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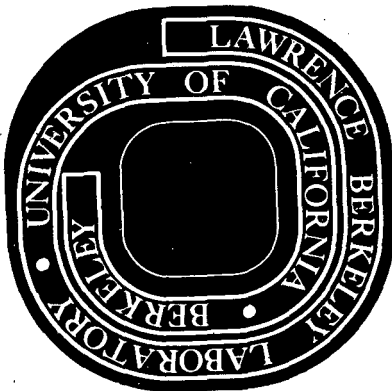
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CONTROLLED-POTENTIAL COULOMETRY

Ray G. Clem

April 1971

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A ROTATED PLATINUM CELL FOR CONTROLLED-POTENTIAL COULOMETRY

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April 1971

BRIEF

A rotated platinum cell for controlled-potential coulometry has been constructed and evaluated with several chemical systems. The highest electrolysis rate constants ever achieved with a platinum electrode, rapid sparging, and low sample volume requirements are some of the advantages of this cell.

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ABSTRACT

A rotated platinum cell which is a conceptual departure from the stationary platinum gauze-stirred solution-type cells has been constructed. It has fast sparging characteristics, low sample-volume requirements, and permits the attainment of the highest electrolysis rate constants ever achieved with a platinum electrode. Constants of 0.13, 0.082, and 0.064 sec<sup>-1</sup> are found for Au(III), Fe(III), and nitrite, respectively. The platinum cell is a gauze-lined cylinder, partially open at the top, and closed at the bottom. Centripetal force holds the sample solution against the cylinder wall in a thin film. The film is contacted and efficiently stirred with a stationary, coaxial, counter electrode-reference combination probe. This cell is freely interchangeable with the rotated mercury cell in an apparatus previously described (1).

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INTRODUCTION

The presented, novel, rotated platinum cell is a conceptual departure from the widely used stationary, platinum gauze, stirred solution designs and is the result of an extension of previous work which lead to the development of the rotated mercury cell (1).

The cell, which is made entirely of platinum, is a gauze-lined cylinder, closed at the bottom, and partially open at the top. It is held inside a plastic cylinder, with a partially open, plastic, screw-cap top. The plastic cylinder is attached to a copper turntable, and the cell-turntable combination is mounted in the previously described 1,800 rpm motor driven apparatus (1). The sample solution, upon rotating the cell, is held against the cell wall with centrifugal force and is contacted and efficiently stirred with the coaxial, combination, reference-auxiliary electrode probe. This efficient stirring combined with a favorable working electrode surface-area to solution-volume ratio results in the attainment of what quite possibly is the highest electrolysis rate constants ever achieved with a platinum electrode. This claim is qualified below.

As expected, many of the desirable qualities of the rotated mercury cell are found in the presented rotated platinum cell since both are based on

the same principles. Hence, it also features very rapid sparging characteristics. Usually, twenty seconds of sparging is sufficient to reduce the oxygen current to a value below the level of the background current. Also, it presently requires only two milliliters of sample solution although there appears to be no reason why a cell with a much smaller capacity could not be constructed. Additionally, surface phenomena are less troublesome since the platinum surface employed in this work is smaller than that of the three, large surface, high-speed cells to which the rotated cell is compared below.

#### EXPERIMENTAL

Instrumentation and Reagents. The digital instrumentation used was described in a previous paper (2). A Beckman #39270 saturated calomel electrode was used as reference.

Stock 0.5M HCl-0.025M sulfamic acid, 0.5M HCl, and 1M acetate buffer, pH 4.7 supporting electrolyte solutions were prepared by dilution of reagent grade chemicals. All water used was distilled. Stock solutions of the electroactive substances were prepared in the following manner. A weighed amount of gold metal was dissolved in aqua regia and the excess aqua regia displaced with hydrochloric acid. Sufficient sulfamic acid was added to give a concentration of 0.025M on final dilution of the stock Au(III) solution. A weighed amount of iron was dissolved in a mixture of hydrochloric acid and hydrogen peroxide. This solution was evaporated to a small volume to remove excess HCl, and to destroy the excess peroxide, then made to volume with water. Working solutions of these stock solutions were prepared by dilution. A stock solution of nitrite was prepared by dissolving a stick of sodium nitrite in water. A diluted working solution was standardized with a coulometric procedure (3).

The high-purity nitrogen employed for sparging was described previously (1).

Construction of the Platinum Cell and Plastic Holder. The platinum cell is constructed from 5 mil foil and 52 mesh gauze as follows. A piece of foil is cut to fit around a length of quartz tubing. The foil is taped at the ends then butt welded with an oxy-hydrogen torch. The seam in the resulting platinum tube is polished out with #600 emery paper, and a section of the cylinder of the desired length is parted, employing a lathe. This section becomes the cell wall. The gauze (each wire is 4 mils in diameter) is rolled and lapped, then severally spot-welded, employing tungsten electrode tips, to the interior wall of the cylinder. The gauze is three layers thick. Two disks of the required diameter are punched from the foil and the disk edges turned in a lathe with a forming tool to make lips. A hole is center punched in one disk which serves as the cell top. The top and bottom disks are welded--lip to cylinder with an oxy-hydrogen torch. The platinum cell is now completed. The weight of the cell is 13.1 g. Drawings 2 through 5 at the left of Figure 1 show an exploded view of the cell.

The plastic holder is machined, externally, to fit the copper turntable described previously (1). Internally, it is machined to center and snugly accommodate, diameterwise, the platinum cell. The screw-cap top serves two functions: it is a retainer for the cell and it forces the cell down against a rubber pad, platinum tab combination through which electrical contact is made to the turntable. "A" view of Figure 1 depicts a cross-section of the completed cell and holder while "B" is a top view.

A shop-copy blue-print of Figure 1 will be sent upon request.



Analytical Procedures. The details of the analytical methods employed were obtained from the literature. The procedures used to align the coaxial probe, to transfer the sample solution to the cell, and to prepare the fumed-silica salt bridges were described in earlier papers (1,4).

Gold is determined by electroreduction at 0.480 V vs. SCE in a 0.5M HCl-0.025M sulfamic acid supporting electrolyte (5). Nitrogen sparging is required. Iron is quantitatively electroreduced at 0.300 V vs. SCE in 0.5 HCl alone, after a 20 sec sparging with nitrogen (5), and nitrite is coulometrically oxidized at 0.950 V vs. SCE in the pH 4.7 acetate buffer medium (3). If the normalization procedure is used (1,2), set the rate meter (2) to terminate the titrations at 10, 10, or 20 ng/sec levels for gold, iron, or nitrite, respectively.

#### RESULTS AND DISCUSSION

Controlled-potential coulometry has long had basic appeal to analysts. Analyses can usually be performed with high selectivity, accuracy, precision, and sensitivity. The measured quantities, time and current, are fundamentally definable and the method is absolute. Additionally, the sample is not contaminated with titrant; generally it can be completely recovered for other tests or chemical applications. This is an important consideration when dealing with rare or expensive samples; i.e., transuranium elements or separated isotopes.

Despite these advantages, coulometry does not enjoy wide popularity because it is time consuming. For example, if the aliquoting time and, if need, sparging time is included in the titration time, only 3 to 6 analyses can be made per hour in the well-designed Harrar cell (6) which the presented cell has

now replaced in this laboratory. Coulometry then is employed only in situations in which its selectivity, accuracy, or precision is unique among the available alternatives and the projected number of analyses, or in the case of non-routine analysis, the value or nature of the sample is great enough to justify the time spent in adapting an existing method or developing a new one. If this statement were not true, why then would one group of workers find it attractive to reduce the titration time through the use of an on-line digital computer as recently as 1970 (7).

In an attempt to overcome this time problem, two schools of thought have appeared. One school prefers the calculational approach (2,7,8-11) which has culminated in the development of a very sophisticated instrument capable of producing results rivaling those obtained with classical weight-volumetric or gravimetric analysis in precision and with classical volumetric procedures in speed (7). The other school has attempted to reduce the time factor, with varying degrees of success, through improved cell design.

These efforts appear to have begun with Bard's work (12). By essentially filling the cell cavity with platinum gauze, he obtained electrolysis rate constants somewhat comparable to those obtained for the presented cell. He reported  $0.05 \text{ sec}^{-1}$  for the reduction of silver ion and  $0.012 \text{ sec}^{-1}$  for the oxidation of hydrazine under the conditions of mass transfer. Sonic warming of the solution titrated probably accounted for the slight increase in the rate constants over those obtained using nitrogen stirring alone. The background and capacitive currents, owing to the very large electrode surface-area, were greater than those of other types, e.g., the Harrar cell (6). This may be the reason why Bard's cell has not been widely used (13).

The work of Goode and Herrington (14) tends to confirm this author's contention that Bard's use of ultrasonic stirring was ineffectual. In the titration of iron(II), employing an annularly shaped platinum gauze electrode of high surface in conjunction with magnetic stirring, they obtained a log  $i$ -time plot of slope  $0.052 \text{ sec}^{-1}$ .

An initial slope steeper than the final slope was reported for both cells and had a value ranging from  $0.1$  to  $0.3 \text{ sec}^{-1}$ . Since the familiar Lingane equation (15,16) is used to describe a log  $i$ -time curve in which the reaction rate is limited only by the rate of mass transfer of the electroactive species to the working electrode, it appears that this equation does not apply to the steeper initial slope for reasons given below. This initial slope has, however, been used as a figure of merit (13). This is misleading.

The third high speed cell, that of Johansson (18), requires separate discussion. Cell 4, upon which most of his results were based, was constructed in such a way as to insure that the control-potential was exceeded over most of the working electrode surface because the reference electrode was placed in a region of minimum current flow. See Figures 4, 6, and 7 of Reference (17). Figure 3 of this author's previous work (1) shows the log  $i$ -time behavior for a cell in which the control-potential is initially exceeded. The initial slope of the curve is much greater than the final major portion, which was under proper potential-control. If, instead of the parallel combination probe used, two separate probes, i.e., an auxiliary and a reference bridge, had been employed and had been separated by  $180^\circ$ , the control-potential, in analogy to the Johansson cell, would have been exceeded during essentially the entire titration. Depending upon the concentration of the electroactive species, rate

constants as high as  $0.8 \text{ sec}^{-1}$  would be obtained and the slope of the log  $i$ -time curve would be quite linear. The background correction would also be a function of the concentration of the electroactive substance, decreasing as the concentration decreases. Precision coulometry under these conditions is obviously not possible. In view of the foregoing, it does not seem reasonable that Johanssen's reported constants of from  $0.10$  to  $0.18 \text{ sec}^{-1}$  should be used to justify a claim to having the fastest cell.

From the design standpoint, his cell 3 is somewhat better than cell 4, yielding constants of from  $0.014$  to  $0.026 \text{ sec}^{-1}$ . Such constants are sufficiently realistic for a properly designed cell which has the area to volume ratio described in his investigations.

These reported steeper initial slopes could be due to three different effects or combinations thereof not related to the phenomenon of mass transfer. They could be, as Bard states, due to "electrolysis of material--within the diffusion layer" (12), or to surface phenomena which include redox of material adsorbed on the platinum surface, or to the exceeding of the control-potential through faulty cell design (17), thus permitting development of deleterious potential gradients across the cell.

To some extent, depending upon the electrode surface-area, the nature of the sample, and the oxidation potential employed, the log  $i$ -time curve obtained with any platinum coulometry cell can be affected by the first two effects. Goode and Herrington found it advantageous, in the titration of plutonium, to use a gold working-electrode for which the surface phenomena are less pronounced.

Judging from the drawings, both of the above cells (12,14) probably suffer to varying degrees from the third effect, i.e., the exceeding of the control

potential. This insidious effect makes its presence known in the following ways. The cell's selectivity in the determination of closely adjacent redox couples could be impaired, yielding a positive error which would increase with increasing concentration of the first couple determined, i.e., the most easily oxidizable or reducible substance, if the second couple is irreversible. Such redox couples could include two or more substances of analytical concern as above, or it could be a single couple whose redox potential is near the decomposition potential of the supporting electrolyte or solvent. The background correction then is not easily obtained since its value depends upon the concentration of the electroactive substance determined. It certainly can not be measured by making a blank titration since the deleterious potential gradients are absent at the very small background current levels encountered in such a titration. Good results can, however, be obtained in cells of marginal design if the control-potential required for a single substance is well within the operating range of the electrode-material and not near the decomposition potential of the solvent or supporting electrolyte. In light of the foregoing, the Harrar-Shain article (17), and the discussion below, it might be of interest to re-examine the  $n$  value obtained for the oxidation of hydrazine (12) employing proper placement of the reference electrode.

The above remarks are in no way meant to fault the authors of their efforts (12,14,18). Their works are senior to the papers (1,17) which form the basis upon which these criticisms stand.

From the foregoing, it is apparent that if further reduction in the 15 to 20 min. electrolysis time is to be realized, some conceptual departure must be made from the conventional designs in such a way that the electrode

area to solution volume ratio is increased, but not at the expense of increasing the background current, or surface phenomena.

Such desirable qualities are obtained readily with the rotated platinum cell. The fundamental consideration and practical limitations underlying this development are the same as for the rotated mercury cell (1). The platinum surface-area is no greater than that of a well designed conventional cell (cf. Reference (3,6)); however, the sample solution-volume required is about one tenth. The electrolysis rate constants are about ten times those calculated for the conventional cell owing in part to the very efficient stirring action provided by the contacting of the rotated solution with the stationary coaxial probe. Also, the background correction is reduced by almost a factor of ten, provided the current is not initially limited.

The three chemical systems selected to test this new cell were the electroreduction of Au(III) and Fe(III), and the electrooxidation of nitrite. They were chosen because: they represent a sampling of different electrolysis rates, ranging from fast (Au III) to moderately slow (nitrite); they involve different kinds of electrode reactions--ion-ion, and ion-metal; and also, they illustrate problems peculiar to the rotated platinum cell.

The electrolysis rate constants calculated (11) for Au(III), Fe(III), and nitrite are 0.13, 0.082, and  $0.064 \text{ sec}^{-1}$ , respectively. These rate constants, as qualified in the preceding discussion, are probably the highest ever attained with a platinum cell. In comparison, constants of 0.014 and  $0.005 \text{ sec}^{-1}$  are found for Au(III) and for nitrite in a conventional cell (3,5,6). These selected chemical systems are diffusionally controlled because the rate constants respond to geometrical cell changes. Only small changes in the electrolysis constants would be anticipated for a kinetically controlled system (7,19,20).

The electrolysis time is sensitive to sample solution volume changes. See Figure 2. The electrolysis constant for a 5 ml sample is no larger than that obtained with a conventional cell (3,6). A 2 ml sample volume was selected for this cell because the rate constants are high, and this volume is convenient. Attempts to contact a much smaller volume can result in the scraping of the platinum gauze against the counter electrode-reference probe.

The log  $i$ -time curves for Fe(III) and Au(III) were similar to curve (a) for nitrite in Figure 2. The curve is initially non-linear because of the cell's current limiting behavior and finally non-linear because of the increasingly greater contribution of the background current to the gross current. The same analysis applies to curve (b). The cell current was not initially limited in the case of curve (c). The higher initial slope is due to surface phenomena. This behavior can also be observed for nitrite in conventional cells under non-current limiting conditions. For other examples see Reference (7), Figures 6 and 9.

The oxidation of nitrite illustrates a problem peculiar to the rotated cell. Nitrous acid is volatile and can be lost from aqueous solutions. Harrar found no losses of nitrite from his cell in pH 4.7 buffer for a period of one hour and a precision of 0.1% was obtained (3). The highest concentration level encountered in his cell was 4 mg nitrite in 25 ml of solution. The precision and accuracy obtained with the rotated cell, however, was much poorer at high concentration levels, owing to serious losses of nitrous acid. See Table I. This is due to the high air-solution contact area and to the high air turbulences in the present cell which do not exist in conventional cells. That these losses are due to volatilization was confirmed in an experiment in which the

rotated solution containing 3.8 mg of nitrite in 2 ml was sparged with nitrogen for 10 min. prior to the titration. Less than 2.6 mg were found as opposed to 3.1 mg when the titration was commenced immediately after aliquoting. These losses were compounded by the fact that the cell-current was limited for several minutes at 750  $\mu$ A at this concentration level. In view of this finding, the rotated cell in its present form should not be used conjunctively with volatile substances.

The titration of Au(III) illustrated another, but much less serious problem. It was observed that variations in the background current existed and were eventually related to variations in the draft velocity in the hood work-area in which the titration results shown in Table I were obtained. Although oxygen is irreversibly reduced over a wide potential range, reduction at +0.480 V vs. SCE was unexpected. In fact, the method employed states that oxygen removal is unnecessary (5). Sparging the cell with nitrogen, however, eliminated these variations and reduced the background current rate by at least 10 ng Au(III)/sec. This observation may lead to development of a new kind of air pollution monitor. Nitrogen sparging is not harmful to methods amenable to the rotated cell and is therefore recommended. The current limiting level for both Au(III) and Fe(III) is 900  $\mu$ A. The iron results are also shown in Table I.

The results for the smallest samples titrated presented in Table I exhibit positive bias. The manual, digital normalization procedure (1,2), which removes a constant number of counts from each memory channel, is not entirely satisfactory for normalizing very small samples. Much better results can be obtained using a FORTRAN program which treats the titration data as the sum of two exponentials. This program will be reported in the near future.



The current noise for this rotated cell is somewhat higher than for a conventional cell. This noise is traceable to the eccentricity of the present cell which results in a cyclic time variation in the working to reference electrode distance and thus appears as a periodic 30 Hz signal. See the dimensions given in Figure 1. Other noise of higher frequency but of lesser intensity is due to small dents in the cylinder wall resulting from the spot-welding operation. Current noise is objectionable because it results in some scattering of data points upon digital normalization of the stored log  $i$ -time curve. This demonstration cell will be replaced with one from a commercial source and will be constructed to rigid dimensional specifications. Construction of a gold and a silver cell is also planned, but no report on these is being considered. The characteristics of these cells should be similar to those given above for platinum.

In conclusion, a cell having rapid sparging behavior, low sample volume requirements and yielding short electrolysis times has been constructed. It should promote the use of controlled-potential coulometry for non-routine analysis and spur the development of new methods. Further, systems involving molecularly bulky organic complexing agents, which in the past have been avoided because of the reduction of the diffusion coefficient and hence prolongation of the titration, should now yield methods of reasonable titration times. A one hour titration in a conventional cell could probably be trimmed to 6 minutes in the rotated cell. Although the titration times presented, assuming the current is not initially limited, are very short--12 runs, including aliquoting, sparging, if necessary, and cell cleaning, can easily be made per hour--some further reduction in electrolysis times may be

made possible through the application of magnetically induced sonic stirring, although not at the 1 MHz frequency employed previously (12). The extent of this time reduction is apt to be much more dramatic for the mercury working electrode than for platinum.

#### ACKNOWLEDGMENTS

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Table I. Reproducibility\*

Au <sup>3+</sup> ( $\mu\text{g}$ )				Fe <sup>3+</sup> ( $\mu\text{g}$ )				NO <sub>2</sub> <sup>-</sup> ( $\mu\text{g}$ )			
Added	Found	Av. Dev.	n	Added	Found	Av. Dev.	n	Added	Found	Av. Dev.	n
1032	1029.8	0.4	5	761	759.0	0.3	5	3882	3104	7	3
516	514.8	0.2	6	380	379.0	0.4	6	1294	1283.6	1.3	5
258	257.5	0.2	5	76	77.2	0.2	5	647	648.2	0.8	6
								517	514.9	0.5	4
								326	323.7	0.3	5
								129	128.8	0.2	4
								65	66.7	0.1	5

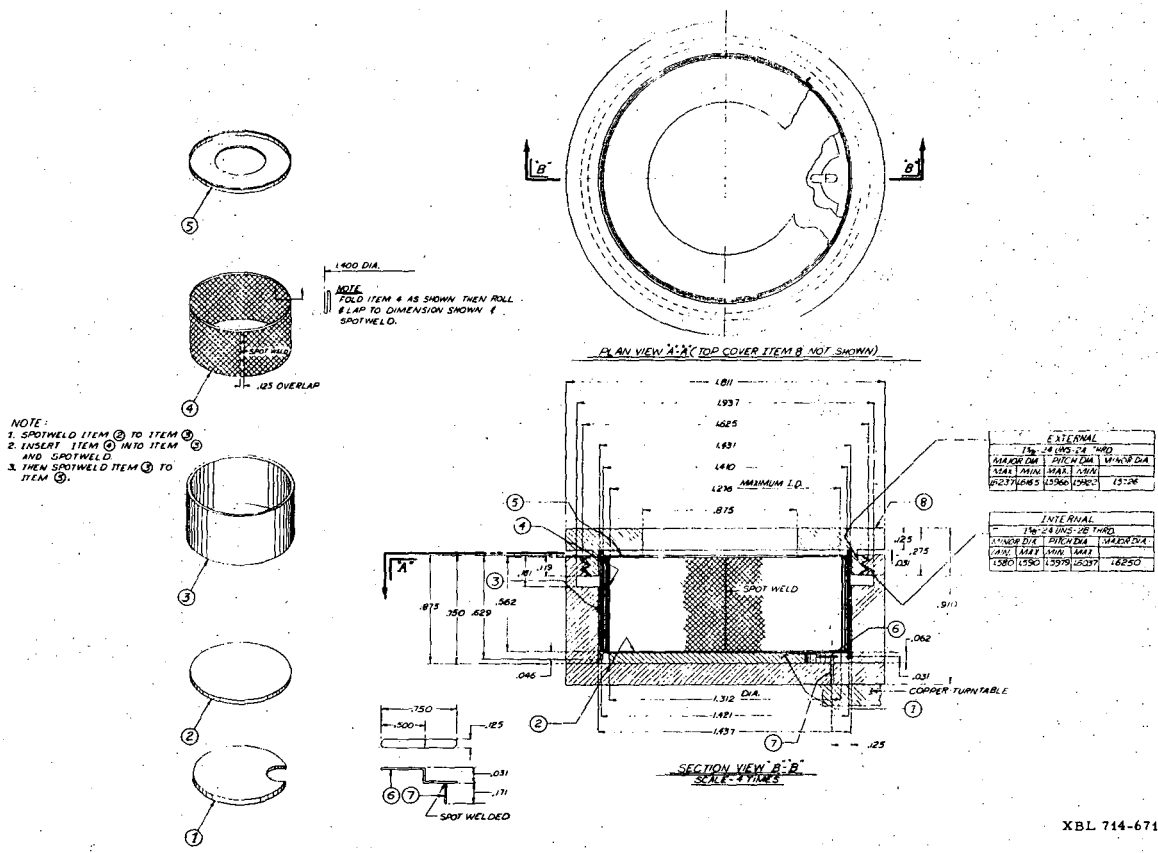
\* All results obtained by normalization (1).

FIGURE CAPTIONS

Fig. 1. Exploded, Top, and Cross-Sectional Views of the Platinum Cell and Plastic Holder.

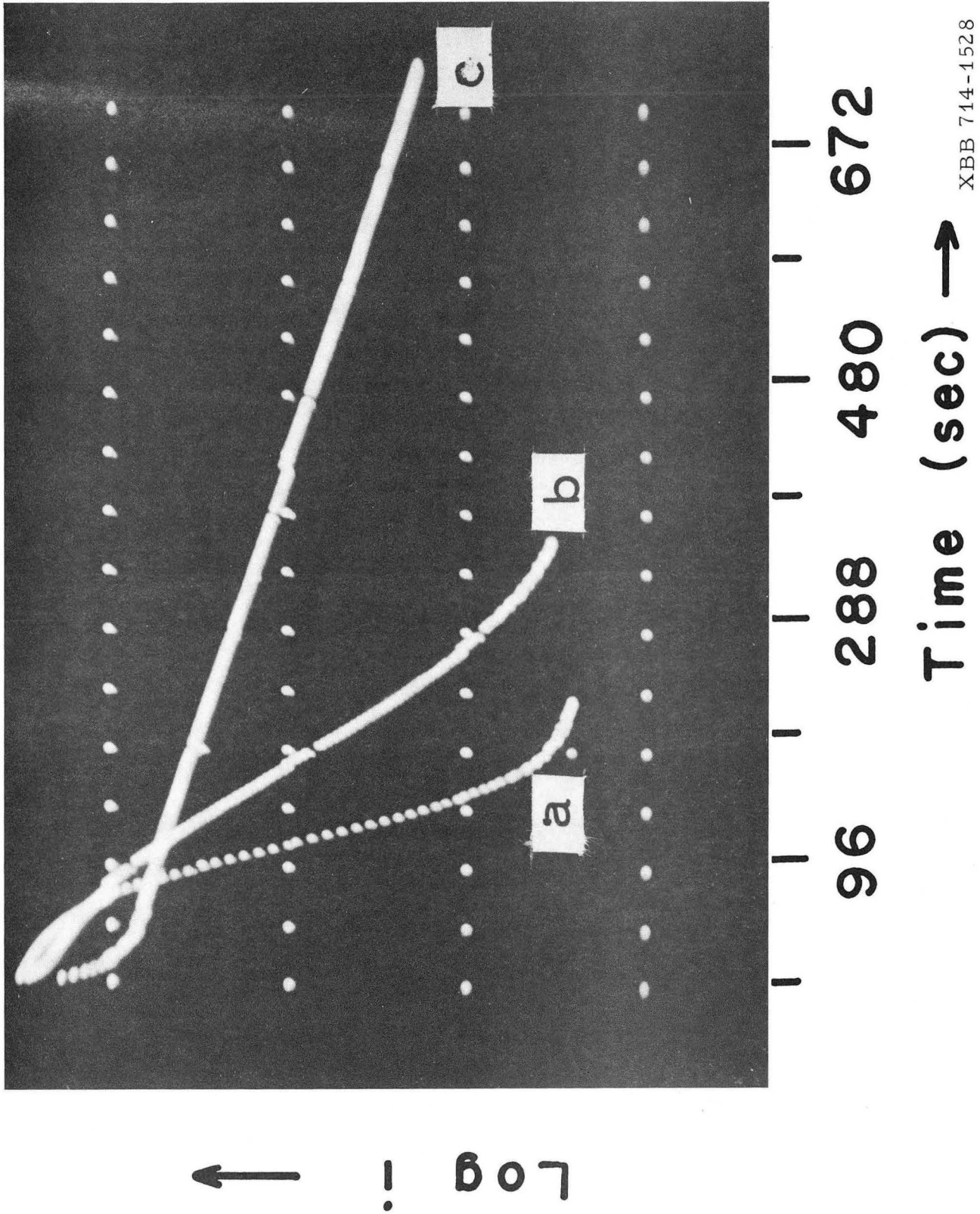
Fig. 2. Effect of Volume on the Electrolysis Rate

647  $\mu\text{g}$  nitrite in: A. 2, B. 3, and C. 5 ml of 1M acetate buffer, pH 4.7. Rate constants for curves A, B, and C are 0.064, 0.023, and 0.005  $\text{sec}^{-1}$ , respectively.



XBL 714-671

Fig. 1



XBB 714-1528

Fig. 2



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