

# Extractive Spectrophotometric determination of palladium with 3-Hydroxy-2-(2'-thienyl)-4H-chromen-4-one in alkaline medium

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## ABSTRACT:

A rapid, simple, selective and sensitive method for the determination of palladium in trace amounts has been developed, which is based on the reaction of 3-Hydroxy-2-(2'-thienyl)-4H-chromen-4-one with the metal ion in alkaline medium (pH 8.5-9.2). The yellow colored palladium complex formed is quantitatively extracted into chloroform, whose absorbance is measured at 455nm. A large number of cations do not interfere; whereas, amongst anions/complexing agents, only nitrite, thiourea and Ascorbic acid show interference. It obeys Beer's law in the range 0.01-0.1  $\mu\text{g. Pd mL}^{-1}$ . The molar absorptivity and Sandell's sensitivity of the system are  $3.301 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$  and  $0.0032 \mu\text{g Pd cm}^{-1}$  respectively. The ratio of metal to ligand in the extracted complex is determined as 1:1. The validity of the method is tested by carrying out analysis of various samples with satisfactory results.

**Key Words:** palladium, 3-Hydroxy-2-(2'-thienyl)-4H-chromen-4-one, Sodium bicarbonate, chloroform, spectrophotometry.

## 1. Introduction:

In a wide variety of samples, palladium is generally present in very low concentrations. This fact calls for laying out better methods of trace determination, based on specific and sensitive reaction of metal ions with different ligands, which will go a long way towards its enrichment in the byproducts of many industrial processes and use in a large number of alloys with other transition elements and also as a catalyst. Though several mono- and di-oximes (1-5) have earlier been employed for complexation of palladium in acid solutions for carrying out determination after extraction into organic solvents, but the methods still

suffer from serious interferences and low sensitivity. An attempt has, therefore, been made to work out a simple spectrophotometric method using 3-Hydroxy-2-(2'-thienyl)-4H-chromen-4-one as a complexing agent in slightly alkaline medium with a view to contain these problems to the minimum, the details of which are as under:

## 2. EXPERIMENTAL

### 2.1 Preparation of 3-Hydroxy-2-(2'-thienyl)-4H-chromen-4-one, (HTC)

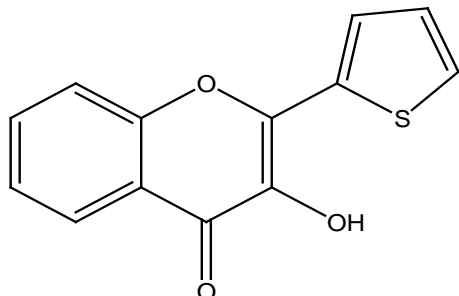
The reagent HTC is prepared by (10) as per details available in the method wherein solution of o-Hydroxyacetophenone (4.08g in 30 ml ethanol) and NaOH (4g in 8 ml in 50% ethanol) are mixed and stirred (2h, below 60°C) after adding thiophene-2-aldehyde (3.6g) drop wise. The orange-red mass (I, m.p. 100°C) thus obtained is neutralized with 0.2 molL<sup>-1</sup> HCL and crystallized from ethanol and water. Solution of compound 1 (2g in 20 ml methanol), NaOH

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(8ml of 20% in methanol) and  $H_2O_2$  (4 ml of 70 volume) are mixed, stirred (2h, below  $10^\circ C$ ) and neutralized with  $CH_3COOH$ . The yellow compound so obtained after crystallization from ethanol and water is HTC (m.p.  $200^\circ C$ ) as under:



### 3-Hydroxy-2-(2'-thienyl)-4H-chromen-4-one (I)

**2.2 Synthetic samples:** Synthetic samples were prepared by mixing solution of palladium and other metal ions in suitable proportion, as shown in Table 2.

**2.3 Pd-Charcoal catalyst** (Aldrich 20,568-0): The sample (0.05g) was dissolved in minimum volume of aqua regia by heating. The Charcoal was filtered off when hot. Nitric acid was destroyed completely by evaporating the solution to dryness. The residue thus obtained was dissolved in water, filtered and the filtrate was processed for the determination of palladium as described in the procedure.

**2.4 Apparatus, reagents and solutions** A UV-VIS. spectrophotometer 140-02(Shimadzu, Japan) with 10 mm matched quartz cell was used. A stock solution of (1mg/mL) of palladium was obtained by dissolving 0.167g of  $PdCl_2$  (Sisco) in  $0.75 \text{ mol L}^{-1}$  HCL and was standardized gravimetrically (6). Working solutions at the concentration level of  $\mu\text{g mL}^{-1}$  were obtained by dissolving their commonly available sodium or potassium salts in deionized water or dilute acids. The solution of 3-Hydroxy-2-(2'-thienyl)-4H-chromen-4-one(HTC), 0.1%(m/v) was prepared by dissolving it in ethanol. Sodium bicarbonate 1M was used. Chloroform (Ranbaxy, A.R.) is employed for extraction

**2.5 Procedure:** To the sample solution containing 10g Pd and/or other ions in a 100ml separating funnel, add 0.9 ml of 0.1% Of HTC solution, and 0.2 ml of  $NaHCO_3$  (1M) and make up to 10 ml with distilled water. The contents were gently mixed and equilibrated

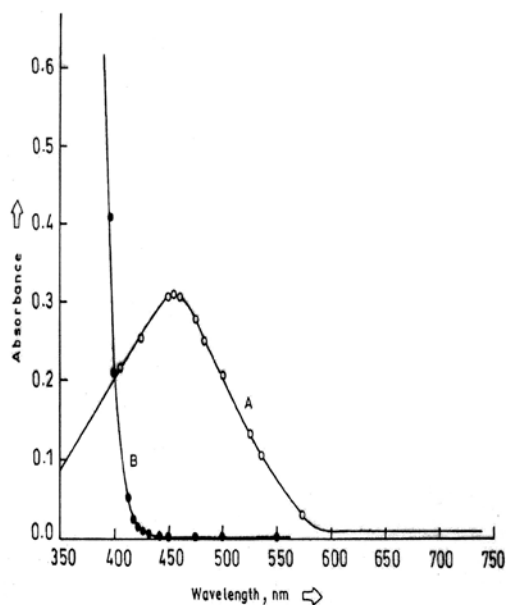
once with an equal volume of chloroform for 30seconds. The two phases were allowed to separate and the organic layer was filtered through a whatman's filter paper no.41 into a 10 ml volumetric flask which was made up to mark with pure chloroform. The contents were gently mixed and absorbance of the yellow colored species was measured at 455nm against pure chloroform using 1cm quartz cells. The amount of the metal ion was determined from standard curve obtained by plotting a graph between different  $\mu\text{g}$  amounts of Pd(II) and corresponding absorbance value following above procedure.

## 3. RESULT AND DISCUSSION

**3.1 Effect of acids/bases;** Palladium (II) forms a yellow colored complex with HTC in alkaline as well as in acidic medium. The extractability and absorbance of the metal complex is high in  $NaHCO_3$  solution, whereas it shows a relatively downward trend in  $Na_2CO_3$  and NaOH. Similarly, there is a decline in absorbance value if  $HClO_4$ , HCl and  $H_2SO_4$  are used under comparable aqueous conditions. Hence alkaline medium,  $NaHCO_3$ , is preferred for the system. The effect of various parameters on absorbance of Pd(II)- complex is shown in Table 1.

In neutral medium, the absorbance of Pd-HTC complex is 0.220 and it keeps increasing with further increase in  $NaHCO_3$  concentration and is 0.310 at 0.1 to 0.3 ml of  $NaHCO_3$  (1M). At still higher alkalinity a downward trend in absorbance is observed and is 0.240 for 1 ml of  $NaHCO_3$ . Therefore, 0.1-0.3 ml of  $NaHCO_3$  (1M) is considered suitable for the system.

**3.2 Effect of Concentration of 3-Hydroxy-2-(2'-thienyl)-4H-chromen-4-one(HTC).** The absorbance is nil if the aqueous solution does not contain HTC. The metal ion starts forming the colored species just on addition of the reagent. The absorbance is 0.140 when 0.1 mL of the reagent is present. It increases with increasing HTC content and becomes 0.310 for 0.8-1 mL of the reagent and thereafter shows a gradual fall. Therefore, 0.9 mL of HTC is considered sufficient for maximum formation of complex under experimental conditions as indicated in Table 1.



**Figure 1: Absorption Spectrum of Pd(II)-HTC Complex**

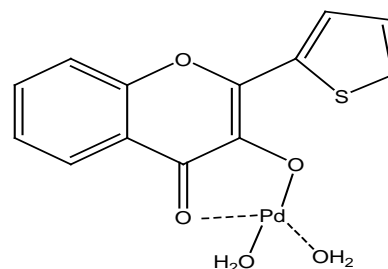
A-Absorbance of Pd complex measured against reagent blank

B- Absorbance of reagent blank measured against pure chloroform

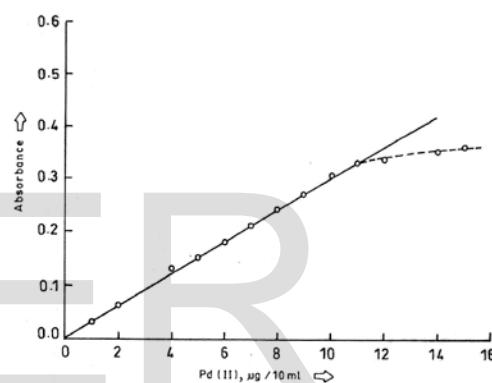
**3.3 Effect of equilibration time:** The absorbance of complex is maximum for an equilibration time of 15- 45s., beyond which it starts showing a downward trend. Hence 30 s. is set as equilibration time for the extraction of complex in different solvents is in the order Chloroform 0.240, 1,2-Dichloroethane 0.220, benzene 0.210, carbon tetrachloride 0.20, Toluene 0.190, ethyl acetate 0.170, amyl acetate 0.150, isobutylmethylketone 0.100, and butyl alcohol 0.110. Therefore, Chloroform is recommended as extracting solvent for the system.

**3.4 Validity of Beer's Law:** The absorption spectrum of the Pd(II)-HTC complex is shown in Fig.1 with the maximum at 448-460nm where reagent blank I does not show any absorbance. Beer's law is obeyed over the palladium concentration range  $0.1-1\mu\text{g mL}^{-1}$ . However, as evaluated from Ringbom plot, the optimum concentration range of determination of Pd is  $0.25-1.09\text{gPd mL}^{-1}$ . The molar absorptivity and Sandell's sensitivity of the complex at 455nm are  $3.301 \times 10^4 \text{ molL}^{-1}\text{cm}^{-1}$  and  $0.0032 \mu\text{gPdcm}^{-2}$  respectively. The ratio of Pd (II) to HTC in the extracted complex was found to be 1:1 by Job's method of continuous variations and the same was further

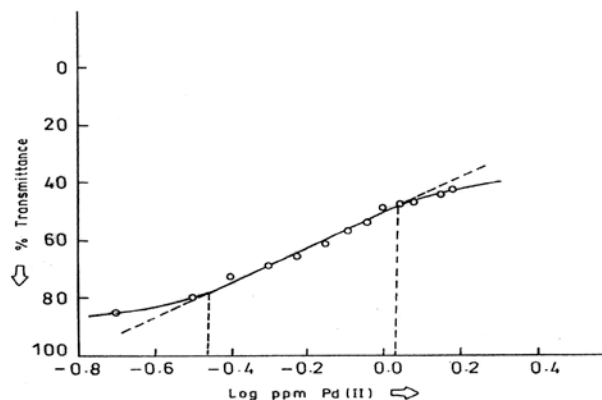
confirmed by mole ratio method(9). The probable composition of the Complex is as under:



**Possible structure of Pd(II)-HTC**



**Fig:2 Beer's Law for Pd(II)-HTC Complex**



**Fig:3 Ringbom Plot for Pd(II)-HTC Complex**

**3.5 Nature of extracted species:** The composition of Pd-ligand complex was determined by Job's continuous variation methods [9] (Fig.4). Equimolar solution of HTC and Pd ( $9.3 \times 10^{-4}$ )

having different volume (1-10 mL) are contracted to obtain the different ratio of HTC and Pd(II). Absorbance of organic phase was plotted against mole fraction of palladium. The ratio of metal ligand was found to be 1:1.

**3.6 The effect of diverse ions** Under the optimum conditions of the procedure in 10 ml aqueous volume, chloride, bromide, sulfate and oxalate, 40mg each; fluoride, acetate phosphate, 30mg each; nitrate and EDTA, 20 mg each; tartrate, sulfosalicylic acid, sodium dithionite, 5 mg each; sulphite and citrate, 1mg each are without effect. However, thiourea, ascorbic acid, iodide and nitrite show interference. Amongst the cations, Sr(II), As(V), Ti(IV), Ag(I), Ca(II), Mg(), 10mg each; Cr(VI), Ba(II), Cr(III) 5mg each, Os(VIII) 2.9 mg; Co(II), Cu(II), V(v), Zr(IV), W(VI), U(VI) Mo(VI), Rh(III), Cd(II) 1mg each; Ru(III), 0.425mg; Re(VII) 0.3 mg; Se(IV) 0.250mg; Ni(II) 0.2 mg; Ta (v) 0.100 mg; Zr(I) 0.08 mg; Nb (v), Zn(II) 0.050 mg each; Pt(II) 0.025mg do not show any absorbance. Fe(II, III) cause interference.

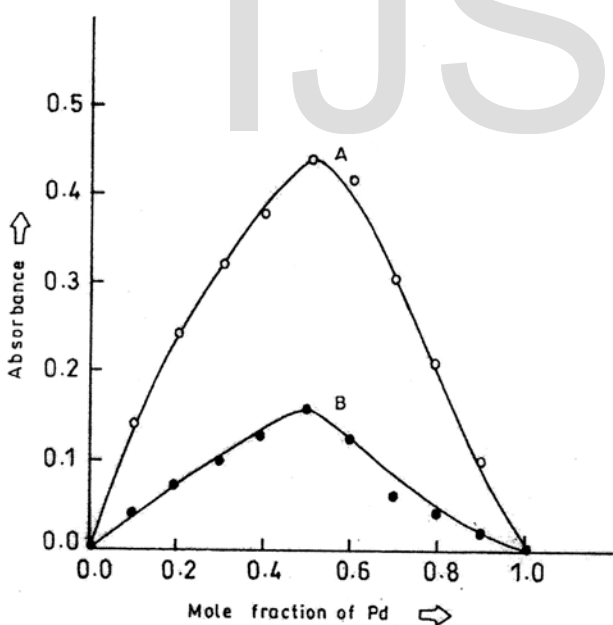


Figure 4: Job's Plot for Pd(II)-HTC Complex

**4. Conclusions**

The proposed method for the micro determination of palladium is satisfactory for carrying out analysis of a wide variety of samples shown in Table -1. The method

is free from the interference of a large number of other elements of analytical interest which are generally found to be associated with the metal ion in natural samples and alloys. The results obtained are quite reproducible with a standard deviation of 0.0021% for ten replicate measurements each time with the same amount of metal ion. The method compares favourably with the existing methods (10-19) in terms of selectivity, sensitivity and rapidity.

TABLE-2

**ANALYSIS OF VARIOUS SAMPLES WITH THE PROPOSED METHOD**

S.No.	Sample Composition Matrix*	Pd added, g	Pd found, **g
1.	Re(0.1), W(0.1), V(0.05)	5	5.3
2.	U(0.1), Mo(0.1), As(0.1)	10	9.7
3.	Rh(0.100), W(0.106)	10	10.5
4.	Cd(0.050), Os(0.05)	4	4.2
5.	Cd(0.010), Re(0.010)	7	7.3
6.	Ni(0.030), Pt(0.0025), V(0.0025)	2.5	2.7
7.	Au(0.04)	10	9.6
8.	Au(0.0025), Cu(0.013), Ag(0.012)	6	5.84
9.	Ag(0.014), Co Ag(0.001)	5	5.0
10.	Au(0.09)	10	9.6
11.	Pd-charcoal catalyst	1%	0.98%

\*Amount of metal ion shown in parentheses is in mg.

\*\*Average of triplicate analyses

\*\*\*Composition of samples 6,7,8,9,10 corresponds to Palau-, Palau-, Palladium-gold, copper and white gold.

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