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Functionalised SBA-15 mesoporous silica in ion chromatography of alkali, alkaline earths, ammonium and transition metal ions

Maria Concetta Bruzzoniti[a,*], Rosa Maria De Carlo[a], Sonia Fiorilli[b,c], Barbara Onida[b,c], Corrado Sarzanini[a]

[a] Dipartimento di Chimica Analitica, Università degli Studi di Torino, Via P. Giuria 5, 10125 Torino, Italy
[b] Dipartimento di Scienza dei Materiali e Ingegneria Chimica, Politecnico di Torino, Corso Duca degli Abruzzi, 24 - 10129 Torino, Italy
[c] CR-INSTM for Materials with Controlled Porosity

(*) Corresponding author:
Dr. Maria Concetta Bruzzoniti, PhD
Department of Analytical Chemistry
University of Torino
Via P. Giuria 5, 10125 Torino, Italy
Phone: +39 011 6707844
Fax: +39 011 6707615
E-mail: mariaconcetta.bruzzoniti@unito.it

Abstract

The retention properties of a SBA-15 mesoporous silica functionalized with –$(CH_2)_3COOH$ groups, synthesized by a co-condensation route, were investigated for the ion chromatography of different cationic species.

A systematic study on the effect of different eluent compositions containing non-complexing (methanesulfonic acid) or complexing (oxalic or pyridine-2,6-dicarboxylic acids) eluents, in the presence of organic modifiers (CH_3CN, CH_3OH, CH_3NH_2) on the retention of cations (Li^+, Na^+, K^+, Ca^{2+}, Mg^{2+}, Sr^{2+}, Ba^{2+}, NH_4^+, Cu^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}, Co^{2+}, Pb^{2+}, Fe^{3+}) chosen as model analytes and for their environmental importance, allowed us to elucidate the mechanisms (cation-exchange or complexation) involved in the retention on the SBA-15 phase. For the first time separations of cations on SBA-15 based stationary phases are investigated, providing the basis for further development of mesoporous silica chemistry for in-flow ion-exchange applications.

1 Introduction

Ordered mesoporous silicas, templated by supramolecular aggregates, are characterized by high specific surface areas and ordered arrays of uniform mesopores [1]. They are widely investigated for applications in, for instance, catalysis, drug delivery, and nanocomposites [2]. In the last decade, several studies dealing with the adsorption and separation capabilities of mesoporous silica have been published. Some of the advantages of the use of mesoporous structured materials in separation methods, mainly liquid chromatography, are their high surface area, high pore volume, and adjustable pore size. These features improve column permeability, molecular selectivity [3] and hence make mesoporous materials promising supports for chromatographic stationary phases. Notwithstanding, the synthesis of mesoporous silica with homogeneous size and shape of the particles, which are required properties in determining column efficiency and separation performance, is still a challenge [4,5]. Mesoporous silica were studied as chromatographic support only for HPLC reversed phase applications and, for instance, phenyl-functionalized ethane-silica [6] was tailored for the chromatographic separation of neutral organic compounds (*e.g.* benzene, naphthalene). Octyl modified mesoporous silicas were used and compared with commercial silicas carrying on similar functionalization, for the separation of uracil, benzene, naphthalene and biphenyl [4,7].

Among mesoporous materials, SBA-15 silica based materials have larger pore size which allows for an even better control of adsorption/desorption processes [8,9]. Moreover, SBA-15 materials have a rich population of silanol groups [10] which allows the loading of functional groups, e.g. alkyl groups, for a surface modification. SBA-15 silica based materials functionalized with C18 moieties, received attention as chromatographic stationary phase for proteins [2], while, recently, when functionalized with immobilized aminoalcohol, SBA-15 have found application as potential chiral stationary phase for chiral ligand exchange chromatography [11].

As far as ion-exchange interactions with mesoporous materials are concerned, SBA-15 functionalized by 2-diethylamino-ethanol was used as weak anion exchange matrix for chromatography to purify Der f2 allergen [12], but to the best of our knowledge, applications of properly functionalized mesoporous silica as cation-exchanger for chromatographic and separative purposes are lacking, with the unique applications being only adsorption measurements in batch conditions for a wide variety of transition metal ions [13,14] and more recently for Na^+, K^+, Cu^{2+}, Ca^{2+} [15] through sulfonic acid functional groups.

In parallel, the evolution of chemistry for column technology in cation-exchange chromatography is currently oriented towards selective weak exchangers with carboxylic or phosphonic groups that can avoid the use of relatively concentrated acidic eluents, and long analysis run, typical of sulfonic cation-exchangers.

In a previous paper we synthesized a SBA-15 sample functionalized with $-(CH_2)_3COOH$ groups by co-condensation from tetraethylorthosilicate and 4-(trethoxysilyl)butyronitrile [16] which exhibited different recoveries for metal ions (*i.e.*: Ag^+, Cu^{2+}, Fe^{3+}, Pb^{2+}, Zn^{2+}) in batch experiments. The different recoveries were interpreted as differences in selectivity of the material towards metal ions; this property is particularly desired if the material must be used as stationary phase for chromatographic separations. The aim of this work is the evaluation of the performance of the -COOH functionalized SBA-15 material as a stationary phase for the retention and/or separation of different classes of cationic analytes. Therefore, alkali (Li^+, Na^+, K^+), alkaline earths (Ca^{2+}, Mg^{2+}, Sr^{2+}, Ba^{2+}), ammonium and transition metal ions (Cu^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}, Co^{2+}, Pb^{2+}, Fe^{3+}) were selected as model cations for their importance in different environmental compartments. Systematic studies on the effect of different eluent compositions on the retention factors of analytes were performed, evaluating the different mechanisms involved during the separation. According to the results obtained, separations for the selected classes of cations are shown.

This is the first application of mesoporous materials, and in particular of SBA-15 based mesoporous silica, as cation-exchanger support in ion chromatography.

2 Experimental
2.1. SBA-15-COOH synthesis and characterization

The synthesis was carried out as described in [16], using Pluronic P123 triblock copolymer as surfactant, tetraethylorthosilicate (TEOS) and 4-(triethoxysilyl)butyronitrile, $(EtO_3)Si$-BuCN, acting as $-(CH_3)_2COOH$ precursor. The final molar composition is: 0.9 TEOS:0.017 P123:2.9 HCl:202.6 H_2O:0.1 $(EtO_3)Si$-BuCN. To remove the template and to hydrolyse the $-CN$ groups to carboxylic groups, the procedure reported by Schüth et al. [17] was followed: 1.0 g dried sample was re-dispersed in 120 ml of 48% H_2SO_4 solution, and the mixture was heated to 368 K for one day. The product was washed with water until the eluent became neutral, then washed with acetone.

Specific surface area, pore size distribution, and pore volume have been evaluated by nitrogen adsorption/desorption isotherms (Quantachrome Autosorb1). Data are collected in Table 1.

The BET specific surface area has been calculated using a cross-section value for the nitrogen of 13.5 Å, as suggested in literature for hydrated silica surfaces [18]. The internal surface of the SBA-15-COOH sample, in fact, is expected to be highly hydrated because the material was not calcined (the surfactant was removed by extraction).

Pore size distribution has been calculated using NLDFT model for cylindrical pore.

The acidic capacity is 0.98 meq/g (rsd%=1.4), whereas the acidic dissociation constant (pK_a), measured according to Soldatov [19], is 4.74. The amount of $-COOH$ groups measured by differential thermo gravimetric analysis (Mettler Toledo thermogravimetric analyzer with a heating speed of 10 K/ min under air in a flow of 50 mL/min) was 1.1 mmol/g.

2.2 Column packing

The SBA-15-COOH was suspended in CH_3OH and stirred. A PEEK tube (50x4 mm i.d.) was slurry packed by a Minipuls 3 peristaltic pump (Gilson Inc., Middleton, WI, USA) set at 13 rpm. The column was subsequently equilibrated with H_2O at 0.5 mL/min under high pressure by connecting a peek tube of 2.6 m with an internal diameter of 0.08 mm (0.003 inches, 1 μl/ft volume), generating a backpressure of about 2850 psi/m at 1 mL/min (Dionex Co., Sunnyvale, USA). The slurry packing and the equilibration was continued until the column was completely filled. The operating back-pressure of the column at 0.5 mL/min ranged between 1130 and 1200 psi. The void volume of the column, evaluated as the water deep in the chromatogram, was 0.6 mL.

2.3 Instrumentation

For the study on alkali and alkaline earths, an ICS3000 (Dionex) chromatograph equipped with a 10 µL loop was used. Detection was performed with suppressed conductivity using a CSRS Ultra-II 2 mm suppressor in the external water mode. After preliminary experiments performed at 1 mM methanesulfonic acid, eluent flow rate was set at 0.1 mL/min; this value ensured the best differences in selectivity among analytes. According to the eluent concentration, the instrument automatically set the current for the suppression (the values ranged from 1-2 mA for 0.1 ml/min eluent flow rate).

The study on transition metal ions was performed on a 4000i model ion chromatograph (Dionex) equipped with a Rheodyne injector Model 7125 (100 µl loop) and with a VDM-II variable-wavelength UV–Vis detector. Eluent flow rate was set at 0.5 mL/min. Spectrophotometric detection was performed at 520 nm after a post-column reaction with 0.4 mM 4-(2-pyridylazo)-resorcinol (PAR) in 0.3 M NaHCO$_3$, 1 M 2-methylamminoethanol, 0.5 M NH$_4$OH, 25% in water. The flow rate for the post-column reagent was set at 0.5 mL/min.

2.4 Reagents and solutions

Deionized water (18.2 MΩ·cm resistivity at 25 °C) from a water purification system (Milli Q Academic, Millipore) was used for the preparation of the eluents and standards. Stock solutions (1000 mgL^{-1}) of analytes were prepared from Titrisol standard solutions (Merck, Darmstadt, Germany). Ammonium standard solution (10000 mg/L) was prepared by dissolving the chloride salt in water. Methanesulfonic acid (MSA) 70% in water and LiNO$_3$ were from Aldrich (Missouri, USA), acetonitrile, methanol (HPLC grade), and pyridyne-2,6-dicarboxylic acid were from Fluka (Sigma-Aldrich, Missouri, USA). Oxalic acid was from Merck. Prior to use, all eluents were filtered through a 0.22 µm filter.

For the preparation of the post-column reagent, 4-(2-pyridylazo)-resorcinol (PAR) and 2-methylamminoethanol were from Fluka, NaHCO$_3$ from Riedel de Haen (Sigma-Aldrich), and NH$_4$OH from Acros Organic (Geel, Belgium).

2.5 Column washing protocol and column performance

Whenever the elution of the analytes was not observed, before changing the eluent composition, and after each day of measurements the column was washed with 7 mL of 0.1 M HNO$_3$ (Merck) at 0.5 mL/min. The re-equilibration of the column was performed with at least 10 mL eluent solution at the desired flow rate and until a stable baseline was obtained. This procedure ensured a good within-day repeatability of retention times (RSD%= 0.8 for retention times as long as about 40 min). After four months of daily use of the column, excellent reproducibility of the column was observed (RSD%= 4.1 for retention times as long as about 40 min).

3. Results and discussion

To evaluate the performance of the SBA-15-COOH material as a stationary phase for the retention of the selected analytes, its behaviour was studied at different eluent compositions.

3.1 Alkali, alkaline earths and ammonium ion
3.1.1 Effect of MSA on selectivity

Due to the presence of the –COOH groups in its structure, SBA-15-COOH can act as a weak cation-exchanger and MSA (in the range 1-5 mM) was used to investigate the cation-exchange properties of the stationary phase.

The retention order obtained at the lowest MSA concentration was: Li$^+$<Na$^+$<NH$_4^+$<K$^+$<Mg^{2+}<Ca^{2+}<Sr^{2+}<Ba^{2+}, see Table 2. The selectivity exhibited by the SBA-15-COOH column is similar to that obtained by the conventional IC columns carrying a –COOH

functional group (*e.g.* IonPac CS12 or IonPac CS16 [20]). Increasing the MSA concentration, retention times for all analytes decrease, as expected by a cation-exchange mechanism and, at the highest MSA concentration studied, selectivity between alkaline earths and K^+ is reversed (Table 2). This behaviour is in agreement with the fact that the divalent ions are the most affected by the increase of the counter-ion concentration in the eluent.

The *k* data obtained were fitted to the ion-exchange mechanism equation [21] (Figure 1):

$$\log k = a - x/y \log[H^+] \qquad\qquad (1)$$

where *x* is the charge of the analyte ion, *y* (=+1) is the charge of H^+, and *a* is a constant.

The slopes calculated according to eq. (1), which are collected in Table 2, are in good agreement with the theoretical charges of the analytes.

As an example, in the inset of Figure 1 a typical chromatogram obtained at 1 mM MSA is also shown, where it is possible to note a certain selectivity among Li^+, Na^+, NH_4^+, and K^+. At these conditions, efficiency expressed as theoretical plates, *N*, ranged from 11 (K^+) to 220 (Mg^{2+}).

3.1.2 Effect of ligands on selectivity

In cation-exchange chromatography, it is usual to promote the formation of weak complexes in the eluent to control the selectivity. Therefore, the effect of the presence of oxalic and pyridyne-2,6-dicarboxylic acid (PDCA) on the separation was investigated.

3.1.2.1 Oxalic acid

Oxalic acid is a mildly acidic complexing agent that is usually employed for the IC separation of transition metal ions and in this study, it was used in the range 0.5-2 mM (four levels).

The retention behaviour of cations is mostly ascribed to the presence of the H^+ in the eluent due to oxalic acid dissociation; this is confirmed by several observations, namely (i): the similar selectivity obtained to that of MSA at the lowest eluent concentrations (see Table 2); (ii) the charges calculated by the ion-exchange equation (see Table 2); and (iii) the similar retention times values obtained for the two eluents at the same pH values. Nevertheless, it is important to underline that the inversion of selectivity between alkaline earths and K^+ occurs for MSA eluent at pH 2.6, whereas for oxalic acid eluent at about pH 3.0. A complexation effect by oxalic acid towards alkaline earths (Mg^{2+}: $\log\beta_2=4.38$; Ca^{2+}: $\log\beta_2=3.49$; Sr^{2+}: $\log K_1=2.54$; Ba^{2+}: $\log K_1=2.54$ [22,23]) can thus contribute to anticipate at higher pH values the inversion of selectivity.

The complexation effect of oxalic acid improves the selectivity against the alkaline earths in respect to the elution with MSA. In fact, at 1 mM oxalic acid, pH 3.1 (Figure 2a) the separation of Li^+, NH_4^+, Mg^{2+} and Ba^{2+} can be obtained. Moreover peak widths and efficiency improved for all the analytes in the presence of oxalic acid, with *N* ranging from 21 (K^+) to 260 (Li^+).

3.1.2.2 PDCA

The effect of PDCA on the selectivity of alkali and alkaline earths was evaluated in the range 0.5-1.2 mM (four levels). As shown in table 2, PDCA completely alters the selectivity within the alkaline earths metals group, with retention order being now: $Li^+<Na^+<NH_4^+<Ca^{2+}<K^+<Sr^{2+}<Ba^{2+}<Mg^{2+}$. The retention order obtained for the alkaline earths is in agreement with the stability constant of the metal-PDCA complexes (Ca^{2+}: $\log K_1=4.6$; Sr^{2+}: $\log K_1=3.80$; Ba^{2+}: $\log K_1=3.43$; Mg^{2+}: $\log K_1=2.32$ [22,23]), with the most stable complex (Ca^{2+}) eluted at first.

The log *k* data plotted against the log*[H^+]* concentration in the eluents containing PDCA still give *x* values close to the charges of the analytes (Table 2), but the r^2 significantly decrease, especially for Ca^{2+} and Sr^{2+} (the species most complexed by PDCA), whose r^2 decrease up to 0.98. With the increase of PDCA concentration an inversion of selectivity between Ca^{2+} and NH_4^+ and between Sr^{2+} and K^+ is observed, in agreement with the charges of the analytes. As previously noted with oxalic acid containing eluents, the inversion of selectivity between K^+ and alkaline earths

metals (Sr^{2+}) is anticipated at even higher pH values (pH=3.25), thus supporting the complexation mechanism contribution of the eluent during the elution. Figure 2b illustrates, as an example, the separation of a mixture of Li^+, Ca^{2+}, Sr^{2+} and Mg^{2+}, with the inset showing overlaid chromatograms obtained for each analyte, at 1.2 mM PDCA, pH 3.1. Peak width and column efficiency globally slightly improve in respect to the eluent 1 mM oxalic acid (pH 3.1), with N ranging from 20 (K^+) to 330 (Li^+).

3.1.4 Effect of organic modifiers on efficiency (CH_3CN, CH_3OH, CH_3NH_2)

The main drawback of the separations achieved so far is the large peak width, especially for the more retained analytes (NH_4^+, K^+ and alkaline earths). This may be related to morphologic and structural properties (shape and dimensions of the particle, pore dimension) [24] but it may also be related to more than one retention mechanism taking place [25]. When MSA is used as the eluent, no additional equilibria in the mobile phase besides the pure ion-exchange are present and the main interactions/equilibria acting on retention, that can affect peak shape and efficiency, are confined to the stationary phase. It should be reminded that the surface of the mesoporous phase is rich of silanol groups. Linden and coworkers [26] have recently demonstrated that 50% or more of the accessible surface groups also in functionalized SBA-15 materials are silanols and that about one fifth of those silanols have a $pK_a=2$. The capacity of the stationary phase in terms of –SiOH groups was estimated by titration (0.06 meq/g) and its influence in the whole retention should not be neglected. It was previously observed that decreasing the MSA concentration from 5 to 2.5 mM (from pH 2.3 to 2.6) does not dramatically increase retention times for alkaline earths with peak width not so large and different, while decreasing the MSA concentration up to 1 mM (pH 3) definitely does increase retention times and peak widths. It should be figured out that approaching to pH values ≤2, the silanol is protonated $SiOH_2^+$ and the carboxylic group is in the form –COOH. Both are Brønsted acids but metal ions can give cation-exchange with –COOH whereas this is not the case for $SiOH_2^+$. The higher the pH, the more the silanol in the –SiOH form, which can now act as fixed cationic sites for the cation-exchange, together with the –COOH groups. This in turn leads to a column of higher capacity and to additional retention equilibria for the analytes, thus supporting enlarged peak widths.

To reduce any additional interactions with the -SiOH groups in the stationary phase and to reduce peak widths, several solvents CH_3R (R= NH_2, OH, CN) of different polarity were added to an eluent containing 1 mM MSA (the eluent conditions in which the presence and the effect of SiOH are maximized). The effect of CH_3CN and CH_3OH were studied in the range 0-25%, while the effect of CH_3NH_2 was studied in the range 0-1 mM.

When CH_3NH_2 is added to the eluent and its concentration is increased in the eluent, the retention times of analytes increase as well. This behaviour is due to the protonation of the amine that causes a lesser availability of counter ions (H^+) for the cation-exchange. Concentrations of methylamine up to 0.5 mM globally improve N (see Figure 3a), but its presence leads to a higher overall retention and to an increase of background noise.

Conversely, the effect of increasing methanol and acetonitrile concentration is to decrease the retention times. Nevertheless, the addition of the same percentage of the two organic solvents causes a reduction of t_r which is more significant for methanol than for acetonitrile. This effect is the reverse of what observed in HPLC-RP separations, where acetonitrile exhibits a higher solvent strength and is more efficacious to reduce hydrophobic interactions. In our study the opposite effect is noticed, supporting that hydrophilic interactions are involved and that CH_3OH gives more interactions with the -OH groups in the stationary phase. This effect appears levelled at 25% of solvent, where methanol and acetonitrile both lead to the same retention times.

Unexpectedly, methanol caused the following peak splitting: (i) 5% CH_3OH: Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+}; (ii): 15% CH_3OH: Mg^{2+} and Ca^{2+}; (iii): 25% CH_3OH Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+} and hence the improve of N values only for certain analytes and for certain CH_3OH percentages (Figure

3b). A possible overloading effect, that could explain the peaks splitting, was excluded by injection of lower amounts of analytes.

On the contrary, acetonitrile provided an increase of efficiency (N up to 500 for alkaline earths) without any peak splitting (Figure 3c and inset).

It must be pointed out that none of the solvents studied altered the selectivity of the separation.

To summarize, SBA-15-COOH exhibits cation-exchange properties against alkali, alkaline earths and ammonium. Differences in the selectivity can be enhanced by the use of complexing eluents so that preliminary separations of Li^+, NH_4^+, Mg^{2+}, Ba^{2+} (with oxalic acid eluent) and Li^+, Ca^{2+}, Sr^{2+}, Mg^{2+} (with PDCA) were obtained; chromatographic performance can be improved by the use of a proper organic modifier.

3.2 Transition metal ions

Based on the characteristics of SBA-15-COOH and on its functionalization, it can be hypothesised that elution of metal ions can be accomplished according to two possible mechanisms: cation-exchange, and chelation. Therefore, different kinds of eluent were tested to evaluate the retention performance of SBA-15-COOH and possibly to achieve a separation among the cations considered (Cu^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}, Co^{2+}, Pb^{2+}, Fe^{3+}).

3.2.1 Effect of MSA

Previous experiments on the evaluation of retention of several transition metals on SBA-15-COOH in batch conditions [16] pointed out that retention yields differ for each metal and vary according to the pH, thus indicating different selectivity of the material towards metal ions. This characteristic was exploited here for chromatographic purposes and hence preliminary investigations on the retention behaviour of Cu^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}, Co^{2+}, Pb^{2+}, Fe^{3+} on SBA15-COOH column were performed at different MSA concentrations (1.5- 2.5 mM, five levels).

Under non-complexing elution condition, the pH affects the conditional stability constants of the complexes formed between the functional group of the stationary phase and the metals. Likewise, these groups can dissociate (or become protonated) with an increase (or decrease) in pH thus altering the electrostatic interactions with the metal ions (*i.e.* the cation-exchange mechanism). Our results, shown in Fig. 4, show that retention for all metal ions decreases with the increase of MSA (that is decreasing pH).

In agreement with the equation proposed by Nesterenko and Jones [27]:

$$\log k = \log \beta_1 + \log \left[H_n R \right] + \log K_{diss} + n \cdot pH + \log \varphi \qquad (2)$$

where β_1, for a cation M^{y+}, is the stability constant of the complex $MR^{(n-y)+}$ formed at the surface in a $H_n R$ chelating resin; K_{diss} is the dissociation constant of $H_n R$ groups, and φ is the phase ratio,

we obtained linear dependences on pH using bilogarithmic axis, as shown in Fig. 4. Similar dependencies were observed for mixed carboxylic and phosphonic ion-exchangers (IonPac CS12A) [28]. The values obtained for *n*, which can give information about the stoichiometry of interaction between metal ion and the chelating group, are shown in Figure 4 and indicate that, for all the cations, two –COOH groups are involved.

According to Fig. 4, few differences in selectivity are obtained except for Pb^{2+}. It is worth of mentioning that the observed retention order corresponds to the stability constants of the complexes formed between metals and ligands having the same carboxylate functionality as the stationary phase, *i.e.* butanoic acid (Pb^{2+} K_1=2.08, β_4=4.43; Cu^{2+} K_1=1.54, β_4=2.95; Cd^{2+} K_1=1.30, β_4=1.98; Zn^{2+} K_1=1.0, β_4=1.53; Ni^{2+} K_1=0.73, β_3=1.34 Co^{2+} K_1=0.66, β_2=0.88 [29]), in full agreement with eq. (2).

3.2.2 Effect of LiNO₃

Under a cation-exchange mechanism, the addition of a counter-cation should decrease the retention of analyte species. Nevertheless, if an additional mechanism, i.e. complexation/chelation, is contributing to the retention, it is expected that the effect of eluent strength upon retention will be less than seen if simple cation-exchange were the only retention mechanism [25].

Keeping constant the eluent pH (1.5 mM MSA), *i.e.* the number of carboxylic sites in the stationary phase, the ionic strength was increased by the addition of LiNO₃ in the range 0.5-2.0 mM (four levels). The effect of Li^+ as counter ion can be appreciated only for concentrations above 1.0 mM, indicating its low affinity for the –COOH groups of the mesoporous silica. Since the slopes obtained plotting the log*k* data *vs* log*[Li⁺]* ranged from -0.64 (Cu^{2+}) to -0.90 (Zn^{2+}), an additional retention mechanism must be assumed, thus confirming the complexation properties of the stationary phase.

3.2.3 Effect of oxalic acid in the eluent

To alter and to control the selectivity of the stationary phase towards metal ions, a weak complexing agent such as oxalic acid, was added in the eluent.

The results obtained in the presence of oxalic acid (0.8 mM $H_2C_2O_4$, pH 3.1) are compared, for selected analytes, with those previously obtained under non-complexing eluent conditions, (2.0 mM MSA, pH 2.8), in Fig. 5(a) and (b), respectively. Interestingly, the retention behaviour of Cu^{2+} (Cu-oxalic acid logß₂=9.3), Pb^{2+} (Pb-oxalic acid logß₂=6.6) and Cd^{2+} (Cd-oxalic acid logß₂=4.2) [23]) is greatly affected by the presence of oxalic acid which alters and improves the selectivity of the separation.

3.2.4 Eluent containing MSA and oxalic acid

Eluents containing both MSA and oxalic acid were recognized successful to achieve separation among transition metal ions in silica-based weak cation-exchangers [30,31] through the optimization of eluent pH. Therefore, the effect of pH on metals retention was studied for eluents containing 2.5 mM MSA and 0.5 mM oxalic acid (Fig. 6); the desired pH was obtained by addition of LiOH. The retention order obtained for Fe^{3+}, Cu^{2+}, Ni^{2+}, Zn^{2+}, Co^{2+}, Pb^{2+} and Cd^{2+} is in agreement with their stability constants with oxalic acid [logß₃: Fe^{3+}(20.0), logß₂: Cu^{2+}(9.3), Ni^{2+} (7.9), Zn^{2+}(7.6), Co^{2+}(6.8) Pb^{2+}(6.6), Cd^{2+}(4.2)], rather than with butanoic acid (the moiety present in the stationary phase): the higher the stability constant, the shorter the retention time.

Eluent pH can affect the cation-exchange mechanism, both in terms of availability of – COO⁻ sites and of competing ion H^+, as well as the formation of complexes with oxalic acid.

The trend for *k vs* pH indicates that the cation-exchange and/or complexation mechanism in the stationary phase is favoured over complexation in the eluent especially for Cd^{2+} and Pb^{2+}. Eq. (1) applied to the retention data provided for *x* values lower than the theoretical charges (e.g. Zn^{2+}=0.5397, Pb^{2+}=0.7480, Cd^{2+}=0.9259), suggesting that both the cation-exchange and complexation interactions in the stationary phase are contributing to the retention mechanism.

Since pH 4.0 ensures the best separation conditions, for this eluent composition, the effect of oxalic acid concentration (0.25-0.75 mM) on separation was evaluated (2.5 mM MSA). The results obtained show that increased ligand concentrations decrease retention times for all the analytes, due to the prevailing of the complexed forms, but at the detriment of the selectivity and that the best separation conditions can be achieved when the lowest oxalic acid concentration (0.25 mM) is in the eluent. Since pH resulted to be a key parameter to enhance differences in selectivity, new experiments were performed evaluating the effect of pH (4-5) at 0.25 mM oxalic acid, as optimized and at lower concentrations of MSA, *i.e.* 1.5 mM. The retention order still follows the order of stability constants for the metal-oxalate complexes; furthermore, at pH higher than 4.2, a poor reproducibility of the system is experienced which indeed can be solved by the addition of 1 mM LiNO₃. At the following eluent conditions 1.5 mM MSA, 0.25 mM oxalic acid, 1 mM LiNO₃,

pH 4.2, the elution of Cu^{2+}, Fe^{3+}, Ni^{2+}, Zn^{2+} and Co^{2+} can be accomplished within 10 min, while Cd^{2+} and Pb^{2+} are not eluted within 30 min.

3.2.5 Gradient elution

To elute all the considered analytes in reasonable run times and to possibly enhance the separation, a gradient elution was optimized. The column was equilibrated with the aforementioned eluent composition (1.5 mM MSA, 0.25 mM oxalic acid, 1 mM $LiNO_3$, pH 4.2, hereafter labelled as E1) and several eluents were attempted to achieve the elution of Cd^{2+} and Pb^{2+}. The main problems encountered during the optimization of the gradient program was the baseline separation of Cd^{2+}/Pb^{2+}. The best results were obtained switching from E1 to a non complexing eluent containing MSA only. Through a further optimization of time programming and final MSA concentration, the following gradient: from 0 to 6.5 min E1 and from 6.5 to 7 min: 1 mM MSA, provided a baseline resolution between Cd^{2+} and Pb^{2+} and the separation of five cations (Cu^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}), as shown in Figure 7.

Conclusions

The retention capabilities of –COOH functionalized SBA-15 mesoporous silica for cation-exchange chromatography were assessed. For the first time, chromatographic elutions of model mixtures of cations (alkali, alkaline earths, ammonium and transition metal ions) were obtained under different eluent conditions which allowed us to discriminate the type of interaction involved in the retention mechanism and to attempt the first examples of separation of cations on SBA-15 based stationary phases.

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Captions

Figure 1. Effect of MSA concentration on retention factors for alkali, alkaline earths and ammonium on the SBA15-COOH column (50 x 4 mm i.d.). The experimental data were fitted to eq. (1). Inset: overlay of chromatograms for all analytes at 1 mM MSA (pH 3.0) Eluent flow rate 0.1 mL/min. Injection loop: 10 µL. Analyte concentrations (mg/L): Li^+ (0.5); Na^+ (2.5); NH_4^+ (2.5); K^+ (12.5); Mg^{2+} (0.5); Ca^{2+} (1.0); Sr^{2+} (6.0); Ba^{2+} (6.0). Detection: suppressed conductivity.

Figure 2. Effect of the presence of (A) oxalic acid and (B) PDCA on the selectivity of the SBA15-COOH column (50 x 4 mm i.d.) vs alkali, alkaline earths and ammonium.

(A): 1 mM oxalic acid (pH 3.1), (B): 1.2 mM PDCA (pH 3.1). Eluent flow rate 0.1 mL/min. Detection: suppressed conductivity. Inset: overlay of chromatograms obtained for each analyte.

Figure 3. Effect of organic modifiers (CH_3OH, CH_3CN and CH_3NH_2) on the number of theoretical plates N, N=5.54 $(t/w_{1/2h})^2$ for alkali, alkaline earths and ammonium. Column: SBA15-COOH (50 x 4 mm i.d.). Eluent: 1 mM MSA and organic modifiers as shown. Eluent flow rate: 0.1 mL/min.

Figure 4. Effect of MSA concentration on retention factors for transition metal ions on the SBA15-COOH column (50 x 4 mm i.d.). Eluent flow rate: 0.5 mL/min. The experimental data were fitted to eq. (2); regression outputs are also shown.

Figure 5. Comparison between (a) complexing (0.8 mM oxalic acid, pH 3.1) and (b) non complexing (2.0 mM MSA, pH 2.8) eluents on the retention of selected analytes. Column: SBA15-COOH (50 x 4 mm i.d.). Injection loop: 100 µL. Analyte concentrations (mg/L): Cu^{2+} (2.5); Zn^{2+} (5.0); Pb^{2+} (5.0); Cd^{2+} (2.5). Detection: post-column reaction with PAR at 520 nm.

Figure 6. Effect of pH on retention factors for transition metal ions. Column: SBA15-COOH (50 x 4 mm i.d.). Eluent: 2.5 mM MSA, 0.5 mM oxalic acid, pH was adjusted with LiOH at the desired value. Eluent flow rate: 0.5 mL/min.

Figure 7. Separation of Cu^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+} under optimized gradient conditions. Column: SBA15-COOH (50 x 4 mm i.d.). Eluent: gradient from 0 to 6.5 min: 1.5 mM MSA, 0.25 mM oxalic acid, 1 mM $LiNO_3$, pH 4.2. From 6.5 to 7 min: 1 mM MSA. Injection loop: 100 µL. Eluent flow rate: 0.5 mL/min. Detection: post-column reaction with PAR at 520 nm.

Table 1. Textural features of SBA-15-COOH

Sample	S_{BET}[a] (m^2/g)	Pore volume (cm^3/g)	D_{DFT}[b] (nm)	$W_{1/2}$[c] (nm)
SBA-15-COOH	400	0.88	9.9	1.8

[a] Specific surface area
[b] Pore diameter calculated according to Density Functional Theory model
[c] Peak width at half-max of pore size distribution.

Table 2. Selectivity for alkali and alkaline earth metals on SBA-15 –COOH

Selectivity (eluent)	Slope[a] (r^2)							
	Li^+	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}
$Li^+<Na^+<NH_4^+<K^+<Mg^{2+}<Ca^{2+}<Sr^{2+}<Ba^{2+}$ (1 mM MSA)	-1.3 (0.9986)	-1.1 (0.9930)	-1.3 (0.9768)	-1.2 (0.9949)	-2.0 (0.9995)	-2.0 (0.9996)	-2.0 (0.9998)	-2.0 (0.9993)
$Li^+<Na^+<Mg^{2+}<NH_4^+<Sr^{2+}<Ca^{2+}<Ba^{2+}<K^+$ (5 mM MSA)								
$Li^+<Na^+<NH_4^+<K^+<Mg^{2+}<Ca^{2+}<Sr^{2+}<Ba^{2+}$ (0.5 mM oxalic ac.)	-1.2 (0.9987)	-1.2 (0.9999)	-1.1 (0.9976)	-1.3 (0,9968)	-2.1 (1.000)	-2.1 (0.9999)	-2.1 (1.000)	-2.1 (1.000)
$Li^+<Na^+<NH4^+<Mg^{2+}<Ca^{2+}<Sr^{2+}<Ba^{2+}<K^+$ (2 mM oxalic ac.)								
$Li^+<Na^+<NH_4^+<Ca^{2+}<K^+<Sr^{2+}<Ba^{2+}<Mg^{2+}$ (0.5 mM PDCA)	-1.3 (0.9923)	-1.3 (0.9955)	-1.4 (0.9894)	-1.3 (0.9983)	-2.1 (0.9899)	-2.0 (0.9839)	-2.1 (0.9889)	-2.2 (0.9907)
$Li^+<Na^+<Ca^{2+}<NH_4^+<Sr^{2+}<K^+<Ba^{2+}<Mg^{2+}$ (1.2 mM PDCA)								

[a] slopes calculated according to regression data on eq.(1)
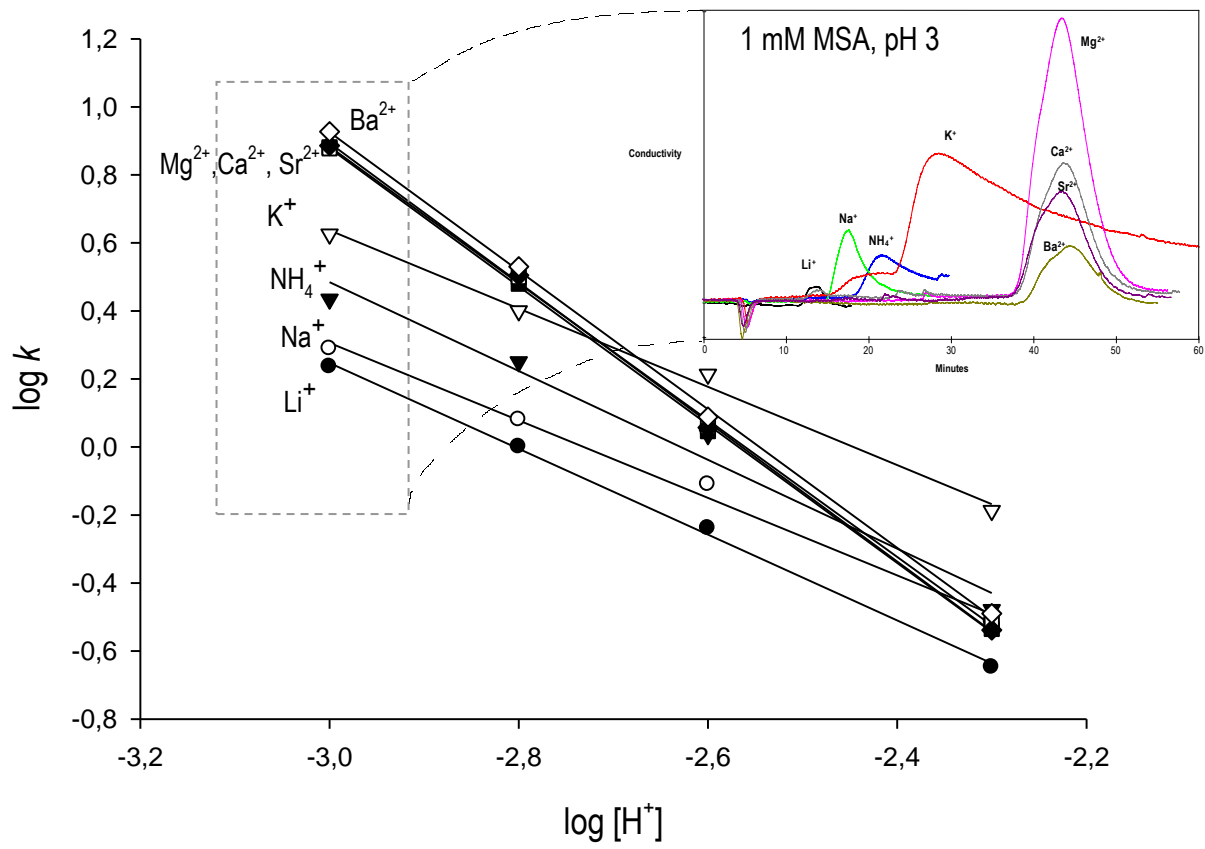
Figure 1

Figure 2

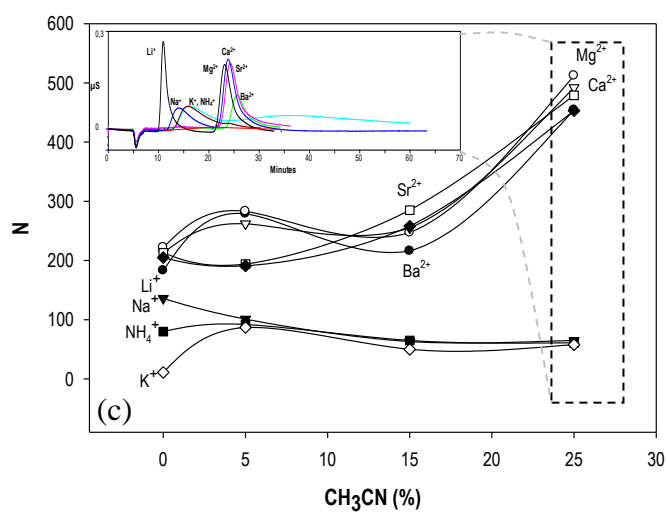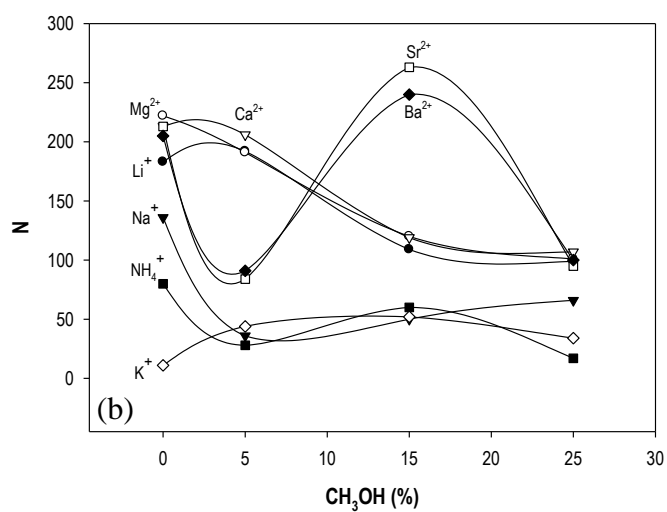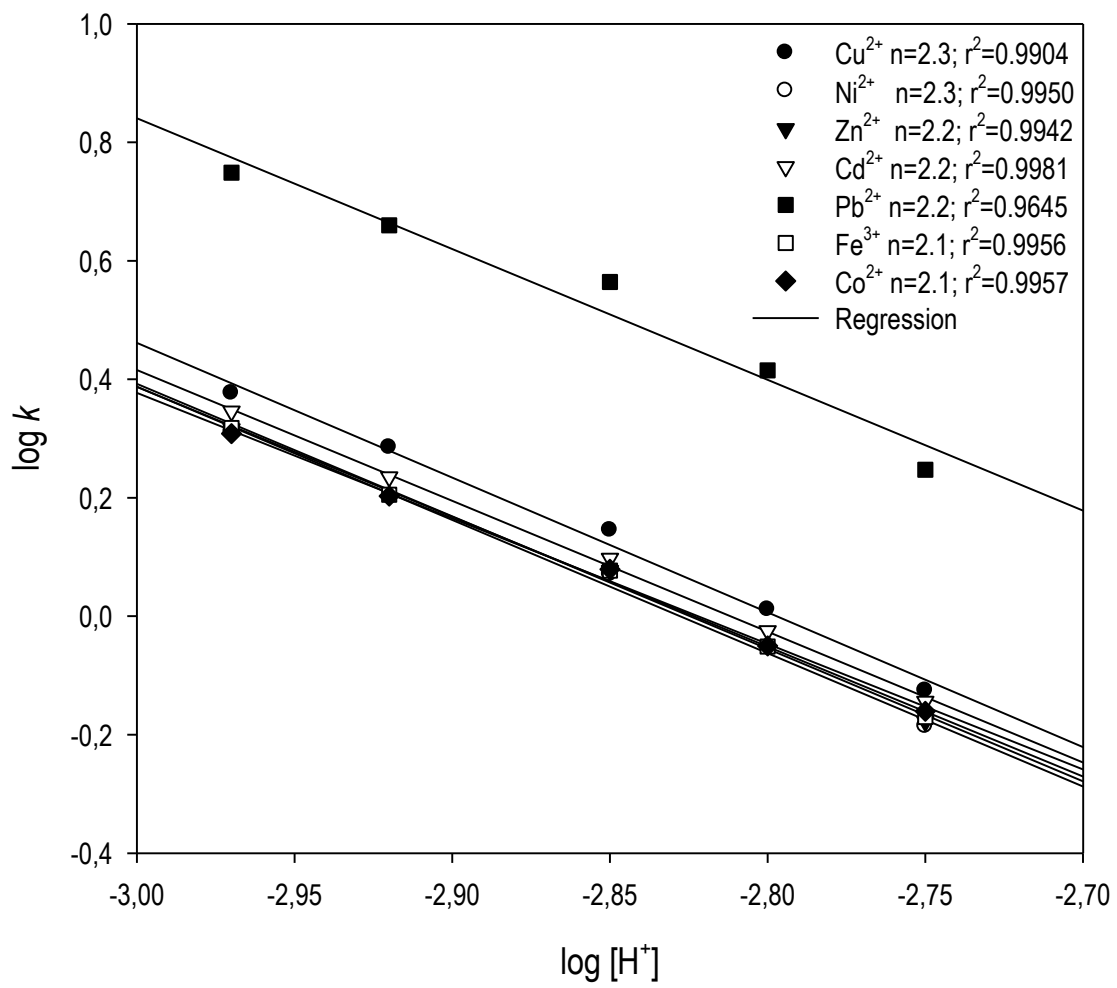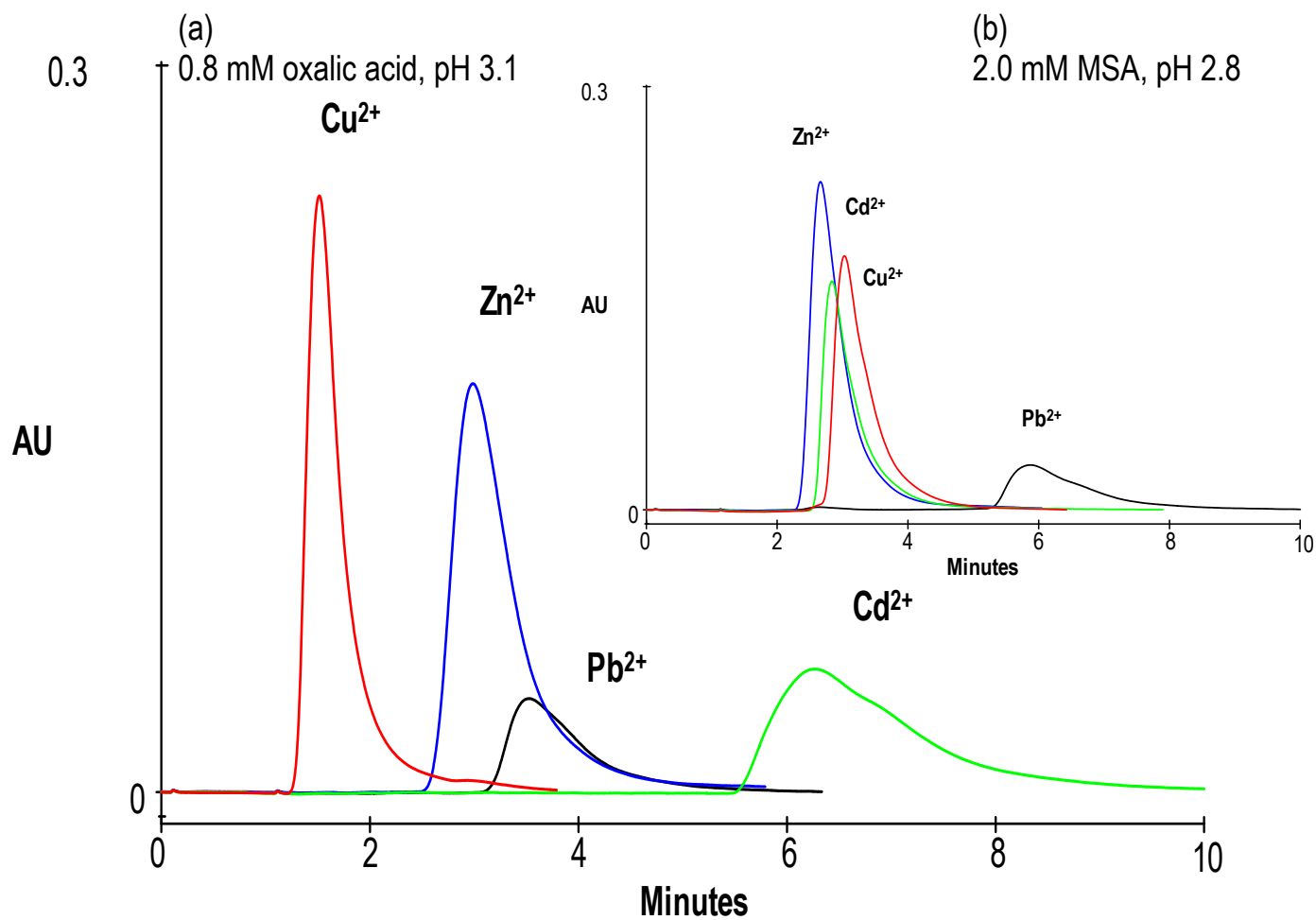Figure 3

(a)

(b)

(c)
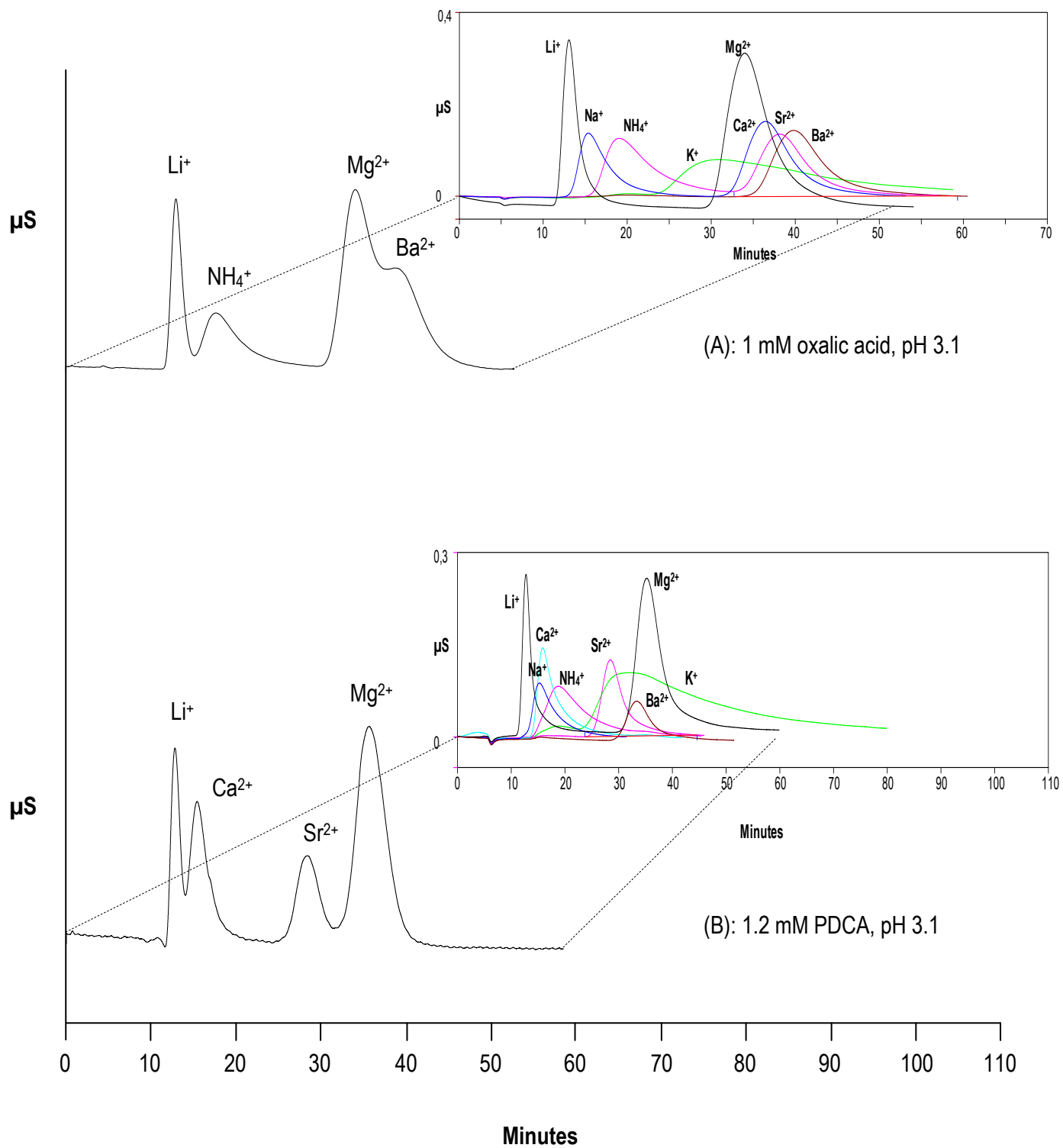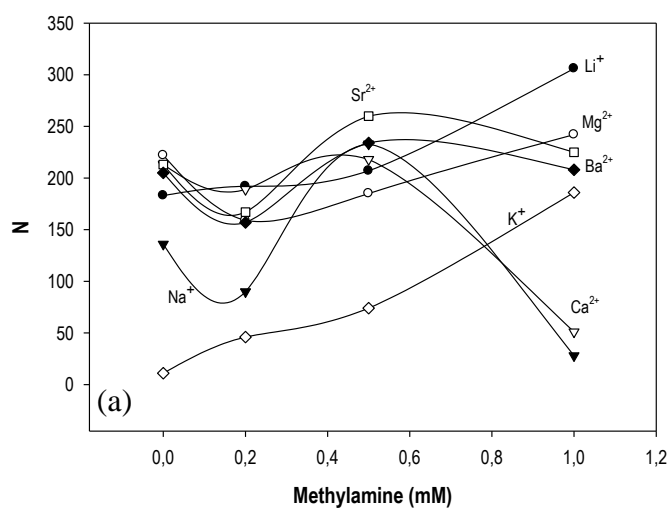
Figure 4

Figure 5

Figure 6

Figure 7