Indirect Polarographic Estimation of Palladium

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Chemical displacement of palladium by mercury at the DME, has been found to be quantitative (that is, instantaneous and proportional to the i_d of mercury). Therefore the mercury(I) wave has been exploited for the indirect estimation of palladium using the DME. The conditions of estimation are standardized and the method applied to a mixture (dental alloy) containing palladium. The results are within experimental accuracy. The indirect method has certain advantages over the direct methods.

Palladium has been directly estimated in the past by several workers mostly by the spectrophotometric technique using a variety of organic reagents, as for example, oximes,[1-3] azoles,[4] substituted ketones,[5-7] substituted phenols,[8-10] and sulfur compounds.[11-14] There has also been an indirect spectral method,[15] based on the catalytic action of palladium on the reduction of molybdophosphate to molybdenum blue. With but a few exceptions[16,17] the spectral estimations were restricted to ranges below 30 ppm. Another short-coming of the spectral method was that an extraction step was often necessary prior to the spectral reading, and this has been the cause to lengthen the procedure and introduce errors.

Less frequently adopted methods for the direct estimation of palladium are amperometry,[18] potentiometry,[19] stripping voltammetry,[20] and polarography.[21]

Polarographic estimations of palladium complexes at the DME (dropping mercury electrode), in the past have not been smooth-sailing. In some cases[22] the half-wave potential had been very close to the decomposition potential of the electrolyte, the wave itself being irregular at the top. In other cases,[23,24] the half-wave potential was reported to vary with concentrations of palladium, indicating the formation of more than one species. The present indirect polarographic method is free from these short-comings.

The direct polarographic estimation of palladium (without complexation) using a DME is difficult, for the reason that palladium salts are spontaneously reduced[22] to the metal by contact with mercury, the latter being more electronegative than palladium in the electromotive series of elements. An accurate method of estimation is outlined here for the indirect estimation of palladium, making use of the mercury(I) wave, which occurs due to the chemical displacement of palladium from solution. The practical range of estimation has been found to be between 10—210 ppm, (wider than many of the spectral methods, and also without encumbrance of the extraction step). This makes it a more rapid method than the conventional spectrophotometric methods.

When a solution of palladium chloride was subjected to polarography at a DME, a single wave was obtained with an half-wave potential of +0.06 V. This curve has been reported by previous workers[25] as due to mercury(I) ion liberated by the reaction.[26]

$$Pd^{2+} + 2\,Hg^0 \rightarrow Pd^0 + Hg_2^{2+}$$

This reaction is instantaneous up to 210 ppm, and the lower limit has been found to be 10 ppm, though theoretically the reaction may be stoichiometric even at much lower concentration ranges.

That the wave with a half-wave potential of +0.06 V is due to the mercury(I) ion, was confirmed by us as follows: Polarograms of palladium using a stationary platinum electrode, under the same conditions as before always showed a wave with an $E_{1/2}$ of +0.16 V. There was no wave at +0.06 V, unlike with the DME.

Polarograms of mercury(I) chloride (10^{-5} M) in the absence of palladium gave the same wave with a half-wave potential of +0.06 V, regardless, whether the electrode used was a DME or a platinum electrode.

Estimation of Palladium. A stock solution of 1×10^{-2} M palladium chloride was prepared from anhydrous palladium chloride (A.R.), by warming the aqueous solution with a drop of concentrated HCl, to ensure complete dissolution before making up to the required volume. This solution was diluted appropriately to get concentrations ranging from 10 to 225 ppm during polarography. Potassium chloride was used as a supporting electrolyte and also to keep the ionic concentration constant at 0.1 M. A 0.01% gelatin solution was used as a maximum suppressor. pH was maintained at 3.5 by the use of an appropriate Britton-Robinson buffer.[27] Polarograms were recorded after deaeration with oxygen-free nitrogen.

Instrument. A polariter PO3 Radiometer of the pen recording type with a built-in saturated calomel anode was used to record the polarograms.

The capillary characteristics were established as follows: m=9 mg/s, t=1.4 s, h=25 cm. A fast dropping capillary was found to be more suitable for the experiment, to minimize the chemical vitiation of the mercury surface.

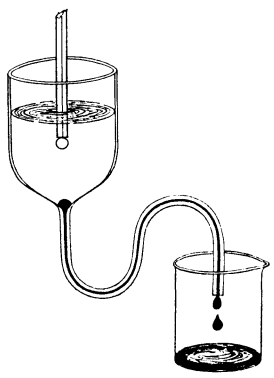

Fig. 1. Vessel used for the indirect polarographic estimation of palladium.

TABLE 1. COMPARISON OF RESULTS OBTAINED BY POLAROGRAPHY AND SPECTROPHOTOMETRY

No.	Quantity of Pd in the dental alloy (ppm)	Polarographically (ppm)	Spectrophotometrically (ppm)	Deviation between the two techniques (ppm)
1	10.65	10.55	10.60	+0.05
2	21.30	21.40	21.35	−0.05
3	31.95	32.00	32.00	0.00
4	53.05	53.00	53.05	+0.05
5	63.70	63.20	63.50	+0.30
6	74.35	74.20	74.30	+0.10
7	95.65	95.50	95.55	+0.05
8	106.30	106.40	106.20	−0.20
9	116.95	117.00	116.90	−0.10
10	137.65	137.50	137.60	+0.10
11	148.30	148.00	148.20	+0.20
12	158.95	159.80	160.00	+0.20
13	180.25	180.30	180.20	−0.10
14	190.90	191.00	190.90	−0.10
15	201.55	201.00	201.50	+0.50

Precaution was taken to avoid undue contact of solution with mercury other than the DME, so that the chemical reaction between palladium ions and non-electrodic mercury is made negligible. The polarographic vessel was drawn out into a capillary, so that the building up of the mercury pool by the drops of mercury was prevented by continuous tapping out of mercury, leaving only a droplet of negligible area of contact inside the capillary (Fig. 1). The scanning of the polarogram was done within 2 min.

The relationship between the diffusion current i_d and the concentration was found to be linear up to 210 ppm. Above this range the linearity is gradually lost by the vitiation of the surface of the mercury drop. A number of estimations were carried out with known concentrations of palladium, and the quantities were estimated by referring the i_d to the working graph.

The results obtained by the above method were checked by parallel determinations conducted by the well known spectrophotometric method[28,29] (λ_{max}= 525 nm), using *p*-nitrosodimethylaniline as the color developer and a Beckman Model B spectrophotometer as the instrument. The results of the two techniques were found totally within experimental error *vide* Table 1. In a series of fifteen experiments with 106.3 ppm of palladium, the standard deviation[30] was found to be 0.0876.

Analytical Applications. Indirect polarographic estimation of palladium through the mercury(I) wave is applicable to micro and semimicro quantities of palladium (below 50 mg). This quantity is below the macro-gravimetric limit. Micro-gravimetry is more tedious and hence the advantage of the polarographic estimation. This technique is suitable for the estimation of palladium present in hydrogenation catalysts and in dental and ornamental alloys. In alloys, palladium is generally found in association with gold, silver, and sometimes base metals like copper and zinc.

TABLE 2. R_f VALUES OF THE DIFFERENT IONS

Ion	R_f value	Remark
Gold	0.96	Moves with the solvent front
Palladium	0.84	Fine, thin band
Copper	0.74	Thin, well defined band
Zinc	0.30	Thick, diffused band, but far separated from the other ions

Before subjecting to polarography, it has to be isolated from its associates by any suitable method, a number of which are available in literature.[31-34] The method adopted in this laboratory was to separate the palladium by means of circular paper chromatography.

Isolation of Palladium from Gold, Copper, and Zinc in a Dental Alloy. The first investigation was to discover the R_f values of individual constituents, which alone will decide whether they can be separated at all. Solutions of pure metal constituents of the dental alloy (10^{-4} M) were prepared in aqua-regia. The solutions were evaporated to dryness to expel the oxides of nitrogen and made up to a required volume with 0.1 M HCl. Chromatograms were run on circular paper of diameter of 12 cm, with a central wick, and the eluent used was ethyl methyl ketone, concd HCl (A.R.) and isoamyl alcohol in the ratio of 6:3:1. After the paper was dried the bands were developed by spraying with the following reagents. (a) Hydrazinium chloride in dilute HCl for gold (Black band), (b) DMG in acid medium for palladium (Yellow band), (c) 0.1% Rubeanic acid in alcohol for copper (Green band), and (d) Dilute dithizone in chloroform for zinc (Pink band).

Table 2 shows the average R_f values of the different ions.

An appropriate quantity of the dental alloy was weighed, dissolved in 10 cm^3 of aqua regia, evaporated to expel the oxides of nitrogen and finally made up to 200 ml with 0.1 M HCl. The chromatogram was run as before. The brown band of palladium was clearly visible second from the outermost. It was cut out from the paper, and the metal extracted with 0.1 M HCl and utilized for quantitative estimation.

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