



CLOUD POINT EXTRACTION FOR PRE-CONCENTRATION AND DETERMINATION OF PALLADIUM IN WATER AND FOOD SAMPLES BY VISUAL AND FLAME ATOMIC ABSORPTION SPECTROMETRY

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The cloud point extraction (CPE) method was successfully employed for the separation and pre-concentration of trace amounts of palladium prior to its determination either by flame atomic absorption spectrometry (FAAS) or using visual spectrophotometry. Palladium(II) reacts with 2-Hydroxyimino-3-(2-hydrazonepyridyl)-butane (HHB) as chelating agent in the presence of *p*-octyl poly ethylene glycol phenyl ether (Triton X-100) as a nonionic surfactant giving a purple to pink surfactant rich phase chelate which could be used for CPE. The effects of experimental conditions such as pH, chelating agent and surfactant concentrations, equilibration temperature and time on CPE were studied. The performance characteristics of the method such as linearity, detection limit, pre-concentration and improvement factors were evaluated. Linearity was obeyed in the range of 0.5–15 and 0.4–18.0 ng mL⁻¹ of Pd(II) with a detection limit of 0.08 and 0.035 ng mL⁻¹ using FAAS and visual spectrometry, respectively. Validation of the method revealed good performance characteristics including good selectivity for Pd²⁺ over a wide variety of other diverse cations and anions, high reproducibility, low detection limit, acceptable accuracy and precision. The proposed method was successfully applied for the assessment of palladium (II) traces in water and food samples with satisfactory results.

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Introduction

Monitoring of trace levels of heavy metal ions in environmental samples is an important task of analytical chemistry due to their positive and/or negative influences on the human life.¹⁻³ Palladium metal has an increasing importance in today's industries because of its catalytic functions, conductivity and resistance to corrosion.⁴ It is essential in key manufacturing processes in the automobile, chemical petroleum refining, pharmaceutical and electronics industries.^{5,6} The toxicity of palladium compounds to mammals, fish and higher plants are causes for environmental concerns. Therefore, these compounds usually considered as environmental pollutants.⁷ Moreover, some of Pd(II) compounds have been reported as potential health risks to humans, causing asthma, allergy, rhino conjunctivitis and other serious health problems.⁸⁻¹⁰ Several analytical techniques have reported for the determination of trace elements in natural water, however, the determination of palladium under microgram concentration levels is generally hampered by insufficient sensitivity of the techniques used and or by a matrix effect.¹¹⁻¹⁶ To overcome the above drawbacks it requires previously separation and pre-concentration technique for enrichment of Pd(II) traces prior to its determination.

Various methods for the separation and pre-concentration of Pd(II) ions, such as co-precipitation, fire-assay, sorption and ion exchange, liquid-liquid micro-extraction, solid phase extraction, and cloud point extraction have been developed and applied.¹⁷⁻²¹ Some advantages of CPE extraction are low cost, safety, simplicity, fast operation, no need for large amounts of toxic organic solvent, high pre-concentration factor, and ease of coupling to analytical instruments.²²⁻²⁴ This method is based on the property that an aqueous solution of surfactants forms micelles and becomes turbid above a temperature defined as cloud point temperature. Above the cloud point temperature, the original surfactant solution separates into a small volume of surfactant rich phase and a bulk of diluted aqueous phase, in which the concentration of surfactant is close to the critical micellar concentration (CMC). Any analyte solubilized in the hydrophobic core of the micelles will be concentrated into the small volume of the surfactant rich phase which can subsequently be determined by different spectrometric techniques such as flame atomic absorption spectrometry (FAAS) and UV/Visible spectrophotometry. The advantages and limitations of this technique have been summarized in recent reviews.^{14,15}

In this work, cloud point pre-concentration method was developed and optimized for the extraction and determination of Pd(II) in the aqueous samples. Pd(II) reacts with 2-hydroxyimino-3-(2-hydrazonepyridyl)butane (HHB) giving colored chelate followed by extraction into *p*-octylpolyethyleneglycolphenylether (Triton X-100) as a non-ionic surfactant. After optimization the main factors affecting the cloud point extraction, the proposed procedure has been applied for the pre-concentration of palladium in water and food samples prior to its determination either by FAAS or using visual colorimetric technique.

Experimental

Instrumentation

Experiments were carried out using a Varian model analyst AA240FS atomic absorption spectrometer equipped with deuterium back ground correction. Air-acetylene burner was used for Pd(II) measurement in both surfactant-rich and poor phases. Palladium hollow cathode lamp was used as radiation source. The instrumental parameters, wavelength (244.8 nm), slit width (0.20 nm) and lamp current (5 mA), for determination of Pd(II) were adjusted according to the manufacturer's recommendations.

The nebulizer flow rate and the burner height were adjusted in order to obtain the maximum absorbance signal by aspirating a solution containing the analyte in methanol containing 0.1 mol L⁻¹ HNO₃. A Unicam UV/Vis. spectrometer controlled by a Hewlett-Packard computer and equipped with 1 cm path length quartz cell was used for absorption measurement. Cole palmer pH/mV meter (model 59003-05) was used for pH adjustment. A GFL Model D-30938 thermostatic bath, maintained at the desired temperature, was used for cloud point temperature experiments. A Hettich, EBA 21 model centrifuge was used to accelerate the phase separation

Chemicals and Reagents

All reagents used were of analytical reagent grade and were used without further purification. PdCl₂, 2-hydrazinopyridine and 2,3-butandione monoxime were purchased from Sigma Chemicals Co (St. Louis, MO). Triton X-100 was obtained from Merck chemicals (Germany).

Standard stock solution of palladium (II) chloride (0.01 mol L⁻¹) was prepared in 100 mL of water acidified with 3.0 mL of concentrated hydrochloric acid. The resulting solution was standardized gravimetrically using the dimethylglyoxime method.²⁵ Working solutions were obtained by suitable dilution of the stock solution with deionized-distilled water.

A 1.0×10⁻³ mol L⁻¹ stock HHB solution was prepared by dissolving the requisite amount in aqueous ethanolic solution and made up to the mark with 100 mL of doubly distilled water.

Synthesis of 2-hydroxyimino-3-(2-hydrazonopyridyl)-butane (HHB)

HHB was synthesized by mixing equimolar amounts of 2-hydrazinopyridine with 0.5 mole 2,3-butanedione monoxime in ethanolic solvent and maintaining the reaction mixture at reflux temperature for 1hr. The products obtained were filtered off, recrystallized from ethanol and finally dried in vacuum desiccators over anhydrous CaCl₂.²⁶

Characteristics of HHB are as follows: (C₉H₁₂N₄O): Yield 92 %. Color: pale yellow. Elemental analysis Calc.(%): C 56.2; H 6.2; N 29.1. Found: C 56.3; H 6.2; N 28.8.

CPE Procedure

Typically cloud point extraction experiments were performed as follows: The pH of an aliquot of 60 mL of standard or sample solution containing Pd(II), was adjusted to pH 6 by introducing 4 mL of phosphate buffer solution. To this solution, 1 mL of NaCl solution (0.5 mol L⁻¹), and 2 mL of 10 % (v/v) Triton X-100 solution were mixed and transferred into a graduated centrifuge tube. This mixture was heated at 70 °C for 20 min in a thermostatic bath. Separation of the two phases was achieved by centrifugation for 10 min at 3500 rpm. The mixture was cooled in an ice bath to increase the viscosity of the surfactant-rich phase, and the supernatant aqueous phase was carefully removed with a pipette. The remaining micellar phase (400 µL) was treated with 600 µL 0.1 mol L⁻¹ HNO₃ in ethanol in order to reduce its viscosity and facilitate sample handling. The final solution was introduced to the flame by conventional aspiration. Alternatively, 0.5 mL of methanol was added to the surfactant-rich phase and a 100 µL of the solution was transferred into a quartz cell containing the blank to measure the absorbance of the solution at 548 nm.

Analytical applications

The extraction efficiency was studied using spiked natural water samples for the recovery of palladium. The natural water samples were filtered through a 0.45 µm pore size membrane filter to remove suspended particulate matter, spiked with known amounts of Pd²⁺ ions standards (5, 10, 20 ng mL⁻¹) and stored at 4 °C in the dark. To 60 mL of water sample, the cloud point extraction experiments were performed as described above.

For Pd determination in food samples, mallow, peas and meat samples were purchased from local markets in Egypt. First, Mallow and peas samples were cleaned with tap water and double distilled water. Then, these samples were dried at 110 °C. Each of the dried varieties of samples and meat sample were ground to reduce particle size and then thoroughly mixed to ensure homogeneity samples individually. Masses of 50 mg of Mallow, peas and meat were transferred into separate 250 mL beakers and 5 mL of 0.5 mol L⁻¹ nitric acid was added to moisten the samples thoroughly. This was followed by adding 10 mL of concentrated nitric acid and heating on a hot plate (130 °C) for 3 h. After cooling to room temperature, 5 mL of concentrated perchloric acid was added dropwise. The beaker was heated gently until completion of sample decomposition resulting in a clear solution. This was left to cool down and then was transferred into a 100 mL volumetric flask by rinsing the interior of the beaker with small portions of 0.1 mol L⁻¹ nitric acid and the solution was filled to the mark with the same acid.²⁷

Results and discussions

Separation of metal ions by CPE has several advantages such as high pre-concentration factor, ease of coupling to analytical instruments, simplicity and fast operation. Herein, 2-hydroxyimino-3-(2-hydrazonopyridyl)butane(HHB) forms a stable complex with palladium ions (Fig. 1), which is extractable into surfactant-rich phase of Triton X-100.

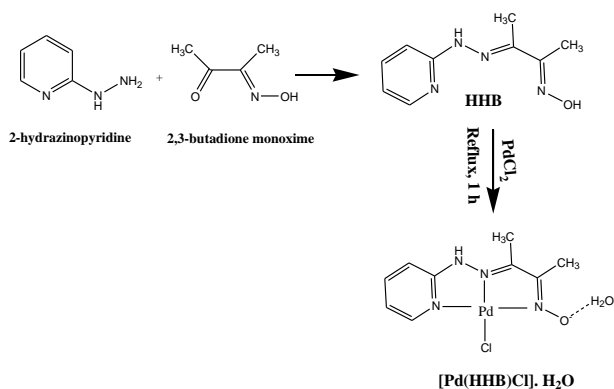


Figure 1. Schematic representation for the preparation of HHB ligand and the structure of the complex formed

The ligand (HHB) forms a stable 1:1 complex with palladium (II) as previously reported²⁸. In order to establish the optimum conditions for the formation and extraction of the complex, the performance features such as pH; concentrations of ligand and surfactant, temperature, and incubation time were evaluated and presented in Table 1.

Table 1. Optimum conditions for the CPE of palladium ion.

Optimum conditions for the CPE of palladium ion	Value
Concentration of chelating agent	3.0×10^{-5} mol L ⁻¹
Concentration of surfactant	0.3 % (w/v)
pH range	5-7
Equilibrium temperature (°C)	70
Equilibrium time (min)	20
Centrifugation rate (rpm)	3500
Centrifugation time (min)	10
Diluent	0.1 mol L ⁻¹ HNO ₃ in methanol

HHB shows maximum absorbance at 296 nm in the pH 2-8 range, and its Pd(II) complex in the extracted surfactant-rich phase has λ_{\max} at 548 nm (Fig. 2).

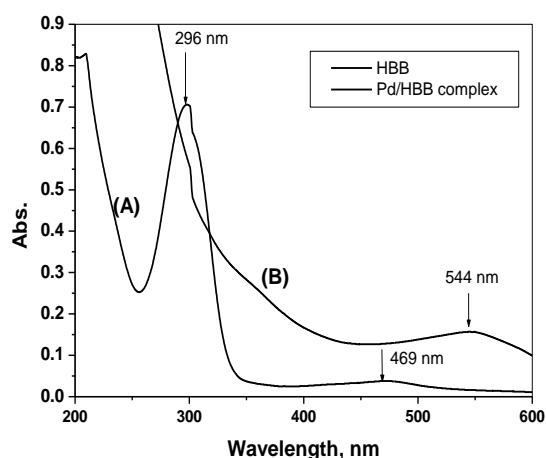


Figure 2. Absorption spectra of (a) 3×10^{-5} mol L⁻¹ HHB, (b) Pd(II)-HHB complex at pH 6.0 in the presence of: 5.00 ng mL⁻¹ of palladium(II), 3×10^{-4} mol L⁻¹ HHB, 0.3% Triton X-100

Effect of pH

The pH of the solution plays a unique role on metal-chelate formation and subsequent extraction. The effect of pH on the complex formation and subsequent extraction was investigated in the range 2-10 as shown in Fig. 3. The recovery is nearly constant in the pH range of 5-7, indicating that the optimum pH value for the quantitative extraction of palladium (II) complexes lies in this range. Due to these results, pH 6.0 was chosen for subsequent measurements. At pH <5, bad recovery was noticed due to unstable formation of Pd(HHB) complex. At pH >7, the recovery decreases due to the formation of some hydroxo complexes of Pd.

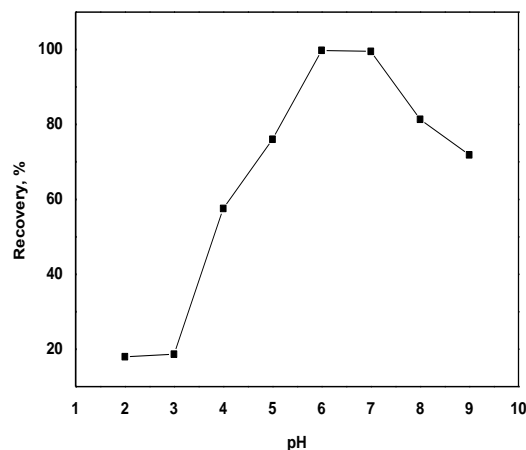


Figure 3. Influences of pH on the recovery of analyte ion. Conditions: $30 \mu\text{g L}^{-1}$ Pd²⁺; Triton X-100 0.3% (w/v); HHB 0.3×10^{-4} mol L⁻¹.

Influence of ligand concentration

The effect of amount of 2-hydroxyimino-3-(2-hydrazinopyridyl)butane (HHB) on the recovery of analyte ion was examined. Concentration of (HHB) was varied in the range of 0.2×10^{-5} - 5.0×10^{-5} mol L⁻¹. Inspection of data presented in Fig. 4 indicated that the recovery of Pd(II) increases by increasing HHB concentration up to a concentration of 3×10^{-5} mol L⁻¹ and thereafter reaches a plateau.

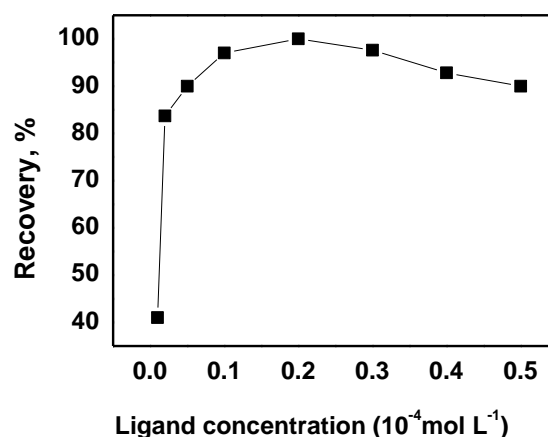


Figure 4. Influence of HHB concentration on the recovery performance of analyte ion. Conditions: $30 \mu\text{g L}^{-1}$ Pd²⁺; 0.3% (w/v) Triton X-100; pH 6.0

Thus, a concentration of 3.0×10^{-5} mol L⁻¹ of (HHB) was chosen for further experiments. When the experiments were performed without HHB at pH 6; the recoveries of the analyte ions were not quantitative. The use of more excess of HHB may adversely affect the system performance especially in AAS detection. This could be attributed to the rise in background signal in the presence of ligand, which presumably is trapped in micelles. However this behavior is not noticed in visual measurements which could be attributed to the great shift of the λ_{\max} of Pd(II) –HHB extracts from that of HHB reagent.

Effect of Triton X-100 concentration

The amount of Triton X-100 not only affected the extraction efficiency, but also the volume of surfactant-rich phase. A successful cloud point extraction should maximize the extraction efficiency by minimizing the phase volume ratio ($V_{\text{org}}/V_{\text{aqueous}}$), thus improving its concentration factor²¹. The effect of Triton X-100 concentration was studied in the range of 0.08–0.8 % (w/v). The extraction efficiency of analyte increased as the concentration of Triton X-100 increased from 0.08 to 0.3 % (w/v). With the increase of triton X-100 concentration above 0.32 %, the signal decrease because of the increment in the overall analyte volumes and the viscosity of the surfactant phase. So, a concentration of 0.3 % (w/v) was chosen as the optimum Triton X-100 concentration in order to achieve the highest possible extraction efficiency as shown in Fig. 5.

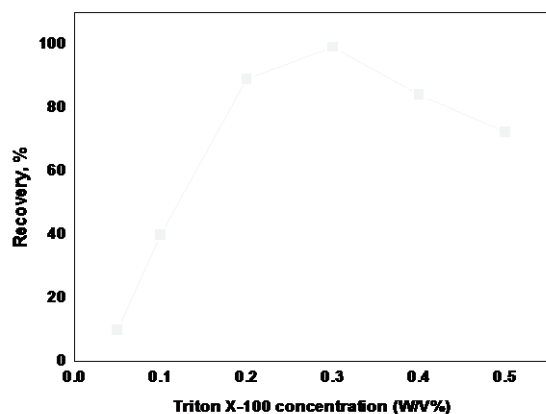


Figure 5. Effect of TritonX-100 concentration on the CPE performance. Conditions: $30 \mu\text{g L}^{-1}$ Pd²⁺; 0.3×10^{-4} mol L⁻¹ HHB; pH 6.0

Effect of ionic strength

The influence of ionic strength on the performance of CPE was investigated. For this purpose, various experiments were performed by adding different amount of NaCl, keeping other experimental conditions constant. The results showed that addition of NaCl in the interval of (0.1–0.6 mol L⁻¹) has no significant effect on the sensitivity and cloud point extraction efficiency. For further studies, the ionic strength was kept constant at 0.5 mol L⁻¹ with sodium chloride.

Effects of the equilibrium temperature and incubation time

Equilibrium temperature and the incubation time were also optimized. The effect of equilibrium temperature was investigated in the range of $t = 20\text{--}80^\circ\text{C}$. Results obtained indicated that the absorbance of the analyte reaches maximum in the $50\text{--}70^\circ\text{C}$ range. The decrease in absorbance at temperature higher than 70°C is probably due to the decomposition of the complex which reduces the extraction efficiency. So, an equilibrium temperature of 70°C was selected as optimum temperature for further studies. The dependence of analytical signal upon incubation time was also investigated in the range of 5–30 min. It was observed that an incubation time of 10 min is adequate for quantitative extraction.

Effect of viscosity on the analytical signal

The surfactant rich phase obtain after cloud point extraction is rather viscous, ethanol containing 0.1 mol L^{-1} nitric acid was added to the surfactant rich phase after separation of phase in order to facilitate its introduction into the nebulizer of the spectrometer. An optimum volume of $600 \mu\text{L}$ methanole solution of 0.1 mol L^{-1} HNO₃ was added to the remaining micellar phase ($400 \mu\text{L}$) which shows the maximum analytical signal. This added volume of methanol was chosen in order to ensure a sufficient volume of sample for aspiration.

Effect of diverse ions

In view of the high selectivity provided by flame atomic absorption spectrometry, the only interference studied were those related to the pre-concentration step. The effect of foreign ions on the determination of Pd(II) by the proposed method was also investigated by measuring the absorbance of the solutions containing 20 ng mL^{-1} of palladium ion in the presence of various amounts of other ions. In order to evaluate the performance of this procedure, the highest tolerability of various common interfering ions were studied. Interferences may occur mainly due to competition of other existing ionic species in the test solution that may form complexes with the HHB. Results obtained indicated that, in spite of the high tendency of HHB to form complexes with different transition metal ions, fortunately, most of these complexes are not extracted in the rich phase and thus remains in the supernatant aqueous phase. Therefore, all of these interferences were completely controlled by adding excess HHB (1.0×10^{-4} mol L⁻¹ especially in visual spectrometric measurements). The tolerable limits of various foreign ions were studied in solution containing 20 ng mL^{-1} of Pd(II), by keeping the relative error between $\pm 5\%$. It was found that most of the investigated species did not interfere even when present in 1000-fold excess over Pd(II). Data presented in Table 2 indicated that palladium recoveries were almost quantitative in the presence of the studied interfering species.

Calibration, precision and detection limits

The calibration graph was obtained by pre-concentration of 60 mL of sample in the presence of 0.3 % Triton X-100 under the optimum instrumental condition.

Table 2. Effect of foreign ions on the preconcentration and determination of Pd²⁺

Interferent	Concentration (mg L ⁻¹)	Recovery (%)
K ⁺	20x10 ³	101.3
Na ⁺	20x10 ³	103.1
Ca ²⁺	100	99.6
Mg ²⁺	50	101.4
Fe ²⁺	1	101.9
Zn ²⁺	1	102.7
Cu ²⁺	2	98.6
Ni ²⁺	2	102.8
Al ³⁺	2	99.8
Pb ²⁺	4	79.5
Hg ²⁺	4	103.5
Cd ²⁺	6	100.6
Ba ²⁺	8	98.5
Mn ²⁺	8	99.7

Table 3 shows the calibration parameters, the standard deviations obtained for 10 samples subjected to the complete procedure and the detection limit. The enrichment factor was calculated as the ratio slope of the calibration curve obtained from the pre-concentrated samples to that obtained without pre-concentration. The precision of the method was established by repeated assays ($n = 10$) using 10 ng mL⁻¹ solutions of analyte ions. The limit of detection was sufficiently low as compared that obtained by FAAS without pre-concentration limits around 2 mg L⁻¹.

Table 3. Analytical characteristic of CPE method using FAAS technique

Parameter	Analytical feature
Enrichment factor	80
Limit of detection (ng mL ⁻¹)	0.08
Regression equation	$Y=1.5955x+0.0095$
Correlation coefficient (r^2)	0.9991
Linear range(ng mL ⁻¹)	0.5-15
%R.S.D	2.2

For visual detection, Table 4 summarizes the analytical characteristics of the optimized method, including regression equation, linear range, limit of detection, pre-concentration and improvement factors. The limit of detection and limit of quantification are defined as $LOD = 3S_b/m$ and $LOQ = 10S_b/m$ where S_b and m are standard deviation of the blank and slope of the calibration curve, respectively. By the use of the foregoing formula 0.035 and 0.116 ng mL⁻¹ were obtained for LOD and LOQ, respectively. Because the amount of palladium (II) in 10 mL of sample solution is measured after pre-concentration by cloud point extraction in a final volume of 0.7 mL (0.2 mL surfactant-rich phase and 0.5 mL methanol), the maximum pre-concentration factor of the solution is 20. The improvement factor defined as the ratio of the slope of the calibration graph for CPE method to that of the calibration graph in micellar media without pre-concentration was 100. The relative standard deviation (RSD) was 3.3 % and 2.9 % for concentrations of palladium of 2.0 and 5.0 ng mL⁻¹, respectively (Table 4).

Table 4. Analytical features of the proposed method for pre-concentration of palladium (II) using visual spectrophotometric technique

Parameter	Analytical feature
Linear range ^(a)	0.4–18.0 (ng mL ⁻¹)
Regression equation ^(a)	$0.014C \text{ ng mL}^{-1} + 0.090$ ($n = 8$)
Correlation coefficient (r^2) ^(a)	0.995
Linear range ^(b)	50–2000 (ng mL ⁻¹)
Regression equation ^(b)	$0.00011C \text{ ng mL}^{-1} + 0.080$ ($n = 10$)
Correlation coefficient (r^2) ^(b)	0.998
Improvement factor	100
Maximum pre-concentration factor	20
Repeatability	RSD 3.5 % (for 2.0 ng mL ⁻¹ , $n = 6$)
Repeatability	RSD, 2.7 % (for 5.0 ng mL ⁻¹ , $n = 6$)
Limit of detection	0.0350 ($3S_b$, ng mL ⁻¹) ($n = 7$)
Limit of qualification	0.110 ($10S_b$, ng mL ⁻¹) ($n = 7$)

(a) After pre-concentration.(b) Before pre-concentration.

Table 5. Determination of analyte ion in tap water, river water and food samples using proposed methodology ($n=4$)

Sample	Added ($\mu\text{g g}^{-1}$)	Found ($\mu\text{g g}^{-1}$)	Recovery, %
Tap water	70	72	97.1
	100	98	98
River water	70	71.5	102.1
	100	102	102
Meat	70	69.7	99.6
	100	97.5	97.5
Malow	70	71.5	102.1
	100	103.5	103.5
Peas	70	68.8	98.3
	100	102.7	102.7

Determination of palladium in real samples

The developed method was applied to the determination of palladium in tap water, river water (El-Mansourah, Egypt) and food samples (meat, mallow and peas). The results were given in Table 5. These samples were subjected to pre-concentration and metal ions determination using the proposed procedure. The percentage recovery (R) was calculated by using the equation:

$$R = 100 \frac{C_m - C_0}{m}$$

where C_m is a value of metal in a spiked sample, C_0 is a value of metal in a sample and m is the amount of metal spiked.²⁹ The obtained recoveries were reasonable for trace palladium analysis in food matrices, in a range of 94–106 %.

Table 6. Comparison of the present method with reported methods for the preconcentration and CPE of palladium

Reagent	Surfactant	Technique	Detection limit	Ref.
2-Hydroxyimino-3-(2-hydrazonepyridyl)butane (HHB) [CHCl ₃ solvent extraction]	Solvent extraction	spectrophotometry	5.0 µg mL ⁻¹	12
Bis((1H-benzo[d]imidazol-2-yl)ethyl)sulfane	TritonX-114	FAAS	1.6 ng mL ⁻¹	21
2-Hydroxyimino-3-(2-hydrazonepyridyl)butane (HHB) [flotation]	Oleic acid (HOL)	Spectrophotometry	80 µg mL ⁻¹	30 31
1,8-Diamino-4,5-dihydroxyanthraquinone	TritonX-114	ICP FAAS	0.3 µg mL ⁻¹ 0.3 ng mL ⁻¹	32
(2-((1H-Benzo[d]imidazole-2-yl)methoxy)phenoxy)-methyl-1H-benzo[d]imidazole (BIMPI)	TritonX-114	FAAS	25 ng mL ⁻¹	33
1-(2-Pyridylazo)-2-naphthol	TritonX-114	ETASS	0.01 ng mL ⁻¹	34
4-(2-Benzothiazolylazo)-2,2-biphenyldiol	TritonX-114	spectrophotometry	0.6 ng mL ⁻¹ 1.8 µg mL ⁻¹	35
1-Phenyl-3-methyl-4-benzoyl-5-pyrazolone	PONPE 7.5	GFAAS		
2-Hydroxyimino-3-(2-hydrazonepyridyl)butane (HHB)	TritonX-100 TritonX-100	FAAS spectrophotometry	0.08 ng mL ⁻¹ 0.033 ng mL ⁻¹	Present work

Conclusions

We described the use of new micellar system as an alternative method for pre-concentration of palladium in water and food samples before analysis using CPE-FAAS or by using visual detection. This study offers a simple, rapid, inexpensive, and nonpolluting technique for the preconcentration and determination of trace metals. This approach offered several advantages over reported method,^{12,21,30-35} as shown in Table 6. The proposed reagent is versatile, as it has been early applied for pre-concentration of Pd(II) either by using solvent extraction or by floatation techniques.^{12,30} Foreign ions did not interfere in the proposed method, which is making the method selective and were successfully applied for the determination of palladium in water and food samples.

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