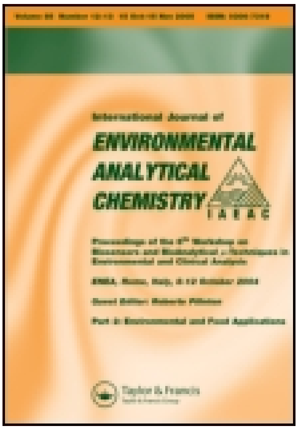

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Synthesis and characterisation of a silicon oxide film solid-phase extraction system for lead traces determination: an all the way green analytical method

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In this work, an all the way green analytical procedure based on a silicon oxide film-solid phase extraction system is proposed for lead traces determination. From the synthesis of a solid phase extraction (SPE) system and throughout the metal preconcentration and determination only aqueous media were employed. Characterisation of the film was carried out by Scanning Electron Microscopy and Attenuated Total Reflectance-Fourier Transform Infrared Spectroscopy. Preconcentration conditions, prior to Pb(II) Electrothermal Atomic Absorption Spectrometry (ETAAS) determination, such as adsorption and desorption time, pH and temperature, were optimised. Langmuir, Freundlich and Dubinin-Radushkevich isotherm models were analysed along with the evaluation of adsorption energy and standard free energy (ΔG^0). The greatest adsorption was obtained with incubation at pH 7 and 37°C. By using a small volume of $0.5\,\mathrm{mol\,L^{-1}}$ HNO_3 (0.5 mL) lead was desorbed from the silicon oxide film after 2 h incubation, generating low amount of waste. The films showed better adjustment for the Langmuir model ($R^2 = 0.989$). The detection limit (3.29σ) for Pb(II) was $0.228\,\mu\mathrm{g\,L^{-1}}$. The developed procedure is 10-fold more sensitive in comparison to direct ETAAS determination. Recovery values from soft tap-water and soft well-water were above 95%. When hard water was analysed, Pb(II) adsorption was found to be interfered by Mg^{2+} and Ca^{2+}. After five preconcentration cycles relative recovery was found not to decay below 90%, indicating that the silicon oxide film could be used for multiple lead determinations.

Keywords: green chemistry; solid-phase extraction; silicon oxide; lead traces; atomic absorption

1. Introduction

Lead, one of the most toxic metals, has been used by man for many centuries. It appears in natural waters and industrial effluents, mainly due to anthropogenic sources [1]. Although natural waters seldom contain more than $5\,\mu\mathrm{g\,L^{-1}}$, lead is cumulative in the

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body and slow acting [2]. This fact means there is a need for a sensitive analytical technique for its determination, which frequently requires a preconcentration step. Lead analytical determination has been studied for a long time by several techniques such as colorimetric, atomic absorption, inductively coupled plasma or anodic stripping voltammetry, among others [3].

Preconcentration is often required to improve sensitivity and to separate the analyte from the matrix components and potential interferences. Lead preconcentration has been achieved by different techniques such as coprecipitation, cloud point extraction, liquid–liquid extraction, on-line preconcentration and solid phase extraction (SPE), among others [4–7].

In the last decades, several green analytical methods have been developed. Green analytical chemistry tries to solve the drawbacks of classical analytical chemistry, which often contributes to environmental pollution through the use of hazardous chemicals in their procedures [8]. Waste amount and toxicity of compounds are parameters to be taken into account, which could be solved by reagent replacement, recycling and waste treatment [9]. The use of solid phase extraction (SPE) has been pointed out as an advantage since it could be used in preconcentration by desorbing analytes in small volumes, thus using low amounts of solvent and generating low quantities of waste [10,11].

Natural and synthetic silica containing composites have been widely studied for preconcentration applications [12–14]. Nevertheless, most preconcentration developments have used chemically modified silica matrices [15–17]. Among these can be mentioned the use of thiolated silica or the bonding of chelating agents such as 5-formyl-3-(1′-carboxyphenylazo) salicylic acid, p-dimethylaminobenzaldehyde, 8-hydroxyquinoline, aminothioamidoanthraquinone [9,18–24]. Most of these developments involve the use of an organic solvent for at least at one step of the synthesis procedure.

Commercially available adsorbents for preconcentration are usually expensive and the preparation of chemically modified silica matrices requires laborious synthesis. In addition, organic chelating agents may not be stable and the reutilisation of preconcentration systems is frequently not possible. On the other hand, unmodified silica matrices are less expensive and they are chemically stable. The sol-gel chemistry is at present the most used methodology to obtain silica matrices because it allows the polymerisation of a wide variety of silicon oxide precursors at mild conditions within a single step [25].

The aim of this work was to generate an all the way green analytical procedure, that is, from the synthesis of a SPE system, throughout the metal preconcentration and its determination, as well as in its waste generation. With this purpose, silicon oxide films were obtained by the silicate sol-gel aqueous route for its study in the solid phase extraction and preconcentration of lead traces and its subsequent determination by Electrothermal Atomic Absorption Spectrometry (ETAAS). The silicon oxide films (Si-SPE films) were obtained within a one step reaction over naked glass surfaces. Conditions of batch preconcentration such as adsorption and desorption times, pHs and temperatures were studied along with the reutilisation of the Si-SPE films. Langmuir, Freundlich and Dubinin-Radushkevich isotherm models were analysed together with the evaluation of adsorption energy and standard free energy (ΔG^0). Lead detection limits and recoveries from tap-water and well-water were also determined.

2. Experimental

2.1 *Apparatus*

Lead determinations were done with a Buck Scientific VGP 210 Atomic Absorption Spectrophotometer (E. Norwalk, CT, USA) by the electrothermal atomisation method using pyrolytic graphite tubes. Nickel nitrate 0.1% was used as matrix modifier [26]. Each sample was injected in triplicate. Other instrumental parameters were used as recommended by the manufacturer. Real water ion composition studies were carried out with a Capillary Electrophoresis System CAPEL-105 M Lumex (St. Petersburg, Russia) and analysis parameters were used as described elsewhere [27]. Scanning electron microscopy (SEM) images were obtained using a Philips 505 microscope. Films were coated with 20 nm gold, before SEM. Attenuated Total Reflectance-Fourier Transform Infrared Spectroscopy (ATR-FTIR) transmission spectra were acquired in the range of 4000–650 cm^{-1}, using a Fourier Transform infrared spectrometer (FT-IR) with a Flat-plate Attenuated Total Reflectance (ATR) (Perkin Elmer, Spectrum One IR). All slides were previously dried for 24 h at 60°C to avoid water related bands interference.

2.2 *Reagents and samples*

Sodium silicate was from Riedel-de Haën (Seelze, Germany). Nitric acid (70%) was from J.T. Baker (Phillipsburg, NJ, USA). Water was filtered and deionised with a Milli-Q, Millipore system (Milford, MA, USA). Standard stock solutions of Pb(II) were carefully prepared by dissolving lead chloride (1 $g\,L^{-1}$) (Merck, Darmstadt, Germany). All working solutions were made by dilution of the standard stock solution and concentration verified against the appropriate dilution of Titrisol® Lead Standard 1000 $mg\,L^{-1}$ (Merck). All other reagents were of analytical grade.

Tap-water samples from Buenos Aires city (Argentina) and San Rafael city (Mendoza province, Argentina) and well-water samples from Monte Grande city (Buenos Aires province, Argentina) were collected and assayed without further treatment.

2.3 *Si-SPE films generation*

Standard microscope slides (75 mm × 25 mm) were used as coating support. They were conditioned by sonication (30 min, 35 kHz), first in acetone and then in ethanol and then dried at 60°C. In order to generate the films (Si-SPE films), the naked glass slides were immersed in a mixture of 4% p/v sodium silicate solution, 0.2 $mol\,L^{-1}$ potassium phosphate pH 5, water and HCl 1 $mol\,L^{-1}$ (2 : 4 : 1 : 1) and left in it for 5 min at 25°C. The resulting slides were then air dried at 25°C. The Si-SPE films thus obtained showed optical transparency after the aging process. The coated slides average mass of the SiO_2 films was 12.9 mg (0.69 $mg\,cm^{-2}$). Before metal adsorption assays, all slides were soaked sequentially in ultrapure water for 2 h, 0.5 $mol\,L^{-1}$ HNO_3 for 4 h and finally in ultrapure water for 2 h.

2.4 *Adsorption and preconcentration procedure*

The effects of incubation pH, temperature, adsorption and desorption times on lead preconcentration were evaluated by batch method. In order to minimise contamination problems by foreign elements and adsorption not related to the films, plastic vessels were used in the study. When the use of volumetric glassware was needed it was previously washed with a nitric acid solution until no lead was detected.

Samples were prepared by spiking known amounts of lead to ultrapure, tap and well-water. For all adsorption assays Si-SPE films were immersed in 200 mL of Pb(II) spiked solutions ranging from 1 to 500 $\mu g\,L^{-1}$. At concentrations of lead below 1 $\mu g\,L^{-1}$ the samples were analysed using 1000 mL and 200 mL in order to compare the experimental performance of the Si-SPE system. Incubation solutions pHs were adjusted within the range of pH 3 and 7. Optimum incubation times for adsorption and desorption were tested at 25°C and 37°C. Adsorption isotherms and preconcentration assays were carried out at optimised conditions: pH, temperature and incubation time within the range between 0.1 and 500 $\mu g\,L^{-1}$ Pb(II). For all tests, blank experiments were performed using naked glass slides.

Preconcentration of the adsorbed metal from the films was carried out as follows: (a) after incubation in Pb(II) spiked solution, slides were air dried and placed in plastic petri dishes; (b) a volume of 0.5 mL 0.5 $mol\,L^{-1}$ HNO_3 was used to cover all slide surface. They were kept at room temperature with a relative humidity no less than 90%. The equilibrium time was deducted from the kinetic experiments. The volume and concentration of HNO_3 were chosen in order to avoid the generation of large and diluted amount of metal containing waste and not to use a concentrated acid that would need large amounts of alkaline solution to neutralise.

Reutilisation of slides was evaluated following the same sequence used for preconcentration assays. In-between preconcentration cycles, the water-nitric-water washing procedure was repeated, after which a 2 h 0.5 $mol\,L^{-1}$ HNO_3 incubation was carried out in order to verify lead presence. Then the slides were washed following the above mentioned procedure before a new lead incubation cycle.

Real water samples were spiked with known amounts of Pb(II) in order to evaluate the recovery of the metal and possible ion interferences. All experiments and measurements were conducted in duplicate under identical conditions.

3. Results and discussion

3.1 *SEM analysis of Si-SPE films*

Sodium silicate being a tetrafunctional monomer, its polymerisation can lead to complex branching of the polymer [25]. Thus, the chains can be joined by crosslinks to form a three-dimensional structure. SEM image of the Si-SPE film shows a characteristic silicon oxide network image, which can be seen as polymeric chains disposed in plane films and branched elevations over the flat naked glass (Figure 1).

3.2 *Infrared spectra*

ATR-FTIR spectra of Si-SPE films and the glass used as support are shown in Figure 2. In the naked glass spectrum, it could be seen characteristic silicon oxide broad bands at 750 cm^{-1} and 900 cm^{-1} corresponding to symmetric Si–O–Si bond stretching and Si–OH bond stretching, respectively [28]. In Si-SPE films spectrum, it could be observed the Si–O–Si bond stretching band together with a narrowing of the Si–OH bond stretching band, which produces a maximum shift to 880 cm^{-1}. It could also be observed the appearance of

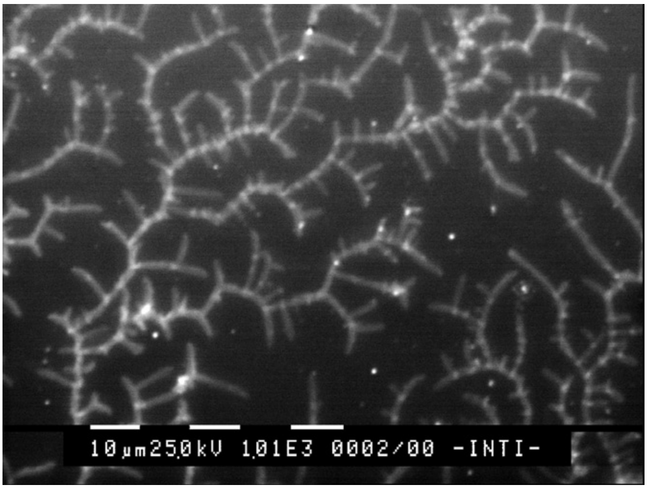

Figure 1. SEM image of Si-SPE film.

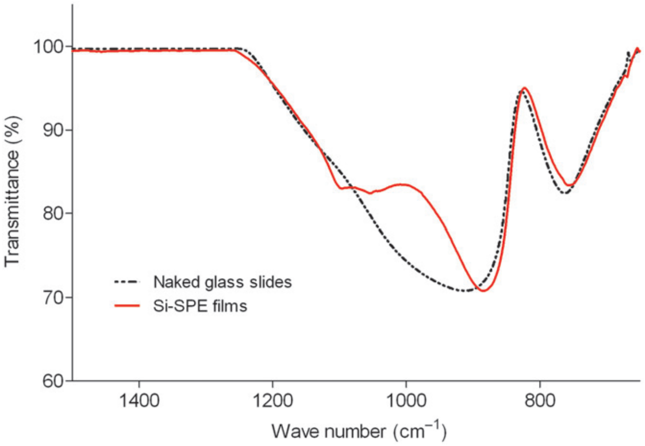

Figure 2. ATR-FTIR spectra of Si-SPE film and naked glass used a support.

bands at the range 1100–1000 cm^{-1}. Other researchers assigned these bands to asymmetric Si–O–Si bond stretchings from condensed polymeric precursors forming oligomeric units typical of silicon oxide polymerisation [29]. Thus, the presence of these bands (absents in the structure of the support) would be indicative of the presence of the Si-SPE films polymeric network.

3.3 *Effect of pH on adsorption*

The influence of aqueous solution pH on Pb(II) adsorption was investigated in the pH range 3–7 (Figure 3). Higher pHs were not evaluated because $Pb(OH)_2$ precipitates above

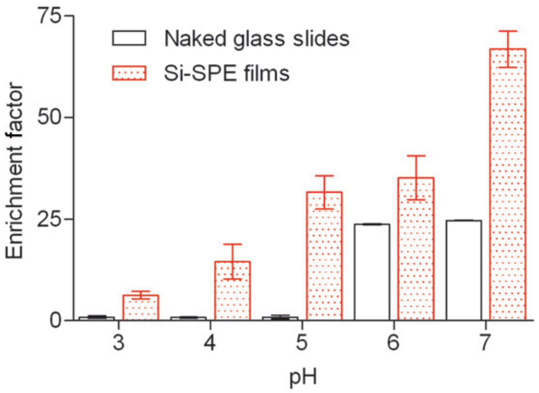

Figure 3. Influence of sample solution pH on Pb(II) preconcentration.

pH 8 [30]. Lead adsorption to the SiO_2 film increased with the rise of solution pH reaching its maximum at pH 7. A similar behaviour was observed by other researchers, who indicated that Si_sOH and H–OH have similar behaviour as ligands, which explains that metal silicon oxide complex is formed at a slightly lower pH than the one at which the metal hydroxide is precipitated [31,32]. This also explains the Pb(II) adsorption increase in naked glass at high pH (Figure 3).

3.4 *Effect of time and temperature on adsorption and desorption assays*

Kinetic experimental results are shown in Figures 4 and 5. These plots show Pb(II) concentration over time in the adsorption (pH 7) and desorption process ($0.5\,\mathrm{mol\,L^{-1}}$ HNO_3) respectively. In order to analyse the influence of incubation temperature on the uptake rate, a kinetic analysis using the pseudo-first-order equation was tested [33,34]:

$$C_t = C_{eq} + C_x \cdot e^{-k.t}, \tag{1}$$

where C_t and C_{eq} are aqueous metal concentration at time t and at equilibrium, respectively ($\mu g\,L^{-1}$), C_x is the difference between metal initial concentration (C_0) and C_{eq} ($\mu g\,L^{-1}$).

Uptake kinetics showed to be faster for incubations at 37°C than those at 25°C (Figure 4). Lead aqueous concentration at equilibrium was found to be higher for incubations at 25°C than for those at 37°C, indicating a greater adsorption at the higher temperature. Thus, Pb(II) adsorption was found to be influenced by temperature, probably due to an increase in diffusion rate given by the rise of temperature. All further experiments were carried out at 37°C incubation temperature.

Lead desorption from the Si-SPE films was evaluated by eluting the metal with $0.5\,\mathrm{mol\,L^{-1}}$ HNO_3. Desorption achieved equilibrium within 2 h incubation at room temperature (Figure 5).

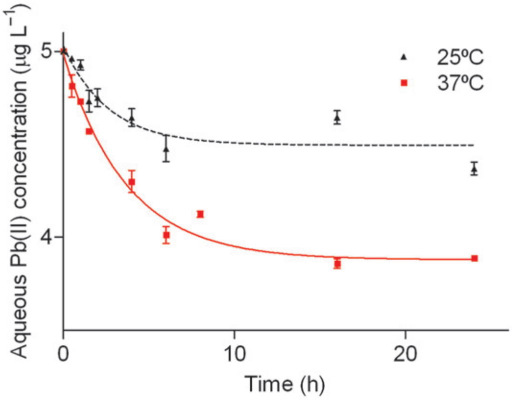

Figure 4. Effect of time and temperature on aqueous Pb(II) concentration exposed to the Si-SPE films at pH 7.

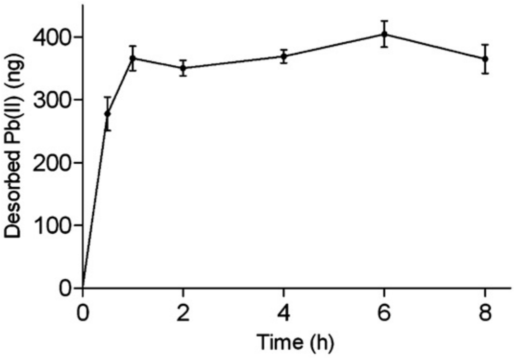

Figure 5. Lead desorption over time by incubation of Si-SPE films in 0.5 mol L^{-1} HNO_3 at room temperature.

3.5 *Adsorption isotherms*

Langmuir and Freundlich isotherms were modeled in order to evaluate its application in the film characterisation. Langmuir and Freundlich adsorption isotherms can be expressed using Equations (2) and (3) respectively as follows [35]:

$$q_{eq} = \frac{q_m \cdot K_a \cdot C_{eq}}{1 + K_a \cdot C_{eq}} \tag{2}$$

$$q_{eq} = k \cdot C_{eq}^{n}, \tag{3}$$

where q_{eq} is the amount of adsorbed metal per unit mass of sorbent at equilibrium (µg g^{-1}), K_a is the adsorption equilibrium constant (L µg^{-1}), q_m is the maximum adsorption capacity (µg g^{-1}), and k and n are arbitrary parameters, the dimensions of k depend on the value of n. The adsorption isotherms are shown in Figure 6, where Langmuir and Freundlich plots are also represented. Parameters obtained for the nonlinear regression of Langmuir and Freundlich models are summarised in Table 1. Both Langmuir and

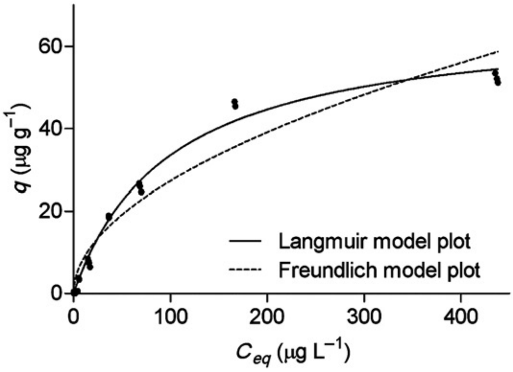

Figure 6. Lead adsorption isotherms at pH 7 and 37°C, Langmuir and Freundlich model fits are represented.

Table 1. Adsorption isotherm parameters for Pb(II) on Si-SPE films.

Langmuir			Freundlich		
q_m (μg g^{-1})	b (L ng^{-1})	R^2	k	n	R^2
66.8 ± 1.7	0.0101 ± 0.0006	0.989	2.51 ± 0.38	0.518 ± 0.028	0.935

Freunlich isotherms can be linearised giving the following Equations (4) and (5), respectively [36]:

$$\frac{C_{eq}}{q_{eq}} = \frac{1}{K_a} + \frac{C_{eq}}{q_m} \tag{4}$$

$$\ln q_{eq} = \ln k + n \ln C_{eq}. \tag{5}$$

Langmuir and Freundlich linear plots present similar results as the non-linear regression demonstrating concordance between both types of plots (Figure 7). The films showed to have a better adjustment for the Langmuir model than for the Freundlich one. Langmuir model presents good experimental agreement for systems with homogeneous monolayer adsorption for a single specie of the metal from the liquid to the solid phase [37]. The maximum adsorption capacity value obtained by the Langmuir model indicates that this sorbent does not have a great adsorption capacity. Applications should be focused on metal preconcentration rather than on water remediation.

3.6 *Evaluation of adsorption energy and standard free energy*

The equilibrium data shown as points in Figure 6 have been analysed by Dubinin-Radushkevich (D-R) Equation (6). For liquid–solid phase adsorption the amount adsorbed corresponding to any adsorbate concentration is assumed to be a Gaussian function of the Polanyi potential, ε [38,39]:

$$q_{eq} = q_{DR} e^{-K_{DR}\varepsilon^2} \tag{6}$$

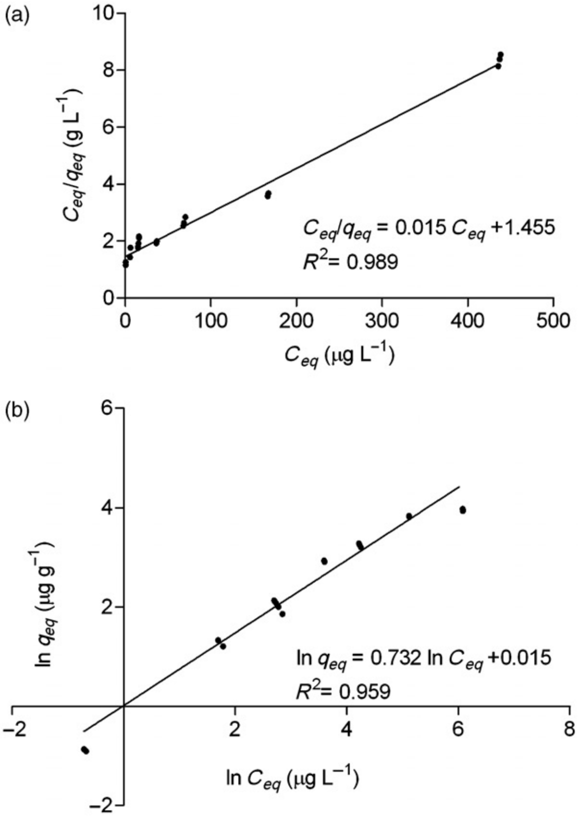

Figure 7. Lead adsorption isotherms at pH 7 and 37°C; linearised Langmuir (a) and Freundlich (b) model fits are represented.

with

$$\varepsilon = RT\ \ln(1+1/C_{eq}), \tag{7}$$

where q_{DR} is the maximum adsorption capacity (mg g^{-1}), K_{DR} is a constant related to sorption energy (mol^2 kJ^{-2}), R the gas constant (kJ mol^{-1} K^{-1}), and T the absolute temperature (K).

For adsorbents with a heterogeneous surface the presence of homogeneous subregions could be considered. In this case, using Equation (8) it could be calculated the average free energy value [40]:

$$E_{DR} = (2K_{DR})^{-1/2}, \tag{8}$$

where E_{DR} is the mean free energy of adsorption (kJ mol^{-1}); this magnitude is useful for estimating the type of adsorption reaction, being the range of 8 to 16 kJ mol^{-1} related to ion exchange reactions [36].

The standard free energy (ΔG^0) of the process is related to the adsorption equilibrium constant (K_a) by the following Equation (9) [12]:

$$\Delta G^0 = -R.T\ \ln K_a. \tag{9}$$

Table 2. R_L values for the Pb(II) initial concentrations used in the isotherms.

	C_0 (μg L^{-1})											
	0.1	0.5	1	2	5	10	25	50	100	250	500	1000
R_L	0.999	0.995	0.990	0.980	0.952	0.908	0.799	0.665	0.498	0.498	0.166	0.090

The Si-SPE films showed good agreement to D-R isotherm model in its interaction with Pb(II) ($R^2 = 0.949$). The values of q_{DR} and K_{DR} were $1.7 \pm 0.3\,\mathrm{mg\,g^{-1}}$ and $0.0024 \pm 0.0001\,\mathrm{mol^2\,kJ^{-2}}$, respectively. The mean free energy of adsorption calculated for this interaction was $14.48 \pm 0.35\,\mathrm{kJ\,mol^{-1}}$, which is indicative of an ion exchange reaction. This would support the theory of the release of hydrogen from the Si–OH group in order to interact with the cation Pb^{2+}. The negative value obtained for the standard free energy ($-55.31 \pm 0.03\,\mathrm{kJ\,mol^{-1}}$) shows the spontaneity of the process at these conditions.

3.7 *Preconcentration of water samples*

Adsorption isotherm results showed that, before adsorption sites begin to be saturated there is a linear relationship between final lead desorbed concentration and the lead initial concentration. This was confirmed by the separation factor (R_L), which indicates the shape of the isotherm and the favourability of the adsorption process. The adsorption is unfavourable when $R_L > 1$, linear when $R_L = 1$, favorable when $0 < R_L < 1$, and irreversible when $R_L = 0$. Table 2 shows the values of R_L for each initial Pb(II) concentration, calculated using Equation (10) [36]:

$$R_L = 1/(1 + K_a \cdot C_0). \tag{10}$$

As could be seen in Table 2, for the lower initial Pb(II) concentrations R_L is almost equal to 1, indicating a linear adsorption. Thus, the linear-regression equation for Pb(II) adsorption before saturation was $y = 68.896x–15.615$ ($R^2 = 0.996$).

3.7.1 *Analysis of real water samples*

No filtration or centrifugation of real water samples was found necessary for these experiments. Spiking experiments demonstrated that the Si-SPE films could be applied to real water samples with good recovery values, as shown in Table 3. Relative recovery values (calculated considering 100% the initial concentration) were above 95% for ultrapure-water and Buenos Aires tap-water. The detection of an initial concentration of $0.5\,\mathrm{\mu g\,L^{-1}}$ was possible with a sample volume of 1000 mL. When Monte Grande household well-water was investigated, $1.77\,\mathrm{\mu g\,L^{-1}}$ was found as the initial concentration. When this water was spiked, the calculated initial concentration values agreed with the spiking concentration added to the original Pb(II) content and relative recovery values were above 99%. Lead in a water supply may come from the dissolution of old lead plumbing or solder pipe joints [2]. Thus, well-water original Pb(II) content probably came from the lead plumbing associated to the well.

Table 3. Determination of Pb(II) in water samples by Si-SPE films preconcentration.

Water sample	Added ($\mu g\,L^{-1}$)	Found ($\mu g\,L^{-1}$)	Enrichment factor	Initial concentration ($\mu g\,L^{-1}$)[a]	Relative recovery (%)	R.S.D. (%)	Monovalent cations ($mg\,Na\,L^{-1}$)	Hardness ($mg\,CaCO_3\,L^{-1}$)
Ultrapure	0[b]	n.d.[c]	–	–	–	–	n.d.	n.d.
	0.1[b]	n.d.	–	–	–	–	n.d.	n.d.
	0.5[b]	21.03 ± 1.40[d]	42	0.53 ± 0.02	106.4	6.7	n.d.	n.d.
	0.5	n.d.	–	–	–	–	n.d.	n.d.
	1	56.71 ± 3.30	58	1.05 ± 0.05	105.0	5.8	n.d.	n.d.
	2	115.32 ± 4.06	58	1.90 ± 0.06	95.1	3.5	n.d.	n.d.
	10	683.33 ± 11.38	68	10.15 ± 0.17	101.5	1.7	n.d.	n.d.
Tap-Buenos Aires	0	n.d.	–	–	–	–	32.4	55.4
	2	115.60 ± 0.83	58	1.91 ± 0.01	95.5	0.7	32.4	55.4
	10	640.15 ± 13.52	64	9.52 ± 0.20	95.2	2.1	32.4	55.4
Well-Monte Grande	0	106.07 ± 3.04	–	1.77 ± 0.04	–	–	100.5	106.6
	2	246.11 ± 1.86	–	3.80 ± 0.03	100.9	0.8	100.5	106.6
	10	793.15 ± 0.11	–	11.74 ± 0.01	99.8	0.01	100.5	106.6
Tap-San Rafael	0	n.d.	–	–	–	–	87.9	309.9
	2	72.53 ± 7.22	36	1.28 ± 0.11	64.0	9.9	87.9	309.9
	10	294.33 ± 25.19	29	4.50 ± 0.37	45.0	8.6	87.9	309.9

Notes: [a] Calculated from $y = xm + b$.
[b] Sample volume = 1000 mL.
[c] Not detected.
[d] Mean ± SD ($n = 6$).

Lead recovery was not affected by water monovalent cation content, but it was affected by water hardness. This is shown in Table 3, where it can be seen that San Rafael tap-water (hard water) recovery values were considerably lower than Monte Grande well-water ones (soft water) although they had similar monovalent cation concentration values. We presume that this difference arises because San Rafael tap-water hardness value is three times higher than well-water. This could probably be due to an efficient competition of polyvalent cations with Pb^{2+} binding sites. Ca^{2+} and Mg^{2+} are the predominant constituents of hard water, therefore the principal contributors in water hardness [2]. Other studies have demonstrated that these cations have, as Pb(II), the ability to adsorb onto silica surface [31].

3.7.2 *Accuracy, precision and detection limits*

The limit of detection (LOD) for ETAAS measurements alone and associated to the preconcentration procedure were calculated using the equation $LOD = 3.29 \times \sigma_{BL}/b$, where σ_{BL} was the standard deviation (SD) of 10 measurements of the blank and b is the slope of the calibration curve [2,41]. The Pb(II) preconcentration procedure, along with the ETAAS measurement, $LOD = 0.228\,\mu g\,L^{-1}$, showed to be 10 times more sensitive than for our direct ETAAS measurement $2.011\,\mu g\,L^{-1}$ and also more sensitive than the typical LOD for ETAAS determination which is around $1\,\mu g\,L^{-1}$ [3]. All the preconcentrated samples were measured within the dynamic linear range of the ETAAS calibration curve ($6–75\,\mu g\,L^{-1}$).

The present method demonstrated good accuracy and precision for soft water samples (Table 3), showing values of recovery greater than 95% and R.S.D. less than 7%. Table 4 shows the comparison of characteristic data of other published SPE methods. A more detailed comparison of separation and preconcentration procedures for the determination of lead is given by Korn *et al.* [5]. Most of these methods involve, in the sorbent synthesis procedure or in the analytical methodology, organic compounds or solvent utilisation or higher amount of waste generation; meanwhile, the method herein proved to have similar analytical performance and to be an all the way green analytical procedure.

3.8 *Reutilisation of the Si-SPE films*

The recovery of $1\,\mu g\,L^{-1}$ Pb(II) by the Si-SPE films was analysed through five consecutives preconcentration cycles in order to evaluate the reutilisation performance. Figure 8 shows the performance of each individual cycle in comparison to the first cycle of preconcentration (considered 100%). The loss of recovery was evaluated compared with the first preconcentration cycle. No lead was detected in supernatants of the washing steps. After five cycles relative recovery was found not to be less than 90%, demonstrating that the Si-SPE films could be used for multiple lead determinations. The possibility of the films reutilisation represents an advantage that unmodified silica matrices have in contrast with most chemically modified silica matrices were the organic component adsorbent is released from the matrix along with the metal. This drawback is usually solved by covalent attachment of the chelating molecule but these process often requires the use of organic solvents and toxic crosslinkers [14].

Table 4. Comparison of the characteristic data between published off-line procedures for Pb(II) preconcentration using SPE.

Sample	Sorbent	Technique	LOD ($\mu g\,L^{-1}$)	R.S.D. (%)	Elution solvent	Elution volume (mL)	Reference
Biological and natural water	Ofloxacin modified silica gel	ICP-OES[a]	0.13	<3	$0.5\,mol\,L^{-1}$ HCl	2	[15]
River and biological water	p-dimethylaminobenzaldehyde-modified nanometer SiO_2	ICP-OES	0.4	<2	$1\,mol\,L^{-1}$ HCl	4	[14]
Tap, pond and drinking water	Aminothioamido anthraquinone modified silica gel	FAAS[b]	22.5	<9	$0.1\,mol\,L^{-1}$ HNO_3	5	[17]
Hot spring and drinking water	Amberlite XAD-2000	ETAAS[c]	0.51	2	$0.5\,mol\,L^{-1}$ HNO_3	5	[42]
Tap and lake water	Silica gel immobilised nanometer TiO_2	ETAAS	0.01	3.2	$1\,mol\,L^{-1}$ HCl	1	[43]
Saline matrices	Dithizone co-crystallised with naphtalene	ICP-OES	47.0	2.5	$8\,mol\,L^{-1}$ HNO_3	15	[44]
Sea water	3-Aminopropyltriethoxysilane modified silica gel	ETAAS	4.0	1.4	$2\,mol\,L^{-1}$ HCl	25	[45]
Certified reference water	Sephadex A-25 loaded with thiacalix[4]arenetetrasulfonate	ETAAS	0.20	—	$1\,mol\,L^{-1}$ HNO_3	0.5	[46]
Black tea and black and hot pepper	Modified hexagonal mesoporous silica	ICP-OES	0.34	2	$3\,mol\,L^{-1}$ HNO_3	5	[47]
Industrial and river water	Silica gel chemically modified with Zirconium phosphate	FAAS	6.10	4.7	$1\,mol\,L^{-1}$ HNO_3	10	[48]
Soft tap and well water	Si-SPE film	ETAAS	0.23	<7	$0.5\,mol\,L^{-1}$ HNO_3	0.5	This work

Notes: [a] Inductively coupled plasma optical emission spectrometry.
[b] Flame atomic absorption spectrometry.
[c] Electrothermal atomic absorption spectrometry.

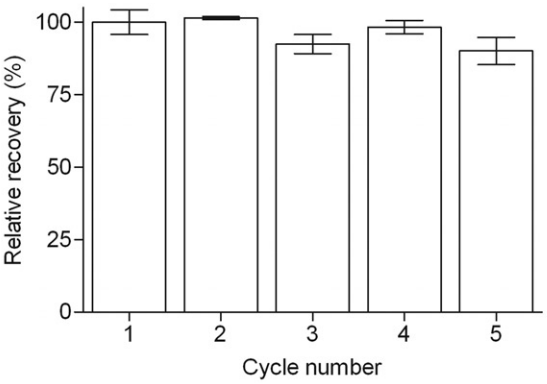

Figure 8. Relative recovery of 1 μg L^{-1} Pb(II) in consecutive Si-SPE preconcentration cycles.

4. Conclusions

Using sol-gel chemistry it was possible to obtain SiO_2 films for solid phase extraction of Pb(II). These films were employed in lead preconcentration from water samples, achieving a ten-fold rise in LOD for ETAAS measurement. This one step silicon oxide film obtaining method is simple and mild, carrying all procedures in aqueous media without the addition of any organic solvent or toxic precursors, which is essential from an environmental and economical point of view. In addition, all reagents included in film generation are non toxic and the metal is desorbed in a small amount of aqueous media (0.5 mL) minimising waste generation. Thus a green analytical method was developed by avoiding the use of organic solvents and toxic reagents in the generation of the SPE system and the analytical procedure, adjusting to the principles of Green Chemistry [10,11]. As pointed out by Keith *et al.* [8], analysis schemes that do not require pretreatment, use few reagents, or work with aqueous solvents, have a greenness advantage.

The SiO_2 matrix can be generated as a film over a support with the desired geometry in order to facilitate its application for the metal preconcentration of a liquid sample. The Si-SPE system can be placed in the liquid sample for metal adsorption and be easily removed for a desorption/preconcentration process without interposing steps that would affect metal recovery. This methodological study demonstrates the applicability of this cost-effective solid phase extraction system in the determination of lead traces from soft water samples.

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