J Incl Phenom Macrocycl Chem (2012) 73:151–159
DOI 10.1007/s10847-011-0038-z

ORIGINAL ARTICLE

Simultaneous separation and extraction of Ag(I), Pb(II) and Pd(II) ions by solid phase method and determination of these ions by flame atomic absorption spectrometry

Gholamreza Khayatian · Shahed Hassanpoor

Received: 30 August 2010 / Accepted: 25 August 2011 / Published online: 9 September 2011

Abstract A simultaneous preconcentration and separation method for determination of trace amount of dissolved Ag^{+}, Pb^{2+} and Pd^{2+} ions by modified octadecyl silica membrane disks with DBzDA18C6 was developed. The adsorbed metal complexes were eluted from disk with 10 mL of 4 M KCl and determined by flame atomic absorption spectroscopy. Several parameters such as anion effect, pH of sample solution, type of eluent, amount of ligand, sample and elution flow rate were evaluated. The effect of diverse ions on preconcentration was also investigated. A precocentration factor of 110 can easily be achieved depending on the volume of the sample. For 100 mL of the solution the linear dynamic rang were found to be 30–1000, 140–6000, 60–900 μg l^{-1} for Ag^{+}, Pb^{2+} and Pd^{2+}, respectively. Based on three standard deviation of the blank the detection limit was obtained as 1.8, 8.0 and 4.2 μg L^{-1} for Ag^{+}, Pb^{2+}, Pd^{2+}, respectively. The formation constants of Ag^{+} and Pb^{2+} ions with DBzDA18C6 at 25 °C were determined from the molar conductance–mole ratio data. This method was applied for the determination of Ag^{+}, Pb^{2+} and Pd^{2+} in environmental water, tea and soil samples.

Keywords Solid phase extraction · Preconcentration · Ag (I) · Pb(II) · Pd(II) · Crown ether

Introduction

The determination of heavy metal ions in natural samples such as waters, soils, foods and biological fluids have been considered as very important part of environmental and public health researches. Direct determination of metal ions of trace level is usually very limited due to their low level of concentration and matrix interferences. Flam atomic absorption spectrometry (FAAS) which has been used for the determination of trace metal ions suffers from insufficient sensitivity for direct determination of ions in environmental samples. Therefore, a preconcentration or separation step is necessary to improve the detection limit and sensitivity of the measurement. For this purpose several separation and preconcentration methods have been developed for determination of trace amount of metal ions. These methods include ion exchange [1], liquid extraction [2], anodic stripping voltammetry [3], cloud point [4], coprecipitation [5] and solid phase extraction [6–10]. Among the various methods, solid phase extraction has received more attraction due to simple application procedure, easy methodology and high sensitivity [11–13].

Among the heavy metals, lead is appeared to be extremely toxic even at very low concentration levels. It is well known that lead can cause blood enzyme changes, hyperactivity and neurological disorders in both human and animals [14].

Silver has been recognized as a toxic element for biological systems. Low level of exposure to silver compounds is widespread owing to the use of soluble silver compounds to disinfect water for drinking and reaction purpose. In many countries silver impregnated filters are being used for water purification, and concentration of silver up to 50–200 μg L^{-1} are permitted to control antimicrobial activity with no risk to human health [15].

G. Khayatian (✉) · S. Hassanpoor
Department of Chemistry, Faculty of Science, University of Kurdistan, P.O. Box 416, Sanandaj, Iran
e-mail: gkhayatian@yahoo.com

Therefore, determination of trace amount of silver is important.

Palladium has been used in different areas of science and technology including coating agents, brazing alloys, petroleum, electrical industries and catalytic chemical reactions. Thus, due to its increasing application in one hand, and the toxicity of Pd(II) compounds to mammals and fishes on the other hand, the separation, preconcentration, and determination of palladium is of special interest in environmental analysis [16].

In SPE procedure, the choice of appropriate ligand is a critical factor to obtain full recovery, high enrichment factor and excellent selectivity. Among the many types of ligands used in SPE, macrocyclic crown ethers and their derivatives have been demonstrated to be excellent ligands, especially for selective and efficient extraction of alkali and alkaline earth ions. In contrast, much less attention has been directed toward the SPE of heavy metal ions by macrocyclic ligands [13, 17, 18].

The aim of this work is to present our experimental results for development of a solid phase extraction procedure for preconcentration of lead, silver and palladium in environmental samples using octadecyl silica membrane disks modified by DBzDA18C6 as a solid phase extractant, prior to flame atomic absorption spectrometric determination.

Experimental

Extra pure methanol, acetonitrile (AN), nitric acid and hydrochloric acid were used as received. Stock standard solution (1.00 g L^{-1}) of Ag^+, Pb^{2+} were prepared by dissolving corresponding $AgNO_3$ (Merck) and $Pb(NO_3)_2$ (Merck) in distilled water. Stock standard solution (1.00 g L^{-1}) of palladium was prepared by dissolving corresponding $PdCl_2$ 59% Pd (Fluka) in 3 mL concentrated HCl and reached to the mark in 1000 mL volumetric flask with distilled water. All reagents for conductometric study ($AgNO_3$ and $Pb(NO_3)_2$) were prepared by dissolving of appropriate amount of desired salt in a few drops of methanol and reached to the mark in volumetric flask with acetonitryl (96% AN-4% MeOH). The ligand that used for extraction procedure was dibenzyl diaza-18-crown-6 (DBzDAz18C6). Figure 1 from Fluka and used without any further purification, except for vacuum drying over P_2O_5.

All pH measurements were made using a Metrohm E-691 digital pH meter with a combined glass electrode. Conductance measurements were carried out using a Metrohm 712 conductometer. A dip-type conductivity cell made of platinum black, with the cell constant of 0.832 cm^{-1} was used. In all measurements the cell was thermostated at 25.0 ± 0.1 °C by using a MLW thermostated-circular water bath as described elsewhere [19–22].

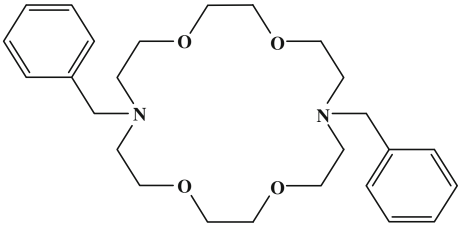

Fig. 1 Structure of ligand DBzDA18C6

In a typical experiment, 10 mL of the salt solution in methanol (1.0×10^{-4} M) was in titration cell, thermostated to 25.0 ± 0.1 °C and its conductance was measured. A known amount of the crown ether solution prepared in the same solvent was then added in a stepwise manner using a precalibrated micropipette. The conductance of the solution was measured after each addition. Addition of crown ether solution was continued until the desired crown ether to metal ion mole was achieved. The 1:1 binding of the metal ions with DBzDA18C6 can be expressed by the following equilibrium:

$$M^{n+} + L \rightleftarrows ML^{n+} \quad (1)$$

The corresponding equilibrium constant, K_f, is given by

$$K_f = [ML^{n+}] / ([M^{n+}].[L]) \times f(ML^{n+}) / (f(M^{n+}) \cdot f(L)) \quad (2)$$

where $[ML^{n+}]$, $[M^{n+}]$, [L] and f represent the equilibrium molar concentration of complexes, free cation, free ligand and the activity coefficient of the species, respectively. Under the dilute conditions used, the activity coefficient of uncharged crown ether, f (L) can be reasonably assumed as unity [19–24]. The use of Deby-Huckel limiting law of 1:1 electrolytes [25], lead to the conclusion that $f(M^{n+}) = f(ML^{n+})$, so the activity coefficient in Eq. 2 is canceled out. Thus the conductances, Λ can be expressed as [26]

$$K_f = [ML^{n+}] / [M^{n+}] \cdot [L] = (\Lambda_M - \Lambda_{Obs}) / (\Lambda_{Obs} - \Lambda_{ML}) \cdot [L] \quad (3)$$

$$K_f = C_L \cdot C_M(\Lambda_M - \Lambda_{Obs}) / (\Lambda_{Obs} - \Lambda_{ML}) \quad (4)$$

Here, Λ_M is the molar conductance of the metal ion before addition of ligand, Λ_{ML} the molar conductance of the complex, Λ_{Obs} the molar conductance of the solution during titration, C_L the analytical concentration of ligand added and C_M the analytical concentration of the metal ion salt. The complex formation constant, K_f and the molar conductance of the complex, Λ_{ML}, were obtained by computer fitting of Eqs. 3 and 4 to the molar conductance–mole ratio data using a non linear least-squares program KINFIT [27]. The details are described elsewhere [19–22].

General extraction procedure

Extraction were performed using Empore™ membrane disks (3 M CO., St. paul, MN, USA): 47 mm diameter, 0.5 mm thickness with 90% octadecyl-bonded silica 18 µm particle size) and 10% PTFE fiber. The disks were used in conjunction with a standard Millipore 47 mm filtration apparatus connected to a vacuum pump.

In order to remove potential interferences and to ensure optimal extraction of the analyte of interest. The recommended disk cleaning and conditioning was performed before use as described elsewhere [9]. After placing the membrane disk in the filtration apparatus, 10 mL of methanol was poured onto the disk and immediately drawn through the disk by applying a slight vacuum. After all of the solvent had passed through the disk, it was dried by passing air through it for few minutes. The disk conditioning was then begun by pouring 10 mL of methanol onto the disk. Immediately, a low vacuum was applied and the solvent was drawn through the disk until solvent surface almost reached the surface of the disk, without allowing the disk to soak without vacuum, nor allowing air to contact with the surface of the disk. Then, a DBzDA18C6 solution (8 mg in 5 mL acetonitrile) was introduced onto the disk and drowns slowly through the disk using a slow vacuum. Finally the disk was washed with 25 mL of water and dried by passing air through it.

The general procedure for the extraction of Ag (I), Pd (II) and Pb(II) on the membrane disk was as follow. The modified disk was first washed with 0.5 mL of methanol followed by 25 mL of water with the same pH as the sample solution. This step wets the surface of the disk pore to the extraction of cations from water and ensures good contact between the analyte and the ligand. The appropriate volume of cation sample solution (adjusted to pH 5 using 0.01 M acetate buffer) was passed through the membrane (flow rate 15 mL min^{-1}). After the extraction, the disk was dried completely by passing air through it for a few minutes. The extracted cations were stripped from the membrane disk using 9 mL of 4.0 M KCl. The eluted solution was collected in a test tube and then transferred into 10 mL calibrated flask.

Results and discussion

The existence of two donating nitrogen atoms in DBzDA 18C6 was expected to increase both stability and selectivity of its complex with transition and heavy metal ions, as reported elsewhere [28–30]. Thus, in order to check the suitability of DBzDA18C6 as an extraction agent for different metal ions, in preliminary experiment, it was used to extraction a wide variety of cations, including : Ag(I), Pb(II), Pd(II), Cd(II), Cu(II), Zn(II), Co(II) and Fe(II). DBzDA18C6 showed the high extraction ability for Ag(I), Pb(II) and Pd(II) ions over the other metal ions. This is probably due to high stability of the DBzDA18C6 cation complexes (Ag (I), Pb(II)) in comparison to the other metal ions. In order to obtain information about the stability of the resulting complexes, the resulting molar conductance, Λ vs. [L]/[M^{n+}] mol ratio in acetonitrile solution is plotted as shown in Fig. 2. As can be seen, for Pb^{2+}, the molar conductance of solution is increasing with ligand content ratios. This behavior indicates that the DBzDA18C6-Pb^{2+} complex in this system is more mobile than free solvated Pb^{2+} cation. In contrast for the case of Ag^{+} ion, the molar conductance of solution is decreasing with increasing ligand content ratios. It seems, when Ag^{+} ion is complexed with large crown ether, it becomes bulkier than free Ag^{+} ion, resulted in decreasing the mobility and then lowering the molar conductivity [31]. In order to clarify this idea the 1:1 [M: L] complexation model, the fitting curve for (DBzDA18C6-Pb^{2+}) complex in acetonitrile at 25 °C is shown in Fig. 3. As is evident in this figure, there is a good agreement between the fitting and experimental data.

The values of stability constants as (log K_{ML}^{n+}) for the metal ions by conductometry were found to be 4.56 ± 0.18 and 4.71 ± 0.17 for Ag^{+} and Pb^{2+} respectively. It is observed that lead happens to form more stable complex with DBzDA18C6 which may be explained on the basis of its relatively larger size that can be fit into the cavity as well as a partial covalent interaction. However, the stability of silver complex is low (even though the ionic radius of Ag^{+} is closer to that of DBzDA18C6). For silver ion being monovalent exerts lesser electrostatic attraction than divalent ion such as lead. Similar behavior was observed in the case of 18C6 complexes of Ag^{+} and Pb^{2+} in ethanol–

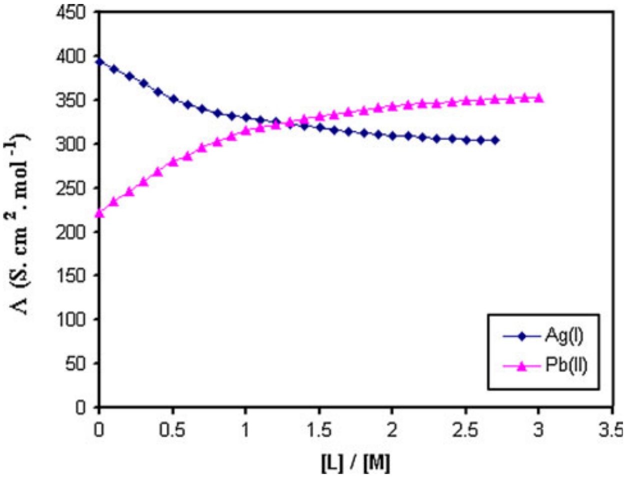

Fig. 2 Molar conductance vs. [DBzDA18C6]/[M^{n+}] curves in AN solution. Condition: [M^{n+}] = 1 × 10^{-4} M, [DBzDA18C6] = 2 × 10^{-3} M

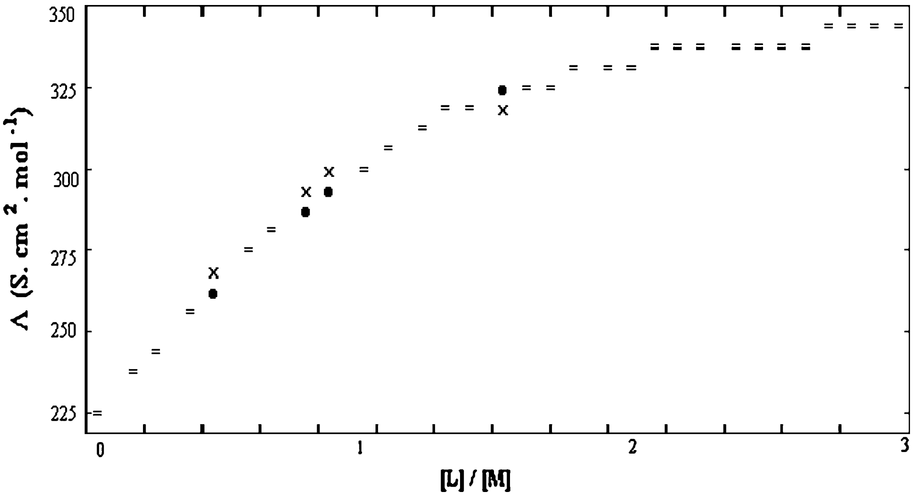

Fig. 3 Computer fit of molar conductance-mole ratio data for DBzDA18C6-Pb^{2+} in AN at 25 °C: (×) experimental data; (○) calculated points; (=) experimental and calculated points are the same within the resolution of the plot

water mixture [32]. Furthermore, it is well known that Ag^+ strongly complexes with acetonitrile [31]. This is probably because polarizable Ag^+ ions has a high affinity for the nitrogen atoms of the –CN group in AN molecules, which results in strong solvation and weak complexation in this solvent. The previously reported stability constant between DBzDA18C6-Ag^+ was 4.1 ± 0.1 in 95.9% AN-4.1% DMF mixture [31] that it seems reasonable in comparison with value obtained in this study (4.56 ± 0.18 in 96% AN-4% MeOH). It is well known that, MeOH is the solvent with a lower donocity (DN = 19.1) than DMF (DN = 26.6). Therefore, it is less competing with the crown ether for Ag^+, which in turn results in the more stable Ag^+-DBzDA18C6 complexes in AN-MeOH ($K_f = 4.56$) mixture than AN-DMF ($K_f = 4.1$) mixture.

Recovery is often improved by the presence of co-extraction ions. In order to investigate the effect of the presence of these ions on the recovery of Ag (I), Pb(II) and Pd(II) by the modified disks, sodium acetate and sodium perchlorate were tested and the results are shown in Table 1. The obtained results indicate that the co-extraction ions with concentration of 1×10^{-3} M of each salts allowed for the quantitative extraction of three analyte from sample solution. The probable mechanisms may be given as follows:

$$\mathrm{Ag^+_{(aq)} + DBzDA18C6_{(org)} + A^-_{(aq)} \rightarrow (Ag - DBzDA18C6)^+(A^-)_{org}}$$

$$\mathrm{Pb^{2+}_{(aq)} + DBzDA18C6_{(org)} + \ 2A^-_{(aq)} \rightarrow (Pb - DBzDA18C6)^{2+}(A^-)_{2org}}$$

$$\mathrm{[PdCl_4]^{2-}_{(aq)} + 2M^+_{(aq)} + 2DBzDA18C6_{(org)} \rightarrow [PdCl_4]^{2-}\left([M - DBzDA18C6]^+\right)_{2(org)}}$$

that the Ag^+ and Pb^{2+} extract in form of cationic complexes but Pd^{2+}(as $PdCl_4{}^{2-}$) extract in the form of anionic complexes by M^+-crown ether complexes (where M^+ is the co-extracted cation)[33].

The effect of pH of the test solution on the retention of Ag (I), Pb(II) and Pd(II) was also studied. The pH values of 100 mL solution containing 100 μg of Ag (I), Pd (II), 200 μg of Pb(II) adjusted in the range of 1–7 using diluted nitric acid or sodium hydroxide. The results of recovery versus pH value are depicted in the Fig. 4. The best recovery values of pH for analytes were obtained at the pH rang of 4.5–7. Thus pH of 5.0 was chosen as working pH for the subsequent work. In order to maintain this pH value, a buffer solution of acetic acid-sodium acetate (0.01 M) is recommended.

In order to choose a proper eluent for the retained ions after the extraction of 100 μg Ag(I), Pd(II) and 200 μg of Pb(II) from 100 mL solution by the modified disk with 10 mg DBzDA18C6, the disk eluted with 10 mL of different reagent of varying concentration. The results are shown in Table 2. As can be seen from Table 2, it is obvious that KCl, KBr and KI with concentration of 4 M can quantitavely strip the retained ions. It might be due to extraction of these salts (KCl, KBr and KI) on the membrane at high concentration compared with Ag^+, Pb^{2+} and $PdCl_4{}^{2-}$ ions. This concentration effect cause Ag^+, Pb^{2+} and $PdCl_4{}^{2-}$ ions release from the membrane phase.

Table 1 Effect of co-extraction ions for extraction of Ag, Pb and Pd[a]

Ion pair	Recovery of Ag^+ %	Recovery of Pb^{2+} %	Recovery of pd^{2+} %
$NaCH_3CO_2$	99 ± 2[b]	98 ± 1	97 ± 2
$NaClO_4$	101 ± 1	97 ± 1	99 ± 3
Without co-extraction ions	99 ± 1	100 ± 1	50 ± 2

[a] Conditions: 100 μg Ag(I), Pd(II) and 200 μg Pb(II) in 100 mL solution, pH 5 and salt concentration of 1×10^{-3} M

[b] Standard deviation (SD) for $n = 3$

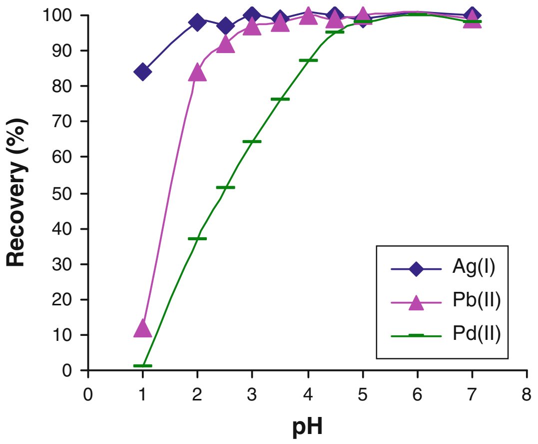

Fig. 4 Effect of pH on the percent of recovery of Ag^+, Pb^{2+} and Pd^{2+}

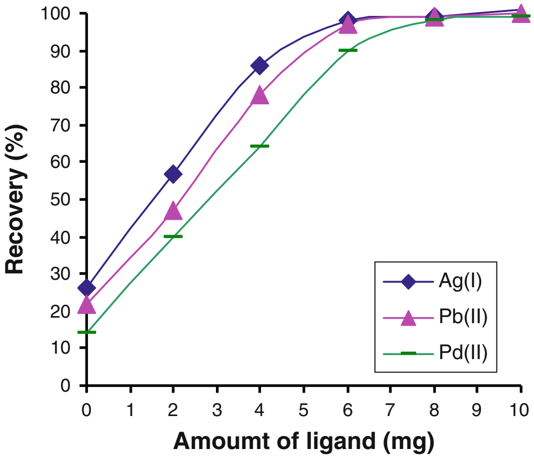

Fig. 5 Effect of amount of ligand on the recovery of Ag^+, Pb^{2+} and Pd^{2+}

Table 2 Effect of various eluents on the recoveries of analytes

Eluent	Recovery (%)		
	Ag^+	Pb^{2+}	Pd^{2+}
$S_2O_3^{2-}$ (1 M)	12 ± 1[a]	56 ± 2.1	68 ± 2.5
$P_2O_7^{2-}$ (1 M)	8 ± 1.5	25 ± 1	58 ± 2
HNO_3 (0.5 M)	9 ± 0.57	99 ± 1	1 ± 1
HCl (1 M)	0 ± 0.57	100 ± 2	2 ± 0.6
EDTA (0.2 M)	1 ± 1	101 ± 1.1	9 ± 0.6
KI (2 M)	55 ± 2.5	79 ± 1.1	85 ± 3
KI (4 M)	99 ± 1	100 ± 0.6	99 ± 2.5
KCl (4 M)	99 ± 1.1	101 ± 1.5	100 ± 1
NaCl (4 M)	25 ± 1.5	30 ± 1.5	96 ± 2
KBr (4 M)	96 ± 2	97 ± 1	99 ± 1

Condition: 100 μg Ag(I), Pd(II) and 200 μg Pb(II) in 100 mL solution and pH 5 (acetate buffer)

[a] Standard deviation (SD) for $n = 3$

The influences of amount of DBzDA18C6 on the retention of the Ag (I), Pb(II) and Pd(II) ions were examined in the range of 0.0-10.0 mg under optimized working condition. The experimental results are shown in Fig. 5. As can be seen, the recovery values for Pb(II), Ag(I) and Pd(II) were quantitative up to 7 mg of ligand. Therefore, 8 mg of DBzDA18C6 were used in the all experiments.

The retention of Ag(I), Pb(II) and Pd(II) ions in modified disk was examined using passes the sample solution through the disk with the flow rate adjusted in the range of 5-55 mL min^{-1}. The optimum flow rate of the sample solution was found to be 15 mL min^{-1}. On the other hand quantitative, striping of three ions from the disk was achieved with KCl 4 M solution at the flow rate of 6 mL min^{-1}.

The influence of foreign ions which interfere the determination of analyte ions was examined with the above optimized condition. In these experiments, 100 mL solution containing 100 μg of Ag(I), Pd(II) and 200 μg of Pb(II) and various amount of foreign ions were prepared and general procedure was applied. The experimental results are given in Table 3. As can be seen from Table 3, the recovery of analytes were higher than 95%, tolerable limit was defined as the highest amount of foreign ions that produced an error not exceeding 5%. As it is seen, large numbers of used ions have no considerable effect on the determination of analyte ions. Also, some of the alkali and alkaline—earth metals at mg L^{-1} levels were not interfered on the recovery of the analyte ions, therefore, it seems that this method can be used for sea water and waste water analysis because in sea water the level of alkali metals and alkaline-earth metals is in the range of mg L^{-1}.

Analytical performance and method validation

The calibration graphs were obtained using the recommended procedure under the optimum condition with 100 mL solution containing 100 μg of Ag (I) and Pd (II) as well as 200 μg of Pb(II). In the initial solution linear graphs were obtained in the range of 30-1000, 140–6000, 60–900 μg L^{-1} for Ag, Pb and Pd, respectively. The equation of lines are found to be $A = 0.502\ C - 0.0241$ with $r = 0.9971$ for silver, $A = 0.115\ C - 0.0079$ with $r = 0.995$ for lead and $A = 0.297\ C - 0.0181$ with $r = 0.9954$ for palladium. The detection limit (LOD) based on three standard deviation of blank ($n = 10$) for the combination of the proposed preconcentration procedure and flame atomic absorption spectrometry method were found to be 1.8, 8, 4.2 μg L^{-1} for Ag, Pb and Pd respectively. The relative standard deviation (R.S.D) for 10 replicate measurement of 100 mL solution containing 100 μg of

Table 3 Influence of some foreign ions on the percent of recovery of analytes[a]

Interference ion	Amount of interfere (mg L^{-1})	Added as	Recovery of Ag^+ (%)	Recovery of Pb^{2+} (%)	Recovery of Pd^{2+} (%)
Na^+	1000	$NaNO_3$	98(2)[b]	96(1)	100(2)
K^+	500	KNO_3	101(3)	96(3)	97(3)
Mg^{2+}	750	$MgCl_2 \cdot 6H_2O$	98(3)	95(3)	97(4)
Ba^{2+}	250	$Ba(NO_3)_2$	99(1)	96(1)	97(1)
Ca^{2+}	350	$Ca(NO_3)_2 \cdot 4H_2O$	100(3)	97(2)	96(2)
Cd^{2+}	250	$CdNO_3 \cdot 6H_2O$	99(1)	99(1)	97(3)
Sr^{2+}	300	$SrBr_2 \cdot 6H_2O$	97(2)	96(1)	100(3)
Cu^{2+}	400	$Cu(NO_3)_2 \cdot 3H_2O$	98(3)	97(2)	96(2)
Co^{2+}	400	$Co(NO_3)_2 \cdot 6H_2O$	98(1)	100(1)	96(3)
Zn^{2+}	400	$Zn(NO_3)_2 \cdot 6H_2O$	98(3)	99(2)	98(3)
Sn^{2+}	250	$SnCl_2 \cdot 2H_2O$	97(1)	95(1)	96(2)
Ni^{2+}	400	$NiCl_2 \cdot 6H_2O$	100(4)	97(3)	95(3)
Fe^{2+}	50	$Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$	99(2)	95(1)	96(4)
Fe^{3+}	50	$Fe(NO_3)_3 \cdot 9H_2O$	98(3)	95(3)	96(2)
Al^{3+}	100	$Al(NO_3)_3 \cdot 9H_2O$	96(3)	97(2)	100(3)
Hg^{2+}	130	$HgCl_2$	97(1)	95(1)	96(2)
NH_4^+	150	NH_4NO_3	98(2)	97(1)	100(1)
PO_4^{3-}	400	$Na_3PO_4 \cdot 12H_2O$	100(3)	97(3)	101(3)
SO_4^{2-}	200	Na_2SO_4	98(2)	97(2)	96(1)
ClO_4^-	1000	$NaClO_4$	97(2)	96(2)	98(1)
SCN^-	200	NaSCN	100(1)	98(1)	99(2)
Br^-	1000	KBr	97(4)	96(3)	96(2)
Cl^-	1500	NaCl	96(3)	95(2)	96(2)
I^-	1000	KI	98(1)	97(2)	98(1)

[a] Condition: 100 μg Ag (I), Pd (II) and 200 μg Pb(II), interference ion with different concentration in 100 mL solution and pH 5 (acetate buffer)

[b] Standard deviation (SD) for $n = 3$

Table 4 The application of presented method in real samples ($N = 3$)

Sample	Ion								
	Ag^+ (μg L^{-1})			Pb^{2+} (μg L^{-1})			Pd^{2+} (μg L^{-1})		
	Added	Found	Recovery (%)	Added	Found	Recovery (%)	Added	Found	Recovery (%)
River water	0	14 ± 2[a]	–	0	57 ± 2	–	0	bdl	–
White river (Iran)	200	221 ± 6	103	200	252 ± 2	97	200	191 ± 3	96
	500	527 ± 3	102	500	579 ± 6	104	500	514 ± 2	102
Tap water	0	bdl	–	0	bdl	–	0	bdl	–
(Sanandaj, Iran)	200	192 ± 5	96	200	201 ± 3	100	200	206 ± 1	103
	500	501 ± 2	100	500	508 ± 2	101	500	511 ± 4	102
Sea water	0	11 ± 2	–	0	43 ± 4	–	0	19 ± 2	–
(Caspian sea, Iran)	200	219 ± 2	104	200	251 ± 5	104	200	225 ± 6	103
	500	517 ± 6	101	500	556 ± 4	103	500	531 ± 4	102

[a] Standard deviation (SD) for $n = 3$

bdl Below detection limit

Ag(I) and Pd(II) as well as 200 μg of Pb(II) was 2.21, 2.51, 2.07% for Ag, Pb and Pd respectively. The maximum capacity of the disk modified by 8 mg DBzDA18C6 determined by passing 100 mL solution containing 500 μg of each metal ions at the optimum condition, followed by the determination of retained metal ions using FAAS. The maximum capacity of the membrane disk obtained from three replicate measurements were found to be 470 ± 8 μg, 230 ± 4 μg and 120 ± 3 μg for Ag, Pb and Pd respectively on the modified disk.

Table 5 The application of presented method in real solid samples ($N = 3$)

Sample	Element								
	Ag (μg g^{-1})			Pb (μg g^{-1})			Pd (μg g^{-1})		
	Added	Found	Recovery(%)	Added	Found	Recovery(%)	Added	Found	Recovery(%)
Tea leaves	0	0.34 ± 0.027[a]	–	0	0.92 ± 0.03	–	0	0.74 ± 0.03	–
	5	5.47 ± 0.09	102	5	6.04 ± 0.07	102	5	5.9 ± 0.07	102
	10	10.61 ± 0.12	103	10	11.32 ± 0.08	103	10	10.81 ± 0.15	101
Soil	0	43.2 ± 0.22	–	0	1784 ± 17.51	–	0	5.9 ± 0.15	–
	50	90 ± 1.9	96	50	1821 ± 18.5	99	50	53 ± 1.2	94
	100	138 ± 2.8	96	100	1864 ± 21	98	100	103 ± 1.9	97
Black tea S_1[b]	0	1 ± 0.02	–	0	1.45 ± 0.03	–	0	0.97 ± 0.03	–
	5	5.11 ± 0.11	100	5	6.37 ± 0.08	99	5	5.82 ± 0.07	97
	10	11.24 ± 0.17	101	10	11.25 ± 0.13	98	10	10.93 ± 0.06	99
Black tea S_2	0	1.1 ± 0.02	–	0	1.31 ± 0.05	–	0	0.94 ± 0.06	–
	5	6.04 ± 0.14	99	5	6.24 ± 0.17	98	5	6.07 ± 0.12	102
	10	10.84 ± 0.25	97	10	11.32 ± 0.21	100	10	11.14 ± 0.1	101
Black tea S_3	0	0.97 ± 0.04	–	0	2.56 ± 0.02	–	0	0.86 ± 0.01	–
	5	5.86 ± 0.16	98	5	7.28 ± 0.15	96	5	5.8 ± 0.18	98
	10	10.74 ± 0.17	97	10	12.41 ± 0.16	98	10	10.8 ± 0.17	99

[a] Standard deviation (SD) for n = 3

[b] Sample

Table 6 Comparison of the present method with other system

Method	Metal ions	LDR(μg L^{-1})[a]	Sorbent	(μg L^{-1})[b]	Concentration factor	Ref.
Present method	Ag, Pb, Pd	Ag(30–1000), Pb(140–6000), Pd (60–900)	ODS[c]	Ag (1.8), Pb(8), Pd(4.2)	110	This work
FAAS	Ag	Ag(30–5000),	Zeolite[d]	Ag(0.07)	140	[34]
FAAS	Pb	Pb(10–200)	Naphthalene	Pb(4.5)	100	[35]
FAAS	Ag, Pd	Ag(40–1000), Pd(20–4000)	ATuSG[e]	Ag(1.1), Pd(17)	–	[36]
FAAS	Pb	–	ODS	16.7	50	[37]
FAAS	Pd	–	ODS	12	100	[16]
FAAS	Ag	–	ODS	0.05	200	[17]

[a] Linear dynamic range

[b] Limit of detection

[c] Octadecyl-bonded silica membrane disk

[d] Clinoptilolite zeolite

[e] Amidinothioureido-silica gel

The validation of present method was evaluated using a spiking water, tea and soil samples. The recoveries of analytes spiked into samples were studied. Satisfactory results were obtained as presented in Tables 4, 5. Good agreement was obtained between the added and recovered analyte contents using the experimental procedure. The recovery values calculated were always higher than 96% confirming the accuracy of the procedure and the absence of matrix effects.

Comparison of this method with other systems

Separation and determination of Ag^+, Pb^{2+} and Pd^{2+} by developed method were compared with the other solid phase extraction methods used for the determination these ions and the results are shown in Table 6. As it is shown, in most cases the enrichment factor and the limit of detections obtained by the present method are better than those reported previously.

Conclusion

A solid phase extraction procedure based on octadecyl silica membrane disk modified with DBzDA18C6 for the atomic absorption spectrometric determination of Ag (I), Pb(II) and Pd(II) at trace level is described. The accuracy of the procedure was verified by analyzing the spiked water, tea and soil samples. The recovery of Pb(II), Ag(I), Pd(II) from the spiked samples up to the high tolerate limit were almost quantitative (>95%). Our experimental results prove the reliability of the presented method for the analysis of these samples.

References

1. Soilack, M., Elci, L., Dogan, M.: Column preconcentration/separation and atomic absorption spectrometric determinations of some heavy metals in table salt samples using Amberlite XAD-1180. Turk. J. Chem. **27**, 235–242 (2003)
2. Okamoti, Y., Nomura, Y., Nakamura, H., Iwamura, K., Fujiwara, T., Kumamura, T.: High preconcentration of ultra-trace metal ions by liquid–liquid extraction using water/oil/water emulsions as liquid surfactant membranes. Microchim. J **65**, 341–346 (2000)
3. Locatelli, C., Torsi, G.: Simultaneous square wave anodic stripping voltammetric determination of Cr, Pb, Sn, Sb, Cu, Zn in presence of reciprocal interference: application to meal matrices. Microchem. J. **78**, 175–180 (2004)
4. Kulichenko, S.A., Doroschuk, V.O., Lelyushok, S.O.: The cloud point extraction of copper (II) with monocarboxylic acids into non-ionic surfactant phase. Talanta **59**, 767–775 (2003)
5. Duran, C., Bulut, V., Gundugdu, A., Osdez, D., Yildrim, M., Soylak, M., Senturk, B., Elci, L.: Carrier element-free coprecipitation with 3-phenly-4-o-hydroxybenzylidenamino-4,5-dihydro-1,2,4-triazole-5-one for separation/preconcentration of Cr(III), Fe(III), Pb(II) and Zn(II) from aqueous solutions. J. Hazard. Mater. **167**, 294–299 (2009)
6. Goswami, A., Sigh, A.K.: 1, 8-Dihydroxyanthraquinone anchored on silica gel: synthesis and application as solid phase extractant for lead(II), zinc(II) and cadmium(II) prior to their determination by flame atomic. Talanta **58**, 669–678 (2002)
7. Yang, G., Huang, Zh., Hu, Q., Yin, J.: Study on the solid phase extraction of Co(II)-QADEAB chelate with C18 disk and its application to the determination of trace cobalt. Talanta **58**, 511–515 (2002)
8. Abou-El-Sherbini, K.S., Kenawy, I.M.M., Ahmed, M.A., Issa, R.M., Elmorsi, R.: Separation and preconcentration in a batch mode of Cd(II), Cr(III, VI), Cu(II), Mn(II, VII) and Pb(II) by solid-phase extraction by using of silica modified with N-propylsalicylaldimine. Talanta **58**, 289–300 (2002)
9. Khayatian, G., Pouzesh, S.: Solid phase extraction and flame atomic absorption spectroscopic determination of trace amounts of iron(III) using octadecyl silica membrane disks modified with 2-mercapto-pyridine-1-oxide. J. Iran. Chem. Soc. **4**, 490–496 (2007)
10. Saracoglu, S., Elci, L.: Column solid-phase extraction with chromosorb-102 resin and determination of trace elements in water and sediment samples by flame atomic absorption spectrometry. Anal. Chim. Acta **452**, 77–83 (2002)
11. Majors, R.E.: Sample preparation for HPLC and gas chromatography using solid phase extraction. LC-GC **4**, 972–976 (1989)
12. Sturgeon, R.E., Berman, S.S., Desaulniers, A., Russell, D.S.: Preconcentration of trace metals from sea water for determination by graphit furnance atomic absorption spectrometry. Talanta **27**, 85–94 (1980)
13. Camel, V.: Solid phase extraction of trace elements. Spectrochim. Acta B Rev. **58**, 1177–1233 (2003)
14. Elci, L., Kartal, A., Soylak, M.: Solid phase extraction method for the determination of iron, lead and chromium by atomic absorption spectrometry using Amberlite XAD-2000 column in various water samples. J. Hazard. Mater. **153**, 454–461 (2008)
15. Gomez, M.M., Haligo Garcia, M.M., Palocios, C.: On-line preconcentration of silver on a sulfhydryl cotton microcolumn and determination by flow injection atomic absorption spectrometry. Analyst **120**, 1911–1915 (1995)
16. Farhadi, K., Teimuri, G.: Flame atomic absorption determination of palladium in solutions after preconcentration using octadecyl silica membrane disks modified by thioridazine·HCl. Talanta **65**, 925–929 (2005)
17. Shamsipour, M., Mashhadizadeh, M.H.: Preconcentration of trace amounts of silver ion in aqueous samples on octadecyl silica membrane disks modified with hexathia-18-crown-6 and its determination by atomic absorption spectrometry. Fresenius J. Anal. Chem. **367**, 246–249 (2000)
18. Yamini, Y., Alizadeh, N., Shamsipor, M.: Solid phase extraction and determination of ultra trace amounts of mercury (II) using octadecyl silica membrane disks modified by hexathia-18-crown-6-tetraone and cold vapor atomic absorption spectrometry. Anal. Chim. Acta **355**, 69–74 (1997)
19. Khayatian, G., Karoonian, F.S., Vaziri, S.: Conductance study of the complexation of NH_4^+ and Tl^+ ion with different crown ethers in binary acetonitrile-methanol mixtures. Polish J. Chem. **82**, 537–554 (2008)
20. Shamsipur, M., Khayatian, G.: Conductance study of the thermodynamics of Tl^+ ion complexes with different 18-membered crown ethers in binary dimethylformamide-acetonitrile mixtures. J. Incl. Phenom **39**, 109–113 (2001)
21. Khayatian, G., Shariati, S., Shamsipour, M.: Conductance study of the thermodynamics of binding of some macrocyclic polyethers with Tl^+ ion in dimethylformamide-acetonitrile mixtures. J. Incl. Phenom. **45**, 117–125 (2003)
22. Khayatian, G., Karoonian, F.S.: Conductance and thermodynamic study of complexation of ammonium ion with different crown ethers in binary nonaqueous solvents. J. Chin. Chem. Soc. **55**, 377–384 (2008)
23. Amini, M.K., Shamsipur, M.: Complex formation of hydronium ion with several crown ethers in 1,2-dichloroethane, acetonitrile, and nitrobenzene solutions. J. Solut. Chem. **21**, 275–288 (1992)
24. Amini, M.K., Shamsipur, M.: Complex formation of silver, thallium and alkali cations with dibenzo-30-crown-10 in some non-aqueous solutions. Inorg. Chim. Acta **183**, 65–69 (1991)
25. Debye, P., Huckel, H.: Phys. Z **24**, 305 (1928)
26. Takeda, Y.: A conductance study of 18-crown-6 and dibenzo-18-crown-6 complexes with K^+ in various solvents. Bull. Chem. Soc. Jpn. **56**, 866–869 (1983)
27. Nicely, V.A., Dye, J.I.: J. Chem. Educ. **48**, 443 (1971)
28. Izat, R.M., Pawlak, K., Bradshow, J.S.: Thermodynamic and kinetic data for macrocycle interaction with cations and anions. Chem. Rev. **91**, 1721–2085 (1991)
29. Thaler, A., Cox, B.G., Schneider, H.: Stability constants of aza-oxa crown ether complexes with silver (I) in nonaqueous polar solvents. Inorg. Chim. Acta **351**, 123–132 (2003)
30. Tar, A., Barboiu, M., Legrand, Y.M., Luca, C.: Stability constants of complexed formed by new schiff-base lariat ethers derived from 4,13-diaza-18-crown-6 with Ag^+, Pb^{2+}, Cu^{2+} cations determined by competitive potentiometry. J. Incl. Phenom. **60**, 35–41 (2008)

31. Rounaghi, G.H., Mohajeri, M., Ashrafi, S., Ghasemi, H., Sedaghat, S., Tavakoli, M.: Complex formation of 1,10-dibenzyl-1,10-diaza-18-crown-6 with Ni^{2+}, Cu^{2+}, Ag^{+}, Cd^{2+} metal cations in acetonitrile–dimethyl formamide binary solutions. J. Incl. Phenom. **58**, 1–6 (2007)
32. Ijeri, V.S., Srivastava, A.K.: Complexation of macrocyclic compound with metal ions: Cd(II), Pb(II), Co(II), Mn(II) and Ag(I) ions in 40 vol.% ethanol–water. J. Chem. Eng. Data **47**, 346–350 (2002)
33. Khayatian, G., Shamsipur, M.: Higly selective and efficient membrane transport of palladium as $PdCl_4^{2-}$ ion using NH_4^{+}-dibenzyldiaza-18-crown-6 as carrier. Sep. Purif. Technol. **16**, 235–242 (1995)
34. Afzali, D., Mostafavi, A.: Flame atomic absorption spectrometry determination of trace amounts of Ag^{+} and Cd^{2+} after simultaneous separation and preconcentration on to modified clinoptilolite zeolite as a new sorbent. Can. J. Anal. Sci. Spect. **53**, 82–89 (2008)
35. Pourreza, A., Hoveizavi, R.: Simultaneous preconcentration of Cu, Fe and Pb as methylthymol blue complexes on naphthalene adsorbent and flame atomic absorption determination. Anal. Chim. Acta **549**, 124–128 (2005)
36. Zhang, S., Pu, Q., Liu, P., Sun, Q., Su, Z.: Synthesis of amidinothioueido–silica gel and its application to flame atomic absorption spectrometric determination of silver, gold and palladium with on-line preconcentration and separation. Anal. Chim. Acta **452**, 223–230 (2002)
37. Hashemi, O.R., Kargar, M.R., Raoufi, F., Moghimi, A., Aghabozorg, H., Ganjali, M.R.: Separation and preconcentration of trace amounts of lead on octadecyl silica membrane disks modified with a new S-containing Schiff's base and its determination by flame atomic absorption spectrometry. Microchem. J. **69**, 1–6 (2001)