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# REMOVAL OF NICKEL(II) AND PALLADIUM(II) FROM SURFACE WATERS

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**ABSTRACT.** A new sorbent was prepared using alumina and 5-Br-PADAP, and its adsorption ability for the removal of Ni(II) and Pd(II) from different waters was investigated. The procedure is based on retention of the analytes on the alumina load with 5-Br-PADAP at pH ~ 6. The separation/preconcentration conditions for the quantitative recoveries were investigated. The limit of detections (LOD) based on three times the standard deviations of the blank, were 0.187 and 0.253 ng mL<sup>-1</sup> for Ni(II) and Pd(II), respectively. Obtained sorption capacities for 1 g sorbent were 6.0 mg Ni(II) and 11.0 mg Pd(II). The linearity was maintained in the concentration range of 0.625 to 6.0 ng mL<sup>-1</sup> for Ni(II) and 0.416 to 7.0 ng mL<sup>-1</sup> for Pd(II) in the original solution. Eight replicate determinations of a mixture containing 2.0 µg mL<sup>-1</sup> each of the elements in the final solution gave relative standard deviation of ±0.82 and ±1.12% for Ni(II) and Pd(II), respectively. The proposed method was successfully applied to the determination trace amounts of Ni(II) and Pd(II) in the surface water samples.

KEYWORDS: Alumina, Surface water, Nickel(II), Palladium(II), Preconcentration

### **INTRODUCTION**

Nickel is widely used in electroplating, in the manufacture of Ni-Cd batteries, in rods for arc welding, in pigments for paint, in ceramics, in surgical and dental prostheses, in magnetic tapes and computer components and in nickel catalysts. Nickel enters waters from dissolution of rocks and soils, from biological cycles, from atmospheric fallout, especially from industrial processes and waste disposal [1]. Nickel was thought be essential to plants and some domestic animals [2], but not considered to be a metal of biological importance until 1975, when Zerner discovered that urease was a nickel enzyme [3, 4]. Nickel is an essential constituent of plant urease. Urease-rich legumes such as jack beans and soybeans generally contain high nickel concentrations [1]. Compared with other transition metals, nickel is a moderately toxic element. However, it is known that inhalation of nickel and its compounds can lead to serious problems, including cancer of the respiratory system [5]. Moreover, nickel can cause a skin disorder known as nickel-eczema [6]. Eczema develops in places where nickel-containing metal is touching the skin.

Palladium is used as a matrix modifier for the determination of several metals by electrothermal atomic absorption spectrometry [7, 8]. Owing to its corrosion resistance nature and alloying ability, it is an important element in metallurgy. Its alloys are used in dental and medicinal devices and in jewellery manufactures. Palladium has an extensive use in electrical industry as grids for electronic tubes and electrodes for high quality spark plugs. It is also used as catalytic converter in motor vehicles. Therefore, this metal may accumulate along motorways and on soil surface and street dust [9].

Nickel and palladium can enter waters from industrial processes and waste disposal, beside; they enter environmental samples such as surface water, from dissolution of soils and street dust. Therefore, it is necessary and important to develop sensitive methods for determining nickel and palladium in environmental samples.

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Owing to the co-existence of various heavy metal ions in industrial effluents or other water resources, selective separation of toxic metal ions attracts much attention in both industries and researches. Selective adsorption of an ion on suitable solid sorbent possessing selectivity is inherently attractive to remove metal ions from dilute aqueous solution. For this purpose, many enrichment methods have been proposed and used to separate and preconcentrate trace elements, according to nature of the samples, the concentration of the analytes and the measurement techniques [10]. Different methods have been applied to extract Ni(II) and Pd(II) ions in water samples including liquid-liquid extraction [11], cloud point extraction [12-16], coprecipitation [17], ion exchange [18], liquid phase micro extraction [19-21], voltammetry [22, 23] and solid phase extraction [9, 24-32]. The liquid-liquid extraction and separation methods are usually time-consuming and labor extensive, and require relatively large volumes of high purity solvents. Of additional concern is disposal of the organic solvent used, which creates a severe environmental problem. Solid phase extraction (SPE) has known as a powerful tool for separation and enrichment of various inorganic and organic analytes. SPE has several advantages over other techniques, including stability and reusability of the solid phase, high preconcentration factors, ease of separation and enrichment under dynamic conditions, no need for organic solvents, which may be toxic and minimal costs due to low consumption of reagents [33].

Aluminum oxide is one of the most widely used adsorbents, as it does not swell and has good mechanical strength, small solubility and stability in a broad pH range [34]. Immobilization of organic compounds on the surface of the solid support is usually aimed at modifying the surface with certain target functional groups for a higher selectivity of the extraction. The selectivity of the modified solid phases toward certain metal ions is attributed to several well-known factors, such as the size of the organic compound used to modify the sorbent, the activity of the loaded surface groups and the type of the interaction of functional group [35].

2-(5-Bromo-2-pyridylazo)-5-diethylaminophenol (5-Br-PADAP), one of commercially available and cheap pyridylazo reagents has been used in determination of trace metals, including cadmium [36, 37] and zinc [38].

There is no report on complexation of PADAP with Pd(II) ions or immobilization on the surface of alumina. The preliminary experiments showed that the bare alumina can adsorb a lot of metal ions, but, adsorption was not selective and the recoveries were incomplete. By immobilization of the ligand PADAP on the alumina, only, Ni(II) and Pd(II) can be adsorbed in the specified pH. On the other hand, the coating of alumina with the ligand increases the adsorption capacity for Ni(II) and Pd(II). Also, since, the conditions of the proposed method, was proper for simultaneous extraction and preconcentration of Pd(II) and Ni(II), only. For example the both elements were adsorbed at pH = 6 and desorbed with 3.0 mL of 1 M thiourea and then 2.0 mL 3 M of HCl, simultaneously. Therefore, these two elements were selected and examined for the proposed method.

This work is devoted to the preparation and evaluation of the sorption properties of alumina modified with PADAP to preconcentration trace amounts of Ni(II) and Pd(II) from surface water samples. The analytical conditions for the selective extraction of analytes elements were investigated.

# EXPERIMENTAL

### Materials

The stock solutions of Ni(II) and Pd(II) (1000.0 mg  $L^{-1}$ ), were prepared by dissolving 0.5196 g of nickel nitrate (99.99%, Merck, Darmstad, Germany), in distilled water and 0.1660 g PdCl<sub>2</sub> (99.999%, Aldrich, Milwaukee, USA) in 2 M HCl (37.0%, Merck, Darmstad, Germany), and

diluting to 100.0 mL with distilled water, separately. The standard working solutions were diluted daily prior to use. A 0.01% (m/v) solution of the 5-Br-PADAP (99.999%, Aldrich, Milwaukee, WI, USA) was prepared by dissolving 0.01 g of this reagent in ethanol (96.0%, Merck, Darmstad, Germany), and diluting to 100.0 mL with ethanol. Buffer solution was prepared from 0.2 M potassium dihydrogen phosphate (99.5%, Aldrich, Milwaukee, WI, USA) and 0.2 M dipotassium hydrogen phosphate (99.5%, Aldrich, Milwaukee, WI, USA) and 0.2 M dipotassium hydrogen phosphate (99.5%, Aldrich, Milwaukee, WI, USA) for pH 6. A solution of thiourea 1.0 M was prepared by dissolving 7.680 g of thiourea (99.0-101%, Merck, Darmstad, Germany), in distilled water and diluting to 100.0 mL with distilled water. $Al_2O_3$  (0.063-0.2 mm or 70-230 mesh ASTM) (Merck, Darmstad, Germany) was used as sorbent.

### Apparatus

An atomic absorption spectrometer model Sens AA (Dandenong, Victoria, Australia) equipped with deuterium lamp background corrector was used for determination of Ni and Pd in airacetylene flame. The instrumental settings of the spectrometer were as follows: wavelength, 232.0 and 244.8 nm; slit width of 0.2 and 0.2 nm; lamp current, 4 and 5 mA; acetylene flow 1.5 L min<sup>-1</sup> and air flow 3.5 L min<sup>-1</sup> for Ni and Pd, respectively. A mechanical shaker KS 130 basic (Deutschland, Germany) having speed control and timer was used for preparation of the sorbent. Funnels-tipped glass tube (5×100 mm) equipped with stopcock were used as column for the preconcentration purposes. The bed height the adsorbent in the column was approximately 10 mm. A 691 Metrohm pH meter (Herisau, Switzerland) was employed for pH measurements.

## Adsorbent preparation

Amount of 3.0 g alumina was added to 50 mL of the solution containing 0.01% PADAP in a stoppered Pyrex glass flask, and the mixture was shaken on mechanical shaker (Model KS 130 basic, Deutschland, Germany) having speed control and timer at room temperature for 2 h. The reagent coated alumina was filtered through a cellulose membrane filter (Millipore) of 0.45  $\mu$ m pore size, washed with distilled water tree times and dried at room temperature for 24 h.

#### General procedure

Funnel-tipped glass tube (ten columns, 10 cm long and 0.5 cm in diameter) equipped to stopcock was used as the column for preconcentration purposes. A small amount of glass wool was placed in the end of the columns to prevent loss of the sorbent during sample loading. Then, the columns were packed with 100 mg of the alumina coated with PADAP and conditioned with a buffer solution at pH ~ 6. The bed height the adsorbent in the column was approximately 10 mm. An aliquot of the sample solution containing Ni(II) (0.25-30.00  $\mu$ g) and Pd(II) (0.25-40.00  $\mu$ g) was taken in a 50 mL beaker and to it was added 2 mL phosphate buffer solution with pH 6. The total volume of the solution was made up to about 30 mL with distilled water. It was then passed through the column containing 100 mg of the sorbent with flow rate of 2 mL min<sup>-1</sup>. The flow rate of solution was controlled by using a stopcock in end of the column. The retained metal ions were eluted from the solid phase with 3.0 mL of 1.0 M HCl and then 2.0 mL of thiourea 1.0 M. This solution was aspirated into an air-acetylene flame for the determination of Ni(II) and Pd(II) by FAAS. Calibration curves for the determination of Ni(II) and (Pd(II) were prepared according to the proposed procedure under the optimum conditions.

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#### Analysis of real samples

The method was applied to determine NI(II) and Pd(II) from water different samples including river and spring water from Baft and Ravar in Kerman, and a sea water from Khazar Sea in Iran. The water samples were filtered through a cellulose membrane filter (Millipore) of 0.45  $\mu$ m pore size. A volume 50.0 mL of water samples was transferred to a beaker, and pH was adjusted to 6 by addition of the buffer solution. Then the proposed procedure was applied to these samples. The levels of analyte ions in the samples were determined by flame atomic absorption spectrometry.

In order to evaluate the accuracy of the procedure, recovery experiments were also carried out with spiked water samples because of certified reference material for the Ni(II) and Pd(II) was not available. The recovery percentages of Ni(II) and Pd(II) ions were evaluated and the results showed that the real samples matrixes did not affect the recovery of these ions.

### **RESULTS AND DISCUSSION**

Preliminary experiments showed that the bare alumina can adsorb a lot of metal ions, but, adsorption was not selective and the recoveries were incomplete (for example Ni: 72%, Cu: 84%, Co: 78%, Fe: 90%, Mn: 80%, Pd: 92%, Ag: 30%, Cd: 87%). By immobilization of the ligand PADAP on the alumina, only, Ni(II) and Pd(II) can be adsorbed in the specified pH. On the other hand, the coating of alumina with the ligand increases adsorption capacity for Ni(II) and Pd(II). In order to achieve the best performance, the separation/preconcentration procedure was optimized for various analytical parameters, such as pH of the sample, the flow rate of eluent and sample solution, amount of the adsorbent, volume and type of the eluent solution, volume of the buffer and volume of the sample solution. Interference effects of various ions were also investigated.

### Effect of the sample pH

Since the pH of the aqueous solutions is an important analytical factor in solid phase extraction studies of metal ions [39], the influence of pH on the recovery of analyte ions was examined in the pH range of 2-10 by using diluted solutions of HNO<sub>3</sub> and NaOH or proper buffers. As can be seen from Figure 1, Ni(II) ions were quantitatively recovered at pH range of 5-10, while Pd(II) ions were recovered at pH range of 6-9. In order to avoid hydrolyzing and determine these elements, simultaneously, pH 6 was selected for further study and was kept constant at 6 using potassium dihydrogen phosphate buffer solution.

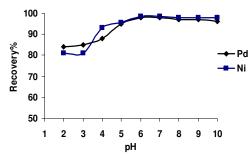


Figure 1. Effect of pH on the recovery of Ni(II) and Pd(II) after preconcentration with the proposed method. Conditions: Ni(II), 10.0 μg; Pd(II), 10.0 μg; pH ~ 6; buffer, 3.0 mL; flow rate, 2.0 mL min<sup>-1</sup>; sorbent, 100.0 mg. Instrumental conditions as in Table 1.

### Effect of type and concentration of eluent

Desorption of the retained Ni(II) and Pd(II) from the column was tested using various eluting agents. Since the complex of the Pd(II) with PADAP is stable, many of the reagents could not elute Pd(II) from the column, completely. As can be seen from Table 1, maximum recoveries have been obtained by using 3.0 mL of 1 M HCl and then 2.0 mL of 1 M thiourea (final volume 5.0 mL). Therefore, in all the experiments 3.0 mL of 1 M HCl and then 2.0 mL of 1 M thiourea were used for simultaneous desorption of Ni(II) and Pd(II).

Table 1. Effect of elution solutions on the recoveries of Ni(II) and Pd(II).

	Recov	Recovery% <sup>a</sup>		
Solution	Ni(II)	Pd(II)		
5.0 mL of 1.0 M HCl	74.6	82.0		
5.0 mL of 1.0 M HNO <sub>3</sub>	81.0	80.0		
5.0 mL of 1.0 M thiourea	83.0	51.0		
5.0 mL of 1.0 M Na <sub>2</sub> SO <sub>3</sub>	65.0	25.0		
5.0 mL of 1.0 M H <sub>2</sub> SO <sub>4</sub>	60.0	11.0		
5.0 mL mixture of 2.0 M HCL and 1.0 M thiourea	93.0	97.5		
3.0 mL 1.0 M thiourea and then 2.0 mL 3.0 M HCl	98.0	98.5		

<sup>a</sup>Average of three determinations,  $\pm$  standard deviation. Conditions: Ni(II), 10.0 µg; Pd(II), 10.0 µg; pH ~ 6; buffer, 3.0 mL; flow rate, 2.0 mL min<sup>-1</sup>; sorbent, 100.0 mg. Instrumental settings: wavelength, 232.0 and 244.8 nm; slit width 0.2 and 0.2 nm; lamp current, 4 and 5 mA; acetylene flow 1.5 L min<sup>-1</sup> and air flow 3.5 L min<sup>-1</sup> for nickel and palladium, respectively.

# Effect of flow rate of sample and eluent solution

The retention of an element on a sorbent also depends on the flow rate of the sample solution [40]. Thus, the effect of flow rate of the sample and elution solution on the retention and recovery of ions was investigated under optimum conditions (pH = 6; elution solution 3.0 mL of 1 M HCl and then 2.0 mL of 1 M thiourea). The solution containing Ni(II) and Pd(II) was passed through the column with the flow rates adjusted in the range 0.5-3 mL min<sup>-1</sup>. It was observed that, a flow rate of 3 mL min<sup>-1</sup> was adequate for Ni(II) and 2 mL min<sup>-1</sup> for Pd(II). At flow rates greater than 2 mL min<sup>-1</sup> there was a decrease in the recovery of Pd(II), probably due to insufficient contact of the metal ions and the sorbent to reach equilibrium [40]. Therefore, a flow rate of 2 mL min<sup>-1</sup> was applied for simultaneous adsorption of Ni(II) and Pd(II) in subsequent experiments. Also, for desorption of metal ions, flow rate was varied between 0.5-3 mL min<sup>-1</sup> and a flow rate of 2 mL min<sup>-1</sup> was found adequate for simultaneous desorption of Ni(II) and Pd(II).

### Effect of amount of the sorbent

The amount of sorbent is another important parameter that affects the recovery [41]. A quantitative retention is not obtained when the amount of sorbent is less [41]. On the other hand, an excess amount of resin prevents the elution of the retained chelates by a small amount of eluent quantitatively [41]. For this purpose, different amounts of the sorbent (10-200 mg) were examined. The results showed that quantitative recoveries (>95%) of the metal ions were obtained when the sorbent quantity was greater than 50 mg. 100 mg of the sorbent was selected for further experiments. The column filled with 100 mg adsorbent can be regenerated over 100 cycles of adsorption-desorption cycles without any significant change in the retention of Ni(II) and Pd(II). It can be recovered with about 10 mL of the elution solution and then water, subsequently.

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### Breakthrough volume

The measurement of breakthrough volume is important in solid phase extraction because breakthrough volume represents the sample volume that can be preconcentrated without loss of analyte during elution of the sample [39]. The volume of the first aqueous phase, containing a fixed amount of the analytes (10.0  $\mu$ g Ni(II) and 10.0  $\mu$ g Pd(II)), was varied in the range of 50.0-1000.0 mL under the optimum conditions, keeping other variables constant, and was passed through column for preconcentration. It was found that recovery was quantitative to 400.0 mL for Ni(II) and 600.0 mL for Pd(II), alone, but for the both elements as simultaneous, at sample volumes >400 mL the recoveries decreased gradually with increasing volume of sample solution. Since the elution solution volume was 5.0 mL; preconcentration factors were obtained 80 for Ni(II) and 120 for Pd(II).

# Sorption capacity of the sorbent

To determine the amount of analyte retained on the column, for a specific mass of sorbent, several solutions differing in concentrations were made and introduced into the column. Ten milliliters of solutions containing Ni(II) and Pd(II) at concentrations in the range of 20.0-150.0 mg L<sup>-1</sup>were passed through the columns containing exactly 100.0 mg of the sorbent under optimum conditions. The eluting solutions were collected and the presence of the analyte in each was tested by FAAS. When Ni(II) and Pd(II) were detected in the eluate, the test was stopped and the sorption capacity calculated. The sorption capacities were found to be 6.0 mg Ni<sup>2+</sup> and 11.0 mg Pd<sup>2+</sup> for 1.0 g sorbent.

# Effect of foreign ions

Various salts and metal ions were added to a solution containing Ni(II) and Pd(II) and the general procedure was applied. The tolerance limit was set as the concentration of the ion required to cause  $\pm 3\%$  error [42, 43]. The results obtained are given in Table 2. Among the metal ions and salts studied, most did not interfere. Thus, this method is selective and can be used for the determination of Ni(II) and Pd(II) in the water samples.

Table 2. Effect of different salts and metal ions on the extraction and preconcentration of Ni(II) and Pd(II).

Salt or ion	Tolerance limit (mg)			
	Ni(II)	Pd(II)		
Na <sub>2</sub> SO <sub>4</sub>	400	500		
KI	400	700		
$Na_2S_2O_3$	200	400		
KBrO <sub>3</sub>	400	500		
Na <sub>2</sub> CO <sub>3</sub>	300	150		
NaCl, KCl, NaF	500	500		
NaHCO <sub>3</sub>	400	400		
CH <sub>3</sub> COONa.3H <sub>2</sub> O	300	400		
Ca <sup>2+</sup>	500	500		
Pb <sup>2+</sup>	2.0	2.0		
Co <sup>2+</sup>	5.0	5.0		
Cu <sup>2+</sup>	3.0	5.0		
Cd <sup>2+</sup> , Cr <sup>3+</sup>	3.0	4.0		
Ag <sup>+</sup>	2.5	2.0		

Conditions: Ni(II), 10.0  $\mu$ g; Pd(II), 10.0  $\mu$ g; pH ~ 6; buffer, 3.0 mL; flow rate, 2 mL min<sup>-1</sup>; sorbent, 100.0 mg. Instrumental conditions are the same as in Table 1.

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#### Analytical performance

The analytical performance of the proposed procedure can be shown for the results of FAAS measurements. The linearity was maintained in the concentration range of 0.05-6.0  $\mu$ g mL<sup>-1</sup> in the final solution or 0.625-6.0×10<sup>3</sup> ng mL<sup>-1</sup> in the original solution for Ni(II) and 0.05-7.0  $\mu$ g mL<sup>-1</sup> in the final solution or 0.416-7.0×10<sup>3</sup> ng mL<sup>-1</sup> in the original solution for Pd(II). The equations of the lines are A = 0.0636C + 8.16×10<sup>-3</sup> for Ni(II) and A = 0.0415C + 5.6×10<sup>-4</sup> for Pd(II) in the final solution, respectively where A is the absorbance and C is concentration of the metal ions ( $\mu$ g mL<sup>-1</sup>). The regression coefficients for the lines are 0.9981 and 0.9967 for Ni(II) and Pd(II), respectively.

The preconcentration factors for Ni(II) and Pd(II) according to 5.0 mL eluent and the workable maximum sample volumes (400 and 600 mL) were calculated as 80 and 120, respectively. Eight replicate determinations of 10.0  $\mu$ g nickel and 10.0  $\mu$ g palladium in the 5.0 mL final solution gave a relative standard deviation of  $\pm$  0.82% for Ni(II) and  $\pm$  1.12% for Pd(II). The limit of detections (LOD) for the analytes ions based on  $3\sigma_{bb}/m$  (n = 8) were 0.187 ng mL<sup>-1</sup> for Ni(II) and 0.253 ng mL<sup>-1</sup> for Pd(II) and limit of quantification (LOQ) were 0.625 and 0.416 ng mL<sup>-1</sup> for Ni(II) and Pd(II), respectively, in the original solution.

# Application to real samples

To assess the capability of the method for real samples with different matrices containing varying amounts of diverse ions, the method was applied to determine nickel and palladium indifferent water samples. The results are given in Table 3. According to the results, the concentrations of Ni(II) and Pd(II) in analyzed water samples were below the LOD of the method. The suitability of the proposed method for the analysis of natural water samples was checked by spiking the samples with 5.0 and 10.0 mL of 2.0  $\mu$ g mL<sup>-1</sup> of the analyte ions. Good recoveries were obtained for all analyzed samples (Table 3).

Table 3. Determination of Ni(II) and Pd(II) in the water samples after preconcentration with the proposed method.

Sample	Added (ng mL <sup>-1</sup> )		Found $(ng mL^{-1})^{a}$		Recovery (%)		
	Ni(II)	Pd(II)	Ni(II)	Pd(II)	Ni(II)	Pd(II)	
River water <sup>b</sup>	0.0	0.0	ND	ND			
	5.0	5.0	5.10±0.04	5.05±0.10	102.0	101.0	
	10.0	10.0	10.07±0.08	10.03±0.14	100.7	100.3	
Spring	0.0	0.0	ND	ND			
water <sup>c</sup>	5.0	5.0	4.94±0.06	5.11±0.10	98.8	102.2	
	10.0	10.0	10.01±0.07	9.71±0.19	100.1	98.9	
River water <sup>c</sup>	0.0	0.0	ND	ND			
	5.0	5.0	$5.04 \pm 0.05$	04±0.05 5.00±0.11 100.8		100.0	
	10.0	10.0	10.15±0.07	10.07±0.09	101.5	100.7	
Sea water <sup>d</sup>	0.0	0.0	ND	ND			
	5.0	5.0	4.88±0.22	5.10±0.10	97.6	102.0	
	10.0	10.0	10.28±0.31	9.70±0.20	102.8	97.0	

ND: not detected; sample volume: 50.0 mL; <sup>a</sup>average of three determinations, ± S.D.; <sup>b</sup>Baft, Kerman, Iran; <sup>c</sup>Ravar, Kerman, Iran; <sup>d</sup>Khazar Sea, Iran. Conditions: pH ~ 6; buffer, 3.0 mL; flow rate, 2 mL min<sup>-1</sup>; sorbent, 100.0 mg.

### Comparison with other methods

Comparative data from some papers on solid phase extraction of trace Ni(II) and Pd(II) are summarized in Table 4. The analytical performance is not significantly different from those achieved by other methods described in the literature. The detection limits of investigated elements are superior to those of some preconcentration/separation methods [9, 29, 44-50]. The sorption capacities are also better or comparable with the other methods. The matrix effects with the method were reasonably tolerable. Good recoveries were obtained for the environmental samples, demonstrating that the method can be successfully applied to these samples.

Table 4. Comparative data from some recent studies on preconcentration of analyte ions.

Sorbent/reagent	Analyte	PF <sup>a</sup>	Sorption capacity	LOD	RSD%	Ref.
-	-		$(\text{mg g}^{-1})$	(ng mL <sup>-1</sup> )		
Silica gel/dimethyl golyoxime	Pd(II)	75.0	4.06	1.20	1.7	[9]
Ambersorb 572/EDTA	Ni(II)	50.0	0.21 <sup>b</sup>	1.42	2.0	[29]
Silica gel/polyethylene glycol	Ni(II)	83.3	8.30	0.71	3.1	[44]
Octadecyl silica/thioridazin	Pd(II)	100	0.44	12.0	1.2	[45]
XAD-2000/diethyldithio carbamate	Ni(II)	100	3.80	0.25		[46]
Chromosorb 108	Ni(II)	80.0	4.90	0.44	1.4	[47]
Nanometer-size TiO <sub>2</sub>	Pd(II)	50.0	11.8	12.0	7.4	[48]
Coprecipitation	Ni(II)	30.0		3.60	2.7	[49]
XAD-7/KI	Pd(II)	37.3		24.9	1.6-8.9	[50]
5-Br-PADAP/alumina	Ni(II)	80.0	6.0	0.19	0.8	Present
	Pd(II)	120	11.0	0.25	1.12	method

<sup>a</sup>PF: preconcentration factor; <sup>b</sup>mmol g<sup>-1</sup>.

# CONCLUSIONS

The new sorbent 5-Br-PADAP/alumina could be successfully applied for simultaneous separation and preconcentration of nickel(II) and palladium(II) in water samples. This solid phase extractant has the following advantages: preparation of the sorbent is simple, rapid and low cost. The modified alumina can be regenerated over 100 cycles of adsorption-desorption without any significant change in the retention of Ni(II) and Pd(II). The accuracy of the results was verified by analyzing the spike water samples. The good precision and high tolerance to interferences from matrix ions are other advantages. Thus, it may be concluded that the method in an effective approach in separation and preconcentration of nickel and palladium in water samples.

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