

Title: POLAROGRAPHIC DETERMINATION OF MERCURY USING A DIPPING ELECTRODE

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POLAROGRAPHIC DETERMINATION OF MERCURY USING A DIPPING ELECTRODE

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Polarographic determination of Hg_2^{+2} and Hg^{+2} using a mercury dropping cathode may be conducted with an inert electrolyte KNO_3 as well as with some complex forming electrolytes, such as Seignette salt, ammonium citrate and others [1]. Mercury ions give clear waves which begin almost from a zero of applied electromotive force, and there is a proportional relation between the wave height and concentration. Application of the solid dipping electrode described in the previous article [2] also permits determination of Hg_2^{+2} and Hg^{+2} in the solution.

The possibility of determining Hg^{+2} by the solid electrode was suggested for the first time by Miller [3].

A microelectrolyzer permitting experiments with volumes of 0.5-2.5 milliliters was used for demonstrating the possibility of microanalysis with a dipping electrode in the case of potassium nitrate electrolyte. The microelectrolyzer represents a tube 10-12 mm in diameter and 35-40 millimeters long with a cock and with a branch piece for connection with the calomel half-cell which serves as an anode. The construction of this electrolyzer permits quick replacement of solution and experimentation with very small volumes. There is a rectilinear relation between wave height and concentrations in a sufficiently wide range. It was stated in a previous article [4] that depolarization of dipping electrodes has a particular importance because it affects the reproducibility of polarographic curves and the linear relation between the wave height and concentration. Experiments with mercury confirmed that conclusion. However, methods suggested for depolarization of electrodes, e.g., washing them with nitric acid and holding them in a short-circuit state, did

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not give any good result in the case of mercury determination. Evidently, mercury and platinum in the electrode form stable amalgams which can not be decomposed by the methods ~~above~~ mentioned above. Heating of the electrode also gave poor results. The most efficient method of depolarization in the determination of mercury is the electric method.

The cathode is placed in ~~the~~ special electrolytic unit with sulfuric acid and has to be connected to the positive pole of a rectifier. A large platinum electrode is used. Complete removal of the mercury deposit from the cathode takes 1-2 minutes at a voltage of 6-8 volts. But after this operation the electrode is polarized anodically and should be heated for its depolarization.

The solid anode being used in polarographic determination is also polarized but heating for 3-4 minutes is sufficient for its depolarization. Use of the calomel half-cell with solution of potassium nitrate as an anode is especially advantageous because in this case anode depolarization may be omitted.

Besides the above described method for polarographic determination of mercury ions on a solid electrode, there is the method of volt-ampere titration. Determination by this method was conducted with the polarograph, model No 8, of the Odessa Institute.

For titration of Hg^{+2} , solutions of potassium iodide and orthoxyquinoline were investigated. A 4-5N solution was found as the optimum concentration for potassium iodide. Pure orthoxyquinoline gives a very shallow titration curve on which determination of the equivalent point is difficult. The shape of the titration curve may be considerably improved by addition of potassium iodide to the orthoxyquinoline. A solution of orthoxyquinoline with 3 percent concentration of potassium iodide shows the best result in titration and may be recommended for volt-ampere determination of Hg^{+2} .

For titration of Hg_2^{+2} solutions of potassium chloride and potassium iodide were investigated and both solutions were found satisfactory.

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The method of volt-ampere titration has many advantages. First of all, results are not dependent upon the conditions of titration, e.g., ~~from~~ the rate of bubble formation, temperature, electrode dimensions — factors which have a considerable effect on polarographic determination. A very essential advantage of volt-ampere titration is also the fact that results are not affected by polarization of electrodes and, therefore, the method does not require any depolarization of the electrode, readjustment of calibrating curves upon replacement of solid electrodes or strict observance of the rate of bubble formation. In addition, the method of volt-ampere titration permits to determine high concentrations of Hg^{+2} and Hg_2^{+2} which may not always be determined polarographically.

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