Solid-Phase Extractors Based on 8-Aminoquinoline and 2-Aminopyridine Covalently Bonded to Silica Gel for the Selective Separation and Determination of Calcium in Natural Water and Pharmaceutical Samples

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Two new silica-gel phases were produced directly *via* the chemical interaction of 3-chloropropyltrimethoxysilane modified silica gel with 8-aminoquioline, phase I and 2-aminopyridine, phase II under reflux conditions. The selectivity properties exhibited by the phases under investigation for the uptake of Ca(II), Mg(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Pb(II) were determined at different pH values and shaking times under static conditions. The immobilization process and binding of metal ions to the phases were proved *via* infrared spectra. The phases showed high performance towards Ca(II) extraction at pH 10.00. The equilibrium data were better fitted with a Langmuir model ($r^2 = 0.985$). The adsorption kinetics data were best fitted with the pseudo-second-order type. Good validation was obtained on applications of the two phases for the separation and determination of Ca(II) in natural water and pharmaceutical samples with no matrix interferences at pH 10.00 under dynamic conditions prior to determination by AAS.

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Introduction

The determination of alkaline earth metals, especially calcium and magnesium, is important in environmental, biological, and industrial applications. They play a crucial role in different vital processes occurring in the human body. Calcium and magnesium are two of the most important minerals the body needs to gain and maintain good health.[1,2] Calcium is needed for growth and bone density, plus it keeps the heart pumping, muscles moving, and nerves communicating; it also plays a key role in a number of physiological processes. Magnesium actives over 100 enzymes and helps nerve and muscle function.[3,4] However, if they are in excess, they can also play an important role in the progression of several types of damage to the human body, including disturbances in energy metabolism or increasing oxidative stress. Depression can also be related to high and low levels of calcium and/or magnesium too, with low levels often being associated with anxieties as well.[2] All examples showed that maintaining a balance of cations in the body is essential to human health. Hence, accurate determination of pharmaceutical products is important, since the intake of even low concentrations of metal ions can cause serious toxic effects.

The determination of trace metals in complex matrices remains one of the most complicated areas of analytical chemistry. In the literature, due to strong environmental and biological impacts, trace-metal ion determination has received particular attention in recent years. These metal ions can be determined by different methods, such as flame spectrophotometry or atomic-absorption methods,[5-7] ion-selective electrodes,[8,9] ion chromatography,[10] fluorometric sequential injection analysis[11] and a solvent extraction–flow injection method.[12,13] These techniques are sensitive and sophisticated, but suffer from inherent interferences; also, all these procedures involve tedious and cumbersome extraction or preparation steps to enhance the analytical utility.

In fact, the separation of Ca(II) and Mg(II) was rather difficult for the purposes of determining metal ions with different methods. Most of them were indirect, since they were nonselective. Thus, the separation and determination of Ca(II) and Mg(II) present together are the main challenges in many respects. In the past, several papers have appeared concerning the separation of calcium and magnesium by using ion-exchanger chromatography.[14-16] Recently, other papers discussed the determination of calcium and magnesium in the presence of each other using different techniques.[17-19]

Researchers are thus focusing on using an important technique that has many advantages, called solid phase extraction (SPE) for the determination of these two selected metal ions in the presence of each other.[20-22] This technique has advantages of simplicity, low cost, ease of use and rapid extraction of analyse, which exists in low concentrations. Accordingly, several selective solid-phase extractors have been prepared either by the physical loading or chemical binding of selected chelating reagents to different solid supports.[23-33] The efficiency of unmodified silica gel to act as a solid-phase extractor for the removal, separation and preconcentration of heavy metal ions is very low due to the weak interaction between these metal ions and surface silanol groups.[34,35] Thus, the modification of a silica-gel surface through the immobilization of organic complexing agents, either chemically[36-38] or physically,[39-42]

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greatly enhances the metal-exchange capacity as well as the selectivity of such produced phases towards metal-ion removal, separation and/or preconcentration prior to their determination by AAS analysis. The selectivity of solid-phase extractors mainly depends on the structure of the immobilized organic compound, the nature of the incorporated donor atoms, the positioning of the functional groups along the surface of the solid support and the steric requirements of the complex formed after uptake of the desired metal ion.[43] Consequently, a large number of silica gel-supported organic moieties have been synthesized and applied regarding in different research aspects. However, a survey of the literature reveals that little work has so far been reported regarding the simultaneous determination of calcium and magnesium using silica-gel phases.

This manuscript introduces two new chemically modified silica gels bearing 8-aminoquioline (phase I) and 2-aminopyridine (phase II) for the selective separation and determination of Ca(II) ions as a function of the pH using both batch and column techniques. The proposed method has been applied to separate and determine Ca(II) in the presence of Mg(II) ions in natural drinking water and pharmaceutical samples prior to determination by AAS.

Experimental

Analysis equipments

The IR spectra of the phases before and after metal-ion sorption were obtained from KBr pellets by using a Perkin Elmer 1430 spectrophotometer. A Fisher Scientific Accumet pH meter (Model 825) calibrated against two standard buffer solutions at pH 4.0 and 9.2 was used for all pH measurements. A Spectronic 20 (Milton Roy Co., USA) and atomic absorption measurements were performed with a GBC (902) atomic-absorption spectrophotometer (Australia) to quantify metal ions present in mixtures.

Activation of silica gel

To remove any adsorbed metal ions and to increase the content of –OH, silica gel (SG) was first activated by refluxing in concentrated hydrochloric acid for 12 h, then filtered and washed thoroughly with doubly distilled water (DDW) until no detectable chloride ion could be found in the filtrate. Such treated silica gel was dried in an oven at 150°C to remove any adsorbed water on the surface.

Synthesis of chloromodified silica-gel immobilized 8-aminoquinoline (CMSG-8AQ, phase I) and chloromodified silica-gel immobilized 2-aminopyridine (CMSG-2AP, phase II).

For the synthesis of these phases I and II, the surface of silica gel, which is characterized by silanol groups, was firstly modified by the immobilization of 3-chloropropyltrimethoxysilane, as previously described.[38] This modification step produced chloromodified silica gel (CMSG) surfaces, which were followed by the reactions with each 8-aminoquinoline and 2-aminopyridine. Thus, 10 g CMSG was refluxed with 12 mmol of each amino compound for 12 h in the presence of 100 ml of toluene and 1 ml of triethanolamine. The two phases (I and II) thus produced were separated by filtration, washed with diethyl ether and finally dried at 60°C for 2 h.

Metal uptake capacity as a function of the pH and contact time

The metal uptake capacities of such new solid-phase extractors, phases I and II towards Ca(II), Mg(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), and Pb(II) ions were determined in triplicate under static conditions by the batch equilibrium technique. Then, 25 mg of the phase was added to a mixture of 0.5 ml of 0.1 M of the metal ion and 24.5 ml of a buffer solution of pH 1.0 – 10.0, except with Fe(III), where the pH used was between 1.0 – 4.0; the total volume was completed to 50 ml by DDW in a 100-ml volumetric flask. This mixture was mechanically shaken for 30 min at room temperature to attain equilibrium. Then, the phase was separated by filtration and washed with DDW; the unretained metal ion in the filtrate was determined by complexometric EDTA titration and/or AAS. Mixed known volumes of 1.0 M of each of hydrochloric acid and sodium acetate, 1.0 M sodium acetate and ammonia buffer were used to cover the pH range of 1.0 – 10.0. Moreover, the effect of the shaking time on the metal uptake was determined under the same batch conditions for different equilibrium periods (2, 5, 10, 20 and 30 min) at the pH of the highest metal-ion uptake (optimum pH value).

Stability of the phases

Prolonged medium effects on the stability of phases I and II were investigated in the pH range 1.0 – 10.0 under static conditions.[43] To investigate the temperature effects,[22] three weights of 50 mg each of the phase were kept for 1 h at 50, 60, 70, 75 and 100°C in an electric oven, and then left to cool. To show the extent of decomposition or hydrolysis of the immobilized chelate on a silica surface, 25 mg of each medium and thermally treated phases along with an untreated one taken as the standard, were used to evaluate the Ca(II) ion sorption capacity under the same conditions as previously described for batch experiments and the pH of the highest uptake, and then comparing the Ca(II) uptake values obtained with that of the standard untreated one.

Chemicals and reagents

The silica gel used was of TLC grade (70 – 230 mesh size and 60 Å pore diameter), purchased from Woelm Pharm, Eschwege, Germany. 3-Chloropropyltrimethoxysilane, 8-aminoquinoline and 2-aminopyridine were purchased from Aldrich Chemical Co., USA. We used Calcium Kits (Fluitest® Ca-CPC) from Biocon® Diagnostik, Germany; vitamin tablets of "Theragran" (stress formula) and "Theragran-M"; "Aquafina" natural drinking-water samples (mineral waters). Organic solvents used were of spectroscopic grade.

Results and Discussion

Infrared spectra and surface coverage of the new solid-phase extractors (phases I and II)

The spectral data of phases I and II showed strong bands appearing at 1620 and 1600 cm^{-1} and at 1640 and 1620 cm^{-1}, respectively, due to aromatic C=N stretching vibrations. In addition, aromatic ν(C=C) at 1610 – 1600 cm^{-1} overlapped with ν(C=N) bands. However, the weak NH and NH_2 stretching vibration bands of amino groups of 8-aminoquinoline and 2-aminopyridine, respectively, could not be detected, since they merged with the strong characteristic band of silanol groups of silica gel at 3400 cm^{-1}.[22] Also, disappearance of CH-aromatic bands located at 3050 and 3100 cm^{-1} for the two ligands and the appearance of CH-aliphatic located at 2800 and 2900 cm^{-1} for phases I and II confirmed the presence of methoxy groups of the 3-chloromodified compound. Sorptions of the calcium ion by silica gel phases I and II were found to affect the N-H and C=N stretching vibration bands, where they are significantly changed regarding either the position or features as a result of the participation of N-H and C=N in binding to Ca(II) for complex formation, where ν(C=N) in the IR spectra of phases I and II was around 1640 and 1600 cm^{-1}, but shifted to locate at 1580 and 1420 cm^{-1}, respectively. This clearly indicates that the heterocyclic and amino-group nitrogen atoms are the main binding sites for the target metal ion. Moreover, the participation of free hydroxyl silanol groups for binding to Ca(II) should not be neglected, although they could not easily be detected due to different overlapping in the ν(-OH) stretching vibration region. Their synergetic effect with the immobilized ligands are significant, as will be proved and discussed when dealing with the results of the uptake of Ca(II) using bare silica gel. On the other hand, the surface concentration of both 8-aminoquinoline and 2-aminopyridine bound to the CMSG surface were found to be 0.390 and 0.553 mmol g^{-1}, respectively based on a probe method.[43] The values of the surface coverage are in harmony with the number of aromatic rings. Thus, the concentrations of 2-aminopyridine (one aromatic ring) on silica surfaces were higher than that of 8-aminoquinoline, regardless of the stability of the metal complex formed, as discussed later. Moreover, the immobilization process of the two organic modifiers is supported by an interesting color change of the white of CMSG to pale brown (phase I) and yellow (phase II). The phenomenon of color change was extended after metal-ion sorption by the two phases due to complex formation. For example, the color of CMSG-2AP (phase II) changed from yellow to pale orange, pale pink, green and pale blue after the sorption of the Fe(III), Co(II), Ni(II) and Cu(II) ions, respectively, at the optimum pH values where the maximum metal uptake was obtained.

Selectivity studies of two new solid-phase extractors phases (I and II)

Effect of different pH values and the contact time. It is obviously known that the high affinity of a solid phase to bind selectively to a certain metal ion, and consequently its potential use for selective separation of this metal ion from other coexisting metal ions largely depend upon the nature of the function groups of the complexing agent immobilized to the surface of a solid support.[44] However, the pH of the medium is one of the most important factors that control the sorption limit of these metal ions from aqueous solutions to the solid phase, and consequently determining the values of the percentage of extraction for a given solid phase. Based on these values, the following could be investigated: the two phases showed low efficiency towards the extraction of metal ions from aqueous solutions at low pH values due to the protonation of chelation sites in the ligands that inhibit their binding to metal ions.[45] The orders of percentage extraction (%) by phase I (CMSG-8AQ) and phase II (CMSG-2-AP) at the optimum pH decrease in the following order: Ca(II) (100.00) > Cd(II) (23.98) > Fe(III) (22.16) > Cu(II) (21.27) > Zn(II) (20.99) > Co(II) (16.65) > Ni(II) (11.08) > Mg(II) (10.08) > Pb(II) (9.24) for phase I; Ca(II) (98.53) > Fe(III) (22.16) > Cu(II) (18.49) > Zn(II) (16.98) > Co(II) (16.32) > Cd(II) (15.0) > Ni(II) (11.08) > Mg(II) (9.8) > Pb(II) (8.03) for phase II.

These results indicate that the highest affinity is towards Ca(II) extraction for phases I and II, Figs. 1(a) and 2(a). On the other hand, interesting results were obtained upon using bare silica gel for the uptake of Ca(II), as shown in Figs. 1(b) and 2(b). The percentage extraction of silica gel for Ca(II) did not exceed 42%, which strongly supports the participation of free silanol hydroxyl groups, especially in the pH range 8 - 10 for interactions with Ca(II) ions. This synergetic effect with the immobilized ligands reflects the high selectivity of the new phases towards Ca(II) binding. Moreover, the high affinity of Ca(II) for binding to silanol oxygen is apparently high compared to the other metal ions sorbed by the two modified silica-gel phases. In fact, the binding of Ca(II) ions to oxygen-containing ligands is predominant, but their binding to oxygen and nitrogen donor sites is also familiar.[3,46] In addition, the highest affinity of the two phases towards Ca(II) was further strengthed based on the obtained distribution coefficient values (log K_d)[44] for the uptake of metal ions under investigation at the optimum pH values using the two new modified SP-extractors, as follows: Ca(II) (6.43), Mg(II) (2.38), Fe(III) (2.75), Co(II) (2.60), Ni(II) (2.39), Cu(II) (2.73), Zn(II) (2.72), Cd(II) (2.79) and Pb(II) (2.31) for phase I; Ca(II) (5.13), Mg(II) (2.34), Fe(III) (2.75), Co(II) (2.59), Ni(II) (2.14), Cu(II) (2.66), Zn(II) (2.61), Cd(II) (2.55) and Pb(II) (2.26) for phase II.

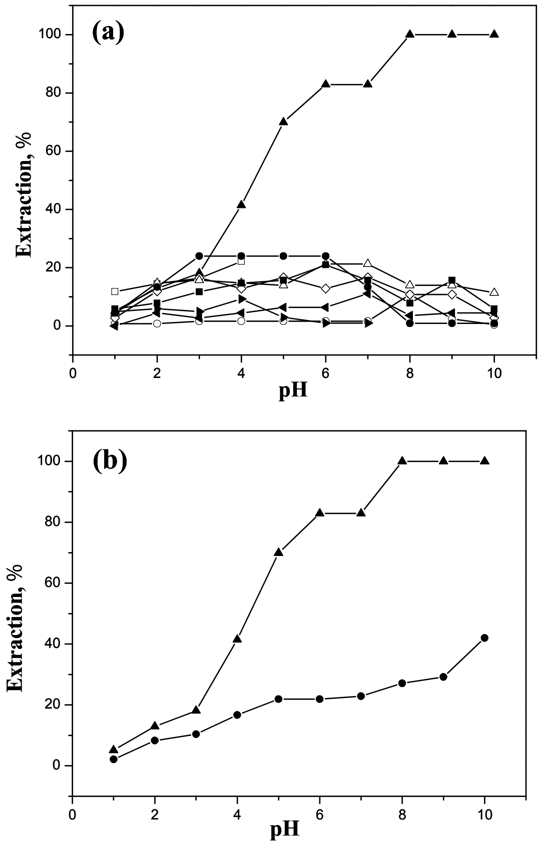

Fig. 1 (a) Percentage extraction of Ca(II) and different metal ions using a batch technique with CMSG-8AQ, phase I at different pH values: ○, Mg(II); ▲, Ca(II); □, Fe(III); ◇, Co(II); ◀, Ni(II); △, Cu(II); ■, Zn(II); ●, Cd(II); ▶, Pb(II). (b) Percentage extraction of Ca(II) using batch technique with SG and CMSG-8AQ, phase I at different pH values: ●, SG-Ca(II); ▲, CMSG-8AQ-Ca(II).

Upon focusing our study of the uptake of Ca(II) and Mg(II) using the two new SP-extractors, it was found that the two phases showed the highest percentage extraction of Ca(II) 100.0, 98.53% and lowest percentage extraction with Mg(II) 0.4, 0.8% using phases I and II, respectively, at pH 10.0. Moreover, the distribution coefficient (K_d) can be taken as a representative value for the selectivity measurements if all of the tested metal ions, not only the individual ones, are brought about in one mixture to compete with each other in binding to selective functional groups of the metal chelate-forming sorbent. Based on the amount of metal ion remaining in the effluent solution and that retained by the phase, the K_d values can be calculated.

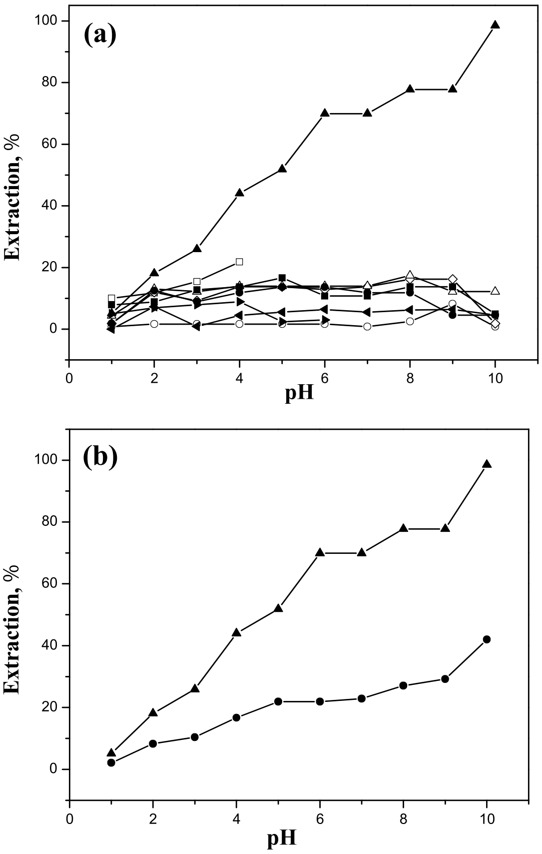

Fig. 2 (a) Percentage extraction of Ca(II) and different metal ions using a batch technique with CMSG-2AP, phase II at different pH values: ○, Mg(II); ▲, Ca(II); □, Fe(III); ◇, Co(II); ◀, Ni(II); △, Cu(II); ■, Zn(II); ●, Cd(II); ▶, Pb(II). (b) Percentage extraction of Ca(II) using batch technique with SG and CMSG-2AP, phase II at different pH values: ●, SG-Ca(II); ▲, CMSG-2AP-Ca(II).

In this context, the remarkably high values of the separation factor (α), 1.41×10^5 and 1.35×10^3, and the selectivity (S), 5.15 and 4.13, for Ca(II) and Mg(II) at pH 10.0 using phases I and II, respectively ($\alpha = K_{dCa(II)}/K_{dMg(II)}$, $S = \log K_{dCa(II)} - \log K_{dMg(II)}$) support the separation process. Thus, it was clearly observed that the separation of calcium from magnesium ions can be performed easily and directly using these two new synthesized phases at the selected pH values.

A modification of the silica-gel surface with organic complexing agents resulted in producing metal-ion extractors that need only a few minutes to complete the metal-ion extraction processes, compared with other organic adsorbents.[44] This represents one of the advantages of using silica gel as an inorganic solid support for the immobilization of chelating compounds. Moreover, the shaking time is another important factor in the process of evaluating the two new SP-extractors, phases (I and II). The relative fastness of extraction of a given metal ion can be used for its selective separation from a mixture containing other coexisting metal ions. To account for the fastness of metal-ion sorption using the phases (I and II), metal capacity values were determined using the batch method at different shaking times (2, 5, 10, 20, and 30 min) to determine the time needed to attain equilibrium. The percentage extraction for each metal ion at the optimum pH value was calculated at each time interval relative to the highest uptake at 30 min.[22] It is evident from the results that the extraction of Ca(II) was the fastest using any of the phase I or II at any time interval used. For example at 10 and 20 min contact times, the percentages of extraction of Ca(II) were 86 and 95% and 65 and 75% using phases I and II, respectively.

Table 1 Parameters of Freundlich and Langmuir isotherm constants for binding of Ca(II) using phases I and II at room temperature

Sorbent	Freundlich constant			Langmuir constant		
	K_f	$1/n$	r^2	Q_o[a]	b[b]	r^2
Phase I	–2.75	3.86	0.934	0.924	0.676	0.985
Phase II	–2.92	1.07	0.934	0.763	0.930	0.985

a. µmol g^{-1}.
b. ml µmol^{-1}.

Sorption isotherms and kinetic studies

The results obtained on the sorption of Ca(II) ions were analyzed by well-known models given by Langmuir and Freundlich. The Langmuir equation, which is valid for monolayer sorption onto a completely homogeneous surface with a finite number of identical sites and with a negligible interaction between the adsorbed molecules, is given by the following equation:

$$C_e/q_e = (C_e/Q_o) + 1/Q_o b,$$

where C_e and q_e are the equilibrium concentrations of adsorbate in the liquid and adsorbed phases in µmol ml^{-1} and µmol g^{-1}, respectively.[47] $Q_o = 0.924$, 0.763 and $b = 0.676$, 0.930 are Langmuir constants for phases I and II, respectively, which are related to the maximum Ca(II) sorption capacity (µmol g^{-1}) and affinity parameter (ml µmol^{-1}), respectively, and can be calculated from the intercept ($1/Q_o b$) and slope ($1/Q_o$) of the linear plot, C_e/q_e *vs.* C_e. The correlation coefficient ($r^2 = 0.99$ for phases I and II) showed that the Langmuir model fitted the results better. Moreover, the essential characteristics of the Langmuir isotherm can also be expressed in terms of a dimensionless constant separation factor or equilibrium parameter, R_L, which is defined as $R_L = 1/(1 + bC_o)$, where b is the Langmuir constant (indicates the nature of sorption and the shape of the isotherm accordingly); C_o the initial concentration of the analyte.[47] The R_L for Ca(II) sorption (0.94) supports a highly favorable sorption process based on the Langmuir model.

The Freundlich isotherm model assumes neither homogeneous site energies nor limited levels of sorption.[48] This model is the earliest known empirical equation, and is shown to be consistent with the exponential distribution of active centers, characteristic of heterogeneous surfaces,

$$\log q_e = \log K_f + 1/n \log C_e.$$

Here, K_f and n are the characteristic Freundlich constants. K_f and n are indicators of the biosorption capacity and biosorption intensity, respectively. The plot of $\log q_e$ *vs.* $\log C_e$ has a slope with a value of $1/n = 3.86$, 1.07, and an intercept magnitude of $\log K_f = -2.75$ and -2.92 for phases I and II, respectively.

It was observed from the isotherm and regression coefficient[47] that the fit is better with the Langmuir model than with the Freundlich model. The different parameters of the Langmuir and Freundlich isotherm constants are collected in Table 1.

The adsorption kinetic study is quite significant in a water

Table 2 Analytical results for calcium and magnesium ions in 100 ml of five natural drinking-water samples using 100 mg of phases I and II at pH 10.0

Phase	n	Ion present in mg/l		Ca(II) found in mg/l			Mg(II) found in mg/l		
		Ca(II)	Mg(II)	Mean + SD	RSD, %	%R	Mean + SD	RSD, %	%R
I	5	5.1	13.6	5.06 ± 0.05	0.98	99.2	13.44 ± 0.89	6.60	98.8
II	5	5.1	13.6	4.90 ± 0.28	5.71	96.1	13.20 ± 0.38	2.90	97.1

treatment, since it describes the solute uptake rate, which in turn controls the residence time of the adsorbate uptake at the solid–solution interface. The sorption kinetic data of calcium measured on phases I and II were analyzed in terms of pseudo-first-order and pseudo-second-order sorption equations.[47] The pseudo-first-order equation is

$$\log(q_e - q_t) = \log q_e - (k_1/2.303)t,$$

where k_1 (min^{-1}) is the rate constant of the pseudo-first-order sorption, q_t (mg g^{-1}) denotes the amount of sorption at time t (min), and q_e (mg g^{-1}) is the amount of sorption at equilibrium. The kinetic plots were drawn for the two phases and the adsorption rate constant ($k_1 = 0.214$, 0.124) and adsorption capacity ($q_e = 0.802$, 0.752) for phases I and II, respectively, were calculated from the slope and intercepts of plots of $\log(q_e - q_t)$ against "t".

The sorption kinetic data of Ca(II) measured on phases I and II were also analyzed in terms of a pseudo-second-order sorption equation.[47] This equation can be written as

$$t/q_t = 1/\upsilon_o + (1/q_e)t.$$

Here, $\upsilon_o = kq_e^2$ is the initial sorption rate (μmol g^{-1} min^{-1}), where, k (gm mmol^{-1} min^{-1}) is the rate constant of sorption, q_e (mmol g^{-1}) is the amount of metal ion sorbed at equilibrium, and q_t (mmol g^{-1}) the amount of meal ion on the surface of the sorbent at any time t (min). υ_o and q_e can be obtained from the intercept and slope of a plot of t/q_t *vs.* t, respectively. They were calculated to be $\upsilon_o = 0.363$, 0.066, $q_e = 0.776$, 0.736 μmol g^{-1} and $k_2 = 0.603$, 0.122 min^{-1} for phases I and II, respectively. Since the kinetics of the uptake has to be determined in order to establish the time course of the uptake process, the previous results showed that the adsorption kinetics data were best fitted with the pseudo-second-order model, which gives a correlation factors of $r^2 = 0.99$ and 0.97 more appropriately than the pseudo-first-order equation, $r^2 = 0.91$ and 0.93, for phases I and II, respectively.

Stability of the phases I and II

The results of medium effects showed that the phases I and II experienced pronounced stability, since no hydrolysis (no loss in the efficiency of the phase for Ca(II) uptake) as experienced by both phases I and II at pH 1.0 - 4.0 or the minimum hydrolysis of 6.2 and 6.6% as exhibited by phases I and II, respectively, at pH 5.0 - 10.0. On the other hand, the results of thermal-stability studies showed that the two phases I and II maintained their efficiency for Ca(II) uptake at 50 and 60°C where no decomposition occurred. However, at 70, 75 and 100°C the values of decomposition did not exceed 44.4%.

Selective separation and determination of Ca(II) and Mg(II) from natural water samples

Silica-gel modified phases were chosen to study the possibility of their potential use for the purposes of selective separation of Ca(II) present in natural drinking-water samples with Mg(II) and other metal ions. Column separation was performed by passing 100 ml of natural drinking-water samples, that contained 5.1 ppm of Ca(II) and 13.6 ppm of Mg(II), the amount of Ca(II) and Mg(II) as on the label of the bottle were 5.2 and 13.2 ppm, respectively, in the presence of other metal ions, like Na(I), K(I), HCO_3^-, SO_4^{2-} and SiO_2^{2-}, in minicolumn (length 10 cm, i.d. 1.65 cm) supported glass wool, with a flow rate of 1.5 ml/min. It was established that Ca(II) ions were completely retained from the solution samples on 100 mg of both two phases I and II at pH 10.00. On the other hand, Mg(II) ions were found in the effluent at this pH value; then, 2 ml of concentrated HNO_3 used for the elution of retained Ca(II) ions with a flow rate of <0.1 ml/min, justify the eluate solution at pH 10.00 to 10 ml volume. We then calculated the value of Ca(II) retained on the phases and Mg(II) ions in the effluent by AAS. The results, as given in Table 2, are successfully explained by saying that we are directly able to determine Ca(II) ions in the presence of excess Mg(II) ion content in natural drinking-water samples. Generally, the results of separation are in accordance with the highest efficiency of phase I or II towards Ca(II) uptake, relative to the other coexisting metal ions.

Selective determination of Ca(II) ions in different pharmaceutical samples

The determination of trace metals in complex matrices remains one of the most complicated areas of analytical chemistry. In the literature, due to a strong environmental and biological impact, trace metal-ion determinations have received particular attention in the last few years.[4]

For phases I and II, more complicated matrices are used as pharmaceutical samples. Five vitamin tablets of two different types of "Theragran" (Theragran (stress formula) (T) and Theragran-M (TM)), were weighed and finally powdered. The powder amount was dissolved in conc. HNO_3 using glass beakers covered with water glasses and heated on a hot plate. For that aim, 10 ml of conc. HNO_3 was used until the digest solutions were clear and light colored. After cooling, another 10 ml of conc. HNO_3 was added, and the heating was gently continued. After evaporation to near dryness, the samples were taken up with DDW. The resulting liquids were quantitatively transferred to 100 ml volumetric flasks and completed with DDW. One element solution of Ca(II), of volume 100 ml, containing the analytes at concentrations of 18.9 mg for T and 42.0 mg for TM, the amounts of calcium contained in each tablet were 20 and 50 mg for T and TM, respectively, was driven through the columns at a given flow rate of 5 ml/min. After passing this volume, about 10 ml of conc. HNO_3 used as eluant was passed through the Ca(II) retained phase at a flow rate 0.1 ml/min. The effluent from the column was collected and buffered to the respective pH 10.0, and then analyzed concerning the content of the metal of interest by means of a spectrophotometer. The results are listed in Tables 3 and 4, which show quantitative recovery. However, it was established from these tables that using phases I and II is convenient for the

Table 3 Analytical results for calcium ions in 100 ml of five different vitamin (T) tablet samples using 100 mg of phases I and II at pH 10.0

Phase	*n*	Ion present in mg/100 mL	Ion found in mg/100 mL		
			Mean + SD	RSD, %	%*R*
I	5	18.97	18.96 ± 1.1	5.80	99.9
II	5	18.97	18.23 ± 0.1	5.70	96.1

Table 4 Analytical results for calcium ions in 100 ml of five different vitamin (TM) tablet samples using 100 mg of phases I and II at pH 10.0

Phase	*n*	Ion present in mg/100 mL	Ion found in mg/100 mL		
			Mean + SD	RSD, %	%*R*
I	5	42.00	41.46 ± 1.70	4.10	98.7
II	5	42.00	41.25 ± 0.58	1.40	98.2

determination of Ca(II) ions in the presence of Mg(II), which is the most interfering metal ion with calcium, or proteins and other macromolecules in the vitamins samples. Moreover, this determination method offers the advantages of simplicity, selectivity and high sensitivity for the determination of calcium ions in complicated matrices.

Conclusion

In the present study, a new solid-phase extraction technique was developed based on using two new solid-phase extractors' phases I and II for the selective determination of Ca(II), compared with eight other investigated metal ions. It was also used, for the selective separation of Ca(II) from Mg(II) ions in natural-water and pharmaceutical samples prior to determination by AAS. These methods are simple, accurate, and economical, and can be applied to the determination of Ca(II) in environmental samples.

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