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Spectrophotometric Determination of Pt (II) and Pd (II) in Environmental Samples Collected from Highly Polluted Areas of Delhi Region of India

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Abstract: A simple and highly selective spectrophotometric method for the determination of platinum and palladium emitted by automobiles catalyzed with catalytic converters in highly polluted areas of Delhi region of India is proposed. The proposed method is based on the formation of mixed complexes of Pt (II) [pH 6.0] and Pd(II) [pH 4.5] with 2-(5-Bromo-2-pyridylazo)-5-diethylaminophenol (5-Br-PADAP) in the presence of dodecyl benzene sulphonate sodium salt. Both the complexes are extractable with dichloromethane. The Pt (II) and Pd (II) complexes have shown maximum absorbance at 570 nm and 550 nm, respectively. The optimum concentration ranges for the determination of Pt (II) and Pd (II) complexes are 1.0 -3.6 and 0.1- 2.0 µg/ mL, respectively. The methods are free from the interference of the platinum group metals.

Keywords: Automobile exhaust, Extraction, Dodecyl benzene sulphonate sodium salt, Platinum (II), Palladium (II)

I. Introduction

The automobile catalytic converter is a part of the automobile exhaust system. It converts harmful compounds like hydrocarbons of unburned gasoline, carbon monoxide and nitrogen oxide in exhaust into harmless compounds like carbon dioxide, water, nitrogen and oxygen. Automobile catalysts are mobile sources of platinum and palladium. The particulate of platinum and palladium released from an auto catalyst ranged from 4 to 108 ng/Km. The increasing use of platinum group metals (PGMs) in vehicle catalytic converters in addition to its use in chemical industry, jewelry making, pharmaceuticals etc. leads to the emission of PGMs into the environment. These metals are naturally found at very low concentration in the earth crust, but the increasing anthropogenic PGMs concentration poses a risk to living organisms and human beings [1].

Some rare metals belonging to PGMs are more environmentally mobile and thus bio-available to plants and trees. Under appropriate pH and redox potential conditions, PGMs can bind with peptides or humic or fulvic acids in the aquatic environment. Concentrations of PGMs in surface fresh water and surface salt water were found to be in the range of 0.4 to 22 ng/L and 19 to 70 pg/L, respectively whereas in the dense traffic road soil samples, concentration of PGMs were found to be in the range of less than 0.7 to 47 µg/Kg. Other PGMs concentrations in sewage sludge, sludge contaminated by discharges from the local jewelry industry and drinking-water samples were 18 to 260 µg/Kg, 4700 µg/Kg, less than 24 ng/L, respectively [2].

A lot of advanced techniques, namely graphite furnace atomic absorption spectrometry (GFAAS) [3,4] and inductively coupled plasma mass spectrometry (ICP-MS) [5-7], stopped-flow injection spectrophotometric determination [8], flow injection analysis (FIA) [9], flame atomic absorption spectrometry (FAAS) [10], electrothermal vaporization inductively coupled plasma mass spectrometry (EVI-CP-MS) [11], electrothermal atomization-laser induced fluorescence ion chromatography [12], polarography [13], have been developed for the determination of trace amount of platinum and palladium in various complex matrices such as ores, alloys, seawater, biological samples and autocatalytic exhaust samples.

Although, all the above techniques are good but spectrophotometric method is more popular due to being cheaper technique. Literature reveals that a small amount of work has been done for the analysis of platinum and palladium in catalytic converter based on spectrophotometric method.

William et al. [14] developed a complicated extraction method for the determination of Pd (II) and Pt (II) complexes with dibenzylthiooxamide in chloroform. Marczenko et al. [15, 16] developed a less sensitive separation method for palladium and platinum which was extracted with dithizone in carbon tetrachloride. Toral et al. [17] developed a method for the determination of Pd and Pt complexes with 3-(2-thiazolylazo)-2, 6-diaminopyridine (2, 6-TADAP) in the presence of 1.7 mol L⁻¹ perchloric acid solution which had drawback of heating upto 90° C for 30 min. Mojski et al. [18] developed a less sensitive extractive separation of platinum from macroamounts of palladium using triphenylphosphine oxide. Kavrentis et al. [19, 20] a less sensitive

method using a reagent 2-allylthiourea and thiocyanate with isoamyl alcohol, benzyltriethylammonium ion and iodide in the presence of EDTA. Manku *et al.* [21] developed a less sensitive method of extraction with oximidobenzotetronic acid which suffered from matrix interferences of common metal ions.

In the proposed method, the reagent, namely 2-[(5-bromo-2-pyridylazo)]-5-diethylaminophenol (5-Br-PADAP), forms mixed-ligand colored stable complexes with Pt(II) and Pd(II) due to the presence of the $-N-(CH_3)_2$ and halogen group. Complexes made with Pt (II) and Pd (II) are extractable with dichloromethane in the pH range of 4.0-6.5. The proposed method is free from interference of most of platinum group elements, even with no interference from Cu (II) and Fe (III) ions.

II. Experimental

A. Reagents

All chemicals used were procured from Sigma Aldrich and E. Merck. Millipore double distilled water was used for the preparation of all solution. The standard solution of platinum was prepared by dissolving a 1 g-ampoule of $PtCl_4$ in 50 mL of 6 mol L^{-1} HCl and then diluting to 1 Liter in a volumetric flask with the double distilled water. The stock solution was standardized by the gravimetric method [22].

The standard solution of 1000 $\mu g mL^{-1}$ palladium was prepared by dissolving weighed amount of $PdCl_2$ (1.66g) in 3.3 mL of concentrated HCl and then diluted to 100 mL in a volumetric flask with water. After the standardization of stock solution by the dimethylglyoxime gravimetric method [23], the exact morality of stock solution was found to be 9.39×10^{-3} mol L^{-1} . A diluted solution of platinum (IV) and palladium (II) was prepared by diluting the stock solution as required. A (5%, w/v) solution of $SnCl_2$ was used in 10 mol L^{-1} HCl. A 8.60×10^{-4} mol L^{-1} or (0.03%, w/v) 2-[2-(5-bromopyridyl) azo]-5-dimethyl-aminophenol (5-Br-PADAP) (97.0% pure) solution in ethanol (95.0% pure) was employed for color development. An aqueous solution of 0.02869 mol L^{-1} or (1%, w/v) of dodecyl benzene sulphonic acid sodium salt (DBSA) was prepared. Acetate buffer was prepared by mixing 0.1 mol L^{-1} solution of sodium acetate with 0.1 mol L^{-1} solution of acetic acid used for pH adjustment [24]. The stock solution of desired diverse ions was prepared as described in the literature and its 1mg/mL solution was prepared by dilution [24].

B. Instrumentation

For the characterization of maximum absorbance at appropriate wavelength of the complexes of Pt (II) and Pd (II), double beam UV-Visible spectrophotometer 54440SS model equipped with 1cm quartz cell was used. A digital pH meter (DB-1011) was calibrated regularly with a standard buffer solution of acid and base before being utilized.

C. General Procedure

Take an aliquot of the standard solution containing up to 0.1-3.5 μg of Pt(IV) in a 125mL separatory funnel. To the above solution, add 0.9 mL of 0.1 mol L^{-1} $SnCl_2$ in HCl for complete reduction of Pt (IV) to Pt (II), then add 0.9 mL of (1%, DBSA) and 1.0 mL of 5-Br-PADAP and then adjust the total volume of 10 mL with acetate buffer solution of pH 6.0 ± 0.2 and shake the violet color aqueous complex vigorously for 2 min with 5 mL dichloromethane. After drying over anhydrous sodium sulfate (≈ 2 gm), all the extracts were transferred to a 10 mL volumetric flask and made up to 10 mL with dichloromethane. Further, absorbance of the complex against solvent at λ_{max} 570 nm was measured.

For the preparation of Pd(II) complex, take an aliquot of 0.5-20 μg of Pd (II) in a 125mL separatory funnel and mix it with 0.4 mL of 1% DBSA and 1.2 mL of 5-Br-PADAP and then adjust the total volume upto 10 mL with acetate buffer solution of pH 4.5 ± 0.2 . In the case of extraction of Pd (II), follow the same extraction procedure as done earlier for Pt (II). Further, absorbance of the Pd (II) complex against solvent at λ_{max} 550 nm was measured.

D. Sampling and Sample Preparation

a. Automobile Exhausts Fume (Sample "A")

With conical flask connected to catalytic converter maintaining temperature between 0-5°C and stand-alone car maintaining speed at 20 Km L^{-1} for 2h, exhaust fume samples collected condense into liquid. The collected exhaust fume samples from 4 different types of four-wheelers, were diluted to 100 mL with distilled water in a volumetric flask, and with 1mL fume sample, the procedure given at para II(C) are to be followed.

b. Automobile Exhaust Scrape (Sample "B")

Automobile exhaust samples were collected from the exhaust scrape of Bharat II type cars equipped with catalytic converter (PGMs). About 1.0 g of usable catalyst obtained as scratches from exhausts pipe, was

weighed and treated with 15 mL of aqua regia on a hot plate for 30 min. After cooling, the solution was filtered and the filtrate was heated to dryness. Another 5 mL of aqua regia was added and then procedure was repeated. The residue was dissolved in 10 mL of 0.1 mol L⁻¹ H₂SO₄ and then solution was filtered off and made up to 50 mL with distilled water.

c. Roadside Dusts (Sample “C”)

The roadside dust was collected from heavy traffic road areas. The samples were crushed in an agate mortar and sieved through 200 meshes. These samples were separately treated with aqua regia (50 mL) with 4-5 mL of HF in a Teflon beaker to dissolve silica, if present. The solution is heated to dryness and treated with 10 mL of 0.1 mol L⁻¹ H₂SO₄ and made up to 25 mL with distilled water in volumetric flask.

d. Vegetation (Sample “D”)

Plant leaves were heated in an oven to dryness and crushed into fine particles in an agate mortar and then sieved through 200 meshes. Samples were treated in a same fashion as described above for the automobile catalyst samples and made up to 25 mL with distilled water in 25 mL volumetric flask. In all sample preparation, the solutions were filtered through Whatman Filter paper no. 42 after digestion.

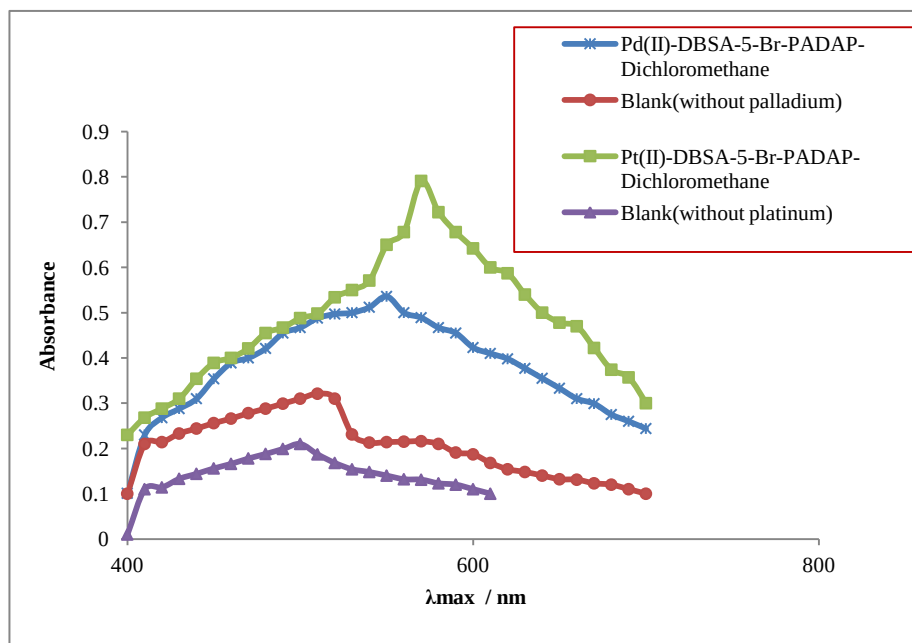
III. Results and Discussion

A. Absorption Spectra

The choice of suitable solvent and use of appropriate amounts of buffer, surfactant and reagent significantly increase the sensitivity, selectivity and molar absorptivity of the system.

The complexes of Pt (II) and Pd (II) in dichloromethane exhibit a maximum absorbance at around 570 and 550 nm, respectively against the solvent in their respective pH ranges of 6.0±0.2 and 4.5±0.2, as shown in Fig. 1. The reagent blank and solvent show negligible absorbance (A=0.05) in this region, hence it was used for whole experimental work.

Figure 1 Absorption spectra of the complexes, Pt(II) at pH 6.0 and Pd(II) at pH 4.5: Pt(IV)= 2.96×10^{-7} mol L⁻¹, SnCl₂= 1.72×10^{-2} mol L⁻¹, DBSA= 2.57×10^{-3} mol L⁻¹, 5-Br-PADAP= 5.72×10^{-5} mol L⁻¹, Pd(II)= 3.38×10^{-6} mol L⁻¹, DBSA= 1.43×10^{-3} mol L⁻¹, 5-Br-PADAP= 1.03×10^{-4} mol L⁻¹



B. Choice of Solvent

Both Pt (II) and Pd (II) complexes are extractable with many organic polar and non-polar solvents, such as ethyl acetate, isobutyl methyl ketone, toluene, benzene, carbon tetrachloride, chloroform, dichloromethane as listed in Table 1. Maximum extraction (>99%) in terms of absorbance of the complexes were observed with dichloromethane as compared with the other solvents. Since dichloromethane is less toxic than the chloroform, therefore, it was chosen as solvent for present work.

Table 1 Effect of solvent on the extraction of Pt(II) and Pd(II) complexes.
 Pt(IV)= 2.96×10^{-7} mol L⁻¹, SnCl₂= 1.72×10^{-2} mol L⁻¹ DBSA= 2.57×10^{-3} mol L⁻¹, 5-Br-PADAP= 5.72×10^{-5} mol L⁻¹
 Pd(II) = 3.38×10^{-6} mol L⁻¹ DBSA= 1.43×10^{-3} mol L⁻¹, 5-Br-PADAP= 1.03×10^{-4} mol L⁻¹

Solvent	Pt(II), $\lambda_{\max}$, nm	Molar absorptivity(ϵ) L mol ⁻¹ cm ⁻¹ $\times 10^5$	Pd(II), $\lambda_{\max}$, nm	Molar absorptivity(ϵ) L mol ⁻¹ cm ⁻¹ $\times 10^4$
Ethyl acetate	400	0.113	500	3.40
Isobutyl methyl ketone	575	0.730	570	4.25
Xylene	560	0.235	550	2.35
Benzene	420	0.122	480	3.66
Toluene	440	0.410	440	3.19
Carbon tetrachloride	560	0.121	550	2.02
Chloroform	570	1.270	550	9.57
Dichloromethane	570	1.270	550	9.57

C. Effect of pH

The effect of pH on the extraction of Pt (II) and Pd (II) complex were studied with different buffer of pH ranges of 1.0-14.0. The Pt (II) complex show stable and maximum absorbance with acetate buffer in the pH range of 3.0-6.5, so pH 6.0 ± 0.2 , at 570 nm was kept constant throughout the experiment. The Pd (II) complex show constant absorbance at the pH range of 4.0-5.5, so pH 4.5 ± 0.2 at 550 nm, using an acetate buffer solution.

D. Effect of Surfactants

Effect of nine surfactants, namely cetyltrimethylammonium bromide, cetylpyridinium bromide, benzyltrimethyltetradecylammonium chloride (Zephiramine), sodium lauryl sulfate, sodium dodecylmethylamino acetate, nonyl phenoxy polyethoxyethanol OP, Tween-60, Tween-80 and dodecyl benzene sulphonic acid sodium salt (DBSA) were tried. It was found that only dodecyl benzene sulphonic acid sodium salt (DBSA) was able to decrease the consuming time of color development increasing the sensitivity and molar absorptivity of both complexes.

E. Effect of Reagents

Pt (IV) reduces to Pt (II) in the presence of tin (II) chloride at room temperature ($30 \pm 0.2^\circ\text{C}$). Tin (II) chloride developed a maximum color in the final aqueous solution with concentration varying between the range (0.95 - 1.90) $\times 10^{-2}$ mol L⁻¹. Hence, a 1.72×10^{-2} mol L⁻¹ solution of tin (II) chloride was kept constant throughout the experiment.

The concentration of DBSA in the range of (1.14 - 2.29) $\times 10^{-3}$ mol L⁻¹ was required for maximum color development and constant absorbance of Pt (II) complex. Hence, a 1.43×10^{-3} mol L⁻¹ solution was kept constant throughout experiment. But for the formation of Pd (II) complex, the reagent range (2.0 - 2.86) $\times 10^{-3}$ mol L⁻¹ was required for maximum color development of Pd (II) complex. So, 2.57×10^{-3} mol L⁻¹ solution was kept constant through experiment.

The reagent 5-Br-PADAP indicated that at least concentration range of (2.86 - 6.29) $\times 10^{-5}$ mol L⁻¹ in methanol was required for maximum color development of Pt (II) complex and therefore 5.72×10^{-5} mol L⁻¹ of 5-Br-PADAP was kept constant throughout the experiment. But for the formation of Pd (II) complex, the reagent range (0.77 - 1.11) $\times 10^{-4}$ mol L⁻¹ solution in methanol was required for constant and maximum absorbance. A 1.03×10^{-4} mol L⁻¹ of 5-Br-PADAP was kept constant throughout the experiment.

F. Effect of Temperature, Electrolyte and Dilution

The study of the variation of temperature on the extraction of the metal complex with dichloromethane showed no change in absorbance of the Pt (II) and Pd (II) complexes between the temperature 10 - 50°C . Beyond this temperature, the absorbance of the complexes decreased. Hence, all the extraction works were carried out at a temperature of $30 \pm 2^\circ\text{C}$.

Addition of electrolytes such as potassium chloride or potassium sulfate or ammonium chloride upto 1.5 mol L⁻¹ did not change the absorbance and $\lambda_{\max}$ of the complexes. The effect of variation in the volume of the aqueous phase, keeping the other variables constant, on the extraction of the metal complexes with dichloromethane was studied. No change in the absorbance of the complex and $\lambda_{\max}$ was observed while varying the volume ratio

of the organic to aqueous phase(1:4 to 1:1. Hence the 1:1 organic:aqueous phase was chosen for the entire experiment.

G. Composition of the Metal Complexes

The composition of the Pt(II) and Pd(II) complexes were determined by using the curve fitting method (Sillen)[25] and Job's continuous variation method [26]. A graph was plotted between log D (distribution ratio) of metal versus log M (concentrations of ligand). The corresponding mole ratio of the metal to ligand for Pt (II) complex and Pd(II) complex are 1:1:2 [M: DBSA: 5-Br-PADAP] and 1:1:3 [M:DBSA: 5-Br-PADAP]. The probable reaction mechanism is given as below:

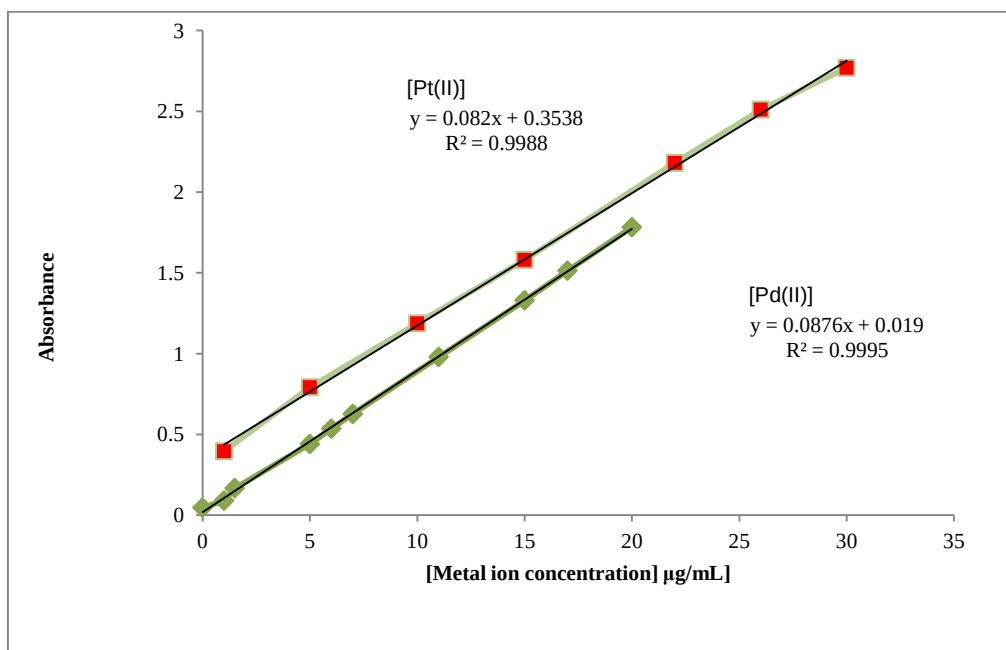


Subscript “₀” here describes the organic phase or dichloromethane.

H. Analytical Parameters

The system obeyed Beer's law upto 1.0-3.6 $\mu\text{g Pt (II) mL}^{-1}$ and 0.5-2.0 $\mu\text{g Pd (II) mL}^{-1}$ in the organic phase as shown in Fig 2. All the parameter such as correlation coefficient, slope, intercept, molar absorptivity, Sandell's sensitivity, detection limit (2σ), standard deviation, relative standard deviation, percentage of error, etc. are listed in Table 2.

Figure 2 Plot of calibration curve for determination of Pt(II) and Pd(II) complexes in dichloromethane.



I. Effect of Diverse Ions

A 10 $\mu\text{g Pt(II) mL}^{-1}$ and a 6 $\mu\text{g Pd(II) mL}^{-1}$ in aqueous phase were used for the study of the effect of diverse ions [28]. Different amount of foreign ions were introduced into a fixed amount of Pt(II) and Pd(II) which changed the absorbance. Foreign ions interfered when there was a change in the absorbance of the Pt(II) and Pd(II) complexes (Absorbance) by $\geq \pm 2\%$. The important feature of the method is that PGEs, namely Ru(IV), Rh(III), Pt(IV), Ir(III) and Os(VIII) do not interfere with the proposed method. The tolerance limit of various diverse ions in the determination of metal complex is summarized in Table 3.

J. Analytical Applications

The samples like automobile engine exhaust scrape, roadside dust, vegetation samples etc were collected from the different polluted places of Delhi region, namely Chandani chowk area of South Delhi, Maduban Chowk area of North Delhi and Janakpuri and Vasantgunj of West Delhi and Dilshad Garden, Modi Nagar and Ghaziabad region of National Capital Territory of Delhi.

The proposed method required minimal volume of the final sample solution with several fold preconcentration of the analyte, deposited at the mouth of exhaust vehicle [29]. The actual concentration of Pt(II) and Pd(II) in samples were determined using the calibration curve. The average concentration of Pt(II) and Pd(II) in automobile exhaust fume, automobile exhaust scrape and in the environmental samples (plants and dust) were found to be in the range of 0.068-185 $\mu\text{g/mL}$ and 0.020-0.81 $\mu\text{g/mL}$, respectively, as shown in Fig. 3 and Fig. 4. The average recovery of Pt (II) and Pd (II) is calculated to be $99.5 \pm 0.1\%$ with RSD value ranging between 0.1-4.6% and the same is listed in Table 4. So, the proposed method is suitable for the spectrophotometric determination of trace amount of Pt(II) and Pd(II) in the automobile exhaust fume and scrape, and environmental samples (plants and dust) in Delhi region of India. ,

IV. Conclusion

A sensitive and selective spectrophotometric method for the determination of Pt (II) and Pd (II) at trace level in automobile exhaust fume and automobile exhaust scrape, and environmental samples (plants and dust) in highly polluted areas of Delhi region is described here. The high concentration of Pt (II) and Pd (II) were found in East and West Delhi region of India because of the densely established industry and also due to emission of toxic gases through unserviceable automobiles running on the road. Some results obtained were: (i) The average concentration of Pt (II) and Pd (II) ranged 0.030-0.085 $\mu\text{g/mL}$ and 0.020-0.090 $\mu\text{g/mL}$, respectively. (ii) The average recovery of Pt (II) and Pd (II) calculated to be $99.5 \pm 0.1\%$ with RSD value ranging between 0.1-4.6%. The methods are very sensitive and selective as it is free from the interference of PGMs element i.e. Ru(IV), Rh(III), Pt(IV), Ir(III) and Os(VIII). The present work provides for a new method for quantitative analysis of Pt (II) and Pd (II) in automobile exhaust and environmental samples as very few literature is available for the determination of Pt (II) and Pd (II) using spectrophotometric method in such samples.

Table 2 Analytical characteristics of Platinum (II) and Palladium (II) complexes in dichloromethane.

Parameters	Pt (IV) to Pt (II)	Pd (II)
Color of the complexes	Violet	Blue
λ_{max}	570 nm	550nm
pH	6.0 $\pm$ 0.2	4.5 $\pm$ 0.2
Concentration of 5-Br-PADAP	5.72 $\times 10^{-5}$ mol L ⁻¹	1.03 $\times 10^{-4}$ mol L ⁻¹
Concentration of DBSA	2.57 $\times 10^{-3}$ mol L ⁻¹	1.43 $\times 10^{-3}$ mol L ⁻¹
Concentration of SnCl ₂	1.72 $\times 10^{-2}$ mol L ⁻¹ at 30°C	-----
Solvent	Dichloromethane	Dichloromethane
Composition of complex (M: L:L)	1:1:3	1:2:3
Stability up to,	12.0h	18.0h
Beer's law	1.0 to 3.6 $\mu\text{g}/10 \text{ mL}$	0.1 to 2.0 $\mu\text{g}/10 \text{ mL}$
Molar absorptivity	1.54 $\times 10^5$ L mol ⁻¹ cm ⁻¹	9.57 $\times 10^4$ L mol ⁻¹ cm ⁻¹
Detection limit (2 σ)	22.4ng mL ⁻¹	21.0ng mL ⁻¹
Sandell's sensitivity	12.0 ng cm ⁻²	11.2 ng cm ⁻²
Standard deviation(S), N=10	0.31%	0.348%
Relative standard deviation(RSD)	1.5%	1.62%
Intercept, slope, correlation coefficient	0.82, 0.0050, $\pm$ 0.995	-0.00070, 0.060, 1.0
Error	$\pm$ 1.2%	$\pm$ 0.52%

Table 3 Tolerance limit of diverse ion in the determination of Pt (II) and Pd (II) complexes.

Ions added	Tolerance limit* in mg 10 mL ⁻¹ aqueous phase	
	10µg Pt (II) /mL	6µg Pd(II) /mL
Cu(II)	0.20	0.20
Ir(III), Rh(III), Os(VIII)	0.05	2.0
Au(III), Zr(IV), Re(VII)	0.9	3.0
Pt(IV), Pt(II)	----	4.0
Pd(II)	1.5	-----
Sb(III), Bi(III), U(VI), Ta(V), Mo(VI)	1.0	4.5
Ni(II), Ti(IV), V(V), Cr(VI), Mn(VII)	2.0	5.0
Al(III)	3.0	6.5
Zr(II)	6.0	7.1
Co(II), Fe(III)	10	7.5
Bromide	18	4.0
Oxalate	20	4.3
EDTA	50	5.5
Fluoride	80	10.0
Acetate	100	14.2
Citrate	20	15.0
Tartrate	80	25.0

*Foreign ions interfere when there is a change in the absorbance by $\geq \pm 2\%$ of the Pt(II) and Pd(II) complexes

Figure 3 Concentration of Platinum (II) in Delhi Region of India

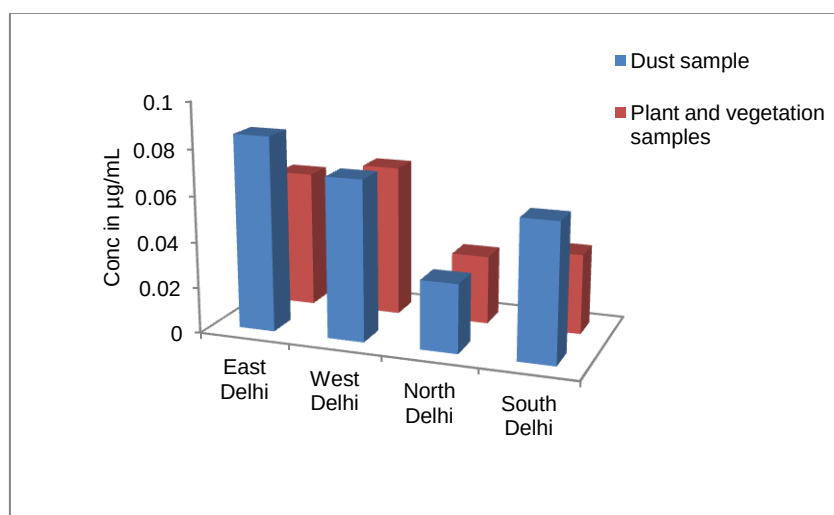


Figure 4 Concentration of Palladium (II) in Delhi Region of India

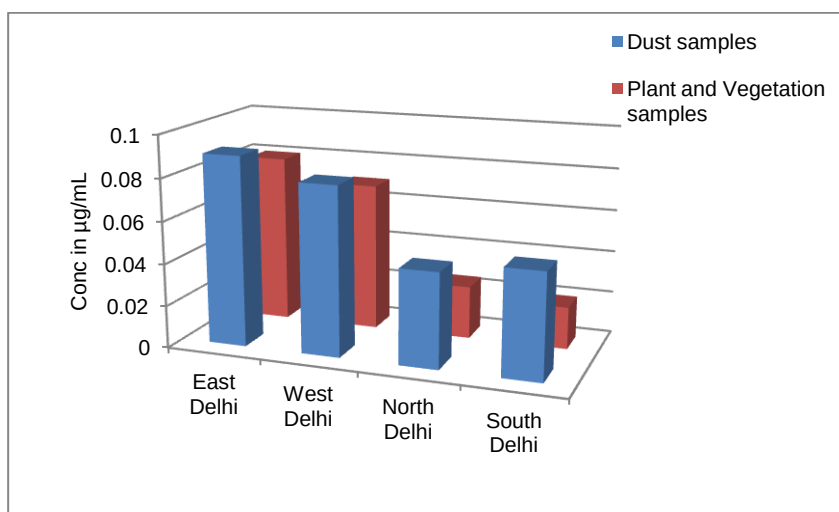


Table 4 Determination of Platinum (II) and Palladium (II) by using standard addition method

Samples	Amount of Pt(IV) & Pd(II) added to the sample (µg/mL)	Present method		Reported method	
		Concentration of Pt ^{II} & Pd ^{II} µg/mL, N=4		Bazel et al.[30] Karthikeyan et al.[31] Concentration of Pt ^{II} & Pd ^{II} in µg/mL, N=4	
		Pt ^{II} , ±%, RSD	Pd ^{II} , ±%, RSD	Pt ^{II} , ±%, RSD	Pd ^{II} , ±%, RSD
A ₁	1.0	1.135 ± 1.9	1.850 ± 4.0	1.136 ± 1.6	1.851 ± 4.2
A ₂	1.0	1.138 ± 2.9	1.550 ± 4.1	1.140 ± 2.8	1.458 ± 4.0
A ₃	1.0	1.068 ± 2.1	1.721 ± 4.3	1.065 ± 2.2	1.718 ± 4.6
A ₄	1.0	1.095 ± 2.2	1.620 ± 4.1	1.092 ± 2.3	1.622 ± 4.2
B ₁	1.0	1.100 ± 2.5	1.135 ± 0.1	1.098 ± 2.5	1.049 ± 1.1
B ₂	1.0	1.152 ± 2.6	1.105 ± 0.2	1.151 ± 2.5	1.038 ± 1.2
B ₃	1.0	1.160 ± 1.1	1.150 ± 0.1	1.161 ± 1.2	1.080 ± 1.1
B ₄	1.0	1.185 ± 1.5	1.180 ± 0.1	1.183 ± 1.6	1.100 ± 1.1
(C1)East Delhi	2.0	2.085 ± 2.0	2.090 ± 1.1	2.082 ± 1.9	2.090 ± 2.2
(C2)West Delhi	2.0	2.070 ± 2.6	2.080 ± 1.1	2.068 ± 2.5	2.085 ± 2.0
(C3)North Delhi	2.0	2.030 ± 2.2	2.045 ± 1.5	2.031 ± 2.2	2.000 ± 2.5
(C4)South Delhi	2.0	2.060 ± 2.1	2.050 ± 1.8	2.033 ± 2.2	1.030 ± 2.6
(D1)East Delhi	2.0	2.060 ± 2.8	2.080 ± 2.1	2.058 ± 2.9	1.078 ± 2.1
(D2)West Delhi	2.0	2.066 ± 2.4	2.070 ± 2.0	2.045 ± 2.9	1.085 ± 2.0
(D3)North Delhi	2.0	2.030 ± 2.5	2.025 ± 2.5	2.032 ± 2.6	1.000 ± 2.2
(D4)South Delhi	2.0	2.035 ± 1.9	2.020 ± 2.8	2.034 ± 1.8	1.030 ± 2.6

LIGENDS:

N : Number of determinations, A₁, A₂, A₃, & A₄ : Automobile exhaust fume samples,

B₁, B₂, B₃, & B₄ : Automobile exhaust scrape samples, C₁, C₂, C₃, & C₄ : Roadside dust samples

D₁, D₂, D₃, D₄ : Vegetation samples collected from road side trees and plants present near highly polluted areas of Delhi region

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