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Preparation, characterization and application of polymethacrylate-based monolithic columns for fast and efficient separation of alkanes, alcohols, alkylbenzenes and isomeric mixtures by gas chromatography

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ABSTRACT

Application of monolithic columns in gas chromatography is still considered very limited. In this work, several polymethacrylate-based monolithic capillary columns were fabricated, characterized and used in gas chromatography. The five monomers used were: methyl methacrylate, (MMA), hexyl methacrylate (HMA), glycidyl methacrylate (GMA), 2-butoxyethyl methacrylate (BEMA) and isobornyl methacrylate (IBMA), while ethylene dimethacrylate was the crosslinker. The monoliths were synthesized in 30 cm length capillaries possessing inner diameters (i.d.) of 0.25 mm. The prepared monolithic columns were applied for separation of 3 series of homologous alkanes, alcohols and alkylbenzenes, as well as some isomeric mixtures. Van Deemter plots were used to optimize and compare the columns performance. The smaller methacrylates (MMA and GMA) exhibited higher porosity and permeability with low column backpressure values and poorer efficiency than the larger methacrylate monomers (HMA and BEMA). The columns prepared from IBMA monomer showed the highest pressure and the least separation efficiency. The fastest full separation of alkanes was achieved on HMA-*co*-EDMA column in about 3.0 min with resolution better than 2.73, while the fastest full separation of alcohols and alkylbenzenes was carried out using BEMA-*co*-EDMA column in less than 0.8 and 1.75 min with chromatographic resolution better than 1.27 and 1.85, respectively. Again, BEMA-*co*-EDMA column gave the best performance with the fastest and complete separation of all studied isomeric mixtures. For all tested series of solutes, the better separation efficiency was reached with tridecane, which gave 25,200 plates/m on the HMA-*co*-EDMA column. Another application was carried out using HMA-*co*-EDMA column for determination of myrcene and limonene, two monoterpenic isomers, in some fruit peels. Under the optimum GC conditions, a rapid separation of myrcene and limonene was achieved in less than 1.0 min with chromatographic resolution of 2.56. The highest contents of myrcene (0.131 mg/g) and limonene (1.225 mg/g) were measured in the hexane extracts of grapefruit and Egyptian orange, respectively. Finally, a comparison between the prepared columns and a commercial capillary column was performed. Based on the measured run time and HETP values, HMA-*co*-EDMA and BEMA-*co*-EDMA monolithic columns exhibited faster separation and higher efficiency for n-alkanes and alkylbenzenes than the TR-5 open tubular column, although they are 100 times shorter.

1. Introduction

The first investigations about monolithic materials and their applications in various fields were reported about five decades ago. Kubin et al. described in 1967 the first preparation of a polymethacrylate-based monolithic column and its application in HPLC [1], while Svec et al. proposed in 1996 the denomination of "monolithic stationary phases" which is now widely accepted [2]. These highly porous materials can be easily prepared *in-situ* inside the column and showed several advantages over conventional particulate stationary phases [3,4]. The development of new and efficient monolithic columns proved to be a prolific and innova-

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tive field which has attracted many fruitful research activities [4,5]. Thousands papers reported various methods for preparation of monolithic stationary phases and improvement of their efficiency in several chromatographic modes [6,7]. Compared to conventional packed columns, monolithic capillaries are a miniaturized separation system with many other advantages such as easy preparation, high separation efficiency, short analysis time and low solvent consumption [8,9]. Beside their main application as stationary phase in many chromatographic techniques, monolithic materials proved to be versatile and efficient adsorbents for extraction and separation of specific analytes. Due to the highly porous structure of monolithic materials which confers them a high specific surface area, their use as specific adsorbents instead of packed cartridges is increasing [9,10].

Three kinds of monolithic materials were developed: inorganic based on silica, organic consisting of a rigid porous polymer and organic-inorganic hybrid monoliths [11,12]. While inorganic silica-based materials are generally prepared by *sol-gel* method, organic based porous polymers are synthesized through a single-step polymerization of a mixture including suitable monomers, cross-linkers, porogenic solvents and an activator. All monolithic materials have a single-piece structure with a dense porous network. The density and size of these interconnected channels can be modulated to control the permeability and efficiency of the prepared monolithic stationary phase [13,14].

A large variety of monolithic columns were prepared, characterized and applied for separation of a wide range of analytes, from small solutes to large biomolecules. The success of this kind of new structures can be explained by their easy and inexpensive preparation, good permeability, low solvent consumption and high efficiency [12]. Many published papers and reviews reported successful applications of different kinds of monolithic columns for separation of various solutes such as pharmaceuticals, pollutants, food, chiral compounds and polymers [8,15–17]. In the last two decades polymer-based monoliths became more popular and many kinds were developed and successfully used for fast separation of various samples [16–18]. Most research efforts focused on preparation of new monolithic organic polymers and improvement of their chromatographic properties because they are easier to synthesize and to modify than silica-based monoliths [19,20]. In addition, these monolithic polymers could be widely used in different chromatographic modes such as reversed-phase liquid chromatography (RPLC), ion exchange chromatography (IEC), hydrophilic interaction chromatography (HILIC) and size exclusion chromatography (SEC) [17,21]. Monoliths based on organic polymers showed their ability to separate efficiently various macromolecules either natural such as peptides, proteins and nucleic acids or synthetic [20–22].

Svec and Frechet described in 1995 the preparation of a monolithic continuous bed based on macroporous copolymer glycidyl methacrylate-ethylene dimethacrylate and its use for HPLC separation of proteins [23]. Compared to other monolithic materials, methacrylate based columns have several advantages such as their simpler preparation, a wider range of pH stability, easy functionalization, as well as the availability of various monomers [24–26]. The main feature of monolithic columns is the single continuous piece of stationary phase which fills all the column volume. A uniform network of interconnected channels allows the flow of mobile phase through this porous material. The macropores, with a size in the μm range, provide this flow path and contribute to increase the column porosity and permeability while reducing the solute retention [9,18,27]. The fine porous structure of a monolith is due to mesopores which have a diameter in the nm range and afford a high active surface area for better separation efficiency. This characteristic structure is a key factor in the success of monolithic columns in terms of low back pressure, fast mass transfer of solutes and high efficiency [7,28,29]. On the other hand, if the monolith contains micropores which correspond to diameters less than 2 nm, the small solutes will tend to stagnate more; this will result in an increase of peak dispersion and a loss of efficiency. Therefore, preparation of highly efficient monolithic stationary phases requires a tight control of their porosity, in terms of pore size and distribution [12,30]. If the prepared monolith suffers from a lack of mesopores, its low specific area will induce a low retention for smaller solutes. Several procedures were applied to correct this defect including use of more suitable monomers and cross-linkers, incorporation of nanoparticles and hyper-crosslinking of the prepared monolith [12,31,32].

The first application of monolithic columns was carried out by Crawley in gas chromatography in 1969, but their use in GC remained very limited compared to their great success in HPLC [33,34]. Thus, most reports published later described their use in high performance liquid chromatography, using mainly fused silica capillary columns. In fact, the performance of monolithic stationary phases tested in GC was notably lower than that of commercially available open tubular capillary columns. While several detailed reviews described a great variety of monolithic columns successfully used in different HPLC modes, the first review about applications of monoliths in GC was published only in 2008 by Svec and Kurganov [4]. It was followed by a second review authored by Kurganov in 2008 [9].

Since polymethacrylate-based monoliths have a relatively low thermal stability, only few investigations were carried out on their applications in gas chromatography. However, some recent papers showed that methacrylate-based monolithic capillary columns can be successfully used in GC for fast separation of gases and light hydrocarbons, using a conventional non-modified chromatograph [34–36]. As for liquid chromatography, application of capillary monolithic columns in gas chromatography has several advantages: ease of preparation, fast and efficient separation, reduced carrier gas consumption [4].

The preparation of organic-based monolith columns is easily achieved in few steps by thermal or photo-induced polymerization inside the capillary of a mixture composed of suitable monomers, crosslinker, porogenic solvents and initiator. Among the available monomers, acrylates, methacrylates, styrenes and acrylamide were widely used; whereas divinylbenzene and ethylene dimethacrylate are common cross-linkers [8,18,20]. Several studies showed that the amount and properties of crosslinker greatly influences the porosity, permeability and chromatographic efficiency of the prepared column [12,18].

Polydivinylbenzene has been widely used as monolithic stationary phase in GC since 2000, because of its remarkable thermal stability until 380 °C. Since the permeability of monolithic columns is much lower than that of conventional open tubular capillaries, some research groups used a modified GC instrument working at carrier gas higher pressure [12,18]. The present work describes fabrication and characterization of five methacrylate-based monolithic materials including MMA-*co*-EDMA, HMA-*co*-EDMA, GMA-*co*-EDMA, BEMA-*co*-EDMA and IBMA-*co*-EDMA, then their use for some applications in gas chromatography.

2. Experimental

2.1. Chemicals and columns

Polyimide coated fused silica tubing (250 μm i.d.) was purchased from Restek (Bellefonte, USA). The chemicals used for preparation of monolithic columns in this work were acquired from Aldrich (Steinheim, Germany) as follows: 3-(trimethoxysilyl) propyl methacrylate (TMSM) 98%, ethylene dimethacrylate (EDMA)

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