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POLAROGRAPHY WITH ACCUMULATION AT A STATIONARY ELECTRODE

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Higher-purity materials are now demanded in many branches of industry, so more sensitive methods of analysis are needed. The best method for trace components (10^{-6} to 10^{-8}%) is storage polarography.

The essence of this method is that the components are concentrated by electrolysis into a small volume of solution or at the surface of an electrode, the amalgam or film being subsequently dissolved by varying the potential. This gives rise to characteristic peaks or steps, whose positions indicate the nature of the components and whose heights indicate the concentrations. The method has attracted much attention in recent years, and many papers have been published. Here we consider papers published in 1961-2 and (in part) 1963. The literature up to 1960 has been dealt with in several reviews [1-4].

Classification of Storage Polarography Methods

There are several forms of storage polarography (SP); all involve accumulation by preliminary electrolysis at a stationary electrode. These may be distinguished by reference to the method of recording the anode polarograms as follows:

1. Classical polarography with accumulation at a stationary electrode (CSP). The anode current is recorded with an ordinary polarograph with a sweep rate of 6-18 mV/sec (0.4-1.2 V/min). Neeb's polarograph [5] uses a high sweep rate.

2. Oscillograph polarography with accumulation at a stationary electrode (OSP). The anode polarogram is recorded with a cathode-ray oscilloscope. Here two different forms can be distinguished: a) linear variation of potential, rate 1-30 V/sec; b) sinusoidal variation. The polarogram is usually plotted as dE/dt against E [6-9].

3. Square-wave polarography with accumulation at a stationary electrode (SSP). A Barker square-wave polarograph [10,11] is used to record the anode polarogram.

The CSP method is the most used, on account of the relative simplicity of the apparatus, high sensitivity, and good resolution [12]. The OSP method is of higher resolving power, but its sensitivity is lower, on account of the larger capacitance current [12,13]. There are also other forms of storage polarography (ac, pulse, radio-frequency, and [15]), but these have not yet found practical use.

The nature of the product deposited at the electrode enables us to distinguish amalgam storage polarography (ASP), in which the metal dissolves in the mercury, and film storage polarography (FSP), in which the product forms an insoluble film on the mercury or solid electrode.

Here we consider mainly amalgam polarography with classical recording, which has been most extensively used. Branina et al. [16-27] have been the principal workers in the field of film polarography.

There is no agreed terminology at present, and many names are current, such as "anode volt-amperometry at a stationary mercury electrode" [28], "hanging mercury drop method" [29], "amalgam polarography at a stationary mercury drop" [17,30], "one-drop square-wave polarography", "inverse polarography" [31,32], and so on.

The names for the various techniques should be standardized. The common name for all should be storage polarography (polarography with accumulation at a stationary electrode, in full), which emphasizes the distinction from ordinary polarography (preliminary electrolytic concentration and use of a stationary electrode instead of a dropping one). The names given above should be used for the various forms of the basic method.

Design of Electrodes and Electrolyzers

Several types of stationary electrode have been described [1,2] for ASP. Two main types of electrode have been used recently:

Stationary Mercury Electrodes with Metal Contacts

Contact material	Solution in Hg at 18-25°C, wt. %	a†, V	Compounds with
Platinum [17, 30, 31, 37, 43—54]*	0.03 [55]	0.1	Zn, Sn, Sb [56]
Silver [5, 28, 39, 40, 57, 58]	0.05 [60]	0.95	Cd, Zn [61]
Gold [62—64]	0.01 [60]	0.8	Cd [62], Sn, Mn [2], Zn, Cd [65]

* Electrodes of type I were used in the last three cases.
† Constant in Tafel's equation [59]; the numerical value corresponds to the hydrogen overvoltage at 1 a/cm^2 for the contact material.

1. A mercury drop suspended at a suitable contact (Pt, Au, Ag), the drop being formed electrolytically from mercury nitrate or being produced via a polarographic capillary.

2. A drop formed and stabilized at the end of a capillary in various ways: by rotation of a stopcock [33,34], by a piston [35-40], or by a needle [41,42]. Important properties of the contact material are inertness, solubility in mercury, formation of intermetallic compounds, and hydrogen overvoltage. The table gives the properties of some metals that have been used.

Intermetallic compounds have been observed [56,65] at relatively high concentrations (10^{-4} to 10^{-5}M) in the solution when a platinum contact is replaced by a platinum sphere coated with mercury or when a mercury drop is saturated with mercury by electrolysis. No effects of the platinum contact have been reported for concentrations of 10^{-6} to 10^{-7}M in the cases of zinc, lead, and antimony [17, 50, 54, 61, 66-68].

The sides of the contact may be insulated with epoxide resin [57]. Polyethylene and PTFE are less suitable, for mercury can penetrate between the film and the wire.

Reproducible and stable drops are produced when certain conditions are observed in the treatment of electrodes of type 1 [46, 54, 69, 70].

A rotating electrode [49,71] of this type has been described.

Improvements in type 2 take the form of devices for making reproducible mercury drops [35,37,39,41,42,57], reduction of the total volume of mercury to 0.1 ml to minimize temperature effects [36,37], reduction of the penetration of electrolyte into the capillary [39,57] (by treatment with water repellent or by construction of the capillary of repellent material), suppression of the diffusion into the capillary [57], and improvements in reliability [42,57].

Theory [40,72] indicates that the film mercury electrode should provide sensitivities in ASP 2-3 orders of magnitude higher; it should also narrow the peaks (improve the resolving power) of ASP. The electrode takes the form of a silver contact coated with a film of mercury 2-4 μ thick [12].

Solid inert electrodes are used in FSP (platinum [20,24,27] or graphite [16,21]); these serve for use with films of metals or insoluble precipitates formed by reaction with anions after charge transfer at the electrode [22]. Use is also made of electrodes (of mercury [17,18] or silver [19]) capable of anodic oxidation and of forming insoluble films with certain anions [17-20, 23,26,73].

Little has been published on the comparison of different types of electrode under identical conditions [33,37,46, 56,68], so it is impossible to say which is best under particular conditions.

Various modifications have also been made in the electrolyzers; cells of volume about 1 ml have been described [5,31,54]. Further, the analysis is performed directly in the vessel used to dissolve or concentrate the specimen, in order to minimize the time required and the possibility of contamination. The tubes for nitrogen, the electrode, and so on are mounted in a removable teflon cover [37].

Effects of Various Factors on the Anode Wave

No theory of the wave was available until recently. A major advance was made when Vinogradova and Vasil'eva [74] and Shain and Lewinson [75] simultaneously deduced that the metal is uniformly distributed in the

droplet before the polarogram is recorded. Reinmuth [76] deduced an equation for the wave (without an inverse Laplace transform). Graphs have been given [53,76] showing the agreement between observed and calculated curves, but the formulas have not been given. Igolinskii [40] proposed a new method of deriving the voltage-current curves for an electrode with a linearly varying potential; he deduced the equation for spherical and film mercury electrodes. However, so far there has been no equation convenient for comparison with experiment; nor has the dependence of peak height on the various factors been given explicitly.

A semiempirical equation has been given for the anode current as a function of time, potential, volume of solution, and radius of drop [77]. The behavior of the peak height is governed by a dimensionless parameter itself determined by the various factors. The solution is not appreciably affected by the electrolysis for values of the factor less than 0.1; the current is then proportional to the electrolysis time and independent of the volume of solution. For values >3.0 the solution is virtually exhausted, whereupon the current is nearly independent of the electrolysis time and is proportional to the volume. A value of 1.26 gives the maximum current as the radius of the droplet is varied. For this reason it is best to state the value of this parameter and those of all the factors.

This enables us to calculate the anode-current constant, which is governed solely by the temperature and the diffusion coeffecient for the metal in mercury; it is not affected by the other factors, including the nature of the background. Numerical values of this constant have been found for Cd, Pb, Tl, and Cu. This constant, if available for all elements, would provide a method of ASP calculation similar to that used for the diffusion current for a mercury dropping electrode.

Theoretical deductions about effects on the wave height [77] have been confirmed [78], as by study of the relation of peak height to time of preliminary electrolysis [5,28,33,34,36,79-81]. The relation is linear, as theory predicts, for large volumes and short times [11]. Studies have been made of the effects of solution volume [78], drop radius [4,11,34,78], electrolysis potential [4,5,11,45,47,82], and mixing [5,11,33,34,45] on the anode wave height; this is reduced by sufactants. For instance, the height for lead is reduced 16% by 0.001% gelatin [34]. These materials have even more effect in SSP [11], which is a disadvantage of the method. The temperature coefficient of the anode current is about 3% [34].

The film electrode has been used in studies of the effects of rate of change of potential [40,46].

Brainina [20,21] deduced equations for the peaks from solid films and tested them [20].

The ease of determination by ASP is related to the position of the element in the periodic system; in particular, this results from the capacity to form an amalgam at room temperature [60,83,84]. Possible ways of extending the use of SP are implied by this; 20-30 elements, in addition to the 9-10 currently used, should be accessible. Of these, 13 elements in series 5, 7, and 9 (groups 1-5) are particularly promising, as well as the alkali and alkaline-earth metals. Waves have already been recorded for 10 elements: nickel, cobalt, iron [29,49,86,87], manganese [4,87], chromium [29], gallium [28,45,88], germanium, barium, potassium, and lithium [89].

FSP enables one to assay other elements, including ones not accessible to ASP, such as the halogens [17-19,23] and cations of variable valency [22].

Intermetallic Compounds in Solution in Mercury

ASP has provided evidence on the compositions and solubility products of intermetallic compounds in mercury; this problem is of considerable practical importance, for the formation of compounds may lead to reduction or elimination of the waves. ASP has been used to detect the formation of many compounds between metals [1], but very little quantitative information is available. A method of composition determination employing ASP has been proposed [90] (with reference to the Zn-Cu system in mercury); the results agree well with ones obtained in other ways [91]. Ficker and Meites [92] have described a current-time method of determining the composition and dissociation constants of the cobalt-zinc compound; they consider that this compound is soluble in mercury, which conflicts with Zebreva's view [91,93].

New Methods of Using Storage Polarography

New methods have provided improved sensitivity and resolution in ASP; difference ASP with one [40] or two [51,94] cells has been proposed. The first method gives higher sensitivity and can separate peaks of smaller spacing provided that the cathode peaks of the elements lie at different potentials. Difference ASP, in conjunction with a mercury-film electrode [72], should give access to 10^{-10} to 10^{-11} M in SP.

The height of the anode wave can be increased by use of catalytic hydrogen waves [95]. Vinogradova and Vasil'eva have used the compound between gold and cadmium in mercury to determine lead in the presence of cadmium [62]. Organic solvents have also been tested for use in ASP.

Several methods have been proposed for the simultaneous determination of several elements, such as stopping of the potentiometer drum when the potential corresponds to that of a more negative element, or alternatively reducing the rate of change [1]; there are also the method of proportional addition [48] and analysis with two cells with transfer of the stationary electrode [52,61,68,96,97]. A cell has been described for the quantitative determination of trace amounts of lead and copper in indium: the trace elements are extracted with 1 M H_3PO_4 as background, while the polarogram is run with a background of 0.25 M KOH + 0.5 M ethylene diamine [97]. The sensitivity is raised by stirring the solution near the drop with bubbles of hydrogen generated at the cathode during preliminary electrolysis [1,31,51]. It is found [40] that the anode peaks are higher and sharper if the solution is stirred during the recording.

A single droplet of mercury (at a contact) can be used for a prolonged period [66]. The drop is purified after use by keeping it slightly below the dissolution potential of mercury for 5-7 min; others [49,50] have used the same method. One of the difficulties with trace components lies in the preparation and storage of standard solutions. For instance, anomalous waves appear with nitric acid stored in polyethylene vessels, or even in quartz ones [98]. These anomalies are suppressed by the addition of 10^{-4}% of gelatin. It has been suggested [31] that standard solutions should be replaced by tablets, e.g. of urea.

Practical Application of SP

Relatively little has been published on SP applied to trace impurities; the last three years have seen papers on 10^{-5} to 10^{-7}% impurities in zinc [36,38], zinc sulfide [98], antimony [32], uranium salts [80,96], indium [44,97,99,100], tin [30,43,67], aluminum [28,62], arsenic [32,82], gallium [4,32], and gallium arsenide [101]. Papers have also appeared on the analysis of reagents [18,31,32,34,50,64,87,102-107]. There is no difficulty if the reagent forms the background (e.g., contains a cation: potassium, calcium, aluminum, etc). The ASP method has been used to examine biological objects [108] and food products [109,110].

Sometimes ASP has been used to determine amounts of the order of 10^{-3}%, as of tin in steel [52], lead and cadmium in mild steel [33], and indium and tin in alloys [53]. ASP may be better than ordinary polarography for 10^{-3} to 10^{-4}% levels if amounts <0.01 g are to be used.

Ways of Increasing the Sensitivity and Resolving Power of ASP

Sensitivity here needs definition. The maximal sensitivity is defined as the minimal concentration that can be detected under optimal conditions (e.g., corresponding to a 2 mm wave). This must be distinguished from the analytic sensitivity for a given level of error (10-20%), the latter being 5-10 times less (wave of 10-20 mm).

The sensitivity of SP can be raised by the use of a more sensitive instrument (in terms of μA/mm) and by improving the ratio of signal to noise. The last (the residual current) is reduced by balance methods in differential circuits, by choice of background, careful removal of oxygen, and so on. The signal can be raised by concentrating the impurities into a small volume of solution, increasing the electrolysis time, improving the stirring, increasing the ratio of surface to volume in the electrode, and use of catalytic effects.

By resolving power is meant the capacity to determine a given element in the presence of larger amounts of other elements; a quantitative measure of this is given by the maximum ratio of interfering to desired element at which the latter is still detectable. This is clearly governed by the width of the waves and increases with the rate of change of potential and also as the thickness of the mercury film decreases. The resolving power in OSP is therefore higher than in classical storage polarography, and the same applies to the film (amalgam) electrode relative to the drop (spherical) one. The resolving power and sensitivity of ASP can be raised if the rate of change of potential is reduced to zero when a peak is reached, the diffusion current being allowed to fall to its residual value before the next peak is recorded [40].

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