Fabrication of methacrylate polymer-based on the silica capillary modified with dimethylamine

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Abstract. Capillary silica is reacted with the monomer through the externally polymerization process so that a capillary silica polymer will be formed. The formed silica polymer will be modified with dimethylamine as an anion exchange group. Modified silica polymers, their morphological form are characterized by SEM and to see the series of functional groups in polymerized silica polymers will be characterized using FTIR. This research begins with the activation of capillary silica to be used, namely capillary silica with an inner diameter of 0.32 mm. After obtaining the optimum conditions of capillary silica to be used, silica will be reacted with several monomers such as glycidyl methacrylate (GMA), azobisisobutyronitrile (AIBN) as an initiator, ethylene dimethacrylate (EDMA) as a crosslinker and porogen 1,4 butanadiol, 1-propanol, and water, by comparison of certain compositions to create a capillary silica polymer. Capillary silica polymers that have been externally polymerized will be modified with dimethylamine (DMA) as an anion exchange group and will be applied as a stationary phase for nitrite and nitrate anion analysis.

1. Introduction
Monolith column is a column that has been modified in such a way from the capillary column as a container to create or synthesize new columns that will be used as a media for separating or analyzing anions or cations from various analytes using ion chromatography. The most important thing in the ion chromatography system is the column separator and detector. The monolith column has high separation efficiency at low pressure work, easily regulates permeability and surface loads and has a higher phase ratio than open tubular columns [1]. Monolith columns are faster and more efficient for separations at relatively lower pressures because monoliths have large porosity, so they have a large hydrodynamic force that can increase the rate of separation compared to packing columns [2].

Polymethacrylate monoliths have been introduced since the 1990s as columns for chromatography. Hjerten in 1989 for the first time introduced a monolith column as a new type of column on chromatography. Since then, the monolith column has become a type of column widely used in research as a stationary phase in liquid chromatography. Monolith technique is a way to enter stationary phase into a column by making several types of monomer, cross linker and parogen solutions and then compounds that have group anion or cation exchange function. Several types of monomers that have been used glycidyl methacrylate (GMA), GMA which has a high porosity which was originally developed for separation with capillary columns [3].
The monolith column has several advantages including; having good permeability, fast transfer of time, very stable, and very easily modified and has a better retention time and optimal number of cycles [4]. The monolith column has strong resistance to high flow rates while maintaining excellent peak efficiency. The monolith column is more permeable and can be carried out under low pressure conditions, due to its large pores, so that a greater hydrodynamic flow can be used to increase the speed of separation. The monolith column is classified into inorganic and organic polymers based on its constituent materials. The inorganic polymer monolith material in the column consists of silica compounds [5]. While organic monoliths can be grouped into three groups: styrene, methacrylate, and acrylamide. The organic monolith column widely used as a stationary phase in the separation of organic compounds has proven to be a good stationary phase with chemical stability over a wide pH range.

The porous structure of the monolith column can simultaneously reduce the diffusion path length and flow resistance compared to the packing column. The absence of intra particles in the monolith column causes the mobile phase to be forced to flow through large pores in the monolith column. As a result mass transportation has a positive effect on separation performance [6]. Polymer-based methacrylate monolith columns have advantages when compared to other types of polymers, namely a simple preparation process, diverse selectivity, easy functionality, and very stable even under extreme pH conditions (pH 2 - 12) [7], and has good mechanical stability and high permeability [8]. The addition of methacrylate monomers in the polymerization mixture can increase the surface area of the monolith so that the molecular separation performance can be improved [6].

In this research, polymers has been made on capillary silica using several monomers such as glycidyl methacrylate (GMA), azobisisobutyronitrile (AIBN) as an initiator, ethylene dimethacrylate (EDMA) as a crosslinker and porogen 1,4 butanediol, 1-propanol, and water. After the polymer is formed, it is continued with modification using dimethylamine (DMA) and finally it is used for the determination of nitrite and nitrate. The characterization of the silica capillary polymer was carried out using SEM and FTIR.

2. Experimental

2.1. Apparatus
Determination of wave number using Fourier Transform Infra Red (FTIR) Perkin Elmer Universal ATR Sampling Accessory 735 B, surface of polymers was determined using a Scanning Electron Microscopy (SEM) S-4800, determination of retention time for nitrine and nitrat anions by Liquid Chromaography, weighing chemicals to make reagents using analytical balance, glassware and reagent bottle.

2.2. Chemicals
All of chemicals are obtained from Merck, unless otherwise noted. Glycidyl methacrylate (GMA), 1,4-butanediol, dimethylamine (DMA), 3-propyl methacrylate, ethylene dimethacrylate (EDMA), water, decanol, azobisisobutyronitrile (AIBN), NaCl, KCl, NH4Cl, NaNO2, NaNO3, HCl, NaOH, HCl, aseton and N2.
2.3. Research Procedure

2.3.1. Manufacture of Capillary Silica Polymers. First the capillary silica was washed with NaOH then with HCl with a concentration of 1 M and a flow rate of 4 µL / min for 30 minutes for each. After cleaning, the keeper's silica was filled with γ-MAPS and both ends of the silica were clogged with PTFE. A 15 mL γ-MAPS solution was prepared by dissolving it in 0.35 mL acetone. Furthermore, the capillary silica is immersed in a waterbath at 60°C for 24 hours, then rinsed with acetone and N₂ gas.

0.002 g AIBN initiator reacted with 0.22 mL GMA (monomer); 0.25 mL EDMA (crosslinker); 0.25 mL 1,4-butandiol; 0.4 mL of 1-propanol; 0.2 mL of water (porogen) to make polymer precursors. The solution was homogenized for 5 minutes by ultrafication. Then the polymer solution was filled into the capillary column and covered both ends with PTFE. Capillary silica polymer is fed into a waterbath for 24 hours at 60°C. The polymer is removed from the water bath rinsed using 0.5 mL methanol to remove the unreacted solution.

2.3.2. Modification of Monolith Silica with DMA. Capillary silica polymers are modified with DMA, the process is 0.5 mL DMA dissolved in 0.5 mL ethanol (1: 1 v / v) then put into the polymer at a rate of 4 µL / min. Furthermore, capillary silica was put into an oven at 80 °C for 4 hours to maximize the DMA bond in the polymer. After that the column was rinsed with 0.5 mL methanol with a flow rate of 4 µL / min.

2.3.3. Characterization with SEM and FTIR. Capillary silica polymers cut with an average length of 2-3 mm are characterized using SEM and FTIR. Before being scanned with SEM, the monolith column was coated or stained with metal or a mixture of gold and palladium using Sputter 8. Some polymers were tested using FTIR to see whether the formation of the polymer was good.

2.3.4. Application Column Monolith to Determine Nitrite and Nitrate Anions. The monolith column is mounted on the system and the mobile phase NaCl 50 mM in the string is flowed into the column with the help of a pump with a flow rate of 3 µL / min. Regulated wavelength of 210 nm on a UV Visible detector. Anion solution is injected for each anion one by one and the peak retention time of each anion is obtained.

3. Results and Discussion

3.1. Making Monolith Capillary Column
Capillary silica polymers in the form of monolith columns are made by in situ polymerization reaction which consists of several steps. The first treatment was given to the capillary column using γ-MAPS which reacts with silica on the capillary walls. After that the polymer matrix is formed using AIBN, GMA, EDMA and porogen mixture consisting of 1-propanol, 1.4 butanadiol and water. After capillary silica monoliths are formed, the final step is to modify the monolith column using DMA. The function of DMA is to provide anion exchange groups so that capillary silica monoliths can be used as anion exchange columns.

3.2. Characterization with SEM
The shape and shaft of the produced silica polymer largely determine the polymer can be modified and can be used as an adsorbent or separator of a mixture. This is an important parameter so that it can affect the ability and efficiency of separation. One method that can be used to see the shape of this silica polymer is by scanning the surface using SEM. The surface shape of the silica polymer that has been modified with DMA can be seen in Figure 2.

The size of particles formed affects the effectiveness of sample separation, if the particle size is small then the particle will provide a large surface area. The results can be seen on a chromatogram, where a small particle size will give a large number of plate numbers so that the resulting resolution will also be
as large. Pore size can also have a large impact if the polymer is used as a stationary phase in the size exclusion method where separation is carried out based on the molecular size of the sample. Samples with larger molecular sizes will come out earlier than particles with smaller sizes. Pores that are formed can be resized using porogens. Porogens with large molecular weights will form large pores, and contrarily.

![Image](image1.png)

**Figure 2.** Magnification of 3000 times, monolithic silica polymers modified with DMA

### 3.3. Characterization with FTIR

Polymer characterization by FTIR is used to see functional groups that change after the polymer is modified with DMA. In Figure 3 we can see that the solid line spectrum is the spectrum for the polymer before it is modified, while the dotted line is the spectrum after being modified with DMA.

There is no noticeable difference between the two spectra, but in the dotted line spectrum there is a peak at the wave number 1700-1800 cm\(^{-1}\) which is the peak of C = O (amide) and the peak at the wave number between 1400-1500 cm\(^{-1}\) which is CN (amide) peak. This shows that there has been a reaction between DMA and C = O (ester) groups of monomers to produce amide compounds with tertiary amides as an anion exchange group.

![Image](image2.png)

**Figure 3.** FTIR spectra of capillary silica polymers. Solid line = before modification and dotted line = after modification with DMA

### 3.4. Application of Diethylamine Modified Monolith Column

Capillary columns that have been polymerized in situ and are characterized subsequently are applied to determine nitrite and nitrate anions. Anion analysis was performed using an ion chromatography system using a mobile phase (NaCl + HCl 0.04 mL) 50 mM and the standard used is a 1 mL nitrite solution and 1 mL nitrate solution with a flow rate of 3μL/min at a wavelength of 210 nm.
The addition of HCl into the mobile phase is expected to be able to maintain the anion exchange group contained in the column. Chromatogram analysis of nitrite ions can be seen that the retention time of nitrite ions is around 9. While the retention time of nitrate ions is about 11. The resulting chromatogram differs between the first and second and third injections. But it is still within the adjacent retention time. This shows the existence of anion exchange groups contained in the column is not strongly bound. So that tends to be separated from the column carried by the mobile phase. Chromatogram for nitrite and nitrate anions can be seen in Figure 4.

![Chromatogram of nitrite (1) and nitrate (2) anions.](image)

**Figure 4.** Chromatogram of nitrite (1) and nitrate (2) anions.

4. Conclusion
Based on the data obtained it can be concluded that the silica capillary polymer which has been modified with DMA can be produced for the determination of nitrite and nitrate anions, but the results obtained cannot separate the two anions simultaneously.

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