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Catalytic ligand exchange reaction between hexacyanoferrate(II) and 4-cyanopyridine applied to trace kinetic analysis of palladium(II)

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ABSTRACT

The present paper describes a novel and fairly inexpensive catalytic kinetic method for the determination of Pd^{2+} in the concentration range 17.71–177.14 ppb ($ng\ mL^{-1}$). The method is based on the catalytic effect of Pd^{2+} on the substitution of cyanide by 4-cyanopyridine (4-CNpy) in hexacyanoferrate(II) in acidic media. The reaction was followed by measuring an increase in the initial rate of the indicator reaction with respect to the product, $[Fe(CN)_5(4\text{-}CNpy)]^{3-}$, formation at 477 nm. The effects of various parameters, such as pH and ionic strength of the reaction medium, concentration of the reactants and temperature, on the rate of the indicator reaction were studied to optimize the reaction conditions to achieve the highest sensitivity and to get lowest limit of detection of $[Pd^{2+}]$. The fixed time procedure, as a measure of the initial rate, was followed to obtain a linear regression equation relating the absorbance and $[Pd^{2+}]$ in the range 17.71–177.14 ppb i.e. 1×10^{-7} to $1 \times 10^{-6}\ mol\ L^{-1}$. The effects of the presence of various cations commonly associated with Pd^{2+} and some anions have also been investigated and discussed. The detection limit of the method was calculated to be 9 ppb. The maximum average error of the proposed method was quite low. The method was successfully applied for the determination of Pd^{2+} in synthetic and environmental water samples. The proposed method is selective, accurate and inexpensive compared to many other methods available in literature for Pd^{2+} determination.

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1. Introduction

Palladium is a silvery white transition metal [1,2]. In the earth's crust this precious metal occurs in a native form, usually associated with traces of platinum, silver, gold, nickel, chromium, etc. and has immensely been used in different areas [1–12]. It belongs to platinum group elements (PGEs) which are used as autocatalytic converters containing Pt, Rh, and Pd [3–5]. The PGEs have successfully been used for reducing emission of pollutants such as CO, hydrocarbons, and NO_x in vehicular exhaust by converting them to less toxic gases CO_2, N_2, and H_2O [3,5]. Thus the most important application of Pd together with Pt and Rh has been associated with three-way catalytic converters for vehicle's engines [3,5,6]. The unique catalytic property of palladium has also been utilized in the synthesis of sulfuric and hydrocyanic acids, hydrogenation of several organic compounds, production of vinyl acetate and petroleum processing [7–10]. Furthermore, due to its strong resistance to corrosion, palladium has a wide range of application, especially in the electrical and electronic industries, catalyst, dentistry, and medical devices, etc. [8]. Recently palladium nanoparticles have been of great importance in the development of new catalytic materials as well as for a number of other applications such

as hydrogen storage and sensing [8–12]. A list of palladium applications has been reported by Rao and Chandrasekhar which shows its uses in the watch bearings, springs and balance wheels, air craft spark plugs, blood sugar test strips and also for mirrors in scientific instruments [8]. Besides its use as a catalyst and in many hydrogenation processes [10], palladium is very much used in medicines, ground water treatment, photographic printing paper, jewelry, electronic devices including computers, mobile phones, televisions, multilayer capacitors, low voltage electrical contacts, etc. [8]. In the field of analytical sciences, palladium is used as a matrix modifier for the determination of various metals by electrothermal atomic absorption spectrophotometry [7].

The consequence of trace metals in biological systems comes from their essentiality as well as toxicity in living organisms. However, having no specific biological role, the palladium compounds have been regarded as toxic and carcinogenic [13–15]. Though palladium has huge applications [1–12], it has some adverse health effects and is cytotoxic damaging cells and inhibits enzyme activity and functions [14]. Palladium causes significant number of allergic reactions as well as contact dermatitis, stomatitis, lichenoid reactions, and periodontal gum disease [8]. Thus palladium and its compounds are not only highly toxic but also cause contact allergies [8,13,14].

Palladium spreads in the atmosphere through its various applications and mainly from the catalytic converters and their recycling [3,5,6]. Therefore, high concentration of Pd has continuously been reported in

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samples of airborne particulate matter, road side dust and soil samples taken from areas of high traffic density [4,16–19]. The discharge of palladium through such anthropogenic activities to the atmospheric deposition is the most important pathways for Pd into the environment. Thus the analysis of river and lake waters and sediments in urban areas has clearly demonstrated that anthropogenic activities have resulted in high concentrations of PGEs [16,17,20,21]. Thus, due to increasing use of palladium, on one hand [5,8,9,12–15] and its toxicity on the other hand [8, 13–15], its determination at trace level is of great public interest in environmental analysis. Although many research articles have been published by several research groups on the determination and the distribution of palladium in the environmental samples from Asian and other developed/developing countries [1–5,7,8,10,13–21] but none from the South Pacific Island countries.

Several sophisticated techniques, such as neutron activation analysis [22,23], atomic absorption spectrometry (AAS) [3,7,13,24–28], graphite furnace atomic absorption spectrometry (GFAAS) [14,29–32], inductively coupled plasma mass spectrometry (ICP-MS) [4,16,33,34], inductively coupled plasma-atomic emission spectrometry (ICP-AES) [2], and high performance liquid chromatography (HPLC) [35–37] have been used for the determination of Pd in different types of samples. Being cost effective, a good number of spectrophotometric methods have also been reported in the literature for the determination of palladium [1,8,15,38–48], which includes stopped-flow injection liquid–liquid extraction spectrophotometric [39] as well as catalytic kinetic spectrophotometric [1,15, 49–51] or spectrofluorimetric methods [52]. Many of these methods require prior separation, pre-concentration, extraction and enrichment to avoid matrix interference, and to enhance sensitivity [27,30–32,35, 39–42] while some uses micellar media which are not practical in environmental analysis [45–48]. Many of the methods are disadvantageous being expensive [2,4,14,22,23,29–37]. Developing kinetics based catalyzed and uncatalyzed reaction rate as well as other inexpensive miscellaneous analytical methods for various types of analytes have been our research interest [53–71]. Therefore, in continuation of our collaborative research interest in developing analytical methods, we have considered it worthwhile to report a sensitive, selective and economically viable kinetic method for the determination of Pd^{2+} in water samples. The present method is based on Pd^{2+} catalyzed substitution of CN^- from $[Fe(CN)_6]^{4-}$ by 4-CNpy which leads to the formation of stable complex, $[Fe(CN)_5(4-CNpy)]^{3-}$, having λ_{max} at 477 nm [72].

2. Experimental

2.1. Reagents and water samples

Analytical reagent grade potassium hexacyanoferrate(II) $(K_4[Fe(CN)_6]\cdot2H_2O)$ and 4-cyanopyridine were purchased from E. Merck (India) and used as received. The standard stock solutions of $K_4[Fe(CN)_6]\cdot2H_2O$ and 4-CNpy were prepared by their accurate weighing. $K_4[Fe(CN)_6]\cdot2H_2O$ solution was stored in amber volumetric flask to avoid any photodecomposition. Palladium(II) chloride $(PdCl_2)$ obtained from Sigma-Aldrich (USA) was used for preparing its standard stock and working solutions. KNO_3 (A.R. Glaxo, India) was used to maintain ionic strength (μ) in the indicator reaction medium. The pH of the reaction mixture was adjusted using potassium hydrogen phthalate (A.R. Qualigens Fine Chemicals, India) buffer solutions prepared as reported in the literature [73]. The standard BDH buffers of pH 4, 7, and 9 were used to standardize the pH meter before its use. Double distilled water was used throughout the present study for preparing all required solutions.

Following standard protocol, the lake water samples were collected from Jamuna Jheel (Lake), one of the largest natural water bodies in Lucknow, while tap water samples were collected from Lucknow University campus and river water samples from the Gomti River. The water samples were filtered through Whatman filter paper no. 40 collecting the filtrate. The filtered water samples were spiked with different concentrations of
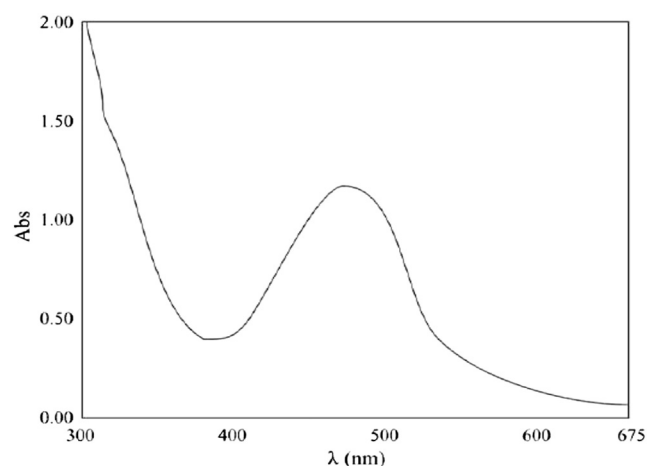

Fig. 1. UV visible spectrum of the product, $[Fe(CN)_5(4-CNpy)]^{3-}$, showing λ_{max} at 477 nm formed due to Pd^{2+} catalyzed exchange of CN^- from $[Fe(CN)_6]^{4-}$ by 4-cyanopyridine under the reaction conditions: $[Fe(CN)_6^{4-}] = 8.0 \times 10^{-2}$ mol L^{-1}, [4-CNpy] = 3.0×10^{-3} mol L^{-1}, $[Pd^{2+}] = 8 \times 10^{-7}$ mol L^{-1}, pH = 3.20 ± 0.02, $\mu = 0.1$ mol L^{-1} (KNO_3) and temperature = 25.0 ± 0.1 °C at 35 min.

Pd^{2+}. 2 mL of the spiked water samples was analyzed, by proposed procedure (2.3). The concentration of palladium(II) in water samples was calculated using linear regression equation.

2.2. Equipment

A self-designed thermostat was used to maintain the desired temperature of the reactants and buffer solutions. The Shimadzu double beam spectrophotometer UV-240, equipped with circulatory arrangement of water for thermostating the cell compartment, was used to monitor the progress of the reaction. The matched quartz cuvettes were used for the absorbance measurements. The pH measurements were made on a Toshniwal (India) digital pH meter model CL46. A Perkin Elmer 2280 atomic absorption spectrophotometer was used to evaluate the proposed method.

2.3. General procedure

In order to maintain required temperature, all the working reactants as well as buffer solutions were equilibrated at 25.0 ± 0.1 °C by hanging
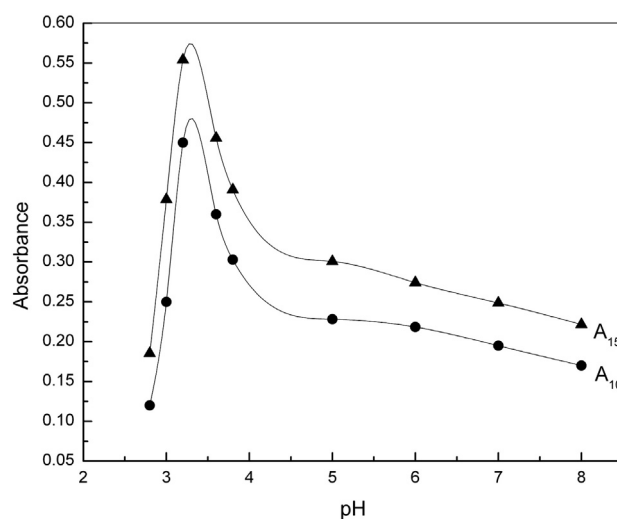

Fig. 2. Effect of pH on the initial reaction rate under the conditions: $[Fe(CN)_6^{4-}] = 8.0 \times 10^{-2}$ mol L^{-1}, [4-CNpy] = 3.0×10^{-3} mol L^{-1}, $[Pd^{2+}] = 8 \times 10^{-7}$ mol L^{-1}, $\mu = 0.1$ mol L^{-1} (KNO_3) and temperature = 25.0 ± 0.1 °C at time interval of 10 and 15 min.
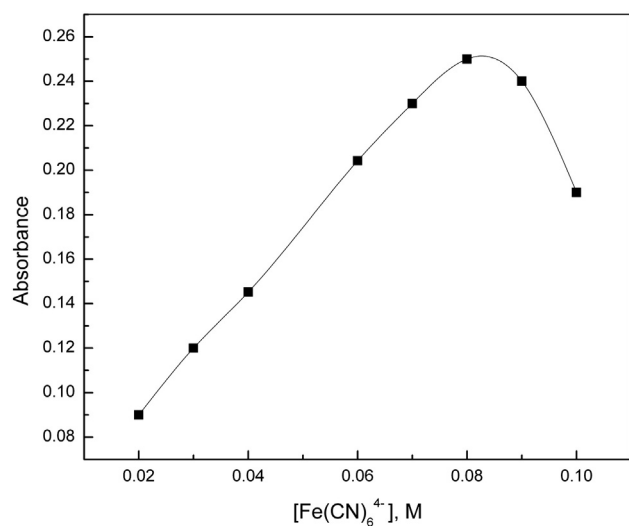
Fig. 3. Effect of [Fe(CN)$_6^{4-}$] on the initial reaction rate under the conditions: [4-CNpy] = 3.0 × 10^{-3} mol L^{-1}, [Pd^{2+}] = 8 × 10^{-7} mol L^{-1}, pH = 3.20 ± 0.02, μ = 0.1 mol L^{-1} (KNO$_3$) and temperature = 25.0 ± 0.1 °C.

them in the volumetric flasks for 30 min in a self-designed thermostat prior to the start of the reaction. Each reactant (2 mL) was mixed in the sequence: 4-CNpy, buffer, and palladium(II) chloride. The reaction was finally started by adding 2 mL of [Fe(CN)$_6$]$^{4-}$ to the reaction mixture solution. (While analyzing real/spiked water samples, in lieu of 2 mL palladium(II) chloride, 2 mL real/spiked water sample was taken.) The reaction mixture was properly shaken and transferred quickly to 10 mm quartz cuvette which was placed in the temperature controlled cell compartment of the spectrophotometer. The progress of the reaction was followed by monitoring the increase in the absorbance, as a measure of the initial rate, at 477 nm due to formation of the product, [Fe(CN)$_5$(4-CNpy)]$^{3-}$ where reactants; K$_4$[Fe(CN)$_6$], 4-CNpy, and Pd^{2+} do not absorb in the region 400–800 nm.

3. Results and discussion

3.1. Indicator reaction

The palladium(II) catalyzed ligand exchange reaction between [Fe(CN)$_6$]$^{4-}$ and 4-CNpy outcomes in the formation of a very stable

Fig. 4. Effect of [4-CNpy] on the initial reaction rate under the conditions: [Fe(CN)$_6^{4-}$] = 8.0 × 10^{-2} mol L^{-1}, [Pd^{2+}] = 8 × 10^{-7} mol L^{-1}, pH = 3.20 ± 0.02, μ = 0.1 mol L^{-1} (KNO$_3$) and temperature = 25.0 ± 0.1 °C.

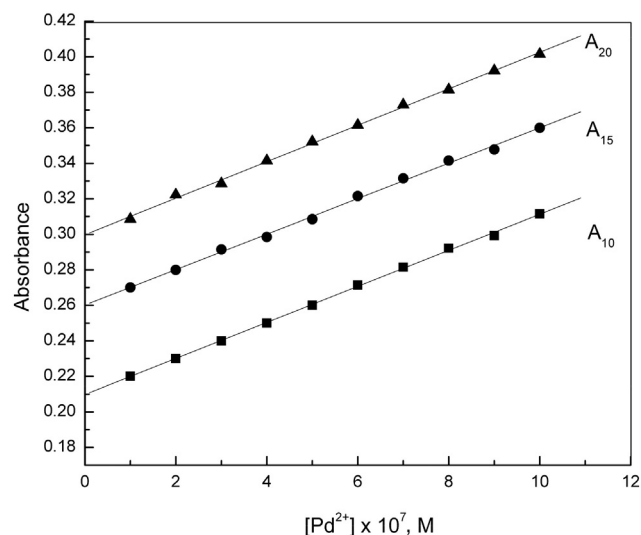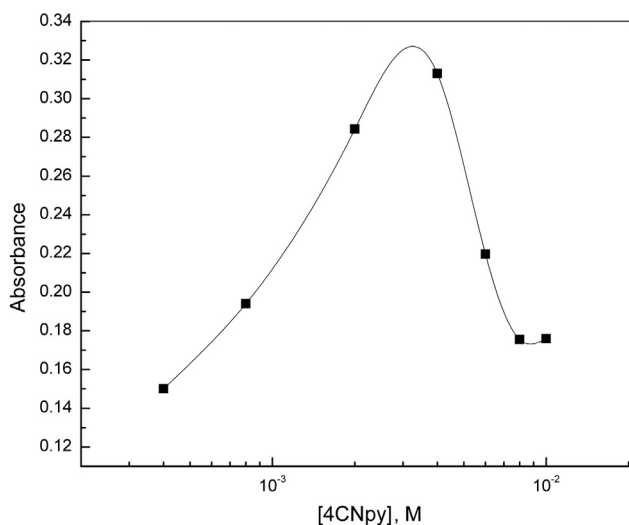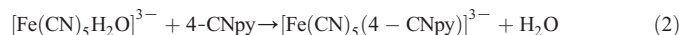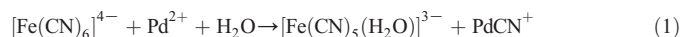**Fig. 5.** Calibration graph at different time intervals under the conditions: [Fe(CN)$_6^{4-}$] = 8.0 × 10^{-2} mol L^{-1}, [4-CNpy] = 3.0 × 10^{-3} mol L^{-1}, pH = 3.20 ± 0.02, μ = 0.1 mol L^{-1} (KNO$_3$) and temperature = 25.0 ± 0.1 °C.

product [Fe(CN)$_5$(4-CNpy)]$^{3-}$. The role of Pd^{2+} in the exchange reaction between [Fe(CN)$_6$]$^{4-}$ and 4-CNpy is attributed to the following catalytic cycle where Pd^{2+} abstracts a CN$^-$ from the complex leading to the formation of [Fe(CN)$_5$H$_2$O]$^{3-}$ which on reaction with 4-CNpy gives the product [Fe(CN)$_5$(4-CNpy)]$^{3-}$ as shown in Eqs. (1) and (2), respectively. The PdCN$^+$ generated in the reaction i.e. Eq. (1) reacts with H$^+$ to regenerate of Pd^{2+} as shown in Eq. (3) and thus the catalytic cycle is maintained [74, 75].

$$[Fe(CN)_6]^{4-} + Pd^{2+} + H_2O \rightarrow [Fe(CN)_5(H_2O)]^{3-} + PdCN^+ \tag{1}$$

$$[Fe(CN)_5H_2O]^{3-} + 4\text{-CNpy} \rightarrow [Fe(CN)_5(4-CNpy)]^{3-} + H_2O \tag{2}$$

$$PdCN^+ + H^+ \rightarrow Pd^{2+} + HCN^-. \tag{3}$$

The absorption spectrum of the product [Fe(CN)$_5$4-CNpy]$^{3-}$ shown in Fig. 1 clearly shows the maximum absorption at 477 nm. Other reactants K$_4$[Fe(CN)$_6$]·2H$_2$O, 4-CNpy, and Pd^{2+} do not absorb in the region

Table 1
The analytical figures of merit at different fixed times for the determination of Pd^{2+} under the optimum reaction conditions: [Fe(CN)$_6^{4-}$] = 8.0 × 10^{-2} mol L^{-1}, [4-CNpy] = 3.0 × 10^{-3} mol L^{-1}, [Pd^{2+}] = 1 – 10^{-7} mol L^{-1}, pH = 3.20 ± 0.02, μ = 0.1 mol L^{-1} (KNO$_3$) and temperature = 25.0 ± 0.1 °C.

Linear regression/calibration equation	Linear range [Pd^{2+}] (ppb)	Coefficient of determination (R^2)	Sensitivity	Detection limit, (ppb)
A$_{10}$ = 1.0 × 10^5[Pd^{2+}] + 0.2097	17.71–177.14	0.9991	1.0 × 10^5	9.0
A$_{15}$ = 1.0 × 10^5[Pd^{2+}] + 0.2602	17.71–177.14	0.9988	1.0 × 10^5	10.2
A$_{20}$ = 1.0 × 10^5[Pd^{2+}] + 0.2797	17.71–177.14	0.9996	1.0 × 10^5	12.5

Linear calibration range: 17.71–177.14 ng mL^{-1} (ppb).

Table 2
Effect of diverse ions in the determination of 50 ppb Pd^{2+} in the aqueous samples under the reaction conditions: $[Fe(CN)_6^{4-}] = 8.0 \times 10^{-2}$ mol L^{-1}, $[4\text{-CNpy}] = 3.0 \times 10^{-3}$ mol L^{-1}, pH = 3.20 ± 0.02, $\mu = 0.1$ mol L^{-1} (KNO_3) and temperature = 25.0 ± 0.1 °C.

Ion added	Tolerance limit ([Interfering ion]/[Pd^{2+}])	Recovery found[a] ± s (%)
Al^{3+}	100	101.0 ± 0.2
V^{5+}	100	101.0 ± 0.4
Mn^{2+}	95	99.5 ± 0.2
As^{5+}	105	100.5 ± 0.2
Mo^{6+}	100	101.0 ± 0.4
Cr^{3+}	50	100.5 ± 0.2
Cr^{6+}	50	100.2 ± 0.2
Mn^{7+}	100	100.4 ± 0.5
Fe^{2+}	20	100.2 ± 0.5
Fe^{3+}	2	100.8 ± 0.2
Co^{2+}	20	100.8 ± 0.2
Ni^{2+}	20	100.6 ± 0.4
Cu^{2+}	2	100.5 ± 0.6
Zn^{2+}	100	100.4 ± 0.2
Tl^{3+}	100	100.6 ± 0.4
Pb^{2+}	100	100.8 ± 0.2
Ti^{4+}	50	100.1 ± 0.4
Ag^{+}	10	100.2 ± 0.5
Se^{4+}	10	100.4 ± 0.4
Hg^{2+}	5	100.2 ± 0.2
Bi^{3+}	10	100.4 ± 0.5
Borate	100	100.2 ± 0.4
Oxalate	100	100.5 ± 0.2
$EDTA^{4-}$	10	100.8 ± 0.2

$EDTA^{4-}$: Ethylenediaminetetraacetate.
The ± s values represent standard deviation for five determinations.
  [a] Mean of five determinations.

400–800 nm. The optimization of the reaction variables were carried out sequentially keeping all fixed except the one to be optimized.

3.2. Effect of pH

In order to select a pH value corresponding to an optimum initial rate, the effect of pH on the reaction rate was first investigated, using the fixed time procedure as a measure of initial rate, in the pH range 2.5–8. The pH up to 6 was maintained using potassium hydrogen phthalate/NaOH or HCl buffer. However in higher pH region, the pH of all the working solutions was maintained using 5 M NaOH. Fig. 2 shows the plot of the initial rate (absorbance A_t measured at 10 and 15 min of mixing the reagents) versus the pH of the reaction media. The initial rate was low at low pH values, attained a maximum at pH 3.20 and then decreased again. The pH 3.20 corresponding to the maximum initial rate was taken as optimum.

3.3. Effect of the reactants

With all the experimental parameters kept constant, the effect of the concentration of $[Fe(CN)_6]^{4-}$ on initial rate was studied in the concentration range $2–10 \times 10^{-2}$ mol L^{-1} and is shown in Fig. 3. The dependence study clearly shows the initial linear increase in the rate at lower concentrations achieved at maximum and then decreased at higher concentration. Therefore, 8×10^{-2} mol L^{-1} $[Fe(CN)_6]^{4-}$, corresponding to maximum rate, was taken as the optimum concentration for further studies.

The effect of [4-CNpy] on the initial rate of the reaction was examined with optimum pH fixed at 3.20 ± 0.02, while the concentration of 4-CNpy was varied from 4×10^{-4}–1.0×10^{-2} mol L^{-1}. A plot of absorbance (initial rate) versus [4-CNpy] on logarithmic scale is shown in Fig. 4. The reaction rate increased with increasing [4-CNpy], attained a maximum and finally decreased at higher concentrations. Thus an optimum concentration 3.0×10^{-3} mol L^{-1} of 4-CNpy was chosen for further studies.

3.4. Effects of temperature and ionic strength (μ)

The effect of the temperature on the initial rate (absorbance) of the Pd^{2+} catalyzed reaction rate was studied, involving optimized reaction conditions and following general procedure (cf. Section 2.3), in the temperature range 20–45 °C. The reaction obeyed Eyring's equation and found to proceed with reasonable rate at 25.0 ± 0.1 °C. The change in the reaction rate at 25 °C was appropriate and hence selected for further studies.

The effect of ionic strength (μ) on the reaction was studied in 0.01–0.40 mol L^{-1} range using KNO_3 to maintain the ionic strength of the reaction medium. The increase in ionic strength decreased the rate of the reaction. A negative salt effect was observed. The ionic strength of 0.1 mol L^{-1} gave a measurable change in the reaction rate. Hence 0.1 mol L^{-1} (KNO_3) was selected for further studies.

3.5. Influence of [Pd^{2+}]

To establish the calibration graph for the chosen indicator reaction system, the catalytic effect of Pd^{2+} on the substitution reaction was studied in the concentration range 1×10^{-7}–2×10^{-3} mol L^{-1} under the optimum reaction conditions. Fixed-time procedure as a measure of the initial rate was adopted to record the absorbance at different times A_t (t = 10, 15 and 20 min) after mixing the reagents. However, the plots of the absorbance (A_t) versus [Pd^{2+}], where other reactants were in their optimum conditions, were found to be linear only in the range 1×10^{-7}–1×10^{-6} mol L^{-1} as shown in Fig. 5 and were used as calibration curves. The linear regression equations correlating the A_t

Table 3
Accuracy and precision of Pd^{2+} determination by proposed catalytic kinetic method under the reaction conditions: $[Fe(CN)_6^{4-}] = 8.0 \times 10^{-2}$ mol L^{-1}, $[4\text{-CNpy}] = 3.0 \times 10^{-3}$ mol L^{-1}, pH = 3.20 ± 0.02, $\mu = 0.1$ mol L^{-1} (KNO_3) and temperature = 25.0 ± 0.1 °C.

Concentration of Pd^{2+} added (ppb)	A_{10}			A_{12}			A_{15}		
	[Pd^{2+}] found[a] ± s (ppb)	Recovery (%)	Error (%)	[Pd^{2+}] found[a] ± s (ppb)	Recovery (%)	Error (%)	[Pd^{2+}] found[a] ± s (ppb)	Recovery (%)	Error (%)
20.22	20.11 ± 0.03	99.46	−0.54	20.44 ± 0.06	101.09	+1.09	20.44 ± 0.16	101.09	+1.09
30.46	30.52 ± 0.03	100.20	+0.28	30.24 ± 0.04	99.28	−0.72	30.72 ± 0.03	100.85	+0.85
41.77	41.98 ± 0.03	100.50	+0.50	41.94 ± 0.04	101.41	+0.41	41.98 ± 0.05	100.50	+0.50
49.88	49.62 ± 0.03	98.48	−0.52	49.44 ± 0.06	99.12	−0.88	49.66 ± 0.08	99.56	−0.44
60.94	60.78 ± 0.02	99.74	−0.26	60.72 ± 0.08	99.64	−0.36	60.22 ± 0.04	98.82	−1.18
90.62	90.99 ± 0.03	100.41	+0.41	90.82 ± 0.02	100.22	+0.22	90.34 ± 0.02	99.58	−0.31
122.18	122.78 ± 0.05	100.49	+0.41	122.40 ± 0.18	100.18	+0.18	122.94 ± 0.04	100.62	+0.62
134.22	134.44 ± 0.06	100.16	+0.16	134.58 ± 0.08	100.27	+0.27	134.76 ± 0.04	100.40	+0.40
162.44	162.33 ± 0.13	99.60	−0.07	162.98 ± 0.02	100.33	+0.33	162.12 ± 0.08	99.80	−0.20
		Av = 0.04			Av = 0.06			Av = 0.15	

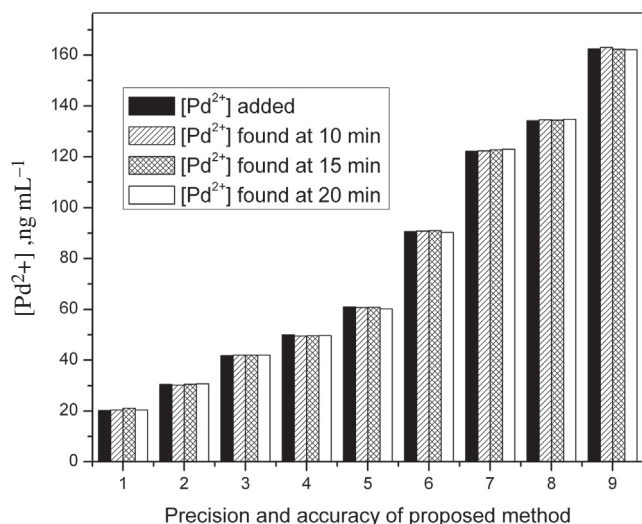The ± s values represent standard deviation for five determinations.
  [a] Mean of five determinations.

Fig. 6. Precision and accuracy of the proposed method under the conditions: $[Fe(CN)_6^{4-}] = 8.0 \times 10^{-2}$ mol L^{-1}, $[4\text{-CNpy}] = 3.0 \times 10^{-3}$ mol L^{-1}, pH = 3.20 ± 0.02, $\mu = 0.1$ mol L^{-1} (KNO$_3$) and temperature = 25.0 ± 0.1 °C.

to $[Pd^{2+}]$ in the range 1×10^{-7}–1×10^{-6} mol L^{-1} (17.71–177.14 ppb) along with other parameters on analytical figures of merit for the determination of Pd^{2+} are given in Table 1. The detection limit (3σ) of the method was calculated to be 9 ppb corresponding to the measurement at 10 min.

3.6. Selectivity, precision, and accuracy studies

In order to assess the applicability of the proposed method for the analysis of real and synthetic samples containing Pd^{2+}, the influence of the presence of various interferents on the kinetic determination of Pd^{2+} was studied. The tolerance concentration of each diverse ion was taken as the highest concentration causing an error not more than ±4%. The results on tolerance limit are shown in Table 2, which clearly indicates that most of the ions examined did not interfere, with the determination of 50 ppb Pd^{2+}, up to 100 folds in excess while some cations like Fe^{3+}, Cu^{2+}, Hg^{2+}, Se^{4+}, Bi^{3+}, and Ag^+ and the complexing agent $EDTA^{4-}$ were found to interfere when present 2–10 fold excess. However, these species generally do not exist with Pd^{2+}.

The precision and accuracy of the developed method were judged by the recovery of Pd^{2+} with five independent experiments using a range of Pd^{2+} concentrations under the optimum conditions and the results are given in Table 3. The maximum average error for the determination of Pd^{2+} by the proposed method was quite low. The excellent recoveries of Pd^{2+} at different time intervals (10, 15 and 20 min) are also shown in Fig. 6 where X-axis values 1–9 simply show different bars for comparison at different concentrations reported on Y-axis.

Table 5
Determination of Pd^{2+} in river, lake, and tap water samples under the reaction conditions: $[Fe(CN)_6^{4-}] = 8.0 \times 10^{-2}$ mol L^{-1}, $[4\text{-CNpy}] = 3.0 \times 10^{-3}$ mol L^{-1}, pH = 3.20 ± 0.02, $\mu = 0.1$ mol L^{-1} (KNO$_3$) and temperature = 25.0 ± 0.1 °C.

Samples	Pd^{2+} added (ppb)	Pd^{2+} found ± s (ppb)	Recovery (%)
River water	30	35.0 ± .02	116.66
	35	40.8 ± .04	116.57
	40	45.6 ± .02	114.00
	40	49.6 ± .04	124.00
Lake water	20	24.2 ± .03	121.00
	80	84.2 ± .03	105.25
	100	102.2 ± .01	102.20
Tap water	105	106 ± .04	100.95
	95	98.8 ± .04	104.00

The ± s values represent standard deviation for five determinations.

3.7. Applications

The developed catalytic kinetic spectrophotometric method was applied for Pd^{2+} determination in various synthetic mixtures (SM) and real samples. The synthetic samples were prepared with different compositions of metal cations including Pd^{2+} and analyzed by the proposed method. This was done because authentic samples containing trace amounts of Pd^{2+} were not available. These cations were chosen to judge their interferences due to the fact that many of these cations catalyze the indicator reaction but to lesser extent than Pd^{2+} and also they generally exist in the environmental water samples. Hg^{2+} was chosen in the synthetic mixture to judge its interference as it shows good catalytic activity, on the used indicator reaction, in comparison to many other metal ions [75]. The results on Pd^{2+} recoveries from the synthetic mixture are shown in Table 4. The recovery in each case is well within the acceptable error limit for environmental monitoring applications. The synthetic samples were also analyzed by atomic absorption spectrophotometry (AAS) method and the results obtained by both methods were in close agreement (Table 4).

The developed method was successfully applied for Pd^{2+} determination in spiked environmental water (river, lake and tap) samples where the water samples were simply filtered using Whatmann no. 41 filter paper and directly analyzed after spiking. The results given in Table 5 shows that slightly high recovery was achieved, especially in case of river and lake water samples may be due to matrix effect. The higher recovery in most of the spiked environmental (river, lake and tap) water samples may be attributed to the synergistic effects by the other ions which are not uncommon [69]. The developed method has adequate precision and accuracy for the determination of Pd^{2+} in synthetic and environmental samples. The proposed catalytic kinetic method, in comparison to various other methods as shown in Table 6 [30,35, 39–42,45,51], is found to be economically more viable. This is because of the fact that in many of these methods extraction of the sample is required [30,39,40,42], one used costly HPLC with spectrophotometric detection [35], another used high temperature of 90 °C for color

Table 4
Determination of Pd^{2+} in synthetic samples under chosen range under the reaction conditions: $[Fe(CN)_6^{4-}] = 8.0 \times 10^{-2}$ mol L^{-1}, $[4\text{-CNpy}] = 3.0 \times 10^{-3}$ mol L^{-1}, pH = 3.20 ± 0.02, $\mu = 0.1$ mol L^{-1} (KNO$_3$) and temperature = 25.0 ± 0.1 °C.

Synthetic mixture (SM)	SM composition; each cation 10 fold excess (ppb)	Pd^{2+} added (ppb)	Pd^{2+} found ± s (ppb)	Error (%)	AAS method (ppb)
SM-1	$Al^{3+} + V^{5+} + Mn^{2+} + Ni^{2+} + Tl^{3+}$	50	50.80 ± 0.08	1.60	50.10
SM-2	$Al^{3+} + V^{5+} + Ni^{2+} + Tl^{3+} + Ag^+ + Zn^{2+}$	70	70.50 ± 0.06	0.71	70.08
SM-3	$Ni^{2+} + Tl^{3+} + Pb^{2+} + Ti^{4+} + Zn^{2+} + Hg^{2+}$	80	81.64 ± 0.10	2.05	80.10
SM-4	$Ni^{2+} + Tl^{3+} + Pb^{2+} + Zn^{2+} + Ti^{4+} + Co^{2+} + Hg^{2+}$	85	85.88 ± 0.40	1.05	85.06
SM-5	$Ni^{2+} + Tl^{3+} + Pb^{2+} + Ti^{4+} + Mo^{6+} + Zn^{2+}$	90	91.08 ± 0.06	1.20	90.08

The ± s values represent standard deviation for five determinations.

Table 6
Comparison of the proposed method with other spectrophotometric methods for the determination of palladium.

Methods	Reagents used and type of reaction	Linear range, limit of detection, type of sample and comments	Ref. no.
Spectrophotometric	Palladium + N,N′-diphenylbenzimidoylthiourea, λ_{max} = 365 nm in chloroform.	Acidic medium, simple, rapid and applicable over 0.3–1.0 M HCl. Free from interferences, detection limit 80 ppb, metals in catalytic material determined.	[45]
Stopped-flow injection liquid–liquid extraction spectrophotometric	Pd^{2+} + 2, 2′-dipyridyl-2-pyridylhydrazone (DPPH) → colored complex Pd^{2+}–DPPH extracted in $CHCl_3$, λ_{max} = 560 nm.	Airborne particulate matter (APM) and in automobile exhaust gas converter catalysts. The linear calibration graph linear up to 12 mg L^{-1} detection limit = 0.007 mg L^{-1}. Extraction required.	[39]
Graphite furnace-atomic absorption spectrophotometric	Prior separation and enrichment of Pd^{2+}-$SnCl_3^-$-N-butylacetamide complex into 1-pentanol based on solvent extraction method, molar absorptivity of the complex in three solvents, ethyl acetate, 1-pentanol, chloroform, lie in the range of $(0.70–2.75) \times 10^4$ L mol^{-1} cm^{-1}, λ_{max} = 360–440 nm.	Applied for the analysis of Pd in soil samples derived from roads and highways. Separation, enrichment and extraction required.	[30]
Kinetic spectrophotometric	Pd^{2+} catalyzed on the oxidation of pyrogallol red with hydrogen peroxide at pH 9.7, at 540 nm.	0.02–1.00 µg mL^{-1} Pd^{2+}, limit of detection = 0.017 µg mL^{-1} Pd(II), liquid samples.	[51]
High-performance liquid chromatographic–spectrophotometric	pH dependent phase-separation phenomenon of water–acetic acid–chloroform ternary solvent system.	5×10^{-8}–8×10^{-7} M, 8×10^{-9} M, liquid samples.	[35]
Extraction-spectrophotometric	Pd^{2+}-di-2-pyridylketone benzoylhydrazone complex formation followed by extraction into benzene from sulfuric acid solution in the presence of chloride ions, λ_{max} = 455 nm.	Range 0–10 µg mL^{-1} of palladium, applied in a dental alloy and in palladium-catalyst samples.	[40]
Spectrophotometric	Pd^{2+} determination after solid–liquid extraction with 1-(2-pyridylazo)-2-naphthol at 90 °C, pH 1.5–7.5, λ_{max} = 678 nm.	0.5–10 ppm, high temp., molar absorptivity and Sandell's sensitivity are 1.2×10^4 L mol^{-1} cm^{-1} and 0.0070 µg cm^{-2}, synthetic samples.	[41]
Extractive spectrophotometric	2,2′-dipyridyl-2-quinolylhydrazone used as a reagent.	Pd^{2+} determination in the presence of chloride ions, liquid samples	[42]
Kinetic spectrophotometric	Hexacyanoferrate(II) + 4-CNpy + Pd^{2+} → $[Fe(CN)_5(4\text{-CNpy})]^{3-}$ pH = 3.2, λ_{max} = 477 nm.	17.71–177.14 ppb, 9 ng mL^{-1}. Aqueous real and synthetic samples, very selective.	Present method

development [41]. The present method also offers advantages of simplicity, instant color development, and much less interference problem.

4. Conclusion

The proposed catalytic kinetic method is quite sensitive, simple, inexpensive and accurate. It has been established that Pd^{2+} can be determined in the range 17.71–177.14 ppb by the proposed method in the presence of a number of cations and anions. The method can be adopted for the determination of Pd^{2+} in environmental water samples. Among the various sophisticated methods, the proposed method may be popular because of its inherent analytical figure of merits.

References

[1] M.F. Mousavi, M. Barzegar, A. Rahmani, A. Jabbari, Catalytic kinetic determination of trace amounts of palladium with photometric detection, Microchim. Acta 140 (2002) 41–44.
[2] H. Zheng, D. Zhang, W.Y. Wang, Y.Q. Fan, J. Li, H.P. Han, Highly selective determination of palladium(II) after preconcentration using Pd(II)-imprinted functionalized silica gel sorbent prepared by a surface imprinting technique, Microchim. Acta 157 (2007) 7–11.
[3] S. Atilgan, S. Akman, A. Baysal, Y. Bakircioglu, T. Szigeti, M. Óvári, G. Záray, Monitoring of Pd in airborne particulates by solid sampling high-resolution continuum source electrothermal atomic absorption spectrometry, Spectrochim. Acta B 70 (2012) 33–38.
[4] J. Wang, R.-H. Zhu, Y.-Z. Shi, Distribution of platinum group elements in road dust in the Beijing metropolitan area, China, J. Environ. Sci. 19 (2007) 29–34.
[5] M.A. Palacios, M.M. Gómez, M. Moldovan, G. Morrison, S. Rauch, C. McLeod, R. Ma, J. Laserna, P. Lucena, S. Caroli, A. Alimonti, F. Petrucci, B. Bocca, P. Schramel, S. Lustig, M. Zischka, U. Wass, B. Stenbom, M. Luna, J.C. Saenz, J. Santamaría, J.M. Torrens, Platinum group elements: quantification in collected exhaust fumes and studies of catalyst surfaces, Sci. Total Environ. 257 (2000) 1–15.
[6] C. Hochfeld, W. Jenseit, Screening life cycle inventory of PGEs and its influence on the overall emission balance of cars fitted with catalytic converters, in: F. Zereini,

F. Alt (Eds.), Anthropogenic Platinum-Group Element Emissions: Their Impact on Man and Environment, Springer, Berlin Heidelberg, Germany 2000, pp. 293–300 (Chapter 6).
[7] A. Tunceli, A.R. Turker, Determination of palladium in alloy by flame atomic absorption spectrometry after preconcentration of its iodide complex on amberlite XAD-16, Anal. Sci. 16 (2000) 81–85.
[8] M.R. Rao, K.B. Chandrasekhar, Sensitive derivative spectrophotometric determination of palladium(II) using 3,5-dimethoxy-4-hydroxybenzaldehyde-isonicotinoylhydrazonein presence of micellar medium, Der Pharma Chem. 3 (2011) 358–369.
[9] Y. Sakai, A. Shimanaka, M. Shioi, S. Kato, S. Satokawa, T. Kojima, A. Yamasaki, Fabrication of high-sensitivity palladium loaded tungsten trioxide photocatalyst by photodeposite method, Catal. Today 241 (2015) 2–7.
[10] H. Tavallali, M.G.P. Jahromi, A novel optode sensor for the determination of palladium(II) in water and a hydrogenation catalyst, J. Serb. Chem. Soc. 74 (2009) 311–315.
[11] Y. Liu, G. Sun, C. Jiang, X.T. Zheng, L. Zheng, C.M. Li, Highly sensitive detection of hydrogen peroxide at a carbon nanotube fiber microelectrode coated with palladium nanoparticles, Microchim. Acta 181 (2014) 63–70.
[12] C.-L. Yang, X.-H. Zhang, G. Lan, L.-Y. Chen, M.-W. Chen, Y.-Q. Zeng, J.-Q. Jiang, Pd-based nanoporous metals for enzyme-free electrochemical glucose sensors, Chin. Chem. Lett. 25 (2014) 496–500.
[13] D.L.G. Borges, M.A.M. Silva da Veiga, V.L.A. Frescura, B. Welz, A.J. Curtius, Cloud-point extraction for the determination of Cd, Pb and Pd in blood by electrothermal atomic absorption spectrometry, using Ir or Ru as permanent modifiers, J. Anal. At. Spectrom. 18 (2003) 501–507 (and references cited therein).
[14] M.R. Jamali, Y. Assadi, R.R. Kozani, Determination of trace amounts of palladium in water samples by graphite furnace atomic absorption spectrometry after dispersive liquid–liquid microextraction, J. Chem. 2013 (2013) (Article ID 671743, 6 pages).
[15] A. Niazi, B. Jafarian, J. Ghasemi, Kinetic spectrophotometric determination of trace amounts of palladium by whole kinetic curve and a fixed time method using resazurine sulfide reaction, Spectrochim. Acta A 71 (2008) 841–846.
[16] S. Rauch, M. Motelica-Heino, G.M. Morrison, O.F.X. Donard, Critical assessment of platinum group element determination in road and urban river sediments using ultrasonic nebulisation and high resolution ICP-MS, J. Anal. At. Spectrom. 15 (2000) 329–334.
[17] F. Zereini, B. Skerstupp, K. Rankenburg, F. Dirksen, J.M. Beyer, T. Claus, H. Urban, Anthropogenic emission of platinum-group elements (Pt, Pd and Rh) into the environment: concentration, distribution and geochemical behaviour in soils, in: F. Zereini, F. Alt (Eds.), Anthropogenic Platinum-Group Element Emissions: Their Impact on Man and Environment, Springer, Berlin Heidelberg, Germany 2000, pp. 733–783.
[18] V.F. Hodge, M.O. Stallard, Platinum and palladium in roadside dust, Environ. Sci. Technol. 20 (1986) 1058–1060.
[19] F. Zereini, E. Heinrich, G. Schmidt, K.L. Kratz, Determination of platinum-group elements (PGE) from catalytic converters in soil by means of docimasy and INAA, Fresenius J. Anal. Chem. 354 (1996) 883–885.
[20] E. De Vos, S.J. Edwards, I. McDonald, D.S. Wray, P.J. Carey, A baseline survey of the distribution and origin of platinum group elements in contemporary fluvial sediments of the Kentish Stour, England, Appl. Geochem. 17 (2002) 1115–1121.

[21] S. Rauch, H.F. Hemond, B. Peucker-Ehrenbrink, Recent changes in platinum group element concentrations and osmium isotopic composition in sediments from an urban lake, Environ. Sci. Technol. 38 (2004) 396–402.

[22] I. Shazali, L.V. Dack, R. Gijbels, Determination of precious metals in ores and rocks by thermal neutron activation/γ-spectrometry after preconcentration by nickel sulphide fire assay and coprecipitation with tellurium, Anal. Chim. Acta 196 (1987) 49–58.

[23] M. Asif, S.J. Parry, H. Malik, Instrumental neutron activation analysis of a nickel sulfide fire assay button to determine the platinum group elements and gold, Analyst 117 (1992) 1351–1353.

[24] S. Lin, C. Zheng, G. Yun, Determination of palladium by flame atomic absorption spectrometry combined on-line with flow injection preconcentration using a micro-column packed with activated carbon fibre, Talanta 42 (1995) 921–926.

[25] M.M. Schnepfe, F.S. Grimaldi, Determination of palladium and platinum by atomic absorption, Talanta 16 (1969) 591–595.

[26] J.C.V. Loon, Determination of platinum, palladium, and gold in a silver assay bead by atomic absorption spectrophotometry, Fresenius J. Anal. Chem. 246 (1969) 122–124.

[27] D. Zhang, P. Yu, Determination of palladium in water by FAAS after preconcentration and separation with the modified barium-strontium titanate powder by dithizone, Asian J. Chem. 24 (2012) 1715–1718.

[28] D. Zhang, Determination of Pd(II) in street dust and water samples by FAAS after preconcentration with dimethylglyoxime-anchored organobentonite, Adv. Mater. Res. 433–440 (2012) 24–28.

[29] M. Schuster, M. Schwarzer, Selective determination of palladium by on-line column preconcentration and graphite furnace atomic absorption spectrometry, Anal. Chim. Acta 328 (1996) 1–11.

[30] K.S. Patel, P.C. Sharma, P. Hoffmann, Graphite furnace-atomic absorption spectrophotometric determination of palladium in soil, Fresenius J. Anal. Chem. 367 (2000) 738–741.

[31] M. Shamsipur, M. Ramezani, M. Sadeghi, Preconcentration and determination of ultratrace amounts of palladium in water samples by dispersive liquid-liquid microextraction and graphite furnace atomic absorption spectrometry, Microchim. Acta 166 (2009) 235–242.

[32] P. Liang, E. Zhao, F. Li, Dispersive liquid–liquid microextraction preconcentration of palladium in water samples and determination by graphite furnace atomic absorption spectrometry, Talanta 77 (2009) 1854–1857.

[33] D.C. Gregorie, Determination of platinum, palladium, ruthenium and iridium geological materials by inductively coupled plasma mass spectrometry with sample introduction by electrothermal vaporization, J. Anal. At. Spectrom. 3 (1988) 309–314.

[34] I. Jarvis, M.M. Totland, K.E. Jarvis, Determination of the platinum-group elements in geological materials by ICP-MS using microwave digestion, alkali fusion and cation-exchange chromatography, Chem. Geol. 143 (1987) 27–42.

[35] S. Igarashi, N. Ide, Y. Takagai, High-performance liquid chromatographic–spectrophotometric determination of copper(II) and palladium(II) with 5,10,15,20-tetrakis(4 N-pyridyl)porphine following homogeneous liquid–liquid extraction in the water–acetic acid–chloroform ternary solvent system, Anal. Chim. Acta 424 (2000) 263–269.

[36] Y. Haichuan, H. Qiufen, L. Qiang, H. Zhangjie, Y. Guangyu, Simultaneous determination of palladium and platinum by on-line enrichment and HPLC with 4-(2-hydroxynaphthalene-1-ylmethylene)-thiazolidine-2,5-dithione as pre-column derivatization reagent, S. Afr. J. Chem. 58 (2005) 57–60.

[37] X. Dong, Y. Han, Q. Hu, J. Chen, G. Yang, Simultaneous determination of palladium, platinum and rhodium by on-line column enrichment and HPLC with 2,4-dihydroxybenzylidenethiorhodanine as pre-column derivatization reagent, J. Braz. Chem. Soc. 17 (2006) 189–193.

[38] M.H. Hashmi, T. Qureshi, F.R. Chughtai, Spectrophotometric determination of palladium, Microchem. J. 17 (1972) 18–25.

[39] N. Anthemidis, D.G. Themelis, J.A. Stratis, Stopped-flow injection liquid–liquid extraction spectrophotometric determination of palladium in airborne particulate matter and automobile catalysts, Talanta 54 (2001) 37–43.

[40] T. Nakanishi, M. Otomo, Extraction-spectrophotometric determination of palladium(II) with di-2-pyridyl ketone benzoylhydrazone, Anal. Sci. 1 (1985) 161–163.

[41] J. Gao, B. Peng, H. Fan, J. Kang, X. Wang, Spectrophotometric determination of palladium after solid–liquid extraction with 1-(2-pyridylazo)-2-naphthol at 90 °C, Talanta 44 (1997) 837–842.

[42] M. Otomo, 2,2′-Dipyridyl-2-quinolylhydrazone as a reagent for the spectrophotometric determination of metals: the extractive spectrophotometric determination of palladium(II), Anal. Chim. Acta 116 (1980) 161–168.

[43] A. Niazi, A. Azizi, M. Ramezani, Simultaneous spectrophotometric determination of mercury and palladium with thio-Michler's ketone using partial least squares regression and orthogonal signal correction, Spectrochim. Acta A 71 (2008) 1172–1177.

[44] G. Bagherian, M.A. Chamjangali, H. Eskandari, Simultaneous determination of cobalt and palladium in micellar media using H-point standard addition method and partial least square regression, Spectrochim. Acta 67 (2007) 378–384.

[45] K.S. Patel, P.C. Sharma, S.G. Aggarwal, P. Hoffmann, Specific spectrophotometric determination of palladium with N, N′-diphenylbenzimidoylthiourea, Anal. Lett. 33 (2000) 503–511.

[46] M. Arab Chamjangali, G. Bagherian, G. Azizi, Simultaneous determination of cobalt, nickel and palladium in micellar media using partial least square regression and direct orthogonal signal correction, Spectrochim. Acta 62 (2005) 189–196.

[47] R.R. Kozani, J. Mofid-Nakhaei, M.R. Jamali, Rapid spectrophotometric determination of trace amounts of palladium in water samples after dispersive liquid–liquid microextraction, Environ. Monit. Assess. 185 (2013) 6531–6537.

[48] A.K. Malik, K.N. Kaul, B.S. Lark, W. Faubel, A.L.J. Rao, Spectrophotometric determination of cobalt, nickel palladium, copper, ruthenium and molybdenum using sodium isoamylxanthate in presence of surfactants, Turk. J. Chem. 25 (2001) 99–105.

[49] A.A. Ensafi, M. Keyvanfard, Catalytic–kinetic determination of palladium(II) by spectrophotometric method in anionic micellar medium, Anal. Lett. 35 (2002) 423–433.

[50] A. Jabbari, M. Barzegar, M. Mohammadi, Catalytic kinetic spectrophotometric determination of palladium(II) and its application to the determination of traces of propylthiouracil, Indian J. Chem. 44A (2005) 1215–1218.

[51] A.A. Ensafi, M. Keyvanfard, Kinetic-spectrophotometric determination of palladium in hydrogenation catalyst by its catalytic effect on the oxidation of pyrogallol red by hydrogen peroxide, Spectrochim. Acta A 58 (2002) 1567–1572.

[52] B. Tang, H. Zhang, Y. Wang, Flow injection kinetic spectrofluorimetric determination of trace amounts of palladium, Anal. Chim. Acta 511 (2004) 17–23.

[53] J. Boken, S. Thatai, P. Khurana, S. Prasad, D. Kumar, Highly selective visual monitoring of hazardous fluoride ion in aqueous media using thiobarbituric-capped gold nanoparticles, Talanta 132 (2015) 278–284.

[54] G.P. Pandey, A.K. Singh, S. Prasad, L. Deshmukh, A. Asthana, Development of surfactant assisted kinetic method for trace determination of thallium in environmental samples, Microchem. J. 118 (2015) 150–157.

[55] G.P. Pandey, A.K. Singh, L. Deshmukh, S. Prasad, L.J. Paliwal, A. Asthana, S.B. Mathew, A novel and sensitive kinetic method for the determination of malathion using chromogenic reagent, Microchem. J. 113 (2014) 83–89.

[56] R.M. Naik, S. Prasad, B. Kumar, S.B.S. Yadav, A. Asthana, M. Yoshida, Ligand substitution kinetic assay of antitubercular drug isoniazid in pure and pharmaceutical formulations, Microchem. J. 111 (2013) 108–115.

[57] R.M. Naik, S. Prasad, B. Kumar, V. Chand, Kinetic assay of D-penicillamine in pure and pharmaceutical formulations based on ligand substitution reaction, Microchem. J. 111 (2013) 97–102.

[58] R.M. Naik, B. Kumar, A. Asthana, Kinetic spectrophotometric method for trace determination of thiocyanate based on its inhibitory effect, Spectrochim. Acta A 75 (2010) 1152–1158.

[59] V. Chand, S. Prasad, Trace determination and chemical speciation of selenium in environmental water samples using catalytic kinetic spectrophotometric method, J. Hazard. Mater. 165 (2009) 780–788.

[60] R.M. Naik, A. Agarwal, S. Prasad, A.K. Verma, Trace determination of thiosulphate and thioglycolic acid using novel inhibitory kinetic spectrophotometric method, Microchem. J. 93 (2009) 43–48.

[61] R.M. Naik, A. Agarwal, S. Prasad, Determination of trace amounts of mercury(II) in water samples using a novel kinetic catalytic ligand substitution reaction of hexacyanoruthenate(II), Spectrochim. Acta A 74 (2009) 887–891.

[62] R. Prasad, R. Kumar, S. Prasad, A fluorescence quenching-based sensor using new metallo-tetraazaporphyrin dye as a recognition element for aniline assay in aqueous solutions, Anal. Chim. Acta 646 (2009) 97–103.

[63] S. Prasad, R.M. Naik, A. Srivastava, Application of ruthenium catalyzed oxidation of [tris(2-aminoethyl)amine] in trace determination of ruthenium in environmental water samples, Spectrochim. Acta A 70 (2008) 958–965.

[64] R.M. Naik, J. Sarkar, S. Prasad, Kinetic determination of cysteine and thiosulphate by inhibition of Hg(II) catalyzed ligand substitution reaction, Microchem. J. 88 (2008) 45–51.

[65] R.M. Naik, R.K. Tiwari, P.K. Singh, S.B.S. Yadav, A. Asthana, Kinetic determination of silver at trace level based on its catalytic effect on a ligand substitution reaction, Transit. Met. Chem. 33 (2008) 615–623.

[66] R.M. Naik, A. Srivastava, S. Prasad, Highly sensitive catalytic spectrophotometric determination of ruthenium, Spectrochim. Acta A 69 (2008) 193–197.

[67] S. Prasad, Kinetic determination of organosulphur ligands by inhibition: trace determination of cysteine and maleonitriledithiolate (MNDT), Microchem. J. 85 (2007) 214–221.

[68] S. Prasad, Kinetic method for determination of nanogram amounts of copper(II) by its catalytic effect on hexacynoferrate(III)–citric acid indicator reaction, Anal. Chim. Acta 540 (2005) 173–180.

[69] S. Prasad, Catalytic abstraction of cyanide in hexacyanoferrate(II) by mercury(II) in the presence of α-nitroso-β-naphthol as indicator reaction for determination of mercury(II) by kinetic method, Anal. Lett. 37 (2004) 2851–2867.

[70] S. Prasad, T. Halafihi, Development and validation of catalytic kinetic spectrophotometric method for determination of copper(II), Microchim. Acta 142 (2003) 237–244.

[71] S. Prasad, P.C. Nigam, Catalytic kinetic determination of ultratrace amount of ruthenium(III) based on the oxidation of benzylamine by alkaline hexacyanoferrate(III), Talanta 38 (1991) 627–630.

[72] A.P. Szecsy, S.S. Miller, A. Haim, Kinetics of formation and dissociation of complexes of pentacyanoferrate(II) with benzonitrile, dicyanobenzenes and cyanopyridines, Inorg. Chim. Acta 28 (1978) 189–200.

[73] R.C. Weast, CRC Handbook of Chemistry and Physics, 49th ed. The Chemical Rubber Co, Ohio, 1969. D79.

[74] M.C. Mehra, R. Garvie, Catalysis by Pd(II) of ligand exchange between pentacyanoamminneferrate(II) and nitroso-R-salt and its use in spectrophotometric analysis of Pd(II), J. Less Common Met. 68 (1979) 17–21.

[75] S. Prasad, Kinetics and mechanism of exchange of cyanide in hexacyanoferrate(II) by N-methylpyrazinium ion in the presence of mercury(II) as a catalyst, Transit. Met. Chem. 28 (2003) 1–8.