

```

C 1 CYCLIC CHRONO, DIFFU-
    SION CONTROL, PLANE
    ELECTRODE, READ IN K
    NOSIG RR FRACT, TWO
    SOLUBLE SPECIES
    READ 900,K,NOSIG, RR,
    FRACT
    DIMENSION X(100),T(100),
    R(100)
C  GENERATION OF EQUA-
    TIONS
    DO 200 N = 1,K
    T(N) = 0.0
    M = 1
    LA = 0
10  DO 80 I = 1,N
    SUM = 0.0
    DO 60 J = I,N
60  SUM = SUM + T(J)
    X(I) = SQRTF(SUM)
80  CONTINUE
    Y = X (1) - 1.0
    IF (1 - N) 81,96,300
81  SIGN = 1.0
    DO 95 L = 2,N
    SIGN = -SIGN
95  Y = Y + SIGN * RR * X(L) -
    SIGN - SIGN * FRACT

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C 2 SOLVE GENERATED EQUA-
    TION BEGIN AT 96 READ
    IN NOSIG FOR ACCURACY
96  IF(M-1)300,100,102
100 Z = Y
    M = M + 1
102 IF (Z) 98,200,99
98  IF (Y) 71,200,73
99  IF (Y) 73,200,71
71  T(N) = T(N) + 10.0 **(-LA)
    GO TO 10
73  T(N) = T(N) - 10.0 **(-LA)
    LA = LA + 1
199 IF (NOSIG - LA) 300,200,71
200 CONTINUE
C 3 EQUATION SOLVED PRINT
    ANSWER
    DO 201 J = 1,K,2
201  R(J) = T(J)/T(J + 1)
    PRINT 903, RR, FRACT
    PRINT 901
    PRINT 902, [N,T(N),R(N),
    N = 1,K]
500 CONTINUE
900 FORMAT (2I10, 2F10.5)
901 FORMAT [4(3X, 1HN, 6X,
    4H TAU, 5X, 5HRATIO)]/]
902 FORMAT [4(1X, 1I3, 2F10.6)]/]

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903 FORMAT (5HRR =, F10.5,
    SHFRACT =, F10.5)
    GO TO 920
300 PRINT 905
905 FORMAT (2X, 5HERROR)
920 STOP
    END
    END

```

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# High Speed Controlled Potential Coulometry

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► An electrolysis cell for rapid controlled potential coulometric determinations, employing a large electrode area-to-solution volume ratio and using ultrasonic and nitrogen stirring, was designed. This cell allowed determinations to be performed with total electrolysis times of less than 100 seconds. The apparatus was tested by determining silver (I) and iodide by electrodeposition of silver and silver iodide, respectively. From 2.5 to 25  $\mu$ moles of each was determined with an average error of 2 to 0.2%. The application of this cell to the study of mechanisms of electrode reactions was also considered.

CONTROLLED potential coulometry has been useful both as an analytical technique and for the investigation of mechanisms of electrode reactions. The time required to perform a controlled potential determination is usually between 20 minutes and 2 hours, depending upon the experimental apparatus employed. Although controlled potential coulometric analysis has the advantage of being an absolute method—i.e., allowing the direct determination of the quantity of a substance without

reference to calibration curves, etc.—the long electrolysis times usually required sometimes discourage potential users of this technique. The aim of this study was to consider the factors governing the speed of an electrolysis, and to design a cell capable of performing a controlled potential coulometric analysis in a short time.

For a single electrode reaction carried out at potentials at which the rate of the reaction is limited by the rate of mass transfer of the electroactive species to the electrode, the current decays according to the equation (7)

$$i_t = i_0 e^{-pt} \quad (1)$$

where  $i_t$  is the current at time  $t$ ,  $i_0$  is the initial current, and  $p$  is a function of the electrode dimensions, solution volume, cell geometry, and rate of mass transfer. For a simple Nernst diffusion layer model of convection,  $p$  is given by the expression

$$p = DA/\delta V \quad (2)$$

where  $D$  is the diffusion coefficient of the electroactive species,  $A$  is the electrode area,  $V$  is the total solution volume, and  $\delta$  is the thickness of the diffusion layer. The actual dependence of  $p$  upon these variables is very complex,

and depends upon such experimental conditions as electrode shape, cell geometry, and turbulence of flow. It is probably better to write simply

$$p = f(A, 1/V, m) \quad (3)$$

where  $m$  is a mass transfer constant. There is frequently no direct proportionality between  $p$  and  $A$ ; the dimensions of the electrode, rather than the area, are more important (3). Completion of electrolysis is generally taken at the time when the current has decayed to 0.1% of its initial value, that is

$$t = 6.9/p \quad (4)$$

To decrease the electrolysis time,  $p$  must be made as large as possible. In this study an electrolysis cell was designed with a large electrode area-to-solution volume ratio, which employed ultrasonic and nitrogen stirring. With this cell an "effective  $p$ " of about 0.1 second<sup>-1</sup> was obtained, so that electrolysis times were only slightly longer than one minute.

#### EXPERIMENTAL

**Apparatus.** With a suitable potentiostat and coulometer, the design of the electrolysis cell usually governs the electrolysis time. After experi-

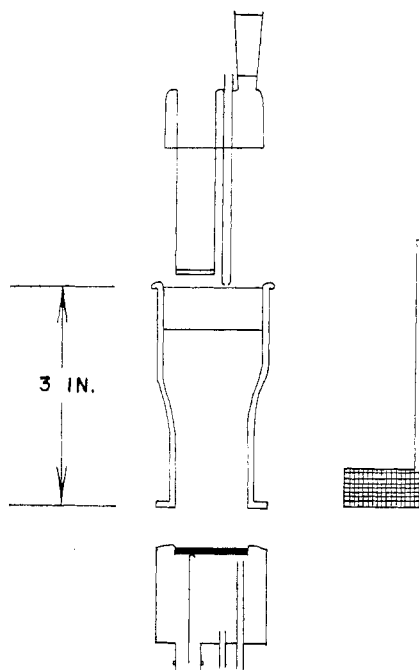


Figure 1. Schematic diagram of electrolysis cell

menting with several types of cells, we found the one shown schematically in Figure 1 to be most useful. Details of the cell construction are shown in Figure 2 and are described below. The solution volume was about 7.5 ml. when the cell was filled to slightly above the bottom of the auxiliary electrode chamber. A platinum gauze electrode, 6, wound in a tight spiral so as to fill the sample solution completely, was used as a working electrode. With this electrode design, the usual types of stirring by rotating the working electrode or by employing a propeller or magnetic stirrer could not be used. Ultrasonic stirring eliminated the need for moving parts within the cell, and by making the base of the cell a barium titanate transducer driven by an ultrasonic generator, effective stirring could be accomplished. A rapid flow of nitrogen through the solution also aided in increasing the mass transfer rate.

The base of the cell consisted of three pieces of machined brass. The bottom piece screwed into the second piece and held the ultrasonic transducer, 5, pressed between two Teflon gaskets, against the upper lip of the second piece. The upper Teflon gasket was shaped so that when the glass cell portion was finally attached, solution would not come in contact with the brass.

Electrical connection to the transducer was made with a BNC connector. The middle terminal, 2, was connected to one contact of the transducer; the

other contact of the transducer was connected by means of a small metal piece, 3, leading around the Teflon gasket and connecting to the brass wall of the piece. This, in turn, connected to the outside (ground) terminal of the BNC connector. An inlet, 1, was used to direct a stream of compressed air or other coolant against the transducer to cool it. The glass cell was held against the transducer by the upper threaded brass piece, which screwed onto the second brass piece and pressed the lip of the cell down against the transducer gasket.

Another Teflon gasket between the upper part of the cell lip and the upper machined brass piece relieved the strain on the glass lip. This rather complex mounting arrangement assured that the transducer and cell would be rigidly held in place and could be easily disassembled for cleaning or for making cell or transducer modifications. A simpler cell and transducer mounting could probably be designed.

The cell cover, which contained a tube closed at the bottom with a fine porosity sintered glass disk, 9, for the auxiliary electrode, 10, fitted to the cell body by means of a standard taper joint. Additional standard taper joint connections in the cell cover permitted the introduction of a reference electrode, 7, nitrogen, 8, and sample aliquots. With this arrangement, and because a stirrer did not have to be positioned, the cell could be assembled very rapidly.

The requirements for the potentiostat and coulometer are somewhat more stringent for high speed electrolysis than for the usual slower methods. The current changes so rapidly, es-

pecially in the early stages of electrolysis, that electromechanical potentiostats and coulometers cannot be used. In this investigation an electronic potentiostat, based on one commercially available from Brinkmann Instruments, Great Neck, L. I., N. Y., as a Wenking Potentiostat, with an output of about 25 volts at 250 ma. and a response time in the order of microseconds, was employed. The coulometer was based on a voltage-to-frequency converter and a digital counter (2). A block diagram of the apparatus is shown in Figure 3. A Sargent Model SR recorder, measuring the voltage drop over a standard resistor, was used to obtain current-time curves. Since the recorder could not follow the rapid current changes during the first few seconds of electrolysis, the ball-and-disk integrator which is connected to this recorder is not suitable for determining the total number of coulombs involved in the electrolysis. A Model 35 ultrasonic generator (McKenna Laboratories, Santa Monica, Calif.), operating at 1 Mc. per second at power levels up to 35 watts, was used with a one-inch barium titanate transducer in these experiments.

**Procedure.** The electrolyses were performed by adding about 7 ml. of supporting electrolyte solution to the cell, deaerating, and pre-electrolyzing the solution at the control potential

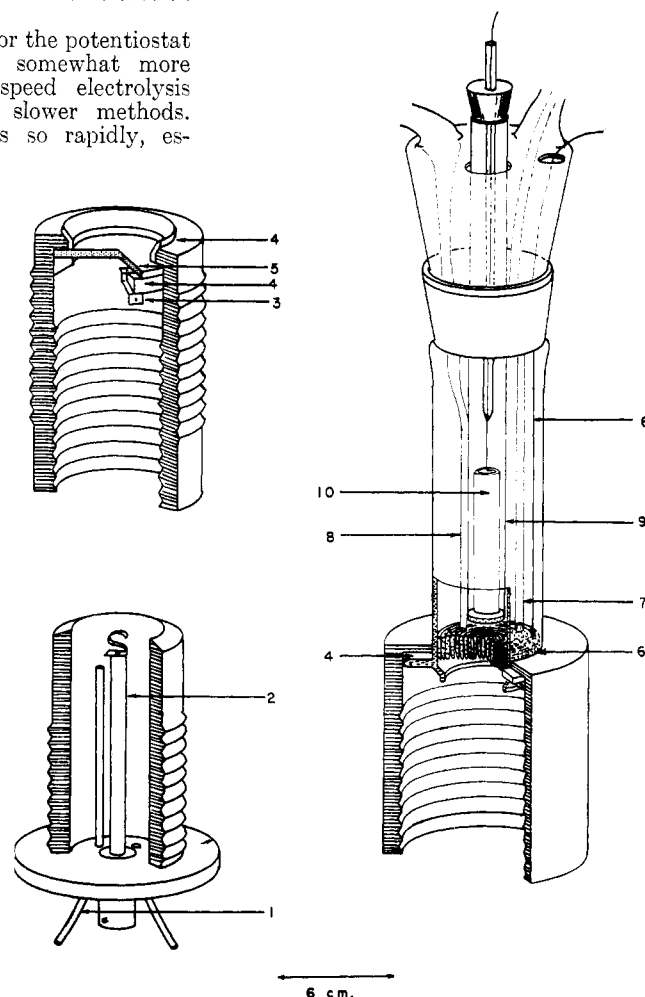


Figure 2. Detailed diagram of electrolysis cell

1. Compressed air inlet for cooling transducer. 2,3. Electrical connection to transducer. 4. Teflon gaskets. 5. Barium titanate ultrasonic transducer. 6. Platinum gauze electrode. 7. Reference electrode. 8. Nitrogen inlet. 9. Auxiliary electrode chamber. 10. Auxiliary electrode. The cell body was borosilicate glass. The transducer mounting was brass

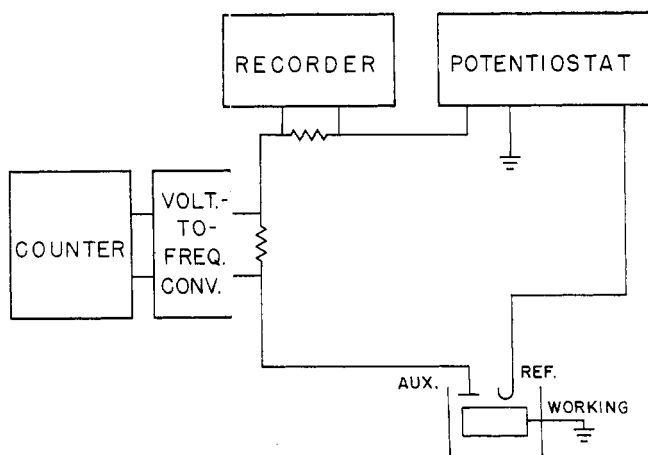


Figure 3. Block diagram of controlled potential coulometric analysis apparatus

until the background current reached a low, constant value. The counter was set for a preset time, the electrolysis started, and the sample introduced. At the completion of the electrolysis, the counter was reset and the correction due to the background current was determined. When sample volumes were kept small (500  $\mu$ l. or less), up to four determinations could be performed before the cell had to be cleaned and refilled with supporting electrolyte solution.

#### RESULTS

**Determination of Silver.** Silver was determined by plating onto the platinum electrode from 1M  $\text{KNO}_3$  at a potential of  $-0.40$  volt *vs.* a saturated mercurous sulfate electrode. Results of the analysis of 2.5 to 25  $\mu$ moles of silver are given in Table I. The total electrolysis time, including the time required for sample addition, was 100 seconds.

**Determination of Iodide.** Iodide was determined by formation of  $\text{AgI}$  upon anodic polarization of a silver-plated platinum electrode by the method of Lingane and Small (8), from a supporting electrolyte of 1M  $\text{KNO}_3$  at a potential of  $-0.20$  volt *vs.* a saturated mercurous sulfate electrode. Results of the analysis of 2.5 to 25  $\mu$ moles of iodide are shown in Table II. The cell has also been used successfully for a number of other electrolyses, including the electro-oxidation of hydrazine and iodide, and the electrolysis of diphenylpicryl hydrazyl in an acetonitrile medium. Details of this work will be presented elsewhere.

**Current-Time Behavior.** Figure 4 illustrates the effect of variation of the electrode area and stirring conditions during the determination of iodide ion upon  $\log i_t$  *vs.*  $t$  behavior. Similar behavior was found during the electroplating of silver. The curves are characterized generally by two slopes. The larger, initial slope of about 0.1 to 0.3  $\text{second}^{-1}$  appears on curves in both stirred and unstirred solutions

and apparently is involved with the electrolysis of material in the immediate vicinity of the electrode (within the diffusion layer). After about 6 to 8 seconds the slope changes to that characteristic of the rate of mass transfer. In unstirred solutions this slope is about 0.01  $\text{second}^{-1}$ , while in a solution with both ultrasonic and nitrogen agitation, it is about 0.05  $\text{second}^{-1}$ . Curve 3 in Figure 4 indicates that the current decays to 1 and 0.1% of its initial value in about 44 and 68 seconds, respectively, indicating an over-all effective- $p$  of about 0.1  $\text{second}^{-1}$ . Since the initial slope is usually not larger than 0.5  $\text{second}^{-1}$  (corresponding to a  $p$  of 1.2  $\text{second}^{-1}$ ), the electrolysis time would probably be no shorter than about 6 seconds with this cell, even with the best possible conditions.

The effect of ultrasonics on electrode reactions has been studied extensively (9, 11). Ultrasonics primarily increase the rate of mass transfer to the electrode, although alteration of the structure of metals deposited under the influence of ultrasonics has also been reported. Too high levels of ultrasonic power caused the solution to heat up very quickly and eventually boil. Ultrasonic radiation is also capable of causing sonochemical reactions (5, 10), such as the dissociation of water into hydrogen and hydroxyl radicals, which might react with the electroactive substance or cause an increase in the background current. Most of the electrolyses performed here were conducted at ultrasonic power levels of below 30 watts. In kinetic studies where a constant temperature is desirable electrolyses can be carried out with only nitrogen stirring at the expense of some increase in  $p$ . Higher levels of ultrasonic power, or radiation of a frequency different than the 1 megacycle per second employed in

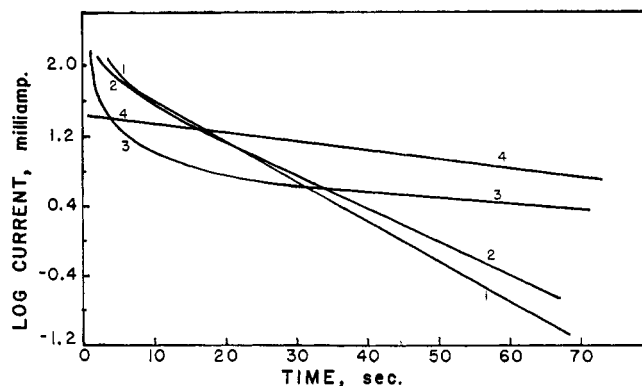


Figure 4. Effect of varying conditions upon log current vs. time behavior for electrodeposition of iodide as  $\text{AgI}$  on a silver anode. Solution contained 12.5  $\mu$ moles iodide in about 6.5 ml. of 1M  $\text{KNO}_3$ . Control potential was  $-0.20$  volt *vs.* saturated mercurous sulfate electrode

1. Gauze electrode, ultrasonic and nitrogen stirring
2. Gauze electrode, only nitrogen stirring
3. Gauze electrode, no stirring
4. Electrode of 16-gauge silver wire coils, ultrasonic and nitrogen stirring

these studies, may prove useful for more efficient mass transfer, especially in larger cells.

Nitrogen stirring had the disadvantage of causing droplets of solution to collect on the walls of the upper portions of the cell, leading to low results. Flushing down the cell walls with a small amount of the electrolysis solution withdrawn during the determination in a dropping pipet decreased errors due to this effect.

**Application to Electrode Mechanism Studies.** When secondary chemical reactions occur along with the electrolysis reaction, the number of coulombs of electricity consumed may be more or less than the amount ex-

Table I. Determination of Silver

Supporting electrolyte, 1M  $\text{KNO}_3$ . Solution volume, above 7 ml. Platinum electrode at  $-0.40$  volt *vs.* saturated mercurous sulfate electrode. Electrolysis time, 100 seconds

No. of determinations	Silver taken, $\mu$ moles	Silver found, $\mu$ moles	Av. dev., $\mu$ mole
4	2.501	2.447	0.035
3	12.50	12.42	0.04
4	25.01	24.94	0.28

Table II. Determination of Iodide

Supporting electrolyte, 1M  $\text{KNO}_3$ . Solution volume, about 7 ml. Silver-plated platinum electrode at  $-0.20$  volt *vs.* saturated mercurous sulfate electrode. Electrolysis time, 100 seconds

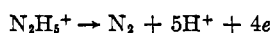
No. of determinations	Silver taken, $\mu$ moles	Silver found, $\mu$ moles	Av. dev., $\mu$ mole
4	2.500	2.463	0.101
3	12.50	12.43	0.03
2	25.00	25.04	0.14

**Table III. Effect of Side Reactions on Coulometric Oxidation of Hydrazine in Usual and High Speed Cell**

Supporting electrolyte, 0.05M H <sub>2</sub> SO <sub>4</sub>	
Hydrazine concentration, mM	$n^0_{app}$
Usual cell; <sup>a</sup>	
$p$ estimated at about $10^{-3}$ second <sup>-1</sup>	
0.1	4.02
1.0	3.80
10.0	3.27
High speed cell;	
$p = 1.2 \times 10^{-1}$ second <sup>-1</sup>	
3.3	3.83
16.0	3.80

<sup>a</sup> Data of Karp and Meites (6).

pected if only the electrode reaction occurs (1, 4). The variation of the amount of electricity consumed during an electrolysis has been used to explain the mechanism of electrode reactions and to estimate the rate constants of the secondary chemical reactions. For example, in a study of the controlled potential coulometric oxidation of hydrazine, Karp and Meites (6) found that because a chemical reaction consumed some electroactive material, the apparent number of coulombs per mole of hydrazine oxidized ( $n^0_{app}$ ) was less than the 4.00 expected on the basis of the electrode reaction alone (Table III).



Note that  $n^0_{app}$  decreases with increasing hydrazine concentration because the competing chemical reaction is second order in hydrazine. The extent of inter-

ference of the chemical reaction decreases as the rate of the electrolysis (governed by  $p$ ) increases. In the high speed cell the  $n^0_{app}$  values were closer to 4, even at high concentrations of hydrazine. Actually, because the potentiostat employed in this study had a limited current output, the cell was not operating under limiting current conditions during the total duration of the electrolysis, and the effective  $p$  was smaller than that obtained under optimal conditions. With a potentiostat of higher output capacity a  $p$  of about 0.1 second<sup>-1</sup> should be obtainable ( $p$  is practically independent of the concentration of the electroactive substance), and an  $n^0_{app}$  even closer to 4.00 should result (1).

#### CONCLUSIONS

Short electrolysis times yield advantages other than merely decreasing the analysis time. High speed controlled potential coulometry diminishes the effect of chemical side reactions during analytical determinations and permits the application of this technique to the study of electrode reactions where side reactions are occurring at faster rates. The accuracy of the coulometric determination should be increased, because the background current is increased less than the current due to the electroactive species. Transfer of solution into and out of the auxiliary electrode chamber is also less for a short electrolysis time. On the other hand, using large effective electrode areas increases the error due to charging of the electrical double layer. However, even for an electrode with an area of 100 sq. cm., this would amount to less than 1 mc.

(or 0.01  $\mu$ eq.) assuming a voltage change of 0.5 volt and a double layer capacity of 20  $\mu$ f. per sq. cm. The cell described here was useful only for electrolyses with solid electrodes. Constructing a cell for use with mercury cathodes is apparently more difficult and is currently being investigated.

#### ACKNOWLEDGMENT

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## Polarography of Selenium(IV)

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► As many as three polarographic reduction waves are found for selenium(IV) depending upon the pH of the medium. The limiting current of all waves is diffusion controlled but only the second wave is reversible. The first wave exhibits a four-electron change while the second wave corresponds to a two-electron change. In basic medium, the third wave is due to a six-electron change. However, in acid medium, coulometric reduction at potentials corresponding to the third wave results in the formation of coagu-

lated elementary selenium which resists further reduction. The polarographic characteristics of selenium(IV) in a number of electrolytes are described.

THERE is considerable confusion in the literature concerning the polarographic behavior of selenium. The first polarography of selenium was reported by Schwaer and Suchy (17) who described three waves for selenium (IV) in 1N hydrochloric acid. These

authors attributed the waves to the stepwise reduction to the +2 elemental, and -2 oxidation states, respectively. In very dilute solution, the first two waves merged. They reported a single wave for the reduction of selenite ion to the element in ammoniacal solution. Lingane and Niedrach (13) found that selenide ion gave a dissolution wave at the dropping mercury electrode (DME) similar to that of sulfide ion. These authors also studied the polarography of selenite and selenate ions (14). They attributed the selenite