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AMPEROMETRIC DETERMINATION OF PALLADIUM WITH 1-HYDROXY-2-ACETONAPHTHONEOXIME*

1-Hydroxy-2-acetonaphthoneoxime was used for the amperometric determination of copper and nickel[1]. We now describe its use in the amperometric determination of palladium. The reagent gives a deep yellow precipitate with palladium in 0·01–0·05 N HCl solution. The reagent[2,3] was recrystallised from rectified spirit and then vacuum dried and a stock solution (0·025 M) prepared.

The apparatus used was the same as described previously[4]. Aliquots of the standard palladium chloride solution in the titration cell were mixed with 25 ml of K_2SO_4 (0·1 M), 5 ml of rectified spirit, 2 ml of chloroform and 2 ml of gelatin (0·2%). The overall acid concentration was adjusted with 0·5 M HCl and the total volume kept at 80 ml with distilled water. The applied potential was −0·1 volt (*vs.* SCE). The solution was titrated with the standard oxime solution deaerating after each addition. The galvanometer readings were plotted against titre values and the end point determined. Palladium in the range of 0·5–4 mg was quantitatively determined by this procedure with an average error of ±0·47%. Five determinations of 1·057 mg of palladium gave a standard deviation of 0·005 mg, the relative mean error being ±0·47%. The method[5] described above gave accurate values when the solution was 0·01–0·05 N with respect to hydrochloric acid. Higher acid concentrations were avoided since the reagent did not give any precipitate with palladium. Carbon dioxide was used for deaeration to prevent the deposition of spongy material supposed to be metallic palladium[5]. Addition of chloroform was necessary to prevent contact between mercury and palladium solution which would otherwise tarnish the surface of mercury due to the adsorption of a black spongy material which was proved to be metallic palladium. In this connection, it may be mentioned that a passing remark was made by Kolthoff and Lingane that solutions of platinum group metals get reduced to metallic state in presence of mercury[6].

Copper, nickel, aluminium, manganese, zinc, platinum, ruthenium and rhodium did not interfere under the above experimental conditions. The interference due to iron(III) was however masked with a 0·5 M solution of sodium fluoride.

The present study thus shows that 1-hydroxy-2-acetonaphthoneoxime can be utilised for the amperometric determination of palladium in presence of metals usually associated with it.

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A NOVEL SYNTHESIS OF 10,11-DISUBSTITUTED TETRAHYDROPROTOBERBERINE ALKALOID XYLOPININE

The tetrahydroprotoberberine alkaloid xylopinine (IV) has been isolated from *Xylopia discreta* (L. Fil) Sprague and Hutchins[1]. The structure (IV) was assigned to it on the basis of spectral studies and unambiguous syntheses[2–5]. The aim of the present investigation was two-fold, firstly, to evolve an efficient route for the synthesis of pharmacologically[6] and biogenetically important[7] 10,11-disubstituted tetrahydroprotoberberine alkaloids, making use of the lactone (II) for the first time and secondly to improve upon the existing procedures of protoberberine synthesis involving the lactones in one or the other steps of their reaction sequences. The approach as developed by us becomes more important in view of the reports that the most general method of the synthesis of 10,11-substituted tetrahydroprotoberberines, the Mannich