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ALTERNATING CURRENT POLAROGRAPHY:
DETERMINATION OF THE TRANSFER COEFFICIENT OF
ELECTROCHEMICAL PROCESSES

by

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ALTERNATING CURRENT POLAROGRAPHY: DETERMINATION OF THE TRANSFER
COEFFICIENT OF ELECTROCHEMICAL PROCESSES

ABSTRACT

The present paper is the second produced as the result of a critical investigation of the methodology of a.c. polarography from the viewpoint of its eventual application to studying the nature of organic electrode processes and the effects of experimental conditions, and to organic analysis.

The apparatus and technic previously described for use in sinusoidal wave alternating current polarography have been simply modified to permit the determination of the transfer coefficients for electrochemical reactions. The procedure developed is a modification of that proposed by van Cakenberghe, which is based on measurement of the even harmonics of the alternating current. The improved procedure is simple and rapid, and permits determination of the transfer coefficient to a precision of about ± 0.01 or ± 0.02 . The apparatus, operation and critical features are described in some detail. The proposed procedure was used to measure the transfer coefficients for the reduction of Cd(II) at the D.M.E. in various media. A significant difference was observed between the values in potassium chloride and sodium sulfate solutions; the value in hydrochloric acid solution is midway between the other two. No significant changes in the transfer coefficient were apparent on varying the concentrations of Cd(II) or of background electrolyte, the temperature, or the amplitude and frequency of the superposed alternating potential.

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ALTERNATING CURRENT POLAROGRAPHY: DETERMINATION OF THE TRANSFER
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Abstract

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The apparatus and technic previously described for use in sinusoidal wave alternating current polarography have been simply modified to permit the determination of the transfer coefficients for electrochemical reactions. The procedure developed is a modification of that proposed by van Cakenberghe, which is based on measurement of the even harmonics of the alternating current. The improved procedure is simple and rapid, and permits determination of the transfer coefficient to a precision of about ± 0.01 or ± 0.02 . The apparatus, operation and critical features are described in some detail. The proposed procedure was used to measure the transfer coefficients for the reduction of Cd(II) at the D.M.E. in various media. A significant difference was observed between the values in potassium chloride and sodium sulfate solutions; the value in hydrochloric acid solution is midway between the other two. No significant changes in the transfer coefficient were apparent on varying the concentrations of Cd(II) or of background electrolyte, the temperature, or the amplitude and frequency of the superposed alternating potential.

Van Cakenberghe (5) has shown mathematically, from the theory of absolute reaction rates, that the alternating current, produced under polarographic conditions as a result of a superposed alternating potential of small amplitude, should contain harmonics of the fundamental frequency. Furthermore, the even harmonics should disappear at the point of symmetry of the polarographic curve, i.e., at the symmetry potential. For a perfectly reversible reaction the latter

would occur at the half-wave potential, $E_{1/2}$; for other than a perfectly reversible reaction, the point of disappearance of the even harmonics would be at some other potential, E_z . The potential difference between $E_{1/2}$ and E_z can be used to calculate the ratio of C_O/C_R where C_O and C_R represent the concentrations of the oxidized and reduced species in the electrode reaction

at the potential E_z , provided that the potential difference is not too great, i.e., does not exceed ca. 0.1 volt. The transfer coefficient can then be calculated from the ratio C_O/C_R .

The transfer coefficient, α , is defined as the coefficient of transformation of electrical energy into energy of activation or, as it is usually described, as the fraction of the applied potential effective in the forward reaction; $(1 - \alpha)$ is then obviously the fraction of the applied potential effective in the reverse reaction. Van Cakenberghe reported values of the transfer coefficient at the dropping mercury electrode (D.M.E.) for the reduction of phenosofranine and of four metal ions [Cd(II), Co(II), Mn(II), Pb(II); no value could be determined for Co(II) under the experimental conditions used.] Despite the possibilities inherent in this approach as a rapid method for determining transfer coefficients, no other work with the method has been published since van Cakenberghe's 1951 paper.

In a previous study of alternating current (a.c.) polarography employing a superposed sinusoidal alternating potential of millivoltage amplitude (2), it was mentioned that the apparatus used could also be used to measure the transfer coefficient in the way suggested by van Cakenberghe, by the incorporation of a suitable frequency filter. Such a filter has now been found. The present paper describes the apparatus and method developed, and reports results obtained for

the reduction at the D.M.E. of cadmium(II) in a variety of media.

APPARATUS SELECTION

Van Cakenberghe (5) used a tuned amplifier to transmit selectively the second harmonic of the alternating current to the screen of a cathode ray oscillograph. The resulting current consisted, near the symmetry potential, of a very appreciable amount of the fundamental frequency as well as of the harmonics. Consequently, the potential of zero harmonics was determined by finding the potential at which the current (fundamental frequency) displayed an undistorted sinusoidal form.

In the apparatus previously described by the authors (2) for a.c. polarography, a vacuum-tube voltmeter is used to measure accurately the magnitude of the alternating current. If it were possible to obtain a frequency filter which would pass a negligible amount of the main frequency compared to the harmonic, this VTVM could be used to measure the actual magnitude of the harmonic current as a function of the polarizing potential. In this way, the potential of zero harmonics could be estimated with more certainty than is involved in deciding whether or not a particular waveform on the CRO is perfectly sinusoidal; this is particularly so since a D.M.E. does not produce a steady trace on the screen.

Furthermore, it seemed desirable for at least two reasons to obtain a frequency filter which could be readily adjusted for work at various frequencies: (a) flexibility in the first instance in permitting the choice of a suitable frequency, which choice could be quite critical because of the frequency dependence of the faradaic and capacitative impedances, and (b) possibility of being able to investigate possible changes of the measured transfer coefficient with frequency. A filter satisfying the requirements outlined has been found in the combination in series of two "Selectoject" units (1). The Selectoject is a circuit which can be used either as a sharp amplifier or as a single frequency rejection filter.

Frequency Filter. Two Selectoject units constructed in accordance with the

published circuit (1; Fig. 1), were placed between the first and second stages of the amplifier previously described, i.e., between switch S_1 and tube V_2 in Figure 8 of reference 2. These units are connected to the amplifier via a four-position switch, permitting the use of neither unit, of either one separately, or of the two in series.

Other Electronic and Electrical Instrumentation. With the exception of the Selectoject units, the electronic instruments used were the same as those previously described (2); the Elecdropode was replaced by a regular potentiometer-galvanometer arrangement.

A Leeds & Northrup No. 141023 potentiometer was used to supply the steady d.c. polarizing potential. Its scale is marked in one-mv. divisions, large enough to permit readings to be made to 0.2 mv.; the slidewire itself is sufficiently long to enable the polarizing potential to be changed by much smaller fractions of a millivolt. The Leeds & Northrup No. 2430D galvanometer used had an internal resistance of 495 ohms and a period of 3.3 secs. Its critical damping resistance of 23,000 ohms was effected by placing a 20,300-ohm resistor in series with an Ayrton shunt of 2000 ohms total resistance. The maximum sensitivity of the galvanometer was 0.46 μ a. full scale (10 cm.) deflection.

Dropping Mercury Electrode. The capillary used was Corning marine barometer tubing, 6 cm. long, and had the following characteristics at -0.6 v. vs. S.C.E. in 0.5 M potassium chloride solution at $h = 26$ cm.: $t = 4.6$ sec. and $m = 2.52$ mg./sec.

Cell. A water-jacketed H-cell, maintained ^{at} ~~at~~ 25° except for the temperature variation runs, was used with a saturated calomel reference electrode for the runs in chloride solution and with a saturated mercurous sulfate electrode for the runs in sulfate solution.

EXPERIMENTAL PROCEDURE: CRITICAL FEATURES

Use of the Frequency Filter. It has been found to be more advantageous to use both Selectojects as selective amplifiers of the second harmonic, rather than as narrow-band rejectors of the fundamental frequency. The reason for this is that in the latter case and under the conditions used in the present study, 60-cycle stray current of magnitude equal to or greater than that of the second harmonic is also passed by the filters. In the former approach, however, the second harmonic is amplified selectively with respect to the 60-cycle stray as well as with respect to the fundamental frequency.

Adjustment of the Frequency Filter. The Selectojects are adjusted in the following manner:

The polarographic cell is replaced by a resistor of a few hundred ohms. The master switch (Fig. 1) is put in position 2, and the ganged switch S_1 - S_2 of Selectoject No. 1 is put in the amplifier position. A potential of a few millivolts is applied across the resistor at a frequency of $2F$ c.p.s., where F c.p.s. is the frequency which is to be used in the experiments.

The amplification control R_{11} is put in an intermediate position; at one extreme setting, no amplification results, while towards the other extreme, the unit oscillates. The frequency control R_{12} - R_{13} is then adjusted until there is a maximum current response on the output VTVM (K in Fig. 2 of reference 2). The alternating potential is then switched off and the amplification control advanced until oscillation occurs, resulting in a large current reading on the VTVM; the control is then turned back until the current just returns to zero. At this point, the Selectoject displays the maximum selective amplification. The setting of the frequency control R_{12} - R_{13} is then checked; it may need slight readjustment. The adjustments outlined are highly critical and must be made very carefully.

With the master switch in position 3, the same adjustments are now made to Selectoject No. 2.

The switch is then put in position 4 and the oscillator is set to deliver the desired frequency of F c.p.s. It is not sufficient for this purpose to use the calibrated scale on the oscillator. Conveniently, use can be made of the fact that some harmonics are produced in the circuit itself: as a result of this, the current response through the Selectojects passes through a maximum not only at a frequency of 2F c.p.s. (B, Fig. 2), but also through a small but usually easily discernible maximum at the frequency of F c.p.s. (A, Fig. 2). The oscillator is set at the peak of the latter maximum.

The polarographic cell is now replaced in the circuit.

Variation of the Harmonics Current as a Function of the Steady Potential.

Outside the potential range where a redox process occurs, the observed alternating current is due to the capacity of the double layer at the D.M.E. and contains no appreciable amount of current due to harmonics. In the potential region where a redox process occurs, the faradaic alternating current is due to harmonics, as well as to the fundamental frequency. These harmonics are at a minimum at some potential in this range (5; Figs. 3 and 4). The magnitude of the harmonics increases more than linearly with increasing amplitude of the alternating potential (Fig. 4). Qualitatively, this can be readily explained: for small amplitudes of the alternating potential the current-potential characteristic, i.e., the d.c. polarographic curve, simulates linearity; with higher amplitudes the section of the curve "scanned" by the alternating potential becomes increasingly non-linear; the production of harmonics is presumably due to the same factors as the non-linearity of the curve.

These facts are of great importance when measurements are made to locate E_2 with the apparatus described. The adjustment of the frequency filter is so delicate that it is inadvisable to attempt to duplicate settings by dial calibration and reading; trial and error procedure, as described, is rapid and yields reproducible

results. If the setting is not the best possible one, results are obtained as shown in Fig. 3: at low amplitudes of the alternating potential, the minimum of the harmonics is not very pronounced, since the current being measured contains a very appreciable amount of the fundamental, and the magnitude of the latter reaches a maximum near the potential where the harmonics are at a minimum (Fig. 5). At higher amplitudes, the faradaic current contains a higher percentage of harmonics, since the latter increase more than linearly with amplitude while the fundamental increases only as $\tanh (nF \Delta V_0 / 2RT)$, i.e., somewhat less than linearly (2). Thus, the minimum of the harmonics current at E_Z can be more accurately located at higher amplitudes. Further, since the actual value of E_Z and E_S (peak of the total alternating current) are not exactly equal (Fig. 5), increasing the amplitude of the alternating potential results in a shift of the observed value of E_Z until a limiting value is reached at higher amplitudes (Fig. 3). However, even at amplitudes of the order of 30 or 40 mv., the minimum of the harmonics, E_Z , can be located to within a fraction of a millivolt.

If the setting of the frequency filter is the best obtainable, E_Z can be located accurately even at amplitudes of the alternating potential of the order of a few millivolts, and does not detectably change with changing amplitude (Fig. 4). This is of practical importance; if the frequency filter setting is not quite ideal, E_Z can still be accurately located by using alternating potential amplitudes of the order of 10 to 30 mv., provided that one is in the range of amplitudes where E_Z is constant. However, the use of high amplitudes can produce disturbances in the dropping of the capillary electrode, which must be avoided (4, 10).

Determination of the Transfer Coefficient. In order to calculate the transfer coefficient, it is necessary to know the relative concentrations of the oxidized and reduced species at the electrode at E_Z . There are at least two possible ways of achieving this:

Van Cakenberghe measured E_2 accurately and tried to measure $E_{\frac{1}{2}}$ equally accurately from the polarographic curve. From the difference, $E_{\frac{1}{2}} - E_2$, the ratio C_O/C_R was calculated by the Nernst equation. It is apparent that the latter will be justified only for reactions which are ideally reversible.

A more generally valid method which was used in the present study, is to measure the direct current, i_2 , at the potential E_2 and, by comparing this current with i_d from the d.c. polarogram, to calculate the ratio C_O/C_R directly from the relation (cf. 7)

$$\frac{C_O}{C_R} = \left(\frac{D_R}{D_O} \right)^{\frac{1}{2}} \frac{i_d - i_2}{i_2} \quad (2)$$

In this procedure, E_2 and $E_{\frac{1}{2}}$ need not be measured accurately. First the d.c. polarogram is plotted, and then the polarizing potential is adjusted until the alternating current flowing (due to the second harmonic) is at a minimum in the potential range where the reduction occurs. The deflection of the d.c. galvanometer at this point then represents the desired current i_2 . This latter method does not depend on the reversibility of the process, but only on the validity of assuming diffusion control, which can be readily verified by measuring the variation of the limiting current with temperature or with drop-time.

Knowing the ratio C_O/C_R , the transfer coefficient can be calculated from the equation (5)

$$\alpha = \frac{-C_R \pm (C_O C_R)^{\frac{1}{2}}}{C_O - C_R} \quad (3)$$

which may be written as follows by setting $p = C_O/C_R$

$$\alpha = \frac{-1 \pm p^{\frac{1}{2}}}{p - 1} \quad (4)$$

TRANSFER COEFFICIENT FOR CADMIUM REDUCTION

The experimental procedure outlined was used to determine the transfer coefficient for the reduction of Cd(II) at the D.M.E. in hydrochloric acid, potassium chloride and sodium sulfate solutions under various experimental conditions. For the calculation of C_O/C_R from equation 2, the values of the diffusion coefficients used were based on $D_O = 0.70 \times 10^{-5} \text{ cm.}^2 \text{ sec.}^{-1}$ in 0.1 M KCl (2); values of D_O in other electrolytes were calculated from the diffusion current constants observed in the present work relative to the value found in 0.1 M KCl (Table I); a value of $1.61 \times 10^{-5} \text{ cm.}^2 \text{ sec.}^{-1}$ was used for D_R (6; mean of the five values quoted). There is a possible uncertainty in using the latter value which was obtained for a dropping amalgam electrode, for a D.M.E.

Variation with Amplitude of the Alternating Potential. Measurements could not be made accurately with alternating potentials of amplitude less than ca. 2 mv. or greater than ca. 40 mv. Within this range, there is no detectable variation in the magnitude of the transfer coefficient, i.e., no change in E_T .

Variation with Frequency of the Alternating Potential. At frequencies below ca. 100 c.p.s., the Selectojects do not discriminate sufficiently to allow useful measurements to be made. At frequencies above several hundred cycles, it was again not possible to observe a sharp minimum of the harmonics current; this limiting frequency was higher, the greater the concentration of the reducible species. The difficulty at these higher frequencies resides not in the frequency filter, but in the electrochemical system itself. At higher frequencies, the major part of the current is not faradaic but capacitative, and consequently the harmonics of the faradaic current become a smaller and smaller fraction of the total current. As a result, the current passed by the filters contains an increasing amount of the fundamental frequency, and the minimum of the harmonics cannot be accurately located.

Thus, the most useful measurements were possible only in a limited frequency range, within which there was no detectable variation of the transfer coefficient with frequency (Table II).

Variation with Temperature. No significant variation was observed in the transfer coefficient in the temperature range of 11° to 45°C. (Table III).

Variation with Concentration. Over a ten-fold Cd(II) range concentration in various media there was no significant change in the value of the transfer coefficient (Table IV).

Variation with Nature and Concentration of Base Electrolyte. There was no significant variation in the magnitude of the transfer coefficient with change in concentration of the background electrolyte, for potassium chloride and sodium sulfate solutions. However, there was a definite difference between the values found in chloride and in sulfate (Table V). In potassium chloride, the transfer coefficient was 0.44 to 0.45; in sodium sulfate, 0.37 to 0.38; and in hydrochloric acid, 0.41. The probable error in these values is about 0.02, as far as the reproducibility of the measurements is concerned.

The uncertainty in the values of the diffusion coefficients used introduces a further possible inaccuracy. However, the possible variations in the values of D_0 will not be great, judging from values currently used in the literature. The error₁ due to this uncertainty in the transfer coefficients calculated in the present study will not be greater than 0.01. Accordingly, the difference between the values found in potassium chloride and in sodium sulfate is almost certainly a significant one, whereas that between potassium chloride and hydrochloric acid solutions, however, may not be significant.

APPLICABILITY AND LIMITATIONS

The method proposed by van Cakenberghe (5) for the determination of the transfer coefficient for an electrochemical reaction by means of measurement of

produced as a result of a superposed alternating potential the harmonics of a superposed alternating current, has been thoroughly investigated and improved. An apparatus is described which can be used to measure the absolute magnitude of the harmonics, rather than only to locate the potential of minimum harmonics. The technique described permits the latter potential to be readily located to fractions of a millivolt.

Calculation of the transfer coefficient from the experimental results requires knowledge of the diffusion coefficients of the oxidized and reduced species. However, an error in these values does not produce an appreciable error in the magnitude of the transfer coefficient, since these quantities enter the calculation only as the square root of their ratio.

The method has been applied to the study of Cd(II) in various media. A significant difference has been observed between the values of the transfer coefficient in potassium chloride solution, and those in sodium sulfate solution. No significant changes in the transfer coefficient could be observed with amplitude of the alternating potential, with frequency, with temperature, with changing concentration of the reducible species, or with changing concentration of the background electrolyte.

Unfortunately, entirely adequate data is not available for comparing the transfer coefficients determined in the present study with the results of other approaches. Van Cakenberghe (5) reported α to be 0.50 for Cd(II) reduction at the D.M.E. electrode from 0.1 M potassium chloride solution; a value of 0.14 was found in the present study for a similar situation. Gerischer (8) who employed electrolysis with superimposed alternating potential found a transfer coefficient of 0.17 ± 0.02 for Cd(II) reduction at a hanging drop cadmium amalgam electrode from 0.5 M sodium sulfate solution; Berzins and Delahay (3), using potential-time curves, found α for similar conditions but in 1 M Na_2SO_4 solution to be 0.21 or

0.23, depending on the method of computation employed. Transfer coefficients found in the present study for Cd(II) reduction at the D.M.E. are 0.38 and 0.37 for 0.5 M and 1.0 M Na_2SO_4 solutions, respectively. It is apparent that future work with the method described in the present paper should include the investigation of Cd(II) solutions employing cadmium amalgam electrodes.

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Table I. Diffusion Coefficients of Cd(II) in Various Media at 25°C.

Base Solution	Diffusion Current Constant	Diffusion Coefficient ^a 10 ⁵ cm. ² sec. ⁻¹
1.0 M KCl	3.90	0.84
0.5 M KCl	3.77	0.77
0.1 M KCl	3.56	0.70 ^b
0.5 M HCl	3.73	0.77
1.0 M Na ₂ SO ₄	2.43	0.33
0.5 M Na ₂ SO ₄	2.72	0.41

^aCalculated from the diffusion current constant
relative to the value in 0.1 M KCl

^bValue taken from literature (9)

Table II. Transfer Coefficient of Cd(II) as a Function of Frequency in Various Media at 25°C.

System Studied	Frequency c.p.s.	Transfer Coefficient	Number of Detns. ^a
9.28×10^{-4} M Cd(II) in 1.0 M Na ₂ SO ₄	100	0.37	2
	200	0.37	1
	350	0.38	3
	500	0.39	1
	750	0.35	1
1.86×10^{-4} M Cd(II) in 1.0 M Na ₂ SO ₄	200	0.38	1
	350	0.36	1
	500	0.37	2
4.64×10^{-4} M Cd(II) in 0.5 M Na ₂ SO ₄	100	0.41	1
	200	0.38	2
	350	0.38	3
	500	0.39	2
	650	0.38	1
3.7×10^{-4} M Cd(II) in 0.5 M HCl	100	0.38	2
	200	0.42	3
	350	0.41	5
1.2×10^{-4} M Cd(II) in 0.5 M HCl	100	0.41	2
	200	0.39	3
	350	0.43	1
9.55×10^{-4} M Cd(II) in 1.0 M KCl	100	0.45	1
	200	0.46	1
	350	0.47	1
	500	0.46	1
	700	0.47	1

^aThe largest spread in any set of replicate determinations of the transfer coefficient was 0.04. The maximum deviation of any individual result in a set from the mean for that set was 0.02.

Table III. Variation of Transfer Coefficient of Cd(II) With Temperature^a

Temperature °C	Transfer Coefficient	Number of Detns.
11	0.46	2
25	0.42	3
45	0.45	2

^aThe data were obtained at 350 c.p.s. for 0.955×10^{-4} M Cd(II)
in 0.5 M KCl solution

Table IV. Variation of Transfer Coefficient of Cd(II)
with Concentration at 25°C.

Base Solution	Cadmium Concn. 10^{-4} M	Transfer Coefficient	Number of Detns.
0.5 M KCl	9.55	0.46	3
	4.78	0.45	2
	0.955	0.44	5
1.0 M Na ₂ SO ₄	9.28	0.37	8
	3.72	0.33	1
	1.86	0.37	4
0.5 M HCl	3.7	0.41	10
	1.2	0.40	6

Table V. Transfer Coefficient of Cd(II) in Various Media at 25°

Base Solution	Transfer Coefficient	Number of Detns.
0.1 <u>M</u> KCl	0.44	5
0.5 <u>M</u> KCl	0.45	10
1.0 <u>M</u> KCl	0.45	3
0.5 <u>M</u> HCl	0.41	16
0.5 <u>M</u> Na ₂ SO ₄	0.38	2
1.0 <u>M</u> Na ₂ SO ₄	0.37	13

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Figure Captions

Figure 1. Frequency filter. The two Selectoject units are identical. Current requirements are ca. 4 ma. for each unit. The 150-volt +B is obtained from the 400-v. power supply by use of a VR 150 and a dropping resistor of ca. 27 K. Master switch positions: 1 - frequency filter shorted; 2 - Selectoject No. 1 operating; 3 - Selectoject No. 2 operating; 4 - both Selectojects operating in series. Selectoject circuit:

C_1	0.01 μ f	R_2	1 K ^b	R_{11}	500 pot ^d
C_2	0.1	R_3	1 K ^b	R_{12}	5 M ^e
C_3	0.1	R_4	2 K ^c	R_{13}	5 M ^e
C_4	0.002	R_5	2 K ^c	R_{14}	120 K
C_5	0.05	R_6	20 K	V_1, V_2	12AX7
C_6	16 ^a	R_7	2 K	S_1-S_2	DPDT ganged
C_7	0.0002	R_8	10 K	positions (1 - Selective amplifier; 2 - Rejection filter)	
C_8	0.002	R_9	6 K		
R_1	1 M ohm	R_{10}	20 K		

^aElectrolytic condenser.

^{b, c}Matched pairs of resistors.

^dFrequency control (carbon potentiometer with 5:1 vernier dial).

^eAmplification control (ganged carbon potentiometers with 5:1 vernier dial).

Figure 2. Current passed by frequency filter, as a function of frequency, with the filter set to amplify selectively at a frequency of 2F c.p.s.

Figure 3. Selectojects imperfectly adjusted (solution of 9.55×10^{-4} M Cd(II) in M KCl). Curves drawn on different, arbitrary scales to show relative ease of location of the minimum. Amplitude of alternating potential

across the cell: (A) 2 mv.; (B) 5 mv.; (C) 15 mv.; (D) 30 mv.

Figure 4. Selectojects properly adjusted (solution of 0.955×10^{-4} M Cd(II) in 0.5 M KCl). Amplitude of alternating potential: (A) 2 mv.; (B) 5 mv.

Figure 5. Total alternating current and harmonics current as a function of steady applied potential (solution of 1.2×10^{-4} M Cd(II) in 0.5 M HCl). Superposed alternating potential of 5 mv. amplitude across the cell at a frequency of 200 c.p.s. Continuous line represents the a.c. polarogram, i.e., the total alternating current flowing. Dashed line represents the harmonics present in the alternating current, measured by use of the frequency filter. The difference between E_s and E_z is less than 5 mv.

Frequency Filter Master Switch

FIGURE 2

FIGURE 3

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FIGURE 4

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FIGURE 5

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