



Simultaneous Determination Of U(VI) and Pd (II) Using 4-Hydroxybenzaldehyde Thiosemicarbazone By Second Order Derivative Spectrophotometric Technique

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Abstract

The metals U(VI) and Pd (II) gives yellow coloration with the reagent 4-Hydroxy benzaldehyde thiosemicarbazone(4-HBTS) in acidic medium simultaneous determination of both the metal ions U(VI) and Pd (II) can be done by using second order derivative spectrophotometric technique. For the determination of composition of metal complexes Job's method and mole ratio method were employed.

Keywords: Derivative Spectrophotometry; Thiosemicarbazone; 4-HBTS

Introduction

Uranium is hexavalent and palladium is divalent transition metals. Uranium is a highly reactive metal, especially at elevated temperatures. Uranium is radioactive, and is the element for which the phenomenon of radioactivity was first discovered. Palladium is little harder than pure platinum and it is catalytically active in the colloidal state. Simultaneous determination of these two metal ions becomes difficult and poses many problems. A second order derivative spectrophotometric method is used for the simultaneous determination of two metal ions based on their reaction with 4-hydroxy benzaldehyde thiosemicarbazone (4HBTS). Thiosemicarbazones have wide range of analytical applications in the determination of metal ions [1-5]. Thiosemicarbazones can be synthesized easily (Figure 1). Thiosemicarbazones forms stable complexes with different metal ions [6-13]. For getting improved resolution of spectral bands derivative spectrophotometry is

chosen, for resolving two overlapped spectra and to eradicating matrix interferences in two component mixtures zero crossing method can employed [14,15]. Two simultaneous equations should be solved for the determination of components in a mixture in the absence of zero crossing point [16,17]. Without solving simultaneous equations, derivative spectrophotometric technique can be employed for analysis of two component mixtures [18,19]. The tolerance limit value of foreign increases using derivative spectrophotometric technique which intern decreases the interference of foreign ions. Resolution of spectral bands can be achieved using derivative spectrophotometry, which allows location and detection of wavelength of complex spectra which is poorly resolved and also decrease the effect of interferences of spectral background. Simultaneous determination of metal ions by derivative spectrophotometric technique is not much exploited [20-22].

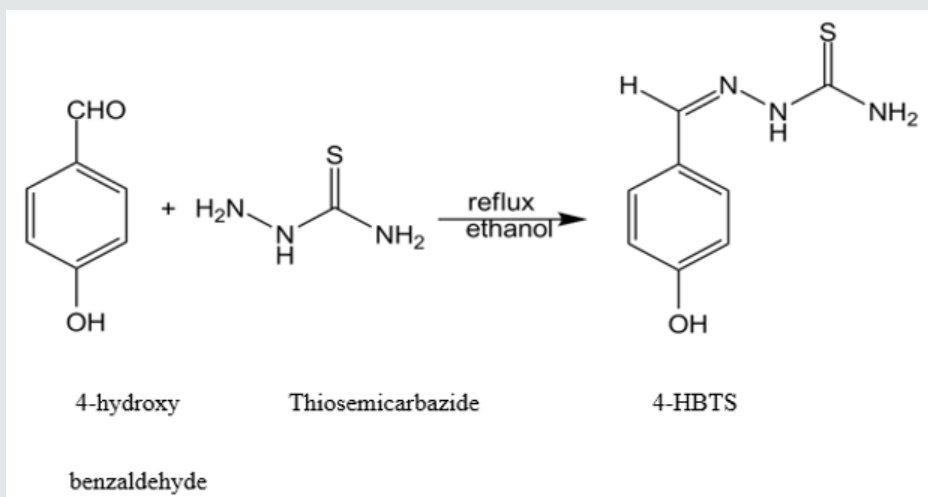


Figure 1: The yield remained 80% by weight and the melting point is 207°C-209°C. The compound structure was originated using infrared and nuclear magnetic resonance spectra.

Experimental Part

Shimadzu UV-Visible spectrophotometer (model UV-160A) used for the measurement of absorbance values and pH measurements were made by Elico digital pH meter (model LI20).

Preparation of 4-hydroxy benzaldehyde thiosemicarbazone

1 mole (1.22gm) of 4-hydroxy-benzaldehyde taken in 100ml of methanol and 1-mole (0.92gm) of thiosemicarbazone taken in hot water were mixed together in a clean 250ml round bottomed flask and refluxed for about 2 hours. Condensation reaction takes place and a brown colour product was observed, which is collected by filtration. With the help of methanol, the reagent was recrystallized and dried up in vacuum.

Characterization

Perkin-Elmer 137 infrared spectrometer is used for IR spectrum of the compound in KBr. The asymmetric as well as symmetric (–N–H) stretching frequencies assigned to primary amino-group are noticed at 3458cm^{-1} and 3342cm^{-1} . Frequency of aromatic proton (Ar–H) is observed at 3218cm^{-1} . The peak noticed at 1595cm^{-1} is ascribed to C=N stretching frequency of azomethine. The peak for –OH group is observed at $3028\text{--}3092\text{cm}^{-1}$. C=S stretching frequency is observed as strong peak at 1056cm^{-1} . The peaks for aromatic ring stretching frequency are observed in the range of $1530\text{--}1360\text{cm}^{-1}$ frequency. DRX 300 NMR spectrophotometer was used to record H-NMR spectrum. The characterization of phenolic –OH gives a peak noticed at δ -value 10.74 (1H), the peak for aromatic proton was observed at a peak attained at δ -value 7.86(4H) the

peak recorded at δ -value 6.8 (2H) can be assigned to –NH₂ proton assigned to thionyl (C=S) group. The aldehydic proton gives a peak detected at δ -value 9.0. The –NH proton (Azomethine) gives a peak at δ value 11.5.

Results and Discussion

The precursors, 1 ml of 1×10^{-3} M uranyl acetate and 1 ml of 1×10^{-3} M palladium chloride are taken in a 25 ml volumetric flask. 10 ml of buffer-solution of pH 5 is added. The reagent 4-hydroxy benzaldehyde thiosemicarbazone (4-HBTS) is taken in such a way that it is ten times in excess of both the metal ions. The mixture in the flask are made up the mark with distilled water. A blank solution is also prepared without adding the metal ion. The zero order spectra of U (VI) and 4-HBTS; Pd (II) and 4-HBTS are recorded in a buffer solution (pH 5). They are shown in (Figures 2,3) respectively. The λ_{max} values of the metal ions are 348.5 nm and 359 nm respectively. The zero-order spectrum of the solution containing both the metal ions is also recorded under the same experimental condition and presented in (Figure 4). It can be observed from this figure that the solution containing the mixture of metal ions shows only one peak at 355 nm. Hence it is not possible to determine U(VI) and Pd (II) simultaneously employing zero order spectrum. Attempts are made by the author to use the first order derivative spectrophotometric technique for the simultaneous determination, but the outcomes are not favorable. The author therefore adopted second order derivative spectrophotometric technique for the simultaneous determination of U(VI) and Pd (II).

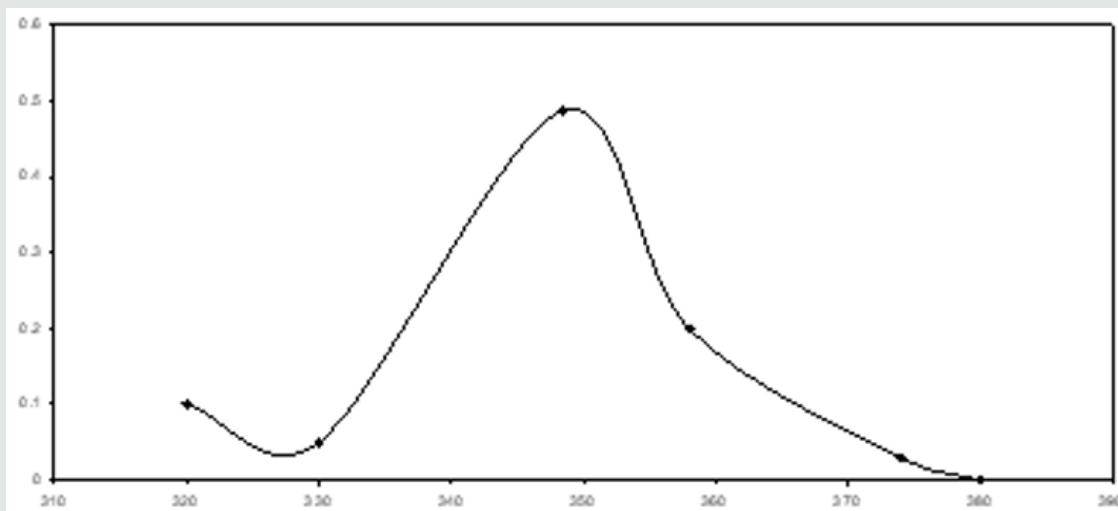


Figure 2: Zero order spectrum of uranium in presence of 4-HBTS, [U]=1 × 10⁻³M, [4-HBTS] =1 × 10⁻²M, pH =5.

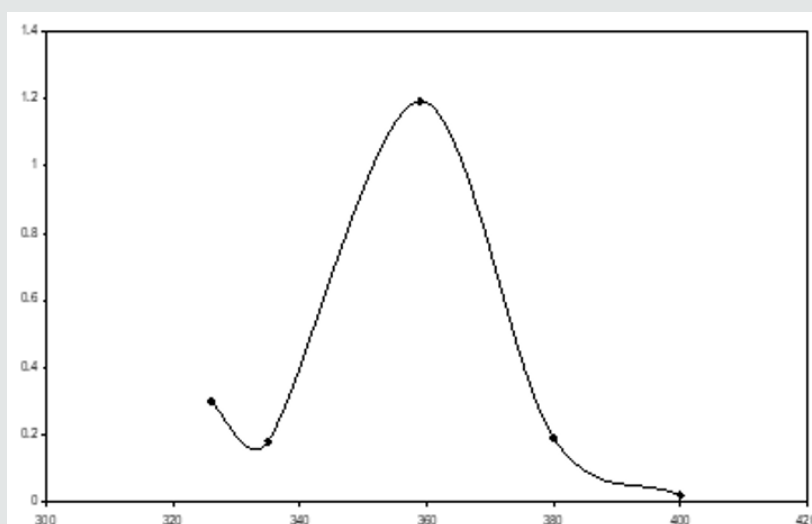


Figure 3: Zero order spectrum of palladium in presence of 4-HBTS, [Pd]=1 × 10⁻³M, [4-HBTS] =1 × 10⁻²M, pH = 5.

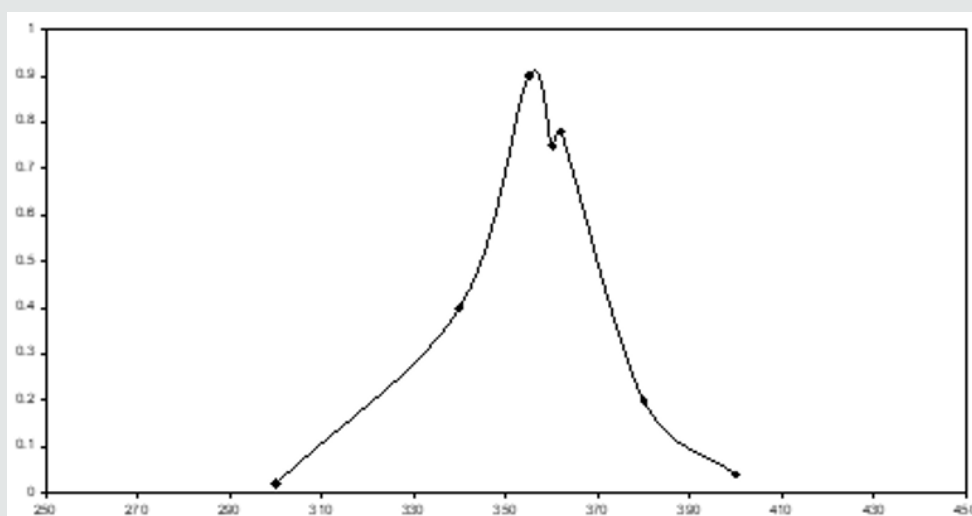


Figure 4: Zero order spectrum of (U + Pd) in presence of 4-HBTS, [Pd]= 1×10⁻³M, [U]=1×10⁻³M, [4-HBTS] = 1×10⁻²M, pH =5.

Simultaneous determination of U(VI) and Pd (II)

A series of solutions are prepared containing varying concentrations of U(VI) and Pd (II). An excess of the reagent is added to each of these solutions. The solution is made up to the mark by adding required volume of buffer (pH 5) and distilled water. An absolute solution is made on the same limes but deprived of metal ions. The second order derivative spectrum is recorded

for the experimental solution. Typical spectrum is presented in (Figure 5). From the figure, it is clear two peaks are observed for corresponding two metal ions 410 nm and 440 nm and two valleys at 429 nm and 454 nm. Under the same conditions, the second order derivative spectra are recorded individually for both metal ions. The outcomes disclosed that the peak and valley at 410 nm and 425 nm correspond to Pd (II) and the peak and valley at 440 nm and 454 nm corresponding to U(VI).

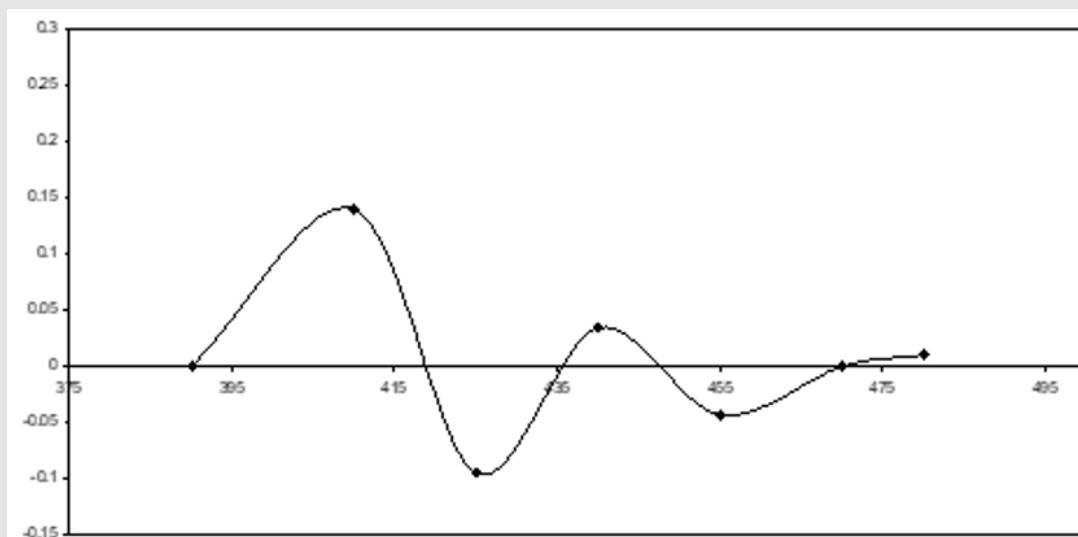


Figure 5: Typical second order spectrum of U + Pd in presence of 4-HBTS, $[U]=3 \times 10^{-4}M$, $[Pd]=3 \times 10^{-4}M$, $[4-HBTS] = 2 \times 10^{-2}M$, pH =5.

In addition, the measurements are made on the respective amplitudes of peak and valley are shown in the (Figure 6) for both metal ions. Graphs are drawn between the respective metal ion concentration and peak amplitude for uranium as well as palladium. Besides, maintaining the same conditions second-order derivative spectra are recorded for individual metal ions. The suitability of this method is established by the linear plots obtained

for the simultaneous determination of U(VI) & Pd(II) in the acidic medium. The straight line plots are obtained when the graphs are plotted by taking the sum of peaks & valleys amplitudes for individual metal ions. Fig.6 indicates the straight lines obtained and uranium is estimated in the range 4.7604 to 38.083 $\mu\text{g/ml}$ and palladium is estimated from 2.128 to 17.024 $\mu\text{g/ml}$ by using this method (Figure 7).

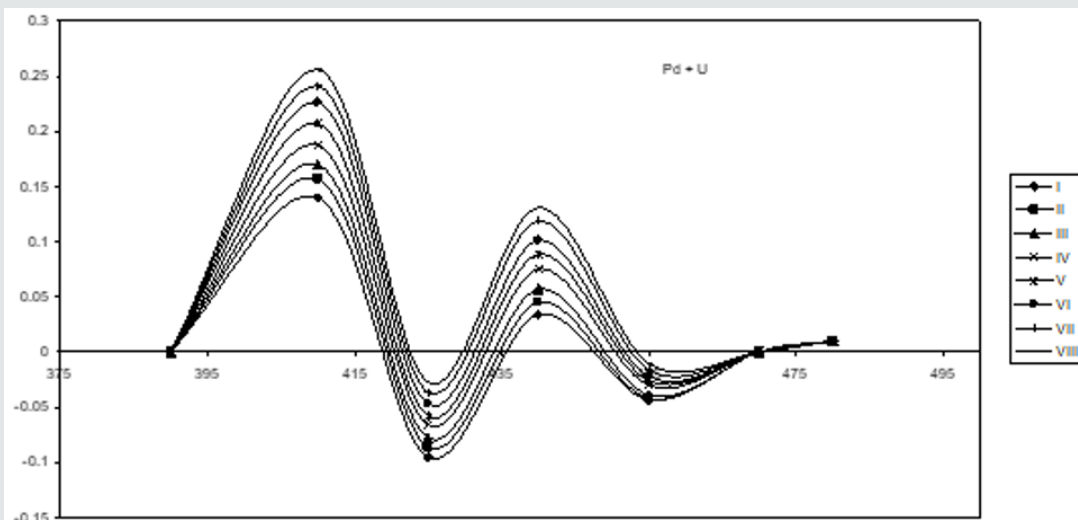


Figure 6: Second order spectra of U + Pd in presence of 4-HBTS, $[U]=3 \times 10^{-4}M$, $[Pd]=3 \times 10^{-4}M$, $[4-HBTS] = 2 \times 10^{-2}M$. pH =5.

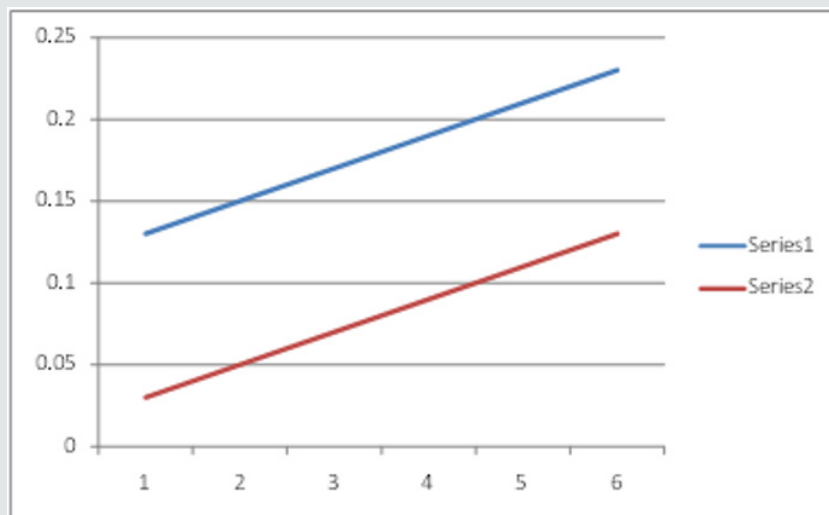


Figure 7: Verification of Beer's law for Series 1- U (VI) and Series 2- Pd (II).

Tolerance effect

Tolerance limit of different metal ions associated with U(VI) and Pd(II) is investigated. Influence of several anions is also studied.

The appropriate data is presented in Table 1. An analysis of the data reveals that Cu (II), Ni (II), V(V) and Cr (VI) did interfere seriously in the determination of metal ions. Utmost of the anions does not interfere.

Table 1: Tolerance limit of foreign ion in the determination of 0.952 $\mu\text{g/ml}$ of U(VI) & 0.424 $\mu\text{g/ml}$ of Pd (II).

Ion added	Tolerance-limit($\mu\text{g/ml}$)		Ion added	Tolerance limit($\mu\text{g/ml}$)	
	U (VI)	Pd (II)		U (VI)	Pd (II)
Chloride	170	142	Cadmium (II)	11.24	4.5
Bromide	319	255	Manganese (II)	17.58	2.2
Acetate	424	236	Nickel (II)	5.86	2.35
Nitrate	496	248	Copper (II)	2.54	2.54
Tartarate	736	736	Vanadium (V)	1.63	12.22
Sulphate	313	313	Chromium (VI)	1.039	1.039

Application

The method developed by the author has been employed for the simultaneous determination of U(VI) & Pd (II) in simulated mixtures. The outcomes are presented in Table 2 and they are satisfactory.

Table 2: Analysis of simulated mixture (U (VI) and Pd (II)), *Average of five determinations.

Amounts taken* ($\mu\text{g/ml}$)	Found ($\mu\text{g/ml}$)	% of error
0.525	0.515	1.9
0.843	0.833	1.18

Conclusion

The current work is simple, sensitive and highly selective for the simultaneous determination of U(IV) & Pd (II) in admixtures by second order derivative spectrophotometric technique without separation as well as solving the simultaneous equations. The technique developed has been applied for the simultaneous determination of U(IV) and Pd (II) in simulated mixtures.

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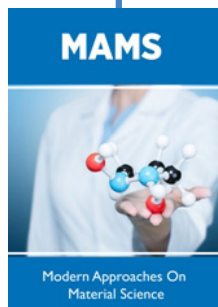
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