



Eco friendly spectrophotometric method for the determination of Palladium (II) with dimethylglyoxime in micellar media

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Abstract

Palladium (II) was determined spectrophotometrically with dimethylglyoxime as complexing reagent in aqueous phase in presence of an anionic surfactant SDS. Beer's law was obeyed, over the concentration range 2.0-16.0 $\mu\text{g mL}^{-1}$ with the detection limit 26.6 ng mL^{-1} . The molar absorptivity and Sandell's sensitivity were $0.4 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ and 28.2 ng cm^{-2} respectively at $\lambda_{\text{max}} 481 \text{ nm}$. Validation of method has been made by comparing the results with those obtained by Atomic Absorption Spectrometry; no significant difference was noted between the two methods at 95% confidence interval. The purpose was to develop rapid, convenient, sensitive, and reproducible spectrophotometric method for the detection of Pd (II) ions at trace level using DMG reagent in 0.02% SDS micellar media and replaced the old solvent extraction method, which was time consuming, costly and use of toxic solvents. The method is simple, accurate and economical and has been successfully applied to the determination of palladium (II) in natural, biological, industrial and environmental samples.

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Introduction

Palladium is the most abundant of the platinum group metals in the earth's crust. Palladium finds extensive applications as catalyst in several chemical reactions (Djingova *et al.*, 2003). Palladium and its alloys cause the risk of illness like metal toxicity in many people (Liang *et al.*, 2009). Palladium is cytotoxic and thus, damages cells. It also causes number of allergic reactions (Begerow *et al.*, 1997). Palladium complexes like $[\text{Pd}(\text{O}_2\text{Me})_2]_3$ are claimed to have antitumor properties. Pd is used mostly in the auto catalyst industry and electronics (Bruzzoniti *et al.*, 2003; Bilba *et al.*, 2004). Owing to its corrosion resistance property and alloying ability, Pd is an important element in metallurgy (Lozynska *et al.*, 2014; Mohammadi *et al.*, 2013). Its alloys are used in dental and medicinal devices and in jewelry manufacture (Azmi *et al.*, 2014; Tavallali and Jahromi, 2009). In chemical analysis, Pd chelation with DMG is followed by solvent extraction and spectrophotometric detection is the preferred mode of analysis for a number of metal ions due to rapidity, simplicity and wide applications. However, during last decade several spectrophotometric methods have been developed in which the solvent extraction step is conveniently replaced by the use of a surfactant (Sarma *et al.*, 2002). Due to the solubility of several compounds in micelles (aggregates of surfactants); many analytical techniques for the determination of metal ions in aqueous system have been developed and modified. Micellar media is mainly used to enhance the absorption sensitivities, thus simplifying the system by replacing the use of toxic organic solvent for extraction (Hosseinzadeh *et al.*, 2013; Hosseinzadeh and Gheshlagi, 2009; Ketola, 2016; Khammas, 2009; Olkowska and Polkowska, 2012; Wani *et al.*, 2017). The dimethylglyoxime is used as chelating agent in the determination of metal ions by spectroscopy. However, dimethylglyoxime metal complexes are water insoluble and therefore a solvent extraction with either chloroform or carbon tetrachloride is required. The determination of metal ions using various chelating agents in micellar media has been reported recently. Dimethylglyoxime has a hydrogen atom of hydroxyl group that is replaceable

by a Pd, and nitrogen atom, which formed stable complexes with several metal ions as shown in Fig. 1. In the present work, a spectrophotometric determination of Pd (II) as dimethylglyoxime complex in micellar aqueous solution of anionic surfactant SDS is described. The method was successfully applied to the determination of Pd (II) in natural, biological, industrial and environmental samples.

Material and method

UV-Vis Cecil CE 9500 spectrophotometer having quartz cells with path length of 10mm. Atomic absorption spectrophotometer (Analyst-800 Perkin Elmer) model. FTIR spectrophotometer (NICOLET iS10). pH/ conductivity meter (Sension 156 HACH Company USA) model.

Preparation of Reagents

Stock solution of 1% solution of dimethylglyoxime was prepared. The Pd (II) ion stock solution of 100 $\mu\text{g mL}^{-1}$ was prepared from chloride salts in deionized water in the volumetric flask (Marczenko, 1986), while other required metal ion solutions were prepared from their nitrate and chloride salts. SDS (0.02%) solution was prepared by dissolving 0.02g of SDS in a 100mL volumetric flask, and diluting to the mark with double distilled water. Insoluble chemicals were solubilized in particular acids as a technique special dissolution (Shar and Soomro, 2014). Buffers of pH 1 to 10 were made according methods (Perrin, 2012), by mixing appropriate volumes of KCl (0.2 M)-HCl (0.2M) of both for pH 1.0 to 4.0, CH_3COOH (0.2 M)- CH_3COONa (0.2 M) volumes for solution of pH 5.0 to 6.0, KH_2PO_4 (0.1 M)-NaOH (0.1 M) volumes for solution of pH 6.5 to 8.0 and sodium borate (0.025 M)-HCl (0.1 M) volumes for preparation of the solution of pH 9.0 to 10.0. All the chemicals were used of analytical grade with high purity (Merck / Fluka).

General method for determination of Pd (II) ions

The different concentrations of Pd (II) ions ranges from 0.5-20 $\mu\text{g mL}^{-1}$, dimethylglyoxime 1% solution 3mL, 2mL of buffer solution of 2 pH and 2mL of SDS surfactant 0.02% were mixed into measuring flask of

10 mL. Mixture was shaken and final volume was made with deionized water. The absorbance for Pd (II) ion at optimum conditions for Pd-complex formation was observed at particular λ_{\max} 481nm with UV-vis spectrophotometer (double beam CE-9500).

Determination of Pd (II) in industrial waste samples

Industrial wastewater sample, 1L obtained from industrial effluent collected from Kotri site area was filtered using Whatman filter paper. Concentrated nitric acid (4mL) and 30% hydrogen peroxide (2mL) were added to the filtrate (Iqbal *et al.*, 2017).

The resulting solution was concentrated in an oven at 110°C to a final volume of 25mL. The samples were transferred in measuring flasks, mixed 3mL volume DMG (1%); 2mL of SDS 0.02% and 2mL buffer of pH 2 in complex formation and the absorbance was measured against reagent blank spectrophotometrically and with AAS as given in Table 3.

Determination of Pd (II) in Pd-Ag alloy

Pd dental alloy sample was treated with 4mL of each aqua-regia and perchloric acid and heated on a hot plate. Then cooled it and again treated with aqua-regia 3mL and evaporated to dryness. The residue was dissolved in HCl (5M) 5mL and diluted to 250mL volume by adding double distilled water (Shar and Soomro, 2014). The samples were transferred in measuring flasks, mixed 3mL volume DMG (1%), 2mL of SDS 0.02% and 2mL buffer of pH 2 in formation of complex and determined spectrophotometrically. The results are given in Table 4.

Determination of Pd (II) in blood samples

About 2mL of the blood samples were mixed with 3mL of nitric acid (2M) and 1mL of hydrogen peroxide in a 100mL volumetric flask. Then the flask was shaken to promote oxidation of the sample and made the volume with distilled water. The solution was transferred into measuring flask and mixed 3mL volumes DMG (1%), 2mL of SDS 0.02% and 2mL buffer of pH 2 for metal chelate formation. Then absorbance was observed spectrophotometrically for Pd (II) ion. The results are given in Table 5.

Determination of Pd (II) in tea samples

The sample of Tea leaves 0.1 g was taken in a measuring utensil and digested with 5mL volume of HNO₃ conc. with warming (Da Antonio, 1982; Mehra and Juneja, 2005).

Then filtered and diluted the sample solution and the solution was transferred into measuring flask and mixed 3mL volumes DMG (1%), 2mL of SDS 0.02% and 2mL buffer of pH 2 for formation of metal chelate. Then absorbance was observed spectrophotometrically for Pd (II) ion. The amount of Pd was calculated and is shown in Table 5.

Analysis of Pd (II) ion in tap water sample

Tap water sample was taken from area of Khairpur, Sindh. Then the solution was filtered using 0.45 μ m filter paper and acidified by adding 1mL of concentrated HNO₃ to prevent from precipitation. Pd was added in the sample in measuring flask, the solution was transferred into measuring flask and mixed 3mL volumes DMG (1%), 2mL of SDS 0.02% and 2mL buffer of pH 2 for formation of metal complex. Then absorbance was observed spectrophotometrically for Pd (II) ion. The results are given in Table 2.

Investigation of Pd (II) in hair samples

The hair samples were washed and subjected to ultrasonic vibration for 1 hour in acetone, water, water and acetone separately in the 100mL volume. The samples were filtered and dried. After weighing the samples, they were digested in nitric acid 2.5mL volume and kept at 60°C overnight in oven. These samples were taken in calibrated flask (Da Antonio, 1982; Mehra and Juneja, 2005).

Then NaOH was mixed to neutralize the samples and working solutions were made in 50mL measuring flask. The solution was transferred into measuring flask and mixed 3mL volumes DMG (1%), 2mL of SDS 0.02% and 2mL buffer of pH 2 for formation of metal chelate. Then absorbance was observed spectrophotometrically for Pd (II) ion. The results are given in Table 5.

Results and discussion

The proposed reaction of the Pd (II) -DMG complex is shown in Fig. 1. UV-vis spectrum of dimethylglyoxime (DMG) showed maximum absorption at λ_{max} 310nm as shown in Fig. 2(a) and UV-vis spectrum of Pd(II)-DMG complex showed maximum absorption at λ_{max} 481nm as shown in Fig. 2(b). The Pd complex gave the same constant maximum absorbance up to 60 minutes. Pd-DMG complex at room temperature showed no any change in absorbances until 24h. The reagent concentration was used 1% whereas the surfactant concentration was 0.02%. Stoichiometric Pd-DMG compositions were determined using Job's method (Cherdantsevaa *et al.*, 2010; Jayanna *et al.*, 2010; Patil *et al.*, 2016; Reddy *et al.*, 2016) by varying both Pd and DMG concentrations by molar-ratio method. Pd-DMG metal against ligand ratio was found 1:2 (M:L₂) as shown in Fig. 4. 0.02% SDS 2mL volume of surfactant solution showed maximum

constant absorbance, which was above the cmc value. In complex formation different pH was kept and investigated the optimum pH where the absorbance was showed maximum. pH 2.0 was measured optimum pH (Kuliev *et al.*, 2017) for Pd (II)-(DMG)₂ complex formation is given in Fig. 5. Calibration linear concentration graph was obtained over the range 2.0-16.0 μ gmL⁻¹, with correlation coefficients 0.9995 is given in Fig. 3. Coefficient of molar absorptivity was obtained ϵ 0.4 \times 10⁴ L mol⁻¹cm⁻¹ at λ_{max} 481 is shown in Table 1.

The Sandell's sensitivity was found 28.2 ngcm⁻² is shown in Table 1, showed improvement. Detection limit was obtained to be 26.6 ngmL⁻¹ is given in Table 1. There was found improvement in the molar absorptivity, determination range, Sandell's sensitivity and detection limit than previous solvent extraction method.

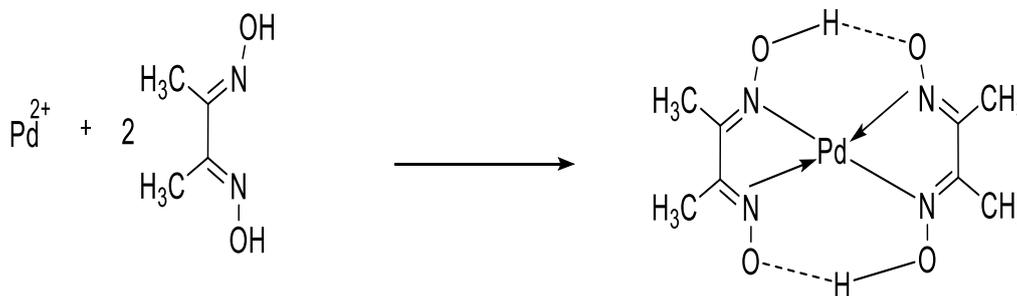


Fig. 1. Proposed reaction of Pd (II) with DMG forming Pd(II)-DMG complex.

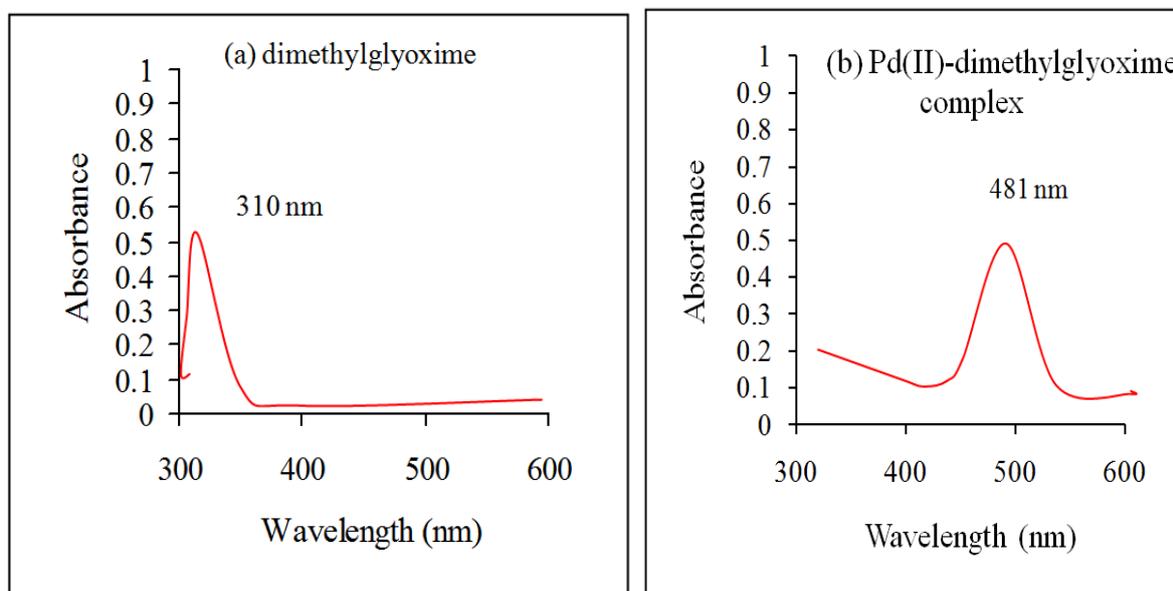


Fig. 2. Absorption spectra of (a) dimethylglyoxime (b) Pd (II)-dimethylglyoxime complex in SDS.

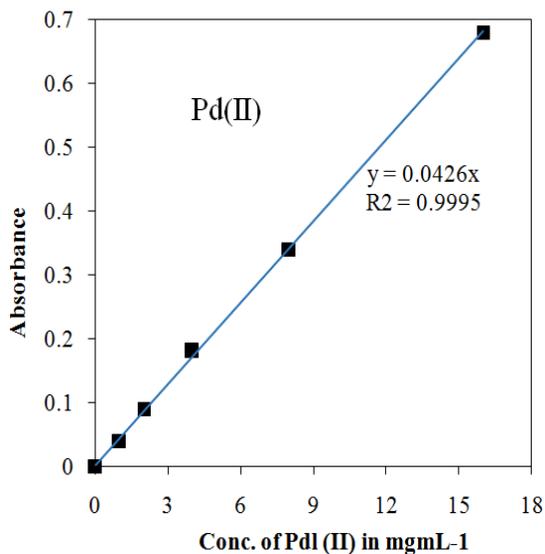


Fig. 3. Calibration graph of Pd(II)-dimethylglyoxime complex in SDS.

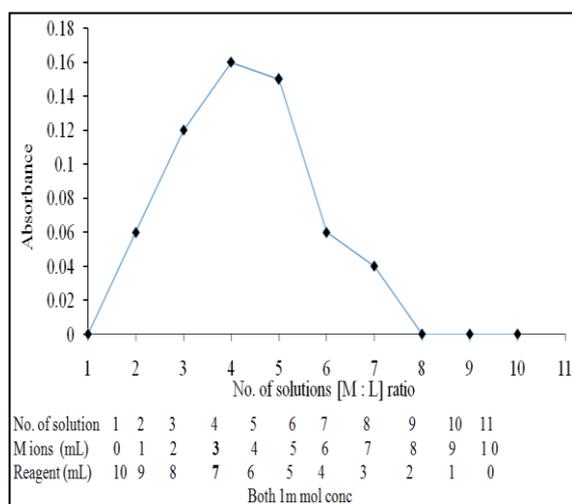


Fig. 4. Job's plot metal : ligand ratio.

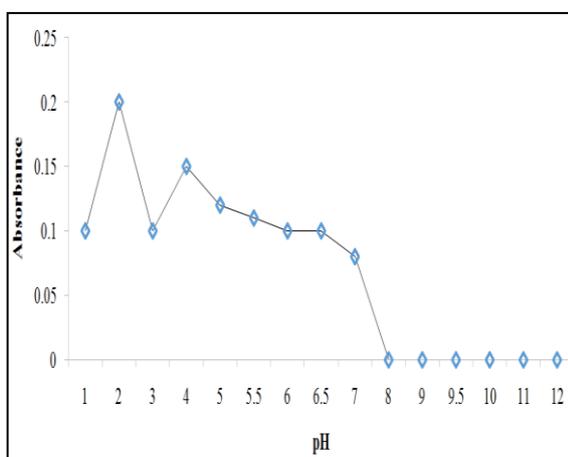


Fig. 5. Effect of pH on the absorbance of Pd(II)-DMG complex.

In the determination of Pd (II) ions with dimethylglyoxime in presence of 0.02% SDS, interference by foreign ions were studied, when Pd(II) ions were 5µg mL⁻¹. Under appropriate conditions dimethylglyoxime is specific for palladium (II). While it forms water soluble complexes with iron (II), cobalt (II) and copper (II). Among the anions examined (amount in mg shown in parenthesis), the following anions did not interfere: acetate (100), sulphate (80), thiosulphate (30), citrate (90), bromide (80), thiocyanate (100), fluoride (95), and chloride (95). Interference was eliminated by adjusting pH of the complex and using masking agent citrate and cyanide.

Table 1. Analytical characteristics of Pd(II)-dimethylglyoxime.

Characteristics	Pd (II)
Beer's law range	2.0 - 16.0 µg mL ⁻¹
Absorption maxima (λ _{max})	481 nm
Molar absorptivity (ε)	0.4×10 ⁴ Lmol ⁻¹ cm ⁻¹
Sandell's sensitivity	28.2 ng cm ⁻²
Detection limit	26.6 ng mL ⁻¹
pH range	2.0
0.02 % SDS	2 mL
1.0% dimethylglyoxime	3.0 mL
RSD	±0.004

at 95 % confidence limit, n = 6.

Table 2. Percent recovery of known amount of Pd(II) added to tap water.

Metal ions	Amount added (ug mL ⁻¹)	Amount found (ug mL ⁻¹)	Recovery (%)
Pd(II)	2.0	1.99	99 ± 1

at 95 %, n = 6

Table 3. Determination of Pd(II) in industrial waste samples.

Sample	Amount of Pd(II) determined (ug)		
	Present method	AAS method	C.V. %
*Industrial waste	0.99 ± 0.32	1.00	2.57

at 95 %, n =6* Kotri SITE area

Table 4. Determination of Pd (II) in Pd-Ag alloy.

Alloy	Metal ions	Certified value (%)	Amount found (ug mL ⁻¹)	RSD %
Pd-Ag Alloy	Pd(II)	25.00	24.98	0.14

Table 5. Determination of Pd (II) in human hair, blood and tea samples.

Sample	Added	Pd (II) found \pm SD	Recovery (%)
Human hair	-	1.25 \pm 0.1	101.3
	0.3	1.57 \pm 0.2 ng/mL	
Blood	-	28.0 \pm 2.0	100.5
	15	43.2 \pm 1.7 ng/mL	
Tea	-	33.5 \pm 1.2	100.4
	15	48.7 \pm 1.3 ng/g	

Validation of method

Proposed method results were validated with AAS, reference materials, % age recovery test at 95% confidence interval and the results were compared with AAS, which are in good agreement as given in Table 3.

Conclusions

The present method is simple, rapid, sensitive, selective, reproducible, non-extractive, and versatile spectrophotometric method for determination of palladium (II) ions at trace level. The proposed method is environment friendly, showed higher selectivity and sensitivity and has replaced the old solvent extraction methods which is time consuming, costly and toxic. The proposed method was successfully applied for the determination of Pd from natural, biological, industrial and environmental samples.

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