Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Chromatography A, 1084 (2005) 18–23
JOURNAL OF CHROMATOGRAPHY A
www.elsevier.com/locate/chroma

Investigations of a new field in gas chromatography: Capillary columns with a super-thick layer of stationary liquid phase

V.G. Berezkin[a,*], A.B. Lapin[a], J.B. Lipsky[b]

[a] *A.V. Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, Leninsky prospect 29, 119991 Moscow, Russian Federation*
[b] *Quadrex Corporation, P.O. Box 3881, Woodbridge, CT 06525 USA*

Available online 18 January 2005

Abstract

Basic characteristics (efficiency, selectivity, non-equilibrium) of capillary columns with a super-thick layer of stationary liquid phase are investigated. In contrast to traditionally used capillary columns with standard stationary phase thickness of 0.1–0.5 um, some new variables are now established. Firstly, the values of relative retention depend on carrier gas linear velocity. Secondly, the asymmetry of chromatographic peaks increased in accordance with the increase in carrier gas velocity. Thirdly, it was theoretically and experimentally shown that dependence of the height equivalent to a theoretical plate (HETP) on carrier gas velocity is linear. The above noted variables are evidences that the new type of GC is realized under these conditions. The use of capillary columns with super-thick layer of stationary liquid phase is practical when the following problems have to be solved: (1) Separation of highly volatile substances; (2) Preliminary concentration of trace compounds from strong diluted samples; (3) Improvements in measurement and accuracy due to the advantages of splitless injection into wide bore columns with super-thick films. Solutions to some analytical tasks while using super-thick stationary liquid phase are shown: (1) Large volume injection into capillary column with sample transfer speed up to 100 μL min^{-1}; (2) Isothermal splitless injection; (3) Separation of low boiling compounds; (4) Separation of polar substances (alcohols).

Keywords: Gas chromatography; Capillary columns; Stationary phases, GC, Ultra thick film; Large volume injection

1. Introduction

Since their development by Golay in 1958, capillary columns have introduced new methodologies in gas chromatography [1–6]. Today, capillary columns play the dominant role in GC analysis [2–7].

However, packed columns still offer some preferable characteristics when compared to capillaries. Primarily, packed columns offer much higher sample capacities, allowing the entire sample to be injected without the need of a splitter. This yields greater sample sensitivity.

The advantages of packed columns are due to the greater volume of stationary phase per unit of column length. An increase in phase loading per unit of a wall-coated open tubular (WCOT) capillary column length ϕ ($\phi = m/L$, where m is the mass of stationary phase in the column and L is the column length) can allow it to have the same capacity as a packed column.

Capillary columns with a greater amount of stationary phase per unit of column length (or with thick phase films) provide optimal conditions for techniques which have been in use in analytical gas chromatography for a long time, i.e., the concentration of high boiling components as narrow bands in the beginning of the column, use of the solvent effect, etc. [6,8]. Therefore, it seemed reasonable to carry out an investigation of the analytical capabilities of capillary columns with ultra-thick stationary phase films, where the thickness was many times greater than that of the traditionally used ones.

At present wide-bore capillary columns with ultra-thick stationary phase films (with films up to 18.0 μm) are available from Quadrex. Columns with such coating should

* Corresponding author. Fax: +7 095 230 2224.
E-mail addresses: berezkin@ips.ac.ru (V.G. Berezkin), tech@quadrexcorp.com (J.B. Lipsky).

0021-9673/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.chroma.2004.12.011

exhibit special properties, provide new data and extend the application range of capillary gas chromatography.

The purpose of the present research was to study the analytical capabilities of open tubular columns with ultra-thick stationary phase coatings.

2. Experimental

The column loading of three different columns were evaluated for the sake of comparison: (1) a standard capillary column of 0.20 mm i.d. with a film thickness of 0.33 μm (methylsilicone); (2) a capillary column of 0.53 mm i.d. with a film thickness of 10.0 μm (methylsilicone); and (3) a capillary column of 0.53 mm i.d. with a film thickness of 18.0 μm (methylsilicone).

The amount of stationary phase per unit length is 132 times greater for column 2 and 238 times greater for column 3 than that for the column with a 0.2 μm film thickness (column 1).

The use of wide-bore capillary columns with an internal diameter of 0.53 mm was considered because for a given film thickness, the amount of stationary phase per unit of column length increases as the column diameter increases and higher flow rates can be employed, which result in shorter injection times.

Therefore, the use of a wide-bore capillary column with a thick layer of stationary phase film allows not only an increase in column loading, but also an increase in the speed of injection.

Chromatographic measurements were made using an HP 5890 (series II) gas chromatograph (Agilent Technologies, USA) equipped with an electronic pressure control, a split/splitless injector, an autosampler and a flame ionisation detection (FID) system. Chromatographic separations were carried out on 30 m × 0.53 mm i.d. columns (Quadrex, USA) coated with methylsilicone (film thickness: 10.0 μm and 18.0 μm). According to the GC manufacturer's recommendations, column position in the injector was 5 mm from the column end to ferrule. A cylindrical liner of 78 mm length and 4 mm i.d. without packing was used. The syringe needle was plunged into the injector for 51 mm. One microlitre sample was introduced quickly with a cold needle using an autosampler while 25–150 μL samples were introduced manually. Septum purge was constant at 4.0 mL min^{-1}. The split ratio was measured by a flowmeter.

Trace compounds in ethanol or vodka were determined using a Trace 2000 gas chromatograph (Thermo Separation/CE Instruments, USA) equipped with an electronic pressure control, a split/splitless injector, an autosampler, FID system, and ChromQuest software. Column position in the injector was 40 mm from the column end to ferrule. A cylindrical liner of 105 mm length and 3 mm i.d. without packing was used. The syringe needle was plunged into the injector for 51 mm. An air-sample-air "sandwich" injection technique was used.

Helium was used as the carrier gas. Carrier gas velocity and column pressure were controlled by the electronic pressure controller.

The online column-concentrator device was very simple, was made as follows: the piece of capillary column with super-thick stationary phase (3 m × 0.52 mm i.d., d_f 18 μm) was pushed into the tin filled with sand. This piece of column was connected to an evaporator and to an analytical column by hollow capillaries. The heater provided with heat the tin with temperature gradient from the evaporator side to the analytical column. This simplest construction has only one goal: to show the new possibility of application of column investigated with ultra-thick films of stationary phase.

3. Results and discussion

3.1. Some general characteristics of capillary columns with ultra thick stationary phase films

As shown by Jennings, the efficiency of WCOT columns began to fall off when the film thickness exceeded 0.5 μm [9]. The comparative study of the dependence of column efficiency on the carrier gas velocity for columns with ultra thick stationary phase films showed a lower column efficiency than expected on the column with 18.0 μm film thickness (Fig. 1). For example, with a carrier gas velocity of $\bar{u} = 25\,cm\,s^{-1}$, the HETP was about 2 mm for the 10.0 μm column and about 7 mm for the column with an 18.0 μm film thickness. Total efficiency of the 30 m long column (film thickness 10.0 μm) was 15 000 theoretical plates.

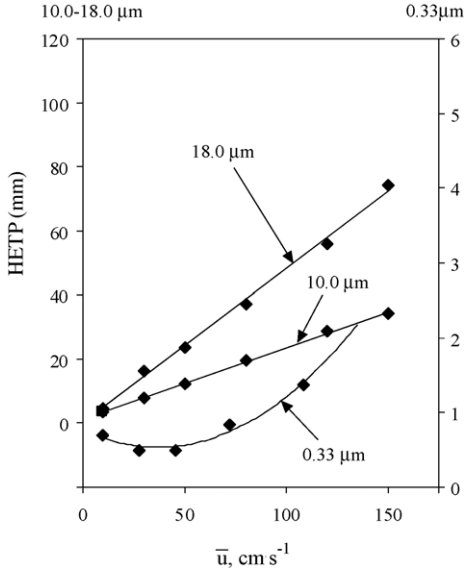

Fig. 1. Relationships between the HETP and the carrier gas velocity (helium) for *n*-decane on capillary columns with film thicknesses of 0.33, 10.0 and 18.0 μm. Oven temperature: 200 °C (125 °C for 0.33 μm column). Split ratio: 1:20.

For description of the dependence of the height equivalent to a theoretical plate (HETP) on the linear velocity of the carrier gas, different forms of Golay's equation [4–6] are used:

$$H = \frac{B}{u} + Cu \tag{1}$$

In the case of WCOT columns, coefficients B and C are calculated using the following equation:

$$B = 2D_g \tag{2}$$

$$C = C_m + C_s \tag{3}$$

$$C_m = \frac{1 + 6k + 1/k^2}{96(1+k)^2} \frac{d_c^2}{D_m} \tag{4}$$

$$C_s = \frac{2k}{3(1+k)^2} \frac{d_f^2}{D_s} \tag{5}$$

where B is the longitudinal diffusion coefficient; C, total mass transfer resistance coefficient; k, retention factor; D_g, diffusion coefficient of the sorbate in the gas phase; C_m and C_s, mass transfer resistance coefficients in the gas phase and in the stationary phase, respectively; d_c, diameter of the column; d_f, film thickness; D_m and D_s, diffusion coefficients of the sorbate in the mobile and in the stationary phases, respectively.

The dependence of HEPT on $\bar{u}$ for the column with $d_f = 0.33\,\mu m$ is described by Eq. (1), but for the columns with $d_f = 10.0$ and $18.0\,\mu m$, the HEPT linearly depends on the linear velocity of the carrier gas. These results can be explained on the basis of Golay's equation. For columns with ultra thick stationary phase films $B/u \ll Cu$. Consequently, from Eq. (1) we can obtain the linear equation

$$H = C_T u \tag{6}$$

where

$$C_T = \frac{1}{3(1+k)^2} \left\{ \frac{1}{32}(1 + 6k + 11k^2) \left(\frac{d_c^2}{D_m} \right) + 2k \left(\frac{d_f^2}{D_s} \right) \right\} \tag{7}$$

Note that Eq. (6) was not considered in theory of capillary chromatography; it is correct for the columns with ultra-thick stationary phase film only, the investigation of which is the main purpose of this work.

Besides, the drastic fall in efficiency from the 10.0 μm film to 18.0 μm is probably due to non-equilibrium effects in chromatographic processes that occur in a column with thick stationary phase film. Also molecules that diffuse through the whole thickness of the stationary phase as the zone moves along the film layer will cause serious band spreading. In this case, some new trends in the basic chromatographic characteristics might be expected.

Relative retention time (in contrast to absolute retention time) does not depend on carrier gas linear velocity (for example, [10,11]), film thickness or phase ratio, and column length. However, the authors have assumed that equilibrium of separated compounds between the mobile phase and the super-thick stationary phase cannot be reached, especially at high flow rates. Therefore, the well-known rule r = constant may not be kept in this case.

Dependence of relative retention r of hydrocarbon gases (*n*-hexadecane and *n*-heptadecane) on the carrier gas average linear velocity (helium) for columns with various film thickness (0.33 and 18.0 μm) are given in Fig. 2. As follows from these data, relative retention significantly changes with an increase in the linear velocity of the carrier gas for the 18.0 μm column with super-thick film (18 μm) and remains nearly uncharged for a classical capillary column with $d_f = 0.33\,\mu m$. Similar dependences for relative retention were obtained for other hydrocarbon gases.

This peculiarity of function (see Fig. 2)

$$r = f(\bar{u}) \tag{8}$$

is non-standard (r is relative retention, $\bar{u}$ is linear velocity of carrier gas). As a rule, r = const., if $\bar{u}$ changes. In our opinion r is dependent on velocity of carrier gas, especially in the field of high speeds (see Fig. 2).

3.2. Trace analysis with ultra-thick film columns

The use of capillary columns with an ultra-thick stationary phase film permits an improved determination of trace components since their permissible sample load is much greater than that for normal capillary columns. In fact, the initial band of heavy components in the beginning of a column is proportional to the mass of stationary phase per unit of

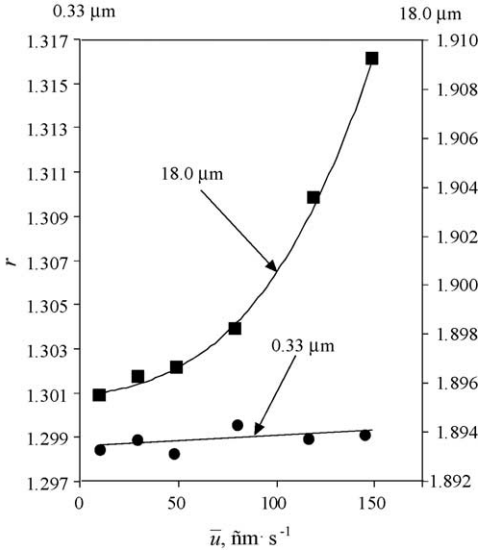

Fig. 2. Dependence of relative retention r for *n*-hexadecane and *n*-heptadecane on the carrier gas average linear velocity (helium) for 0.33 and 18 μm film thickness. Oven temperature: 100 °C for 0.33 μm and 200 °C for 18 μm.

column length. Note that sample introduction into a column with ultra-thick stationary phase coating can be achieved using standard gas chromatographic equipment and standard techniques.

During splitless injection [8,12] at the moment of sample introduction and for a short period after, it the column is kept at a temperature below the boiling points of the sample components. After the transfer of the sample into the column, the split line is opened and the injector is purged with carrier gas to remove the residual solvent and sample. Then the column temperature is increased rapidly assisting fast evaporation of the solvent and sample. Thus, thermal focusing occurs in the column. Under the same conditions but in other operational modes, solvent effects can be realized.

The formation of a large evaporated sample volume occurring when the liquid solvent turns into gaseous state and its subsequent transfer into the capillary column are the main problems of splitless injection. For example, when 1 μL of chloroform is introduced at 250 °C at a carrier gas pressure of 4.5 p.s.i. (1 p.s.i. = 6894.76 Pa), a volume of vapour of 0.32 mL is formed. When 1 μL of methanol is introduced under the same conditions, the volume of the evaporated sample is 0.75 mL. The common range of carrier gas flow rates through a column is 0.5–3.0 mL min^{-1}. Thus, the transfer of the evaporated sample into the column can take considerable time and this process occurs under conditions of mixing of the evaporated sample with the carrier gas. Due to the small volume of the injector, introduction of samples over 1–1.5 μL can cause sample loss because of injector "overflow". In some cases these problems can be solved by an increase in the carrier gas flow rate at the moment of sample introduction and sample transfer into the column [12,13]. However, this technique leads to additional band-broadening of the initial zone and to a loss in efficiency.

The application of wide-bore capillary columns permits high speed transfer of large sample volumes into the column and avoids considerable pressure increase in the injector due to relatively high volumetric flow rate of carrier gas.

Fig. 3 shows the dependence of the peak areas and peak resolution of *n*-hexadecane and *n*-heptadecane on the volume of sample introduced into the gas chromatograph during 1 min. As seen, the dependence of the peak areas is linear up to 100 μL. Apparently, non-observance of the linearity for larger samples is due to a partial loss of sample during its introduction. Resolution does not decrease abruptly (less than 23%) for samples up to 100 μL. Under these conditions the speed of sample introduction of 100 μL s^{-1} can be considered as maximal.

The experiments described above show that the application prospects of this type of columns is suitable for the determination of trace components, allowing an increase in the sample volume (and, therefore, sensitivity) without distortion of the main chromatographic characteristics.

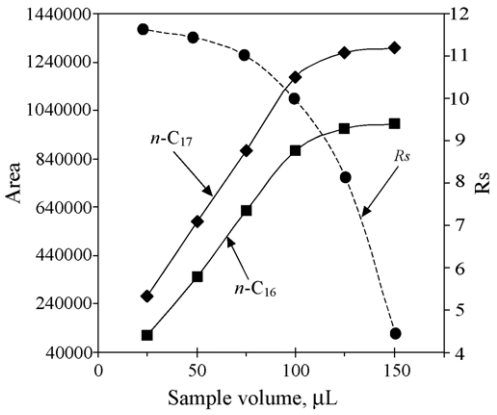

Fig. 3. Relationships between the peak areas of *n*-hexadecane and *n*-heptadecane, peak resolution and the sample volume introduced into the gas chromatograph over 1 min. Column 30 m × 0.53 mm i.d. coated with methylsilicone (film thickness: 10.0 μm). Oven temperature: isothermal at 80 °C for 1.5 min, then programmed to 120 °C at 30 °C min^{-1}, and then to 200 °C at 10 °C min^{-1}. Carrier gas velocity (helium): 150 cm s^{-1}. Injector temperature 250 °C. Splitless sample injection. Duration of sample injection: 1 min.

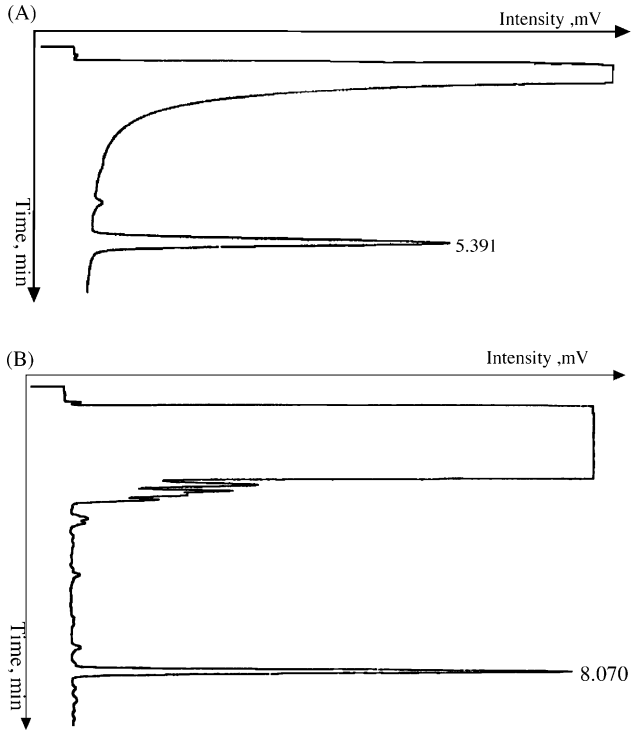

Fig. 4. (A) Isothermal splitless injection. Column 30 m × 0.53 mm i.d. coated with methylsilicone (film thickness: 10.0 μm). Oven temperature 150 °C isothermal. Carrier gas: helium, 32.5 mL min^{-1} (180 cm s^{-1}). Sample volume: 1 μL, the sample contained 10 ppm of trichlorfon in chloroform. The peak with retention time 5.391 min is trichlorfon. (B) Introduction of a 100 μL sample into the capillary column for 1 min. Column 30 m × 0.53 mm i.d. coated with methylsilicone (film thickness: 10 μm). Oven temperature: isothermal at 80 °C for 1.2 min, then programmed to 120 °C at 30 °C min^{-1}, and then to 190 °C at 10 °C min^{-1}. Carrier gas: helium, 27.6 mL min^{-1} (150 cm s^{-1}). Splitless period: 1.2 min. Sample: 0.1 ppm trichlorfon in chloroform. The peak with retention time 8.070 min is trichlorfon.

Fig. 4A shows the trace analysis in splitless mode, without temperature programming (without solvent focusing, thermal focusing and purging after splitless period). The relatively narrow symmetrical zone of the target component (a widely used pesticide, trichlorfon) is an evidence of the rapid transfer of the sample into the column. We did not find any references to splitless injection under isothermal conditions.

As noted earlier, the application of wide-bore capillary columns with ultra-thick stationary phase film is reasonable for increasing the sample volume. Slow sample introduction is reasonable for the separation of large samples [13,14]. The speed of sample introduction is proportional to the speed of sample transfer into the column if the evaporated sample volume is not to exceed the volume of injector. However, as a rule, it is very difficult to introduce a sample with a speed above 1 μL for 10 s in columns of small internal diameter [8,14].

A chromatogram of trichlorfon in chloroform when introducing a 100 μL sample for 1 min is shown in Fig. 4B.

As it seems to us, it is a very interesting way to concentrate the target compounds by using the capillary columns with super-thick stationary phase. For this purpose online column-concentrator was placed between an evaporator and analytical column. The column-concentrator was pushed into the device independently from GC oven heater. The device provides heating of the column-concentrator with temperature gradient from an evaporator to analytical column. We do not describe the whole system in details, as our purpose was to show expediency of such an approach only. The results are shown on Fig. 5. It is apparent that the above described method with online column-concentrator can be used for trace analysis with large volume injection.

3.3. High selectivity and ultra-thick stationary phase film

A well-known concept "*similia similibus solvuntur*", according to which stationary phases were selected earlier, is not the only possible approach for choosing a selective stationary phase.

In some cases, stationary phases with a poorer dissolution ability for sample components than the traditionally used phases demonstrate better selectivity. However, it is preferable to carry out separations with thick stationary phase films, where the components are poorly dissolved but are selectively separated, because the retention of poorly dissolved components is much greater on such columns.

Another advantage of columns with non-polar ultra-thick stationary phases is the small role of adsorption phenomena on the interfaces between the coatings and the capillary wall (solid support).

Considering all the above-mentioned points, we have used capillary columns with ultra-thick phase coatings of non-polar polydimethylsiloxane for the separation of polar traces in alcoholic beverages.

Determination of volatile traces in ethanol and alcoholic beverages is an example of such gas chromatographic analysis [15,16]. Columns coated with polyethylene glycol

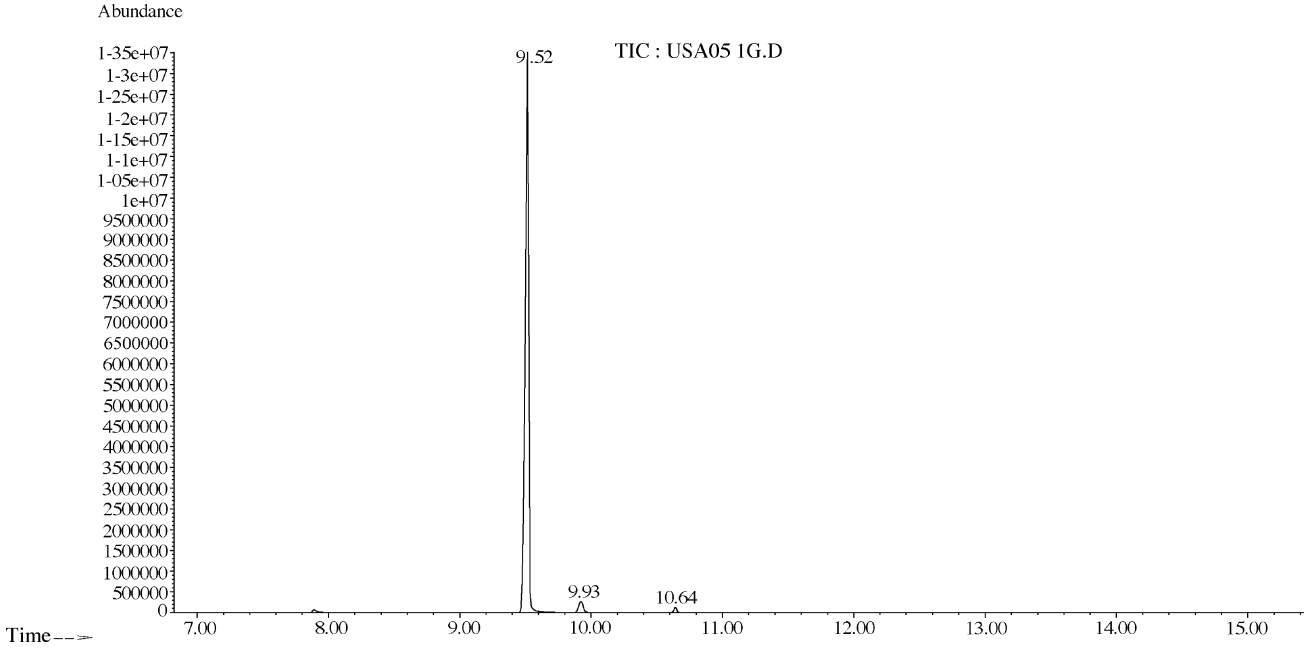

Fig. 5. Introduction of 25 μL sample into traditional analytical column with use of the online column-concentrator device. Analytical column 30 m × 0.25 mm i.d. coated with methylsilicone (film thickness 0.25 μm). Column concentrator temperature: initial 80 °C (5 min), then up to 250 °C. Oven temperature: isothermal at 80 °C (5.5 min), then programmed to 200 °C at 30 °C min^{-1}. Carrier gas: helium. Sample: 0.1 ppm trichlorfon in chloroform. Time scale in min. The peak with retention time 9.52 min is trichlorfon.

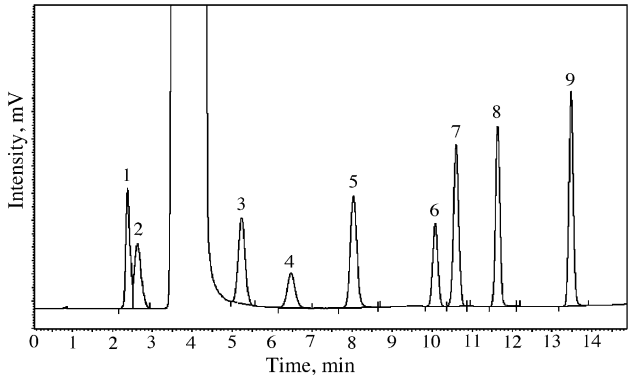

Fig. 6. Chromatogram of volatile traces in ethanol. Solutes: (1) acetaldehyde, (2) methanol, (3) isopropanol, (4) methyl acetate, (5) *n*-propanol, (6) ethyl acetate, (7) isobutanol, (8) *n*-butanol, (9) isopentanol. Column 30 m × 0.53 mm i.d. coated with methylsilicone (film thickness 10.0 μm). Column temperature: isothermal at 40 °C for 6.5 min, then programmed from to 150 °C at 10 °C min^{-1}. Carrier gas: helium, 30 cm s^{-1}. The sample was ethanol–water (4:6, v/v) containing 0.001% (v/v) of each component.

(Carbowax 20M, Innowax, FFAP) are in common use for this purpose. In this case, acceptable separation is achieved for all components except isopropanol, which forms an unresolved peak with the larger ethanol peak. This problem cannot be solved by decreasing the initial oven temperature. As a rule, it is necessary to increase split ratio for the determination of isopropanol, which leads to a decrease in the sensitivity of the determination for all sample components. Traditional columns coated with non-polar phases, with traditional film thickness and phase ratio, have not been in common use for such analysis because of the low retention of the components to be separated (especially, methanol and acetaldehyde). As seen in Fig. 6, acceptable separation of ethanol can be achieved in a short time on a column with an ultra-thick stationary phase film, and isopropanol and ethanol are well separated. Note that ethanol elutes as a narrow peak and it does not prevent the determination of other components.

4. Conclusion

The study performed indicates the expediency of application of capillary columns with ultra-thick stationary phase coatings for gas chromatographic analysis and, especially, for the determination of traces in volatile solvents.

Acknowledgment

We express our gratitude to Dr. Leslie Ettre for useful discussions and valuable remarks.

References

[1] L.S. Ettre, in: H.J. Issaq (Ed.), A Century of Separation Science, Marcel Dekker, New York, 2002, p. 1.
[2] V.G. Berezkin, E.N. Viktorova, J. Chromatogr. A 985 (2003) 3.
[3] E. Soczewinski, Chem. Anal. (Warsaw) 48 (2003) 647.
[4] G. Guichon, C.L. Guillemin, Quantitative Gas Chromatography, Elsevier, Amsterdam, 1988.
[5] M. Lee, F. Yang, K. Bartle, Open Tubular Column Gas Chromatography, Wiley-Interscience, New York, 1984.
[6] C.F. Poole, The Essence of Chromatography, Elsevier, Amsterdam, 2003.
[7] V.G. Berezkin, Russ. Chem. J. 46 (2000) 115 (in Russian).
[8] K. Grob, Split and Splitless Injection in Capillary GC, Hüthig Buch, Heidelberg, 1993.
[9] W. Jennings, E. Mittlefehdt, P. Stremple, Analytical Gas Chromatography, Academic Press, London, 1997.
[10] A.T. James, A.J.P. Martin, Biochem. J. 50 (1952) 678.
[11] S. Dal Nogare, R.S. Juvet, Gas-Liquid Chromatography, Interscience, New York, 1962.
[12] P.L. Wylie, J. High Resolut. Chromatogr. 15 (1992) 763.
[13] S.S. Stafford, Electronic Pressure Control in Gas Chromatography, Hewlett-Packard, Wilmington, DE, 1993.
[14] K. Grob, K. Grob, J. High Resolut. Chromatogr. Commun. 1 (1978) 57.
[15] F.J. Yang, A.C. Brown, S.P. Cram, J. Chromatogr. 158 (1978) 91.
[16] A. Antonelli, M. Galli, Chromatographia 41 (1995) 772.