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ARTICLES

Polycapillary (Multichannel) Chromatographic Columns in Liquid Chromatography

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Abstract—The use of polycapillary (multichannel) columns with channels 3–10 μm in diameter in liquid chromatography was studied. It was shown that, in a number of cases, polycapillary columns can give analytical results more rapidly than conventional packed columns. The polycapillary columns studied in this work were not used in liquid chromatography before.

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Currently, the diameter of interparticle channels in packed columns used in high-performance liquid chromatography is 4–6 μm. These sizes are determined by the particle size of adsorbents (3–5 μm), which, in its turn, is caused by the necessity to drastically reduce the diffusion resistance in a liquid medium. Works on decreasing the channel diameters in columns for liquid chromatography were started in 1965–1967 [1–3]. A polytetrafluoroethylene column with inner diameter approximately 0.5 mm was used packed with a fine-particle adsorbent [3]. Steel columns with a diameter of 1 mm and less were also used [1–2]. The decrease in the particle sizes of adsorbents and, consecutively, the diameter of interparticle channels resulted in a sharp increase in the efficiency of columns and enabled the use of difficultly available and expensive reagents, because in this case, the consumption of the mobile and stationary phases is small. Moreover, it became possible to improve the sensitivity of detection and to use highly sensitive detection systems, including mass spectrometry, for recording separated compounds and determining their chemical nature.

Open-tubular columns [1–7], such as glass capillaries of small diameters and flexible quartz capillaries with an external polyimide coating, usually 20–60 m in length and 10–30 μm in inner diameter [8–9], are also used in high-performance liquid chromatography.

Polycapillary columns have so far been used only in gas chromatography. In 1990–1995, researchers from the Novosibirsk Design and Technological Institute of Instrument Making for Geophysics and Ecology developed a technology for manufacturing glass multicapillary tubes. These tubes have some 10^3 individual channels with only slightly varying sizes of 30–40 μm [10–12]. Besides, a technique was developed for coating the inner walls with the stationary phase, which made it possible to produce gas-chromatographic columns with a specific performance of up to 10000–12000 theoretical plates (**TP**) per meter [13, 14]. Similar technical approaches allowed the use of multichannel (polycapillary) columns with channels 5–10 μm in diameter and a total number of channels of about 10^6 in gas chromatography [15–17]. Such columns allowed separation efficiency up to 2000 to 3000 TP at a column length of 20–30 cm.

Success attained in the use of polycapillary columns in gas chromatography initiated the interest for the possible use of similar columns in liquid chromatography. However, the parameters of columns used in liquid chromatography considerably differ from the parameters of polycapillary columns designed for gas chromatography. The main and most important difference is that polycapillary columns with channels 30–50 μm in diameter cannot provide adequate efficiency in high-resolution liquid chromatography because of significant diffusion resistance [7–9, 18–23]. Polycapillary columns with channels 3–10 μm in diameter are required in this case. Such columns were developed at the Institute for Roentgen Optics (Moscow, Russia). They are thoroughly described in [16] and have some 10^6 channels 3–6 μm in diameter. In liquid chromatography, the efficiency of these columns reached 500–600 TP at the column length of 20–30 cm. The time of analysis was less than 10 min. The first results of studying such columns for gas and liquid chromatography have been published earlier [17]. The goal of the present work was the more detailed investigation of multicapillary columns with a channel size of 3–6 μm and a total number of channels of some 10^6 in liquid chromatography.

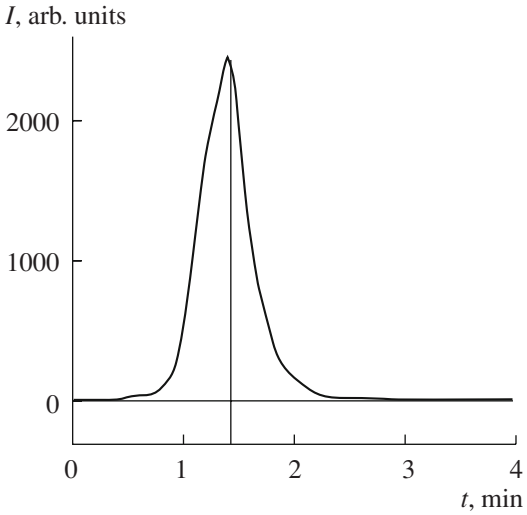

Fig. 1. Chromatogram of a naphthalene solution in acetonitrile; mobile phase flow rate, 0.5 mL/min.

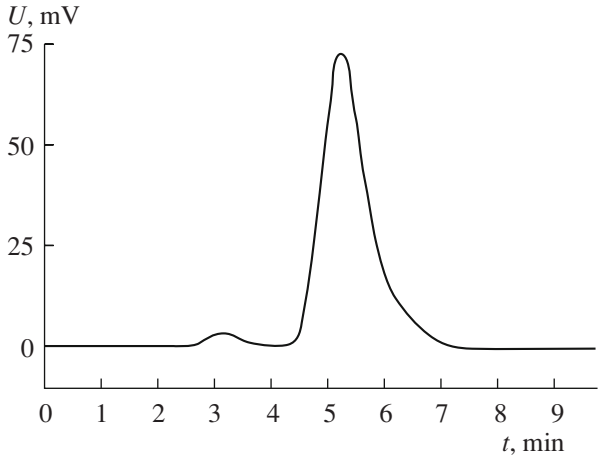

Fig. 3. Chromatogram of Preduktal cardiac preparation obtained with the elution by acetonitrile. The mobile phase flow rate, 3 mL/min; column length, 20 cm; number of channels, 10^6; diameter of a channel, 5 μm; stationary phase, polysiloxane E-301; separation efficiency, 150 TP; time of analysis, 8 min.

EXPERIMENTAL

Multicapillary tubes made of lead glass with a relatively low softening point were used in the study [15, 16]. These tubes had an outer diameter of 3–6 mm and a total number of channels of $(0.7–1) \times 10^6$ with the size of each channel of 3–6 μm.

The columns were tested on a liquid chromatograph (Finnigan) with a UV detector with the wavelength set at 254 nm.

Films of stationary phases were dynamically applied onto the inner walls by extruding their solutions in an appropriate solvent. All the solvents and other reagents used in this study were of analytical or chemically pure grade. In the cases of high-molecular stationary phase polysiloxane E-301, its 10% solution in benzene was used. After passing the solutions of stationary phases, the solvent was evaporated by purging nitrogen through the columns (30–40 mL/min) at room temperature for 4–5 h. Then, the permeability and performance of the obtained columns were examined at 20–60°C by the retentions of test compounds. A chromatogram of naphthalene obtained at the flow rate of the mobile phase (acetonitrile) of 0.5 mL/min is presented in Fig. 1. All samples were injected into chromatographic columns as 10% solutions in acetonitrile. To record the dead time, 0.2–0.5% of benzene was added to a sample solution, because benzene is almost not retained in the column if acetonitrile is used as the mobile phase.

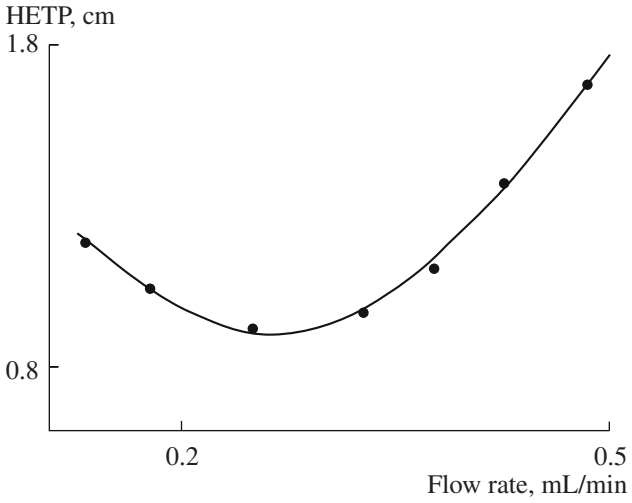

Fig. 2. The height equivalent to a theoretical plate (HETP) of the polycapillary column as a function of the mobile phase flow rate for naphthalene. Column length, 20 cm; number of channels, 10^6; diameter of a channel, 5 μm; stationary phase, polysiloxane E-301.

RESULTS AND DISCUSSION

A chromatogram of naphthalene in elution with acetonitrile (flow rate, 0.5 mL/min) is presented in Fig. 1. The dependence of the performance of polycapillary columns on the mobile phase flow rate for naphthalene is given in Fig. 2. Some chromatograms obtained with such columns are presented in Figs. 3–5. It can be seen that the results are comparable with the data for conventional packed columns but can be obtained within considerably shorter time. Polycapillary columns have not been used in liquid chromatography before; therefore, these data were obtained for the first time. Although the performance of polycapillary columns is relatively

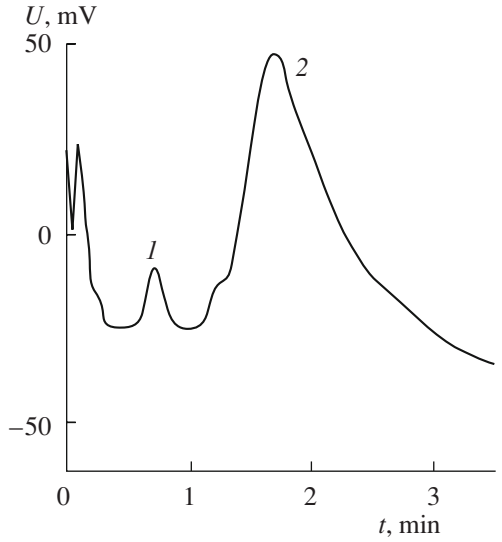

Fig. 4. Chromatogram of (*1*) salicylic acid and (*2*) naphthalene obtained with the elution by acetonitrile. Chromatographic conditions are given in the caption of Fig. 3.

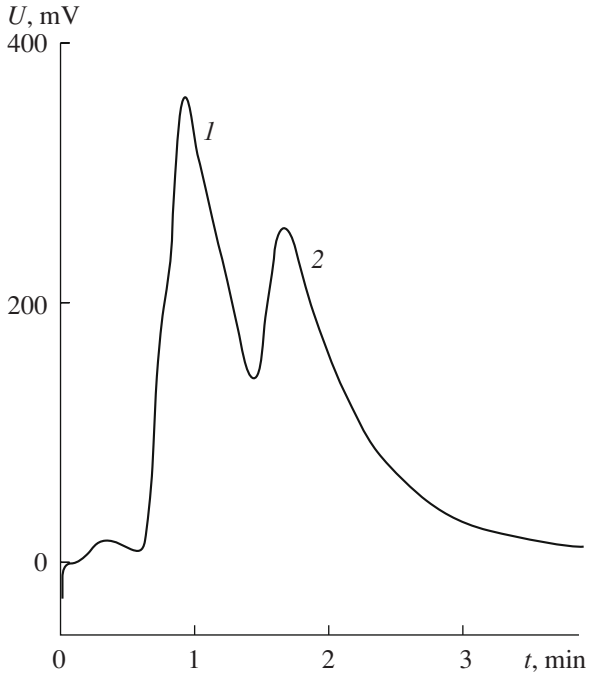

Fig. 5. Chromatogram of a pharmaceutical preparation containing (*1*) phenobarbital and (*2*) codeine obtained with the elution by acetonitrile. Chromatographic conditions are given in the caption of Fig. 3.

poor with respect to the packed columns, the investigations in this field should be considered prospective, because polycapillary columns enable rapid determinations.

An important feature of the studied columns is that the pressure of the mobile phase at the column inlet did not exceed 3 atm in all experiments; this allows the use of these columns in portable analytical devices.

The use of polycapillary columns with the activated adsorption surface also has considerable promises. The operation time of chromatographic columns for liquid chromatographs is determined by the durability and mechanical properties of the stationary phase and usually is 1–3 months. It was shown in the first experiments that polycapillary columns without an applied stationary phase but with the activated adsorption surface of channels (without applying the stationary phase) can operate considerably longer than conventional columns with fine-grained adsorbents, that is, for 6–8 months.

The precision of the retention parameters was comparable with the certified values for the used chromatograph (0.3–1.0%) even at low retention times (2–5 min).

The columns described in this work are inferior to the best columns packed with fine-grained adsorbents in performance; the efficiency of a 20-cm column with 10^6 channels with a channel diameter of 5 μm was 150–200 TP (Fig. 3). However, it is reasonable to suppose that further investigations will allow the development of polycapillary columns with operational characteristics close to or even better than those currently obtained for packed columns.

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