ANODIC STRIPPING VOLTAMMETRY WITH SUPERIMPOSED A.C. POTENTIAL*

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ABSTRACT

The combination of a.c. polarography with linear scan anodic stripping voltammetry has been investigated, employing a self-constructed, phase discriminating a.c. attachment. The resolution and sensitivity of the method was compared with those obtainable, under similar experimental conditions, by plain anodic stripping voltammetry. Changes in the concentration of the supporting electrolyte and the presence of dissolved oxygen frequently affect the sensitivity and must be carefully controlled. The practical application of the method is illustrated by applying it to the determination of zinc in solutions and in a standard silicate sample.

The application of anodic stripping voltammetry to the solution of analytical problems concerning the determination of low concentrations is well on the way to become an established technique [1, 2]; the hanging mercury drop electrode is most frequently employed [3], although some recent applications involve other electrodes and especially graphite [4]. The method allows the determination of metals deposited as amalgams, as a thin metallic film (on solid electrodes) or as an insoluble film [5].

A.C. polarography, as compared to classical linear voltage scan polarography, offers improved sensitivity and resolution; the quantitative evaluation of successive peaks is convenient. The method is also useful for the study of the kinetics of electrochemical reactions.

In this work, the combination of A.C. polarography with Anodic Stripping Voltammetry has been investigated. It was compared to plain (linear voltage scan) anodic stripping, critical attention having been paid to the points of difference of the two methods.

The combination of anodic stripping and a square wave pulse has been attempted [6]; the equation describing the current-potential relationship applicable to the combination of A.C. and anodic stripping has been elaborated [7].

Apparatus

A. C. polarographs have been known for a considerable time and a number
are available commercially. These instruments may be classified as
follows: a. instruments recording the total a. c. current; b. instruments
discriminating between the capacity current and the faradaic current,
by exploiting the phase difference between them. The advantages of the
second class are well known [8].

The availability of operational amplifiers greatly simplifies the
construction of a. c. polarographs; these may be readily adapted to
required specifications and are often preferable to available commercial
apparatus. The instrument employed in the present work was constructed
in our laboratory, from inexpensive transistorised amplifiers, as an
attachment to a linear scan polarograph. Compared to the apparatus
proposed by Smith [9] it has one limitation: a small (5×10^{-8} A) current
passes through the reference electrode (vs 10^{-10} A in Smith's apparatus);
while this current is too small to polarize the usual electrodes employed
in polarography, it obviously precludes the use of commercial electrodes
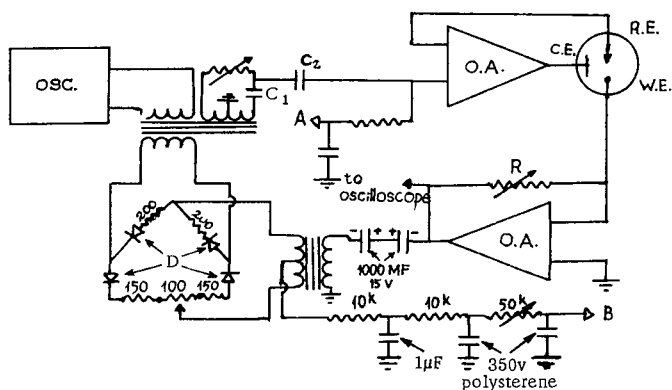of the kind often employed in potentiometry.

Figure 1

Outline of A. C. attachment

A   – to polarograph voltage supply   C. E.– Counter Electrode
        terminal (Leeds and   D   – Silicon diode 1001
        Northrop type E Electro-   O. A.– Operational Amplifier type ADO –
        chemograph)   3, Fairchild
B   – to polarograph current   OSC. – Audio oscillator
        measuring terminal   R   – Sensitivity determining resistor
C_1 – phase shift capacitor   R. E. – Reference Electrode
C_2 – attenuation capacitor   W. E. – Working Electrode

An outline of the A. C. attachment is given in Figure 1. An outlet to
an oscilloscope allows the total current passing through the cell to be
monitored; the oscilloscope image should have the shape of a sinusoidal
current superimposed on a d. c. current. However, owing to distortions

of the sinusoidal voltage, the current, too, is distorted (Figure 2).
Whenever circuit resistance rises (owing to a malfunction of the electrode,
etc.) these distortions disappear, indicating at once the presence of a
fault in the system.

Regular and A. C. polarograms, obtained with a 10^{-5} M zinc ion solution,
are compared in Figure 3.

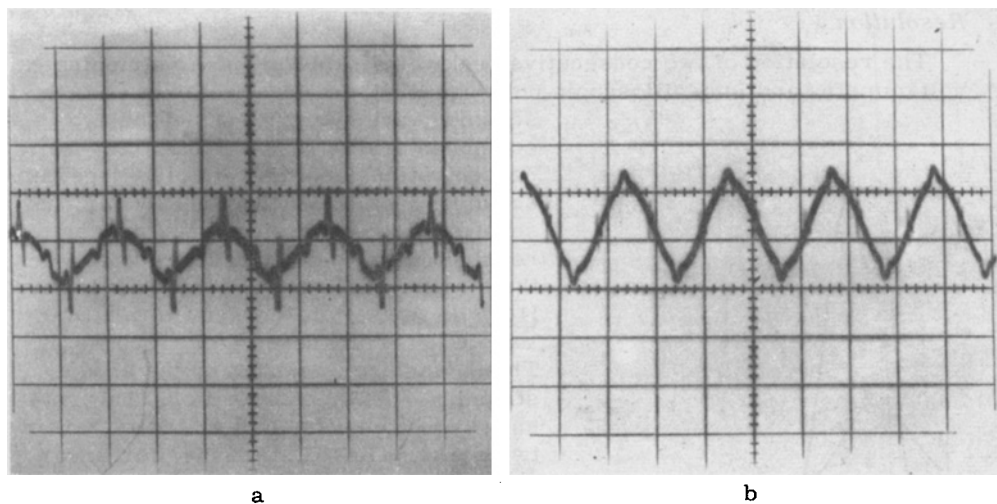a   b

Figure 2

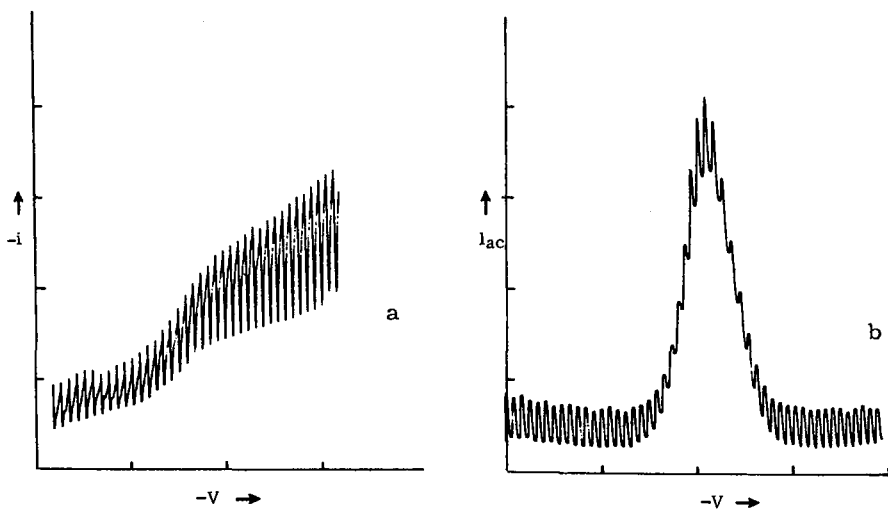a. Distortions in cell current; b. Smoothed out cell current, indicating faulty system.

Figure 3

Comparison of (a) regular and (b) A. C. polarograms obtained with a 10^{-5} M Zn^{+2}, 0.1 M KCl solution.

Experimental and Results

The experiments discussed below are described in detail under each figure in which the results are displayed. In principle, the methodology employed in the pre-electrolysis, rest period and scanning steps, is an exact replica of that accepted in regular anodic stripping voltammetry [2]; the only difference is the superposition of an a. c. potential on the linear voltage scan.

Resolution

The resolution of two consecutive peaks obtainable in anodic stripping voltammetry and in oscilloscopic polarography, for equal rates of voltage scanning, are similar. When the two components are present in similar concentrations and the rate of voltage scanning does not exceed 100 mv per second, two consecutive peaks may be resolved, provided the difference between their half-wave potentials, $\Delta E_{\frac{1}{2}} \geqslant 150 \, \mathrm{mv}$ [10]. In A. C. Polarography with a DME, resolution is improved ($\Delta E_{\frac{1}{2}} \geqslant 50 \, \mathrm{mv}$ [11].) This advantage is shared by the anodic stripping — A. C. combination. Figure 4 shows the comparison of the resolution of two peaks, with $\Delta E_{\frac{1}{2}} \approx 60 \, \mathrm{mv}$, for linear scan and a. c. anodic stripping.

For a species undergoing a two electron reaction, 10% of the peak height is reached when the potential difference: $E - E_p$ (between the electrode potential and the peak potential) is 47 mv (at 27°C); at 5% peak height, $E - E_p$ is 56 mv, and at 1% — 78 mv. These figures allow the calculation of the error resulting from the overlapping of two consecutive peaks: for two peaks of equal height, and whose peak potentials differ by 75 mv, this error does not exceed 1% (no quantitative evaluation is possible, in the parallel case, when plain anodic stripping is employed, owing to almost complete overlapping of the peaks).
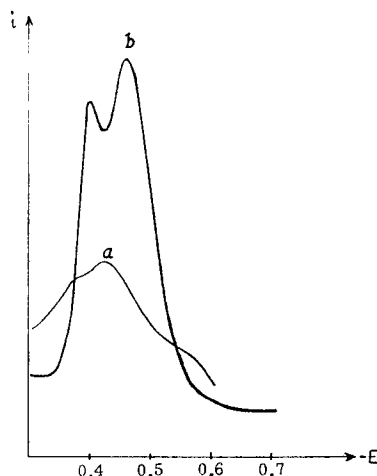

Figure 4

Comparison of resolution of consecutive peaks in the methods of plain anodic stripping and the A. C. - anodic stripping combination $2 \times 10^{-7} \mathrm{M} \, Pb^{+2}$ and $2 \times 10^{-7} \mathrm{M} \, Tl^{+1}$ in 0.1M KCl solution; $\Delta E_{\frac{1}{2}} = 60 \, \mathrm{mv}$; electrolysis potential: - 1.0 v vs SCE; stripping scan range :- 0.7 v to - 0.35 v vs SCE.
a. anodic stripping: electrolysis period: 10 min; rate of linear voltage scan: 3 mv/sec; sensitivity 1 μA/full scale
b. A. C. - anodic stripping combination; electrolysis period: 1 min; alternating potential: 10 mv p-p; frequency: 80 cps; rate of linear voltage scan: 3 mv/sec.

Sensitivity

The sensitivity of A. C. Polarography exceeds that of the classical D. C. method; this has been illustrated in Figure 3.

Increased sensitivity is limited to ions undergoing reversible electrochemical reactions; irreversible reactions are accompanied by a

significant decrease in sensitivity (parallelling the decrease in the rate
constant of the electrochemical reaction). This sensitivity may be
exploited in the case of low concentrations of a reversibly reacting species
in the presence of considerable amounts of an irreversible reactant. In
favorable cases no interference due to the presence of the latter is evident.

The absence of oxygen interference has been cited by numerous authors
with regard to a. c. determinations of lead, cadmium, etc.

For reversible reactants, a comparison of plain anodic stripping with
the a. c. — anodic stripping combination (given the same experimental
conditions of stirring, pre-electrolysis, etc.) shows that the latter allows
sensitivity to be increased by one order of magnitude [7]. This increase
is retained, though to a lesser degree for slightly irreversible reactions.
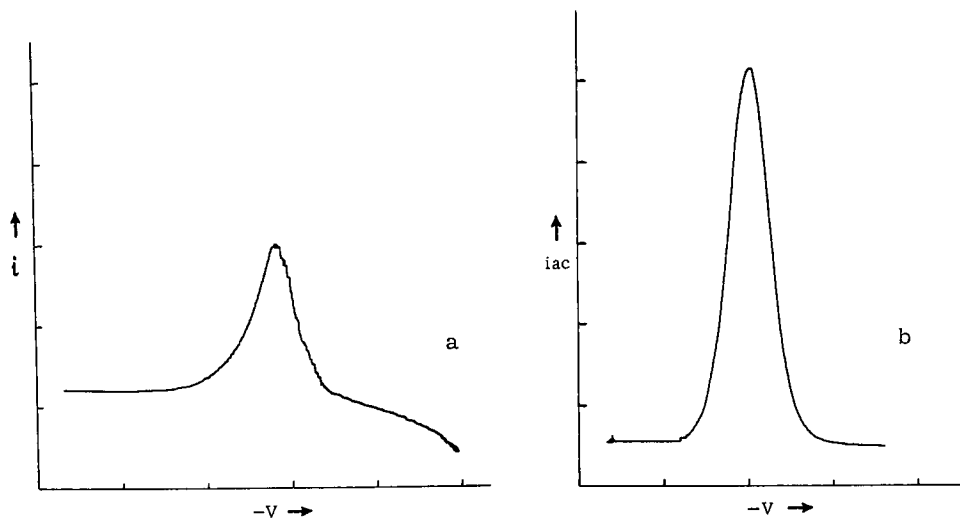

Figure 5

Comparison between: a. plain anodic stripping voltammetry and b. A. C. - anodic stripping combination
in 5×10^{-7}M Cd^{+2} solution, 0.1 M KCl; a. electrolysis period: 3 min; recorder sensitivity: 0.1 μA/div;
b. electrolysis period: 1 min; recorder sensitivity: 0.3 μA/div. Alternating potential: 10 mv p-p; frequency:
80 cps; rate of linear voltage scan: 3 mv/sec.

A 5×10^{-7} M zinc ion solution in 0.1 M HOAc buffer (pH 4.5) was used to
illustrate the method. The comparative results are shown in Figure 5.

Quantitative determinations

The a. c. current is proportional to the concentration of metal in the
amalgam, reaching its peak value when the electrode potential reaches the
value of the half-wave potential of the metal in the given supporting electro-
lyte (for reversible reactions) [7]. The concentration of the metal in
the amalgam is proportional to the concentration of the metal ion in
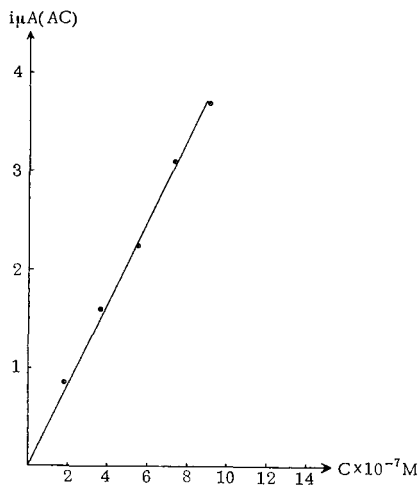
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iμA(AC)

Figure 6

Calibration graph for Zn^{+2}

Suporting electrolyte: 0.1 M KCl, (+ HCl,
pH 3); rate of linear voltage scan: 3 mv/sec;
frequency: 80 cps; alternating potential:
10 mv p-p.

the sample solution and may be calculated according to [12]. With careful control of all the experimental parameters of anodic stripping (stirring, cell geometry, pre-electrolysis time, etc.) a linear correlation between the peak height and the concentration of the metal ion in the original sample solution is obtained.

As in anodic stripping, quantitative evaluation is best effected by the method of standard addition (based, obviously, on the assumption of linear peak current — concentration correlation). Figure 6 shows a calibration curve obtained by this method.

The supporting electrolyte

The peak current depends, among other things, on the rate constant of the electrochemical reaction, which in turn is influenced by the nature and concentration of the supporting electrolyte. This effect has been observed, in the case of zinc and cadmium, in KCl — HCl solutions, for square wave polarography [13]; a similar effect was detected when a combination of anodic stripping and square wave polarography were used [6].

In this work the cadmium peak was found to be unaffected by variations in KCl concentration of the supporting electrolyte, while the height of the zinc peak decreased appreciably with increased KCl content (up to about 0.1 M KCl). The shape of the peak height vs KCl concentration curves obtained were similar to those reported by Sturm and Ressel [13]. Similar results were obtained when KNO_3 was substituted for KCl (Figure 7).

As a consequence of the above, the amount of reagents employed in sample preparation should be kept as low as possible, so that the final supporting electrolyte is sufficiently dilute and sensitivity is not unduly impaired (for the determination of a metal ion present at the 10^{-6} M concentration level, the concentration of the supporting electrolyte need not exceed 10^{-3} M; a three electrode cell, exploiting potential control, removes difficulties resulting from solution resistance).

Polarographic experiments with a 10^{-4} M zinc ion solution, at varying concentrations of KCl (0.03 M to 0.4 M KCl) confirmed that the reversibility of the electrochemical zinc reaction decreases with increasing KCl concentration.
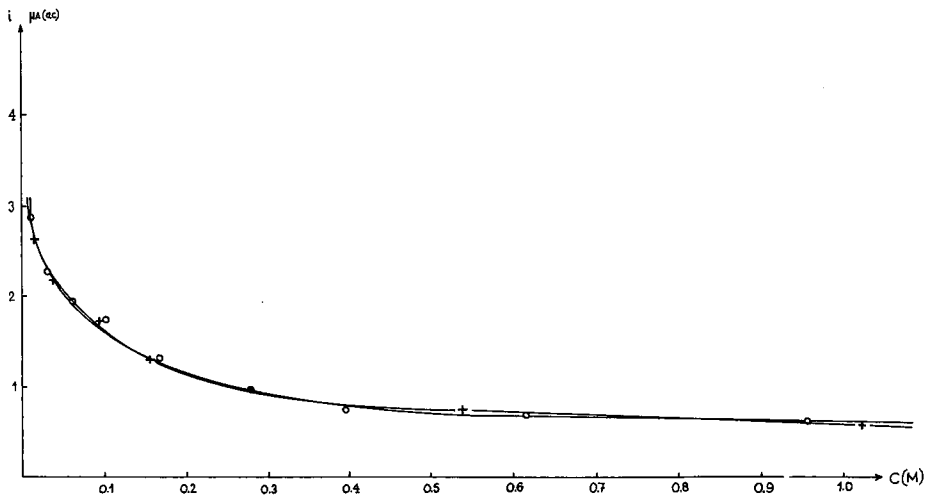
Figure 7

Height of zinc peak as a function of the supporting electrolyte concentration

Concentration of zinc ion solution: 6.5×10^{-7} M; pH 4.5; electrolysis period: 1 min; frequency: 80 cps; alternating potential: 10 mv p-p; rate of linear voltage scan: 800 mv/min. + —KNO$_3$ solution; o — KCl solution.

Oxygen

Oxygen is reduced irreversibly at the mercury electrode and has, therefore, been considered harmless in the course of the a. c. polarography of reversibly reduced species [11].

In this work the zinc oxidation peak was recorded at -0.96 v vs SCE (in 0.1 M KCl); however, an additional peak was frequently observed at -1.10 v, disappearing whenever oxygen had been scrupulously removed from the sample solution.

The splitting of the zinc peak has been reported for 10^{-3} M zinc ion solution [14]. It seems that during pre-electrolysis, at -1.2 v vs SCE, oxygen present in the sample solution is reduced according to: $O_2 \rightarrow 2OH^-$; as a result, during the subsequent rest period (without stirring), the pH of the solution in the vicinity of the electrode rises; if the sample solution has a pH in the 5—6 range, the vicinity of the electrode becomes suffi- ciently basic for zinc hydroxide to form, giving rise to the additional peak. At the same time, the height of the normal zinc oxidation peak is decreased. This effect is also observed in KCl — HCl solutions of pH 4.5.

The decreased height of the normal zinc peak, in the presence of the additional (zinc hydroxide) peak, may be ascribed to the impeding influence of film formation on the electrode surface.

Applications of the method

The determination of zinc in NBS sample No. 91 (Opal Glass containing 0.08% ZnO) was chosen to illustrate the practical potentialities of the method. The sample was dissolved by acid attack, diluted and its pH

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adjusted to 3; an aliquot was introduced into the electrolysis cell
containing 0.05 M KCl (adjusted to pH 3) and analysed. The results obtained
agreed with those obtained by regular anodic stripping [15]. For samples
with low zinc content, a considerable saving of electrolysis time is obtained.

The presence of traces of platinum (frequently introduced from the
platinum utensils, during sample attack) diminishes the height of the zinc
peak in anodic stripping voltammetry [15]; this effect has been observed
in this work. The zinc peak decreases linearly with increased platinum
concentration, finally disappearing entirely (Figure 8). In contrast to
anodic stripping voltammetry the base line is unaffected by the catalytic
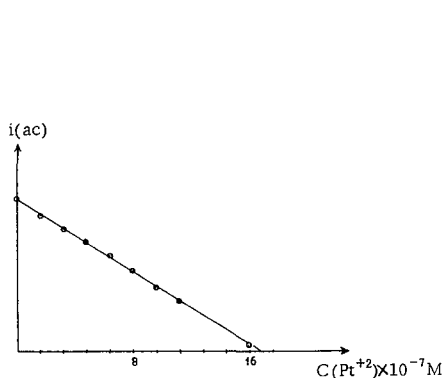hydrogen reduction [15].

Figure 8

Figure 9

Height of zinc peak as function of the concentra-
tion of platinum ions.
6.9×10^{-7} m Zn^{+2} in 0.1 M KCl (+HCl, pH = 2.5)
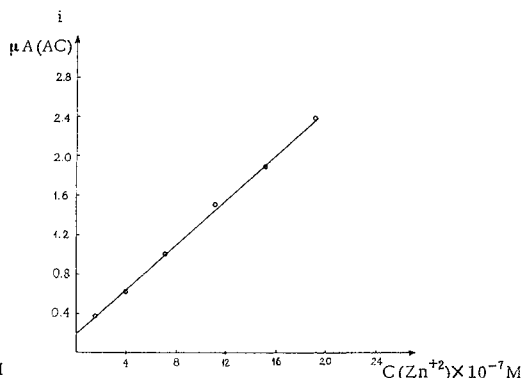solution. Frequency: 180 cps; alternating
potential: 10 mv p-p.

Calibration graph for Zn^{+2} in the presence of
1.6×10^{-4} M Fe^{+3}.
Supporting electrolyte: 0.1 M KCl solution (+HCl,
pH 2.8); rate of linear voltage scan: 3 mv/sec;
alternating potential: 10 mv p-p; frequency: 80 cps.

The simultaneous reduction of iron was shown to be a source of potential
interference in the determination of zinc in silicates by anodic stripping
voltammetry [15]; no such interference is observed in the a. c. — anodic
stripping combination, since the $Fe^{+3} \rightarrow Fe^{+2}$ reduction proceeds
irreversibly in the medium employed (KCl solution); zinc may, therefore,
be determined in the presence of considerable iron (Figure 9).

The choice of pre-electrolysis potential becomes critical in this case;
at the potential chosen (-1.2 v vs SCE), the reduction of ferrous iron to
metal does not occur; whenever more negative (up to - 1.5 v) potentials
were used, the height of the zinc peak decreased. A similar effect has
been reported [16] and attributed to the formation of compounds of the
type $Fe_x Zn_y$.

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