CAPILLARY ION CHROMATOGRAPHY WITH CONTACTLESS CONDUCTIVITY DETECTION FOR THE SEPARATION OF INORGANIC CATIONS USING POLYMER MONOLITHIC COLUMN

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ABSTRAK

Since two decades ago, the innovations of many gifted analysts have brought us to a new era phase in chromatography, i.e., monolithic materials, both silica- or polymer-based. These materials have high permeability, no need to frits preparation and fast mass transfer. In this research, polymer monolithic columns were used for separation of inorganic cations by using contactless conductivity detector. Glycidyl methacrylate (GMA) and polyethylene glycol dimethacrylate (PEGDMA) were used as monomer and crosslinker. Methanol and decanol were used as binary porogenic solvents. The monolith columns were prepared by two-step procedures: polymerization and sulfonation of GMA. This polymer monolitic column could separate lithium, sodium and rubidium with the5mMMSA in 50% methanol as eluent.

Keywords: polymer monolithic column, contacless conductivity detector,separation of inorganic cations.

INTRODUCTION

During the last 15-20 years, there has been a trend to alleviate the column size in HPLC in order to take the advantages such as improved mass sensitivity, reduced consumption of packing material, mobile phases and sample amount and easiness of coupling to MS [1]. In some cases for example proteomics, the downsizing of sample made a significant problem. The increasing of demand for the throughput analysis with the high efficiencies encouraged development of high speed LC techniques and tools [2, 3]. The important thing to get a rapid and highly efficient separation is to reduce the column length with a smaller packed particle and also to increase the flow rate. Unfortunately, these conditions increased back pressure. To relieve the backpressure problem and get higher efficient separation, researchers started to develop monolith columns.

Monolithic columns have a great attention because easiness of modifications, improved chromatographic properties, fast mass transfer, easy control of permeability and no need of frits preparation. In 1989, Hjerten*et al.* firstly developed compressed soft polyacrylamide gels called "continuous bed" and used them to separate protein [4]. Another researchers reported rigid macroporous organic polymer monolith and produced the different procedure and vision for the preparation [5]. There are two types of monolithic columns based on their components: organic and inorganic polymers. Silica based monolith belongs to inorganic polymers. Organic polymer monolithic materials can be classified into three general categories: polystyrene, methacrylate and acrylamide [6]. Methacrylate-based polymer becomes the most popular among the other organic polymer monolithic materials because of its advantages such as high stability in a broad pH range, fast and simple preparation, when using glycidyl methacrylate (GMA) as monomer, it is easy to modify because it has epoxy groups [7,8].

Nowadays, the sensitivity of detection techniques becomes one of the important research field on monolithic columns. UV absorption detection is most commonly preferred because of its low cost and wide applications [9]. Besides that, amperometry[10], mass spectrometry [11], chemiluminescence [12] are used for monolithic column detection.

Conductivity detection has been simple and universal detection technique in IC because it can detect many kind of ionized species with good sensitivity. There are two

general types of conductivity detections: the metal electrodes can be directly contacted with liquid (galvanic detection) and separated from liquid with insulating film (contactless detection). Contactless conductivity detection has gained increasing attention in capillary liquid chromatography in recent years [8,13].

Karmarker*et al.* [14] analyzed the effect of different matrix formulation on mechanical properties of bis-glycidyl methacrylate (GMA) and poly(ethylene glycol) dimethacrylate(PEGDMA). Linda's group [15] reported methacrylate-based diol monolithic columns for separation of polar and non-polar compounds in capillary LC. Preparation and modification of poly GMA/PEGDMA with diethylamine to separate inorganic anions was studied by Rahmah and co-workers [16]. In this work, GMA as a monomer, PEGDMA as a crosslinker and this polymer monolith reacted with Na_2SO_3 to introduce sulfonate groups in order to get cation-exchange monolithic columns inside 0.32 mm i.d. fused silica column. Strong cation-exchange monolith containing sulfonic groups were successfully synthesized from poly(GMA/PEGDMA) with methanol and decanol as porogenic solvents by *insitu* copolymerization. The synthesized monoliths were used to separate cations such as $Li^{+,}$ Na^+, Rb^+. The effect of temperature condition, reaction time condition, and addition of organic solvent were studied.

EXPERIMENTAL

Apparatus

All experiments were assembled with a capillary LC system constructed by an L.TEX-8301 Micro Feeder (L. TEX Corporation, Tokyo, Japan) equipped with an MS-GAN 050 gas-tight syringe (0.5 mL; Ito, Fuji, Japan) as a pump, a model 7520 injector with an injection volume of 0.2 µL (Rheodyne, Cotati, CA, USA) as an injector, a 0.32 mm i.d.×100 mm microcolumn, and a Tracedec contactless conductivity detector (Istech, Strasshof, Austria). The flow-rate of the pump was kept at 3 µL/min. The data were acquired by a Chromatopac C-R7Ae plus data processor (Shimadzu, Kyoto, Japan).

Reagents and materials

3-(Trimethoxysilyl)propyl methacrylate (γ-MAPS), PEGDMA and 1-decanol were purchased from Tokyo Chemical Industry (Tokyo, Japan). GMA (97% pure), 2,2'-azobis(isobutyronitrile) (AIBN), methanol were obtained from Wako Pure Chemical Industries (Osaka, Japan). Purified water was produced in the laboratory by using a Millipore Simplicity UV system (Darmstadt, Germany). All the solutions in this study were prepared using the purified water.

Cation-exchange monolithic column preparation

The capillary column was washed with 1M NaOH, 1M HCl andpurified water for 2 h, respectively. The inner wall of capillary was pretreated withγ-MAPS to make sure the anchoring the matrix of monolithic polymer. γ-MAPS in methanol were injected into the capillary column, and both ends of the capillary were sealed with teflon tube. The pretreatment was left to proceed in water bath at 60 ^oC for 24 h. Subsequently, the capillary was washed with acetone to flush out the residual reagent and dried with N_2 for 30 min.

The monolithic columns were prepared by *in situ* polymerization consisting of the monomer GMA, PEGDMA, the porogens of methanol and decanol. After sonicated for 5 min, AIBN were added to the monomer solutions (1% w/w corresponding to the total monomers), and purged with $N_2$for 3 min. The pretreated capillary was filled with the monomer solutions and immediately sealed with teflon tube. Finally, the capillary was submerged in the water bath at 60 ^oC for overnight. After polymerization, the capillary was washed with acetonitrile to remove the unreacted monomers and porogenic solvents present in the column.

The poly (GMA-PEGDMA) was flushed with 1M Na_2SO_3 in order to attach the sulfonate groups [5]. Then, the cation-exchange columns were rinsed with 5mM HNO_3 and water.

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Results and Discussions

Column characterization

Cation-exchange monolith columns firstly were prepared from polymerization of GMA and PEGDMA with methanol and decanol as porogenic solvents. After that, poly(GMA-PEGDMA) was reacted with the Na_2SO_3 to introduce the sulfonate groups. The ratio between the monomer and the porogen phases will influence the flow-through pore size within a broad range, and the morphology of the monolith columns is depended on the composition of the porogen solvents, as well as on the composition of the monomer and crosslinker [17]. Figure 1 shows the SEM images of poly (GMA-PEGDMA)monolithic columns. In this monolith column, decanol was used as a porogen solvent to produce the throughpores in the polymer, while methanol was used to produce the mesopores, and could give the best flow-through characteristic [18]. The skeleton of monolith is approximately 2-3 µm.

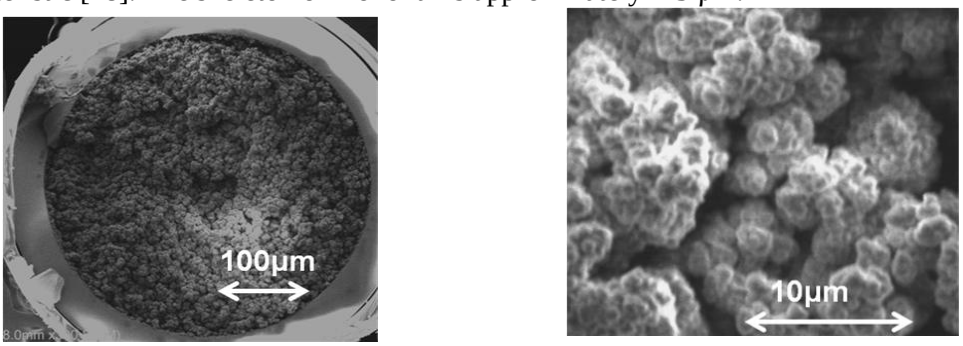

Fig. 1The SEM images of poly (GMA-PEGDMA) monolithic columns.

Effect of temperature in modification

Temperature will take an important part in modification condition. In this work, we tried to modify at the temperature from 70-90 ^oC.

Table 1 The composition of polymerization of the column with the variation of temperature

Column	Monomer mixture		Porogen %(v/v)			% Porogen	1M Na_2SO_3
	GMA	PEGDMA	MeOH	Decanol	(^oC/h)		ml
A	12	20	4	64	80/8	68	0.5
B	12	20	4	64	90/8	68	0.5
C	12	20	4	64	100/8	68	0.5

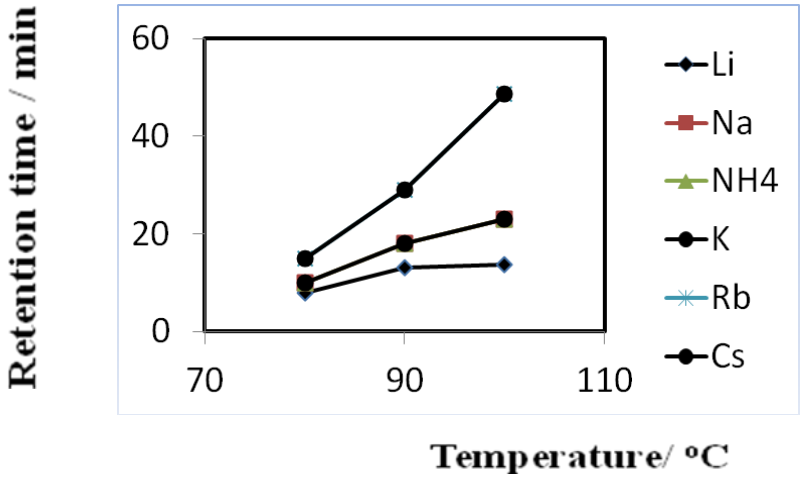

Fig. 2 The effect of temperature in modification with 1 M Na_2SO_3.

Figure 2 illustrates the retention time of analytecations as a function of modification temperature of polymer monolith. It can be seen that the retention time of analytecations increased with increasing temperature. By increasing the modification temperature, it could be expected more $Na_2SO_3$is introduced on the polymer monolithic column and retained the analytecations.

Effect of reaction time in modification

Beside temperature, the reaction time could be considered in modification of polymer monolithic column. We tried to modify for the reaction time from 8-16h.

Table 2The polymerization composition of the column with the variation of reaction time

Column	Monomer mixture		Porogen %(v/v)			% Porogen	Na_2SO_3 1M
	GMA	PEGDMA	MeOH	Decanol	(°C/h)		ml
A	12	20	4	64	80/8	68	0.5
B	12	20	4	64	80/12	68	0.5
C	12	20	4	64	80/16	68	0.5

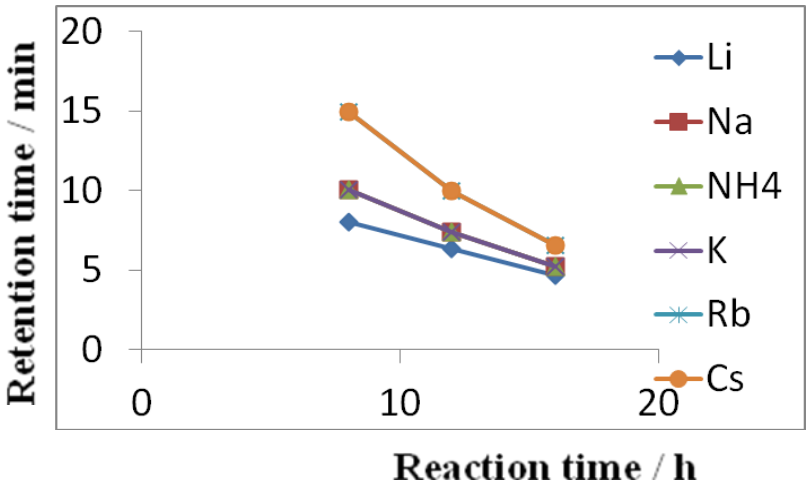

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Fig. 3 The effect of reaction time in modification with 1M Na_2SO_3.

Retention time of inorganic monovalent cations as a function of the reaction time for modification of polymer monolith column is shown in Figure 3. It can be seen that the shorter the reaction time, the longer is the retention time of analytecations. Attaching Na_2SO_3 into the poly(GMA/PEGDMA) at 80 ^oC for 8h shows the best profile.

Effect of the organic solvent in the eluent

Figure 3 demonstrates the separation of the monovalent cations on the poly(GMA/PEGDMA) modification with 1 M Na_2SO_3. In some cases, adding methanol into the eluent can give the better selectivity of the performance in chromatographic system. From the chromatogram, it can be seen that methanol gives a better selectivity than acetonitrile. Unfortunately, in our work from the six monovalent cations were injected, only three cations could be separated which is lithium, sodium and rubidium.

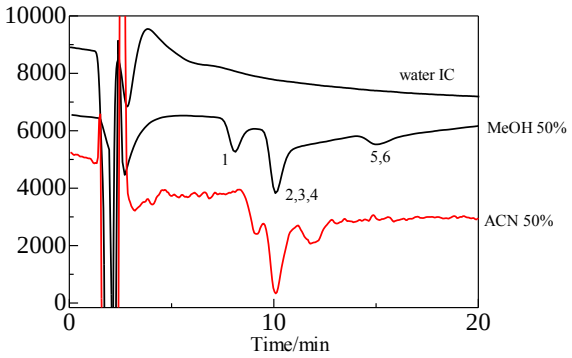

Fig 4Separation of monovalent cations on poly(GMA/PEGDMA) modified with1M Na_2SO_3.

Column, poly(GMA/PEGDMA)/1M Na_2SO_3, 100 × 0.32 mm i.d.; eluent, 5 mM MSA; flow-rate, 3.0μL min^{-1}; concentration of analytes,analytes (concentration in 1 mM), 1=Li^+, 2=Na^+, 3=NH_4^+,4=K^+, 5=Rb^+, 6=Cs^+; injection volume, 0.2□ L; detection, contactless conductivity detector.

CONCLUSIONS

Polymer-based strong cation-exchange monolithic stationary phases were prepared by thermal copolymerization of GMA as monomer, PEGDMA as crosslinker using binary porogenic solvents in the fused silica capillary with diameter of 0.32 mm. There are two step procedures to build up polymer monolithic stationary phases: synthesis of rigid polymer matrix (step 1) and sulfonation (step 2). Polymer monolithic GMA/PEGDMA modified with 1 M Na_2SO_3 (80 ^oC, 8H) and 68%porogen content could separate lithium, sodium and rubidium with the5mMMSA in 50% methanol as eluent.

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