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A Highly Selective Visible Spectrophotometric Estimation of Pd (II) Using Ambroxol Hydrochloride.

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ABSTRACT

The present paper reports a simple, accurate, precise, sensitive, and highly selective visible, spectrophotometric method for the estimation of Pd(II) using ambroxol hydrochloride. The method is based on the colour reaction between ambroxol and palladium (II) in the pH range 3.0 – 8.0 forming a yellow coloured complex solution. The coloured species has maximum at 410 nm. Studies were carried at the maximum absorption at pH 6.0. A 0.1% sodiumdodesylsulphate (SDS) keeps the complex in solution. The colour intensity attains a maximum value after 30 minutes of mixing the various components. Under the optimum conditions Beer's law is obeyed in the range 1.5-18.5 µg/ml. The straight line plot obeyed the equation $A = 0.0572 C + 0.0007$. The molar absorptivity and Sandell's sensitivity are $6.10 \times 10^3 \text{ l mol}^{-1} \text{ cm}^{-1}$ and $0.0175 \text{ µg cm}^{-2}$ respectively. The standard deviation of the method for ten determinations of 5.0 µg/ml ambroxol is 0.0021. The correlation coefficient (r) of the experimental data of the calibration plot is 0.9999. The effect of various foreign ions was studied. The composition of the complex is established as 2:1[(Pd(II) : Ambroxol)]. The stability constant of the complex is 2.090×10^{11} . The proposed method is successfully applied for the determination of Pd(II) in alloy steels and natural water samples .

Keywords: Pd(II) , Ambroxol hydrochloride, Visible spectrophotometric selective method

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INTRODUCTION

Palladium is a platinum group metal discovered by W.H. Wollaston in 1803. It is rare and lustrous silvery metal. Palladium and its alloys have wide range of applications both in chemical industry and instrument making [1]. Palladium forms a good catalyst and is used to speed up hydrogenation and dehydrogenation reactions, as well as in petroleum cracking. Palladium is employed in many electronic devices including computers, cellphones, multi-layer capacitors and low voltage electrical contacts as well as in dentistry and medicine [2]. Palladium is used in jewellery, watch making and blood sugar strips. Palladium is one of the three most popular methods used to make white gold alloys [3]. Due to its wide applications there is a need for the development of a sensitive, highly selective and precise method for its determination at micro levels. Several analytical techniques such as atomic absorption spectrometry [4], neutron activation analysis [5] and pre-concentration and separation methods such as flow injection method, hollow fiber micro extraction, solid phase micro extraction and spectrophotometry [6-33]. Among them spectrophotometric methods are preferred because of their low cost and simplicity of operation.

However, the survey of literature revealed that there is no report of a sensitive and specific spectrophotometric method for determination palladium (II). In this communication we report a specific, sensitive and precise visible spectrophotometric method for the determination of palladium (II) using ambroxol hydrochloride.

MATERIALS AND METHODS

All chemicals and solvents used were of analytical reagent grade.

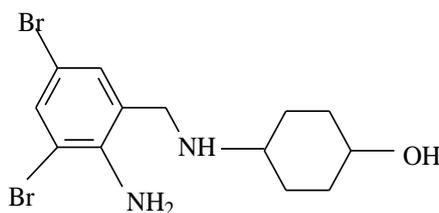
Solutions

Palladium (II) solution

1 g of palladium chloride (Loba Chime Ltd.) is dissolved in distilled water in a 100ml standard flask and standardized [34]. Working solution is prepared by suitably diluting the stock solution.

Ambroxol solution

Ambroxol is 4-[[2-amino-3,5-dibromophenyl) –methyl]amino] cyclohexanol (or) N – (trans –P –hydroxy cyclohexyl) – (2 – amino -3,5 – dibromobenzyl) amine. It is a white crystalline powder freely soluble in water and its molecular formula is $C_{13}H_{18}Br_2N_2O$ (M. W. = 378.11). Its molecular structure is



100 mg of ambroxol hydrochloride was weighed accurately and transferred into a 100 ml standard flask, dissolved and made up to the mark in double distilled water. This solution was diluted as required.

Buffer solutions were prepared by adopting the standard procedures reported in the literature [20]. The solutions employed for the preparation are given below.

pH	Constituents
0.5 – 3.0	1 M Sodium acetate + 1 M Hydrochloric acid
3.0 – 6.0	0.2 M Sodium acetate + 0.2 M Acetic acid
7.0	1.0 M Sodium acetate + 0.2 M Acetic acid
8.0 – 12.0	2.0 M Ammonia + 2.0 M ammonium chloride

Instruments

A Shimadzo UV-Visible recording spectrophotometer (UV-160A) measuring wavelength at 200-1100 nm, and wave length accuracy $\pm 0.5\text{nm}$ with automatic wavelength correction.

An ELICO digital pH meter was used for measuring the pH of buffer solutions. The reproducibility of measurements is within ± 0.01 pH.

Procedures

Preparation of alloy steel samples

A 0.1-0.5g of steel sample was dissolved in a minimum volume of aquaregia by slow heating an sand bath and then heated to fumes of oxides nitrogen. After cooling, 5-10 ml of 1:1 H_2SO_4 were added and evaporated to dryness. Sulphuric acid treatment was repeated three times to remove all the nitric acid. The residue was dissolved in 20 ml of distilled water and filtered. The filtrate was made up to the mark in a 100 ml volumetric flask with distilled water. The solution was diluted to obtain the concentration in the required range.

Absorbance spectrum

5ml of buffer solution of pH 6.0, 1ml of Pd(II) [$2 \times 10^{-3}\text{M}$] solution and 1 ml of ambroxol [$1 \times 10^{-2}\text{M}$] were taken in a 10 ml volumetric flask and made up to the mark with distilled water. The absorbance of the solution was measured in the wavelength region 300-600 nm against a blank consisting of 5 ml of buffer solution made up to the mark with distilled water in a 10 ml volumetric flask.

Determination of Palladium(II)

5ml of buffer solution of pH 6.0, 1ml of ambroxol [$1 \times 10^{-2}\text{M}$] solution and varying volumes of Pd(II) [$2 \times 10^{-3}\text{M}$] solution were taken in a series of 10 ml volumetric flasks and

the contents of each flask were made up to the mark with distilled water. The absorbance of the solution was measured at 410 nm using buffer blank.

Effect of SDS Concentrations

In order to improve the sensitivity the method and to avoid precipitation of the complex species, the effect of various surfactants on the ambroxol –Pd(II) complex solution was studied. Of all the surfactants studied sodium dodecyl sulphate (SDS) is found to enhance the absorbance. The effect of varying concentration of SDS on the absorbance studies are reported in Table-1. The study reveals that 0.1% of SDS gives maximum absorbance for the system.

Interference studies

In order to assess the applicability of the method, the effect of presence of various foreign ions that are generally associated with Pd(II) in real samples is assessed by adding varying amounts of foreign ions to a fixed amount of Pd(II) (5.0 µg/ml) solution and the absorbance measurements are carried out under optimal conditions. The concentration (µg/ml) at which various ions can cause an error $\pm 3\%$ in absorbance is taken as its tolerance limit. The results are given in Table-2

RESULTS AND DISCUSSION

Pd(II) reacts with Ambroxol hydrochloride in the pH range 3.0-8.0 forming a yellow coloured complex in solution. The absorption spectrum of the yellow coloured Pd(II) – Ambroxol complex shows (Fig-1) absorption maximum at 410 nm. At this wavelength either Pd(II) or ambroxol has no significant absorbance. The colour intensity of the complex is maximum in pH range 5.5-6.5. Hence studies were carried at pH 6.0. The colour formation attains maximum intensity after 30 minutes of mixing the various components. Thereafter the colour of the complex remains stable for more than 24 hours. A five fold molar excess of ambroxol hydrochloride is sufficient to produce maximum absorbance. To increase the sensitivity a one percent SDS solution is added. The absorbance varied linearly with the concentration of Pd(II). Beer's law is obeyed in the range 1.5-18.5 µg/ml of Pd(II). The straight line plot obeyed the equation $A = 0.0572 C + 0.0007$. The molar absorptivity and Sandell's sensitivity are $6.100 \times 10^3 \text{ l mol}^{-1} \text{ cm}^{-1}$ and $0.0175 \text{ µg cm}^{-2}$ respectively. The standard deviation of the method for ten determinations of 5.0 µg/ml Pd(II) is 0.0021. The correlation coefficient (r) of the experimental data of the calibration plot is 0.9999. The effective range of concentration for accurate determination of Pd(II) as ascertained from Ringbom's plot is 2.0 - 18.0 µg/ml. The limit of detection is 0.1213 µg/ml.

The composition of the complex was studied by Job's method and molar ratio method. Both the methods confirm that the ratio of [Pd(II) : Ambroxol] is 2:1. The stability constant of the complex as evaluated from the Jobs method is 2.090×10^{11} .

The effect of associated metal ions studied and the results are shown in table -2. The data reveal that the method is specific at pH 6.0 as none of the associated metal ions show any interference.

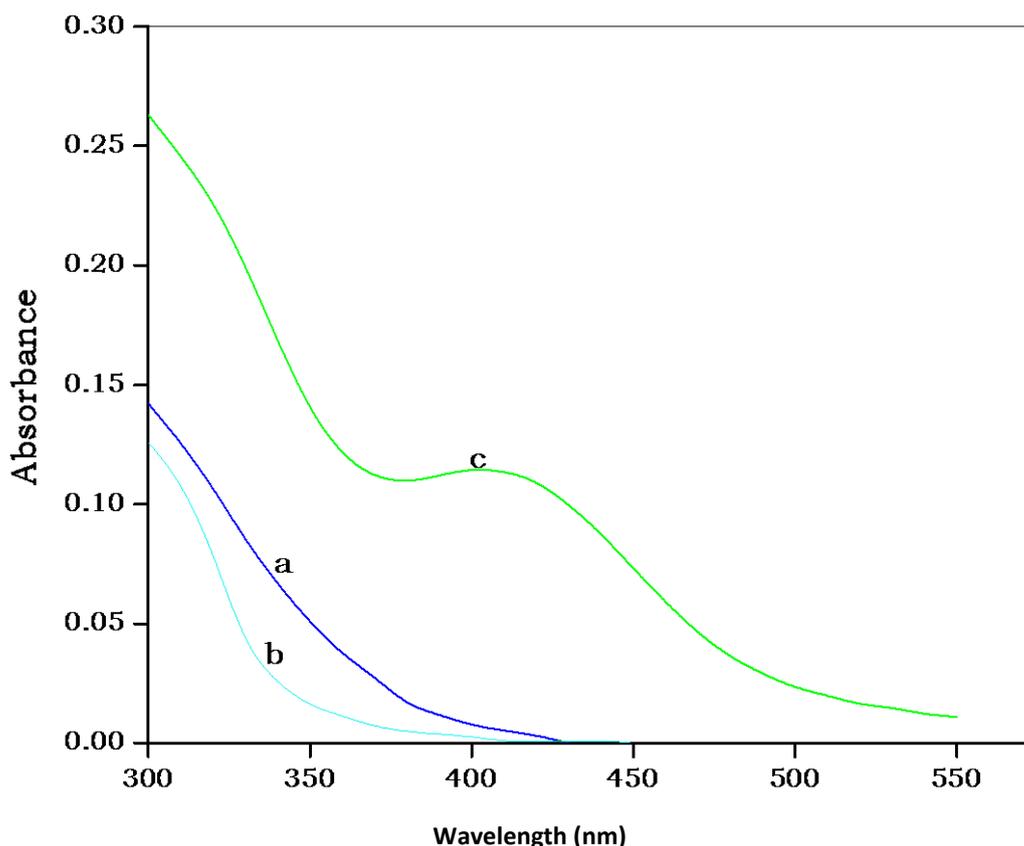


Fig.:1. Absorption spectra of a) Pd(II) vs. buffer blank; b) ABX vs. buffer blank; c) ABX – Pd(II) vs. buffer blank
 $[Pd(II)] = 5.0 \times 10^{-4}M$; $[ABX] = 2.0 \times 10^{-5}M$

Table 1: Effect of SDS Concentration on the absorbance

S. No	Volume of 1% SDS solution	Absorbance
1	0.20	0.316
2	0.50	0.438
3	1.00	0.450
4	1.50	0.451
5	2.0	0.449

$[ABX] = 1 \times 10^{-3} M$
 $[Pd(II)] = 1.25 \times 10^{-4} M$

$\lambda = 410 \text{ nm}$
 $pH = 6.0$

Applications

The method developed was successfully applied for the determination of Pd(II) in alloy steel samples and water samples. The alloy solution prepared as described above was analysed by the present method and results are reported in table-4. Water samples were spiked with known amounts of Pd(II) and were analysed by the proposed method and samples were simultaneously analysed by atomic absorption spectrophotometry and the results are compared[table-5].

Table 2: Tolerance limits of foreign ions

Ion	Tolerance limit($\mu\text{g/ml}$)	Ion	Tolerance limit($\mu\text{g/ml}$)
Iodide	10	Mo(VI)	349
Bromide	530	Ir(III)	629
Chloride	610	Co(II)	123
Fluoride	420	Ba(II)	236
Carbonate	725	Zn(II)	313
Sulphate	1520	Ce(IV)	218
Nitrate	948	W(VI)	397
Phosphate	1630	Mn(II)	108
Oxalate	1190	V(V)	103
Thiocyanate	356	Ag(I)	281
EDTA	1091	U(VI)	428
Tartrate	1462	Zr(VI)	149
Citrate	687	Se(IV)	215
Acetate	878	Th(IV)	350
Ascarbate	1191	Te(IV)	430
Na(I)	355	Pb(II)	267
K(I)	936	Ga(III)	138
Mg(II)	548	In(III)	252
Ca(II)	926	Y(III)	289
Ru(III)	357	La(III)	685
Cr(VI)	159	Ti(IV)	212
Fe(III)	328	Ni(II)	253
Cu(II)	257	Al(III)	102
Cd(II)	457	Au (III)	120
Hg(II)	367	NH ₄ (I)	268
Pt(II)	96		

[palladium (II)] = 5 $\mu\text{g/ml}$ pH = 6.0

Table 3: Optical and regression characteristics, precession and accuracy of the Proposed method for Pd(II)

Parameter	Pd(II)
Analytical Wavelength (nm)	410
Beer's law limits ($\mu\text{g/ml}$)	1.5 – 18.5
Limits of detection ($\mu\text{g/ml}$)	0.1213
Limits of quantization ($\mu\text{g/ml}$)	0.3640
Molar absorptivity ($\text{l.mol}^{-1}\text{cm}^{-1}$)	6100
Sandell's Sensitivity ($\mu\text{g/cm}^2$)	0.0175
Regression equation ($y = a + b x$)	
Slope (b)	0.0571
Intercept (a)	0.0007
Correlation coefficient (γ)	0.9999
Standard deviation(SD)(5.0 $\mu\text{g/ml}$)	0.0021

Table 4: Analysis of alloys

Alloy	Composition	Palladium found * (μg)	Error (%)
(Pd-Au alloy)	Pd, 50: Au, 50	50.28	+0.56
Pd-Cu alloy	Pd,60; Cu:40	59.5	-0.86
Pd- Ag alloy	Pd,60; Ag,40	60.40	0.60

* Average of seven determinations

Table 5: Determination of Pd(II) in water samples

Sample No	Amount of Pd(II) added(μg)	Pd(II) found present method* (μg)	Pd(II) found AAS method (μg)
1	6.0	5.89	6.91
2	8.0	7.88	7.93
3	10.0	9.96	9.99

* Average of seven determinations

CONCLUSIONS

As reported already literature survey do not reveal the report of any specific spectrophotometric method for the determination of Pd(II). The present method for the determination of Pd(II) is a simple, selective and sensitive. The present visible spectrophotometric procedure which is not only fairly rapid, precise and highly sensitive but also is within the reach of an ordinary chemical laboratory. The linearity parameter and the corresponding regression data indicates excellent linear relationship ($r = 0.9999$). Other spectrophotometric methods reported for its determination either use of costly instrumentation or suffer from interference of associated ions. The method is easily applied for the determination of Pd(II) in alloy steels and natural waters.

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