



Anion separations for liquid chromatography using propylpyridinium silica as the stationary phase

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ABSTRACT

This work describes the characterization and potential applications of a silica-based anion-exchange phase prepared by a two-step modification process that incorporates a propylpyridinium group. The effects of pH and eluent concentration on anion separation were examined using 150 mm × 3.9 mm HPLC columns packed with the new phase. The mobile phase pH values ranged from 3.8 to 6.6 using phthalic acid/Tris solutions. The best separation was achieved using 2.5 mmol L⁻¹ phthalate/2.4 mmol L⁻¹ Tris solution at pH 4.2 as mobile phase with non-suppressed conductivity detection. The new stationary phase was used for the separation of some inorganic and organic anions showing good resolution. The stability of the silica-based anion exchange phase was also evaluated.

Analytical curves, for concentrations ranging from 0.25 to 10 mg L⁻¹ for the inorganic anions chloride, nitrite, bromide and nitrate, showed good linear correlations ($r > 0.998$). The method was tested with certified rainwater samples. The measured and certified values were in good agreement, indicating that the new phase holds significant promise for the analysis of these anions in environmental samples.

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1. Introduction

Pure silica modified with 3-chloropropyltrimethoxysilane has found several applications, such as the adsorption of divalent cations [1], reaction with an aromatic amine [2], functionalization with glutamic acid for the formation of a zwitterionic stationary phase [3], and also functionalization with benzimidazole molecules for the concentration of metallic ions dispersed in ethanol solution [4]. Reaction of 3-chloropropylsiloxysilica with pyridine yields a pyridinium substitution [5]. The anion exchange properties of a silica gel surface modified with covalently bound pyridinium salts were first described by Tundo et al. for application as a catalyst [6]. Later the exchange kinetics and selectivity of several anions using silica functionalized with the pyridinium ion were studied and this material was used as a support in the adsorption of metallic ions from aqueous and non-aqueous solutions [5,7–10]. The functionalized silica was also used as a catalyst in the epoxidation of alkenes [11].

Electrochemical applications have also been performed using propylpyridinium chloride immobilized onto the silica surface, including as a potentiometric sensor for perchlorate ion [12], in electrooxidation of ascorbic acid [13], and as a substrate in the immo-

bilization of Fe(II) and Co(II) tetrasulfonated phthalocyanines for application as an oxygen sensor and as an electrode for the determination of oxalic acid [14].

Stationary phases developed for the analysis of organic and inorganic anions usually have an organic polymer as the support for the positively charged species. However polymeric phases for use in HPLC require significant crosslinking for mechanical stability and this reduces access to the fixed charge by the species being separated. Silica modified with covalently bonded organofunctional groups [15,16] such as aminopropyl [17] or phenylaminopropyl groups [18] present appropriate mechanical stability for use in HPLC.

Recently, an anion exchange stationary phase was synthesized by silanization of silica with chloropropyltrimethoxysilane followed by reaction with N-methylimidazole [19]. This phase is reported to present both a reverse phase mechanism and anion exchange and has been used for amino acid and protein separations. This same research group has also synthesized similar reversed-anion exchange phases by grafting other imidazoles onto silica for the separation of diverse test mixtures [20,21].

In an earlier paper [22] we described the preparation of a new anion exchange stationary phase based on silica with a propylpyridinium group on the surface, obtained by chemical modification of silica with 3-chloropropyltrimethoxysilane followed by functionalization with pyridinium groups, using a modification of an earlier procedure [2]. From the physical and chemical characterization of this new material, it was observed that the silylant agent is covalently

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lently bonded to the surface and remains bound in the presence of several electrolytes [22,23].

Thus, the objective of the present work is to evaluate the effects of concentration and pH on the separation and quantification of some anions using propylpyridinium chemically bonded to silica as a new stationary phase for high performance anion exchange chromatography.

2. Materials and methods

2.1. Materials

HPLC-grade methanol, hexane, dichloromethane (Merck, Rio de Janeiro, Brazil) and Milli-Q water (Millipore, Bedford, USA) were filtered (0.22- μm membrane) before use. Toluene, the reaction solvent, was also purchased from Merck and was dried over sodium and distilled before use. Pyridine and triethylamine were dried over KOH pellets and purified by distillation. The silylant agent, 3-chloropropyltrimethoxysilane (97%) was obtained from Aldrich (Milwaukee, USA). The anions for the anion-exchange experiments were standard solutions from Merck. Phthalic acid and tris(hydroxymethyl)methylamine (Tris) were both from Merck. Davisil silica from Alltech Associates (Deerfield, IL, USA) with 10 μm irregular porous particles, an average pore diameter of 15 nm, and a specific surface area (S_{BET}) of 263 $\text{m}^2 \text{g}^{-1}$ was used as support. The column used for comparison of the results was a Shim-pack IC-A1 column (100 mm \times 4.6 mm i.d.) (Shimadzu, Kyoto, Japan), packed with anion-exchange resin on a polymethacrylate support incorporating a quaternary ammonium base as functional group. A Shim-pack IC-GA1 guard column (100 mm \times 4.6 mm) was attached.

2.2. Synthesis of the propylpyridinium silicas

The new silica-based phase was prepared by a two-step modification process as previously described [22]. In the first step of the synthesis, chloropropyl silica was obtained under two different conditions: in the absence (SilprCl) and in the presence of trace amounts of water (SilprCl-H₂O) in the reaction medium. The presence of water promotes polymerization of the trialkoxysilane. The procedures and the reagents used in the two syntheses were the same, differing only in the reaction medium. In the second step the chloropropylsilicas were reacted with an excess of pyridine under anhydrous conditions, yielding the propylpyridinium silicas SilprPy and SilprPy-H₂O, respectively.

2.3. Characterization of the propylpyridinium silicas

Since the first step of the synthesis was performed in two different media the integrity of the exchanger was checked by elemental analysis, thermogravimetry, and infrared and solid state ¹³C and ²⁹Si nuclear magnetic resonance spectroscopies, as previously described [22].

2.4. The specific exchange capacity of the propylpyridinium silicas

The specific exchange capacities of the chloride ion of the two functionalized silicas were determined through Cl[−] counter-ion exchange with NO₃[−] ions. The concentrations of the exchanged chloride ions were determined by k_0 -instrumental neutron activation analysis (k_0 -INAA) [24].

The irradiation was performed in the TRIGA Mark I IPR-R1 reactor located at CDTN/CNEN (Nuclear Technology Development Center/National Nuclear Energy Commission). Aliquots of 0.10 g of propylpyridinium silica (SilprPy or SilprPy-H₂O) were added to 10.0 mL of aqueous potassium nitrate (0.1 mol L^{−1} KNO₃, pH 4.2) and stirred for 1 h. Afterwards, the sample was allowed to settle

and 1.0 mL of the supernatant was placed into polyethylene vial, which was sealed and put into an irradiation rabbit suitable for use in the reactor. The same procedure was performed with 10.0 mL of aqueous nitric acid (0.1 mol L^{−1} HNO₃). Samples were prepared in duplicate and irradiated individually for five minutes in the reactor at 100 kW under a thermal neutron flux of 6.6×10^{11} neutrons cm^{−2} s^{−1} for determination by k_0 -INAA. The standards used as Na comparators were also irradiated for 5 min.

During irradiation, the reaction ³⁷Cl(n, γ)³⁸Cl occurs. After 15 min of decay time, gamma spectroscopy was performed with a high purity germanium detector with resolution of 1.85 keV for the 1332 keV peak of ⁶⁰Co and 15% nominal efficiency. The spectra obtained were analyzed with the software Maestro from ORTEC. k_0 -INAA was applied to determine the elemental chlorine concentrations based on the radionuclide ³⁸Cl, which has a 37.24 min half-life with a 1642.59 keV gamma emission.

2.5. Chromatographic evaluations

2.5.1. Column packing

HPLC columns (150 mm \times 3.9 mm i.d. or 60 mm \times 3.9 mm i.d.) were made from type 316 stainless steel tubes whose internal surfaces were polished using a technique developed in our laboratory [25]. The columns were downward packed using 10% (w/v) stationary phase slurries in chloroform with methanol as propulsion solvent. A constant packing pressure of 34.5 MPa from a Haskel packing pump (Burbank, USA) was used. After packing, the column was conditioned by passing 20 column volumes of isopropanol to remove the propulsion solvent and then a normal mobile phase (hexane:dichloromethane) 95:5 (v/v) at 0.2 mL min^{−1} prior to testing.

2.5.2. Normal phase separations

Chromatographic evaluations of column performances under normal phase conditions were carried out with a mixture of benzene, benzyl alcohol, anthracene, benzonitrile and nitronaphthalene using a modular HPLC from Waters (Milford, USA) composed of a Waters 510 pump, a Rheodyne 7125 injection valve (Cotati, USA) with sample loop of 5 μL and a Waters 486 UV-Vis detector at 254 nm. The test mixture was separated with a hexane-dichloromethane (95:5 (v/v)) mobile phase. The optimal flow-rate was determined by a van Deemter plot. Data collection and treatment were carried out with Chrom Perfect for Windows from Justice Innovations (Mountain View, USA). Chromatographic performance was evaluated by means of efficiency (plates per meter, calculated at half peak height (N/m)), reduced plate height (h), retention factor (k), resolution (R_s) and asymmetry (A_s) measured at 10% of peak height [26].

2.5.3. Ion exchange separations

These separations were performed with a Shimadzu system (Kyoto, Japan) equipped with a LC10A Shimadzu pump, a 7125 Rheodyne injection valve with sample loop of 20 μL and a LC10A Shimadzu conductivity detector. Before using an aqueous mobile phase for these evaluations the hexane-dichloromethane mobile phase was substituted by passing 20 column volumes each of isopropanol followed by pure methanol and then a mixture of methanol:water (70:30 (v/v)). Finally a pH 3.8 solution of 250 mmol L^{−1} phthalate was passed at 0.5 mL min^{−1} for 2 h before starting the anion exchange separations. The mobile phases were phthalate/Tris buffer solutions prepared by mixing a 2.5 mmol L^{−1} phthalic acid solution with 2.4 mmol L^{−1} Tris. The pH of the resulting solutions were measured with a freshly calibrated model 744 Metrohm pH meter. The test mixture, containing inorganic anions, was prepared by diluting commercially available 1000 mg L^{−1} stock

Table 1

Exchange capacity for the functionalized silica synthesized in an anhydrous medium (SilprPy) and in the presence of water (SilprPy-H₂O), determined by chloride counter-ion concentration.

Conditions	Ionic exchange capacity (mmol g ⁻¹)	
	HNO ₃ (0.1 mol L ⁻¹)	KNO ₃ (0.1 mol L ⁻¹ , pH = 4.2)
SilprPy	0.36 ± 0.02	0.38 ± 0.01
SilprPy-H ₂ O	0.44 ± 0.01	0.55 ± 0.01

Table 2

Chromatographic parameters for the SilprPy stationary phase using normal phase conditions.

Compounds	N/m	As ^a	k ^b	Rs
Benzene	30,800	1.1	–	–
Anthracene	33,900	1.1	1.1	12.7
Benzyl alcohol	32,900	1.2	1.4	2.5
Benzonitrile	26,800	1.6	1.7	1.3
Nitronaphthalene	32,500	1.1	2.7	5.7

^a Asymmetry factor at 10% of peak height.

^b t_M measured with benzene.

standards of chloride, nitrite, bromide, and nitrate. Standard working dilutions of 10 mg L⁻¹ of each anion were prepared daily.

2.6. Effect of pH on anion retention

One of the ways of evaluating stationary phases by chromatography is to verify the separation of anions at different pH values. For this experiment, a 60 × 3.9 i.d. chromatographic column was used. Mixtures of 2.5 mmol L⁻¹ phthalic acid having different concentrations of Tris to obtain the desired pH were used as mobile phases. 20 µL of a standard mixture made of chloride (5.0 mg L⁻¹), nitrite (10.0 mg L⁻¹) and nitrate (10 mg L⁻¹) ions were injected into the mobile phase at 0.6 mL min⁻¹ at 30 °C.

2.7. Stability test

The changes in efficiency, retention factor and asymmetry, as a function of the mobile phase volume that passed through the column, were evaluated with the SilprPy-H₂O stationary phase in a 60 mm × 3.9 mm column. A solution having a mixture of chloride and nitrate ions with concentrations of 5 mg L⁻¹ and 10 mg L⁻¹, respectively, was injected twice a day during the course of the experiment.

To simulate prolonged and continuous use, fresh eluent was used with a flow rate of 0.1 mL min⁻¹ at night and 0.8 mL min⁻¹ during the day.

2.8. Applications

2.8.1. Separation of some inorganic and organic anions

The phase SilprPy-H₂O was used to separate several organic and inorganic anions at the optimized buffer concentration. The

Table 3

Chromatographic parameters for the SilprPy-H₂O stationary phase using normal phase conditions.

Compounds	N/m	As ^a	k ^b	Rs
Benzene	33,500	1.5	–	–
Anthracene	33,800	1.3	0.7	9.3
Benzyl alcohol	32,300	1.4	1.0	2.6
Benzonitrile	29,800	1.7	1.3	2.3
Nitronaphthalene	33,500	1.3	2.0	4.6

^a Asymmetry factor at 10% of peak height.

^b t_M measured with benzene.

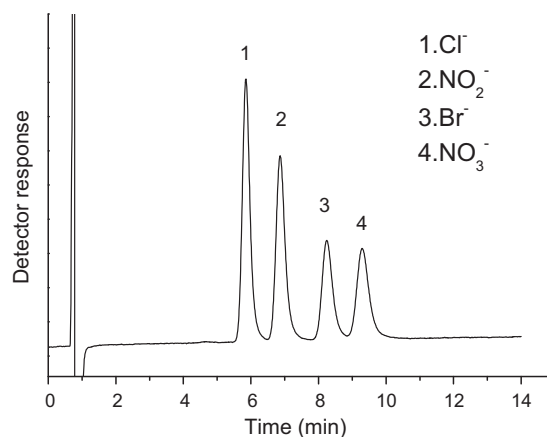


Fig. 1. Chromatogram obtained with a 150 mm × 3.9 mm column packed with SilprPy-H₂O for the separation of chloride (1), nitrite (2), bromide (3), nitrate (4). Chromatographic conditions: mobile phase 2.5 mmol L⁻¹ phthalic acid/2.4 mmol L⁻¹ Tris, pH 4.2; flow rate: 1.5 mL min⁻¹; injection volume: 20 µL; detector: non-suppressed conductivity.

retention times and resolutions of inorganic anions, such as azide, chloride, bromide, nitrite, nitrate and dihydrogenphosphate, were tested as well as those of some organic anions such as lactate, acetate and succinate.

Solutions of the inorganic anions were prepared from their salts with initial concentration of 100 mg L⁻¹, after which the necessary dilutions were made. The organic anions were prepared with similar concentrations by dilution of the appropriate compounds in deionized water. All these solutions were filtered through a 0.45 µm membrane filter before injection.

The separations of these inorganic and organic anions were carried out on the Shimadzu chromatograph using a 150 mm × 3.9 mm i.d. column packed with the stationary phase SilprPy-H₂O under the following optimized conditions: mobile phase buffer solution: 2.5 mmol L⁻¹ phthalate acid/2.4 mmol L⁻¹ Tris, at pH 4.2; mobile phase flow rate: 1.3 mL min⁻¹; oven temperature: 30 °C, injection volume: 20 µL; detection conditions: gain: 0.1 µS cm⁻¹, attenuation: 4, polarity: positive.

2.8.2. Quantification of some inorganic anions

Solutions of four monovalent anions, chloride, nitrite, bromide, and nitrate, were used in the construction of the analytical curves and in the statistical evaluation of some validation parameters such as limit of detection and quantification, precision and accuracy [26]. Individual anion standard solutions (CertiPur, Merck) were diluted to give solutions of each of the anions with concentrations ranging from 0.25 to 10 mg L⁻¹.

Analytical curves were constructed from the peak areas of each anion using the least squares method. Two reference samples, CRM 408, with chloride and nitrate ion concentrations of 2.4 mg L⁻¹ and 1.2 mg L⁻¹, respectively, and CRM 409, with chloride and nitrate ion concentrations of 4.0 mg L⁻¹ and 4.8 mg L⁻¹ were used to verify quantitation by interpolation of the analytical curve. These samples, in sealed quartz vials sterilized by gamma irradiation, were obtained from the European Community and are certified to correspond to simulated rainwater with high levels of electrolytes.

3. Results and discussion

3.1. Synthesis and physical characterization of the propylpyridinium silicas

The silica surface modification procedures have already been outlined [22]. Physical characteristics of the new materials were

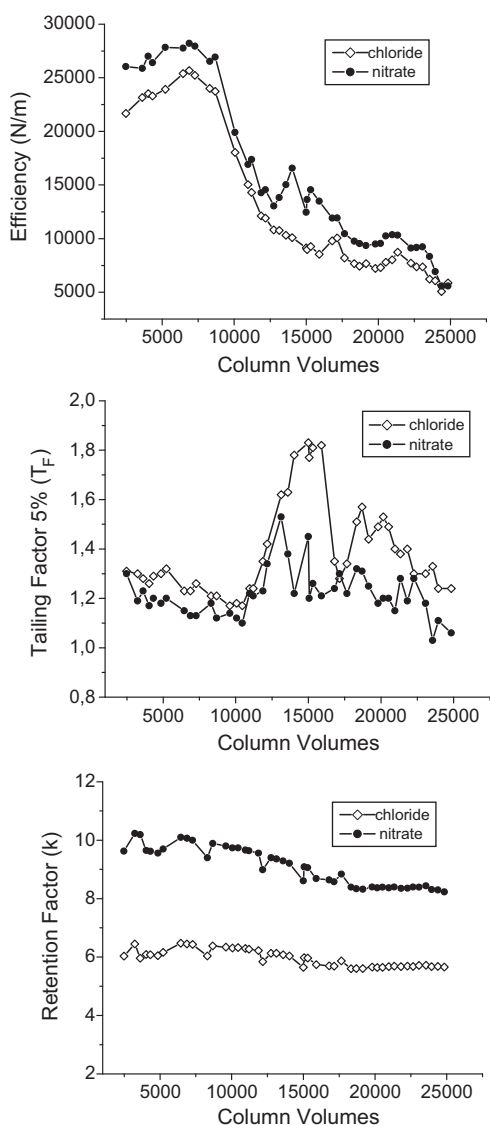


Fig. 2. Chromatographic parameters from the stability test using a 60 mm \times 3.9 mm i.d. SilprPy-H₂O column. Mobile phase: phthalate/Tris buffer solution at pH 4.2; flow rate: 0.8 mL min⁻¹; injection volume: 20 μ L; detection: non-suppressed conductivity. The initial point at \sim 500 column volumes represents the mobile phase (of varying concentrations) that passed through the column during the pH tests.

evaluated by thermogravimetry and infrared and nuclear magnetic resonance (¹³C and ²⁹Si) spectroscopies. The results conformed to those reported earlier [23]. As expected, the results of elemental analysis indicated less chloropropylsilane incorporation for the synthesis carried out in the absence of water.

3.2. The specific exchange capacity of the propylpyridinium silicas

The specific capacities of the two functionalized silicas were evaluated by determining the exchange capacity of the counter-ion chloride of the propylpyridinium group (Table 1). That for SilprPy-H₂O was higher, confirming that the product of the reaction carried out in the presence of water has a higher number of exchangeable sites, as also reported by Gushikem and collaborators using large particle diameter silica [5,7].

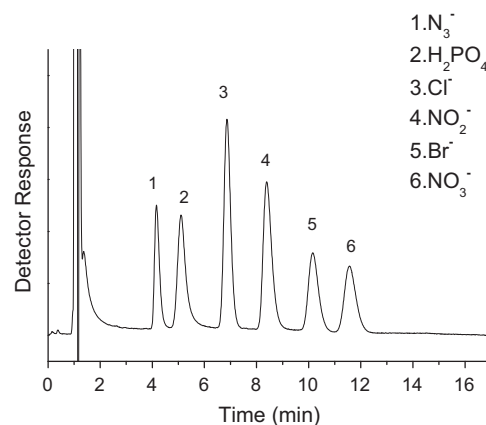


Fig. 3. Separations of some inorganic anions. 150 mm \times 3.9 mm column packed with SilprPy-H₂O. Chromatographic conditions: mobile phase: phthalate/Tris buffer at pH 4.2; flow rate: 1.3 mL min⁻¹; injection volume: 20 μ L; detection: non-suppressed conductivity.

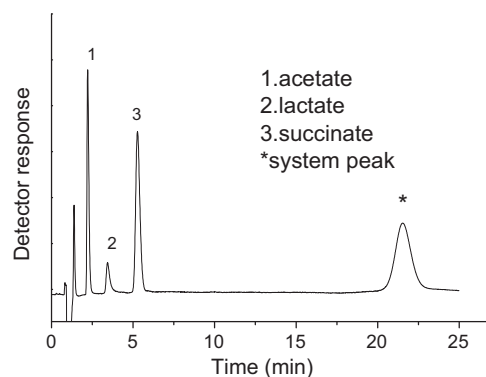


Fig. 4. Separation of some organic anions. 150 mm \times 3.9 mm column packed with SilprPy-H₂O. Chromatographic conditions as in Fig. 3.

3.3. Chromatographic evaluations

Four 150 mm \times 3.9 mm i.d. chromatographic columns were packed, one with the stationary phase SilprPy and three with phase SilprPy-H₂O. The chromatographic parameters and optimal flow rates were determined for each column by injecting test mixtures under normal phase conditions at different mobile phase flow rates ranging from 0.1 to at least 1.2 mL min⁻¹. The columns showed very similar behaviors under the same analysis conditions. The optimal flow rates for maximum efficiency were 0.4 mL min⁻¹.

Chromatographic parameters for both phases are shown in Tables 2 and 3. The retention time of an unretained compound

Table 4

Parameters of analytical curves obtained using the SilprPy-H₂O column and the Shim-pack IC-A1 column.

Anions	Concentration range ^a (mg L ⁻¹)	Linear correlation	R	LD (mg L ⁻¹)
150 mm \times 3.9 mm SilprPy-H ₂ O column				
Chloride	0.25–10	$Y = 1579.8x + 22.0$	0.9999	0.04
Nitrite	0.40–10	$Y = 918.7x + 179.3$	0.9990	0.17
Bromide	0.70–10	$Y = 504.3x + 16.0$	0.9987	0.20
Nitrate	0.90–10	$Y = 530.4x + 158.4$	0.9991	0.24
100 mm \times 4.6 mm Shim-pack IC-A1 column				
Chloride	0.50–10	$Y = 1568x + 58.7$	0.9994	0.05
Nitrite	0.25–7.5	$Y = 1102x - 179.3$	0.9999	0.10
Bromide	0.25–7.5	$Y = 772.5x - 32.8$	0.9999	0.05
Nitrate	0.50–10	$Y = 743.4x - 25.7$	0.9996	0.10

^a 8 points were used for construction of the curve.

Table 5

Comparison of results obtained for chloride anion in simulated rain water reference samples CRM 408 and CRM 409.

Reference sample	Nominal concentration (mg L ⁻¹)	SilprPy-H ₂ O		IC-A1	
		Experimental concentration (mg L ⁻¹)	Recovery (%)	Experimental concentration (mg L ⁻¹)	Recovery (%)
<i>Chloride</i>					
CRM 408	2.40	2.42	101	2.55	106
CRM 409	4.00	4.07	102	4.17	104
<i>Nitrate</i>					
CRM 408	1.25	1.58	126	1.24	99
CRM 409	4.80	4.70	98	4.70	98

was taken from benzene, although benzene might interact with the propylpyridinium stationary phase to a degree. These results indicate that the chromatographic parameters are very similar under these normal phase conditions. After the normal phase tests the mobile phase was changed to one more appropriate for anion exchange using a series of steps ending by passing a pH 3.8 phthalate/Tris solution through each column to displace the chloride counter ion from the propylpyridinium phase. After this, the column were conditioned with more dilute buffer solutions in which the total buffer concentration was never higher than 10 mmol L⁻¹.

Using a test mixture composed of chloride, nitrite and nitrate, separations varying the total buffer concentrations and pH were performed. A phthalate solution offers good buffer capacity over a wide pH range due to its two dissociation constants ($pK_{a1} = 3.1$ and $pK_{a2} = 5.4$).

Although both the SilprPy and SilprPy-H₂O phase showed similar chromatographic parameters under normal phase conditions, when tested for their ion exchange capacities using a phthalate/Tris buffer, the separation of the anion mixture on the SilprPy column was not adequate, perhaps as a result of its lowered exchange capacity, also indicated from the capacity results shown in Table 1.

Using the SilprPy-H₂O phase separations at low pH values showed longer retention times even for high buffer concentrations. In addition, separations at pH values lower than 3 should be avoided to prevent hydrolysis of siloxane bonds and consequent loss of the bonded phase. Separations at pH values of 5 were faster and the retention factors were lower. However, at this pH a system peak interferes. System peaks were observed at pH between 4.2 and 6.0 and are due to the presence of amphoteric biphtalate. At pH 6.0, it was possible to separate sulphate and thiocyanate with good efficiency although resolution was lost for several monovalent anions. The buffering capacity is very low at pH 7.0 and resolution was totally lost. The best separations were achieved with 2.5 mmol L⁻¹ phthalate/TRIS buffer at pH 4.2 (Fig. 1).

3.4. Stability test

The stability of the SilprPy-H₂O stationary phase in a 60 mm × 33.9 mm column was evaluated by periodic injections of a chloride plus nitrate standard mixture with concentrations of 5 and 10 mg L⁻¹, respectively. The test was carried out by running the mobile phase continuously to 25,000 column volumes over 5 weeks.

The modifications that the column underwent during this period were evaluated by following the chromatographic efficiency (N/m), retention factor (k) and tailing factor (T_F), as shown in Fig. 2. Not surprisingly, the retention factor hardly changes throughout the test, while the efficiency shows a significant drop, accompanied by an increase in the tailing factor, at about 10,000 column volumes. However the resolution of this pair of anions was sufficient to permit separation up to the final injection.

3.5. Applications

3.5.1. Separation of anions

Separations involving some organic and inorganic anions were carried out using the optimized mobile phase. The chromatogram in Fig. 3 shows that the inorganic anions of the injected mixture are eluted in 12 min of analysis time with good resolution and excellent selectivity. The applicability of the new phase was also evaluated for some organic anions. The results indicate a rapid elution of several anions, such as acetate, lactate and succinate (Fig. 4).

3.5.2. Anion quantification

The SilprPy-H₂O column was compared with a commercial polymeric column that has quaternary ammonium bound to the support and is considered appropriate for the analysis of low content environmental samples for the quantification of several anions. Analytical curves were constructed with concentration ranging from 0.10 to 10 mg L⁻¹ with a concentration interval of 0.05 mg L⁻¹. Table 4 compares the analytical parameters of the curves for the two columns.

Two European Community reference samples, CRM 408 and CRM 409, with different concentrations of chloride and nitrate, were used to simulate rainwater samples. These samples have several anions and cations in their composition and allow the evaluation of the selectivity of the new phase. Table 5 shows the results obtained for chloride and nitrate concentrations in the two certified reference samples for the SilprPy-H₂O and IC-A1 columns. Although the sensitivity of the SilprPy-H₂O is somewhat lower than that of the commercial column, both columns adequately quantify the concentrations of these reference samples.

4. Conclusions

A silica support having positively charged propylpyridinium groups chemically bonded to the surface is a potentially interesting stationary phase for anion exchange chromatography of small inorganic and organic anions. The best separations were achieved using a 2.5 mmol L⁻¹ phthalate/2.4 mmol L⁻¹ Tris buffer solution at pH 4.2 as a mobile phase.

Analytical curves for several inorganic anions, including chloride, nitrite, bromide and nitrate, showed good linear correlations ($r > 0.998$) for concentrations ranging from 0.25 to 10 mg L⁻¹. The method was tested with certified rainwater samples and the values measured were in good agreement with the certified values. The new SilprPy-H₂O stationary phase showed promising results for the separation and quantification of some inorganic anions often found in actual environmental samples, while the good results obtained for separations under normal phase conditions do not exclude the possibility of using this new stationary phase in normal phase chromatography as well.

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