Spectrophotometric Determination of Pt (IV) Using a Schiff Base Derived from Substituted Triazole

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Platinum (IV) forms a bright red coloured complex in acid medium with a Schiff base derived from 3-methyl-4-amino-5-mercapto-1,2,4-triazole and piperonal. The complex absorbs at 400 nm with a molar absorptivity of $4.98 \times 10^4 \, dm^3 \, mol^{-1} \, cm^{-1}$ and a Sandell's sensitivity of 20.9 ng. cm^{-2} Beer's law is valid over the range of 1.8 to 24.0 ppm.

Substituted 1,2,4-triazoles have found extensive applications in analytical chemistry as gravimetric reagents for copper[1] and silver[2,3], as demasking agents for complexometric determination of mercury[4], thallium[5] and palladium[6] as reagents for spectrophotometric determination of serum triglycerides[7,8], fatty acids[8] and uric acid[9]. The present paper describes the spectrophotometric determination of Pt (IV) in ppm levels using the Schiff base derived from piperonal and 3-methyl-4-amino-5-mercapto-1,2,4-triazole (MPMT).

The ligand MPMT was prepared by the condensation of 3-methyl-4-amino -5-mercapto-1,2,4-triazole[10] with piperonal in ethanol and recrystallised from ethanol-water mixture. A 0.1% solution of the reagent in absolute alcohol was used. A stock solution of Pt (IV) was prepared by dissolving a 1 gm. ampoule of chloroplatinic acid (Johnson Mathey, London) in 100 ml. dil hydrochloric acid and standardized by gravimetric method[11]. The stock solution was further diluted as required. A potassium biphthalate buffer of pH 4.0 was used. The solutions of various anions and metal ions were prepared by dissolving AnalaR grade salts. A Beckman DU–6 spectrophotometer with matched 10 mm cells was used for absorbance measurements.

To an aliquot containing 45 µg of Pt (IV) 4 ml. of the ligand solution and 10 ml. buffer solution of pH 4.0 were added and heated for 30 min. The intense red coloured solution was carefully transferred to a 25 ml. standard flask and made up to the mark. The absorbance of the solution was measured at 400 nm against reagent blank.

MPMT forms a water-soluble complex having absorption maxima at 400 and 510 nm, the former being more sensitive. The development of colour at laboratory temperature was very slow and hence heating for a minimum period of 30 min.

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was needed to achieve maximum colour intensity. The colour was stable for at least 48 hrs. without any substantial change in absorbance. For maximum colour development at least 10 fold excess of the reagent was needed. The reagent and Pt (IV) solution do not absorb at 400 nm.

The coloured species was found to be absorbed on a cation exchanger indicating cationic nature of the Pt (IV)–MPMT complex and the composition was found to be $[ML_3]^+[Cl^-]$ by Job's method of continuous variation and mole ratio method. The Beer's law was found be valid over a range of 1.2–27.8 ppm. and the optimum range was found to be 1.2 to 24.0 ppm by Ringbom's plot. The method was found to be quite accurate and the results were reproducible. At 11.25 ppm concentration of Pt (IV), the standard deviation and coefficient of variance were 0.028 and 0.17% respectively.

The interference by various cations and anions were studied. The results are presented in Table 1. Among the noble metals, Pd (II) interfered seriously above 8 ppm level, but the interference up to 16 ppm could be avoided using dimethylglyoxime as masking agent. Ru (III) interferes very seriously. Among the base metals Cu (II) interferes. The method was applied to analysis of artificial mixtures corresponding to the compositions of Pt–Ir, Pt–Rh and Pt–Ni alloys.

TABLE 1
TOLERANCE LIMIT OF DIVERSE IONS IN THE DETER-
MINATION OF 9 PPM OF PLATINUM (IV)

Ion added	Tolrance limit ppm	Ion added	Tolerance limit ppm
F^-	2250	Cl^-	6400
Br^-	3500	I^-	100
NO_3^-	8000	SO_4^{2-}	8000
PO_4^{3-}	1500	$C_2O_4^{2-}$	250
Citrate	800	Tartarate	3000
Acetate	2500	EDTA	32
DMG	80		
Co (II)	270	Ni (II)	240
Cu (II)	5**	Zn (II)	1400
Cd (II)	1500	Fe (III)	60***
Ag (I)	10	Hg (II)	300
Al (III)	800	W (VI)	40
V (V)	50	Ti (IV)	25
Zr (IV)	25	Pd (II)	16*
Rh (III)	4	Ir (III)	2
Os (VIII)	5		

*in the presence of 80 ppm of dimethyl glyoxime
**in the presence of 30 ppm EDTA
***in the presence of 1000 ppm of tartarate.

The proposed reagent is quite selective and the method is selective. The accuracy of the method is comparable to that of most of the methods reported in literature.

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