# HIGHLY SPECIFIC SPECTROPHOTOMETRIC METHOD FOR PALLADIUM(II) DETERMINATION WITH 3-(5′-TETRAZOLYLAZO)-2,6-DIAMINOTOLUENE IN THE PRESENCE OF CHLORIDES. KINETIC AND EQUILIBRIUM STUDY OF REACTIONS

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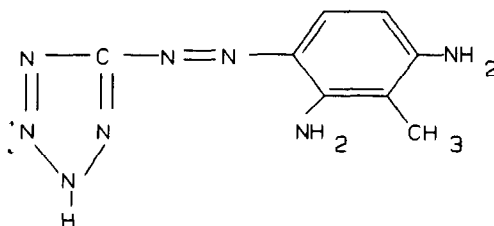
**Summary**—3-(5′-tetrazolylazo)-2,6-Diaminotoluene (TEADAT, $H_3L^{2+}$) forms stable 1:1 and 1:2 (metal:ligand) pink-red complexes ($\lambda_{max}$ 506 and 536 nm) with palladium(II). The apparent molar absorptivity of 1:2 complex is $5.2 \times 10^4$ l. $mol^{-1}$. $cm^{-1}$ at 536 nm. Equilibrium constants $\beta^*_{n1}$ for reactions $PdCl_4^{2-} + nH_3L^{2+} \rightleftharpoons PdCl_{4-n}(H_2L)_n^{2n-2} + n$ $Cl^- + n$ $H^+$ were determined: $\log \beta^*_1 = 4.09 \pm 0.05$, $\log \beta^*_2 = 8.40 \pm 0.02$, corresponding stability conditional constants of $PdCl_3(H_2L)$ and $PdCl_2(H_2L)_2^{2+}$ were $\log \beta_1 = 19.03$, $\log \beta_2 = 26.74$. The formation of complexes was rather slow but could be speeded up considerably by the catalytic effect of trace amounts of thiocyanate. Constant absorbance values were thus reached in 2–5 min. A rapid, sensitive and highly specific method for the determination of palladium(II) at pH 1.42 in 0.25$M$ NaCl has been worked out with a detection limit of 0.54 $\mu$g. Interference of precious and common metal ions have been studied and the method has been applied for the determination of palladium in Pd asbestos, oakay alloys and various catalysts and for the determination of palladium in precious metals.

There is an increasing interest in the spectrophotometric determination of palladium(II) in catalytic, biological and other materials using thiazolylazo, or triazolylazo reagents.[1–7] Among the many azodyes those with functional groups (*e.g.* —COOH, —NH₂, arsonic) *ortho* to the azo group are the most frequently employed.

Some time ago, thiazolylazo and triazolylazo derivatives of 2,6-diaminotoluene were synthesized and used for the determination of cobalt and palladium;[8,9] while the preliminary result of equilibrium and kinetic study between Pd(II) and 3-(1′H-1′,2′,4′-Triazolyl-3′-azo)-2,6-diaminotoluene have been reported elsewhere.[10,11] In acid medium a limited number of metal ions reacts with these azo dyes derivatives, *i.e.* Cu(II), Co(III), Fe(III) and Pd(II).

In the present work, 3-(5′-tetrazolylazo)-2,6-diaminotoluene (TEADAT), a similar reagent to the previous ones, has been synthesized and a detailed study of the complexation equilibria

in the system Pd(II)-TEADAT-chloride has been done, with the aim of establishing optimal conditions to carry out the determination of Pd(II) in various materials and precious metal ions mixtures.



**TEADAT**

## EXPERIMENTAL

*Reagents*

3 - (5′ - tetrazolylazo - 2,6 - Diaminotoluene (TEADAT) 0.15 m$M$ solution in absolute

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ethanol. A standard 1 mg/ml solution of palladium chloride in 10% hydrochloric acid (AAS standard, Aldrich) was diluted with double distilled water. The ionic strength was kept constant at various levels using sodium chloride (Merck).

The reagent was synthesized and purified as described earlier.[8] 5-Amino-1H-tetrazol was dissolved in $1M$ hydrochloric acid, ice-cooled, and diazotized with a solution of sodium nitrite. The solution of the diazotate was then poured, while stirring, into a well cooled solution of 2,6-diaminotoluene in $0.3M$ sodium hydroxide. The mixture was then neutralized. A dark red precipitate began to settle immediately. The mixture was filtered and the precipitate washed with water and dried in air. The crude product was purified by successive recrystallizations in ethanol–water mixtures. Elemental analysis gave a content of 43.93%C, 51.23%N and 4.57%H, in a good agreement with the theoretical values (44.04%C, 51.38%N and 4.58%H).

Analytical reagent grade chemicals and double distilled water were used, with no further purification.

## Apparatus

The pH measurements were made with a Radiometer PHM 64 digital pH-meter with a combined glass–calomel electrode 9810, Ingold. The electrode was standardized using at least two buffers. No correction with respect to the ionic strength, concentration of the salts or ethanol was done, thus the pH values referred should be considered as conditional.

Absorption measurements were made with a HP 8452A diode array spectrophotometer equipped with 1-cm quartz cells and interfaced to a Hewlett–Packard Vectra ES computer and a Think Jet printer and processed with the aid of the spectrophotometer's bundled software.

The experimental set-up was completed by a RM6 Lauda thermostatic batch with a built-in compressor.

## Computation

For the calculation of equilibrium the LETAGROP-SPEFO[12] program (PC version[13]) was used on an IBM PC/AT. Factor analysis of the absorbance matrix was done using the SIBYLA program,[14] kinetic data were evaluated using the KILET[15–17] program (version

KILET-MINUIT[17]) or the updated version of KILET(92)[18], on a PC computer.

## General procedure used for the measurement

In a 25 ml standard flask were placed, in sequence, a sample containing no more than 35 $\mu$g of Pd(II), 2.5 ml of $2.5M$ sodium chloride, adjusted to the required pH 1.42 with hydrochloric acid, and 10 ml of an ethanolic solution of TEADAT 0.15 m$M$ (40% of the overall volume), make up to the mark with double-distilled water, mixed and thermostated the mixture at 25°C for 5 min. The spectra of this mixture were recorded between 300 and 600 nm against a solution containing 2.5 ml of $2.5M$ sodium chloride in ethanol–water (40% v/v) as a reference.

## RESULTS AND DISCUSSION

### Acidity constants of the reagent

TEADAT forms $H_4L^{3+}$, $H_3L^{2+}$, $H_2L^+$, HL and $L^-$ species, with $pK_{a1}$–$pK_{a4}$. In this work acidity constants have been determined spectrophotometrically analyzing $A = f(pH)$ curves for selected wavelengths with the LETAGROP-SPEFO program. The mean values found in 40% (v/v) ethanol–water medium and $I = 0.25M$ were $pKa_1 = -1.63 \pm 0.02$; $pKa_2 = 2.74 \pm 0.01$; $pKa_3 = 5.24 \pm 0.01$; and $pKa_4 = 9.25 \pm 0.14$. The $pKa_1$, is assigned to the deprotonation of one of the ring nitrogen atoms, (probably the one in position 2, as it originates a great number of resonant structures), $pKa_2$ and $pKa_3$ correspond to the deprotonation of the *ortho* and *para* amino groups, respectively and $pKa_4$ to the dissociation of the =NH ring group.

The acidity constants in 40% ethanol–water and $I = 2M$ shifted to higher values than in $I = 0.25M$ (sodium chloride), so in former condition the values of $pKa_2$ and $pKa_3$ are 3.10 and 5.33 respectively.

### Effect of acidity

In a 40% ethanol–water medium, the TEADAT reacts with Pd(II) in acid medium forming pink-red complexes species only when chloride ions are added, in spite of the fact that chlorides form a fairly strong complexes with palladium (II).[19] When the hydrochloric acid was changed by perchloric, nitric or sulphuric acid no reaction was observed between Pd(II) and TEADAT, which is evidence that the chloride ions are necessary for the formation of the complex species.
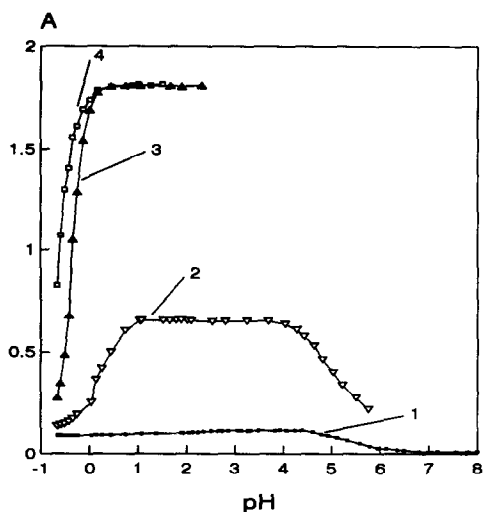
Fig. 1. Absorbance–pH curves for Pd(II)–TEADAT system. $C_L = 6.0 \times 10^{-5}M$, 40% (v/v) ethanol–water, $I = 2M$ (NaCl), $\lambda = 536$ nm and $C_M = $ (1) 0; (2) $1.1 \times 10^{-5}$; (3) $6.0 \times 10^{-5}$ and (4) $6.0 \times 10^{-4}M$. Absorbance were measured at equilibrium (after 60 min).

The variations of the absorbance with pH $(H_o)$ at 536 nm, for solutions with different $C_{Pd}/C_L$ ratios after reaching equilibrium, are given in Fig. 1, and indicate that complexation begins at higher acidities as $C_{Pd}/C_L$ increases.

## Effect of time

The reaction between Pd(II) and TEADAT proceeds slowly, the equilibrium is reached in about 20–60 min. The kinetic spectra are shown in Fig. 2; for solutions with an excess of the metal ion (Fig. 2a) and for solutions with an excess of the reagent (Fig. 2b).

It follows from Fig. 2a, b that the limiting values of absorbance obtained after a sufficiently long time are almost double for solutions with excess of the reagent with respect to those obtained for solutions with an excess of Pd(II).

Factor analysis of spectra was performed. The rank of the matrix calculated by the SIBYLA program[14] for spectra in Fig. 2a was equal to 2, while a value equal to 3 was obtained for a rank of the matrix of spectra as shown in Fig. 2b. As reported in the literature,[14,20] the rank of the absorbance matrix is less or equal to the number of the colored species present. Therefore, the results provide evidence that except absorbing form of the reagent, one complex is formed in solutions with an excess of the metal ion and at least two different complexes can be suggested in solutions with excess of the reagent.
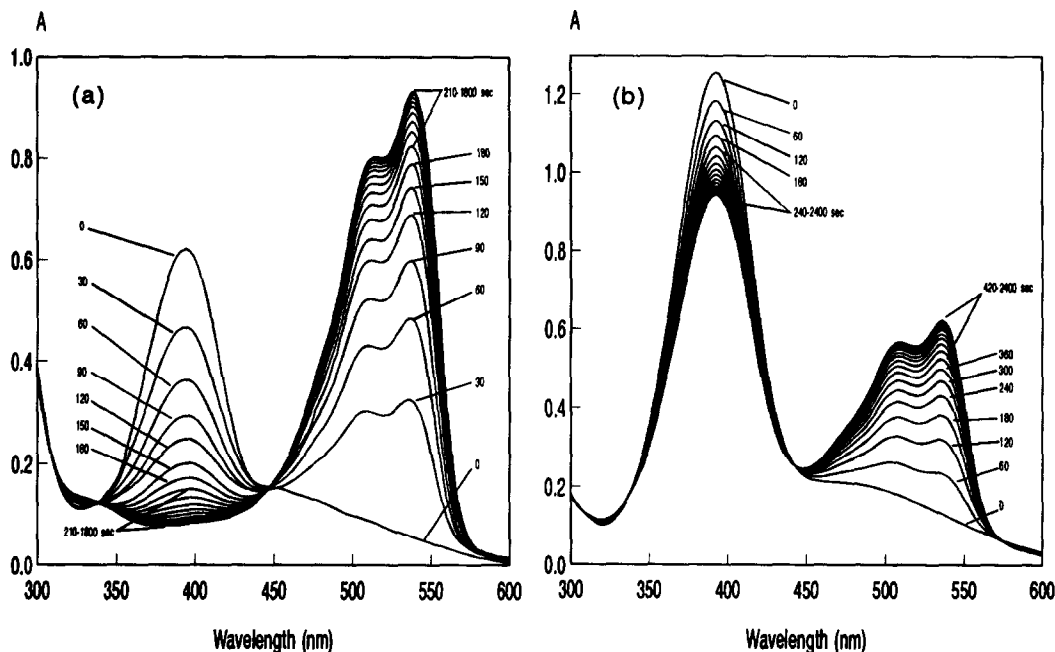


Fig. 2. Kinetic spectra of the Pd(II)–TEADAT–chloride complex formation. (a) $C_{Pd} > C_L$. $C_{Pd} = 7.5 \times 10^{-5}M$, $C_L = 3 \times 10^{-5}M$, pH 1.42, ionic strength $0.25M$ (NaCl), 40% ethanol–water, time interval 30 sec and starting time 30 sec. (b) $C_{Pd} < C_L$. $C_{Pd} = 1.2 \times 10^{-5}M$, $C_L = 6 \times 10^{-5}M$, pH 1.42, ionic strength $0.25M$ (NaCl), 40% ethanol–water, time interval 60 sec and starting time 60 sec.

Table 1. Results of equilibrium data analysis with a general least square program LETAGROP-SPEFO

| Data set | Conditions | Model* | $\log \beta^* \pm 3\sigma (\log \beta^*)$ | $\epsilon_{\lambda_{max}}$ $(l.mol^{-1}.cm^{-1})$ | $U \times 10^2$ | $\sigma(A) \times 10^3$ |
|---|---|---|---|---|---|---|
| 1 | Excess of metal ion $C_M = 3.76 \times 10^{-4}M$ | 1. $Pd(LH_3)$ | Not evaluated | Not evaluated | 8.04 | 30.50 |
| | $C_L = 4 \times 10^{-5}M$ | 2. $Pd(LH_2)$ | $4.09 \pm 0.05$ | 29,700 | 0.20 | 4.84 |
| 2 | Excess of the reagent $C_M = 7.52 \times 10^{-6}M$ | 1. $Pd(LH_2)$ | $4.09 \pm 0.02$ | 72,100 | 33.30 | 9.25 |
| | $C_L = 3.2 \times 10^{-5}M$ | 2. $Pd(LH_2)$ $Pd(LH_2)_2$ | $4.70 \pm 0.08$ $9.07 \pm 0.01$ | 3,200 56,700 | 1.03 | 3.19 |
| | | 3. $Pd(LH_2)_2$ | $8.40 \pm 0.02$ | 55,200 | 0.63 | 4.02 |
| 3 | Joined data set 1 + 2 | 1. $Pd(LH_2)$ | $4.08 \pm 0.14$ | 29,900 | 178.59 | 59.80 |
| | | 2. $Pd(LH_2)_2$ | $8.49 \pm 0.05$ | 59,700 | 17.72 | 18.85 |
| | | 3. $Pd(LH_2)$ $Pd(LH)_2$ | $4.69 \pm 0.06$ $8.44 \pm 0.08$ | 29,600 58,700 | 17.10 | 18.70 |
| | | 4. $Pd(LH)$ $Pd(LH)_2$ | $3.85 \pm 0.05$ $7.26 \pm 0.05$ | 30,000 51,800 | 2.51 | 7.17 |
| | | 5. $Pd(LH)$ $Pd(LH_2)_2$ | $3.27 \pm 0.03$ $8.11 \pm 0.04$ | 29,800 68,000 | 1.94 | 6.31 |
| | | 6. $Pd(LH_2)$ $Pd(LH_2)_2$ | $3.91 \pm 0.05$ $8.44 \pm 0.02$ | 30,000 61,000 | 0.89 | 4.27 |

$U$ is the sum of squares of residuals.
$\sigma(A)$ is the standard deviation of absorbance.
*The number of chlorides and charges are omitted for the sake of clarity.
Recommended values: $\log \beta_1^{*'} = 4.09 \pm 0.05$, $\log \beta_2^{*'} = 8.40 \pm 0.02$.

### Complex equilibria of Pd(II) with TEADAT

Equilibrium data were analyzed using the LETAGROP-SPEFO/PC program. The calculations are based on the application of a general least squares regression method searching minimum of $U$, the sum of squares of residuals, defined by equation (1)

$$U = \sum_{i=1}^{N} \sum_{j=1}^{N_\lambda} (A_{exp, ij} - A_{calc, ij})^2, \qquad (1)$$

where $N$ is the number of experimental points, $N_\lambda$ the number of wavelengths used, $A_{exp}$ the experimental absorbances and $A_{calc}$ the absorbances calculated by the program from equilibria (or rate) constants. The best model is that for which the lowest value of $U$ and the lowest standard deviation $\sigma(A)$ are obtained.

Some of the models tested are given in Table 1, where the number of chlorides and charges are omitted for sake of clarity. To simplify the calculations, the curves for excess of Pd(II) and for excess of reagent were analyzed separately. From the analysis of the curves for Pd(II) in excess, the best fit was obtained when the model assumes the presence of the species $Pd(LH_2)^{2+}$ only, with $\lambda_{max} = 536$ nm and with $\epsilon_{\lambda max}$ equal to 29,700. It follows from different models tried that the number of protons splitted off from $LH_3^{2+}$ reagent equals one.
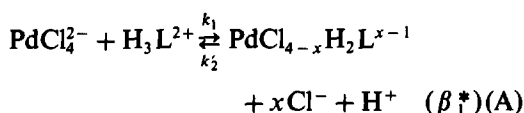
However, from the analysis of the curves with excess reagent, (Table 1, Data set 2) the best fit was achieved for a model formed by the species $Pd(LH_2)_2^{2+}$ (model 3) and almost the same standard deviation was reached when the model assumed both $Pd(LH_2)$ and $Pd(LH_2)_2^{2+}$ species complexes (model 2). In this case, splitting off one proton from the $LH_3^{2+}$ form of the ligand was also proved.

The formation of two complexes was then confirmed by analyzing the whole data set together (Table 1, Data set 3). From several models tried, model 6 assuming the formation of $Pd(LH_2)$ and $Pd(LH_2)_2^{2+}$ gave the best fit with the lowest standard deviation of the absorbance. As for the calculation of the constants given in Table 1, the chloride concentration has not been taken into account, so those values must be considered as conditional and correspond to equilibria:
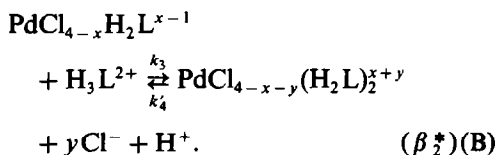
$$PdCl_4^{2-} + LH_3^{2+} \rightleftharpoons PdCl_3(LH_2) + H^+ \quad (\beta_1^{*'})$$

$$PdCl_4^{2-} + 2LH_3^{2+} \rightleftharpoons PdCl_2(LH_2)_2^{2+} + 2H^+ \quad (\beta_2^{*'})$$

On the other hand, because palladium(II) in chloride medium exists in chloride complexes $PdCl_x^{(2-x)}$ with a high stability ($\log \beta_n = 4.47$, 7.74, 10.2, 11.5 for $n = 1$, 2, 3, 4),[19,21] and at chloride concentration equal to $2.0M$ the species

$PdCl_4^{2-}$ predominates, the complexes formation reactions can be written as

$$PdCl_4^{2-} + H_3L^{2+} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} PdCl_{4-x}H_2L^{x-1}$$
$$+ xCl^- + H^+ \quad (\beta_1^*)(A)$$

and

$$PdCl_{4-x}H_2L^{x-1}$$
$$+ H_3L^{2+} \underset{k_4}{\overset{k_3}{\rightleftharpoons}} PdCl_{4-x-y}(H_2L)_2^{x+y}$$
$$+ yCl^- + H^+. \quad (\beta_2^*)(B)$$

Thus, it can be assumed that the chloride anions in palladium $PdCl_x^{(2-x)}$ complexes are partly or totally replaced with the reagent.

Where $\beta_1^*$ and $\beta_2^*$ are the equilibria constants, which included the chloride concentration, they are related to $\beta_1^{*\prime}$ and $\beta_2^{*\prime}$ by the following expressions:

$$\log \beta_1^* = \log \beta_1^{*\prime} + \log[Cl^-] = 4.39$$

$$\log \beta_2^* = \log \beta_2^{*\prime} + 2\log[Cl^-] = 9.00.$$

Equilibria constants $\beta_n^*$ were recalculated to stability constants using the values of Pd(II) chloro complexes, cf. above:

$$\log \beta_1 = \log \beta_1^* + \log \beta_4 [PdCl_4^{2-}] + pKa_3$$
$$= 19.03$$

$$\log \beta_2 = \log \beta_2^* + \log \beta_4 [PdCl_4^{2-}] + 2pKa_3$$
$$= 26.74.$$

The formation of 1:2 complex was also supported using the molar ratio method. The curves $A = f(x_L)$ show maximum for ratio $x_L = C_L/(C_M + C_L)$ near to 0.66, which means that at the ratio $C_L/C_M = 2$, the 1:2 complex is already formed (Fig. 3).

### Effect of chloride concentration and catalytic effect of the thiocyanate

In the presence of small concentrations of thiocyanate ($\approx 2 \times 10^{-5}$ mol/l.) the rate of the formation reactions are greatly increased and the constant absorbance values can be obtained after 2–5 min, which considerably simplifies the spectrophotometric procedure of the palladium determination. The catalytic effect of thiocyanate can be explained by the formation of mixed $PdCl_x(SCN)_y^{(2-x-y)}$ species[21] where the replacement reaction of a halide with the reagent molecule is easier. This is analogous to the observation of Al-Bari and Freiser[22] who

reported a 600 times increase of Pd(II) extraction from chloride solutions by KELEX 100 in the presence of thiocyanate. In our case we can also suggest that the formation of $PdCl(SCN)_3^{2-}$, $PdCl_2(SCN)_2^{2-}$ or $PdCl_3(SCN)^{2-}$ species is the explanation for the faster replacement of chloride ions with the reagent. Higher concentrations ($> 10^{-2}M$) of thiocyanate interfere, due to the strong complexation of Pd(II) with the formation of a stable $Pd(SCN)_4^{2-}$ complex.

In order to ascertain the number of chlorides in the complexes formed, absorbance as a function of chloride concentration $A = f(C_{Cl^-})$ was measured and analyzed. The $A = f(C_{Cl^-})$ was measured up to $0.2M$ chloride concentration at pH 1.42 and for Pd(II) concentration $1.1 \times 10^{-5}M$ with excess reagent, $C_L = 6.0 \times 10^{-5}M$, and for thiocyanate concentration 0.1 mM. By a logarithmical graphical analysis[20] it was proved that two chlorides are bound with the formation of the 1:2 complex, thus the reaction can be written as

$$Pd(SCN)_4^{2-} + 2Cl^- + 2H_3L^{2+}$$
$$\rightleftharpoons PdCl_2(H_2L)_2^{2+} + 4SCN^- + 2H^+.$$
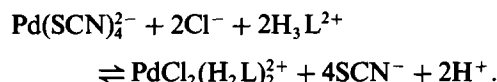
Evaluation of the stability constant of $PdCl_2(H_2L)_2^{2+}$ gave $\log \beta_2 = 26.4 \pm 0.1$, in good agreement with the value obtained by LETAGROP treatment of data where no thiocyanate was present ($\log \beta_2 = 26.74$). As two chlorides are present in the 1:2 complex, it is natural to suggest that each reagent replace one chloride only.
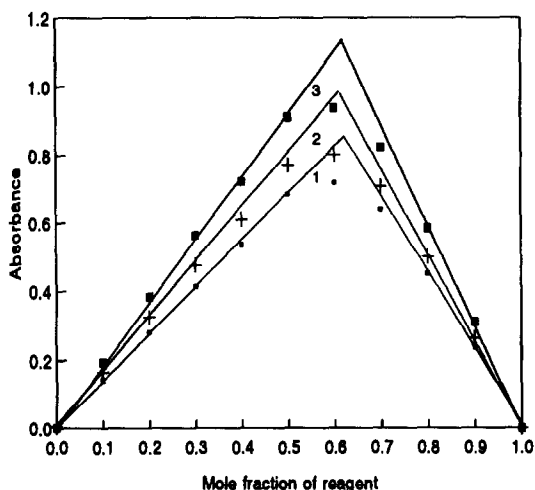


Fig. 3. Job plots. [Pd] + [TEADAT] = $6 \times 10^{-4}M$; wavelength = (1) 500, (2) 530 and (3) 538 nm.

Table 2. Rate contants and molar absorptivities calculated by the KILET-MINUIT program

| Series | Conditions | Model* | $k_i \pm (\sigma(k_i)\dagger$ $(mol^{-1}. sec^{-1})$ | $\epsilon_{\lambda_{max}}$ $(l. mol^{-1}.cm^{-1})$ | $U \times 10^3$ | $\sigma(A) \times 10^3$ |
|---|---|---|---|---|---|---|
| 1 | $C_M = 1.13 \times 10^{-5}M$ $C_L = 1.2 \times 10^{-5}M$ | Pd(LH$_2$) | $k_1 97.2 \pm 0.02$ $K_2'(7.60 \pm 0.01) \times 10^{-5}$ | 35,800 | 2.43 | 1.46 |
| 2 | $C_M = 1.13 \times 10^{-5}M$ $C_L = 6 \times 10^{-5}M$ | Pd(LH$_2$) Pd(LH$_2$)$_2$ | $k_1 90.0 \pm 0.10$ $k_2'(2.21 \pm 0.01) \times 10^{-5}$ $k_3 14.2 \pm 0.10$ $k_4'(1.30 \pm 0.01) \times 10^{-3}$ | 30,800 62,600 | 1.72 | 1.19 |
| 3 | $C_M = 3.76 \times 10^{-6}M$ $C_L = 4 \times 10^{-5}M$ | Pd(LH$_2$) Pd(LH$_2$)$_2$ | $k_1 92.13 \pm 0.57$ $k_2'(4.50 \pm 0.45) \times 10^{-5}$ $k_3 13.8 \pm 0.50$ $k_4'(1.30 \pm 0.02) \times 10^{-3}$ | 30,000 62,800 | 0.86 | 7.55 |

$U$ is sum of squares of residuals.

$\sigma(A)$ = standard deviation of absorbance.

*Number of chlorides and charges omitted.

†$\sigma$I($k_i$) standard deviation of $k_i$.

$I = 0.25$ (NaCl) and pH 1.42 in all series.

$k_2'$ and $k_4'$ are conditional rate constants.

### Kinetic analysis

Further evidence for the stepwise complex formation was obtained from the kinetic analysis of absorption spectra as a function of time. The absorbance matrix data were analyzed using the KILET-MINUIT program[17] at selected wavelengths or analyzing the absorbance matrix as a whole applying the KILET(92) program.[18] The results of analysis are given in Table 2, where $k_1 - k_2'$ and $k_3 - k_4'$ are rate constants of forward and backward reactions (A) and (B), respectively.

It follows from the results in Table 2 that $k_1 > k_3$ and $k_4' > k_2'$, which is logical. The replacement of the first chloride anion (with the lowest stability) is easier than the replacement of the next one $(k_1 > k_3)$. The second backwards reaction is slightly faster than the first one $(k_4' > k_2')$ for the same reason. The stability constants calculated from the rate constants (Table 2) and correcting for chloride concentrations yield the values,

$$\log \beta_1^* = \log k_1 / \log k_2' + \log[Cl^-] + \log[H^+]$$

$$= 18.37$$

and

$$\log \beta_2^* = \log \beta_1 + \log K_2 + pKa_3 = 23.12,$$

where

$$\log K_2 = \log k_3 / \log k_4' + \log[Cl^-] + \log[H^+]$$

$$= 2.01,$$

in good agreement with those obtained by equilibrium analysis. The values may be lower than those obtained by LETAGROP because of

difference in ionic strength in both cases (2$M$ NaCl and 0.25$M$ NaCl).

For species complexes of the type of PdCl$_2$(LH$_2$)$_2$, it is well known that the formation of the *cis* isomer is kinetically favoured, whilst the *trans* isomer is thermodynamically more stable,[23] so that the catalytic effect of thiocyanate on the kinetic process could be the formation of the *cis* isomer PdCl$_2$(SCN)$_2^{2-}$ in a first step which is transformed into the *trans* isomer PdCl$_2$(SCN)$_2^{2-}$ in a second one, the latter species is easier attached to by TEADAT to form PdCl$_3$(LH$_2$) and PdCl$_2$(LH$_2$)$_2^{2+}$ species.

In conclusion, two complexes have been found, which can be formulated as PdCl$_3$(LH$_2$) and PdCl$_2$(LH$_2$)$_2^{2+}$, thus in equations (A) and (B) the values of $x$ and $y$ are equal to one. Finally, spectra of the complexes and a
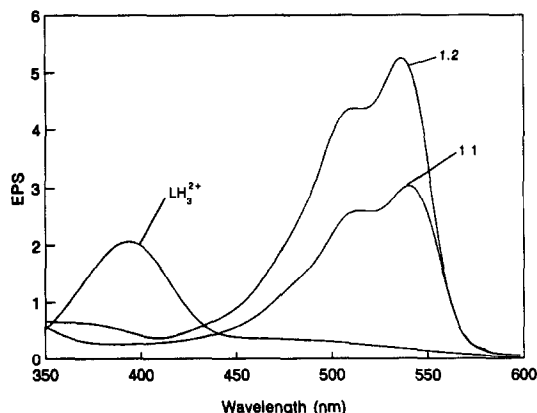


Fig. 4. Absorption spectra of TEADAT (LH$_3^{3+}$) and Pd–TEADAT 1:1 and 1:2 complexes. EPS is the molar absorptivity [l. mol$^{-1}$. cm$^{-1}$].

Table 3. Determination of palladium in synthetic mixtures corresponding to the composition of some alloys

| Sample no. | Synthetic mixture composition (%) | Pd($\mu g$) | | Relative % error |
|---|---|---|---|---|
| | | Taken | Found* | |
| 1 | Au 50.0; Pd 50.0 | 30.0 | 30.78 | 2.60 |
| 2† | Pd 35.0; Ag 30.0; Pt 10.0; Cu 14.0; Au 10.0; Zn 1.0 | 30.0 | 30.81 | 2.70 |
| 3 | Pd 34.0;; Ni 34.0; Co 22.0; Au 10.0 | 30.0 | 31.01 | 3.36 |
| 4 | Pd 10.5; Ni 60.0; Pt 20.0; V 9.5 | 33.0 | 32.84 | −0.53 |
| 5 | Pt 39.6; Rh 19.8; Os 39.6; Pd 1.0 | 30.0 | 30.03 | 0.10 |
| 6 | Pt 36.2; Rh 27.1; Os 36.2; Pd 0.5 | 15.0 | 14.21 | −5.26 |
| 7 | Ti 49.8; Se 49.8; Pd 0.4 | 30.0 | 29.33 | −2.23 |
| 8 | Pt 18.2; V 9.1; Ni 54.5; Pd 18.2 | 30.0 | 29.12 | −2.93 |
| 9 | Cd 38.3; Fe 38.3; Co 23.0; Pd 0.4 | 27.0 | 27.93 | 3.44 |
| | | | Average | 2.57 |

*Mean of three determinations
†Ag was masked with NaCl ($1M$).

comparison to that of the reagent are given in Fig. 4. The spectra of the complexes are very similar to each other and confirm almost the same way of coordination of the ligand molecules in complexes.

## Optimization of the conditions and method of palladium(II) determination

From Fig. 1 it follows that in solutions with excess of reagent a plateau is obtained at $0.5 \leqslant pH \leqslant 4.0$. We recommend $1.0 \leqslant pH \leqslant 2.5$ as the optimal pH range to carry out the determination.

*Effect of ethanol concentration.* The concentration of ethanol has been optimized. At low ethanol content (6% v/v) and pH $\approx 1.42$, the apparent molar absorptivity is lower while optimum results have been obtained for 40% ethanol (v/v). This stabilizing effect of ethanol has also been observed for many thiazolyl-azo reagents.

*Effect of TEADAT concentration.* For Pd concentration up to $1.5 \times 10^{-5}$ mol/l., $6.0 \times 10^{-5}$ mol/l. reagent concentration is enough to complete the reaction. For optimal conditions [40% ethanol (v/v), $I = 0.25$ (NaCl), pH 1.0–2.5, $C_L = 6.0 \times 10^{-5}M$] Lambert–Beer's law is obeyed in the range 0.02–2.00 $\mu$g/ml Pd

Table 4. Determination of palladium in hydrogenation catalyst

| Catalysts (Fluka) | Palladium found (%) | |
|---|---|---|
| | AAS | Proposed method* |
| Pd–charcoal | 4.56 | 4.58 |
| Pd–asbestos | 4.38 | 4.32 |
| Pd–Al$_2$O$_3$ | 4.26 | 4.32 |
| Pd–CaCO$_3$ | 4.89 | 4.77 |
| Pd–BaSO$_4$ | 4.34 | 4.25 |

*Mean of three determinations.

with apparent molar absorptivity value equal to 52,000 l. mol$^{-1}$. cm$^{-1}$.

*Procedure for* Pd(II) *determination.* In a 25 ml measuring flask were added, in the following order, a sample containing less than 35 $\mu$g of Pd(II), 2.5 ml of 2.5$M$ NaCl, the pH adjusted over the range 1–2 with 1$M$ HCl, 2.5 ml of 0.2 m$M$ KSCN, and 10 ml of an ethanolic solution of 0.15 m$M$ TEADAT. The solution were made up to volume with double-distilled water, left for 5 min and the absorbance measured at 536 nm.

*Effect of diverse ions.* Under the optimum conditions specified above, it was found that even 100-fold excess of Co(II), Fe(III), Zn(II), Cd(II), Pt(IV), (1000 excess), Os(IV), Au(II), Rh(III), Hg(II), Pb(II), Cu(II), Ni(II), Al(III), Ca(II), Sr(II), Ba(II), Zr(IV), Se(IV), $UO_2^{2+}$, $VO^{2+}$, Ti(IV) did not interfere. Chlorides up to saturated solution, EDTA, nitrates, sulfates, perchlorates and hydrogen peroxide also did not interfere. The Ag(I) interference could be eliminated by using chloride ($1M$) as a masking agent. Thiocyanate in 60-fold excess did not interfere. Because none of the precious metal ions interfered and Ir(IV) did not interfere up to higher concentrations than $1.3 \times 10^{-5}M$ ($1.3 \times 10^{-5}M < [Ir(IV)] < 1.3 \times 10^{-4}M$) can be eliminated by the presence of EDTA) the reagent is specific for the determination of palladium(II).

## Practical applications of the method

The proposed method was used for the microdetermination of palladium. It is very simple, highly sensitive and free from the interference of a large number of elements, particularly the other platinum group metal ions, which otherwise seriously affect most of the methods of

palladium(II) determination. The detection limit estimated as $3\sigma$ from the analysis of calibration curve was found to be 0.54 $\mu$g and relative error $\pm$ 2.6% for the determination of 30 $\mu$g of palladium. The validity of the method was further tested by analyzing several synthetic samples and hydrogenation catalysts. The results are given in Tables 3 and 4 where it can be seen that average relative error is less than 2.6% for synthetic mixtures of precious metals, and the obtained results are in a very good agreement with those obtained by AAS for hydrogenation catalysts.

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