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Extractive spectrophotometric determination of palladium (II) with isonitroso p-nitro acetophenone thiosemicarbazone (HINATS)

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ABSTRACT

Isonitroso p-Nitro Acetophenone thiosemicarbazone (HINATS) extracts palladium (II) quantitatively (99.60%) into from an aqueous solution of pH 0.0 – 4.0 and from 0.1 – 1 M solution of acetic acid and mineral acids. The chloroform extract shows an intense peak at 410 nm (λmax.). Beer's law is obeyed over the Pd (II) concentration range 5.0 – 80 µg/m.. The molar absorptivity is 910 L mole^{-1} cm^{-1} at 410 nm. The composition of extracted and Mole ratio method. Interference by various ions has been studied. The proposed method has been applied for determination of Pd (II) in catalyst sample.

Key words: HINATS, Palladium, Spectrophotometry.

INTRODUCTION

Various reagents are available for the spectrophotometric determination of palladium of which isonitrosoketone constitutes an important class[1-4]. In the present communication, we describe the extractive spectrophotometric determination of Pd (II) with Isonitroso p – Nitro Acetophenone thiosemicarbazone (HINATS).

MATERIALS AND METHOD

ELICO – SL 159 spectrophotometer with optically matched quartz or glass cells of 1cm path length were used for absorbance measurement. An ELICO – LI 127 pH meter was employed for pH measurements. The reagent HINATS was synthesized by condensation of Isonitroso p-Methylacetophenone[5] with thiosemicarbazide as procedure recommended by Vogel[6] and characterized by elemental and spectral analysis. Its solution was prepared in alcohol (1:1). A stock solution of Pd (II) was prepared by dissolving palladium chloride in water containing dilute hydrochloric acid. It was standardized by dimethylglyoxime mthod[7]. Working solutions of Pd (II) were made by suitable dilution. All other reagents used were of AR grade and all the solutions were prepared in doubgly distilled water.

Extractive Spectrophotometric Determination of Pd (II)

To an aliquot of aqueous solution containing 50 – 800 µg of Pd (II), 2ml of 1 M acetic acid and 1 ml of 1% solution was made up to 10 ml with distilled water. The solution was then equilibrated for 1 min with 10 ml of chloroform and the phases were allowed to separate. The chloroform extract was collected in a 10 ml measuring flask and made up to mark with chloroform. The absorbance of chloroform extract was measured at 410 nm against a reagent blank prepared under identical conditions. The Palladium content of the sample solution was determined from 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 (Pd-charcoal, Pd- $BaSO_4$ and Pd-$CacO_3$ catalyst):

Boiling with 10 ml of aquaregia dissolved 0.1 to 0.2 gm. sample of catalyst. The solution was evaporated to dryness and the residue was dissolved in 10 ml of 1 N HCl filter, if required and resulting solution was diluted to 100 ml with water. 1 ml aliquot of this solution was analyzed fro Pd (II) by the procedure as described earlier.

RESULTS AND DISCUSSION

Palladium (II) could be extracted quantitatively (99.60%) by HINATS into chloroform from an aqueous solution of pH 0.0 to 4.0 and from 0.1 to 1 M solution of acetic acid and mineral acids. Organic solvents used for extraction of Pd (II) can be arranged on the basis of their extraction coefficient values as chloroform > carbon tetrachloride > n – butanol > benzene > n-amyl alcohol > ethyl acetate > toluene > xylene > benzyl alcohol > nitrobenzene. Chloroform was found to be the best extracting solvent; hence, it was selected for extraction throughout the work. The chloroform extract of Pd – HINATS complex showed an intense peak at 410 nm. The absorbance due to the reagent is negligible at this wavelength, so the absorption measurements were taken at this wavelength. The result shows that the system confirmed to Beer's law at this wavelength over a palladium concentration range 5.0 to 80 µg/m. The molar absorptivity of the extracted complex on the basis of PD (II) content was calculated to be 910 L mol^{1-} cm $^{-1}$. It was fount that 1 ml of 1% solution of HINATS was sufficient to extract 800 µg of Pd (II). The colour of the toluene extract was found to be stable at least 48 hrs. at room temperature.

Effect of Other IOns

Pd (II) (100 µg) 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) (100 µg): 10 mg each of Mg(II), Al(II), Ca(II), Cr(II), Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Mo(VI), W(VI), Be(II), Sn(II), Zr(II), Fe(II), Fe(III), Hg(II), Ba(II), Bi(III), Th(IV), Sr(II), Li(I), 5 mg each V(V), Ce(IV), Ru(III) Rh(III) and Pt(IV). 20 mg each of chloride, bromide, fluoride, chlorate, bromate, nitrate, nitrite, phosphates, acetate and 10 mg of citrate and thiosulphate. The interference by iodide and iodate can be removed by adding potassium persulphate and boiling the solution with nitric acid. EDTA and thiourea do not interfere in the presence of copper sulphate.

Composition of the extracted complex

The composition of the extracted complex was found to e 1:2 (Pd:HINATS) by Job's continuous variation and Mole ratio methods.

Precision, Accuracy, Sensitivity and Application of Method

The precision and accuracy of the method were tested by analyzing the solution containing a

Table 1: Determination of Pd (II) in alloy and catalyst samples

Sample	Pd(II) found % Present method*	Dimethyl glyoxime Method
Silver alloy	0.094	0.096
Pd charcoal catalyst	25.96	27.03
Pd – $BaSo_4$ catalyst	0.884	0.890
Pd – $Caco_3$ catalyst	4.43	4.54

* Average of three determinations

known amount of Pd (II) following the recommended procedure. The average of 10 determination of 50 µg of Pd (II) in 10 cm^3 solutions ws 49.80 µg, which is varied between 48.10 and 51.50 at 95% confidence limit and standard deviation was ± 3.25. 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 method[7] for Pd (II) (Table-1).

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