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4-(N,N-DIETHYLAMINO) BENZALDEHYDE THIOSEMICARBAZONE IN THE SPECTROPHOTOMETRIC DETERMINATION OF PALLADIUM

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Summary - 4-(N,N-diethylamino)benzaldehyde thiosemicarbazone(DEABT) is proposed as a sensitive and selective analytical reagent for the spectrophotometric determination of palladium(II). The reagent reacts with palladium (II) in a potassium hydrogen phthalate-hydrochloric acid buffer of pH 3.0, to form a yellow complex. Beer's law is obeyed in the concentration range up to 3.60 μgmL^{-1}. The optimum concentration range for minimum photometric error as determined by Ringbom plot method is 0.36- 3.24 μg mL^{-1}. The yellow Pd(II)-DEABT complex shows a maximum absorbance at 408 nm, with molar absorptivity of 3.33 x 10^4 dm^3 mol^{-1} cm^{-1} and Sandell's sensitivity of the complex from Beer's data, for D=0.001, is 0.0032 μg cm^{-2}. The composition of the Pd(II)-DEABT 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 and model mixtures with a fair degree of accuracy.

INTRODUCTION

Palladium and its alloys find extensive application in electronic industry[1], dental alloys[2], magnetic materials[3] and are also used as hydrogenation catalysts[4]. Considering these excellent and extensive applications of palladium and its compounds, a reliable and rapid method is often essential for the determination of palladium in real samples. Many sensitive methods, like spectrofluorimetry, X-ray fluorescence spectrometry, atomic absorption spectrometry and neutron activation analysis have widely been used for the determination of palladium. However, spectrophotometric methods have gained popularity for palladium determination as advantageous in respect of simplicity and low operating costs.

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The chemistry of transition metal complexes of thiosemicarbazones has been receiving considerable attention largely because of their biological and carcinostatic activities[5, 6]. These biological activities include antitumour, antibacterial, antiviral, antimalarial and anticancer activities[7]. Besides they are potential pesticides and fungicides. Thiosemicarbazone are good complexing agents too[8, 9]. They are also excellent analytical reagents, used in the gravimetric and spectrophotometric determinations[10, 11]. The literature survey shows that a wide variety of thiosemicarbazones have been reported for the spectrophotometric determination of palladium.

The present work describes the spectrophotometric determination of Pd(II) using 4-(N,N-diethylamino)benzaldehyde thiosemicarbazone (DEABT). The proposed method, when compared with other spectrophotometric methods, is found to be sensitive and selective. These are summarized in Table 1. The method is rapid as the palladium-DEABT complex is soluble in water-ethanol-DMF mixture and not requiring any extraction for the complex. The method is employed for the estimation of palladium in its alloys, complexes, catalysts and model mixtures.

TABLE 1. - Comparison of the proposed method with other spectrophotometric method

Reagent	λ_{max} (nm)	pH	Beer's law range, ppm	Molar absorpti--vity (dm^{-3} mol^{-1} cm^{-1})	M:L	Remarks	Ref
Salicylaldehyde thiosemicarbazone	405	1.8 – 4.0	1.3-6.5	6400	1:1	Less sensitive. Sandell's sensitivity is 0.017μg cm^{-2}	12
5-Bromo-salicyaldehyde – 4-phenyl-3-thiosemicarbazone	412	0.25M H_2SO_4	0.2-8	14200	1:2	Less sensitive, Hg(II), Cr(III) & Cu(II) interfere.	13
O-Hydroxy acetophenone thiosemicarbazone	370	5-9	1.1-9.5	9000	1:2	Co(II), Cu(II), Ni(II), Cr(III), Fe(III) interfere.	14
4-Dimethyl amino benzaldehyde thiosemicarbazone	405	2.2 -3.6	0.5-1.75	45900	1:2	Moderately sensitive Sandell's sensitivity is 2.33 x 10^{-3} μg cm^{-2}	15
3-thiophenaldehyde -4-phenyl-3-thiosemicarbazone	355	1M H_2SO_4	0.4-6	25000	1:2	Moderately sensitive . Sandell's sensitivity is 4.3 x 10^{-3} μg cm^{-2}	16
Nicotinaldehyde – 4-phenyl-3-thiosemicarbazone	365	3	0.5 – 8	28100	1:2	Moderately sensitive	17
2,4-Dihydroxy-aceto phenone thiosemicarbazone	NR	3.5	0.7 – 12	13000	1:2	Ag(I), Hg(II) & Cu(II) interfere.	18

TABLE 1. – (Continued)

Pyridoxal-4-phenyl-3-thiosemicarbazone	460	3.0	0.4-6.4	21900	1:1	Moderately sensitive	19
Piperonal thiosemicarbazone	363	0.5M HCl	0.5-2.45	38000	1:2	Moderately sensitive Sandell's sensitivity is 2.8×10^{-3} μg cm^{-2}	20
4-(N,N-diethylamino)benz--aldehyde thiosemicarbazone	408	3.0	0.36 - 3.24	33370	1:2	Moderately sensitive	PM

PM – Present method. NR – Not reported.

EXPERIMENTAL

Reagents and apparatus

A Shimadzu (Model – 160A) double beam UV/VIS spectrophotometer with 1.0 cm quartz cell and ELICO pH meter (LI 127) with combined electrode is used for the measurements of absorbance and pH respectively. All reagents and chemicals used were of analytical or chemically pure grade.

Stock solution of palladium(II) chloride solution

A stock solution of palladium(II) chloride was prepared by dissolving 1.00 g of $PdCl_2$ in minimum amount of 2 mol dm^{-3} hydrochloric acid and the solution was made up to one litre using doubly distilled water. The solution was standardized gravimetrically by the dimethylglyoxime method[21] and volumetrically by thioacetamide method[22]. This stock solution was further diluted to get 9 μg mL^{-1} of palladium with double distilled water.

Synthesis of 4-(N,N-Diethylamino)benzaldehyde thiosemicarbazone

4-(N,N-diethylamino)benzaldehyde thiosemicarbazone (4-DEABT) was synthesized and recrystallized as per the reported procedure[23]. A mixture containing equimolar ethanolic 4-(N,N-diethylamino)benzaldehyde (Aldrich, used as received) and thiosemicarbazide (Aldrich, used as received) were taken into a round bottom flask. The reaction mixture was refluxed on a hot water bath for about 60 minutes. The light yellow colored product obtained was separated by filtration and dried. The product was recrystallized from ethanol. The recrystallized product was checked by elemental analysis and melting point.

4-(N,N-diethylamino)benzaldehyde thiosemicarbazone solution (0.008 %)

This solution was prepared by dissolving of 4-(N,N-diethylamino)benzaldehyde thiosemicarbazone in a known volume of pure acetone.

Buffer solutions

Solutions of 0.2mol dm^{-3} potassium hydrogen phthalate and hydrochloric acid were prepared in double distilled water. The solutions are mixed in required portions to get the desired pH.

Procedure

Different aliquots of solutions, containing 9.00 – 81.00 μg of Pd (II) were pipetted out into a 25 mL standard flask, 5 mL of buffer(pH 3.0), 2-3 mL of 4-DEABT [Pd:R:1:2], 5 mL dimethylformamide, 5 mL of ethanol were added and the mixture was diluted to 25 mL with distilled water. After 5 minutes the absorbance was measured at 408 nm against a reagent blank. The palladium content was determined using a concurrently prepared calibration graph.

RESULTS AND DISCUSSION

Absorption spectra

The absorption spectrum of the Pd(II)- DEABT complex is recorded against the reagent blank. Similarly, the absorption spectrum of the reagent is recorded against the solvent as blank. The absorption spectra of both the reagent and the complex are shown in Fig. 1.

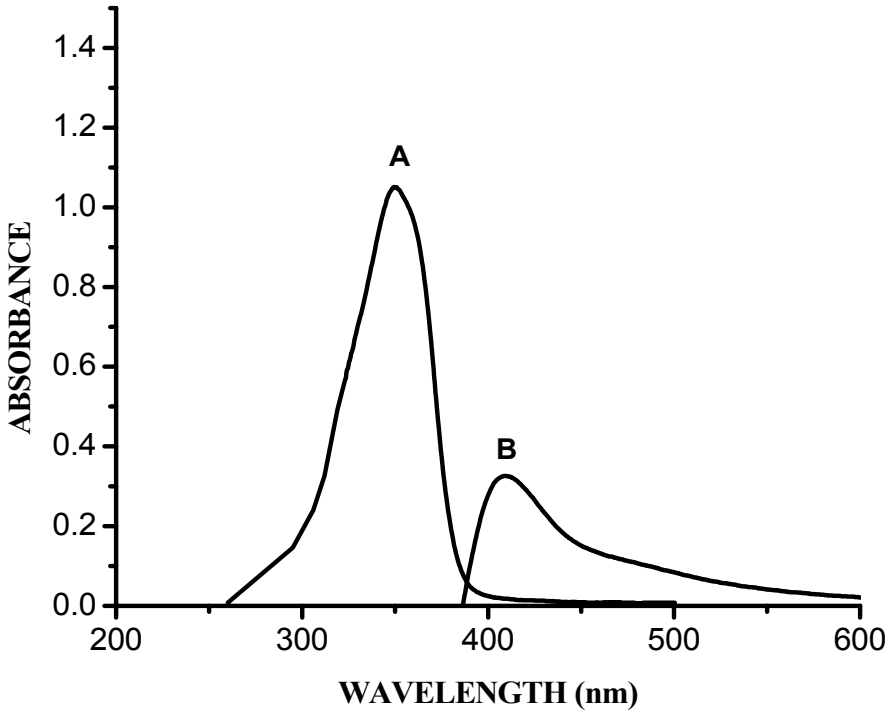

FIGURE 1. – (A) Absorption spectra of DEABT vs acetone blank. (B) Absorption spectra of Pd(II)-DEABT Complex vs reagent blank.

The spectra obtained reveal that the Pd(II)- DEABT complex and the reagent have maximum absorbance at 408 nm and 360 nm, respectively. The reagent has a negligibly small absorbance at the λ_{max} of the complex, and hence, does not interfere with the determination of palladium. Thus, further absorbance measurements of the complex were made at 408 nm.

Effect of the pH

The reagent forms a sparingly soluble yellow complex with Pd(II) in aqueous medium and the complex was found to be completely soluble in DMF-ethanol medium. Preliminary investigations of pH studies using different buffer solutions, each differing by 0.2 pH units were prepared and the color was developed at different pH, in presence of these buffers. The absorbance values of each of the solutions were measured. It was observed that the absorbance values were maximum and remained steady in the pH range 2.6-3.4. But, outside this pH range, the observed absorbance values were lower. Therefore, for all subsequent studies, the pH was maintained at an optimum level of 3.0.

Composition of the Pd(II)- DEABT complex and effect of reagent concentration

The composition of the Pd(II) – DEABT complex was studied by Job's method of continuous variation[24] and also by the mole ratio method.[25] In these methods, equimolar solutions of Pd(II) and DEABT were used. The continuous variation method shows a maximum at the mole fraction of palladium is 0.335, indicating the formation of a 1:2 complex (Pd:R). Further support to this, comes from the results of mole-ratio method.

The effect of reagent concentration on the color development was studied by varying the concentration of the reagent with a fixed amount of Pd(II). It was found that 2 moles of DEABT per mole of Pd(II) was required for maximum color development. Further more, 10 fold excess of the reagent did not show any substantial change in the absorbance.

Order of addition of reagents, rate of reaction and stability of color

The order of the addition of the reagent did not have any effect on the absorbance of the complex. The color reaction between Pd(II) and DEABT was found to be fast and color development took place soon after the mixing of the reagents. However, the reaction mixture was allowed to stand for five minutes before measuring its absorbance to ensure the maximum color development. The color of the solution remained stable for about 120 minutes.

Validity of Beer's law, molar absorptivity, Sandell's sensitivity

In order to determine the concentration range in which Beer's law is valid, absorbance values were measured at various concentrations of Pd(II) in the solution. The Beer's plot (Fig 2) shows that, Beer's law is obeyed up to 3.60 μg of Pd(II). The optimum working range, obtained from Ringbom plot[26] was found to be 0.36 – 3.24 μg mL^{-1} (Fig. 3). Molar absorptivity of the complex was calculated and is 3.33 x 10^4 dm^3 mol^{-1} cm^{-1}. The Sandell's sensitivity of the method is 0.0032 μgcm^{-2}.

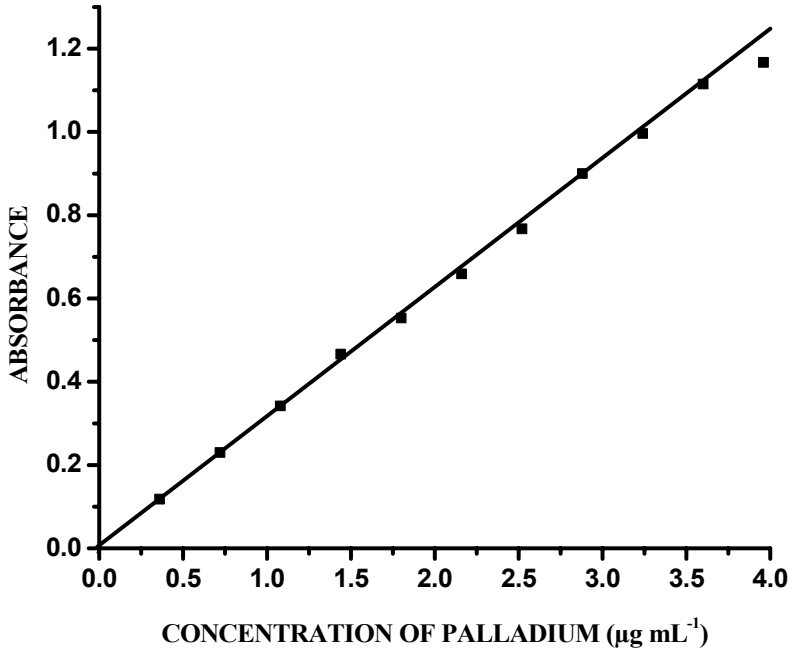

FIGURE 2. – Beer's law plot for Pd(II)-reagent complex.

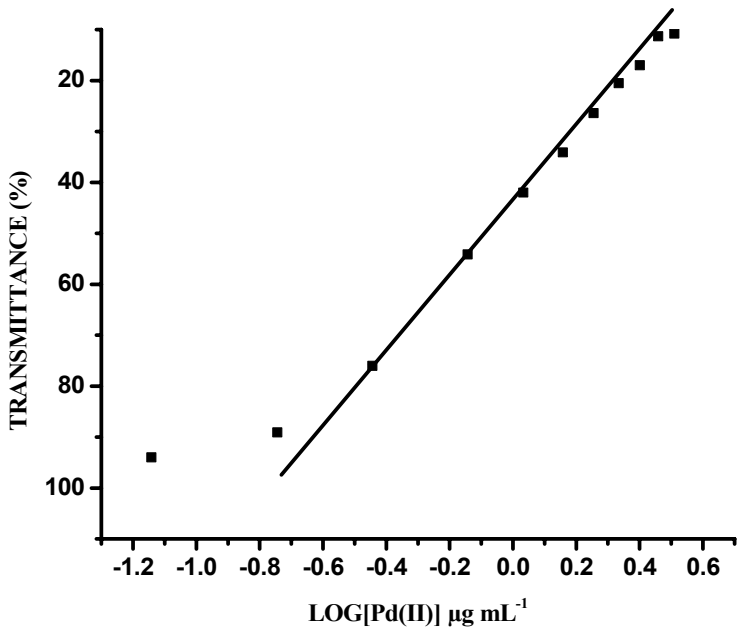

FIGURE 3. – Ringbom plot for Pd(II)-reagent complex.

Accuracy and precision

To assess the precision and accuracy of the method, determinations were carried out for a set of six measurement of 0.48-3.24 μg mL^{-1} of Pd(II), under the optimized experimental conditions. The results are presented in Table 2. These result reveal that the relative error, standard deviation and co-efficient of variation do not exceed 1.38 %, 0.014 and 1.52 % respectively. From these results it is reasonable to infer that the proposed method is precise and accurate.

TABLE 2. - Precision and accuracy in the determination of palladium(II)(n=6)

Palladium, μg mL^{-1}		Relative error (%)	Standard deviation	Students "t" value*	Coefficient of variation (%)
Taken	Found				
0.48	0.48	0.00	0.002	0.00	0.43
0.72	0.71	-1.38	0.011	2.23	1.52
0.96	0.95	-1.04	0.011	2.23	1.15
1.20	1.19	-0.83	0.010	2.45	0.84
1.44	1.42	-1.38	0.011	4.45	0.76
1.68	1.66	-1.18	0.007	6.36	0.42
1.92	1.90	-1.04	0.007	7.00	0.31
2.16	2.15	-0.46	0.010	2.45	0.46
2.40	2.39	-0.42	0.011	2.23	0.46
2.64	2.62	-0.75	0.010	4.90	0.38
2.88	2.86	-0.69	0.012	4.08	0.41
3.24	3.22	-0.62	0.014	3.50	0.43

n=Number of average determination

* Students 't' test value for 5% level of significance is 2.57

Effect of foreign ions

The influence of the presence of various diverse ions on the absorbance value of Pd(II) – DEABT complex system was studied with 0.72 μg mL^{-1} Pd(II) in the presence of foreign ions. An error of ±2 % in the absorbance value was considered as tolerance limit. No interference was observed for the following ions at the amounts in μgmL^{-1} shown: Pb(II) (40), Zn(II)(200), Cd(II) and Mn(400), Co(II) (40), Ni(II) (400), Mg(II) and Hg(II) (20), Ba(II) (160), La(III) and Y(III), (200), Zr (III)(400), Ru(III)(8), Rh(20), Fe(III)(40), Cr(III) and Tl(III)(2), Se(IV)(50), Sn(IV)(5), U(VI)(400), chloride(200), fluoride(300), sulfate, acetate and phosphate (400), borate, nitrate and tartarate (120), citrate(80). However, the presence of Cu(II), Pt(VI) and iodide cause severe interference. The interference of 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.

Analytical applications

The proposed spectrophototmetric method is employed for the determination of palladium(II) in alloys, catalysts, complexes and model mixtures of ions.

Determination of the palladium alloys

0.1-0.2 g of the alloy sample was carefully dissolved in aqua-regia, evaporated to near dryness, and cooled to room temperature. The residue was then dissolved in minimum amount of dilute HCl and made up to a 250 mL. The stock solution was standardized gravimetrically by the dimethylglyoximate method[21] and volumetrically by thioacetamide method[22]. Aliquots of this solution were used for the estimation of palladium as per the proposed procedure. The results are presented in the Table 3.

TABLE 3. – Analysis of palladium alloys (n=5)

Palladium alloys	Pd(II) taken μg mL^{-1}	Pd(II) found μg mL^{-1}	Relative error (%)	Standard deviation	*Students "t" test	Coefficient of variation (%)
Pd – Rh (90 %)	1.65	1.64	-0.61	0.005	4.47	0.36
Pd – Ni (40 %)	2.14	2.15	+0.46	0.007	3.14	0.33

* Students 't' test value for 5% level of significance is 2.57

Determination of palladium in complexes

Palladium complexes with thiosemicarbazide, dimethylglyoxime, thiocarbohydrazide and salicyloylhydrazide were prepared and purified as per the reported procedures.[27-29] A known weight of the complex was carefully decomposed with minimum amount of aqua-regia and evaporated to near dryness. The residue was dissolved with minimum amount of dilute HCl and made up to a known volume using double distilled water. Then the stock solution was standardized gravimetrically by the dimethylglyoximate method[21] and volumetrically by the thioacetamide method[22]. It was used for the estimation of palladium as per the proposed procedure. The results are presented in Table 4.

TABLE 4. – Determination of palladium(II) in complexes (n=5)

Complex	Palladium calculated (%)	Palladium found (%)	Relative error (%)
[a]$Pd(CH_5N_3S)_2Cl_2$	29.59	29.51	-0.27
[b]$Pd(C_4H_7O_2N_2)_2$	31.61	31.54	-0.22
[c]$Pd(CH_6N_4S)_2Cl_2$	27.31	27.26	-0.18
[d]$Pd(C_7H_8O_2N_2)_2Cl_2$	22.09	22.02	-0.32

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

Determination of palladium in catalysts

A known weight (0.3g) of the catalyst such as palladium-charcoal and palladium-asbestos was digested with aqua-regia to nearly dryness. The residue was treated with dilute HCl, filtered and made up to a known volume with double distilled water. The stock solution was standardized gravimetrically by the dimethylglyoximate method[21] and volumetrically by the thioacetamide method[22]. Suitable aliquots of this solution were used for the estimation of palladium as per the proposed procedure. The results are presented in Table 5.

TABLE 5. – Determination of palladium(II) in catalysts(n=5)

Palladium catalyst	Palladium (Certified value) (%)	Palladium found (%)	Relative error (%)
Pd-Charcoal catalyst	5.00	5.01	+0.20
Pd-Asbestos catalyst	5.00	5.02	+0.40

Determination of Palladium in model mixtures

Several model mixtures of varying compositions, containing palladium(II) and diverse ions of known concentrations were analyzed for palladium by the proposed method. The results are given in Table 6.

TABLE 6. – Determination of palladium(II) in model mixtures of metal ions (n=4)

Composition of mixtures ($\mu g\ mL^{-1}$)	Found ($\mu g\ mL^{-1}$)	Relative error (%)
Pd(II) (0.720 ($\mu g\ mL^{-1}$) (A)	0.71	-1.38
(A) + Ru (III)(0.5($\mu g\ mL^{-1}$)	0.71	-1.38
(A) + Rh (III)(0.5($\mu g\ mL^{-1}$)	0.71	-1.38
(A) + Co(II) (2$\mu g\ mL^{-1}$) + Ni(II) (1.0 $\mu g\ mL^{-1}$)	0.72	0.00
(A) + Ni(II) (1.0 $\mu g\ mL^{-1}$) + Rh(III) (0.5 $\mu g\ mL^{-1}$)	0.71	-1.38
(A) + Mn(II) (1 $\mu g\ mL^{-1}$) + Rh(III) (0.4 $\mu g\ mL^{-1}$)	0.72	0.00
(A) + Pb(II) (0.5 $\mu g\ mL^{-1}$) + Mn(II) (0.1 $\mu g\ mL^{-1}$) + La(III)(0.2 $\mu g\ mL^{-1}$)	0.72	0.00

CONCLUSIONS

The DEABT forms a 1:2 yellow complex with Pd(II) .Beer's law is valid up to 3.60 $\mu g\ mL^{-1}$ and optimum concentration range for the determination palladium is 0.36 – 3.24 $\mu g\ mL^{-1}$. The molar absorptivity and Sandell's sensitivity of the method are found to be 3.33×10^4 $dm^3\ mol^{-1}\ cm^{-1}$ and 0.0032 $\mu g cm^{-2}$ respectively. The relative error and coefficient of variation (n=5) for the method does

not exceed 1.38 % and 1.52 % 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 model mixtures.

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