

Cloud Point Extraction of Palladium as Chelate with 1-(2-pyridylazo)-2-naphthol Using Triton X-114 Prior to Determination in Real Samples by ETAAS

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Abstract

A pre-concentration and determination methodology for palladium in real samples at ultra-trace levels by 1-(2-pyridylazo)-2-naphthol (PAN) was developed. The analyte in the initial aqueous solution, acidified with HCl, was complexed with PAN and Triton X-114 was added as a surfactant. The surfactant-rich phase was diluted with concentrated HNO₃ (65%, w/w) after phase separation. Then, the concentrations of analyte were determined by graphite furnace atomic absorption spectrometry (GF-AAS). The variables affecting the complexation and extraction steps were optimized. Under the optimum conditions, namely a pH of 4.5, a cloud point temperature of 55 °C, the concentration of PAN of 1.2×10^{-4} mol l⁻¹, 0.1% (W/V) Triton X-114, a sample volume of 1.0 ml, (centrifuged at 3500 rpm) an enhancement factor of 26-fold was reached. Triton X-114 allowed the detection limit of 0.01 ng ml⁻¹ of Pd. The precision measured as relative standard deviation (R.S.D.) for 10 replicate determinations at 10.0 μg l⁻¹ Pd was 2.5%. Analytical graphs were rectilinear in the concentration range of 3-200 μg l⁻¹ and relative standard deviations were lower than 5%. The method affords recoveries in the range of 97 to 101%. The method was successfully applied for the determination of Pd in dust, drinking water, and rainwater samples.

Key words: Cloud Point Extraction, Graphite Furnace Atomic Absorption Spectrometry, Pd, 1-(2-pyridylazo)-2-naphthol, Triton X-114

Introduction

Palladium is used in jewelry, dentistry applications and fine instruments such as watches and some surgical tools, for electrical contacts, and for the purification of hydrogen gas [1]. The accumulation of Pd has already been detected in road dust [2-4] and airborne particulate matters. The effect of environmental concentrations of Pd on human beings is still unknown, but hypersensitivity and allergic reactions have been observed in susceptible individuals following chronic occupational exposures [5], car exhaust fumes [6], and urban water [7], and it correlates with traffic density and distance from the road. Thus, the determination of this pollutant in environmental matrices is of considerable importance for human exposure assessment and for the investigation of its correlations with health effects. However, the direct determination by all these techniques is restricted owing to the interferences caused by environmental sample matrices and usually a preliminary separation and/or enrichment step is required. In recent years, some authors have presented

the inductively coupled plasma mass spectrometry (ICP-MS) methods that enable interference-free or almost interference-free direct determination of noble metals in environmental samples. However, they have not been verified in the common use yet [8-16]. Although in the literature, many graphite furnace atomic absorption spectrometry (GF-AAS) methods for the determination of a group or individual noble metals in various types of samples may be found, their determination at low trace concentration levels in such difficult matrices as environmental samples causes still many problems [17]. In the determination of trace or ultra-trace amounts of Pd in environmental and pharmaceutical samples, because of their very complex sample matrices, a preconcentration/separation procedure is required even when relying on the high sensitivity and selectivity of modern instrumental techniques, such as electrothermal atomic absorption spectrometry (ETAAS) [5], inductively coupled plasma atomic emission spectrometry (ICP-AES) [3], and ICP-MS [2,4,7,8]. Conventional off-line procedures for pre

concentration and separation, although effective, are usually tedious and time-consuming, require large quantities of sample and reagents, and are vulnerable to contamination and losses of analyte.

Flow injection techniques have played an important role in the automation, acceleration, and miniaturization of solution handling in sample pretreatment. Several on-line preconcentration and separation methods, such as ion exchange [2] and sorption [4, 8] have been adopted for the flow injection analysis of palladium. Solid phase extraction based on ion-exchange properties of platinum metal ions or formation of chelate complexes is a very effective preconcentration method in combination with atomic absorption spectrometry [18-20].

The use of micellar solution in different areas of analytical chemistry has attracted much attention in recent years and separations based on cloud point extractions (CPE) are becoming an important and practical application in the use of surfactants in analytical chemistry [21-23]. The present study, describes a CPE method for separation and preconcentration of Pd using PAN as a ligand, HNO₃ (65%, w/w) as a diluting solvent, and Triton X-114 as a nonionic surfactant, prior to its (ETAAS) determination. Although PAN forms a very strong and stable complex with palladium, it has not been yet used for the cloud point extraction of palladium. The proposed method was optimized for Pd determination in water samples and road dusts in ppb levels.

Experimental

Apparatus

A Shimadzu, model 6300 pc/Zeman atomic absorption spectrometer equipped with a GFA-4A graphite furnace atomizer, an AS-60 furnace auto sampler and a circulating cooling unit were used for the determination of palladium in the surfactant-rich phase and Zeeman background correction was employed to correct for the non-specific absorbance. A palladium hollow cathode lamp (Shimadzu, wavelength of 247.6 nm) was used as the radiation source. Pyrolytically coated graphite tubes were used throughout. Argon 99.999% (Roham gas Co., Tehran, Iran), with a flow rate of 1.5 l min⁻¹, was used as a protective and purge gas, Aliquots of 20 µl for all the samples and calibration solutions were injected directly into the graphite tube by the auto sampler. Microwave digestion was performed with a domestic microwave oven (Philco, Ushuaia, Argentina) operating at a maximum power of 700 W, equipped with a magnetron of 2450 MHz and milestone hermetically sealed 100 ml internal volume, 1 cm wall thickness polytetrafluoroethylene (PTFE) reactors. A Metrohm 744 pH-meter furnished with a combined glass-saturated calomel electrode was used for pH measurements. A G.F.L. thermostatic bath (Soofer Company) was used to reach the cloud point temperature and phase separation was assisted using a centrifuge (Hettich, universal II) for accelerating the separation process, in 50-ml calibrated centrifuge tubes.

Reagents

All the reagents were of analytical reagents grade. The

nonionic surfactant Triton X-114 was obtained from E. Merck and used without further purification. The stock standard Pd solution (1000 ppm) was prepared from pure Pd (II) chloride (Merck-Schuchardt) in 0.01M hydrochloric acid (Merck). A stock solution (1.2 × 10⁻² M) of PAN (Fig.1), (E. Merck, Darmstadt Germany) was prepared by dissolving 0.3 g of this reagent in absolute ethanol (E. Merck, Darmstadt Germany). Working stan-

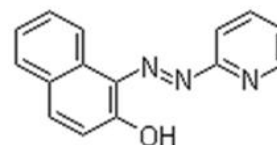


Figure1- Molecular Structure of PAN

dard solutions were obtained by appropriate dilution of the stock standard solution daily as required and all of other reagents were of analytical reagent grade. All the glassware and vessels used for trace analysis were previously washed with a 10 % (V/V) HNO₃ solution and then rinsed with ultrapure water. Ultrapure water was used throughout the work.

General Cloud Point Preconcentration Procedure

For the cloud point extraction, 0.5 ml of Triton X-114 surfactant solution (0.1% V/V) and 1 ml of PAN chelating solution (1.2 × 10⁻² M) were added to a 1.0 ml aliquots of the sample solutions. After the addition of buffer solution (acetate buffer, pH 4.5), the mixture was diluted up to 50 ml with ultrapure water (the Pd content of this solution should be in the range of 3 to 200 µg l⁻¹), and then the mixture was heated in a thermostated bath to 55 °C for 5 min (well above cloud point temperature of the system, 25 °C). Centrifuging at 3500 rpm for 5 min accelerates the separation of the two phases. The supernatant aqueous phase was then separated with the aid of a syringe after cooling in ice-acetone mixture (5 min.), and as a result the surfactant rich phase became viscous; then, it was diluted with concentrated HNO₃ (65%, w/w) and the resultant solution was introduced into the GF-AAS.

Dust Sample

Road dust samples were taken from Tehran-Qom road and Tabriz-Tehran road (Iran), using a small brush and a plastic pan. The samples were dried in an oven at 100 °C for 24 hr; sieving of the material was not required. 0.2 g of the dust (road dust) sample was weighed in a PTFE vessel. 3 ml of aqua regia were added. The mixture was heated almost to dryness. After the addition of 3 ml aqua regia and 1 ml of 40% HF, the mixture was heated again for 2 hr. Then, 2 ml of 65% HNO₃ were added, and the mixture was heated to dryness. The last step was repeated twice to ensure the total elimination of HF. The residue was diluted to 50 ml with MQ water. The digest was centrifuged for 20 min at 3000 rpm in order to sepa

rate the solid residue. The sample acidity was adjusted to pH 4.5 with acetate buffer. A blank solution characterizing the procedure was prepared in the same way.

Water Samples

Drinking and rainwater were filtered using a 0.45- μm pore size membrane filter to remove suspended particulate matter and homogenates, then adjusted to approximately pH 4 by adding concentrated HCl, and finally stored in a refrigerator in the dark. Two aliquots of water samples (25 ml), 0.4 ml of 0.1 M KF, 0.5 ml of 0.2 M EDTA, and sodium citrate solution were added before making up the volume to 50 ml in order to remove possible interferences. The final solution was then subjected to the CPE methodology.

Results and Discussion

Study of the ETAAS Conditions

In the present work, the selection of an appropriate pyrolysis temperature is very important for removing as much the matrix as possible and preventing the pyrolysis loss of the analytes prior to atomization. However, when the pyrolysis temperature was over 1200 °C, the signal of analyte decreased rapidly by increasing the pyrolysis temperature. Therefore, 1100 °C was selected as the optimized pyrolysis temperature for the determination of palladium. At the selected pyrolysis temperature of 1100 °C, the effect of pyrolysis time on the absorbance of palladium was investigated. The results showed that the absorbance was increased when the pyrolysis time was changing from 10 to 35 s and no appreciable improvements were observed for longer times. As a result, a pyrolysis time of 35 s was chosen. The effect of the atomization temperature, in the range of 2000–3000 °C, on the analytical signal of palladium was also studied. The maximum signal was obtained at about 2300 °C and remained unchanged with a further increase in temperature up to 2700 °C. Hence, the atomization temperature of 2400 °C was selected for further experiments. The experimental results show that atomization time has a little effect on the atomic signal of palladium. Therefore, an atomization time of 5 s was selected. The unusual low pyrolysis and atomization temperatures used in this work is probably due to the fact that the components used in the CPE procedure are reducing the thermal stability of Pd. The graphite furnace temperature/time program used for Pd determination is summarized in Table 1.

Table 1- Furnace temperature program for Pd determination

Step	T (°C)	Ramp (s)	Hold (s)
Dry	90	12	25
Pyrolysis	1100	15	35
Atomization	2400	0	5
Cleaning	2600	1	6

Effect of pH on the Extraction Recovery

Cloud point extraction of Pd was performed using the pH range of 1 to 8 adjusted with appropriate buffer solutions. It was found that the signal reached a maximum at

pH values greater than 4. Hence, a pH of 4.5 was taken as the optimum solution pH and was adjusted with acetate buffer (a pH of 4.5 and 0.01M).

Effect of PAN Concentration

The extraction recovery of palladium as a function of PAN concentration was investigated. For this study, a 50 ml solution containing PAN in the range of 0.9×10^{-4} to 6×10^{-4} M in the presence of $10 \mu\text{g l}^{-1}$ Pd and 0.1% (V/V) Triton X-114 was subjected to the cloud point preconcentration. The results indicated that the signal increases up to a PAN concentration of 2.4×10^{-4} M and reaches the plateau afterwards, which is considered as the 100% extraction. Thus, the PAN concentration of 2.4×10^{-4} M was employed throughout the work.

Effect of Triton X-114 Concentration

The variation of the percentage of extraction (calculated as percent ratio of the mass of Pd in the extract to the mass of Pd present in the standard solution) versus the surfactant concentration was examined within the range of 0.05 to 1.0 % (V/V). Extractions close to 100% were observed for a surfactant concentration higher than 0.1% (V/V). In order to achieve a good enrichment factor, 0.1% (V/V) was chosen as an optimal value of surfactant concentration.

Cloud Point Temperature

The enrichment factor of CPE is affected by equilibration time and temperature. The preliminary extractions indicated that the Pd and PAN complexation reaction completed within 5 min at 55 °C. Hence, a reaction time of 5 min and the temperature of 55 °C were taken as the optimum conditions.

Calibration, Accuracy, and Precision

A linear calibration graph with regression coefficient of 0.999 was obtained for the concentrations of 3 to 200 $\mu\text{g l}^{-1}$. The relative standard deviation for the determination of $10 \mu\text{g l}^{-1}$ Pd was 2.5% (for 10 replicate determinations). The limit of detection (blank signal plus three times the standard deviation of blank) was 0.01 ng ml^{-1} .

Interferences

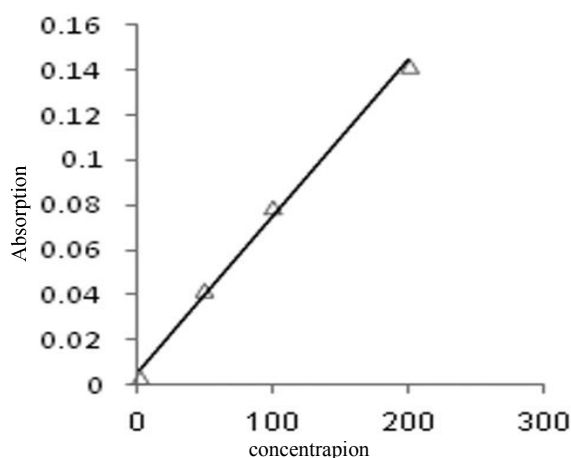
For the study of the interferences, the effect of interfering ions on the absorbance of a solution containing $10 \mu\text{g l}^{-1}$ of analyte was studied at different concentration ratios. The tolerance limits of the indicated ions are the limits that do not affect the analyte signal by more than 5%. Among the ions tested, Cl^- , NO_3^- , CO_3^{2-} , N_a^+ , K^+ , PO_4^{3-} , F^- , Mg^{2+} , CH_3CO_2^- , $\text{C}_2\text{O}_4^{2-}$, $\text{C}_{10}\text{H}_{14}\text{O}_8^{2-}$, SO_4^{2-} , SCN^- , Ir (III), Pt (IV), Au (III), and Rh (III) did not interfere even at concentrations 1500 times higher than that of the analyte. However, as shown in Table 2, Fe (III), Fe (II), and Co (II) proved to interfere at concentrations 25 times higher than the analyte concentrations. The interferences of Fe (III) and Co (II) were completely avoided by KF (8×10^{-4} M) and EDTA (0.002 M) respectively.

Characteristics of the Method

Under the optimum experimental conditions, the calibration curve for palladium was linear in the range of 3 to 200 $\mu\text{g l}^{-1}$ (Fig. 2).

Table 2- Tolerance limits of interfering ions in the determination of 10 µg l⁻¹ of Pd (II)

<i>Tested ions</i>	<i>Tolerance limit</i> (Ratio of interference concentration to Pd)
[Cl ⁻ , NO ₃ ⁻ , CO ₃ ²⁻ , Na ⁺ , K ⁺ , PO ₄ ³⁻ , F ⁻ , Mg ²⁺ , CH ₃ CO ₂ ⁻ , C ₂ O ₄ ²⁻ , C ₁₀ H ₁₄ O ₈ ²⁻ , SO ₄ ²⁻ , SCN ⁻ , Ir (III), Pt (IV), Au (III), Rh (III)]	<1500 <150
Ag (I), Cr (III)	
Ni (II)	<200
Hg (II), AL (III), Cd (II)	<200
Cu (II)	<100
Fe (III), Fe (II), Co (II)	<25

**Figure 2-** Calibration curve of palladium (3-200 µg l⁻¹)

The phase volume ratio (V_s/V_w the ratio of the volume of the surfactant rich phase to that of the aqueous phase) was 0.02.; the limit of detection was also sufficiently low.

Determination of Palladium in Dust, Drinking Water, and Rainwater Samples

In order to confirm the reliability of proposed method, the method was applied to the determination of Pd in several spiked water and dust samples after digestion. For this purpose, 0.5 ml of spiked sample solutions were preconcentrated with 0.1% Triton X-114 and a PAN concentration of 2.4×10^{-4} M. The results are shown in Table 3. As can be seen, the results of three analysis of each

sample show that the Pd recovery is successful.

Conclusion

Cloud point extraction was used for the preconcentration of Pd as a prior step to its determination by GF-AAS. The method allows the determination of Pd at ppb levels by GF-AAS. The method is selective, leads to an effective separation, and constitutes an inexpensive alternative to other preconcentration methods. The method gives a low limit of detection. Table 4 also compares present method with reported methods for the preconcentration and CPE of palladium [31].

Table 3- Results of Pd determination in dust samples after digestion (95% confidence level; n=6)

Sample	Content (µg l ⁻¹)	Added (µg l ⁻¹)	Found (µg l ⁻¹)	Recovery (%)
Qom-Tehran road	<DL*	0.25	0.23 ± 0.02	92
		0.30	0.29 ± 0.02	97
Tabriz-Tehran road	<DL	0.25	0.24 ± 0.02	96
		0.30	0.28 ± 0.03	93
Drinking water	<DL	0.25	0.24 ± 0.02	97
		0.30	0.29 ± 0.02	97
Rainwater	<DL	0.25	0.25 ± 0.02	100
		0.30	0.29 ± 0.03	97

Table 4- Comparison of the present method with reported methods for the preconcentration and CPE of palladium

Reagents	surfactant	Technique	Detection limit	Rference
1-(2-Thiazolylazo)-2-naphthol	TritonX-114	FAAS	0.24 ng ml ⁻¹	[24]
1-(2-Pyridylazo)-2-naphthol	TritonX-114	FAAS	0.38 ng ml ⁻¹	[25]
1-Nitroso-2-naphthol	PONPE 7.5	FAAS	1.22ngml ⁻¹	[26]
N-Benzoyl-N-phenyl hydroxylamine	TritonX-114	FAAS	2.08 ng ml ⁻¹	[27]
1-Phenyl-3-methyl-4-benzoyl-5-pyrazolone	TritonX-100	FAAS	0.64 ng ml ⁻¹	[28]
4-(2-Naphthalenyl)thiozol-2yl azo chromotropic acid	TritonX-114	FAAS	0.067 ng ml ⁻¹	[29]
Ammonium pyrroline dithiocarbamate	TritonX-114	GFAAS	0.1ngml ⁻¹	[30]
2-(5-Bromo-2-pyridylazo-5(diethylamino)-phenol)	TritonX-114	GFAAS	0.08ngml ⁻¹	[31]
8-Hydroxyquinoline	TritonX-114	GFAAS	0.012 ng ml ⁻¹	[32]
1-(2-Pyridylazo)-2-naphthol	TritonX-114	GFAAS	0.01 ng ml ⁻¹	present work

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