

Simultaneous determination of Cu(II) and Pd(II) as 4-phenylpiperazinecarbodithioate complex using H-point standard addition method and derivative spectrophotometry

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A new, simple, inexpensive, and sensitive method for the simultaneous spectrophotometric determination of Cu(II) and Pd(II) by H-point standard addition method and derivative spectrophotometry is described. 4-Phenylpiperazinecarbodithioate (PPDTC) in an anionic micellar solution of SLS was used as a reagent at pH 4. The experimental parameters, such as pH, type of surfactant, concentration of reagent, and surfactant used, were optimized to minimize the errors. The linear ranges of the method were 0.1-10 and 0.1-11 $\mu\text{g mL}^{-1}$ for Cu(II) and Pd(II), respectively. The results of applying H-point standard addition and fourth derivative spectrophotometry showed that Cu(II) and Pd(II) can be determined simultaneously with detection limits of 0.12 and 0.11 $\mu\text{g mL}^{-1}$ respectively. Therefore, the method of H-point standard addition and fourth derivative spectrophotometry was used for resolving overlapped spectra for the determination of Cu(II) and Pd(II). This method was successfully applied to the determination of these metals in synthetic and real samples.

Introduction

Palladium is obtained from copper ores. Both metals are used in jewelry and for improving the electrical properties of alloys. Simultaneous determination of copper and palladium in different alloys is difficult by

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normal spectrophotometry due to overlap of spectra of copper and palladium complexes.

A number of selective techniques have been proposed for simultaneous determination of copper and palladium. Some of the simultaneous determination methods of different metal ions are reported in the literature, such as derivative spectrophotometry,¹⁻³ GC-AES,⁴ differential pulse polarography,⁵ derivative solid phase spectrophotometry,⁶ atomic emission spectrometry,⁷ extraction-AAS,⁸ SPME-HPLC,⁹⁻¹¹ and chemometric based techniques such as H-point standard addition¹² and the partial least square method.¹³ Due to low selectivities, some methods are used in the presence of masking agents or accompanied by steps involving separation of metal ion from the complex matrix.¹⁴

These techniques have various limitations including high cost, requirement of tedious preliminary separation techniques, and excessive use of organic solvents. A large volume of solvents is required for these techniques, which are expensive, hazardous to health, and harmful to the environment. HPLC requires precolumn derivatization without preliminary separation. It requires either an organic solvent extraction or use of surfactants and alcohols in the mobile phase. Other methods such as NAA, ICP-AES, and XRF are very sophisticated and expensive.

These metals cannot be determined simultaneously by the use of ordinary spectrophotometric methods due to the overlapping of absorption spectra. The H-point standard addition method introduced by Bosch-Reig et al.^{15,16} is able to correct both proportional and constant errors produced by the matrix. It is based on the principle of dual wavelength spectrophotometry and standard addition. In this method, the analytical signal due to 1 of the species is measured at those 2 wavelengths at which the signal due to other species is constant. In the same way, derivative spectrophotometry¹⁷ is an economical technique that resolves overlapping spectra of metal complexes. It is a function of bandwidth of zero order absorption spectra. In this method, broad bands are suppressed relative to sharp bands to an extent that increases with derivative order. Use of derivative spectra can increase the detection sensitivity of minor spectral features^{18,19} and can separate superimposed curves for quantitative measurements.

In this method, we employed 4-phenylpiperazinecarbodithioate (PPDTC) as a reagent for the simultaneous determination of Cu(II) and Pd(II) based on their complexation in micellar media. In the present study, we introduced 2 simple, sensitive, selective, and low cost procedures for simultaneous spectrophotometric determination of Cu(II) and Pd(II) using fourth derivative spectrophotometry and H-point standard addition with satisfactory results.

Equipment

An Elico SL-164 double beam UV-Vis spectrophotometer was loaded with Spectra Treatz software and interfaced to a computer in conjunction with an HP Laserjet 1010 printer to record the spectra and calculate their derivatives. A Century CP 901 Digital pH meter was used to adjust the pH and 1 cm quartz cuvettes were utilized for absorbance studies.

Chemicals and reagents

All chemicals used were of analytical grade and water was double distilled. A stock solution of copper sulfate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) was prepared by dissolving 3.93 g of copper sulfate pentahydrate in double distilled water

containing a few drops of dilute H_2SO_4 and was made up to 1 L and standardized by iodometry. The stock solution was diluted further to $10 \mu\text{g mL}^{-1}$. Similarly stock solution of palladium chloride was prepared by dissolving 1.66 g in double distilled water containing 1 mL of conc. HCl. It was standardized by gravimetry and further diluted as desired. The reagent PPDTC was prepared using a method reported by Macrotrigiano et al.²⁰ A fresh reagent solution was prepared by dissolving 0.1 g of PPDTC in 100 mL. The pH of buffer solution was adjusted by using 0.1 N NaOH and 0.1 N acetic acid solutions. The final pH 4 was adjusted by using sodium acetate buffer. Then 1% solution of each surfactant (SLS, CTAB, TX-100 and CPB) was prepared by dissolving 10 g of each in 1 L of double distilled water.

Procedures

Individual calibration

For the preparation of each standard sample solution, 1 mL of reagent solution, 1 mL of sodium acetate buffer of pH 4, 1 mL of SLS, and an aliquot of solution containing 1-10 μg Cu(II) or 1-11 μg of Pd(II) were added to a 10 mL flask. The volume was made up to the mark with triple distilled water. A portion of solution was transferred into a quartz cell to measure the absorption against reagent blank.

H-point standard addition method

An aliquot of solution containing 1-10 μg of Cu(II) and 1-11 μg of Pd(II), 2 mL of reagent solution, 1 mL of pH 4 sodium acetate/acetic acid buffer, and 1 mL of SLS were added to a 10 mL volumetric flask. Appropriate amounts of analyte were added for standard addition and made up to the mark with water. Absorption spectra of the solution were recorded at 440 nm and 465 nm when Cu(II) was considered an analyte. On the other hand, for Pd(II) determination, 350 and 365 nm were selected for recording absorbance.

Derivative spectrophotometry

For the simultaneous determination of copper and palladium by derivative spectrophotometry, a sample or standard solution containing 1-15 $\mu\text{g mL}^{-1}$ of copper and 1-10 $\mu\text{g mL}^{-1}$ of palladium was placed in a calibrated 10 mL flask. Then 1.0 mL of reagent solution and 1 mL of SLS were added to the mixture. The pH of the solution was adjusted to 4 by adding sodium acetate/acetic acid buffer. The volume was made to 10 mL with triple distilled water. The spectra were recorded against a reagent blank. The absolute values of the fourth derivative were measured at 408.5 nm and 358.5 nm for the determination of copper and palladium, respectively.

Instrumental parameters such as $\Delta\lambda$ and scan speed were optimized to give a constant position of isodifferential/zero cross-over points. The optimum $\Delta\lambda$ for the first and second-order derivative was found to be 0.5 nm. A scan speed of 300 nm (lowest) was found suitable for simultaneous determination of cobalt and nickel. Response time is automatically selected by the spectrophotometer in accordance with the optical energy and speed of scan. For recording derivative spectra, Box Car smoothing was used to improve the signal to noise ratio. Derivative spectra were prepared by using Savitzky Golay differentiation in which group size was kept 1 and 15 for the first and second derivative, respectively at a polynomial degree of 2.

Results and discussion

Preliminary study of system

4-Phenylpiperazinecarbodithioate is a very good reagent for the determination of trace amounts of Cu(II) and Pd(II). The absorption spectra of Cu(II) showed maxima at 305 nm and 450 nm and Pd(II) showed maxima at 315 nm (Figure 1). The determination of Pd(II) is difficult in the presence of Cu(II) by ordinary spectrophotometry due to overlapping of spectra. The metal complexes were insoluble in water, but soluble in the presence of surfactants.

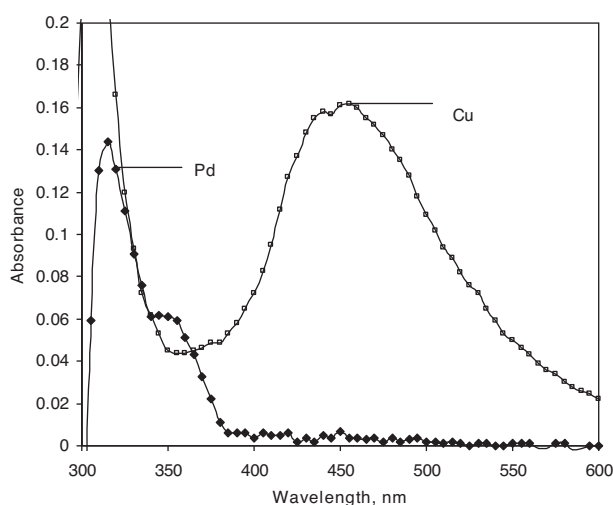


Figure 1. Absorption spectra of Pd(II)- PPDTC and Cu(II)- PPDTC complex in the presence of SLS ($1 \mu\text{g mL}^{-1}$ Cu(II) and $1 \mu\text{g mL}^{-1}$ Pd(II), 0.5 mL of 0.1% PPDTC, 1 mL of 1% SLS).

Optimization of conditions

The working conditions were optimized by studying the effect pH of solution, nature of the concentration of the surfactant, concentration of the surfactant, and concentration of the reagent. Formation of Cu(II)- PPDTC and Pd(II)- PPDTC complex was affected by hydrogen ion concentration. Absorbance for both complexes was studied over a wide range of pH from 1 to 10 using 0.1 N NaOH and 0.1 CH_3COOH acid solutions. The studies showed that the maximum absorbance is in the pH range 4-10 for copper and up to pH 4 for palladium complex as shown in Figure 2. Hence, further studies were carried out at pH 4.0 using sodium acetate/acetic acid buffer.

Various surfactants such as TX-100, CTAB, SLS, and CPB were tested as solubilizing agents. The effects of different surfactants on metal complexes are shown in Figure 3. Less absorbance was observed in other surfactants as compared to SLS. It was observed that the complex formation is faster and stable in the presence of SLS and showed maximum absorbance; therefore, it was selected as the micellizing agent for further studies.

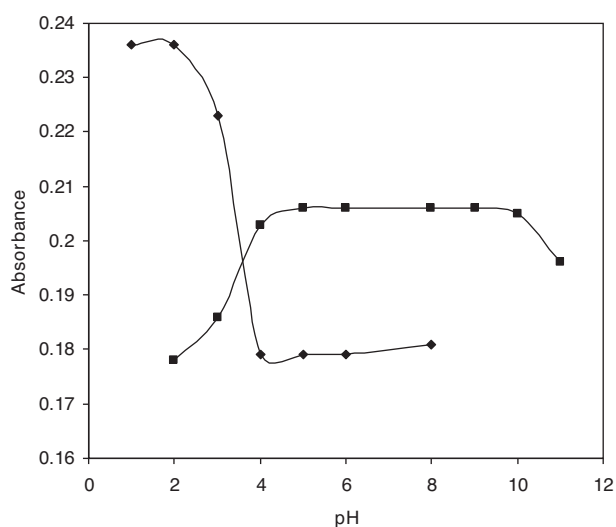


Figure 2. Effect of pH on Cu(II)- PPDTC and Pd(II)- PPDTC complex, $2 \mu\text{g mL}^{-1}$ Cu(II) and $2 \mu\text{g mL}^{-1}$ Pd(II), 0.5 mL of 0.1% PPDTC, 1 mL of 1% SLS, 2 mL of buffer pH 4.

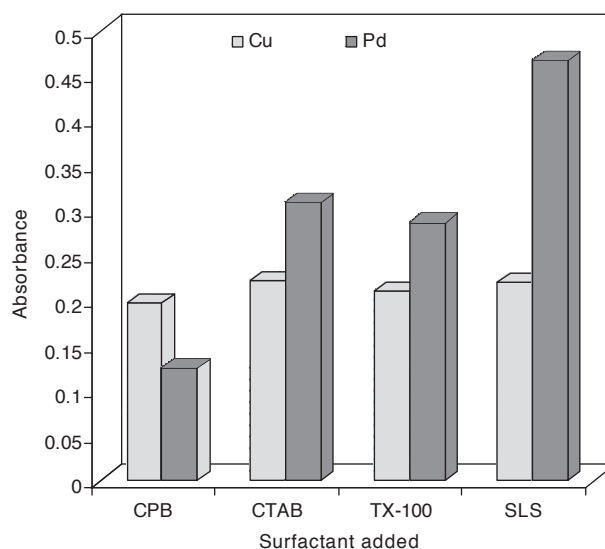


Figure 3. Effect of surfactant on Cu(II)- PPDTC and Pd(II)- PPDTC complexes, $2 \mu\text{g mL}^{-1}$ Cu(II) and $4 \mu\text{g mL}^{-1}$ Pd(II), 0.5 mL of 0.1% PPDTC, 1 mL of 1% surfactant, 2 mL of buffer pH 4.5, at 300 nm for Pd(II) and 430 nm for Cu(II).

Optimization of PPDTC concentration was performed spectrophotometrically for both metal ions by varying the amount of 0.1% PPDTC solution in the presence of 0.1% SLS. The obtained results showed that sensitivity was maximum and constant in 0.75-1.25 mL of the 0.1 % PPDTC solution. Therefore, 1 mL of reagent was considered for the further studies.

H-point standard addition method

This is used for an unknown sample containing an analyte A and an interferent B. In this work, either Cu(II) can be considered as the analyte and Pd(II) as interferent or vice versa. The main requirement of HPSAM is the selection of 2 wavelengths λ_1 and λ_2 at which the B should have same absorbance and the difference between the slopes of 2 straight lines must be as large as possible in order to get more accurate results. When Cu(II) was considered as the analyte, the pair of wavelengths selected was 440 and 465 nm, which gave the greatest slope increment and good accuracy. Then known amounts of Cu(II) were successively added and absorbances were recorded at the 2 wavelengths. These can be expressed as the 2 equations given below:

$$X_{(440)} = Y_o + Y + M_{440}C_{Cu(II)} \quad (i)$$

$$X_{(465)} = Z_o + Z + M_{465}C_{Cu(II)} \quad (ii)$$

where $X_{(440)}$ and $X_{(465)}$ are the analytical signals measured at 440 and 465 nm, respectively,

Y_o and Z_o ($Y_o \neq Z_o$) are original analytical signals of Cu(II) at 440 and 465 nm, respectively, Y and Z are analytical signals of Pd(II) at 440 and 465 nm, respectively, M_{440} and M_{465} are slopes of standard addition calibration lines at 440 and 465, respectively, and

C_i is the added concentration of Cu(II).

On plotting a graph, 2 straight lines intersect at a point called the H-point ($-C_{Cu(II)}$, $A_{Pd(II)}$) as shown in Figure 4. At the H-point,

$$X_{(440)} = X_{(465)}$$

$$C_{Cu(II)} = -C_H$$

Therefore, equations (i) and (ii) are

$$Y_o + Y + M_{440}(-C_H) = Z_o + Z + M_{465}(-C_H) \quad (iii)$$

Hence,

$$-C_H = [(Y_o - Z_o) + (Y - Z)] / (M_{440} - M_{465}) \quad (iv)$$

If the concentration of Pd(II) is known, and the analytical signal corresponding to Pd(II) i.e. Z and Y at 440 and 465 nm does not change with standard additions of Cu(II), i.e. X = Y = constant, then

$$-C_H = (Y_o - Z_o) / (M_{440} - M_{465}) = -Y_o / M_{440} = -Z_o / M_{465} \quad (v)$$

On putting the value of $-C_H$ in equation (i), the analytical signal at H-point is

$$A_H = Y_o + Y + M_{440}(-C_H) \quad (vi)$$

As from equation (v)

$$Y_o = M_{440}(C_H)$$

Therefore, equation (vi) becomes

$$A_H = Y$$

$$\text{and } A_H = Z$$

Hence, A_H is related to the signal of Pd(II) at 440 and 465 nm. The concentration of Pd(II) can be calculated from the regression equation obtained from the individual calibration curve of Pd(II).

If the interferent is unknown, the concentration of Cu(II) is independent of the interferent signal at the H-point. Similarly, if Pd(II) is considered as the analyte and Cu(II) as the interferent, 350 and 365 nm (Figure 5) can be used as working wavelengths for achieving the highest accuracy. Both metals can be determined in the mixture from the H-point.

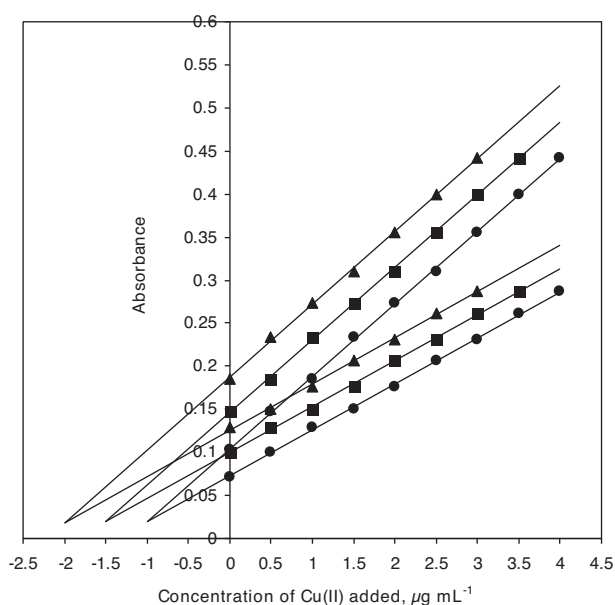


Figure 4. Plots of the H-point standard addition method for fixed Pd(II) concentration (equal to $0.5 \mu\text{g mL}^{-1}$) and different concentrations of Cu(II) (\bullet) $1 \mu\text{g mL}^{-1}$, (\blacksquare) $1.5 \mu\text{g mL}^{-1}$, and (\blacktriangle) $2 \mu\text{g mL}^{-1}$.

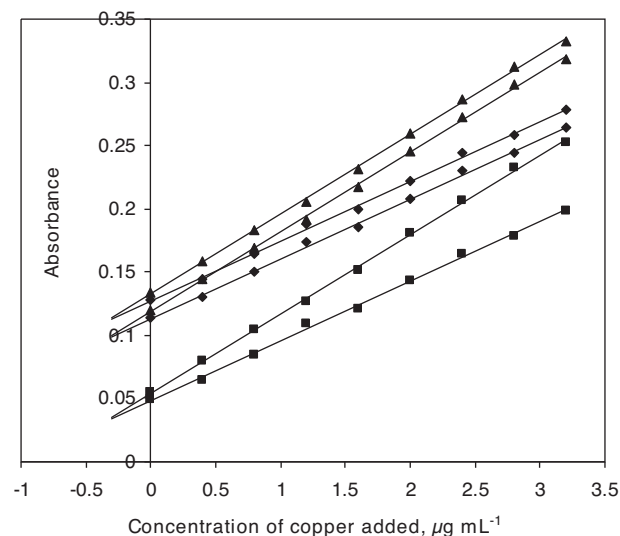


Figure 5. Plots of the H-point standard addition method for fixed Cu(II) concentration (equal to $0.5 \mu\text{g mL}^{-1}$) and different concentrations of Pd(II) (\blacksquare) $0.4 \mu\text{g mL}^{-1}$, (\bullet) $0.8 \mu\text{g mL}^{-1}$, and (\blacktriangle) $1 \mu\text{g mL}^{-1}$.

Fourth derivative mode for simultaneous determination of Cu(II) and Pd(II)

A zero-crossing method was utilized for derivative spectrophotometry. Zero-crossing wavelengths for the fourth derivative are 358.5 nm and 408.5 nm for copper and palladium complexes, respectively.

A set of fourth derivative spectra of mixtures containing $1 \mu\text{g mL}^{-1}$ of Pd(II) and increasing amounts of Cu(II) (0.2 - $1 \mu\text{g mL}^{-1}$) (Figure 6) was studied. A further set was performed by keeping the Cu(II) concentration at $0.2 \mu\text{g mL}^{-1}$, while Pd(II) concentration was varied over 0.2 - $1 \mu\text{g mL}^{-1}$ (Figure 7). The results in Figures 4 and 5 indicate that when the concentration of Pd(II) (Cu(II)) was kept constant and the concentration of Cu(II)(Pd(II)) was varied, peak amplitudes at 358.5 nm (408.5 nm) were unaltered. Amplitudes at 358.5 nm (h_2) and 408.5 nm (h_1) were proportional to Pd(II) and Cu(II) concentration, respectively. Similarly, amplitudes at the different wavelengths given were proportional to Pd(II) and Cu(II) concentration for first-, second-, and third- derivative spectrophotometry. To select derivative order, first- and second-derivative spectra of Cu(II) and Pd(II) complexes were studied (Table 1). Studies revealed that fourth-derivative spectra were simple, and gave results of highest accuracy and lowest detection limits.

Reproducibility of method

To check the reproducibility of the method, 6 replicate measurements of Cu(II) and Pd(II) were performed. The concentration of Pd(II) was calculated from standard additions and the H-point (A_H). The concentration of Cu(II) was directly obtained from $-C_H$. The relative standard deviations were 1.1% and 1.5% for Cu(II) and

Pd(II), respectively. Similarly, the standard deviations were calculated for fourth-derivative spectrophotometry and were less than 4% as shown in Table 1.

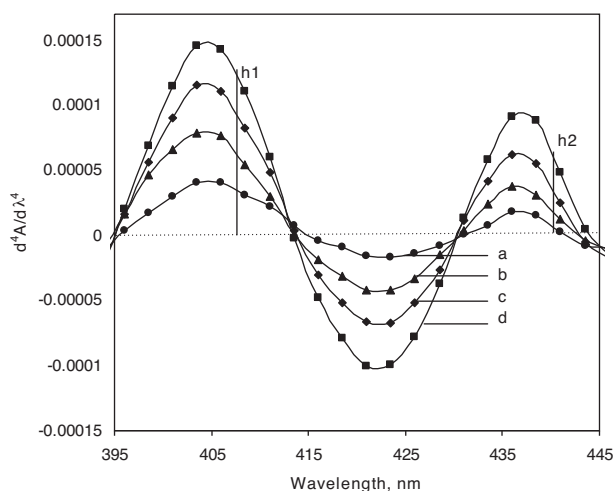


Figure 6. Second-derivative spectra of Cu(II)- and Pd(II)- PPDTC complexes, [(e) Pd(II) = 0.5 $\mu\text{g mL}^{-1}$, (Cu(II) = (a) 0.2, (b) 0.4, (c) 0.6, and (d) 0.8 $\mu\text{g mL}^{-1}$), 1 mL of 1% PPDTC, 1 mL of 1% SLS sodium acetate/acetic acid pH 4.

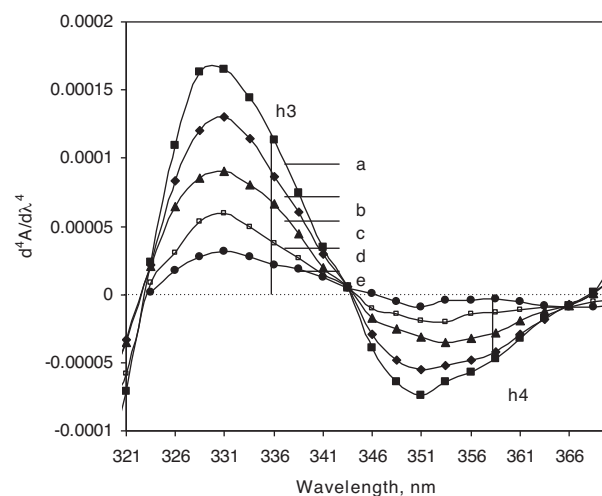


Figure 7. Second derivative spectra of Cu(II)- and Pd(II)- PPDTC complexes, [(a) Cu(II) = 0.2 $\mu\text{g mL}^{-1}$, (Pd(II) = (b) 1, (c) 0.8, (d) 0.6, (e) 0.4, and (f) 0.2 $\mu\text{g mL}^{-1}$), 1 mL of 1% PPDTC, 1 mL of 1% SLS sodium acetate/acetic acid pH 4.

Table 1. Statistical analysis of the determination of Cu(II) and Pd(II) in mixtures with PPDTC in the presence of SLS by derivative spectrophotometry.

Metal ion	Order of derivative	λ nm	Regression equation	r^2	R.S.D. (%)	Limit of detection, $\mu\text{g mL}^{-1}$
Cu(II)	1 st	433.5	$D = 0.0039x - 0.0007$	0.9939	0.5	1.25
	2 nd	401.0	$D = 0.0006x - 0.00008$	0.9966	0.3	0.24
	3 rd	393.5	$D = 0.0001x + 0.00001$	0.9993	0.6	0.15
	4 th	408.5	$D = 0.00005x + 0.000004$	0.9994	0.3	0.12
Pd(II)	1 st	356.0	$D = 0.0112x - 0.0004$	0.9982	0.6	0.25
	2 nd	363.5	$D = 0.0011x + 0.0002$	0.9955	0.2	0.25
	3 rd	348.5	$D = 0.0002x + 0.00002$	0.9985	0.5	0.14
	4 th	353.5	$D = 0.0001x + 0.000005$	0.9999	0.4	0.11

Accuracy of method

In order to ensure the accuracy of the method, several synthetic mixtures were prepared with different concentration ratios of Cu(II) and Pd(II) and analyzed by the proposed method. The developed methods were applied for determination of copper in various environmental samples such as pharmaceutical samples and alloys and palladium in activated charcoal. The results are given in Tables 2 and 3. It was observed that the accuracy and precision of the method were satisfactory.

Table 2. Results obtained by the HPSAM for mixtures of Cu(II) and Pd(II) as PPDTC complex.

A-C equation	r	Added in sample, $\lambda\text{g mL}^{-1}$		Found in sample, $\lambda\text{g mL}^{-1}$ (% recovery)	
		Cu(II)	Pd(II)	Cu(II)	Pd(II)
$A_{440} = 0.1684C + 0.1039$ $A_{465} = 0.1069C + 0.0725$	0.9995 0.9993	1.0	0.5	1.0 (100.0)	0.5 (100.0)
$A_{440} = 0.1689C + 0.1876$ $A_{465} = 0.107C + 0.1258$	0.9991 0.9985	1.5	0.5	1.49 (99.3)	0.5 (100.0)
$A_{440} = 0.168C + 0.1465$ $A_{465} = 0.1067C + 0.0994$	0.9994 0.9990	2.0	0.5	2.0 (100.0)	0.5 (100.0)
$A_{350} = 0.1259C + 0.0539$ $A_{365} = 0.0947C + 0.0482$	0.9991 0.9979	0.5	0.4	0.5 (100.0)	0.39 (97.0)
$A_{350} = 0.1265C + 0.0786$ $A_{365} = 0.0951C + 0.0667$	0.9988 0.9971	0.5	0.8	0.5 (100.0)	0.8 (100.0)
$A_{440} = 0.1259C + 0.0539$ $A_{465} = 0.0947C + 0.0482$	0.9991 0.9979	0.5	0.4	0.5 (100.0)	0.41 (102.5)
$A_{440} = 0.1259C + 0.1329$ $A_{465} = 0.0947C + 0.1132$	0.9991 0.9979	0.5	0.8	0.5 (100.0)	0.79 (98.7)
$A_{440} = 0.1259C + 0.1189$ $A_{465} = 0.0947C + 0.1272$	0.9991 0.9979	0.5	1.0	0.5 (100.0)	1.0 (100.0)

Effect of diverse ions

The effect of various ions was studied. Different amounts of some alkali metal salts and metal ions were added individually to aliquots containing 5 μg of Cu(II) and 5 μg of Pd(II). Each of these metal ions can be determined without any interference in the presence of Pb(II), Zn(II), Bi(III), Cd(II), Cr(III), In(III), Mn(II), Se(IV), As(III), Hg(II), Co(II), Ni(II) etc. Amongst the anions examined were acetate, sulfate, citrate, bromide, thiocyanate, fluoride, and chloride. EDTA interfered strongly in determination of these metal ions due to its ability to form stronger complexes than the ligand used. The tolerance limit of different ions is given in Table 4.

Table 3. Determination of Cu(II) and Pd(II) in different samples.

Metal and S.No.	Sample and composition	Amount of metal taken (μg) Cu(II)/Pd(II)	Amount of metal found by fourth derivative method (μg)	Amount of metal found by HPSAM	Recovery (%) by 4 th derivative method	Recovery (%) by HPSAM
(1) Pharmaceutical samples						
(a)	Supradyn (Nicholas Piramal India Limited) CuSO ₄ .5H ₂ O = 3.39 mg ZnSO ₄ = 2.20 mg Na ₂ MoO ₄ .2H ₂ O = 0.25 mg Sodium borate = 0.88 mg	8.62/2.0 ^a	8.50/1.8	8.60 /1.9	98.6/90.0	99.7/95.0
(b)	Vimgran (Sarabhai Chemicals) ZnSO ₄ = 15 mg CuSO ₄ = 2 mg SeO ₂ = 50 μg Chromium picolinate = 200 μg	5.08/1.5 ^a	5.01/1.49	5.0/1.35	98.6/90.0	98.4/99.3

Table 3. Continued.

(2) Alloys						
(a)	Brass alloy Copper 58.18% Lead 2.56 % Zinc 38.99 % Iron 0.09 % Tin 0.12 %	6.0/2.0 ^a	6.2/1.8	6.1/1.99	103.3/90.0	101.6/99.5
(b)	Pd-Charcoal Pd 5 C 950	2.0 ^a /5.0	1.9/4.6	1.99/4.9	95.0/92.0	98.0/99.5
(c)	Oakay alloy Pd = 10% Ni = 60% Pt = 20% V = 9.5%	1.0 ^a /1.0	0.098/0.095	0.099/1.0	98.0/95.0	99.0/100
(d)	JSS 653-7 stainless steel Mn = 1.72% Cr = 22.53% Ni = 13.91% Co = 0.35% Cu = 0.03%	0.03/0.05 ^a	0.025/0.045	0.026/0.047	86.6/90.0	86.6/94.0
(e)	Drinking water sample I ($\mu\text{g mL}^{-1}$) ³ Co(II) = 0.5 ^a Pd(II) = 1.0 ^a Ni(II) = 0.5 ^a Cu(II) = 0.5	0.5 ^a /1.0 ^a	0.49/0.97	0.49/0.99	98.0/97.0	98.0/99.0
(f)	Drinking water sample II ($\mu\text{g mL}^{-1}$) ³ Co(II) = 2.5, ^a Pd(II) = 2.5 ^a Ni(II) = 2.5, ^a Cu(II) = 2.5	2.5 ^a /2.5 ^a	2.3/2.2	2.4/2.4	92.0/88.0	96.0/96.0

^aamount of metal added in sample.Table 4. Effect of diverse ions on the determination of 5 μg of Cu(II) and 5 μg of Pd(II).

Anions added	Tolerance limit (μg)	Cation added	Tolerance limit (μg)
Bromide	45	Lead	400
Iodide	53	Zinc	500
Chloride	55	Bismuth	350
Fluoride	40	Cadmium	450
Acetate	78	Manganese	800
Oxalate	26	Indium	500
Citrate	140	Mercury	300
Phosphate	42	Silver	700
Thiocyanate	55	Cobalt	100
Sulfate	75	Nickel	150
Tartrate	5	Chromium	800
Cyanide	33	Arsenic	600
Nitrate	45	Platinum	600
EDTA	0.1	Selenium	500

Conclusion

The suggested method shows that either HPSAM or the fourth derivative can be well adopted for the simultaneous determination of Cu(II) and Pd(II) ions using PPDTTC as a reagent in the presence of SLS. This method eliminates the need for extraction of analytes in organic solvents. The proposed method offers good accuracy and precision and can be applied for a wide range of concentration ratios.

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