

## SHORT GLASS MICRO-PACKED COLUMNS FOR GAS CHROMATOGRAPHY

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For a quick analysis of simple mixtures of lower chlorinated hydrocarbons a possible application has been studied of short glass micro-packed columns packed with commercial sorbents for extraction by solid phase. For analyses of lower alcohols, carboxylic acids, and other oxygen-containing substances the columns were packed with the organic porous sorbent, a copolymer of divinylbenzene and 1,4-di(methacryloyloxymethyl)naphthalene. The chosen sorbents were placed into glass capillary columns of 0.4 – 0.7 m length and 0.7 mm i.d. As the sorbent amount in the column is small, the columns are cheap. Whenever necessary, they can be prepared in any laboratory. The analyses of simple mixtures of above-mentioned classes of compounds lasted from 90 to 270 s.

The present commercial capillary columns for analyses of multicomponent mixtures of organic compounds are predominantly made of fused silica, less often of glass or metal (WCOT or PLOT types<sup>1–9</sup>). The stationary phase in the columns is either only introduced or immobilized<sup>3–9</sup>.

A number of reports deal with studies of possibilities of application of either short packed micro columns or micro-packed capillary columns to quick analyses, i.e. fast obtaining information about the qualitative as well as quantitative composition of volatile substances in a sample. Commercial classical sorbents (however, with fine grain size) for gas chromatography have been used as the packing of these columns, e.g. charcoal<sup>10</sup>, molecular sieve<sup>10</sup>, alumina<sup>11</sup>, silica gel<sup>12</sup>, Porapak Q (ref.<sup>12</sup>), Chromosorb 102 (ref.<sup>13</sup>),  $\beta$ -cyclodextrin stationary phases on Chromosorb W AW (ref.<sup>14</sup>), OV 17 (ref.<sup>15</sup>), and SE 30, Carbowax 20M, OV 1, Fractonil III, Triton X, OV 225, Fomblin 1, Carbowax 300, OV 275 (ref.<sup>16</sup>) on Volasphere A 2, and Carbowax 20M on Carbo-pack B (ref.<sup>17</sup>). For separating lower aliphatic and aromatic hydrocarbons we described even the use of several sorbents for extraction by solid phase, e.g. Separon SGX, Separon SGX C18, and Separcol ALU OH (ref.<sup>18</sup>). For preparation of micro-packed columns also used were the commercial sorbents for LC and HPLC (refs<sup>19–26</sup>).

The present communication deals with the preparation of short micro-packed glass columns. For the packing of columns we used the commercial sorbents for extraction by solid phase (Solid Phase Extraction – SPE) and a porous organic copolymer of

divinylbenzene (DVB) and 1,4-di(methacryloyloxymethyl)naphthalene (1,4-DMN) prepared by us<sup>27</sup>.

## EXPERIMENTAL

Short micro-packed glass columns were prepared from glass capillaries made from thick-walled borosilicate glass tubes Simax on an apparatus described by Desty et al.<sup>28</sup>. The capillary was not wound to a circular spiral form in a heated metal bending tube, but was broken off in regular pieces of 0.5 – 0.8 m length. These pieces were shaped on a little flame to an U-shape according to the distance between the inlet and outlet to detector. The outlet part of the glass capillary column, ca 15 mm from the end, was narrowed in a small flame so that a small piece of silylated fused silica capillary of 0.32 mm i.d. could be attached in the same way as in the connection procedure of two fused silica columns by means of commercial press fit. A skilled worker can carry out this narrowing of the outlet end of column as late as after its filling with sorbent to ca 20 mm from the end and after insertion of a piece of quartz wool. The chosen sorbents were filled into the prepared glass U-capillaries. The uniformity of filling of columns was achieved by using a vibrator and subsequent 5 min insertion into water ultrasonic bath. After filling the capillary up to ca 5 mm from its beginning and from the narrowing, small pieces of quartz wool were inserted into these empty sections. Then a 10 – 12 cm piece of silylated fused silica capillary of 0.32 mm i.d. was attached to the outlet narrowed end of the column. The columns prepared in this way were packed with the following sorbents: Separcol ALU H, Separcol SI NH<sub>2</sub>, 60 μm (Centre of Chemical Research, Slovak Academy of Sciences, Bratislava, The Slovak Republic) and the DVB/1,4-DMN copolymer, 100 – 150 μm (University of M. Curie-Skłodowska, Lublin, Poland). The columns packed with inorganic sorbents were heated in a thermostat at 250 °C for 10 h while nitrogen was passed through. The column with the porous organic copolymer was heated under argon flow at 180 °C for 10 h.

The micro-packing glass columns with activated and/or thermally stabilized sorbent were installed into a gas chromatograph Fractovap model 2150 with FID and temperature programmer model 232 (Carlo Erba, Milan, Italy). The inlet part of column was introduced in split-splitless injector and the attached piece of fused silica capillary was introduced as far as into the detector nozzle. The detector signal was recorded with a Speedomax W recorder (Leeds and Northrup) and CI-105 integrator (Laboratorni pristroje, Praha). For all the columns, helium was used as the carrier gas at a volume flow rate of 4 ml min<sup>-1</sup> ( $\Delta p = 0.4 - 0.5$  MPa). The dividing ratio was splitted at 1 : 10.

The model mixtures were prepared by mixing the individual components of p.a. purity grade (Lachema Brno). The samples were injected by means of a Hamilton micro syringe.

## RESULTS AND DISCUSSION

The columns prepared can be installed either directly into a capillary gas chromatograph or into one adapted for operation with capillary columns using the pipe union and sealing adopted in handling with commercial fused silica or glass capillary columns. For separation packing we chose the sorbents commercially delivered for SPE: Separcol ALU H and Separcol Si NH<sub>2</sub>, and moreover the copolymer of DVB with 1,4-DMN. The grain size of inorganic sorbents (60 μm) and organic porous copolymer (100 – 150 μm) ensured a pressure below 0.5 MPa at the inlet of the prepared column. Therefore, the common commercial injecting system for capillary columns could be used. The inner

diameter of columns (0.7 mm) enabled the column to be filled with a sufficient amount of sorbent, hence fairly large samples could be injected therein.

The prepared micro-packed glass columns filled with the above-mentioned sorbents are suitable for quick analyses of chloroethylenes (Fig. 1): the chromatograms show the analysis times of 150 and 100 s (Figs 1a and 1b, respectively). The columns packed with the porous organic copolymer of DVB and 1,4-DMN proved successful in analyses of mixtures of lower aliphatic alcohols (Fig. 2), lower free aliphatic monocarboxylic acids (Fig. 3), and mixtures of miscellaneous compounds (Fig. 4) with acceptable resolution at both isothermal and programmed temperature regimes of column. The analysis times ranged from 90 to 270 s.

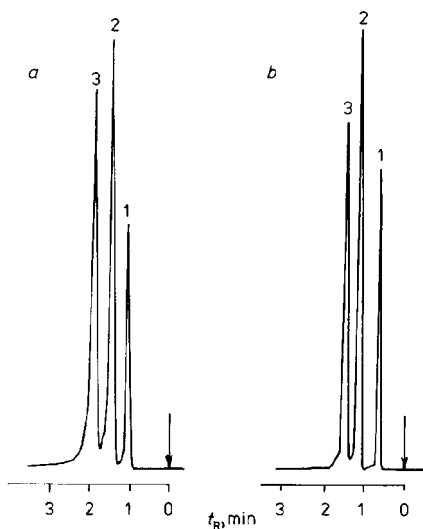


FIG. 1

Separation of chloroethylenes: 1 1,2-dichloroethylene; 2 trichloroethylene; 3 tetrachloroethylene. Sample volume: 0.4  $\mu$ l vapour mixture. **a** Glass column 0.4 m  $\times$  0.7 mm; sorbent: Separcol Si NH<sub>2</sub>, 60  $\mu$ m;  $\Delta p$  = 0.42 MPa; temperature 140 °C; **b** Glass column 0.43 m  $\times$  0.7 mm; sorbent: Separcol ALU H, 60  $\mu$ m;  $\Delta p$  = 0.50 MPa; temperature 170 °C

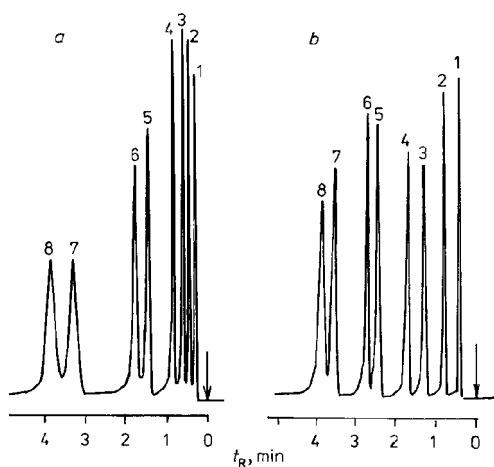


FIG. 2

Chromatogram of lower aliphatic alcohols at isothermal (**a**) and programmed temperature (**b**) regimes. Glass column 0.7 m  $\times$  0.7 mm; sorbent: DVB/1,4-DMN copolymer, 100 – 150  $\mu$ m;  $\Delta p$  = 0.38 MPa; sample volume 0.6  $\mu$ l vapour mixture. Peaks: 1 methanol, 2 ethanol, 3 2-propanol, 4 1-propanol, 5 2-methyl-1-propanol, 6 1-butanol, 7 3-methyl-1-butanol, 8 1-pentanol. Column temperature: **a** 170 °C; **b** 150 °C 1 min, programmed at 39 °C min<sup>-1</sup>, 170 °C 3 min

The separation efficiencies of the columns with inorganic sorbents and with the DVB/1,4-DMN copolymer were estimated by means of injection of a model mixture of  $C_5 - C_8$  n-alkanes (1 : 1.3 : 1.6 : 1.8) and a model mixture of  $C_2 - C_4$  n-alcohols, respectively, at the column temperature of 160 °C. Because of the rather low flow rate range used, the graphical plotting of the height equivalent to a theoretical plate against the mean linear flow rate used for the carrier gas [ $H = f(u)$ ] with heptane gave only the front descending sections of hyperbolas for both the inorganic sorbents. It stands to reason that at higher flow rates of carrier gas the ascending sections of curves would be obtained too. For the larger-grained porous organic copolymer studied within a broader range of flow rates of carrier gas the mentioned dependence (with 1-propanol) exhibits the usual shape with a minimum (Fig. 5).

The efficiency of the columns prepared from both inorganic sorbents, characterized by the minimum value of height equivalent to a theoretical plate (Fig. 5), is comparable with that of e.g. quartz micro-packed columns of 0.32 mm i.d. with alumina of 50 – 63  $\mu\text{m}$  grain size ( $H_{\text{min}} = 0.22$  mm) prepared for analyses of mixtures of lower

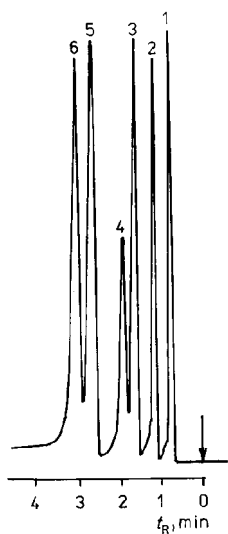


FIG. 3

Chromatogram of lower aliphatic monocarboxylic acids at programmed temperature regime of column. Glass column see Fig. 2, temperature 220 °C 2 min, programmed at 39 °C  $\text{min}^{-1}$ , 240 °C 4 min; sample volume 1  $\mu\text{l}$  vapour mixture. Peaks: 1 acetic acid, 2 propanoic acid, 3 2-methylpropanoic acid, 4 butanoic acid, 5 3-methylbutanoic acid, 6 pentanoic acid

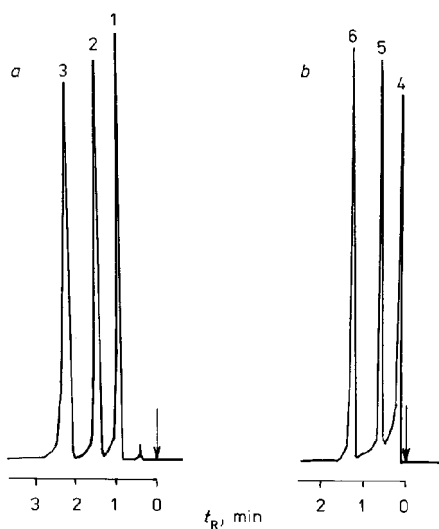


FIG. 4

Separation of solvent mixture (a) and solvent traces (10 ppm) in water (b). Glass column see Fig. 2; temperature 180 °C; sample volume: a 0.4  $\mu\text{l}$ , b 200  $\mu\text{l}$  vapour mixture. Peaks: 1 nitromethane, 2 1,2-dichloroethane, 3 dioxane, 4 unidentified component, 5 acetone, 6 2-butanone

aliphatic hydrocarbons<sup>11</sup>. Also the efficiency of the column prepared with the porous DVB/1,4-DMN copolymer is comparable with e.g. the micro-packed column of 1 mm i.d. packed with 5 wt.% Carbowax 300 on Volasphere A-2, 100 – 125  $\mu\text{m}$  ( $H_{\text{opt}} = 0.5 \text{ mm}$ )<sup>16</sup>.

A higher efficiency of columns could be achieved by decreasing either both the inner diameter of column and the grain size of sorbent<sup>11,12,16</sup> or only the latter parameter<sup>11,12</sup>. Either case would be connected with a big increase in the pneumatic resistance of column, which would bring the necessity of special modifications of commercial gas chromatographs for applications of high inlet pressures.

It is likely that the sorbents used will obey the known rule that the specific efficiency of columns decreases if the same sorbent is placed in columns with gradually increasing inner diameter, which can be seen in the case of micro-packed columns e.g. with the classic packing of 4 wt.% OV-1 on Volasphere A-2, 100 – 125  $\mu\text{m}$  or with that of alumina<sup>11</sup> and Silasorb 600 (ref.<sup>12</sup>).

With respect to the fact that the analysis of the given or other similar mixtures is rapid, these columns could also be used in process gas chromatographs.

As the amount of packing used for the preparation of the described short micro-packed columns made from drawn glass capillaries is small, and the preparation is simple, the columns are cheap. In some cases they may replace expensive capillary columns of WCOT or PLOT types, e.g. in analyses of simple mixtures of low-boiling organic compounds or in cases where there is a risk of damage of the separation layer of column at the inner wall e.g. by reaction with a component of injected sample.

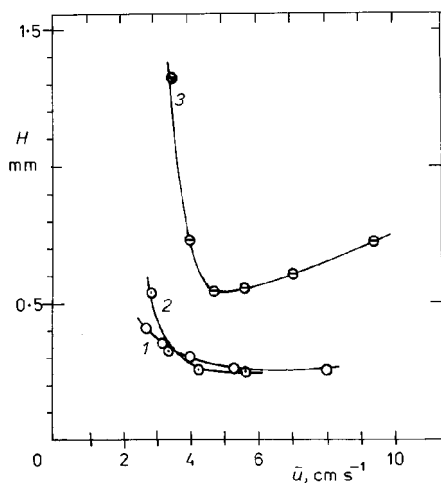


FIG. 5

Dependence of height equivalent to a theoretical plate ( $H$ ) upon mean linear flow rate of carrier gas ( $\bar{u}$ ) for heptane and 1-propanol. Column temperature 160  $^{\circ}\text{C}$ ; sample volume: 0.1  $\mu\text{l}$  vapours of  $\text{C}_5 - \text{C}_8$  n-alkanes or 0.2  $\mu\text{l}$   $\text{C}_2 - \text{C}_4$  n-alcohols. Sorbents: 1 Separcol Si  $\text{NH}_2$ , 2 Separcol ALU H (for heptane), 3 DVB/1,4-DMN copolymer (for 1-propanol)

## REFERENCES

1. Cowper C. J., De Rose A. J.: *The Analysis of Gases by Chromatography*. Pergamon Series in Analytical Chemistry, Vol. 7. Pergamon, Oxford 1983.
2. Kiselev A. V., Yashin J. I.: *Adsorptionsnaya Gazovaya i Zhidkostnaya Khromatografiya*. Khimiya, Moscow 1979. *Adsorpční plynová a kapalinová chromatografie*, SNTL, Praha 1988.
3. Smolkova E., Feltl L.: *Analyza latek v plynnem stavu*. SNTL, Praha 1991.
4. Schulte E.: *Praxis der Kapillar-Gas-Chromatographie*. Springer, Berlin 1983.
5. Jennings W.: *Gas Chromatography with Glass Capillary Columns*. Academic Press, New York 1980.
6. Tesarik K., Komarek K.: *Kapilarni kolony v plynove chromatografii*. SNTL, Praha 1984.
7. Lee M. L., Yang F. J., Bartle K. D.: *Open Tubular Column Gas Chromatography*. Wiley-Interscience, New York 1984.
8. Grob K.: *Making and Manipulating Capillary Columns for Gas Chromatography*. Huethig, Heidelberg 1986.
9. Borek V., Hubacek J., Rehakova V.: Chem. Listy 79, 364 (1985).
10. Malik A., Gavrichev V. S., Berezkin V. G., Voloshina N. V. in: *Chromatography '85* (H. Kalasz and L. S. Ettre, Eds), p. 437. Akademiai Kiado, Budapest 1986.
11. Gavrishev V. S., Voloshina N. V., Berezkin V. G., Korolev A. A., Malisova A. D., Okhotnikov B. P., Simongauz S. E.: J. Chromatogr. 509, 59 (1990).
12. Malik A., Berezkin V. G., Gavrichev V. S.: Chromatographia 19, 327 (1984).
13. Al-Thamir W. K.: J. High Resolut. Chromatogr., Chromatogr. Commun. 8, 143 (1985).
14. Smolkova-Keulemansova E., Pokorna S., Feltl L.: J. High Resolut. Chromatogr., Chromatogr. Commun. 11, 670 (1988).
15. Olano A., Calvo M. M., Reglero G.: Chromatographia 21, 538 (1986).
16. Reglero G., Herraiz M., Cabezudo M. D., Sanchez E. F., Dominguez J. A. G.: J. Chromatogr. 348, 327 (1985).
17. Schindler S., Wasserfallen K.: J. High Resolut. Chromatogr., Chromatogr. Commun. 10, 371 (1987).
18. Komarek K.: J. High Resolut. Chromatogr., Chromatogr. Commun. 16, 59 (1993).
19. Malik A., Yumaev A. R., Berezkin V. G.: J. High Resolut. Chromatogr., Chromatogr. Commun. 9, 312 (1986).
20. Malik A., Berezkin V. G., Gavrichev V. S.: Chromatographia 22, 117 (1986).
21. Takeuchi T., Hamanaka T., Ishii D.: Chromatographia 25, 993 (1988).
22. Lagesson V., Newman J. M.: J. High Resolut. Chromatogr., Chromatogr. Commun. 11, 577 (1988).
23. Takeuchi T., Ohta K., Ishii D.: Chromatographia 27, 182 (1989).
24. Liu Y., Yang F. J.: J. Microcol. Sep. 3, 249 (1991).
25. Gavrichev V. S., Berezkin V. G., Yumaev A. R., Malik A., Borisov M. Yu., Lvov I. A., Lyubotov M. Yu., Mikhailov V. I., Sokovikh V. O.: J. Chromatogr. 365, 237 (1986).
26. Berezkin V. G., Malik A., Gavrichev V. S. in: *Chromatography '85* (H. Kalasz and L. S. Ettre, Eds), p. 429. Akademiai Kiado, Budapest 1986.
27. Matyina T., Gawdzik B.: Angew. Macromol. Chem. 147, 123 (1987).
28. Desty D. H., Haresnape J. N., Whyman B. H. F.: Anal. Chem. 32, 302 (1960).

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