



Original Research Article

Separation of Inorganic Anion using Methacrylate-based Monolithic Column Modified by Diethylamine in Capillary Ion Chromatography

Athika Rahmah¹, Edison Munaf^{1*}, Rahmiana Zein¹, Toyohide Takeuchi²,
Lee Wah Lim², Fitri Mairizki¹, Hilma¹, and Radhia Putri¹

¹Departement of Chemistry, Faculty of Mathematics and Natural Sciences, Andalas University, 25163, Padang, Indonesia

²Department of Chemistry and Biomolecular Science, Faculty of Engineering, Gifu University, 1-1 Yanagido, Gifu 501-1193, Japan

*Corresponding author

A B S T R A C T

Keywords

Anion exchange;
Glycidyl methacrylate;
Diethylamine;
Anion inorganic.

The polymeric monolithic column for anion-exchange capillary liquid chromatography of inorganic anions (iodate, bromate, nitrite, bromide and nitrate) were prepared in a single step by thermally copolymerization of *glycidyl methacrylate* (GMA) and *poly ethylene glycol dimethacrylate* (PEGDMA), in the presence of a binary porogenic solution. The resulting monoliths contained functionalities of diethylamine (DEA) as anion exchanger in monolith column. This work represents a successful attempt to prepare functionalized monoliths via direct thermally copolymerization. Important physical and chromatographic properties of the synthesized monoliths were characterized. The permeability and capacity ion exchange was $2.25 \cdot 10^{-12} \text{ m}^2$ and 40 mmol/mL in 7 cm of length. Separation and determination of anions in ion chromatography by using GMA-PEGDMA-DEA as stationary phase which using NaCl 50 mM + HCl 1 mM in 50% acetonitril as mobile phase given the optimum condition. Precision of monolith column ranged 0.223-2.394%. Linearity was established for range concentration of 0.25-1.25 mM with coefficient correlation 0.972-0.999. Limit of detection (LOD) was 0.019-0.540 and limit of quantification (LOQ) was 0.062-1.798. Anion nitrate level in ground water of Lubuk Lintah area, Padang City, West Sumatera, Indonesia was 0.079 mM.

Introduction

Ion chromatography was first time introduced by Small et al. in 1975 as a new analytical analysis. Then, ion chromatography widely applied as a new technology to separate and analyze

inorganic anions, cation and anion. The interest improvement in ion chromatography was low reagent consumption, rapid and efficient separations, analysis of small sample

volumes of high matrix complexity, and simple interfacing, therefore since in 1983 of capillary ion chromatography columns had been used (Takeuchi, T., 2005; Haddad et al., 2003; Ríordáin et al., 2007). In 1989, Hjerten *et al.* introduced time monolith column for the first time through research which made a new column in chromatography that have been fast to separate biomolecule using *polyacrylamide-based* as supporting materials (ALothman et al., 2011; Arrua et al., 2012). Since that time, monolith column have attracted much attention by researchers as stationary phase in liquid chromatography. Due to their good permeability, fast mass transfer, high stability, and ease of modification, monolithic column have been regarded as the new generation study for HPLC.

According to their components, monolithic materials divided into inorganic and organic polymers. Inorganic polymer monolithics materials is a column that consist of silica-based. Organic polymer monolithics materials can be classified into three main groups, according to the monomer system used, *styrene*, *methacrylate* dan *acrylamide* (Svec and Huber, 2006). Organic monolithic column widely used for separations of large molecules. *Polymethacrylated-based* monoliths column as stationary phase have been proved to be a good stationary phase with chemical stability in a broad pH range, which have been widely used for separation of organic compounds (Mangeling et al., 2007). Li-Qun et al. succeeded in preparing organic polymer methacrylate-based as stationary phase for separate *thiourea*, *toluene*, *naphthalene*, and *biphenyl* (Fan et al., 2010).

Preparation and function of methacrylate-based as organic polymer monolithics

column was studied by Vlakh and Tennikova (Vlakh and Tennikova, 2007). The former monoliths are generally made by *in situ* polymerization of monomers, cross-linkers, and porogens (Hilder et al., 2004). For Methacrylate-based monolithics column, the polymer network is generally formed inside the capillary by a chain-polymerization reaction with the help of thermal or photo-initiated polymerization, irradiation (Li et al., 2008, 2009; Zhang et al., 2008; Bandari et al., 2008) and free-radical polymerization technique (Liu et al., 2011). Different temperature of polymerization will give different shape and size of porous, and also give effect in homogenous of polymeric stationary phase structure (Mihelic et al., 2001). Once the polymerization is complete, unreacted components such as the porogenic solvents are removed from the monolith using a syringe pump. Karmaker et al. analyzed the effect of different matrix formulation on mechanical properties of polymer Bis-GMA and *polyethylene glycol dimethacrylate* (PEGDMA) (Karmaker et al., 1997). The glass transition temperature and flexural strengths of Bis-GMA/PEGDMA were found to be influenced by amount of concentration of PEGDMA.

Zein et al. reported about separated inorganic anions using *Bovine Serum Albumin* (BSA) as modifier stationary phase and tartaric acid as stationary phase (Zein et al., 1996). Beside that Jiang et al. also reported about separated inorganic anions in seawater using silica-based and modified by *cetyltrimethylammonium* (Jiang et al., 2009). Sykora et al., (1999) was introduced first time weak anion exchanger (WAX), their used diethylamine as anion exchanger. *Diethylamine* was introduced into

copolymer monolithics column stationary phase *poly(glycidyl methacrylate-co-ethylene glycol dimethacrylate)* (GMA-co-EDMA) by reaction between epoxy group with *diethylamine* (DEA). The separated selectivity of stationary phase depend on functional group properties where it bend (Nesterenko and Haddad, 2000). The monolithics column consist of *poly2-(diethylamino)ethyl methacrylate* (DEAEMA)-co-*polyethylene glycol diacrylate* (PEGDA) and *poly2-(acryloyloxy)ethyl trimethylammonium chloride* (AETAC)-co-*polyethylene glycol diacrylate* (PEGDA) modified with diethylamine (DEA) in 0.75 mm i.d. capillaries and NaCl in buffer solution produced good chromatographic efficiencies and resolution for protein separation, but the chromatogram of separation show that the separation is not completely good, the chromatogram stil overlapping between the analites.

Based on previous researchs in the design of successful funtionalized monoliths, in this research monolithic column with in situ polymerization of charged monomers of *glycidyl methacrylate* (GMA) and *Poly ethylene glycol dimethacrylate* (PEGDMA) as cross-linker, *methanol* and *decanol* as porogens, *2,2'-azobisisobutyronitrile* (AIBN) as the thermal initiator and also *diethylamine* as modifier were prepared, which showed reaction between epoxy group and amine group to make anion exchanger. These anion-exchange monolithic columns were prepared in a capillary format using 0.32 mm i.d capillaries and then the separation were evaluated by UV detector. Characterization and physical properties of the monolithics column were throughly investigated. The column was then evaluated and applied to the separation of inorganic anion mixtures, ground water and tap water.

Materials and Methods

Reagents and materials

The reagents employed were of guaranteed reagent grade, and were obtained from Wako Pure Chemical Industries (Osaka, Japan), Nacalai Tesque (Kyoto, Japan) and Trade TCI Mark. HPLC-grade distilled water was obtained from GS-590 water distillation system (Advantec, Tokyo, Japan), sodium Chloride, chloride acid, acetonitrile, and copper (II) sulphate pentahydrate were obtained from Nacalai Tesque, Wako Pure Chemical Industries and Trade TCI Mark, and they were employed for preparing sample solutions and mobile phases.

Monolith column were preparing by *Glycidyl methacrylate* (GMA), *Poly Ethylene Glicol Dimethacrylate* (PEGDMA), *Diethylamine* (DEA) and *Buffer Tris-HCl* pH 8.0 all reagents were obtained from Wako Pure Chemical Industries, Trade TCI Mark, and Nacalai Tesque.

Samples

The metropolitan area of Padang City is one of the most urbanized and industrialized areas in Indonesia. Padang City is located at the western part of the extreme centre of Sumatra island of Indonesia and in front of the Hindia Ocean. In the present work, Tap water samples were collected from a house in Pegambiran area and ground water from lubang lintah, Indonesia.

Apparatus

The chromatographic measurements were carried out by using Capillary LC system that was constructed by an L.TEX

Microfeeder (L.TEC Cooperation, Tokyo, Japan) equipped with an MS-GAN 050 gas-tight syringe (0.5 mL; Ito, Fuji, Japan) as a pump, a model microinjection valve with an injection volume 0.2 μ L (Upchurch Scientific, Oak Harbour, WA, USA) as an injector, a 0.32-mm i.d x 70 mm microcolumn, and a Model Detector UV-2070 (Jasco, Japan). The flow-rate of the pump was kept at 4 μ L/min. A fused-silica capillary with 50 μ m i.d (GL Sciences, Tokyo, Japan) was inserted into a cell block attached to the detector. The data were acquired by a Chromatopac C-RR4A data processor (Shimadzu, Kyoto, Japan).

The inlet pressure was monitored by an DLS-5028 Pressure Sensor (Toyo Sokki, Kyoto, Japan). The microcolumn was prepared from a fused-silica capillary tube (0.32 mm i.d x 70 mm) using a monolith packing method. PTFE 1/16 mm i.d x 0.25 mm o.d (GL Sciences, Tokyo, Japan) as a sealed of microcolumn. *Fourier Transform Infrared Spectrometer* FT/IR-460 Plus (Jasco, Japan). *Scanning Electron Microscope* (SEM) S-4800 (Hitachi, Japan)

Preparation of Monolithic Column

Prior to the polymerization, the capillary column was pretreated with the following procedure : first, the capillary column with a length of 12 cm was rinsed with 0.1M NaOH for 30 minutes and then with water until the outflow reached pH 7.0, after subsequent flushing with HCl 1 M for 30 minutes. The capillary was filled with silanization solution containing 30% (v/v) γ - MAPS in acetone, was injected into the capillary with a syringe 0.5 mL. Then, the capillary was sealed with PTFE at both ends and then submerged in water bath at 60 °C for overnight. After silanization, the

capillary was flushed with acetone to flush out the residual reagent and dried by the purge of nitrogen gas. Thereby, Si–O–Si–C bonds were formed between the capillary wall and the reactive methacryloyl groups, which were available for subsequent attachment of monolith to the wall during the polymerization reaction.

The monolithic columns were prepared from polymerization reaction of mixtures, consisting of the monomers GMA, PEGDMA, the porogens of methanol and decanol using AIBN (0.3%, w/w, with respect to the monomers) as an initiator. The polymerization mixtures were sonicated for 5 min to obtain homogeneous solution, and then purged with nitrogen for 30 min. After the pretreated capillaries was completely filled with the mixture, they were sealed at both ends with PTFE. The sealed capillaries were submerged into a water bath and allowed to react for at 60 °C for overnight. The resultant monolithic capillary columns were washed with methanol about 2 h using an HPLC pump to remove unreacted monomers and the porogenic solvents.

Diethylaminoethyl (DEAE) functionalities could be introduced after polymerization of the rod of copolymer (GMAPEGDMA) by reaction of the epoxy groups with DEA. Typically, DEA was pumped through the column to completely “wet” the polymer first, and then the column was sealed at both ends by a closed loop filled with DEA, and heated at 55 °C for 12 h in an oven. Residual epoxy groups were blocked by washing the column with 1.0 M Tris buffer, pH 8.0. After preparation, both ends of the monolithic column were sealed at both ends with PTFE and placed in water to keep the monolith wet (Li et al., 2009).

Results and Discussion

Morphology and Permeability of Monolithic Column

The morphology of the monoliths column is controlled by the quality of the porogen solvent, the percentage of the monomer and cross-linker, the ratio between the monomer and the porogen phases, and the polymerization temperature, which affect the flow-through pore size within a broad range (Urban and Jandera, 2008). The SEM image of the monolithic column is shown in Fig. 1, which that the largest channels was existent using decanol as porogen for formation of throughpores in the polymer reached several μm , resulting in higher permeability. In other hand, monolith prepared using methanol as a porogen for formation mesoporous of had a pore size of around 3 μm and provided the best flow-through characteristics (Vlakh and Tennikova, 2007).

The monolith column filled with interconnected pores that influence for high permeability and therefore flow rates at moderate pressures. The high flow rates with the convective mass transfer, possibilities shorter separations times in chromatographic separations (Arrua et al., 2010). In general, the permeability of monolithic columns was higher than that of packed columns. The permeability (Shu et al., 2004), K , calculated according to Darcy's law, Eq. (1), was $K = 2.248 \times 10^{-12} \text{ m}^2$. Normally a separation monolith should possess appropriate permeability around $1.9 \times 10^{-12} \text{ m}^2$ (Chen et al., 2012).

The results show that the column head pressure was directly proportional to the flow-rate of mobile phase and exhibited a good linearity in the range of 0.5–4 $\mu\text{L}/\text{min}$ ($R^2 = 0.996$).

Fig.2 this should be attributed to the stable structural characteristics of the synthesized monolithic material. On the other hand, the good linearity between column head pressure and the mobile phase flow-rate clearly demonstrates that the cross-linked monoliths were mechanically stable to with stand the pressure of the liquid passing through the column.

$$K^o = \frac{V\eta L}{\pi r^2 P} \quad (1)$$

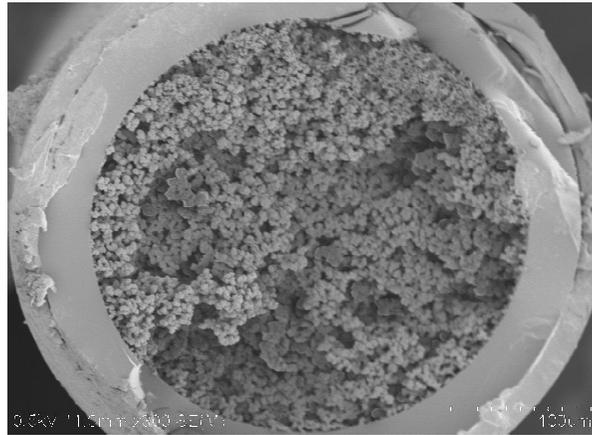
where η is the viscosity of the mobile phase; L the column length; P the back pressure; and u the linear velocity of mobile phase.

Chromatographic Performance

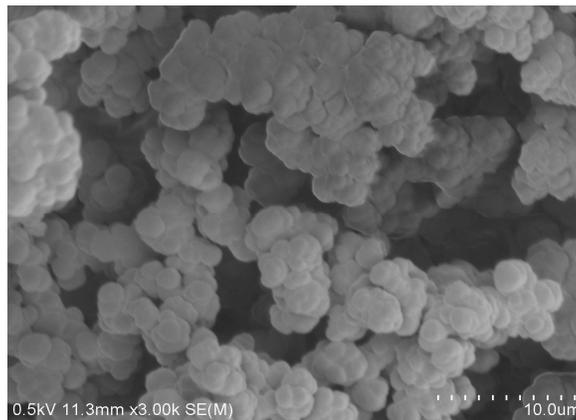
The anion-exchange monoliths reported in this study demonstrated efficient separations of inorganic anions of varying mobile phase and also evaluate the performances of the monolith. Fig. 3 demonstrates the separation of iodate, nitrite, and nitrate using varying sodium chloride as mobile phase in monolith column poly(GMA-PEGDMA). The lower concentration give good separation of inorganic anions, however it showed higher retention and resolution compared to the higher concentration. Compared to other concentration, 50 mM of sodium chloride faster and showed good separation peak and resolution of inorganic anions. Furthermore, 50 mM sodium chloride provided better inorganic anions separation due to lower back pressure of monolithic column.

Copolymerization of hydrophilic functional monomers and crosslinkers is a seemingly straight forward approach to

Figure.1 Scanning-electron micrograph of the end of the *poly*(GMA-co-PEGDMA) monolithic stationary phase in a fused-silica capillary column (0.32 μm i.d) (a) 300 \times , (b) 3000 \times .



(a)



(b)

Figure.2 Back pressure dependency on linear velocity for the poly (GMA-PEGDMA) functionalized monoliths. Conditions: 70 mm \times 0.32 mm i.d. columns; mobile phase, IC Water

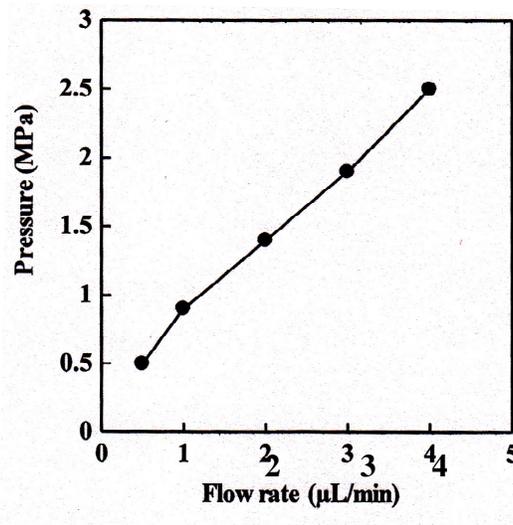


Figure.3 Effect of sodium chloride concentration on the separation of inorganic anion. Column, *poly*(GMA-PEGDMA) monolith, 70x0.32 mm i.d; mobile phase, sodium chloride with concentration a. 10 mM, b. 20 mM, c. 30 mM, d. 40 mM, e. 50 mM, f. 100 mM; flow μ L rate, min 4^{-1} ; injection μ L; wavelength volume, 0. of 2 UV detection, 210 nm; 1. IO_3^- , 2. NO_2^- , 3. NO_3^-

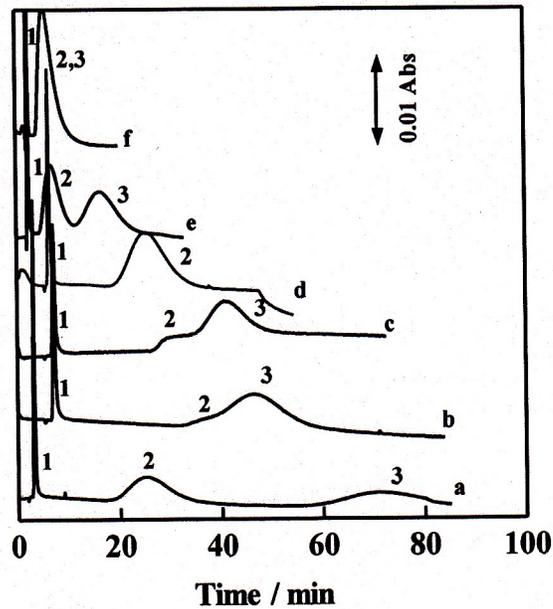


Figure.4 Effect of addition Acetonitrile concentration in 50 mM sodium chloride + 1 mM chloride acid on the separation of inorganic anions. Column, *poly*(GMA-PEGDMA) monolith, 70x0.32 mm i.d; mobile phase 50 mM sodium chloride + 1 mM chloride acid in acetonitrile with concentration a. 20 %, b. 30 %, c. 40 %, d. 50 %, e. 60 %; flow μ L rate, min 4^{-1} ; injection μ L; wavelength volume, 0. of 2 UV detection, 210 nm; 1. IO_3^- , 2. BrO_3^- , 3. NO_2^- , 4. Br^- , 5. NO_3^-

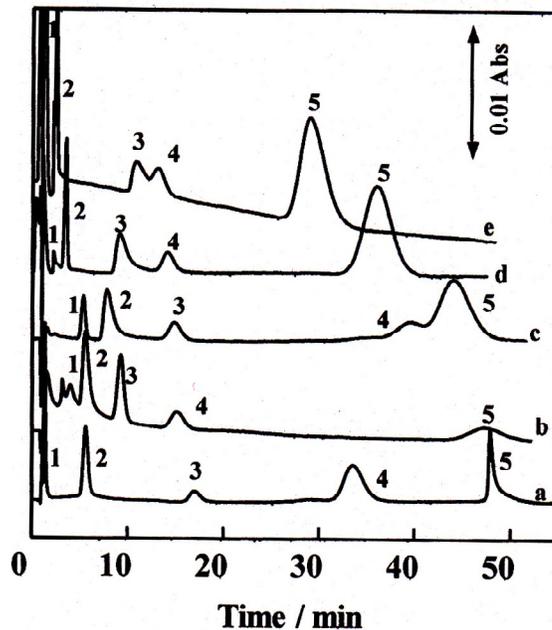


Figure.5 Calibration curves for five inorganic anions. Conditions : column, *poly*(GMA-PEGDMA) monolith, 70x0.32 mm i.d; mobile phase, 50 mM sodium chloride + 1mM chloride acid in 50 % acetonitrile; flow rate, 4⁻¹; injection volume, 0.2 μL; wavelength 210 nm; ●=iodate, ▼=bromate, ■=UV ▲nitrite, detection, 210 nm; = bromide, ◆ = nitrate

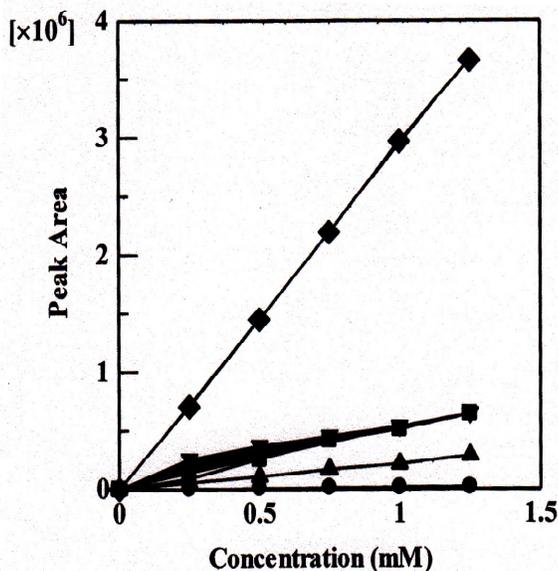


Figure.6 Separation of inorganic anions in tap water and ground water in Indonesia, Column, *poly*(GMA-PEGDMA) monolith, 70x0.32 mm i.d; mobile phase, 50 mM sodium chloride + 1 mM chloride acid in 50% acetonitrile; flow rate, 4.0 μl min⁻¹; injection volume, 0.20 μl; wavelength of UV detection, 210 nm; samples, 0.5 mM each of standard solution(a), ground water (b), tap water (c); 1. IO₃⁻, 2. BrO₃⁻, 3. NO₂⁻, 4. Br⁻, 5. NO₃⁻

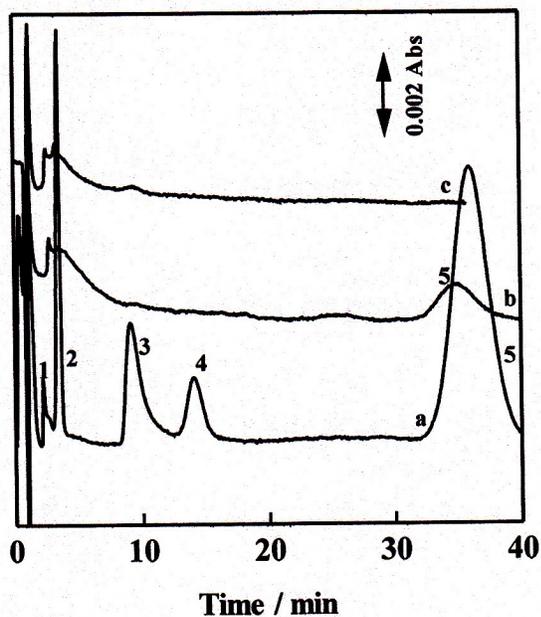


Table.1 Capillary repeatability RSD for retention factor of iodate, bromate, nitrite, bromide, and nitrate and for ion-exchange capacity

No.	Analite	RSD (%)
1	IO ₃	1.98
2	BrO ₃	2.40
3	NO ₂	1.16
4	Br	0.47
5	NO ₃	0.22

obtain materials. PEGDMA as cross-linker was based on the fact that these monomers contain hydrophobic sites which are essential in the design of stationary phases to be used in (Arrua et al., 2012). Minimizing non-specific interactions is also important from a view point of avoiding slow adsorption-desorption kinetics that lead to band broadening and peak asymmetry. The addition of 20% (v/v) acetonitrile was still required in order to lessen hydrophobic interactions, good separation and resolution and also increased elution of anions in column (Gu et al., 2006, 2007). And also the addition of up to 20% (v/v) acetonitrile in the eluents suggesting negligible hydrophobic interaction. The effect of acetonitrile concentration in the mobile phase on the retention factors of iodate, bromate, nitrite, bromide, and nitrate is shown in Fig. 4. It can be seen that the separation peak linear decreased by decreasing concentration of acetonitrile. It can deduce that the separation of inorganic anions on poly(GMA-PEGDMA), 50 mM of acetonitrile provided faster and good separation peak and resolution and also the maintainance of baseline resolution for all peaks.

Capillary repeatability of monolith

We investigated the repeatability of the preparation of poly (GMA-PEGDMA)

monoliths for five inorganic anions mixtures. The results presented in Table 1 shows capillary RSD values below 2.4 % for IEC. The RSD results indicated the good run-to-run reproducibility could be easily obtained.

Application

WAX chromatography of inorganic anions from tap water and ground water in West Sumatra, Indonesia was achieved using poly(GMA-PEGDMA) monolith, shown in Fig. 6. The separation of monolith column was demonstrated that in tap water were not identified of inorganic anions. In ground water were identified only nitrite could be separated using this column. From the curve calibration, Fig. 5, we could find the concentration of nitrite in ground water is 0.079 mM.

Monolith column poly(GMA-PEGDMA) were prepared by direct thermally copolymerization of functional monomer and cross-linker using binary porogenic solutions in 0.32 mm i.d capillaries in the presence of new monolith column modified with weak anion exchanger. They were then evaluated as stationary phase in anion exchange LC of inorganic anions. Poly(GMA-PEGDMA) monoliths contain DEA functionality that are required for WAX chromatography, respectively. These monolith produced

comparable chromatographic efficiencies, resolution and repeatability compared to anion exchange monolith reported previously.

Acknowledgement

The author wish to extend special thanks to JASSO and Gifu University for all supported in Student Research Program and all members of Prof. Takeuchi laboratory.

References

- ALothman, Z. A., A. Aqel, H.A., AlAbdelmoneim, A.Y. Badjah-Hadj-Ahmed and Al-Warthan, A. A. 2011, "Preparation and evaluation of long chain alkyl methacrylate monoliths for capillary chromatography," *Chromatographia*, 74: 1-8
- Arrua, R. D., C. Moya, E. Bernardi, J. Zarzur, M. Strumia and Igarzabal, C. I. A. 2010. "Preparation of macroporous monoliths based on epoxy-bearing hydrophilic terpolymers and applied for affinity separations," *European Polymer J.* 46: 663–672
- Arrua, R. D., M. Talebi, T.J. Causon and Hilder, E. F. 2012, "Review of recent advances in the preparation of organic polymer monoliths for liquid chromatography of large molecules," *Anal. Chim. Acta*, 738: 1 - 12
- Bandari, R., W. Knolle, A. Prager-Duschke, H. Glaesel and Buchmeiser, M. R. 2007. "Monolithic media prepared via electron beam curing for proteins separation and flow-through catalysis," *Chem. Phys.* 208 (13): 1428–1436
- Chen, M.L., L. Li, B. Yuan, Q. Ma and Feng, Y. 2012, "Preparation and characterization of methacrylate-based monolith for capillary hydrophilic interaction chromatography," *J. Chromatog. A.* 1230: 52-60
- Fan, L. Q., Y.P. Zhang., Na-Cheng, G. Wen-Jun, L.B. Qu and Lee, K. P. 2010, "Rapid preparation and characterization of methacrylate-based monoliths for chromatographic and electrophoretic separation," *J. Chromatogr. Sci.* 48: 399-405
- Gu, B., Y. Li and Lee, M. L. 2007. "Polymer Monoliths with Low Hydrophobicity for Strong Cation-Exchange Capillary Liquid Chromatography of Peptides and Proteins," *Anal. Chem.* 79: 5848–5855.
- Gu, B., Z. Chen, C.D. Thulin and Lee, M. L. 2006, "Efficient Polymer Monolith for Strong Cation-Exchange Capillary Liquid Chromatography of Peptides" *Anal. Chem.* 78: 3509–3518
- Haddad, P. R., P.E. Jackson and Shaw, M. J., 2003, "Developments in suppressor technology for inorganic ion analysis by ion chromatography using conductivity detection," *J. Chromatogr. A*, 1000: 725-742
- Hilder, E. F., F. Svec and Frechet, J. M. 2004, "Development and application of polymeric monolithic stationary phases for capillary electrochromatography," *J. Chromatogr. A.* 1044: 3 – 22
- Jiang, X., L.W. Lim and Takeuchi, T. 2009, "Determination of trace inorganic anions in seawater samples by ion chromatography using silica columns modified with cetyltrimethylammonium ion," *Anal Bioanal Chem.* 393: 387–391
- Karmaker, A. C., A.T. Dibenedetto and Goldberg, A. J. 1997, "Extent of conversion and its effect on the mechanical performance of Bis-GMA/PEGDMA-based resins and their composites with continuous glass fibres," *J. Materials Sci., Mater. Med.*

- 8: 369-374
- Li, L., J. Wang, S. Zhou and Zhao, M. 2008, "Development and characterization of an immunoaffinity monolith for selective on-line extraction of bisphenol A from environmental water samples," *Anal. Chem. Acta.* 620: 1-7
- Li, Y., B. Gu, H.D. Tolley and Lee, M. L. 2009, "Preparation of polymeric monoliths by copolymerization of acrylate monomers with amine functionalities for anion-exchange capillary liquid chromatography of proteins," *J. Chromatogr. A.* 1216: 5525-5532
- Liu, M., H. Liu, Y. Liu, L. Bai, G. Yang, C. Yang and Cheng, C. 2011, "Preparation and characterization of temperature-responsive poly(N-isopropylacrylamide-co-N,N'-methylenebisacrylamide) monolith for HPLC," *J. Chromatogr. A.* 1218: 286-292
- Mangeling, D., I. Tanret, V. Meert, S. Eeltink, P.J. Schoenmakers, W.T. Kok and Heyden, Y.V. 2007, "Evaluation of polymeric methacrylate-based monoliths in capillary electrochromatography for their potential to separate pharmaceutical compounds," *J. Sep. Sci.* 45:578-586
- Mihelic, I., M. Krajnc, T. Koloni and Podgornik, A. 2001, "Kinetic Model Of A methacrylate-based monolith polymerization" *Ind. Eng. Chem. Res.* 40: 3495-3501
- Nesterenko, P. N., and Haddad, P. R. 2000, "Zwitterionic ion-exchange in liquid chromatography," *Anal. Sci.* 16: 565-574
- Ríordáin, C., E. Gillespie, D. Connolly, P.N. Nesterenko and Paull, B., 2007, "Capillary ion chromatography of inorganic anions on octadecyl silica monolith modified with an amphoteric surfactant," *J. Chromatogr. A.* 1142: 185-193
- Shu, X., L. Chen, B. Yang and Gua, Y. 2004, "Preparation and characterization of long methacrylate monolithic column for capillary liquid chromatography," *J. Chromatogr. A.* 1052: 205-209
- Svec, F., and Huber, C. G. 2006, "Monolithic materials promises, challenges, achievements," *Anal. Chem.* 78: 2100-2107
- Sýkora, D., F. Svec and Fréchet, J. M. 1999, "Separation of oligonucleotides on novel monolithic columns with ion-exchange functional surfaces" *J. Chromatogr. A.* 852: 297-304
- Takeuchi, T., 2005, "Development of Capillary Liquid Chromatography," *Chromatogr.* 26: 7-11
- Urban, J., and Jandera, P. 2008, "Polymethacrylate monolithic columns for capillary Polymethacrylate monolithic columns for capillary liquid chromatography," *J. Sep. Sci.* 31: 2521-2540
- Vlakh, E. G., and Tennikova, T. B. 2007, "Preparation of methacrylate monoliths," *J. Sep. Sci.* 30: 2801-2813
- Zein, R., E. Munaf, T. Takeuchi and Miwa, T. 1996, "Microcolumn ion chromatography of inorganic UV-absorbing anions using bovine serum albumin as stationary phases," *Anal. Chem. Acta.* 335: 261-266
- Zhang, Y., X. Ye, M. Tian, L. Qu, S. Choi, A.L. Gopalan and Lee, K. P. 2008. "Novel method to prepare polystyrene-based monolithic columns for chromatographic and electrophoretic separations by microwave irradiation," *J. Chromatogr. A.* 1188 (1): 43-49.