Solid Phase Extraction of Au and Pd by Silica Gel Functionalized With Triethylenetetramine for Determination by FAAS

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INTRODUCTION

Gold (Au) and palladium (Pd) are both noble and precious metals. Their main features include rare occurrence in the world, high economic value, and attractive physical and chemical properties. Au and Pd have been used in many fields such as bio-medicine, the electroplating industry, electrical industry, information technology, petro-chemical industry, aerospace construction, jewelry, electronics, energy and process technology (1-3). Au and Pd are found in rocks, ores, and soil at very low levels. For example, gold concentration in soil and ores is approximately 4 and 1 ng/g, respectively (4). Also, the wide use of catalytic converters in cars to reduce harmful species in exhaust gases results in an increase of Pd pollution of the environment. Pd concentration should be monitored because of its toxicological effects on living organisms (5). Hence, accurate and precise determination of Pd and Au is a very important analytical task (6).

Flame atomic absorption spectrometry (FAAS) (6,7), electrothermal atomic absorption spectrometry (ETAAS) (3,8), ultraviolet-visible spectrophotometry (UV-Vis) (9,10), inductively coupled plasma optical emission spectrometry (ICP-OES) (11), inductively coupled plasma mass spectrometry (ICP-MS) (12), neutron activation analysis (NAA) (13), and electro-analytical

ABSTRACT

Selective solid phase extraction (SPE) of Pd(II) and Au(III) ions were investigated using a column loaded with triethylenetetramine-bonded silica gel (TETA-SG). The presented method was optimized by investigating various effective parameters, including the pH of the sample solution, sample volume, flow rate of the sample solution, eluent volume and type, and matrix ions. TETA-SG has a high affinity towards Pd(II) and Au(III) ions at slightly acidic conditions. Both analytes were successfully eluted from the column with 5 mL of 1.0% thiourea in 1 M HCl solution.

The recovery of Pd(II) and Au(III) ions at the optimum conditions was obtained as $99.4 \pm 1.0\%$ and $99.5 \pm 1.0\%$ at the 95% confidence level, respectively. Moreover, the Pd(II) and Au(III) ions were selectively recovered from the aqueous solution containing base metal ions such as nickel(II), copper(II), and iron(III).

Flame atomic absorption spectrometry (FAAS) was used throughout the study for the determination of Au, Pd, and other metal concentrations. The detection limits of FAAS (3 σ) for Pd(II) and Au(III) were 0.26 and 0.24 $\mu\text{g L}^{-1}$, respectively, using a preconcentration factor of 100. The developed method was applied to certified reference material SARM 7B for the determination of palladium and gold with good agreement.

methods (14) have been used for the determination of Au and Pd in various samples. Unfortunately, high concentrations of matrix components in rock, sediment, and metallurgical samples usually necessitate a preconcentration and/or separation procedure prior to the determination step. Some of these techniques also suffer from insufficient detection limits for the determination of Pd and Au at trace levels as encountered in most real sample analyses (4,6). In order to increase the concentration of Pd and Au, and to separate them from matrix ions, methods including fire assay (15), ionic liquid extraction (16), co-precipitation (17), dispersive liquid-liquid microextraction (3), cloud point extraction (18), and SPE (19-22) have been used. SPE is basic, widely used, and the preferred preconcentration method due to the productiveness of a high preconcentration factor, ease of use, etc. (23). Many materials including XAD resins (24), polymeric resin (25), modified silica gel (26,27), modified activated carbon (1), and carbon nanotubes (19) have been investigated for use as a sorbent in the SPE procedure.

Chelating resins are important solid phase extractants due to their selective extraction capabilities. The resins can be prepared by immobilizing the chelating organic functional groups bearing N, O, S, and P atoms on the solid phase consisting of polymers or silica gel (28-36). For this purpose, various chelating resins have been prepared and investigated for the preconcentration of trace elements including 9-acridinylamine functionalized silica (27), γ -alumina

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functionalized with pyridine groups (20), dipyridylamine-modified nanoporous silica (26), activated carbon modified with ethyl-3-(2-aminoethylamino)-2-chlorobut-2-enoate (37), and alkyl amines bonded silica gels (38,39). Our literature survey revealed that there are no published studies using the preconcentration of Pd(II) and Au(III) on triethylenetetramine-bonded silica gel for their subsequent determination by FAAS.

In this study, the separation and preconcentration of Pd(II) and Au(III) ions by TETA-SG were investigated using the column solid phase extraction (SPE) technique. Optimum conditions for SPE of Pd(II) and Au(III) ions were determined by examining various effective parameters including pH, flow rate and volume of the model solution, and type and volume of the eluent solution. Also, the separation of Pd(II) and Au(III) ions from base metals such as iron(III), nickel(II), and copper(II) was studied. The developed method for the determination of palladium and gold was validated by application of the method to certified reference material for the determination of the Pd and Au concentration.

EXPERIMENTAL

Instrumentation

A Shimadzu AA6701F atomic absorption spectrometer (Kyoto, Japan) was used for the determination of palladium, gold, and other metal ion concentrations. Deuterium lamp for background correction and an air-acetylene flame type were used. The Pd and Au wavelengths used were 244.8 and 242.8 nm, respectively, with a slit width of 0.5 nm. The pH values of the Pd(II) and Au(III) solutions were adjusted by adding dilute HCl or NaOH solution and controlled with a Hanna 213 pH meter (Hanna Instruments, RI, USA). Deionized water (chemical resistivity 18 M Ω

cm⁻¹ at 25 °C) from Millipore® Milli-Q™ water system (Millipore, MA, USA) was used for all experiments.

Chemicals

Spectroscopic grade standard solutions of Au and Pd (1000 mg/L) and other chemicals were obtained from Merck KGaA (Darmstadt, Germany) and working solutions were prepared daily by step dilution. Preparation, characterization, and structure of triethylenetetramine-propyl-bonded silica gel were given in our previous study (21). Briefly stated, silica gel was activated in HCl solution, then it was reacted with 3-chloropropyltrimethoxysilane in dry toluene under N₂ atm. The product, 3-chloropropyl-bonded silica gel, was reacted with triethylenetetramine in the presence of triethylamine. The obtained product of TETA-bonded silica was characterized and its functional group content was found to be 0.89 mmol triethylene-tetramine group per gram of the modified silica.

SPE Procedure

A glass column packed with 0.3 g of TETA-SG was used throughout this study. The column was connected to a peristaltic pump in order to percolate the solutions at the desired flow rate. A 100 mL amount of individual solution of Au(III) and Pd(II) at 0.2 mg L⁻¹ was passed through the column using a flow rate of 10 mL min⁻¹. Then, the retained analyte was eluted with 5 mL of 1.0% thiourea in 1.0 M HCl. The metal ions in the eluates were determined by FAAS. The method was optimized by investigating the effective factors such as pH of the solution in the range of 1 and 5, sample volume in the range of 100 and 1000 mL, and flow rate in the range of 1 and 20 mL min⁻¹. The recovery of Au and Pd was obtained using the following equation:

$$\text{Recovery (\%)} = \frac{C_e}{C_s \cdot P_f} \times 100$$

where C_e and C_s are the analyte concentration in the eluate and sample solution, respectively, and P_f is the preconcentration factor obtained by the ratio of the sample solution volume to the final volume.

Sample Preparation

The certified platinum ore (SARM 7B) purchased from the South African Bureau of Standards was used to examine the accuracy of the column SPE method described in this study. The decomposition of ore (2.00 g) was carried out by reverse *aqua regia* as described in the literature (22,39). The pH of the obtained solution (100 mL) was adjusted to 1.0 or 1.7 for the preconcentration of Pd(II) and Au(III) ions, respectively, using the proposed preconcentration method at the optimum conditions.

RESULTS AND DISCUSSION

Effect of pH

The pH of the sample solution is one of the most important parameters which affects the retention of the metal ions onto the sorbents. The Pd(II) and Au(III) solutions (100 mL) were adjusted to various pH values with HCl or NaOH solution, and passed through the column loaded with TETA-SG at a flow rate of 10 mL min⁻¹. The effect of sample solution pH on the recovery of Pd(II) and Au (III) is shown in Figure 1. The Pd(II) ions were recovered quantitatively at the pH between 1.0 and 2.5. The recoveries of the Pd(II) ions decreased at a pH lower than 1.0 and higher than 2.5. The Au(III) ions were quantitatively recovered at pH values between 1.5 and 5.0.

Mixed adsorption mechanisms including ion-exchange and chelation may be proposed for the retention of Au(III) and Pd(II) on TETA-SG. The modified silica gel contains nitrogen atoms. At the acidic conditions, N atoms will be protonated and, hence, its charges will be positive. On the other hand, it is well known that Au(III) and Pd(II) can exist as anionic form $[\text{AuCl}_4]^-$ and $[\text{PdCl}_4]^{2-}$ in the solution containing ≥ 0.01 M HCl. Ionic interaction can occur between positively charged organic functional groups on TETA-SG and negatively charged chloro-anionic metal complexes. On the other hand, according to the classification of Pearson (40), Au and Pd were accepted as soft metals and the metal ions can be chelated by donor atoms with the affinity range of $\text{S} > \text{N} > \text{O}$. Hence, at higher pH values, the ability of N atoms to chelate Au(III) and Pd(II) ions appears to play an important role in their retention on the column. The ion-exchange and the chelation mechanism on the nitrogen-containing resin are listed in the literature (41-44).

It should also be noted that nitrogen atoms can attract to other heavy metal ions such as iron, copper, etc., especially at high pH values. To eliminate their retention on TETA-SG, the most acidic pH values

in which quantitative recoveries of Au(III) and Pd(II) can be obtained were chosen as optimum pH values. Therefore, the following experiments were carried out at pH 1.0 for Pd(II) ions and 1.7 for Au(III) ions.

Effect of Eluent

Some of the advantages of the eluent for use with the metal ions are as follows:

- (a) Small volume of eluent should be sufficient for complete recovery of the analytes.
- (b) Eluent should be appropriate for the instrument used for the determination of the analyte.
- (c) Eluent should not be toxic and hazardous.
- (d) Eluent cannot destroy the structure of the sorbent.

Several acids (mainly hydrochloric or nitric acid), bases, and complexing agents have been used for the elution of analytes. The elution step in the SPE procedure will be difficult when the analytes are adsorbed strongly on the sorbent. For successive elution, a high concentration and volume of the eluents or heating of the eluents will be required. Hence, easy elution of the analytes is important.

For the elution of Pd(II) and Au(III) on the TETA-SG-loaded column, the mixture of thiourea and hydrochloric acid were tested. According to the results listed in Table I, thiourea 0.1–1.0% (m/v) in HCl solution at concentrations between 0.1 and 1.0 M is sufficient for the elution of Pd(II) or Au(III) adsorbed by the TETA-SG. It is well known that Au(III) and Pd(II) can form a stable complex with thiourea (TU) consisting of $[\text{Au}(\text{TU})_2]^+$ and $[\text{Pd}(\text{TU})_4]^{2+}$, respectively, and the complex cannot be adsorbed on the TETA-SG, and the elements will be eluted from the column.

Effect of Sample Flow Rate

100 mL of Pd(II) and Au(III) solutions (0.2 mg L^{-1}) at their optimum pH values were percolated through the column at flow rates varying from 10 to 40 mL min^{-1} . According to the results given in Table II, the retention of Pd(II) and Au(III) was not significantly affected from the sample flow rate, and quantitative recoveries were obtained for both ions at high flow rates. The sample flow rate is an important parameter which determines the duration of the SPE procedure. Many of the resins can adsorb the analytes only at low flow rates, maybe due to the slow sorption kinetics (41). The usability of the TETA-SG filled column at high flow rates, i.e., 40 mL min^{-1} for the SPE of Au(III) and Pd(II) ions, is the great advantage of the proposed method. This property of the developed method is very useful, especially for the recovery of Pd(II) and Au(III) ions from large solution volumes.

Effect of Sample Volume

The effects of sample volume on the recovery of Pd(II) and Au(III) ions were studied in order to find the maximum applicable sample volume. Sample solutions containing 0.020 mg of Au(III) or Pd(II) at volumes between 100 and 1000 mL

Fig. 1. Effect of pH on recovery of Pd(II) and Au(III) ions. Sample volume, 100 mL; initial concentration of Pd(II) and Au(III) ions, 0.2 mg L^{-1} ; eluent, 10 mL of 1.0% thiourea in 1.0 M HCl; flow rate of sample solution, 10 mL min^{-1} .

were prepared. The recovery results after application of the SPE procedure are listed in Table III.

The recovery of the Au(III) and Pd(II) ions did not significantly decrease by increasing the sample volume from 100 to 1000 mL. It was found that the recovery rates of the Pd(II) and Au(III) ions were quantitative at a high sample volume (i.e., 1000 mL). It can, therefore, be concluded that TETA-SG

can adsorb Pd(II) and Au(III) ions at low concentrations from large solution volumes. Finally, a preconcentration factor of 100 was obtained by using 10 mL of eluent and 1000 mL of sample solution.

Analytical Performance

The precision of the Pd(II) and Au(III) preconcentration on the TETA-SG loaded column was investigated at the optimum conditions (see Table IV) using their individual

solution (100 mL) at the concentration of 0.2 mg L⁻¹ (n=8). The recoveries of Pd(II) and Au(III) were found to be 99.5±1.0% and 99.4±1.0% at the 95% confidence level, respectively. It can be concluded that this method can be reliably used for SPE of the Pd(II) and Au(III) ions. Some characteristics including preconcentration factor, limit of detection, and relative standard deviation of previously reported methods were compared

TABLE I
Effect of Eluents on Recovery of Pd(II) and Au(III)
(sample volume, 100 mL; initial concentration of Pd(II) and Au(III), 0.2 mg L⁻¹; flow rate of the sample solution, 10 mL min⁻¹; pH of the Pd(II) solution, 1.0; pH of the Au(III) solution, 1.7)

Eluent		Eluent Volume (mL)	Recovery (%)	
			Pd(II)	Au(III)
Thiourea, 0.1%	in 0.1 M HCl	10	98 ± 2	100 ± 1
	in 0.5 M HCl	10	98 ± 3	95 ± 2
	in 1.0 M HCl	10	100 ± 1	98 ± 2
Thiourea, 0.5%	in 0.1 M HCl	10	99 ± 1	96 ± 1
	in 0.5 M HCl	10	99 ± 1	98 ± 2
	in 1.0 M HCl	10	99 ± 1	99 ± 2
Thiourea, 1.0%	in 0.1 M HCl	10	98 ± 1	99 ± 1
	in 0.5 M HCl	10	99 ± 1	99 ± 1
	in 1.0 M HCl	10	99 ± 1	100 ± 1
	in 1.0 M HCl	5	98 ± 1	99 ± 2
	in 1.0 M HCl	5	98 ± 1	99 ± 2

TABLE III
Effect of Sample Solution Volume on the Recovery of Pd(II) and Au(III) Ions
(flow rate of sample solution, 10 mL min⁻¹; pH of Pd(II) solution, 1.0; pH of Au(III) solution, 1.7; eluent, 10 mL of 1.0% thiourea in 1.0 M HCl)

Sample Volume (mL)	Conc. of Pd(II)& Au(III) (mg L ⁻¹)	Recovery (%)	
		Pd(II)	Au(III)
100	0.2	99±1	100±1
250	0.08	99±2	100±2
500	0.04	99±2	98±1
1000	0.02	98±2	97±2

TABLE II
Effect of Flow Rate on Recovery of Pd(II) and Au(III)
(sample volume, 100 mL; initial concentration of Pd(II) and Au(III), 0.2 mg L⁻¹; eluent, 10 mL of 1.0% thiourea in 1.0 M HCl; pH of Pd(II) solution, 1.0; pH of the Au(III) solution, 1.7)

Flow rate (mL min ⁻¹)	Recovery (%)	
	Pd(II)	Au(III)
10	99 ± 1	100 ± 1
25	98 ± 3	99 ± 1
40	97 ± 1	100 ± 2

TABLE IV
Optimum SPE Conditions of Au(III) and Pd(II) on TETA-SG Loaded Column

Parameter	Optimum Conditions	
	Au(III)	Pd(II)
pH of the solution	1.7	1.0
Sample flow rate	≤ 40 mL min ⁻¹	≤ 40 mL min ⁻¹
Eluent	Thiourea (0.1-1.0) % in HCl (0.1-1.0 M)	Thiourea (0.1-1.0) % in HCl (0.1-1.0 M)
Maximum applicable sample volume	1000 mL	1000 mL

with the present method. As seen in Table V, the analytical performance of the developed method is good.

The stability of triethylene-tetramine-bonded silica gel is satisfactory and its Au(III) and Pd(II) uptake properties did not change by using it up to 20 times.

The instrumental detection limits (3δ) of Pd and Au based on three times the standard deviation of the blanks ($n=10$) was found to be 26 and 24 $\mu\text{g L}^{-1}$, respectively. The analytical detection limits were found to be 0.26 and 0.24 $\mu\text{g L}^{-1}$ with an enrichment factor of 100.

Effect of Matrix Ions

For investigation of matrix ion effects on Pd(II) and Au(III) preconcentration, various amounts of some alkaline and alkaline earth metal salts were added to 100 mL of Pd(II) or Au(III) sample solutions. The solution pH was adjusted to their optimum pH values and then passed through the column at a flow rate of 10 mL min^{-1} . The retained Pd(II) or Au(III) on the column was eluted with 10 mL of 1.0% thiourea in 1.0 M HCl. The results presented in Table VI show that the recoveries of Pd(II) and Au(III) are quantita-

tive and not affected significantly from high concentrations of alkali and alkaline earth metal ions.

The effects of Cu(II), Ni(II), and Fe(III) on the recovery of Pd(II) and Au(III) ions and their separation from Pd(II) and Au(III) were investigated. Various amounts of FeCl_3 , CuSO_4 , and $\text{Ni(NO}_3)_2$ were added to the Pd(II) and Au(III) solutions. The prepared solutions were passed through the column at the optimum conditions. As the results listed in Table VII show, the recoveries of Pd(II) and Au(III) were not affected significantly from Cu(II), Ni(II), and Fe(III) metal ions. The Cu(II),

TABLE V
Comparison of the Developed Method With Some Studies
on Preconcentration of Au(III) and Pd(II) Ions Reported in Literature

Sorbent	Analyte	PF ^a	LOD ^b ($\mu\text{g L}^{-1}$)	RSD(%)	Ref.
DowexM-4195	Au	31	1.61	5	45
NH ₂ -MCM-41	Au	833	0.056	0.7	23
Benzoylthiourea-bonded silica gel	Au	267	1.4	1.2	46
Diol, poly(p-CMS-DVB) microbeads	Au	500	-	-	47
Multi-walled carbon nanotubes	Pd	165	0.3	5.3	48
Polyamine metalfix-chelamine resin	Pd	20	9	3.2	49
Amberlite XAD-2 anchored 2,3-dihydroxypyridine	Pd	500	0.59	3.32	50
Triethylenetetramine bonded silica gel	Au	100	0.24	1	Present study
Triethylenetetramine bonded silica gel	Pd	100	0.26	1	Present study

^a Preconcentration Factor.

^b Limit of Detection.

TABLE VI
Effect of Some Alkaline and Alkaline Earth Metals
on Recovery of Pd(II) and Au(III)

Matrix Compounds	Concentration (mg L^{-1})	Recovery (%)	
		Pd(II)	Au(III)
NaCl	1 000	99 $\pm$ 1	100 $\pm$ 2
	10 000	97 $\pm$ 3	96 $\pm$ 1
KCl	1 000	99 $\pm$ 3	100 $\pm$ 2
	10 000	98 $\pm$ 2	99 $\pm$ 3
CaCl ₂	1 000	99 $\pm$ 1	98 $\pm$ 2
	10 000	96 $\pm$ 2	95 $\pm$ 2
MgCl ₂	1 000	99 $\pm$ 2	99 $\pm$ 2
	10 000	99 $\pm$ 1	94 $\pm$ 3

TABLE VII
Effect of Some Heavy Metal Ions
on Recovery of Pd(II) and Au(III) Ions

Heavy Metal Ions	Concentration (mg L^{-1})	Recovery (%)	
		Pd(II)	Au(III)
Fe ³⁺	172.1	99 $\pm$ 2	99 $\pm$ 1
	344.3	98 $\pm$ 3	98 $\pm$ 1
Cu ²⁺	199.1	98 $\pm$ 1	100 $\pm$ 1
	398.2	97 $\pm$ 2	96 $\pm$ 2
Ni ²⁺	160.6	98 $\pm$ 1	98 $\pm$ 3
	321.2	96 $\pm$ 1	97 $\pm$ 5

Ni(II), and Fe(III) ion concentrations in the eluates were between 0.4 and 7.2 mg L⁻¹. The results show that while the concentrations of the base metal ions seriously decreased, the Au(III) and Pd(II) concentrations increased nearly 10-fold. Consequently, TETA-SG can also be used for the recovery and separation of Pd(II) and Au(III) from base metal ions for industrial purposes.

Validation of Proposed Method

The SPE method presented in this study was applied to the determination of palladium and gold concentration in certified reference material SARM 7B Platinum Metal Ore, purchased from the South African Bureau of Standards. According to the results (Table VIII), the obtained values by the developed method correspond well with the certified values.

CONCLUSION

In this study, the separation and preconcentration of Pd(II) and Au(III) ions was carried out by using TETA-SG loaded column. Pd(II) and Au(III) ions can be quantitatively recovered from their aqueous solutions at pH of 1.0 and 1.7, respectively. The TETA-SG loaded column can be used at high flow rates of the sample solution. The elution of Pd(II) and Au(III) was easily carried out with 10 or 5 mL of 1.0 % thiourea in 1.0 M HCl. Also, the modified silica gel can uptake Au(III) and Pd(II) from large volumes of the solution. The recoveries of Au(III) and Pd(II) ions were not affected from metal ions including Ni(II), Cu(II), and Fe(III).

The method can be applied to highly saline samples for the recovery and preconcentration of Pd(II) and Au(III). Moreover, the modified silica shows less affinity to the base metal ions at slightly acidic conditions. Hence, it is possible to separate Pd(II) and Au(III) from Cu(II),

Ni(II), and Fe(III) metal ions for industrial or other analytical purpose. In conclusion, the proposed method provides a simple, accurate, and efficient separation and preconcentration method of Pd(II) and Au(III) for their determination at trace levels by flame atomic absorption spectrometry (FAAS).

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TABLE VIII
Determination of Pd and Au in Ore
(Certified Reference Material, SARM 7B)

Analyte	Certified Value (ppm)	Found Value (ppm)	Relative Error (%)
Au	0.27 ± 0.015	0.268 ± 0.017	- 0.7
Pd	1.54 ± 0.032	1.547 ± 0.026	+ 0.5

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