



Behavior of short silica monolithic columns in high pressure gas chromatography



Adrien Maniquet^b, Nicolas Bruyer^a, Guy Raffin^a, Franck Baco-Antonial^b,
Claire Demesmay^a, Vincent Dugas^a, Jérôme Randon^{a,*}

^a Univ Lyon, CNRS, Université Claude Bernard Lyon 1, Ens de Lyon, Institut des Sciences Analytiques, UMR 5280, 5 rue de la Doua, F-69100 Villeurbanne, France

^b IFP Énergies nouvelles – établissement de Lyon, Expérimentation Procédés, Rond-point de l'échangeur de Solaize, BP3, 69360 Solaize, France

ARTICLE INFO

Article history:

Received 1 June 2016

Received in revised form 4 July 2016

Accepted 5 July 2016

Available online 6 July 2016

Keywords:

Silica monolith

Gas chromatography

Hydrodynamic flow

Light hydrocarbons

Holdup time marker

ABSTRACT

In order to analyze light hydrocarbons mixtures with silica monolithic columns, a conventional gas chromatograph was modified to work with carrier gas pressure as high as 60 bar. To understand hydrodynamic flow and retention with short columns (less than 30 cm), special attention was required due to the temperature difference between the oven area and the FID detector which contain a significant length of the column. Efficiency and selectivity using various carrier gases (helium, nitrogen and carbon dioxide) at different inlet pressure for different oven temperature were studied. Carrier gas nature was a very significant parameter: on one side, linked to adsorption mechanism for gases like nitrogen and carbon dioxide onto the stationary phase modifying retention and selectivity, on the other side in relation to the minimum theoretical plate height which was as low as 15 μm (66 000 plate m^{-1}) using carbon dioxide as carrier gas. The chromatographic system was then used to separate methane, ethane, ethylene, acetylene, propane, cyclopropane, and butane in less than 30 s.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Even if monolithic capillary columns have been widely used for nano-liquid chromatography or capillary electrochromatography, several studies have been carried out in gas chromatography and some reviews have been recently published on this topic [1,2]. Such monolithic columns have been used mainly for separation of light hydrocarbon mixtures which was previously performed using porous layer open tubular (PLOT) columns. The monolithic columns can indeed overcome some issues related to PLOT columns such as the low efficiency per column length of PLOT columns (which is rarely above 5000 plate m^{-1}), the low sample capacity of PLOT column for industrial applications, and the limited number of commercially available materials used as PLOT columns.

The first organic monolithic columns were used in GC in the 1970s as an alternative to packed columns [3], but after the commercial release of open tubular capillary columns during the same decade their interest dramatically decreased. Nowadays, organic monoliths can be prepared based on several polymers having dif-

ferent polarities: polyurethane foams, polydivinylbenzene (PDVB) or polymethacrylate [4]. Even if very good mechanical, chemical and thermal stability (up to 300 °C [5]) have been obtained with one specific PDVB monolithic columns, the main drawback of organic monoliths is still related to their poor thermal stability (usually limited to 200 °C) and their very low permeability [6].

Based on a thermally resistant inorganic material, the first silica monolithic columns were introduced by Tanaka's group in the middle of the 90's for liquid phase separations [2]. These columns showed very high porosity (90–95%) compared to packed columns, so their permeability were somewhere between open tubular capillary columns and packed columns with comparable particle sizes [7]. Up to now, Kurganov's group has published several papers based on Tanaka's columns and Azzouz et al. have reported the preparation of silica monolith for GC. In these articles, the analyzed sample is mainly based on methane, ethane, propane and butane mixtures and various carrier gases have been considered in relation to the adsorption process on the silica surface. Despite these few studies, there is today a lack of publication concerning silica based monolithic columns in order to use them for the separation of more complex mixtures.

Considering packed columns, when high efficiency per unit of column length was required (low HETP), the particle diameter was

* Corresponding author.

E-mail address: randon@univ-lyon1.fr (J. Randon).

reduced and according to Darcy's law, the column resistance to the mobile phase transfer which is inversely proportional to the square value of the particle diameter increased dramatically [8]. With silica monolithic columns in LC, the same efficiency per unit of column length (same low HEPT) was obtained with higher permeability compared to packed columns. However, monolith permeability cannot be in the same order of magnitude as the one observed for open tubular (OT) columns, so separations have to be performed using inlet pressure which is significantly higher than the conventional operating conditions used for gas chromatographs with OT columns. To overcome this issue, column length has to be reduced, and instrument modifications were also required to allow higher inlet pressure of the carrier gas [9]. Moreover, with such miniaturized columns, the control of column temperature all along the column (inside the injector, inside the oven, inside the detector) can be critical and is discussed in this paper.

To study the chromatographic characteristics of short monolithic columns for gas separation, GC instrument has been modified and optimized to work with a carrier gas pressure as high as 60 bar. Then, this device has been used to study the hydrodynamic properties of short silica monolithic columns as well as the chromatographic properties of silica material facing different carrier gases (helium, nitrogen and carbon dioxide). Unconventional results have been observed and have been related to the geometry of the different parts of the instrument (split, oven, FID) which can be critical for an optimal use of short monolithic column.

2. Materials and methods

2.1. Chemical and reagents

Fused-silica capillaries (75 μm I.D., 375 μm O.D.) were obtained from Cluzeau (France). Ethanol, TMOS (Tetramethylorthosilicate), PEG (Polyethylene glycol 10 000), urea, pentane, heptane, nonane, decane, undecane, dodecane and naphthalene were purchased from Sigma-Aldrich (France), acetic acid was from Prolabo (France), and sodium hydroxide from Laurylab (France). Nitrogen and carbon dioxide were from Air Liquide (France). Helium and gas sample mixtures were from Messer (France) mixture A: methane (998 ppm), ethane (970 ppm), ethylene (994 ppm), acetylene (1019 ppm), propane (987 ppm), cyclopropane (1016 ppm), *n*-butane (989 ppm), 1-butene (989 ppm), carbon monoxide (996 ppm), carbon dioxide (1008 ppm), *n*-pentane (100 ppm), *n*-hexane (100 ppm), hydrogen (98.6 ppm) in nitrogen; mixture B: hydrogen (15 mol%), carbon monoxide (15 mol%), carbon dioxide (15 mol%), methane (15 mol%) and ethane (15 mol%) in nitrogen.

2.2. Preparation of the silica capillary monolithic columns

Columns have been prepared by sol-gel process according to previous report [10].

The inner wall of the fused-silica capillary was rinsed with 1 M KOH (1 h, 2 bar, 25 °C) to eliminate any impurities present in the capillary. Then the ends were sealed with silicone rubber and the capillary was kept at 60 °C for 1 h. After that, the capillary was rinsed with water and dried at 150 °C under nitrogen stream. Monolithic silica capillary columns were prepared from a mixture of tetramethoxysilane/methyltrimethoxysilane (85:15; v/v). A total of 18 mL of this mixture was added to 40 mL acetic acid (0.01 mol L⁻¹) containing 1.9 g PEG and 4.05 g urea at 0 °C and stirred for 30 min. Then the temperature was increased up to 40 °C and the mixture was stirred for 10 min before it was charged into pretreated fused-silica capillaries. After that, the capillary was stored at 40 °C overnight in order to start hydrolysis and condensation of reactants. Then the temperature was raised slowly with an increment of 0.1 °C min⁻¹

and allowed to react at 120 °C for 4 h to form mesopores with the ammonia generated by the hydrolysis of urea. The monolithic silica columns were cooled and washed with methanol. Column permeability was determined using nano-LC 400 from Eksigent (France) with UV detector (model ActiPix D100) using naphthalene as hold-up time marker and in GC under CO₂ at 120 °C. A scanning electron microscope (SEM) Neoscope JCM-5000 from JEOL (France) was used to measure the internal diameter of the silica capillaries and to estimate the pore size diameter of the monoliths.

2.3. Silica capillary monolithic columns

Several columns were made from different batches (Table 1). Columns name are represented as follow: M[batch number-column number]. Columns were compared in terms of internal diameter, pore diameter, length, permeability, relative retention time of C₂ over C₁ (at 25 °C under 60 bar of helium, from mixture A and B) and H_{min} (minimum plate height). Results were very similar comparing different parts of the same column and inter batch columns. This set of homogenous columns from different batches has been used in order to be sure that the reported results were representative of the silica column behavior.

2.4. Gas chromatography

Agilent Technologies 7820 gas chromatograph (GC) with a split/splitless injector and a flame ionization detector (FID) was lent by SRA Instruments (France), and gas injection valve and high pressure regulators have been added to the GC: Fig. 1. Valves, lines, ferrules and nuts were in stainless steel 316 L from Swagelok (France). Pressure regulators were bought from Messer (France) and Air Liquide (France). Pressures gauges were obtained from Keller AG (Switzerland). The injection valve was from VICI Valco (Switzerland): the model used has an internal sample loop of 0.06 μL and a pressure limit of 1000 psi (69 bar). Actuation was made with helium. Split injection was designed using open capillary tubing with controlled flow resistance based on internal diameter and length of the capillary.

3. Results and discussion

3.1. Validation of the chromatographic instrument for high pressure gas chromatography

In order to validate the chromatographic system, a Wall Coated Open Tubular column (WCOT 10 m x 50 μm x 0.05 μm , DB-5MS) has been used. The column was initially connected to the conventional split/splitless injector using helium as carrier gas to determine the intrinsic efficiency value of the column (N and HETP) according to Gritti and Guiochon [11] with a sample mixture of C₉-C₁₂ in solution in heptane. At the optimum velocity of the column, the HEPT value was 53 \pm 6 μm which is in agreement with the expected value of 50 μm (i.e. the internal diameter of the column). The column was then directly connected to the VICI valve and the corresponding Van Deemter curve has been plotted (carrier gas pressure from 5 to 30 bar) using hexane in mixture A as test solute. Even with a detector time constant as low as 0.004 min, the observed H_{min} value without split was 400 μm , which was clearly higher than the intrinsic H value of the WCOT column. Setting up the split, using an open capillary (L = 1 m, 50 μm I.D.) to obtain a split ratio close to 50, lead to the expected H_{min} value of 53 \pm 5 μm with an optimum gas velocity of 32 cm s⁻¹. Relative Standard Deviation (RSD) of retention times, areas and efficiency have been measured with ethane in mixture B (n = 10) and the low observed values, respectively <0.3%, <1.5% and <1.0%, confirmed the correct setup of the instrument for

Download English Version:

<https://daneshyari.com/en/article/1199992>

Download Persian Version:

<https://daneshyari.com/article/1199992>

[Daneshyari.com](https://daneshyari.com)