VOLTAMMETRIC ULTRA TRACE DETERMINATION OF PALLADIUM (II) IN PRESENCE OF IRIDIUM (III) AND RUTHENIUM (III)

Dr. P.Sharma[1], Dr. S. Sharma[2], Dr. R. Bais[3] and S. Barmera[4]

[1,2,3,4] *Electroanalytical Laboratory, Department of Chemistry,*

J.N.V. University, Jodhpur- 342001 (India)

ABSTRACT

A simple and convenient method is described for the determination of low concentration palladium based on differential pulse polarographic reduction of Pd(II) in presence of ethylenediamine. Linearity of the calibration curve was achieved upto 27 ppm with a limit of determination 0.01 µg/ml. The possible interference of usually present other platinum group metals was examined and ruled out. The method has been successfully applied for the determination of palladium in industrial waste water samples.

Keywords: Differential Pulse Polarography, Industrial Waste Water Analysis, New Method Development, Palladium, Platinum Group Metals.

I INTRODUCTION

Palladium is a platinum group metal of great importance and utility because of its remarkable catalytic properties and ability to readily absorb hydrogen. It is mainly used as auto catalyst. Other applications of palladium include in jewelry along with platinum [1]. Therefore it is appropriate to develop a simple and convenient analytical method for the determination of palladium.

Several methods such as flameless atomic absorption [2], X-ray fluorescence [3] and NAA [4] are reported in determination of microgram level palladium. The procedure requires preliminary treatment of the sample to bring an element (Pd) to the proper state for measurement [5]. The voltammetric methods are more suitable, as these can identify and determine different forms of an element as in case of palladium, which exists in three oxidation states of +6, +4 and +2 [6]. Differential pulse polarography (DPP) and anodic stripping voltammetry have proved useful in such determinations [7]. Thus, it is of interest to investigate the suitability of these methods in the determination of palladium, which is usually present at ultra trace concentration.

The electrochemical data on palladium revealed that the standard reduction potential (E^0) of Pd(II) is rather high (>0.90V) [8]. Therefore, it will be quite necessary to employ a complexing ligand so that the reduction potential of the complexed ion might be shifted towards a sufficiently negative potential so as to be measurable at mercury

electrode [9]. On this basis several authors have reported polarographic studies of Pd(II) complexes with dithioacetylacetone [10], caprolactum [11], organic sulfides [12], pyridine [13] and thiocarbazone [14]. Ahmed and Magee [15] have used organic solvents in electrochemical studies of Pd(II).

Cyclic voltammetric and single sweep polarographic studies of palladium complexes have been reported by Munichandraiah [16] and Zhao et al [17], respectively. The utility of glassy carbon [18] and carbon paste electrodes [19] has also been reported in these investigations.

The author has utilized the complexing ability of ethylenediamine in 0.1 M potassium chloride medium to study Pd/Pd(0) system at mercury electrode. Further in stripping analysis intermetallic compound formation on the electrode surface significant interference during the deposition [20]. Therefore the authors have used differential pulse polarography. The observations have enabled in developing of optimal conditions for the determination of ultra trace amount of palladium in aqueous matrices. The DPP determination of molybdenum [21], silver [22], osmium [23] and gallium [24] were reported earlier.

II RESULTS AND DISCUSSION

2.1 Electrochemical Characteristics of Palladium

Different supporting electrolytes, viz. acetate buffer, ammonia buffer, monoethanolamine in potassium chloride, glycine in sodium perchlorate and alanine in sodium perchlorate were studied to observe electroreduction of palladium at dropping mercury electrode. A combination of ethylenediamine with 0.1 M potassium chloride was found to be suitable medium where a distinct wave was obtained for the reduction of palladium (II) as shown in Fig. 1.

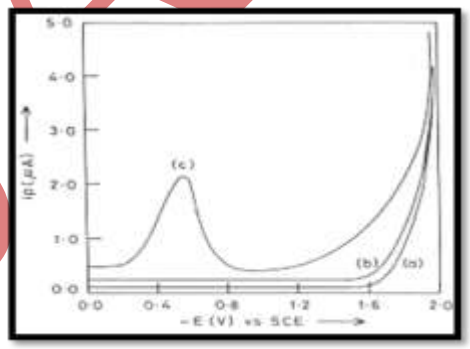

Fig. 1: DP polarogram of Palladium (II)-ethylenediamine in 0.1 M KCl

Pd(II) = 20 ppm
(a) Blank solution of 0.1 M KCl
(b) 2 x 10^{-2} M ethylenediamine in 0.1 M KCl
(c) Pd(II)- ethylenediamine in 0.1 M KCl

The variation of ethylenediamine concentration revealed that the wave height increases with the concentration of ethylenediamine upto 2×10^{-2} M. Subsequent addition of ligand did not increase the wave height. Therefore, all the

measurements were made at this concentration. Direct current polarographic observations revealed that the electrode reaction of palladium with ethylenediamine was not fully reversible. The wave appears to be diffusion controlled.

2.2 Optimal Conditions For Palladium Determination

Pd(II) also showed sharp differential pulse peak (DP) at -0.59V. A linearity of peak height was observed in 0.01-27 ppm range of Pd(II) concentration. The characteristics of the calibration curve were as follows: slope, 0.099; coefficient of correlation (π), 0.997 and intercept, 0.069. The plot of calibration is drawn in Fig. 2.

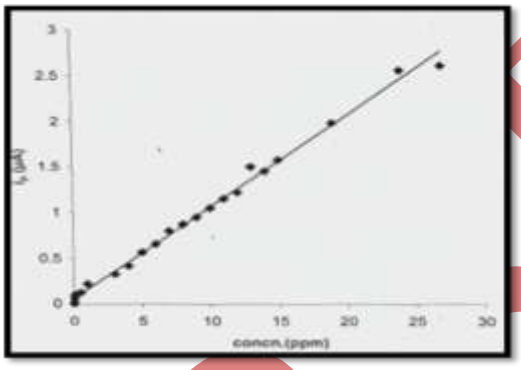

Fig. 2: Peak current vs concentration curve of Pd(II)- ethylenediamine in 0.1 M KCl

The detection limit of 0.01 µg/ml was achieved under the experimental conditions.

2.3 Interference

The metals of platinum group generally are present together and often occur as by product of the mining of some other metals, usually nickel or copper. Therefore, the expected interferants such as Cu(II), Ir(III), Ni(II) and Ru(III) were monitored during the determination of palladium. The peak potential of copper was found at -0.25V, and thus copper does not interfere. Similarly, Ir(III) and Ru(III) in presence of ethylenediamine are reduced at more negative potentials (-1.05V and -1.65V, respectively) than Pd(II) which gets reduced at -0.59V. The DP peak of Ni(II) was noticed at -1.22V, which was distinguishable, illustrating no interference as clarified in Fig. 3.

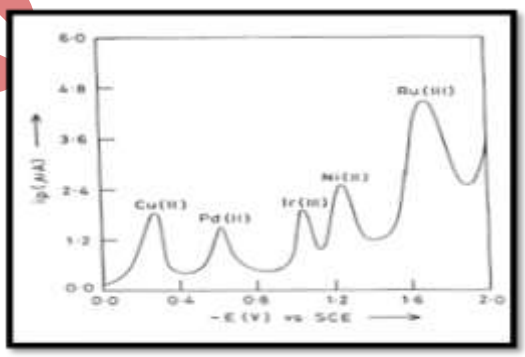

Fig. 3: DP polarogram of Pd(II) in presence of Cu(II), Ir(III), Ni(II) and Ru(III) in 0.1 M KCl

Cu(II)= 8ppm, Pd(II)= 15 ppm, Ir(III)= 10 ppm, Ni(II)= 15 ppm and Ru(III)= 15 ppm

III ANALYTICAL APPLICATIONS

The DPP reduction of Pd(II) in polarographic medium of 2×10^{-2} M ethylenediamine in 0.1 M KCl was made the basis for palladium determination in industrial waste samples. The prepared samples were taken into the polarographic cell and DP polarograms were recorded in the potential range of 0.0V to -1.0V. Peak currents were measured at -0.59V after making the blank correction.

Quantitation in all observations was made by applying the standard addition method [25]. The results of palladium determination are summarized in table Table 1.

Table 1: DPP Determination of Pd (II) In Industrial Waste Water Samples

S. No.	Pd(II) added (µg/ml)	Pd(II) determined (µg/ml)	SD (±)	RSD (%)	Average recovery (%)
1.	0.5	0.475	0.014	2.9	95.1
2.	1.0	0.94	0.021	2.2	
3.	2.0	1.93	0.030	1.5	
4.	3.0	2.86	0.054	1.8	
5.	4.0	3.79	0.089	2.3	

Atomic absorption spectrophotometry was used to compare the results obtained by DPP. The comparative data are presented in Table 2.

Table 2: The results of Pd(II) determined by DPP and AAS

Sample	Pd (II) present (µg/ml)	Pd (II) determined (µg/ml)	
		DPP	AAS
A	2.0	1.87	1.80
B	5.0	4.85	4.79
C	8.0	7.70	7.65
D	3.5	3.41	3.40

IV CONCLUSION

The DPP method for the determination of palladium is of simple approach and specific in terms of measurement, detection limit (0.01 µg/ml) and precision (RSD, 2.14%). Furthermore, the peak potential of palladium in presence of ethylenediamine (-0.59V) has enabled the determination of palladium together with other platinum group metals. The method will be useful in research and automobile industries where palladium is used as catalytic convertor.

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