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BRIEF

A rotated mercury cell for controlled potential coulometry has been developed and evaluated with several chemical systems. Electrolytic rate constants that are relatively large, rapid sparge and low cell noise are some of the advantages of this cell.

Elimination of continuous background current by digital normalization is discussed.

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ABSTRACT

A cell which is rotated at high speeds and contains a thin-layer, mercury, working electrode has been developed for controlled potential coulometric determinations. The cell, which is the first successful departure from stirred mercury pool types, has several advantageous features. Constant mercury geometry assures very low noise operation and background currents that are substantially less than stirred mercury pool cells of similar capacity. A large solution surface area to solution volume ratio results in sparge times that can be as short as 20 seconds. Electrolytic rate constants of 0.020, 0.017, and 0.012 sec^{-1} were obtained for the determination of Pb, Cd, and U, respectively. A unique arrangement of the reference and auxiliary electrodes has been developed. This very compact combination, contains both reference and auxiliary electrodes in a single probe configuration. With this electrode it should be possible to produce scaled down versions of the rotated mercury cell, which currently requires 2 ml of mercury and 2 ml of solution.

A new procedure termed "normalization" which requires the use of digital equipment permits the elimination of the continuous background current from individual titrations. The result is improved precision.

INTRODUCTION

To the best of our knowledge, the rotated cell reported in this paper embodies the first successful conceptual departure from the stirred mercury pool design first proposed by Lingane more than 25 years ago (1). The reported cell is a cylinder which is closed at the bottom, partially opened at the top, and is mounted on a turntable rotated at 1,800 rpm with a synchronous motor. Owing to density differences and the high centripetal force, the mercury phase is held rigidly as a thin film on the wall of the cell, while the solution is forced into a film lying on top of the mercury. Contacting of the solution film with a novel, stationary, fumed-silica (2)- reference electrode combination probe generates a very efficient stirring action which, together with the favorable mercury-electrode surface-area to solution-volume ratio proveded by the cell's geometry, results in the attainment of quite high electrolysis rates. The cell's noise level is substantially less than that found in conventional cells since the surface area of the mercury electrode is not free to fluctuate in time. The high solution-surface to solution-volume ratio results in very short sparging times. A 20 sec sparging is recommended in the general procedure. Although solution and mercury volumes of 2 ml of each phase are employed presently, there are probably no reasons why cells with much smaller capacities could not be fabricated.

Briefly mentioned in a previous paper (3), but detailed here for the first time is a new procedure termed "normalization" which allows the subtraction of the continuous background current from individual controlled-potential coulometric titration curves. The precision of the titration results are improved by more than a factor of 4 in the example cited, i.e., the determination of U(VI) in sulfuric acid. Implementation of this normalization procedure

requires the use of digital recording equipment, some arithmetic data processing capabilities, and the ability to electronically display the stored data in a log-linear fashion.

EXPERIMENTAL

Instrumentation, Reagents, and Materials. The digital instrumentation used has been described previously (3). In addition, a General Radio Model 1538-A strobe light was employed. A Beckman #39270 saturated calomel electrode was used as reference.

Stock, 2M KCl and 1M H_2SO_4 supporting electrolyte solutions were prepared by dilution of reagent grade chemicals. All water used was distilled. Stock, standard metal-ion solutions were prepared in the following manner. Weighed, gram amounts of reagent-grade cadmium and lead were dissolved individually in nitric acid and converted to the chloride form by repeated evaporations with hydrochloric acid. The excess hydrochloric acid was removed by evaporation to near dryness, and these solutions were made to volume with water. Gram amounts of N.B.S., U_3O_8 (assay 99.95%) were similiarly weighed and dissolved in nitric acid, and the excess of this acid removed by repeated fumings with sulfuric acid. After being cooled, the residue was made to volume with water. Working solutions of the cadmium and lead stock solutions were prepared by dilution with water. Working solutions of the uranium stock solution were made 1M in H_2SO_4 and 0.2 M in sulfamic acid on dilution. All volumetric ware (flasks and T.C. pipets) was of class A tolerance. The calibration of the wash-out, micro-pipets was confirmed by weighing mercury.

The high-purity nitrogen employed, to sparge oxygen from the solutions prior to titration, contained nominally less than 10 ppm. and averaged 3 ppm. oxygen by mass-spectrographic analysis. It was necessary to saturate this dry

gas with water prior to admitting it to the coulometry cell, to prevent evaporation of the sample solution during the electrolysis.

Masero Laboratories' "high-purity", instrument-grade mercury was aliquoted into the cell using a luer-tipped, "Tomac" disposable, 2.5 ml hypodermic syringe. The plunger-tip of the syringe was sheathed in Teflon, when it was learned from x-ray fluorescence analysis that the original rubber tip contained considerable amounts of metals, noteably zinc. Oxide-free mercury can be drawn by inserting the luer-tip beneath the mercury surface since the dross has no tendency to cling to the plastic syringe. The need for pin-holing the mercury is thus eliminated.

Construction of the Rotated Cell and Assembly. Figure 1 shows an exploded view of the rotated cell apparatus. A set of detailed drawings of the apparatus are available upon request. The following is supplimentary information complementary to the drawings.

The Lucite cell is constructed in the following manner. Two inch rod stock is turned down to 1 13/16 in. in a lathe, and center bored to a 40 mm i.d. to form the walls of the cell. The machining marks are removed by turning the piece against, first, #600 sandpaper, followed by a polishing step with "Brilliant Shine" polishing liquid until the cylinder is optically transparent. The cylinder is then parted into rings 1.5 cm in length. Two 2 in. diameter saw-cut circles of 1/8 in. Lucite sheet are mounted in the lathe and machined to a 1 13/16 in. diameter. One circle serves as the cell bottom. A 7/8 in. hole is center drilled through the other piece to form the cell top. The three pieces are then united using a glue made from Lucite shavings dissolved in ethylene-dichloride. The article is held together with a C-clamp until the glue

hardens. The cell is now essentially completed, except for the installation of the platinum, mercury-contact wire. A hole is drilled and tapped in the side of the cell a few millimeters from the bottom to receive an 0-80 threaded, 1/16 in. diameter platinum wire. The wire is dipped into the Lucite glue, then screwed into the hole until it extends ~ 1 mm inside. When the glue sets, the excess is scraped away exposing the platinum metal. See Figure 1, Detail 1.

The cell must now be subjected to the cleaning and preconditioning procedures given below.

The turntable, to which the cell and its platinum, mercury-contact wire is mounted, is made of copper and is electrically isolated from the motor by sleeving the center of the copper shaft with Lucite and by using a nylon set screw to secure the turntable to the shaft of the 1,800 rpm, synchronous Bodiene motor, Model NSY-12. It is important that the eccentricity of the cell, when installed on the turntable and mounted on the motor shaft, be less than 2 mils T.I.R.

Electrical connection to the cell-turntable is made through a bronze-wool brush contact. Bronze-wool is compacted into the holder using a small screwdriver. The excess wool is cut with shears about 1/4 in. from the end of the holder and the holder is mounted in the bracket attached to the positioning collar. The brush pressure should be such that the turntable does not heat up, even after prolonged operation.

This contact is relatively trouble free provided it does not become contaminated with mercury. Amalgamated bronze is a hard substance, completely lacking in resiliency and therefore useless as a contact material. If mercury

is spilled on the wool, the entire tuft must be discarded and a new one taken. Contact bounce can occur when using a brush type contact; however, if it does occur in this system, the time width is less than 0.1 μsec.

Note that the brush and all the associated metal parts are ultimately mounted on the Lucite base and are thus electrically isolated from the motor and housing.

The stainless-steel probe holder is made specifically to accommodate a variety of 6-mm o.d. glass probes and is open at the end to facilitate easy tube mounting and demounting without the necessity of removing the positioning collar or disturbing the probe holder alignment. The probe is so designed that it cannot move in either the horizontal or the verticle plane when locked.

The Lucite hinged cell cover is mounted less than 10 mils from the top of the rotated cell. In its open position, it permits the aliquoting of the sample and mercury into the cell. In its closed position, it blocks entry of air into the cell. The channel in the cover, which terminates in a short tube, permits the directing of nitrogen into the cell.

Cell Cleaning and Preconditioning Instructions. Before the cell can be used, it is necessary to remove the contaminents introduced during its fabrication. The cell, as received, must be thoroughly washed with dilute hydrochloric acid, rinsed with water, then ethanol. After being dried, the cell is soaked overnight in 2M H_2SO_4. The following day, it is washed with water and filled with 0.1 M $HClO_4$, and the platinum, mercury-contact wire is anodized against another platinum wire for a short time using a 10 V source. This acid is discarded and the cell is refilled with 0.1 M $HClO_4$. This time, the contact wire is cathodized and after a few moments, ~ 0.5 ml of mercury is introduced. The cell is tilted

so that the mercury touches the contact wire; the mercury will flow onto and thoroughly coat the exposed platinum. The solution and excess mercury is discarded and the cell is then washed with water, dried, then mounted on the copper turntable. It is now ready for use.

Failure to heed these cleaning and preconditioning instructions will result in very high background currents.

Probe Construction. The two probes used in this work are shown in Figure 1, upper left. The first probe consists of parallel arrangement of the reference-analyte salt bridges. The reference bridge terminates in an asbestos wick, and the analyte bridge terminates in a glass frit. These parallel probes are easy to construct. The second probe consists of a coaxial arrangement in which the reference bridge is located at the center of the analyte bridge. This type of probe is more difficult to construct. See Figure 2. Drawings 1 through 5 show the steps required for the fabrication of the coaxial probe, Drawing 6 is a side view of the completed probe, and Drawing 7 is an end view of the tip.

The probe tip design is very important and will be discussed below.

Salt Bridge Preparation and Alignment. Both probes are prepared for use in the following manner: the reference electrode salt-bridge is filled with 1M KCl. Using a polyethylene spitzer, the analyte compartment is injected, as described in a previous paper (2), with either a fumed-silica, gelled solution of 1M KCl when titrating cadmium or lead, or a fumed-silica, gelled solution of 1M H_2SO_4 when titrating uranium. The analyte compartment is then filled with the same solution as the gelled one.

Position the arm of the stainless-steel probe holder along an imaginary line passing through the center of the cell, then lock it into this position by

tightening the jam nut. Clamp the probe in the holder so that the center of the probe tip is just below the center of the cell and facing toward the probe holder's vertical support. Aliquot 4 ml of water into the cell and start it rotating. Turn the horizontal positioning screw, located in the probe holder's arm, counter-clockwise until the probe-tip just touches the moving wall of water. Orient the probe in such a way that the pointed end of the tip is the first part to contact the water. Continue turning the positioning screw counter-clockwise until the entire tip surface contacts the water. When thus correctly positioned, the solution will course around and over the horizontal section of the probe, but no dripping will occur and no spray will be formed. Lock the probe-holder in this position by tightening the set-screw.

General Procedure. Calibrate the digital integrater to read out directly in nanograms of material titrated by using the voltage equivalent of the nF to atomic weight ratio. Start nitrogen flowing into the cell at a rate of 2.9 l/min or more. The recommended sample size depends upon the type of probe employed and is discussed below. Open the hinged cell-cover and aliquot the sample into the cell using a 500-μℓ pipet. Employing standard micro-techniques, rinse the pipet twice by filling it to the miniscus with the 2M KCl stock, supporting-electrolyte solution and once with water when titrating cadmium or lead, or three times with 1M H_2SO_4 when titrating uranium. It is convenient to draw up the rinse from droplets distributed over Parafilm. Add these rinsings to the cell. The total volume of sample plus rinsings must be 2.0 ml. Aliquot 2.0 ml of mercury into the cell, using the plastic syringe, then close the hinged cell-cover. Bring the cell up to its designed speed over a 10 to 15 sec interval by slowly increasing the output voltage of a 0 to 120 V Variac.

The solution is sparged of oxygen in part during the aliquoting operation. Allow it to rotate for 20-sec to complete the sparging, then apply the pretitration voltage. Cadmium, lead, or uranium is pretitrated at -0.400 V, -0.200 V, or +0.075 V vs. SCE, respectively. The pretitration electrolysis rates as observed on the rate-meter should fall to a value of < 5 ng/sec for cadmium or lead and to ≤ 10 ng/sec for uranium within one to three minutes. After the pretitration set the appropriate titration voltage and start the titration. Cadmium, lead, or uranium is titrated at -0.825 V, -0.650 V, or -0.275 V vs. SCE, respectively. The titration termination times used for the three elements are 7, 8, or 12 min., respectively.

The cell is not conveniently demountable for cleaning between titrations. Remove the titrated solution and mercury from the cell using a polyethylene spitzer connected through a 500 ml filter flask trap to a vacuum line. Rinse the cell several times with water then aliquot the next sample.

Carry blanks through the above procedure for the element titrated and correct the raw data for the background current.

Normalization Procedure. Normalization of coulometric data contained in the memory of a multi-channel analyzer is an alternate and time saving route to coulometric analysis (3). After pretitrating the sample, adjust the potentiostat to the required titration potential. Adjust the rate meter to terminate the experiment when the electrolysis rate decreases to 7 ng/sec for cadmium or lead, or 10 ng/sec for uranium. Start the titration and store the digital information in the first half of the memory, using a time-dwell of 3-sec per channel. After the rate-meter termination, transfer the stored data, while simultaneously multiplying it by a factor of 10, to the last half of the memory

using the data processor. Switch the data processor to its normalize mode of operation and change the storage sense of the analyzer to subtract. While observing the 5-cycle log display of the data on the analyzer's oscilloscope, repeatedly initiate the normalization program until all the data points of the curve in the second half of the memory fall on a straight line. Determine the number of channels involved in recording the titration data, using the analyzer's peak select function, and multiply this number by one-tenth the normalization value per channel. Subtract this product, after rounding to the nearest count, from the total number of counts shown on the accumulate scaler. The scaler data is now corrected for the continuous background current.

If the sample titrated is very small, it will have a significant positive bias owing to the lack of compensation for the charging and the supporting electrolyte impurity currents. Run a blank, normalize this data, and using the data processor, integrate all non-empty channels. Subtract this integrated value from the scaler data above.

DISCUSSION AND RESULTS

Fundamental considerations, tempered by experimental limitations, served as a guide in the development of the presented cell.

The current-time relationship in a controlled-potential coulometric determination, which is free of chemical complications and is carried out at a potential at which the rate of the reaction is limited solely by the rate of mass transfer of the electroactive species to the working electrode, is given by the Lingane equation (1,4).

$$i = i_o e^{-kt} \qquad (1)$$

The current i is expressed in milliamperes at some time t expressed in seconds; i_o is the initial current, and k is the electrolysis rate constant. The Nernst diffusion layer concept allows one to relate the electrolytic rate constant to several important experimental parameters. The relationship derived for this model is

$$k = D\left(\frac{A}{V}\right)\left(\frac{1}{\delta}\right) \qquad (2)$$

where D is the diffusion coefficient of the electroactive species, A is the working electrode area in square centimeters, V is the volume of solution in milliliters, and δ is the Nernst diffusion layer thickness in centimeters.

Examination of Equation 2 reveals three ways in which the value of k could be increased. The diffusion coefficient could be increased by heating the solution titrated, but the practical consideration of providing some thermostating at the elevated temperature because of shifts in the required control potential militates against this. Also, the background current increases with increasing temperature. Increasing A while decreasing V would increase k. However, space limitations in the cell void restrict the size and the effective area of the auxiliary electrode thus causing localization of the current distribution pattern. Other probes essential to the operation of the cell must also share the same void. For these reasons, the effective A to V quotient is usually near unity. The third alternative--providing more efficient mass transfer by making δ small through efficient stirring, has attracted the widest attention, because it is the most effective and the easiest to effect.

Making k large is desirable for two reasons: the titration time is reduced, and the contribution of the background current to the total electrolysis

current is decreased. The precision of the results and the sensitivity of the method is thus improved, provided the cell is free from deleterious potential gradients and the noise level of the cell is low.

A paper by Harrar and Shain (5), in which they investigated potential gradients in coulometry cells, was an invaluable guide in the present study. They showed how improper placement of the references electrode could produce localized excursions of the working electrode potential in which the control potential was sufficiently exceeded to produce undesired reactions. A general conclusion of these workers is that the reference electrode should be placed on a line of minimum separation between the auxiliary and working electrodes.

Cell current noise is caused by stirring which produces electrode-area fluctuations in time. These fluctuations cause variations in the reference to working electrode distances and, if the iR drop between the electrodes is appreciable, considerable fluctuations in the control-potential can occur. The net effect is an increase in the background current which decreases the sensitivity of the coulometric method.

The last cell design criteria, sparging time, is largely a matter of convenience although it is of great practical importance if coulometry is to be considered for a control application. Dissolved oxygen interferes with coulometric titrations and must be removed prior to the analysis. The time need to sparge the coulometry cell of oxygen adds to the total time required for a determination. Sparging time should, therefore, be as short as possible.

The following is an account of the way in which the rotated cell evolved. The rugged, easily fabricated salt-bridge described in an earlier paper (2) was the precursor of the salt-bridge probes developed for this work. Our most

difficult developmental problem was that of designing a satisfactory probe with an acceptable tip geometry. Initially, various shapes patterned after boat-hull designs, were cut into the end of a piece of 1/4 in. diameter, aluminum rod-stock and were tested by holding them against the rotated wall of water. Without exception, considerable spray was formed. Also, the water had a tendency to run onto the horizontal section of the probe and form drops which, upon striking the floor of the rotated cell, produced spray. Spray formation is objectionable because the spray droplets can be deposited on the cell-cover or probe stem and thus escape titration. This problem was, however, overcome when it was observed that a piece of small diameter (1/32 in.) copper wire did not cause spraying or dripping on contacting the water, and produced a wake with the horizontal of about 15° at 1,800 rpm. It was reasoned that a much larger diameter object could similiarly contact the water without causing the deleterious effects characteristic of the other designs provided it too had a wake-matching 15° triangular shape cut into it. This reasoning proved to be correct. Any attempt to streamline the trailing edge of the design shown in Figure 2, Drawing 7 will probably result in the reappearance of spray. The probe tip surface selected was plane since the ratio of the probe length to the circumference of the cell used for this work is small.

Once a satisfactory probe tip was designed, the next problem was one of selecting the correct geometry for the reference and analyte probes with respect to the rotating mercury electrode.

In the first titration experiments, two probe holders were employed, mounted on two positioning collars which fitted concentrically on the two stepped collar holder. See Figure 1. The cell used, at this stage of the

development, was 4.0 cm in diameter and 4.0 cm in height. These dimensions were selected because they were physically convenient. The cell was charged for each run with 7-ml of mercury and 7-ml of 1M KCl containing 200-μg of lead and was sparged of oxygen with a strong jet of nitrogen from a tube inserted through the center of the cell-top opening. The angular separation between the probes had an effect on the normalized results. As the angular separation decreased from 180°, the positive titration error decreased, and approached zero as the separation approached 0°. From these results it was obvious that the control-potential was being exceeded sufficiently to cause a secondary electrolysis at wide reference-anode separations, hence the high results. See Figures 4 and 6 of Reference 5. Based upon this experimental information the parallel probe design was developed and is shown in the upper left corner of Figure 1.

The parallel salt-bridges are situated one directly above the other to avoid placing one probe in the compression wake of the first which would be the case if one were allowed to lead the other as, for example, in a side by side configuration. This latter configuration is avoided because it is electronically very noisy. Examination of it with strobatic light revealed the cause. Depending upon which probe is allowed to trail, either the control-loop or the reference-lead is being opened intermittently by the turbulence.

Although these first experiments showed that it was possible to do precision coulometry using a rotated cell provided certain geometrical requirements were met, the electrolytic rate constant for this electrode (e.g. 0.006 sec^{-1} for lead in 1M KCl) was disappointing. It was reasoned that a considerable area of the mercury electrode was inactive because of the small

anode surface area and the probable high collimation of the field. To test this, the cell height was reduced from 4.0 cm to 1.5 cm while keeping the same cell diameter. Upon reducing the rotated electrode's surface area by a factor of 2.7 and by decreasing the cell's capacity to 2 ml of mercury and 2 ml of solution, the electrolysis constant increased by more than 300% to 0.020 sec^{-1}. This increase is due to an increase in the value of k in Equation 2 made possible through a reduction in δ with more efficient stirring. Although the geometrical ratio of A to V is 9 to 1 for the 1.5 cm cell, the effective ratio is probably near unity.

Reduction of the cell height and solution-mercury volume also reduced the starting inertia of the motor resulting in the entrapment of as much as 20-μl of solution beneath the mercury which lead to low titration results. Interposing a transformer between the motor and the line to initially limit the voltage to the motor permitted a much slower and controllable start up and thus eliminated the formation of solution pockets. This was verified by examination of the cell under strobatic light conditions. Coincidental with the cell alteration, a more sophisticated means of protecting the cell from the ingress of air became necessary. This took the form of the hinged cell cover.

There is a definite upper limit to the amount of material titrated when using a parallel probe. Figure 3 shows the log $\underline{i}$ - time behavior for a cadmium sample which exceeds the upper limit. The positive deviation from the expected linear log $\underline{i}$ - time relation does not conform with the logarithmetic form of Equation 1 and is due to the control-potential being exceeded sufficiently to cause a secondary electrolysis, hence the high positive error. Again see Figures 4 and 6 of Reference 5. This phenomenon can be explained by assuming that the probe

changes from configuration II to configuration III type behavior depending upon the cell current demand. This behavioral transition occurs abruptly so if the upper limit is determined, and care taken that it is not exceeded, a parallel probe can be used without trepidation. Replacement of the parallel probe with the coaxial probe discussed below eliminates these problems.

In conjunction with the above, it seemed advisable to make a potential map of the rotated mercury electrode when it was in its configuration II state. The cell was converted to essentially a constant current operation in the following manner. The cell cover was removed to allow air into the cell, then a potential of -0.600 V vs. SCE was imposed. The cell current became constant at 400 μA within a short time owing to the equilibrium between the rate of entry of oxygen into the cell with the rate of its reduction. Using the second positioning collar and probe holder as described above, a moveable reference probe was introduced into the cell and potential measurements were made against the working electrode at various angular settings with respect to the stationary parallel probe. Figure 4 shows the results. Even though the working electrode potential is less than the control potential over much of the electrode surface, this will not harm the analysis provided the final electrode potential corresponds to that of complete electrolysis (5), although there are some exceptions (6). The electrode potential of the rotated cell, of course, approaches the control potential at all points on its surface as the current-demand approaches zero, a fact confirmed by experiments in which the cell was sparged of oxygen during the potential measurement.

Figure 5, trace A, shows the ac noise superimposed on the 400 μA constant cell current while simultaneously trace B shows the variation in the

control potential. Qualitatively, this cell has one of the lowest noise levels of any efficiently operated, mercury coulometry cell studied by these authors. The cell noise which is due to stirring and/or mechanical shocks transmitted to the mercury by the motor appears to be of a high frequency nature (msec range). Intuitively, however, low frequency noise could occur from a precession in the mercury and would occur if the cell had appreciable eccentricity. A frequency analyzer was, unfortunately, not available for this work.

An outstanding feature of this cell is its outgas characteristics. Figure 6 is in log-linear presentation of the change in the oxygen current with time. Curve A is the recorded data, and curve B is a normalization of curve A. Curve A indicates that a solution, initially saturated with air, can be sparged to background in about one minute. It is reasonable to assume that the sparge characteristic of the cell is exponential in nature and that an empirical "sparging constant" could be calculated, since curve B is fairly linear. This constant, as might be expected, is related to the volume of the aqueous phase which, in turn, is related to solution thickness. Sparging constants of 0.11, 0.10, and 0.05 sec^{-1} were found for 1.5, 2.0, and 3.0 ml of 1.0M KCl, respectively. The thickness of these solutions, in millimeters, is almost identical with the solution volumes. Under the conditions of the general procedure, the sparging time is less than one third that calculated (69 sec) because the sample is being sparged in part during the aliquoting step.

The minimum nitrogen flow rate to maintain the sparging constant of 0.10 is 2.9 l/min. This value is also the minimum flow necessary to maintain an oxygen free cell environment when the cell-cover is mounted 0.01 in. above the rotating cell.

Although the parallel probe is easy to construct, the fact that there is an upper limit on the size of the sample titrated impares its usefulness, if it is to be used in non-routine work. To circumvent these problems, the coaxial type salt-bridge was developed. See Figure 2. Since the reference electrode is located center of and flush with the analyte bridge, the control potential is reduced by the iR drop between the reference and the rotated mercury electrode; therefore, it is impossible to exceed the control potential. This behavior, which limits the cell current to approximately 600 μA in 1M KCl is about 1/3 the total current available. If the initial cell current demand is above the current limiting value, the titration time is extended. Figure 7 illustrates this phenomenon. If current limiting is a problem, it can be overcome in one of two ways. An iR drop compensator can be installed in the potentiostat or the probe tip can be redesigned in such a way that the reference electrode salt-bridge is placed nearer the rotated mercury electrode. It is the considered opinion of the authors that the former suggestion would be the easier to implement.

The two probes compare favorably. The current noise levels of the two probes are the same but the variations of the control potential (Figure 5) is reduced by roughly 50% through the use of the coaxial probe.

It would be interesting to compare the performance of our cell with that of previous workers. Unfortunately, it has not generally been the practice of past workers to evaluate the electrolysis constants for their cells; rather, the amount of material which can be titrated to background within 15 minutes is usually reported as an upper limit for their methods. If one assumes that the electrolysis current obeys Equation 1 and decays by three orders of magnitude in this time, a constant of 0.008 sec^{-1} is calculated for a typical

conventional cell. In comparison, the measured electrolysis constants for our cell were 0.020, 0.017, and 0.012 sec^{-1} for lead, cadmium, and uranium, respectively.

A large value for the electrolysis constant is desireable because, in addition to reducing the time necessary to do a titration; the size of the blank titration is reduced; smaller samples can be titrated with good precision; and, when normalizing data, the uncertainity in the visually determined linearity is greatly reduced because the slope of the titration curve is increased. Table I gives, what we consider an objective time comparison of our cell with a conventional cell. The rate of reduction of U(VI) is kinetically controlled and depends upon the rate of disproportationation of the U(V) species (7,8). The time disparity would be larger had a diffusionally controlled species been considered.

Calculated electrolysis times of 7, 8 or 12 min. for Pb, Cd or U, respectively, based on the observed rate constants are shorter than those actually employed. The electrolysis was allowed to continue for a time equal to 120% of the calculated value to assure an adequate deviation from the linear log $\underline{i}$ - time relation to permit the evaluation of the background current by normalization. A computer program which is currently under development will automate this normalization procedure.

Both kinds of probes were used in obtaining the results shown in Table II. A constant titration time interval was used to obtain the reported values for cadmium and lead, whereas the normalization procedure was used for the uranium analyses. Table III details the data reduction steps necessary to arrive at the information shown in the previous table for uranium at the 1124 μg

level. This ability to analyze coulometric titration data for a continuous background current contribution on an individual basis rather than on a statistical basis considerably improves the precision of the final results. Note that the average deviation of 0.2 μg would have been greater by a factor of 4.5 had the average blank correction been used.

Normalization of titration data should also permit the accurate determinations of radioactive elements where the radiolysis products are created at a constant rate.

FUTURE WORK

Although we have attained our original objectives; a cell having very efficient stirring action, low noise characteristics, a very high sparging rate, and low sample volume requirements, several other studies probably are suggested by this work. If a very low-play, bearing-mount arrangement were developed, it should be possible to scale down the cell size and titrate samples in volumes of 100-μℓ or less. The probes could be maintained at their present dimensions and thus still be physically easy to handle. Sonic stirring (9) could be employed in conjunction with the rotated mercury electrode since the centripetal force would prevent fragmenting of the liquid metal surface.

A fairly large sample volume is generally required for platinum coulometry cells to cover the electrodes. Construction of a rotated platinum gauze or wool electrode would reduce the volume required and make the electrode surface-area to sample-volume ratio quite favorable and at no increase in the background current over the conventional application. Sonic stirring (9) could be applied to this arrangement too.

If by sonic stirring an increase by a factor of 5 in the electrolysis rate constants is realized, potential scanning coulometry would become practical for use in routine analysis.

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LITERATURE CITED

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(1) J. J. Lingane, J. Am. Chem. Soc., 67, 1916 (1945).

(2) R. G. Clem, F. Jakob, and D. Anderberg, Anal. Chem., 43, 292 (1971).

(3) R. G. Clem and W. W. Goldsworthy, University of California, Lawrence Radiation Laboratory Report UCRL-19956 (1970).

(4) J. J. Lingane, "Electroanalytical Chemistry", 2nd Edition, Interscience, New York (1958), pp. 224-229.

(5) J. E. Harrar and I. Shain, Anal. Chem., 38, 1148 (1966).

(6) J. E. Harrar, Anal. Chem., 35, 893 (1963).

(7) G. L. Booman, W. B. Holbrook, and J. E. Rein, ibid., 29, 219 (1957).

(8) I. M. Kolthoff and W. E. Harris, J. Am. Chem. Soc., 68, 1175 (1946).

(9) A. J. Bard, Anal. Chem., 35, 1125 (1963).

Table I. Time Comparison of the Rotated Cell with a Conventional Cell

Operation	Time, minutes	
	Rotated Cell	Conventional Cell
Aliquot	1	1
Sparge	0.3	7 to 10
Pretitrate	1 to 3	1 to 3
Titrate[a]	12	15[†]
Time Totals	14.3 to 16.3	24 to 29

[a]For U^{6+} in 1M H_2SO_4

[†]See text

Table II. Titration Results

μg Cd				μg Pb				μg U			
Taken	Found	Av. Dev.	No. of Analyses	Taken	Found	Av. Dev.	No. of Analyses	Taken	Found	Av. Dev.	No. of Analyses
1030[a]	1029.9	±1.4	5	1250[a]	1250.0	±0.9	6	1124[a,c,d]	1123.5	±0.2	5
258[b]	257.8	±0.3	5	500[b]	500.2	±0.4	5	562[a,c]	561.7	±0.1	5
26[b]	26.2	±0.2	5	100[b]	99.9	±0.1	5	281[a,c]	280.4	±0.5	6
				10[b]	9.9	±0.2	6	56[a,c]	57.0	±0.2	5

[a]Coaxial probe used

[b]Parallel probe used

[c]Normalization procedure used

[d]Also see Table III

Table III. Normalization of Uranium Results

Run No.	1	2	3	4	5
Scaler Counts	1128373	1128259	1129566	126863	1126666
Correction	3400	3840	5120	2560	2048
Normalized Value	1124973	1124419	1124446	1124303	1124618
Nominal Value μg	1125.0	1124.4	1124.4	1124.3	1124.6
Less charging current U equivalent (1.0 μg)	1124.0	1123.4	1123.4	1123.3	1123.6
Av.			1123.5 ± 0.2		

FIGURE CAPTIONS

Fig. 1. Rotated Cell Apparatus--Exploded View.

Fig. 2. Coaxial Probe Construction.

Fig. 3. Coulometric Titration in which the Control Potential is Exceeded

Taken: 501.5 μg Cd^{2+}, Found: 554.6 μg Cd^{2+}, Conditions: See General Procedure.

Fig. 4. Potential-Map of the Rotated Cell

Solution: 0.1M KCl.

Fig. 5. Cell Noise

A. Cell current noise; 1 mV = 1 μA.

B. Variations in the control potential; 1 mV = 1 mV.

Conditions: 400 mA total current, -600 mV vs. SCE, 1M KCl.

Fig. 6. Sparging Behavior of the Rotated Cell

A. Current-time data as recorded.

B. Curve A expanded by a factor of 10 and normalized.

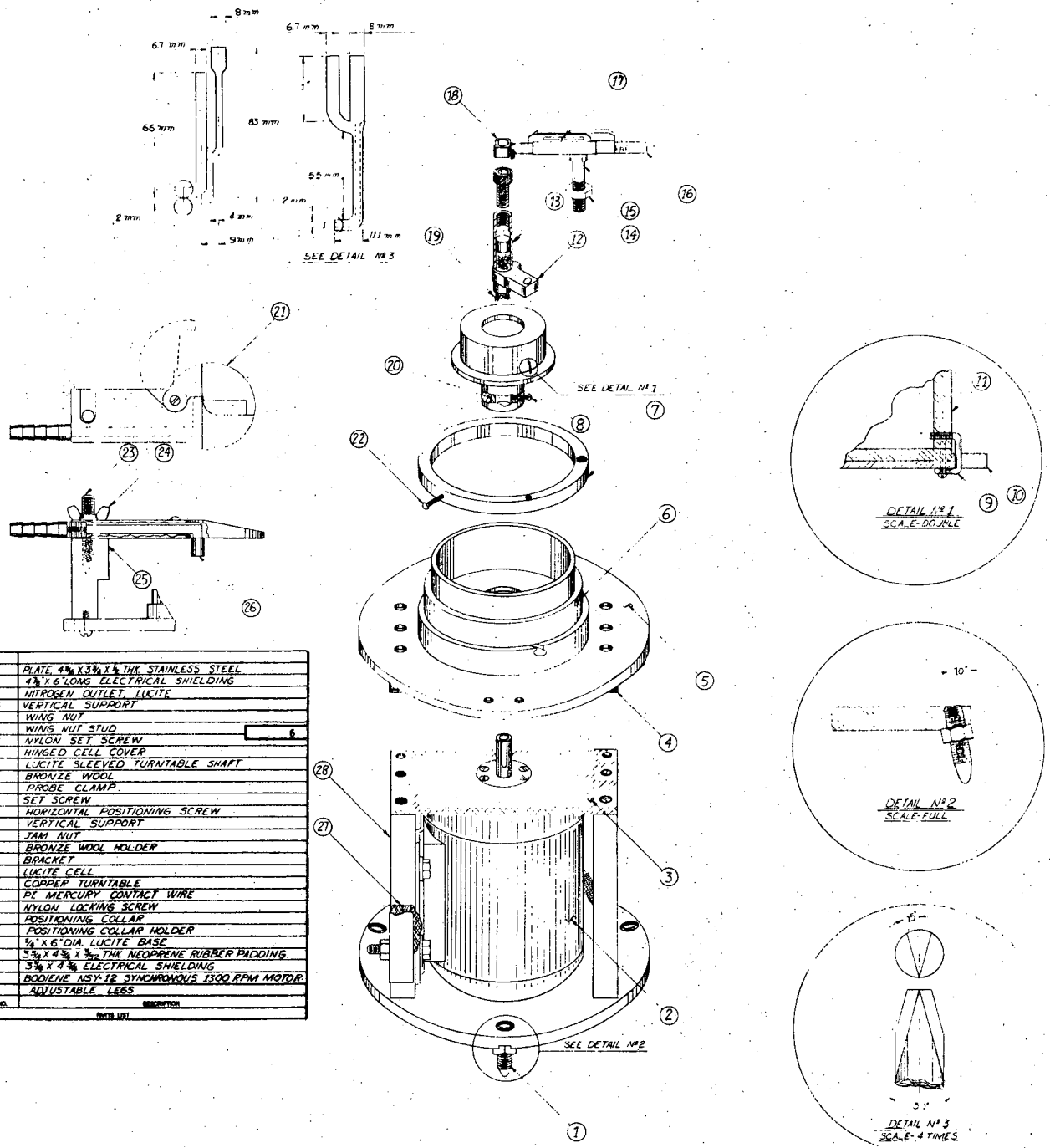
Arrow denotes the point in time at which the N_2 was turned on.

Fig. 7. Current Limiting Behavior of the Coaxial Probe

A. Curve B expanded by a factor of 10 and normalized

B. Current-time data as recorded.

1,030 μg Cd^{2+} taken, 1,032 μg Cd^{2+} found before normalization, curve B, 1,029 μg Cd^{2+} found after normalization, curve A.



REQ'D	ITEM	PART NO.	DESCRIPTION
2		28	PLATE 4 9/16 X 3 9/16 X 1/4 THK. STAINLESS STEEL
2		27	4 9/16 X 6" LONG ELECTRICAL SHIELDING
1		26	NITROGEN OUTLET, LUCITE
1		25	VERTICAL SUPPORT
1		24	WING NUT
1		23	WING NUT STUD
1		22	NYLON SET SCREW
1		21	HINGED CELL COVER
1		20	LUCITE SLEEVED TURNTABLE SHAFT
1		19	BRONZE WOOL
1		18	PROBE CLAMP
1		17	SET SCREW
1		16	HORIZONTAL POSITIONING SCREW
1		15	VERTICAL SUPPORT
1		14	JAM NUT
1		13	BRONZE WOOL HOLDER
1		12	BRACKET
1		11	LUCITE CELL
1		10	COPPER TURNTABLE
1		9	PT. MERCURY CONTACT WIRE
1		8	NYLON LOCKING SCREW
1		7	POSITIONING COLLAR
1		6	POSITIONING COLLAR HOLDER
1		5	1/4" X 6" DIA. LUCITE BASE
1		4	5 5/16 X 4 3/16 X 3/32 THK. NEOPRENE RUBBER PADDING
1		3	3 3/16 X 4 3/16 ELECTRICAL SHIELDING
1		2	BODIENE NSY-12 SYNCHRONOUS 1300 RPM MOTOR
3		1	ADJUSTABLE LEGS

PARTS LIST

XBL 711-40

Fig. 1

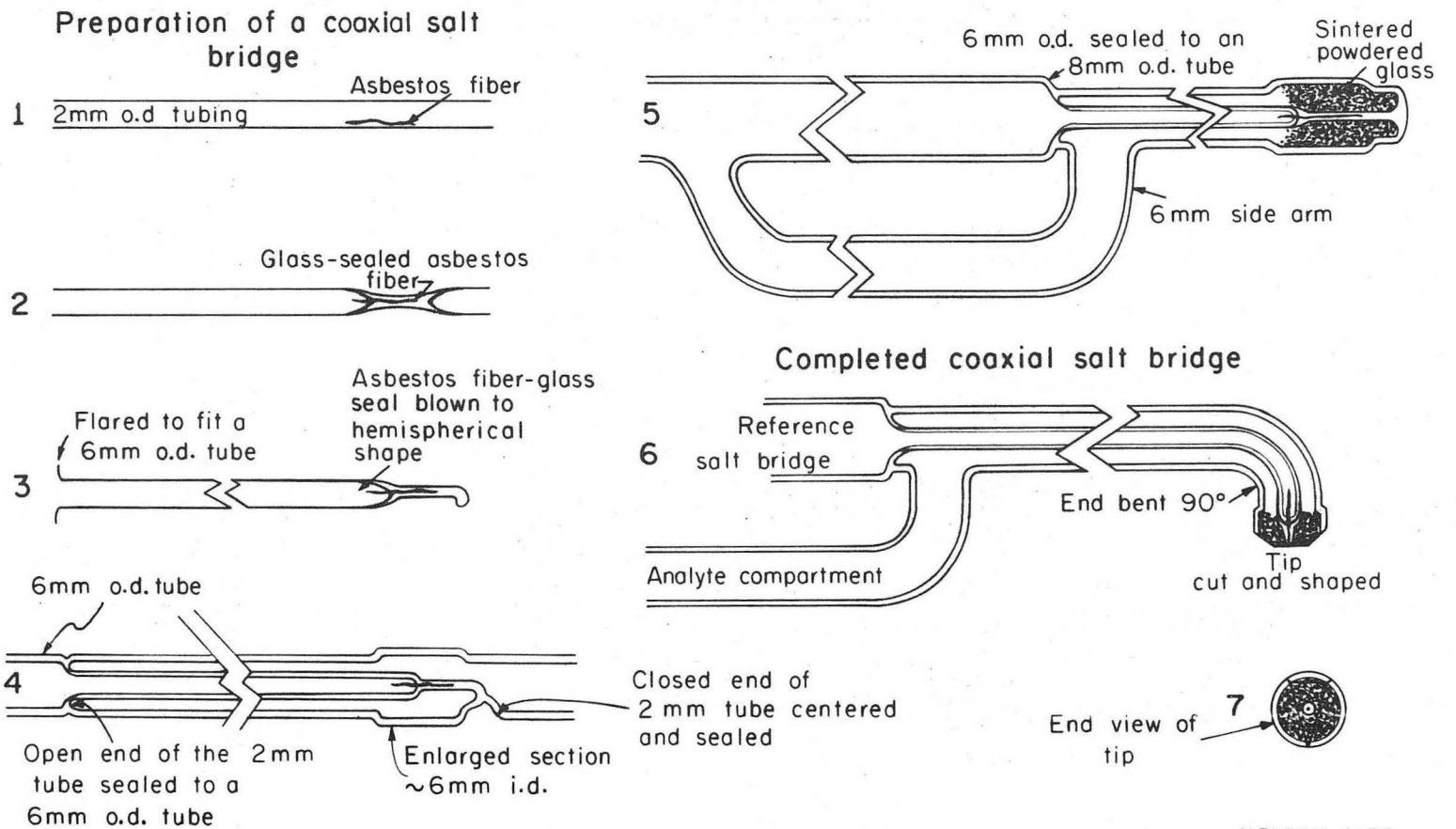

Preparation of a coaxial salt bridge
1
2mm o.d tubing
Asbestos fiber
2
Glass-sealed asbestos fiber
3
Flared to fit a 6mm o.d. tube
Asbestos fiber-glass seal blown to hemispherical shape
4
6mm o.d. tube
Open end of the 2mm tube sealed to a 6mm o.d. tube
Enlarged section ~6mm i.d.
Closed end of 2 mm tube centered and sealed
5
6 mm o.d. sealed to an 8mm o.d. tube
Sintered powdered glass
6 mm side arm
Completed coaxial salt bridge
6
Reference salt bridge
Analyte compartment
End bent 90°
Tip cut and shaped
7
End view of tip
XBL7011-4138

Fig. 2

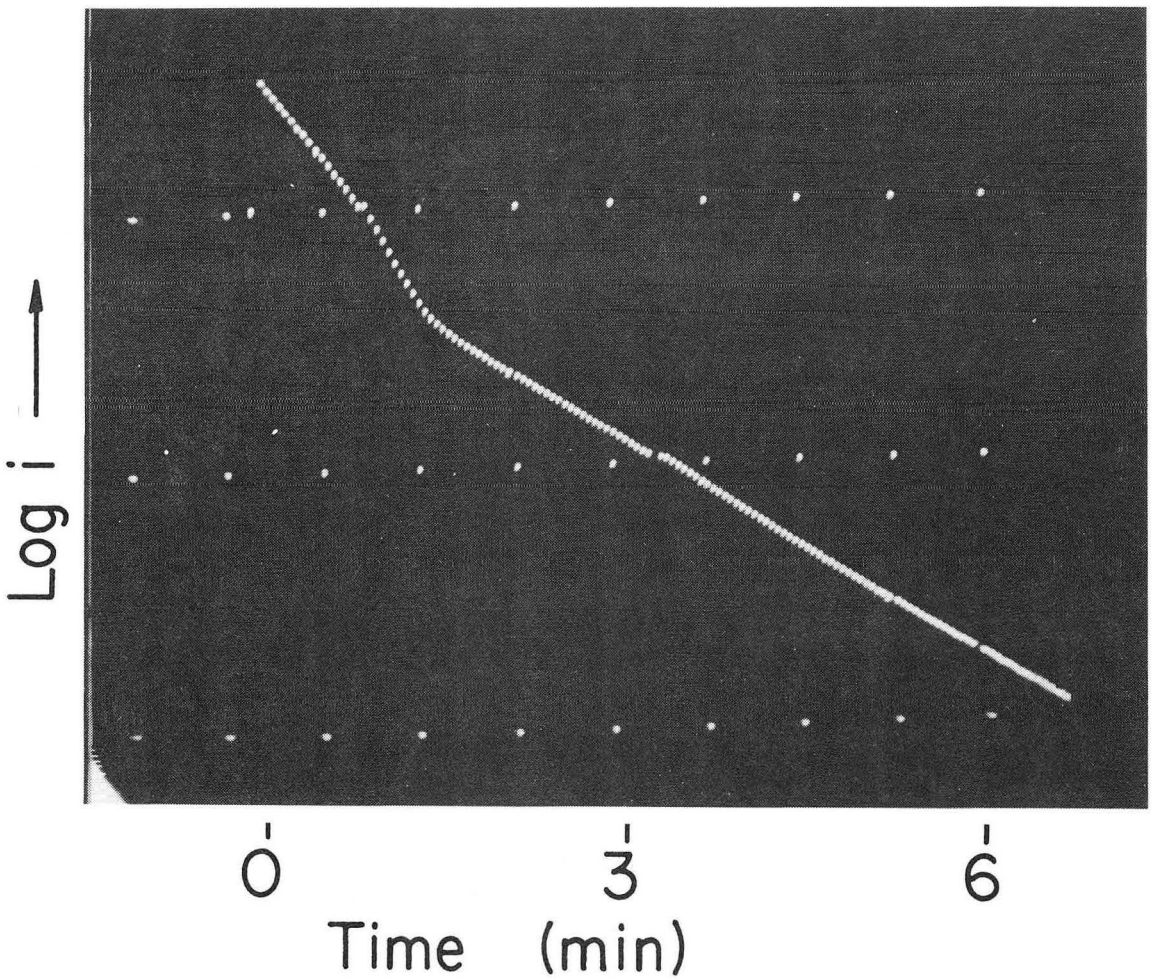


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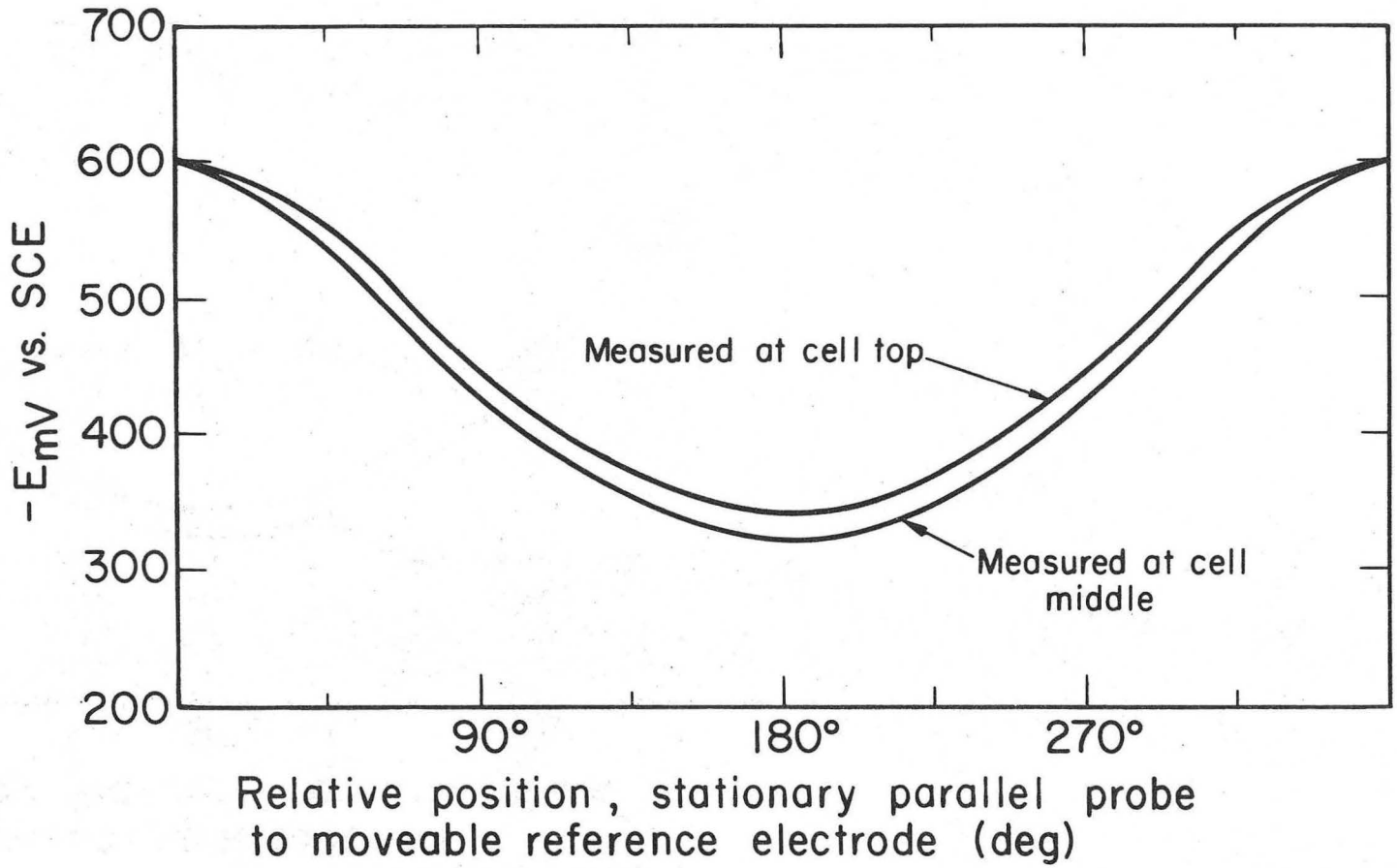
Fig. 3



XBL 711-2650

Fig. 4

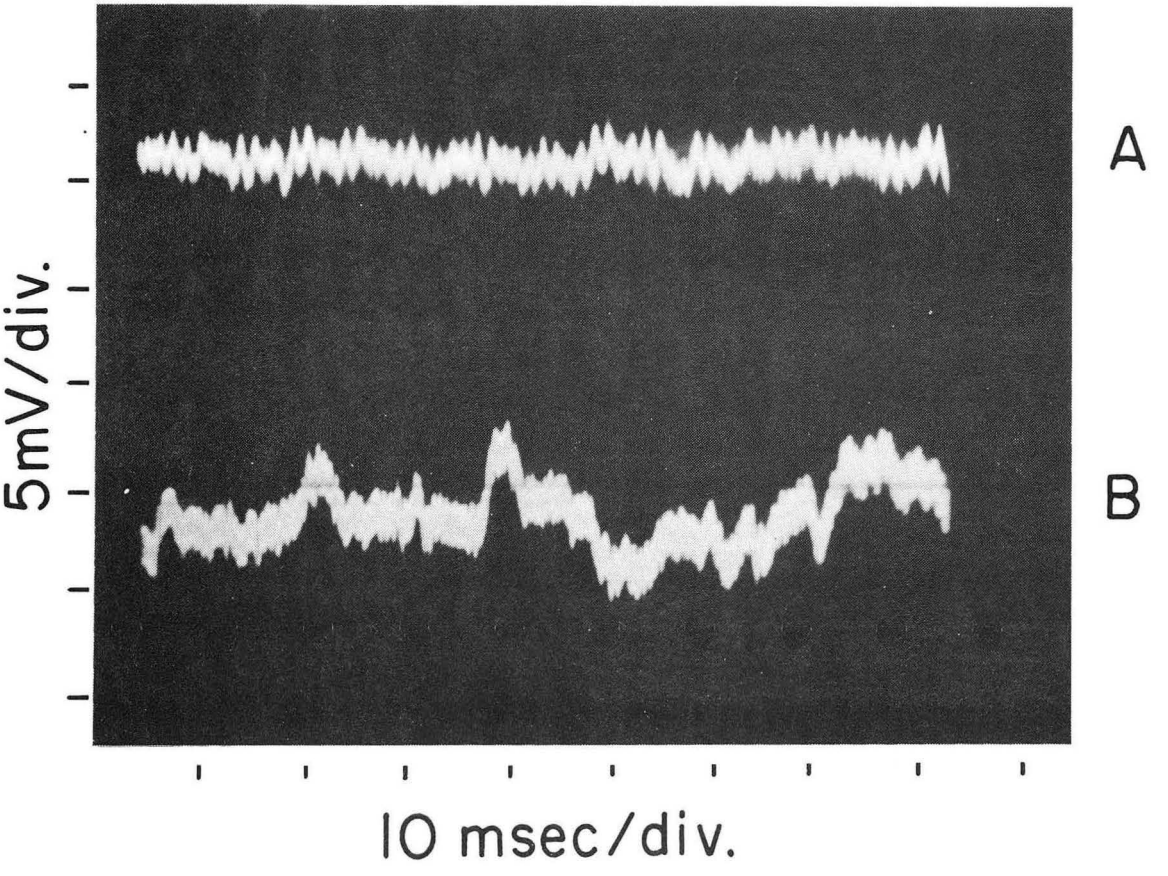


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Fig. 5

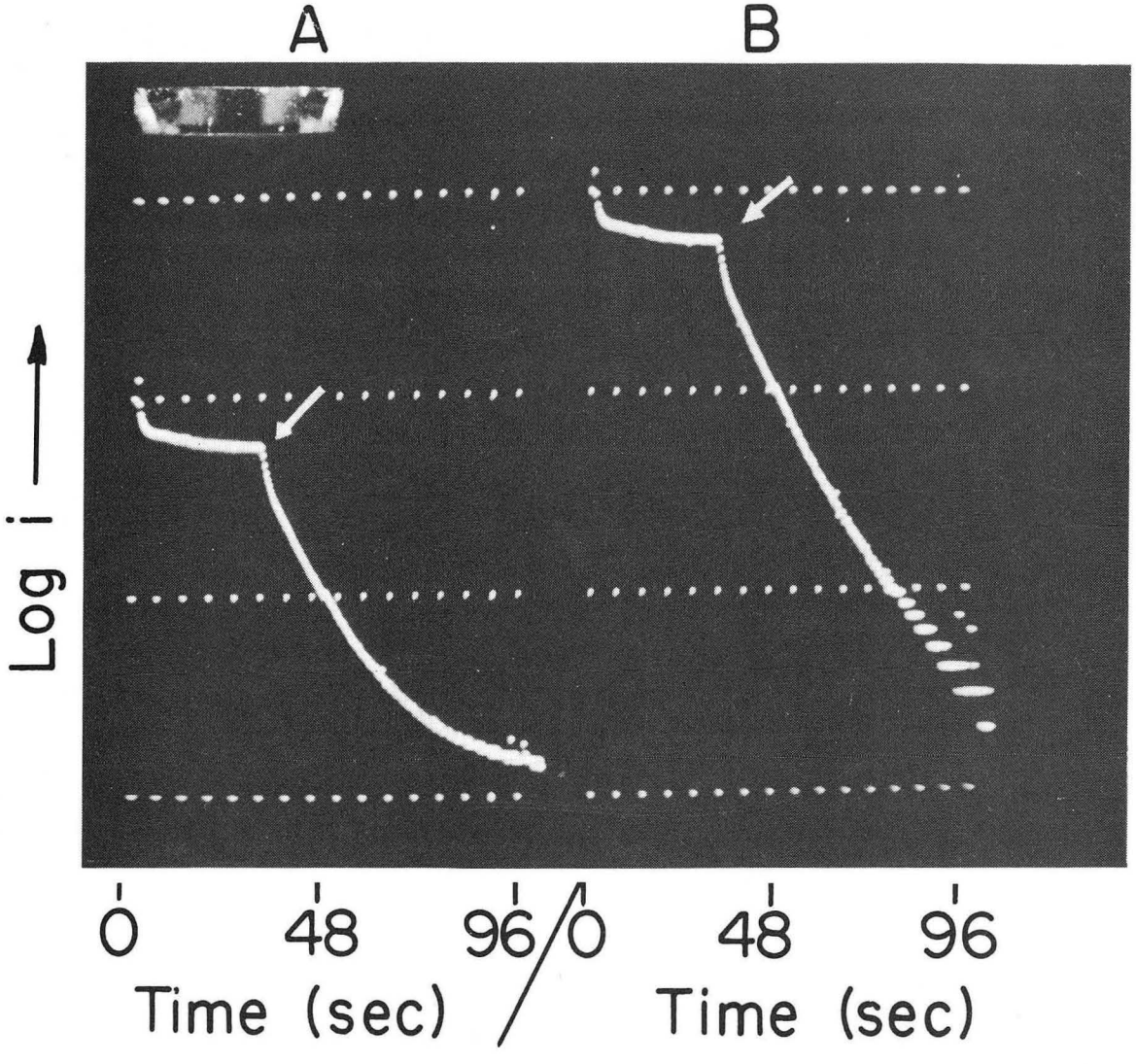

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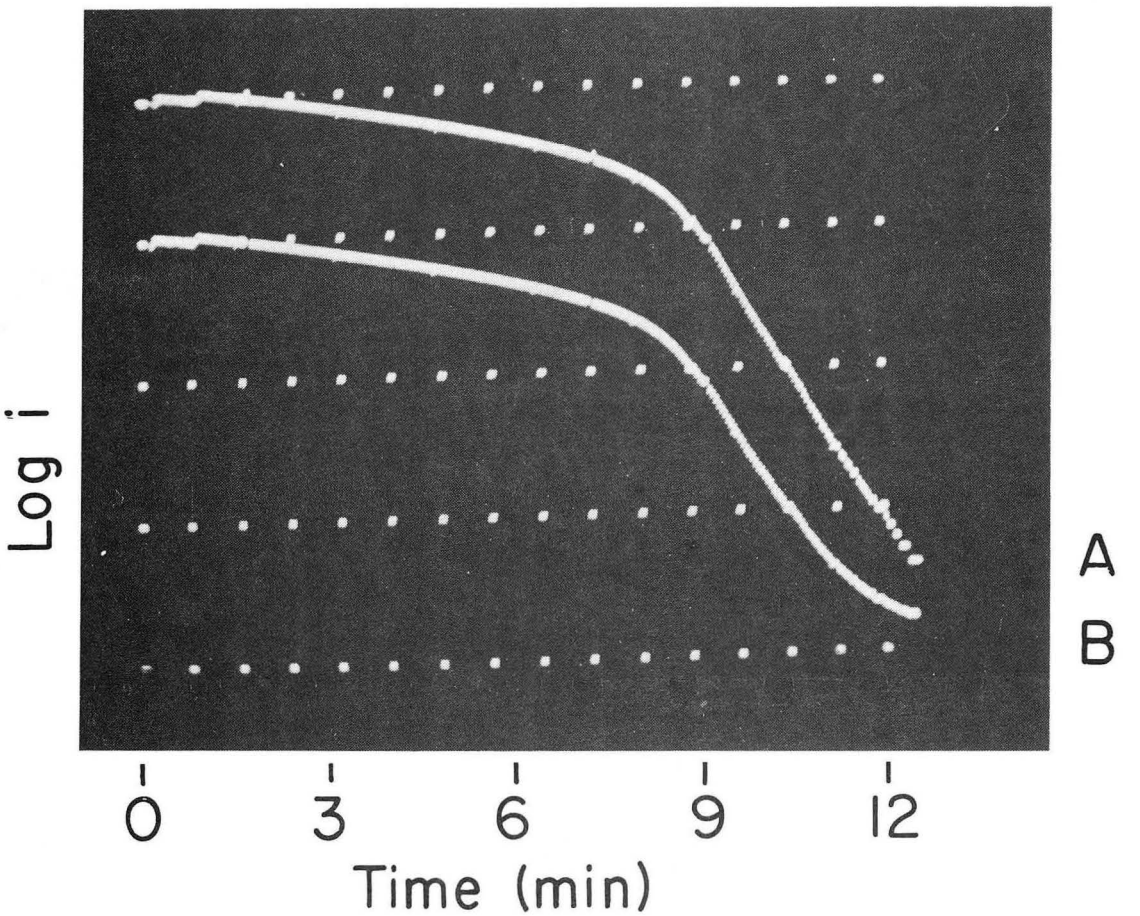
Fig. 6



XBB711-149

Fig. 7

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