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Rapid Palladium Preconcentration and Spectrophotometric Determination in Water and Soil Samples

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Cloud Point Extraction (CPE) is an economic, rapid, and environmentally friendly method. It was performed by preconcentration samples (water and soil) that contained palladium. An ion-pair association complex was formed when the chromogenic reagent 2-(4-hydroxy phenyl azo)-4-benzene naphthol (HPBN) reacted with palladium in HCl media. It was then extracted into a surfactant (Triton X-114) rich phase. After diluting the cloud point layer with acidic methanol, the concentration of enriched samples was determined by UV-Vis spectroscopy. The effects of Triton X-114 and HCl concentrations, heating time, temperature, centrifuge rate, incubation duration, and interferences on cloud point extraction were analyzed and improved. The short extraction time (8 min) is an advantage of this method. The limit of detection (LOD) and the limit of quantification (LOQ) are low (0.10 and 0.30 $\mu\text{g l}^{-1}$, respectively). The enrichment factor (EF) and preconcentration factor (PF) are calculated to be 40 and 100, respectively. The precision for the approach was determined to be (RSD 1.10%, n = 6). For collected samples, the FAAS was used to assess the accuracy of the modified preconcentration technique. The method can be used to detect palladium in natural samples, with relative recovery values ranging from 93 to 109% for various concentrations, demonstrating its accuracy.

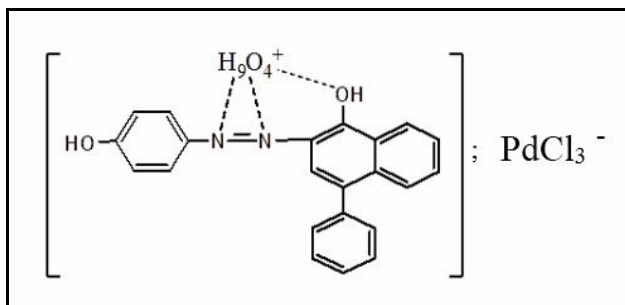
Keywords: Cloud point extraction, Palladium, Preconcentration method, Liquid ion exchange

INTRODUCTION

Palladium's importance has grown in recent years, as additional applications for dentistry, medical equipment, jewels, and automobile catalytic converters have developed [1]. Despite the obvious benefits of automobile catalysts, palladium emissions into the environment are tied to the fabrication and recovery of emissions controls in the manufacturing industries and the functioning of car catalysts. Palladium ions are associated with asthma, rhino conjunctivitis, allergies, and other medical disorders in humans [2]. As a result, developing analytical methods for determining palladium is critical for the effective detection

of low concentrations. Inductively coupled plasma emission spectrometry (ICP-OES) is the most widely utilized methodology for detecting palladium and trace elements in environmental analysis. Also, the researchers used electrothermal atomic absorption spectrometry (EAAS), spectrophotometry, co-precipitation, and flame atomic absorption spectrometry (FAAS) [3-6]. However, the direct determination of palladium is currently not possible due to a lack of accuracy and selectivity. A preconcentration step is usually needed before the determination step. In this regard, several preconcentration procedures to determine palladium have been developed, like solidified floating organic drop micro extraction (SFODME), dispersed liquid-liquid micro extraction (DLLE) [7-9], and micellar extraction [10-15]. Because of its high extraction efficiency and

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Scheme 1. Suggested structure of extracted ion-pair association complex

preconcentration factor, the CPE method has become a prominent alternative methodology in recent years. CPE uses water instead of expensive, toxic, and dangerous solvents since the volume of a surfactant-rich layer is around 10-100 times smaller than the size of an aqueous layer [16,17]. Compared to solvent extraction, it allows for a substantially larger concentration of solute to be extracted [18,19]. The cloud point extraction method is related to the fact that when the sample temperature is changed, the aqueous solution of surfactants displays clouding behavior. The optimal temperature, also known as the "cloud point," is determined by the surfactant's amphiphilic type and concentration [20-22]. The hydrophobic layer and an aqueous layer form when the temperature rises above the cloud point. Temperature increases micellar volume while dehydrating the hydrated exterior cloud point layers [23-25]. The Cloud Point Extraction was developed to extract tiny quantities of palladium in a short time (8 min) from water and soil samples with the addition of HCl to make a liquid ion exchanger. An organic reagent (HPBN) was synthesized depending on the method reported in the literature [26]. Triton X-114 was used as a non-ionic surfactant in this method. The suggested structure of the ion-pair association shows a (1:1) palladium ion and ligand using slope analysis and slope ratio methods. Scheme 1 explains the structure of the extracted species.

EXPERIMENTAL

Instrumentations

The Biochrom spectrophotometer (UV-Vis) was made

in the United Kingdom (Biochrom Libra560). The samples were centrifuged by a centrifuge (Hettich, EBA 20). A water bath (Hamburg-90) from the United Kingdom measures the temperature. A D₂ background corrector and a flame burner were installed on a Varian AA 240 FS FAAS (Varian, Australia). For all spectral analysis, a 10 cm long slot-burner head, a hollow cathode lamp, and an air-acetylene flame were utilized. The FAAS wavelength was 247.6 nm.

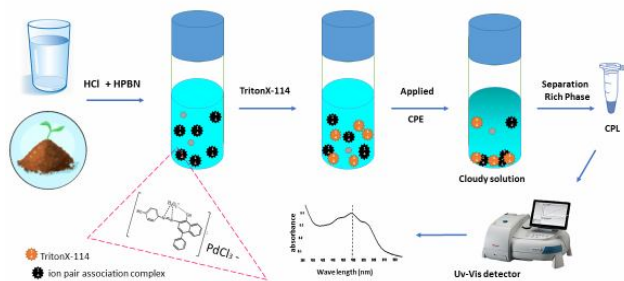
Chemicals and Solutions

Fluka (Bunch., Switzerland) or Sigma-Aldrich (St. Louis, Missouri) provided all of the chemicals applied in this research. All of the tests were carried out using ultra-pure deionized water. The water was purified using a Milli-Q system (Millipore, Bedford, Massachusetts). For one day, the glassware was immersed in an acidic solution (10% HNO₃). Deionized water is used to clean the glassware, which is subsequently dried in the atmosphere. Triton X-114 (1.0% v/v) was used without any purification.

The palladium standard stock solution (1000 mg l⁻¹) was provided by dissolving the required weight of pure PdCl₂ in 1.0 ml of HCl. A suitable dilution of stock solutions creates operating solutions. Potassium iodide KI solution at a 20% concentration was created by dissolving 20 g in 100 ml of distilled water. A stock solution (1 × 10⁻² M) of organic reagents, HPBN, was made by dissolving a sufficient quantity of the reagent in an amount of water with drops of Triton X-114 and bringing the total volume to 100 ml. The required dilution applies to produce a workable solution.

Applied Procedure

The sample solution (25 ml) containing Pd(II), 0.8 M HCl, 1 × 10⁻⁴ M HPBN, and 0.6 ml of (1.0% v/v) Triton X-114 were added, and deionized water was added to the line of the 50 ml centrifuge tube. At a 40 °C cloud point temperature, the solution could stand for around 8.0 min in a water bath. The mixture was centrifuged for 12 min at 4000 rpm and then refrigerated for 4 min in the freezer. The viscosity of the hydrophobic layer increased as it cooled. By inverting the tube, the supernatant is decanted. Then, the cloud point layer (0.5 ml) dissolves in 5 ml of an acidic methanol solution containing nitric acid (1.0 M). A palladium concentration in the cloud point layer (CPL) was



Scheme 2. Applied method for separation and determination of palladium in water and soil samples

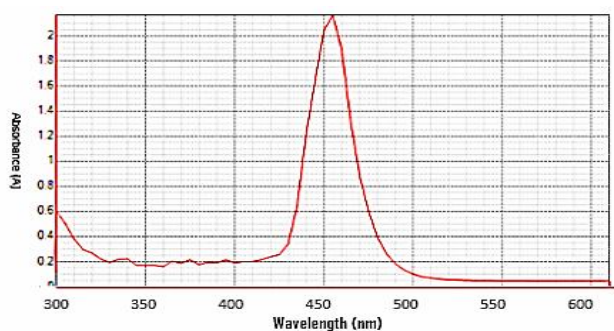
calculated using UV-Vis spectroscopy at $\lambda_{\max} = 455$.

Scheme 2 shows the applied procedure for recovering palladium. The recovery rate (R%) was calculated by using Eq. (1). In which C_m denotes the palladium content of a spiked test, C_0 denotes the test's metal value, and m denotes the palladium content spiked.

$$R\% = \{(C_m - C_0)/m\} \times 100 \quad (1)$$

RESULTS AND DISCUSSION

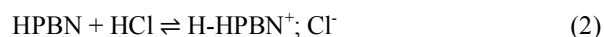
Analytical parameters such as chemical concentrations, heating time, temperature, and interfering effects are controlled using the cloud point extraction process for palladium solutions. Spectrometric studies involved the extraction of Pd(II) ions according to the procedure detailed in the general method. The spectrum for dissolved CPL appeared to have the maximum absorbance at $\lambda_{\max} = 455$ nm. The results were as in Scheme 3.



Scheme 3. UV-Vis spectrum for extracted palladium via CPE.

The Effect of HCl Concentration

The concentration of HCl is critical in the production of the liquid ion-pair association complex ($H\text{-HPBN}^+$; Cl^-) with organic agent and the palladium chloride complex ($PdCl_3^-$). So, the effect of HCl on the applied procedure was examined by varying the HCl concentrations from 0.1 to 1.5 M. The results are as illustrated in Fig. 1 and Eqs. ((1)-(3)). The results demonstrate that 0.8 M HCl was the best concentration, providing improved extraction efficiency and a higher quantity of ion-pair association for palladium creation by reaching the appropriate thermodynamic equilibrium to create the ion-pair complex with good selectivity [26]. As a result, 0.8 M HCl was used in the following studies.



The Effect of Surfactant Volumes

The effect of Triton X-114 volume on applied CPE efficiency for preconcentration and separation of palladium was investigated within the Triton X-114 volume range of 0.1-1.5 ml (1.0% v/v). The high-density cloud point layer and low cloud point temperature of Triton X-114 enhance phase separation *via* centrifugation. The results are presented in Fig. 2. By turning up the volume of Triton X-114 to 0.6 ml, the extraction efficiency improves. After that,

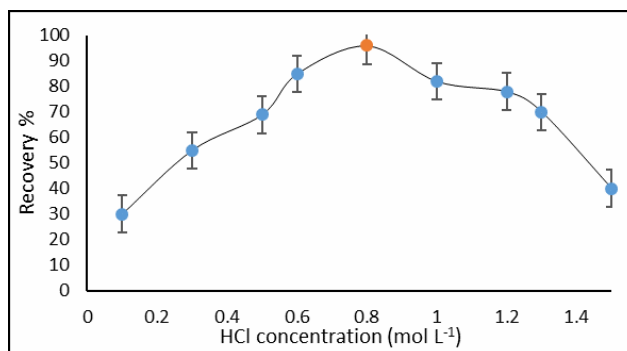


Fig. 1. The effect of HCl concentration on the CPE recovery of palladium ions.

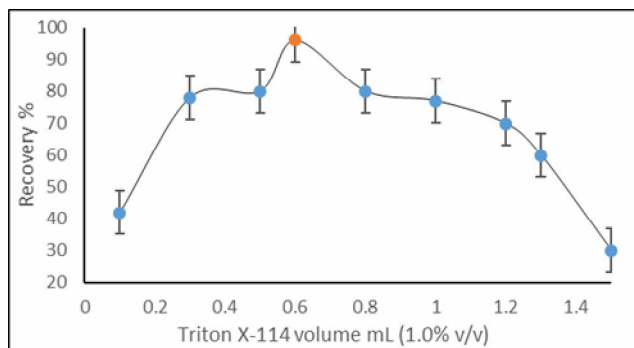


Fig. 2. Triton X-114 volume effect on CPE recovery of palladium ions.

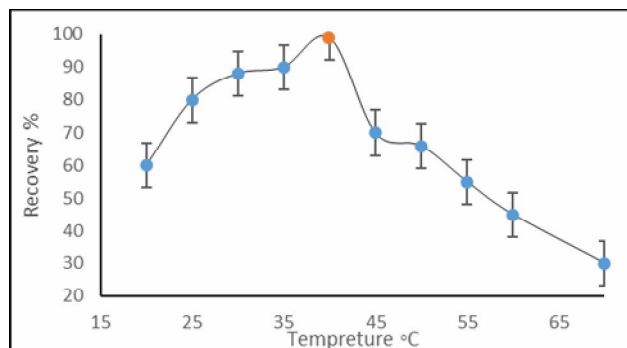


Fig. 4. Effect the temperature on CPE of recovery palladium ions.

the surfactant quantities above the optimum result in a significant reduction in extraction efficiency. For the other studies, a volume of 0.6 ml of Triton X-114 was chosen to produce the maximum extraction efficiency.

The Effect of Heating Time and Temperature

The optimum heating time and temperature are optimized in CPE procedures to generate an efficient and fast cloud point layer. The effects of heating time and temperature were investigated in the 2.0-24 min and 20-70 °C ranges, respectively. The results revealed that a heating time of 8 min and an equilibria temperature of 40 °C would yield the best extraction efficiency. The optimal time for perfect separation was determined to be 10 min at 4000 rpm in a centrifuge [48]. Figures 3 and 4 show the final results.

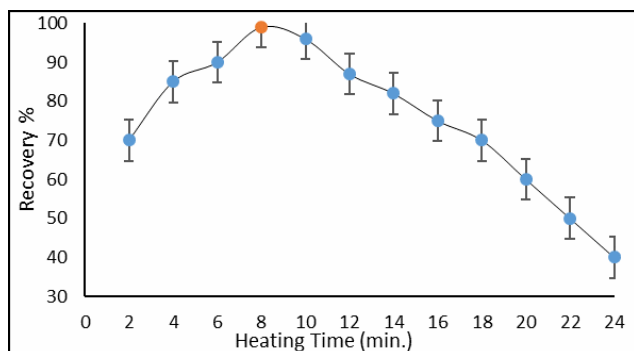


Fig. 3. Effect heating time on CPE recovery of palladium ions.

The Interference Effect

Matrix influences are a significant issue in determining metals in biological samples [26,32]. Palladium is extracted in the presence of metal cations (0.01 M) by using the CPE method. The limit values for a total error of $\leq \pm 5.0\%$ were calculated. Each test was carried out six times, and the average findings are shown in Table 1. As can be seen, the presence of transition metals did not affect the extraction process of palladium ions. As a result, palladium ions can be detected in biological samples (water, blood, and urine) using the CPE methodology [48].

Table 1. Effects of Interferences on the CPE Recovery of Palladium ions

Ions	Interferences effective	
	Added as	Recovery% \pm SD
Ag(I)	AgCl	93.0 \pm 4.0
Cd(II)	CdCl ₂	89.0 \pm 1.0
Fe(III)	FeCl ₃	97.0 \pm 4.0
Hg(II)	HgCl ₂	94.0 \pm 5.0
Ni(II)	NiCl ₂	93.0 \pm 7.0
Pb(II)	PbCl ₂	90.0 \pm 2.0
Pt(II)	PtCl ₂	89.0 \pm 7.0
Zn(II)	ZnCl ₂	95.0 \pm 1.0
Without	-	99.0 \pm 1.1

Comparison of the Applied CPE Procedure with Other Procedures Listed

Table 2 compares the applied CPE approach to other palladium determination methods reported in the literature [2,3,15,28-49]. The LOD obtained was better than the reporting method utilizing the CPE procedure [3,15,40,43,46,47], whereas the best LOD value reported by the CPE method in research was 0.03 ng ml⁻¹ [31]. The linearity of this proposed CPE approach was greater than that of some of the other methods described in Table 2

[3,35,38,41,42]. The proposed approach was below the RSD of previous methods reported [28-34]. The enrichment factor was excellent in the paper [31]. Also, the applied CPE procedure has good value.

Analytical Merits

The analytical merits of the enhanced approach are summarized in Table 3. The linear and practical range of the applied approach is determined to be 0.2-500 µg l⁻¹. The limit of detection (LOD) and the limit of quantification

Table 2. Comparing the Reported Methods with the CPE Method

Applied method	RSD%	LOD (a or b)	Linearity (a or b)	Detector	EF	Ref.
LL-CPE	1.85	0.30 a	1-500 a	FAAS	27.6	[28]
CPE	0.6	1.40 a	-	AAS	21.0	[36]
CPE	3.8	0.30 a	0.5-1000 a	ICP-OES	20.2	[29]
CPE	2.7	1.60 a	-	FAAS	32.0	[30]
CPE	5.0	0.03 a	0.3-60 a	LITLSS	460	[31]
CPE	1.36	0.60 a	2-240 a	UV-Vis	-	[32]
CPE	-	0.15 a	1-100 a	GFAAS	48	[38]
CPE	-	1.00 a	-	FAAS-FI	51	[39]
CPE	0.6	1.80 b	-	FAAS	17	[40]
CPE	2.7	25.0 b	57-72 b	UV-Vis	28	[41]
CPE	1.85	0.12 b	0.05-25 b	GFAAS	104	[42]
CPE	-	0.52 b	5-100 b	ICP-OES	-	[15]
DLLME	0.7	90.0 a	100-2000 a	FAAS	45.7	[33]
DLLM	1.5	1.40 a	15-7000 a	FAAS	-	[34]
DLLME	4.3	2.40 a	-	GFAAS	156	[37]
SPE	0.5-1.1	3.4 b	-	ICP-OES	-	[35]
SPE	-	10.0 b	-	ICP-OES	-	[43]
SPE	-	1.17 b	-	ICP-AES	-	[44]
SPE	-	0.13 b	500 b	FAAS	200	[2]
SPE	3.2	0.20 a	-	ICP-AES	100	[45]
SPE	-	2.80 b	5.0-500 b	FAAS	-	[46]
SPE	-	0.19 b	-	FAAS	250	[47]
SFODME	±2	0.60 a	2-400 a	FAAS	-	[49]
USAE-SFODME	±2.1	0.30 b	1.5-100 b	FI-FAAS	55	[3]
CPE	1.1	0.10 b	0.2-500 b	UV-Vis	40	This work

The a = ng ml⁻¹, b = µg l⁻¹

ICP-OES = Inductively Coupled Plasma-Optical Emission Spectrometry, LL-CPE= Ligand less Cloud Point Extraction, LITLSS = Laser-induced- thermal lens spectrometer, DLLME = Dispersive liquid-liquid microextraction, ICP-AES = inductively coupled plasma atomic emission spectrometer.

Table 3. Analytical Merits of the Applied CPE Procedure

Parameters	Analytical merits
	Values
Linearity ($\mu\text{g l}^{-1}$)	0.2-500
Regression equation	$y = 1.4 \times 10^{-3}x + 0.228$
Correlation coefficient after CPE	$R^2 = 0.9996$
Regression equation	$y = 35 \times 10^{-6}x + 0.11$
Correlation coefficient before CPE	$R^2 = 0.9991$
LOD ($\mu\text{g l}^{-1}$) (3σ , $n = 6$)	0.10
LOQ ($\mu\text{g l}^{-1}$)	0.30
RSD% ($n = 6$)	1.10
Enrichment factor	40
Preconcentration factor	100

(LOQ) are so low as to be $0.10 \mu\text{g l}^{-1}$ and $0.30 \mu\text{g l}^{-1}$. So the enrichment factor (EF) and preconcentration factor (PF) are calculated to be 40 and 100, respectively.

The detection limit has the formula $\text{LOD} = 3\text{Sb}/m$, where LOD, Sb, and m stand for detection limit, blank standard deviation, and slope of the calibration curve, respectively ($n = 6$). The relative standard deviation (RSD) and relative error for six replicate analyses carried out in solutions containing $60 \mu\text{g l}^{-1}$ of palladium, which was reported to be 1.1%, were used to determine the precision of the CPE process. The enrichment factor (EF) is based on a division of the slopes of calibration curves with and without preconcentration CPE. The preconcentration factor (PF) is calculated by the ratio between the initial aqueous sample and the final extracted surfactant-rich phase volumes.

Preparation and Analysis of Water and Soil Samples

Water samples. Several water samples were collected during March 2021 in Kufa City, Iraq. The samples are stored in polyethylene bottles. The samples were filtered in the lab using a $0.45 \mu\text{m}$ pore-size membrane filter and acidified with (1.0% v/v) HNO_3 before being maintained at $4 \text{ }^\circ\text{C}$ to collect particles in a refrigerator. In the presence of 1.0% H_2O_2 and strong nitric acid, the organic interferences in the samples oxidize. A buffer solution is used to adjust the pH to 7.0. Water samples from the understudy were then preconcentrated using the CPE method. The amounts of analytes in the samples were determined using a UV-Vis

spectrophotometer and FAAS [38-40].

The substantial recovery of varied concentrations in Table 4 indicates that the test was accurate (93-109%). As a result of the approach, palladium was recovered from water samples. The findings repeat six sample analyses on average.

Soil samples. Street sand, clay, and stone samples were taken from several locations in Baghdad, Iraq. The samples were dried at $90 \text{ }^\circ\text{C}$ for three hours, crushed, and homogenized through a 120-mesh screen. In a 100 ml beaker, three grams of each sample were weighed. To break it down, 10 ml of aqua regia was placed in a volumetric glass, and the mixture was heated until it was nearly dry. Afterward, the residue was treated with 5 ml of both aqua regia and H_2O_2 , and the mixture evaporated until it was dry. Insoluble components were filtered using filtrate and washed with double-distilled water before the beaker was filled with water. Deionized water is used to fill a 25 ml volumetric flask after the pH adjusters to about 3. As described above, the CPE technique uses 5 ml of digested material [38]. The results are in Table 5.

CONCLUSIONS

In comparison to similar extraction processes utilizing organic solvents, cloud point extraction provides several advantages, including ease of use in experiments, affordability, simplicity, and safety in the preconcentration of tiny metals in an aqueous medium. Triton X-114 has

Table 4. The Suggested CPE Procedure and FAAS Analyze Water Samples (n = 6)

Samples	Palladium quantity in water samples ($\mu\text{g l}^{-1}$)			
	Added	Found \pm RSD%	Recovery (%)	FAAS \pm RSD%
Drinking water	-	-	-	-
	5.00	4.95 \pm 0.3	99.0	4.44 \pm 0.7
	10.0	9.90 \pm 0.5	99.0	9.85 \pm 0.9
	15.0	14.7 \pm 0.2	98.0	14.9 \pm 0.2
	20.0	21.8 \pm 0.1	109.0	20.9 \pm 1.2
River Kufa water	-	-	-	-
	5.00	5.10 \pm 0.3	102.0	4.99 \pm 1.2
	10.0	10.2 \pm 0.5	102.0	10.42 \pm 0.7
	15.0	15.9 \pm 0.2	106.0	16.0 \pm 0.3
	20.0	19.3 \pm 1.1	96.5	22.7 \pm 0.2
Tap water	-	-	-	-
	5.00	4.65 \pm 0.3	93.0	4.77 \pm 2.1
	10.0	9.50 \pm 0.5	95.0	9.48 \pm 0.1
	15.0	14.9 \pm 0.2	99.3	14.2 \pm 0.4
	20.0	19.5 \pm 1.0	97.5	19.2 \pm 0.7

*All water samples were collected from various locations within Al-Kufa city, Iraq. *Mean \pm standard deviation. All values were repeated six times.

Table 5. Palladium Ions in Soil Samples Measured Using the CPE and FAAS Techniques

Sample (ng g ⁻¹)	Palladium concentration (Mean \pm standard deviation)	
	Applied Procedure	FAAS
Street sand	24.5 \pm 4.2	25.0 \pm 3.8
Clay	29.0 \pm 0.7	29.5 \pm 1.0
Stone	39.5 \pm 4.0	39.9 \pm 3.4

been selected for use in the project because of its excellent physical and chemical properties. Also, the low required temperature, the density of the cloud point layer (which facilitates easy separation by centrifugation), chemical stability, cheaply priced, and non-toxicity. The CPE method was applied to preconcentration of palladium ions before measuring them with a UV-Vis spectroscopic detector. Palladium was successfully derived from the bulk aqueous phase (50 ml) into tiny amounts of CPL (0.5 ml) utilizing the CPE technique. Low detection limits and precision are achieved with this approach. Water and soil samples were

also used to validate the method, which resulted in significant improvements. This procedure was very rapid.

Conflicts of Interest Statement

There are no conflicts of interest declared by the authors.

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