

Simultaneous Third order derivative Spectrophotometric Determination of Vanadium and Palladium Using 2-Hydroxy-1-Naphthaldehyde-P-hydroxy Benzoichydrazone (HNHBH)

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Abstract: A highly sensitive and selective third order derivative spectrophotometric method is proposed for the simultaneous determination of Vanadium and palladium. V(V) and Pd(II) react with the Chromogenic reagent 2-hydroxy-1-naphthaldehyde-p-hydroxybenzoichydrazone (HNHBH) at pH 4 to form deep yellow and greenish yellow coloured solutions with λ_{max} at 430 nm. Both the metal ions were simultaneously determined by measuring the third derivative amplitudes at 465.5 nm and 482.5 nm (zero cross method) against the reagent blank and plotting against the amount of the corresponding metal ion. Beer's law was obeyed in the range 0.050 – 1.935 $\mu\text{g mL}^{-1}$ and 0.022-2.021 $\mu\text{g mL}^{-1}$ for V(V) and Pd(II) respectively. No interference from associated anions and cations was observed. The method was applied for the determination of V (V) and Pd (II) in plant, pharmaceutical, water and alloy samples.

Keywords: Simultaneous determination, Third order spectrophotometry, Vanadium and Palladium, HNBH

I. Introduction

Vanadium and Palladium are chemically and industrially important as Vanadium is an important component of ferrous alloys used in jet-aircraft engines and in turbine blades and Palladium is used in instrument making [1], in aircraft spark plugs and in the production of surgical instruments and as electrical contacts.

On the other hand Vanadium compounds are toxic to human beings and animals. They inhibit biosynthesis of cholesterol in mammals, present in human blood and plasma [2] (in the range 0.005-8.4 μM). Its poisoning is treated as an industrial hazard [3], air pollutant,[4] which causes nervous depression, vomiting, coughing, anemia, diarrhea and increased risk of lung cancer, that are sometimes fatal. [5-6] and Palladium is thought to be one of the allergent in view of health hazards[7] so it is an important research activity for a analytical and bio-analytical chemist to determine vanadium [8] and palladium [9] in trace levels or ultra trace levels. Review of literature reveals that simultaneous spectrophotometric determination of V (V) and Pd (II) are not exploited so far, so we are now proposing third derivative spectrophotometric method for the simultaneous determination of V (V) and Pd (II) by zero cross method without the need for solving simultaneous equations.

II. Materials And Methods

1. Experimental

The absorbance and pH measurements were made on a Shimadzu UV-visible spectrophotometer (Model UV -160A) fitted with 1 cm Quartz cells and ELICO digital pH meter model LI – 120 respectively. The pH meter has temperature compensate arrangement and has reproducibility of measurement within ± 0.01 pH.

2. Reagent and solutions

All chemicals used were of analytical-reagent grade of the highest purity available procured from Merck. Doubly distilled de-ionized water was used throughout the experiment. Glass vessels were cleaned soaking in acidified solutions of $\text{K}_2\text{Cr}_2\text{O}_7$ followed by washing with conc. HNO_3 and were rinsed several times with high purity deionized water.

2.1. Preparation of 2-Hydroxy-1-naphthaldehyde-p-hydroxybenzoichydrazone (HNAHBH)

The reagent (HNHBH) was prepared by simple condensation of 1 mol of 2-hydroxy-1-naphthaldehyde and 1 mol of p-hydroxybenzoichydrazide. In a 250-ml Erlenmeyer flask, a hot ethanolic solution of 2-hydroxy-1-naphthaldehyde (5ml, 0.0438mol in 5ml of ethanol), thiosemicarbazide (4g, 0.0438 mol, dissolved in 10 ml of hot water) were taken in 250-ml round bottom flask. Suitable quantity (~ 2ml) of glacial acetic acid was added

to the reaction mixture and refluxed for 3 hours. [10] On cooling the reaction mixture, the reddish brown coloured solid obtained was then separated by filtration, washed and dried. The product was recrystallized from aqueous ethanol in the presence of norit and dried *in vacuo*, yield 4.2 g; m.p. 273⁰c as shown in Scheme 1

2.2. HNHBH solution

The reagent solution (0.01M) was prepared by dissolving 31 mg of the compound in dimethylformamide (DMF) in 25-ml standard flask. The reagent solution is stable for at least 12h.

2.3. Vanadium (V) solution

0.1219 g of ammonium meta vanadate (NH₄VO₃) (AR Qualigens) was dissolved in hot distilled water and the solution was made up to 100 ml in a volumetric flask after cooling with distilled water. The stock solution was standardized titrimetrically [11, 12].

1.4. Palladium (II) solution

A 0.01 M solution of palladium (II) was prepared by dissolving 0.1774 g of palladium chloride (Sigma-Aldrich) in minimum volume of 2N hydrochloric acid and diluting to 100 ml with distilled water in a 100 ml volumetric flask. This stock solution was standardized gravimetrically using dimethyl glyoxime. Solutions of lower concentrations were prepared freshly by diluting the stock solution to carry out the analysis.

1.5. Buffer solutions

Buffer solutions of various pH values were prepared by mixing 1 M HCl and 1 M of CH₃COONa (pH 1.0-3.0), 0.2 M CH₃COOH and 0.2 M CH₃COONa (pH 3.5-7.0), 0.2 M CH₃COOH and 0.1 M CH₃COONa (pH 7.0) and 2M NH₄Cl and 2 M NH₄OH (pH8.0-10.0) solutions in appropriate ratios. The pH of the solutions was checked with pH meter.

1.6. Procedure

1.6.1. Determination of V(V) and Pd(II) in binary mixtures

To different aliquots containing V(V) and Pd(II) in variable proportions in 10 ml volumetric flasks, 4 ml of buffer solution (pH 4.0), 0.5 ml of 1% triton X-100 and 0.4 ml of HNHBH (1x10⁻² M) were added to each flask and made upto the mark with distilled water. The third order derivative spectra were recorded in the wave length range of 350-600 nm and the derivative amplitudes were measured at 465.5 nm and 482.5 nm. The amounts of V(V) and Pd(II) present in the binary mixtures were calculated from the measured derivative amplitudes with the help of pre-determined calibration plots ("Fig"1 & 2). The results obtained are shown in Table .1.

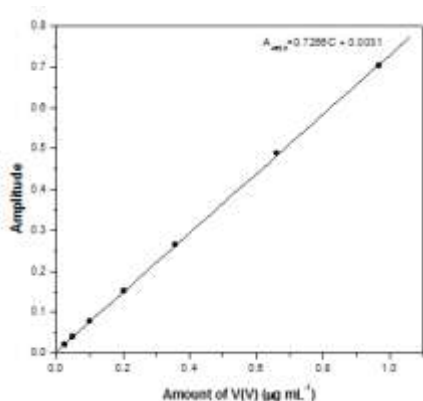


Fig. 1. Calibration plot of [V(V) – HNAHBH]

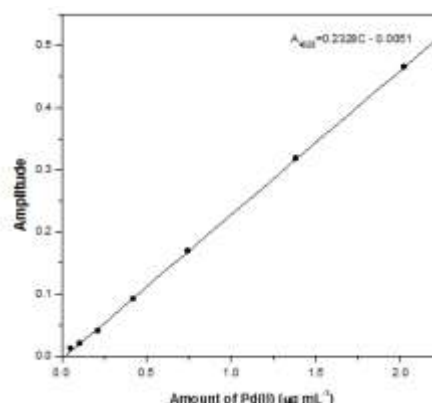


Fig.2. Calibration plot of [Pd(II) – HNAHBH]

Table. 1 Simultaneous third derivative spectrophotometric determination of V (V) and Pd(II)

Amount taken (µg mL ⁻¹)		Amount found* (µg mL ⁻¹) (% of recovery)		Relative error (%)	
V(V)	Pd(II)	V(V)	Pd(II)	V(V)	Pd(II)
0.101	1.277	0.100 (99.01)	1.260 (98.67)	-0.99	-1.33
0.203	1.277	0.207 (101.97)	1.302 (101.96)	+1.97	+1.95
0.305	1.277	0.300 (98.36)	1.260 (98.67)	-1.64	-1.33
0.610	1.277	0.618 (101.31)	1.294 (101.33)	+1.31	+1.33
0.814	1.277	0.810 (99.51)	1.270 (99.57)	-0.49	-0.55
0.305	0.053	0.300 (98.36)	0.052 (98.11)	-1.70	-1.88
0.305	0.106	0.308 (100.98)	0.107 (100.94)	+1.01	+0.94
0.305	0.212	0.305 (100.00)	0.211 (99.53)	-0.26	-0.47
0.305	0.425	0.306 (100.33)	0.426 (100.23)	+0.19	+0.23
0.305	0.851	0.305 (100.00)	0.849 (99.57)	-0.13	-0.23
0.305	1.064	0.306 (100.33)	1.065 (100.09)	+0.06	+0.09
0.305	1.276	0.305 (100.00)	1.277 (100.08)	-0.06	+0.07

*Average of four determinations

III. Results and Discussion

The third order derivative spectra recorded for the various solutions containing different amounts of vanadium (V) or palladium (II) are shown in “Figure 3”. The [Pd(II)-HNHBH] solution showed maximum amplitude at 472.5 nm where the [V(V)-HNHBH] solution showed zero amplitude. Similarly in [V(V)-HNHBH] species showed maximum amplitude at 509 nm where the Pd(II) complex showed zero amplitude. The simultaneous determination of V(V) and Pd(II) was carried out by measuring the third derivative amplitudes at 465.5 nm and 482.5 nm respectively. The plots constructed between the derivative amplitudes measured and the amount of V(V) or Pd(II) showed that the Beer’s law was obeyed in the range 0.050 – 1.935 µg mL⁻¹ of V(v) and 0.022-2.021 µg mL⁻¹ of Pd(II) respectively. Since no amplitude was observed for Pd(II) complex at 482.5 nm where the V(V) complex showed maximum and no derivative amplitude by V(V) complex at 465.5 nm where the Pd(II) complex has maximum amplitude, the zero cross method was adopted for the simultaneous determination of V(V) and Pd(II) in the binary synthetic mixtures by measuring their derivative amplitudes 465.5 nm and 482.5 nm respectively. The results obtained along with recovery percentages are shown in “Table”.1. The relative errors obtained in these determinations indicate the suitability of the proposed method for the simultaneous determination of V(V) and Pd(II). The study on the effect of diverse cations on the derivative amplitudes showed that Tl(III), Pb(II), Cd(II), and Hg(II) do not interfere in any levels., Sn(II), and Zn(II) were tolerable upto 5 fold excess. Y(III), La(III), In(III) and Al(III) interfered when present in more than equal amounts.

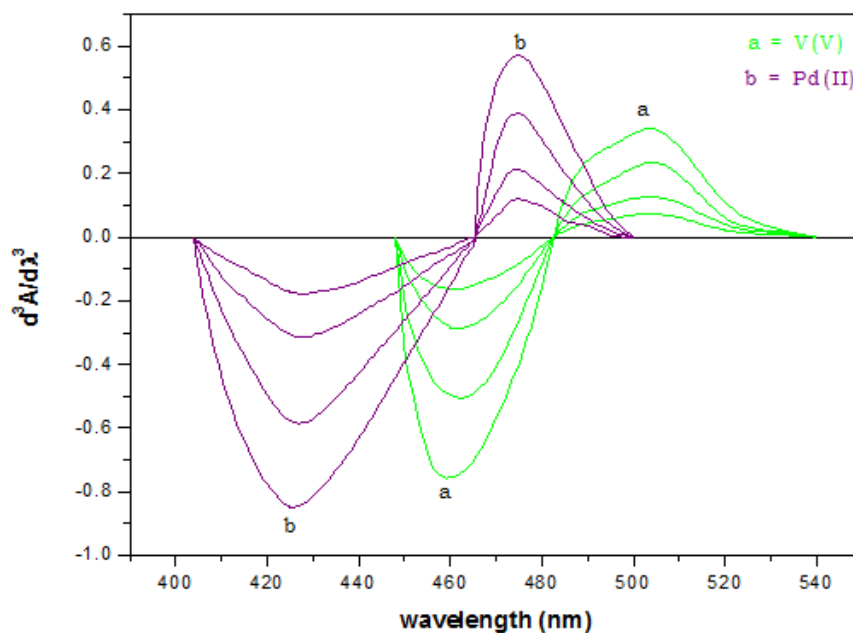


Fig. 3. Third order derivative spectra of (a) V(V) – HNAHBH and (b) Pd(II) – HNAHBH

V(V) ($\mu\text{g mL}^{-1}$): 0.203; 0.356; 0.661; 0.967.

Pd(II) ($\mu\text{g mL}^{-1}$): 0.425; 0.744; 1.383; 2.021

2. Applications

The proposed simultaneous method was applied for the determination of V(V) and Pd(II) in environmental, pharmaceutical and alloy samples.

IV. Preparation of sample solutions

4.1 Plant sample

The raddish roots were washed thoroughly with water, wiped with filter paper and weighed. Then the samples were dried, ashed and brought into solution as per the standard procedures [13, 14] and neutralized with NH_4OH solution. Since the sample did not contain any detectable levels vanadium or palladium, known amounts the metal ions were spiked into the resultant solution and finally diluted to known volume with distilled water. Suitable aliquot of the sample solution was analyzed according to the simultaneous procedure and the vanadium and palladium contents were determined. The results are presented in “Table. 2.”

4.2 Pharmaceutical sample solution

10 ml of Neogadine Elixer syrup were treated with 10 ml conc. HNO_3 and the resultant mixture was evaporated to dryness. The residue was leached with 5 ml 0.5 M H_2SO_4 . The solution was neutralized with dilute NH_3 . As the sample did not contain known levels of palladium, a known aliquot of palladium solution containing fixed amount of palladium was introduced and finally the solution was made upto known volume with distilled water. Suitable volumes of the sample solution were analyzed by the proposed derivative method and the amounts of V(V) and Pd(II) present were calculated. The results are presented in “Table. 2.”

4.3 Water sample

Known amounts of vanadium and palladium were spiked into mineral water and tap water and the resultant solutions were diluted to known volumes with distilled water. The sample solutions were analyzed using the proposed simultaneous derivative method and the vanadium and palladium contents were evaluated. The results are presented in “Table. 2.”

4.4 Alloy sample [15]

Synthetic mixtures of Okay alloy and Palau alloy were prepared by mixing vanadium and palladium along with other associated metals as shown in “Table. 3.” in suitable ratio and dissolved in HCl-HNO_3 mixture according to the standard procedure. The solution was filtered and finally diluted to known volume with distilled water. Known aliquots of sample solutions were treated with 400 μg of EDTA (to mask Ni) and the vanadium and palladium contents were determined by the proposed simultaneous derivative method. The results along with the recovery percentages are given in “Table. 3.”

Table.2. Determination of V(V) and Pd(II) in plant, pharmaceutical and water samples

Sample	Amount of vanadium ($\mu\text{g mL}^{-1}$)			Amount of palladium ($\mu\text{g mL}^{-1}$)		
	Added	Found*	Recovery Percentage (%)	Added	Found*	Recovery Percentage (%)
Plant material (raddish)	5.0	5.01 ± 0.04	100.20	8.0	8.02 ± 0.01	100.25
Pharmaceutical sample ^a	-	5.24 ± 0.06	104.80	4.0	4.03 ± 0.05	100.75
	5.0	10.32 ± 0.03	100.58	6.0	5.97 ± 0.02	99.50
Tap water	10.0	10.25 ± 0.03	102.50	10	9.98 ± 0.05	99.80
mineral water	5.0	4.96 ± 0.08	99.20	5.0	5.06 ± 0.02	101.20

*Average of five determinations \pm SD

a = Neogadine Elexer (Raptakos Brett & Co. Ltd, India)

(Each 15 ml contains 29 mg iodised petone, 20 mg MgCl_2 , 4 mg MgSO_4 , 0.66 mg NaVO_3 , 6 mg ZnSO_4 , 0.7 mg pridomine HCl, 0.5 mg cyanocobalamine, 10 mg nicotinamide, 0.95 ml alcohol (95%). Vanadium taken $5.26 \mu\text{g mL}^{-1}$)

Table.3. Determination of V(V) and Pd(II) in synthetic alloy samples

Sample & composition	Amount of vanadium ($\mu\text{g mL}^{-1}$)			Amount of palladium ($\mu\text{g mL}^{-1}$)		
	Taken	Found*	Recovery Percentage (%)	Taken	Found*	Recovery Percentage (%)
Oakay alloy 18.2Pd;18.2Pt; 54.2Ni; 9.4V(%)	0.846	0.844 ± 0.004	99.76	1.468	1.472 ± 0.002	100.27
Palau alloy 0.45Ni;0.15Pt; 0.075V; 0.15 Pd (mg)	0.686	0.688 ± 0.01	100.29	1.980	1.985 ± 0.009	100.25

*Average of four determinations \pm SD

V. Conclusions

The proposed third order derivative spectrophotometric method is simple, rapid, sensitive, and accurate without any type of extraction and does not require the solving of simultaneous equations. The applicability of the method in various samples have been studied which gave encouraging results in the simultaneous determination of V(V) and Pd(II) (table 2 and 3).

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References

- [1]. R. Sahu, S.M. Sondhi and B. Gupta, *Talanta*, 42(3), 1995, 401-405
- [2]. J.Versieck, and R.Cornelis, *Anal. Chim. Acta*, , 116, 1980, 217.
- [3]. G.D. Clayton and F.E.Calyton, *Patty's Industrial Hygiene and Toxicology*, vol. 2A, 3rd Ed., Wiley New York, 1981, P. 2013.
- [4]. S.Langard, T. Norseth, L. Friberg, G.R.Nerberg, and V.B. Vouk, (Eds.), *Hand Book on toxicology of metals*, Elsevier, Amserdam, 1986.
- [5]. B.Venugopal and T.D Luckey, *Metal Toxicity in Mammals 2*, plenum press, New York, 1979, P. 220.
- [6]. A.Safavi, M.R. Hormozi Nezhad, and E.Shams, *Anal Chim. Acta*, 409, 2000, 283.
- [7]. S. Caroli, A. Alimonti, F. Petrucci, B. Bocca, M. Krachler, F. Forastere, M T Sacerdote and S. mallone *Spectro chim acta Part B.*, 56(7), 2001, 1241.
- [8]. P. Govinda Chowdary and V. Saleem Basha. *Der Pharma Chemica*, 7(12), 2015, 338-345
- [9]. P. Govinda Chowdary and V. Saleem Basha, *WJPR*, 4(5) , 2015, 1168-1180
- [10]. Brown, E.V., Caglioti, L., Paoluca, G., Sucrow, W., *Hydrazones and hydrazones*, In: *Methodicum chemicum*, C-N compounds, Academic Press, New York, 6, 1975
- [11]. A.Ali Ensafi, M.K. Amini, and M. Mazloun, *Anal. Lett*, 32, 1999, 1927
- [12]. K.Gavazov and A.Alexandrov, *Talanta*, 52, 2000, 539
- [13]. S.A.Abbasi, *Anal. Lett*. 20, 1987, 1347.
- [14]. D.Glick (Ed.), *Methods of Biological Analysis*, vol. 21, John Wiley, 1973, p.39
- [15]. W. Yang, Q. Hu, Z. Huang, J. Yin, G. Xie and J. Chen, *J.Serb.Chem.Soc*, 71(7), 2006, 821-828.