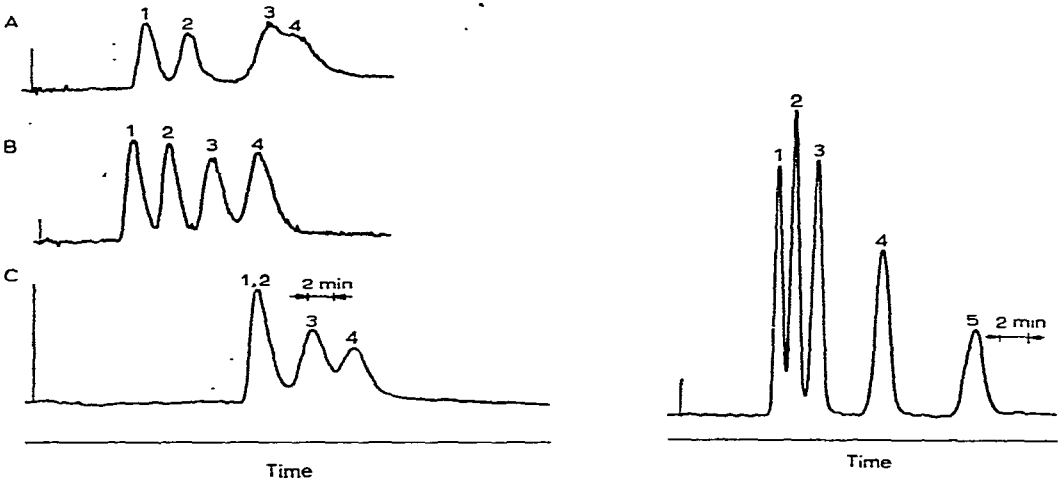

Fig. 7. Chromatograms A and B: Adsorbent, silica gel, 100–200 mesh; column temperature, 150° column length, 50 cm; sample, 6 μl of ethanol solution containing 0.05–0.2% (1) unknown, (2) *o*- (3) *p*- and (4) *m*-phenylenediamine. Carrier vapour is 1.0% ethylenediamine–ethanol vapour (B) or pure ethanol vapour (A). Chromatogram A was obtained by using silica gel that was pre-treated by passing over it ethylenediamine–ethanol carrier vapour for 1 h. Chromatogram C: carrier vapour is 1.2% cyclohexylamine–ethanol; column temperature, 190°; column length, 1.5 m.

Fig. 8. Chromatogram of N-substituted anilines: carrier vapour, 1.2% cyclohexylamine–ethanol vapour; adsorbent, silica gel; column temperature, 180°; column length, 1.5 m; sample, 3 μl of ethanol solution containing about 0.2% (1) aniline, (2) N-methyl-, (3) N-ethyl-, (4) N,N-diethyl- and (5) N-*n*-butylaniline.

When silica gel and helium were used as adsorbent and carrier gas, respectively, aniline was eluted only when injected in large amount, and its peak was very broad and peak height very small. With ethanol vapour as carrier gas, aniline was usually eluted, but its peak was also broad. When cyclohexylamine (about 1.6%) was added to the ethanol vapour, the peak of aniline was greatly improved, without any tailing.

Similar phenomena were more strictly observed in the case of the isomers of phenylenediamine. When ethanol vapour was used as carrier gas, these isomers were not eluted reproducibly. When, however, about 1% of cyclohexylamine or ethylenediamine was added to the ethanol carrier vapour, the isomers were eluted with good reproducibility and their peaks were so improved as to be symmetrical. Next, after passing ethanol vapour containing about 1% of each amine through the silica gel column for about 1 h, the carrier vapour was changed to pure ethanol and we ob-

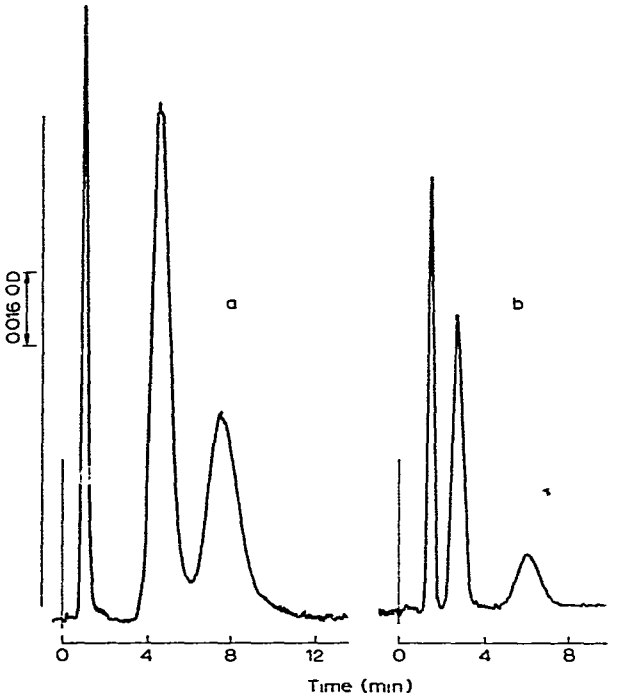

Fig. 9. Chromatogram using Spherosil. (a) Separation of N-phenylnaphthylamine isomers: adsorbent, Spherosil XOB 075, particle diameter 40–100 μm; carrier vapour, ethanol; column temperature, 150°; column length, 50 cm; sample, 3 μl ethanol solution containing about 0.1% benzylamine, N-phenyl-α-naphthylamine and N-phenyl-β-naphthylamine, eluting in that order. (b) Separation of nitroaniline isomers: sample, 1 μl of ethanol solution containing about 0.2% *o*-, *m*- and *p*-nitroaniline, eluting in that order; experimental conditions as in (a).

tained the chromatograms of N-substituted anilines and phenylenediamines. The two chromatograms of N-substituted anilines, which were obtained by using pure ethanol and ethanol containing amine, were identical, but the chromatograms of the phenylenediamines were different from each other, as partly shown in Figs. 7A and B.

From the above results it is suggested that the presence of an amine in the carrier vapour, which is physically adsorbed on the surface of silica gel, has the effect of improving the chromatogram of the sample of strong amines, such as the phenylenediamines, owing to the displacement effect. It is also suggested that the chemical modification of the surface of silica gel by an amine, such as cyclohexylamine or ethylenediamine, and the displacement effect of ethanol molecules, are sufficient for the separation of N-substituted anilines.

Although the chromatograms of phenylenediamine isomers show similar patterns when about 1% of cyclohexylamine, 1,3-diaminopropane or 1,2-diaminocyclohexane was added to ethanol carrier vapour, the chromatogram using ethanol carrier vapour containing ethylenediamine differed from the others, as typically shown in Figs. 7B and C, and shows the best pattern. Ethylenediamine has the function of separating phenylenediamine isomers. It is not apparent why ethylenediamine has

this function, but it is suggested that it is partly because this amine has the strongest basicity. When the concentration of ethylenediamine is increased from 0.5 to 4%, there is no remarkable variation in the retention volume of phenylenediamines.

Comparison of carrier vapours

When Spherosil XOB 075 is used as adsorbent, the retention time of *o*-nitroaniline is 6 min, under the following conditions: column length, 50 cm; column temperature, 150°, carrier vapour, 100% ethanol. However, its retention time using silica gel is 14.5 min, under the following conditions: column length, 50 cm; column temperature, 200°, carrier vapour, ethanol containing cyclohexylamine. By using Spherosil XOB 075 instead of silica gel, samples such as the nitroanilines are eluted very rapidly. Samples such as N-phenyl-*α*-naphthylamine (m.p. 60°) and N-phenyl-*β*-naphthylamine (m.p. 108°), which have very low vapour pressures, are also eluted within 10 min, as shown in Fig. 9. By using Spherosil XOB 075 and ethanol vapour, biphenyl and fluorene are eluted within 1 min, under the following conditions: column length, 50 cm, column temperature, 150°. Their retention times are about one third of the retention time of isobutene using nitrogen carrier gas saturated with water[14]. It is suggested that ethanol vapour has a stronger function in eluting the sample than nitrogen carrier gas saturated with water, and that ethanol vapour has a stronger function than water, as the following results indicate: high-boiling hydrocarbons, such as anthracene, are eluted from the column of activated alumina using ethanol vapour as carrier gas, while only lower hydrocarbons are eluted using water vapour as carrier gas[3,8].

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