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# Functionalized anion exchange stationary phase for separation of anionic compounds



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## ABSTRACT

Synthesis of the multilayered stationary phases containing quaternary ammonium functional groups on the silica support was described. Bonded phases were characterized by elemental analysis, solid state  $^{13}\text{C}$  NMR spectroscopy and chromatographic methods. The surface of silica support was coated with different number of polymeric layers formed by condensation polymerization of primary amine (methylamine) with diepoxide (1,4-butanedioldiglycidyl ether). A series of stationary phases with different number of polymerized layers were tested. Separation of an inorganic anions sample ( $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{NO}_2^-$ ,  $\text{Br}^-$ ,  $\text{NO}_3^-$ ) and nucleotides was performed.

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## 1. Introduction

Ion chromatography (IC) is one of the most common applied techniques for the separation of various ionic compounds, inorganic and organic [1–3]. Since IC offers many possibilities of application it is used in different branches of current analytical chemistry [4–6]. During last few years, the number of ion-exchange materials that have been developed for ion chromatography has significantly increased [4,7].

The most ion exchangers used for ion chromatography are synthesized on organic polymers [8,9]. The most commonly used supports for ion exchangers synthesis are: styrene/divinylbenzene (PS/DVB) copolymers [10,11], ethylvinylbenzene/divinylbenzene (EVB/DVB) copolymers [12], and polyvinyl and polymethacrylate resins [13–15]. Outside of the ion chromatography, silica gel is the most important material applied in separation techniques as both the bulk adsorbent (unmodified) and the support for the stationary bonded phases (modified) [16–18]. Physical stability and well defined porous structure are the main advantages of silica-based packings. These properties assure rapid mass transfer, good loadability, and high reproducibility [19,20]. Unfortunately, silica reveals limited stability in the pH range 2–10. In opposite, porous copolymers are stable in wider pH range, also in alkaline solution. On the other hand, silica-based bonded phases serve higher

chromatographic efficiency and greater mechanical stability in comparison to organic polymers. Dissolving of silica gel at high and low pH can be prevented by using a precolumn packed with pure large-particle silica gel. The precolumn should be placed between the pump and injector. This precolumn presaturates the mobile phase with silicate which should hamper the silica support in the analytical ion-exchange column against dissolving [21].

Ion exchange silica based bonded phases are usually formed by direct reaction of an appropriate silane with a silica support. The bonded silane must contain a functional group which can either be converted to an ion exchange group or permit to attach an ion exchange group to it.

One of the most popular anion-exchange groups used in IC are the quaternary ammonium groups and amine groups [22,23]. Anion exchangers are classified as strong or weak. This classification bases on how much the ionization state of the functional groups changes with pH. A strong ion exchanger over a wide pH range has the same charge density on the surface. The charge density of a weak ion exchanger changes with a pH. As a result, the selectivity and the capacity of a weak ion exchanger are different at different pH of the mobile phase in the opposite to strong anion exchangers.

Packings containing quaternary ammonium groups possess positive charge in pH range 1–14, thus they are strong anion exchangers. On the other hand, tertiary, secondary and primary amino groups can be positively charged below pH~9.

The stationary phases with quaternary ammonium groups exhibit good selectivity for separation of inorganic and organic

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anions. One of the new method of preparation stationary phase with quaternary ammonium groups is the methodology introduced by Pohl and coworkers [24,25]. During the synthesis hyperbranched anion-exchange polymer stationary phase is created, which contains quaternary ammonium groups as well as tertiary and secondary amine groups.

The main aim of this work was to synthesize dendrimer anion exchanger on the silica gel surface which exhibits high efficiency and selectivity of chromatographic separation. The goal of the study is to obtain materials providing better separation of both inorganic and organic compounds. Stationary phases were tested according to separation of inorganic anions and applied for separation of nucleotides.

## 2. Experimental

### 2.1. Instrumentation

The packing material under study was packed into 150 mm × 2.1 mm. PEEK columns. All columns were packed using a DT 122 packing pump (Haskel, Burbank, CA, USA) under the pressure of 25 MPa.

Chromatographic analyses of inorganic anions were performed with an ion chromatograph Dionex model, ICS-3000 consisting of pump, a degasser, an autosampler, a thermostat, and a conductometric detector. Data collection and analysis were performed on a personal computer using the Chromeleon Chromatography Management 6.8 software (Dionex Corporation, Sunnyvale, USA). The Dionex Suppressor ASRS-ULTRA II 2-mm was installed between the analytical column and conductometric detector.

Analyses of nucleotides were performed using a Shimadzu 10 liquid chromatograph (Kyoto, Japan) equipped with a multisolvent

delivery system (LC-10AD), a manual injector with a 20- $\mu$ l loop, a diode-array UV-vis detector (SPD-M10A), and a computer data acquisition station with Class VP software.

### 2.2. Chemicals and eluents

The packing material was prepared by a modification of silica gel Kromasil 100 (Akzo Nobel, Bohus, Sweden) with particle size 5  $\mu$ m and pore diameter 100 Å. Specific surface area of bare silica gel was 313 m<sup>2</sup>/g and pore volume was 0.87 cm<sup>3</sup>/g.

The following reagents were used for the chemical modification of the silica gel support material: methylamine (MA 40% in H<sub>2</sub>O, v/v) and 1,4-butanedioldiglycidyl ether (BDDE 95% in H<sub>2</sub>O, v/v) purchased from Sigma-Aldrich Chemie (Steinheim, Germany).

Sodium fluoride, sodium chloride, sodium nitrite, potassium nitrate, potassium bromide, and sodium hydrogen carbonate were from POCh (Gliwice, Poland). The concentration of the tested anions was 20 mg/l.

Water was purified using a Mili-Q system. All eluents were prepared daily and were pure per analysis grade.

Standards of uridine 5'-monophosphate disodium salt (U), adenosine 5'-monophosphate disodium salt (A), cytidine 5'-monophosphate (C), guanosine 5'-monophosphate disodium salt hydrate (G) were purchased from Sigma-Aldrich (Gillingham, Dorset, UK).

The buffers solutions for nucleotides analysis were prepared with the use of high purity substances ammonium formate (HCOONH<sub>4</sub>) and formic acid (HCOOH) (Sigma-Aldrich, Gillingham, Dorset, UK).

Nucleotides were analyzed with the mobile phases composed of 50 mM HCOONH<sub>4</sub>/HCOOH pH 3.0. The fresh buffer solution was daily prepared. The flow rate was 0.5 ml/min. UV-vis detection was performed at wavelength  $\lambda$ =254 nm.

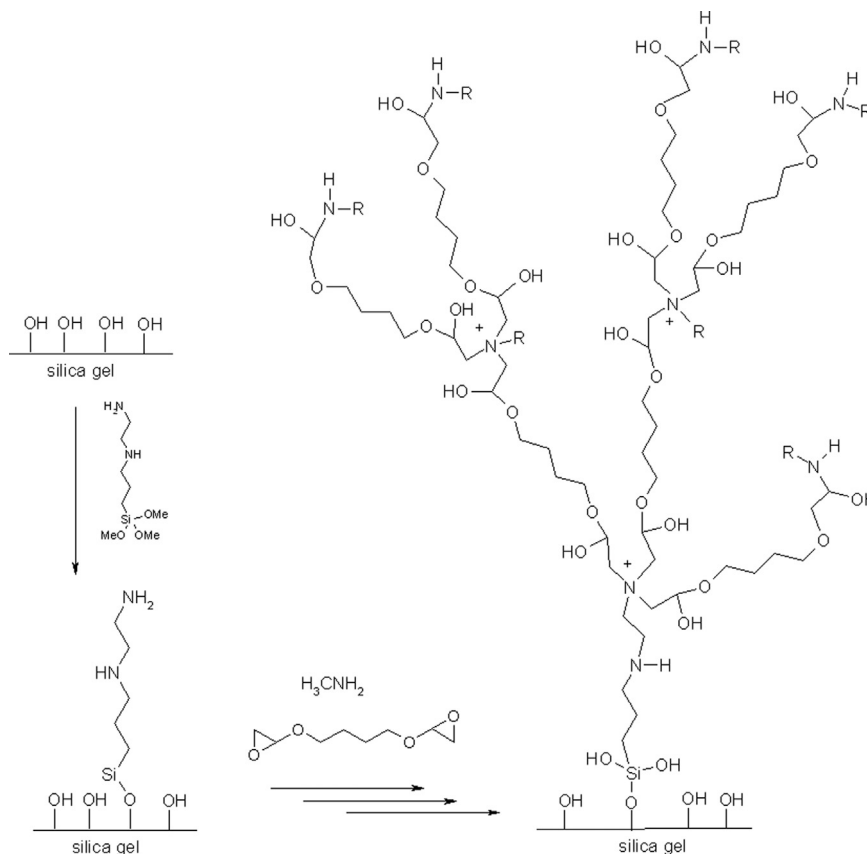


Fig. 1. Synthesis procedure of the anion-exchanger (structure with two layers of anion exchange sites).

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