SOME APPLICATIONS OF THE POLAROGRAPH IN SOIL INVESTIGATIONS

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THE polarograph, developed largely by Heyrovsky and his associates, is an instrument designed for the photographic recording of current-voltage curves obtained upon electrolysis of solutions at a dropping mercury electrode under a steadily increasing applied E.M.F. The electrochemograph (1) is an American instrument designed for the same purpose but differing in details of construction and operation. The principle involved can be illustrated by Fig. 1. An excellent review of principles and details of operation can be found in Chemical Reviews (3).

In polarographic work the dropping mercury most frequently serves as a cathode, while a large mercury surface serves as the anode. In such cases, the curves obtained are the result of electro-reduction phenomena. Under appropriate conditions, it is also possible to use the dropping mercury as an anode and study electro-oxidations.

The authors have confined their attention to electro-reductions and have been concerned with two general types of applications, namely, (a) quantitative analysis for certain cations and (b) the behavior of oxidation-reduction systems involving organic complexes.

The E.M.F. at which an increase in current (inflection in the curve, Fig. 1) is registered is characteristic for the substance being reduced, and the magnitude of the current increase is a function of its concentration in solution. The E.M.F. characteristic for a given reduction is that measured at the half-wave point of the inflection, and it can be demonstrated in many cases that this corresponds closely to the reversible oxidation-reduction potential of that system being reduced.

QUANTITATIVE ANALYSIS

In the use of the polarograph for quantitative analysis, it is necessary to choose conditions such that no substance other than the one under study is reduced at a potential sufficiently close as to cause two inflections to coalesce. In many cases, inflections which coalesce may be resolved by the addition of some substance which forms a more stable complex with one ion than with the other. Also, no substance reduced at a potential smaller than the one under study should be present in concentrations exceeding more than a few fold that of the one under study. Once this is established, one is concerned with the choice of conditions such that the magnitude of the current step for the reduction under study is a reproducible function of its concentration in solution.

This involves the use of a single clean capillary dropping at a constant rate under a constant head of mercury and in a solution whose electrolyte content is above a certain minimum.

The authors have established the limits of such conditions in the determination of zinc and copper in plant materials and soil extracts. (For details see literature references 4 and 5.) In establishing limits for these determinations, the authors used a synthetic ash (Table 1) containing the principal mineral constituents likely to be encountered in plant materials and in many cases in amounts considerably above those to be expected in practice.

Fig. 1.—Principle of operation of the polarograph (after Kolthoff and Lingane).