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New Spectrophotometric Method for the Determination of Trace Amounts of Palladium

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Summary. A simple, rapid, selective, and sensitive method for the spectrophotometric determination of palladium is developed based on the reaction of Pd(II) with 1-amino-4-hydroxyanthraquinone (*AMHA*). The reaction is carried out at *pH* 3.8 in 50% (*v*/*v*) ethanol-water medium. The molar absorptivity of the complexed ligand is $1.1 \cdot 10^4 \, \mathrm{l \, mol^{-1} \, cm^{-1}}$ at 620 nm. Calibration plots are linear up to 17 µg Pd $\mathrm{cm^{-3}}$. The optimum concentration range (Ringbom plot) is between 3–14.5 µg $\mathrm{cm^{-3}}$. The spectral study of the reaction in solutions containing equimolar concentrations or an excess of one component, in the *pH* range ~ 0.3–6.5, indicate the possible complex transitions that occur in solution. Complete graphical and logarithmic analysis of the absorbance-*pH* graphs was performed to demonstrate and characterize the complexation equilibria in solution. Under the optimum conditions, palladium can be determined as the noncharged complex $\mathrm{Pd}(AMHA)_2$ in the presence of a large number of foreign ions. Interferences caused by zirconium(IV) could be masked with fluoride ions.

Keywords. Palladium(II) determination; 1-Amino-4-hydroxyanthraquinone; Spectrophotometry; Complexation equilibria.

Eine neue spektrophotometrische Methode für die Bestimmung von Palladium in Spuren

Zusammenfassung. Eine einfache, schnelle und empfindliche Methode für die spektrophotometrische Bestimmung von Palladium wurde auf der Basis der Reaktion von Pd(II) mit 1-Amino-4-hydroxyanthrachinon (*AMHA*) entwickelt. Die Reaktion wird in 50% (*v*/*v*) Ethanol/Wasser bei *pH* 3.8 ausgeführt. Die molare Absorption des komplexierten Liganden beträgt $1.1 \cdot 10^4 \, \mathrm{l \, mol^{-1} \, cm^{-1}}$ bei 620 nm. Kalibrierungskurven verlaufen bis zu 17 µg Pd $\mathrm{cm^{-3}}$ linear. Der optimale Konzentrationsbereich (Ringbom-Plot) liegt zwischen 3 und 14.5 µg $\mathrm{cm^{-3}}$. Spektroskopische Untersuchungen der Reaktion in Lösungen, entweder mit equimolaren Konzentrationen oder mit einem Überschuß an einer Komponente im *pH*-Bereich ~ 0.3 – 6.5, lassen Rückschlüsse auf mögliche Komplex-Übergänge in Lösung zu. Es wurde eine vollständige graphische, logarithmische Analyse der Absorptions-*pH*-Graphen durchgeführt, um die Komplexgleichgewichte in Lösung aufzuklären und zu charakterisieren. Unter den Optimalbedingungen kann Palladium als nichtgeladener Komplex $\mathrm{Pd}(AMHA)_2$ in Gegenwart einer großen Anzahl an Fremd-Ionen bestimmt werden. Schwierigkeiten mit Zirkonium(IV) konnte durch Maskierung mit Fluorid-Ionen umgangen werden.

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Introduction

Previous studies from this laboratory have shown that amino-substituted anthraquinones have some advantages among other anthraquinone dyes for further application in analytical chemistry [1–7]. During the course of investigating the potentialities of some of these compounds as analytical reagents, an extensive study has been made with 1-amino-4-hydroxyanthraquinone (*AMHA*). The analytical aspects of *AMHA* for Zr(IV) [7] have recently been explored. *AMHA* possesses a unique combination of properties that enable this reagent to be utilized in some novel applications. The reagent has three variously colored acid-base forms: LH_4^+, LH_3 and LH_2^- which are dependent on the acidity of the medium. The neutral form (LH_3) is the prevalent species of the reagent present in solution within a wide pH interval (~ 1.5–10) and hence any contribution from the other two forms of the reagent in the complexation equilibria within this pH range can be precluded. In 50% (*v*/*v*) ethanol, the acid-base equilibria liable to set in *AMHA* solution can be represented as

$$\underset{(pH < 1.0)}{LH_4^+} \overset{-H^+}{\rightleftharpoons} \underset{(pH\ 1.5\text{–}10)}{LH_3} \overset{-H^+}{\rightleftharpoons} \underset{(pH > 10.5)}{LH_2^-}.$$

The acid dissociation constants (pK_{a_i}) corresponding to these ionization steps have been calculated by treating the nonlinear dependences $A = f(pH)$ as described elsewhere [8]. The mean pK_{a_i} values are given in Table 1. The experimental data can be obtained from the authors of this work.

Based on preliminary results of a study of the complex equilibria of the platinum metals with *AMHA*, Pd(II) was chosen for a detailed spectrophotometric study in aqueous-ethanol medium. The work was aimed to give a complete picture of the solution equilibria in the pH range studied. The basic characteristics of the complex species have been determined. The study enables us to determine the optimum conditions favouring the direct spectrophotometric determination of trace levels of palladium on the basis of the suitably selected complex equilibrium.

Experimental Part

Analytical-grade reagents and deionized water (or pure ethanol) were used for preparation of solutions. A stock solution of palladium was prepared by dissolving chloride-free palladium hydroxide obtained from 1 g palladium(II) chloride in perchloric acid and was standardized as recommended [9]. A

Table 1. Values of pK_a and λ_{max} for various forms of *AMHA* in 50% (*v*/*v*) ethanol (species in parentheses)

pK_{a_i}	λ_{max}, nm
	395 (LH_4^+)
0.82 ± 0.02	525, 565 (LH_3)
10.46 ± 0.03	555, 595 (LH_2^-)

$2 \cdot 10^{-3}$ mol dm^{-3} stock solution of *AMHA* was prepared by dissolving the accurately weighed amount of the reagent in ethanol. Standard solutions of NaOH (0.1 mol dm^{-3}) and $HClO_4$ ($5 \cdot 10^{-2}$ mol dm^{-3}) were also prepared. More dilute solutions of the reagents were obtained as required by accurate dilution. Solutions of diverse ions used for interference studies were prepared using AnalaR products of the nitrate, acetate or perchlorate salts of metal ions and potassium or sodium salts of the anions to be tested. The acidity of the solutions investigated was adjusted by the addition of either dilute perchloric acid or sodium hydroxide.

A model Lambda 3B Perkin-Elmer Spectrophotometer with 1 cm quartz cells and a model M63 Radiometer *pH* meter with a combined glass electrode of the type Radiometer (GK 2301C) were used. Measurements were carried out in a 50% (*v*/*v*) ethanol-water medium at 20°C. The ionic strength of solutions was kept constant at 100 mmol dm^{-3} ($NaClO_4$) except for some measurements that were performed in stronger perchloric acid. Correction of *pH* readings in aqueous-ethanol medium was made as described previously [10]. IR spectra of the solid chelates were recorded as CsBr discs on a Perkin Elmer 599 B IR spectrophotometer. Elemental analysis were performed at the Microanalysis Laboratory, School of Chemistry at Leads University, U.K.

Standard Procedure

A solution containing 75–320 µg of Pd(II) was transfered into a 25 ml calibrated flask and 4 ml of $2 \cdot 10^{-3}$ mol dm^{-3} *AMHA* solution and 2.5 ml of 1 mol dm^{-3} $NaClO_4$ were added. After mixing with the requisite amount of pure ethanol, the *pH* of the solution was adjusted to 3.8 with suitably selected dilute $HClO_4$. The resulting solution was diluted to volume with de-ionized water and the absorbance was measured at 620 nm by using 1 cm quartz cell against a similarly prepared reagent blank of the same *pH*.

Results and Discussion

The complexation equilibria of Pd(II) with *AMHA* were studied in 50% (*v*/*v*) ethanol-water medium in the *pH* range 0.3–6.5. The visible absorption spectra of solutions were recorded in the presence of an excess of the metal ion, in equimolar solutions and in presence of excess reagent. The absorption spectra of equimolar solutions and of solutions with excess of metal ion at various *pH* values are analogous and exhibit an absorption band with λ_{max} at 595 nm. In presence of excess reagent, the solution spectra reflect the formation of a complex with λ_{max} 595 nm at $pH < 0.9$ and of another complex with $\lambda_{max} = 620$ nm at $pH < 3.2$–4.0. The absorbance versus *pH* graphs for the above solutions show the range of formation and existence of the basis complex equilibria within the *pH* range studied, that are sufficiently separated (representative curves are given in Fig. 1). The first complexation equilibrium in strongly acidic solutions ($pH < 0.9$) probably involves complexation through interaction of Pd(II) with LH_4^+ forms of the reagent according to the general Eq. (1).

$$mM^{2+} + nLH_x \rightleftharpoons M_mL_nH_z + qH^+. \tag{1}$$

The absorbance-*pH* graphs for solutions with excess metal ion or with equimolar concentrations show a decrease of absorbance within the *pH* range 1.2–3.1 followed by a nearly flat part up to $pH \sim 4.2$, which denotes a complex transition of the type:

$$M_mL_nH_z \rightleftharpoons M_mL_nH_{z-q} + qH^+. \tag{2}$$

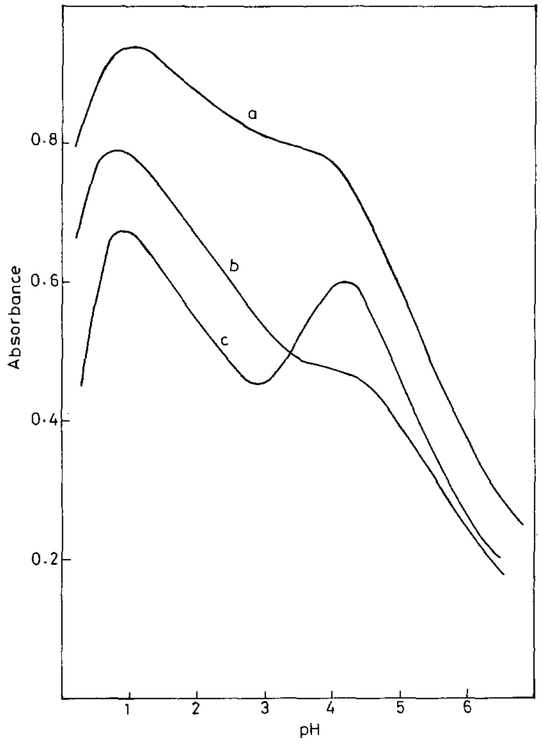

Fig. 1. Absorbance vs. *pH* graphs for Pd(II)-*AMHA* systems of various concentrations of components, 50% (*v*/*v*) ethanol. *a* $C_L = 1 \cdot 10^{-4}$ mol dm^{-3}, $C_M = 5 \cdot 10^{-4}$ mol dm^{-3}, *b* $C_L = C_M = 1 \cdot 10^{-4}$ mol dm^{-3}, *c* $C_L = 5 \cdot 10^{-4}$ mol dm^{-3}, $C_M = 1 \cdot 10^{-4}$ mol dm^{-3}, $\lambda = 610$ nm

Above $pH \sim 4.5$, the absorbance decreases rapidly owing to the hydrolysis of the complexed ligand according to equilibrium (3).

$$M_mL_nH_c + y\,H_2O \rightleftharpoons M_ml_nH_d(OH)_y + q\,H^+ . \qquad (3)$$

The absorbance vs. *pH* graphs for solutions containing excess ligand indicate the existence of three basic equilibria within the *pH* range 0.3–4.2 that are sufficiently separated. In addition to equilibrium (1), and the deprotonation equilibrium (2) the second ascending part of these graphs (at *pH* range 3.3–4.2) is probably due to a stepwise complex transition with further ligand species coordinated.

$$M_mL_nH_z + pLH_x \rightleftharpoons M_mL_bH_c + q\,H^+ . \qquad (4)$$

The absorbance-*pH* graphs have also a descending branch above *pH* 4.5 due to the hydrolysis of the complex.

The absorbance curves of solutions with an excess of one component or equimolar solutions in dependence on the *pH* were interpreted using the early-derived slope-intercept transformations [11] of the equilibrium constants of conditional stability constants of the assumed chelates for conditions under which a single complex equilibrium predominates and for chosen wavelengths.

The absorbance vs. *pH* graphs for equimolar solutions or solutions with an excess of one component exhibit two sufficiently separated formation branches in the *pH* range 0.3–3.2. The first branch shifts to more acidic region with increasing Pd(II) concentration and reaches its upper limit at $pH \sim 0.8$–1.2 which denotes quantitative formation of the first complex species. This complex is presumably transformed to a complex with less protons in the *pH* range 1.4–3.2 along with the absorbance decreases gradually until reaches a limiting value at *pH* 3.5–4.0. The second formation branch of the absorbance vs. *pH* graphs for solutions containing excess metal ion is considerably distorted by simultaneous hydrolysis of the Pd(II) ions. The two formation branches were treated independently by graphical analysis considering the complex formation according to equilibrium (1) in the first part of the graph and conversion of the complex to a less protonated complex with the same nuclearity (Eq. 2).

By considering the values of the dissociation constants of *AMHA* under our experimental conditions, we can assume the following complexation equilibria during direct graphical and logarithmic analysis of the absorbance *pH* graphs:

$$\mathrm{Pd}^{2+} + L\mathrm{H}_4^+ \rightleftharpoons [\mathrm{Pd}(L\mathrm{H}_2)]^+ (\varepsilon_1) + 2\,\mathrm{H}^+, \tag{A}$$

$$\mathrm{Pd}^{2+} + L\mathrm{H}_4^+ \rightleftharpoons [\mathrm{Pd}L\mathrm{H}_3]^{2+} (\varepsilon_{1\,\mathrm{H}}) + \mathrm{H}^+, \tag{B}$$

$$[\mathrm{Pd}L\mathrm{H}_3]^{2+} (\varepsilon_{1\,\mathrm{H}}) \rightleftharpoons [\mathrm{Pd}(L\mathrm{H}_2)]^+ (\varepsilon_1) + \mathrm{H}^+, \tag{C}$$

$$[\mathrm{Pd}L\mathrm{H}_2]^+ + L\mathrm{H}_3 \rightleftharpoons \mathrm{Pd}(L\mathrm{H}_2)_2 (\varepsilon_2) + \mathrm{H}^+, \tag{D}$$

$$[\mathrm{Pd}L\mathrm{H}_3]^{2+} + L\mathrm{H}_3 \rightleftharpoons \mathrm{Pd}(L\mathrm{H}_2)_2 + 2\,\mathrm{H}^+, \tag{E}$$

$$[\mathrm{Pd}(L\mathrm{H}_2)]^+ + 2\,\mathrm{H}_2\mathrm{O} \rightleftharpoons [\mathrm{Pd}(L\mathrm{H}_2)(\mathrm{OH})_2]^- + 2\,\mathrm{H}^+, \tag{F}$$

$$\mathrm{Pd}(L\mathrm{H}_2)_2 + 2\,\mathrm{H}_2\mathrm{O} \rightleftharpoons [\mathrm{Pd}(L\mathrm{H}_2)(\mathrm{OH})_2]^- + L\mathrm{H}_3 + \mathrm{H}^+. \tag{G}$$

The graphical and logarithmic analysis of the first part of the absorbance-*pH* graphs for solutions of varying component ratios did not prove the existence of equilibrium (A), but a complex equilibrium involving dissociation of only one proton, in accordance with Eq. (B) was unambiguously confirmed. This may be interpreted on the basis that chelate formation with the $L\mathrm{H}_4^+$ form of the reagent takes place through the carbonyl oxygen and the hydroxyl group and leads to proton displacement. The deprotonation of the amino-nitrogen at this stage is precluded.

The graphical and logarithmic analysis of the second part of the absorbance-*pH* graphs proved that the protonated complex $[\mathrm{Pd}L\mathrm{H}_3]^{2+}$ is converted into the $[\mathrm{Pd}L\mathrm{H}_2]^+$ complex with the dissociation of one proton according to Eq. (C).

On the other hand, the formation of the $\mathrm{Pd}(L\mathrm{H}_2)_2$ complex according to Eq. (D) was confirmed by the analysis of the second ascending branch of the absorbance-*pH* graphs for solutions with excess of ligand in the *pH* range 3–4.3 using transformations I and II; assuming an equilibrium of the type (4).

$$C_M/\Delta A = 1/\varepsilon_2 + (\Delta A - \varepsilon_1 C_M)[\mathrm{H}]^q z^p/\Delta A\,{}^*K_2\,\varepsilon_2\,C_L^p, \tag{I}$$

$$\log\,[(\Delta A - \varepsilon_1 C_M) Z^p/(\varepsilon_2 C_M - \Delta A) = q\,pH + p\log C_L + \log{}^*K_2. \tag{II}$$

The distortion of the C_M/A or $\log\,[(\Delta A - \varepsilon_1 C_M)Z^p/(\varepsilon_2 C_M - \Delta A)] = \mathrm{f}(pH)$ dependences at the ends ($pH < 3.2$ and $pH > 4.2$) is probably caused by overlapping of the equilibria of the $[\mathrm{Pd}L\mathrm{H}_2]^+$ complex formation and its conversion into the $[\mathrm{Pd}(L\mathrm{H}_2)_2]$ complex according to reactions (C) and (D) respectively, or by formation of the $[\mathrm{Pd}(L_2\mathrm{H}_5)]^+$ complex species according to the reaction

$$[\mathrm{Pd}L\mathrm{H}_3]^{2+} + L\mathrm{H}_3 \rightleftharpoons [\mathrm{Pd}(L_2\mathrm{H}_5)]^+ + \mathrm{H}^+ \tag{H}$$

and its conversion to the less protonated $\mathrm{Pd}(L\mathrm{H}_2)_2$ complex.

It was found by measuring the dependence of absorbance on the reagent concentration at *pH* 3.5–4.0 that a concentration excess of reagent of $C_L/C_M \simeq 3$ (at

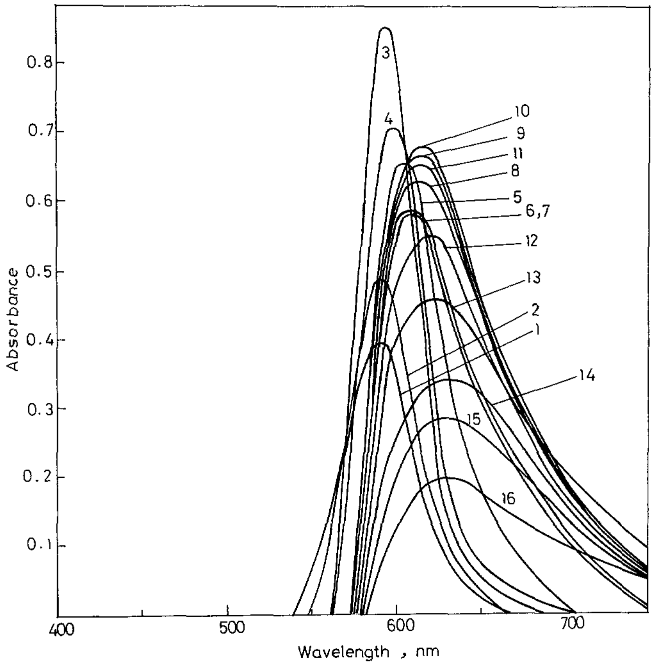

Fig. 2. The absorption spectra of Pd(II)-*AMHA* solutions at different *pH* values. $C_M = 1 \cdot 10^{-4}$ mol dm^{-3}, $C_L = 3 \cdot 10^{-4}$ mol dm^{-3}, 50% (*v*/*v*) ethanol; *pH*: *1* 0.35; *2* 0.50; *3* 0.95; *4* 1.75; *5* 2.05; *6* 2.75; *7* 3.10; *8* 3.45; *9* 3.70; *10* 3.90; *11* 4.25; *12* 4.60; *13* 5.0; *14* 5.35; *15* 5.70; *16* 6.45

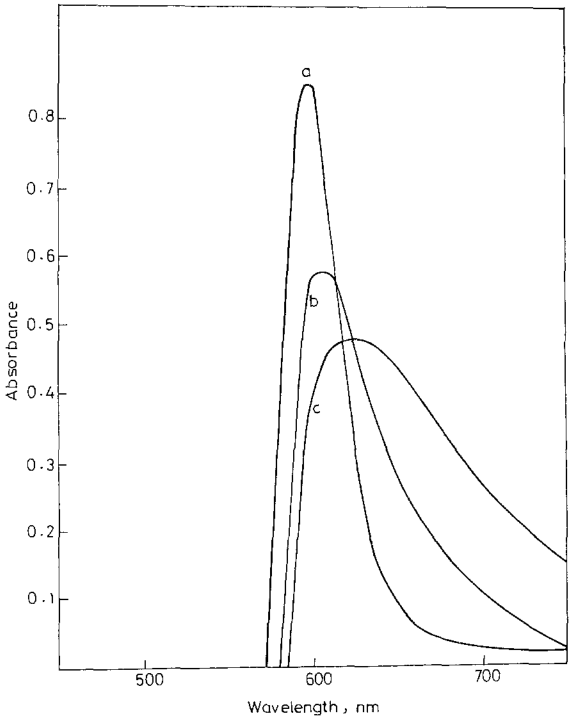

Fig. 3. The absorption spectra of Pd(II)-*AMHA* complexes, 50% (*v*/*v*) ethanol, $C_M = 1 \cdot 10^{-4}$ mol cm^{-3}, $C_L = 3 \cdot 10^{-4}$ mol dm^{-3}; *a* $pH = 1.05$, *b* $pH = 2.25$, *c* $pH = 3.85$

pH 3.8) is sufficient for quantitative formation of the $Pd(LH_2)_2$ complex. A series of absorption spectra of solutions with excess *AMHA* at various *pH* values indicating successive formation of the $[Pd(LH_3)]^{2+}$, $[Pd(LH_2)]^+$, and $Pd(LH_2)_2$ complexes and the spectra of the individual complexes of Pd(II) with *AMHA* are given in Figs. 2 and 3, respectively.

Table 2. Mean values of equilibrium (log $^*K$), stability constants (log B) and molar absorptivities of palladium(II)-*AMHA* complexes. Values are taken as averages for various component concentrations, $I = 0.1$ mol dm^{-3} ($NaClO_4$), 20°C, 50% (*v*/*v*) ethanol

Equilibrium$^{()}$	Constant	log constant	Molar absorptivity l mol^{-1} cm^{-1}
$[PdLH_3][H]/[Pd][LH_4]$	$^*K_{11}$	$(4.91 \pm 0.02)^a$, $(4.52 \pm 0.01)^b$, $(4.83 \pm 0.02)^c$	(ε_{1H}) 5 600
$[PdLH_2][H]/[PdLH_3]$	$^*K_{kal}$	$(-2.15 \pm 0.01)^a$, $(-1.92 \pm 0.02)^b$, $(-1.68 \pm 0.02)^c$	(ε_1) 7 600
$[Pd(LH_2)_2][H]/[PdLH_2][LH_3]$	K_{21}	$(-1.01 \pm 0.01)^c$	(ε_2) 11 000
$[PdLH_2(OH)_2][H]^2/[PdLH_2]$	$k_{(2OH)}$	$(-8.86 \pm 0.03)^a$, $(-8.94 \pm 0.02)^b$	
$[PdLH_2(OH)_2][H][LH_3]/[Pd(LH_2)_2]$	$k'_{(2OH)}$	$(-9.4 \pm 0.02)^c$	
$[PdLH_3]/[Pd][LH_3]$	β_{1H}	5.71^d	
$[PdLH_2]/[Pd][LH_2]$	β_1	14.21^e	
$[Pd(LH_2)_2]/Pd][LH_2]^2$	β_2	23.66^f	
$[PdLH_2(OH)_2]/[Pd][LH_2][OH]^2$	$\beta_{(OH)}$	31.81^g	

$^{()}$ Charges are omitted

[a] From the absorbance vs. *pH* graphs for solutions of equimolar concentrations

[b] From the absorbance vs. *pH* graphs for solutions with excess metal

[c] From the absorbance vs. *pH* graphs for solutions with excess ligand

[d] $\beta_{1H} = {}^*K_{11}/K_{a1}$

[e] $\beta_1 = {}^*K_{11} \cdot K_{kal}/K_{a2}$

[f] $\beta_2 = \beta_1 \cdot K_{21}{}^*K/K_{a2}$

[g] $\beta_{OH} = k_{(2OH)} \cdot \beta_1/K_w^2 = k'(2OH) \cdot \beta_2 \cdot K_{a2}/K_w^2$

All the absorbance vs. *pH* graphs at various wavelengths and concentration ratios of components have a descending branch above $pH \sim 5$ which is due to the hydrolysis of the complexed ligand. The graphical analysis of this part of the absorbance-*pH* graphs for solutions with excess metal ion according to Eq. (3) indicate unambiguously the hydrolysis of the $[Pd(LH_2)]^+$ complex to the hydroxo-complex $[Pd(LH_2)(OH)_2]$. This complex transition is also confirmed in equimolar solutions above *pH* 4.5. The results obtained indicate that two protons are liberated during the complex transition and the equilibrium (F) is predominant. On the other hand, the analysis of the descending branch (at *pH* 4.5–6.0) in solutions with excess ligand confirmed the existence of the hydrolytic reaction (G) of the $Pd(LH_2)_2$ complex.

The calculated values of the molar absorptivities, equilibrium constants and stability constants of the Pd(II)-*AMHA* complexes are given in Table 2.

The stoichiometry of the Pd-*AMHA* chelates was further verified by the method of continuous variation [12]. In solutions having $C_0 = C_M + C_L = 6.0 \cdot 10^{-4}$ mol dm^{-3} at *pH* 2.5, the maximum of the Job plot corresponds to a component ratio of 1 : 1 (metal to ligand). At *pH* 3.5–4 a component ratio of 1 : 2 was confirmed.

As far as the analytical aspects of the complexation reaction of Pd with *AMHA* are concerned, the formation of the protonated $[Pd(LH_3)]^{2+}$ complex seems to be an unsuitable base for the determination of palladium. This is because of the low stability of the complex and its extreme sensitivity to changes in acidity. The quantitative formation of this complex is attained at $pH \sim 0.6$. The reagent, however, begins to deprotonate at this *pH* value yielding the strongly absorbing LH_3 form (λ_{max} 525, 565 nm, $\varepsilon = 1 \cdot 10^4$ l mol^{-1} cm^{-1}) so that the *pH* of the sample solution and of the reagent blank solution must be accurately maintained.

On the other hand, the predominancy of the complex $Pd(LH_2)^+$ is uncertain unless a favourable adjustment of the *pH* value and component concentration ratio is carried out. As a consequence, the above complex is not very promising for the analytical determination of palladium. According to the results of this work, the most suitable basis for the spectrophotometric determination of palladium under our experimental conditions is the complex formation of $Pd(LH_2)_2$ which possesses greater stability and does not require a rigid control of *pH*. The optimum *pH* range for quantitative formation of this complex according to equilibrium (D) is 3.2–4.3 which makes the LH_4^+/LH_3 acid-base equilibrium of the reagent to have no role in the complexation reaction since the only reacting species of *AMHA* at this *pH* range is the molecular form LH_3.

The $Pd(LH_2)_2$ chelate was prepared and characterized. The salient features of the IR spectrum of the complex showed unambiguously that chelate formation takes place via the carbonyl oxygen and hydroxyl group and leads to proton displacement. The spectrum revealed that any possibility of the co-ordination of *AMHA* occurring through the amino nitrogen can be eliminated. The formulation of the isolated complex as $Pd(LH_2)_2$ (LH_3 symbolizing the neutral form of *AMHA*) was confirmed by elemental analysis and conductivity measurements. The molar electrical conductance, Λ_m, of reagent grade *DMF* solution of the complex at a concentration of 10^{-3} mol dm^{-3} showed that the complex is essentially nonelectrolyte.

Calibration Graph and Reproducibility

Under the optimum conditions given under Standard Procedure, a linear calibration graph was obtained up to a concentration of 17 μg cm^{-3} of Pd(II). The molar absorptivity of the complex at 620 nm was $1.1 \cdot 10^4$ l mol^{-1} cm^{-1}. A Ringbom plot showed that the optimum range for the determination of Pd(II) was 3–14 μg cm^{-3}. The sensitivity of the reaction was found to be $2.4 \cdot 10^{-3}$ μg cm^{-2} of palladium(II). The reproducibility of the method was checked by analysing two series of solutions having palladium(II) concentrations of 6.4 and 10.6 μg cm^{-3}. The relative standard deviations were found to be 0.7 and 0.5% respectively.

The application of numerous organic reagents for the spectrophotometric determination of palladium is well known. From comparison with other conventional or recently described reagents (Table 3), *AMHA* was proved to act as potential reagent for direct spectrophotometric determination of palladium. The present method is simpler and faster than many other sensitive methods. It has the advantages of reasonable selectivity, good sensitivity and reproducibility and highly stable reagent solution.

Table 3. Comparison of spectrophotometric reagents for palladium(II)

Reagent	Range of concentration $\mu g\,ml^{-1}$	Molar absorptivity $l\,mol^{-1}\,cm^{-1}$	Ref.
4,4,6-Trimethylpyrimidine-2-thiol	5.3–20	$3.7 \cdot 10^3$/430 nm	13
2-Chlorophenethiazine	0.36–6.4	$4.63 \cdot 10^3$/525 nm	14
Mepazine hydrochloride	$\leqslant 12$	$4.46 \cdot 10^3$/510 nm	15
Phenylazobenzaldehyde oxime	2–16	$3.6 \cdot 10^3$/550 nm	16
Nitrosodibenzylaniline	$\leqslant 1$	$1.1 \cdot 10^5$/522 nm[a]	17
4-(4,5-Dimethyl-2-thiazolylazo)-2-methylresorcinol	0.08–0.76	$1.46 \cdot 10^4$/560 nm	18
Isonitrosobenzoylacetone	1–13	$1.02 \cdot 10^4$/405 nm[a]	19
Quindine-2-aldehydethiosemicarbazone	2.5–20	$2.6 \cdot 10^3$/510 nm[a]	20
Ethylene dithiodiacetic acid	0.4–4	$2.01 \cdot 10^4$/290 nm	21
Solochrome Red B	0.1–1	$1.2 \cdot 10^4$/488 nm	22
Methiomeprazine hydrochloride	0.4–21	$3.6 \cdot 10^3$/480 nm	23
2-thiobarbaturic acid	0.18–6	$7.5 \cdot 10^3$/388 nm	24
2-(5-Bromo-2-pyridylazo)-5-(diethylamino)phenol	$\leqslant 40$	$4.5 \cdot 10^4$/620 nm	25

[a] By solvent extraction

Effect of Diverse Ions

To determine the effect of diverse ions on the determination of palladium, solutions were prepared containing 175 μg of Pd(II) and varying concentrations of each ion to be tested. The palladium was then determined as $Pd(LH_2)_2$ under the optimum conditions as described in the given procedure. The tolerance criterion for a given ion was taken to be the deviation of the absorbance values by more than ± 2% from the value expected for palladium alone. The presence of 15 mg (~ 85-fold excess) of the following ions caused no interference; Li^+, K^+, Na^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Mn^{2+}, Co^{2+}, Zn^{2+}, Mo^{6+}, Ru^{3+}, Rh^{3+}, Ag^+, Cd^{2+}, W^{6+}, Au^{3+}, Os^{8+}, Ir^{3+}, Pt^{2+}, Pt^4, Tl^{3+}, La^{3+}, U^{6+}, Ce^{4+}, Cl^-, Br^-, F^-, NO_3^-, SO_4^{2-}, SO_3^{2-}, ClO_4^-, and acetate ions. The determination of palladium was also possible in presence of Ni^{2+}, and Pb^{2+}, Al^{3+} (7.5 mg) or Hg^{2+}, Th^{4+} (3 mg). Using the present experimental conditions, it was observed that Pd(II) could not be determined in the presence of *EDTA* or CN^- ions. Accordingly the above reagents could not be used as masking agents. Interference from the presence of Zr(IV) could be eliminated by adding ammonium fluoride solution (ca. 50-fold excess) as a masking agent, whereas the interference caused by large amounts of Hg^{2+} or Th^{4+} (up to 10 mg) could be prevented in presence of salicylic or thiosalicylic acid (~ 20-fold excess) as masking agents.

The recommended procedure for the determination of palladium(II) was applied to some dental alloys with an appropriate palladium(II) content, to evaluate its effectiveness. The recovery of the analysis was 96.8% [Pd(II) taken, 15 $\mu g\,ml^{-1}$].

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Symbols used (Eqs. I and II). C_L = total concentration of the ligand; C_M = total concentration of the metal ion; $\Delta A = A - A_L$, differences in the overall absorbance and the absorbance of the reagent blank under the same conditions; ε_1 and ε_2, molar absorptivities of $[\mathrm{Pd}(L\mathrm{H}_2)]^+$ and $\mathrm{Pd}(L\mathrm{H}_2)_2$ complexes, respectively; q, number of protons liberated during the formation of the complex $K_a = [L\mathrm{H}_{i-1}][\mathrm{H}]/[L\mathrm{H}_i]$; $Z = 1 + [\mathrm{H}]/Ka_1$, K_2 is the equilibrium constant of the complexation reaction.

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