INDIRECT SPECTROPHOTOMETRIC DETERMINATION OF PALLADIUM (II)

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An indirect spectrophotometric determination of Palladium is described. The method is based on the chemical reaction between metallic mercury and bivalent Palladium to form an equal amount of mercurous ions. The mercurous ion is further oxidised to mercuric which is measured spectro-photometrically by dithizone method. Various experimental parameters have been studied. The method is found useful for estimating Palladium in dental alloy, jewellery metal and catalysts.

Key words: Palladium (II), Indirect photometric method, Extraction.

INTRODUCTION

There are several procedures for the estimation of palladium by both instrumental and classical methods [1-4]. Although there are some merits to these methods, there needs to be control of special conditions and the lower limits of estimations are generally poorer than the method reported in this paper.

This paper describes a simple, sensitive and relatively selective method for the estimation of palladium. It is known from the literature [5,6] that palladous ion chemically interacts with mercury to give mercurous ions as per the equation,

$$Pd(II) + 2Hg \rightarrow \underset{\text{(Blackdeposit)}}{Pd^{o} + 2Hg(I)}$$

Reduced palladium metal exists as a black solid deposits. The oxidised mercurous ion (liberated by Pd(II)) is further oxidised to mercuric ions, in response, are determined by using dithizone as spectrophotometric reagent [7]. The method described is based on the above reduction reaction.

MATERIALS AND METHODS

Reagents and equipment. Analytical grade reagents and doubly distilled water were used for the entire work. Mercury metal (E.Merck,India) of 99.8 % purity was washed successively with 5 % nitric acid, conductivity water and doubly distilled under vacuum.

A Varian DMS-80 UV/Vis spectrophotometer equipped with a digital read out system was used for absorbance measurements. An Elico pH meter (model LI-120) was used for measuring pH (accuracy, ± 0.01 pH unit)

Stock solution of palladium. A stock palladium solution was prepared by dissolving Pd(II)Cl2 (Arora-Mett-hey, India) in minimum volume of 1M HCl (approximately 0.01M solution) and was standardised gravimetrically by DMG method [8]. An aliquot of this solution was diluted suitably to get 100 μg ml^{-1} of palladium.

Calibration graph. An aliquot containing 12-60 μg palladium (II) was transferred to a 100 ml conical flask; nitrogen gas was passed for a few minutes then 3-5 drops of mercury was added and shaked for 5 minutes and the contents were allowed to settle. The liquid phase alone was carefully powered off into 100 ml separating funnel containing 10 ml water. The mercury residue was successively washed with 5-10 ml portions of water and washings were added to the separating funnel. To the above solution 3 ml of 4 N nitric acid was added in order to keep the mercury in the bivalent state in solution.

The mercuric ion from the separating funnel solution was extracted with small aliquots of 0.001 % dithizone solution in carbon tetrachloride. The orange coloured extractions were collected in a 50 ml measuring flask and the volume was made upto the mark with carbon tetrachloride. Absorbance of calibrating solutions was measured at 485 nm against the compensatory blank. Calibration graph was obtained by plotting the absorbance against palladium (II) concentration.

RESULTS AND DISCUSSION

Effect of shaking time and nitrogen atmosphere. To obtain the minimum shaking period required to complete the chemical reaction (reduction of Pd(II) with concomitant liberation of Hg(I) ions), Pd(II) sample was shaken with mercury metal for different intervals of time.

The mercuric ions absorbance obtained were plotted against different shaking time intervals. From the above experiments it was found that 2 minutes shaking of the contents was quite enough to complete the reaction and

also that further shaking did not produced any considerable effect on results.

To check the effect of atmospheric oxygen, reduction of Pd(II) was carried out with and without inert atmosphere. In the presence of air random positive errors appeared; indicating some additional oxidation of mercury. Hence, to avoid this error, reduction process was carried out under nitrogen flow.

Effect of volume and concentration of nitric acid. In order to oxidise the mercury from univalent state (liberated from the chemical reaction) to bivalent state, the effect of nitric acid volume and concentration was carried out. It was found that 2 ml of 4 N nitric acid was quite enough to keep the mercury in the bivalent state and also that higher volume of acid did not produced any adverse effect on results.

Effect of temperature. When the reduction of Pd(II) was carried out at high temperatures, it was found that the rate of chemical reaction is significantly fast and the reaction is completed within 30 sec. itself (at $60^\circ \pm 1^\circ$). Therefore, higher temperatures can also be recommended for rapid estimation.

Effect of other ions. Of the various cations and anions tested individually in the determination of Pd(II), no interference was observed (error being less than ± 2 % in absorbance) in the presence of 100, 50, 30, 20, 10, 5, 2 and 1 fold excess of (oxalate, sulphate and acetate), (Ca(II), Zn(II), Ba(II) and chloride), (Al(III) and phosphate), (Ni(II), Co(II), CD(II), Fe(III) and Ir(III)), (Rh(III) and Ru(III)), (bromide and sulphide), (iodide and Cu(II)) and (thiosulphate, Au(III), Ag(I) and Pt(II), respectively.

Analytical application of the proposed method. Synthetic mixtures simulating the composition of a dental alloy, catalysts and jewellery metal made of palladium in which other heavy metals were also present had been selected for analytical study [9,10]. Because among the cations Pt(II), Ag(I) and Au(III) interfere seriously in this method. Palladium was separated from such combination alloy systems by adopting well established procedure [11] prior to indirect spectrophotometric estimation of Pd(II) as liberated mercury ions. The results presented in Table 1 show that this method is highly selective and sensitive for the assay of Pd(II).

Statistical treatment of the proposed method. The precision of the proposed method was evaluated by determining the same amount of Pd(II) in 6 different samples and the average amount found by the proposed method as well as by 2,2'-dipyridyl ketoxime method [12] and the corresponding standard deviation were presented in Table 2. From the test of linearity observations (correlation coeffi-

Table 1. Results of indirect estimation of palladium (II).

Constituent metals (simulated)	Concentration (in μg)		Palladium found[a] (μg)	Error (μg)
	I	II		
Dental alloy				
Platinum	20.3	40.4	20.7 (48.5)	– 0.40
Palladium	20.3	49.2		(– 0.70)
Copper	48.6	60.2		
Zinc	48.6	75.6		
Catalysts[b]				
Palladium	16.6			
Alluminium Oxide	353.0[c]	16.8	16.8	+ 0.2
Palladium	13.4		(13.2)	(– 0.2)
Calcium chloride	258.8[d]			
Jewellery metal[b]				
Palladium	27.6	55.2	27.5	– 0.1
Ruthenium	1.2	2.4	(54.8)	(– 0.4)

a = average of four determinations; b = determination (without isolation of palladium); c = concentration as Al(III); d = concentration as Ca(II).

Table 2. Comparison with 2,2'-dipyridyl ketoxime method.

Amount of Pd(II) taken (μg)	Amount of Pd(II) found[a] (μg)		Standard deviation (μg)	
	Proposed method	2,2'-diphyridyl ketoxime method	Proposed method	22'-diphyridyl ketoxime method
20.0	19.8	19.9	0.924	0.516
25.0	25.1	25.2	0.852	0.964
30.0	30.3	30.8	0.844	1.132
40.0	40.4	40.6	0.786	0.966
45.0	45.7	45.5	0.906	0.928
55.0	56.1	55.9	0.818	1.176

a = average of six determinations.

cient, r) gave the value of r = 0.9924 which implied best linear association between the experimental signal and true (theoretical) concentration.

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