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# The properties of capillary columns with silica organic–inorganic MCM-41 type porous layer stationary phase

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ABSTRACT

In this work, we report the method of capillary columns preparation for gas–solid chromatography with a porous layer of MCM-41 type silica sorbent. The porous layer was synthesized by the sol–gel method inside the column. Scanning electron microscopy (SEM) measurements were performed to obtain information about the porous layer. The loading capacity of the prepared columns was investigated. An adsorbent selectivity was changed by using different relative contents of organic–inorganic precursors: vinyltriethoxysilane (VTEOS) and tetraethoxysilane (TEOS). Properties of the columns prepared are discussed. Separating examples of $C_1$–$C_4$ hydrocarbons and some other compounds are presented.



## 1. Introduction

Capillary columns with a sorbent porous layer (porous layer open tubular (PLOT) columns) are widely employed in the cases where separations cannot be successfully performed on the columns with a stationary liquid phase layer. Although PLOT columns are capable of separating different classes of chemical compounds, their main application fields are related to low-boiling compounds, in particular, $C_1$–$C_5$ hydrocarbons [1], sulfur-containing gases [2], permanent and noble gases, volatile oxides [3,4] and organic solvents [5]. Commercial columns are prepared mostly with the stationary phases based on alumina with deactivation agents, divinylbenzene based porous copolymers, carbon molecular sieves, zeolite 5A/13X, and porous silica [6].

A porous layer in the columns can be formed by different ways. There are examples of the particles synthesized outside the column and then deposited by static [7] or dynamic [8] methods. A porous layer can be created directly in the capillary column using sol–gel synthesis [9,10] or radical polymerization of organic monomers for porous divinylbenzene based copolymers [11,12].

The above listed sorbents, which are employed in capillary gas chromatography, are represented by unstructured materials whose pore space is a disordered labyrinth of narrowings and widenings. Such structure of a sorbent leads to uncertainty of the integrated residence time of molecules in the pore labyrinth, thus restricting the sorbent surface area and increasing the time of establishing the equilibrium between stationary and mobile phases. Irregular porosity produces broadening and asymmetry of a chromatographic peak and hence decreases the separation efficiency. Another limitation of the sorbents with disordered pores is related to a low loading capacity of the porous layer capillary columns.

The loading capacity of porous layer columns is known to be approximately two orders of magnitude lower than the value typical of columns with a stationary liquid phase film [6]. This phenomenon is caused by the low surface area of sorbent in the column, which limits the number of sorption sites per unit surface area of the porous layer.

A possible way to increase specific surface area of sorbent in a column without deterioration of its separation performance is the use of an MCM-41 type material having the ordered mesopores [13]. It was shown that MCM-41 silicas can be used not only as catalyst supports [14,15] and functional coatings [16], but also as stationary phases for size-exclusion [17], normal-phase [18,19] and chiral HPLC [20]. A substantial improvement of chromatographic quality of a stationary phase in HPLC with the use of a sorbent containing MCM-41 spheres was reported in [21].

As for gas chromatography, the application of MCM-41 material in packed columns was reported in [22–24]. In all cases, the sorbent was represented by a powder synthesized outside the column or by an MCM-41 layer synthesized on the grain surface of a prefabricated non-porous sorbent.

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**Table 1**
Molar ratio of precursors for sol synthesis in different columns.

| Column | Molar ratio of precursors | | | | | |
|---|---|---|---|---|---|---|
| | V00 | V10 | V20 | V30 | V50 | V70 |
| TEOS | 100 | 90 | 80 | 70 | 50 | 30 |
| VTEOS | 0 | 10 | 20 | 30 | 50 | 70 |

An attempt to apply this approach to capillary gas chromatography, i.e. to create a porous layer capillary column where a sorbent prepared outside the column is located on its wall as a mesoporous powder, did not provide a satisfactory quality of the columns [25].

The present work is devoted to capillary columns for gas chromatography with a porous layer of MCM-41 type sorbent based on silica. The sorbent layer was synthesized by the sol–gel method inside the column. Some improvements of an ordered porous structure compared to a disordered silica gel as a commercial porous layer column were shown. Selectivity of the porous layer in the sol–gel reaction was changed using an organic–inorganic precursor.

## 2. Experimental

### 2.1. Reagents

The study was carried out with tetraethoxysilane (99.0%) (TEOS) and vinyltriethoxysilane (98.0%) (VTEOS) (Sigma–Aldrich Chemie GmbH, Steinheim, Germany); cetyltrimethylammonium bromide (98.0%) (CTAB) (Acros, Geel, Belgium); hydrochloric acid (36.5%), ethanol (96%) (ZAO NPO Ekros, St. Petersburg); and deionized water (specific conductance of 0.1 μS/cm).

### 2.2. Sol synthesis

To obtain the initial sol, a solution of precursor, ethanol, $H_2O$, HCl and CTAB taken in a molar ratio of 1.0:12.0:5.4:0.004:0.16 was prepared. Either TEOS or a mixture of TEOS and VTEOS was used as a precursor to obtain films with specified features. Table 1 lists different combinations of precursors for preparation of a porous layer in the columns. The porous layer of V00 sorbent consists only of silica. Other columns of Table 1 show the composition of precursors used for the synthesis of organic–inorganic porous layer with different relative contents of organic component.

The reaction mixture containing a precursor dissolved in ethanol was supplemented with the CTAB surfactant as a pore forming agent and with a hydrochloric acid solution as a catalyst of the condensation reaction. The solution was stirred for an hour to obtain a transparent sol. Thus obtained sol was used to prepare the columns.

### 2.3. Column preparation

A sorbent was deposited on the inner surface of capillaries by the static high-pressure method first described in [26]. The prepared sol was filtered and poured into a fused silica capillary (Fiberguide Industries Inc., Stirling, NJ, USA) of 0.32 mm diameter and 10–30 m length. The column was filled by sol as described in [27]. Depending on the column length, a gas pressure required for filling the column was 0.5–2.0 bar. After filling, one of capillary ends was sealed.

The open end of the capillary filled with the sol was then introduced in an air thermostat at a temperature of 200 °C. The column was brought into the oven at a rate of 300 mm/min. The solvent evaporated from the open end and the sorbent layer remained on its inner surface. To provide a more intense evaporation, a segment of the cold column was preheated to 250 °C at the thermostat inlet using a 5 cm additional oven [28]. When the column completely entered the thermostat, the sealed end of the capillary was cut, the column was connected to a source of inert gas (argon) and blown off with the inert gas for an hour at 200 °C.

The thermostat temperature was then raised to 220 °C and the column was blown off with argon for an hour. After that the column temperature was increased to 320 °C, and then the column was kept at the final temperature for 4 h to remove the surfactant from the resulting porous layer. These deposition conditions were employed to prepare all the tested columns. In the study, each column was prepared in duplicate. The film thickness was 8–12 (μ)m for all the prepared columns.

### 2.4. Column testing

The test mixtures were separated on an Agilent 7890 chromatograph with a flame-ionization detector. The temperature in the detector and injector was 250 °C; helium was used as a carrier gas to investigate the height equivalent to a theoretical plate (HETP) dependence on a flow rate. In all other cases, dinitrogen was used as a carrier gas. Gas mixtures were prepared for tests by mixing the individual $C_1$–$C_4$ hydrocarbons. The dependences of HETP on the linear rate of carrier gas flow were obtained with respect to n-butane using the columns of 20 m length. The temperature was chosen so that capacity factor for n-butane was higher than 5 ($k > 5$). At each value of the linear rate, three parallel values of efficiency were obtained for the tested substance.

The Kovatz retention indices for the tested columns were determined at a temperature of 80 °C with dinitrogen as a carrier gas.

A procedure for measuring the loading capacities of columns was described in [29]. A 20% loss in efficiency served as the overload criterion. The loading capacities were measured using cis-2-butene. Three parallel determinations were made for each point.

### 2.5. Study of the properties of the synthesized materials

Thickness of the synthesized sorbent film in the columns was estimated using a JSM-6460LV (JEOL, Japan) scanning electron microscope.

Infrared spectra of the sorbent films were recorded on a FTIR 8300 (Shimadzu, Japan) spectrometer.

For IR spectroscopy study, films of organic–inorganic sorbents were synthesized on the surface of aluminum wafers under the conditions close to those used for preparation of the columns. A drop of the synthesized sol was placed on an aluminum wafer and heated to 100 °C to remove the solvent. The wafer was then heated to 320 °C under argon flow and kept at this temperature during 4 h.

## 3. Results and discussion

The V00 column with a porous layer containing TEOS was prepared by the following procedure. The sol obtained by hydrolysis of a precursor was brought into the column and the solvent was removed; as a result, a solid porous layer remained on the column wall. In our case, the formation of a sorbent film is based on fast heating of the sol and differs from conventional procedures for obtaining the MCM-41 type sorbent films [30]. As shown in [31], thus synthesized porous layer has a specific surface area of ca. 1200 $m^2/g$ and the average pore diameter of 3.5 nm. The width of pore size distribution is ca. 1 nm. The adsorption isotherm of the synthesized material is identical to that of MCM-41 type materials [32]. Let us consider other properties of the column.