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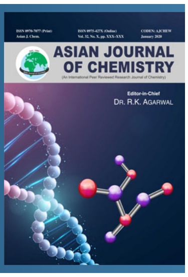

Microdetermination of Palladium(II) using 6-Chloro-3-hydroxy-7-methyl-2-(2′-thienyl)-4-oxo-4*H*-1-benzopyran

N. KAUR[1], N. AGNIHOTRI[1,*] and U. BERAR[2]

[1]Department of Chemistry, Maharishi Markandeshwar (Deemed to be University), Mullana, Ambala-133207, India
[2]Department of Applied Science, University Institute of Engineering and Technology, Kurukshetra University, Kurukshetra-136119, India

*Corresponding author: E-mail: nivagni11@gmail.com; niveditachem@mmumullana.org

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A simple, rapid, sensitive and selective extractive spectrophotometric method is developed for the trace determination of palladium(II) from $NaHCO_3$ medium using 6-chloro-3-hydroxy-7-methyl-2-(2′-thienyl)-4-oxo-4*H*-1-benzopyran (CHMTB) as a colouring agent. The proposed metal complex can be quantitatively extracted into ethyl acetate and absorbs maximum in the wavelength range 415-426 nm. The 1:1 yellow complex obeys linearity over the Pd(II) concentration range of 0-2.6 $\mu g\ mL^{-1}$; the correlation coefficient being 0.9998. The molar annihilation coefficient and Sandell′s sensitivity when applying spectrophotometric determination at 420 nm, were 6.173×10^4 L $mol^{-1}\ cm^{-1}$ and 0.0017 μg Pd(II) cm^{-2}, respectively. The proposed method is free from the interference of Os(VIII), Cr(VI), Mo(VI), V(V), Nb(V), Ce(IV), Se(IV), Zr(IV), Pt(IV), Ru(III), Ir(III) and Fe(III) . The method was effectively applied to the determination of Pd(II) in various samples including palladium charcoal catalyst and water.

Keywords: Palladium(II), 6-Chloro-3-hydroxy-7-methyl-2-(2′-thienyl)-4-oxo-4*H*-1-benzopyran, Extraction, Spectrophotometry.

INTRODUCTION

Palladium, a rare lustrous silvery-white element belongs to platinum group metals (PGMs), has extensive utility in different fields like catalysis, alloying, jewellery and cosmetic industries, dentistry, production of surgical instruments, electrical contacts and hydrogen storage materials [1,2]. Also, it is associated with some toxic biological effects [3-5]. All palladium compounds are exceptionally dangerous and cancer-causing whenever inhaled or retained through skin. It causes bone marrow, liver and kidney harm in laboratory animals [6].

The mentioned behaviour lays a strong stress for study of the methods of its determination from different industrial and natural products. The increasing use of palladium as an alloying element and as a catalyst and also its environmental effects lays further stress on the urgent need for the study of its determination techniques. Numerous methods of palladium determination have been reported in the past including gravimetric [7], titrimetric [8], atomic absorption spectroscopy [9,10], X-ray flourescence [11,12], UV-Vis spectrophotometry [13,14], neutron activation analysis [15] and inductively coupled plasma emission spectroscopy [16].

The observations indicate that the gravimetric and volumetric methods employed for the determination of palladium suffer seriously from interference of a large number of metal ions. For the microdetermination of palladium, neutron activation, atomic absorption, inductively coupled plasma emission spectroscopy and X-ray fluorescence methods are certainly quite sensitive but require costly equipments and also prior concentration and separation of the element is essential. Hence, out of the number of techniques that can be employed for determination of Pd(II), spectrophotometric methods being better involving less instrumentation and technique are extensively used.

Although several procedures using a number of organic reagents are available for extractive microdetermination of Pd(II), the situation is still away from satisfaction in terms of rapidity, selectivity and sensitivity [17-24]. Incidentally, while working with 4*H*-1-benzopyran derivatives [25], it is observed that 6-chloro-3-hydroxy-7-methyl-2-(2′-thienyl)-4-oxo-4*H*-1-benzopyran (CHMTB) is highly advantageous in terms of its chelating ability with Pd(II) enhancing significantly the speed, selectivity and sensitivity of extractive spectrophotometric determination.

EXPERIMENTAL

Palladium(II) solutions: The standard stock solution of Pd(II) containing 1 mg mL^{-1} of metal ion was prepared by dissolving the precisely gauged accessible salt, palladium chloride, hydrate, $PdCl_2·2H_2O$ (CDH, A.R. grade) in doubly distilled water and standardized gravimetrically by the known method. The µg mL^{-1} level concentrations were prepared by appropriate dilutions.

The other metal ions were brought into solutions at mg mL^{-1} level by dissolving their commonly available chemically pure sodium or potassium salts in doubly distilled water or dilute mineral acids and diluted further as per the requirements.

6-Chloro-3-hydroxy-7-methyl-2-(2′-thienyl)-4-oxo-4*H*-1-benzopyran (CHMTB) solution: The compound CHMTB having molar mass = 292.5 and m.p. = 212 ºC was synthesized as described procedure [26] and dissolved in ethanol to the concentration 0.1% (w/v) solution.

Moreover, 0.5 M solution of sodium bicarbonate (CDH, A.R. grade) was freshly prepared and ethyl acetate (CDH, A.R. grade) was utilized as extractant for the determination.

Instrumentations: An UV-VIS Electronics India-2375 spectrophotometer equipped with 1 cm coordinated quartz cells was used for absorbance estimations and spectral investigations.

Synthetic samples: Synthetic samples (such as braggite, palau I, palau II, palladium alloy, watch alloy, white gold and Cooper′s alloy) were composed for the determination of Pd(II) by mixing its solution with the solution of other metal ions in suitable proportions.

Technical samples: Technical samples including water (from different sources) and palladium charcoal catalyst (Oxford Lab Fine Chem) were brought into desired solutions according to the accompanying procedures.

Palladium-charcoal catalyst: The sample was brought into solution by heating with aqua regia [25]. After isolating charcoal by filtration, excess of nitric acid was evaporated by heating with conc. HCl to dryness. The acquired residue was treated with distilled water and dil. HCl. It was then exposed to the determination of palladium (II) according to the proposed procedures.

Water samples: Water samples (1000 mL each from tap and well) were mixed with 500 µg Pd(II), heated upto dryness, treated with 2 mL 6% H_2O_2 (w/v) in ammonical medium and the resulting volume was raised up to 25 mL of 1 M strength using HCl. Palladium(II) was determined in aliquots (0.5 mL for each) under conditions of the proposed procedure.

Standard procedure for extraction and spectrophotometric determination: An aliquot of the working solution containing up to 26 µg of Pd(II) was placed in a 125 mL separating funnel. Sufficient $NaHCO_3$ solution to make the final aqueous strength of 0.02 M was added followed by 1.5 mL of 0.1% (w/v) solution of CHMTB in ethanol in a final aqueous volume of 10 mL. The aqueous content thus prepared was equilibrated once with 10 mL of ethyl acetate for 30 s. After phase separation, the organic layer was filtered into a 10 mL volumetric flask through a Whatman filter paper No. 41 (9 cm diameter) and diluted up to the mark with pure ethyl acetate. The contents were gently mixed and absorbance of the yellow extract was measured at 420 nm against a blank solution prepared analogously using 1 cm quartz cuvettes.The palladium content was determined from the standard calibration plot prepared under identical conditions.

RESULTS AND DISCUSSION

Absorption spectra: CHMTB forms an extractable and stable dark yellow 1:1 complex with Pd(II) under basic conditions provided by $NaHCO_3$. Comparatively small colour intensity was observed in acidic solutions and bases other than $NaHCO_3$ as shown in Fig. 1. The complex was extractable into ethyl acetate and under optimized conditions of the procedure shows maximum absorption band at 415-426 nm in the visible region (Fig. 2, curve A), where the reagent also absorbs a less (Fig. 2, curve B).

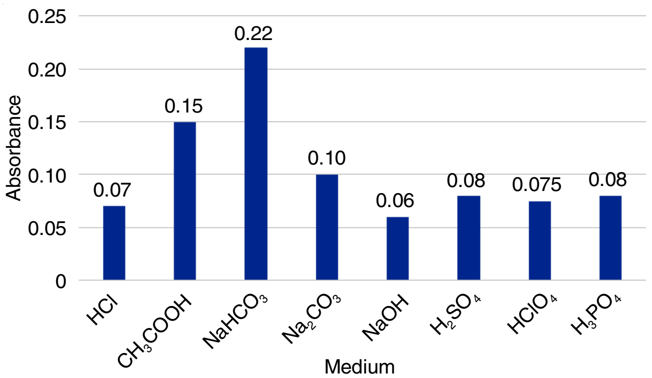


Fig. 1. Variation of absorbance of Pd(II)-CHMTB complex with medium

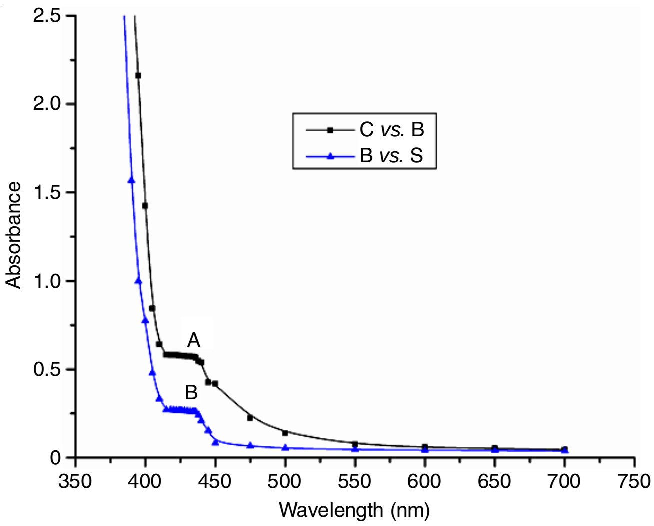


Fig. 2. Absorption spectra of Pd(II)-CHMTB complex

Experimental conditions and stability of chromogenic system: The influence of different physical variables like basic strength, CHMTB concentration and equilibration time on the extraction of Pd(II) has been studied. It was analyzed that to attain the optimum and constant intensity of complex containing 26 µg Pd(II) in 10 mL aqueous phase, 0.01-0.025 M $NaHCO_3$ and 1.3-2.0 mL of 0.1% (w/v) ethanolic solution of CHMTB

TABLE-1
EFFECT OF PHYSICAL PARAMETERS ON THE ABSORBANCE OF Pd(II)-6-CHLORO-3-HYDROXY-7-METHYL-2-(2'-THIENYL)-4-OXO-4*H*-1-BENZOPYRAN COMPLEX

$NaHCO_3$ (M)[a]	0.005	0.010-0.025	0.03	0.035	0.040	0.045	0.050			
Absorbance	0.140	0.220	0.170	0.160	0.140	0.130	0.120			
CHMTB (mL)[b]	0.1	0.3	0.5	0.7	1.0	1.1	1.3-2.0	2.2	2.5	3.0
Absorbance	0.050	0.130	0.220	0.310	0.400	0.560	0.580	0.540	0.480	0.330
Equilibration time (s)[c]	0	5	15-120							
Absorbance	0.300	0.450	0.580							

Conditions: [a]Pd(II) = 20 µg; $NaHCO_3$ = variable; CHMTB [0.1% (m/v) in ethanol] = 0.5 mL; aqueous volume = solvent volume = 10 mL; solvent = ethyl acetate; equilibration time = 30 seconds; λ_{max} = 420 nm; [b]$NaHCO_3$ = 0.02 M; remaining parameters same as in (a) except for the variation in CHMTB concentration; CHMTB = 6-chloro-3-hydroxy-7-methyl-2-2'-thienyl-4-oxo-4*H*-1-benzopyran; [c]CHMTB[0.1% (m/v) in ethanol] = 1.5 mL; remaining conditions same as in (b) excepting variation in equilibration time.

added in the same order as per the applied procedure are adequate (Table-1). The aqueous mixture thus obtained was equilibrated once with an equal volume of ethyl acetate for 15-120 s. The developed Pd(II)-CHMTB complex can be smoothly extracted into a number of non-aqueous organic solvents such as ethyl acetate, dichloromethane, 1,2-dichloroethane, cyclohexane, benzene, chloroform, toluene, carbon tetrachloride, isobutyl methyl ketone, isoamyl alcohol and isoamyl acetate with the absorbance decreasing in same order as indicated in Fig. 3. Ethyl acetate providing maximum and sufficiently stable absorbance of the complex is selected as the most appropriate extractant. The intensity of the complex in ethyl acetate remains practically constant for more than 2 days.

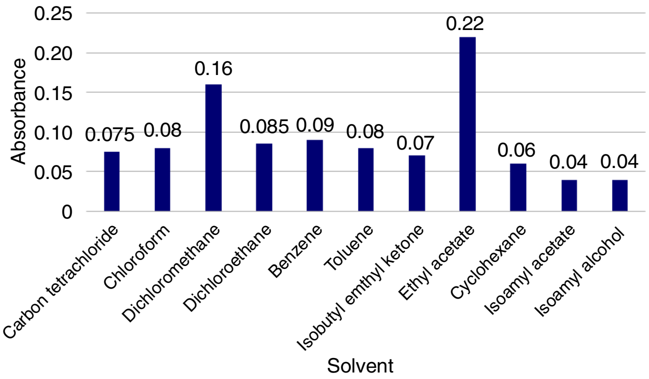


Fig. 3. Variation of absorbance of Pd(II)-CHMTB complex with extractant

Interference study: To study the effect of diverse ions, the ions were added under the ideal states of the proposed strategy to 20 µg concentration of Pd(II) in a complete 10 mL aqueous volume taken all through. The impact of different anions or complexing agents and the cations on the extraction and spectrophotometric determination of Pd(II) have been explored to assess selectivity and tolerance limit as shown in Tables 2 and 3. The tolerance limit was adjusted as the amount of diverse ion causing an error ≤ 1% in the extraction recovery of Pd(II).

Samples containing other metal ions require an altered system involving addition of the appropriate masking agents before the addition of CHMTB like for 0.1 mg of Zn(II), 50 mg of thiourea; for 0.1 mg of Cu(II), 10 mg of nitrite; for 0.1 mg of Ce(IV), 10 mg of ascorbic acid and for 0.01 mg of V(V); 10 mg of fluoride when applied do not affect determination. However, of the various foreign ions studied citrate and oxalate interfere.

TABLE-2
EFFECT OF ANIONS OR COMPLEXING AGENT ON Pd(II)-CHMTB COMPLEX

Anion or complexing agent	Pd(II)-CHMTB complex	
	Tolerance limit (mg/10 mL)	Absorbance
None	–	0.580
Chloride, bromide	100	0.580
Nitrate, sulphate, carbonate	80	0.580
Thiourea, acetate, phosphate, sulphite, hydrazine sulphate	50	0.580
Thiocyanate	40	0.580
Nitrite, ascorbic acid, dithionite, fluoride	10	0.580
Disodium EDTA	1	0.580
Tartarate	0.05	0.580
H_2O_2 (30 %)*	0.1	0.580

*Amount added in mL.

TABLE-3
EFFECT OF CATION ON Pd(II)-CHMTB COMPLEX

Cation	Pd(II)-CHMTB complex	
	Tolerance limit (mg/10 mL)	Absorbance
None	-	0.580
Co(II), Hg(II), Ni(II), Ba(II), Al(III), Pb(II), Ca(II)	10	0.580
Sr(II), Mg(II)	5	0.580
Mn(II), Zn(II)[a], Cu(II)[b], Au(III), Th(IV)	1	0.580
Se(IV), Cr(VI), Pt(IV), Ag(I), Ce(IV)[c], Os(VIII)	0.5	0.580
Fe(III), Mo(VI) Ru(III), Sn(II), Zr(IV), W(VI), Ir(III), V(V)[d]	0.1	0.580

[a]In the presence of 50 mg thiourea; [b]In the presence of 10 mg nitrite; [c]In the presence of 10 mg ascorbic acid;[d]In the presence of 10 mg fluoride.

Stoichiometry of Pd(II)-CHMTB complex: The stoichiometric ratio of Pd(II) and CHMTB in the extracted species was established as 1:1 by the Job's continuous variation method [27] as modified for a two phase system by Vosburgh and Cooper [28]. The 1:1 proportion of the complex constituents was further confirmed by mole ratio [29] and equilibrium shift methods [30]. The slope of the plot of log $A_1/(A_1 - A_o)$ *versus* log C_L

was found to be 0.85 (Fig. 4) confirming the metal to ligand ratio of 1:1. Where A_o denotes maximum absorbance value at complete complex formation, A_l denotes the absorbance value at a reagent concentration C_L (C_L = total molar concentration of reagent added). The stability constant as estimated by the mole ratio method was 1.1204×10^{-5}.

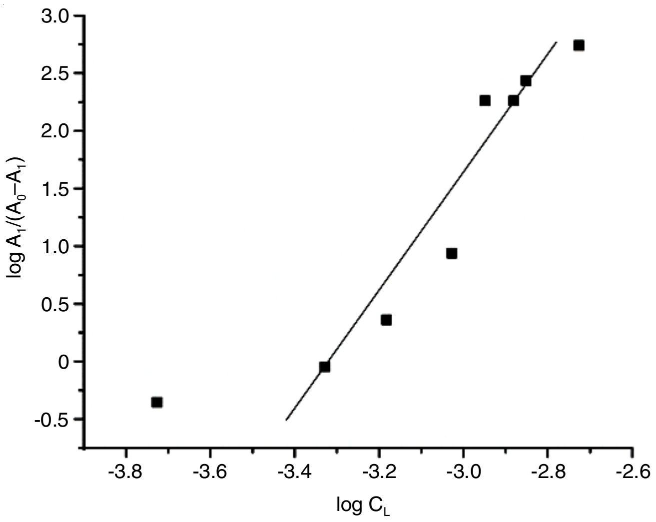
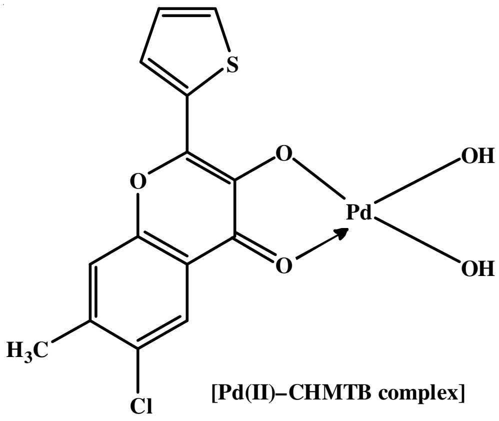


Fig. 4. Equilibrium shift method

Thus, the feasible structure of dark yellow coloured Pd(II)-CHMTB complex is proposed as:



[Pd(II)–CHMTB complex]

Spectral characteristics: The dark yellow complex of Pd(II)-CHMTB obtained under the optimum conditions of the procedure showed linear response up to 2.6 μg mL^{-1} of Pd(II). Linearity of the calibration plot was confirmed by evaluation of the correlation coefficient as having the value 0.9998. Various optical and statistical characteristics as calculated by statistical methods are shown in Table-4.

Structural elucidation: The metal complex was demonstrated with Avogadro 1.01 program [31] and optimized using molecular mechanics. Several cycles of optimization were carried out. Energy found for the complex was 1860.74 KJ mol^{-1} before optimization and 366.468 KJ mol^{-1} after several cycles of optimization. The optimized structure is square planar which is the confirmed characteristic of Pd(II) complexes dicussed on the basis of Jahn-Teller distortion. The optimized metal- oxygen bond length lied in the range 1.901-1.912 Å whereas the ideal bond length was 3.00 Å. Some other optimized bond lengths and bond angles are also calculated and shown in Table-5. The optimized structure is shown in Fig. 5.

TABLE-4
SPECTRAL CHARACTERISTICS,
PRECISION AND ACCURACY DATA

Parameter	Value
λ_{max} (nm)	415-426
Beer's law limits (μg mL^{-1})	0-2.6
Optimum range of determination (μg mL^{-1})	0.74-2.39
Molar absorptivity (L mol^{-1} cm^{-1})	6.173×10^4
Sandell's sensitivity (μg cm^{-2})	0.0017
Correlation coefficient (r)	0.9998
Regression equation (Y)*	Y = 0.287 X + 0.008
Slope (b)	0.287
Intercept (a)	0.008
Standard deviation	± 0.0022
Relative standard deviation (%)	0.38
Limit of detection (μg mL^{-1})	0.0039
Stability constant	1.1204×10^{-5}

*Y = bX + a; where Y = absorbance and X = Concentration of Pd(II) in μg mL^{-1}

TABLE-5
COMPUTATIONAL PARAMETERS OF
Pd(II)-CHMTB COMPLEX

Atom type	Bond length (Å)	Atom type	Bond angle (°)
Pd-O(1)	1.901	O(1)-Pd-O(3)	91.7
Pd-O(2)	1.912	O(2)-Pd-O(4)	91.7
Pd-OH(3)	1.937	O(1)-Pd-O(2)	91.7
Pd-OH(4)	1.937	O(3)-Pd-O(4)	91.7

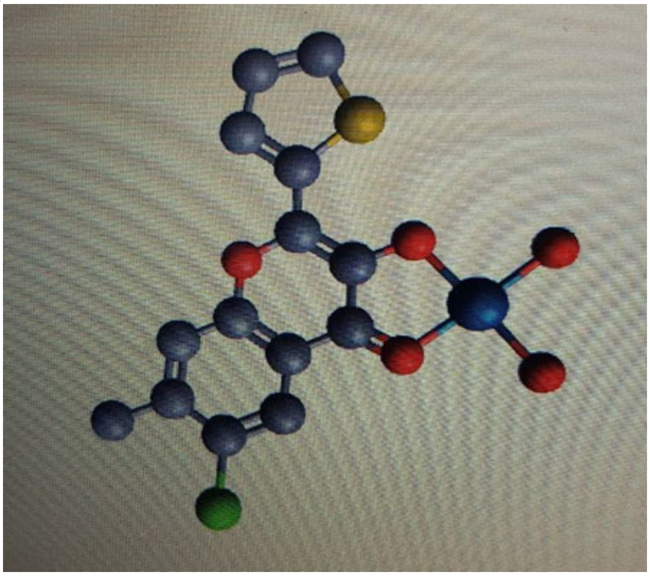


Fig. 5. Optimized structure of Pd(II)-CHMTB complex

Analytical applications: The proposed spectrophotometric method for the trace determination of palladium is quick to apply (2-3 min for a single determination), requires less equipment, highly sensitive, reproducible and has a large tolerance limit of the foreign ions including Fe, Cr, Mo, W, Zr, Nb, Ru, Ir, Os and many other important elements thereby increasing its scope of application. The wide usefulness of the method is further tested by analyzing a large variety of real samples and synthetic mixtures of varying composition (Table-6). The obtained results were in excellent agreement with the amount of metal ion initially added. The proposed method is reproducible and accurate with the relative standard deviation of 0.38% for 10 replicates containing 2 μg Pd(II) mL^{-1} each time. The method proposed is well compared to existing methods in respect of rapidity, selectivity and sensitivity (Table-7).

TABLE-6
Pd(II)-CHMTB COMPLEX: ANALYSIS OF SYNTHETIC AND TECHNICAL SAMPLES BY THE PROPOSED METHOD

Composition of sample*	Pd added (μg)	Pd found (μg)**
Pt(0.045), Ni(0.01)^{a}	20	20.06
Au(0.04)^{a}	10	10.10
Ni(0.09), Pt(0.003), V(0.0015)^{a,b}	15	14.89
Ag(0.006)^{a}	12	12.06
Cu(0.07), Ag(0.001),Ni(0.0002)^{a,c}	20	19.93
Au(0.16)^{a}	18	17.93
Ag(0.030),Co(0.002)^{a}	10	10.10
Co(2), Zn(0.5), Cr(0.1)^{d}	14	13.93
Ni(5),Hg(2),W(0.01)	22	22.06
Ba(5),Al(2), Zr(0.01)	10	9.90
Pd Charcoal catalyst	5***	5.05
Water sample: Tap	10	9.93
Well	10	10.16

*Figure in bracket indicates the amount of metal ion in mg/10 mL. **Average of triplicate analyses. ***Certified value; ^{a}Composition analogous to braggite, palau I, palau II, palladium alloy, watch alloy, white gold and cooper's alloy respectively; ^{b}In the presence of 10 mg fluoride. ^{c}In the presence of 10 mg nitrite. ^{d}In the presence of 50 mg thiourea.

Conclusion

6-Chloro-3-hydroxy-7-methyl-2-(2′-thienyl)-4-oxo-4*H*-1-benzopyran (CHMTB) has been used for the first time as an analytical reagent for the spectrophotometric determination of palladium. Palladium(II) in presence of several cations and anions or complexing agents except oxalate and citrate forms a dark yellow 1:1 complex with CHMTB, which is extractable into ethyl acetate from 0.010-0.025 M $NaHCO_3$ and 1.3-2.0 mL of 0.1% CHMTB solution in ethanol and stable for approximately 2 days. The complex shows an absorption maximum at 415-426 nm with a molar absorptivity of 6.173×10^4 L mol^{-1} cm^{-1} and Sandell′s sensitivity equal to 0.00172 μg Pd(II) cm^{-2}. The linear regression equation was $Y = 0.287 X + 0.008$ and the correlation coefficient, $r = 0.9998$. The detection limit of the method was 0.0039 μg mL^{-1}. Beer′s law obeyed over the concentration range of 0-2.6 μg Pd(II) mL^{-1}. The method is simple, selective, precise, rapid and applied to the determination of palladium in synthetic and technical samples.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

REFERENCES

1. C. Drahl, *Chem. Eng. News*, **86**, 53 (2008); https://doi.org/10.1021/cen-v086n035.p053
2. R.W.Hesse, Jewellery Making through History: An Encyclopedia, Greenwood Publishing group: London, p. 146 (2007).
3. J.A. Marcusson, *Contact Dermat.*, **34**, 320 (1996); https://doi.org/10.1111/j.1600-0536.1996.tb02215.x
4. D. Downey, *Contact Dermat.*, **21**, 54 (1989); https://doi.org/10.1111/j.1600-0536.1989.tb04688.x
5. P. Koch and H.P. Baum, *Contact Dermat.*, **34**, 253 (1996); https://doi.org/10.1111/j.1600-0536.1996.tb02195.x
6. J. Kielhorn, C. Melber, D. Keller and I. Mangelsdorf, *Int. J. Hyg. Environ. Health*, 205, 417 (2002); https://doi.org/10.1078/1438-4639-00180
7. P. Chattopadhyaya and S.K. Majumdar, *Indian J. Chem.*, **26A**, 896 (1987).
8. B. Naryana, B. Rao, K. Muralidhara, T. Girish and K.V. Karuna, *Asian J. Chem.*, **5**, 29 (1993).
9. A. Shams, N. Ashraf, M.H. Arbab-Zavar and M. Masrournia, *J. Anal. At. Spectrom.*, **32**, 2173 (2017); https://doi.org/10.1039/C7JA00145B

TABLE-7
COMPARISON OF THE PROPOSED METHOD WITH REPORTED METHOD

Aqueous conditions	λ_{max}(nm), Solvent	Molar absorptivity (L mol^{-1} cm^{-1})	Interference	Ref.
Pd(II), 4-(2-pyridylazo)-resorcinol, 90 °C, pH 9.0-11.0.	520, naphthalene-chloroform	8.0×10^5	Co(II), Fe(II), Bi(III)	[17]
Pd(II), *p*-[N,N-bis(2-chloro ethyl)amino]benzaldehydethiosemicarbazone, pH 1.0-2.0, HCl medium, 5 minutes colour development time	395, –	4.05×10^4	Cu(II), Pt(IV)	[18]
Pd(II), isonitroso *p*-nitroaceto phenonethiosemicarbazone, pH 0.0-4.0	410, chloroform	9.10×10^2	–	[19]
Pd(II),4-(N,N-diethylamino)benzaldehydethio semicarbazone, pH 2.6-3.4 in potassium hydrogen phthalate-HCl buffer medium, 5 min colour development time	408, -	3.33×10^4	Cu(II) , Pt(IV)	[20]
Pd(II),Phthalaldehydic acid thiosemicarbazone, pH 3.7-7.0, acetic acid- sodium acetate buffer, 5 minutes colour development time	355, Methyl isobutyl ketone	5.1×10^4	–	[21]
Pd(II), 5,6-Diphenyl-2,3-dihydro-1,2,4-triazine-3-thione	385, methanol	6.67×10^3	–	[22]
Pd(II), 4-(2'-furalideneimino)-3-methyl-5-mercapto-1,2,4-triazole, pH range 4.8-6.5	410, *n*-Butanol	1.4×10^3	–	[23]
Pd(II), 5-methyl-2,3-hexanedione dioxime, pH 0.5-1.5	379, Chloroform	3.894×10^3	–	[24]
Pd(II), $NaHCO_3$, 6-chloro-3-hydroxy-7-methyl-2-(2'-thienyl)-4-oxo-4*H*-1-benzopyran (CHMTB)	415-426, Ethyl acetate	6.173×10^4	28 metal ions donot interfere	Proposed method

10. J.X. Liu, C.C. Ran, C.H. Du, D. Chen and Y. Jiang, *Fenxi Shiyanshi*, **34**, 583 (2015).
11. E. Marguí, K. Van Meel, R. Van Grieken, A. Buendía, C. Fontàs, M. Hidalgo and I. Queralt, *Anal. Chem.*, **81**, 1404 (2009); https://doi.org/10.1021/ac8021373
12. N.S. Marinkovic, K. Sasaki and R.R. Adzic, *J. Electrochem. Soc.*, **165**, J3222 (2018); https://doi.org/10.1149/2.0281815jes
13. S. Nain, N. Agnihotri and L.R. Kakkar, *J. Indian Chem. Soc.*, **85**, 228 (2008).
14. S. Nain, N. Agnihotri and L.R. Kakkar, *J. Indian Chem. Soc.*, **83**, 707 (2006).
15. K.K. Chakrahari, R.P.B. Silalahi, T.-H. Chiu, X. Wang, N. Azrou, S. Kahlal, Y.-C. Liu, M.-H. Chiang, J.-Y. Saillard and C.W. Liu, *Angew. Chem. Int. Ed.*, **58**, 4943 (2019); https://doi.org/10.1002/anie.201814264
16. V. Kandathil, S. Patil and S. Patil, Biosynthesized Palladium Nanoparticles Mediated by Black Pepper Extract as Highly Efficient and Reusable Nanocatalystin Aryl Halide Cyanation and Hiyama Cross-Coupling Reactions under Ligand Free Conditions, Abstracts of Papers, 255th ACS National Meeting & Exposition, New Orleans, LA, United States, pp 18-22 (2018).
17. Y. Dong and K. Gai, *Bull. Chem. Soc. Korea*, **26**, 943 (2005); https://doi.org/10.5012/bkcs.2005.26.6.943
18. J. Karthikeyan, P. Parameshwara and A.N. Shetty, *Environ. Monit. Assess.*, **173**, 569 (2011); https://doi.org/10.1007/s10661-010-1405-8
19. V.D. Barhate, P. Madan, A.K.S. Gupta and D.B. Mandhare, *Orient. J. Chem.*, **25**, 731 (2009).
20. P. Parameshwara, J. Karthikeyan, A.N. Shetty and P. Shetty, *Ann. Chim.*, **97**, 1097 (2007); https://doi.org/10.1002/adic.200790093
21. F. Salinas, A.E. Mansilla, L.L. Martinez, L.D. Alba and L. Pedro, *Chem. Anal.*, **46**, 239 (2001).
22. M.B. Tehrani, M. Tahmasebi, E. Souri and H. Shamsa, *Chem. Sci. Trans.*, **4**, 227 (2015); https://doi.org/10.7598/cst2015.878
23. S.H. Gaikwad, T.N. Lokhande and M.A. Anuse, *Indian J. Chem.*, **44A**, 1625 (2005).
24. S.P. Tandel, S.B. Jadhav and S.P. Malve, *Indian J. Chem.*, **40A**, 1128 (2001).
25. S. Nain, N. Agnihotri and L.R. Kakkar, *Int. J. Sci. Eng. Res.*, **4**, 1204 (2013).
26. J. Algar and J.P. Flynn, *Proc. R. Ir. Acad.*, **42**, 1 (1934).
27. P. Job, *Ann. Chim.*, **9**, 113 (1928).
28. W.C. Vosburgh and G.R. Cooper, *J. Am. Chem. Soc.*, **63**, 437 (1941); https://doi.org/10.1021/ja01847a025
29. J.H. Yoe and A.L. Jones, *Ind. Eng. Chem. Anal. Ed.*, **16**, 111 (1944); https://doi.org/10.1021/i560126a015
30. H. Puzanowska-Tarasiewicz, A. Grudniewska and M. Tarasiewicz, *Anal. Chim. Acta*, **94**, 435 (1977); https://doi.org/10.1016/S0003-2670(01)84546-3
31. P. Rathi, K. Sharma and D.P. Singh, *Spectrochim. Acta A Mol. Biomol. Spectrosc.*, **130**, 72 (2014); https://doi.org/10.1016/j.saa.2014.03.046