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## Preparation of suppressor column for capillary ion chromatography with conductivity detection

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# Preparation of suppressor column for capillary ion chromatography with conductivity detection

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**Abstract.** A capillary suppressor column was prepared by packed column and monolith columns. The packed column prepared using HyperSep SCX as packing material. The sulfonate group was introduced from benzenesulfonic acid that could be used as a suppressor material. The slurry of packing material was packed to capillary fused silica 0.53 mm I.D x 0.66 mm O.D with 30 mm of length. Monolith suppressor column was prepared from methacrylate based modified with Na<sub>2</sub>SO<sub>3</sub> for strong cation exchanger and iminodiacetic acid for weak cation exchanger. A suppressor column was connected to a capillary chromatography system for separating 5 inorganic anions (Cl<sup>-</sup>, NO<sub>2</sub><sup>-</sup>, Br<sup>-</sup>, NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup>) using conductivity detection. The suppression system could reduce the background conductivity of the mobile phase sodium bicarbonate and sodium carbonate properly up to 67.72% using packed suppressor column with size 0.53 mm I.D x 0.66 mm O.D with 30 mm length. It column could be used about 1.5 hours before breakthrough.

## 1. Introduction

Ion chromatography was first introduced in 1975 as an analytical method. In a short time, ion chromatography has also developed rapidly as one of the technologies for separating and determining inorganic ions, especially anions [1, 2]. Inorganic anions were also successfully separated using Bovine Serum Albumin (BSA) and tartaric acid as a stationary phase with a UV detection [3]. Inorganic anions in seawater samples were perfectly analyzed using silica modified with cetyltrimethylammonium as a stationary phase [4]. For the sensitivity of ion detection, conductivity detection methods are often used. In order of its, the suppressor column was needed to reduce the conductivity of the mobile phase and increase the conductivity of the sample signal.

The development of technology for reducing conductivity in the analysis of inorganic ions using ion chromatograms has been carried out [5-8]. The use of suppressor columns is optimized in the



determination of inorganic ions by using a contactless conductivity detector (CCD). The suppressor column is the main component related to its function in ion chromatography. In the previous decades, several types of suppressors have been developed to achieve high sensitivity including containerized columns, hollow fiber, and electrolytic mode [9]. However, most of the several types of suppressor columns are designed for conventional system chromatography and less are used in capillary system ion chromatography, whereas in fact there are some advantages when using capillary system ion chromatography such as high sensitivity reducing waste to be generated, minimal use of mobile phase, easy in the operation and optimization of the mobile phase and packaging materials. The packed column is one of the suppressor columns that are widely used in ion chromatographic capillary systems. TSKgel SCX 10  $\mu\text{m}$  of particle size was packed into capillary fused silica (0.32 mm ID  $\times$  0.45 mm OD) with 30 mm length as a material for suppressor and has succeeded in reducing 495  $\mu\text{S}/\text{cm}$  conductivity from sodium carbonate/sodium bicarbonate which is used as a mobile phase with slightly high pressure system [5].

In this research, a suppressor column was made using packing material containing sulfonate group that has a larger particle size is used as a suppressor column in order to refrain from high pressure system. The suppressor columns will be used in ion chromatography capillary systems to reduce the conductivity of the mobile phase in the separation of inorganic ions in particular 5 anions.

## 2. Research methods

### 2.1. Capillary chromatography system

A capillary chromatography system was comprised of micro feeder (L.TEX Corporation, Tokyo Japan) that uses gas-tight syringes (0.5 ml; Ito, Fuji, Japan) as pumps, Two 6-way switching valves with a volume of 0.2  $\mu\text{l}$  as injectors and suppressor connectors (Upchurch Scientific, Oak Harbor, WA, USA), micro columns prepared from fused-silica capillary tubes (100 mm, 0.32 mm ID  $\times$  0.45 mm OD; GL Science, Tokyo, Japan) as separator columns and fused-silica capillary tubes (30 mm; 0.53 mm ID  $\times$  0.66 mm OD; GL Science, Tokyo, Japan) as a suppressor column. Tracedec Conductivity Contactless Detector (Istech, Strasshof, Austria) as a detector. Fused silica tube with a size of 50  $\mu\text{m}$  I.D is used as a flow cell in the detector.

### 2.2. Preparation of separation column

The separation column was prepared using a fused silica capillary tube with a length of 100 mm with a size of 0.32 mm I.D and 0.45 mm O.D. The stationary phase material is put into the capillary column by sprinkling PWxl anion IC using methanol. The Anion PWxl IC stationary separation column is used in anion separation by connecting to the ion chromatography system using UV detector at a wavelength of 210 nm.

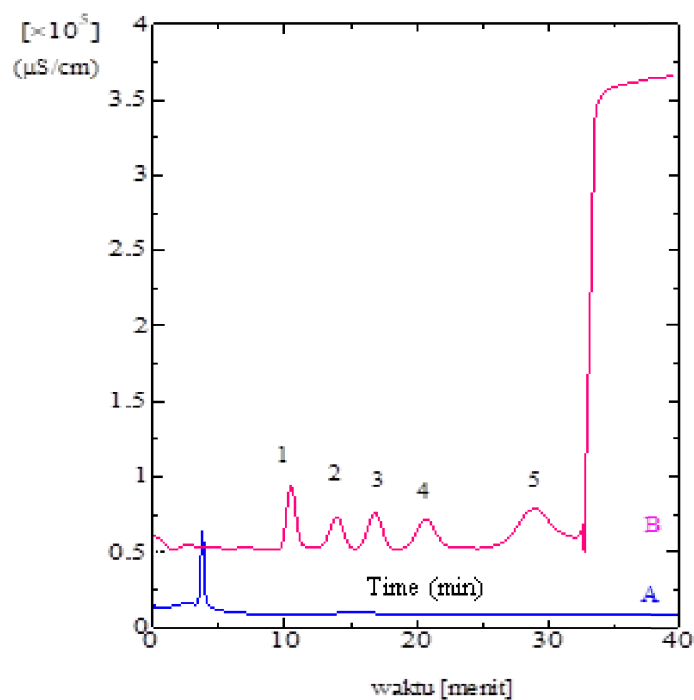
### 2.3. Preparation of suppressor column

Suppressor column was prepared from packed suppressor column and monolith column. A Fused silica with length 30 mm with size 0.53 mm for I.D and 0.66 mm O.D was used as suppressor column that packed using stationary phase material consist of sulfonate functional group. The stationary phase material is put into the capillary column by spreading HyperSep SCX using methanol. As comparison, the monolith suppressor columns were prepared from methacrylate based. Methacrylate based were prepared from glycidyl methacrylate, ethylene glycol dimethacrylate, water, 1-propanol and 1,4-butanediol. Then, the methacrylate based were modified with  $\text{Na}_2\text{SO}_3$  for strong cation exchanger and Iminodiacetic acid for weak cation exchanger. All the suppressor columns were tested for its ability to reduce the conductivity of the mobile phase in term of sodium bicarbonate and sodium carbonate [7:6] by connecting

it to the ion chromatography system in the separation of 5 anions ( $\text{Cl}^-$ ,  $\text{NO}_2^-$ ,  $\text{Br}^-$ ,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$ ) by using a Contactless Conductivity Detector (CCD) conductivity measurement detector.

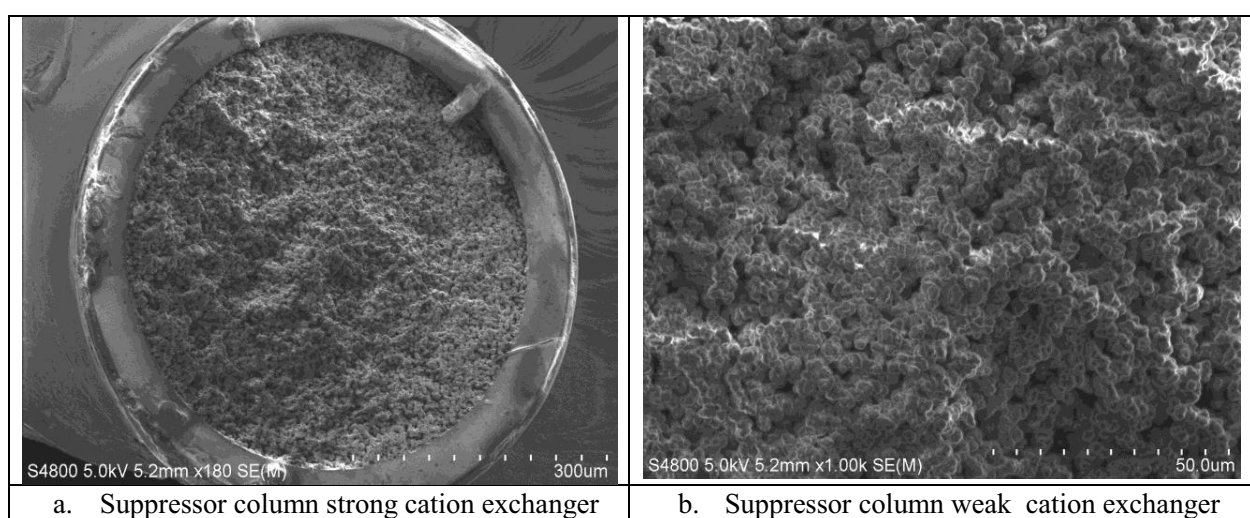
### 3. Result and discussions

The ability of the suppressor column has been tested to reduce the conductivity of the mobile phase (sodium bicarbonate and sodium carbonate) which have high conductivity. When monovalent and divalent anion are separated using sodium bicarbonate and sodium carbonate [7:6] as mobile phase without using a suppressor column, then the entire peak of the analyte will be covered by the high conductivity of the mobile phase. This is because the conductivity of the mobile phase is higher than the conductivity of the separated analyte. Figure 1 shows a chromatogram of separation of 5 anions by ion chromatography system without using a suppressor column as well as using a suppressor column (packed column). The existence of suppressor column was important to decrease the conductivity of the mobile phase, so the peaks of the separated analyte can appear. The suppressor column with packing material in the term of HyperSep SCX contains a sulfonate functional group. It was introduced from benzenesulfonic acid. The sulfonate functional group has ability to reduce the conductivity of the mobile phase up to 67.72%.



**Figure 1.** Separation of 5 anions: A. Without using a suppressor column, B. Using a column suppressor (packed column) with HyperSep SCX material in separation (1)  $\text{Cl}^-$ , (2)  $\text{NO}_2^-$ , (3)  $\text{Br}^-$ , (4)  $\text{NO}_3^-$  and (5)  $\text{SO}_4^{2-}$  by using PWxl IC anion stationary phase with column size capillary 0.32 mm ID x 0.45 mm OD, mobile phase sodium bicarbonate and sodium carbonate [7:6] concentration 1.75 M: 1.5 M, flow rate  $3\mu\text{L}/\text{min}$ , contactless conductivity detector (CCD) injection volume  $0.02\mu\text{L}$ .

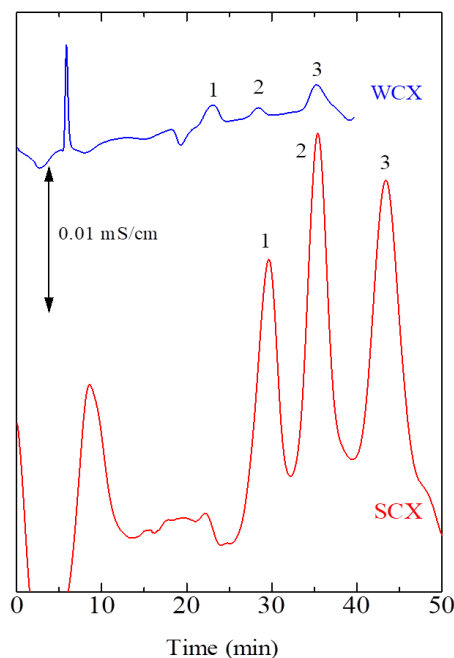
Monolith suppressor columns which prepared from methacrylate based formed using glycidyl methacrylate (GMA) and ethylene glycol dimethacrylate (EDMA) to form the epoxy contained in the polymer matrix, then modified with Iminodiacetic acid for attaching carboxyl active site as weak cation exchange and  $\text{Na}_2\text{SO}_3$  for attaching sulfonate as strong cation exchanger. Figure 2 show the morphology surface of the monolith suppressor column. The polymers were attached tightly into the inner wall of the capillary fused silica tube and the monolith formed packed and filled.



**Figure 2.** Scanning electron Microscopy (SEM) photo of monolith suppressor columns with column size capillary 0.32 mm ID x 0.45 mm OD .

The present of the epoxy group acted as the based to attached functional group. Both of monolith column weak cation exchanger (WCX) and strong cation exchanger (SCX) could apply for separating anions as shown in Figure 3. The SCX monolith column and WCX monolith column have ability to reduce the conductivity of the mobile phase 28.18% and 6.81%, respectively.

In the chromatographic system series the weak cation exchange monolith column has the ability to reduce the background conductivity of the mobile phase from 1349  $\mu\text{S}/\text{cm}$  - 1257  $\mu\text{S}/\text{cm}$  or has a decrease in the conductivity of 6.81% and a system pressure of 3.2 MPa. The ability of a weak cation exchange monolith column is obtained by flowing a mobile phase with a flow rate of 3  $\mu\text{m}$  into a weak cation exchange monolith column with a column length of 3 cm. it was directly connected to the flow cell of the conductivity detector in the ion chromatography system without using a separator column. The use of strong cation exchange monolith columns using  $\text{Na}_2\text{SO}_3$  which contribute sulfonate groups as suppressor columns has sufficient ability to reduce the background conductivity of sodium bicarbonate and sodium carbonate mobile phase with a lifetime of 1 hour.



**Figure 3.** Separation of 5 anions using SCX monolith column suppressor and WCX monolith column suppressor in separation (1)  $\text{Cl}^-$ , (2)  $\text{NO}_2^-$ , (3)  $\text{Br}^-$ , (4)  $\text{NO}_3^-$  and (5)  $\text{SO}_4^{2-}$  by using PWxl IC anion stationary phase with column size capillary 0.32 mm ID x 0.45 mm OD, mobile phase sodium bicarbonate and sodium carbonate [7:6] concentration 1.75 M: 1.5 M, flow rate  $3\mu\text{L}/\text{min}$ , contactless conductivity detector (CCD) injection volume  $0.02\mu\text{L}$ .

#### 4. Conclusion

The capillary suppressor columns were prepared using HyperSep SCX as packing material for packed column and monolith suppressor column from methacrylate based. The sulfonate group was introduced from benzenesulfonic acid that could be used as a suppressor material. The strong cation exchanger site in monolith suppressor was introduced from  $\text{Na}_2\text{SO}_3$  and Iminodiacetic acid. The packed suppressor column could reduce background conductivity of the mobile phase sodium bicarbonate and sodium carbonate properly up to 67.72%. The suppressor column with size 0.53 mm I.D x 0.66 mm O.D with 30 mm length could be used about 1.5 hours before breakthrough.

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## References

- [1]. Small H, Stevens T S and Bauman W C 1975 Novel ion exchange chromatographic method using conductimetric detection *Anal. Chem.* **47**(11) pp 1801-9.
- [2]. Haddad P R, Jackson P E and Shaw M J 2003 Developments in suppressor technology for inorganic ion analysis by ion chromatography using conductivity detection *J. Chromatography A* **1000** pp 725-42.
- [3]. Zein R, Munaf E, Takeuchi T and Miwa T 1996 Microcolumn ion chromatography of inorganic UV-absorbing anions using bovine serum albumin as stationary phases *Analytica Chimica Acta* **335** pp 261-66.
- [4]. Jiang X, Lim L W 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** pp 387-91.
- [5]. Sedyohutomo A, Lim L W and Takeuchi T 2008 Development of packed column suppressor system for capillary ion chromatography and its application to environmental water *J. Chromatography A* 2008 **1203** pp 239-42.
- [6]. Zhang X X, Liu Y Q, Yu H and Zhang R Q 2017 Rapid and simultaneous determination of piperidinium and pyrrolidinium ionic liquid cations by ion pair chromatography coupled with direct conductivity detection *Chinese Chemical Letters* **28** pp 126-30.
- [7]. Ma Y J, Li M, and Li R S 2013 Fast analysis of thiocyanate by ion-pair chromatography with direct conductivity detection on a monolithic column *Chinese Chemical Letters* **24** pp 1067-69.
- [8]. Yang B, Zhang F, Li Y dan Liang X 2011 A cation exchanger resin bead based microscale electrolytic suppressor for capillary ion chromatography *Talanta* **83** pp 1496-500.
- [9]. Li Y M, Liao J L, Nakazato K dan Mohammad J 1994 Continuous beds for microchromatography cation exchange chromatography *Analytical Biochemistry* **223** pp 153-6.