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Spectrophotometric Determination of Palladium(II) Using 4-(Dimethylamino)benzaldehyde Thiosemicarbazone

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A simple, rapid, and selective spectrophotometric method is proposed for the determination of palladium(II), using 4-(dimethylamino)benzaldehyde thiosemicarbazone (DMABT) as a spectrophotometric reagent. The reagent forms a 1:2 complex (Pd:Reagent) with Pd(II) in the pH range 2.2—3.6. The complex is soluble in aqueous solution containing 20% acetone and 30% ethanol by volume. Beer's law is valid upto 2.3 ppm of palladium. The molar absorptivity is 4.59×10^4 dm^3 mol^{-1} cm^{-1} and Sandell's sensitivity 2.33×10^{-3} μg cm^{-2}. The method tolerates large number of cations and anions.

Thiosemicarbazones are a class of compounds which are widely employed as analytical reagents for wide variety of metals in different quantitative methods of analysis. Spectrophotometry is one of the methods, in which thiosemicarbazones are extensively used as colorimetric reagents for several metals. Thiosemicarbazones act as chelating agents by bonding through the sulfur atom and the hydrazino nitrogen atom. Depending upon the types of aldehyde or ketone used for condensation, thiosemiacarbazones can act as monodentate, bidentate or multidentate complexing agents for metal ions, producing highly colored complexes. These colored complexes are then used in the selective and sensitive determination of metal ions.

Several thiosemicarbazones have been reported in the literature as spectrophotometric reagents for palladium. Some of the simple thiosemicarbazones used are 4-(ethylsulfonyl)benzaldehyde thiosemicarbazone,1) nicotinaldehyde thiosemicarbazone,2) phthalimide dithiosemicarbazone,3) glyoxal dithiosemicarbazone,4) Furoin thiosemicarbazone,5) 2-quinolinecarbaldehyde thiosemicarbazone,6) phenanthraquinone monothiosemicarbazone,7) 2- furaldehyde thiosemicarbaone,8) 1, 3- cyclohexanedionebis(thiosemicarbazone),9) *p*-anisaldehyde thiosemicarbazone,10) and salicylaldehyde thiosemicarbazone.11)

In the present work, DMABT has been proposed as a new spectrophotometric reagent for palladium(II). The optimum conditions for maximum color development, the sensitivity and selectivity of the method and the effect of the presence of various ions on the accuracy of the method have been investigated.

Experimental

Reagents and Apparatus. The chemicals used were of Anala R or chemically pure grade.

A Shimadzu UV-visible spectrophotometer (UV-160A) and 10 mm fused silica cells were used for the absorbance measurements.

Palladium(II) Chloride Solution. A stock solution of palladium(II) was prepared by dissolving about 1.0 g of palladium chloride in minimum volume of concd HCl and then diluted to one liter with doubly distilled water. The stock solution was standardised gravimetrically by dimethylglyoximate method.12) This solution was further diluted so as to give palladium content of 7.25 μg ml^{-1}.

Reagent Solution. The reagent, DMABT (Fig. 1) was prepared following the procedure reported in the literature13) and recrystallized from 40—60% ethanol (mp 208 °C). The purity of the compound was checked by elemental analyses. A twice recrystallized product was used for the preparation of 0.5% reagent solution in acetone.

Solutions of Foreign Ions. Solutions of various metal ions were prepared by dissolving the salts of the metals in distilled water or in suitable dilute acids and making up to a known volume. The solutions of various anions were prepared by dissolving the alkali metal salts in water.

Buffer Solution. A buffer solution of pH 3.0 was prepared by mixing proper proportions of hydrochloric acid and potassium phthalate solutions.

Procedure. An aliquot of palladium chloride solution containing 10—100 μg of palladium was taken in a 50 ml standard flask. Ten ml of buffer solution containing hydrochloric acid and potassium phthalate was added followed by the addition of 2 ml of 0.5% solution of DMABT. Then 10 ml of acetone and 15 ml of ethanol were added and finally, the solution was made up to 50 ml with distilled water. The contents were mixed well and kept standing for five minutes to develop the color fully. The absorbance of the complex was then measured at 405 nm using 10 mm matched cell against a reagent blank.

Analysis of Palladium Complexes. Palladium complexes of some sulfur–nitrogen donor ligands were prepared as per the reported procedures14—16) and their purities checked by elemental analyses. A known weight of the complex was decomposed with aqua regia, heated to near dryness, dissolved in minimum volume of dilute hydrochloric acid and made up to a known volume. The solution was diluted to the required concentration levels and appropriate known volume of the solution was subjected to color development with the reagent, as per the recommended procedure. The absorbance of the solution was measured at 405

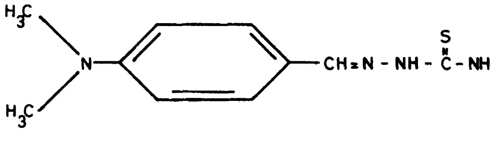

Fig. 1. 4-(Dimethylamino)benzaldehyde Thiosemicarbazone.

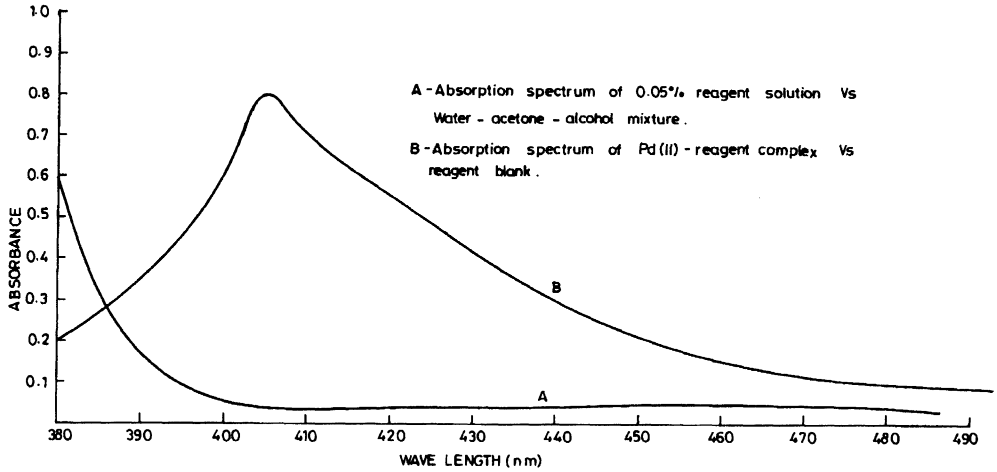

Fig. 2. Absorption spectra of the reagent and Pd(II)–reagent complex.

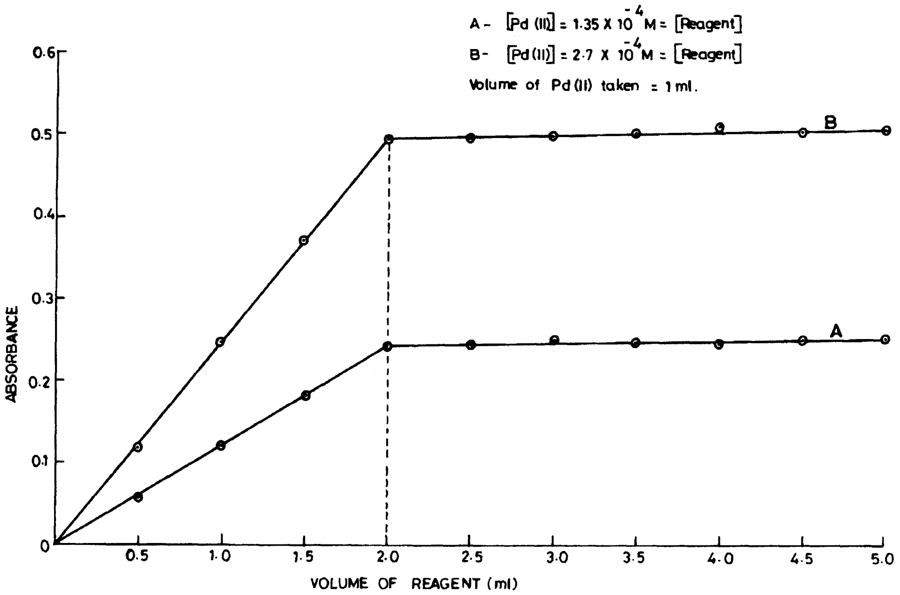

Fig. 3. Mole ratio graph for Pd(II)–reagent system.

nm against a reagent blank.

Results and Discussion

Spectral Characteristics. DMABT forms a yellow colored, sparingly soluble complex with palladium(II). The complex is however, found to be soluble in a solution containing 20% acetone and 30% ethanol. The yellow solution of the palladium complex shows an absorption maximum at 405 nm, in the visible region. The absorbance of the reagent at the wavelength, is found to be negligibly small (Fig. 2).

Composition of the Complex. The composition of the palladium(II) complex with DMABT was studied by the method of Job's continuous variation[17,18] and also by the mole ratio method.[19]

In both of these methods equimolar solutions of Pd(II) and the reagent were used. The graphs plotted for the mole ratio method and continuous variation method are as shown in Figs. 3 and 4 respectively. Both methods conclusively confirm the composition of the complex as 1 : 2 (Pd : L).

Effect of pH. In order to study the effect of pH on the absorbance values of the colored palladium complex, the color reaction was carried out at different values of pH. A series of buffer solutions, each differing by 0.3 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 is evident from the results that the absorbance values are maximum and remain steady in the pH range 2.2—3.6. But, outside this pH range, the observed absorbance values are lower. Therefore, for all subsequent studies, the pH is maintained at an optimum level of 3.0.

Rate of Reaction and Stability of Color. The reaction between palladium(II) and DMABT is found to be very fast and the reaction is almost complete instantaneously. The time required for the maximum color development is less than 5 min at room temperature.

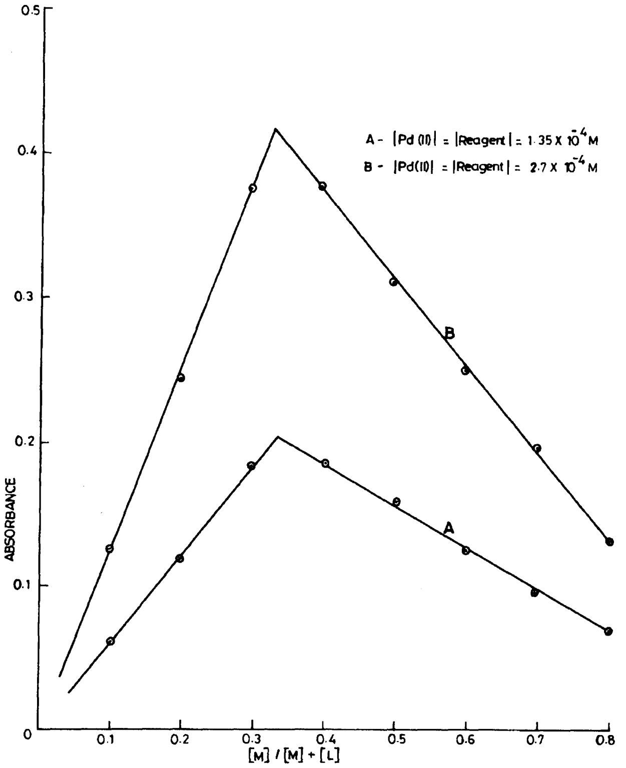

Fig. 4. Continuous variation graph for Pd(II)–reagent system.

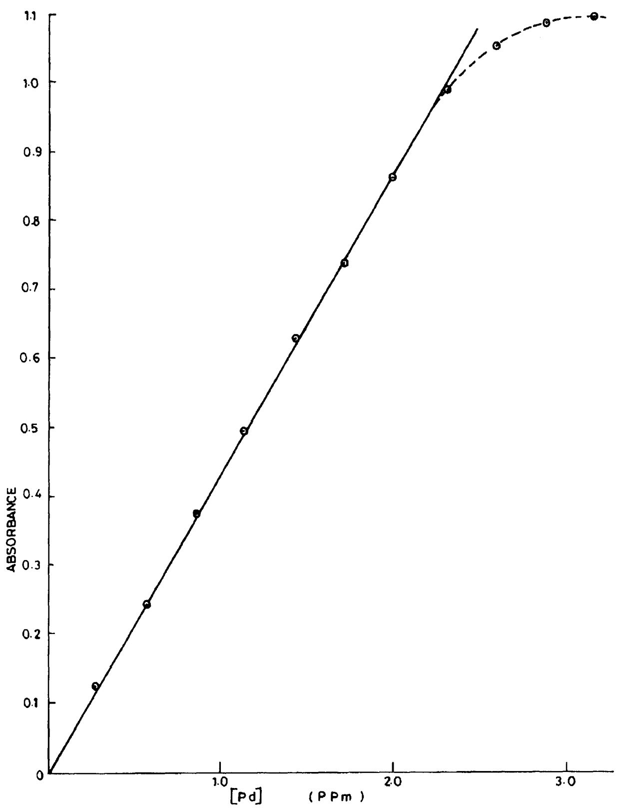

Fig. 5. Verification of Beer's law for Pd(II)–reagent system.

To ensure the maximum color development, in all subsequent studies, the solution is allowed to stand for 5 min before measuring the absorbance of the solution. Thus, the method does not require any stringent conditions for the completion of the color reaction. Further, the intensity of the color developed remains stable for at least 36 h without any substantial change in the absorbance values. For a maximum color intensity, the minimum amount of reagent required is just above 1 : 2 (Pd : L) molar ratio. No adverse effect on the absorbance of the solution is noticed on the addition of a slight excess of the reagent over this molar ratio. However, the addition of a large excess causes the precipitation of the reagent itself under experimental conditions.

Adherence to Beer's Law and Optimum Concentration. The validity of Beer's law for the system was studied by measuring the absorbance values of a series of solutions having different palladium contents. These results are shown in the form of a plot of absorbance (A) vs. molar concentration of Pd, in Fig. 5. It is evident from the graph that Beer's law is valid up to 2.3 ppm of Pd(II).

The optimum concentration range for maximum precision was determined by Ringbom's Plot method.[20] The percentage transmittance of the solution was plotted against log [Pd] (Fig. 6). The linear portion of the curve indicates that palladium can be precisely determined in the range 0.5—1.75 ppm.

Sensitivity and Molar Absorptivity. The molar absorptivity at the wavelength corresponding to the maximum absorbance was calculated by measuring the absorbances of solutions at different concentration levels of palladium(II). The mean value of molar absorptivity is found to be 4.59×10^{4} $\mathrm{dm^{3}\ mol^{-1}\ cm^{-1}}$, which indicates that the method is quite sensitive. The Sandell's sensitivity was also calculated for the method and was found to be $2.33\times10^{-3}\,\mu\mathrm{g\,cm^{-2}}$.

Precision and Accuracy. To assess the accuracy and precision of the method, determinations were carried out at different concentrations of palladium(II), under optimum conditions. The standard deviation of the method is found to be not more than 0.005 and the coefficient of variation does not exceed 0.8%. It is evident from these results that, the method is precise besides being accurate.

Effect of Foreign Ions. The effect of the presence of various cations and anions on the absorbance value of Pd(II)–DMABT complex was studied by carrying out the determination of 1.16 ppm of palladium in the presence of various ions, according to the recommended procedure. An error of 2% in the absorbance value was considered as tolerable limit.

Anions such as fluoride (500 ppm), chloride (5000), bromide (1000), iodide (2000), nitrate (2000), sulfate (1000), phosphate (1000), citrate (800), tartrate (1200), acetate (2000), borate (1500), and EDTA (1000) do not show any interference. Zn(II) (800 ppm), Ba(II) (600),

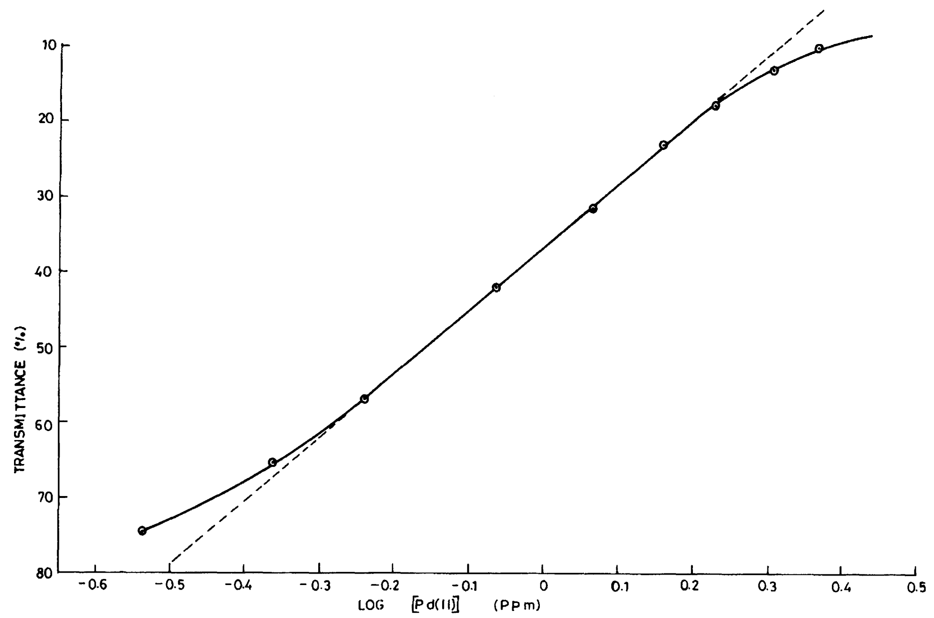

Fig. 6. Ringbom's plot for Pd(II)–reagent system.

Table 1. Comparison of the Proposed Method to Some of the Reported Methods

Reagent used	Wave length	Range	Molar absorptivity (ε)
	nm	ppm	$dm^3\ mol^{-1}\ cm^{-1}$
Phthalimide dithiosemi carbazone	415	1—3.5	2.8×10^4
Furoin dithiosemicarbazone	360	2—4	1.98×10^4
Phenanthraquinone mono thiosemicarbazone	600	2.5—18	2.2×10^3
1,3-Cyclohexanedione bis(thiosemicarbazone)	360	0.5—4.5	1.1×10^4
p-Anisaldehyde thio semicarbazone	370	0.06—3.3	2.16×10^4
DMABT	405	0.5—1.75	4.59×10^4

Table 2. Determination of Palladium in Artificial Mixtures

Pd present	Metal ions added/ppm				Pd found
ppm	Ru(III)	Rh(III)	Ir(III)	Ni(II)	ppm
0.87	2.5	1.2	—	—	0.87
1.16	0.8	2.8	0.5	—	1.15
1.45	—	4.0	1.5	10.0	1.46
1.16	1.0	—	1.0	5.0	1.16
1.45	0.5	0.6	0.8	2.0	1.45

Co(II) (600), Cd(II) (800), Mg(II) (1000), Mn(II) (500), Sr(II) (800), Ca(II) (925), Tl(I) (400), Al(III) (500), Pb(II) (1000), Cr(III) (5), Ru(III) (5), Ir(III) (10), Ni(II) (40), Th(IV) (200), Ti(IV) (60), U(VI) (250), Rh(III) (100), and Fe(III) (50) do not interfere in the method.

Among the anions studied, thiosulfate and oxalate ions show severe interference even at very low concentration levels. The presence of thiosulfate, substantially decreases the intensity of the color. Thiocyanate does not interfere when present in less than 5 ppm, but above this level it shows severe interference.

Among the metal ions, Ag(I), Hg(II), Cu(II), Sn(II), and Pt(IV) show severe interference at all levels. The interference of Hg(II) can be removed by masking mercury with iodide. In the presence of Sn(II), the color is not at all developed. The interference of Ag(I), Cu(II), and Pt(IV) is due to the formation of their respective complexes with the reagent, having appreciable absorbance at 405 nm. The interference of Bi(III) and Ce(III) is due to the formation of precipitates in the medium. The interference of these ions can however, be avoided, when present in small amounts by using EDTA

Table 3. Analyses of Palladium Complexes

Complex	Pd present	Pd found
	%	%
$Pd(CH_5N_3S)_2Cl_2$[a]	29.60	29.80
$Pd(CH_6N_4S)_2Cl_2$[b]	27.30	27.20
$Pd(C_{11}H_{11}N_4S)_2$[c]	18.70	18.75
$Pd(C_4H_7O_2N_2)_2$[d]	31.71	31.82

a) Palladium complex of thiosemicarbazide. b) Palladium complex of thiocarbohydrazide. c) Palladium complex of 3-ethyl-4-benzylidene-5-mercapto-4*H*-1,2,4-triazole. d) Palladium complex of dimethylglyoxime.

as masking agent. The color of the solution turns green on the addition of the reagent in the presence of V(V) thereby causing interference. Ru(III) and Cr(III) also show interference when they are present above 5 ppm level. Zr(IV) interferes at all levels and Ir(III) when present above 10 ppm.

Comparison with Other Methods. A comparison of the proposed method with some of the reported ones has been given in Table 1. It is observed that the method is comparable with other methods and is even more sensitive as indicated by higher molar abosorptivity values. The method can be used for the determination of palladium at lower concentration ranges.

Applications. In order to extend the utility of the proposed method, it was used for the determination of palladium content in artificial mixtures corresponding to palladium alloys. The results are presented in Table 2.

The method was also extended for the estimation of palladium in its complexes. The results pertaining to the analysis of palladium complexes are presented in Table 3. These results clearly indicate that the method is dependable and can be employed in the analysis of palladium complexes, alloys and mixture of ions.

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