

Influence of liquid solvents on the properties of immobilized film of poly(ethylene glycol) type stationary phase on the basis of polyurethane

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Static and dynamic action of organic solvents and water on chromatographic properties of capillary columns with the film of the poly(ethylene glycol) type stationary phase — Carbowax 20M — crosslinked on the basis of polyurethane has been studied. Long-term contact of the film with water decreases capacity of the separation system; by action of benzene both capacity and efficiency of the studied column change. The capillary column can be washed dynamically with benzene, methyl alcohol, ethyl alcohol, hexane, acetone, chloroform, acetonitrile, and tetrahydrofuran without any danger of affecting the homogeneity of the stationary phase film. Dynamic action of 0.02 M-CH₃COOH in distilled water on the stationary phase film causes a slight increase of both capacity ratio and efficiency.

Было изучено статическое и динамическое действие органических растворителей и воды на хроматографические свойства капиллярных колонок с пленкой неподвижной фазы типа полиэтиленгликоля — Carbowax 20M — сшитого на основе полиуретана. Продолжительное взаимодействие пленки с водой снижает емкость разделительной системы; под влиянием бензола изменяется как емкость, так и эффективность колонки. Капиллярную колонку можно промывать динамически бензолом, метиловым и этиловым спиртами, гексаном, ацетоном, хлороформом, ацетонитрилом и тетрагидрофураном без опасности нарушения однородности пленки неподвижной фазы. Динамическое действие 0,02 М-СН₃СООН в дистиллированной воде на пленку неподвижной фазы обуславливает слабое повышение как коэффициента емкости, так и эффективности.

Advantage of capillary columns, currently used in analytical practice at present, lies mainly in their high total efficiency and high permeability in comparison with the packed columns [1, 2]. Recently, they have been preferred also for advantages resulting from the possibility of immobilizing the film of the stationary phase on the inside surface of the capillary. From the chromatographic point of view, the film should also be resistant against stripping effect during splitless or on-column injection while preserving selectivity of the original nonimmobilized stationary phase and sufficient efficiency. Regenera-

tion of the columns should be possible by means of organic solvents, or even by water [3, 4]. Increase of thermostability of the stationary phase film is also desirable [1, 3—6].

At present a large number of stationary phases are used in gas chromatography, the most widely used being polysiloxanes, less used are polyglycols, poly(phenyl ethers), and hydrocarbons. Most of the so far published papers deal with immobilization of polysiloxane stationary phases [1]. Immobilization of the polyglycol film of the stationary phase on the inside surface of the capillary can be reached by means of several methods [4, 7—20]. Majority of the described methods make use of radical reactions with the same initiators as for crosslinking of the silicon phases.

Formation of spatially stable film of the poly(oxyethylene) (poly(ethylene glycol)) type stationary phase with the above-mentioned physical and chemical properties can be reached using the reaction for creation of polyurethane bonds [21—25]. The urethane bond in polyurethanes is formed by means of polyaddition of diisocyanate, or also pluriisocyanate, with a bifunctional donor of hydrogen (often polyester or polyol), multiple block copolymer being formed at the same time [23]. The reaction must often be catalyzed [22]. For immobilization of poly(ethylene glycol) with the relative molecular mass of 15 000—20 000 (Carbowax 20M), the authors [8, 19] made use of the reaction of its end hydroxy groups with —NCO groups of hexamethylene diisocyanate or Desmodur L75 or Desmodur N75 catalyzed by dibutyltin dilaurate or by a catalyst commercially known as DABCO R-8020 in dichloromethane. The reaction resulted in chains of polyadduct of initial components.

Capillary columns coated with the film of the poly(ethylene glycol) type stationary phase crosslinked on the basis of polyurethane are suitable for analysis of basic and neutral substances, organic substances with hydroxy groups as in essential oils and others. Such capillary columns, in comparison with capillary columns coated with noncrosslinked Carbowax 20M, show higher temperature stability while preserving the lower limit of operating temperature. The operating temperature of Carbowax 20 M itself is in the range of 60—225 °C; the upper limit of operating temperature of Carbowax 20 M crosslinked with hexamethylene diisocyanate is 305 °C, when crosslinked with Desmodur N75, it is 310 °C, when with Desmodur L75, it is 330 °C.

This study is concerned with behaviour of the stationary phase film on the inside surface of the capillary column after long-term action of distilled water or benzene. It is also concerned with the possibility of long-term dynamic washing of the capillary column with this type of the stationary phase with distilled water enriched with acetic acid as an example of making use of the mobile phase for capillary liquid chromatography with electrochemical detection. In the end, it concentrates on checking the resistance of capillary columns

to be used for on-column sampling after extraction or concentration in different common solvents.

Experimental

Simax glass tubes (Kavalier, Sázava), quartz capillaries (Slovak Academy of Sciences, Bratislava), γ -glycidoxypropyltrimethoxysilane (Union Carbide, USA), Desmodur L75, Desmodur N75 (Bayer, GFR), DABCO R-8020 (Air Products, U.S.A.), Carbowax 20M (Erba, Milan), and other chemicals supplied by Lachema, Brno were used.

The device for drawing glass capillaries was manufactured in the Institute of Analytical Chemistry, Czechoslovak Academy of Sciences, Brno; capillary columns were thermostated and tested by Fractovap, Model 2300 AC, gas chromatograph equipped with a flame ionization detector (Erba, Milan).

Preparation of capillary columns with the immobilized film of the stationary phase

Glass capillaries (i.d. = 0.25 mm) of Simax glass were drawn in a usual way [26]. The inside surface of the capillary was silylized with a 5% solution of γ -glycidoxypropyltrimethoxysilane [27, 28] in diethyl ether [29]. Before silylation, the quartz capillary columns were washed with 2 cm³ of 1% hydrogen chloride in distilled water and then with 1 cm³ of acetone. Capillaries deactivated by silylation were filled with a solution consisting of 3×10^{-4} M Carbowax 20M, 5×10^{-5} M DABCO R-8020 catalyst, and 2×10^{-3} M Desmodur L75 or 3×10^{-3} M Desmodur N75 pluriisocyanate in dichloromethane and coated by a static method. Crosslinking of the stationary phase was accelerated by heating the sealed columns at the temperature of 145°C for 5 h. After completing the reaction, the columns were blown with nitrogen for about 1 h. Prepared columns 11–16 m long, with the film thickness $d_f = 0.3$ – 0.4 μm , were tested at 110°C with 2,6-dimethylphenol (P) for efficiency and capacity ratio. The linear velocity of nitrogen as a carrier gas was 10–11 cm s⁻¹. After completing the tests, the columns were washed [30] with 1 cm³ of benzene and 1 cm³ of methyl alcohol at the rate of 1 cm s⁻¹, blown with nitrogen for 1 h and then retested.

The degree of crosslinking of the stationary phase was calculated from the relation $z = k'_p/k_p \cdot 100\%$, where k_p or k'_p are the capacity ratios for 2,6-dimethylphenol before or after washing the column with benzene and methyl alcohol.

Resistance of the immobilized film against washing with solvents

Influence of long-term static action of solvents

Influence of long-term static action of water or benzene [21, 22, 30] on the homogeneity of the stationary phase film was studied for both the used crosslinking agents — Desmodur L75 and Desmodur N75. Capillary columns were filled with water or benzene. Then they were sealed and left at the room temperature for 72 h. After that period the solvent was forced out of the column and the column was blown with nitrogen

for about 30 min. Before testing, the capillary columns were heated to 200 °C with the temperature program of 5 °C min⁻¹.

Influence of dynamic action

Different organic solvents

Capillary columns with the stationary phase film crosslinked with Desmodur L75 were washed successively with the following solvents — benzene and methyl alcohol, 2 times with 1 cm³, then with 2 cm³ of ethyl alcohol, hexane, acetone, chloroform, acetonitrile, and tetrahydrofuran at the rate of 1 cm s⁻¹. After each washing, the columns were blown with nitrogen for about 15 min and then heated to 200 °C with the temperature program of 5 °C min⁻¹ and conditioned at this temperature for about 1 h. Then they were tested for efficiency and capacity ratio for 2,6-dimethylphenol.

0.02 M-CH₃COOH in distilled water

The capillary columns with the stationary phase film crosslinked with Desmodur L75 were, after washing with solvents, dynamically washed with 250 multiple of their volume of 0.02 M-CH₃COOH in distilled water under the pressure of nitrogen of 0.8 MPa. After washing, the columns were blown with nitrogen for about 15 min. Before starting the tests, the capillary columns were heated to 200 °C with the temperature program of 5 °C min⁻¹ and conditioned at this temperature for 1 h.

Results and discussion

One of the fundamental requirements to quality of capillary columns with the immobilized stationary phase is the possibility of on-column injection of liquid samples and column regeneration with organic solvents or water. The influence of action of different kinds of solvents [21, 22, 30] on the prepared capillary columns with respect to the assumed needs of gas and liquid chromatography has been studied. A static and dynamic way of regeneration of the capillary column by means of solvents has been chosen as a model.

Influence of long-term static action of solvents

Influence of long-term static action of water or benzene on the homogeneity of the stationary phase film has been studied on capillary columns with the stationary phase crosslinked with Desmodur L75 and Desmodur N75. As shown in the literature [30], both the solvents — water and benzene — are examples of different action of solvents on the structure of polyurethanes. They are resistant against water; with benzene, on the contrary, the polymeric structure is affected. The tests show that by action of water the efficiency for 2,6-dimethylphenol slightly increases. The capacity ratio for 2,6-dimethylphenol

decreases by 10 % when Desmodur L75 is used, with Desmodur N75 by 20 %. By action of benzene the capacity ratio of both types of crosslinking agents decreased by about 3 %. The efficiency for 2,6-dimethylphenol decreases to 50 % when Desmodur L75 is used, in case of Desmodur N75 to 80 % of its original value, while peaks of chromatographic substances remain symmetrical in spite of the fact that the stationary phase film was quite certainly affected.

Influence of long-term static action of water and benzene may be statistically evaluated against Desmodur N75 when used for crosslinking. This is the reason why further study concentrated on dynamic action of solvents on the capillary column with the stationary phase film crosslinked with Desmodur L75.

Influence of dynamic action of different organic solvents

Current dynamic washing of the capillary column with the stationary phase film crosslinked with Desmodur L75 or Desmodur N75 with 2 cm³ of the solvent (benzene and methyl alcohol) at the rate of 1 cm s⁻¹ followed by drying the capillary column with nitrogen has no practical influence on the chromatographic properties of capillary columns.

Influence of dynamic action of different solvents on the properties of the stationary phase film crosslinked with Desmodur L75 is shown in Fig. 1. The degree of crosslinking of the stationary phase (z) varies after washing with different solvents in the range of about 1 %, the efficiency of capillary columns for 2,6-dimethylphenol varies after washing with solvents in the N range of 600 m⁻¹. The efficiency of the capillary column after washing is most negatively but reversibly influenced by chloroform, with which it decreases approximately by $N = 200$ m⁻¹ in comparison with the efficiency of the capillary column after washing with benzene and methyl alcohol. Positive influence, on the contrary, appears when the capillary columns are washed with tetrahydrofuran; in that case the efficiency of capillary columns for 2,6-dimethylphenol increases by $N \approx 400$ m⁻¹ in comparison with the efficiency of capillary columns after washing with benzene and methyl alcohol and by $N = 300$ m⁻¹ in comparison with the original nonwashed capillary column.

The results are in accordance with the literature [21] testifying exceptional resistance of polyurethanes against a number of organic and inorganic solvents including water.

Influence of dynamic action of 0.02 M-CH₃COOH

Influence of dynamic action of 0.02 M-CH₃COOH in distilled water on the homogeneity of the stationary phase film is shown in Fig. 1 (AA). The capillary columns with the stationary phase film crosslinked with Desmodur L75 showed,

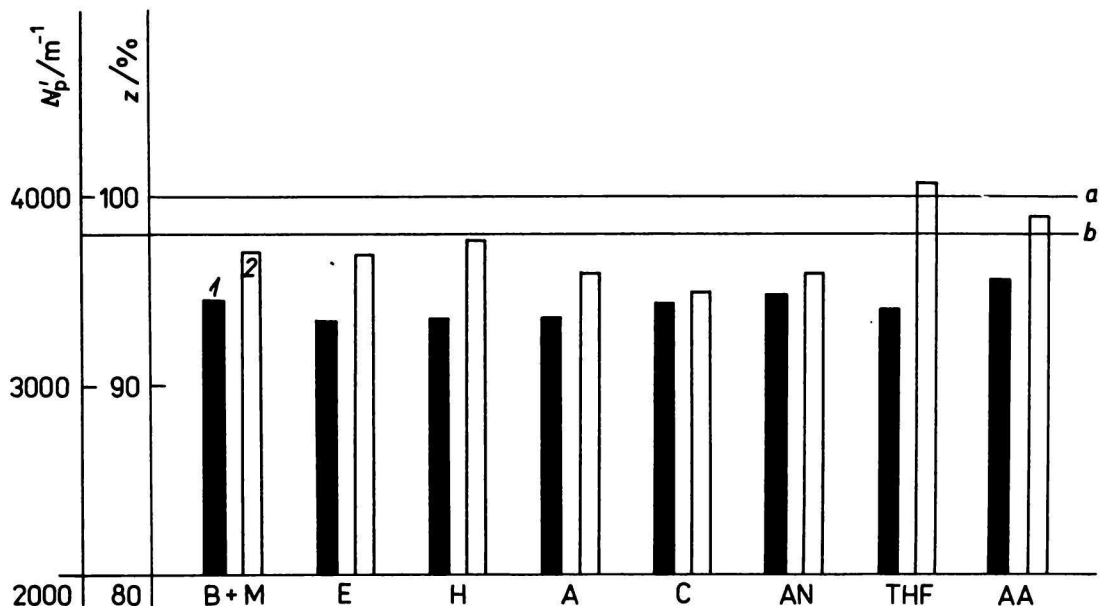


Fig. 1. Influence of dynamic action of different solvents on the properties of the stationary phase film crosslinked with Desmodur L75.

1. Degree of crosslinking of the stationary phase z ; 2. efficiency of the column for 2,6-dimethylphenol after washing with N'_p (the number of theoretical plates within 1 m).

a) Initial state of the capillary column before washing with benzene and methyl alcohol ($z = 100\%$); b) initial state of the capillary column before washing with benzene and methyl alcohol ($N'_p = 3800\text{ m}^{-1}$).

The state of the capillary column after further washing with 2 cm^3 of the solvent: B + M — benzene + methyl alcohol (volume ratio = 1 : 1 cm^3); E — ethyl alcohol; H — hexane; A — acetone; C — chloroform; AN — acetonitrile; THF — tetrahydrofuran; AA — 0.02 M- CH_3COOH in distilled water (250 volumes of the capillary column).

after washing with 250 multiple of their volume of 0.02 M-CH₃COOH in distilled water, *i.e.* 135—195 cm³ of the solute — according to the column length, a slight increase of the efficiency of capillary columns for 2,6-dimethylphenol by N about 200 m⁻¹ in comparison with the efficiency of capillary columns for the same solute after washing with benzene and methyl alcohol. The degree of crosslinking of the stationary phase (z) after washing with benzene and methyl alcohol remained the same.

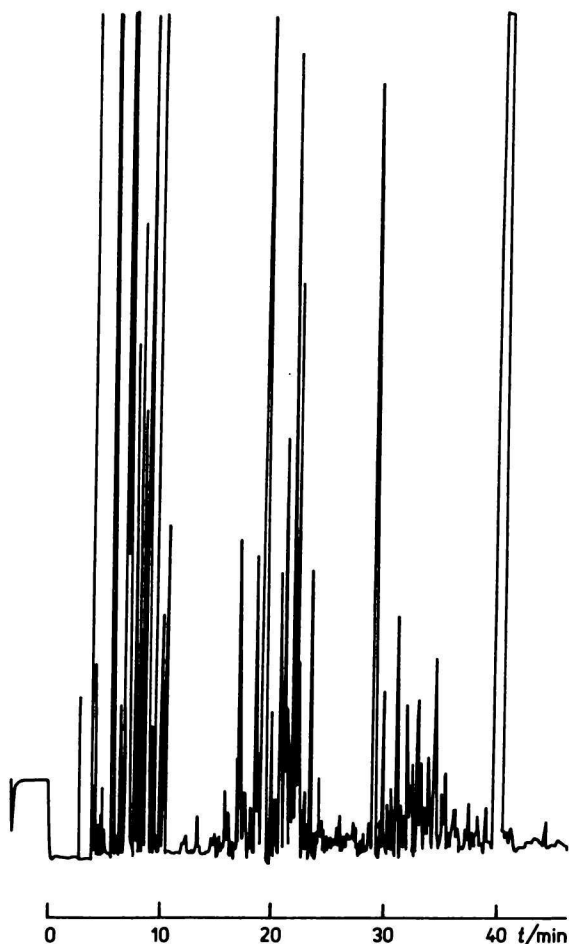


Fig. 2. Chromatographic separation of essential oil.

A quartz capillary column ($l = 15.5$ m; i.d. = 0.20 mm), $d_f = 0.3$ μ m, linear velocity of nitrogen 10 cm s⁻¹.

Chromatogram of separation of milfoil oil (*Achillea millefolia*) — the column temperature programmed from 60 to 200°C at the rate of 5°C min⁻¹.

Conclusion

The capillary columns coated with the film of poly(ethylene glycol) type stationary phase crosslinked on the basis of polyurethane can be washed with benzene, methyl alcohol, ethyl alcohol, hexane, acetone, chloroform, acetonitrile, and tetrahydrofuran without any danger of affecting the homogeneity of the stationary phase film.

Long-term static action of water (72 h), when using the crosslinking agents Desmodur N75 and Desmodur L75, causes decrease of the capacity ratio; long-term static action of benzene affects the homogeneity of the stationary phase film and consequently causes decrease of efficiency. The capillary columns, however, remain further applicable for chromatographic purposes.

Dynamic action of 250 multiple of the volume of the capillary column of 0.02 M-CH₃COOH in distilled water on the stationary phase film crosslinked with Desmodur L75 causes a slight increase of both capacity ratio and efficiency. The film of the poly(ethylene glycol) type stationary phase (Carbowax 20M) crosslinked with Desmodur L75 has been also used for preparation of quartz capillary columns, the properties of which are fully identical with the properties of glass capillary columns. One of these columns has been used for chromatography of one sample of essential oil — milfoil (*Achillea millefolia*, Fig. 2).

The studied type of stationary phase — Carbowax 20M crosslinked with pluriisocyanates — can be generally assessed, on the basis of the above-mentioned results, as fully conforming with the requirements for regeneration of the immobilized stationary phase in gas chromatography and also with respect to the demands made on the stationary phase of capillary liquid chromatography with electrochemical detection.

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