



## A polar-copolymerized method to prepare silica-based anion exchanger for ion chromatography

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### ABSTRACT

A novel silica-based strong anion exchanger was developed for ion chromatography by copolymerizing methyltrichlorosilane and 3-chloropropyltrichlorosilane. The method allows the column capacity to be easy control simply by adjusting the ratio of silanes. The unwanted residual silanol groups onto the surface of silica gel could also be greatly reduced by this strategy. The effective column capacity of the column used was measured to be 50.8  $\mu\text{equiv}/\text{column}$  (2.03  $\mu\text{equiv}/\text{cm}$ ). The exchanger was characterized by solid state CP/MAS  $^{13}\text{C}$  NMR and elemental analysis and its separation performance was evaluated for the separation of common inorganic anions. The results showed that the column had good separation efficiency (e.g. the plate number of nitrite is 80,000/m) and the separation mechanism was observed to be dominantly governed by ion exchange mechanism. The utility of the column was demonstrated for the determination of nitrite and nitrate in saliva sample.

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## 1. Introduction

Ion chromatography (IC) is widely employed for the determination of ionic compounds. Since the introduction of IC, several types of ion exchangers for the separation of anions have been developed, including silica-based anion exchangers [1,2], poly(styrene-divinylbenzene) (PS-DVB)-based anion-exchangers [3–6], and macroporous hydroxyethyl methacrylate-based anion exchangers [7]. Among them, PS-DVB-based resins are widely used in present IC system due to their wide pH tolerance. Although the silica-based exchangers have the drawback of limited pH tolerance, they have some specific features, e.g., higher chromatographic efficiency, higher mechanical stability, no swelling or shrinking problems when contacting with high content of organic solvent in the eluent. In addition, the rich silanol groups onto the surface of silica gel are easily bonded chemically to introduce various kinds of functional groups. Since our aim is to develop anion exchangers, here only the work related with the anion exchanger was mentioned. Lin et al. developed a silica-based strong anion

exchanger (SAX) by immobilizing a quaternary ammonium salt of cyanuric chloride onto the silica surface [2]. Effective separation of anions using tartaric acid or o-phthalic acid as eluent was achieved while relative strong unwanted matrix effect was also observed. By immobilizing N-methylimidazolium ionic liquid onto silica gel, Liu et al. prepared an anion exchanger for the separation of anions [8]. They demonstrated good separation of organic anions and inorganic anions and multimode retention mechanism were observed. More recently, Takeuchi et al. demonstrated the effective separation of inorganic anions on a commercial available silica column designed for hydrophilic interaction liquid chromatography [9]. The pyridine functional group containing in the stationary phase served to be the effective ion exchange sites when operated in acid eluent. In addition, the use of commercial available silica monolithic column coated by cationic surfactant demonstrated great benefits for fast anion analysis [10–12]. Some silica-based anion columns with relative high efficiency have been commercial available and have found lots of specialized applications [13].

The problems associated with the common preparation method of silica-based ion exchanger are 1, difficult to control the content of the functional groups introduced onto the silica surface, always leading to extremely high column capacity. 2, unwanted effect from the residual silanol groups onto the silica surface, then leading to significant nonspecific interactions. In addition, the final prepared

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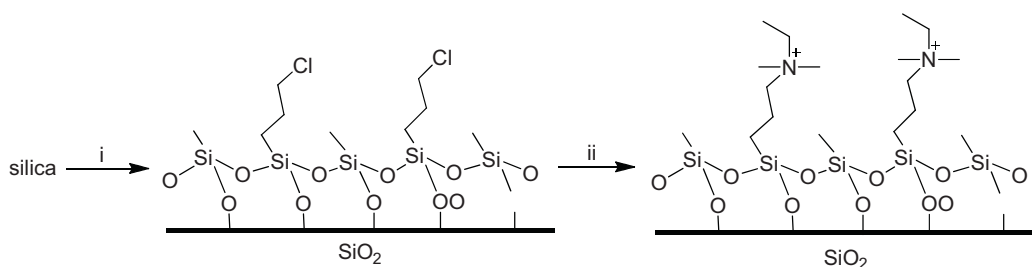


Fig. 1. Synthesis scheme for the preparation of PCP-SAX.

stationary phase with more hydrophilic characteristic would be favorable since it is beneficial to the effective elution in the ion exchange process.

In this study, we attempted to seek another route to the synthesis of a silica-based strong anion exchanger (SAX) based on polar-copolymerized approach [14]. This is an extension of our recent work in which a silica-based stationary phase for high performance liquid chromatography was prepared via polar-copolymerized approach [14]. Methyltrichlorosilane and 3-chloropropyltrichlorosilane has been copolymerized onto the surface of silica gel by using horizontal polymerization technique [15–17], followed by introducing quaternary ammonium functional groups. The effective ion exchange capacity could be easily controlled by adjusting the ratio of silanes, and the unwanted residual silanol groups could be effectively shielded by methyl group as well. The effective separation of common inorganic anions has been demonstrated and ion exchange mechanism was observed to dominate the separation process.

## 2. Experimental

### 2.1. Apparatus

A Waters HPLC system consisting of a 515 pump, a 20  $\mu$ L Rheodyne injector, and a 2487-UV absorbance detector was used to perform the chromatographic experiments. In some cases, an IC equipment (Techcomp Corp. Shanghai, China) was also used. Unless otherwise stated, the results were achieved at 30 °C with the flow rate of 1 mL/min. Solid state <sup>13</sup>C CP/MAS NMR characterization was performed on a Bruker (USA) DSX 300 NMR Spectrometer (300 MHz, 7.0T). Elemental analysis was measured on a Vario EL III elemental analysis system (Elementar, Germany). The void time was measured from the eluent signal in the UV detection. The plate numbers,  $N$  (N/m) of the separation to the tested anions were calculated from the equation  $N = 5.54(t_r/W_{1/2})$  where  $t_r$  is the net retention time of the analyte and  $W_{1/2}$  is the peak width at half peak height.

### 2.2. Synthesis of silica-based strong anion exchanger

A schematic diagram of the synthetic approach for the preparation of silica anion exchanger was outlined in Fig. 1. Firstly, silica gel (Fuji Silysia, 5  $\mu$ m particle size; 10 nm pore size; 315 m<sup>2</sup> g<sup>-1</sup> surface area) is silanized by the copolymerization between methyltrichlorosilane and 3-chloropropyltrichlorosilane to yield 3-chloropropyl silica. The pre-silanization procedures of the original silica particle were similar to our previous work [14]. After humidification, 10 g of silica was placed in a flask under a blanket of nitrogen, along with a stirring bar and 30 mL of anhydrous toluene. A solution of 1.2 mL of methyltrichlorosilane, 3 mL of 3-chloropropyl trichlorosilane and 20 mL of toluene was added to the pretreated silica gel. The reaction was allowed to continue for 24 h. The silanized silica was filtered and washed with dichloromethane,

methanol, water and methanol with 20 mL of each solvent successively. The silanized silica was dried at 80 °C overnight. Then 10 g of the above 3-chloropropyl silica was treated by 10 mL of N,N-dimethylethanamine in DMF at 80 °C for 24 h to produce positively charged groups on the surface of the silica particles. Stainless steel column (4.6 mm I.D.  $\times$  250 mm) was packed in common slurry method, in which the column was upward packed using slurries of the stationary phase in methanol. 40 MPa packing pressure was used and methanol was also used as the propulsive solvent. In this study, the polar-copolymerized strong anion exchanger column was named as PCP-SAX.

### 2.3. Measurement of effective ion-exchange capacity of PCP-SAX column

The effective ion exchange capacity of silica-based PCP-SAX column was roughly estimated through the breakthrough method [10]. Briefly, the column was completely flushed with 50 mM NaCl eluent for 2 h at 1 mL/min and then flushed with water for 0.5 h at 1 mL/min, finally flushed with 5 mM NaNO<sub>3</sub> eluent at 0.4 mL/min and at the same time the effluent was monitored by UV absorbance detector operated at 210 nm until the breakthrough curve was achieved. The column capacity ( $Q$ ) could then be calculated by the equation of  $Q = CF(t_b - t_0)$ . In the equation,  $C$  is the concentration of NaNO<sub>3</sub> eluent (mol/L),  $F$  is the flow rate of NaNO<sub>3</sub> eluent (mL/min),  $t_b$  is the time for complete breakthrough of NaNO<sub>3</sub> (min) and  $t_0$  is the void time of the column (min).

### 2.4. Preparation of saliva sample

A 1.02-g amount of saliva drawn from a healthy male volunteer was diluted in 10 mL of ultrapure water by using a volumetric flask, and centrifuged at 3000 rpm for 5 min, followed by filtration with a 0.45- $\mu$ m membrane filter. The saliva sample was then stored in a refrigerator.

## 3. Results and discussion

### 3.1. Synthesis and characterization

The synthesis scheme of PCP-SAX was shown in Fig. 1. The copolymerization between 3-chloropropyl trichlorosilane and methyl trichlorosilane onto the surface of silica gel was designed to control the surface coverage of reactive chlorine groups and at the same time to increase the stability of the resulting stationary phase. Chloropropyl group was used to be changed into the quaternary ammonium group in the following reaction. Methyl groups introduced served as linkers of the horizontal chloropropyl groups and also covered the silanols of the silica gel surface to a great extent. The column capacity could be easily controlled easily by adjusting the coverage amount of chloropropyl group introduced, and then controlling the final amount of quaternary ammonium charged groups. In addition, the unwanted interaction from resid-

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