Spectrophotometeric Determination of Pd(II) in Tea Leaves by using 4 (4-antipyrilazo) -8- Hydroxyl Quinoline agent in Presence Tween – 80 Micellar solution.

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***Abstract*--** **A direct method has been developed for the spectrophotometeric determination of trace amounts of Pd(II) using 4(4-antipyril azo)-8- hydroxyl quinoline (APAHQ) as a reagent in the presence of surfactant as solubilizing agent. The reagent (APAHQ), as a sensitive chromogenic complexing agent formed a purple colored Pd(II)- APAHQ in Tween- 80 with satisfactory solubility. Various condition such as pH, APAHQ concentration, type and concentration of micelling agent were optimized. Molar absorptivity of Pd complex was found $0.65x10^4$ $L.cm^{-1}.moL^{-1}$ at 470 nm. Calibration graph was derived by zero derivative spectrophotometry at maximum wavelength with linear ranges of 0.1-3.0 p.p.m of Pd(II). Precision as standard deviation as well as accuracy as recovery percent was (0.14%, 0.36%) , (0.1, 0.4) of Pd(II).The recommended procedure was applied to tea leaves with satisfactory results .**

***Index Term*--** **4(4- antipyrilazo)-8-hydroxy quinoline, spectrophotrophotometry, Palladium determination , Tween-80.**

1. INTRODUCTION

Azo compounds have attracted much attention as they are chromogenic reagents and play a vital role in analytical chemistry due to highly sensitive colour reaction ,stability towards various metal ion[1-6].Various instrumental methods that have been developed or modified for deter mention of Pd (II) , these include spectrophometric methods [7,8], Flow injection,[9,10] Flow injection related with flame atomic absorption spectroscopy [11], ion selective electrode [12], solid Phase Extraction[13].

Azo dyes have N=N group which makes them more reactive toward various metals . These compounds form water-insoluble complexs with most of the metal ions; therefore ,their complexes are either dissolved in water or extracted in a suitable solvent for their spectrophotomeric determination, which is quite tedious and time consuming, and so there is a need for simpler and more rapid methods[14-17].

The objective of the investigation reported in this paper was to evaluate a spectrophotometric method for the determination of Pd (II) based on the reaction of this ion with (APAHQ) and in the presence of Tween - 80 as surfactant .

Experimental section

Apparatus

All spectral and absorbance measurements were carried out on a shimadzu UV- Visible 1700 double beam spectrometer using 1cm glass cells. Measurements of pH were made using an Inolab, WTW,720 pH-meter equipped with a glass – saturated calomel combined electrode.

Preparation of 4(4-ontipyriylazo) 8hydroxy quinoline (APAHQ) was prepared by coupling diazotized 4- amino antipyrine with 8-hydroxy quinoline in alkaline at 0-$5c^0$ according to the method described by Amal.[18]

General procedure

To an aliquot of Pd (II) taken separately in the Beer's law rang given in Table. added 3 ml of(APAHQ) reagent solution with concentration (Table I) and the pH was adjusted at 10 .The complex formed was solubilized by adding 3 ml of surfactant Table I and diluted up to 10ml in a standard flask. The absorbance of the resulting solution was measured at the absorption maxima against a reagent blank prepared under similar condition but Pd(II) no.

Reagents

All reagents used were of analytical grade.

Pd stock solution (lmg.L^{-1}) :- prepared by dissolving (0.033)gm of palladium chloride in 200ml distilled water , working standard of Pd (II) solutions was prepared by simple dilution of the appropriate volume of the standard Pd (II) solution (200) p.p.m with distilled water.

4(4-antipyriyL/azo) 8-hydroxy quinoline (1mM):- 0.09gm of reagent with dissolved in 250ml of ethanol.

Sodium dodecylsulfate (SDS) (3%): prepared by dissolving 3 g of SDS in 100 ml of demineralized water.

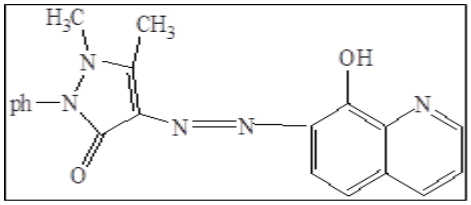
Tritonx 100 solution (3%) : prepared by dissolving 3g of Tritonx-100 in 100 ml of demineralized water..

Tween -80 (3 %) : prepared by dissolving 3 g of Tween -80 in 100ml of demineralized water..

2. RESULTS AND DISCUSSION

Properties of(APAHQ) and its Metal Chelates .APAHQ is a tridentate with coordination of azo group nitrogen and one

hydroxide groups and one carboxyl groups; it has the following structure:



APAHQ

Owing to the large conjugated system, the compound showed excellent chelating ability to form inner metal chelates.APAHQ and its metal chelates can be easily solubilized in an aqueous micellar solution of Tween-80.

Spectra

The results of this investigation indicated that the reaction of Pd (II) with (APAHQ) in the presence tween -80 yield highly soluble colored complex which can be utilized as suitable assay procedures for determinations of Pd (II) This coloured complex have a maximum absorption at 470 nm.Fig.1. The effect of various parameters on the absorption intensity of the formed product was studied and the reaction condition was optimized.

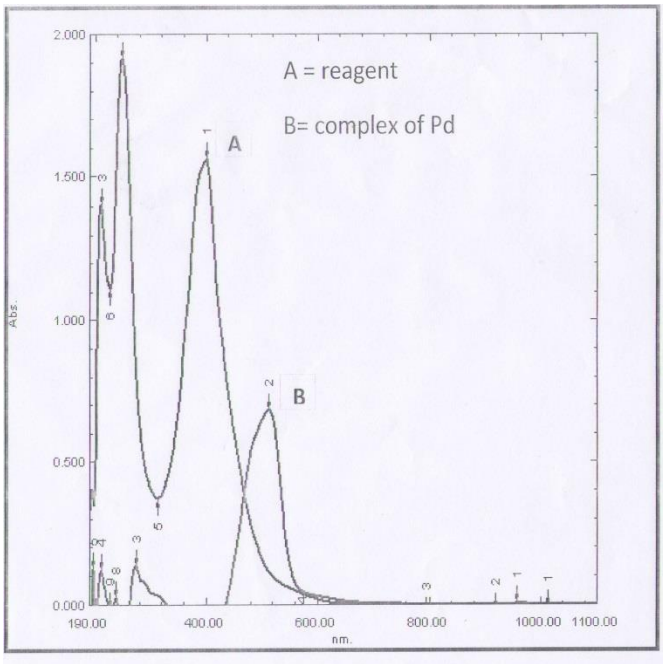


Fig.1. Spectrophotometric spectra of A-APAHQ Reagent and B-Pd(II)-APAHQ complex

Effect of pH

Dilute solution (0.05) of NaOH, 0.05 hydrochloric acid and were used for the study of pH effect on absorbance. The absorbance of the complex was maximum and constant in the pH rang given in table. 1 Fig .2

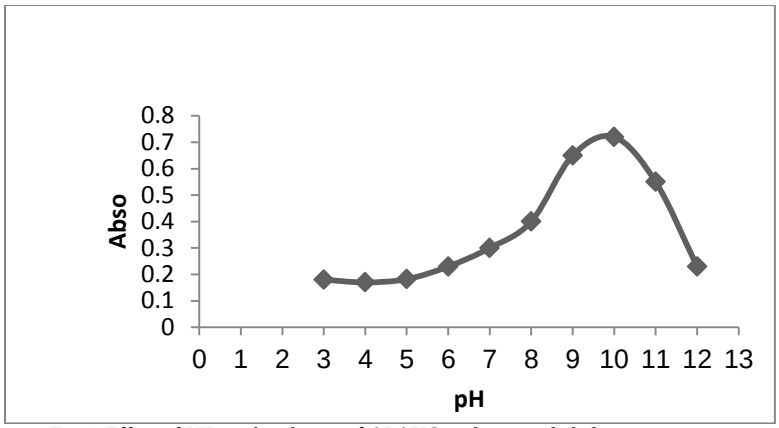


Fig. 2.Effect of PH on absorbance of APAHQ and its metal chelates

Table I
Analytical characteristics of Pd (II) – complex.

Characteristic	**Pd (II)**
Absorption(λmax, nm)	470
PH range	9-11
Beers law range(mg/L)	0.1- 3.0
Molar absorptivity($L.moL^{-1}.cm^{-1}$)	$0.65x10^4$
Concentration of reagent	0.001
Amount of tween-80 100(w/v)	(1,2,3)
RSD%(n=6)	(0.21- 0.36)
Error%	(0.1- 0.4)

Effect of mice llizing agents

Various micellizing agents such as tween – 80 in concentration of (3%) was tasted as solubilizing agents .The absorbance of Pd (II) complex with APAHQ at 470 nm was measured and was .considered for the Pd (II) determinations methods. Less sensitivity was observed in tween – 80 solution .Nonionic micelles are often preferred to .anionic micelles for the determination of metal ion due to attraction forces between the negative head of micelles and the positive charge of metal ion causes lower apparent formation constant between metal ion and ligand.

Faster Formation and high stability for Pd(II) complex was observed in tween-80 Therefore tween – 80 was selected as the micellizing agents further studies.

Effect of reagent concentration

When various concentration of APAHQ solution was added to a fixed amount of Pd(II) . 3ml of 1mM was found enough to develop the colour to its full intensity and give a minimum blank and was considered to be optimum for the concentration range of (0.1- 3.0 µg/ml) of pd (II) Fig.3.

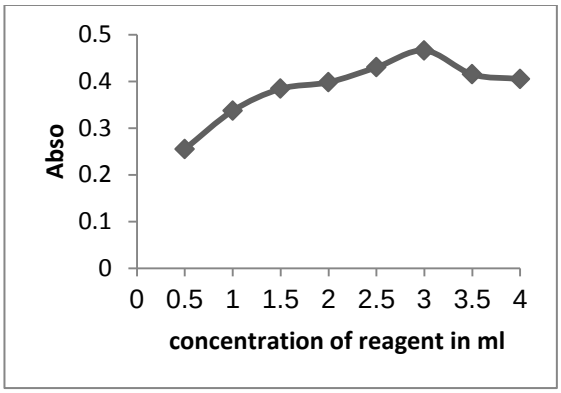


Fig. 3.Effect of the concentration of APAHQ on the coloured

Reaction product

Effect of concentration of Tween -80

Different of amounts of tween -80 was added for metal ion and it was observed that the absorbance was constant and maximum in the amounts given in Table.1. The complex was readily soluble in the presence of Tween -80, and an increase in absorbance was observed in all cases due to miceller action.

Effect of time

The absorbance was constant for more than 24h in the case of Pd(II). This stability period was sufficient to allow several measurements to be performed sequentially .

Composition of the complex

The composition of the complex was studied in the excess of reagent solution by Job's method and mole – ratio method . A break at a 1:2 (M:L) Mole ratio suggested the Formation of M $(C_{20}.H_{19}N_4O_2)_2$ where M=pd (II) under the given conditions .

Beers law and sensitivity

Under the optimum conditions described above ,calibration curve for palladium ion was constructed at respective absorption maxima. Beer's law was obeyed over a wide concentration range of Pd(II) Table I. The molar absorptivity and RSD' are given in Table. I.

Interferences

The effect of diverse ions on the determination of these metals ions were studied in detail .To test the effect of drivers ions, pd(II) was determined by the general procedure, in the presence of their respective . foreign ions. Each of these metal ions can be determined without any interference in the presence of a 50 fold excess of the foreign ions Table. II.

Table II
Effect of foreign ions

Foreign Ions	**Tolerance limit Added µg**	**Interferences With pd(II)**
Hg^{+2}	100	-0.6
Cu^{+2}	100	+0.4
Cr^{+3}	100	+0.14
Mn^{+2}	100	+0.30
Ba^{+2}	100	+0.2
Cd^{+2}	100	+1.06
Fe^{+3}	100	+0.18
Ni^{+2}	100	+0.85
$No3^{-}$	100	-0.32
F^{-}	100	-0.44
I^{-}	100	-0.5
Br^{-}	100	-0.36

Applications

1-Determination of Pd (II) in practical samples .

To determine the accuracy and precision of the method, Pd(II) was determined at two different concentration. The results show in Table III as at is factory precision and accuracy with the proposed method.

Table III
Accuracy and precision of the method.

Amount Taken (µg/ml) of Pd(II)	**Recovery%**	**R.S.D%**
0.5	**99.60%**	**0.36%**
1	**99.90%**	**0.21%**

*** For six determinations**

2- Determination of palladium in tea leaves .

A 2g tea leave put in 50 ml round-bottom flask and digested in 8ml concentrated nitric acid after 3hrs heating . The Solution was cooled, neutralized with sodium hydroxide and filtered. The filtrate was made up to 25ml in volumetric flask with double distilled water[19]. Sample was left for 60 min and then ready for UV-Visible spectrophotometric analysis, 1 ml of the solution was analyzed by the standard addition method Table IV.

Table IV
Determination of Pd(II) in tea leaves

Sample of Tea leaves	**mg .g^{-1} Certified value**	**mg.g^{-1} Amount found**
Pd	**0.84**	**0.82**

Conclusions

In the present work, a new, simple and sensitive micelle-mediated method with the Pd(II)- APAHQ complex was developed for the determination of palladium (II) in biological, and certified samples .The analytical results were satisfactory. The proposed method should be useful for accurate, precise and rapid determination of Pd (II).

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