

## New Amperometric Methods for the Trace Determination of Pd(II) and Pt(IV)

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Amperometric determination of Pd(II) and Pt(IV) was successfully carried out with the help of thioglycolic acid at dropping mercury electrode (d.m.e.). 0.1 M NH<sub>3</sub> + 0.1 M NH<sub>4</sub>Cl medium has been employed for Pd(II) and acetate buffer of pH 4.99 medium for Pt(IV). Both cathodic and anodic titrations were carried out successfully for Pd(II) in respective medium. Only cathodic titrations were carried out in case of Pt(IV). Metal species-TGA stoichiometry obtained was 1:2 for both the metal ions in respective mediums. Solutions as dilute as 1.06 ppm (Pd) and 9.75 ppm (Pt) were estimated in case of cathodic titrations and 10.64 ppm (Pd) was estimated in case of anodic titrations with high degree of accuracy. Tolerance limit for foreign ions has also been worked out.

**Key Words:** Amperometric determination, Thioglycolic acid, Pd(II) and Pt(IV).

### INTRODUCTION

Amperometry being simple and low cost technique is suitable for developing country like India. It is used for diagnosis of hepatitis C virus<sup>1</sup>, in detection of insulin<sup>2</sup>, detection of ultra trace amount of Hg(I)<sup>3</sup>, in cathodic electrochemical detection<sup>4</sup>, in micellar liquid chromatography<sup>5</sup>. Many sulphur containing organic ligands have been used in amperometry for the trace determination of metal ions. Thioglycolic acid (TGA) formulated as HS-CH<sub>2</sub>-COOH has often been used as a complexing agent and analytical reagent<sup>6-13</sup>. This acid has also been used in grafted on silica gel<sup>14</sup>, in preparation and characterization of glass embedding<sup>15</sup>, as a potentiometric sensor<sup>16</sup> and also in synthesizing nanorods and nanosheets<sup>17</sup>. This ligand has also been exploited earlier for the amperometric determination of coinage metal, some transition metals and non-metals<sup>18-20</sup>. The present work was undertaken with a view to extend the use of this ligand for the amperometric determination of Pd(II) and Pt(IV) in traces at d.m.e.

### EXPERIMENTAL

All the titrations were performed at d.m.e. vs. S.C.E. using a Toshniwal manual polarograph (Toshniwal India, Model CLO2A). Analytical grade chemicals and doubly distilled water were used. Palladium chloride (PdCl<sub>2</sub>·2H<sub>2</sub>O) and Hexachloroplatinic acid (H<sub>2</sub>PtCl<sub>6</sub>·xH<sub>2</sub>O) were used as a source compounds for Pd(II) and Pt(IV), respectively. Stock solution of Pd(II) and Pt(IV) were standardized amperometrically<sup>21</sup>. TGA solution was prepared fresh daily and standardized.

Amperometric determination of metal solution of any particular concentration was carried out at least thrice. Purified nitrogen gas was employed for deaeration. The selected potential was kept constant throughout. Limiting current corrected for dilution by the titrant was recorded as a function of the volume of the titrant. Dilution correction was made with the help of equation:  $i_{\text{corr}} = i_{\text{obs}} (V + v)/V$ , where  $i_{\text{corr}}$  is the corrected current,  $i_{\text{obs}}$  is the observed current, V is the volume of solution taken initially and v is the volume of titrant added. Null point was obtained graphically taking  $i_{\text{corr}}$  along y-axis vs. volume of titrant added along x-axis.

### RESULTS AND DISCUSSION

**Determination of Pd(II):** Amperometric determination of Pd(II) was carried out in 0.1 M NH<sub>3</sub> + 0.1 M NH<sub>4</sub>Cl medium. Pd(II) is known<sup>22</sup> to give diffusion controlled wave in 1 F NH<sub>3</sub> + 1 F NH<sub>4</sub>Cl with half wave potential -0.75 V. Same wave was observed in 0.1 M NH<sub>3</sub> + 0.1 M NH<sub>4</sub>Cl medium with  $E_{1/2} = -0.70$  V. Complexation of Pd(II) with 2-mercapto and 3-mercaptopropanoic acid has been reported<sup>23</sup>. Titration of Pd(II) with the TGA solution (cathodic titration) was carried out at -1.20 V. This voltage fell in the limiting region of Pd(II) alone; no anodic current of TGA was present here. The titration resulted in L-shaped amperometric curve shown in Fig. 1. The null point corresponded to the metal species: TGA molar reaction ratio of 1:2. Titration of TGA (anodic titration) with metal species solution were carried out at -0.10 V. This voltage fell in the limiting region of TGA alone; no cathodic current of Pd(II) was present here. The

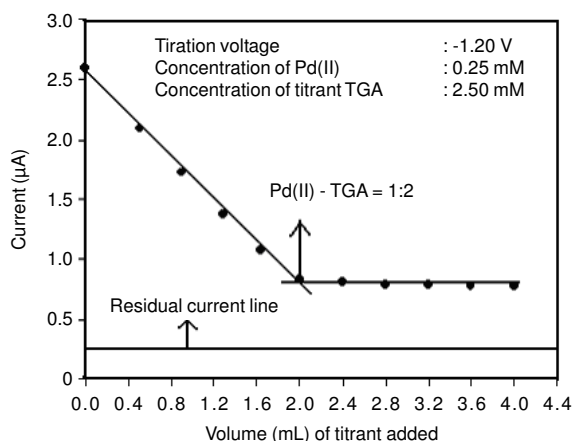


Fig. 1. Amperometric titration curve of Pd(II)-TGA system in 0.1 M  $\text{NH}_3$  + 0.1 M  $\text{NH}_4\text{Cl}$  medium

titration resulted in curve shown in Fig. 2. The null point corresponded to the metal species: TGA molar reaction ratio of 1:2. The method enabled the estimation of Pd(II) solution in the concentration range of 532.10 ppm through 1.06 ppm for cathodic and 532.10 ppm through 10.64 ppm for anodic titration. Maximum error ( $\pm 2\%$ ) was encountered in the case of most dilute solution only. The efficiency of new method was quite good to other d.c. amperometric method<sup>24</sup> and had shown superiority over common spectrophotometric method<sup>25</sup> in being valid over a much wider range of concentration of the metal solutions.

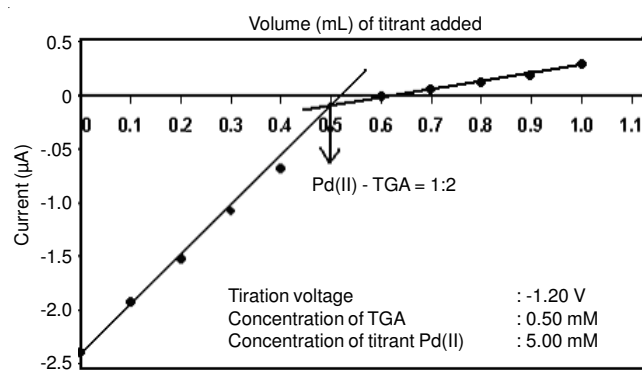


Fig. 2. Amperometric titration curve of Pd(II)-TGA system in 0.1 M  $\text{NH}_3$  + 0.1 M  $\text{NH}_4\text{Cl}$  medium

**Determination of Pt(IV):** Amperometric determination of Pt(IV) was carried out in 0.1 M KCl and acetate buffer of pH 4.99 mediums with 0.005 % gelatin. Titration of Pt(IV) with the TGA solution (cathodic titration) was carried out at -0.50 and -1.00 V in 0.1 M KCl and acetate buffer of pH 4.99 mediums, respectively. Complexation of Pt(IV) with 2-mercapto and 3-mercaptopropanoic acid has been reported<sup>23</sup>. This voltage fell in the limiting region of Pt(IV) alone; no anodic current of TGA was present here. The titration resulted in L-shaped amperometric curve (Fig. 1). The null point corresponded to the metal species: TGA molar reaction ratio of 1:2. The method enabled the estimation of Pt(IV) solution in the concentration range of 975.4 ppm through 1.95 ppm in both of respective mediums. Maximum error ( $\pm 2\%$ ) was encountered in the case of most dilute solution only. This new amperometric

method is quite efficient. Results were also supported by previous studies of our laboratory<sup>24</sup>.

#### Checking of interference of foreign ions and selectivity:

Study of interference of foreign ions in the new amperometric methods was carried out for three concentrations of each metal species *viz.*, 5.00, 1.00 and 0.50 mM. Table-1 includes safe limits of foreign ions in the cell solution. Non-interfering species did not interfere even when present simultaneously in the cell solution. However, for these selectivity tests, the maximum concentration of each species taken was 0.25 mM to avoid super saturation.

TABLE-1  
SAFE LIMIT OF THE CONCENTRATION OF FOREIGN IONS IN THE CELL SOLUTION WITH RESPECT TO THE CONCENTRATION OF THE METAL SPECIES

Metal ion	Pd(II)	Pt(IV)	
Medium	0.1 M $\text{NH}_3$ + 0.1 M $\text{NH}_4\text{Cl}$	Acetate buffer of pH 4.99	
Foreign ion	Cathodic titration	Anodic titration	Cathodic titration
$\text{Cl}^-$	B	B	B
$\text{NO}_3^-$	B	B	B
$\text{CH}_3\text{COO}^-$	B	B	B
$\text{Ox}^{2-}$	B	B	B
$\text{WO}_4^{2-}$	B	B	B
Mg(II)	B	B	B
Al(III)	B	B	B
V(V)	1/10	B	5t
Cr(III)	B	B	B
Cr(VI)	Equal	Equal	A
Mn (II)	B	B	B
Mn (VII)	1/10	1/10	1/10
Fe(II)	Equal	B	5t
Fe(III)	B	B	B
Co(II)	A	A	10t
Ni(II)	A	A	Equal
Cu(II)	A	A	Equal
Zn(II)	A	A	B
Mo(VI)	B	B	Equal
Cd(II)	Equal	1/5	1/10
Hg(II)	1/10	1/5	1/5
Au(III)	A	A	A
As(III)	A	A	5t
$\text{SCN}^-$	B	B	B
Pd(II)	-	-	Equal

A = Serious interference even when the conc. of foreign ion is 1/20 times to the metal ion. B = No interference even when foreign ion is 20 times that of metal t = times.

#### Conclusion

The study shows that thioglycolic acid is suitable for the determination of trace quantities of Pd(II) and Pt(IV). The methods give reproducibility with standard deviation of 0.05 only. The techniques have the added advantages for the developing country like India in being relatively quick, cheap and simple.

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