Determination of Palladium by Ultrasonic Nebulization Coupled to ICP-OES
After On-line Preconcentration on Activated Carbon

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INTRODUCTION

Noble metals, particularly palladium, find extensive use in the electrical industry as contacts in telephone relays and printed circuits, as grids for electronic tubes and electrodes for high quality spark plugs. The determination of traces and ultra-traces of palladium in the environment, as well as in body fluids of living species, at low concentrations is an urgent problem (1–5). Palladium affects the environment increasingly in the form of pollution, especially by its technical use in catalysts containing the active Pd metal. The use of catalytic converters has led to an anomalous increase in the concentrations of palladium in several natural matrices such as soil, water, and vegetation, in areas near intensive vehicle traffic, thus causing a new environmental risk (6–8). The effects of palladium, as well as of the other platinum group elements (PGE), on human health are still not clearly defined. Man comes in contact with this element directly, through inhalation of dust, and indirectly, through food and water. Palladium is currently the element of most concern for man and it is considered a powerful allergen (9). A critical evaluation of possible risks for human health can only be given if reliable analytical data are available.

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ABSTRACT

A system for the on-line preconcentration and determination of palladium by ultrasonic nebulization (USN) coupled to inductively coupled plasma optical emission spectrometry (ICP-OES) was studied. It is based on the chemical sorption of palladium-thiocyanate complex on a conical minicolumn packed with activated carbon (AC). The proposed procedure allowed the determination of palladium with a detection limit of 10 ng/L. The precision for 10 replicate determinations at the 500-ng/L Pd level was 2.9% relative standard deviation (RSD), calculated from the peak heights obtained. The calibration graph using the preconcentration system for palladium was linear with a correlation coefficient of 0.9995 at levels near the detection limits up to at least 100 µg/L. A total enhancement factor of 375-fold was obtained with respect to ICP-OES using pneumatic nebulization (15 for USN and 25 for preconcentration). A sampling frequency of 20 samples per hour was obtained. The effect of other ions in concentrations agreeing with water samples was studied. The addition/recovery experiments in the samples analyzed demonstrated the accuracy and applicability of the system for the determination of palladium in tap water samples.

The determination of trace amounts of palladium in geological, environmental, and biological samples requires modern instrumental techniques, among them flame atomic absorption spectrometry (FAAS) (10,11), electrothermal atomic absorption spectrometry (ETAAS) (12–14), inductively coupled plasma optical emission spectrometry (ICP-OES) (15–17), inductively coupled plasma mass spectrometry (ICP-MS) (18–21), neutron activation analysis (NAA) (22,23), capillary electrophoresis (CE) (24,25), X-ray fluorescence (XRF) (26), and spectrophotometry (27).

A separation/preconcentration step is often applied in order to remove matrix interferences and to preconcentrate the analyte to a level which can be reliably determined.

Various methods have been developed for palladium separation and preconcentration from diverse matrices such as anion exchange (20,22,28), precipitation (6,12), cloud point extraction (19), biosorption (13,14), co-precipitation (29) and sorption (5,10,15, 16,30), among others.

Activated carbon (AC) has been widely used for many purposes both in laboratory and industrial settings due to its ability to adsorb organic compounds and inorganic metal complexes. Since its introduction in analytical chemistry, enrichment of trace metals using AC has had favorably results resulting in very high concentration factors in different matrices (31–33).

The mechanism of sorption on AC is still under investigation and the adsorption of metals on activated carbon could be explained using Langmuir and Freundlich equations. Adsorption equilibrium studies have revealed that the pH is the dominant parameter controlling the adsorption (34).

In the present work, a method for preconcentration and determination of palladium in spiked water samples at low concentration levels is proposed. It was based on solid phase extraction of palladium as thiocyanate complex onto activated carbon. The determination was carried out using ultrasonic nebulization associated with inductively coupled plasma optical emission spectrometry (USN-ICP-OES).

EXPERIMENTAL

Instrumentation

The measurements were performed with a Model ICP2070 sequential ICP spectrometer (Baird, Bedford, MA, USA). The 1-m Czerny-Turner monochromator had a holographic grating with 1800 grooves/mm. The flow injection (FI) system used is shown in Figure 1. A Model U 5000 AT ultrasonic nebulizer (CETAC Technologies, Omaha, NE, USA) equipped with a desolvation system was used. The ICP and ultrasonic nebulizer operating conditions are listed in Table I. A Minipuls™ 3 peristaltic pump (Gilson, Villiers-Le-Bell, France) was used. Sample injection was achieved using a Rheodyne® Model 50, four-way rotary valve (Cotati, CA, USA). A home-made conical minicolumn (40 mm length, 4.5 mm internal upper-diameter and 1.5 mm internal lower-diameter) was used as the activated carbon holder. Tygon®-type pump tubing (Ismatec, Cole-Parmer, Vernon Hills, IL, USA) was employed to propel the sample, reagent, and eluent. The 340.458-nm spectral line was used and flow injection system

measurements were expressed as peak height emission, which was corrected against the reagent blank.

Reagents

Palladium standard solution was prepared by appropriate dilutions of a 1000-mg/L stock solution (Fluka, Switzerland) immediately before use. The palladium solution's pH was adjusted with hydrochloric acid solution.

The hydrochloric acid was Suprapur" grade (Merck, Darmstadt, Germany).

A 1×10^{-2} mol/L potassium thiocyanate (KSCN) solution was prepared by dissolving the reagent in water. Lower concentrations were prepared by serial dilution in water.

A 5% (w/v) thiourea (Fluka, Switzerland) solution was prepared by dissolving the reagent in 0.2 mol/L hydrochloric acid.

The activated carbon (Merck, Darmstadt, Germany, 50–70 mesh) was used after pretreatment with acid [activated carbon was heated to 60ºC with 10% (v/v) hydrochloric acid for 30 minutes and then with 10% (v/v) nitric acid for 20 minutes, and finally washed with deionized water until a neutral pH was reached].

Ultrapure water (18 MΩ cm) was obtained from an EASY pure RF (Barnstedt, Iowa, USA). All other solvents and reagents were of analytical reagent grade or better, and the presence of palladium was not detected in the working range.

Column and Sample Preparation

The conical minicolumn was prepared by placing 100 mg of activated carbon into an empty column using the dry packing method. To avoid loss of activated carbon when the sample solution passes through the conical minicolumn, a small amount of quartz wool was placed at both ends of the conical minicolumn. The column was then connected to a peristaltic pump with PTFE tubing to form the preconcentration system. The average lifetime of the column is more than 300 cycles. All columns prepared in this way show good reproducibility, as proven by the precision of the signals obtained for the different columns.

The water samples were filtered through 0.45 μm pore size membrane filters immediately after sampling, adjusted to pH 3.0 with hydrochloric acid solution, and stored at 4ºC in Nalgene® bottles (Nalge Nunc International, Rochester, NY, USA).

TABLE I
ICP and Ultrasonic Nebulizer Instrumental Parameters

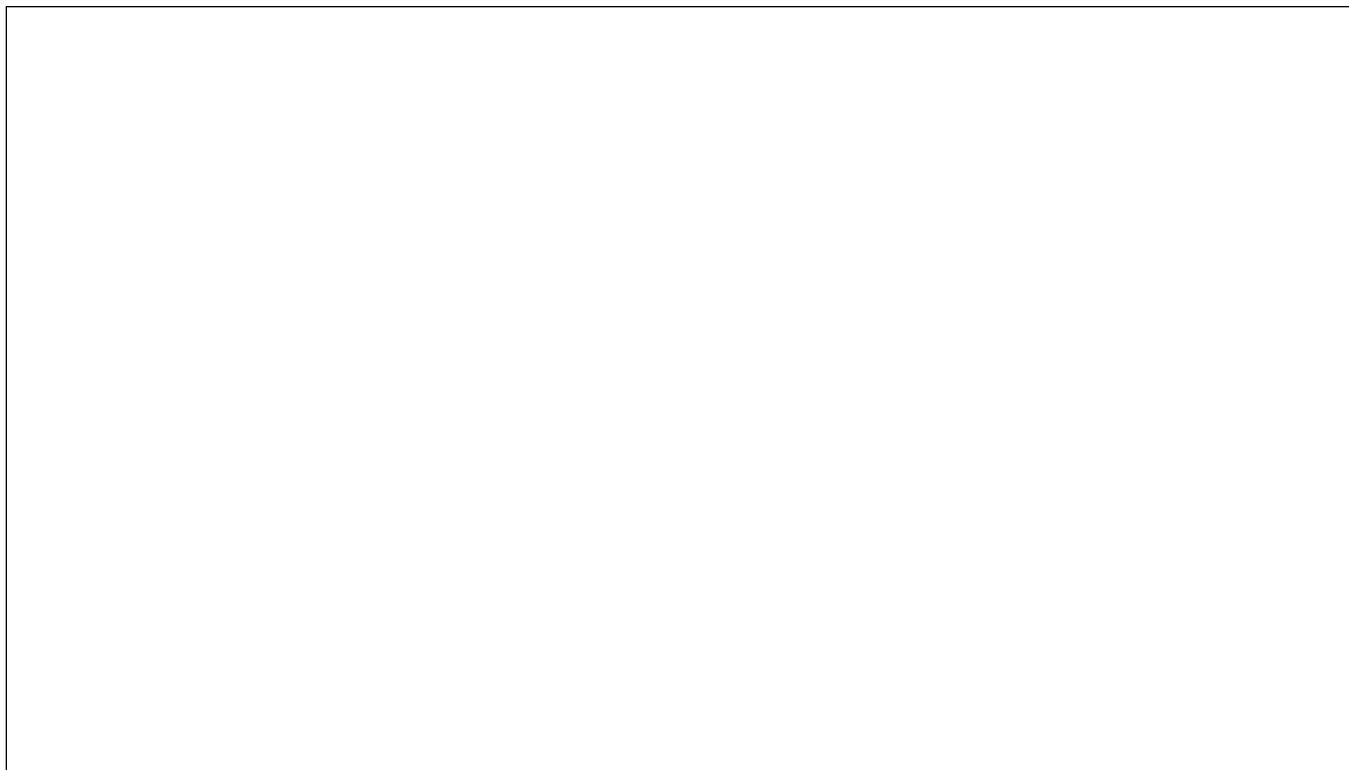| ICP Conditions	
RF Generator Power	1.0 kW
Frequency of RF generator	40.68 MHz
Outer Gas Flow Rate	8.5 L/min
Auxiliary Gas Flow Rate	1.0 L/min
Observation Height	15 mm
Ultrasonic Nebulizer Conditions	
Heater Temperature	140°C
Condenser Temperature	4ºC
Carrier Gas Flow Rate	1 L/min

Fig. 1. Schematic diagram of the instrumental setup. S: Sample (flow rate: 10 mL/min); R: reagent (flow rate: 5.0 mL/min); E: eluent (flow rate: 1.5 mL/min); A: Ar (flow rate: 0.7 L/min); W: waste; P1, P2: peristaltic pumps; C: minicolumn packed with activated carbon; V: injection valve. Valve positions: (a) sample loading; (b) injection.

All glassware and plasticware used was previously washed with a 10% (v/v) HNO_3/water solution and then with ultrapure water.

Preconcentration Step

A 25-mL sample (buffered at pH 3.0) and the complexing reagent (potassium thiocyanate 1×10^{-4} mol/L) at 10.0 and 5.0 mL/min loading flow rates, respectively, were mixed on-line to form the metal complex. Palladium was retained by chemical sorption as the palladium-thiocyanate complex on the minicolumn packed with activated carbon and the remaining solution was discharged; valve V in load position (a) (Figure 1). Finally, the peristaltic pump was stopped, the injection valve V switched to the injection position (b), and the retained complex eluted with 5% (w/v) thiourea at a flow rate of 1.5 mL/min directly into the ultrasonic

nebulizer and ICP-OES. The operating conditions were established and the determination was carried out.

Method Validation

A certified reference material of natural water with a certified value for Pd does not exist. However, using the method of standard addition, it is considered a validation method (35). In order to demonstrate the validity of this method, 125 mL of tap water was collected and divided into 5 portions of 25 mL each. Then, increasing quantities of palladium were added to the sample aliquots and palladium was determined by means of the preconcentration method (Table II).

RESULTS AND DISCUSSION

Sample Loading Variables

In order to optimize the sorption conditions for the retention of the

TABLE II
Recovery Study (Tap Water)

Aliquots	Quantity of Pd Added (ng/L)	Found (ng/L)	Recovery (%)
1	100.0	98.0	98.0
2	150.0	149.3	99.5
3	200.0	201.4	100.7
4	250.0	247.5	99.0
5	500.0	500.5	100.1

metal complexes, the palladium signal was monitored by measuring with USN-ICP-OES while changing the pH of the solution that passes through the minicolumn. The procedure was similar to the Preconcentration step section, the optimum pH values were in the 2.5–4.0 range at the 500-ng/L Pd level (Figure 2). This phenomenon

the throughput was about 20 samples per hour. A sensitive enhancement factor of 375-fold was obtained with respect to ICP-OES using pneumatic nebulization (15 for USN and 25 for preconcentration).

The precision for 10 replicate determinations at the 500-ng/L Pd level was 2.9% relative standard deviation (RSD) calculated from the peak heights obtained. The calibration graph was linear with a correlation coefficient of 0.9995 up to at least 100 μg/L. The detection limit (DL) was calculated as the concentration of palladium required to yield a net peak that was equal to three times the standard deviation of the blank signal (3σ). The value of the detection limit obtained for the preconcentration of 25 mL of sample solution was 10 ng/L.

Application to Tap Water Samples

Finally, the results of the method applied to the determination of palladium in spiked tap water samples are shown in Table II. The recovery of palladium ranged between 98.0 and 100.7 %.

CONCLUSION

The methodology described above was successfully applied to the determination of palladium in spiked water samples. The developed manifold permitted high sample flow rates in order to achieve good sensitivity. This method proved to be rapid, reliable, and flexible with limited interference. The high enhancement factor (375-fold) obtained is a great advantage of this procedure in comparison to the many methods existing for palladium preconcentration.

TABLE III
Performance of the FI-On-Line Activated Carbon Sorption Preconcentration-USN-ICP-OES System Determination of Pd Under Optimized Conditions

Correlation Coefficient	0.9995
Working Range	0.01–100 μg/L
Sampling Frequency (f)	20 h^{-1}
Precision (at 500-ng/L Pd level)	2.9 %RSD, n=10
Detection Limit (3σ)	10 ng/L
Enhancement Factor	375

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is understandable since better complexation occurs within this range. Based on these results, the final pH selected was 3.0.

The sample flow rate through the minicolumn packed with activated carbon is a very important parameter, since this is one of the steps that controls the analysis time. The influence of the sample loading rate on the analytical response obtained was studied between 1.0–15.0 mL/min. We could verify that the optimum sample loading flow rate was achieved at 10.0 mL/min, which, under optimum conditions, allowed us to reach an enhancement factor of 375-fold. At higher flow rates than 10.0 mL/min, the response decreased as is shown in Figure 3.

As regards the response variation with the molar concentration of the reagent potassium thiocyanate, the signal remained constant between 10^{-5} mol/L and 10^{-3} mol/L. A 1×10^{-4} mol/L potassium thiocyanate concentration was adopted for further experiments. The optimum load rate adopted was 5.0 mL/min.

Optimization of Elution Conditions

Thiourea has been successfully used to elute Pd, Pt, and Au from exchange resins and other types of sorbents (13–15,20,30). Thiourea also turned out to be a good eluent for the palladium-thiocyanate complex. Various concentrations of thiourea, thiourea + HCl, were used as the eluents. The results showed that Pd was quantitatively desorbed with 5% (w/v) thiourea solution prepared in 0.2 mol/L HCl. The effect of the flow rate of the eluent was studied and the best ICP-OES signal was achieved at 1.5 mL/min.

Interferences

The effects of potentially interfering species (at the concentration levels at which they may occur in the sample concerned) were tested under the optimum preconcentration conditions. Thus Cu^{2+}, Zn^{2+}, Co^{2+}, Cd^{2+}, Ni^{2+}, Mn^2, and Fe^{3+} could be tolerated up to at least 2500 µg/L.

Analytical Performance

Under the optimum conditions described above, the performance data obtained for the on-line minicolumn preconcentration-USN-ICP-OES system for palladium determination are summarized in Table III. The overall time required for the preconcentration of 25 mL of sample (2.5 minutes, at a flow rate of 10 mL/min), conditioning (~0.3 minutes) and elution (~0.2 minutes, at a flow rate of 1.5 mL/min) was about 3.0 minutes;
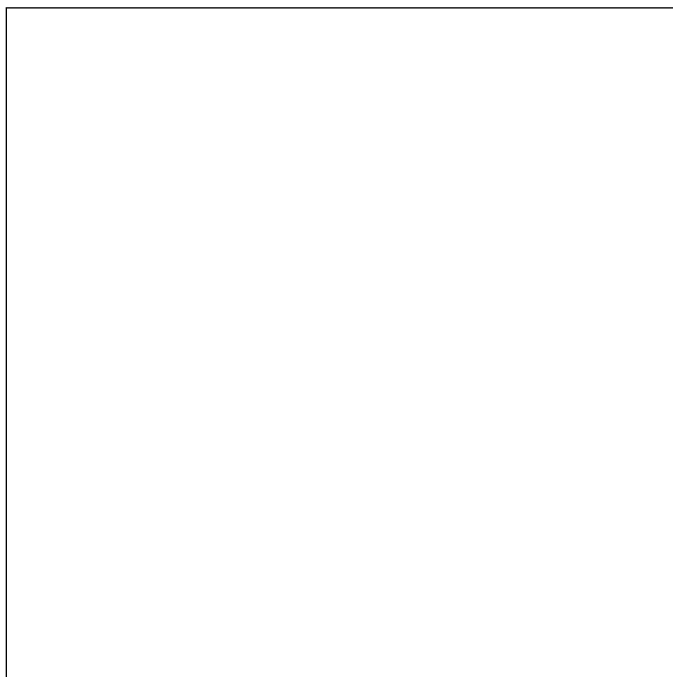
Fig. 2. Dependence of Pd preconcentration with pH of loading solutions. Sample loading volume 25 mL; loaded flow rate was 10.0 mL/min; the elution flow rate was 1.5 mL/min; Pd concentration was 500 ng/L.
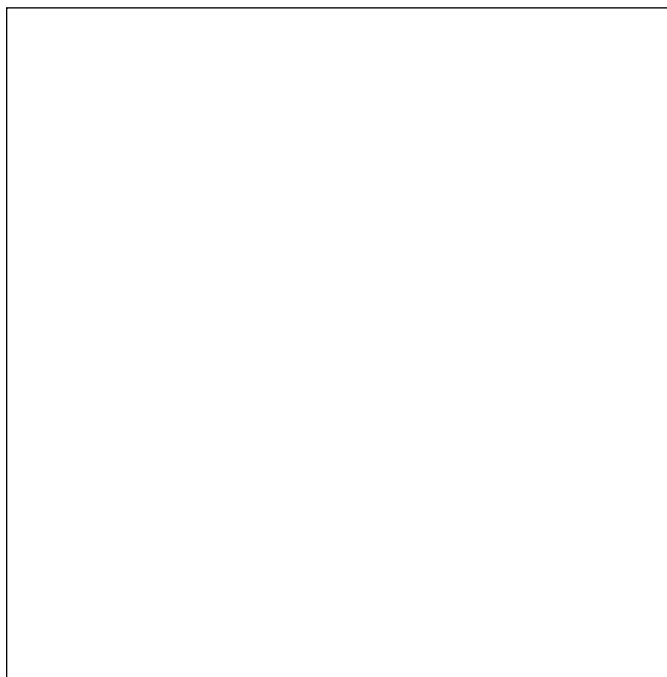
Fig. 3. Dependence of metal recovery with loading flow rate. Sample loading volume was 25 mL; the elution flow rate was 1.5 mL/min; Pd concentration was 500 ng/L.