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Less common applications of monoliths III. Gas chromatography

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Abstract

Porous polymer monoliths emerged about two decades ago. Despite this short time, they are finding applications in a variety of fields. In addition to the most common and certainly best known use of this new category of porous media as stationary phases in liquid chromatography, monolithic materials also found their applications in other areas. This review article focuses on monoliths in capillaries designed for separations in gas chromatography.

Keywords

Monolith; Gas chromatography; Silica; Polymer; Capillary; Separation

1. Introduction

It is a little known fact that the very first monolithic columns have initially been used in gas chromatography (GC) more than 30 years ago [1-6]. However, they did not attract much attention at that time since they emerged in the same time at which Dandenau and Zerenner developed the open capillary columns [7]. Thus, these early monolithic GC columns were forgotten for a long time. Thanks to pioneering work of several research groups [8-10], the monolithic stationary phases re-emerged in the late 1980s and early 1990s.

Meanwhile, monoliths were prepared from diverse materials and in a variety of shapes [11]. A very simplified depiction compares monoliths to a single large piece of porous material. By definition, this material fills entirely the column volume and does not leave any interparticular voids typical of packed beds. Therefore, all the mobile phase must flow through the stationary phase. The unique feature of monolithic columns is that the size of the channels in the monolithic structure does not depend on the size of microglobules or domains forming the monolith. This allows for varying the size of channels and size of microglobules independently and facilitates optimization of the monolithic structure for a particular application. In contrast, the size of interparticular voids in a well-packed column strictly relates to the bead size and approximately equals 20% of the particle diameter. Also, monoliths do not require packing in the column. In a typical implementation, this “single piece” of separation medium is prepared by a simple *in situ* polymerization in a column tube.

Monoliths in several applications offer numerous advantages compared to particulate packings as demonstrated with a large number of studies concerning porous monolithic materials

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published in the scientific literature. This activity led to acceptance of monolithic columns in the large family of chromatographic stationary phases. Their applications in a variety of liquid chromatographic modes including high-performance liquid chromatography (HPLC) and capillary electrochromatography (CEC) has recently been described in several reviews [12-25] and books [11,26]. However, the less common applications of monolithic materials that include supports for solid phase and combinatorial synthesis [27-29], scavengers [30,31], carriers for immobilization of enzymes [32-34], static mixers [35], thermally responsive gates and valves [36-38], as well as solid phase extractors and pre-concentrators [39] are escaping the awareness of the scientific community. The recently started series of review articles aims at popularization of these applications. So far, this series detailed achievements in microscale protein mapping with proteolytic enzymes immobilized on monolithic supports and in preconcentration and solid-phase extraction [34,39]. Present contribution focuses on use of monolithic materials in gas chromatography. Although this application of monoliths is one of the least common, the interesting studies published in literature deserve to be summarized to attract more attention.

2. Column in gas chromatography

Gas chromatography was first demonstrated by James and Martin in 1952 with a home made column comprising a 4 or 11 ft. long and 4 mm I.D. glass tube filled with irregular silica support particles (Kiesselgur) coated with a silicon oil serving as the stationary phase [40]. This column separated volatile aliphatic carboxylic acids in the gas-liquid chromatographic (GLC) mode. For many following years, packed column became the industry standard and hundreds of stationary phases have been described in the literature [41].

Bare porous solids have been used as GC stationary phases in the gas-solid chromatography (GSC) mode. These solid adsorbents are generally more stable over a wider temperature range and less sensitive to oxygen than their coated counterparts. GSC often affords much better selectivity for the separation of geometric and isotopic isomers, and is also well suited for the separation of permanent gases and small hydrocarbons, for which coated capillaries afford insufficient selectivity and retention. Inorganic particles [41] and porous polymer beads introduced by Hollis in 1966 [42] were the most commonly used stationary phases in GSC [43]. Polymer-based stationary phases such as Porapak, Chromosorb, and Tenax became icons of the early GSC. However, the development of this promising technique has been slowed by its intrinsic difficulties. For example, adsorption isotherms in GSC are often non-linear, leading to retentions that vary with sample volume, to asymmetric peaks, and to incomplete resolutions. Additionally, the very large surface area typical of some solids have led to excessively long retention times, thus limiting the broader use of GSC. Despite this drawback, the specific advantages of GSC and its unique separation abilities in some applications have recently led to increased interest in the technique.

The introduction of fused silica capillaries by Dandenau and Zerenner in 1979 [7] quickly led to the current overwhelming popularity of the open tubular capillary format. Since the column cross section is open along its entire length, resistance to the flow of the gas stream is low. Typical open capillary columns exhibit relatively low specific efficiency (efficiency per 1 m of column length). However, a large number of theoretical plates per column can easily be achieved using long capillary which length can vary from tens to hundreds meters. Unfortunately, long columns require long time for an analyte to leave the column, which precludes these columns from use in high speed separations. Thus, development of highly efficient capillary columns enabling high speed analysis is a challenge for modern GC.

The liquid stationary phase is most often coated on the internal wall surface. Nowadays, these liquid phases are crosslinked to improve their thermal and mechanical stability. Although these

crosslinked stationary phases may resemble solid phases featuring good mass-transfer kinetics and low degree of crosslinking, they are most often considered as liquids. In contrast, the mixture of carrier gas and analytes has to percolate through a bed of porous stationary phase in a packed column, and the separation is achieved as a result of the interactions of the analytes with a solid surface or liquid phase immobilized on the surface of the solid packing.

Poole [41] divides columns used in GC in five categories: (1) Classical columns with a diameter exceeding 2 mm packed with 100-250 μm particles, (2) micropacked columns with a diameter of less than 1 mm, (3) packed capillaries with a diameter of less than 0.6 mm and packing size of 5-20 μm, (4) wall-coated open tubular (WCOT), and (5) support-coated open tubular (SCOT). Porous-layer open-tubular (PLOT) capillary columns for GSC are actually SCOT columns that do not include the liquid stationary phase. They represent a compromise combining the good flow properties of open-tubular capillaries with the separation power of solid packings used in the GSC mode. The porous layer of a PLOT column can be prepared by dynamic or static coating of the capillary wall with fine particles [41], or by an *in situ* polymerization process [44-46]. Columns prepared using a coating procedure may suffer from the release of particles from the coated layer. These liberated particles are swept through the column creating a spiky signal and possibly even blocking the detector. In contrast, polymerized layers of crosslinked polymer are physically more stable, and their preparation is more reproducible. The PLOT technique has recently been detailed in an excellent review article [47].

PLOT columns prepared by polymerization *in situ* can also be considered predecessors of today's monolithic columns since the porous polymer layer forms a continuous layer. Although the PLOT columns represent a significant advance, they still must be several tens of meters long since the amount of the polymeric stationary phase they contain is small. However, the same volume of the solid stationary phase could be accommodated within a much shorter length if the column were completely filled with a monolithic separation medium. At the same flow rate, the shorter column then affords separation at a reduced period of time. This feature together with the advantageous properties of i*n situ* prepared stationary phases became motivation for the development of monolithic GC columns described in this review.

3. Polymer-based monolithic columns

3.1. Polyurethane foams

In the early 1970s, two groups, one in USA and another in Europe, independently experimented with polyurethane foams prepared *in situ* within the confines of gas chromatographic columns [3,4]. The former group combining researchers of Monsanto and Aerospace Research Laboratories adopted the original Albert Zlatkis' idea of shaping polymer foams and inserting them into a column. They extended the concept and prepared open pore polyurethane foams directly in the column [3].

Although their first communication falls short on details concerning the preparation of these monolithic columns, most likely to avoid interference with their patent application prosecuted at the same time [2], it clearly demonstrates that a decent gas chromatographic separations of various hydrocarbon mixtures could be achieved. Fig. 1 shows the separation of C_6-C_9 alkanes as an example. The second publication that followed in 1973 has already fully revealed the specifics of the technology [6]. The polyurethane foams were produced from a mixture containing various proportions of polymethaneisocyanate 1 and a polyol 2, which was defined as a reaction product of diethylenetriamine with propylene oxide, dissolved in an isodensity solvent composed of 60:40% toluene-carbon tetrachloride mixture. This mixture was drawn in the 1 m long and 4 mm I.D. glass column tube, sealed, and polymerized at room temperature. The polymerization reaction was initiated by the tertiary amine functionalities of the polyol

component and continued for 18 h upon continuous tumbling that prevented settling of the polymer and eliminated channeling. Once the reaction was completed, the solvent was removed from the pores of the monolith by pressure of nitrogen and the column conditioned at 100 °C for 24 h.

The crosslinked polyurethane formed during this process was not soluble in the polymerization mixture and separated from the system as a new phase in a shape of interconnected spherical units that the authors called spherules. Except for the size of these spherules, the structure shown in Fig. 2. is quite similar to that of the typical current macroporous polymer monoliths. The size of the spherules could be controlled in a broad range of 1-10 μm by varying the dilution of the reaction mixture. These building units were nonporous as can be inferred from a low specific surface area of only 0.4 m^2/g found for the foam [3]. Obviously, the larger the spherules, the larger the pores, and the better the permeability of the monolithic foam. The best chromatographic properties characterized by column efficiency of 800 plates/m determined for decane and an average resolution of 5.50 for the separation of C_{12}, C_{13}, and C_{14} alkanes were achieved with an optimized material that had a bulk density of 0.178 g/mL. The polyurethane was stable at temperatures up to about 200 °C, a limit that seriously restricted its application in GC [6].

The surface of the “bare” polyurethane is rather polar and the tertiary nitrogen atoms and carbonyl groups made this material susceptible to hydrogen bonding. It could be used directly for the GC separations of volatile compounds in the gas-solid mode. For example, 2-propanol eluted before ethanol and methanol leading to a suggestion that these columns could be used for trace analysis of 2-propanol in excess of the other low alcohols.

The surface polarity, which is given by the chemical composition of the polymer, could also be readily changed using a variety of liquid phases anchored at the surface. This was achieved either by admixing the liquid stationary phase to the polymerization mixture prior to the preparation of the porous structure or using the more common approach, i.e. coating of the surface of the monolithic polyurethane with the liquid such as silicon fluid DC 550 or Carbowax 400. The coated GC columns operating in the gas-liquid mode had both higher efficiency and sample capacity. Fig. 3 shows separation of aliphatic alcohols using this column [6].

The authors claimed several advantages of their material [3]: “Glass and metal columns of various configurations, lengths, and diameters (including capillary columns) could be readily filled because of the low viscosity of the precursor reagent. The polyurethane structure adhered tightly to the interior walls of columns of most types of materials of construction, thus preventing channeling along the support-column wall interface and providing “built in” continual baffles. The porosity, density, surface area, and flow characteristics could be controlled by varying reaction conditions. The material could be used as a gas-solid, gas-liquid, liquid-liquid, and thin layer chromatographic support. Stationary phases could be added either by incorporation with the reactants or by a solution method after the support is formed. Compounds with relatively low vapor pressures could be analyzed at low column temperatures.”

By today’s standards, the performance of the monolithic polyurethane columns was poor. However, it was comparable with the packed columns of the early 1970s. In fact, one of the reports [6] indicates that these monolithic columns were commercially available from Analabs (North Haven, CT, USA). It is now difficult to speculate why these columns were not accepted more widely. Perhaps their preparation appeared more complicated compared to a simple packing of columns with particulate solids. Their thermal stability was also much lower that that of the inorganic packings and supports typically used in GC at that time. Interestingly, the polyurethane monoliths have been recently “reinvented”. A monolithic polyurethane foam was

used as a template for the preparation of large blocks of macro/microporous zeolites with the potential application in catalysis [48].

The German group [4] operating in Dunlop Forschung that independently explored the polymer foams demonstrated two techniques: First, they discussed the preparation of polyurethane foam stationary phase in a 1 m long 6 mm I.D. glass column. However, this approach was not successful. They wrote: “Although the in situ procedure is easily done, the columns contain air pockets which cause band broadening. We were not able to prepare material free of shrinkholes”. And they add: “With a more refined technique this could probably be achieved.” However, they did not attempt the optimization of the *in situ* foaming. Instead, they used powdered foam and packed the columns with these materials. This approach enabled expanding the arsenal of polymers. In addition to polyurethane foam particles, they also used other polymer foams such as styrene copolymers, natural rubber, polyvinyl chloride, polyamide (nylon), polymethacrylimide, polyisocyanurate, and polyethylene. All these columns were tested in gas-solid GC. Unfortunately, this single paper completely lacks both characterization of the used materials and experimental details to enable reproduction of the experiments. In addition, only a very short discussion section is presented in this report.

3.2.Poly(divinylbenzene) monoliths

Polymers and copolymers of divinylbenzene (DVB) are not unknown in the GC arena. Many members of both Porapak and Chromosorb series GC packings are based just on this type of chemistry [42]. Monolithic versions of these polymers were also thoroughly studied in liquid chromatography [49-57]. The typical poly(divinylbenzene) monoliths used in HPLC separations of large molecules featured large through pores and no appreciable volume of small pores. Therefore, those monoliths typically exhibit only a very small surface area of 20 m^2/g or less. In contrast, stationary phases for GC typically possess much higher surface areas to provide large number of interaction sites and good separation.

The concept of GC using poly(divinylbenzene) monolith was initially demonstrated in Berkeley [58] with a capillary column prepared in the fused-silica capillary that was first treated with 3-(trimethoxysilyl)propyl methacrylate to assure good adhesion of the monolith to the wall. After running a number of experiments, the optimized polymerization mixture consisted of 40% divinylbenzene (a mixture containing 80% DVB isomers and 20% ethylstyrenes), 52% 1-dodecanol, 8% toluene and azobisisobutyronitrile (1% with respect to divinylbenzene). The polymerization proceeded at a temperature of 70 °C for 20 h to achieve the complete conversion of monomer to polymer. The resulting monolith was washed with methanol and dried in a stream of helium.

The SEM micrographs shown in Fig. 4 reveal several interesting features of the poly (divinylbenzene) monolith. First, the size of through pores is rather large. Pore size determined by mercury intrusion porosimetry exhibits a maximum centered at 8.3 μm, which correlates well with the size of the pores seen in the SEM micrographs. In addition, this material has a large specific surface area of 460 m^2/g as determined from the adsorption and desorption isotherms of nitrogen using monolith prepared from the same mixture in a glass vial. This large surface area indicates that the microglobules are permeated by a large number of small mesopores and micropores that are not visible in SEM. The other feature resulting from copolymerization of divinylbenzene chains with the acryloyl moieties bound to the capillary wall is an outer polymer layer surrounding the porous monolith. This impervious tubular layer minimizes direct contacts of the analytes in the gas phase with the surface of the fused-silica capillary [58].

An important feature of poly(divinylbenzene) is its thermal stability. An increase in the temperature generally accelerates the rate of processes occurring in the gas phase. For example,

elution times in GC become shorter at higher temperatures thus decreasing the time required for analysis. Typically, gradients spanning a wide range of temperatures are used in GC to achieve good resolution. Therefore, the thermal stability of the porous monolith is an important characteristic. TGA measurement shown in Fig. 5 indicates that the porous poly (divinylbenzene) monolith does not undergo any significant thermal degradation until a temperature of 380 °C is reached. This excellent thermal stability enables the monolith to operate routinely at temperatures up to 300 °C, and up to 350 °C for short periods of time, without observing any deterioration of its properties.

Fig. 6 shows the separation of 11 model compounds using the monolithic poly(divinylbenzene) column with temperature gradient from 120 to 300 °C at a rate of 20°C/min. All of the peaks are baseline separated and exhibit very low asymmetries. The narrow peaks are indicative of the efficient separations that can be achieved under specified conditions using this column. These separations suggest that the monolithic capillary column is well suited for the GC analysis of organic compounds. Since the poly(divinylbenzene) matrix is very hydrophobic, non-polar analytes such as hydrocarbons are retained more strongly than polar alcohols, ethers, ketones, and chlorinated hydrocarbons having similar boiling points. The retention data clearly shows that hydrophobic interactions, and perhaps solvation of the matrix by the analytes, are more important factors than volatility in controlling the order of elution [58].

In contrast to standard liquid stationary phases typical of the current coated open tubular columns used for GC, the hydrophobic polymer-based packings were found to be more tolerant of any water present in the injected samples. Fig. 7 shows that this is also true for the monolithic column. No differences were seen in the separations of a mixture of four alcohols injected either neat or as a 10% aqueous solution. Even several successive splitless injections of water followed by an analysis of the test mixture did not result in any changes in retention or efficiency. Obviously, water did not interact with the surface of the hydrophobic polymer, and therefore it eluted rapidly from the column without being monitored by the flame ionization detection (FID) system .

This preliminary study demonstrated that the application range of the rigid porous polymer monoliths can be extended to include gas-solid chromatography. Despite a good injection-to-injection and column-to-column reproducibility and reasonable efficiencies of the monolithic columns, it was clear that more thorough study had to be carried out. Therefore, an extensive set of experiments has been run in Moscow that enabled much better insight in the GC performance limits of the monolithic poly(divinylbenzene) capillary columns [59].

Polymerization mixtures consisting of the same components as in the above study were used again but their proportions were varied to see the effect of composition of the polymerization mixture, polymerization temperature, and time on the chromatographic performance of the monolithic poly(divinylbenzene) columns. These columns were characterized by (i) total porosity determined gravimetrically from the difference in weight of the column containing monolith with empty pores and monolith, which pores were filled with tetrachloromethane as well as (ii) permeability calculated from pressure drop and linear flow velocity using Poiseuille-Darcy equation.

According to the generally accepted rule, porosity of macroporous polymers including porous polymer monoliths should only slightly exceed the content of porogenic solvent in the polymerization mixture. The excess is explained by the shrinkage accompanying all polymerizations of vinyl monomers. Thus, the porosity of monolithic columns prepared in the presence of 59-65% porogenic solvents should not be much larger than these values. Surprisingly, porosity of all monolithic columns prepared within the framework of this study significantly exceeded these values with the maximum at about 88%. Fig. 8 indicates that one

the explanation of this difference can be the incomplete polymerization since the porosity decreases with the increase in reaction time asymptotically approaching the expected values. Some of the difference may also result from the use of 65% grade divinylbenzene that may contain non-polymerizable components such as diethylbenzene that would then count as a part of the porogen. However, the same trend was observed for monoliths prepared at varying temperatures and this contribution appears to be negligible [59].

While porosity was clearly affected by the length of the polymerization reaction, permeabilities of the poly(divinylbenzene) columns were not. Whereas all the pores can be completely filled with tetrachloromethane, the permeability is affected even with a local inhomogeneity within the porous structure. For example, the structure of ends of the monoliths often varies from that of the bulk due to the effect of polymerization mixture-empty capillary interface. The open front and back parts of the capillary may contain traces of oxygen from air that is an efficient inhibitor of free radical polymerization. Even a thin layer of gel-like polymer at the end then increases the resistance to flow in less controlled manner. Obviously, this thin layer does not affect the separation performance of the column that is governed by the bulk properties.

The large number of experiments also allowed for assessment of effects the selected reaction conditions had on the column efficiency. The efficiency expressed as a height equivalent to theoretical plate (HETP) depends on both structure of the monolith and flow velocity of the carrier gas. The Van Deemter curves [60] plotted for each monolithic column characterize these effects. For example, the column efficiency increases as the polymerization time at 75 °C extends from 30 to 110 min reaching the best HETP of 40 μm representing 25,000 plates/m. However, further extension of the polymerization time deteriorates the efficiency. Clearly, the porous structure of the monoliths develops with the reaction time. At a certain point of conversion of divinylbenzene to crosslinked polymer, the structure consists of enough solid materials to make it stable, the through pores are large, and the microglobules contain sufficient number of small pores to afford large surface area. These pores are then partly or completely filled with polymer as the polymerization continues, the structure changes, the mass transport is slower, and the column efficiency gets poorer.

Polymerization time not only affects column efficiency but also retention as shown in Fig. 9 for both butane and 2-methylpropane [59]. The retention increases to a certain point at about 100 min and then levels off. In general the retention depends both on the number of interacting sites located at the pore surface within the stationary phase and its chemistry. The effect of porous structure is easier to comprehend and has already been discussed. In contrast, there should not be any difference in chemistry since the monolithic matrix always consists of poly(divinylbenzene). The issue is that divinylbenzene has two double bonds and the product used in this study contained only 65% of this monomer and 35% of other compounds with some of them being monovinyl monomers. Therefore, the surface chemistry of the monolith is controlled by reactivity rations of all the polymerizable double bonds. It is then possible that some components comprising the technical divinylbenzene polymerize faster than other thus leading to monolith with chemical composition depending on polymerization time. To confirm this, more experiments with artificial mixtures of divinylbenzene with other potential components are needed.

Polymerization temperature also exerts large effect on efficiency. While columns prepared at 70 °C do not separate the model mixture of butane and 2-methylpropane (isobutane), columns prepared at a temperature of 78 °C afford the highest efficiencies. Fig. 10 demonstrates the effect of temperature with Van Deemter's plots for both tested hydrocarbons. It has been shown earlier for monoliths prepared in bulk that materials with smaller through pores and larger surface areas are formed at higher temperature [61]. Similarly, an increase in percentage of divinylbenzene in the polymerization mixture also leads to columns with improved efficiency

(Fig. 11). However, the polymerization temperature, composition of the polymerization mixture and some other parameters, being correlated with column efficiency, indicate a rather narrow window affording efficient columns. Deviation from the optimal values always results in decrease in column efficiency. For example, a subtle change in the temperature by 5 °C or an increase in percentage of monomer in the polymerization mixture from 35 to 41% makes a large difference in the performance of the monolithic column. These effects have been observed in the past and the reason is likely the very high concentration of crosslinking monomer in the polymerization mixture.

The gain in the column efficiency described above always occurs on the account of reduced permeability requiring a higher pressure to be applied at the column inlet to achieve the desired flow velocity. This is not completely surprising since each time the through pores are getting smaller. Variation in percentage of toluene in the polymerization mixture confirmed this effect that has also been observed earlier for other polymers [52]. An excess of toluene affords monoliths with small pores and high resistance to flow. In contrast, use of dodecanol as the single porogen leads to monolith with large through pores, good permeability but with a very small surface area hardly enabling any retention of sorbates in gas phase. As this project continues, it will also be interesting to relate the chromatographic properties with specific surface areas of the monolithic materials. However this is a difficult task because the amount of monolith in a capillary is very small and insufficient for surface area measurements using conventional techniques. Preparation of the same monolith in bulk is not reliable. Despite the same polymerization conditions, the monolith structure can be different due to the difference in the dissipation of heat of polymerization. It appears that reliable characteristics of the monolith in capillary columns can be obtained employing te chromatographic techniques.

Another interesting result of the study including numerous poly(divinylbenzene) columns concerns performance at different flow rates of the carrier gas typically described in terms of Van Deemter plots [60,62]. The original equation derived for packed columns

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

relates the height equivalent to a theoretical plate H with the linear flow velocity u. A, B, and C are constants reflecting respectively contribution of non-uniformity of the packed bed, diffusion of the analyte in the mobile phase, and resistance to mass transfer to zone broadening. Typically, the experimental curves are fitted using Eq. 1 and values of the A, B, and C terms then calculated.

Surprisingly, most of the A values calculated for butane and 2-methylpropane are negative. This would suggest that instead of contribution to peak broadening, the monolithic structure narrows the peaks, which is unlikely. The reason for this paradox appears to be the high pressure that has to be applied at the inlet of monolithic capillary columns to achieve the desired flow velocity. As the pressure increases, the diffusion coefficients of the sorbates change. This factor is neglected in the classical Van Deemter model. Indeed, at moderate pressures, these changes are generally small and can be ignored. Giddings model expressed in Eq. 2 [63] takes into consideration the effect of pressure drop on flow rate in the column.

$$H = (9/8)\,A + (27/16)\,B\left(1/Ku^2\right) + (3/4)\,C_M K u^2 + C_s u \tag{2}$$

where $C = C_M + C_S$ and K relate to the pressure drop across the column and the linear flow velocity. Although use of this equation affords higher values of A, they still remain negative for many of the tested columns and explanation of this unexpected behavior needs yet to be found.

In contrast, values of the *B* term for both butane and 2-methylpropane calculated from the Gidding's equation are close to those calculated from Eq. 3:

$$B = 2\gamma D_M \quad (3)$$

where γ has a value of 0.6-0.8 and D_M is the diffusion coefficient of the sorbate in the carrier gas (mobile phase). The *B* parameter decreases with the increasing polymerization time. Since the porosity of the columns also decreases with increasing polymerization duration, it seems likely that these two parameters are interrelated although this assumption is not supported by the theory.

The last term of Van Deemter equation relates to mass transport, which for monoliths, according to numerous liquid chromatographic studies, compares favorably to columns packed with particles [64]. While Fig. 12 shows a smooth parabolic profile of effect of polymerization time on the *C* parameter, some of the calculated C_S values are negative; again, with no physical meaning.

Analysis of Van Deemter plots done for monolithic poly(divinylbenzene) capillary columns reveals that the main contribution to the peak broadening stems from diffusion processes within the mobile phase since the *B* parameter exhibits the large values. In contrast, mass transport between the mobile and stationary phase appears to play only a minor role. This finding is similar to that observed for separation in liquid chromatographic mode.

Despite the current lack of theoretical support for processes occurring during the gas chromatographic separation in monolithic columns, their performance is very promising. Fig. 13A presents a fast, yet highly efficient separation of aliphatic hydrocarbons using 30 cm long monolithic poly(divinylbenzene) column. Further acceleration can be achieved using heavy carrier gas - carbon dioxide [65]. A high efficiency base line separation of all five hydrocarbons is achieved in less then 80 s (Fig. 13B). It is worth noting that the use of heavy carrier gases such as carbon dioxide and nitrous oxide allows to achieve HETP of about 10-15 μm, a value comparable with that typical for liquid chromatography. The effect of the nature of carrier gas is even stronger expressed for silica based monolithic columns.

4. Silica-based monoliths

Monolithic columns based on silica were introduced by Tanaka's group in the mid of 1990s and first used for the separations in the liquid phase [10]. Fig. 14 shows the typical pore size distribution profile of a silica-based monolith. In addition to the through pores with a size of about 1 μm determined be mercury intrusion porosimetry, they also contain a significant fraction of mesopores sized around 30 nm measured by nitrogen adsorption that cannot be observed in mercury intrusion experiment. The mesopores provide the silica monoliths with a much larger surface area of about 300 m^2/g. Thus in contrast to common porous polymer monoliths used in liquid chromatographic mode exhibiting only about 10 m^2/g, the silica-based monoliths afford much higher number of interactive sites and has proven to be excellent stationary phases for the separation of small molecules [16,66-70]. While liquid chromatographic separations were studied in great detail, very little was known until recently about their performance in gas chromatography.

4.1. Porosity and permeability

One of the most favorable features of all monolithic columns is their high permeability to flow first demonstrated with liquid mobile phases. For example, a standard format silica based monolithic column with a through pore size of 2 μm has a permeability comparable with that of column packed with 11 μm beads, yet exhibiting efficiency equivalent to column packed

with beads smaller than 3 μm [16]. This excellent permeability allows application of high flow rates or long columns without exceeding pressure limits of the equipment.

Permeability of gas chromatographic column is defined by modified Darcy's equation:

$$\Delta p j' = L\eta u / B_o \quad (4)$$

where $\Delta p = p_i - p_o$ with p_i and p_o are the pressures of the carrier gas at the inlet and outlet of the column, respectively, $j'$is the Halasz compressibility correlation factor $j' = 3/2(P^2 - 1)(P + 1)/4(P^3 - 1)$ with P being p_i / p_o, L is the column length, η and u are the carrier gas viscosity and the mean velocity, respectively, and B_o is the column permeability. Since p_o has a typical value of 1 bar, Eq. 1 can be simplified to

$$\Delta p j' = 3\left(p_i^2 - 1\right)^2 / 4\left(p_i^3 - 1\right) \quad (5)$$

Fig. 15 shows the flow velocity as a function of pressure of helium applied at the column inlet. Linearity of this plot confirms validity of Darcy's law even for monolithic columns and under high pressures used. Eq. 4 then enabled calculation of the permeability B_o for a series of silica-based monolithic capillary columns. Selected examples are shown in Table 1 [71]. These results are very interesting and correspond to observations made in the initial experiments [72]. First, permeability of the columns is very similar for both liquid and gaseous mobile phase. Since permeability of open capillaries can be easily calculated as $B_{o,open} = d_c^2/32$, the permeability of monolithic 200-250 μm I.D. columns correspond to that of open tube with a diameter of 2-3 μm. Columns of this size did not prove practical since they have a low sample capacity and working with them is difficult. The routinely used GC capillary columns have an I.D. of 100 μm and their permeability is 3.10^{-6} cm^2, a value three orders of magnitude higher than that found for the monolithic columns. For comparison, permeability of a column packed with 4 μm silica particles has also been determined and found much lower compared to the monolithic counterparts. Since permeability of packed column is calculated from equation $B_{o,packed} = d_c^2/1012$, it is possible to find particles sizes that would afford permeabilities similar to the monolithic columns. Data in Table 1 show that rather large beads with diameter of 12-16 μm would have to be packed in the column that would then exhibit equivalent resistance to flow. The permeability also enables calculation of the cross section area of the column open for flow. Dividing this value by the open capillary cross section affords the apparent porosity ε shown in Table 1. Despite the very high values of porosity reaching one, which normally stands for an open tube, the monolithic columns exhibit a significant resistance to the gas flow. Their permeability is almost three orders of magnitude lower compared to that of the open capillaries from which they were made. However, at the same time, the permeability of monolithic capillary columns is almost two orders of magnitude higher than that of columns packed with particles, which size equals the size of skeletons forming the monolith. Again, this finding is not a surprise since similar effects were also found for monolithic columns used in HPLC mode.

We have already discussed above that the parameters B and C of the Van Deemter equation in gas chromatography depend on the diffusion coefficients of the sorbate in both mobile and stationary phases. Since the mobile phase in gas chromatography is compressible, the diffusion coefficient of the sorbate is inversely proportional to its density, which in turn is proportional to pressure. The pressure decreases along the length of the column and therefore, the magnitude of the diffusion coefficient depends on position within the column. For example, the calculated diffusion coefficient D_M for butane in helium decreases from 0.403 cm^2/s at 1 bar to 0.080 at 5 bar, and to 0.0040 cm^2/s at 100 bar [73]. Such changes in the diffusion coefficient are likely to affect the parameters of the Van Deemter equation. Therefore, several modifications of the original simple Eq. 1 were suggested for gas chromatography [63]. However, Fig. 16 clearly demonstrates that despite differences in the included mechanisms of zone broadening, all three equations fit rather well the experimental data [73]. These equations also enable calculation of

the parameters *A*, *B*, and *C*. Similar to observation made for poly(divinylbenzene) columns, most of the calculated *A* parameters had a negative value except for those calculated using Giddding's Eq. 2. However, the values once more did not relate to the structural characteristics of the monoliths.

4.2. Column efficiency

Fig. 17 shows an example of Van Deemter plots characterizing efficiency of the silica-based monolithic column as a function of flow velocity of the helium used as the carrier gas [74]. The plots for all four hydrocarbons, ethane, propane, 2-methylpropane, and butane have U-shapes predicted by Eq. 1. If column efficiency were governed by size and shape of the hydrocarbon molecule and therefore the ease of access into the micropores, ethane should be most affected and column efficiency for this compound should have the lowest value. However, the experiments show otherwise. The same column efficiency defined by HEPT of about 0.3 mm was found for the first three sorbates no matter of their size. In contrast, column efficiency for butane was about half of that observed for the other homologs. This result suggests that the separation in monolithic columns is also controlled by some other effects. The analysis of the parameters *A*, *B*, and *C* of the Van Deemter equation indicates that the peak broadening is controlled by the diffusion in the mobile phase since the value of *B* is high while the contribution of the mass transport between the mobile and stationary phases plays only a minor role as indicated by the small value of *C*.

4.3. Carrier gas

It is known that the nature of the carrier gas has a significant effect on the separation in GSC [75]. This effect is attributed to the heterogeneity of the surface of the stationary phase, which is characterized by a wide distribution of sorption sites differing in the energy of sorption. While interacting with a carrier gas, the most active sorption sites that contribute substantially to the overall retention interact first and lose their activity. As a result, a decrease in the retention time of the analytes is then observed while using more reactive gases.

Series of experiments with monolithic silica column using helium, hydrogen, nitrogen, carbon dioxide, and nitrous oxide as the carrier gas and butane and 2-methylpropane as sorbates were performed [76]. Table 2, which summarizes the results, clearly shows that the retention times of the alkanes decrease by a factor of about 2 when switching from helium affording the longest retention times to nitrous oxide in which the retention is the shortest. Taking into account a wide variety of processes involved in the adsorption of analytes on the sorbent surface, the effect on retention is difficult to characterize quantitatively. One option is to relate the retention to solubility of the carrier gas in water because surface of silica is also polar and hydrophilic. Indeed, Fig. 18 demonstrates a linear correlation between retention time for both sorbates and solubility of helium, hydrogen, nitrous oxide, and carbon dioxide in water [76]. The slope of the straight line is larger for butane than for 2-methylpropane indicating that the former has better access to the active sites at the surface. This can be explained by an easier access of the linear molecule in small pores in which the most active sites are located. Out of all gases studied, only nitrogen does not fit in the pattern. The retention times in this gas are shorter than predicted from its solubility. Although not completely clear, this behavior may be attributed to the higher polarizability of the nitrogen compared to helium and hydrogen, since the alkanes have no dipole moment.

Table 2 also shows that the choice of carrier gas also significantly affects selectivity and column efficiency. For example, the selectivity of separation of butane and 2-methylpropane decreases from 1.36 in helium to 1.14 in nitrous oxide. Since the retention of 2-methylpropane is less affected by the deactivation of the highly active sites than that of butane, the selectivity decreases. Although diffusion in the carrier gas has been shown to affect processes occurring

during the GC separations using monolithic columns, no good correlation between the square root of diffusion coefficient and column efficiency could be found. However, the minimum HETP appears to be a function of a product of three variables: pressure required to attain flow velocity giving the minimum at the Van Deemter curve, viscosity of the carrier gas, and diffusion coefficient in the mobile phase. The actual Van Deemter curves support this claim [76]. The effect of the nature of the carrier gas on column efficiency is well know in GLC and heavier carrier gases typically provide for 20 to 30% better efficiency than their lighter counterparts. Surprisingly the effect observed for silica based monolithic capillary columns was much stronger and, as it can be seen from Tab.2, replacing helium with nitrogen dioxide results in an increase in the column efficiency by a factor of 10. It is difficult to currently speculate about the reason for such a strong effect. No doubt the nature of the monolith is certainly one of the important parameters because for monolithic poly(divinylbenzene) columns the effect was on the same level known for open capillary columns in GLC. Another interesting aspect of this strong dependency of the column efficiency on the type of carrier gas are very fast separations that can be achieved with heavy carrier gases. This observation clearly supported by the resolution of the standard test mixture shown in Fig.19 [77], is in contrast with the well-known situation typical of open capillary columns in GLC.

5. Loading capacity

Overloading of a chromatographic column negatively affects efficiency of the separation and therefore is undesirable. Since the monolithic columns exhibit much larger surface area than their open tubular counterparts, it is conceivable that their sample loading capacity can also be higher.

Two common parameters - retention time of butane and 2-methylpropane as well as HETP for both these sorbates - were chosen to assess loading capacity of monolithic columns using nitrogen and carbon dioxide as the carrier gas, respectively. For comparison, a typical open tubular capillary column coated with a 250 nm layer of SE-54 phase was also included in these experiments [65]. Properties of all columns are described in Table 3. The retention time is less sensitive to diffusion effects and only reflects deviation of sorption isotherm from linearity. In contrast, column efficiency depends on both sorption isotherm and diffusion coefficients of the sorbate. Indeed, almost no effect of sample quantity on retention time has been observed within the measured range for all four tested columns. However, the column efficiency decreases with an increase in the injection volume.

A comparison of results obtained with both sorbates and both carrier gases presented in Table 4 reveals that indeed the monolithic columns are superior to the open capillary column in loading capacity. In reality, this nominal comparison only indicates that it is possible to inject a larger sample volume in the monolithic columns compared to an open capillary column of the same length. Yet, these columns differ in diameter and volume of the stationary phase. Therefore, a more appropriate way is to consider loading capacities related to unit volume or unit surface of the stationary phase accessible for sorption of analytes. While the surface area of the sorbent in a monolithic column cannot be measured directly, the volume of the stationary phase in the capillary can be accessed more reliably by calculation from porosity and dimensions. Based on the volume, the monolithic column contains 35-50 times more stationary phase than the open capillary. Thus, to achieve a similar loading capacity in the same length of the open capillary assuming that the volumetric capacity is equal for both column formats, the stationary phase layer in the open capillary column would have to be at least 7 μm thick. Preparation of this column would be very difficult and the mass transfer slow resulting in low column efficiency. In contrast, the relatively short monolithic columns provide rapid and efficient separations without overloading as shown in Fig. 13 and 19.

Table 4 also reveals another important information concerning the monolithic columns. The loading capacity of silica-based column is 6-7 times higher than the loading capacities of poly (divinylbenzene) columns while using nitrogen as the carrier gas. However, its loading capacity is only one half of that found for poly(divinylbenzene) columns when using carbon dioxide. This result suggests that in addition to the amount of the stationary phase, the chemical nature of both stationary and mobile phases plays also an important role in determining the loading capacity of the monolithic capillary columns.

6. Concluding remarks

Although gas chromatography remains least common among other applications of both polymer and silica-based monoliths, it represents an area in which continuing research may reveal many new and unexpected facts. Negative values of A-term of Van Deemter equation being systematically found for the monolithic capillary columns or the pronounced effect of pressure on the diffusion of sorbates in the carrier gas and thus on separation performance are just two examples of the numerous surprising findings discussed in this review. Clearly, most of the experiments carried out so far seem to raise more questions than answers and a significantly larger extent of work has to be done to understand the separation mechanism and all related effects that control the separations in the GSC mode. On the other hand, it has already been sufficiently demonstrated that monolithic columns enable very fast separations and provide column efficiency comparable with other packed columns typically used in GC. For example, a 57 cm long capillary column packed with nonporous 3 μm ODS particles afforded 1130 plates/s using carbon dioxide at a pressure of 9.5 MPa [78]. This column efficiency is similar to that obtained with monolithic column (971 plates/s) obtained at a much lower pressure of 5.6 MPa [77]. Obviously, comparing efficiencies of monolithic GC columns with very long open tubular capillary columns typically used in GC makes less sense since each of these technologies is different in their application range.

Polymer-based monolithic columns are likely to attract more attention. It is rather easy to modify their surface polarity and retention properties by varying chemistry of monomers used for their preparation. They also enable separation of compounds in mixtures containing large percentage of water, which can be an advantage when analyzing environmental samples. It is our hope that this review summarizing all the current discoveries may draw attention of other research groups and further extend exploration of this exciting field and guide it from its current infancy in the mature reality.

Acknowledgements

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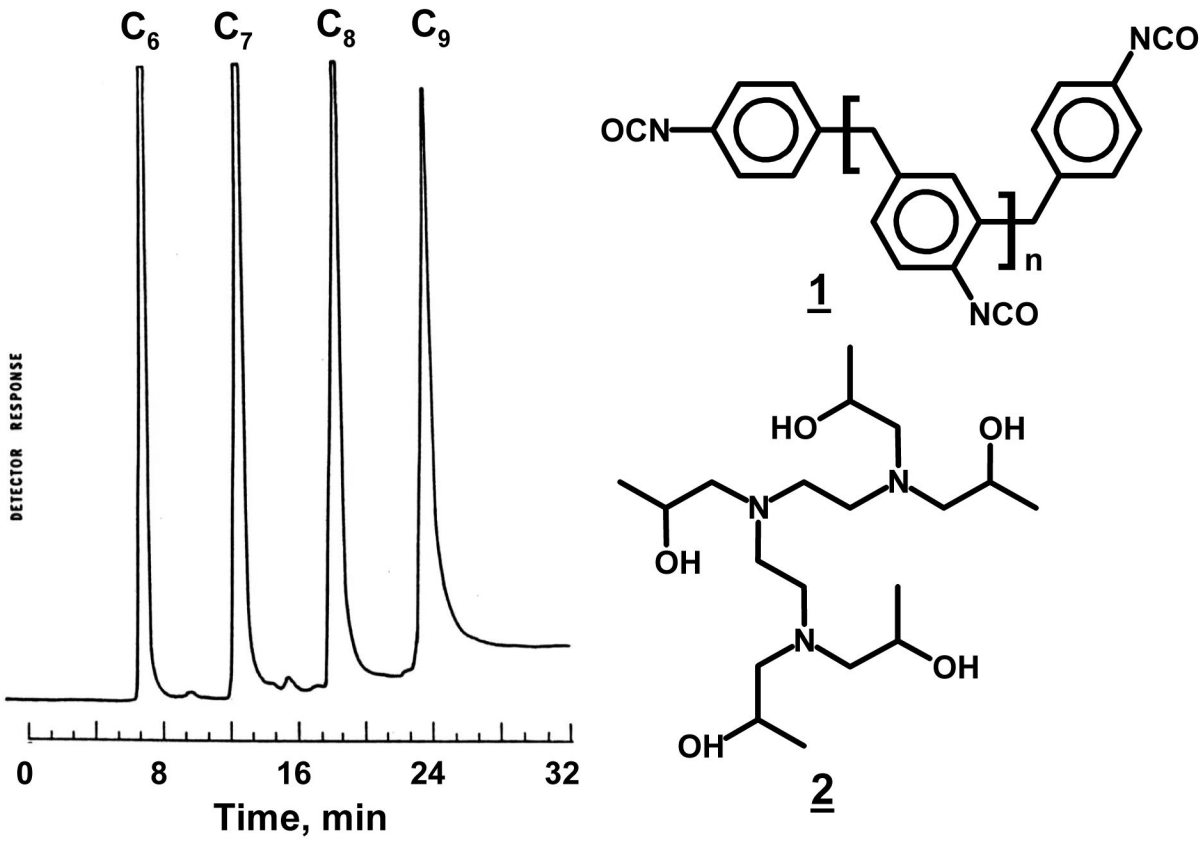

Fig. 1.

GC separation of C_6-C_9 alkanes on open pore polyurethane column containing 10% (w/w) of Dow Corning Silicone Fluids 550 included in the polymerization mixture. Conditions: Glass column 50 × 0.6 cm I.D., temperature gradient 50-140 °C in 5 min. (Reprinted with permission from [3]. Copyright 1974 Preston Publ.).

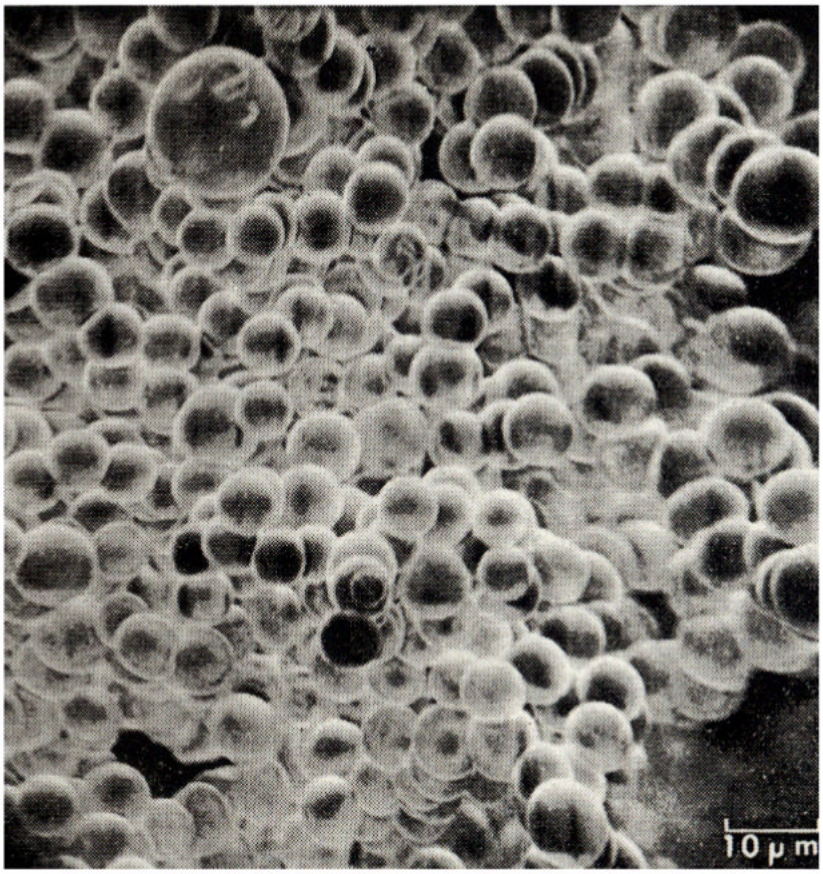

Fig. 2.
Micrograph of open pore polyurethane structure (Reprinted from [3]. Copyright 1970 Preston Publ.)

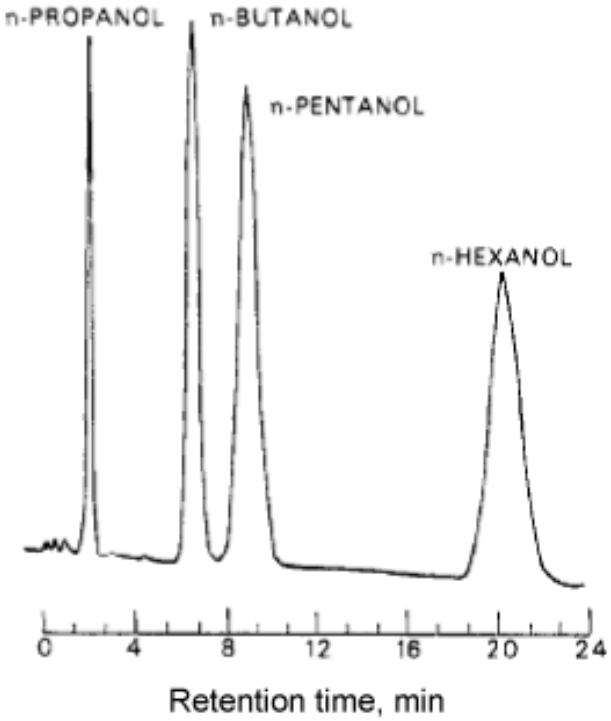

Fig. 3.
GC separation of alcohols using 1 m × 4 mm I.D. column filled with polyurethane foam at a temperature of 100 °C (Reprinted from ref. [6], Copyright 1973 American Chemical Society). Carrier gas helium 55 mL/min.

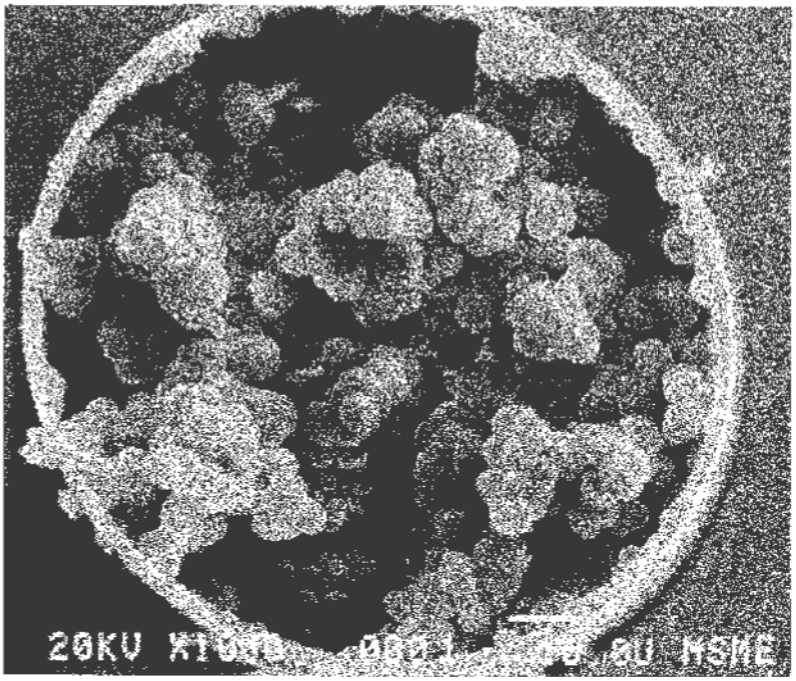

Fig. 4.
Scanning electron micrographs of monolithic poly(divinylbenzene) capillary column (Reprinted from ref. [58]. Copyright 2000 Wiley-VCH).

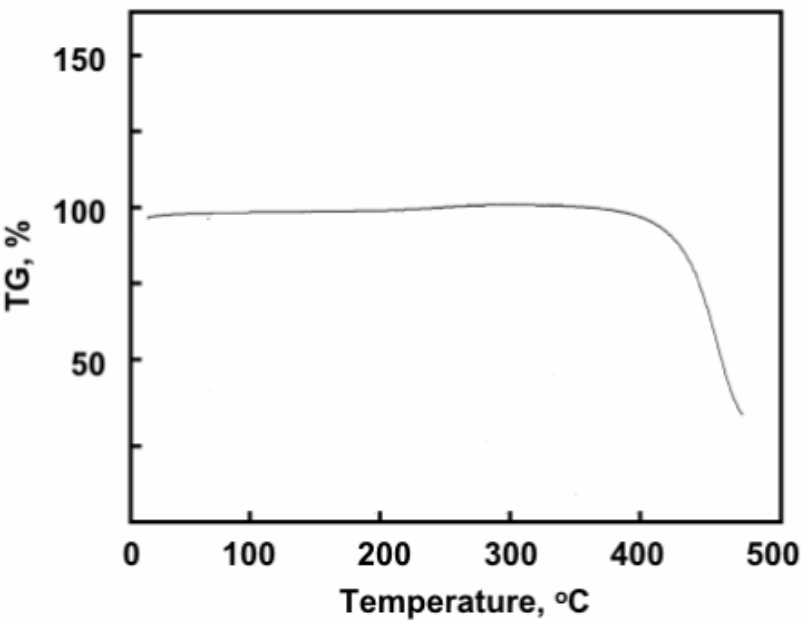

Fig. 5.

Thermal gravimetric curve of the poly(divinylbenzene) monolith in air at a heating rate of 20 °C/min. (Reprinted from ref. [58]. Copyright 2000 Wiley-VCH).

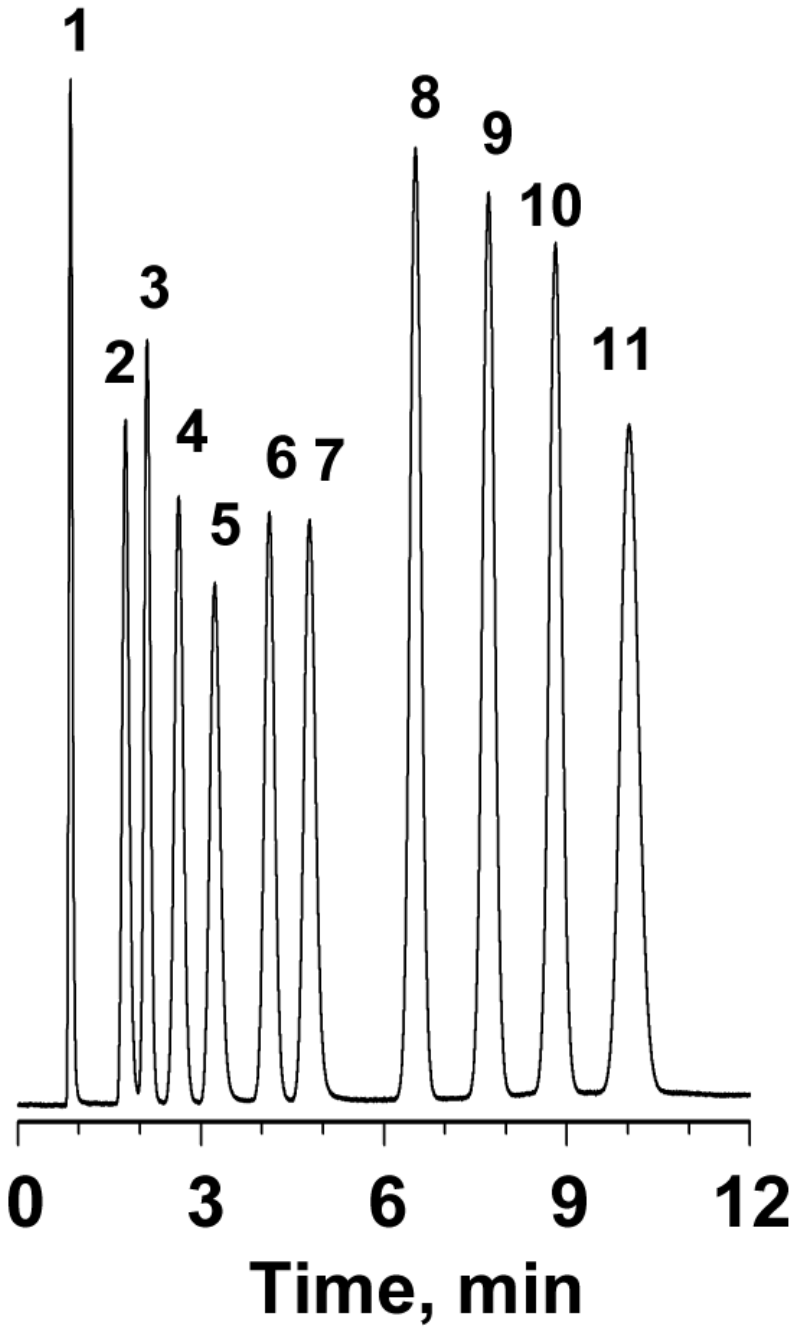

Fig. 6.

Separation of a mixture of organic solvents using 50 cm long and 100 μm I.D. monolithic poly (divinylbenzene) capillary columns. Conditions: Temperature gradient 120-300 °C, 20 °C/min; inlet pressure 0.55 MPa; split injection. Peaks: methanol (1), ethanol (2), acetonitrile (3), acetone (4), 1-propanol (5), methyl ethyl ketone (6), 1-butanol (7), toluene (8), ethylbenzene (9), propylbenzene (10), butylbenzene (11). (Adapted from ref. [58]. Copyright 2000 Wiley-VCH).

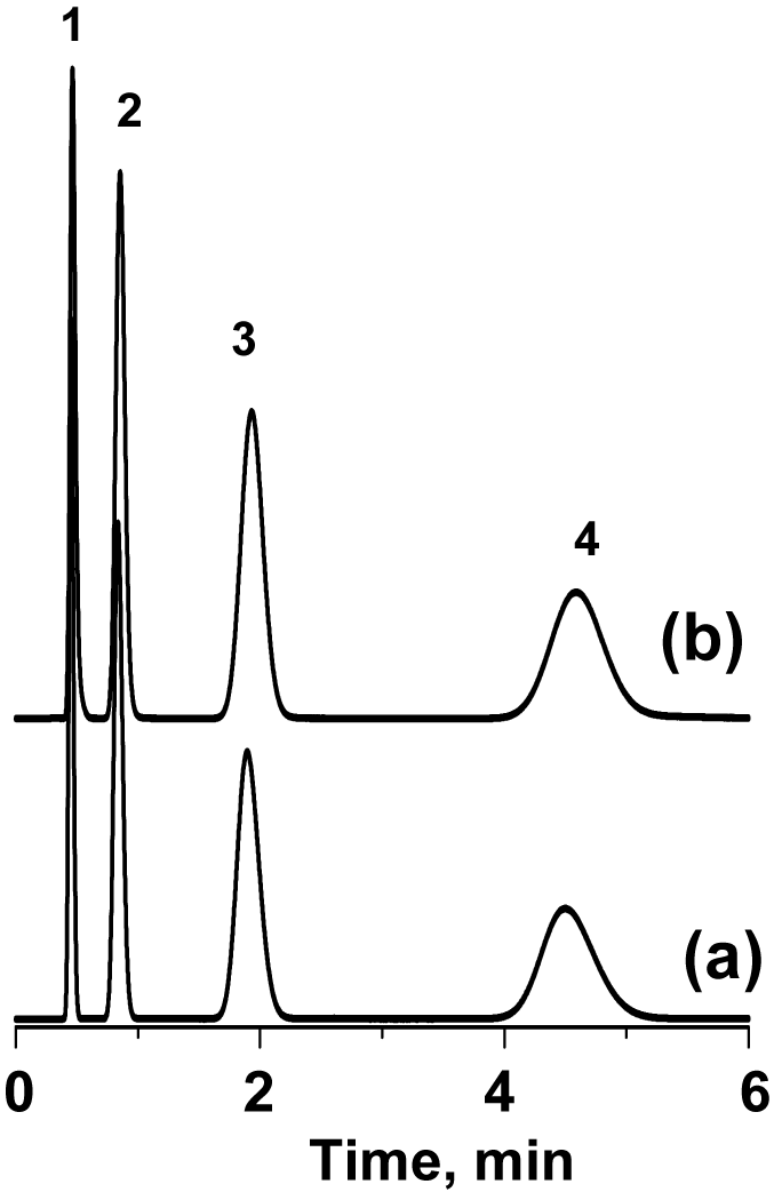

Fig. 7.

Isothermal separation of a straight mixture (a) and 10% aqueous solution (b) of methanol (1), ethanol (2), 1-propanol (3), and 1-butanol (4) using 50 cm × 320 μm I.D. monolithic poly (divinylbenzene) capillary column at 180 °C. For other condition see Fig. 6. (Reprinted from ref. [58]. Copyright 2000 Wiley-VCH).

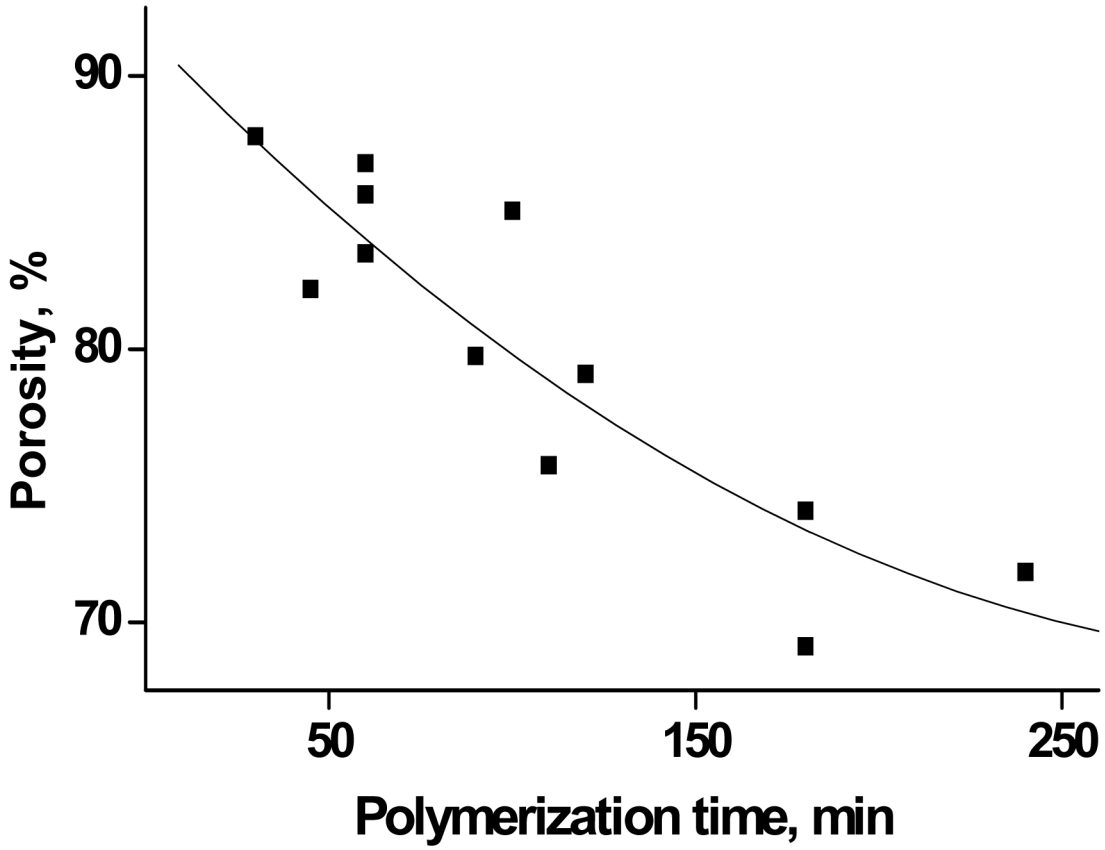

Fig. 8.
Effect of polymerization time on porosity of the poly(divinylbenzene) monolith (Reprinted from ref. [59]. Copyright 2006 Springer). Conditions: Polymerization mixture: divinylbenzene (65% purity) 38%, dodecanol 54%, toluene 8%, initiator azobisisobutyronitrile (1% w/w, with respect to monomers), temperature 75 °C.

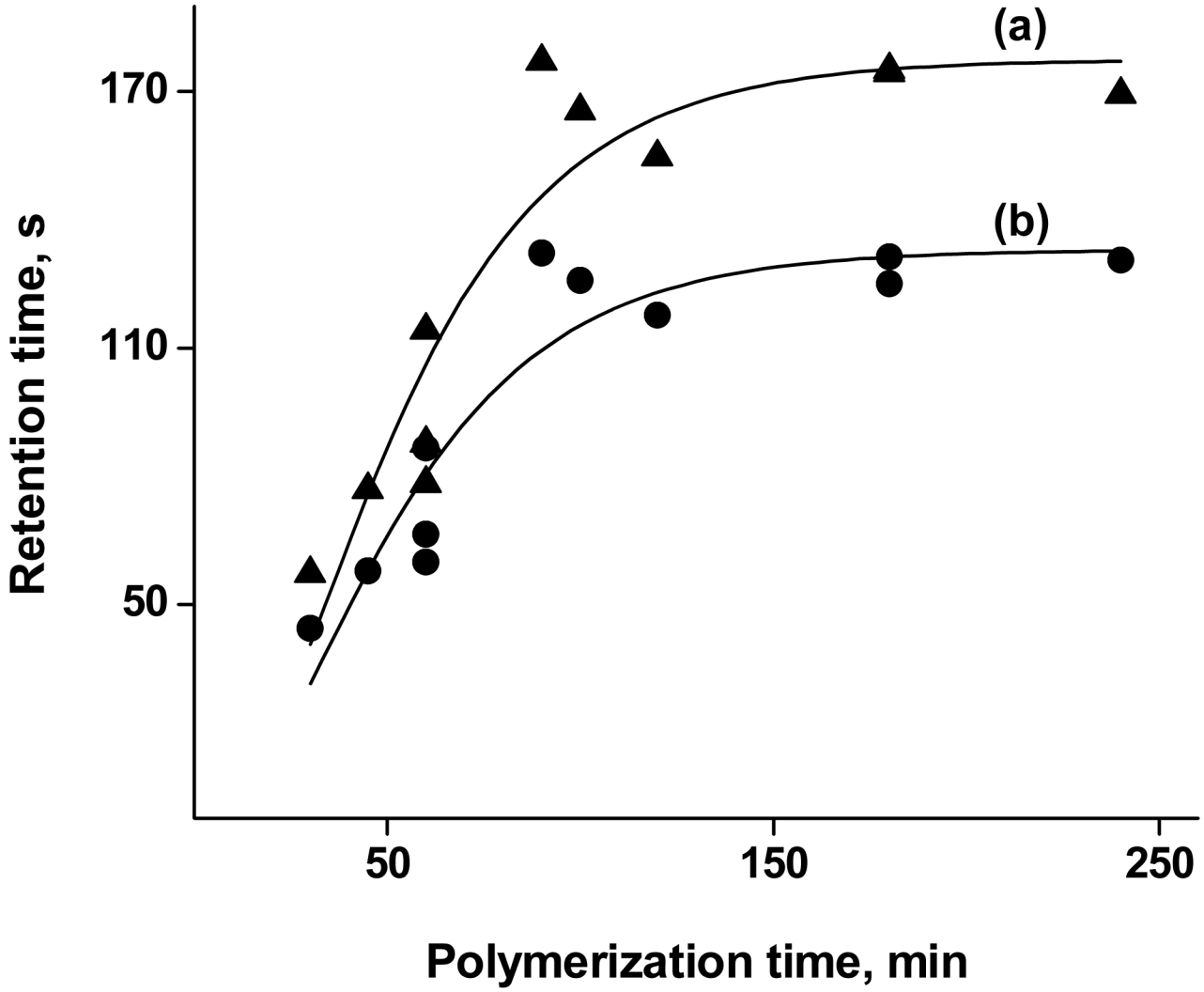

Fig. 9.
Retention of butane (a) and 2-methylpropane (b) as a function of polymerization time (Reprinted from ref. [59]. Copyright 2006 Springer). Conditions: Column length 50 cm, flow velocity 25 mm/s. For polymerization conditions see Fig. 8.

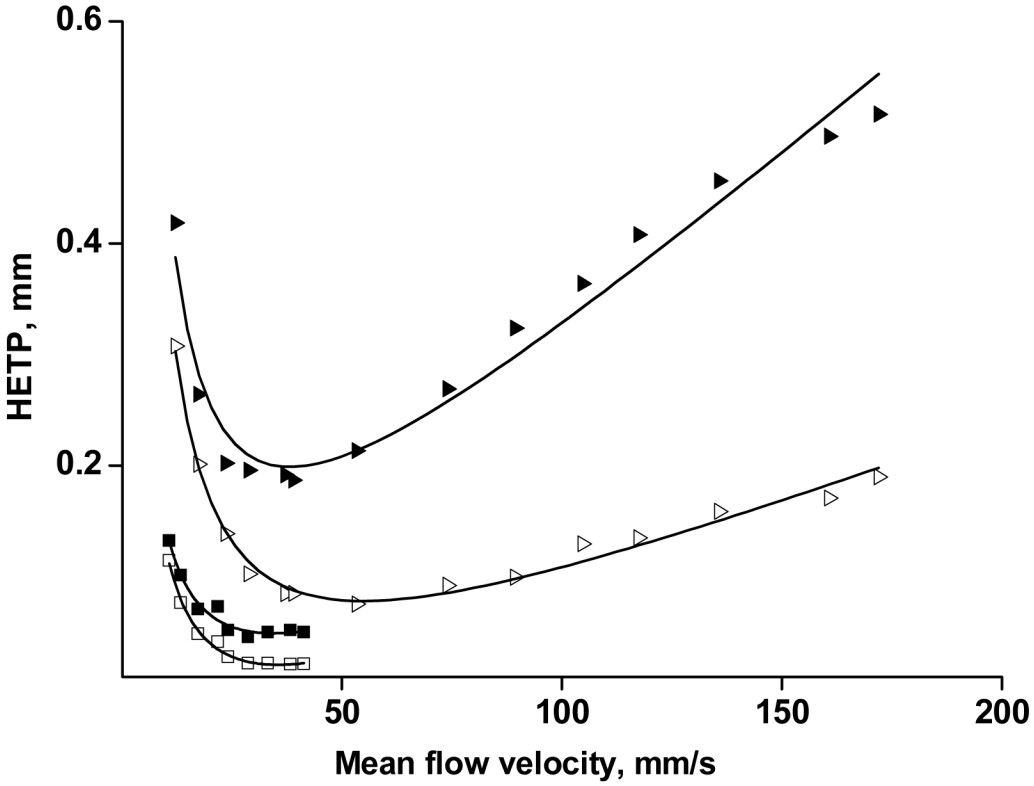

Fig. 10.

Van Deemter plots relating height of a theoretical plate HETP and flow velocity of the carrier gas for butane (closed symbols) and 2-methylpropane (open symbols) in monolithic poly (divinylbenzene) columns prepared at different temperatures (Reprinted from ref.[59]. Copyright 2006 Springer). Polymerization mixture: divinylbenzene (65% purity) 38%, dodecanol 54%, toluene 8%; temperature 75 (triangles) and 78 °C (squares), polymerization time 120 min.

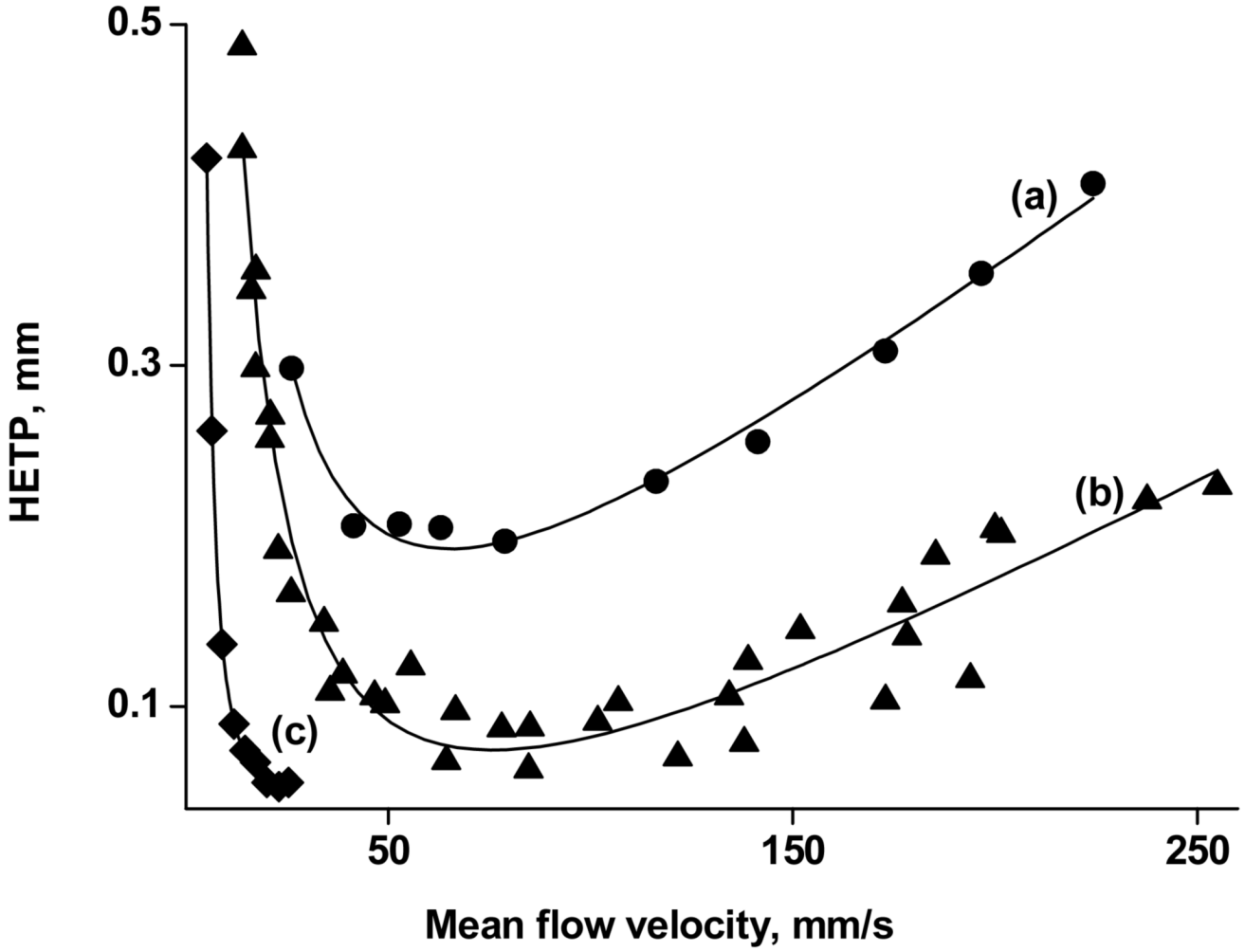

Fig. 11.

Van Deemter plots for 2-methylpropane using monolithic poly(divinylbenzene) columns prepared from polymerization mixtures differing in content of monomer (Reprinted from ref. [59]. Copyright 2006 Springer). Conditions: Polymerization mixture: (a) divinylbenzene (65% purity) 35%, dodecanol 57%, toluene 8%; (b) divinylbenzene (65% purity) 38%, dodecanol 54%, toluene 8%; (c) divinylbenzene (65% purity) 42%, dodecanol 50%, toluene 8%; polymerization temperature 75 °C.

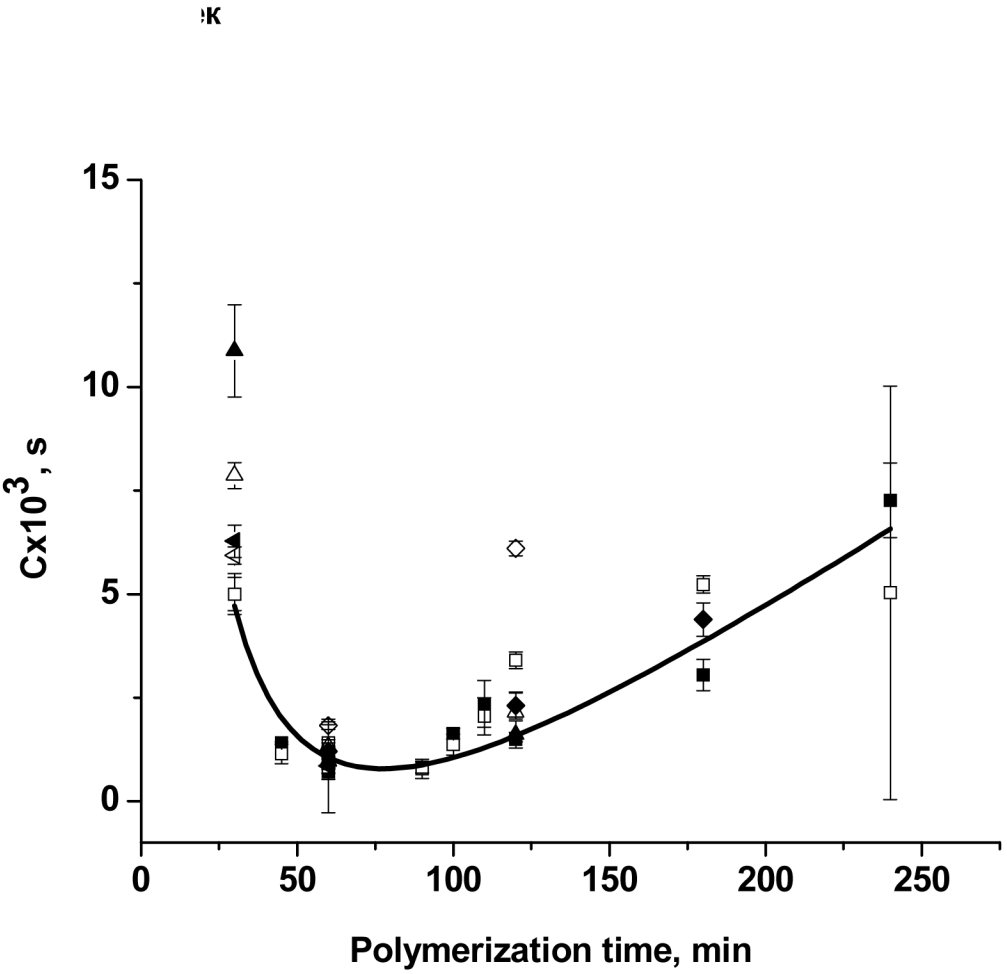

Fig. 12.

Effect of polymerization time used to prepare various monolithic polydivinylbenzene columns on the value of parameter *C* of Van Deemter equation for butane (closed symbols) and 2-methylpropane (open symbols) (Reprinted from ref.[62]. Copyright 2007 Springer).

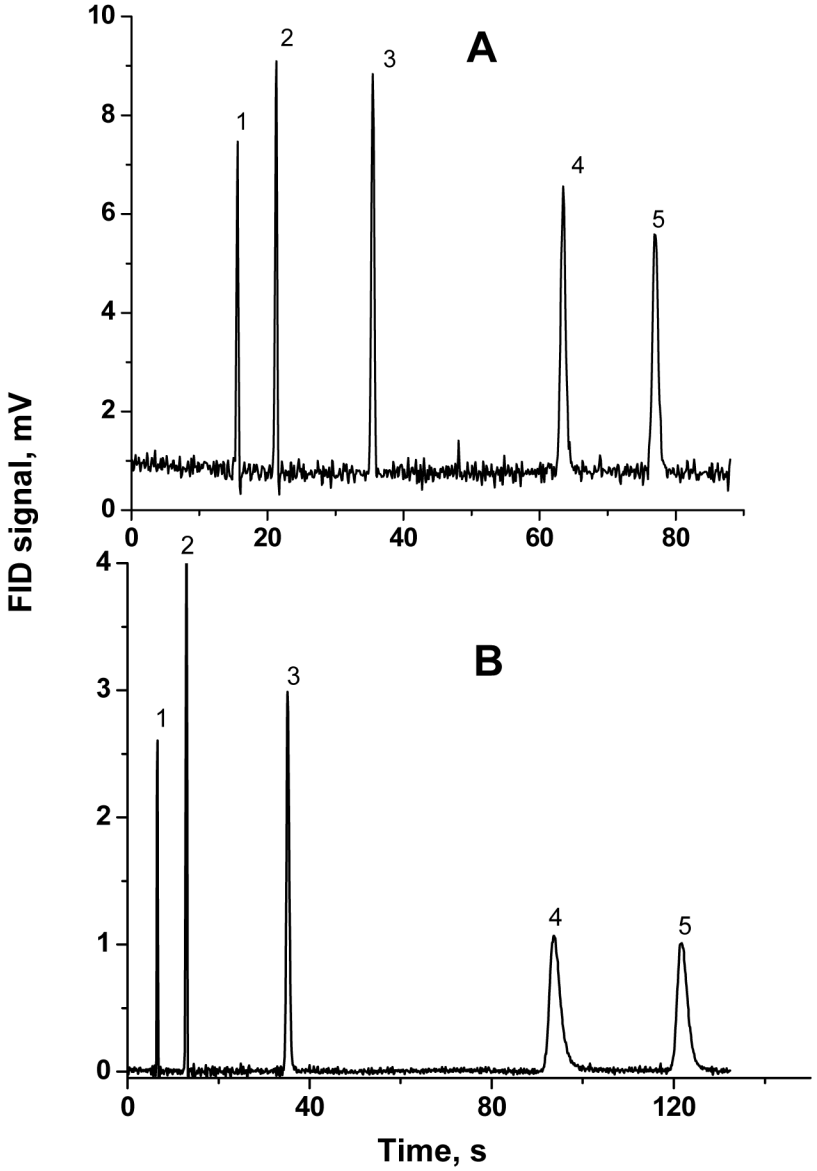

Fig. 13.

Gas chromatographic separation of methane (1), ethane (2), propane (3), 3-methylpropane (4), and butane (5) using monolithic poly(divinylbenzene) capillary column (Adapted from refs. [62] and [65]. Copyright 2007 Springer). Polymerization conditions: divinylbenzene (purity 65%) 35%, dodecanol 57%, toluene 8%, polymerization temperature 75 °C, time 100 min; column: 28.9 cm × 100 μm, flow velocity 44.3 mm/s, column temperature 80 °C; carbon dioxide, pressure 5.42 MPa (A) and carrier gas nitrogen, pressure 6.8 MPa (B).

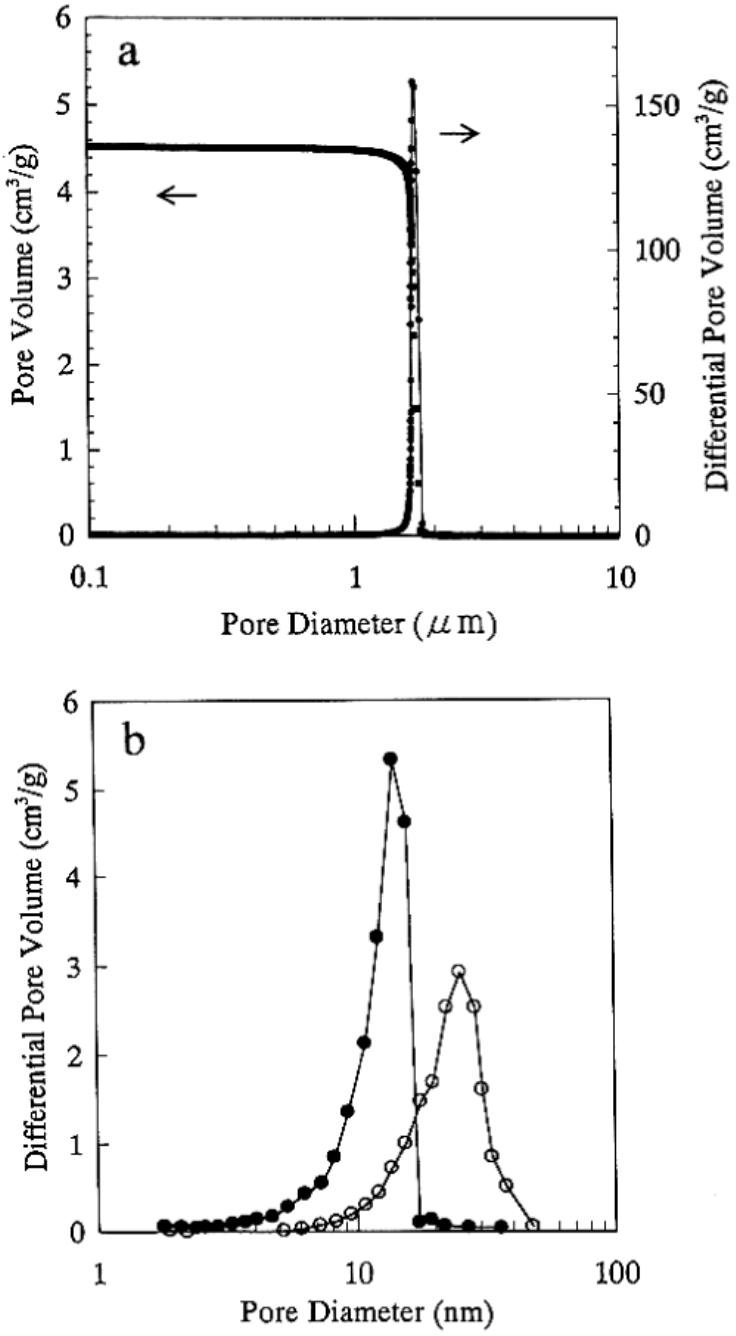

Fig. 14.

Pore size distribution of two different silica based monolithic column measured using mercury intrusion (a) and nitrogen adsorption/desorption (b) metods (Reprinted from ref. [10]. Copyright 1996 American Chemical Society).

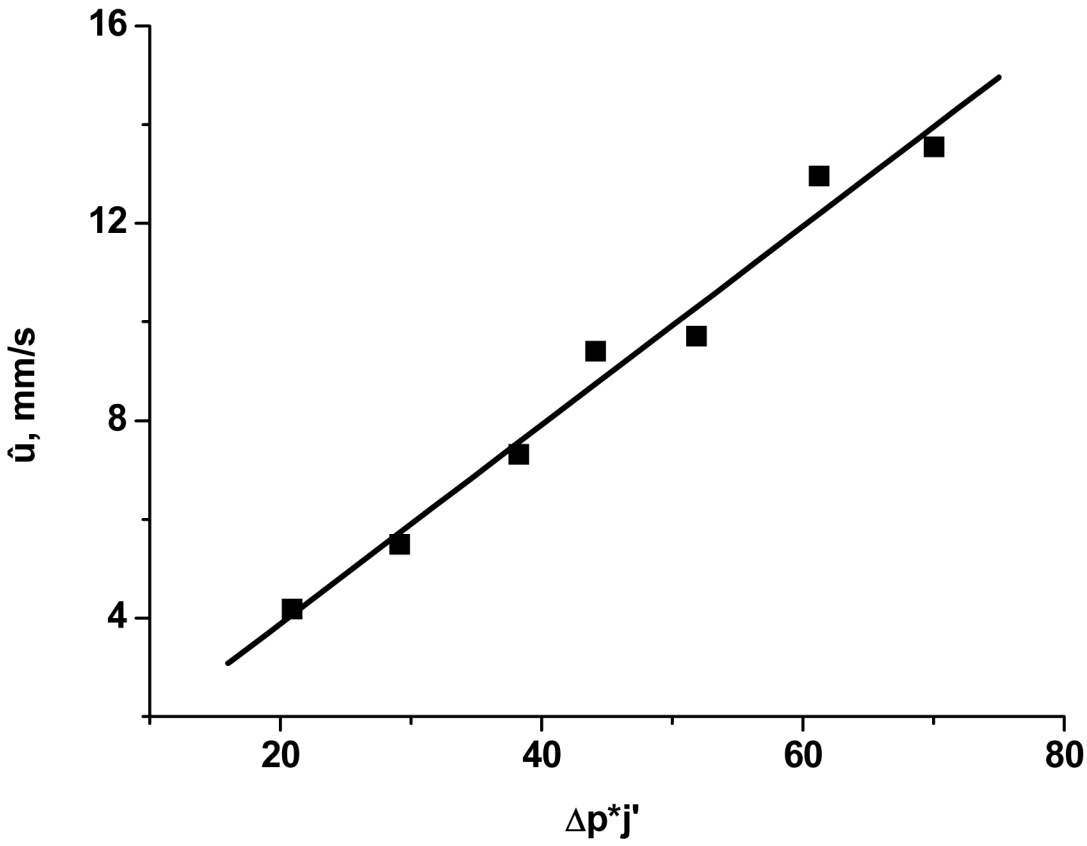

Figure 15.
Effect of helium pressure at the column inlet on flow velocity troug a monolithic column at 60 °C (Reprinted from ref.[71]. Copyright 2006 Springer).

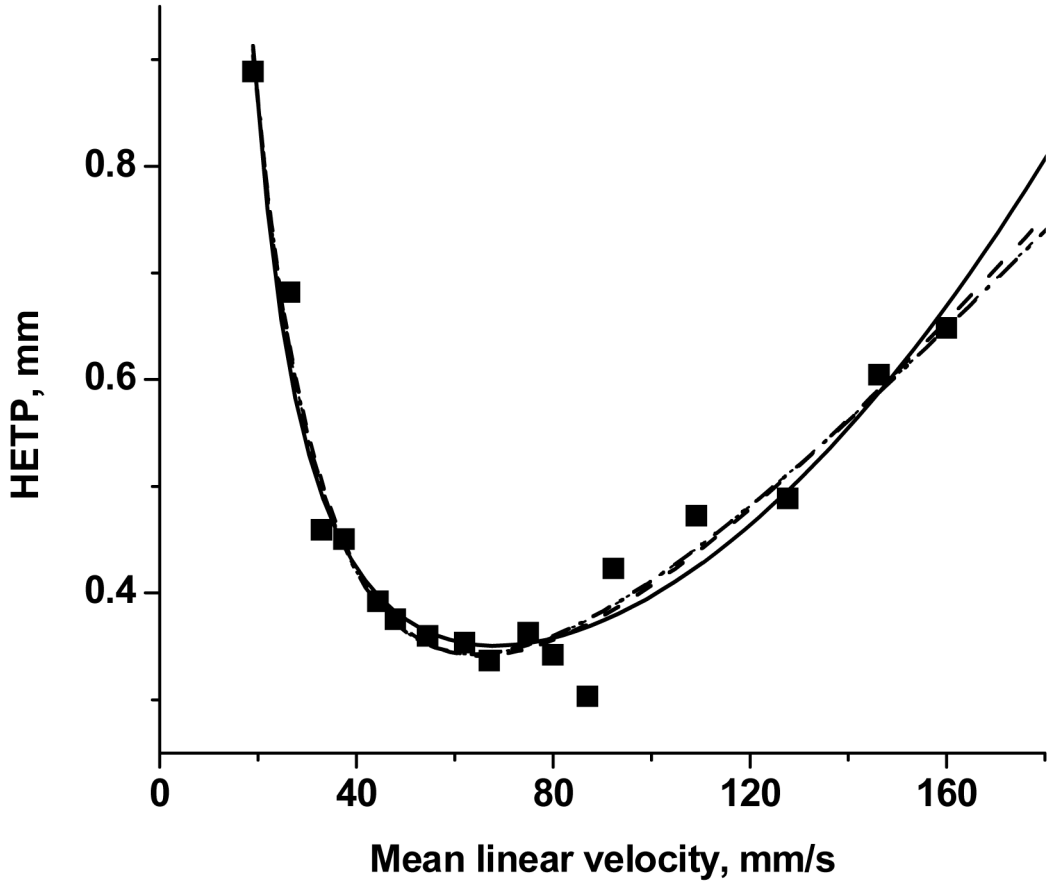

Figure 16.

Fitting experimental points showing effect of flow velocity on HETP using various forms of Van Deemter equation (Reprinted from ref.[73]. Copyright 2006 Springer). Silica-based column 115 cm × 200 μm I.D., carrier gas helium, sorbate butane, temperature 60 °C.
Full line: $H = (9/8)A + (27/16)B(1/K\,u^2) + (3/4)C_M\,K\,u^2 + C_S\,u$
Hatched line: $H = A\,u^{0.33} + B/u + C\,u$
Dotted line: $H = A + B/u + Cu$

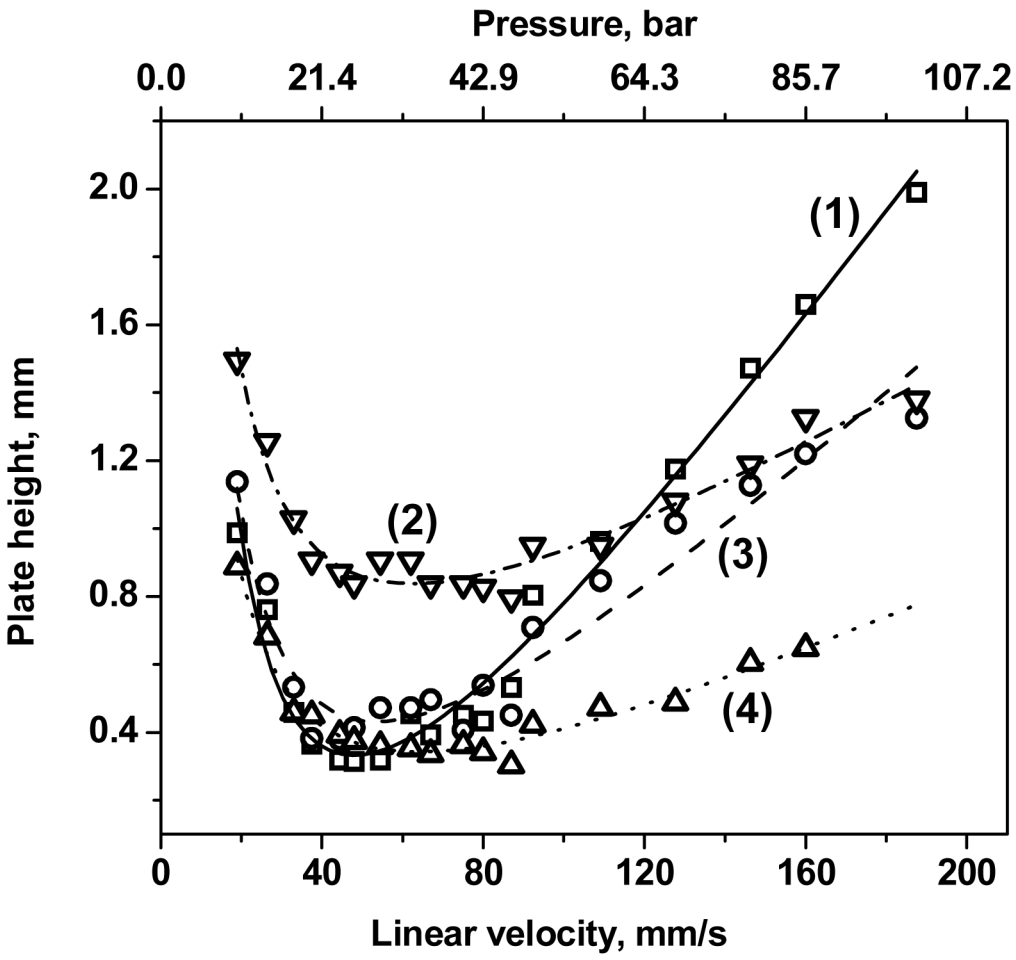

Fig. 17.

Van Deemter plots demonstrating effect of flow velocity of carrier gas on HETP of a silica-based monolithic column for ethane (1), propane (2), 2-methylpropane (3), and butane (4) (Reprinted from ref. [74]. Copyright 2006 Springer). Column 115 cm × 100 μm I.D., carrier gas helium, temperature 60 °C.

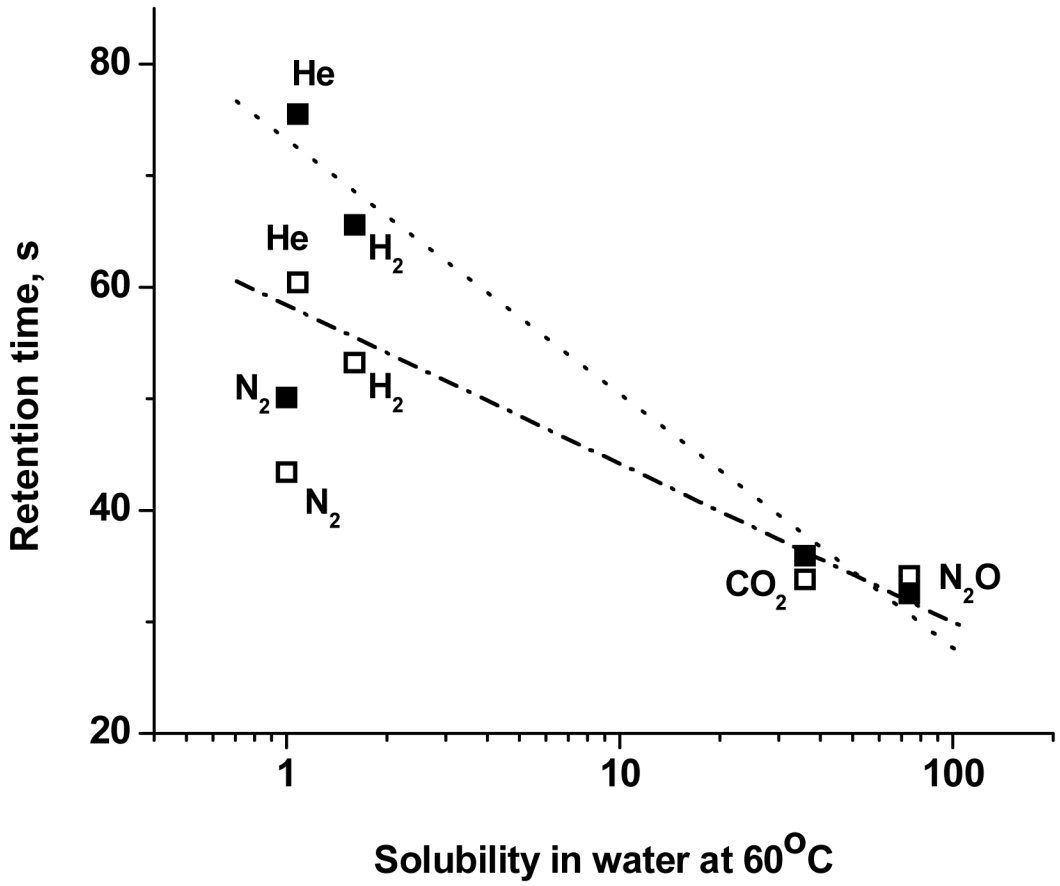

Fig. 18.
Correlation between retention time of butane (closed symbols) and 2-methylpropane (open symbols) and solubility of the carrier gas in water. (Reprinted from ref. [76] Copyright 2007 Springer).

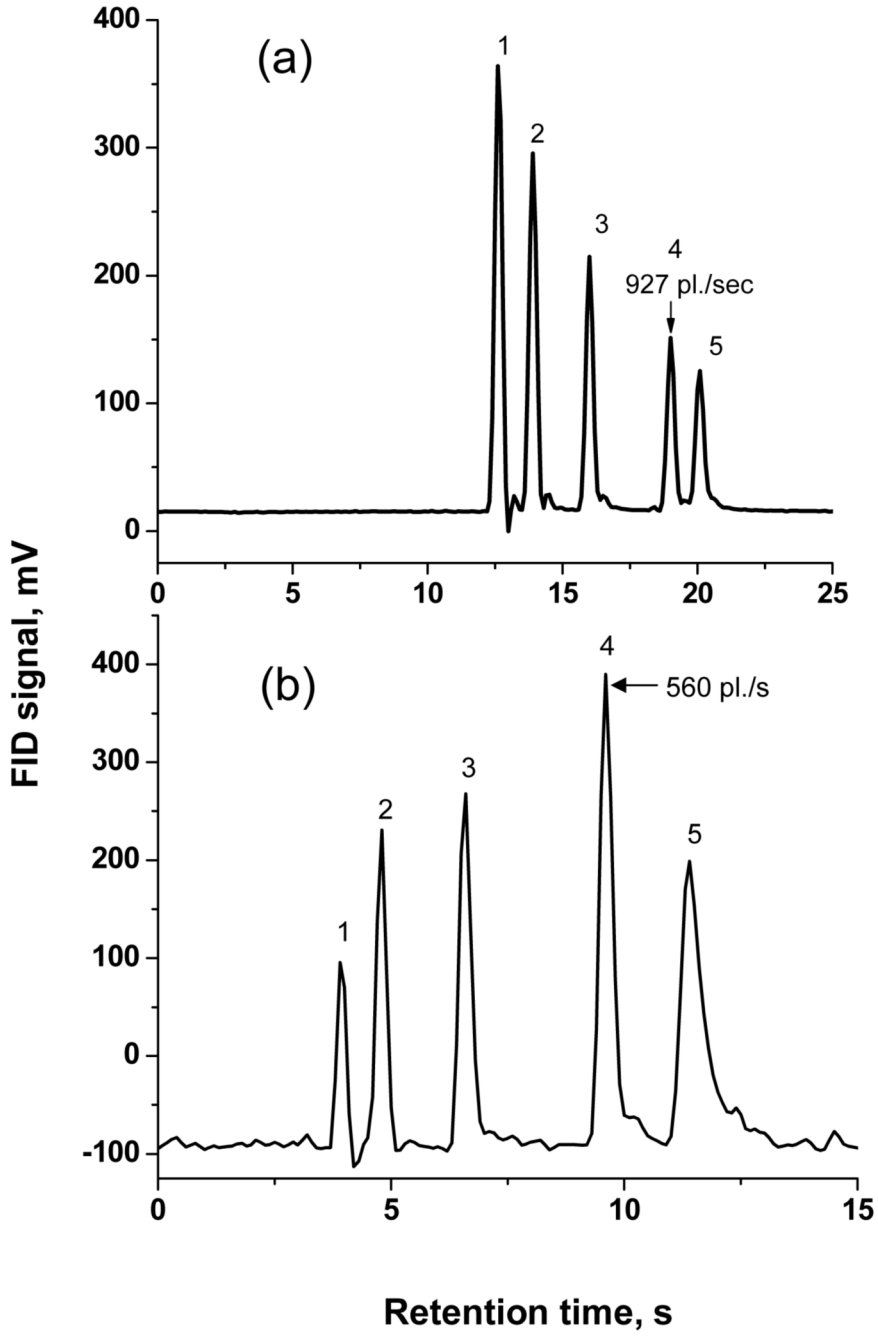

Fig. 19.

Separation of five light hydrocarbons using silica-based monolithic capillary columns and carbon dioxide and hydrogen as carrier gas.(Reprinted from ref. [77]. Copyright 2007 Springer). Column 58,5 cm × 200 μm I.D.; (a) carbon dioxide, pressure 4.33 MPa, mean flow velocity 42,5 mm/sec, (b) hydrogen, pressure 8.5 MPa, mean velocity 136,6 mm/sec; temperature 60 °C. Peaks: methane (1), ethane (2), propane (3), 2-methylpropane (4), butane (5).

Table 1

Permeability and porosity of selected silica-based monolithic capillary columns (adapted from [71])

Column	D_{col}, [a] µm	L_{col}, [b] cm	$B_o \times 10^9$, [c] cm^2		$d_{p,eqv}$, [d] µm	ε, % [e]
			LC	GC		
A	200	58.5	1.4	1.5	12	0.96
B	200	50.0	2.9	2.8	17	1.05
C	250	50.0	2.5	2.4	16	1.01
Supersphere[f]	100	14.3	0.12	-	4	-

[a] Column internal diameter

[b] Column length

[c] Permeability

[d] Particle size of packing that would afford equivalent column permeability

[e] Porosity

[f] Column packed with 4 µm particles

Table 2

Effect of type of carrier gas at a constant flow velocity of 30 mm/s on chromatographic performance of silica-based monolithic capillary column

Carrier gas	Retention time, s		Selectivity	HETP, mm	
	butane	2-methylpropane		butane	2-methylpropane
He	75.7	60.8	1.36	0.464	0.221
H_2	66.5	53.5	1.38	0.192	0.089
N_2	50.7	43.0	1.31	0.067	0.043
CO_2	36.7	34.2	1.17	0.035	0.032
N_2O	34.4	32.5	1.14	0.029	0.027

Table 3

List and properties of monolithic and open tubular capillary columns tested for loading capacity

Type	Chemistry	Length cm	Diameter μm	Permeability 10^{-9} cm^2	Porosity %
Monolith	Silica	58.5	200	1.3	95
Monolith	Poly(DVB)[a]	28.0	100	1.9	86
Monolith	Poly(DVB)[a]	54.0	100	0.8	81
Open tube	Coated	500	250	19,500	99.8

[a] Poly(divinylbenzene)

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Table 4

Loading capacities expresses as the peak area for monolithic and open tubular capillary columns normalized to 1 m length

Type[a]	Chemistry	Loading capacity, mV/s [c]			
		Carrier gas N_2		Carrier gas He_2	
		Butane	2-Methylpropane	Butane	2-Methylpropane
Monolith	Silica	795	1176	154	140
Monolith	Poly(DVB)[b]	139	257	-	-
Monolith	Poly(DVB)[b]	157	191	233	283
Open tube	Coated	-	-	7	21

[a] For column characteristics see Table 3.

[b] Poly(divinylbenzene)

[c] Value of loading capacity is determined as the crossing point of extended horizontal and increasing parts of the HETP vs. peak area plots.