



SEPT—2009

DEVELOPMENT OF VARIOUS THIOSEMICARBAZONE REAGENTS FOR EXTRACTIVE SPECTROPHOTOMETRIC DETERMINATION OF Pd(II)



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Introduction

Solvent extraction method is the method of analysis of ions, impurity detection, enrichment, and complex formation. Thiosemicarbazone reagents form colored complexes with metal ions. These complexes are also found to have biological activities, which have medicinal values in the treatment of diseases like Influenza, Protozoa, Small pox and some tumors and which also have antitubercular activity. Metal chelates of these reagents are used as pesticides and fungicides in Agriculture.

These reagents forms stable complexes with Pd(II). It is found in pharmaceutical, commercial, agricultural and analytical samples. Among the various analytical methods of determination of Pd(II), at micro level, the spectrophotometric methods are less expensive and more sensitive. Literature survey reveals that only few thiosemicarbazone reagents are synthesized for extractive spectrophotometric determination of Pd(II).

The present work constitute the development of various thiosemicarbazone reagents for such determination of Pd(II) and selection of a special reagent which will extract

Pd(II) at working range of P^H and with minimum folds of moles of reagent, with more stability and to develop a practical method for determination of Pd(II). To develop the practical method by use of selected thiosemicarbazone which is applied for pharmaceutical, commercial, and analytical samples of Pd(II).

Preparation of reagents: The Thiosemicarbazones were prepared by condensation of selected aromatic and heterocyclic substituted aldehydes with thiosemicarbazide. 0.02M of aldehydes dissolved in 15 mL of methanol taken in a round bottom flask. Further 0.02M of thiosemicarbazide dissolved in 15 mL of methanol is added to flask. Then 1-2 mL of glacial acetic acid is added to the flask and refluxed for 2-3 hours. The reagents so formed are separated by physical method. The formation of reagents are checked by TLC. The structures of reagents have been established on the basis of IR and NMR spectra, and the melting points.

Preparation of metal solutions: The standard Pd(II) solution was prepared using AR grade $Pd(OAc)_2$ and 10^{-3} to $10^{-4}M$ Pd(II)

aliquot solutions were prepared in double distilled water, first dissolving the $\text{Pd}(\text{OAc})_2$ in few volumes of glacial acetic acid.

Buffer Solution : Buffer solutions of desired P^{H} are prepared using 1M Acetic Acid and 1M Sodium acetate. Suitable proportions of these solutions are mixed to get desired P^{H} .

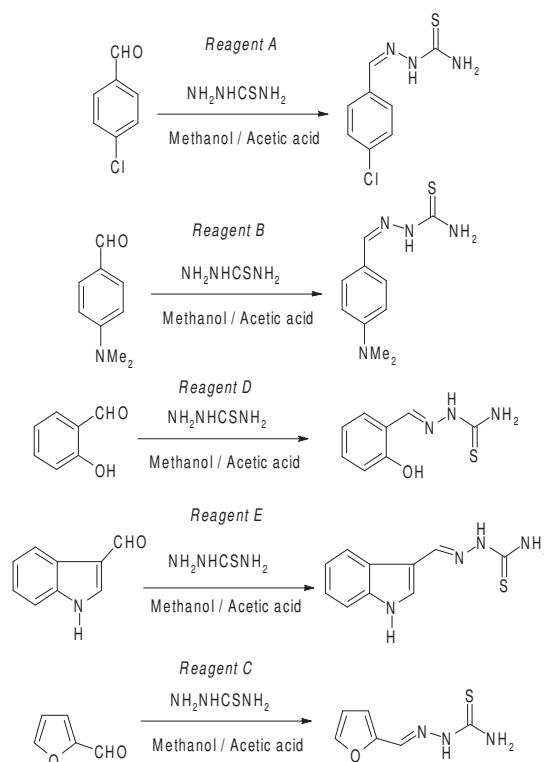
Apparatus : UV-Vis spectrophotometer with pathlength of 1cm. quartz cell has been used for the absorbance determination. P^{H} meter (EQ 614, Elico, Mumbai) has been used for P^{H} adjustment by using buffer solutions.

Recommended Procedures : 5 mL of 0.01M reagent solutions in CCl_4 and 5 mL Pd(II) solution (10^{-3} to 10^{-4} M) is taken in 25 mL separatory funnel. The above solution is shaken for 2 minutes and is allowed to stand for 1 minute. The organic phases are then collected in beaker and desired P^{H} has been adjusted using buffer solution. The contents are transferred to 25 mL flask and volumes are made up to mark using CCl_4 . The absorbance are measured at λ_{max} of reagents against reagent blank (10^{-2} M). The absorbance are measured for all reagents at varying P^{H} . The stability constants and stoichiometry of the complexes of thiosemicarbazones with Pd(II) are

determined by Job's continuous and mole ratio method.

Physicochemical and analytical parameters of reagents:

Reactions:



Characterization of reagents:

Parameter	A(4-CBTS)	B(4-DMABTS)	C(FATS)	D(SATS)	E(I3ATS)
Color	Yellow	green	Brown	Greenish yellow	Orange
Melting point °C	208	190	134	222	224
λ_{max} nm	465	432	498	400	485
P^{H} range	4-5	4.2-5.2	4.5-5.5	4.5-6	5.5-6.5
Moles of folds required	8	5	4	6	3
K (Stability constant)	7×10^5	9.5×10^5	10.1×10^5	8.3×10^5	11.6×10^5

Effect of solvent: The effect of various solvents such as chloroform, diethylether, ethyl acetate, xylene, isopropyl alcohol, carbon tetrachloride on extraction of Pd(II) with the

reagents is determined. Among the various solvents studied Carbon tetrachloride is selected as most suitable solvent due to its maximum absorbance.

Result and discussion: Among the various thiosemicarbazones developed reagents, the reagent E gives required results. The I3ATS(E) reagent gives required extraction of Pd(II) at working range of P^H and with minimum folds of moles of reagent.

This is a novel method of determination of Pd(II) of Pharmaceutical, Commercial and Analytical samples. The reagent I3ATS(E) is most suitable Thiosemicarbazone for extractive spectrophotometric determination of Pd(II)

with minimum folds of moles of reagent for complex formation. All developed thiosemicarbazones extract Pd(II) with good stability of complexes. The heterocyclic ligands shows greater stability of Pd(II) complexes. The selected heterocyclic ligand (E), Indole-3-aldehyde thiosemicarbazone (I3ATS) extract Pd(II) at 5.5 - 6.5 range of P^H Fig.(b) and with about 3 folds of moles of reagent for complete color development.

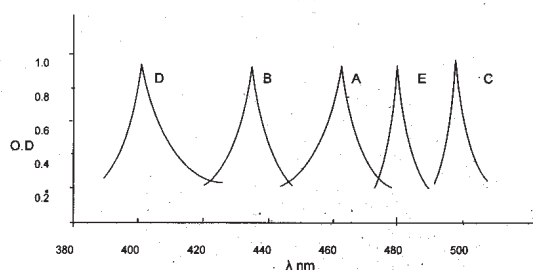


Fig.(a) Plot of O.D. versus λ for Thiosemicarbazones.

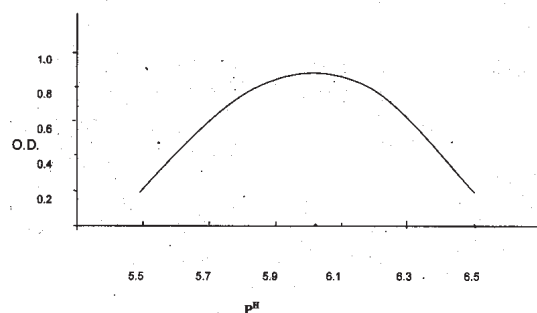


Fig.(b) Plot of O.D. versus P^H for I3ATS(E) Reagent

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