



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}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 (F^- , Cl^- , NO_2^- , Br^- , 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 $\text{pH} \sim 9$.

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- μ 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 μ m and pore diameter 100 Å. Specific surface area of bare silica gel was 313 m²/g and pore volume was 0.87 cm³/g.

The following reagents were used for the chemical modification of the silica gel support material: methylamine (MA 40% in H₂O, v/v) and 1,4-butanedioldiglycidyl ether (BDDE 95% in H₂O, 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 (HCOONH₄) and formic acid (HCOOH) (Sigma-Aldrich, Gillingham, Dorset, UK).

Nucleotides were analyzed with the mobile phases composed of 50 mM HCOONH₄/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 λ =254 nm.

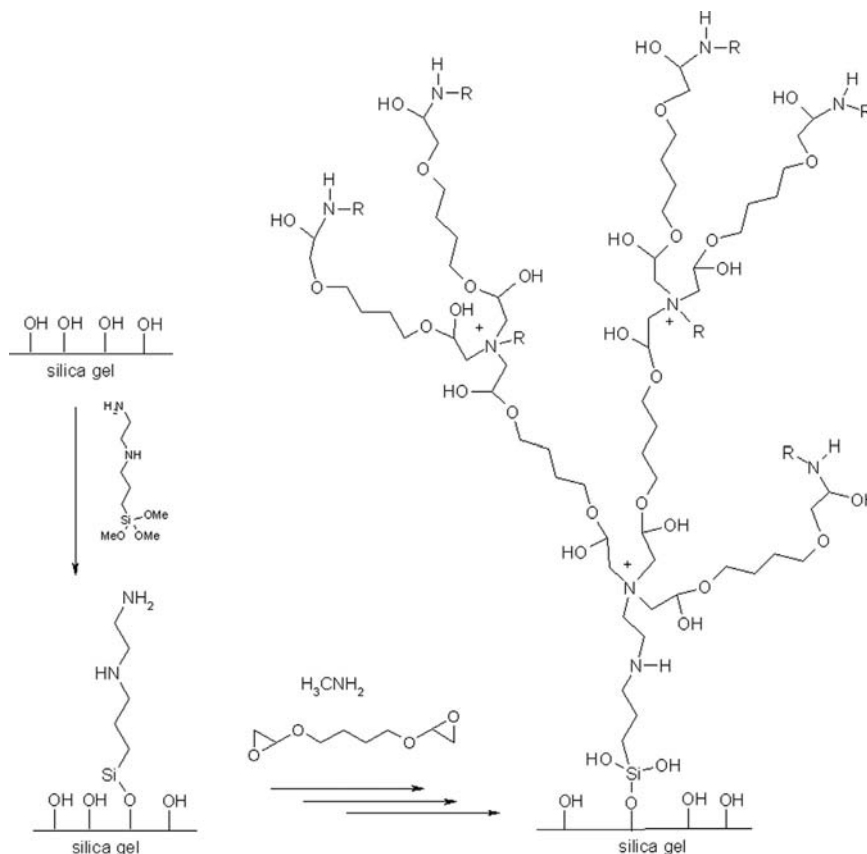


Fig. 1. Synthesis procedure of the anion-exchanger (structure with two layers of anion exchange sites).

2.3. Preparation of the anion-exchanger

Modification of the silica gel with organic ligands containing primary and secondary amine groups was performed according to methodology described earlier [18]. Five grams of silica gel was dried at 180 °C under vacuum to remove adsorbed water. Further, the 3-(2-aminoethylamino)propyl-trimethoxysilane was added. Reaction was carried out for 12 h at the temperature 80 °C. The modified silica gel was flushed with toluene, methanol, hexane and dried under vacuum. The amine-bonded silica material was used as a support for anion-exchanger synthesis during condensation polymerization.

The basic condensation polymerization chemistry depends on methylamine (MA) and, 4-butanedioldiglycidyl ether (BDDE) as monomers to build a branching polymer that possesses quaternary ammonium anion exchanger sites. Reaction was carried out at 60–70 °C. A 15 ml of BDDE monomer (7.0–7.4%) was added to the modified silica gel and reacted for 30 min. After reaction the mixture was filtered and rinsed with redistilled water. Following the addition of 15 ml 3.0–5.0% (v/v) of MA was added to the modified silica gel and reacted for 30 min, filtered and rinsed with redistilled water. These two steps allowed creating quaternary ammonium group which constitute the anion exchange center. The process was repeated two, three, four, seven, eleven and fifteen times to make material with increased number of quaternary ammonium groups. The chemical structure of the anion-exchanger after two reaction cycles is shown in Fig. 1.

3. Results and discussion

3.1. Physico-chemical characterizations of the stationary phases

The obtained materials were a subject for physico-chemical characterization. Elemental analysis, Fourier Transform Infrared spectroscopy (FT-IR) and solid state NMR spectroscopy (^{29}Si and ^{13}C CP-MAS) give information about the structure of synthesized anion-exchanger.

Basis of the elemental analysis, the percentage of carbon and hydrogen in the structure of anion-exchanger were determined. The results are presented in Table 1. The number of anion exchange sites increases with the number of reaction cycles. It allows to control the anion capacity of the stationary phase preparing given number of synthesis cycles on the support.

Dendrimer anion exchanger synthesized on the silica gel contains more nitrogen in the structure than analogous material synthesized on the porous polymer support. The nitrogen percentage on silica base material is around two times higher than in the polymer-based material after the same number of reaction cycles. As a result, the number of anion exchange sites is significantly higher in the case of silica based stationary phase. More anion exchange sites per surface unit of the stationary phase should

Table 1
Elemental composition of prepared series of anion exchangers, compared with analogous material synthesized on the polymer support.

Number of reaction cycles	Nitrogen content (%)	Carbon content (%)	Hydrogen content (%)	Nitrogen content (%) in polymer based stationary phase
1	1.72	10.63	1.87	–
2	1.78	12.67	2.19	–
3	1.82	14.42	2.45	0.650
4	1.88	16.45	2.80	–
7	2.02	22.17	3.84	1.095
11	2.35	28.71	5.06	1.295
15	3.07	39.53	6.78	1.440

result in higher anion capacity of the material and provide higher efficiency of the separation.

Bonding of the silane to silica gel was confirmed by ^{29}Si CP-MAS NMR spectroscopy. After modification the intensity of signals geminal silanols (Q_2 ; $\delta = -92$ ppm), single silanols (Q_3 ; $\delta = -102$ ppm) decrease and signal of siloxane groups (Q_4 ; $\delta = -112$ ppm) increase [26]. New signals appeared at chemical shifts: T_3 ; $\delta = -66.3$ ppm and T_2 ; $\delta = -59.2$ ppm [27]. The absence of T_1 signals at $\delta = -48$ ppm indicates a high degree of the cross-linking of ligands on the silica surface [26–30]. The ^{29}Si NMR spectrum is presented in Supplement S1A.

In the ^{13}C CP-MAS NMR spectrum one can observe signals: at $\delta = +26.1$ ppm belongs to the methylene group ($-\text{CH}_2-$), as a result of carbon chain formation. Signals in the range between $\delta = +60$ –75 ppm correspond to methylene groups connected with oxygen ($-\text{O}-\text{CH}_2-$), nitrogen ($-\text{CH}_2-\text{N}-$) and carbon connected to ether bond and hydroxyl group. The ^{13}C NMR spectrum is presented in Supplement S1B.

The structure of synthesized material was also confirmed by FT-IR spectroscopy. In the spectra few characteristic signals may be recognized. The N–H stretches of amines are in the region 3300–3000 cm^{-1} [31]. These bonds are in the same region as O–H stretches which are also present in the bonded ligand (hydroxyl group). After support modification two new signals that correspond to bonded organic moiety (C–H bending vibrations at 1450 cm^{-1} and stretch at 2900 cm^{-1}) are observed [31]. Signals corresponding to C–N and C–O stretch vibrations may be observed under large unsymmetrical signal in the range 1000–1200 cm^{-1} (C–N at 1080–1200 cm^{-1} and C–O at 1050–1150 cm^{-1}) [31]. The IR spectrum is presented in Supplement S2.

Synthesized adsorbent possess quaternary ammonium groups which function as an anion exchange center. Additionally, because of an incomplete dendrimer structure, tertiary and secondary amines are also presented. These functional groups may constitute anion exchanger sites depending on the pH. In the case of secondary amines, they can be protonated and possess positive charge in the pH lower than 8.

The synthesized stationary phases exhibit good thermal stability, suitable for their use in ion chromatography even carried out with higher temperatures. Thermogravimetric measurements (DSC and TG) indicated that initial decomposition temperatures of the investigated anion exchangers is in the range of 236–362 °C [32].

3.2. Chromatographic characterization of the stationary phases

All of synthesized stationary phases containing 1, 2, 3, 4, 7, 11 and 15 bonded layers were tested using five inorganic anions. Separated mixture contained fluoride, chloride, nitrite, bromide and nitrate anions. As a mobile phase a series of buffers were used: sodium hydrogen carbonate (2–10 mM, pH=8.52–8.591), sodium benzoate (1–10 mM, pH=6.55–7.18), sodium salicylate (2 mM, pH=6.42), *o*-phtalic acid (2 mM, pH=3.70), and tartaric acid (1 mM, pH=3.72). Satisfactory results were obtained using sodium hydrogen carbonate and sodium benzoate. Other buffers did not provide separation and/or caused unsymmetrical peaks and very low efficiency. The most common buffers, sodium carbonate and sodium hydroxide were not tested due to the high pH. High pH causes the leaching of the stationary phase. The column void volume was obtained from the solvent peak.

The highest pH of the mobile phase used was 9 in the case of sodium hydrogen carbonate. In these conditions the stationary phase works stable without any evidence of stationary phase leaching. Additionally, in this condition synthesized anion exchanger allows to separate the mixture of inorganic anions. This is a very important property of these materials. Although anion analyses are usually carried out with alkaline eluents (pH in the

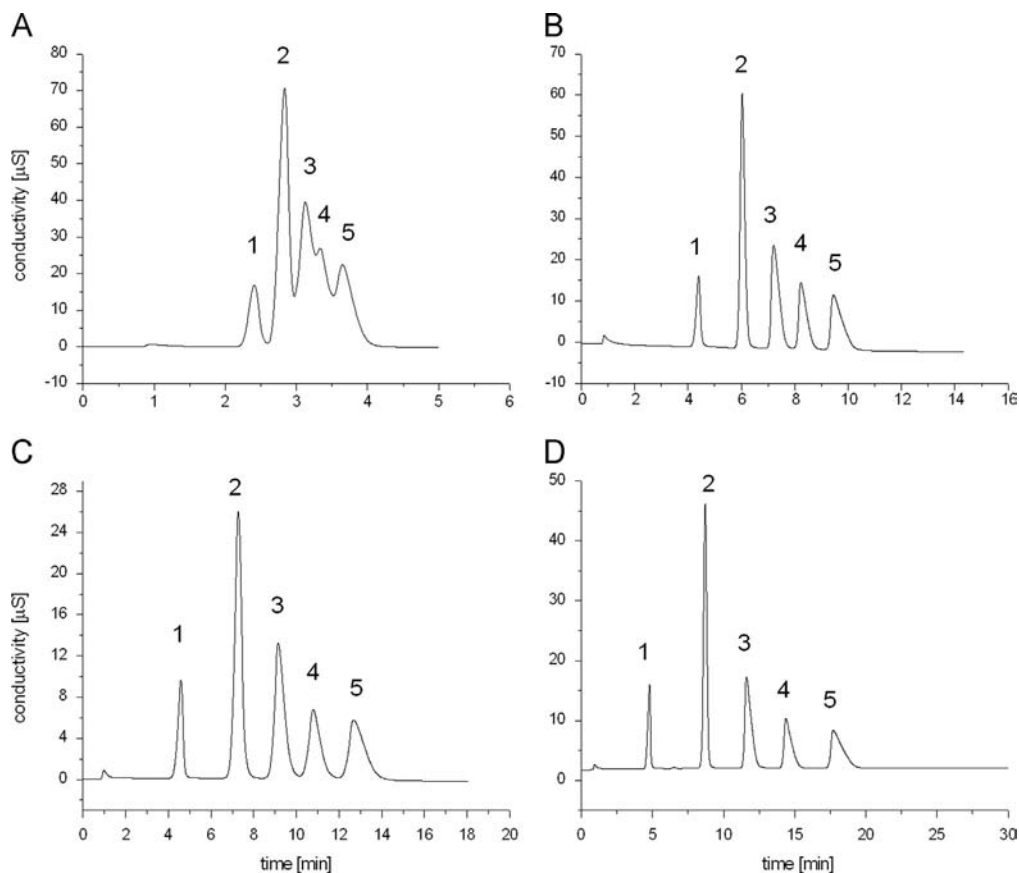


Fig. 2. Separation of inorganic anions on the stationary phases synthesized during 1-A, 2-B, 3-C add 4-D reaction cycles. Mobile phase: 2 mM NaHCO₃ (pH=8.52), sample: (1) F⁻, (2) Cl⁻, (3) NO₂⁻, (4) Br⁻, (5) NO₃⁻.

range of 8–13), the separation carried out using 2 mM NaHCO₃ (pH=8.52) was sufficient. Unfortunately, because of too high pH, the typical eluents, sodium carbonate and potassium hydroxide cannot be applied as a mobile phase for anion-exchangers synthesized on the silica gel.

Exemplary chromatograms for separation mixture of inorganic anions on the anion exchanger after 1–4 reaction cycles using 2 mM NaHCO₃ (pH=8.52) as an eluent are given in Fig. 2. Under these conditions, the stationary phase with 1 bonded layer shows low retention and not allows to separate test mixture. Other stationary phases exhibit sufficient retention and selectivity. Stationary phases with higher than 4 bonded layer exhibit extremely high retention which result in retention times longer than one hour. This fact eliminates mentioned materials from practical applications.

Detailed parameters of the five anion separations were listed in Table 2. As it was discussed before, stationary phase with one bonded layer is insufficient for the proper separation. Increasing number of bonded layers caused increase of the retention and selectivity. Two bonded layers of dendrimer anion exchanger guarantee the proper separation with sufficient selectivity and resolution. Further increase of number of bonded layers causes the increase of the retention, but the selectivity remains almost constant. Higher retention results also in worse peak symmetry. The values of the efficiency change between columns and reaches values up to 46,000 plates per meter. This provides a huge peak capacity, which is extremely important in chromatographic separations.

The change of mobile phase from sodium hydrogen carbonate to sodium benzoate influences significantly the result of separation. First of all it has to be mentioned that the stationary phase with one bonded layer does not provide separation of any

compound. An application of sodium benzoate offers better chromatographic parameters of separation on stationary phases with 2, 3 and 4 bonded layers. This mobile phase provide lower retention with comparable selectivity and resolution (see Table 3). It enables sufficient separation in shorter time what is important from the practical point of view. Additionally, when the sodium benzoate is used as a mobile phase, the symmetry of obtained peaks is better (f_{AS} in the range 0.86–1.57). Stationary phase with 4 bonded layers offers efficiency in the range 20,900–46,586, which is comparable with commercially available columns [8,33]. Moreover, sodium benzoate exhibits lower pH (pH=7.05 for concentration 5 mM) than sodium hydrogen carbonate (pH around 8.6), that is better for the stationary phase synthesized on the silica gel. It confirms that application of proper mobile phase with lower pH allow to use anion exchangers synthesized on the silica gel, which are not so popular than materials synthesized on the polymer support. The synthesis of dendrimer anion exchanger during given number of reaction cycles (given number of anion-exchange sites) allows obtaining stationary phases with desired anion capacity. As a result, the retention of anions may be controlled twice: during the synthesis of the stationary phase and by the selection of the mobile phase.

The increase of the buffer concentration in the mobile phase (from 2 mM to 10 mM of sodium hydrogen carbonate and from 1 mM to 10 mM for sodium benzoate) causes the decrease of the retention of all anions. The concentration of the buffers does not influence the peak symmetry, selectivity and resolution. It suggests that the selectivity of anions separation depends mostly on the properties of anion exchanger—the type of anion exchange sites and depends less on the number of bonded layers. The results are listed in Table 4.

Table 2Chromatographic parameters of separation on the stationary phases with different number of bonded layers using 2 mM NaHCO₃ (pH=8.52) as a mobile phase.

Number of bonded layers	Ion	Retention factor (<i>k</i>)	Selectivity (α)	Resolution (R_s)	Efficiency (N/m)	Asymmetry factor (f_{AS})
1	F ⁻	1.19			8,318	1.57
	Cl ⁻	1.57	1.32	0.66	11,914	–
	NO ₂ ⁻	1.84	1.17	–	–	–
	Br ⁻	2.03	1.10	–	–	–
	NO ₃ ⁻	2.31	1.14	–	–	–
2	F ⁻	3.00			24,780	0.89
	Cl ⁻	4.48	1.49	5.35	37,726	1.16
	NO ₂ ⁻	5.55	1.24	2.72	18,540	1.83
	Br ⁻	6.48	1.17	1.88	23,846	1.81
	NO ₃ ⁻	7.59	1.17	1.82	15,253	2.43
3	F ⁻	3.16			11,347	0.82
	Cl ⁻	5.61	1.77	5.16	15,753	1.02
	NO ₂ ⁻	7.31	1.30	2.64	13,247	1.38
	Br ⁻	8.81	1.21	1.84	13,220	1.29
	NO ₃ ⁻	10.53	1.20	1.64	9,487	1.69
4	F ⁻	3.35			20,833	0.80
	Cl ⁻	6.92	2.06	10.32	46,266	0.98
	NO ₂ ⁻	9.55	1.38	4.67	21,066	1.97
	Br ⁻	12.07	1.26	3.14	24,800	2.00
	NO ₃ ⁻	15.09	1.25	2.76	15,433	2.60

Table 3

Chromatographic parameters of separation on the stationary phases with different number of bonded layers using mobile phase 5 mM sodium benzoate (pH=7.05) as a mobile phase.

Number of bonded layers	Ion	Retention factor (<i>k</i>)	Selectivity (α)	Resolution (R_s)	Efficiency (N/m)	Asymmetry factor (f_{AS})
2	F ⁻	2.13			11,913	1.57
	Cl ⁻	3.13	1.47	3.45	21,686	1.15
	NO ₂ ⁻	4.05	1.29	2.76	19,080	0.90
	Br ⁻	4.65	1.15	1.57	21,520	1.06
	NO ₃ ⁻	5.50	1.18	1.91	18,473	1.43
3	F ⁻	2.25			11,860	1.13
	Cl ⁻	3.61	1.60	4.37	13,353	0.86
	NO ₂ ⁻	4.76	1.32	2.62	15,873	0.89
	Br ⁻	5.61	1.18	1.71	17,533	0.95
	NO ₃ ⁻	6.69	1.19	1.89	16,073	1.01
4	F ⁻	2.37			20,900	1.37
	Cl ⁻	4.45	1.88	8.01	40,200	1.13
	NO ₂ ⁻	6.13	1.38	5.28	42,900	1.15
	Br ⁻	7.44	1.21	3.43	44,840	1.13
	NO ₃ ⁻	9.08	1.22	3.69	46,586	1.15

Table 4

Changes of the retention factor of inorganic anions with the buffer concentration.

NaHCO ₃ concentration (pH)	Retention factor (<i>k</i>)				
	F ⁻	Cl ⁻	NO ₂ ⁻	Br ⁻	NO ₃ ⁻
2 mM (pH=8.52)	1.88	4.10	5.64	7.01	8.57
5 mM (pH=8.61)	1.63	3.10	4.17	5.10	6.18
8 mM (pH=8.70)	1.11	2.24	3.12	3.84	4.73
10 mM (pH=8.91)	1.02	2.08	2.10	3.59	4.42

3.3. Analysis of nucleotides

The silica-based dendrimer stationary phases may be successfully applied for the separation and determination of four 5'-monophosphate nucleotides (CmP, UmP, AmP, GmP). Fig. 3 presents results of their separation on four packing materials differing in the number of anion-exchange layers on the surface. Increasing the number of bonded layers (from 1 to 4) causes the greater retention of each nucleotide. This is a result of increasing number of anion-exchange centers on the surface of studied chromatographic materials. Consequently, the retention of nucleotides depends mainly on the number of NR₄⁺ groups. Furthermore, additional effect is also important, namely the penetration of

nucleotides inside the robust dendrimer ligands and next their interaction with quaternary ammonium groups localized inside the pores of the support.

Results presented in Fig. 3 prove that increasing the number of anion-exchange layers on the silica surface causes not only the greater analysis time, but also greater resolution. On the other hand it may be concluded that regardless the number of layers the separation of studied mixture is complete in case of all packing materials used in the experiments. Therefore, the dendrimer silica-based stationary phase covered with only one anion-exchange layer should be used in the routine analysis of nucleotides by ion chromatography. The separation of nucleotides for this packing material was achieved within 9 min (Fig. 3A).

4. Conclusions

In this work a synthesis of the functionalized stationary phases with quaternary ammonium groups on the silica surface was presented. From the practical point of view it may be reasonable to synthesize stationary phases with only 2 or 3 layers, that provide satisfactory selectivity and relatively low retention. The amount of anion exchange sites may be controlled during

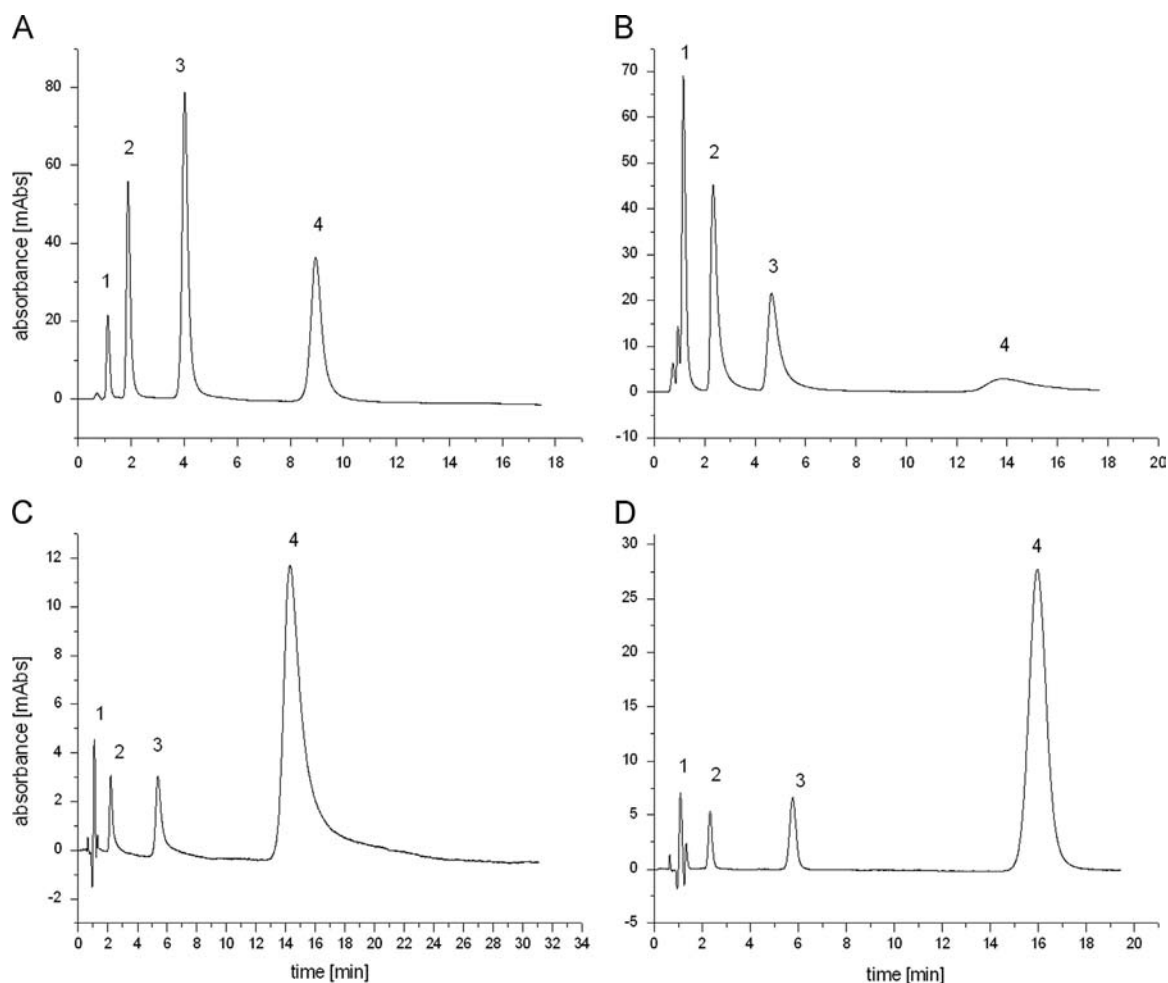


Fig. 3. The chromatograms of nucleotides separation with the use of silica-based dendrimer stationary phases for ion chromatography: (A) one anion-exchange layer, (B) two anion-exchange layers, (C) three anion-exchange layers, (D) four anion-exchange layers. Chromatographic conditions: mobile phase 50 mM $\text{HCOONH}_4/\text{HCOOH}$ pH=3; flow rate 0.5 ml/min, UV-vis detection λ 254 nm. Notification: 1—CmP, 2—UmP, 3—AmP, 4—GmP.

synthesis because anion capacity increases with the number of reaction cycles.

Although the silica based anion exchanger may be operated with lower number of mobile phases, the application of sodium benzoate (pH around 7) provide better chromatographic parameters than commonly used sodium hydrogen carbonate, which is more alkaline. Synthesized material offers properties (resolution, efficiency) comparable to commercially available columns. Silica based anion exchangers with dendrimer structure may be an efficient material for ion-chromatographic separation of inorganic anions as well as for separation of nucleotides, depending on the mobile phase used.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at <http://dx.doi.org/10.1016/j.talanta.2014.04.016>.

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