Analytical properties of *p*-[*N,N*-bis(2-chloroethyl)amino]benzaldehyde thiosemicarbazone: spectrophotometric determination of palladium(II) in alloys, catalysts, and complexes

J. Karthikeyan · P. Parameshwara · A. Nityananda Shetty

Abstract *p*-[*N,N*-bis(2-chloroethyl)amino]benzaldehyde thiosemicarbazone (CEABT) is proposed as a new, sensitive, and selective analytical reagent for the spectrophotometric determination of palladium(II). The reagent reacts with palladium(II) in the pH range 1–2 to form a yellow-colored complex. Beer's law is obeyed in the concentration range up to 2.64 µg cm^{-3}. The optimum concentration range for minimum photometric error as determined by Ringbom's plot method is 0.48–2.40 µg cm^{-3}. The yellowish Pd(II)-reagent complex shows a maximum absorbance at 395 nm, with molar absorptivity of 4.05×10^4 dm^3 mol^{-1} cm^{-1} and Sandell's sensitivity of the complex from Beer's data, for $D =$ 0.001, is 0.0026 µg cm^{-2}. The composition of the Pd(II)–CEABT reagent complex is found to be 1:2 (M–L). The interference of various cations and anions in the method were studied. The proposed method was successfully used for the determination of Pd(II) in alloys, catalysts, complexes, water samples, and synthetic alloy mixtures with a fair degree of accuracy.

Keywords Spectrophotometric determination · Pd(II) determination · *p*-[*N,N*-bis(2-chloroethyl)amino]benzaldehyde thiosemicarbazone · Chromogenic reagent

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Introduction

Palladium and its alloys find extensive application in electronic industry (Barnard and Russell 1987), dental alloys (Ohta et al. 1979), and magnetic materials (Loebich and Raub 1973) and are also used as hydrogenation catalysts (Gragor and Henry 1981). Considering these excellent and extensive applications of palladium and its compounds, a reliable and rapid method is often essential for the determination of palladium at micrograms per cubic centimeter level.

The chemistry of transition metal complexes of thiosemicarbazone has been receiving considerable attention largely because of their biological

Table 1 Comparison of the proposed method with other spectrophotometric method for the determination of palladium(II)

Reagent	λ_{max} (nm)	pH	Beer's law range, $\mu g\ cm^{-3}$	ε_{max}	M:L	Reference
Salicylaldehyde thiosemicarbazone	405	1.8–4.0	1.3–6.5	6,400	1:1	Palaniappan (1989)
5-Bromo-salicyaldehyde-4-phenyl-3-thiosemicarbazone	412	0.25 M H_2SO_4	0.2–8	14,200	1:2	Uesugi et al. (1991)
O-Hydroxy acetophenone thiosemicarbazone	370	5–9	1.1–9.5	9,000	1:2	Murthy and Reddy (1992)
4-(Dimethylamino)benzaldehyde thiosemicarbazone	405	2.2–3.6	0.5–1.75	45,900	1:2	Shetty and Gadag (1993)
3-thiophenaldehyde-4-phenyl-3-thiosemicarbazone	355	1 M H_2SO_4	0.4–6	25,000	1:2	Uesugi et al. (1994)
Nicotinaldehyde—4-phenyl-3-thiosemicarbazone	365	3	0.5–8	28,100	1:2	Lee et al. (1995)
Pyridoxal-4-phenyl-3-thiosemicarbazone	460	3.0	0.4–6.4	21,900	1:1	Sarma et al. (2002)
Piperonal thiosemicarbazone	363	0.5 M HCl	0.5–2.45	38,000	1:2	Prakash et al. (2003)
4-(N,N-diethylamino) benzaldehyde thiosemicarbazone	408	3	0.36–3.24	33,300	1:2	Parameshwara et al. (2007)
N-ethyl-3-carbazolecarbaxaledehyde thiosemicarbazone	410	4	0.0–6.6	16,470	1:1	Reddy et al. (2008)
p-[N,N-Bis (2-chloroethyl) amino] benzaldehyde thiosemicarbazone	395	0.2 M HCl	0.48–2.40	40,500	1:2	Present method

PM present method, NR not reported

and carcinostatic activities. These biological activities include antitumor, antibacterial, antiviral, antimalarial, and anticancer activities. Besides they are potential pesticides and fungicides. Thiosemicarbazone are good complexing agent too. They are also excellent analytical reagents used in gravimetric and spectrophotometric determinations. The literature survey shows that a large number of thiosemicarbazones have been reported for the spectrophotometric determination of palladium. The proposed work describes the spectrophotometric determination of Pd(II) using p-[N,N-bis(2-chloroethyl)amino]benzaldehyde thiosemicarbazone (CEABT). The proposed method, when compared with other spectrophotometric methods, is found to be sensitive and selective. These are summarized in Table 1. The interference of other ions has been studied. The method is also employed for the micrograms per cubic centimeter level estimation of palladium in its alloys, complexes, catalysts, water samples, and synthetic alloy mixtures.
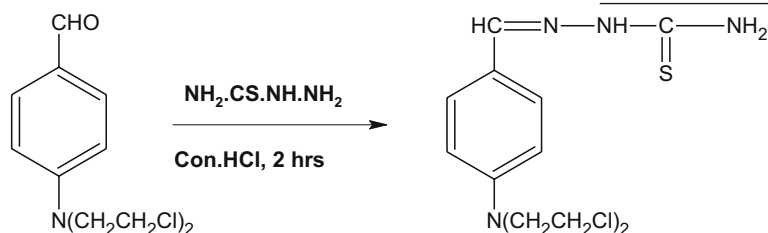
Experimental

Apparatus and reagents

A Shimadzu (Model-160A) double beam UV/VIS spectrophotometer with 1.0 cm quartz cell and ELICO pH meter (LI 127) with a combination of electrodes were used for the measurements of absorbance and pH, respectively. All reagents and chemicals used were analytically or chemically pure grade.

Stock solution of palladium chloride solution

A stock solution was prepared by dissolving calculated amount of $PdCl_2$ (1 g) in minimum amount 2 mol dm^{-3} hydrochloric acid and the solution was made up to 1 l using doubly distilled water and standardized by dimethylglyoxime method (Vogel 1964) and thioacetamide method (Parameshwara et al. 2006). This stock solution was further diluted to get 5×10^{-4} mol dm^{-3} with double-distilled water.

Synthesis and characterization of CEABT

The starting material *p*-[*N*,*N*-bis(2-chloroethyl)amino]benzaldehyde prepared by the reported procedure (Elderfield et al. 1958). The purity of the compound checked by the elemental analysis and by melting point. The title compound was prepared by simple condensation reaction of ethanolic solution of *p*-[*N*,*N*-bis(2-chloroethyl)amino]benzaldehyde (20 cm³) with thiosemicarbazide in water (5 cm³) with hydrochloric acid (35%, 0.5 cm³) taken into a 250-mL round-bottom flask, which was refluxed using steam bath for around 2 h. The yellow powder precipitated after cooling to 5°C. The resulting precipitate were collected by filtration and then washed with ethanol followed by ether and small quantities of the product was recrystallized from acetone to get a pure shiny yellow crystals. The product is characterized by the spectrochemical method and also by the elemental analysis (yield 80%; decomposition point 195 ± 5°C). [Found (Calcd), % are C = 45.70 (45.14), H = 5.19 (5.02), N = 17.45 (17.55), S = 9.81 (10.03)], IR (KBr, υ, cm^{-1}), 3,302 and 3,140 (–NH–), 1,604 (C = N), and 1,180 (C = S). The mass spectrum of the reagent shows signal at 319 (*m/z*) corresponding to its molecular ion peak.

p-[*N*,*N*-bis(2-chloroethyl)amino]benzaldehyde thiosemicarbazone solution (1.27×10^{-4} mol dm^{-3})

This solution was prepared by dissolving the requisite amount of *p*-[*N*,*N*-bis(2-chloroethyl)amino]benzaldehyde thiosemicarbazone in a known volume of pure acetone.

Preparation of HCl solution

Solutions of 0.2 mol dm^{-3} HCl prepared in double-distilled water.

General procedure

Different aliquots of solutions, containing 0.48–2.40 μg of Pd(II) was pipetted out into a 25 cm³ standard flask, 2–3 cm³ of CEABT (5×10^{-4} mol dm^{-3}), 1 cm³ of 0.2 mol dm^{-3} HCl, 5 cm³ dimethylformamide (DMF), and 5 cm³ of ethanol were added and the mixture was diluted up to the mark with double-distilled water (25 cm³ standard flask). After 5 min, the absorbance was measured at 395 nm against a reagent blank. The palladium content in an unknown sample was determined using a concurrently prepared calibration graph.

Analysis of Pd(II) in alloys

Dissolve 0.1–0.2 g of the alloy sample was carefully decomposed with minimum amount of concentrated HCl by evaporating to near dryness. The residue was then cooled, dissolved in minimum amount of dilute HCl, and made up to a 250-mL standard flask. Then the stock solution was standardized by the dimethylglyoximate method and thioacetamide method. Aliquots of this solution were used for the estimation of palladium as per the proposed procedure.

Determination of Pd(II) in complexes

Palladium complexes with thiosemicarbazide, dimethylglyoxime, thiocarbohydrazide, and sali-

cyloylhydrazide were prepared and purified as per the reported procedure (Yoe and Jones 1944; Vogel 1964). A known weight of the complex was carefully decomposed with minimum amount of concentrated HCl and evaporated to near dryness. The residue was dissolved with minimum amount of dilute HCl and in distilled water and made up to a known volume. Then the stock solution was standardized by the dimethylglyoximate method and thioacetamide method. It was used for the estimation of palladium as per the proposed procedure.

Determination of Pd(II) in catalysts

A known weight (0.3 g) of the catalysts such as palladium–charcoal and palladium–CaCO$_3$, palladium–asbestos (supplied by S.D.fine) was digested with concentrated HCl to near dryness. The residue was treated with dilute HCl, filtered, if necessary, and made up to a 250-mL standard flask with double-distilled water. Then the stock solution was standardized by the dimethylglyoximate method and thioacetamide method. Suitable aliquots of this solution were used for the estimation of palladium as per the proposed procedure.

Determination of Pd(II) in synthetic mixtures

Several synthetic mixtures of varying compositions containing palladium(II) and diverse ions of known concentrations were analyzed for palladium by the proposed method.

Results and discussion

Absorption spectra

CEABT forms a yellow-colored sparingly soluble complex with Pd(II) in the aqueous medium. The complex was found to be soluble in the aqueous solution containing 20% (*v/v*) of DMF and 20% (*v/v*) of ethanol. The absorption spectrum of the Pd(II)–CEABT complex was recorded against the reagent blank. Similarly, the absorption spectrum of the reagent was recorded against the solvent as blank. The absorption spectra of both the reagent
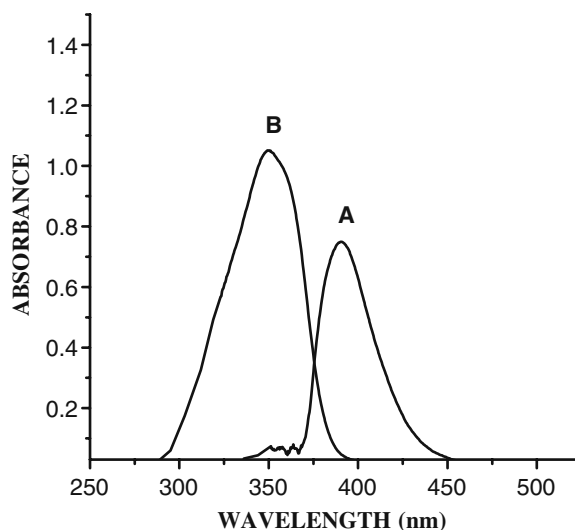

Fig. 1 (*A*) Absorption spectra of Pd(II)–CEABT complex vs CEABT blank, (*B*) absorption spectra of CEABT vs acetone blank. [Pd(II)] = 0.96 μg cm^{-3}

and the complex are shown in Fig. 1. It is evident from the spectra that the Pd(II)–CEABT complex and the reagent have maximum absorbance at 395 and 350 nm, respectively. The reagent has a negligibly small absorbance at the λ$_{max}$ of the complex. Thus, further absorbance measurements of the complex were made at 390 nm.

Composition of the Pd(II)–CEABT complex

The composition of the Pd(II)–CEABT complex was studied by Job's method of continuous variation and also by the mole ratio method. In these methods, equimolar solutions of Pd(II) and CEABT were used {[Pd(II)] = [CEABT] = 1.127×10^{-4} M}. The results shows that continuous variation method shows a maximum at the mole fraction of palladium 0.335, indicating the formation of a 1:2 complex (Pd–CEABT). Further support to this comes from the results of mole-ratio method as 1:2 (Pd–CEABT).

Effect of the medium

The reagent forms a sparingly soluble yellow complex with Pd(II) in aqueous medium and the

complex was found to be completely soluble in aqueous DMF–ethanol medium, containing 20% (*v/v*) of DMF and 20% (*v/v*) of ethanol. Preliminary investigations of the pH studies using different buffers showed that the complex had higher absorbance in acid medium. Further attempts were made to investigate the effect of different acids such as HCl, H_2SO_4, HNO_3, and CH_3COOH on the absorbance of the complex. These studies revealed that the maximum absorbance of the complex was in the hydrochloric acid medium. In order to find out the optimum concentration of hydrochloric acid for complete color development, absorbance measurements were carried out at different concentrations of hydrochloric acid. The results are presented in the form of a plot of absorbance versus molarity of HCl (Fig. 2). It is clear from the plot that the absorbance is constant and maximum in the concentration range 0.08–0.40 M of HCl.

Rate of reaction and stability of color

The absorbance of Pd–CEABT complex was measured at regular intervals of time. The results are presented in a plot of absorbance versus time (Fig. 3). These results show that the color reaction between Pd(II) and CEABT is fast and color development takes place soon after the mixing of
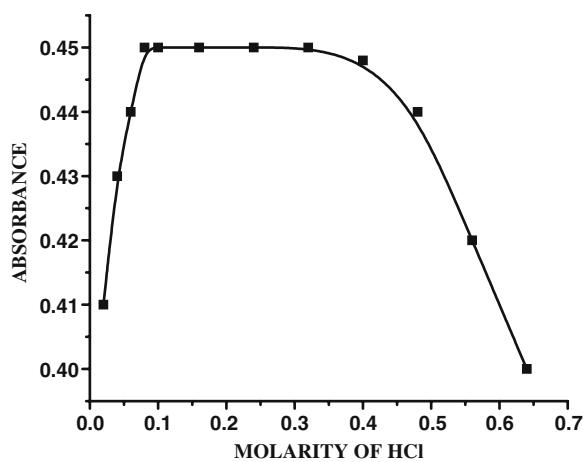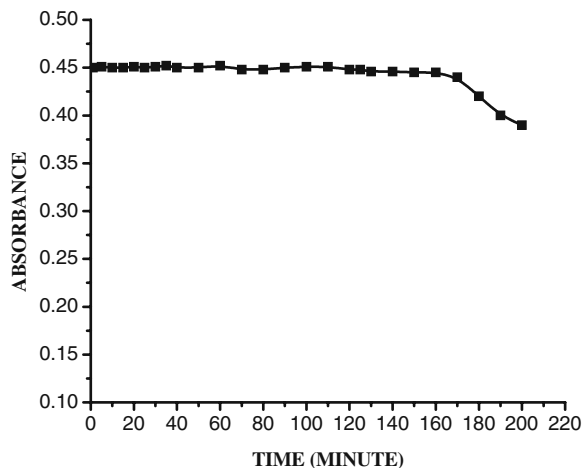

Fig. 3 Color stability of Pd(II)–CEABT complex, $[Pd(II)] = 1.5 \ \mu g \ cm^{-3}$

the reagents. However, the reaction mixture was allowed to stand for 5 min before measuring its absorbance to ensure the maximum color development. It is also seen from the graph that the color of the solution remains stable at least for about 120 min.

Effect of reagent concentration

The effect of reagent concentration on the color development was studied by measuring the absorbance of the solutions containing varying concentrations of the reagent and a fixed amount of Pd(II). The results are presented as a plot of absorbance against concentration of the reagent (Fig. 4). It is evident from the graph that 2 moles of CEABT per mole of Pd(II) are required for the maximum color development. It is also observed that tenfold excess of the reagent over the quantity of the reagent required does not show any substantial change in the absorbance.

Order of addition of reagents

Experiments were carried out with a fixed amount of Pd(II) and changing the order of addition of the reagents. The results indicate that the order of the addition of reagent does not have any effect on the absorbance of the complex.
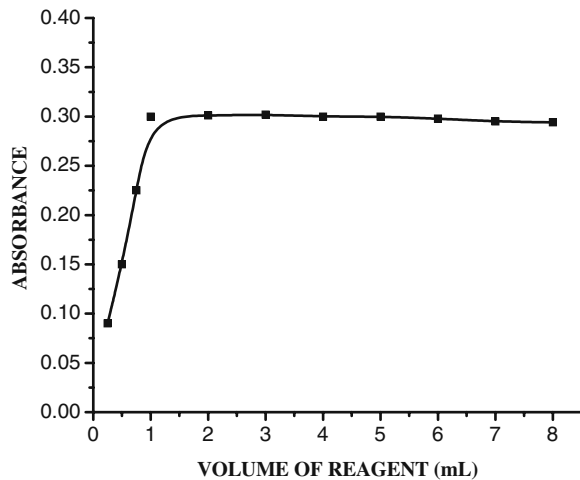

Fig. 2 Effect of concentration of HCl on absorbance, $[Pd(II)] = 1.5 \ \mu g \ cm^{-3}$

Fig. 4 Effect of reagent concentration on absorbance of Pd(II) – CEABT complex [Pd(II)] = 1.127×10^{-4} M:[CEABT] = 2.254×10^{-4} M, volume of Pd(II) taken = 1 mL
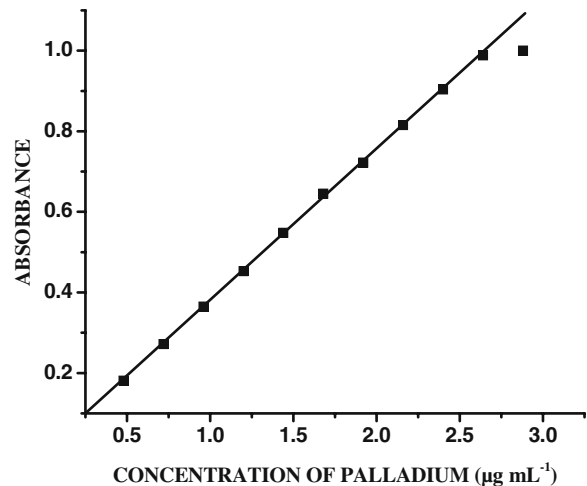

Fig. 5 Beer's law plot of Pd(II)–CEABT complex, [Pd(II)] = 0.40–2.40 μg cm^{-3}

Effect of temperature

The effect of temperature on the maximum color development was studied by performing the color reactions at different temperature and measuring absorbance as per the procedures. These results show that there is no appreciable change in the absorbance values of both the complexes up to 60°C. But at higher temperature, the absorbance value tends to decrease gradually. In the present work, the color reaction is carried out at laboratory temperature (27–30°C).

Beer's law and optimum concentration range

The spectrophotometric determination are based on Beer–Lambert's law, the mathematical expression of which is as follows $A = \varepsilon c l$, where 'ε' is molar absorption coefficient, 'c' is concentration of the color absorbing species in the solution, and 'l' is length of the colored medium. When 'l' is kept constant, absorbance is directly proportional to concentration. In order to determine the concentration range in which Beer's law is valid, absorbance values of Pd(II)–CEABT complex were measured under optimum conditions at various concentrations of Pd(II) in the solution. The results are presented in the form of a plot of absorbance versus molar concentration of palladium

(Fig. 5). It is seen from the graph that Beer's law is obeyed up to 2.64 μg of Pd(II). The optimum concentration range for minimum photometric error was determined by Ringbom plot method. The percentage transmittance of the complex solutions were plotted versus log of Pd(II) concentration (Fig. 6). The linear portion of the graph indicates that Pd(II) can be precisely determined in the range 0.48–2.40 μg mL^{-1}.
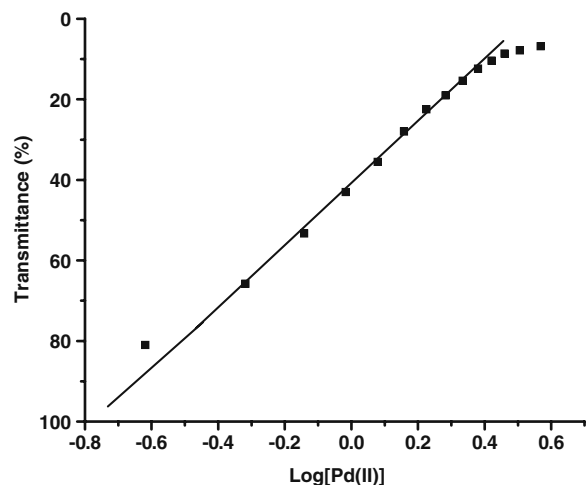

Fig. 6 Ringbom plot of complex. Pd(II)–CEABT, [Pd(II)] = 0.40–2.40 μg cm^{-3}

Table 2 Tolerance limit of diverse ions in the determination of 0.96 μg mL^{-1} Pd(II)

Ion added	Tolerance limit (μg mL^{-1})	Ion added	Tolerance limit (μg mL^{-1})
Ba(II)	200	Se(IV) and Sn(IV)	70
Ca(II)	50	U(VI)	400
Mg(II)	30	Mo(VI)	30
Zn(II)	4,000	Fluoride	2,000
Pb(II)	800	Chloride	4,000
Cd(II) and Mn(II)	4,000	Bromide	400
Co(II)	406	Acetate	80
Ni(II)	46	Sulphate	500
Fe(II)	2	Nitrate	500
Fe(II)*	20		
Hg(II)	30	Phosphate	75
La(III), Y(III), Ce(III), Zr(III), and Al(III)	500	Thiocyanate	15
Ru(III)	5	Borate	200
Rh(III)	47	Thiosulphate	60
Tl(III) and Cr(III)	2	EDTA	2

* Using 5% Sodium fluoride as secondary masking agent

Molar absorptivity and Sandell's sensitivity

The molar absorptivity of the Pd(II)–CEABT complex was calculated by measuring the absorbance values of the complexes at different concentration levels of Pd(II). The mean value of molar absorptivity was found to be 4.05×10^4 dm^3 mol^{-1} cm^{-1}. The Sandell's sensitivity of the method is 0.0026 μg cm^{-2}.

Precision and accuracy of the method

To assess the precision and accuracy of the method, determinations were carried out for a set of six measurement of 0.40–2.40 μg mL^{-1} of

Table 3 Determination of palladium(II) in alloys ($n = 5$)

Palladium alloys	Pd(II) taken (%)	Pd(II) found (%)	Relative error (%)
Pd–Rh (90%)	10	9.95 ± 0.04	0.5
Pd–Ni (40%)	10	9.96 ± 0.04	0.4

Table 4 Determination of palladium(II) in catalyst ($n = 5$)

Palladium catalyst	Palladium (certified value) (%)	Palladium found (%)	Relative error (%)
Pd–charcoal catalyst	5	5.01	−0.20
Pd–asbestos catalyst	5	4.98	−0.40

Pd(II), under the optimized experimental conditions. These result reveal that the relative error, standard deviation, and coefficient of variation do not exceed 1.66%, 0.002, and 1.04%, respectively. From these result it is reasonable to infer that the proposed method is precise and accurate.

Effect of foreign ions

The influence of the presence of diverse ions on the absorbance value of Pd(II)–CEABT complex system was studied with 0.96 μg mL^{-1} Pd(II) in the presence of foreign ions. An error of ±2% in the absorbance value was considered as the tolerance limit. The results are presented in Table 2. No interference was observed for the following ions at the amounts in micrograms per milliliter shown: Pb(II) (800); Zn(II), Cd(II), and Mn (4,000); Co(II) (406); Ni(II) (46); Fe(II) (2); Mg(II) and Hg(II) (30); Ba(II) (50); La(III), Y(III), Ce(III), Zr(III), and Al(III) (400); Ru(III) (5); Rh (40); Cr(III) and Tl(III) (2); Se(IV) (50); Sn(IV) (50); U(VI) (400); chloride (4,000); fluoride (2,000); sulfate (500); bromide and acetate (400); and citrate and tartarate (15). However, the presence of Cu(II), Pt(VI), and iodide cause severe interference. The interference of

Table 5 Determination of palladium(II) in complexes ($n = 5$)

Complex	Pd(II) calculated (%)	Pd(II) found (%)	Relative error (%)
Pd(CH$_5$N$_3$S)$_2$Cl$_2$[a]	29.59	29.47	−0.40
Pd(C$_4$H$_7$O$_2$N$_2$)$_2$[b]	31.61	31.51	−0.32
Pd(CH$_6$N$_4$S)$_2$Cl$_2$[c]	27.31	27.30	−0.04
Pd(C$_7$H$_8$O$_2$N$_2$)$_2$Cl$_2$[d]	22.09	22.00	−0.41

[a]Palladium complex of thiosemicarbazide
[b]Palladium complex of dimethylglyoxime
[c]Palladium complex of thiocarbohydrazide
[d]Palladium complex of salicyloylhydrazide

Table 6 Determination of palladium(II) in synthetic alloy mixtures ($n = 5$)

Composition of mixtures ($\mu g\ mL^{-1}$)	Found ($\mu g\ mL^{-1}$)	Relative error (%)
Pd(II) (0.960 ($\mu g\ mL^{-1}$) (A)	0.95 ± 0.03	-1.04
(A) + Ru (III) (0.5 $\mu g\ mL^{-1}$)	0.96 ± 0.04	0.00
(A) + Rh (III) (0.5 $\mu g\ mL^{-1}$)	0.95 ± 0.04	-1.04
(A) + Co(II) (4 $\mu g\ mL^{-1}$) + Ni(II) (0.4 $\mu g\ mL^{-1}$)	0.96 ± 0.05	0.00
(A) + Ni(II) (0.4 $\mu g\ mL^{-1}$) + Rh(III) (1 $\mu g\ mL^{-1}$)	0.95 ± 0.05	-1.04
(A) + Co(II) (2 $\mu g\ mL^{-1}$) + Al(III) (2 $\mu g\ mL^{-1}$)	0.95 ± 0.05	-1.04
(A) + Mn(II) (2 $\mu g\ mL^{-1}$) + Rh(III) (1 $\mu g\ mL^{-1}$)	0.96 ± 0.05	0.00
(A) + Co(II) (0.1 $\mu g\ mL^{-1}$) + Zn(II) (0.5 $\mu g\ mL^{-1}$) + Al(III) (0.5 $\mu g\ mL^{-1}$)	0.95 ± 0.05	-1.04
(A) + Pb(II) (0.5 $\mu g\ mL^{-1}$) + Mn(II) (0.1 $\mu g\ mL^{-1}$) + La(III) (0.5 $\mu g\ mL^{-1}$)	0.96 ± 0.05	0.00

Cu(II) and Pt(IV) is attributed to the formation of their respective colored complexes and hence cause higher absorbance. The presence of iodide decreases the intensity of color.

Applications

The utility of the proposed method was studied by analyzing samples of palladium alloys, catalyst, complexes, and synthetic mixtures of ions. The results are presented in Tables 3, 4, 5 and 6. The results show that the palladium content in the above samples can be estimated by the proposed method with a fair degree of accuracy.

Conclusions

The CEABT forms a 1:2 yellow complex with Pd(II) in the pH range 1–2. Beer's law is valid up to 2.64 $\mu g\ cm^{-3}$ and optimum concentration range for the determination is 0.48–2.40 $\mu g\ cm^{-3}$. The molar absorptivity and Sandell's sensitivity of the method are found to be 4.05 $\times 10^4$ $dm^3\ mol^{-1}\ cm^{-1}$ and 0.0026 $\mu g\ cm^{-2}$, respectively. The relative error and coefficient of variation ($n = 5$) for the method does not exceed 1.66% and 1.38%, respectively. Since the method tolerates a number of metal ions commonly associated with palladium alloys, it can be employed for the determination of palladium content in alloys, complexes, catalysts, and synthetic alloy mixtures without needing elaborate separation.

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