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## طريقة قياس طيفي محسنة ومحققة لتعيين بلاديوم (II) في عينات من خليط محضر ومن منطقة ورشة للسيارات

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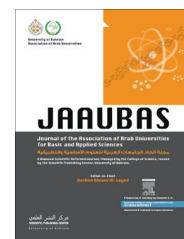
### الملخص:

تم تطوير طريقة قياس طيفي محسنة ومحققة لتعيين بلاديوم (II) في عينات من خليط محضر ومن منطقة ورشة للسيارات. اعتمدت الطريقة على تكون معقد من البلاديوم (II) والسيفيكزيم في وسط ميثانول-ماء وفي وجود مثبت الأس الهيدروجيني فوسفات ثنائي الصوديوم-حمض السيتريك الذي له أس هيدروجيني 2.6 عند درجة حرارة الغرفة. لقد كان أعلى طول موجي للمركب عند 352 نانوميتر. كما ان المحاليل المستخدمة في المدى التركيزي 0.7502-16.5004 ميكروجرام/ملتر اتبعت قانون بيبير وعند امتصاصية مولارية ظاهرية  $1.244 \times 10^4$  لتر/(مول سم) وبحساسية ساندل تعادل 0.002 ميكروجرام/سم<sup>2</sup> وحدة امتصاص. حدود الكشف وحدود الكمية للطريقة المقترحة كانتا عند 0.07 و 0.21 ميكروجرام/ملتر على التوالي. كما تمت دراسة تأثير الأيونات المختلفة مثل Cu(II) و Mg(II) و Mn(II) و Ca(II) و Fe(II) و Cr(III) و Ni(II) و Al(III) و Fe(III) و Cd(II) و Zn(II) في وجود Pd(II) وتم حساب حد التحمل الأعلى لكل فلز. لقد تم تطبيق هذه الطريقة المقترحة بنجاح على تعيين البلاديوم في العينات المحضرة معمليا وفي عينات أخذت من منطقة ورشة سيارات



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ORIGINAL ARTICLE

# Optimized and validated spectrophotometric method for the determination of palladium(II) in synthetic mixture and automobile workshop area samples



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## KEYWORDS

Palladium (II);  
Spectrophotometric determination;  
Environmental samples;  
Validation

**Abstract** An optimized and validated spectrophotometric method has been developed for the determination of Pd(II) in synthetic mixture and automobile workshop area samples. The method was based on the complex formation of Pd(II) with cefixime in methanol-distilled water medium in the presence of Na<sub>2</sub>HPO<sub>4</sub>-citric acid buffer solution of pH 2.6 at room temperature. The complex showed the maximum absorption wavelength at 352 nm. Beer's law was obeyed in the working concentration range of 0.7502–16.5004 μg mL<sup>-1</sup> with apparent molar absorptivity of 1.224 × 10<sup>4</sup> L mol<sup>-1</sup> cm<sup>-1</sup> and Sandell's sensitivity of 0.002 μg/cm<sup>2</sup>/0.001 absorbance unit. Limits of detection (LOD) and quantitation (LOQ) for the proposed method were 0.07 and 0.21 μg mL<sup>-1</sup>, respectively. The effect of diverse ions such as Cu(II), Mg(II), Mn(II), Ca(II), Fe(II), Cr(III), Ni(II), Al(III), Fe(III), Cd(II) and Zn(II) has been studied in the presence of Pd(II) and the maximum tolerance limit of each metal was calculated. The proposed method was successfully applied for the determination of Pd(II) in synthetic mixture and automobile workshop area samples.

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## 1. Introduction

A tremendous effort has been taken for the determination of traces of palladium in a variety of sample types (Sharma

et al., 2012; Ozturk et al., 2011; Soylok and Altin, 2013; Soylok et al., 2000; Serencam et al., 2013). Pd is used in jewelry, dentistry applications, fine instruments such as watches and some surgical tools for electrical contacts and for the purification of hydrogen gas (Bruzzoniti et al., 2003). The largest application of palladium is in the catalytic field. The extensive use of Pd in automotive catalytic converters

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and in chemical industry has led to increasing concentrations of this metal in the environment. The accumulation of Pd has been detected in road dust (Dimitrova et al., 2004; Kovacheva and Djingova, 2002; Gomez et al., 2003), tunnel dust (Dimitrova et al., 2004), airborne particulate matter (Tilch et al., 2000; Limbeck et al., 2003), car exhaust fumes (Moldovan et al., 1999), plants (Djingova et al., 2003), seaweed (Yang, 1989) and food additives (Vaezzadeh et al., 2010). Palladium is emitted in a particulate form together with a relatively high soluble fraction. Further contamination of aquatic systems may result from the transport of these particles through storm water. Under appropriate pH and redox potential conditions, it is assumed that palladium undergoes methylation reactions in the aquatic environment and could be concentrated along the food chain (WHO, 2000). The effect of environmental concentrations of Pd on humans is still unknown, but hypersensitivity and allergic reactions have been observed in susceptible individuals following chronic occupational exposures (Begerow et al., 1997). Therefore, because of its increasing use and also due to toxicity of palladium(II) compounds to mammals, fish and higher plants (Lee, 1983), the determination of this pollutant in environmental matrices is of considerable importance for human exposure assessment and for the investigation of correlations with health effects. Several analytical methods have been reported based on atomic absorption spectrometry (Cetin et al., 2013; Tillery and Johnson, 1975; Tokalioglu et al., 2004; Chwastowska et al., 2004; Rojas et al., 2006; Liang et al., 2009), inductively coupled plasma spectrometry (Moldovan et al., 2003), differential pulse polarography (Dias and Nozaki, 1998), high performance liquid chromatography (Dong et al., 2006), derivative spectrophotometry (Vojkovic and Druskovic, 2003; Kumar et al., 2009), kinetic spectrophotometry (Niazi et al., 2008), extractive spectrophotometry (Kanetake and Otomo, 1988; Reddy et al., 2008; Safavi et al., 1997; Davis, 1969) and spectrophotometry (Mori et al., 1999; Marczenki and Kus, 1985; Otomo, 1963; Horiuchi and Nishida, 1967; Mizuno and Miyatani, 1976; Marczenki, 1986).

The determination of trace amounts of Pd in environmental samples required a preconcentration/separation procedure when relying on the reported methods (Cetin et al., 2013; Tillery and Johnson, 1975; Tokalioglu et al., 2004; Chwastowska et al., 2004; Rojas et al., 2006; Liang et al., 2009; Moldovan et al., 2003; Dias and Nozaki, 1998; Dong et al., 2006; Vojkovic and Druskovic, 2003; Kumar et al., 2009; Niazi et al., 2008; Kanetake and Otomo, 1988; Reddy et al., 2008; Safavi et al., 1997; Davis, 1969; Mori et al., 1999; Marczenki and Kus, 1985; Otomo, 1963; Horiuchi and Nishida, 1967; Mizuno and Miyatani, 1976; Marczenki, 1986), because of their very complex sample matrices. Conventional extractive spectrophotometric procedures for preconcentration and separation, although effective, are tedious, time-consuming, require large amount of sample and reagents and sometimes vulnerable to contamination and losses of analyte. Therefore, there is a need for a simple, sensitive and selective spectrophotometric method for the determination of palladium in synthetic mixture and environmental samples. The proposed method is based on the formation of the yellow colored complex between Pd(II) and cefixime in methanol-distilled water medium in the presence of Na<sub>2</sub>HPO<sub>4</sub>-citric acid buffer solution of pH 2.6 at room temper-

ature ( $25 \pm 1$  °C) which absorbs maximally at 352 nm. The reaction conditions are optimized and validated as per the International Conference on Harmonisation guidelines (ICH, 1995).

## 2. Materials and methods

### 2.1. Apparatus

All spectral and absorbance measurements were made on a Helios Alpha UV-Vis Spectrophotometer (Thermo Electron Corporation, England, UK) with 1 cm matched quartz cells.

An air-acetylene flame type atomic absorption spectrometer (Model iCE 3000, Thermo Scientific) was used to determine Pd(II) in synthetic mixture and automobile workshop area samples.

IR spectra were recorded on an IRAffinity-1 spectrophotometer (Shimadzu, Kyoto, Japan) in wave number region 4000–400 cm<sup>-1</sup> using KBr pellet technique.

Centrifuge machine (Centro 8, J.P. Selectra, Barcelona, Spain) was used to separate the unwanted residue from filtrate of palladium. pH meter (Hanna, USA) was used to measure the pH of analyte solution.

### 2.2. Reagents and standards

All reagents used were of analytical reagent grade.  $1.41 \times 10^{-3}$  M (0.025%) palladium chloride (CAS: 7647-10-1, 150.04 ppm Pd; M.W.: 177.32, Iqba Chemie Pvt. Ltd., Mumbai, India) solution was prepared by dissolving 0.025 g of palladium chloride in 5 mL of 0.5 M HCl and the mixture was heated until the solute dissolved completely and cooled at room temperature before diluting with distilled water up to 100 mL in a volumetric flask.

$9.852 \times 10^{-4}$  M (0.05%) cefixime trihydrate (CAS: 79350-37-1, M.W.: 507.5) solution was freshly prepared in methanol. The pure cefixime trihydrate (Batch No. XMEO 110023) was provided by National Pharmaceutical Industries Company, Oman. The solution was stable up to 12 h.

Buffer solutions of pH ranging from 2.2, 2.4, 2.6, 2.8, 3.0, 3.2, 3.4 and 3.6 were prepared by mixing varying volumes of 0.4, 1.24, 2.18, 3.17, 4.11, 4.94, 5.70 and 6.44 mL of 0.2 M Na<sub>2</sub>HPO<sub>4</sub> and 19.60, 18.76, 17.82, 16.83, 15.89, 15.06, 14.30 and 13.56 mL of 0.1 M citric acid in a total volume of 20 mL (Britton, 1942).

Ghala automobile workshop area (Oman) sample was collected with a brush and afterwards sieved to discard small stones or unwanted particles.

### 2.3. Recommended procedure for the determination of Pd(II)

Aliquots of 0.05–1.1 mL of  $1.41 \times 10^{-3}$  M standard palladium chloride solution corresponding to 0.750–16.5004 µg mL<sup>-1</sup> were pipetted, followed by the addition of 2.5 mL of Na<sub>2</sub>HPO<sub>4</sub>-citric acid buffer solution of pH 2.6 into a series of 10 mL standard volumetric flasks. To each flask, 1.1 mL cefixime (0.05%) solution was added and diluted up to the mark with methanol. The contents of the flask were mixed well and the absorbance was measured at 352 nm against reagent blank prepared similarly except Pd(II) within the stability time

period of 6 h. The amount of Pd(II) was obtained either from the calibration graph or the regression equation.

#### 2.4. Procedure for reference method (Safavi et al., 1997)

Into a series of 150 mL separating funnels, an aliquot (0.159–8.33 mL) of 0.01% PdCl<sub>2</sub> solution (60.016 ppm Pd) corresponding to 9.5–500 µg Pd was taken and the pH of the solution was adjusted to pH 2 by adding dilute HCl or sodium hydroxide in a total volume of 50 mL distilled water. To each separating funnel, 5 mL of  $1 \times 10^{-3}$  M 1,2-bis[methyl (2-aminocyclopentene carbodithioate)] ethane was added with 5 mL dichloromethane. The contents of the separating funnel were shaken in a shaker for a period of 15 min and then allowed to separate for two layers. The absorbance of the organic layer was recorded at 475 nm against a reagent blank prepared similarly except palladium. The amount of Pd(II) was obtained either from the calibration graph or the regression equation.

#### 2.5. Determination of Pd(II) in synthetic mixture sample

The synthetic mixture of Pd(II) chloride sample solution was prepared by taking 25 mg of palladium chloride with 1.4 mg CuSO<sub>4</sub>, 8.48 mg MgSO<sub>4</sub>, 35.7 mg MnSO<sub>4</sub>·H<sub>2</sub>O, 31.1 mg CaCl<sub>2</sub>, 9.80 mg FeSO<sub>4</sub>·7H<sub>2</sub>O, 48.9 mg Cr<sub>2</sub>Cl<sub>3</sub>·6H<sub>2</sub>O, 4.63 mg NiSO<sub>4</sub>·6H<sub>2</sub>O, 13.22 mg Al<sub>2</sub>(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, 19.8 mg Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·9H<sub>2</sub>O, 10.85 mg 3CdSO<sub>4</sub>·8H<sub>2</sub>O and 4.03 mg ZnSO<sub>4</sub>·7H<sub>2</sub>O in a 100 mL standard volumetric flask and diluted up to the mark with distilled water. The amount of Pd(II) was determined by the proposed and reference procedures.

#### 2.6. Determination of Pd(II) in workshop area sample

The sample digestion was performed as per the procedure published in scientific reputed journal (Dimitrova et al., 2004). The palladium sample was dried in an oven at 100 °C for 24 h. 2.5 g of the road dust sample of the workshop area was weighed and crushed. The larger particles were sieved and discarded. 0.5 g of the powdered sample was transferred in a 100 mL beaker and slurred with 3 mL of aqua regia. The contents of the beaker were heated on a hot plate and stirred with the help of small magnetic bead. On drying the mixture, again 3 mL of aqua regia was added and the mixture was heated to dryness. Then 2 mL of 65% HNO<sub>3</sub> was added and the mixture was heated to dryness. The residue was diluted to 50 mL with doubly distilled water. The digest was centrifuged for 30 min at 3000 r min<sup>-1</sup> in order to separate the solid residue. The filtrate from all centrifuge tubes were collected in a 50 mL standard volumetric flask and diluted up to the mark with distilled water. The sample acidity was adjusted to pH 2.1 with NaOH. 0.5 mL of the aliquot of the workshop area sample was pipetted into a 10 mL standard volumetric flask with 1.1 mL of cefixime (0.05%) solution and 2.5 mL of the buffer solution of pH 2.6. The contents of each flask were mixed well at room temperature and diluted up to the mark with methanol. The absorbance of each solution was recorded at 352 nm against the reagent blank, prepared similarly except Pd(II). The amount of Pd(II) in ghala workshop area sample was obtained either from the calibration graph or the regression equation. The amount of Pd(II) in workshop area sample was also estimated by the reference method (Safavi et al., 1997).

#### 2.7. Determination of stoichiometry

The stoichiometry of the reaction between palladium and cefixime was studied by the Mole ratio method (Likussar and Boltz, 1971). For this purpose, different volumes (0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9 and 1.0 mL) of  $9.852 \times 10^{-4}$  M cefixime were added with 1.0 mL of  $9.852 \times 10^{-4}$  M palladium chloride followed by the addition of 2.5 mL of buffer solution of pH 2.6 in 10 mL standard volumetric flasks. The contents of the flasks were diluted up to the mark with methanol. The absorbance was recorded at 352 nm and plotted against the mole ratio of cefixime and palladium.

#### 2.8. Validation

The specificity of the proposed method was evaluated by determining 15.004 µg mL<sup>-1</sup> Pd(II) in the presence of metal ions such as Cu(II), Mg(II), Mn(II), Ca(II), Fe(II), Cr(III), Ni(II), Al(III), Fe(III), Cd(II) and Zn(II) added in the form of CuSO<sub>4</sub>, MgSO<sub>4</sub>, MnSO<sub>4</sub>·H<sub>2</sub>O, CaCl<sub>2</sub>, FeSO<sub>4</sub>·7H<sub>2</sub>O, Cr<sub>2</sub>Cl<sub>3</sub>·6H<sub>2</sub>O, NiSO<sub>4</sub>·6H<sub>2</sub>O, Al<sub>2</sub>(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·9H<sub>2</sub>O, 3CdSO<sub>4</sub>·8H<sub>2</sub>O and ZnSO<sub>4</sub>·7H<sub>2</sub>O.

The precision of the proposed method was evaluated by intra-day and inter-day precisions. For this purpose, the standard solution of palladium chloride at 3 concentration levels (4.5012, 10.5028 and 16.5044 µg mL<sup>-1</sup>) was taken and assessed with 5 replicates for each of 3 working sample concentrations in a single day (intra-day precision) and over five days (inter-day precision).

The accuracy of the proposed method was determined by the standard addition method. For this purpose, 0.5 mL of the synthetic mixture of Pd(II) and Ghala workshop area sample solutions were spiked with 0, 0.1, 0.2, 0.3 and 0.4 mL standard Pd(II) solution corresponding to 0, 1.5004, 3.0008, 4.5012 and 6.0016 µg mL<sup>-1</sup> Pd(II).

The robustness of the proposed method was evaluated by analyzing 15.004 µg mL<sup>-1</sup> Pd(II) in synthetic mixture sample by varying the volume of cefixime (1.1 ± 0.2 mL) at room temperature (25 ± 1 °C).

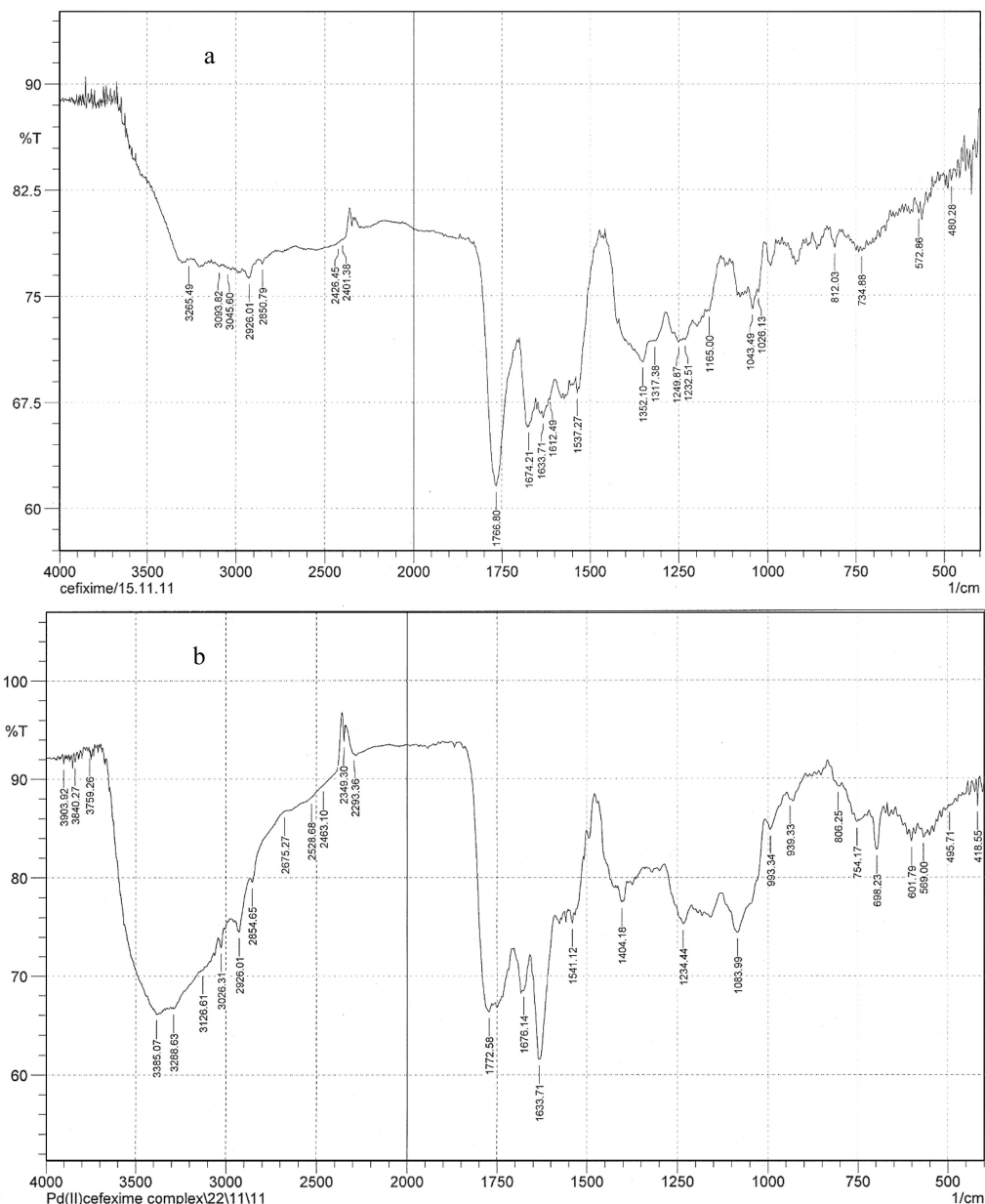
The linearity of the proposed method was assessed at 9 concentration levels (0.7502, 1.5004, 3.0008, 4.5012, 7.502, 10.5028, 13.5036, 15.004 and 16.5044 µg mL<sup>-1</sup>) of Pd(II). Each concentration level was independently analyzed repeatedly for five times. The absorbance obtained at each concentration was plotted against the initial concentration of Pd(II) in µg mL<sup>-1</sup>. The linear regression equation was evaluated by least square treatment of the calibration data. The other statistical parameters of the proposed method were calculated using Origin Software. Limits of detection (LOD) and quantitation (LOQ) were calculated by the following expressions:

$$\text{LOD} = 3.3 \times \frac{S_0}{b} \quad (1)$$

$$\text{LOQ} = 10 \times \frac{S_0}{b} \quad (2)$$

where  $S_0$  and  $b$  are standard deviation and slope of calibration line, respectively.

The bias of the proposed and reference method has been evaluated by point and interval hypothesis tests. The proposed method was compared with the reference method and considered to be acceptable, if mean recovery of the proposed method is within ±2.0% of that of the reference method.



**Figure 1** Infrared spectra of (a) pure cefixime and (b) Pd-cefixime complex in KBr (2 mg sample/200 mg KBr).

The lower ( $\theta_L$ ) and the upper ( $\theta_U$ ) acceptance limits can be calculated by the following quadratic equation (Hartmann et al., 1995):

$$\theta^2 \left( \bar{x}_1^2 - S_p^2 t_{tab}^2 / n_1 \right) + \theta \left( -2\bar{x}_1 \bar{x}_2 \right) + \left( \bar{x}_2^2 - S_p^2 t_{tab}^2 / n_2 \right) = 0 \quad (3)$$

where  $\bar{x}_1$  and  $\bar{x}_2$  are mean values at  $n_1$  and  $n_2$  measurements, respectively.  $S_p$  is the pooled standard deviation and  $t_{tab}$  is the tabulated one-sided  $t$ -value at 95% confidence level.

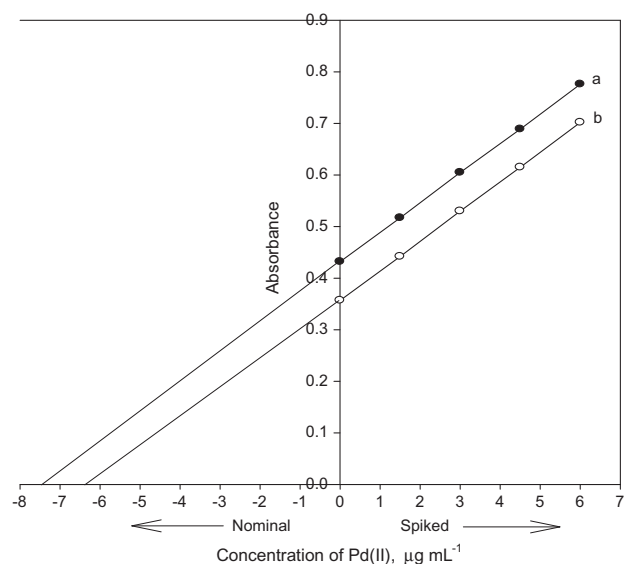
### 3. Results and discussion

The absorption spectrum of aqueous solution of palladium chloride (pH 2.1) showed two bands were maximally absorbed at 208 and 236 nm while the methanolic solution of cefixime was peaking at 210 and 290 nm. When the two

solutions were mixed together in the presence of  $\text{Na}_2\text{HPO}_4$ -citric acid buffer solution of pH 2.6, a red shift in the wavelength was observed due to the complexation reaction of Pd(II) with cefixime. The Pd(II)-cefixime complex exhibited only one band with  $\lambda_{\text{max}}$  of 352 nm. The absorbance measurement at 352 nm as a function of Pd(II) concentration was exploited to develop a new and accurate spectrophotometric method for the determination of Pd(II) in synthetic mixture and automobile workshop area samples. The reaction was carried out at room temperature (25 °C) and the colored complex was stable up to 6 h.

#### 3.1. Stoichiometry

The stoichiometric ratio between Pd(II) and cefixime was evaluated by the Mole ratio method. The mole ratio plot showed a



**Figure 2** Standard addition plot: 0.5 mL of each synthetic mixture and Ghala workshop area samples was spiked with 0, 0.1, 0.2 0.3 and 0.4 mL standard solution of 0.025% palladium chloride.

maximum absorbance at a fraction of 0.5 indicating the formation of 2:1 Pd(II)-cefixime complex. The apparent formation constant ( $K_f$ ) for Pd(II)-cefixime complex was calculated using the following expression:

$$K_f = \frac{(A_{\text{obs}}/A_{\text{extp}})\bar{C}}{[C_M - 2\left(\frac{A_{\text{obs}}}{A_{\text{extp}}}\right)\bar{C}][C_L - (A_{\text{obs}}/A_{\text{extp}})\bar{C}]} \quad (4)$$

where  $A_{\text{obs}}$  and  $A_{\text{extp}}$  are observed and extrapolated absorbance values of Pd-cefixime complex, respectively.  $C_M$ ,  $C_L$  and  $\bar{C}$  are initial concentration of palladium, cefixime and limiting concentration (cefixime) in  $\text{mol L}^{-1}$ , respectively. The  $K_f$  of the complex was found to be  $6.97 \times 10^{14}$ . The apparent Gibbs free energy ( $\Delta G^\circ$ ) was calculated using  $\Delta G^\circ = -2.303 RT \log K_f$  and found to be  $-84.69 \text{ kJ mol}^{-1}$ , confirming the feasibility of the reaction.

The literature survey revealed a very important research paper for the determination of cefixime with palladium, based on the formation of yellow complex absorbed maximally at 347 nm (El-Walily et al., 2000). The same reaction was exploited to develop a spectrophotometric method for the determination of palladium based on the formation of yellow complex at 352 nm. El-Walily and coworkers reported that the resulting Pd-cefixime chelate (2:1) was obtained due to complexation of palladium ions with the thiazole ring and sulfur atom of the  $\beta$ -lactam of the cefixime. Similarly, in the

proposed method, 2 mol of palladium was coordinated with 1 mol of cefixime. The infrared spectra of pure cefixime and Pd(II)-cefixime complex are shown in Fig. 1a and b, respectively.

### 3.2. Optimization of variables

The optimization of variables was investigated by testing reaction time, concentration of cefixime, solvents and buffer solution of different pH.

The effect of reaction time on the absorbance of Pd(II)-cefixime complex and its stability was investigated. The Pd(II)-cefixime complex got stabilized immediately at  $25 \pm 1^\circ \text{C}$  and remained stable for 6 h.

The effect of the volume of  $9.852 \times 10^{-4} \text{ M}$  cefixime on the absorbance of complex was examined in the range of 0.1–1.3 mL. The maximum absorbance was obtained with 0.9 mL of  $9.852 \times 10^{-4} \text{ M}$  cefixime. Above this volume up to 1.3 mL of  $9.852 \times 10^{-4} \text{ M}$  cefixime, the absorbance remained unchanged. Therefore, 1.1 mL of  $9.852 \times 10^{-4} \text{ M}$  cefixime was used in the determination of Pd(II).

The influence of pH on the absorbance of Pd(II)-cefixime complex with  $15.005 \mu\text{g mL}^{-1}$  Pd(II) using disodium hydrogen phosphate-citric acid buffer was investigated in the pH range of 2.2–3.00. The maximum absorbance was obtained in the pH range of 2.2–2.8. Above pH 2.8, the absorbance value decreased. Therefore, the buffer solution of pH 2.6 was selected for all absorbance measurements in the determination of Pd(II) in automobile workshop area and synthetic mixture samples.

The effect of solvents such as methanol, acetone, acetonitrile, ethanol, 1,4-dioxan, dimethylformide (DMF) and distilled water was investigated using  $15.005 \mu\text{g mL}^{-1}$  Pd(II) on the absorbance of Pd(II)-cefixime complex. The reaction mixture was turbid in distilled water and therefore, it is not a suitable solvent for dilution purpose. The highest absorbance was obtained in methanol. Therefore, methanol was selected as the best solvent for the dilution of the reaction mixture.

### 3.3. Validation

Beer's law was obeyed in the concentration ranges of  $0.7502$ – $16.5044 \mu\text{g mL}^{-1}$  with apparent molar absorptivity of  $1.22 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$  and Sandell's sensitivity of  $0.017 \mu\text{g}/\text{cm}^2/0.001$  absorbance unit. The linear regression equation was obtained by statistical treatment of the calibration data and found to be  $A = 1.01 \times 10^{-4} + 5.74 \times 10^{-2} C$  with standard deviation of calibration line of  $1.22 \times 10^{-3} \mu\text{g mL}^{-1}$ . LOD and LOQ were calculated and found to be 0.07 and  $0.21 \mu\text{g mL}^{-1}$ , respectively. The high value of correlation coefficient (0.9999) indicated excellent linearity. The experimental

**Table 1** Significance of testing: point and interval hypothesis tests for the determination of Pd(II) in synthetic mixture sample at 95% confidence level.

| Proposed method |                      | Reference method |                      | Paired $t$ -value <sup>b</sup> | $F$ -value <sup>b</sup> | $\theta_L^c$ | $\theta_U^c$ |
|-----------------|----------------------|------------------|----------------------|--------------------------------|-------------------------|--------------|--------------|
| Recovery (%)    | RSD <sup>a</sup> (%) | Recovery (%)     | RSD <sup>a</sup> (%) |                                |                         |              |              |
| 99.96           | 0.35                 | 100.11           | 0.42                 | 0.60                           | 1.443                   | 0.995        | 1.008        |

<sup>a</sup> Mean for 5 independent analyses.

<sup>b</sup> Theoretical  $t$  ( $v = 8$ ) and  $F$ -values ( $v = 4, 4$ ) at 95% confidence level are 2.306 and 6.39, respectively.

<sup>c</sup> A bias, based on recovery experiments, of  $\pm 2\%$  is acceptable.

**Table 2** Comparison of the proposed spectrophotometric methods with existing related techniques for the assay of cefixime in pharmaceutical formulations.

| Reagents  | $\lambda_{\max}$ , nm | Molar absorptivity, $L \text{ mol}^{-1} \text{ cm}^{-1}$ | Linear dynamic range, $\mu\text{g mL}^{-1}$ | RSD, %    | References                |
|---|-----------------------|--|---|-----------|---------------------------|
| Spectrophotometry: 2,4-dihydroxyl acetophenone-p-hydroxylbenzoylhydrazone in the presence of sodium acetate-HCl buffer solution | 375                   | $8.5 \times 10^3$  | 1.06–8.51                                   | -         | Challa and Reddy (2011)   |
| 2,4-Dihydroxy benzaldehyde isonicotinoyl hydrazone  | 435                   | $2.08 \times 10^4$                                       | 0.213–2.129                                 | 0.1–0.43  | Reddy et al. (2011)       |
| 2-(2-Quinolinyazo)-5-diethylaminobenzoic acid in HCl and Cetyl trimethylammonium bromide medium                                 | 625                   | $1.51 \times 10^5$                                       | 0.01–0.6                                    | 0.75      | Huang et al. (2005)       |
| 5-(5-Nitro-2-pyridylazo)-2,4-diaminotoluene in HCl medium   | 592                   | $1.25 \times 10^5$                                       | 0–0.9                                       | –         | Yang et al. (1996)        |
| o-Hydroxyacetophenone thiosemicarbazone   | 370                   | $9 \times 10^3$  | 0.42–10.6                                   | –         | Murthy and Reddy (1992)   |
| 1-(2-Pyridylazo)-2-naphthol (Solid–liquid extraction at 90 °C)  | 678                   | $1.20 \times 10^4$                                       | 0.1–1.8                                     | –         | Gao et al. (1997)         |
| Flow injection spectrophotometry: 2,2'-furyldioxime in nitric acid nitric acid medium   | 410                   | –  | 0.01–10                                     | 0.1–1.2   | Sacmaci and Kartal (2013) |
| Extractive spectrophotometry: 1,2-bis[methyl(2-aminocyclopentene carbodithioate)] ethane and extraction in dichloromethane      | 475                   | $1.2 \times 10^4$  | 0.19–10                                     | 0.7–1.1   | Safavi et al. (1997)      |
| Pyridoxal-4-phenyl-3-thiosemicarbazone, extracted into benzene  | 460                   | $2.2 \times 10^4$  | 0.4–6.4                                     | 1.84      | Sarma et al. (2002)       |
| Spectrophotometry: cefixime in methanol–water medium in the presence of $\text{Na}_2\text{HPO}_4$ -citric acid buffer solution  | 352                   | $1.224 \times 10^4$                                      | 0.750–16.500                                | 0.09–0.44 | This work                 |

intercept of the calibration line was tested for significance of deviation from the theoretical intercept i.e. zero. For this justification,  $t$ -value was calculated using relation,  $t = a/S_a$  (Nalimov, 1963) and found to be 0.143, which did not exceed the tabulated  $t$ -value (2.365,  $\nu = 7$ ) at 95% confidence level. This indicated that the intercept in the calibration equation of the proposed method was not significantly different from zero. Thus, the proposed method is free from procedural error.

The intra-day and inter day precisions for the proposed method were evaluated. Results of analyses for percentage recovery and RSD (intra-day and inter-day precisions) were in the ranges of 99.92–100.15% and 0.09–0.44%, respectively, indicated that the proposed method is very precise and thus, can be used to determine Pd(II) in synthetic mixture and automobile workshop area samples.

The accuracy of the proposed method was investigated by performing recovery experiments through the standard addition technique. The absorbance for standard added sample solutions was recorded and plotted as shown in Fig. 2. It is clear from the graph that the linearity of the regression lines for synthetic mixture and workshop area samples was good ( $r = 0.999$ ) with slope of 0.0573, 0.0575 and intercept of 0.4318, 0.3566, respectively. The concentration of Pd(II) in synthetic mixture and workshop area samples was calculated

by the ratio of the intercept to the slope and subjected to standard deviation,  $S_{x_E}$ , which can be calculated by the following expression:

$$S_{x_E} = \frac{S_{y/x}}{b} \sqrt{\frac{1}{n} + \frac{\bar{y}^2}{b^2 \sum_i (x_i - \bar{x})^2}} \quad (5)$$

and found to be 0.038 and 0.028  $\mu\text{g mL}^{-1}$ , respectively for synthetic mixture and automobile workshop area samples. The confidence limit for the concentration of Pd(II) in synthetic mixture and workshop area samples was calculated by  $x_E \pm tS_{x_E}$  at  $n - 2$  degrees of freedom and found to be  $7.533 \pm 0.038$  and  $6.200 \pm 0.028$ , respectively. The most attractive feature of the proposed method using the standard addition method is its relative freedom from various non targeted cations. Hence the proposed method is accurate.

The robustness of the proposed method was established by deliberately changing the volume of  $9.852 \times 10^{-4}$  M cefixime, 0.9 mL ( $\pm 0.2$  mL) for the determination of Pd(II). The synthetic mixture sample solution containing 15.004  $\mu\text{g mL}^{-1}$  Pd(II) was analyzed five times repeatedly by the proposed method. Percentage recovery and RSD were found to be 99.96% and 0.345%, respectively, indicating the robustness of the proposed method.

The effect of other ions on the determination of  $15.004 \mu\text{g mL}^{-1}$  Pd(II) was studied. For this purpose, varying concentrations of metal ions such as Cu(II), Mg(II), Mn(II), Ca(II), Fe(II), Cr(III), Ni(II), Al(III), Fe(III), Cd(II) and Zn(II) with  $15.004 \mu\text{g mL}^{-1}$  Pd(II) were taken and the absorbance which did not exceed  $\pm 2\%$  was considered for calculating maximum tolerance amount of metal ions. The maximum tolerance amount of Cu(II), Mg(II), Mn(II), Ca(II), Fe(II), Cr(III), Ni(II), Al(III), Fe(III), Cd(II) and Zn(II) was calculated and found to be 0.56, 1.71, 11.60, 8.48, 1.97, 9.54, 1.03, 0.95, 1.97, 1.58 and  $0.92 \mu\text{g mL}^{-1}$ , respectively indicating that the proposed method is more selective.

The applicability of the proposed method for the determination of Pd(II) in synthetic mixture and automobile workshop area samples has been tested. Results of the proposed method were statistically compared with those of the reference method using point and interval hypothesis tests. The paired  $t$ - and the  $F$ -values at 95% confidence level were calculated and found to be less than the tabulated  $t$ - (2.036 at  $\nu = 8$ ) and the  $F$ -values (6.39 at  $\nu = 4,4$ ) at 95% confidence level (Mendham et al., 2002), thus confirming no significant difference between the performance of the proposed method and the reference method (Table 1). The bias calculated by interval hypothesis test in the form of lower limit ( $\theta_L$ ) and upper limit ( $\theta_U$ ) was in the range of 0.98–1.02.

The performance of the proposed method was also tested in automobile workshop area sample collected from Ghala (Muscat, Oman) and checked for its accuracy with the reference method. The amount of Pd(II) obtained by the proposed method ( $6.205 \mu\text{g mL}^{-1}$ ) was in good agreement with the reference method ( $6.200 \mu\text{g mL}^{-1}$ ). Thus, the proposed method is suitable for routine analysis of Pd(II) in real samples of soil. The speed of analysis and less number of reagents utilized in the proposed method are the main advantages of the proposed method as compared to the reference method.

The performance and utility of the proposed method are compared with other methods for determining Pd(II) in workshop area samples (Table 2). It can be seen from the table that the sensitivity of the proposed method is higher than most of the compared methods. Only methods with sample preconcentration (Gao et al., 1997; Huang et al., 2005) yielded higher sensitivity but the instrumental set-up is much more complex and expensive.

#### 4. Conclusions

The proposed method is a direct UV–Visible spectrophotometric method as compared to the reference method (extractive spectrophotometric method). The proposed method is simple and accurate for the determination of Pd(II) in synthetic mixture and automobile workshop area samples. The method has the advantage of using a commonly available solvent i.e. methanol with the use of cefixime as a reagent. The proposed method has avoided the use of heating the reaction mixture and can be used as an alternate method for routine quality control analysis of Pd(II) in soil, water and catalyst samples.

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