



# Poly(ethylene oxide)-bonded stationary phase for separation of inorganic anions in capillary ion chromatography



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## ABSTRACT

A tosylated-poly(ethylene oxide) (PEO) reagent was reacted with primary amino groups of an amino-propylsilica packing material (TSKgel NH<sub>2</sub>-60) in acetonitrile to form PEO-bonded stationary phase. The reaction was a single and simple step reaction. The prepared stationary phase was able to separate inorganic anions. The retention behavior of six common inorganic anions on the prepared stationary phase was examined under various eluent conditions in order to clarify its separation/retention mechanism. The elution order of the tested anions was iodate, bromate, bromide, nitrate, iodide, and thiocyanate, which was similar as observed in common ion chromatography. The retention of inorganic anions could be manipulated by ion exchange interaction which is expected that the eluent cation is coordinated among the PEO chains and it works as the anion-exchange site. Cations and anions of the eluent therefore affected the retention of sample anions. We demonstrated that the retention of the analyte anions decreased with increasing eluent concentration. The repeatability of retention time for the six anions was satisfactory on this column with relative standard deviation values from 1.1 to 4.3% when 10 mM sodium chloride was used as the eluent. Compared with the unmodified TSKgel NH<sub>2</sub>-60, the prepared stationary phase retained inorganic anions more strongly and the selectivity was also improved. The present stationary phase was applied for the determination of inorganic anions contained in various water samples.

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## 1. Introduction

Ion chromatography (IC) has been a well-established analytical technique and the preferred method for the analysis of inorganic or small organic anions and cations. Various types of stationary phases and separation modes have been developed in IC since its introduction in 1975 [1]. IC stationary phases are mainly polymer-based and silica-based. Although silica-based packings cannot be used in strongly acidic or alkaline mobile phases, and have residual silanols which affect separation of biological samples, they have specific advantages such as resistance to organic solvents, high rigidity, and fast mass transfer. In addition, the rich silanol groups onto the surface of silica gel allow easy introduction of many functional groups onto the gel. Thereby, many researchers have been interested in developing silica-based stationary phases for IC [1–3]. Liu et al. prepared ammonium anion-exchange stationary phases by chemical bonding, deactivation, and quaternization on silica. Anions in oil field water were determined successfully on this column [4]. Phenylpropanolamine modified silica for the separation of acidic, basic, and uncharged drugs, and inorganic

anions by reversed-phase and anion-exchange interactions was prepared by Wongyai modifying the pH of the mobile phase manipulated the retention of anions [5]. The preparation and characterization of a novel multi-interaction stationary phase based on 4,4'-dipyridine modified silica were described [6]. Different series of analytes including PAHs, phenols, inorganic and organic anions were successfully separated on this multi-interaction stationary phase, respectively. The multi-interaction mechanism including  $\pi$ - $\pi$ , hydrophobic, electrostatic and anion-exchange interactions is involved in the chromatographic separation.

A poly(ethylene glycol) (PEG) stationary phase was used as the stationary phase in reversed-phase LC by Guo et al. for the separation of phenyl compounds and in Chinese medicine [7]. Besides the hydrophobic interaction, PEG moieties can provide some other interactions such as hydrogen bonding and dipole-dipole interaction. The PEG moiety also could form a helix-like conformation in the organic aqueous media. PEG-bonded silica-based columns such as, Discovery HS PEG column (Supelco; Bellefonte, PA) are now commercially available and they have been applied in the analysis of natural products [8,9].

Most stationary phases employed in IC have functional groups with charged or chargeable moieties, where ionic analytes experience electrostatic attractive or repulsive forces. Inorganic anions could also be separated even if the stationary phase possesses

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no ion exchange site. Lamb and Smith prepared a crown ether-bonded stationary phase and a cryptand-bonded stationary phase for the separation of alkali metal cations as well as anions. It was reported that the permanently coated alkylated macrocycles such as *n*-tetradecyl-18-crown-6 ether (18C6) or *n*-decylcryptands onto a reversed-phase column formed positively charged anion-exchange sites when they combined with eluent cations. Using 18C6 as the eluent additive, it was found that anion retention increased with increasing eluent strength and organic modifier content [10]. Rong et al. developed and examined PEG or poly(ethylene oxide) (PEO) as the stationary phase for IC by physically coating or chemically bonding [11–15]. For physically coated or chemically bonded PEG/PEO on C30, partitioning was dominantly involved for the retention of analyte anions [11–13]. On the other hand, the chemically bonding on aminopropylsilica improved the selectivity for anions, where it was expected that anions retained in the ion exchange mode. It was suggested that the cations of eluent coordinated among the multiple PEO chains *via* ion-dipole interaction work as the anion exchange sites [14,15]. The present work examines a new PEGylation reagent for the preparation of the PEO-bonded stationary phase for the separation of inorganic anions in capillary IC. The tosylated-poly(ethylene oxide) reagent was cheaper compared with previous PEGylation reagent such as methyl-PEO-NHS (*N*-hydroxysuccinimide) ester which is very expensive.

## 2. Experimental

### 2.1. Apparatus

The chromatographic measurements were carried out by using a  $\mu$ LC system. The eluent was supplied by a pump 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). A model M435 micro injection valve (Upchurch Scientific, Oak Harbor, WA, USA) with an injection volume of 0.2  $\mu$ L, was used as the injector. A UV-970 UV-vis detector (Jasco, Tokyo, Japan) was operated at 210 nm and all of the data were collected by a CDS data processor (LASOFT, Chiba, Japan). The inlet pressure was monitored by an L.TEX-8150 Pressure sensor (L.TEX). Elemental analysis of the packing materials was carried out by using an MT-6 CHN Corder (Yanaco, Kyoto, Japan).

### 2.2. Reagents and materials

Reagents employed were of guaranteed reagent grade and were obtained from Wako Pure Chemical Industries (Osaka, Japan), unless otherwise noted. Polyethylene glycol monomethyl ether *p*-toluenesulfonate (Tosylated-PEO, M.W. 1000,  $n \approx 18.5$ ) was obtained from Aldrich (Rockford, IL, USA). Purified water was produced in the laboratory by using a GS-590 water distillation system (Advantec, Tokyo, Japan). All solutions used in this work were prepared using the purified water. Porous 3-aminopropylsilica, TSKgel NH<sub>2</sub>-60 (5  $\mu$ m particle diameter, 60 Å mean pore diameter) was taken from the packed column obtained from TOSOH (Tokyo, Japan).

### 2.3. Preparation of PEO-bonded stationary phase

A 0.21 g of TSKgel NH<sub>2</sub>-60 and 0.35 g of tosylated-PEO added into 5 mL of acetonitrile in a 20-mL vial, and the solution was then poured into the stainless steel column. The reaction took place in oven at 75 °C for 24 h, followed by washing with methanol. Fig. 1 shows the expected scheme of the reaction. The separation column was prepared from a fused silica capillary tube (0.32 mm

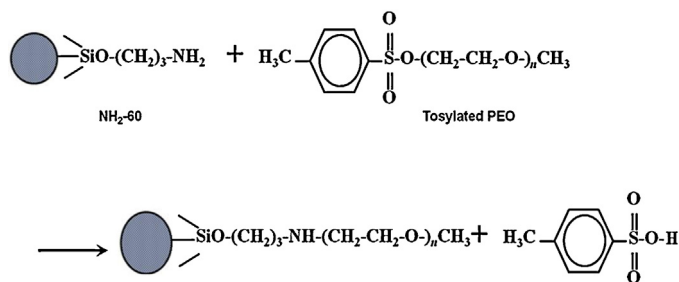


Fig. 1. The structure of the PEO reagent employed as well as the expected reaction scheme.

i.d.  $\times$  100 mm) using a slurry packing method previously reported [16], followed by washing with a phosphate buffer (pH 7.5) for 1 h.

### 2.4. Preparation of water and saliva samples

For saliva sample, a 0.4 mL of saliva diluted in 2 mL deionized water, 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 the refrigerator. Tap water samples were centrifuged at 3000 rpm for 3 min, followed by filtration using a 0.45  $\mu$ m membrane filter.

## 3. Results and discussion

### 3.1. Column characterization

The aminopropylsilica and the PEO-bonded stationary phase were characterized by elemental analysis. The percentages by weight for carbon and hydrogen that contained in aminopropylsilica (1.1 mmol/g) were 5.18 and 1.55%, respectively, while the percentages by weight for the latter stationary phase were 10.08 and 2.30% for carbon and hydrogen, respectively. The increase of the carbon and hydrogen content for the latter demonstrated that PEO was bonded to aminopropylsilica successfully. According to the results, carbon and hydrogen contained in the PEO-bonded stationary phase were 8.40 and 22.8 mmol/g, respectively. The surface coverage of the PEO on the present stationary phase was 0.12 mmol/g, which was calculated from the difference in the carbon content between the aminopropylsilica and the PEO-bonded stationary phase. In other words, 11% of amino groups of the aminopropylsilica were bonded with PEO.

### 3.2. Retention behaviors of anions on PEO-bonded stationary phase

The prepared stationary phase could retain six anions satisfactorily. The separation was achieved in reasonable time. It was suggested that the cations of eluent coordinated with the oxygen atoms of multiple POE chains *via* ion-dipole interaction, work as the anion exchange sites. The eluent and analyte anions can compete for the trapped cation [14,15]. The proposed coordination of cation structure is shown in Fig. 2. Inorganic anions can therefore be separated on the POE-bonded phases in the ion-exchange mode. The elution order was iodate, bromate, bromide, nitrate, iodide, and thiocyanate. The elution order of the anions observed was similar to that observed in common IC. It was also found that bromide and nitrite could not be separated on the prepared PEO-bonded stationary phase, such retention behavior was also observed in other works using PEO-bonded stationary phases [14,15].

Aminopropylsilica as based material has amino group that will be an anion exchange site but the prepared stationary phase provided better selectivity and strong retention for the six anions, compared with the unmodified NH<sub>2</sub>-60 stationary phase. Using

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