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AD NUMBER

ADC950573

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AUTHORITY

DSTL, WO 189/5046, 8 Oct 2009; DSTL, WO 189/5046, 8 Oct 2009

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STUDIES OF THE ELECTROCHEMICAL DETECTION OF THIOLS PART II AN INVESTIGATION OF THE REACTION OCCURRING IN NAIAD, AND THE EFFECT OF HCN, GUAIACOL AND GB ON THESE REACTIONS [C]

by

B.W. Ford, D. Pletcher*, P. Watts and R.G. Wilkinson

Technical Paper No. 213

January 1977

Chemical Defence Establishment,
Porton Down, Salisbury, Wilts.

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7 [STUDIES OF THE ELECTROCHEMICAL DETECTION OF THIOLS
 PART II. AN INVESTIGATION OF THE REACTIONS OCCURRING IN NAIAD,
 AND THE EFFECT OF HCN, GUAIACOL AND GB ON THESE REACTIONS] (C)

10 by
 B.W. FORD, D. PLETCHER*, P. WATTS and R.G. WILKINSON

SUMMARY

The anodic and cathodic reactions occurring in NAIAD have been investigated using a platinum anode. The effects of HCN and guaiacol (substances which are likely to arise from burning vegetation) on these reactions have been studied. The cell has been exposed to GB and the concentration change of thiocholine when NAIAD gives an alarm has been measured.

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STUDIES OF THE ELECTROCHEMICAL DETECTION OF THIOLS

PART II AN INVESTIGATION OF THE REACTIONS OCCURRING IN NAIAD,
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1. INTRODUCTION

The electrode system adopted for NAIAD comprising a pyrolytic graphite anode and a platinum cathode is similar to that used in the early laboratory studies (1) and in the main its performance is satisfactory. However, the details of the electrochemical performance of the electrode system are not understood (2). Since the response of NAIAD to several interfering substances in the atmosphere could be electrochemical in origin, it was essential if these interferences were to be overcome that further investigations of the electrochemical reactions occurring or likely to occur in NAIAD should be undertaken.

The investigation of the electrochemical performance falls into two distinct phases. The first concerns the phase heterogeneity occurring in NAIAD, i.e. solid, liquid and air, and the second concerns the use of pyrolytic graphite, a poorly defined electrode material (3). A separation of these two aspects of NAIAD has been achieved experimentally by initially substituting a better defined electrode material to investigate the electrochemistry.

This paper presents the results of an electrochemical investigation of NAIAD using an experimental cell similar in construction to that used in NAIAD with platinum, a well defined electrode material as the anode. Using various electrochemical techniques both the anodic and cathodic reactions and the effect of the anode geometry upon the magnitude of the electrochemical reactions have been studied. The interaction of hydrogen cyanide (an interfering substance likely to arise from various sources) and of guaiacol (the main interfering substance occurring in smoke from burning vegetation (4)) with the experimental cell have been investigated. Finally, the thiocholine concentration in the experimental cell was monitored during an exposure to GB and an estimate was made of the magnitude of the concentration change of thiocholine necessary to cause NAIAD to alarm.

2. EXPERIMENTAL

The apparatus and experimental techniques have been described previously (2).

The experimental cell used in the present work (Figure 1) was a more advanced version of that used previously and is similar to the electrochemical cell in NAIAD. The anode and cathode were pieces of platinum gauze ca. 1 cm diameter and the silver - silver chloride reference electrode was a coated wire separated from the anode by a piece of nylon gauze. In some experiments the anode was a $\frac{1}{2}$ mm thick platinum plate drilled according to the specification for pyrolytic graphite electrodes - 40 holes 0.03 mm diameter (5).

In all experiments substrate, or thiocholine, in 0.05M phosphate buffer, pH 7.4, containing 0.1M sodium chloride was passed through the cell at a flow rate of 12 ml/h using a syringe drive unit (Sage Instruments Model 355). Air was drawn through the cell at 1 l/min using a diaphragm pump (Charles Austen Model DYMAX Mk.I).

Butyrylthiocholine methanesulphonate, thiocholine methanesulphonate and immobilised cholinesterase pads were provided by Detection and Analysis Division. Thiol analyses were made using the Ellman method (6).

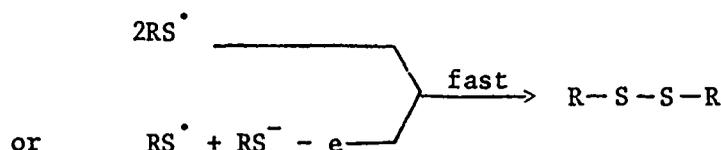
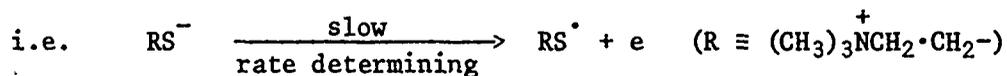
3. RESULTS AND DISCUSSION

3.1 Definition of electrode reactions in NAIAD

Current - potential curves were recorded for thiocholine methanesulphonate at a series of potential scan rates. A typical curve is shown in Figure 2 and that recorded under steady state conditions in Figure 3. Thiocholine methanesulphonate was used rather than butyrylthiocholine and cholinesterase enzyme pads for convenience when the experiment did not require the use of an enzyme pad. The $i - E$ curves show an oxidation wave ($E_{\frac{1}{2}} \sim 0.6V$) similar to that for thiocholine obtained under stationary conditions (2), and it will be reported later that this wave has a magnitude proportional to thiocholine concentration. Under the conditions prevailing in the experimental cell where the solution contains a large concentration of oxygen, a large cathodic current is observed at + 0.1V and more negative potentials. This current obscures the thiocholine desorption wave obtained under stationary conditions in deoxygenated solutions (2).

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The cell effluent was shown to contain thiocholine and choline disulphide, the oxidation product of thiocholine,



which is capable of being reduced at the cathode in NAIAD.

To define the cathodic reaction more clearly, a cyclic voltametric study was carried out. Voltamograms were recorded under stationary deoxygenated conditions using a platinum electrode in the normal cell (Ref. 2, Fig.2), and are recorded in Figure 4. The data from the voltamograms are summarised in Table 1.

TABLE 1

RESULTS FROM CYCLIC VOLTAMETRIC STUDIES OF THE REDUCTION OF CHOLINE DISULPHIDE ($5 \times 10^{-4}M$) AT A PLATINUM ELECTRODE UNDER STATIONARY, DEOXYGENATED CONDITIONS

Sweep rate (V/min)	Cathodic current, i_{p_c} , μA (-0.9V)	Anodic current, i_{p_a} , μA (-0.7V)
0.1	300	300
0.3	500	500
1.0	900	800
3.0	1500	1400

The reduction of choline disulphide occurs at E_p -0.9V, much more negative than oxygen reduction E_p = -0.1V, and the reduction leads to a product stable on the time scale of cyclic voltametry (10 - 100 s) which reoxidises at E_p = -0.7V. This product is not thiocholine, which is oxidised at E_p = +0.8V, and was not identified.

Thus, in NAIAD oxygen reduction will be the cathodic reaction and the reduction is not inhibited by thiocholine or choline disulphide.

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In NAIAD thiocholine is produced, together with a stoichiometric amount of butyric acid, by enzymic hydrolysis of butyrylthiocholine. It has been shown from steady state $i - E$ curves (Fig.3) that there is only a small contribution to the current flowing due to oxidation of butyrylthiocholine and butyric acid; oxidation of thiocholine provides the only significant contribution to the current.

3.2 Quantitative studies in an experimental cell

3.2.1 Calibration of the dependence of cell current upon thiocholine concentration

The dependence of the anodic current, i , upon the concentration of thiocholine, c , at a series of potentials was studied in the experimental cell. The results are reported in Table 2 and shown in the form of $\log i - \log c$ plots in Figure 5.

The best correlation of current with concentration is obtained at the highest potential +0.8V where the reaction is largely subject to mass transport control. The concentration dependence was investigated at lower potentials to see if the signal to noise ratio was dependent upon the nature of the rate controlling process, i.e. electron transfer or mass transfer. However, as the potential was decreased the contribution of the background current became too significant to allow the dependence to be determined.

At 0.8V the current flowing at a thiocholine concentration $5.0 \times 10^{-6}M$ was $0.2 \mu A$, which it was just possible to discriminate from the background current of $1 \mu A$. Hence $5 \times 10^{-6}M$ thiocholine represents the minimum concentration detectable.

TABLE 2

CALIBRATION OF THE RESPONSE OF THE EXPERIMENTAL CELL TO VARIOUS CONCENTRATIONS OF THIOCHOLINE AT A RANGE OF APPLIED POTENTIALS

10^6 [Thiocholine] (M)	Applied potential, V vs. Ag/AgCl:	0.3	0.4	0.5	0.6	0.7	0.8
		Current, i_{p_a} (μA)					
5		-	-	-	-	0.1	0.2
10		-	-	-	0.1	0.2	0.4
25		-	0.1	0.2	0.3	0.5	0.8
50		0.1	0.2	0.3	0.6	0.9	1.8
100		0.2	0.4	0.6	1.0	2.0	3.7
250		0.3	0.8	1.4	2.3	6.0	9.5
500		0.6	1.7	4.1	6.0	9.5	18

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3.2.2 Calibration of the dependence of cell current upon the concentration of thiocholine produced by hydrolysis of butyrylthiocholine with an immobilised cholinesterase pad

(a) Gauze electrode

The experimental cell was used to calibrate the electrode response when thiocholine, produced by enzymic hydrolysis of butyrylthiocholine, was passed through the cell. The cell effluent was analysed for thiol (using the Ellman method) both before and during electrolysis. Typical results are summarised in Table 3 and the calibration for several experiments is shown in Figure 6.

TABLE 3

CALIBRATION OF THE RESPONSE OF AN EXPERIMENTAL CELL TOWARDS THIOCHOLINE PRODUCED BY HYDROLYSIS OF BUTYRYLTHIOCHOLINE WITH A CHOLINESTERASE PAD.

APPLIED POTENTIAL = 800 mV vs. Ag/AgCl

10 ⁶ [BuSch] (M)	10 ⁶ [Thiol] (M)	ip _a (µA)	% Thiol lost	
			Based on current	Based on analyses
5	5	0.3	18.4	14.2
10	10	0.6	18.4	16.2
50	34	2.3	19.3	17.5
100	62	3.6	17.0	20.1
250	91	6.9	23.0	24.1
500	180	11.7	19.1	20.5

There was a good correlation between the current and the thiocholine concentration produced in the cell. The correlation was similar to that obtained using thiocholine but the results should not be compared on an absolute basis because of slight differences occurring in cell configuration during assembly of the cell. All the results recorded from Table 3 onwards were obtained using a gauze electrode in a single cell assembly and these are therefore directly comparable. The enzyme pads used had nominally the same activity (0.77 units/pad) and gave very similar conversions to thiol.

[One unit is defined as that enzyme which will hydrolyse 1 µM butyrylthiocholine per min at pH 8.0 and 25°]. Throughout a series of ca. thirty experiments, the variation in the conversion of substrate (at any fixed concentration) to thiol was never more than 10%.

(b) Plate electrode

The experimental cell was assembled as in Figure 1, but using a drilled platinum plate as anode rather than a piece of gauze. The plate was drilled to a similar specification to that for the pyrolytic graphite electrodes in prototype model NAIAD systems (5).

The cell was then used to calibrate the electrode response when substrate was passed through an immobilised enzyme pad and into the cell. The conversion of substrate into thiol was measured as before and the results are given in Table 4. The current level with buffer only was ca. 4 μ A, rather higher than that for the gauze electrode (ca. 1 μ A). The higher background current level for the plate may be a function of the different cell flow characteristics.

TABLE 4

CALIBRATION OF THE RESPONSE OF AN EXPERIMENTAL CELL (PLATE ANODE) TOWARDS THIOCHOLINE PRODUCED BY HYDROLYSIS OF BUTYRYLTHIOCHOLINE WITH A CHOLINESTERASE PAD. APPLIED POTENTIAL = 800 mV vs. Ag/AgCl

10^5 [BuSCh] (M)	10^5 [Thiol] (M)	Current (μ A)
1	1	0.5
2.5	2.1	1.4
5	3.4	1.9
10	7.0	3.8
25	9.4	5.6
50	18.0	11.6

(c) Comparison of a gauze and plate electrode

Comparison of the results for a plate electrode in Table 4 with those given in Table 3 for the cell with a gauze anode showed that the response of the two cells was very similar. Comparative experiments in a stationary cell using both the gauze and plate anodes showed that the electrodes had similar surface areas. With the plate electrode there was the problem of where on the surface the main electrode reaction was occurring. With this in mind, experiments were carried out with the top surface of the plate coated with paraffin wax so that no reaction could occur on this surface.

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This left the surface within the holes and the bottom face of the plate as surfaces for the electrode reaction to occur. The results for the calibration of the cell with the top surface wax coated are given in Table 5.

TABLE 5

CALIBRATION OF THE RESPONSE OF AN EXPERIMENTAL CELL (PLATE ANODE,
TOP SURFACE WAX COATED) TOWARDS THIOCHOLINE PRODUCED BY HYDROLYSIS
OF BUTYRYLTHIOCHOLINE WITH A CHOLINESTERASE PAD
APPLIED POTENTIAL = 800 mV vs. Ag/AgCl

10^5 [BuSch] (M)	10^5 [Thiol] (M)	Current (μ A)
2.5	2.1	0.6
5.0	3.3	0.9
10	6.6	1.6
25	9.3	2.8
50	18	5.8

It can be seen by comparison of the results in Tables 4 and 5 that about half of the electrode reaction probably occurred on the top surface of the plate, and the remainder of the reaction in the holes and bottom surface of the plate. The uncertainty arises as the wax coating may have caused different flow characteristics. (The surface area of each face of the plates was ca. 25 mm² and of the surface in the holes ca. 20 mm²). Since solution is drawn through the holes it probably does not make sufficient contact with the bottom surface of the plate for this to contribute markedly to the total electrode reaction.

3.2.3 Noise levels

The recorded current levels fluctuated about a mean value. This variation was possibly caused by uneven solution flow through the cell and variations in the air flow. There was more random noise, both in frequency and amplitude, with the plate electrode than with the gauze electrode, probably indicative of a more variable solution flow through the cell. Under the conditions used, the signal to noise ratio was ca. 20:1 but should be improved by a more even solution flow through the cell.

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3.2.4 Effect of HCN on the experimental cell

3.2.4 (i) HCN in solution

Cyclic voltamograms recorded at a stationary platinum electrode for thiocholine, HCN and a mixture of thiocholine and HCN are shown in Figure 7. The HCN was oxidised at a potential close to that for thiocholine. Calibrations of the response of the NAIAD cell to different concentrations of HCN in solution were obtained and the results are given in Table 6. Experiments with both commercial HCN and with AR KCN (ex BDH) dissolved in buffer (pH 7.4) gave identical results.

TABLE 6

CALIBRATION OF THE RESPONSE OF AN EXPERIMENTAL CELL TO VARIOUS CONCENTRATIONS OF HCN. APPLIED POTENTIAL = 800 mV vs. Ag/AgCl
([Thiocholine] = 2.5×10^{-4} M)

10^5 [HCN] (M)	Current (μ A)
-	15
5	16
10	18
50	25

(ii) HCN in air sample

(a) Using thiocholine and laboratory generated HCN

HCN was generated by drawing air across an acidified solution of KCN, and the concentration of HCN in the air was measured using a Dräger HCN tube.

A typical experimental run is shown in Figure 8. As expected the current increased when the air sample contained HCN and fell to the original level when the HCN sample was removed. A peak occurs on exposure to HCN and the current then levels off to a steady value.

The current response for different concentrations of HCN in the air has been measured and the results are given in Table 7.

TABLE 7

CALIBRATION OF THE RESPONSE OF AN EXPERIMENTAL CELL TOWARDS VARIOUS
 CONCENTRATIONS OF HCN. APPLIED POTENTIAL = 800 mV vs. Ag/AgCl
 ([Thiocholine] = 2.5 x 10⁻⁴M)

[HCN] µg/l	Current, µA
-	16
2	17
4	18
6	19
10	22
12	25

Comparison of the data shown in Tables 6 and 7 indicates that about 15% of the HCN goes into solution.

(b) Using thiocholine and HCN generated in an exposure chamber (100 m³)

The results obtained are in close agreement with those obtained using laboratory generated gas shown in Fig.8. The HCN was generated by blowing warm air over the appropriate weight of liquid HCN.

(c) Using butyrylthiocholine + enzyme pad and laboratory generated HCN

A typical experiment is shown in Figure 9. The results are very similar to those obtained using thiocholine. Repeated exposures to HCN did not cause the initial current level for oxidation of the thiol to change after removal of the HCN. Analysis for thiol in the cell effluent before and after exposure to HCN showed that the concentration produced was unchanged, viz. 1.8 x 10⁻⁴M. A prototype NAIAD (A2 Model) with a two electrode system (C anode, Pt cathode) was used in one experiment for comparison. The initial potential was reduced on exposure to HCN peaked as in the constant potential work (a) and returned to the initial level on removal of the HCN.

(d) Using butyrylthiocholine + enzyme pad and chamber generated HCN

A typical experiment is shown in Figure 10. It can be seen that the results obtained are completely different from those with laboratory generated HCN, and also from those obtained using thiocholine and chamber generated HCN. On exposure to HCN the current increased but peaked and fell off rapidly.

Removal of the HCN resulted in a depression of the current below that initially obtained for the thiol produced. Re-exposure to HCN resulted in a smaller current response, and again the current fell off during the exposure. Analysis for thiol produced before and after exposure shows that a reduced amount was formed. Before exposure the thiocholine concentration produced was $1.7 \times 10^{-4}M$ (using $5 \times 10^{-4}M$ butyrylthiocholine) and after exposure the thiocholine concentration was $1.1 \times 10^{-4}M$ (ca. 6 min exposure to $10 \mu g/l$ HCN). There was, however, necessarily some delay in analysing this sample and the value may be 10% low.

Comparison of these results with those obtained using a NAIAD Model A2 system showed that similar effects were observed. The initial potential due to thiol only is reduced after exposure to HCN but rapidly increases during the exposure. After removal from the HCN the potential due to the thiol only was ca. 10% higher than the initial value. Repeated exposures were not carried out.

From these experiments it was apparent that HCN produced in the chamber caused inhibition of the enzyme pad, but this inhibition was an artefact of the experimental system and was not due to HCN. No attempt was made to determine the nature of this artefact.

3.2.5 Response of the experimental cell to guaiacol

Cyclic voltamograms were recorded for the oxidation of thiol only, guaiacol only and thiol plus guaiacol at a stationary platinum electrode and these are shown in Figure 11. It can be seen that guaiacol was oxidised at 0.6V vs. Ag/AgCl and would therefore be co-oxidised with thiol in NAIAD.

Passage of a solution containing $5 \times 10^{-4}M$ butyrylthiocholine and $10^{-4}M$ guaiacol (the maximum level likely from burning straw) through an experimental cell fitted with an enzyme pad caused a gradual reduction in the current, and after about an hour the current levelled off at ca. 3 - 4 μA . Analysis for thiol produced before and after electrolysis in the presence of guaiacol showed that the concentration produced was unchanged. Replacing the enzyme pad with a fresh pad, and passing only substrate caused no change in the reduced current level measured. Additionally, analysis for thiol in the cell effluent before and during electrolysis showed that no thiol was being oxidised. If the pad was removed so that substrate only passed through the cell, the current was unchanged. Allowing solution to flow through the cell for about an hour with no potential applied caused the current level to be restored to its original level when a potential was again applied.

Passage of a solution containing guaicol again caused the current to fall as before. The results obtained are summarised in Table 8.

TABLE 8
THE RESPONSE OF AN EXPERIMENTAL CELL TO GUAICOL

	10^4 [Thiol]			Current μ A
	before electrolysis	during electrolysis	after electrolysis	
BuSCh only	1.8	1.4	1.8	12
+ 10^{-4} M guaicol	1.8	1.7	1.7	Falls to 4
BuSCh only	1.8	1.8	1.8	3
Pad removed	-	-	-	3
New pad, BuSCh only	1.9	1.8	1.8	3
After 1 h washing	1.9	1.5	1.8	11

The results indicated that after passage of guaicol through the cell, the electrode system was unable to oxidise thiocholine. This poisoning of the anode surface was reversible and the electrode can be reactivated in situ after a period of washing.

3.2.6 Response of the experimental cell to GB

The results of experiments carried out using two concentrations of GB are given in Table 9 which also includes the data obtained using a NAIAD Model A2 system so that the time for the alarm to trigger could be noted for the potentiostatted cell.

TABLE 9

THE RESPONSE OF NAIAD AND AN EXPERIMENTAL CELL TO GB

[GB] $\mu\text{g/l}$	Experimental cell, Pt electrodes Ag/AgCl reference electrode				NAIAD Model A2 (Two-electrode cell)	
	Current, μA		10^4 [Thiol] (M)		Change of potential mV/min	Time to trigger s
	Initial	At trigger ^a	Initial	At trigger ^b		
0.005	11.2	10.7	1.8	1.75	15	120
0.05	11.5	11.0	1.8	1.75	75	20

^a NAIAD will give an alarm for a change of potential of > 25 mV at a rate > 6 mV/min.

^b Thiol level at trigger was interpolated from the data presented in Table 4 and Figure 7.

It can be seen from the results in Table 9 that the thiol concentration changed by $< 5\%$ when the NAIAD alarm triggered, in good agreement with the change used in work with a simulation model of NAIAD (7, 8).

4. CONCLUSIONS

1. The electrode reactions which occur in NAIAD are oxidation of thiocholine at the anode and reduction of oxygen at the cathode.
2. The performances of a platinum gauze and of a drilled plate anode are very similar. However, the minimum detectable thiol concentration is higher with the plate anode because of the higher background current level, which probably arises from different cell flow characteristics.
3. The response of the experimental cell to HCN is reversible.
4. Guaicol causes the anode surface to become incapable of oxidising thiocholine.
5. Exposure of an experimental cell and NAIAD (Model A2) to GB shows that NAIAD will alarm when the thiol concentration falls by 5%.

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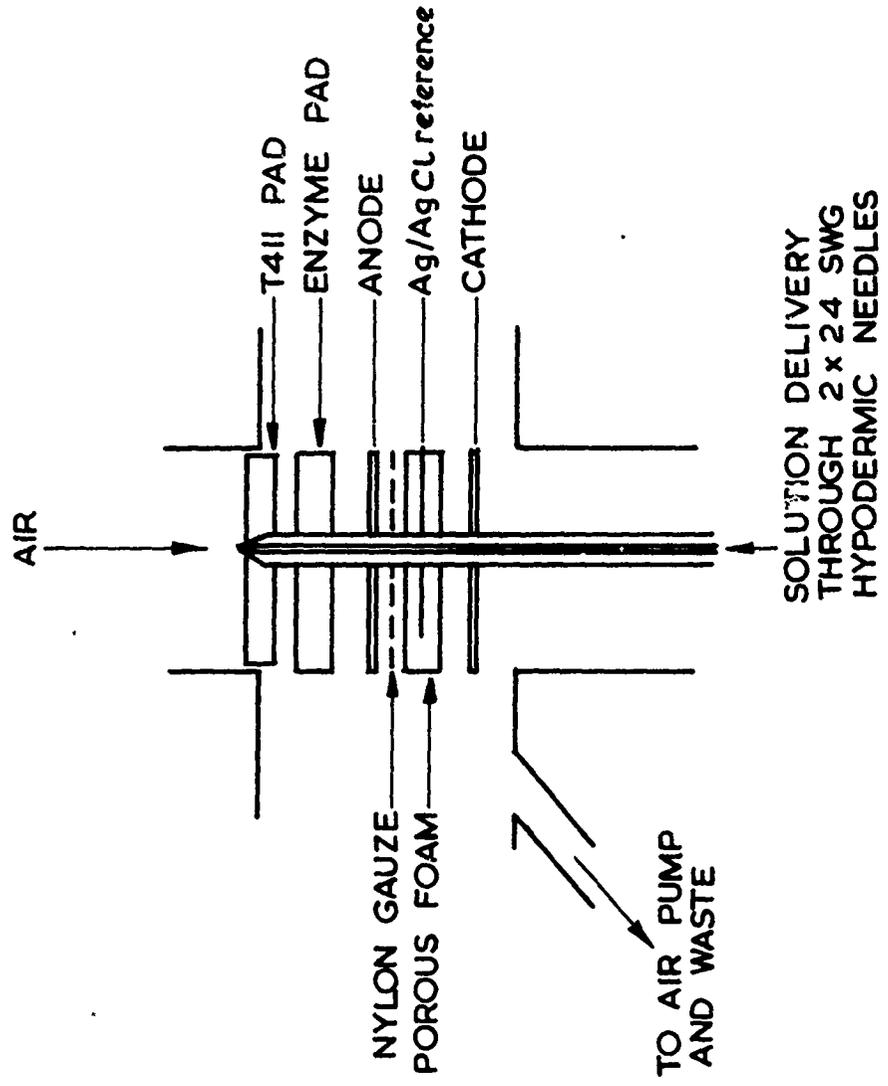
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SCHEMATIC REPRESENTATION OF NAIAD FLOW CELL (MODEL B)

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FIG. I.

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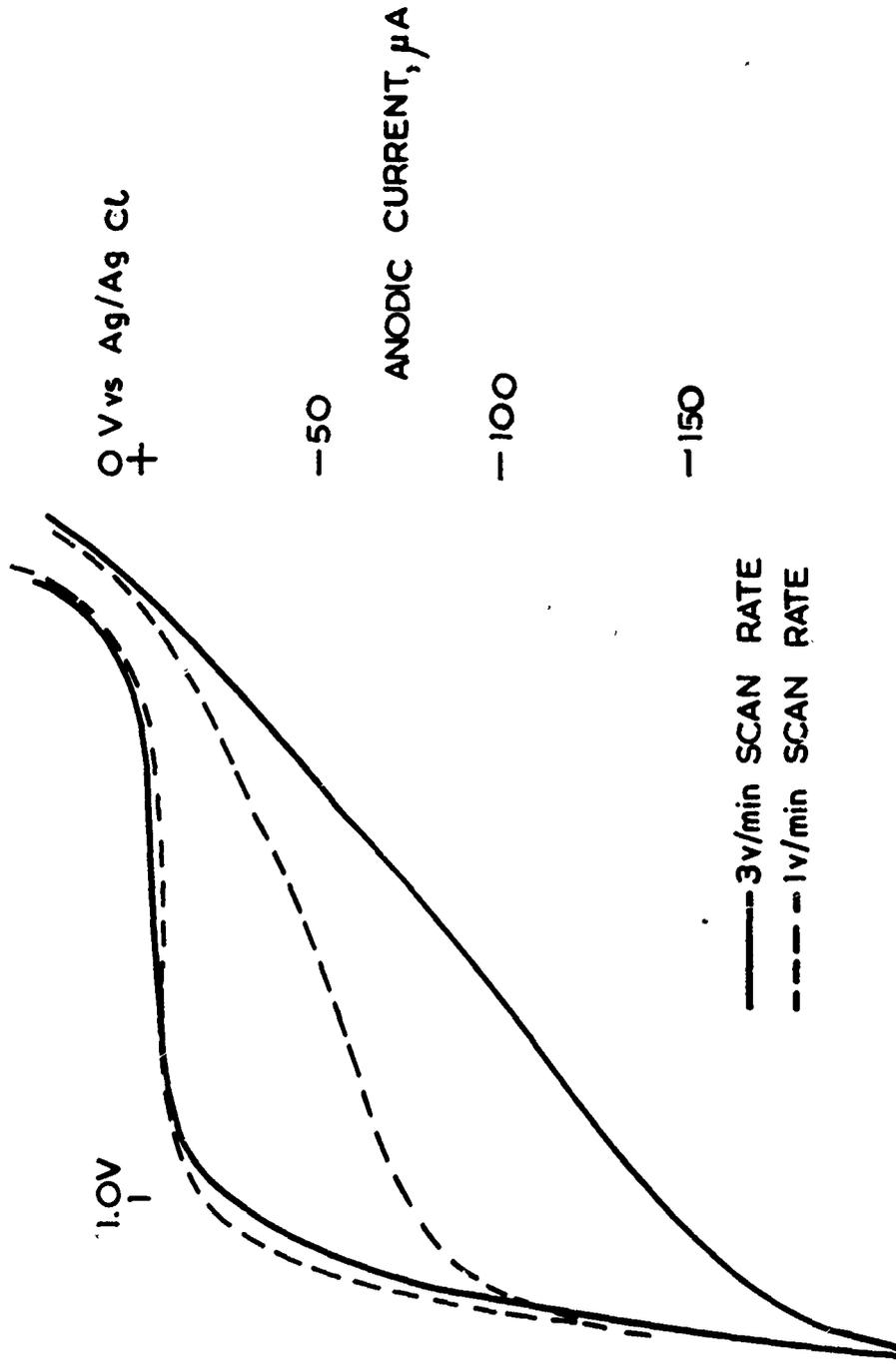
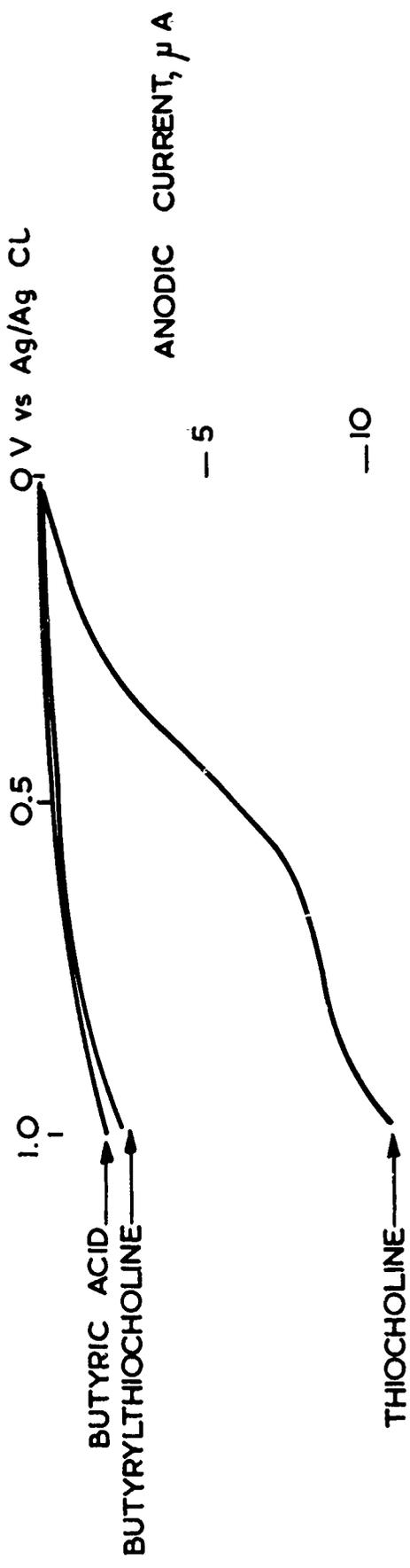


FIG. 2. CYCLIC VOLTAMMOGRAMS OBTAINED FOR THE OXIDATION OF THIOCHOLINE (5 x 10⁻⁴ M) IN AN EXPERIMENTAL CELL

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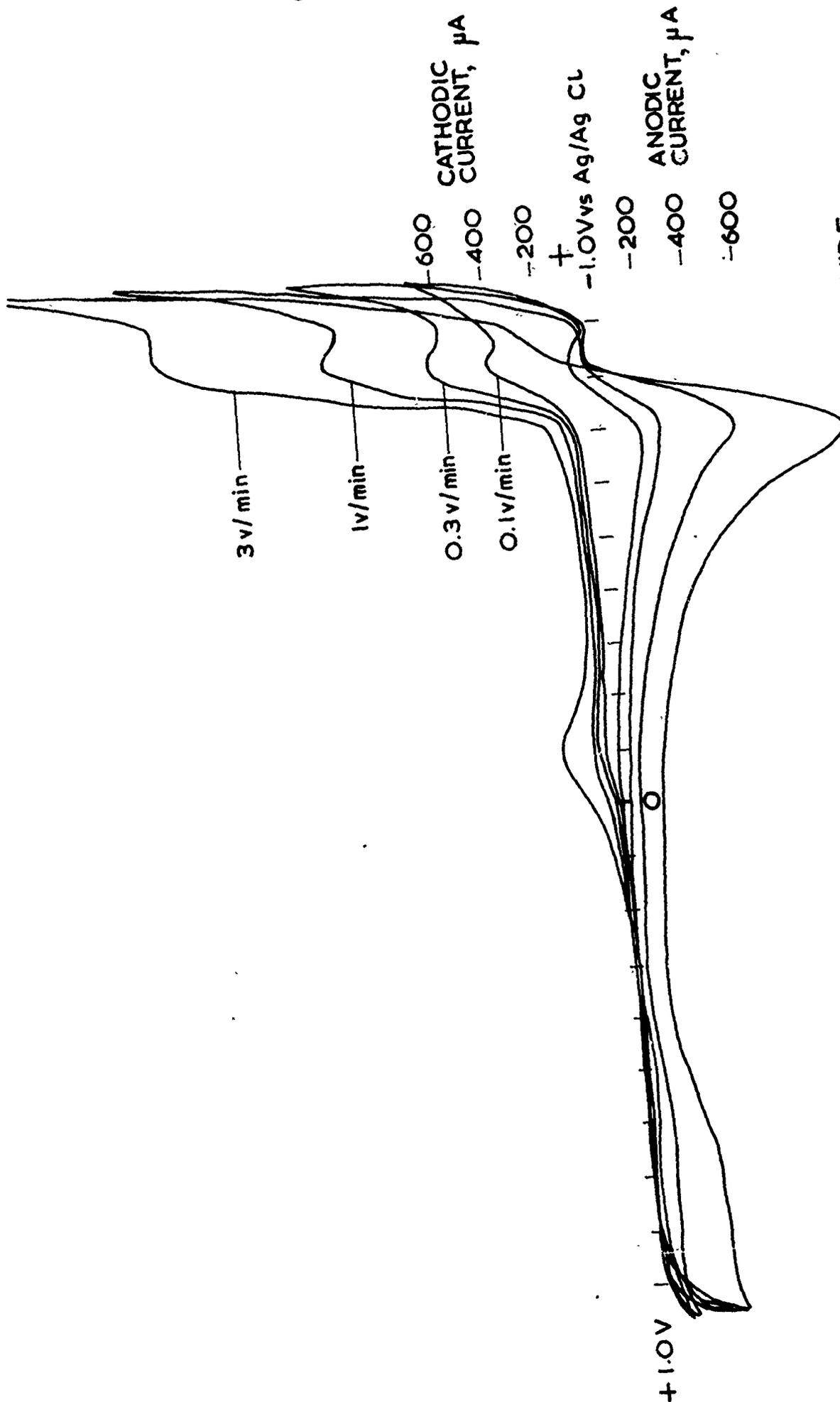
STEADY STATE CURRENT-POTENTIAL CURVES FOR THIOCHOLINE, BUTYRYLTHIOCHOLINE AND BUTYRIC ACID (ALL 5×10^{-4} M)

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FIG. 3.

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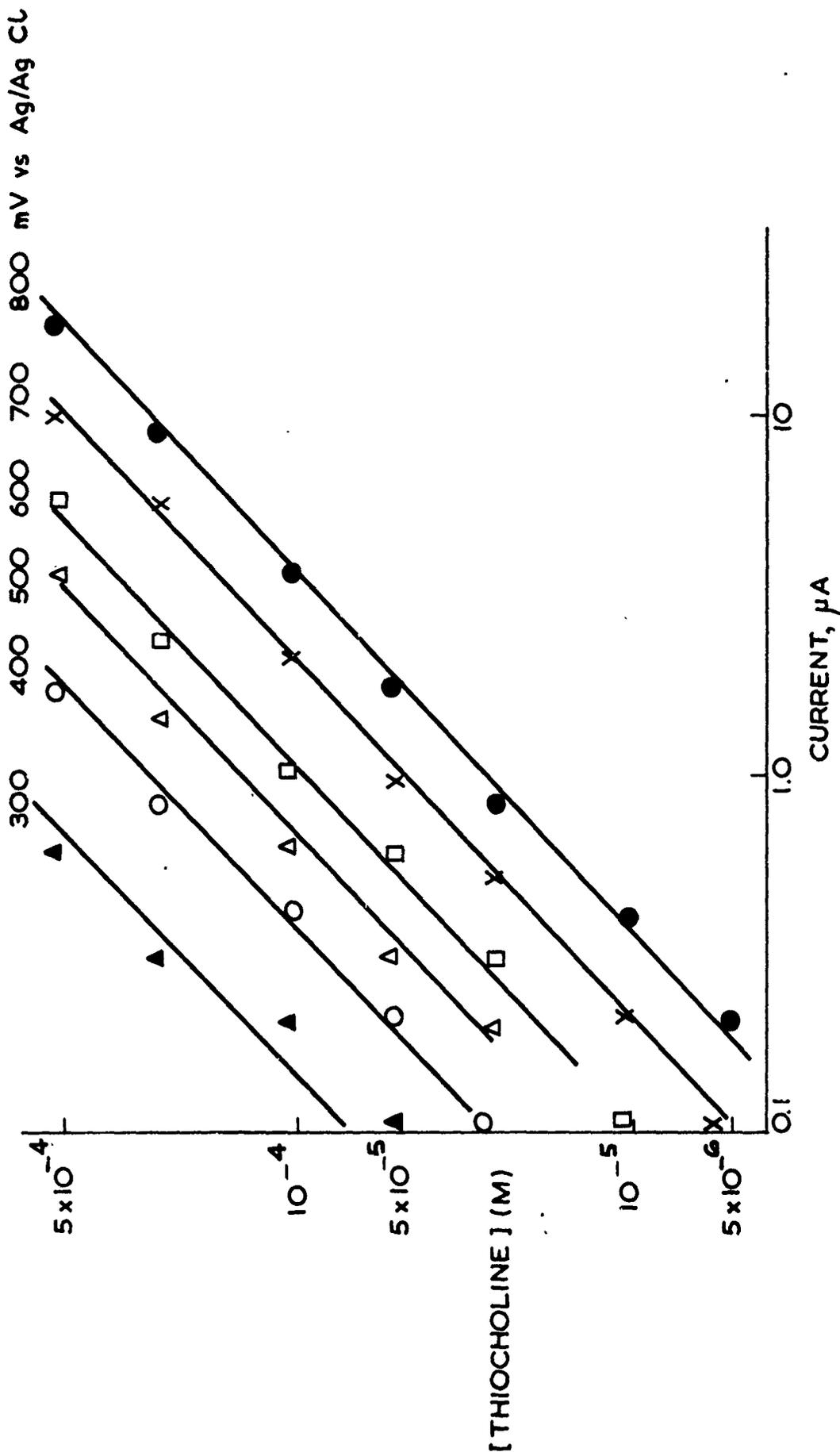


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CYCLIC VOLTAMMOGRAMS FOR THE REDUCTION OF CHOLINE DISULPHIDE

FIG. 4.

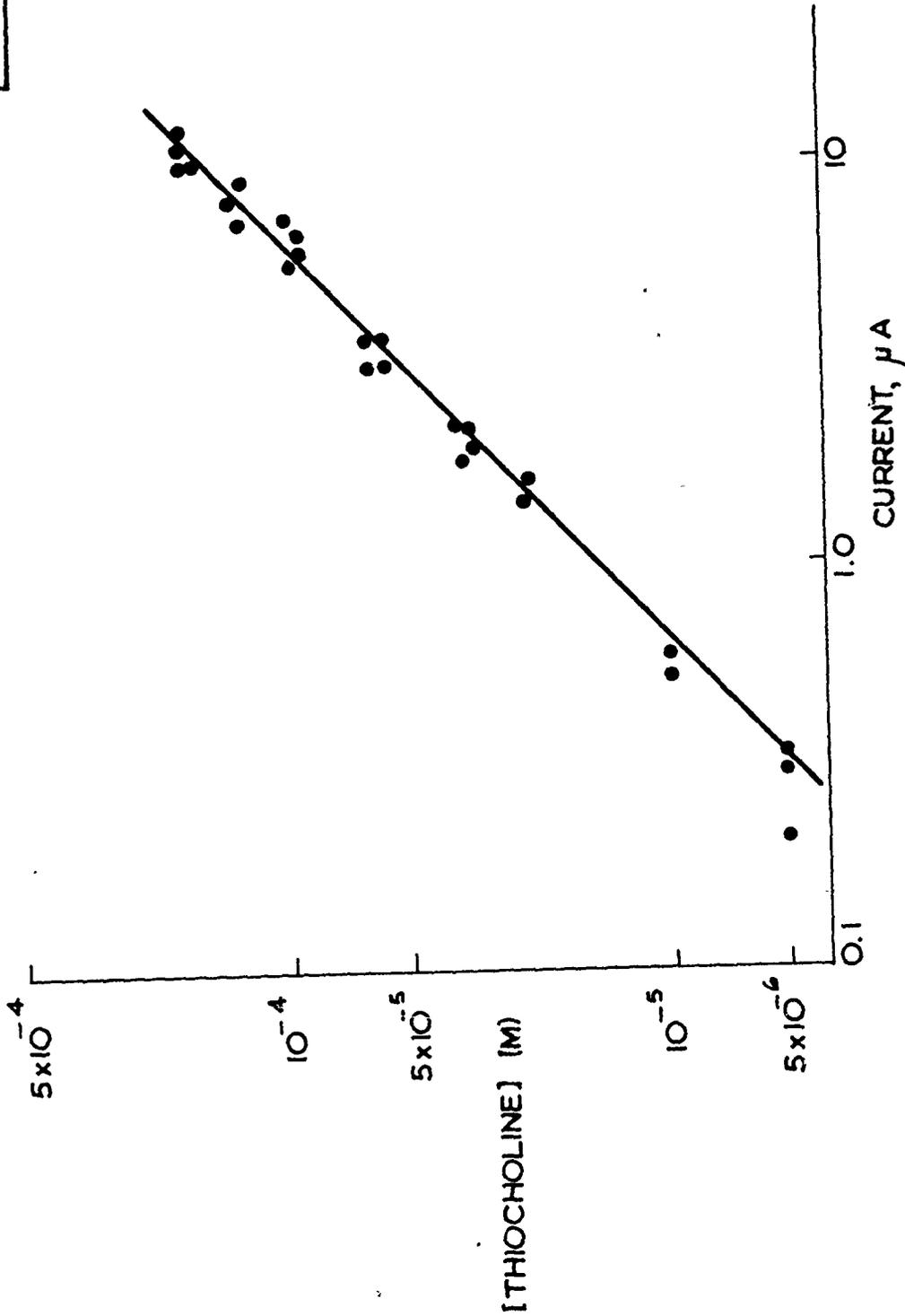
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CALIBRATION OF THE RESPONSE OF AN EXPERIMENTAL CELL TO VARIOUS CONCENTRATIONS OF THIOCHOLINE AT VARIOUS POTENTIALS

FIG. 5.

TP213 PT7119



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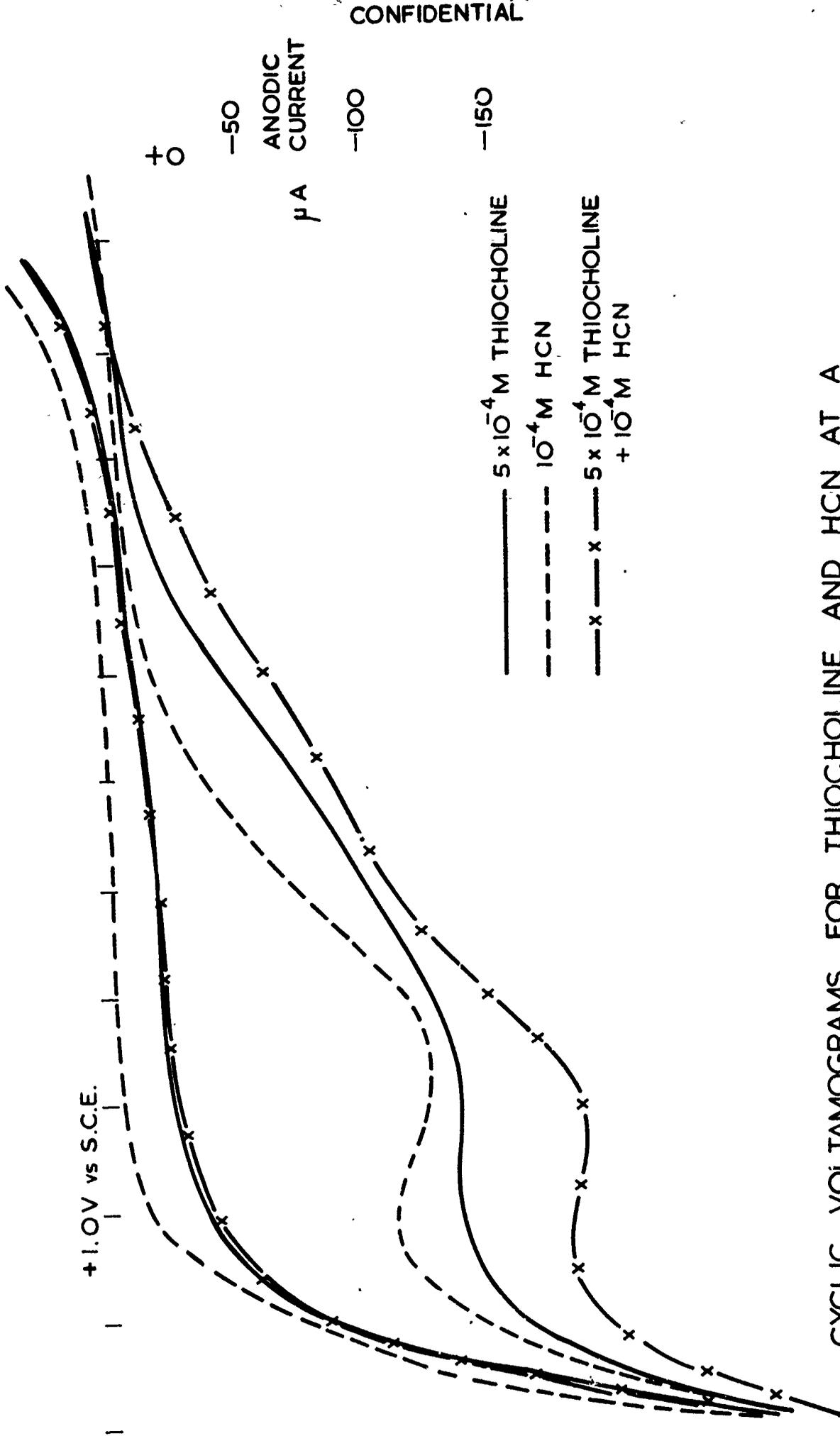
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CALIBRATION OF THE RESPONSE OF AN EXPERIMENTAL CELL TOWARDS THIOCHOLINE PRODUCED BY HYDROLYSIS OF BUTYRYLTHIOCHOLINE WITH AN ENZYME PAD. THIOCHOLINE PRODUCED ELECTROLYSED AT 800mV vs Ag/AgCl

FIG. 6.

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PT7120



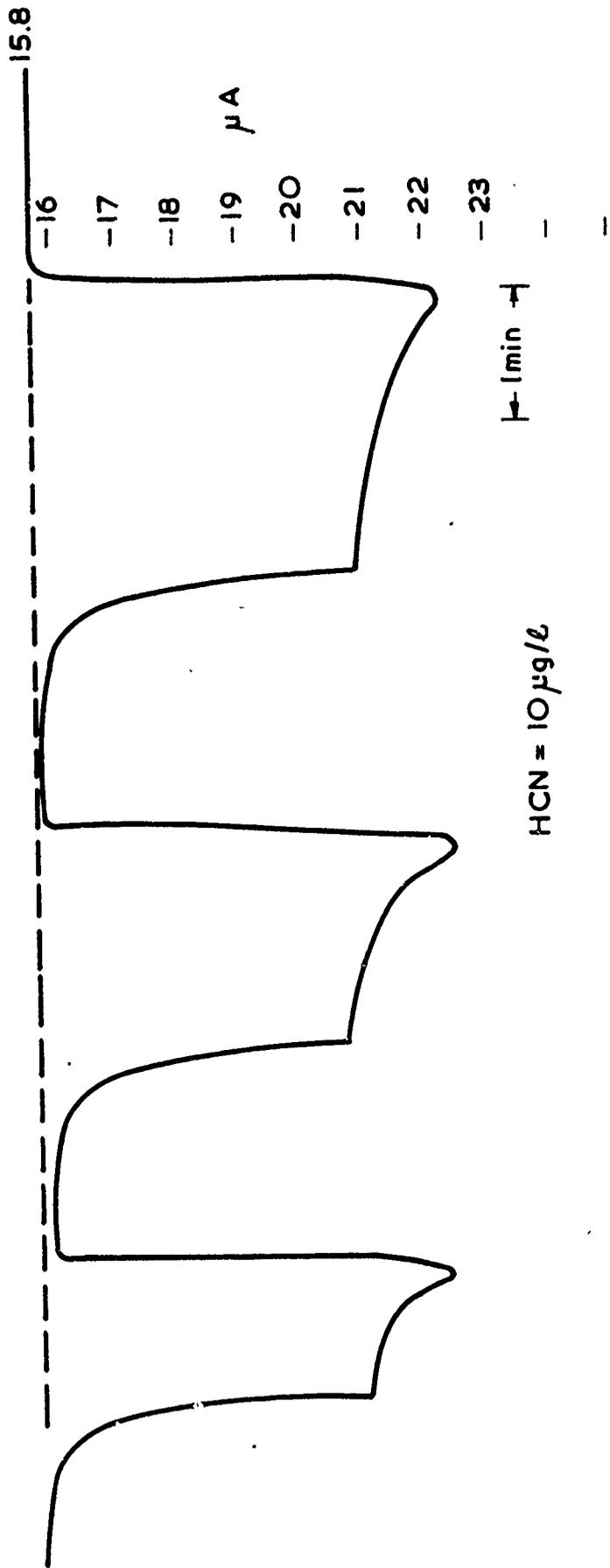
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FIG.7.

CYCLIC VOLTAMMOGRAMS FOR THIOCHOLINE AND HCN AT A STATIONARY PLATINUM ELECTRODE.

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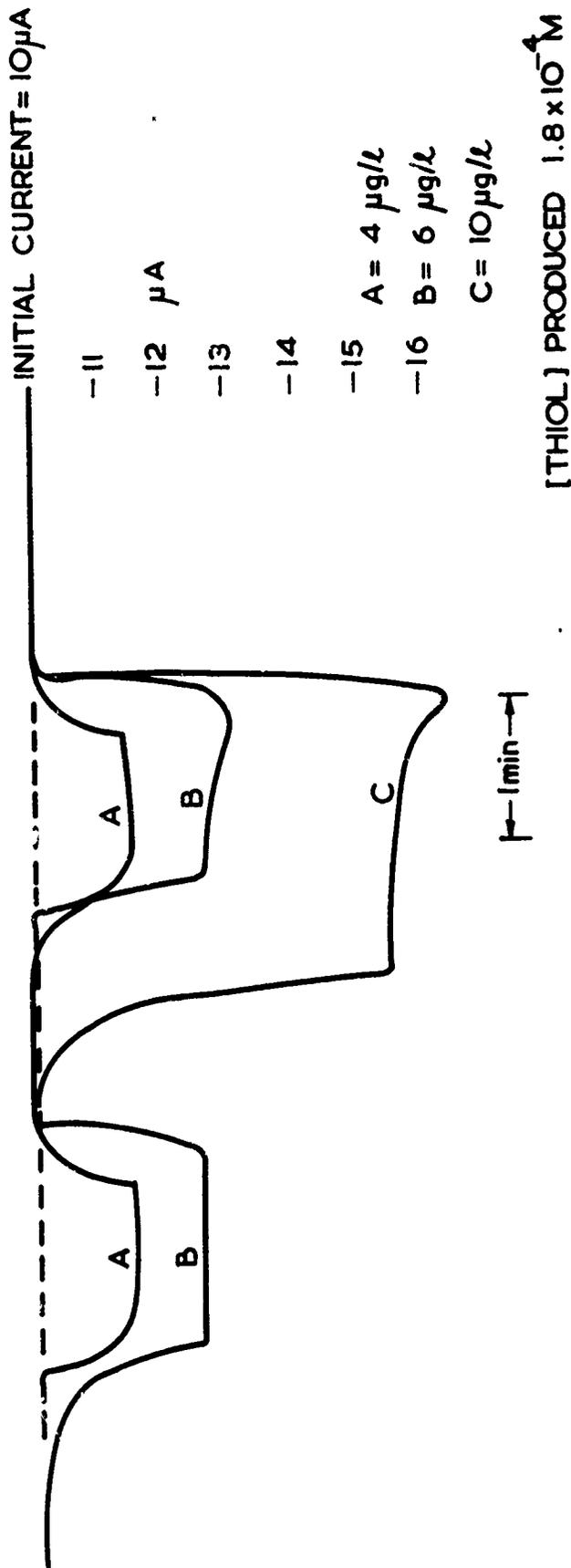
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EFFECT OF HCN (LABORATORY GENERATED) ON THE CURRENT IN AN EXPERIMENTAL CELL USING THIOCHOLINE AND A POTENTIAL OF 800mV vs Ag/Ag CL

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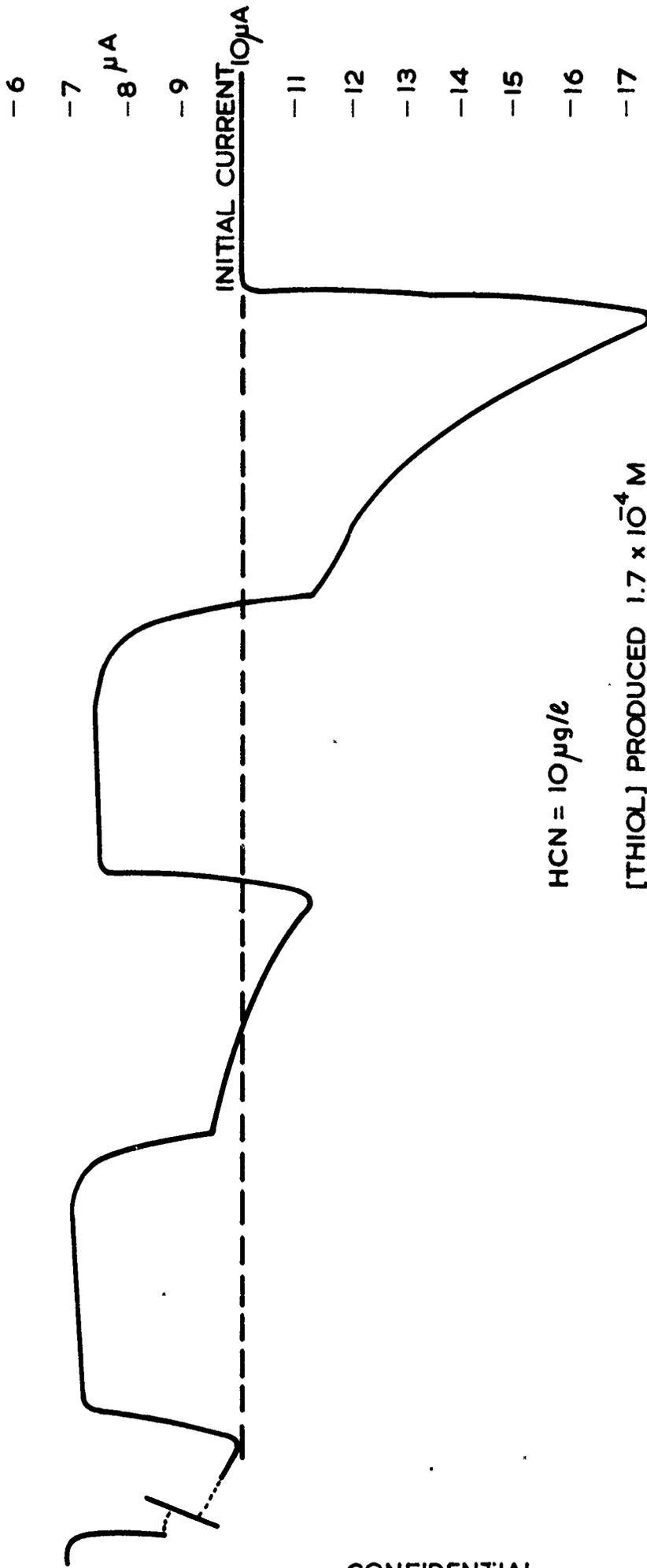
EFFECT OF HCN (LABORATORY GENERATED) ON THE CURRENT FLOWING IN AN EXPERIMENTAL CELL USING BUTYRYLTHIOCHOLINE, ($5 \times 10^{-4} \text{M}$) & AN ENZYME PAD. POTENTIAL 800mV vs Ag/Ag Cl

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FIG.9.

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PT 7123



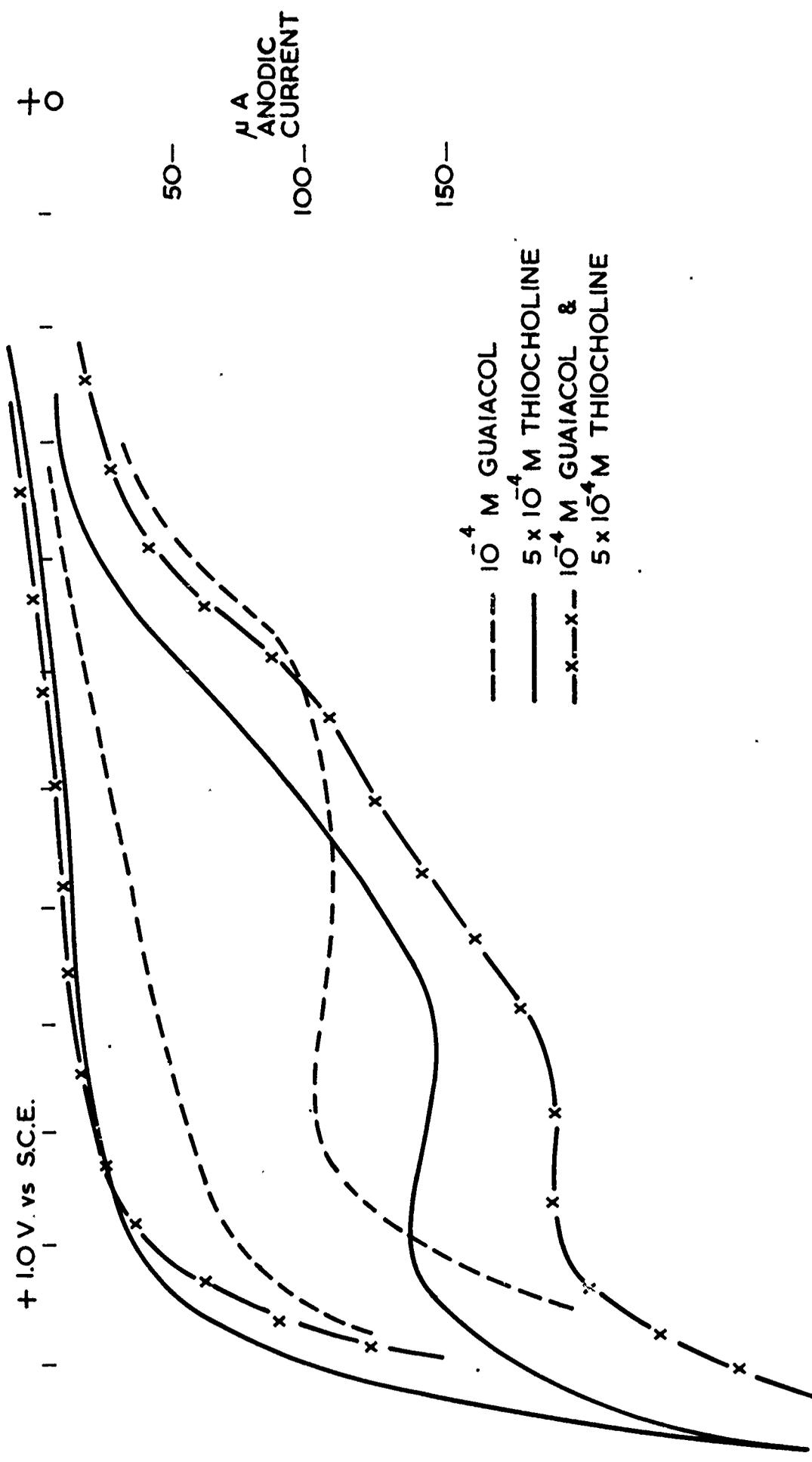
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EFFECT OF HCN (CHAMBER GENERATED) ON THE CURRENT FLOWING IN AN EXPERIMENTAL CELL USING BUTYRYLTHIOCHOLINE ($5 \times 10^{-4} M$) & AN ENZYME PAD. POTENTIAL 800mV vs Ag/AgCl

FIG. 10.

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CYCLIC VOLTAMMOGRAMS FOR THIOCHOLINE AND GUAIACOL AT A STATIONARY PLATINUM ELECTRODE

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