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RAPID EXTRACTIVE SPECTROPHOTOMETRIC DETERMINATION OF PALLADIUM(II) USING 5-CHLOROSALICYLALDEHYDE THIOSEMICARBAZONE

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ABSTRACT

Quantitative extraction of the Pd(II) complex with 5-Chlorosalicylaldehyde thiosemicarbazone (CSTSC) was achieved at pH levels ranging from 3.6 to 4.4 after a 30-second equilibration period in n-butyl acetate. When the concentration of Pd(II) does not exceed 9.0 µg mL^{-1}, the complex formed between Pd(II) and 5-Chlorosalicylaldehyde thiosemicarbazone complies with Beer's law, and it displays the highest absorbance at 400 nm. By means of the mole ratio method and the Jobs continuous variation method, it was determined that the stoichiometry of the Pd(II)-CSTSC complex is 1:2. The stability of the extracted complex persisted for 96 hours. The calculated Sandell's sensitivity was 9.92 x 10^{-3} µg cm^{-2}, while the molar absorptivity was found to be 1.072 x 10^4 L mol^{-1} cm^{-1}. Utilizing this method, effective analysis has been carried out on synthetic samples, complexes, and water samples.

Keywords: n-Butyl Acetate, Extraction, Palladium, CSTSC, Water Samples.

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INTRODUCTION

Materials with palladium have useful chemical and physical characteristics. As such, their significance is felt across various sectors. Along with the jewelry industry, they are also widely used in dental and medical devices.[1] The determination of palladium has been carried out using a range of analytical techniques, including atomic absorption spectrometry, spectrophotometry, voltammetry, ICP-OES, and ICP-MS.[2-10] Solvent extraction is increasingly recognized as a vital separation method in the field of chemistry. Several reagents, including hydrazone, thiosemicarbazone, oxime, and thiourea, have been reported in the extractive spectrophotometric examination of palladium. Thiosemicarbazones have garnered attention in the field of pharmacology and medicine due to their well-established pharmacological and medicinal attributes. Notably, these compounds exhibit antiparasitic, antiviral, antimicrobial, antifungal, and antitumor activities.[11-18] The utilization of thiosemicarbazone compounds in the extraction procedure is prevalent owing to their remarkable reactivity towards metal ions and the formation of exceptionally stable-colored complexes. For spectrophotometric determination of Pd(II), there are multiple methods utilizing various organic reagents, but the situation is still unsatisfactory concerning speed, sensitivity, and selectivity. The present research primarily focuses on the utilization of 5-chlorosalicylaldehyde thiosemicarbazone (CSTSC) as a reagent in the extractive spectrophotometric analysis of Palladium (II). When compared to previously published palladium analysis methods, this method stands out as an extremely selective, reliable, and sensitive approach (Table-1).

Table-1: Reviewing the Suggested Method Against Reported Methods

Reagents	pH/HCl/ $NaHCO_3$	Wavelength nm	Beer range	Molar absorptivity	Remark	Ref.
3-Phenoxybenzaldoxime	4.0	435	0.4–4.0	0.2434×10^4	Less sensitive	19
4-(N,N-diethylamino)benzaldehyde thiosemicarbazone	3.0	408	0.36 - 3.24	3.3370×10^4	Narrow Beer's range	20
Isonitroso p-nitro acetophenone thiosemicarbazone	0.0 – 4.0	410	5.0 – 80	0.910×10^3	Less sensitive	21

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p-[N,N-bis(2-chloroethyl)amino]benzaldehyde thiosemicarbazone	0.2 M HCl	395	0.48–2.40	4.05×10^4	Narrow Beer's range	22
o-Methoxyphenyl thiourea	HCl 1.0	325	0–15	3.38×10^3	Absorbance in UV region,	23
3-Methoxysalicylaldehyde-4-hydroxybenzoyl hydrazone	4.5	412	0.287-4.256	1.03×10^3	Less sensitive, use of surfactant	24
o-Methyl phenyl thiourea	0.8M HCl	340	0-12.5	2.85×10^3	Absorbance in UV region	25
4-(4'-fluorobenzylideneimino)-3-methyl-5-mercapto-1, 2, 4-triazole	HCl 0.6-2.0	390	4.12-17.5	5.404×10^3	less sensitive	26
6-Chloro-3-hydroxy-7-methyl-2-(2′-thienyl)-4-oxo-4H-1-benzopyran	0.5M $NaHCO_3$	415-426	0-2.6	6.173×10^4	Narrow Beer's range	27
3-Hydroxy-2-[2'-(5'-methylthienyl)]-4-oxo-4H-1-benzopyran	0.5M $NaHCO_3$	418	0-1.3	6.597×10^4	Narrow Beer's range	28
5-Chlorosalicylaldehyde thiosemicarbazone	4.0	400	0.5-9.0	1.072×10^4	Rapid, Highly sensitive and selective	PM

PM. – Present method

EXPERIMENTAL

Instruments/Chemicals

The UV-VIS spectrophotometer (Jasco V-730) was utilized to determine absorbance using a quartz cell measuring 1.0 cm in length. pH was adjusted using a pH meter (Equiptronics). For the study, chemicals of AR grade were acquired from commercial suppliers. Freshly prepared, double-distilled water was used in all of the experiments. By utilizing double-distilled water and hydrochloric acid, Palladium (II) chloride was dissolved to form a solution containing 1000 ppm of palladium. Gravimetry using dimethylglyoxime was used to standardize the solution.[29] Portions were diluted every day, to get a functional solution.

Foreign-ion Solutions

The process involved dissolving anions in double distilled water and metal salts in the respective acids. Subsequently, a known volume of water was then added to prepare stock solutions containing different anions and cations.

Synthesis of Reagent

Equimolar amounts of thiosemicarbazide (0.911 g) in 25 mL aqueous ethanolic solution were condensed with 25 mL of ethanolic solution of 5-Chlorosalicylaldehyde (1.567 g). A water bath was utilized to reflux the reaction mixture for a total of five hours. The addition of the mixture to crushed ice resulted in the formation of a precipitate. This precipitate was then filtered, washed with water repeatedly, recrystallized using ethanol and dried. A recrystallized product was used to prepare a 0.1% reagent solution.

Procedure

In a 10.0 mL volumetric flask, Pd(II) solution of concentration 5.0 - 90.0 µg, 1.0 mL of 0.1% reagent solution in methanol, and 4.0 mL buffer of pH 4 were combined. The final volume of 10.0 mL was attained by the addition of distilled water. Following the addition of 10.0 mL of n-butyl acetate, the mixture was equilibrated and both the layers were subsequently separated. The organic phase was dried using anhydrous

Na_2SO_4, and with a matched cell of 1.0 cm, its absorbance was measured at a wavelength of 400 nm against a reagent blank.

RESULTS AND DISCUSSION

pH Study

The extraction of Pd(II)-CSTSC complex by n-butyl acetate was conducted according to the procedure outlined above at pH levels ranging from 1.0 to 10.0. The highest extraction of Pd(II) ions occurred at pH levels between 3.6 and 4.4, where the organic phase displayed the maximum absorbance. Hence, pH 4.0 was maintained for the extraction process.

Absorption Spectra

The yellow complex of Pd(II)-CSTSC was quantitatively extracted in the pH range of 3.6–4.4 into n-butyl acetate. When considering wavelengths between 300 and 500 nm, the absorption spectra of the Pd(II)-CSTSC complex reveal two distinct absorption maxima, specifically at 375 nm and 400 nm. The reagent's negligible absorbance at 400 nm ensures that it does not influence the palladium (II) determination process as indicated in Fig.-1. Therefore, a wavelength of 400 nm was specifically chosen for all absorbance measurements of the Pd(II)-CSTSC complex.

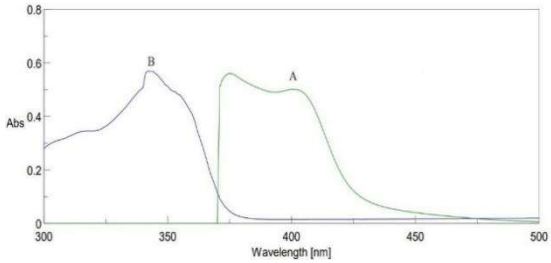

Fig.-1: A - Absorption Spectra of Pd(II)-CSTSC Complex; B - Absorption Spectra of CSTSC

Effect of Solvent

By utilizing a variety of organic solvents, the impact of solvents on extraction and absorbance of the Pd(II)-CSTSC complex was investigated. The solvents are arranged based on the percentage of palladium (II) ion extraction as follows: n-butyl acetate > ethyl acetate > n-butanol > isoamyl alcohol > cyclohexanone > toluene > xylene > benzene > chloroform > carbon tetrachloride > hexane. All extractions were performed with n-butyl acetate due to its ability to achieve the highest percentage of palladium (II) ion extraction.

Equilibration Time and Effect of Reagent Concentration

By equilibrating for just 30 seconds, the Pd(II)-CSTSC complex can be entirely extracted, and it remains stable for more than 96 hours. It was found that 1.0 ml of 0.1 % CSTSC solution in methanol was sufficient to extract 90.0 µg of Pd(II) ion.

Effect of Salting Out Agents

Salts like calcium chloride, ammonium sulfate, potassium carbonate, magnesium sulfate, and sodium chloride, were introduced as salting out agents. Notably, the absorbance of the solution did not change following the addition of a salting-out agent.

Beer's Range

Beer's law applies to Pd(II) at 400 nm with concentrations ranging from 0.5-9.0 µg mL^{-1} (Fig.-2). 1.072 x 10^4 L $mol^{-1}cm^{-1}$ and 9.92 x 10^{-3} µg cm^{-2}, respectively, were calculated to be the molar absorptivity and Sandell's sensitivity.

Determination of the Composition of Pd(II)-CSTSC Complex

Equimolar solutions (4.698 x 10^{-4}M) of palladium (II) and CSTSC were combined in different proportions while maintaining a constant total volume of 2.0 ml. The 1:2 composition of the Pd (II)-CSTSC complex was determined with the help of Job's Continuous Variation technique, as seen in Fig.-3. The mole ratio method is illustrated in Fig.-4.

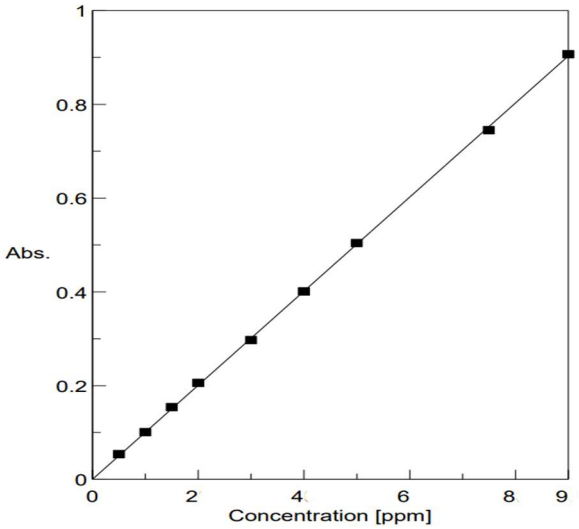

Fig.-2: Calibration Plot

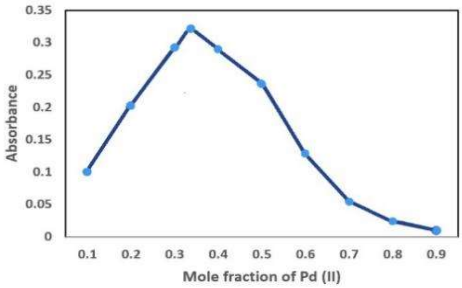

Fig.-3: Job's Continuous Variation Method

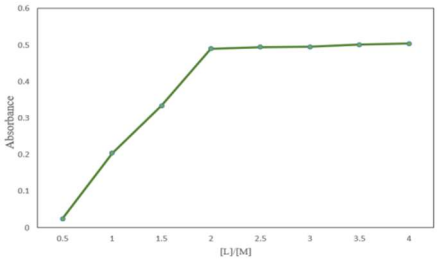

Fig.-4: Mole Ratio Method

Foreign Ions Study

To study the impact of foreign ions on absorbance, 50.0 µg of palladium (II) and various concentrations of each foreign ion were used to measure the absorbance of Pd(II)-CSTSC. A tolerance level of ±2% was set for the absorbance measurement (Table-2): Cu (II), Co (II), Ag (I), Hg (II), and Ru (III) were found to interfere at all levels of concentration, which was eliminated by applying an appropriate masking agent of 1.0 mL of 0.1 % EDTA, 20.0 mg sulfite, 40.0 mg chloride, 40.0 mg iodide, and 20.0 mg thiourea, respectively.

Table-2: Effect of Interfering Ions on Pd(II)-CSTSC Complex Extraction

Interfering ions	Tolerance limit in µg	Interfering ions	Tolerance limit in µg	Interfering ions	Tolerance limit in µg
Fluoride	40000	Oxalate	20000	V(V)	2000
Chloride	40000	Bromate	10000	Bi(II)	2000
Bromide	40000	Iodate	10000	U(VI)	2000
Iodide	40000	Chlorate	10000	Al(III)	2000
Nitrite	40000	Permanganate	2000	Pb(II)	1000

Nitrate	40000	Na(I)	10000	Zn(II)	1000
Thiosulfate	40000	K(I)	10000	Ag(I)[a]	1000
Peroxydisulfate	40000	Ca(II)	4000	Sn(IV)	500
EDTA	40000	Mg(II)	4000	Hg(II)[b]	500
sulphate	20000	W(VI)	4000	Ru(III)[c]	500
Sulfite	20000	Mn(II)	4000	Cd(II)	200
pyrophosphates	20000	Th(III)	4000	Ce(IV)	200
Urea	20000	Ba(II)	2000	Co(II)[d]	100
Thiourea	20000	Sr(II)	2000	Cu(II)[e]	100
Tartrate	20000	Cr(III)	2000	Fe(III)	75
Acetate	20000	La(III)	2000	Ni(II)	50

[a]masked with 40 mg chloride, [b]masked with 40 mg iodide, [c]masked with 20 mg thiourea chloride, [d]masked with 20 mg sulfite, [e]masked with 1 ml 0.1% EDTA.

Accuracy and Precision

To test accuracy and reproducibility, the absorbance of ten different 5.0 µg mL^{-1} palladium solutions was measured. The standard deviation was found to be 0.0288, while the relative standard deviation was 0.58%. Based on the standard deviation, the reproducibility of results can be attained with a 95% confidence level, resulting in a value of 4.988 $\pm$ 0.01783.

Applications

The current method is utilized to analyze the palladium content in synthetic mixtures, complexes, and water samples.

Analysis of Palladium Ion Concentration in Synthetic Mixture

The proposed method was utilized to estimate Pd(II) in several synthetic mixtures, with the results shown in Table-3.

Detection of Pd(II) ions in Water Samples

1000 mL of well and tap water samples were combined with 1000 µg Pd(II), heated until dry, and treated with 2.0 mL 6% hydrogen peroxide in ammonical medium and the volume was then increased to 50 mL using dil. HCl. Under the guidelines of the suggested procedure, palladium (II) was measured in 1.0 mL of aliquot. Table-3 shows the results.

Table-3: Palladium (II) Concentration Estimation in Synthetic Mixtures and Water Samples.

Composition (µg)	Amount of Palladium (II) present (µg)	Amount of Palladium (II) found (µg)
Pd (30), Cd (200), Zn (200)	30.0	29.92
Pd (30), Fe (50), V (100)	30.0	30.05
Pd (30), Ag (150), Cr (150)	30.0	29.88
Pd (30), Sn (50), Ni (50)	30.0	29.96
Well water	20.0	20.08
Tap water	20.0	19.95

Detection of Pd(II) Level in Complexes

Palladium complexes of benzohydrazide and dimethylglyoxime were made and purified in accordance with the reported procedures.[30] The process involved using 5.0 mL of aqua regia for each complex sample, heating it until it reached a nearly dry state. Afterward, 5.0 mL of diluted HCl was added, and the solution was diluted to 100 mL with the help of double-distilled water. The recommended approach was used to examine appropriate aliquots for palladium (II), as shown in Table-3.

Table-4: Pd (II) Content Analysis in Complexes

Complexes	% of Palladium (II) calculated	% of Palladium (II) found by present method
$Pd(C_4H_7O_2N_2)_2$	31.61%	31.52%
$Pd(CH_5N_3S)_2Cl_2$	29.59%	29.53%

CONCLUSION

In microgram amounts, the spectrophotometric detection of Pd(II) is facilitated by this method, offering both high sensitivity and selectivity. The Pd(II)-CSTSC complex in n-butyl acetate exhibits conformity to Beer's law up to a concentration of 9.0 µg mL^{-1}. At a wavelength of 400 nm, the complex demonstrates its highest absorbance and remains stable for a duration of 96 hours. The molar absorptivity was 1.072 x 10^4 L mol^{-1} cm^{-1} and 9.92 x 10^{-3} µg cm^{-2} was Sandell's sensitivity. The extraction efficiency of palladium remained unaffected despite the presence of multiple foreign ions. The concentration of Pd(II) can be rapidly determined in synthetic mixtures, complexes, and water samples due to the simple and rapid nature of the method.

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CONFLICT OF INTERESTS

The absence of any conflicting financial interests is declared by the authors.

AUTHOR CONTRIBUTIONS

All the authors contributed significantly to this manuscript, participated in reviewing/editing, and approved the final draft for publication. The research profile of the authors can be verified from their ORCID IDs, given below:

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