

**K** : Palladium; Spectrophotometry; Tween 80; Natural waters; Micellization

**I** ☒

Amphiphilic molecules (i.e. molecules possessing both hydrophobic and hydrophilic regions) such as surfactants exhibit some fascinating features because of their tendency to self-association in water and / or apolar solvents. The internal structure of the microscopically-ordered molecular aggregates formed (aqueous and reverse micelles, bilayers, microemulsions and vesicles) is determined by the nature of the surfactant monomer, the nature of the solvent and also by other possible surrounding ions. These surfactant aggregates constitute 'ordered' media because they mimic the organisational ability of membranes by bringing reactants together in highly structured specific microenvironments [1-3].

Among the existing surfactant-based organised assemblies micelles and vesicles are possibly the most interesting and investigated organised media in analytical chemistry. Micelles are microscopically organised chemical assemblies formed by self-aggregation of individual surfactant molecules. These molecules exist as monomers in very dilute solutions, but when their concentration exceeds a certain minimum the so-called "Critical Micellar Concentration", CMC, of the surfactant), the monomers associate spontaneously forming aggregates of colloidal dimensions termed micelles. As the surfactant moate 5sti and also by other .

diazo-component form colored complexes with many metal ions in solution [22]. Several analytical techniques have reported for the determination of trace elements in natural water like ICP-AES, ICP-MS, ETAAS, GFAAS, NAA, and CE which are very expensive and in addition to that direct determination of trace metal ions by following methods is not sufficiently sensitive. So, many spectrophotometric methods have been developed for the determination of palladium [23].

Phenanthraquinone monophenyl thiosemicarbazone (PPT) combines with numerous metal ions [24] such as nickel, zinc, copper, cadmium, lead and so forth, to form colored metal complexes. While this chelating agent has been used to determine some metal ions by ultraviolet-visible (UV-Vis) spectrophotometry, [25-28] these metal-PPT complexes do not dissolve in aqueous solution. So it is needed to realize a solvent extraction. These complexes can be extracted with chloroform, which was found to be carcinogenic [29] and was later banned by Food and Drug Management from use in drug, cosmetic, and food packaging products [30].

Phenanthraquinone monophenyl thiosemicarbazone (PPT) has been rarely used for the spectrophotometric determination of palladium (II) in the presence of non-ionic surfactants.

In the present study, a non-ionic surfactant, polyoxyethylene sorbitan monooleate (Tween 80), is used to determine the Pd (II)-PPT complex spectrophotometrically since Pd(II) was chelated with PPT. The method is based on the reaction of PPT in Tween 80 micellar solution with palladium (II) to produce a highly absorbent brownish-violet chelate product, followed by direct measurement of the absorbance in the Tween 80 solution. With suitable masking, the reaction can be made highly selective for palladium. Tween-series surfactants are more soluble in aqueous solution than any other non-ionic surfactants and have polyoxyethylene chains in which the metal complex can be well solubilized. Among Tween-series surfactants, it was empirically noticed for Tween 80 to be less foamed.

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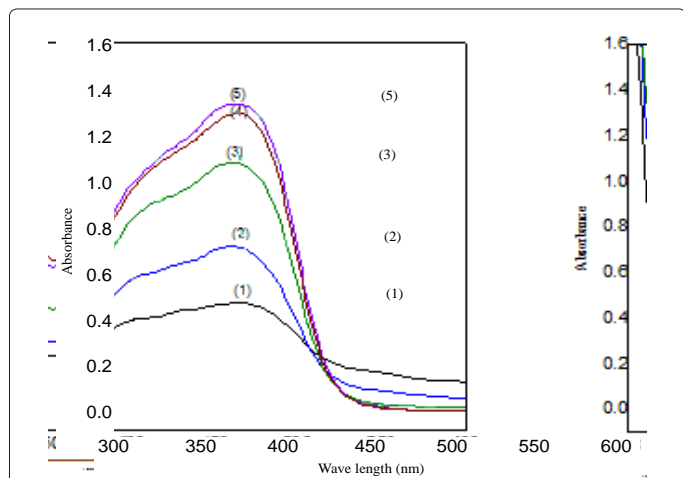


Figure 2: Absorption spectra of 7.5 mg/mL PPT in various percent concentrations of Tween 80 solution. The concentrations of Tween 80: (1) respectively.

outside sphere. Organic compounds and metal chelates that have large attraction power to the polyoxy ethylene group may be combined into this area [31]. PPT could be dissolved by this phenomenon, because this species has a hydroxyl group that interacts with the ether oxygen of polyoxyethylene group by hydrogen bonding. It appears that micelle in solution was formed because 5% Tween 80 solution was above the CMC (0.0013%, w:v) [32]. It is, also, shown from Figure 2, that the solubility of PPT increased in proportion to the percent concentration of the Tween 80 solution.

### E

**E H:** The effect of the pH on the absorbance of the Pd(II)-PPT complex in a 4% Tween 80 medium was considered over the range 2 – 9. The optimum pH value was determined by comparing the absorbances at various pH values. The pH range where Pd(II)-PPT complex had its maximum absorbance in the 4% Tween 80 solution is shown in Figure 3. The Pd(II)-PPT complex had the maximum and constant absorbance through the pH range of 3-5. The data in Figure 3 shows that a maximum and constant absorbance of the analyte is achieved over a wide range of pH. The direct addition of the reactants acquires the solution pH=3.5. Accordingly, pH 3.5 is selected as a suitable value to facilitate the proposed method due to the progress in this experimental investigation. Subsequent experiments were performed at pH 3.5.

### E

Different molar excesses of PPT were added to a fixed Pd(II) concentration, and the absorbance was measured according to the standard procedure. It was observed that at  $1 \times 10^{-5}$  mol l<sup>-1</sup> of Pd(II), the reagent molar ratio of [Pd]: [PPT] = 1:2 produced a constant absorbance of the Pd(II)-PPT chelate (Figure 4). Addition of excess ligand has no deleterious effects on the analysis of Pd(II).

### E

The effect of temperature on the absorbance of the Pd(II)-PPT complex in the Tween 80 medium is shown in Figure 5. As it can be seen that the Pd(II)-PPT complex had its maximum absorbance in the temperature range of 25-60°C, but released slowly with an increase in temperature above 60°C. This behavior can be explained as follows: the present technique is based on a property of most non-ionic surfactants

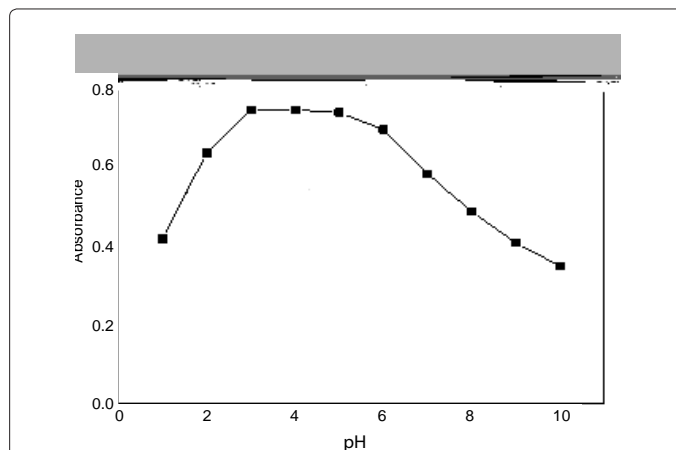


Figure 3: Effect of the pH on the absorbance of the Pd(II)-PPT complex in a 4% Tween 80 medium.

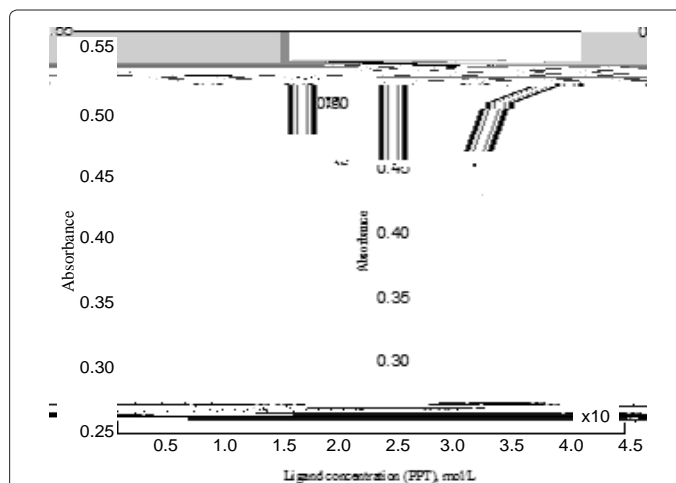


Figure 4: Effect of the concentration of PPT on the determination of Pd(II) in a 4% Tween 80 medium.

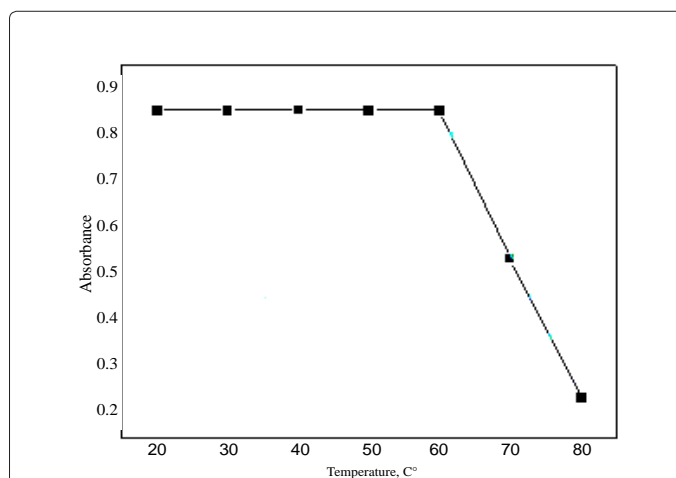


Figure 5: Effect of the temperature on the absorbance of the Pd(II)-PPT complex in the Tween 80 medium.

and the molar absorptivities of absorption spectra of PPT complexes of Pd(II) in 2.5% Tween 80 solution and in chloroform are presented in Table 2. It was also shown that the sensitivity of Pd(II) in Tween 80 medium was higher than in chloroform.

**A** : The absorption spectra of the ligand PPT and its complex with Pd(II) in Tween 80 are shown in Figure 6 (curves b, f). It is evident that the maximum absorption of the free ligand is at 450 nm and that of the complex is at 520 nm with a difference of 70 nm.

**B** : To study the stability of PPT in Tween 80 solution, after the concentration of PPT in a 4% Tween 80 solution was made to 0.5 mg l<sup>-1</sup>, the absorbance was measured as a function of time. Then, to measure the stability of the Pd(II)-PPT complex in Tween 80, the 5 ml of PPT saturated in 5% Tween 80 was added to 5 ml of 0.5 mg l<sup>-1</sup> metal solution buffered at optimum pH. At once, the absorbance was measured as a function of time. The obtained results indicated that PPT and Pd(II)-PPT were observed to be stable in the Tween 80 medium for more than 24 h.

**C** : Palladium (II) reacts with the PPT to form 1:2 complex in aqueous solution (Chart 2).

The infrared spectrum of PPT (Figure 7a) had bands at 1680 and 1630 cm<sup>-1</sup> that were assigned to (C=O) and (C=N), bands at 790 and 1240 cm<sup>-1</sup> assigned to (C=S) and the combination of (C=S) with (C=N) [34], bands at 3290 and 3080 assigned to (N=N) stretching vibrations and bands at 3450-3500 cm<sup>-1</sup>

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As it can be noticed, the sensitivity of Pd(II) in Tween 80 medium is higher than that in chloroform. The composition ratio of the Pd(II)-PPT complex obtained using Job's method was 1:2.

**M** (II)- **80**

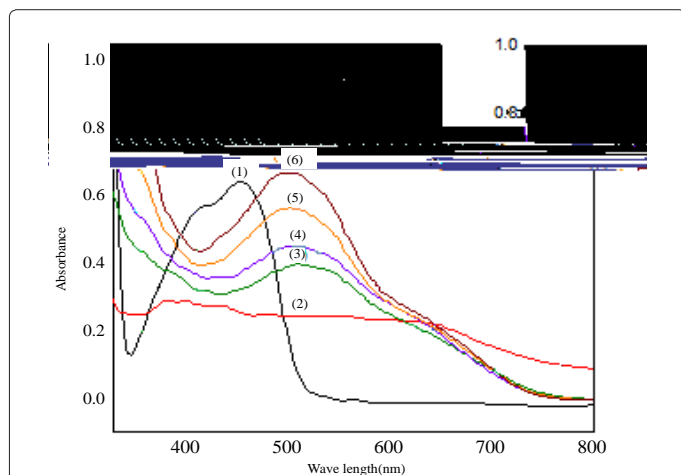
The expected formation mechanism of Pd(II)-PPT complex in Tween 80 medium could be explained by considering the fact that the dissolution process is dynamic. It seems that PPT dissolved in micelle, combines with Pd(II) ions to form non-polar complex that was instantaneously extracted into the local non-polar environment of micelle. This is the advantage of this method over liquid-liquid extraction that needs more time.

**A**

The present method was applied successfully to the determination of palladium in a series of synthetic mixtures (Table 3) and in a simulated silver alloy sample (Table 4). The method was also extended to the determination of palladium in natural water samples (Table 5).

**I** : Several synthetic mixtures of varying compositions containing palladium and diverse ions of known concentrations were determined by the present method using tartrate or KCN as masking agents and the results were found to be highly reproducible. The results are shown in Table 3. Accurate recoveries were achieved in all solutions.

**I** : It is well established in the literature [38] that the spectrophotometric determination of Pd in a solvent extraction is hampered by the presence of silver. Thus, the applicability of this procedure was extended to the determination of Pd(II) in a simulated silver alloy (Table 4).



**Figure 6:** (1) Absorption spectra of PPT without tween 80, (2) Pd(II)-PPT complex without tween 80, various percent

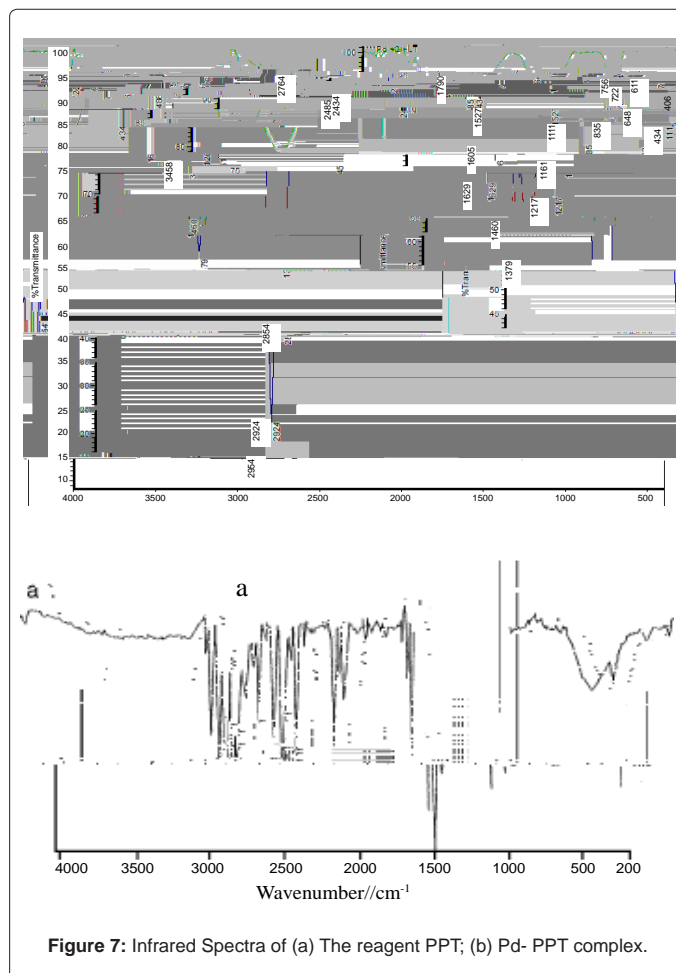
Synthetic mixtures, ( $\mu\text{g ml}^{-1}$ )	Palladium(II) ( $\mu\text{g ml}^{-1}$ )		Recovery, (R %)
	Expected	Found	
Mo VI (10), Ni (10), Ag(10), Zn (25)	10	9.9 $\pm$ 0.2	99.00
Co (12), Mg (80) Ca (20), Mo VI (10), Ni (10), Zn (25), K (25), Cu (10)	10	9.85 $\pm$ 0.4	98.50
Co (12), Mg (80), Ca (20), Mo VI (10), Ag (10)	10		99.20

\*Relative standard deviation (RSD) < 4.0

**Table 3:** Analysis of palladium(II) in synthetic mixtures (n = 5).

Composition	Found	
	Ag, 99.90, Cu: 0.049	0.048

**Table 4:** Comparative results for the analysis of palladium in simulated alloy sample (n=5).



**Figure 7:** Infrared Spectra of (a) The reagent PPT; (b) Pd-PPT complex.

**I** : In order to investigate the applicability to a natural-water sample, the recoveries of known amounts of Pd(II) added to bi-distilled, domestic and river water samples were examined by such a procedure. The results are presented in Table 5.

**C**

In this paper, a new, simple, sensitive, selective and inexpensive micelle mediated method was developed for the analysis of palladium in environmental and certified samples, for continuous monitoring to establish the trace levels of palladium in different sample matrices. Although many sophisticated techniques such as pulse polarography, HPLC, AAS, ICP-AES, and ICP-MS are available for the determination of palladium at trace levels in numerous complex materials, factors such as the low cost of the instrument, easy handling, lack of requirement for consumables, and almost no maintenance have caused spectrophotometry to remain a popular technique, particularly in laboratories of developing countries with limited budgets. The sensitivity in terms of molar absorptivity and precision in terms of relative standard deviation of the present method are very reliable for



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