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Flame atomic absorption determination of palladium in solutions after preconcentration using octadecyl silica membrane disks modified by thioridazine·HCl

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Abstract

A new simple and reliable method for rapid and selective extraction and determination of trace level of Pd(II) ion is developed. Palladium ions are adsorbed quantitatively during passage of aqueous samples through octadecyl silica membrane disks modified with thioridazine·HCl (TRH). The influence of flow rates of eluent and sample solution, amount of ligand, types and least amount of eluent, and pH of samples were studied. Almost all matrix elements were found to pass through the disk to drain. Break through volume and limit of detection of the membrane disks modified by 5 mg of TRH was found to be 1.0 l and 12 μg l^{-1}, respectively. The retained Pd(II) ions are then stripped from the disk with a minimal amount of sulfite solution as eluent and subsequently measured by atomic absorption spectrometry. The proposed method permitted large enrichment factors of about 100 and higher. The method was applied to the recovery of Pd(II) ions from different industrial samples and waters.

Keywords: Solid phase extraction; Pd(II); Thioridazine·HCl; Membrane disk; Atomic absorption spectrometry

1. Introduction

Palladium was used in different areas of science and technology, including coating agents, brazing alloys, petroleum, electrical industries and catalytic chemical reactions [1,2]. Thus, due to its increasing use on one hand, and the toxicity of Pd(II) compounds to mammals, fish, and higher plants on the other hand [3], the separation, concentration, and determination of palladium is of special interest in environmental analysis.

The complexity of matrix and low concentration levels of palladium in samples make a direct measurement of metal difficult. The application of highly sensitive techniques, ICP-MS [4–6], GFAAS [7] coupled with an enrichment procedure is necessary.

Liquid–liquid extraction has been widely used for separation of platinum metals [8–11]. Because of some disadvantages of solvent extraction methods such as emulsion formation, different extracting efficiencies and low sensitivity, much interest has been recently focused in repairing conventional solvent extraction methods for isolating environmental pollutants with SPE techniques. Various sorbents such as amberlit Chelex 100 [12], alumina [7], activated alumina [13], activated carbon [14], and amberlite XAD-16 [15] have been used in the development of preconcentration methods for platinum group metals (PGM). The application of solid–liquid extraction for the adsorption of Pd and platinum groups has been reviewed by Pyrzynska [16]. However, in recent years, various solid phases modified with the various organic compounds are attracting great interest because of high selectivity, high enrichment capacity and operational simplicity. Generally, in solid phase extraction methods, immobilization of organic ligands on the surface of an inorganic or organic solid support is aimed to modify the surface with

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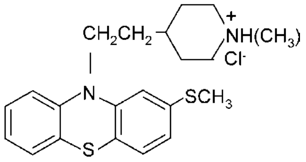
certain target functional groups that can be exploited for further analytical proposes. Similar to various metal cations, several modified solid phases for preconcentration and determination of palladium have been reported in literatures [17–27].

Thioridazine·HCl (TRH) has been used as a reagent for spectrophotometric determination of palladium [28]. The aim of this work is the development of an efficient and relatively rapid method for the selective extraction and concentration of Pd(II) ions using octadecyl silica disks modified with TRH as a selective and stable reagent, from different synthetic and water samples and its determination with flame atomic absorption spectrometry. The influences of some experimental parameters, such as sample matrix, pH, flow rates of sample solution and eluent, type and least amount of eluent for elution of Pd(II) ions from membrane were investigated. The method has also been extended to the separation of Pd(II) from a large number of other elements. To the best of our knowledge, only one separation and preconcentration system as a microcolumn containing C18 silica gel modified by *N*,*N*-diethyl-*N*′-benzoylthiourea (DEBT) for the determination of palladium has been reported until now [21]. Therefore, the present work describes the first attempt for the separation and preconcentration of palladium ions from aqueous samples using octadecyl silica membrane disks modified with TRH.



Thioridazine.HCl (TRH)

2. Experimental

2.1. Reagents

All reagents used were of the analytical reagent grade. Working standard of thioridazine·HCl (THR) were obtained from Pars Minoo Co., Tehran, Iran. Double distilled water was used in this work. A standard solution of palladium was prepared by dissolving 0.443 g of $PdCl_2$ in 10 ml of hydrochloric acid and diluted to 25 ml with water in a standard flask. Solutions of lower concentration required were prepared by diluting standard solution.

2.2. Apparatus

The palladium determinations were carried out on a Shimadzu AA-670 atomic absorption spectrophotometer with a hallow cathode lamp at a wavelength of 363.4 nm using an air–acetylene flame. The AAS determination of all other cations was carried out under recommended conditions for each metal ion. The pH measurements were made at 25 ± 1 °C with a digital WTW multilab 540 Ionalyzer (Germany) equipped with a combined glass-calomel electrode.

2.3. Procedure

2.3.1. Membranes activation

Extraction were performed with 47 mm diameter × 0.5 mm thickness Empore membrane disks containing octadecyl-bonded silica (8 μm particle, 60 A pore size, 3M Co., St. Paul, MN) with a standard Millipore 47 mm filtration apparatus. The membrane disk was placed in the filtration apparatus and it was washed with 10 ml methanol and 10 ml acetonitrile to remove all contaminants. After drying the disks by passing air through it for several minutes, it was dried inside an oven at 60 °C. Then a solution of 5.0 mg TRH dissolved in 10 ml of acetonitrile was introduced to the reservoir of the apparatus and was drown slowly through the disk by applying a slight vacuum until the ligand completely penetrate membrane. Finally, the disk was washed with 25 ml water and dried by passing air through it. The membrane disk modified with TRH is now ready for sample extraction. The activated membranes should be stored in a dry and dark place. Such membranes are stable up to nearly two months.

2.3.2. Sample extraction

The general procedure for the extraction of Pd(II) ions on the membrane disk was as follows: the modified disk was first washed with 2 ml methanol followed by washing with 25 ml water. This step prewets the surface of the disk prior to the extraction of palladium ions from water. Then 50 or 1000 ml of the sample solutions (pH 2.5–3.5) containing microgram amounts of Pd(II) was passed through the membrane, at flow rate of 10 ml min^{-1}. With this procedure, all Pd(II) ions in water samples are quantitatively adsorbed on the modified disk and consequently were eluted by five 2 ml of 1.0 M sodium sulfite at a flow rate of 5 ml min^{-1}, collected in a 10 ml volumetric flask and diluted to the mark with water (if necessary). The palladium concentration was then determined by AAS.

3. Results and discussion

It is well known that phenothiazine derivatives can form stable colored complexes with Pd(II) in hydrochloric acid media [29,30] which can be successfully used for the spectrophotometric determination of palladium [28,31,32]. Thioridazine·HCl (TRH), 10-[2-(1-methyl-2-piperidyl) ethyl]-2-methyl thiophenothiazine hydrochloride, is a N-substituted phenothiazine derivative and commonly used as psychotropic drug [33]. In addition to pharmacological properties, TRH has been used as a sensitive reagent for the spectrophotometric determination of chromium [34], palladium [28] and adsorptive stripping voltammetric determination of palladium [35] in aqueous media at carbon paste electrodes. The palladium(II) (as $PdCl_4^{2-}$) might react with TRH and form the $Pd(TRH)_2Cl_4$ complex as follows [28]:

Table 1
Effect of TRH used in the preparation of modified octadecyl silica membrane on percent recovery of Pd(II)

TRH (mg)	Recovery of Pd(II) (%)
0	31
1	68
2	81
3	89
4	95
5	100
7	100
10	100

Conditions: palladium, 20 μg (pH 2.5); sample volume, 50 ml; eluent, 10 ml of 1.0 M SO_3^{2-}; flow rate, 5 ml min^{-1}.

$$2TRH^+Cl^-_{(ads)} + PdCl_4^{2-}{}_{(aq)} \rightleftharpoons \underset{\text{(Red)}}{[Pd(TRH)_2Cl_4]_{(ads)}} + 2Cl^-_{(aq)}$$

where TRH^+ Cl^- is the real form of thioridazine·HCl.

The interaction between palladium(II) and TRH^+ Cl^- is believed to involve H-bonding between the protonated nitrogen and one of the chlorine atoms on the palladium complex anion [28]. Since most of the phenothiazine derivative-palladium complexes are readily extractable in lipophilic liquids [35–37], we previously used TRH as a potential ion carrier for the selective transport of Pd(II) ion through a chloroform liquid membrane [38]. In the present work, we were interested in studying the possibility of using TRH as a selective sorbent for palladium on octadecyl silica membranes. Thus, some preliminary experiments were carried out in order to investigate the quantitative retention of Pd(II) ions by the octadecyl silica membrane disks in the absence and presence of TRH. The obtained results are summarized in Table 1. As can be seen, while the membrane disk adsorb only 31% of total Pd(II), the membrane modified by TRH are capable to retain 20 μg Pd(II) ions from 50 ml of sample solutions quantitatively. The optimal amount of TRH, which must be adsorbed, on the octadecyl silica membrane disks for the quantitative recovery of 20 μg palladium ions from aqueous sample solutions was found to be approximately 5 mg. Use of TRH amounts higher than 5 mg did not change the recovery results (see Table 1).

3.1. Choice of eluent

In order to choose the most effective eluent for the quantitative stripping of the retained Pd(II) ions by the modified membrane with 5 mg TRH, after the extraction of 20 μg from 50 ml water (pH 2.5–3.5), the palladium ions were stripped with five 2 ml portions of various potential stripping agents. The results are summarized in Table 2. Results showed that the elution of the retained palladium ions was quantitative with SO_3^{2-} ion. The effect of varying concentration of SO_3^{2-} ion on the recovery of palladium ions was also studied and the results are included in Table 2. As seen, 10 ml of 1.0 M SO_3^{2-} solution can accomplish the quantitative elution of Pd(II) from the modified disk.

Table 2
Percent recovery of palladium from the membrane disk using various eluents stripping agent volume of eluent

Stripping agent	Volume of eluent					
	First 2 ml	Second 2 ml	Third 2 ml	Forth 2 ml	Fifth 2 ml	Total
$HONH_3Cl$ (1 M)	38.0	8.3	5.7	0.8	71.0	18.2
$HONH_3Cl$ (2 M)	35.7	27.6	16.1	6.3	3.5	89.2
KNO_2 (1 M)	17.4	14.7	9.4	3.3	–	44.8
HCl (0.5 M)	2.3	2.3	–	–	–	4.6
NH_4SCN (1 M)	16.3	9.6	5.2	–	–	31.1
EDTA (0.1 M)	37.0	23.3	12.0	5.2	3.4	80.9
KI (1 M)	11.0	4.5	3.4	–	–	18.9
Na_2SO_4 (1 M)	22.9	10.8	5.4	–	–	9.18
Na_2SO_3 (0.05 M)	25.0	12.2	4.5	2.5	0.8	45.0
Na_2SO_3 (0.1 M)	37.1	21.1	12.5	6.5	3.2	80.4
Na_2SO_3 (0.5 M)	42.6	23.5	12.5	6.8	3.1	88.5
Na_2SO_3 (1.0 M)	49.7	12.6	6.3	5.0	100	26.4

Conditions: palladium, 20 μg (pH 2.5); sample volume, 50 ml; eluent, 10 ml of each stripping agent; flow rate, 5 ml min^{-1}.

3.2. Effects of flow rate and pH

The effect of flow rates of sample and stripping solutions from the membrane disk on the retention and recovery of palladium ions was investigated. It was found that adsorption of the metal ion was quantitative and reproducible in the range of 10–20 ml min^{-1}. The flow rate was maintained at 10 ml min^{-1} throughout the experiments. On the other hand, quantitative stripping of ions from the membrane was achieved in a flow rate range of 1.0–5.0 ml min^{-1}, using 10 ml of 1.0 M SO_3^{2-}. At higher flow rates (up to 5 ml min^{-1}) quantitative stripping of palladium needed larger volumes of SO_3^{2-}.

In order to study of the effect of pH on the recovery of Pd(II) on modified membrane disks, 50 ml solutions containing 20 μg Pd(II) were adjusted in the pH range 1.0–7.0 by using 1 M HCl or 1 M NaOH and the resulting solutions were passed through the modified membranes and then stripped with 1.0 M SO_3^{2-}. The obtained results are shown in Fig. 1. As seen, high deposition efficiency was achieved at a pH

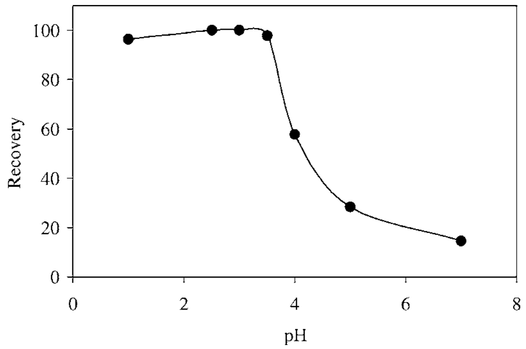


Fig. 1. Effect of pH of sample solutions on percent recovery of Pd(II). Conditions: palladium, 20 μg; sample volume, 50 ml; eluent, 10 ml of 1.0 M SO_3^{2-}; flow rate, 5 ml min^{-1}.

Table 3
Separation of Pd(II) ions from the binary mixtures

Diverse ion	Amount taken (mg)	Found (%)	Recovery of Pd(II) (%)
Ni^{2+}	5	NAPD[a]	100
Cu^{2+}	5	NAPD	100
Hg^{2+}	5	5	96
Fe^{3+}	5	NAPD	100
Zn^{2+}	5	2.5	100
Cr^{3+}	5	4.5	100
Pb^{2+}	5	NAPD	100
Cd^{2+}	5	3.4	100
Mg^{2+}	5	NAPD	100
Ca^{2+}	5	NAPD	100
Co^{2+}	5	NAPD	100

Conditions: palladium, 20 μg + mg of diverse ion (pH 2.5); sample volume, 50 ml; eluent, 10 ml of 1.0 M SO_3^{2-}; flow rate, 5 ml min^{-1}.

[a] No adsorption passes through disk.

Table 4
The tolerance limit of the diverse ions on the determination of palladium

Diverse ion	Tolerance limit (mg)
Cr^{3+}	12.5
Cu^{2+}	15.0
Ni^{2+}	15.0
Ca^{2+}	>20
Mg^{2+}	>20
Hg^{2+}	16.0
Pb^{2+}	14.5
Fe^{3+}	13.5
Cd^{2+}	18.0

Conditions: sample volume, 50 ml; eluent, 10 ml of 1.0 M SO_3^{2-}; flow rate, 5 ml min^{-1}. Samples contained 20 μg Pd(II) and different amounts of diverse ions (pH 2.5).

range of 1.0–3.5. The progressive decrease of palladium recovery at pH > 3.5 is probably due to weak complex formation of Pd with immobilized TRH on solid phase particles [28]. To achieve high efficiency and good selectivity, a pH of ∼2.5 was selected for further experiments.

3.3. Analytical performance

The maximum capacity of the membrane modified by 5 mg of TRH was determined by passing 50 ml portions of an aqueous solution containing 100 μg Pd(II) ions through the membrane, followed by determination of the retained Pd(II) ions using atomic absorption spectrometry. The maximum capacity of the membrane was found to be 440 μg of Pd(II) ions.

The break through volume of sample solution was examined by passing 50, 100, 250, 500, 750 and 1000 ml water containing 20 μg of Pd(II) ions through the modified membrane and the recommended procedure under optimal conditions was performed. In all tested solutions, the extraction by membrane was found to be quantitative. Thus, the break through volume for the proposed method should be greater than 1000 ml. Consequently, by considering the final elution of 10 ml and the sample solution volume of 1000 ml, the enrichment factor of 100 was achievable.

The repeatability of the extraction of palladium ion with modified membrane disk was studied and percent recovery of metal ion (20 μg Pd(II) in 500 ml water) obtained from five replicate experiments was found to be 99.8 ± 1.2%.

The selectivity and utility of the proposed method were examined in the presence of various ions. For this purpose, the effect of diverse ions at milligram levels on the recovery percent of 20 μg palladium in a 500 ml aqueous sample solution was studied. The results obtained are summarized in Table 3. As the results indicate, none of the metals interfered with the recovery of palladium. The tolerance limit was set as the ion concentration required to cause a ±3% error in the recovery values of 20 μg Pd(II) (Table 4). As seen, the proposed method is free from interference from a large number of transitions, non-transition ions at high concentration ranges. Also, the presence of Pt (as $PtCl_6^{2-}$) as a typical noble metal in a mixture containing palladium and platinum (in equimolar concentration) shows no considerable effect on the palladium recoveries. A decrease of ∼8% in palladium recoveries was obtained for mixtures with Pt/Pd = 2. It is noteworthy that, no decrease in recovery values was observed for palladium in the presence of various anions at the milligram ranges.

In order to assess the applicability of the proposed method to real samples with different matrices containing varying amount of a variety of diverse ions, it was applied to the separation and recovery of Pd(II) ions from two different synthetic samples which are used as catalyst in industry and also, for the determination of palladium in three water samples. The matrix of seawater sample as a more complex than others is as follows: pH = 8.0, conductivity = 17.5, SO_4^{2-} = 2320 ppm, Cl^- = 4950 ppm, Ca^{2+} = 420 ppm, Cu^{2+} = 265 ppb, total Cr = 1.8 ppb, Pb^{2+} = 30 ppb, Cd^{2+} = 0.8 ppb, NH_4^+ = 50 ppb, NO_3^- = 35 ppb, NO_2^- = 5.2 ppb, total Fe = 245 ppb and total dissolved solids = 10.1 g l^{-1}. The results of three replicate analyses of each sample are presented in Table 5. As seen, in all cases, the palladium recovery is approximately quantitative.

Table 5
Recovery results of 20 μg palladium added to 200 ml solution of synthetic and water samples (pH 2.5)

Sample	Recovery of Pd(II) (%)
Sample 1 (Pb^{2+}, Ba^{2+}, Fe^{3+}, Hg^{2+}, Ni^{2+}, Zn^{2+}, Cu^{2+}, Cr^{3+}, Cd^{2+}, 12 mg of each cation), Na^+ and K^+, 20 mg of each	102 ± 1[a]
Sample 2 (Pb^{2+}, Ba^{2+}, Fe^{3+}, Hg^{2+}, Ni^{2+}, Zn^{2+}, Cu^{2+}, Cr^{3+}, Cd^{2+}, 6 mg of each cation)	97.8 ± 0.9
Seawater	99 ± 1
Tap water	100.1 ± 0.9
Spring water (local)	102 ± 1

Conditions: eluent, 10 ml of 1.0 M SO_3^{2-}; flow rate, 5 ml min^{-1}.

[a] Mean of triplicates with percent RSD.

4. Conclusions

The proposed solid phase extraction procedure based on modified octadecyl silica membrane disk is very simple, reproducible, and selective and an atomic absorption method can be performed after the high efficient recommended enrichment method. Due to relative high preconcentration factor, trace metal ion at ppb level can be determined by this proposed method. It is free from interference for a large number of diverse ions, which are associated with Pd in its natural occurrence and industrial samples. The use of organic solvents in the proposed method is eliminated. The reproducibility of the method is at the most 1.2%. The method is economical and its toxity is low.

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