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Determination of palladium(II) in presence of micellar medium by derivative spectrophotometric technique

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ABSTRACT

A simple and sensitive spectrophotometric method has been developed for the determination of palladium(II) using newly synthesized 3-methoxysalcilaldehyde-4-hydroxybenzoylhydrazone (MSHBH) reagent in a micellar medium of CTAB (acidic surfactant). Palladium(II) forms an orange yellow colored water soluble complex with the MSHBH reagent in acidic buffer medium pH 4.5. Beer's law obeyed in the range 0.2876 to 4.2568 µg/mL of Pd(II) λ_{max} at 412 nm. The molar absorptivity and Sandell's sensitivity of colored species are 1.03 x10^{4} L.mol^{-1}.cm^{-1} and 0.0103 µg.cm^{-2} respectively. Palladium(II) forms (M: L) 1:1 complex and stability constant of the complex is 9.32x10^{4}. The developed first and second order derivative spectrophotometric methods were employed for the determination of palladium(II) in alloy samples and hydrogenation catalyst samples.

Key Words: Derivative spectrophotometry, 3-methoxysalcilaldehyde-4-hydroxybenzoylhydrazone (MSHBH), Cetyltrimethyl ammoniumbromide (CTAB), Palladium(II).

INTRODUCTION

The potential application of hydrazone derivatives for the spectrophotometric determination of metal ions has been reviewed by Singh.et.al [1]. Hydrazones are important organic analytical reagents for the determination of metal ions in microgram quantities. They react with many metal ions forming colored complexes and act as chelating agents. In general, the technique of solvent extraction is widely used in the spectrophotometric determination of metal ions [2-3]. However, organic solvents such as benzene and chloroform are often carcinogenic, toxic and cause environmental pollution. It is significant to develop a method which does not involve solvent extraction. In the light of good analytical characteristics of hydrazones, herein we report direct (zero order), first order and second order derivative spectrophotometric determination of Pd(II) using 3-methoxysalcilaldehyde-4-hydroxybenzoylhydrazone (MSHBH) in presences of micellar medium without involving any extraction.

Derivative spectrophotometry is a very useful technique, in the sense that, it decrease the interference i.e. increase the tolerance limit value of the foreign ions. The great interest towards derivative spectrophotometry is due to the increased resolution of spectral bands, allowing the detection and location of the wavelengths of poorly resolved components of complex spectra and reducing the effect of spectral background interferences. Because of these characteristics, the process of isolation and pre-concentration of active components, usually required in qualitative and quantitative spectrophotometric procedures applied in the analysis of complex systems, is completely avoided. Derivative spectrophotometric methods for the determination of metal ions [4-6] are not exploited much. A micellar solution of a surfactant has the ability to enhance the stability of metal complex and has been utilized as a medium for the spectrophotometric determination of the metal chelate [7-9].

MATERIALS AND METHODS

Apparatus

All absorption measurements were made in a Shimadzu 160A microcomputer based UV-Visible spectrophotometer equipped with 1.0 cm quartz cells. The instrumental parameters were optimized and the best results were obtained in the wavelength range 300- 650 nm with a scan speed fast, spectral band width 2 nm, wavelength readability 0.1 nm increment and wavelength accuracy ± 0.5 nm with automatic wavelength correction.

ELICO LI-120 digital pH meter was used for the pH adjustments. The reproducibility of the measurements is within 0.01 pH.

Sartorius BS/BT 2245 model (Germany make) electronic analytical balance having maximum capacity of 220 g and sensitivity of ± 0.1 mg was used for weighing purpose.

Reagents

Palladium(II) stock solution: The standard Pd(II) solution (0.01 M) was prepared by dissolving accurately weighed 0.1773 g of $PdCl_2$ (AR Johnson Matthey & Co. Ltd, London) in a few mL of dilute hydrochloric acid and made up to the mark with doubly distilled water in a 100-mL of volumetric flask and standardized [10]. The working solutions were prepared by diluting the stock solution to an appropriate volume.

Buffer Solutions: Buffer solutions were prepared by 1.0 M Hydrochloric acid- 1.0 M Sodium acetate (pH 0.5-3.5); 0.2 M Acetic acid – 0.2 M Sodium acetate (pH 4.5- 7.0); 0.25 M Sodium tetra borate decahydrate - 0.1 M Hydrochloric acid (pH 8.0 – 9.1); 0.25 M Sodium tetra borate decahydrate - 0.1 M sodium hydroxide (pH 9.2-10.8).

Solutions of various diverse ions of suitable concentrations were prepared using AR grade chemicals. All solutions were prepared with doubly distilled water.

CTAB Solution: A 5% solution was prepared by diluting 5.0 g of Cetyltrimethyl ammonium bromide (CTAB) (AR Romali) to 100 mL with doubly distilled water.

3-methoxysalcilaldehyde-4-hydroxybenzoylhydrazone Solution:
The reagent 3-methoxysalcilaldehyde-4-hydroxybenzoylhydrazone (MSHBH) was synthesized by refluxing equimolar amounts of 3-methoxysalcilaldehyde and 4-hydroxybenzoylhydrazide [11]. The structure of MSHBH was given in figure 1.

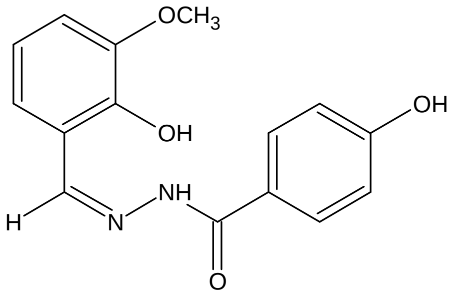

Figure 1 - Structure of 3-methoxysalcilaldehyde-4-hydroxybenzoylhydrazone (MSHBH)

The pKa values are determined by following Phillip and Merritt method [12]. The UV-Visible spectra of µM (2 x 10^{-5} M) solution of ligand was recorded at various pH values and by taking the arithmetic mean of the values obtained from the measurements at five different wavelengths. The values of deprotonation of ligand are 4.6 (pK_1) and 9.5 (pK_2). The possible species which may be formed at different pH values are shown in figure 2.

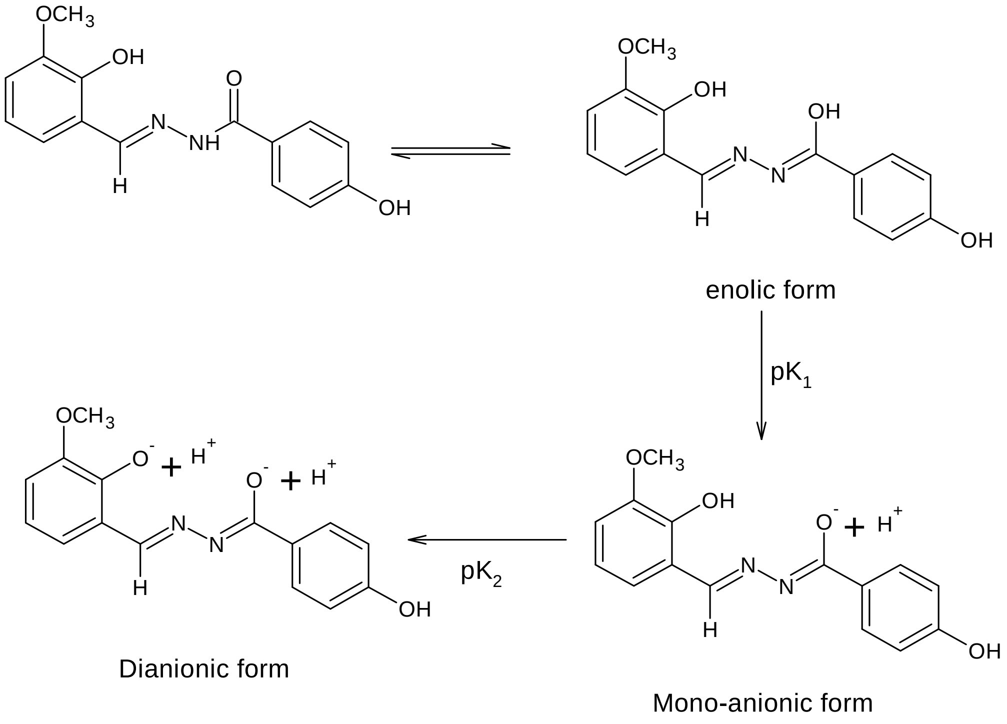

Figure 2 - Different species of MSHBH at different pH

The reagent solution (0.01 M) was prepared by dissolving 0.2863 g of MSHBH in 100 mL of Dimethylformamide (DMF). The reagent solution is stable for 48 hours.

Recommended procedures

Determination of palladium(II) (Zero order):

An aliquot of the solution containing 0.2876 to 4.2568 µg/mL of Pd(II), 10 mL of buffer pH 4.5, 0.5 mL of DMF, 1.0 mL of CTAB (5%) and 1.0 mL of MSHBH reagent 1x 10^{-2} M were taken in a 25-mL volumetric flask and the solution was diluted up to the mark with doubly distilled water. The absorbance of the solution was recorded λ_{max} at 412 nm in a 1.0 cm cell against reagent blank prepared under identical conditions. The measured absorbance was used to compute the amount of palladium(II) from the calibration plot.

Determination of palladium(II) by first order derivative spectrophotometry:

For the above solution of Pd(II)-MSHBH first order derivative spectrum was recorded with a scan speed having degrees of freedom 9 in a wavelength range 300 to 650 nm. The first order derivative peak-height (h) was measured by peak-zero method at 438 nm. The peak-height was plotted against the amount of Pd(II) to obtain the calibration curve.

Determination of palladium(II) by second order derivative spectrophotometry:

For the above solution, second order derivative spectrum of Pd(II) - MSHBH system was recorded with reference to reagent blank with 9 degrees of freedom, in a wavelength range 300 nm to 650 nm. In the second order derivative spectrum peak-height at 451 nm was measured from the zero line of spectrum. Calibration plots were constructed by plotting the derivative amplitude against the amounts of palladium(II).

Analysis of alloy samples

0.5 g sample of alloy was digested in 15 mL of aqua-regia by warming and the solution was evaporated to dryness. The residue was dissolved in 10 mL of diluted HCl and resulting solution concentrated to 5.0 mL, diluted to 50 mL with doubly distilled water, filtered and made up to the mark in a 100-mL volumetric flask.

Analysis of hydrogenation catalyst samples

About 0.3 g of catalyst sample was transferred into 250-mL beaker, treated with 5.0 mL of 2.0 M HNO_3 and covered. When the solution of gas had diminished 10 mL of aqua-regia was added and the solution was evaporated to near dryness on a sand-bath. The residue was dissolved in 5.0 mL of 2.0 M HNO_3 and diluted to mark with doubly distilled water in a 250-mL volumetric flask. Suitable aliquots were taken and analyzed for palladium(II) using recommended procedure discussed above.

RESULTS AND DISCUSSION

The reagent 3-methoxysalcilaldehyde-4-hydroxybenzoylhydrazone (MSHBH) was easily synthesized as any other schiff base reagent. The color reactions are mainly due to complex formation of MSHBH with divalent, tetravalent, pentavalent and hexavalent metal ions in aqueous medium. In acidic medium, ligand presumably exists in enolic form and co-ordinates the metal ion as mono-anion to give neutral complexes.

Palladium(II) reacts with MSHBH over a wide range of pH (2.0- 10.0) to form a sparingly soluble orange yellow colored complex. The colored complex is soluble in DMF. However, the complex was stabilized by employing surfactants.

Absorption spectra:

The absorption spectra of CTAB (5%), MSHBH and [Pd(II)-MSHBH] complex recorded in optimum conditions against buffer solution and reagent blank respectively shown in figure 3. The complex shows absorption maximum at 412 nm, where the CTAB (5%), reagent (MSHBH) solution does not show appreciable absorbance. Therefore, analytical wavelength 412 nm was used for all measurements.

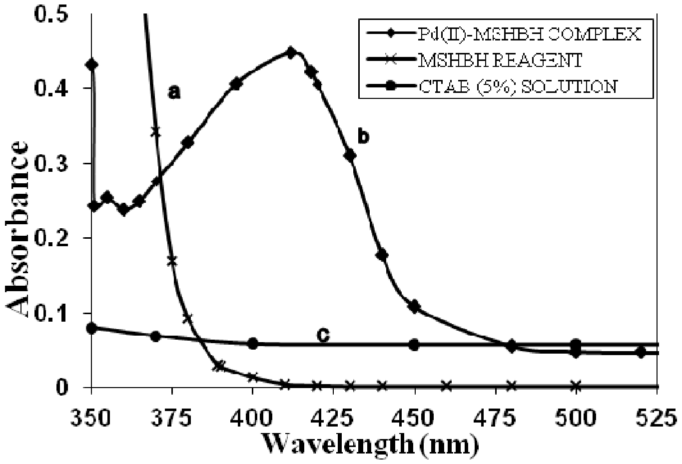

Figure 3 - Zero order absorption spectra of,

a) Reagent (MSHBH) vs. buffer blank.
b) Pd(II)-MSHBH complex vs. reagent blank.
c) CTAB (5%) vs. buffer blank.
Pd(II) = 4.2568 µg/mL, [MSHBH] = 4 x 10^{-4} *M,*
pH (4.5) = 10 mL, CTAB (5%) = 1.0 mL, DMF = 0.5 mL.

Effect of pH:

It was observed that the color reaction between Pd(II) and the reagent MSHBH was instantaneous in pH range 2.0 to 7.0. The study of the effect of pH on the color intensity of the complex showed that the maximum constant absorbance was obtained in the pH range 3.0 to 6.0. Therefore, pH 4.5 was kept constant throughout the experiment.

Color stability of the complex:

The absorbance of palladium(II)-MSHBH complex was measured at different time intervals to ascertain the stability of the complex. The full color development of the complex remains constant for five hours after the incubation period of 25 minutes, in presence of surfactants.

Effect of Surfactants:

The effect of various surfactants such as Triton X-100, Sodium dodecyl benzene sulphonate (SDBS) and Cetyl trimethyl ammonium bromide (CTAB) on the absorption profiles of the Pd(II)-MSHBH system has been investigated and presented in table 1. In presence of CTAB the complex is more stable and exhibited maximum absorbance. Hence, CTAB is selected for further studies.

Table 1 - Effect of various surfactants on the Pd(II)-MSHBH complex.

Surfactant (5%)	Nature of Surfactant	Absorbance at 412 nm
None	-	0.385
Triton X-100	Neutral	0.390
CTAB	Cationic	0.420
SDBS	Anionic	0.247

Effect of CTAB:

A study on the effect of volume of CTAB on absorbance of the complex indicates that, absorbance of the metal complex remains constant over a range of 0.8 to 2.5 mL of CTAB (5%). Therefore, 1.0 mL of CTAB (5%) was sufficient in all analytical studies. CTAB serves to stabilize and sensitize the metal complex.

Effect of MSHBH concentration:

The amount of reagent necessary for full color development of Pd(II)-MSHBH was established. The studies revealed that a 5-fold molar excess of MSHBH reagent is sufficient for complete and constant color development. Excess of reagent has no effect on the absorption of the complex.

Order of addition of reactants:

The order of addition of metal ion, buffer solution, DMF, surfactant and MSHBH reagent has no adverse effect on the absorbance of the colored complex.

Applicability of Beer's law:

From the calibration plots (figure 4) it was observed that, the system obeyed Beer's law in the range 0.2876 to 4.2568 μg/mL of Pd(II) with excellent linearity in terms of correlation coefficient value (r = 0.99). However, the practical range of determination of Pd(II) obtained from Ringbom's curve is 0.8514 to 4.2568 μg/mL at 412 nm. The molar absorptivity and Sandell's sensitivity of the Pd(II)-MSHBH complex are 1.03 x 10^4 L.mol^{-1}.cm^{-1} and 0.0103 μg.cm^{-2} respectively. The specific absorptivity of the complex is 0.097 mL.g^{-1}.cm^{-1}.

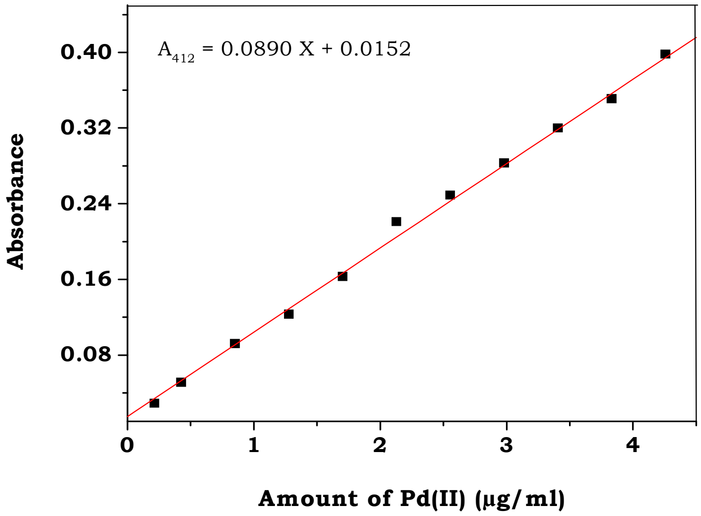

Figure 4 - Absorbance vs. amount of Pd(II) (μg/mL).

[MSHBH] = 4 x 10^{-4} M, pH (4.5) =10 mL,
CTAB (5%) = 1.0 mL, DMF = 0.5 mL,
Wavelength = 412 nm.

The precision of the method in terms of relative standard deviation (n =10) for the determination of 2.1284 μg/mL of Pd(II) is 0.01%. Important analytical parameters of Pd(II)-MSHBH are summarized in table 2.

Table 2 - Important analytical parameters of Pd(II)–MSHBH complex.

Parameter	Results		
	Zero order	First order derivative	Second order derivative
λmax (nm)	412	438	451
Limit of Detection (µg/mL)	0.0959	-	-
Limit of Quantization (µg/mL)	0.2876	-	-
Beer's law range (µg/mL)	0.2876 to 4.2568	0.2876 to 4.6825	0.2876 to 4.6825
Regression equation Y= a + bx			
Slope (b)	0.0890	0.0547	0.0864
Intercept (a)	0.0152	-0.0014	-0.0020
Correlation coefficient (r)	0.9987	0.9996	0.9993

Composition and stability of the complex:

The composition of the complex is determined by Job's continuous variation method and molar ratio method is found to be 1:1 [Pd(II): MSHBH]. The stability constant of the complex is determined as 9.32×10^4 by Job's method.

Derivative spectrophotometry is a useful technique because it decreases the interference i.e. increase the tolerance limit value of foreign ions and may be advantageously used for the determination of metal ion having overlapping spectra. The conceptual simplicity, relatively quick and easy realization, increased selectivity in the analysis of minor components is the main reasons why the interest in derivative spectra is constantly growing for practical applications. The recommended derivative procedure has been employed for the determination of palladium(II).

The typical first order and second order derivative spectra are shown in figure 5 and figure 6 respectively. This shows that, the derivative amplitude measured at 438 nm for first order and 451 nm for second order was found to be proportional to the amount of palladium(II).

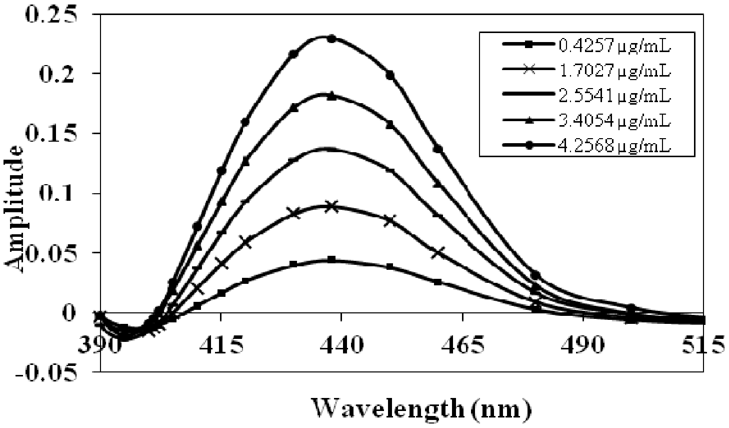

Figure 5 - Typical first order derivative spectra of Pd(II)-MSHBH vs. reagent.

Pd(II) (µg/ml) = 0.4257; 1.7027; 2.5541; 3.4054; 4.2568,
[MSHBH] = 4×10^{-4} M, pH (4.5) = 10 mL,
CTAB (5%) = 1.0 mL, DMF = 0.5 mL.

Effect of diverse ions:

The effect of various diverse ions in the determination of Pd(II) was studied to determine the tolerance limit of foreign ion in the present method. The tolerance limit of a foreign ion was taken as the amount of foreign ion required to cause an error ± 2% in the absorbance or amplitude. The results are given in table 3.

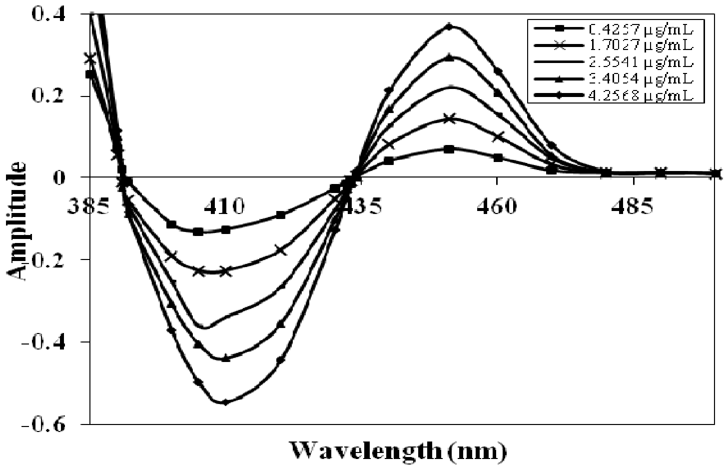

Figure 6 - Typical Second order derivative spectra of Pd(II)-MSHBH vs. reagent.

Pd(II) (µg/mL) = 0.4257; 1.7027; 2.5541; 3.4054; 4.2568,
[MSHBH] = 4×10^{-4} *M, pH (4.5) = 10 mL,*
CTAB (5%) = 1.0 mL, DMF = 0.5 mL.

Table 3 - Tolerance limit of foreign ion in the determination of 2.1284 µg/mL of palladium(II).

Ion added	Tolerance limit (µg/mL)			Ion added	Tolerance limit (µg/mL)		
	Zero order	First order	Second order		Zero order	First order	Second order
Tartarate	2967	2967	3656	La(III)	33	56	56
Tetraborate	2456	2456	2846	Ce(IV)	28	56	56
Sulphate	1921	1921	2171	Ru(III)	50	50	50
Bromide	1917	1918	1918	Cd(II)	18	45	45
Phosphate	1899	1899	2125	Hg(II)	16	40	40
Nitrate	1240	1240	1856	Ag(I)	26	26	26
Urea	1206	1206	1206	Au(III)	16	16	16
Acetate	709	945	945	W(VI)	6.0	15	15
Fluoride	380	380	406	Zn(II)	8.0	13	13
Citrate	76	152	152	Mo(VI)	0.2, 10[a]	0.2, 10[a]	0.2, 10[a]
Ascorbic acid	35	212	212	Zr(IV)	3.0	7.0	7.0
Oxalate	35	176	176	U(VI)	4.0	4.0	4.0
Thiourea	61	61	61	Fe(III)	2.2 [b, c]	2.2 [b], 4.5 [c]	3.4 [b],4.5 [c]
Pb(II)	414	560	602	Ti(IV)	4.0	4.0	4.0
Sb(III)	244	244	303	Li(I)	3.0	4.0	4.0
Ba(II)	165	220	220	Cr(VI)	2.0	3.0	4.0
Bi(III)	167	167	167	Rh(II)	2.5	2.5	2.5
Se(IV)	158	158	158	Co(II)	2.0	2.0	2.0
Mn(II)	110	110	110	Ni(II)	1.0	1.0	1.0
As(III)	75	75	75	Th(IV)	1.0	1.0	2.0
Sn(II)	57	95	95	Cu(II)	0.2 [d], 0.1 [e]	1.0 [d], 0.1 [e]	1.0 [d], 0.1 [e]
Sr(II)	35	53	53	V(V)	0.2	0.4	0.4

'a' Masked with 1187 µg/mL of tartarate,
'b' Masked with 228 µg/mL of fluoride,
'c' Masked with 760 µg/mL of phosphate,
'd' Masked with 61 µg/mL of thiourea,
'e' Masked with 35 µg/mL of ascorbic acid.

The data obtained in derivative method is also incorporated. The data suggest that several commonly associated anions and cations do not interfere in the determination of Pd(II) using MSHBH reagent, when they present in large excess. However, metals like Ni(II), Th(IV) and V(V) were seriously interfered. The tolerance limit of many anions and cations are more in derivative method when compared to zero order. This shows that derivative method is more selective than zero order spectrophotometric method. The Cu(II) metal was interfered even masking with thiourea or ascorbic acid. The interference of associated metal ions such as Mo(VI) decreased on masking with tartarate and the interference of Fe(III) was decreased by masking with fluoride and phosphate.

Applications

The spectrophotometric determination of Pd(II) in the alloy samples and hydrogenation catalyst samples were carried out by employing the recommended procedure. A known aliquot of the sample solution was taken in a 25-

mL volumetric flask containing 10 mL of buffer solution pH 4.5, 0.5 mL of DMF, 1.0 mL of CTAB (5%) and 1.0 mL of MSHBH reagent 1x10^{-2} M solutions. The contents in the flask were made up to the mark with doubly distilled water. The amount of palladium(II) present in these samples was computed from a pre-determined calibration plot and results are summarized in table 4 and table 5 respectively.

Table 4 - Determination of Pd(II) in alloy samples.

Sample composition	Amount found* (%)			RSD (%)		
	Zero order	First order	Second order	Zero order	First order	Second order
Pd, 72; Ag, 26; Ni, 2 %;	72.6	72.4	71.7	- 0.83	- 0.55	+ 0.42
Pd, 60; Au 40%;	58.9	59.1	59.3	+ 1.83	+ 1.50	+ 1.11
Pd, 95, Ru, 4; Rh, 1%;	94.2	94.6	95.3	+ 0.84	+ 0.42	- 0.31
Stibio palladinite mineral (Pd,75;Sb, 25%;)	74.3	75.4	74.6	+ 0.93	- 0.53	+ 0.53

** Average value of five determinations.*

Table 5 - Determination of Pd(II) in hydrogenation catalyst samples.

Sample	Amount of Pd(II) present (%)	Amount found* (%)			RSD (%)		
		Zero order	First order	Second order	Zero order	First order	Second order
Pd-$CaCO_3$	5	4.91	4.92	4.94	+ 1.8	+ 1.6	+1.2
Pd-$BaCO_3$	5	4.89	4.91	4.96	+ 2.2	+ 1.8	+ 0.8
Pd-$BaSO_4$	5	5.12	5.09	4.93	- 2.4	- 1.8	+ 1.4
Pd-charcoal	10	9.87	9.91	10.08	+ 1.3	+ 0.9	- 0.8

** Average value of five determinations.*

CONCLUSION

The present method, using MSHBH as spectrophotometric reagent for the determination of Pd(II) in presence of CTAB is simple, rapid, reasonably sensitive and selective. This method was favorably compared with previously reported spectrophotometric methods [13-19]. Most of the spectrophotometric methods involve either extraction [13-15] or heating of the reaction mixture [16]. However, heating at a specific temperature for a long time or extraction of components is laborious and time consuming. The present method is not laborious and there is no need of heating the components or pre-extraction. Large amounts of tartarate, tetraborate, sulphate, bromide, phosphate, nitrate, lead(II), antimony(III), barium(II), bismuth(III), selenium(IV) and manganese(II), moderate amount of the tin(II), mercury(II), silver(I), zinc(II) and molybdenum(VI) do not interfere in the present method. This method is also free from the interference of lanthanum(III), arsenium(III) and other rare earth metals. Further the CTAB enhances the stability of the metal complex.

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