Talanta 105 (2013) 340–346

Contents lists available at SciVerse ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Synthesis/characterization of a new chelating resin and on-line solid phase extraction for the determination of Ag(I) and Pd(II) from water, cream, anode slime and converter samples by flow injection flame atomic absorption spectrometry

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ARTICLE INFO

Article history:
Received 21 May 2012
Received in revised form
15 October 2012
Accepted 16 October 2012
Available online 23 October 2012

Keywords:
Silver
Palladium
Chelating resin
Synthesis
On-line FI-FAAS preconcentration

ABSTRACT

On-line preconcentration procedures for the determination of Ag(I) and Pd(II) by flame atomic absorption spectrometry have been described. A new chelating resin, poly (N,N′-dipropionitrilemethacrylamide-co-divinylbenzene-co-2-acrylamido-2-methyl-1-propane sulfonic acid) was synthesized and used as a new adsorbent material. The resin was characterized by Fourier transform infrared spectroscopy and elemental analysis. Ag(I) was adsorbed on the chelating resin at pH 5.0 and eluted with 1.0 mol L^{-1} HNO_3. Pd(II) was retained at pH 9.5 and eluted with 1.5 mol L^{-1} HCl. The experimental parameters (pH, type and concentration of eluent, flow rates of sample and eluent solutions, elution time and the effect of interfering ions) for both Ag(I) and Pd(II) were investigated in detail. The detection limit for Ag(I) was 2.4 μg L^{-1} and the relative standard deviation was 2.9% for 0.2 μg mL^{-1} Ag(I). The detection limit for Pd(II) was 1.7 μg L^{-1} and the relative standard deviation was 2.8% for 0.3 μg mL^{-1} Pd(II). Accuracy was confirmed by analyzing a certified reference material (TMDA-70), recovery studies on real samples and comparison with electrothermal atomic absorption analysis. The proposed methods were successfully applied to the on-line determination of Ag(I) in bottled water, pharmaceutical cream and anode slime samples and Pd(II) in bottled water and catalytic converter samples.

1. Introduction

Silver is a metal of commercial importance for use in high strength and corrosion resistance alloys and jewelry. Its compounds and alloys have been widely used in dental and pharmaceutical preparations and in implanted prosthesis due to their marked antibacterial properties. It is also widely used in the photographic and imaging industry [1]. The wide use of silver compounds and silver containing procedures in industry, medicine, jewelry, cloud seeding and in the disinfection of drinking water has resulted in an increasing silver content in environmental matrices [2]. Silver enters the environment through industrial discharges because it often occurs as an impurity in copper, zinc, arsenic and antimony ores. Low-level exposure to silver compounds is widespread due to the use of soluble silver compounds to disinfect drinking water [3,4].

Palladium is attracting a lot of attention in various fields, such as industry, technology and medicine, due to its excellent chemical and physical characteristics. Its main industrial uses are as a raw material for catalysts (e.g. auto catalyst), semiconductors and alloys. Palladium finds extensive use in the electrical industry as contacts in telephone relays and printed circuits and as grids for electronic tubes and electrodes for high quality spark plugs. Palladium impacts on the environment to an increasing degree as an emerging pollutant, especially via the technical use of catalysts containing active palladium metal [5,6]. Platinum group metals (PGMs) occur in the environment mainly due to emissions from automobile and industrial processes. Currently, significant amounts of PGMs supported catalyst are disposed of annually from automobile and chemical industries as a hazardous solid waste [7].

Solid phase extraction is an effective separation/preconcentration technique for heavy metal ions because of its simplicity, its amenability to automation, high enrichment factor, low cost and the availability of a wide variety of sorbent phases [8]. Conventional off-line solid phase extraction procedures are usually effective, but they are time-consuming and tedious, requiring

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http://dx.doi.org/10.1016/j.talanta.2012.10.054

large quantities of sample and reagents, and thus methods are potentially prone to sample contamination and analyte losses. On-line flow injection (FI) preconcentration coupled with atomic spectrometry has been shown to be very powerful in eliminating many of the above drawbacks for trace elements determination [2].

Stationary phases used in FI with on-line solid phase extraction coupled with FAAS detection for the determination of silver in various samples include immobilized or modified silica gel [9–12], immobilized alumina [13], sulfhydryl cotton fibers [14] and polytetrafluoroethylene (PTFE) turnings [2].

Highly sensitive and selective techniques such as electrothermal atomic absorption spectrometry (ETAAS) [15,16], inductively coupled plasma-atomic emission spectrometry (ICP-AES) [17] and inductively coupled plasma-mass spectrometry (ICP-MS) [18] have been used for the determination of trace palladium in various matrices. In these samples, the low concentration of palladium ($\mu g\ L^{-1}$ levels) together with the high concentration of interfering matrix components often requires an enrichment step combined with a matrix separation for the accurate and precise determination of Pd in samples with very low analyte content [19]. For this purpose, solvent extraction [20,21], co-precipitation [22], ion exchange [23] and solid phase extraction [24,25] techniques have been widely used for the determination of Pd. Different solid phase extractors such as activated carbon [26], silica gel [27–29], multi-walled carbon nanotubes [19] and QuadraSil TA [6] have been the most widely used collectors.

In the present work, a new on-line column separation/preconcentration method for FAAS determination of both Ag(I) and Pd(II) in various matrices using N,N′-dipropionitrilemethacrylamide-co-divinylbenzene-co-2-acrylamido-2-methyl-1-propane sulfonic acid, poly (DPMAAm-co-DVB-co-AMPS) chelating resin is reported.

2. Experimental

2.1. Reagents and solutions

All the chemicals used were of analytical reagent grade and distilled water was used in all the experiments. The stock solutions of silver and palladium (1000 $\mu g\ mL^{-1}$) were purchased from Sigma and standard solutions used for calibration were prepared daily by appropriate dilutions of stock solutions. The pH of the solutions was adjusted with buffer solutions. Buffer solutions of pH 4.0–6.0 were prepared by mixing of appropriate volumes of 1 mol L^{-1} acetic acid and 1 mol L^{-1} sodium hydroxide and buffer solutions of pH 8.0–10.0 were prepared by mixing appropriate volumes of 1 mol L^{-1} ammonia and 1 mol L^{-1} hydrochloric acid. The pH 2.0 and pH 3.0 buffer solutions were prepared with 1 mol L^{-1} phosphoric acid and 1 mol L^{-1} sodium dihydrogenephosphate. 3,3′-iminodipropionitrile (Aldrich) and methacryloyl chloride (Alfa Easer, MA, USA) were used as received. 2,2′-azobisisobutyronitrile (AIBN, Merck) was purified by successive crystallizations from chloroform-methanol mixture. The crosslinker divinylbenzene (Merck) was used as received. 2-acrylamido-2-methyl-1-propanesulfonic acid (Merck) was used without further purification.

2.2. Instrument

A Perkin Elmer AAnalyst 800 model flame atomic absorption spectrometer (Shelton, CT, USA) equipped with a deuterium-lamp background corrector and an air–acetylene burner was used for the determination of silver and palladium. The wavelength used for silver was 328.1 nm and for palladium was 244.8 nm. A spectral bandwidth for silver of 0.7 nm and for palladium of 0.2 nm were used as working parameters. For the direct determination of Ag(I) in anode slime and Pd(II) in converter samples, a Perkin Elmer AAnalyst 800 model atomic absorption spectrometer with Zeeman-effect background correction, equipped with a THGA (Transverse Heated Graphite Atomizer) graphite furnace was used. An automatic sampler was used to inject the solution into the furnace. All experiments were performed using pyrolytically coated graphite tubes. The signals were measured as peak area. The sample volume was 10 μL and 5 μL of $Pd(NO_3)_2$ and $Mg(NO_3)_2$ mixed matrix modifier was used for the determination of Ag(I). Instrumental parameters were adjusted according to the manufacturer's recommendations. All pH measurements were made using a WTW pH315i pH meter equipped with combined pH electrode. The FT-IR spectra of the resin were recorded on a PerkinElmer Spectrum 400 FT-IR spectrometer (Waltham, MA, USA). Elemental analyses were carried out using a Leco CHNSO-932 auto microanalyser (St. Joseph, MI, USA).

The FI system consisted of a multichannel peristaltic pump (Ismatec SA, Glattbrugg, Switzerland) furnished with silicone tubes connected to the sample, buffer and washing solutions, a variable speed peristaltic pump (Watson-Marlow Inc., Wilmington, MA, USA) connected to the eluent solution, two electromechanic valves (Cole-Parmer Inc. Co., Illinois, USA, 3-way pinch valve) to select solution ways, a glass minicolumn (2 cm length × 2.6 mm i.d.) connected to the peristaltic pumps and a timer which has five channels. Peristaltic pumps and valves were controlled by the timer. This system was designed in our laboratory. The flow system was operated in the time-based mode. The measurements were expressed as peak area.

2.3. Preparation of the minicolumn

The minicolumn was prepared by packing 25 mg of the chelating resin. The ends of the column were fitted with glass wool to retain the packing material. Before use, distilled water was passed through the column in order to clean it. The resin bed volume was approximately 0.05 mL.

2.4. Sample preparation

The described method was successfully applied for the on-line determination of Ag(I) in bottled water, pharmaceutical cream and anode slime samples and of Pd(II) in bottled water and catalytic converter samples. The bottled water from a local market and cream sample from a pharmacy in Kayseri, Turkey were purchased. Anode slime and converter samples were taken from Kayseri Organized Industrial Region, Turkey.

2.4.1. Preparation of bottled water, anode slime and cream samples for Ag(I) analysis

The described method was applied to the 50 mL of bottled water. For pharmaceutical cream sample, 100 mg of the sample was taken into 100 mL of the beaker. It was dissolved by adding 10 mL of concentrated HNO_3 (65%, w/w) and by evaporating near to dryness on a hot plate. Then 10 mL of concentrated HNO_3 and 2 mL of H_2O_2 (30%, w/w) were added to the residue. The mixture was again evaporated near to the dryness. The cooled residue was dissolved with distilled water and made up to 50 mL. The pH of the 25-fold diluted samples from this solution was adjusted to pH 5.0 and the procedure given above was applied for the preconcentration and separation of Ag(I).

In order to decompose the anode slime (100 mg), 10 mL of aqua regia was added to the beaker. The mixture was evaporated near to dryness on a hot plate. Then, 10 mL of aqua regia was

added again to the residue and the mixture was again evaporated near to dryness. The residue was filtered through a filter paper with blue band by using distilled water. The pH of the filtrate was adjusted to pH 5.0 and the solution was diluted to 50 mL with distilled water. The on-line preconcentration procedure was used to separate and preconcentrate of Ag(I).

2.4.2. Preparation of bottled water and catalytic converter samples for Pd(II) analysis

The described method was applied to an aliquot of 50 mL of bottled water. The catalyst sample (50 mg) was decomposed with twice aqua regia by using portions of 20 mL. The insoluble material was removed by filtration. The pH of the filtrate was adjusted to pH 9.5 and this solution was diluted to 100 mL with distilled water. Then the procedure given above was applied to these sample solutions.

2.5. On-line FI preconcentration system

The on-line preconcentration method was evaluated using model solutions before its application to real samples. The on-line FI system is shown in Fig.1(a–d) and the conditions of the FI system are given in Table 1. Firstly, the minicolumn was preconditioned using buffer solutions of pH 5.0 for Ag(I) and pH 9.5 for Pd(II). During this period, PP1 and valve 2 were active and valve 1 was off (a). Then the sample or standard solution was adjusted to pH 5.0 for Ag(I) and pH 9.5 for Pd(II) and passed through the minicolumn at a flow rate of 4.3 mL min^{-1}. Ag(I) and Pd(II) ions were retained on the resin. Meanwhile, PP1 and valve 1 were active while PP2 and valve 2 were off (b). Then the minicolumn was washed with distilled water to remove the impurities from the resin. In this step, PP1 was active while PP2 valve 1 and valve 2 were off (c). In order to elute the retained ions, 1.0 mol L^{-1} HNO_3 for Ag(I) and 1.5 mol L^{-1} HCl for Pd(II) at a flow rate of 5 mL min^{-1} were aspirated into FAAS using PP2. During the elution, PP2 was activated while PP1 was stopped (d). The elution time was 3.6 s. The resin was then regenerated with distilled water.

3. Results and discussion

3.1. Synthesis and characterization of the chelating resin

N,N′-dipropionitrile methacrylamide (DPMAAm) has been synthesized according to the literature [30]. The preparation of poly (DPMAAm-co-DVB-co-AMPS) resin was carried out with a radical initiator in dimethylformamide solution. The two appropriate monomers, DPMAAm (1.09 g, 6.0 mmol) and AMPS (0.41 g, 2.0 mmol), the crosslinking reagent, DVB (0.26 g, 2.0 mmol), and the initiator AIBN (0.018 g, 0.1 mmol) were added to a polymerization flask. The solution was purged with nitrogen for 10 min, and the reaction mixture was heated at 70 °C in an oil bath for 3 h. The mixture was then cooled to room temperature and the liquid slowly decanted. Solid chelating resin was filtered and washed with abundant diethylether and dried under vacuum at 50 °C until a constant weight was obtained. The structure of the

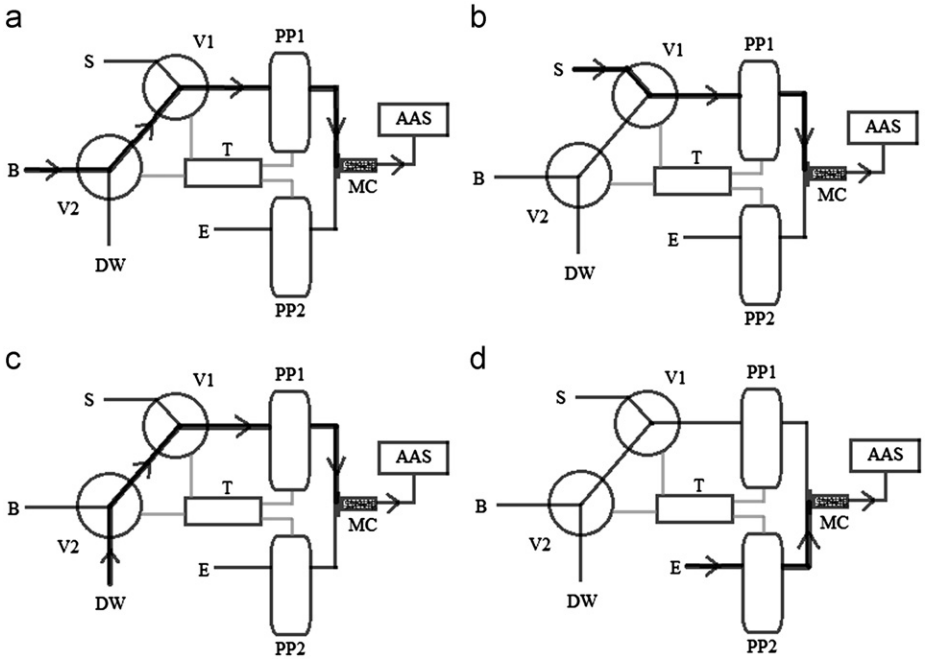

Fig. 1. Schematic diagram of FI-FAAS system: (a) preconditioning, (b) sample loading, (c) washing, (d) elution. S, sample; B, buffer; E, eluent; DW, distilled water; PP1 and PP2, peristaltic pumps; MC, minicolumn; V1 and V2, valves; T, timer. The solution flow paths are shown in bold.

Table 1
The operational sequence for the FI system.

Step	Time (s)	Valve on	Peristaltic pump on	Solution	Flow rate (mL min^{-1})	Function
(a)	52.8	V2	PP1	Buffer	4.3	Preconditioning
(b)	135	V1	PP1	Sample	4.3	Sample loading
(c)	34.2	–	PP1	Distilled water	4.3	Column washing
(d)	3.6	–	PP2	HNO_3 for Ag(I)/HCl for Pd(II)	5.0	Elution

synthesized poly (DPMAAm-co-DVB-co-AMPS) resin is shown in Fig. 2. The chelating resin obtained was weighed 1.408 g (yield: 80%). The resin yield was calculated from the conversion of monomer to polymer resin as follows:

$$\text{Yield } (\%) = (w_r/w_o) \text{ x } 100$$

Where, w_r and w_o denote the weights (g) of chelating resin and total feed monomers, respectively.

The elemental analysis results of poly(DPMAAm-co-DVB-co-AMPS) resin are given in Table 2. The agreement between experimentally found and theoretical values is good. The key FTIR frequencies (cm^{-1}) for a KBr pellet of the chelating resin were: 3320(υ_{NH}), 3050 (υ_{CH} in aromatic ring), 2980, 2927 and 2860 ($\upsilon_{a\ C-H}$ and $\upsilon_{s\ C-H}$ in CH_3 and CH_2), 2245 ($\upsilon_{C\equiv N}$) 1651 ($\upsilon_{N-C=O}$), 1446 (υ_{C-N} of –N–C=O), 1600, 1538, 1480 ($\upsilon_{C=C}$ in aromatic ring), 1380, 1365 (υ_a and υ_s CH_3), 1034 (υ_{SO}), 799, 623 (υ_{CH} and $\upsilon_{C=C}$ out of thiazole ring).

3.2. Effect of pH

The sample pH plays a very important role in the adsorption process. The pH values of 100 mL of model solutions containing 0.2 μg mL^{-1} of Ag(I) and 0.3 μg mL^{-1} of Pd(II) ions were adjusted to 2.0–6.0 for Ag(I) and 8.0–10.0 for Pd(II) using appropriate buffer solutions. The solutions were passed through the column at a flow rate of 3.6 mL min^{-1}. The retained Ag(I) and Pd(II) ions were eluted with 2.0 mol L^{-1} HNO_3 at a flow rate of 7.5 mL min^{-1} for both Ag(I) and Pd(II) and then introduced into the FAAS nebulizer. The analytical signals obtained as peak area are shown in Fig. 3. The highest signals were obtained at pH 5.0 for Ag(I) and at pH 9.5 for Pd(II). At lower pHs (< 5.0), there was competition between H^+ ions and Ag(I) ions to occupy the resin active sites while at higher pHs (> 5.0), a decrease in absorbance signal was observed due to metal hydrolysis. Ag(I) is more stable at acidic pH. Also, at highly alkaline pH, the precipitation of $Pd(OH)_2$ occurs, which reduces the concentration of Pd(II) ions able to interact with the sorbent [13,31]. In the light of these results, the optimum pH was chosen as 5.0 for Ag(I) and 9.5 for Pd(II).

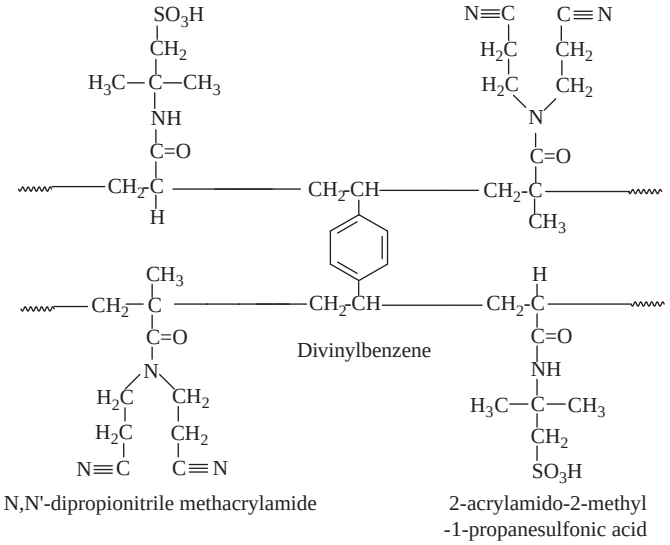

Fig. 2. Structure of synthesized poly (DPMAAm-co-DVB-co-AMPS) resin.

3.3. Effect of eluent type and concentration

For elution of the retained silver and palladium ions, HNO_3 and HCl acid solutions at various concentrations (0.1, 0.5, 0.75, 1.0, 1.5 and 2.0 mol L^{-1}) were examined as the eluent for the FI-on-line preconcentration system. The signals (as peak area) were highest in the concentration range of 0.75–2.0 mol L^{-1} HNO_3 for Ag(I) and at 1.0–2.0 mol L^{-1} HCl for Pd(II). Therefore, 1.0 mol L^{-1} HNO_3 was used as the eluent for Ag(I) and 1.5 mol L^{-1} HCl was used as the eluent for Pd(II) in all subsequent experiments. In acidic solutions containing chloride ions, Pd(II) occurs in anionic form (mainly as $PdCl_4^{2-}$ and $PdCl_3(H_2O)^-$) and does not interact with the active sites of the resin [31].

3.4. Effect of sample and eluent solution flow rates

The sample flow rate is a very important parameter since it is one of the steps that controls the analysis time. At high sample flow rates, metal ions do not equilibrate with the resin due to the increased velocity of the ions, which reduces the contact time between the phases. At low flow rates however there is a decreased sample throughput due to longer residence times [32]. The model solutions containing 0.2 μg mL^{-1} Ag(I) at pH 5.0 and 0.3 μg mL^{-1} Pd(II) at pH 9.5 were passed through the column at flow rates of 1.5–6.9 mL min^{-1}. Fig. 4 shows that the highest signals for both Ag(I) and Pd(II) were obtained in the flow rate range of 3.6–5.1 mL min^{-1}. Flow rates below 4.3 mL min^{-1} were resulted in broader and split peaks and also the precision of the signals (especially for silver ion) was poor. The optimum sample flow rate was therefore selected to be 4.3 mL min^{-1} for

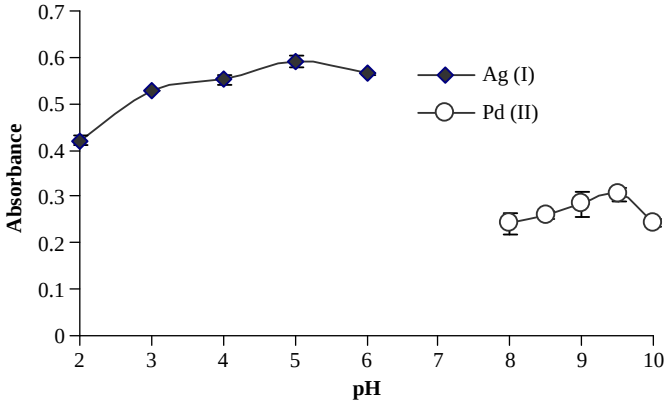

Fig. 3. Effect of pH on Ag(I) and Pd(II) signals. Conditions: sample flow rate, 3.6 mL min^{-1}; eluent flow rate, 7.5 mL min^{-1}; eluent solution, 2 mol L^{-1} HNO_3.

Table 2
Synthesis parameters and chemical analysis of poly (DPMAAm-co-DVB-co-AMPS) resin.

Feed monomers (mol%) in DPMAAm/DVB/AMPS resin	Found value (%)					Yield (%)
	C	H	O	N	S	
60/20/20	[a](61.36) [b](61.55)	[a](6.98) [b](6.95)	[a](14.52) [b](14.44)	[a](10.76) [b](10.81)	[a](6.38) [b](6.25)	80

[a] From elemental analysis.
[b] Theoretical value.

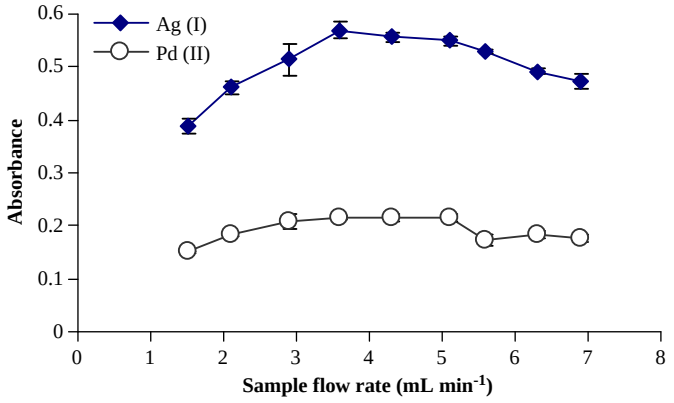

Fig. 4. Effect of sample flow rate on Ag(I) and Pd(II) signals. Conditions: pH 5.0 for Ag(I) and pH 9.5 for Pd(II); eluent solution, 1 mol L^{-1} HNO_3 for Ag(I) and 1.5 mol L^{-1} HCl for Pd(II).

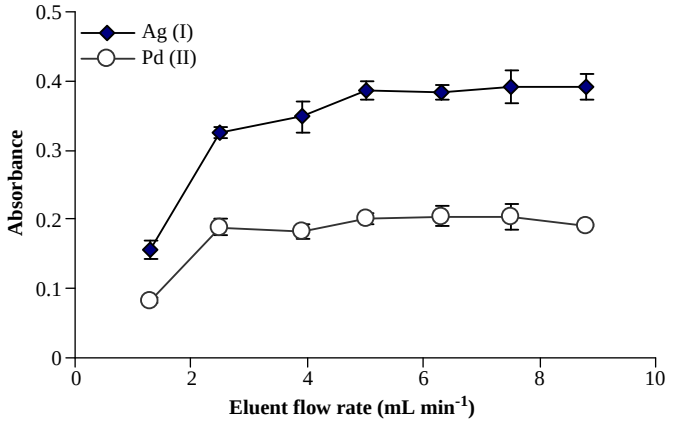

Fig. 5. Effect of eluent flow rate on Ag(I) and Pd(II) signals.

both Ag(I) and Pd(II) as a compromise between sample consumption, sufficient sensitivity and higher sampling frequency.

The effect of flow rate of the eluent was studied in the flow rate range of 1.3–8.8 mL min^{-1}. and the results are shown in Fig. 5. The absorbance was constant at flow rates $\geq$5.0 mL min^{-1} for both Ag(I) and Pd(II) ions. Above this flow rate, analytical signals resulted in broader and split peaks. Thus an eluent flow rate of 5.0 mL min^{-1} was used for both Ag(I) and Pd(II) in all subsequent experiments.

3.5. Effect of elution time

The effect of the elution time was studied over the range 2.4–9.9 s because the elution time is an important parameter affecting the peak area signals of the analytes. As can be seen in Fig. 6, Ag(I) signals decreased rapidly at elution times >3.6 s. Pd(II) signals were constant for elution times of 5.1–9.9 s. When the elution time was short, the peaks shapes obtained were good for both analyte ions but at longer elution times the broader peaks were observed for both Ag(I) and Pd(II) ions. Considering these results, the optimal elution time was selected as 3.6 s for both ions.

3.6. Effect of matrix ions

The effect of interferences on the determination of Ag(I) and Pd(II) was investigated using the optimized on-line preconcentration system. Model solutions containing 0.2 μg mL^{-1} Ag(I) ions at pH 5.0 and 0.3 μg mL^{-1} Pd(II) ions at pH 9.5 and different

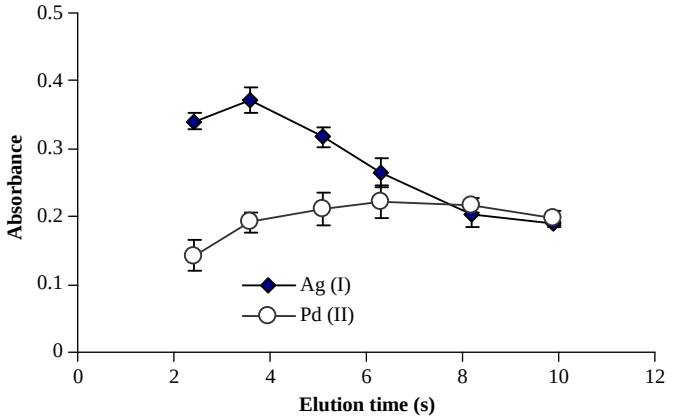

Fig. 6. Effect of elution time on Ag(I) and Pd(II) signals. Conditions: pH 5.0 for Ag(I) and pH 9.5 for Pd(II), sample flow rate, 4.3 mL min^{-1}; eluent flow rate, 5.0 mL min^{-1}.

Table 3
Effect of matrix ions on determination of Ag(I) and Pd(II) ions, $n=3$.

Ion	Added as	Concentration (μg mL^{-1})	R ± s (%), for Ag (I)	Concentration (μg mL^{-1})	R ± s (%), for Pd (II)
Na^+	$NaNO_3$	1000	97 ± 3	2500	100 ± 1
K^+	KNO_3	500	103 ± 3	1000	136 ± 1
				1000[a]	102 ± 2
Ca^{2+}	$Ca(NO_3)_2 \cdot 4H_2O$	50	100 ± 4	75	101 ± 1
Mg^{2+}	$MgCl_2 \cdot 6H_2O$	25	99 ± 5	50	99 ± 2
SO_4^{2-}	Na_2SO_4	250	101 ± 4	100	102 ± 3
NO_3^-	$NaNO_3$	250	97 ± 2	250	104 ± 1
PO_4^{3-}	$NaH_2PO_4 \cdot H_2O$	250	103 ± 2	100	98 ± 3
Cl^-	NaCl	1000	15 ± 1	1000	103 ± 4
Pb^{2+}	$Pb(NO_3)_2$	10	94 ± 1	10	102 ± 3
Zn^{2+}	$Zn(NO_3)_2 \cdot 6H_2O$	10	98 ± 1	10	102 ± 3
Ni^{2+}	$Ni(NO_3)_2 \cdot 6H_2O$	10	94 ± 4	10	99 ± 3
Al^{3+}	$Al(NO_3)_3 \cdot 9H_2O$	5	95 ± 4	10	101 ± 1
Cd^{2+}	$Cd(NO_3)_2 \cdot 4H_2O$	5	96 ± 4	10	99 ± 1
Co^{2+}	$Co(NO_3)_2 \cdot 6H_2O$	10	96 ± 1	10	96 ± 3
Fe^{3+}	$Fe(NO_3)_3 \cdot 9H_2O$	5	100 ± 4		
Mn^{2+}	$Mn(NO_3)_2 \cdot 9H_2O$			10	101 ± 3

[a] 2 mL of trisodium cobalt (III) hexanitrite solution of 1% (w/v) was added to the solution.

concentrations of the interfering ions were treated according to the proposed procedure. The results for Ag(I) and Pd(II) are given in Table 3. Most of the cations and anions examined did not interfere in the determination of Ag(I) and Pd(II) under optimum experimental conditions. However, Cl^- and K(I), interfered with the determination of Ag(I) and Pd(II) ions, respectively. It is well known that Cl^- reacts with Ag(I) ion. The interference of K(I) was eliminated using 1% (w/v) trisodium cobalt (III) hexanitrite solution as a masking agent. Because of the enhancing effect of the K(I) ion on the Pd(II) signal, 2 mL of trisodium cobalt (III) hexanitrite solution was added to the model solutions containing 0.3 μg mL^{-1} Pd(II) and 1000 μg mL^{-1} K(I) ion. The results showed that the recovery of Pd(II) was not affected by solutions containing 1000 μg mL^{-1} K(I).

3.7. Analytical performance of the method

Under the optimum conditions described above, the analytical characteristics of the proposed method were investigated. The flow system showed good linearity within the concentration range from 0.01 to 1.0 μg mL^{-1} for Ag(I) and from 0.05 to 1.0 μg mL^{-1} for Pd(II) with a 3.76 min preconcentration time. Linear regression equations were obtained for calibration curves under the optimum chemical

and flow conditions, $A=0.0019+1.471C$ ($r^2=0.9993$), where A is the absorbance and C is the Ag(I) concentration in the standard solution and $A=-0.0041+0.456C$ ($r^2=0.9992$), where A is the absorbance and C is the Pd(II) concentration in the standard solution. The calibration graph obtained using direct FAAS aspiration without preconcentration was $A=-0.0025+0.034C$ in the concentration range 0.5–5.0 μg mL^{-1} ($r^2=0.9998$) for Ag(I) and $A=0.0023+0.008C$ in the concentration range 1.0–12.0 μg mL^{-1} ($r^2=0.9994$) for Pd (II).

The experimental preconcentration factors [33] calculated as the ratio of the slopes of the calibration curves with and without preconcentration were 43 for Ag(I) and 57 for Pd(II). The overall time required for the preconcentration of 10.4 mL of sample (2.25 min, at a flow rate of 4.3 mL min^{-1}), elution (0.06 min, at flow rate of 5.0 mL min^{-1}), washing (0.57 min, at a flow rate of 4.3 mL min^{-1}) and preconditioning (0.88 min, at a flow rate of 4.3 mL min^{-1}) was 3.76 min; hence sample throughput was 16 samples h^{-1}.

The detection limit (DL, $n=21$) calculated using 3 s/b criterion was 2.4 μg L^{-1} for Ag(I) and the DL based on 3 s ($n=21$) for Pd(II) was found to be 1.7 μg L^{-1}. The precision (RSD,%) was 2.9% for 0.2 μg mL^{-1}Ag(I) and 2.8% for 0.3 μg mL^{-1} Pd(II).

3.8. Accuracy of the method and analytical applications

The accuracy of the described method was verified by analyzing a certified reference material (TMDA-70 lake water) for Ag(I). The found value (10.5 ± 1.0 μg L^{-1}) was in good agreement with the certified value (10.9 ± 0.13 μg L^{-1}). The method was validated by spiking various samples (bottled water, cream, anode slime and catalytic converter) with known amounts of both Ag(I) and Pd(II) ions and the results are given in Tables 4 and 5. The recovery values were satisfactory (94–107%).

The performance of the proposed method was also compared with the results obtained from the ETAAS. The concentration of Ag(I) in anode slime was 31 ± 1 μg g^{-1} and the palladium content of the catalytic converter sample was 942 ± 5 μg g^{-1} which are in good agreement with those given in Tables 4 and 5, respectively.

Table 4
Determination of Ag(I) in bottled water, cream and anode slime samples.

Sample	Unit	Added	Found[a]	$R\pm s$ (%)
Bottled water	(μg L^{-1})	0	< DL	
	(μg L^{-1})	20	20 ± 1	100
	(μg L^{-1})	40	40 ± 2	100
Cream	(μg g^{-1})	0	1875 ± 125	
	(μg g^{-1})	1250	3215 ± 100	107
	(μg g^{-1})	2500	4500 ± 25	105
Anode slime	(μg g^{-1})	0	30 ± 2	
	(μg g^{-1})	25	55 ± 3	100
	(μg g^{-1})	50	78 ± 1	96

[a] $x\pm s$, $n=3$.

Table 5
Determination of Pd(II) in bottled water and catalytic converter samples.

Sample	Unit	Added	Found[a]	$R\pm s$ (%)
Bottled water	(μg L^{-1})	0	< DL	
	(μg L^{-1})	50	47 ± 1	94
	(μg L^{-1})	80	75 ± 2	94
Catalytic converter	(μg g^{-1})	0	940 ± 2	
	(μg g^{-1})	100	1040 ± 14	100
	(μg g^{-1})	200	1136 ± 60	98

[a] $x\pm s$, $n=3$.

Table 6
Comparison of the analytical performances of the present methods with those reported in the literature for on-line FAAS preconcentration of Ag(I) and Pd(II).

Analyte	Sorbent	Sample	Sampling frequency (h^{-1})	Sample consumed (mL)	DL (μg L^{-1})	PF	Sorbent mass (mg)	Refs.
Ag	PTFE-turnings/Pb-DDTC	Tap, lake, sea, and waste water	19	15	0.2	110	100	[2]
Ag, Pd	Silica gel modified with thiourea	Certified ore sample, nickel alloy, anode slime, and $CoCl_2$ solution	–	–	1.3, 21	15–20	–	[10]
Ag	Alumina immobilized with DDTC	Tap water, well water, rain water, sea water, radiology film and lead concentrate samples	16	20	1.7	125	70	[13]
Pd	Various sorbents	Certified reference material	30	–	5	–	20	[24]
Pd	Metalfix-Chelamine	Synthetic geological samples	17	4.7	9	20	100	[34]
Pd	Silica gel	Tap water and catalytic converter	–	–	5.0	335	50	[35]
Ag, Pd	Poly (DPMAAm-co-DVB-co-AMPS) chelating resin	Bottled water, cream, anode slime and catalytic converter	16,16	10.4, 10.4	2.4, 1.7	43, 57	25	This work

A comparison of the reported methods with other on-line solid phase extraction methods is given in Table 6. The developed methods for Ag(I) and Pd(II) show good analytical characteristics such as low detection limits (especially for Pd), comparable sampling frequency, good preconcentration factors, and a smaller mass of resin. The stability of the resin (25 mg) was excellent and its adsorption properties did not change after 450 cycles of adsorption and desorption.

4. Conclusions

In this study, a new chelating resin was synthesized and used for the first time for the on-line FAAS determination of Ag(I) and Pd(II) ions in samples having various matrices with preconcentration time of 3.76 min. The coupling of an on-line system with FI-FAAS increases the speed of the preconcentration and analysis process and reduces sample consumption and contamination risks. The certified reference material (TMDA-70 lake water) analysis for Ag(I) as well as ETAAS analysis and recovery studies for both Ag(I) and Pd(II) in real samples show the reliability and accuracy of the methods. The two methods are also simple, rapid, selective and precise.

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