Spectrophotometric determination of platinum(IV) in alloys, complexes, environmental, and pharmaceutical samples using 4-[*N,N*-(diethyl)amino] benzaldehyde thiosemicarbazone

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Abstract 4-[*N,N*-(Diethyl)amino] benzaldehyde thiosemicarbazone (DEABT) is proposed as an analytical reagent for the spectrophotometric determination of platinum(IV). The DEABT forms 1:2 yellow complex with Pt(IV), which is sparingly soluble in water and completely soluble in water–ethanol–DMF medium. The Pt(IV)–DEABT complex shows maximum absorbance at 405 nm. Beer's law is valid up to 7.80 μg cm^{-3}, and optimum concentration range for the determination of platinum(IV) is 0.48–7.02 μg cm^{-3}. The molar absorptivity and Sandell's sensitivity of the method are found to be 1.755×10^4 dm^3 mol^{-1} cm^{-1} and 0.0012 μg cm^{-2}, respectively. The relative error and coefficient of variation ($n = 6$) for the method does not exceed ±0.43% and 0.35%, respectively. Since the method tolerates a number of metal ions commonly associated with platinum, it can be employed for the determination of platinum in environmental samples, pharmaceutical samples, alloys, catalysts, and complexes. The method is rapid as the Pt(IV)–DEABT complex is soluble in water–ethanol–DMF medium and not requiring any time consuming extraction method for the complex.

Keywords Spectrophotometric determination · Pt(IV) determination · 4-[*N,N*-(Diethyl)amino] benzaldehyde thiosemicarbazone · Chromogenic reagent

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Introduction

Platinum has important roles in environmental and biological fields. Platinum-group metals are widely used as catalysts in many chemical processes (Hartley 1991). A platinum-based catalyst removed 90% of the carbon monoxide, unburned hydrocarbons and nitrogen oxides in exhaust gas from vehicles. Platinum-based catalysts are very effective, e.g., in ammonia oxidation, petroleum reforming, pharmaceutical industry, and fuel cells. Platinum-containing compounds have found important application in treatment of cancerous tumors and rheumatoid arthritis. The most

active complexes of platinum were found to be *cis* isomers of dichlorodiammine–platinum(II), $Pt(NH_3)_2Cl_2$, and tetrachlorodiammine platinum(IV), $Pt(NH_3)_2Cl_4$. Trans-complexes were found to be inactive and are toxic but do not have antitumor properties (Hughes 1988). A study of platinum levels in the diet was conducted in 1986 on market-basket samples in Sydney, Australia (Vaughan and Florence 1992). The major pathway of platinum into the human body at the population level is via the diet, with an average dietary intake of 1.44 µg/day. The toxicological effects of platinum in humans are confined to certain of its complex halides, salts, and to the antitumour agents, cis-platin of its analogs. The platinum group compounds like chloroplatinate is not highly toxic but may cause allergic reactions to human beings. Owing to its corrosion-resistant nature and alloying ability, platinum and its alloys are used in dental and medicinal devices and in manufacturing jewelry (Pillai et al. 1997). Considering these excellent and extensive applications of platinum and the toxic nature of its compounds, there is always a need for monitoring the level of platinum in various samples. Several analytical techniques have been reported for the determination of platinum in various samples using inductively coupled plasma (ICP) atomic emission spectrophotometry, ICP mass spectroscopy, atomic absorption spectrometry, graphite furnace atomic absorption spectrometry, neutron activation analysis, and capillary electrophoresis which are very expensive compared to spectrophotometric method; this method have gained popularity as an analytical tool for platinum determination of such samples in respect of simplicity and low operating costs.

Thiosemicarbazones as spectrophotometric reagents for platinum(IV)

Several organic reagents are used for the spectrophotometric and extractive spectrophotometric determination of platinum(IV). Recently, there has been a rapid growth in the popularity of sulfur-bearing ligands, such as thiosemicarbazone, for the spectrophotometric and extractive spectrophotometric determination of metals. The striking property of thiosemicarbazone is that they form intensely colored complexes with many metal ions particularly with those of platinum group metals. The formation of such highly colored complexes is the basis for its potential use as spectrophotometric reagent. Many complexation reactions of platinum with different ligands were investigated for the development of spectrophotometric reagents for platinum. Beamish (1966); Beamish and Van Loon (1972); Boltz et al. (1966, 1968, 1970, 1972, 1974, 1976); Howell et al. (1978, 1980, 1982, 1984) have reviewed the spectrophotometric methods for the determination of platinum. A survey of literature reveals that a large number of reagents are suitable, either directly or after extraction into a suitable solvent. The conditions for maximum color development, sensitivities, and selectivity of the methods proposed differ very widely. A search in the literature also reveals that only a limited number of thiosemicarbazones have been reported for the spectrophotometric determination of platinum. This is in contrast to copper and palladium, for which a large number of thiosemicarbazones have been suggested as reagents. A brief account of these methods is given Table 1.

Present work

In the present work, 4-(*N*,*N*-diethylamino) benzaldehyde thiosemicarbazone (DEABT) is proposed as a chromogenic reagent for the trace determination of platinum(IV). The color reaction between platinum and DEABT, the optimum conditions for its determination, composition of the complex, molar absorptivity, sensitivity, selectivity of the method, and effect of diverse ions on the accuracy of the method have been studied. The applications of the proposed method for the determination of platinum in alloys, catalysts, complexes, and environmental and pharmaceutical samples have also been explored.

Experimental

Apparatus and reagents

A Shimadzu (Model 160A) double-beam UV/VIS spectrophotometer with 1.0-cm quartz cell and

Table 1 Thiosemicarbazones as spectrophotometric reagents for Platinum(IV)

Reagent	pH	Beer's law range μg mL^{-1}	λ_{max} (nm)	$\varepsilon_{max} \times 10^4$ l mol^{-1} cm^{-1}	M/L	Remarks	Ref.
Furyl acrolein thiosemicarbazone	2.5–5.5	6.2–78	390	0.57	1:1	Requires heating at 60–70°C for 30 min	Kerentseva et al. (1972)
Phthalimide dithiosemicarbazone	5.0	1–10	450	1.50	1:1	Requires heating at 85°C for 1 h	Guzman et al. (1974)
1,3-Cyclohexanedione bis thiosemicarbazone monohydrochloride	4.0	0.78–18.7	375	1.00	1:1	Aqueous DMF medium. Requires 20 min for complete color development. Sandell's sensitivity is 0.0195 μg cm^{-2}. Pd(II), Fe(III), Au(III), and Os(VIII) interfere	Reddy et al. (1984)
Phenanthrenequinone monothiosemicarbaz-one	0.8–4.4	0.75–15	495	1.63	1:2	The complex was extracted into molten naphthalene and dissolved in CHCl$_3$. Sandell's sensitivity is 0.0119 μg cm^{-2}	Wasey et al. (1984)
Acenapthenequinone monothiosemicarbaz-one	1.9–4.1	2.83–11.6	515	1.20	1:2	70% DMF medium. Requires 40 min heating on a water bath. Sandell's sensitivity is 0.01 μg cm^{-2}. Ag(I), Ir(III), and Os(VIII), interfere	Singh et al. (1986)
Anisaldehyde-4-phenyl-3-thiosemicarbazone	1.7–3.0	0.1–20	360	1.58	1:2	Involves extraction with ethyl acetate. Sandell's sensitivity is 0.0123 μg cm^{-2}. Zn(II), Cu(II), Pd(II), Ir(III), Au(III), and Ru(III) interfere	Prakash et al. (1987)
Salicylaldehyde thiosemicarbazone	3.5	0.5–8	388	–	1:2	The method suffers interference from many metal ions	Palaniappan et al. (1988)
2-Hydroxy-1-acetonaphthone thiosemicarbazone	5–6	2.34–13.4	346	0.64	2:3	Aqueous DMF medium. Sensitivity is 0.0301 μg cm^{-2}. Involves heating on a water bath for 30 min	Murthy et al. (1993)
Piperonal thiosemicarbazone	0.008–0.03 M H$_2$SO$_4$	0.1–6.5	360	3.239	1:2	Sandell's sensitivity is 0.006 μg cm^{-2}. Cu(II), Hg(II), Pd(II), and Au(III) interfere	Shetty et al. (2002)
4-(N,N-diethylamino) benzaldehyde thiosemicarbazone	3	0.48–7.02	405	1.755	1:2	Direct method, no need of elaborate separation techniques	PM

PM present method

ELICO pH meter (LI 127) with combined electrode were used for the measurements of absorbance and pH, respectively. All reagents and chemicals used were of analytical or chemically pure grade.

Stock solution of platinum(IV) chloride solution(4.0 × 10⁻⁴ M)

A stock solution of platinum(IV) was prepared by dissolving 1 g of chloroplatinic acid in distilled water and making the solution up to 500 mL. The solution was standardized gravimetrically by the formic acid method (Vogel 1975) and spectrophotometrically by using piperonal thiosemicarbazone (Shetty et al. 2002). The stock solution was further diluted with double-distilled water to get working solutions of appropriate concentrations.

Synthesis of 4-(*N,N*-diethylamino)benzaldehyde thiosemicarbazone (4.0 × 10⁻⁴ M)

DEABT was synthesized and recrystallized as per the reported procedure (Sah and Daniels 1950). The purity of the compound was checked by the elemental analysis and by the melting point. A product recrystallized twice was used for the preparation of DEABT solution in acetone.

Solutions of foreign Ions

The stock solutions of various metal ions and anions were prepared by dissolving the appropriate metal salts in distilled water or with suitable dilute acids and making up to a known volume.

Buffer solutions

A buffer solution of pH 3.0 was prepared by mixing 0.2 M potassium hydrogen phthalate solution and 0.2 M hydrochloric acid in suitable proportions.

Procedure

An aliquot of the solution, containing 12.0–175.5 µg of Pt(IV) was pipetted out into a 25-mL standard flask; 2 to 3 mL of DEABT (M/L : 1:2), 5 mL of buffer (pH 3.0), 5 mL of dimethyl-

formamide, 5 mL of ethanol were added, and the mixture was diluted up to the mark with distilled water. After 15 min, the absorbance was measured at 405 nm against a reagent blank. The platinum content in the unknown sample was determined using a concurrently prepared calibration graph.

Results and discussion

Absorption spectra

The reagent forms a sparingly soluble yellow colored complex with Pt(IV) in aqueous medium. The complex was found to be soluble in the aqueous solution containing 20% (*v/v*) DMF and 20% (*v/v*) ethanol. The absorption spectrum of the Pt(IV)–DEABT complex was recorded against the reagent blank. Similarly, the absorption spectrum of the reagent was recorded against the solvent as blank. The absorption spectra of both the reagent and the complex are shown in Fig. 1. The spectra obtained show that the Pt(IV)–DEABT complex and the reagent have maximum absorbance at 405 and 360 nm, respectively. The reagent has a negligibly small absorbance at the λ_{max} of the complex. Thus, further absorbance

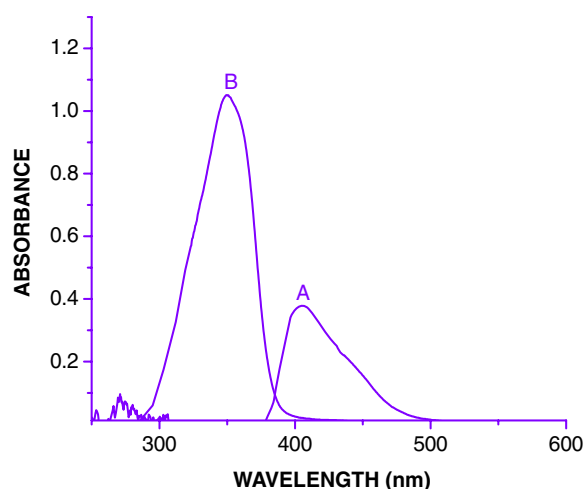**Fig. 1 a** Absorption spectra of Pt(IV)–DEABT complex vs DEABT blank; **b** absorption spectra of DEABT vs Ethanol blank. [Pt(IV)] = [DEABT] = 4.0 × 10⁻⁴ M

measurements of the complex were made at 405 nm.

Effect of pH

The influence of pH on the color of Pt(IV)–DEABT complex was studied by carrying out the reaction between Pt(IV) and DEABT in the presence of a series of buffer solutions differing in their pH by 0.2 units and measuring the absorbance of each of the solutions. The results are shown in the form of absorbance versus pH in Fig. 2. It is evident from the results that the absorbance values are maximum and remain steady in the pH range 2.6–3.4. But, outside this pH range, the observed absorbance values were lower. Therefore, for all subsequent studies, the pH was maintained at an optimum level of 3.0 using potassium hydrogen phthalate–hydrochloric acid buffer medium.

Effect of reagent concentration

The effect of reagent concentration on the color development was studied by varying the concentration of the reagent with a fixed amount of Pt(IV). The results are presented as a plot of absorbance against concentration of the reagent shown in Fig. 3. It is evident from the graph that
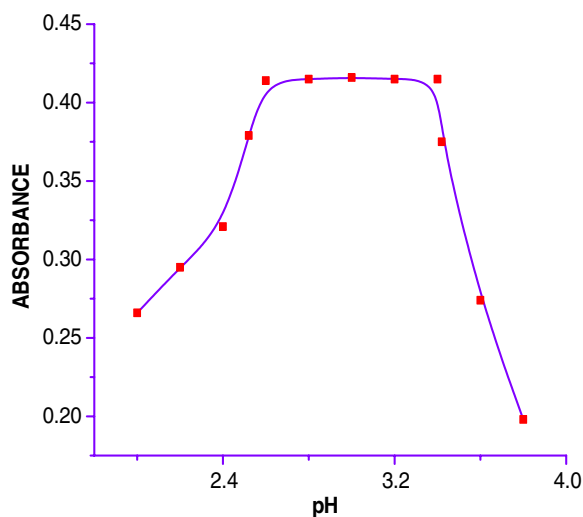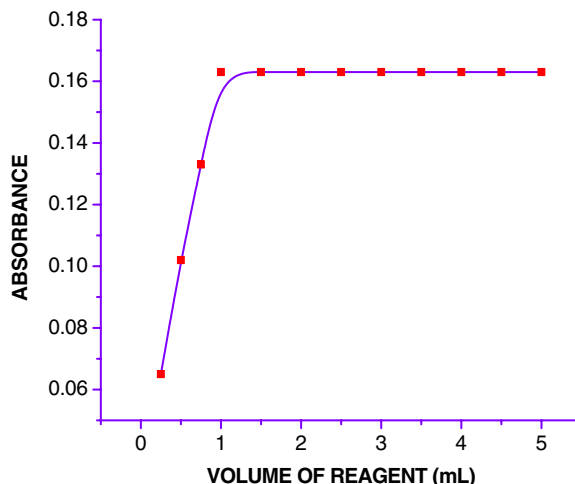

Fig. 3 Effect of reagent concentration on the absorbance of Pt(IV)–DEABT complex, $[Pt(IV)] = 2.0 \times 10^{-4}$ M; $[DEABT] = 4.0 \times 10^{-4}$ M

2 mol of DEABT per mole of Pt(IV) are required for the maximum color development. Furthermore, 10-fold excess of the reagent did not show any substantial change in the absorbance.

Composition of the complex

The composition of the Pt(IV)–DEABT complex was studied by Job's method of continuous variation and also by the mole ratio method. In these methods, equimolar solutions of Pt(IV) and
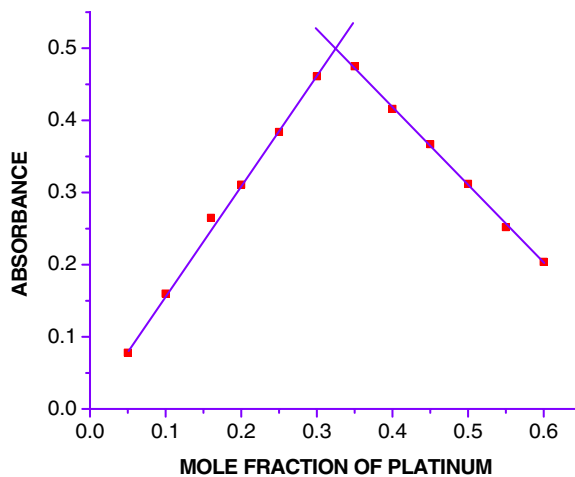

Fig. 2 Effect of pH on Pt(IV)–DEABT complex, $[Pt(IV)] = 4.0 \times 10^{-4}$ M

Fig. 4 Continuous variation plot for Pt(IV)–DEABT complex. $[Pt(IV)] = [DEABT] = 4.0 \times 10^{-4}$ M
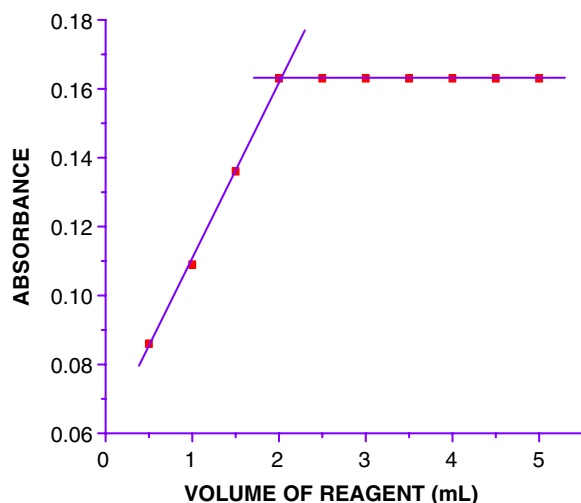
Fig. 5 Mole ratio plot for Pt(IV)–DEABT complex, $[Pt(IV)] = [DEABT] = 2.0 \times 10^{-4}$ M, Volume of Pt(IV) solution taken $= 1$ mL

DEABT were used. The graphs plotted for continuous variation and the mole ratio method are shown in Figs. 4 and 5, respectively. The continuous variation method shows a maximum at the mole fraction of platinum 0.333, indicating the formation of a 1:2 complex (Pt/R). Further support to this comes from the results of mole ratio method.

Order of addition of reagents

Experiments were carried out with a fixed amount of Pt(IV) by changing the order of addition of reagents. The results are presented in Table 2. The results indicated that the order of addition of the reagent did not have any effect on the absorbance of the complex.

Rate of reaction and stability of color

Experiments were carried out with a sample solution containing constant amount of Pt(IV) and

measuring its absorbance at regular intervals of time. The results are presented as plot of absorbance versus time as shown in Fig. 6. These results show that the color reaction between Pt(IV) and DEABT is fast and maximum color development takes place in less than 10 min. However, the reaction mixture was allowed to stand for 15 min before measuring its absorbance to ensure the maximum color development. The color of the solution remained stable for about 120 min.

Effect of temperature

The effect of temperature on the maximum color development was studied by carrying out the color reaction at different temperatures and measuring the absorbance values as per the procedure. These results showed that the absorbance attains the maximum value at the laboratory temperature itself and did not require any heating. However, heating of the solution above 60°C produced substantial decrease in the absorbance values. In all our experiments, the color reaction was carried out at laboratory temperature (27–30°C).

Validity of Beer's law

The validity of Beer's law for the system was studied by measuring the absorbance values of a series of solutions having different known concentrations of Pt(IV) in the solution. These results are shown in the form of a plot of absorbance versus concentration of Pt(IV) in Fig. 7. It is evident from the graph that Beer's law is obeyed up to 7.80 μg cm^{-3} of Pt(IV). The optimum working range for the maximum precision was determined by Ringbom plot. The percentage transmittance of the complex solutions was plotted against log[Pt] as shown in Fig. 8. The linear portion of the plot indicates that the platinum(IV) can be

Table 2 Effect of the order of addition of reagents

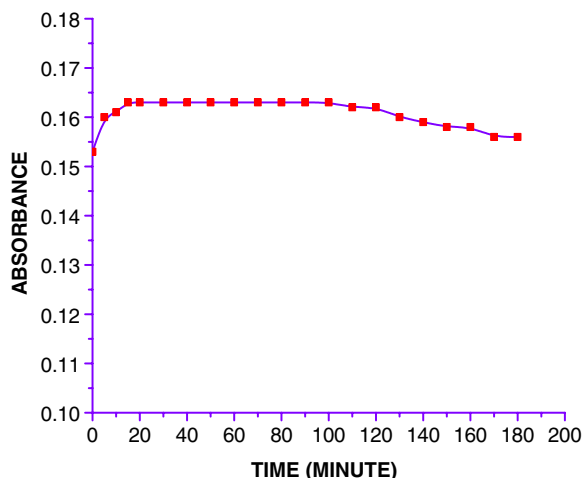| Order of addition of reagents	Absorbance at 405 nm[a]
Pt(IV) + Buffer + DEABT + DMF + Ethanol + Water	0.511
Pt(IV) + DEABT + Buffer + DMF + Ethanol + Water	0.510
Pt(IV) + DEABT + DMF + Ethanol + Buffer + Water	0.509
Pt(IV) + Buffer + DMF + Ethanol + DEABT + Water	0.510
Pt(IV) + DMF + Ethanol + DEABT + Water + Buffer	0.509

[a] Average of four determinations

Fig. 6 Color stability of Pt(IV)–DEABT complex, $[Pt(IV)] = 2.0 \times 10^{-4}$ M

precisely determined in the concentration range 0.48–7.02 μg cm^{-3}.

Molar absorptivity and Sandell's sensitivity

The molar absorptivity at the wavelength corresponding to maximum absorbance was calculated by measuring the absorbance at different concentration levels of platinum(IV). The mean value of molar absorptivity was found to be 1.755×10^4 dm^3 mol^{-1} cm^{-1}. The Sandell's sensitivity of the method is 0.0012 μg cm^{-2}.
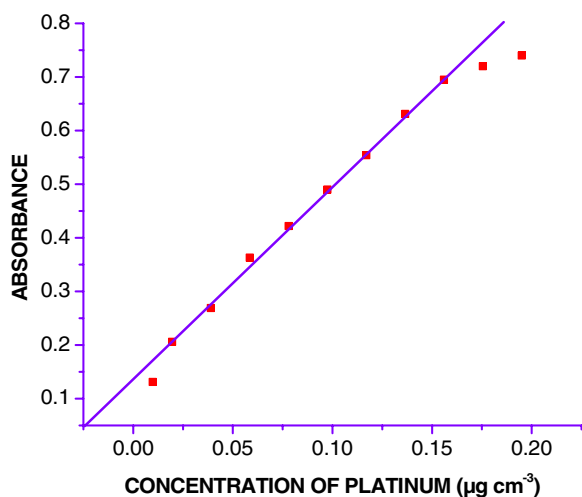
Fig. 7 Beer's law plot for Pt(IV)–DEABT complex. $[Pt(IV)] = 2.0 \times 10^{-4}$ M; $[DEABT] = 4.0 \times 10^{-4}$ M
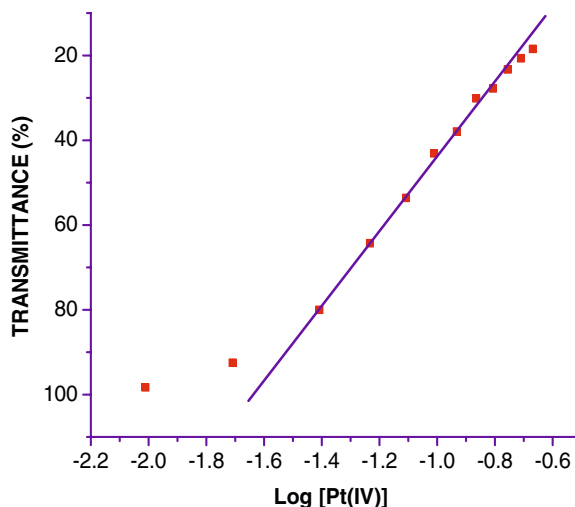

Fig. 8 Ringbom plot for Pt(IV)–DEABT complex. $[Pt(IV)] = 2.0 \times 10^{-4}$ M; $[DEABT] = 4.0 \times 10^{-4}$ M

Precision and accuracy

To assess the precision and accuracy of the method, determinations were carried out for a set of six measurement of 0.48–7.02 μg cm^{-3} of Pt(IV), under the optimized experimental conditions. The results are presented in the Table 3. These results reveal that the relative error and coefficient of variation do not exceed ±0.43% and 0.35%, respectively. From these results, it is reasonable to infer that the proposed method is precise and accurate.

Effect of foreign ions

The influence of the presence of diverse ions on the absorbance value of Pt(IV)–DEABT complex system was studied with 3.12 μg cm^{-3} Pt(IV) in the presence of foreign ions. An error of ±2% in the absorbance value was considered as the tolerance limit. The results are presented in Table 4. No interference was observed for the following ions at the amounts in micrograms per cubic centimeter shown: Pb(II) and Ni(II) (400); Zn(II) and Cd(II) (2,000); Mn(II) (100); Ba(II) (160); Co(II) (100); Ca(II) (50); Mg(II) and Hg(II) (10); Fe(II) (02); La(III), Y(III), Ce(III), Al(III), and Zr(III) (200); Ru(III) (8); Rh(III) (20); Cr(III) and Tl(III) (02); Se(IV) (50); Sn(IV) (05); Mo(VI) (30); U(VI) (400); chloride (2,000); fluoride (3,000); sulfate,

Table 3 Precision and accuracy in the determination of platinum(IV)

Pt(IV) $\mu g\ cm^{-3}$		Relative error (%)	Standard deviation (mg)	Coefficient of variation (%)
Taken	Found[a]			
1.56	1.56	0.00	0.003	0.19
2.34	2.33	−0.43	0.008	0.34
3.12	3.11	−0.32	0.011	0.35
3.90	3.90	0.00	0.005	0.13
4.68	4.67	−0.21	0.012	0.26
5.46	5.45	−0.18	0.011	0.20
6.24	6.24	0.00	0.010	0.16
7.02	7.01	−0.14	0.013	0.18

[a] Average of six determinations

phosphate, and acetate (400); bromide (300); citrate, nitrate, and tartarate (120); borate (100); thiocyanate (20); and thiosulfate (60). However, the presence of Cu(II), Pd(II), and iodide caused severe interference. The interference of Pd(II) and Cu(II) is attributed to the formation of their respective colored complexes and, hence, cause higher absorbance. The presence of iodide decreases the intensity of color.

Applications

Determination of platinum in alloys

A known weight of the alloy sample was carefully dissolved in aqua-regia, evaporated to near dryness and cooled to room temperature. The residue was dissolved in double distilled water and made up to a known volume. The stock solution was standardized gravimetrically by the formic acid

method (Vogel 1975) and spectrophotometrically by using piperonal thiosemicarbazone (Shetty et al. 2002). Aliquots of the solution were used for the estimation of platinum as per the proposed procedure. The results are given in the Table 5.

Determination of platinum in complexes

Platinum complexes with thiosemicarbazide and 4-amino-3,5-dimercapto-1,2,4-triazole were prepared and purified as per the reported procedures (Mahadevappa et al. 1976). A known weight of the complex was carefully decomposed with minimum amount of aqua-regia and evaporated to near dryness. Then the residue was dissolved with minimum amount of distilled water and filtered. The filtrate was made up to a known volume with distilled water. The stock solution was standardized gravimetrically by formic acid method (Vogel 1975) and spectrophotometrically by using piperonal thiosemicarbazone (Shetty et al. 2002).

Table 4 Tolerance limit of diverse ions in the determination of 3.12 $\mu g\ cm^{-3}$ Pt(IV)

Metal ion added	Tolerance limit $\mu g\ cm^{-3}$	Metal ion added	Tolerance limit $\mu g\ cm^{-3}$
Ba(II)	160	Se(IV)	50
Ca(II)	50	U(VI)	400
Cd(II)	2000	Mo(VI)	30
Zn(II)	2000	Fluoride	3000
Pb(II)	400	Chloride	2000
Mn(II)	100	Bromide	300
Co(II)	100	Acetate	400
Ni(II)	400	Sulfate	400
Mg(II) & Hg(II)	10	Nitrate	120
Fe(II)	02	Phosphate	400
La(III), Y(III), Ce(III), Zr(III) & Al(III)	200	Tartarate	120
Ru(III)	08	Borate	100
Rh(III)	20	Thiosulfate	60
Tl(III) & Cr(III)	02	Citrate	120
Sn(IV)	05	Thiocyanate	20

Average of four determinations

Table 5 Determination of platinum in alloys, complexes and catalysts

Samples	Platinum present (%)	Platinum found[a] (%)	Relative error (%)
In alloys			
Pt–Ru	95.20	95.02	−0.19
Pt–Ir	80.00	79.86	−0.18
In complexes			
$Pt(CH_5N_3S)_2Cl_2$[b]	43.53	43.39	−0.32
$Pt(C_2H_2N_4S_2)_2$[c]	40.05	39.91	−0.35
In catalysts			
Pt–Al_2O_3 catalyst	5.00	4.98	−0.40
Pt–charcoal catalyst	5.00	4.99	−0.20

[a] Average of five determinations
[b] Platinum complex of thiosemicarbazide
[c] Platinum complex of 4-amino-3,5-dimercapto-1,2,4-triazole

Aliquots of the solution were used for the estimation of platinum as per the proposed procedure. The results are given in Table 5.

Determination of platinum in catalysts

A known weight of the catalyst was digested with aqua-regia and evaporated to near dryness. The residue was dissolved in distilled water and filtered. The filtrate was made up to a known volume with distilled water. The stock solution was standardized gravimetrically by the formic acid method (Vogel 1975) and spectrophotometrically by the piperonal thiosemicarbazone method (Shetty et al. 2002). Suitable aliquots of the solution were used for the estimation of platinum as per the proposed procedure. The results are given in the Table 5.

Determination of platinum in pharmaceutical samples

Solution from cisplatin injection containing 10 mg/ml cisplatin and carboplatin containing 10 mg/ml carboplatin were added to aqua-regia (5 ml) and was heated to near dryness. The process was repeated for two to three times,

and then residue was dissolved in water and made up to 25 ml with double-distilled water. Suitable volumes of these solutions were taken and analyzed as per the proposed procedure are shown in Table 6.

Determination of platinum in environmental water samples

Water samples were collected in polythene bottles from tap water, river water, and spring water taken from different locations of Tamilnadu particularly in Chennai. After collection nitric acid (1 cm^3 dm^{-3}) was added as a preservative and filtered (with Whattman filter paper No. 40). Each filtered environmental water samples (1,000 mL) was evaporated nearly to dryness with a mixture of 2 mL of con. H_2SO_4 and 5 mL of con. HNO_3. After cooling, addition of 5 mL of con. HNO_3

Table 6 Analysis of Platinum(IV) in pharmaceutical samples ($n = 5$)

Sample	Amount Pt(IV) present		Relative error (%)
	Certi. value(mg)	Present method[a]	
Platosin (cisplatin)injection	10.00	9.89	−1.10
Carboplatin injection	10.00	9.91	−0.90

[a] Average of five determinations

Table 7 Determination of platinum in environmental water samples

Sample	Platinum µg mL^{-1}		Recovery (%)
	Added	Found[a]	
Distilled water		ND	
	0.480	0.477	99.4
	0.640	0.639	99.8
River water		ND	
	0.480	0.475	99.0
	0.640	0.637	99.5
Lake water		ND	
	0.480	0.476	99.1
	0.640	0.635	99.2
Well water		ND	
	0.480	0.476	99.1
	0.640	0.637	99.5

ND nondetectable
[a] Average of five determinations

Table 8 Determination of platinum in synthetic mixtures of ions

Composition of mixtures ($\mu g\,cm^{-3}$)	Found[a] ($\mu g\,cm^{-3}$)	Relative error (%)
Pt(IV) (3.12 $\mu g\,cm^{-3}$) (A)	3.12	0.00
(A) + Ru (III) (0.5 $\mu g\,cm^{-3}$)	3.11	−0.32
(A) + Rh (III) (0.5 $\mu g\,cm^{-3}$)	3.11	−0.32
(A) + Ir(III) (0.5 $\mu g\,cm^{-3}$)	3.12	0.00
(A) + Co(II) (1 $\mu g\,cm^{-3}$) + Pb(II) (1 $\mu g\,cm^{-3}$)	3.11	−0.32
(A) + Ni(II) (1 $\mu g\,cm^{-3}$) + Rh(III) (0.5 $\mu g\,cm^{-3}$)	3.12	0.00
(A) + Co(II) (1 $\mu g\,cm^{-3}$) + La(III) (0.5 $\mu g\,cm^{-3}$)	3.11	−0.32
(A) + Ba(II) (1 $\mu g\,cm^{-3}$) + Rh(III) (0.5 $\mu g\,cm^{-3}$)	3.12	0.00

[a] Average of five determinations

were repeated and heating to dense white fumes continue or until the solution becomes colorless. The solution was then cooled and neutralized with dil. NH_4OH in the presence of 1 to 2 mL of a 0.01% (w/v) tartrate solution. The resulting solution was then filtered and quantitatively transferred into 100-mL standard flask and make up to the mark with distilled water. Suitable volumes of these solutions were taken and analyzed as per the proposed procedure are given the Table 7.

Determination of platinum in synthetic mixtures of ions

Several synthetic mixtures of varying compositions containing platinum(IV) and diverse ions of known concentrations were analyzed for platinum as per the proposed method, and the results are presented in Table 8.

Conclusions

The DEABT complex forms a 1:2 yellow complex with Pt(IV), which is sparingly soluble in water and completely soluble in water–ethanol–DMF medium. The Pt(IV)–DEABT complex shows maximum absorbance at 405 nm. Beer's law is valid up to 7.80 $\mu g\,cm^{-3}$ and optimum concentration range for the determination of platinum(IV) is 0.48–7.02 $\mu g\,cm^{-3}$. The molar absorptivity and Sandell's sensitivity of the method are found to be $1.755 \times 10^4\,dm^3\,mol^{-1}\,cm^{-1}$ and 0.0012 $\mu g\,cm^{-2}$, respectively. The relative error and coefficient of variation ($n = 6$) for the method does not exceed ±0.43% and 0.35%, respectively. Since the method tolerates a number of metal

ions commonly associated with platinum, it can be employed for the determination of platinum in environmental samples, pharmaceutical samples, alloys, catalysts, and complexes. The method is rapid as the Pt(IV)–DEABT complex is soluble in water–ethanol–DMF medium and not requiring any time-consuming extraction method for the complex.

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