

Extraction and spectrophotometric determination of Palladium (II) with isonitroso p-methyl acetophenone phenyl hydrazone (HIMAPH)

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(Received: February 15, 2010; Accepted: April 30, 2010)

ABSTRACT

Isonitroso p – methyl acetophenone phenyl hydrazone (HIMAPH) extracts palladium (ii) quantitatively (99.79%) into toluene from an aqueous solution of pH 0.0-5.0 and from 0.1-1M solution of acetic acid and mineral acids in the presence of 1ml of 2M solution of sodium acetate followed by digestion on boiling water bath for 4-5 minutes. The toluene extracts shows an intense peak at 470nm (? Max) and Beer's law is obeyed over the Pd (ii) concentration range of 0.1-10 μ /ml. the molar absorptivity for Pd (ii)-HIMAPH system is 13,305L mole⁻¹cm⁻¹. the composition of extracted species is found to be 1:2 (Pd : HIMAPH) by job's continuous variation and mole ratio method. Interference by various ions has been studied. The proposed method has been satisfactorily applied for determination of Pd(ii) in alloy and catalyst samples.

Key words : HIMAPH, Palladium, extraction Spectrophotometry.

INTRODUCTION

A solvent extraction is becoming important separation technique in chemistry. It has grown into one of the most promising method in the separation of metal ions at trace level because of its simplicity, rapidity and varsaliyt¹. literature survey reveals that various reagents²⁻⁴ are available for the spectrophotometric determine of palladium of which isonitrosoketone and its derivatives constitute an important class⁵⁻⁹. Isonitroso p-methyl acetophenone phenyl hydrazone (HIMAPH) has been used for the extractive spectrophotometric determination of noble metal ions¹⁰⁻¹². in the present communication we describe the extractive spectrophotometric determination of Pd (ii) with Isonitroso p-methyl acetophenone phenyl hydrazone (HIMAPH).

MATERIAL AND METHODS

ELICO – SL 159 spectrophotometer with optically matched quartz or glass cells of 1cm path length was used for absorbance measurement. An ELICO LI 127 pH meter was employed for pH measurements. The reagent HIMAPH was synthesized by refluxing equimolar amount of ethanolic solution of fisonitroso p – methylacetophenone ⁺⁺¹³.with phenyl hydrazine for 4 hours. On cooling the reaction mixture, a yellow coloured product separated out which was collected by filtration and washed with ethanol. The resulting HIMAPH was recrystallised using aqueous ethanol as the procedure recommended by vogel¹⁴. and characterized by elemental and spectral analysis. Its solution was prepared in Dimethylformamide (DMF). A stock solution of Pd (ii) was prepared by

dissolving accurately weighed palladium chloride in water containing dilute hydrochloric acid and it was standardized by dimethylglyoxime method¹⁵. working solutions of Pd (ii) were made by diluting the stock solution to an appropriate volume. All other reagents used were of A.R. grade and all the solutions were prepared in doubly distilled water.

Extractive spectrophotometric determination of Pd (II)

To an aliquot of aqueous solution containing 1-100µg of Pd (ii), 2ml of 1M acetic acid, 1ml of 2M-sodium acetate and 1ml of 0.2% solution of HIMAPH prepared in DMF added. The volume of solution was made up to 10ml with distilled water followed by heating on boiling water bath for 4-5 minutes. The solution was first cooled at room temperature and then equilibrated for 1 min. with 10ml of toluene and the phases were allowed to separate. The toluene extract was collected in a 10ml measuring flask and made upto mark with toluene, if necessary. The absorbance of toluene extract was measured at 470 nm against a reagent blank prepared under identical conditions. The measured absorbance was used to compute the amount of palladium present in the sample solution from predetermined calibration curve. To study the effect of other ions, the respective foreign ions were added to aqueous phase before the extraction and adjustment of pH or acidity.

Determination of Pd (II) in catalyst sample

For the determination of Pd (ii) in catalyst sample, 0.1 to 0.2 gm. Sample of catalyst was dissolved in boiling with 10ml of aquaregia. The resulting solution was evaporated to dryness and the residue was dissolved in 10ml of 1N HCL filter, if required and solution was diluted to 100ml with doubly distilled water. 1ml aliquot of this solution was analyzed for Pd (ii) by the procedure as described earlier

RESULTS AND DISCUSSION

The composition of HIMAPH has been confirmed by elemental analysis.

Palladium (ii) could be extracted quantitatively (99.79%) by HIMAPH into toluene from an aqueous solution of pH0.0 to 5.0 and from 0.1 to 1M solution of acetic acid and minerals acids in the presence of 1ml of 2M sodium acetate followed by digestion on boiling water bath for 4-5 minutes. Organics solvents used for extraction of Pd (ii) can be arranged on the basis of their extraction of Pd (ii) can be arranged on the basis of their extraction coefficient valules as toluene >benzene >n-amly alcohol > n-butanol > ethylacetate >chloroform> xylene> carbon tetrachloride > benzyl tetrachloride>benzyl alcohol > nitrobenzene. Toluene was found to be the best

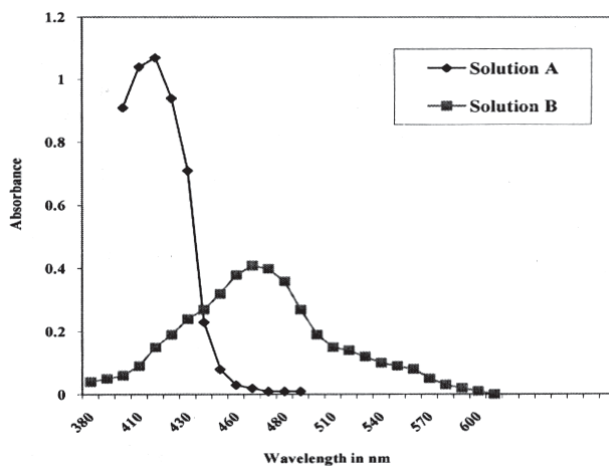
Table 1.

Elements	%C	%H	%N	%O(By difference)
Found	70.10	6.36	16.68	6.86
Required for C ₁₅ H ₁₅ N ₃ O	71.15	5.93	16.06	6.32

Table 2: Determination of Pd (II) in alloy and catalyst samples

Sample	Pd(III) found%* Present method	Dimethyl glyoxime method
Silver alloy	0.094	0.096
Pd charcoal catalyst	25.54	26.17
Pd – BaSO ₄ catalyst	0.840	0.860
Pd – CaCO ₃ catalyst	5.43	5.54

* Average of three determination



Solution A:
Absorbance spectra of HIMAPH
Solution B :
Absorbance spectra of
Pd – HIMAPH Complex

Fig. 1:

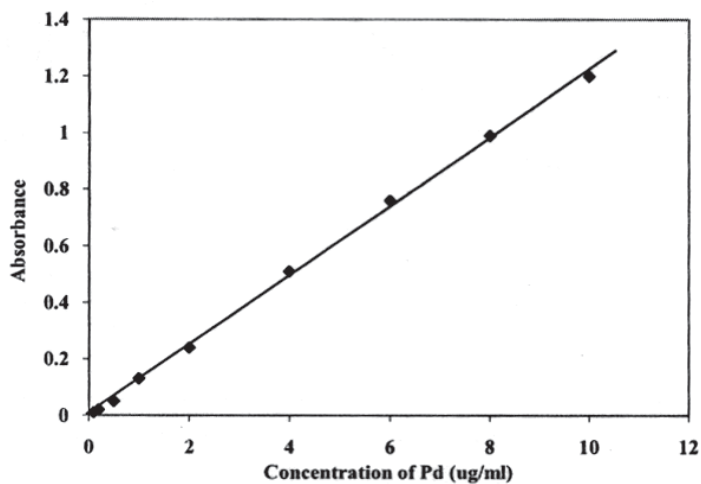


Fig. 2: Callibration curve for palladium (IV)

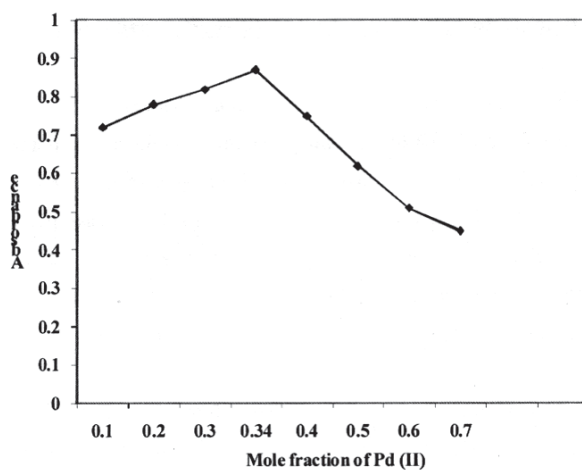


Fig. 3: Job's Continuous variation method

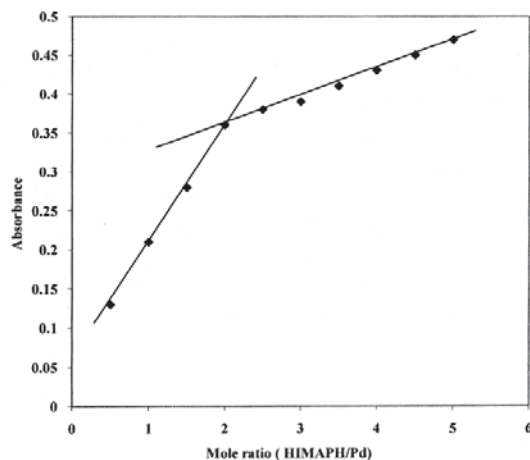


Fig. 4: Mole ratio methods

extracting solvent, hence it was selected for the extraction throughout the work. The toluene extract of Pd-HIMAPH complex showed an intense peak at 470nm [fig-i] the absorbance due to the reagent is negligible at this wavelength. So the absorption measurements were taken at this wavelength over a palladium concentration range of 0.1 to 10 μ g/ml [fig-ii]. The molar absorptivity of the extracted complex on the basis of Pd (ii) content was calculated to be 13,305L mol⁻¹cm⁻¹. It was found that 1ml of 0.2% DMF solution of HIMAPH was sufficient to extract 100 μ g of Pd (ii). The color of the toluene extract was found to be stable at least 48 hrs. at room temperature.

Effect of other ions

Pd (ii) (60 μ g) was determined in the presence of various ions. The following ions in the amount indicated, did not interfere in the spectrophotometric determination of Pd (ii) (60 μ g) 10mg each of Mg (II), Al(III), Ca(II), V(IV), Cr(III), Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Mo(VI), W(VI), Be(II), Sn(II), Zr(IV), Hg(II). 5mg each of Ba(II), Bi(III), Th(IV), Sr(III), Li(I), Ce(III), 1 mg of Ru (III), Rh(III), Pt(IV) and 20 mg each of chloride, bromide iodide, fluoride chlorate, bromate, iodate, sulphide, phosphate, acetate and 10mg of nitrate, nitrite, citrate and thiosulphate interference by the various ions were removed by using appropriate masking agent. In the presence of sodium sulphite and citrate metal ions like Cu(II), Fe(II), Fe(III), did not interfere respectively.

Composition of the extracted complex

The composition of the extracted complex was found to be 1:2 (Pd: HIMAPH) by job's continuous variation [fig – III] and mole ratio methods [fig-IV]

Precision, Accuracy, Sensitivity and Application of method

The precision and accuracy of the method were tested by analyzing the solution containing a known amount of Pd (II) following the recommended procedure. The average of 10 determination of 20 μ g of Pd (II) in 10 cm⁻³ solution was 19.80 μ g, which is varied between 19.38 and 20.22 at 95% confidence limit. Standard deviation and Sandell's sensitivity of the extracted species is found to be ± 0.587 and 7.89ng cm⁻². The proposed method has been applied for the determination of Pd(II) in catalyst and alloy samples.

The results of the analysis of the samples were comparable with those obtained by the Dimethyl glyoxime method¹⁵ for Pd (II) (Table – II)

ACKNOWLEDGEMENTS

Authors are thankful to the principal Dr. (Mrs). J.K. Phadnis, V.E.S. College of Arts, Science and Commerce, Sindhi Society Chembur Mumbai – 71 for providing necessary research facilities.

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