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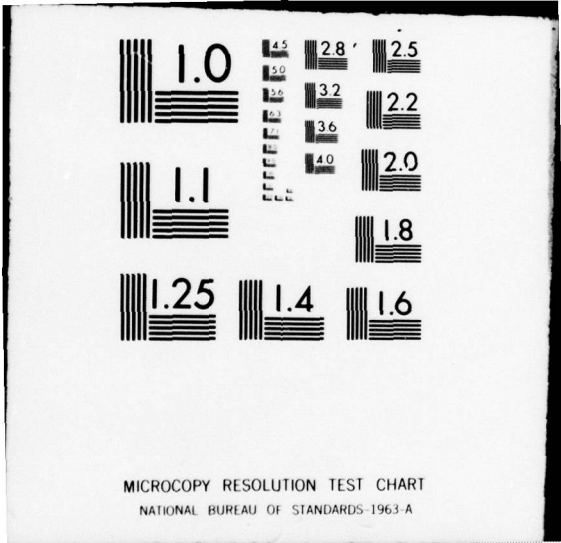
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**BARNACLE ELECTRODE MEASUREMENT SYSTEM
FOR HYDROGEN IN AIRCRAFT STEEL**

Florian Mansfeld
ROCKWELL INTERNATIONAL SCIENCE CENTER
Thousand Oaks, California 91360

12 JANUARY 1979

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FINAL REPORT
CONTRACT N62269-77-C-0351
AIRTASK NO. WRO220101
Work Unit No. DG202B

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Prepared for
NAVAL AIR DEVELOPMENT CENTER
Aircraft and Crew Systems Technology Directorate
Warminster, Pennsylvania 18974

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19) REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM	
1. REPORT NUMBER (18) NADC-77112-36	2. GOVT ACCESSION NO. (9) Final Rept. 22	3. RECIPIENT'S CATALOG NUMBER Sep 77-21 Sep 78	
4. TITLE (and Subtitle) (6) BARNACLE ELECTRODE MEASUREMENT SYSTEM FOR HYDROGEN IN AIRCRAFT STEEL.		5. TYPE OF REPORT & PERIOD COVERED Final Report 9/22/78 through 9/21/78	
7. AUTHOR(s) (10) Florian Mansfeld		6. PERFORMING ORG. REPORT NUMBER (14) SC5128.2FR	
9. PERFORMING ORGANIZATION NAME AND ADDRESS Rockwell International Science Center 1049 Camino Dos Rios Thousand Oaks, CA. 91360		8. CONTRACT OR GRANT NUMBER(s) (15) N62269-77-C-0351 ^{rev}	
11. CONTROLLING OFFICE NAME AND ADDRESS Naval Air Development Center Warminster, PA 18974		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS	
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) (12) 69 p. 1		12. REPORT DATE (11) November 1978	
		13. NUMBER OF PAGES	
		15. SECURITY CLASS. (of this report) Unclassified	
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE	
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited			
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)			
18. SUPPLEMENTARY NOTES			
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) hydrogen permeation, electrodeposition, hydrogen embrittlement, high strength steels.			
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) A portable measurement system for determination of the hydrogen concentration in steels has been developed under contract with the Naval Air Development Center (NADC). This system which is based on the electrochemical permeation technique consists of the "barnacle cell", so called because of its magnetic attachment to steel surfaces, and the electronic measurement system. Three prototypes of the combined system have been delivered to NADC. cont. <i>over</i>			

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February 1979

SC5128.2FR

**BARNACLE ELECTRODE MEASUREMENT SYSTEM FOR
HYDROGEN IN AIRCRAFT STEEL**

Final Report for the Time Period

9/22/77 through 9/21/78

Contract N62269-77-C-0351

Prepared for:

NAVAL AIR DEVELOPMENT CENTER
Warminster, PA. 18974

by

Florian Mansfeld
Principal Investigator



Rockwell International
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SUMMARY

A portable measurement system for determination of the hydrogen concentration in steels has been developed under contract with the Naval Air Development Center (NADC). This system which is based on the electrochemical permeation technique consists of the "barnacle cell", so-called because of its magnetic attachment to steel surfaces, and the electronic measurement system. Three prototypes of the combined system have been delivered to NADC.

This report contains a description of the barnacle cell and the measurement system including all drawings for the cell components and for the electronic circuits. Complete descriptions of the operating procedures are included. Experimental results obtained with the combined system on 4130 steel and cadmium plated 4340 steel obtained from NADC are presented.

INTRODUCTION

The electrochemical permeation method, which was first described by Devanathan and Stachurski^{1,2} has been used to determine the diffusion coefficient D and the concentration C_0 of hydrogen in iron and steels and to a lesser extent also in other metals. In this method, hydrogen is produced on one side of a metal foil either as the result of the corrosion reaction in acids or by application of a cathodic current. On the other side of the foil, hydrogen which has diffused through the metal, is removed by application of an anodic constant potential which leads to oxidation of hydrogen to water. The measurement is carried out in an alkaline solution in which iron is passive and the background current due to iron oxidation is very low.

A modification of the permeation method is the technique which is used in the "barnacle cell"^{3,4}, so-called because of its magnetic attachment to steel surfaces. With this technique use is made only of the oxidation process to determine the hydrogen concentration in steels. A laboratory model of the barnacle cell has been evaluated for the past few years by Berman and co-workers at the Naval Air Development Center (NADC)^{3,4}. Under contract with NADC a portable barnacle cell system has been developed for field use such as determination of the hydrogen concentration in plated steel parts, landing gears, etc. The cell system has been developed at the Science Center, Rockwell International, while the electronic measurement system has been designed and fabricated at the Chemistry Department of Portland State University. Three prototypes of the combined system have been delivered to NADC in September 1978.

For the barnacle cell technique the diffusion equations:

$$I = -zDF \left(\frac{\partial C}{\partial x} \right)_{x=L} \quad (1)$$

$$\frac{\partial^2 C}{\partial x^2} - \frac{1}{D} \frac{\partial C}{\partial t} = 0 \quad (2)$$

are solved with the boundary conditions:

$$x = 0, t > 0, \frac{\partial C}{\partial x} = 0$$

$$x = L, t > 0, C = 0 \quad (3)$$

$$0 < x < L, t \leq 0, C = C_0$$

The time dependence of the hydrogen oxidation current I_p is found to be:

$$I_p = zFC_0 \left(\frac{D}{\pi t} \right)^{1/2} \left[1 - e^{-L^2/Dt} + e^{-4L^2/Dt} + \dots \right] \quad (4)$$

where z is the number of electrons involved in the oxidation reaction ($z=1$), F is the Faraday constant, D is the diffusion coefficient for hydrogen, C_0 is the concentration of hydrogen in the metal and L is the thickness of the foil.

For $e^{-L^2/DT} \ll 1$, Eq. 4 reduces to:

$$I_p = zFC_o \left(\frac{D}{\pi t}\right)^{1/2} \quad (5)$$

Eq. 5 holds for a maximum measurement period $t_{\max} = \frac{L^2}{4D}$. For 4340 steel ($L = 1 \text{ mm}$, $D = 2.5 \cdot 10^{-7} \text{ cm}^2/\text{sec}$) $t_{\max} \approx 10^4 \text{ sec}$.

According to Eq. 5 the hydrogen concentration C_o can be determined from a plot of $\log I_p$ vs $\log t$ in the form:

$$\log I_p = \log \frac{zFD^{1/2}}{\pi^{1/2}} C_o - \frac{1}{2} \log t \quad (6)$$

as the intercept at $t = 1 \text{ sec}$ or can be calculated from the current measured at a given time $t < t_{\max}$. Since at the beginning of the surface oxidation a certain amount of current is due to passivation of the steel, the hydrogen concentration has been calculated after 1800 sec in the experiments described below. For a current density of $1 \mu\text{A}/\text{cm}^2$, the hydrogen concentration C_o is:

$$C_o = 0.203 \text{ ppm for } D = 2.5 \cdot 10^{-7} \text{ cm}^2/\text{sec}$$

or

$$C_o = 0.064 \text{ ppm for } D = 2.5 \cdot 10^{-6} \text{ cm}^2/\text{sec}.$$

II. The Barnacle Cell

1. General Description

The barnacle cell developed under this contract consists of a cell body (Kel-F) pressed into a cylindrical magnet (Alnico 5). The cell body shown in Fig. 1 contains a cavity which houses the Ni/NiO counter electrode (Fig. 2), the epoxy tube with the seal and the sponge which contains the test electrolyte. The Ni/NiO reference electrode (Fig. 3) which is used to check the counter electrode and to indicate that sufficient electrolyte is present also has access to the center cavity. A vent, which reaches the cavity as shown in Fig. 4, is used to relieve pressure when the center electrode is pressed down. Two additional compartments house spring loaded nickel rods which are used to make electrical contact to the test sample (Fig. 5). Figure 6 shows a photograph of the barnacle cell. The present design is suitable for flat surfaces only.

The mold which was used to produce the silicone seal is shown in Fig. 7a-c. The seal bonded to the epoxy tube is shown in Figure 8. Table I lists the materials used for fabrication of the barnacle cell.

2. Fabrication of Cell Components

a. Seal

The procedure for fabrication of the seal is given in Table II. The time allowed for curing of the silicone rubber may vary depending on the relative humidity in step 7 and the age of the silicone rubber adhesive sealant. The older the material gets, the longer will be curing time required. Trimming the seal in step 17 was generally required because of small variations in the dimensions of the plastic body of the barnacle cell and variations of the seal itself. If too much silicone rubber is trimmed from the seal assembly such that it protrudes less than 0.003 inch, it may not seal properly.

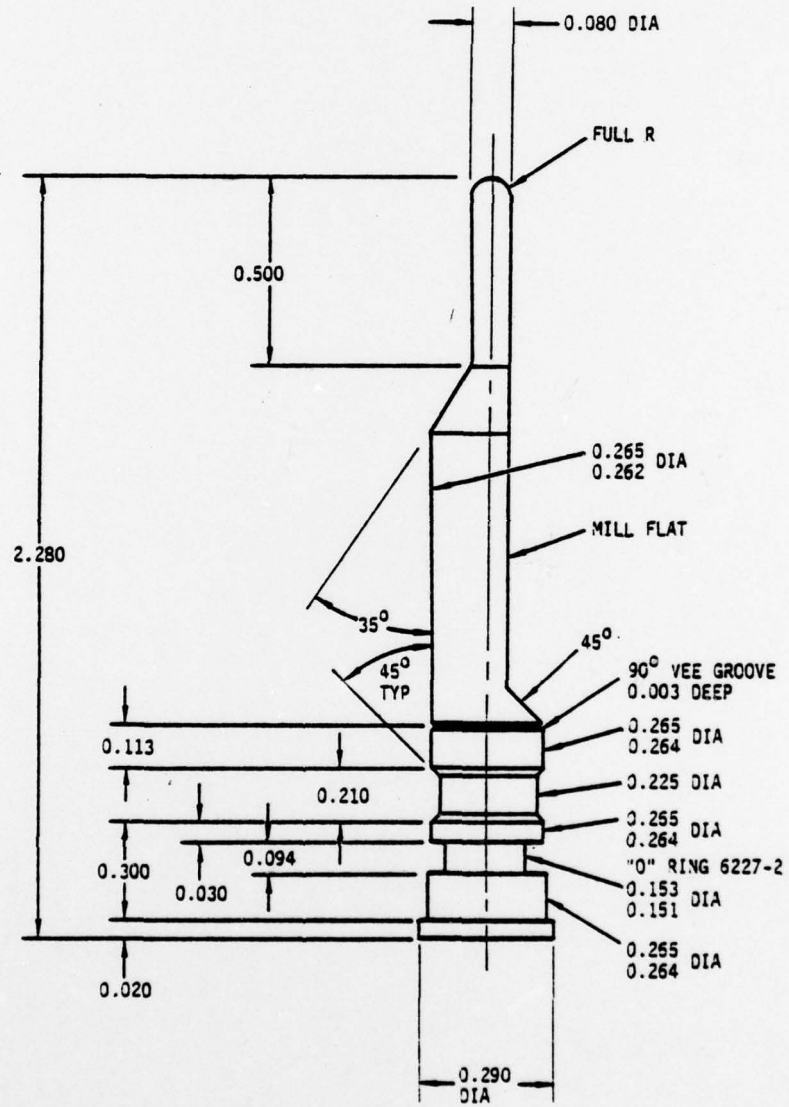


Figure 2

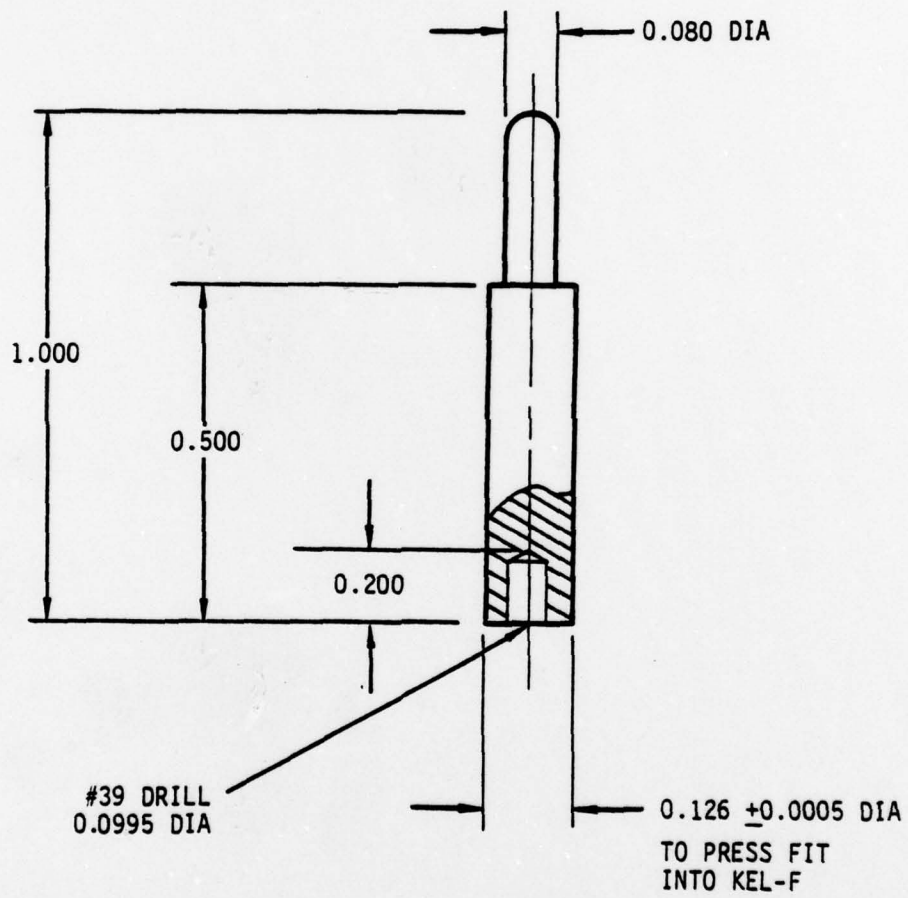


Figure 3

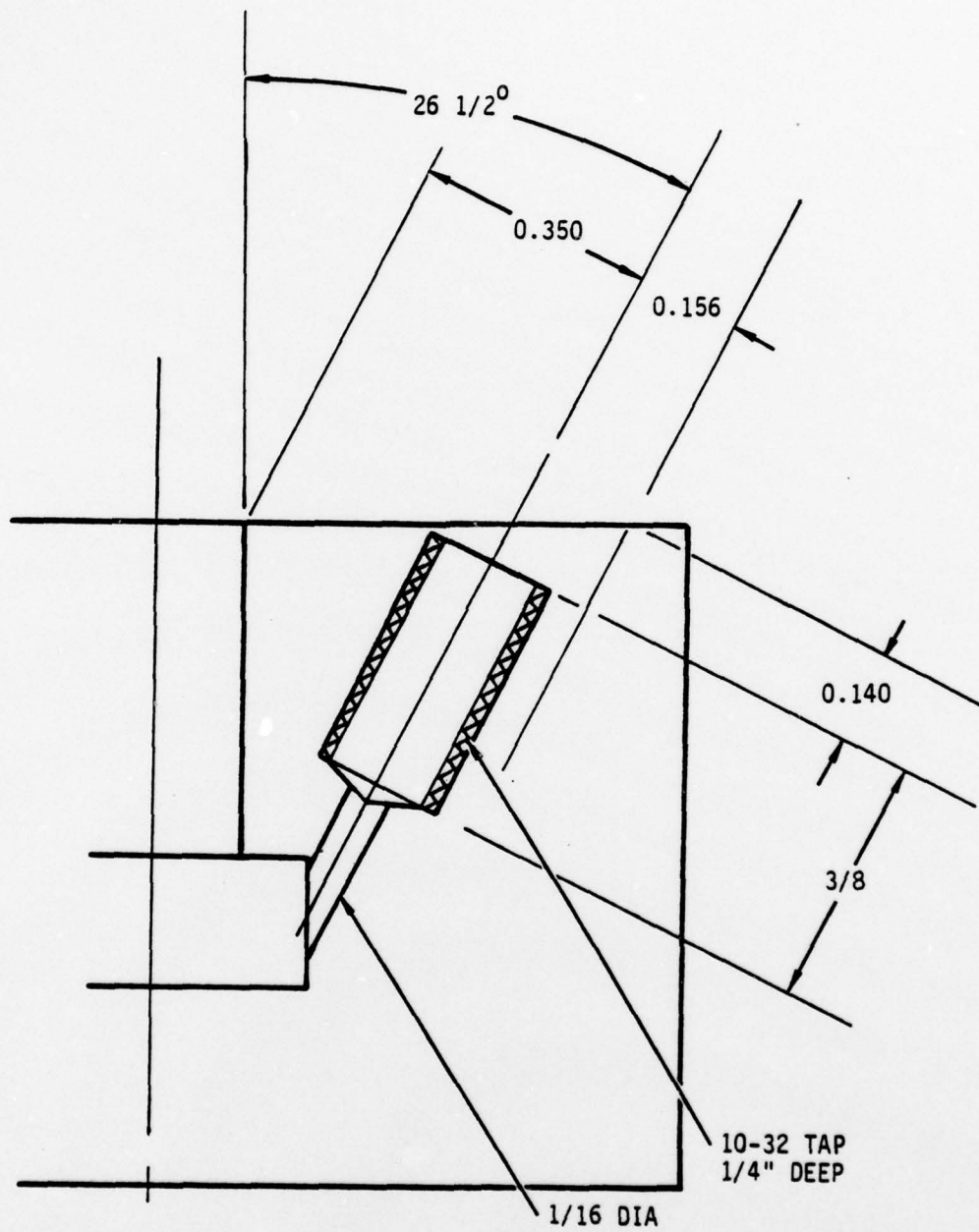


Figure 4 a

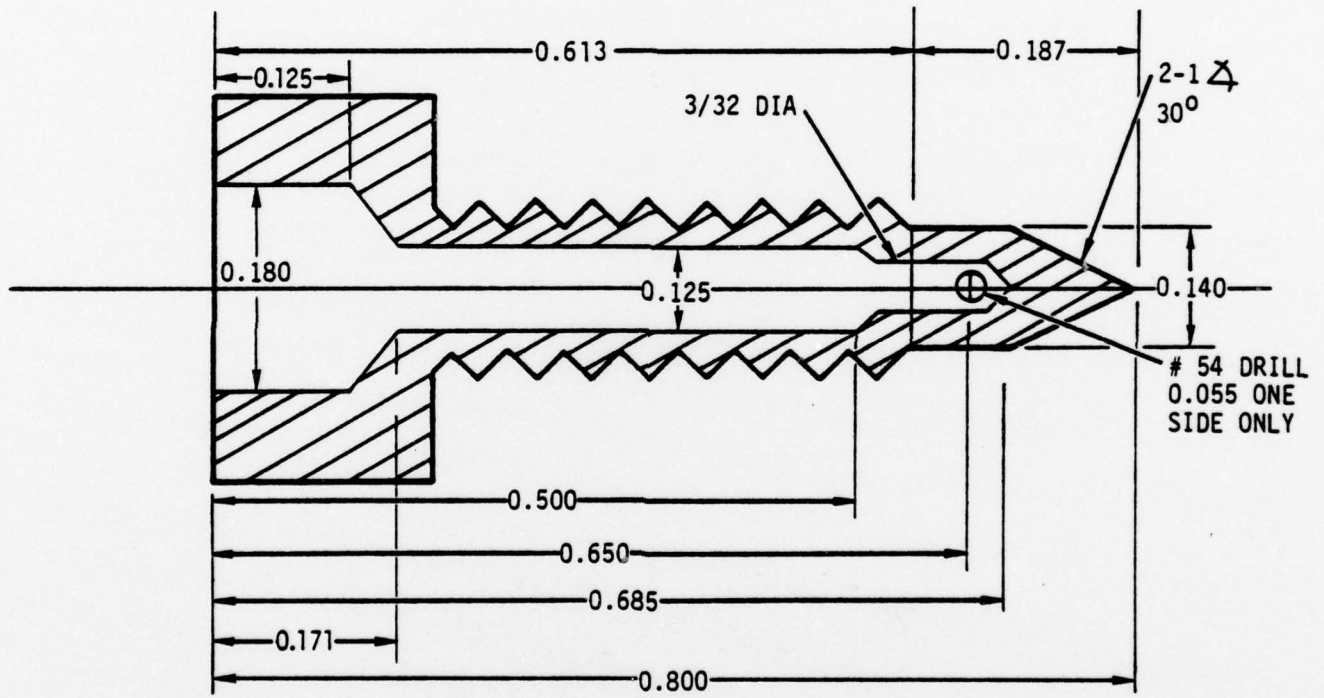


Figure 4b

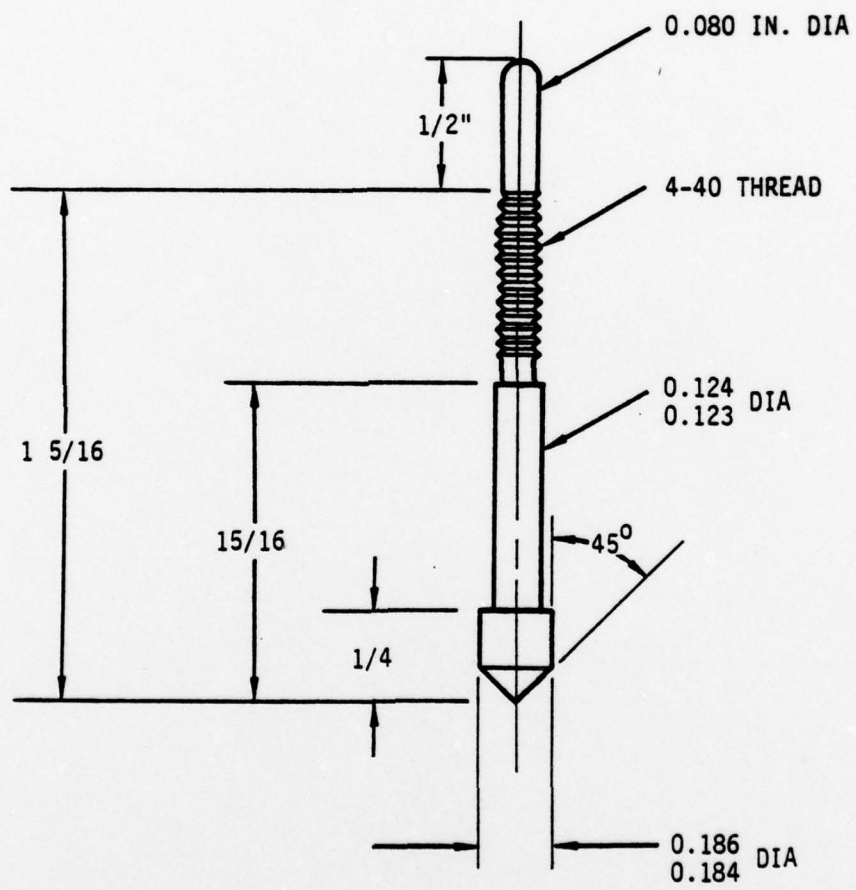


Figure 5

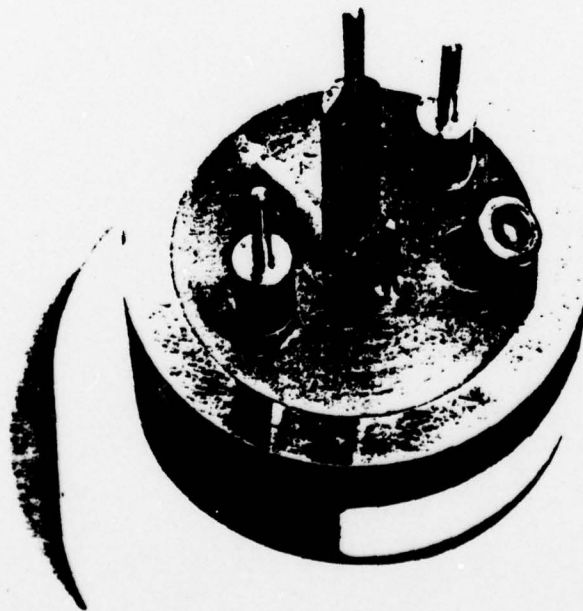
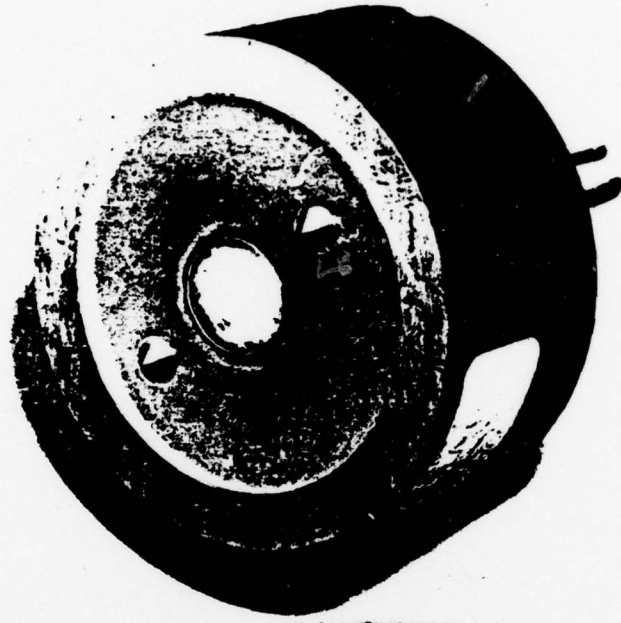
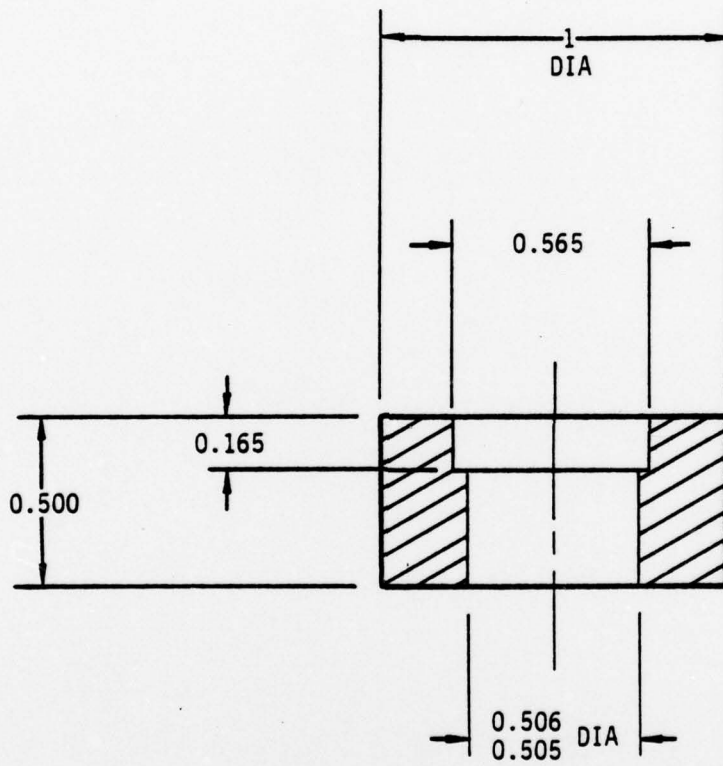
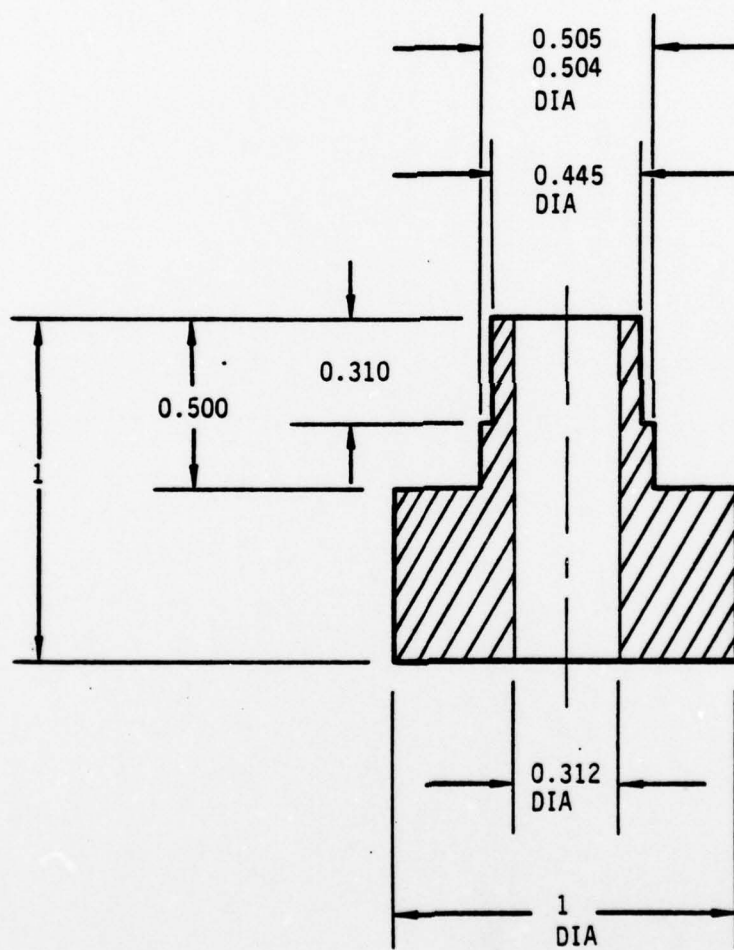


Figure 6



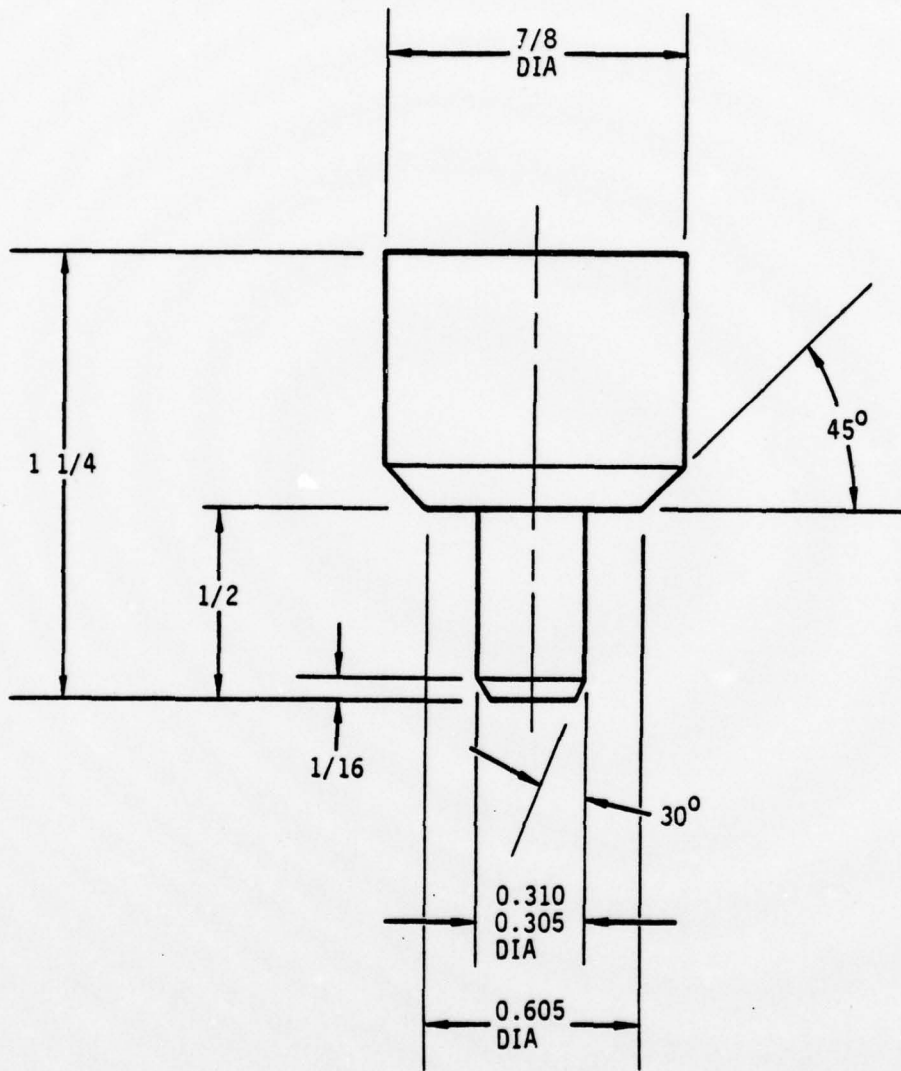
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Figure 7a



b,

Figure 7b
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(C)

Figure 7c

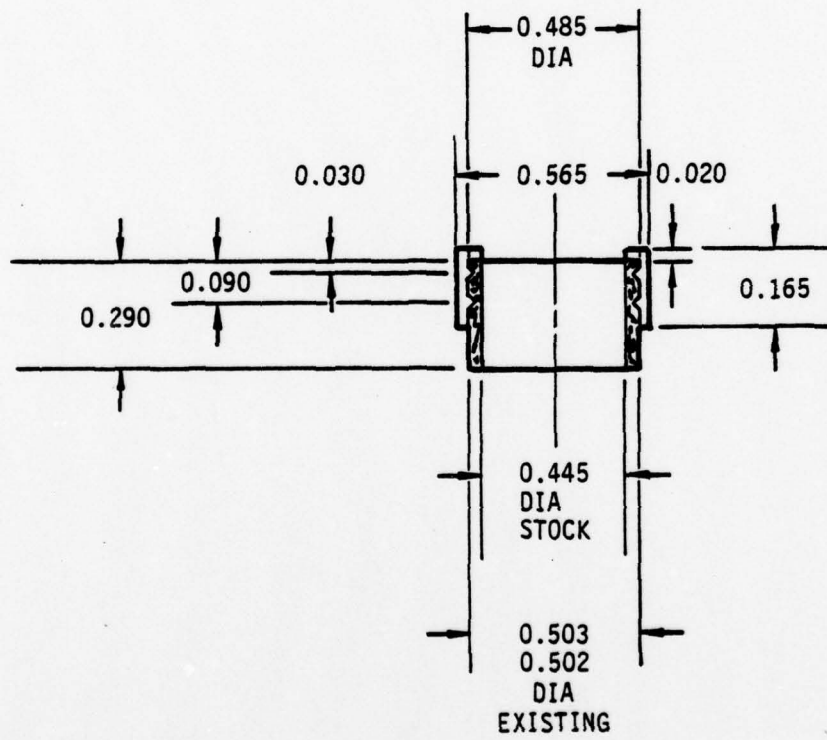


Figure 8

Table I

BARNACLE CELL MATERIALS

1. Silicone Rubber Adhesive Sealant, Permatex 66BR,
Permatex Company, Inc., Kansas City, Kansas.
2. Epoxy tube, Orion Resdel Corporation,
Rio Grande, N.J. (Epoxy is a black, silica-filled compound).
3. Cellulose sponge - fine porosity. Muf-L-Cote, Inc., Akron, Ohio.
4. Mold Release Spray-on No. 205 Silicone Mold Release,
Industrial Supply - Sprayon Products Division,
The Sherman Williams Company, Bedford Heights, Ohio.
5. Nickel-Nickel Oxide electrode - From Nickel-Cadmium battery module
AC-22
General Electric Company, Gainesville, Florida.
6. O-ring AN6227-B-2 (2-007) Parker Compound PS-1-30-5, MIL-P-5516,
a nitrile (Buna N) polymer.
7. Magnet Alnico 5, McMaster-Carr, Los Angeles.

Table II
FABRICATION OF SEAL ASSEMBLY

<u>Step</u>	<u>Procedure</u>
1.	Clean mold parts and epoxy tube ultrasonically with methanol.
2.	Spray mold parts with silicone mold release (not epoxy tube).
3.	Install epoxy tube on inner part of mold, keep clean from mold release agent.
4.	Install the outer mold piece over the inner one using a shim so that the bottom of the outer mold piece is flush with the top of the inner one.
5.	Fill the bottom of the mold cavity with silicone rubber adhesive sealant (Permatex 66BR).
6.	Remove the shims and slowly slide the outer mold down.
7.	Let set in air for 10 min. to form skin on silicone rubber.
8.	Install the top of the mold (teflon), press it down firmly and put a weight on it (approx 1 Kg).
9.	Place assembly in covered jar containing a few ml water (curing agent).
10.	After at least 24 hr rotate and slowly remove top, return mold to covered jar.
11.	After another 8 hr rotate inner part of mold and remove.
12.	Return mold to covered jar for another 24 hrs.
13.	If the seal requires trimming on inner circumference, reinstall inner part of mold and trim with scalpel under a binocular microscope.
14.	Trim outer circumference of seal if required.
15.	Press out seal assembly and allow another 24 hr to cure.
16.	Place seal on insertion tool and install in cell.
17.	If seal protrudes more than 0.005 in beyond cell face, carefully (under microscope) trim excess silicone from back of seal.

b. Nickel/Nickel Oxide Electrode

The procedure for the Ni/NiO electrode is given in Table III with accompanying sketches. Care must be used in cutting open the Ni-Cd cell so that the electrodes are not damaged. The cadmium electrode is used as the counter electrode when charging the Ni/NiO electrode.

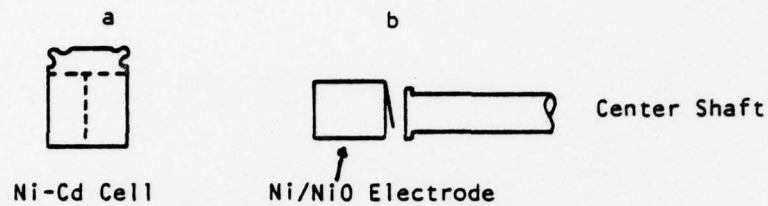
3. Assembly of Cell

After machining and fabrication of the components and cleaning with methanol the nylon positioning pin with its spring and allen screw are installed first. The threaded hole is then sealed with silicone rubber adhesive sealant to ensure that no electrolyte path between the cell and the magnet can be established. The cylindrical magnet is pressed on. The reference electrode is pressed into the cell body and filled as discussed in Table IV. The springs for the spring-loaded sample contact electrodes are cut so that the pointed tips of the electrodes protrude 1-2 mm beyond the face of the cell. The seal assembly is installed as shown in Table IV. The nickel/nickel oxide electrode is charged and installed according to the procedure in Table V.

Table III

FABRICATION OF Ni/NiO ELECTRODE

1. Remove nickel oxide electrode from Ni-Cd cell by cutting on dotted lines around circumference and from end to end. Use abrasive wheel or jewelers saw. (Fig. a)



2. Remove nickel oxide electrode and shape to fit into barnacle cell body.
3. Retain the tab, but trim to about 0.7 cm length.
4. Spot weld metal tab to Ni center electrode. (Fig. b)

Table IV
ASSEMBLY OF CELL COMPONENTS

Filling of Reference Electrode

1. Fill reference electrode compartment to about 1/4 capacity with nickel oxide electrode material from a fully charged Ni/NiO electrode of a nickel-cadmium battery. The nickel oxide is easier to handle when moistened with 0.2 N NaOH first.
2. The compartment is then packed full with dacron cloth from the Ni-Cd battery followed by a small piece of sponge.

Installation of Seal

1. Place seal on insertion/removal tool.
2. Moisten with 0.2N NaOH.
3. Align seal in barnacle cell.
4. Press seal into cell with slight rocking motion.
5. The seal should protrude about 0.005 in beyond the face of the cell body.
6. Removal of the seal is accomplished by a rocking motion while retracting the tool (wet outside of seal w/10 M NaOH).

Table V

Charging and Installation Ni/NiO Electrode

1. NiO should be recharged after 2 hr use or when its potential varies more than 50 mV from the reference electrode.
2. To charge remove the sponge.
3. Remove the NiO electrode.
4. Position electrodes about 1 cm apart during charging.
5. Charge at 20 mA in 10M NaOH vs a cadmium electrode.
6. End charge when cell voltage reaches 1.52V.
7. Rinse NiO electrode with water and reassemble cell.
8. Short NiO and reference electrode for 60 min. or more.
9. Remove short, cell is ready for use.

4. Operating Procedure

The various steps in carrying out a measurement with the barnacle cell and the electronic equipment are the following:

1. Clean the surface of the specimen with abrasive "Scotchbright" to remove grease, paint and dirt. Surface should appear smooth and polished.
2. Invert the barnacle cell, pull the long center electrode down and see that the surface of the sponge has retracted from the edge of the cell opening about one millimeter. If necessary push the sponge into the cell this distance. Wipe the seal surface off. Add two drops of gelled electrolyte (0.2N NaOH + 2% Agar) to center of the sponge. Position the cell on the specimen and allow it to attach itself. Open vent valve.
3. Switch the instrument ON. Connect the cable to the cell by connecting the black plug to the center electrode, the red plug to the reference electrode and the white plugs to the two other electrodes. The long, center electrode will move into the cell about 1/8 inch under slight pressure; be certain that it is pushed in the full distance, indicated by the mark on the electrode. Close the vent valve.
4. Set the desired times on the thumbwheel switches for Recorder Delay, Current Hold, Integration Delay and Integration Time.
5. Set Current Range to 2000 μ A position. Press Start button firmly. Adjust Current Range until meter pointer is in green range of the scale; Current Range may be changed during measurement if current drops below 10% of full scale (below green range) but only during Integration Delay period. Do not change Current Range during Integration Time.
6. When Cycle On light goes off, push Stop button, record Current and Charge readings. Open the vent valve, pull the center electrode out about 1/8 inch, remove cell and switch instrument OFF. Close vent valve and clean the cell surface before storing.

7. To abort measurement cycle, push Stop button firmly. Cell is disconnected and circuit is ready for another measurement cycle.
8. When not in use the barnacle cell should be stored in its base. Place an auxilliary sponge in the well in the base and saturate it with 0.2N NaOH electrolyte. The Ni-NiO electrode and sponge should be kept wet during storage.
9. Fresh agar gel should be made periodically since it promotes bacterial growth. The agar gel (3 wt%) should be dissolved in hot water, cooled and then made 0.2N NaOH. Hot aqueous sodium hydroxide hydrolyzes agar.

III. The Measurement System

1. General Description

The measurement system for electrochemical determination of hydrogen in steel using the barnacle cell is shown in Fig. 9. This instrument controls the operation of a barnacle cell, and provides analog and digital measurements of current and charge due to the oxidation of hydrogen dissolved in steel. A detailed circuit description is given in the Appendix. When the barnacle cell is attached to the specimen, the instrument performs the following functions:

1. Indicates by Check Cell light if cell cathode has adequate capacity and if cell contains electrolyte.
2. Upon depressing the Start button, the cell circuit is completed and cell current is displayed by both an analog and a digital meter.
3. After a preselected time interval, the cell current reading is held by the digital current display until another measurement is made or power is switched off.
4. After a preselected time delay, the cell current is integrated for a selected time interval and the total charge is digitally displayed in units of millicoulombs. Display is held until another measurement is made or power is switched off.
5. Output jacks allow a strip chart recorder to display the time variation of the cell current. Analog signal is switched to the output jacks after a preselected time delay and a Strobe signal goes high (+6 V) at the end of the delay period. This signal may be used to control the recorder chart drive through a transistor and relay.



Figure 9 Measurement System

2. Instrument Specifications

Current Ranges: 200 nA to 2000 μ A full scale in five ranges, manually switched.

Accuracy of Analog Meter: +2% of full scale.

Accuracy of Digital Current Meter: +2% of full scale.

Resolution of Digital Current Meter: $\pm 0.05\%$ of full scale, ± 1 count.

Charge Ranges: Depends upon Integration Time: at five minute Integration

Time and full scale current, range is 0.0600 to 600 millicoulombs.

Counter capacity is 9999.

Accuracy of Charge Measurement: $\pm 1\%$ of current display, ± 1 count.

Recorder Out: 100 mV full scale on any current range; source resistance

1 $k\Omega$, within $\pm 1\%$ of current signal.

Recorder Strobe: -0.6 V during Recorder Delay rising to +6V at end of delay

time. Source resistance 10 $k\Omega$.

Start: When switch button is depressed, cell circuit is completed,

charge display is cleared, timing circuits start and Cycle On light

is illuminated. Cell circuit remains closed until stop switch is

depressed.

Stop: When switch is depressed, cell circuit is opened, current and charge

displays are held, timing circuits are reset and Cycle On light is

extinguished.

Recorder Delay: 0 to 30 min. in steps of one minute; accuracy within $\pm 1\%$.

At end of set time, Recorder Out signals is active and Strobe is +6V.

Current Hold: 0 to 30 min. in steps of one minute; accuracy within $\pm 1\%$.

Cell current at end of set time is held in digital current display.

Integration Delay: 0 to 30 min. in steps of one minute; accuracy within $\pm 1\%$.

Integrator starts at end of set time.

Integration Time: 0 to 5 min. in steps of one minute; accuracy within $\pm 1\%$.

Integrator operates during this time interval.

Cycle On Light: Light Emitting Diode is ON from Start until end of the longer of Current Hold Time and Integration Delay plus Integration Time. Not affected by Recorder Delay.

Check Cell Light: Light Emitting Diode is ON if potential between cell cathode and reference electrode exceeds 100 mV or if there is high resistance between electrodes due to insufficient electrolyte.

Low Battery Light: Light Emitting Diode is ON if battery voltage is less than 12.2V. About one hour more of operating time remains.

High Rate Charging Light: Light Emitting Diode is ON when instrument is connected to 110 V ac outlet and battery is not fully charged. When fully charged, light will blink occasionally. Power switch must be in OFF position.

Battery Power Supply: Six D-size, sealed lead acid cells (Gates 0810-0004) 2.0V nominal, 2.5 Ah capacity. Will power instrument for six hours.

Battery Charge: Constant current with two charging rates: high rate 165 mA, low rate 6 mA. Power requirements: 110V ac at 5 w. Fuse: 3AG, 0.3 to 0.5 A. (Gates 0833-3002).

Instrument Weight: 3.5 kg

Specifications apply over temperature range of -10 to $+45^{\circ}\text{C}$.

IV. Test Results

A number of test runs were performed during the various phases of the development of the barnacle cell system. Earlier measurements were carried out with a potentiostat (PAR 173 with a Model 376 plug-in) in the zero resistance ammeter (ZRA) mode. A number of samples received from Dr. D. Berman of NADC were tested with the barnacle cell system. Each of the three barnacle cells which have been delivered to NADC in September 1978 were also tested with the electronic system which had been designed and assembled by Prof. D. Roe.

1. Test of NADC Samples

Specimens of 4340 steel were prepared at NADC in two pairs to give high and low hydrogen concentration. After cleaning, the samples were cathodically charged for three hours in NaOH/NaCN (10 wt% each), rinsed and immediately cadmium plated. For the electrochemical measurement the cadmium plate was removed using NH_4NO_3 solution. The sample was then rinsed with water and methanol and blown dry under a stream of nitrogen. For a background measurement the specimens were stored for two days in a dessicator under vacuum. The test was then performed in the area from which the Cd had been removed previously.

Since the permeation current I_p decays with the square root of time according to:

$$I_p = C_o F \sqrt{\frac{D}{\pi t}} \quad (5)$$

All electrochemical data are shown in $\log I_p$ vs. $\log t$ plots. For the case that the measured current corresponds entirely to oxidation of hydrogen atoms diffusing to the metal surface, straight lines with a slope of -0.5

should be obtained. Figure 10 a and b show for charged samples (both sides were measured) that for times larger than 5 to 10 min. straight lines with slopes close to -0.5 are obtained. In some cases, slight leaks occurred during the 30 min. tests. This was due in part to the samples not being entirely flat and in part to a weakness in the cell design which was subsequently corrected. For the blank samples slopes between -0.5 and -1.0 were found (Fig. 10 c and d). These results most likely reflect the passivation of the steel surface in the alkaline solution.

2. Evaluation of Cell Design Parameters

In order to evaluate whether certain changes in the original design (such as the use of Agar gel, stability of the Ni/NiO electrode, the occurrence of leaks and the nature of the compound used to form the seal) influence the results obtained in barnacle experiments a number of measurements were carried out under different test conditions.

Tests in bulk solutions were run under two different arrangements:

- a. The sample (4130 steel rod) was potentiostated at the potential of the Ni/NiO electrode (+ 308 mV vs SCE) and the oxidation current recorded.
- b. The galvanic current flowing between the sample and the Ni/NiO electrode was recorded using the potentiostat as a ZRA.

There is remarkable agreement between both measurements (Fig. 11). In experiment b, it was found that the potential of the Ni/NiO electrode did not change (within ± 1 mV) when the steel electrode was connected or disconnected. This result shows that a fully charged Ni/NiO electrode used in our design is indeed functioning as a potentiostat.

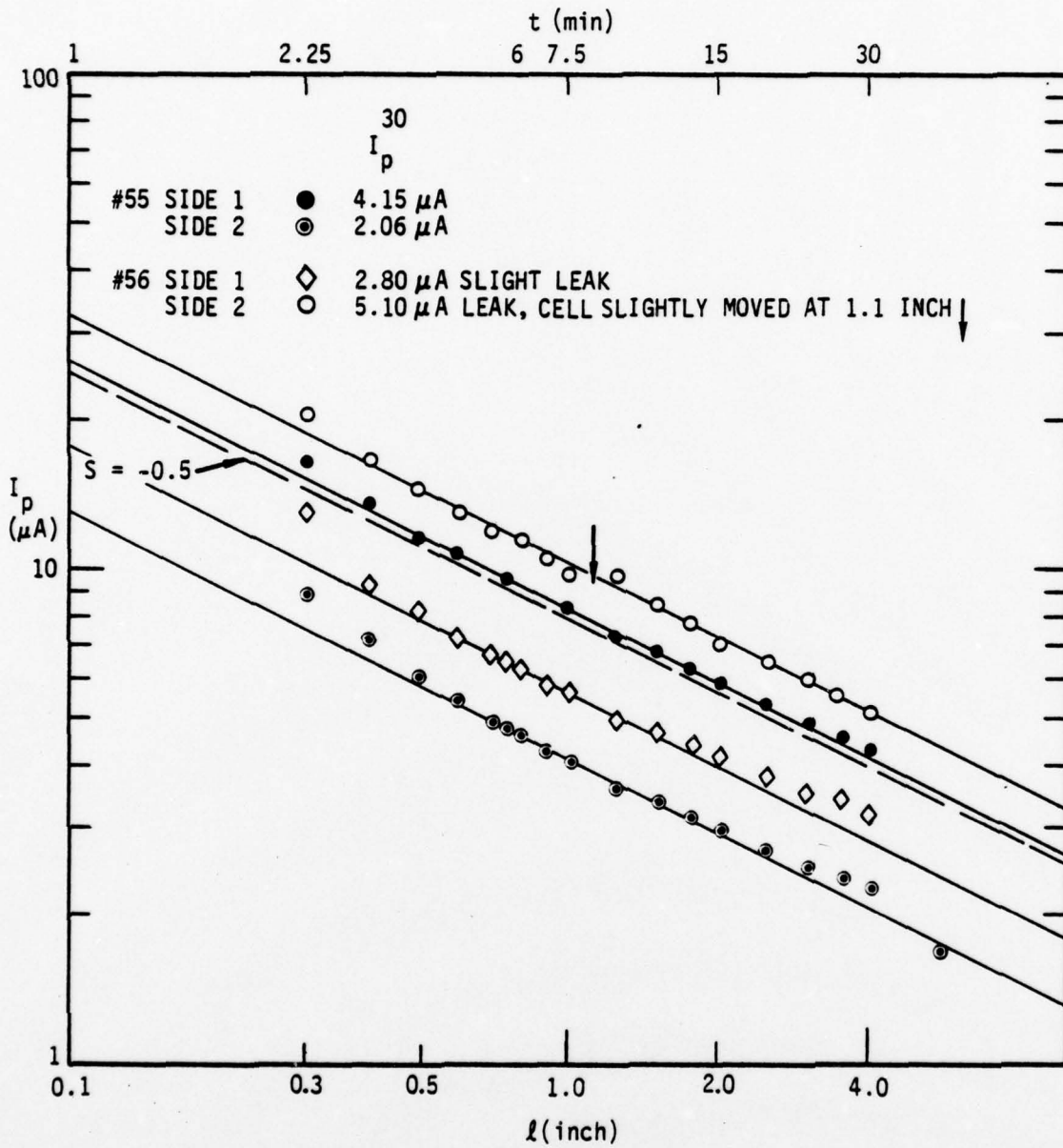


Figure 10a

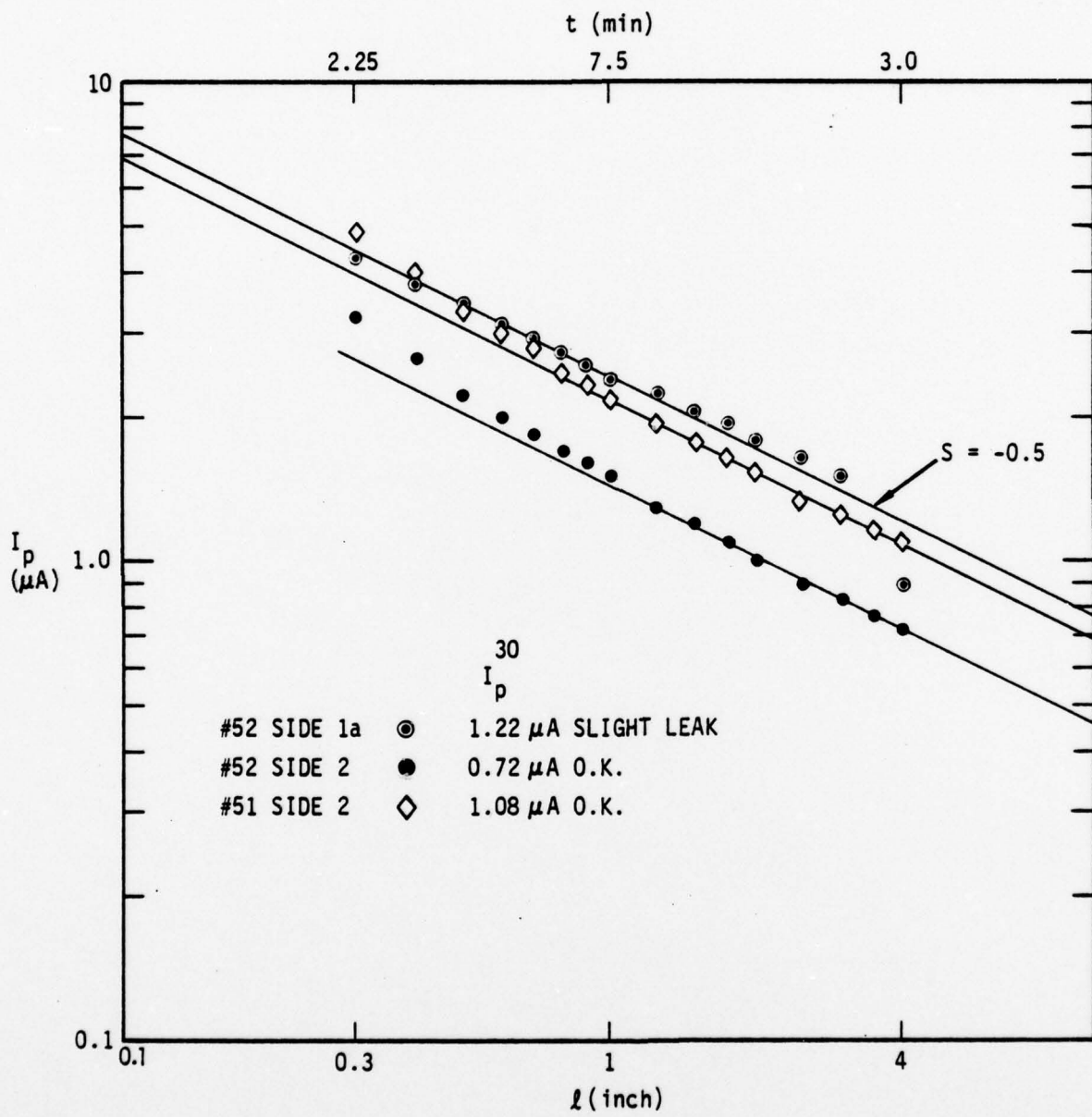


Figure 10b

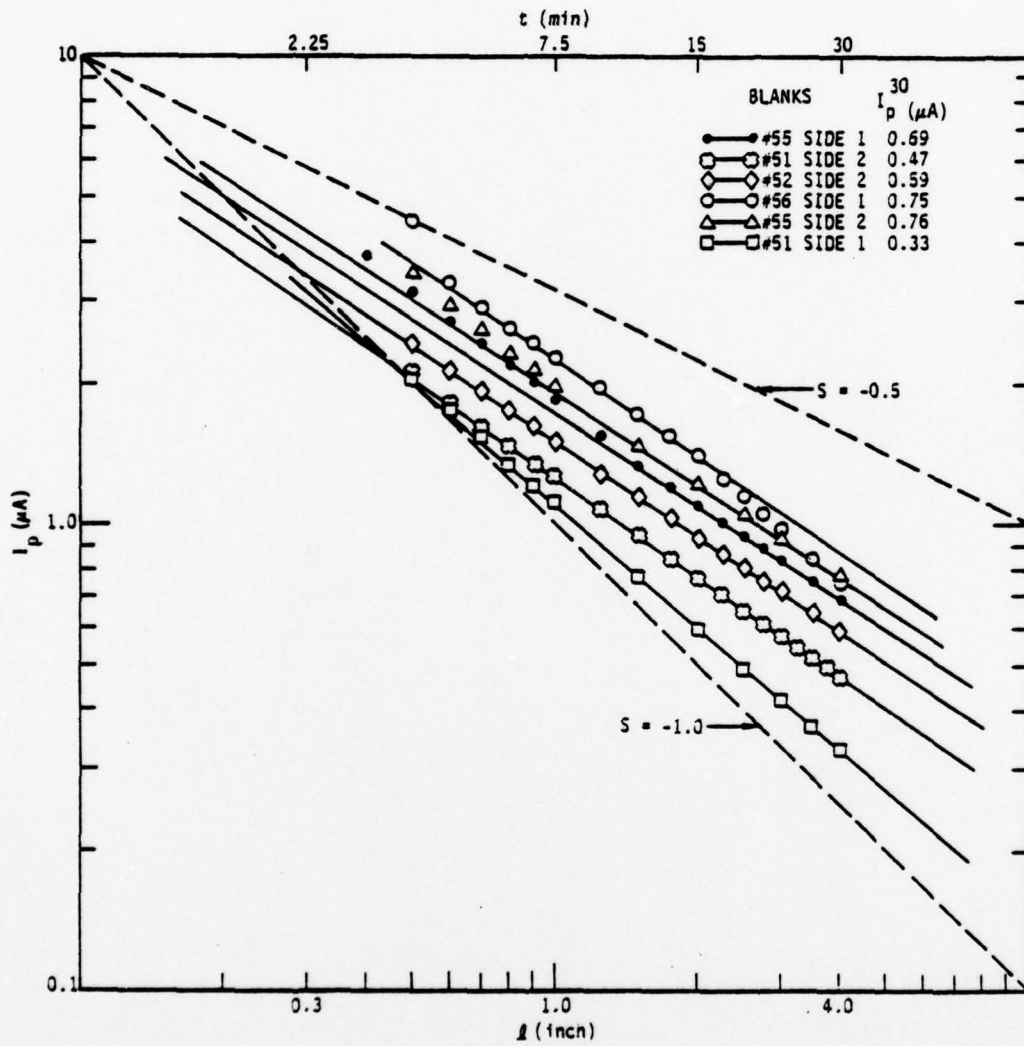


Figure 10c

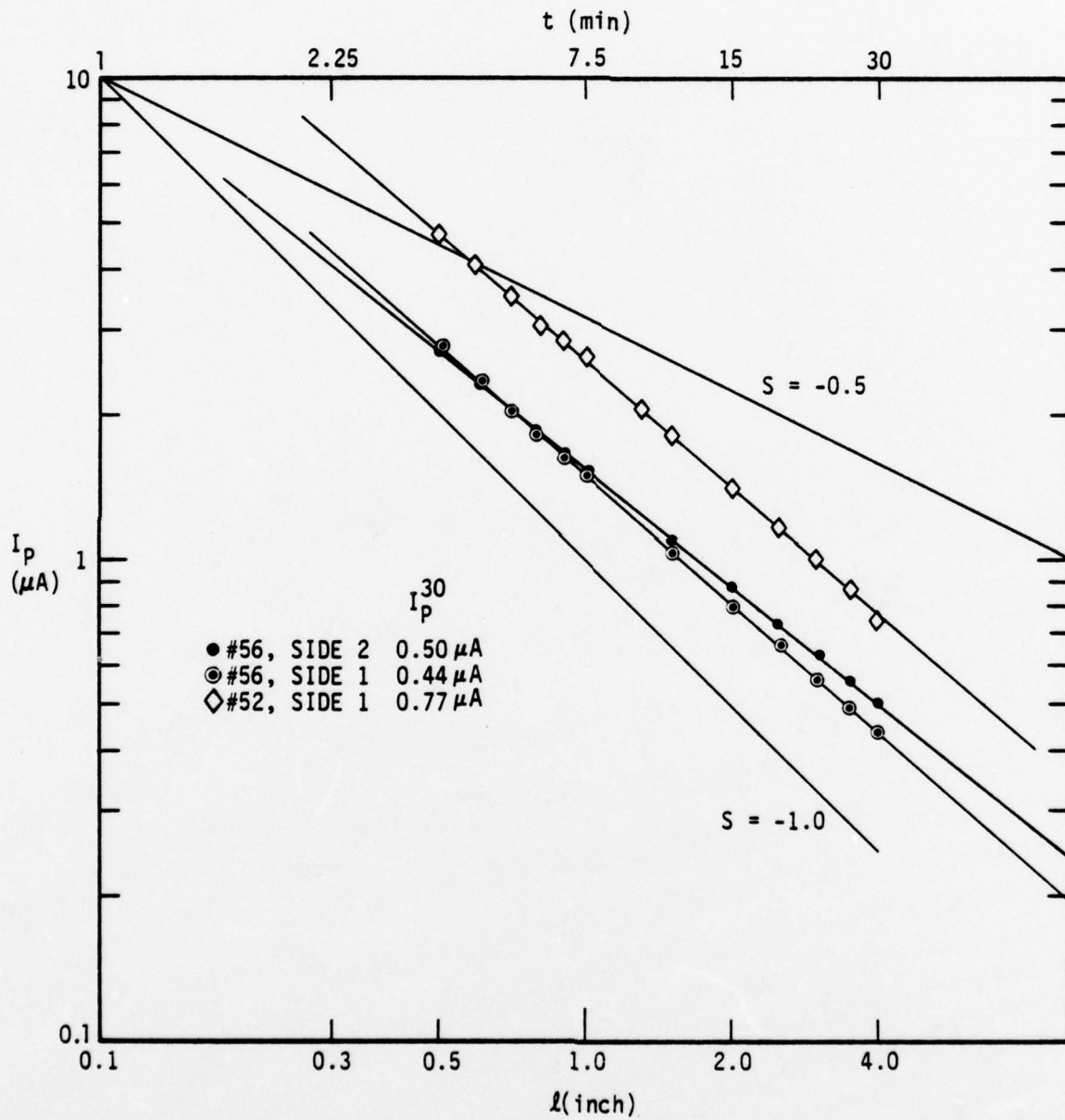


Figure 10d

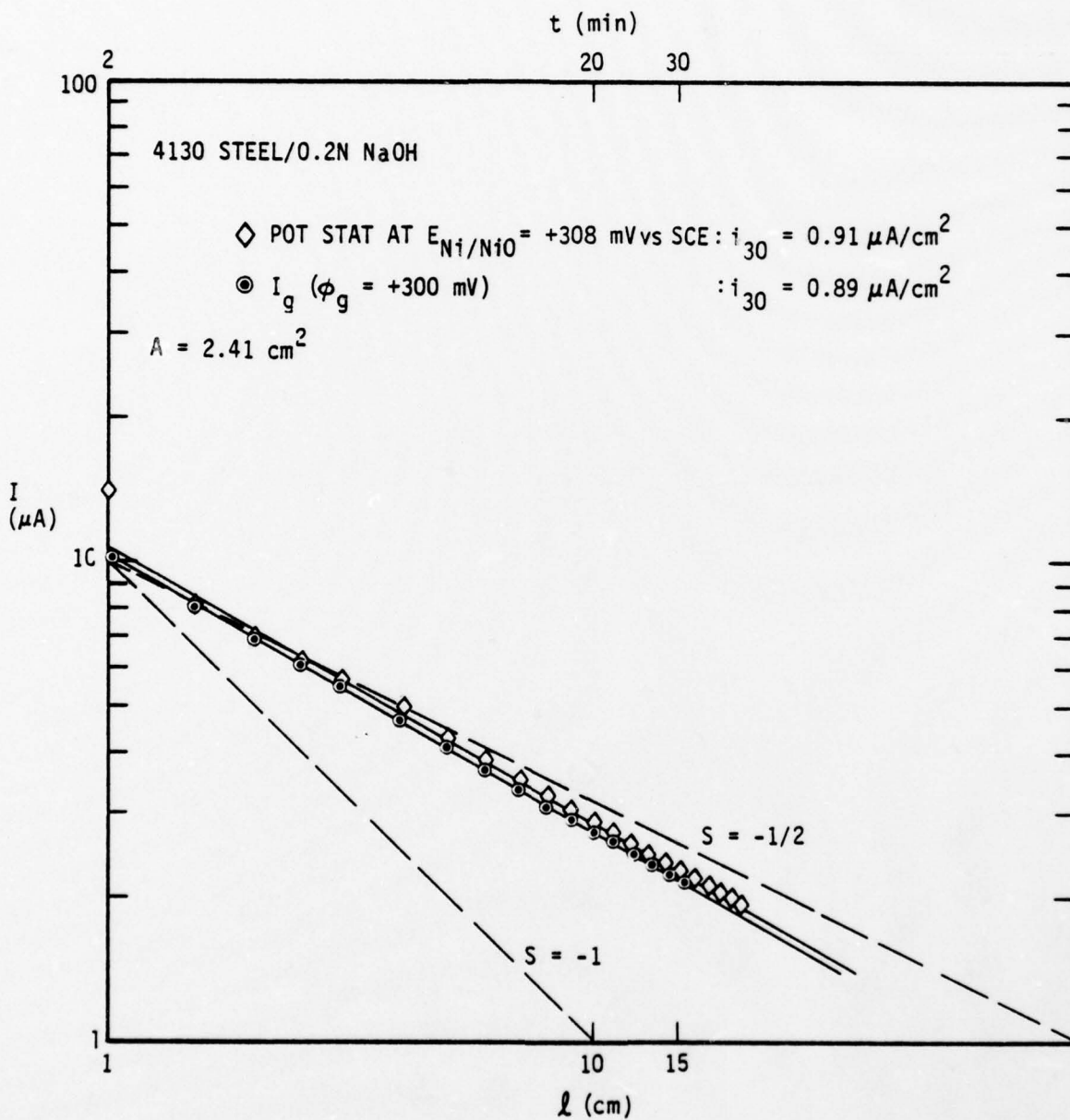


Figure 11

Figure 12a shows results obtained with the barnacle cell and the electronic system developed under this contract. The results obtained in Fig. 12a and b were obtained with Agar gel on the sponge in an attempt to provide 100% contact area, in Fig. 12c the barnacle cell was inverted while a seal was established, no sponge was used. Measurements were performed in the normal cell position. Good agreement is found for all measurements, the blank samples fall between 0.4 and 0.6 $\mu\text{A}/\text{cm}^2$, while for the charge samples (4130 steel) values between 1.4 and 1.9 $\mu\text{A}/\text{cm}^2$ were recorded at the end of the 30 min. test. The blank samples data indicate some variations in the steel surface itself.

The results of these tests show that the Ni/NiO is stable and that there are no problems due to the use of the sponge or the seal.

3. Evaluation of Final Design of Barnacle Cell

The three barnacle cells which were to be delivered to NADC were tested after the final design changes (plunger, vent) had been made. Tests were run on blank 4130 samples since it was felt that this approach would lead to more reproducible results.

Figure 13 a-d show the results obtained. Table VI summarizes the average current after 30 min for each cell and the integrated current over the last 5 min. Good reproducibility is obtained. The range of 0.4 to 0.7 μA compares very well with the data shown in Fig. 12a-c, where various cell design parameters were evaluated. Assuming that the measured current corresponds entirely to oxidation of hydrogen, a concentration of about 0.1 ppm is obtained for the 4130 steel blanks. Cell 1a had a new cell body to correct a leak occurring around the plunger which was due to a defect in the material which had occurred during remachining.

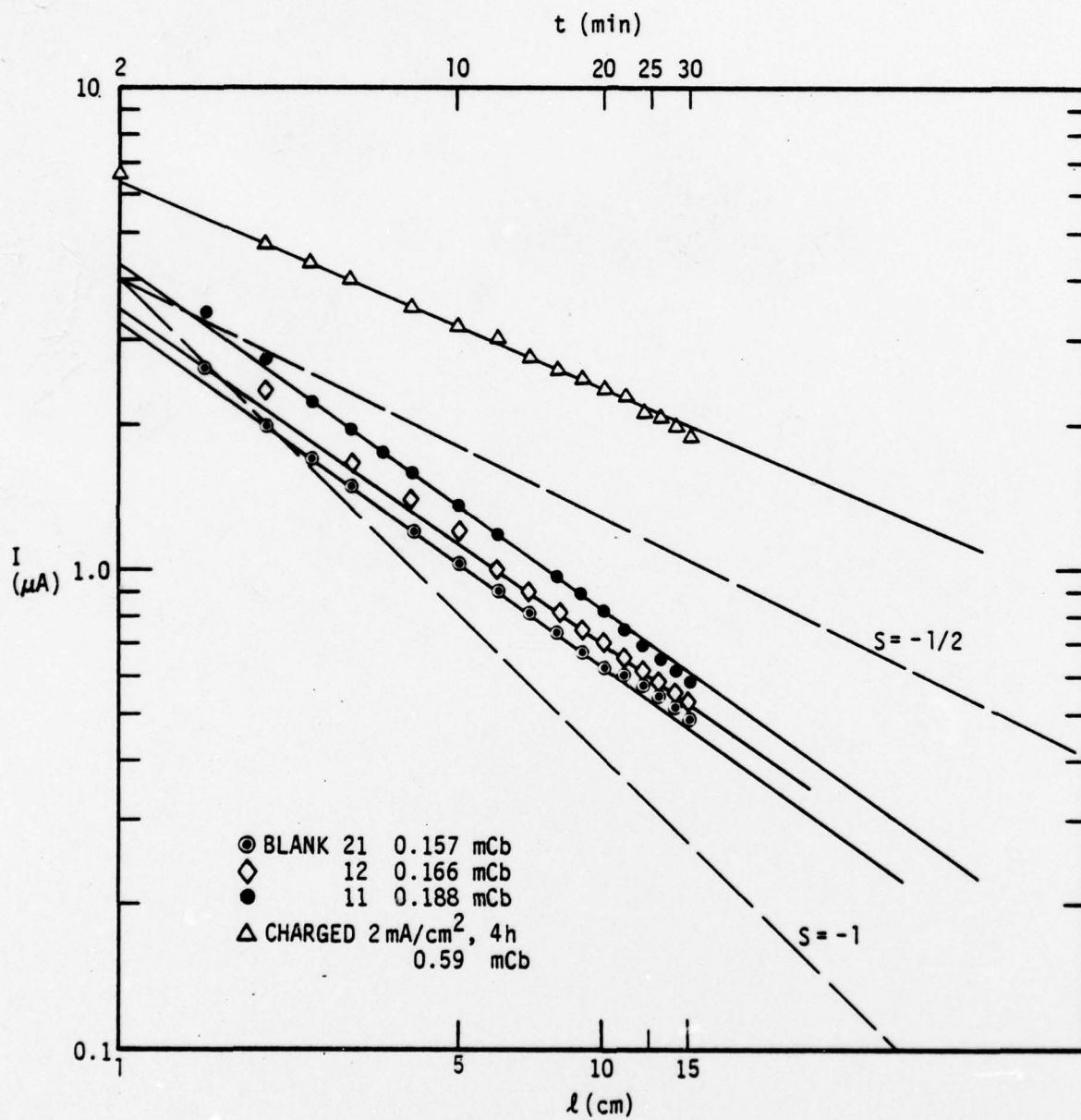


Figure 12a

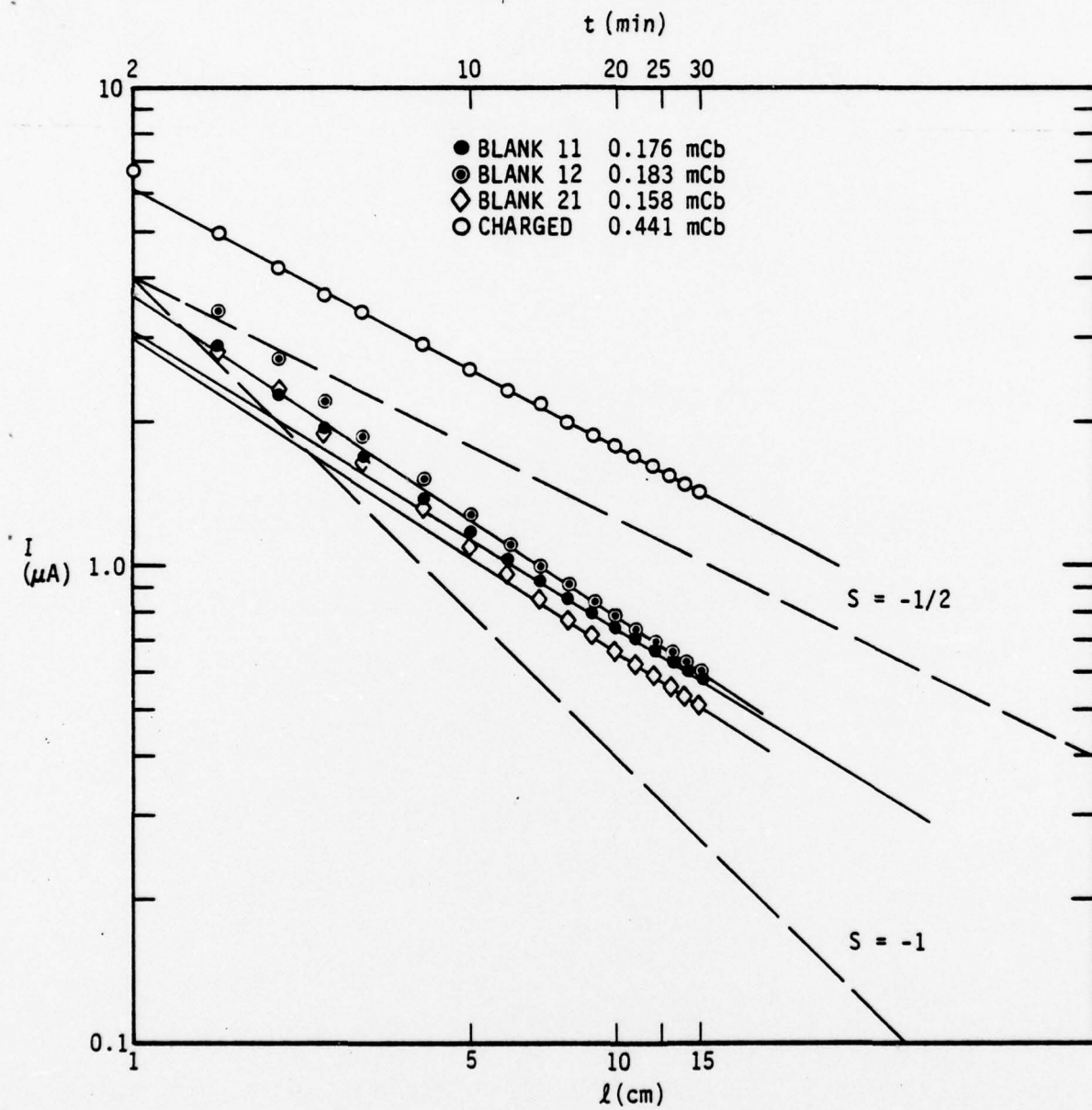


Figure 12b

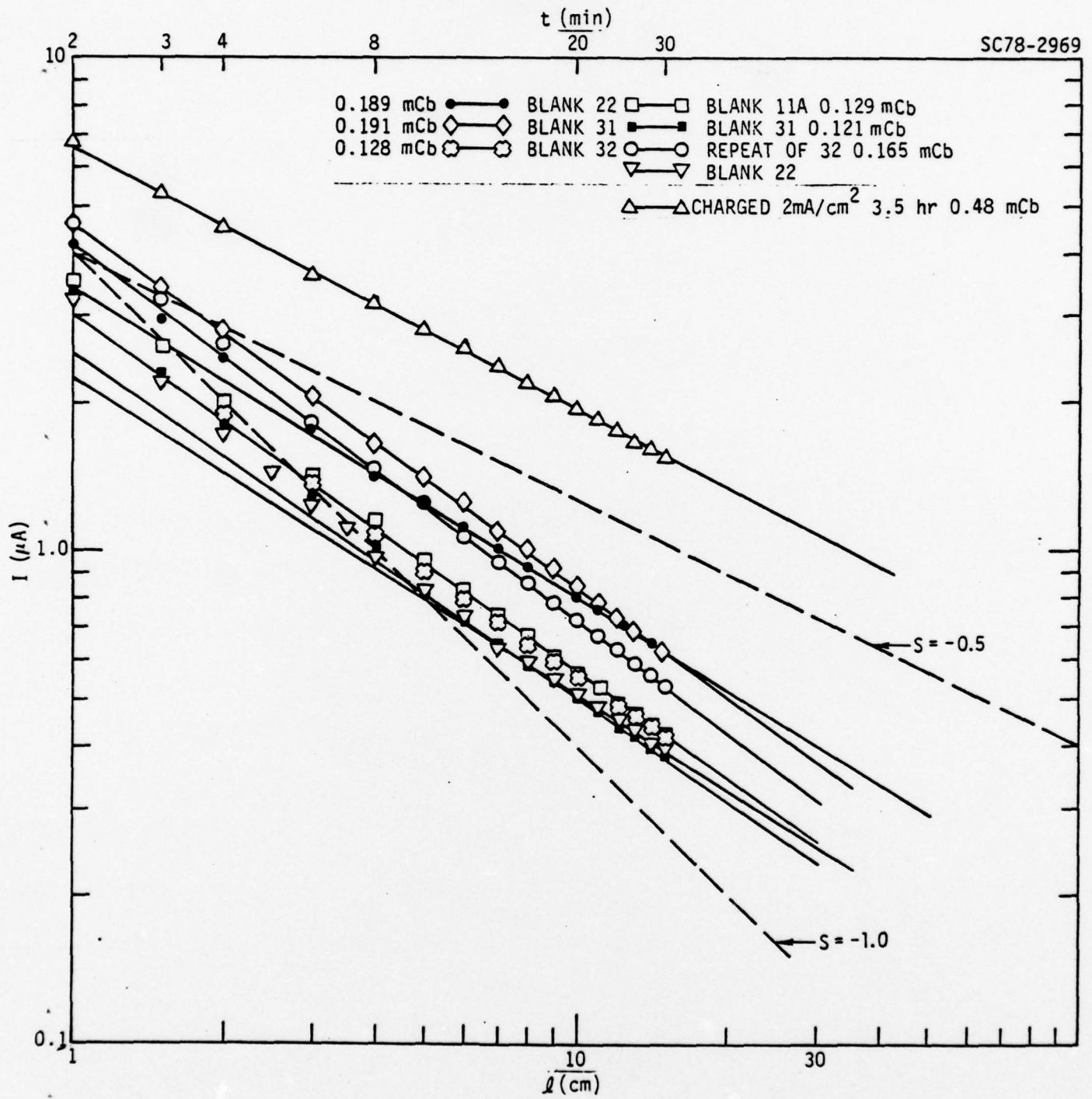


Figure 12c

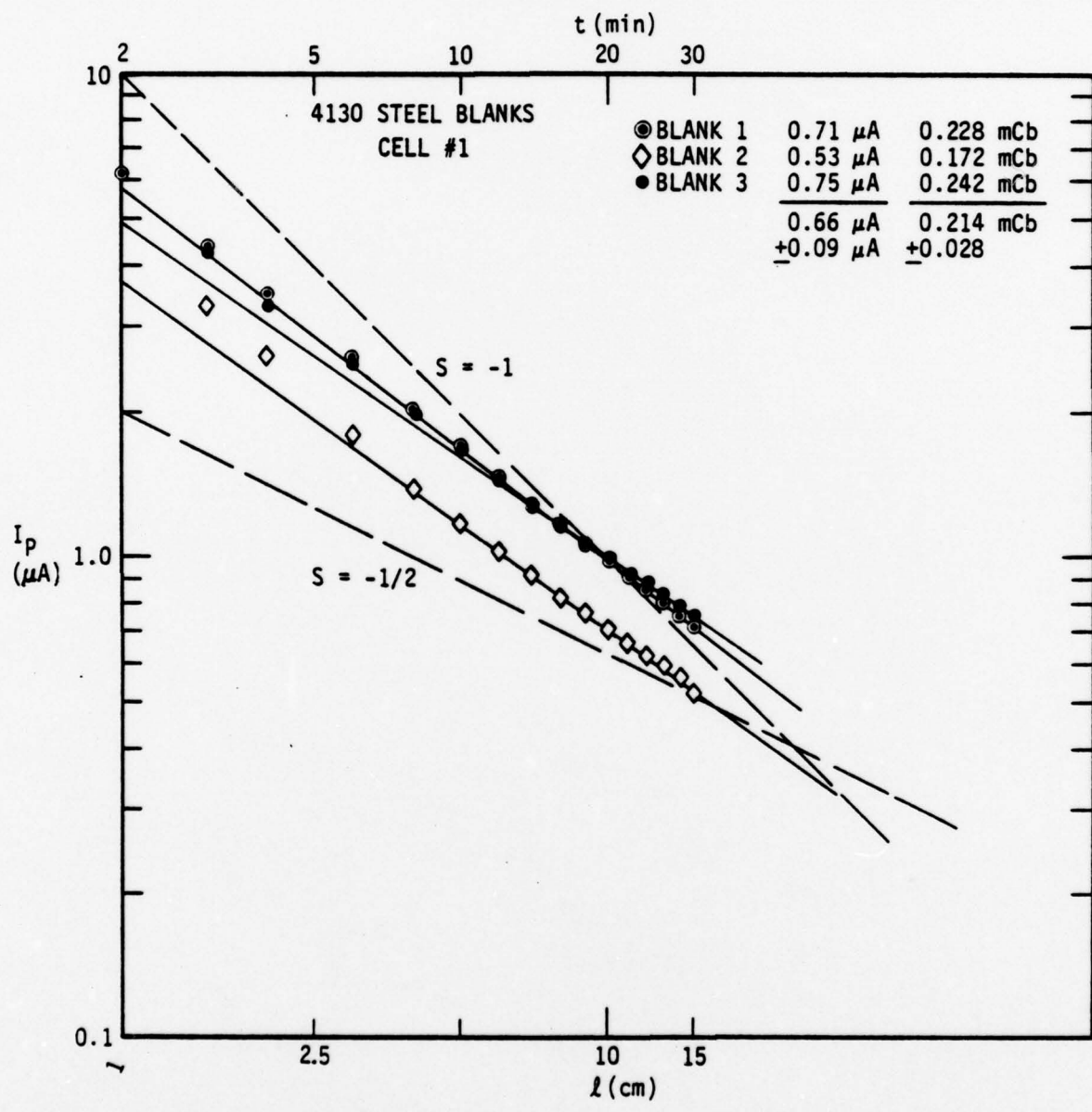


Figure 13a

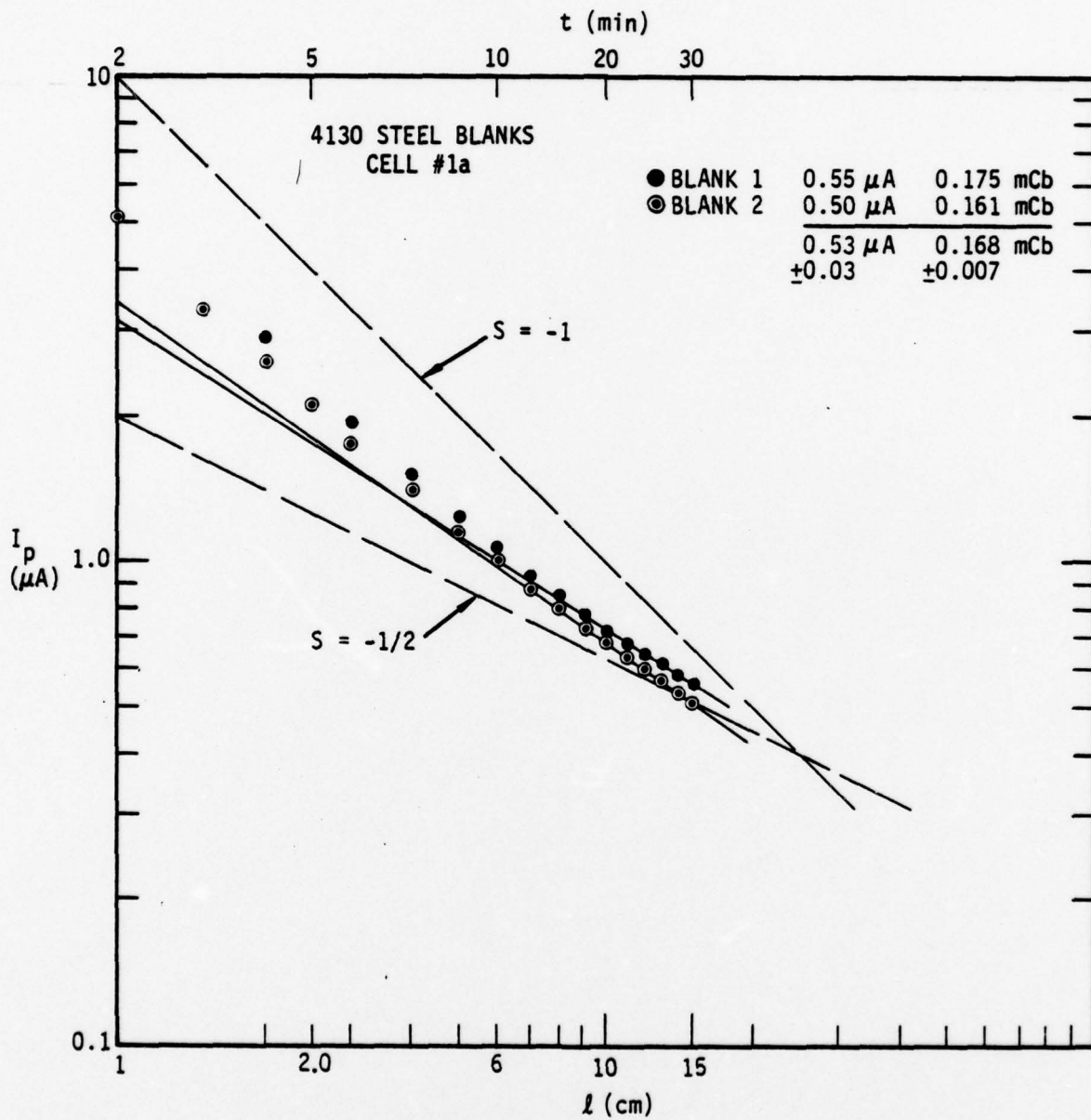


Figure 13b

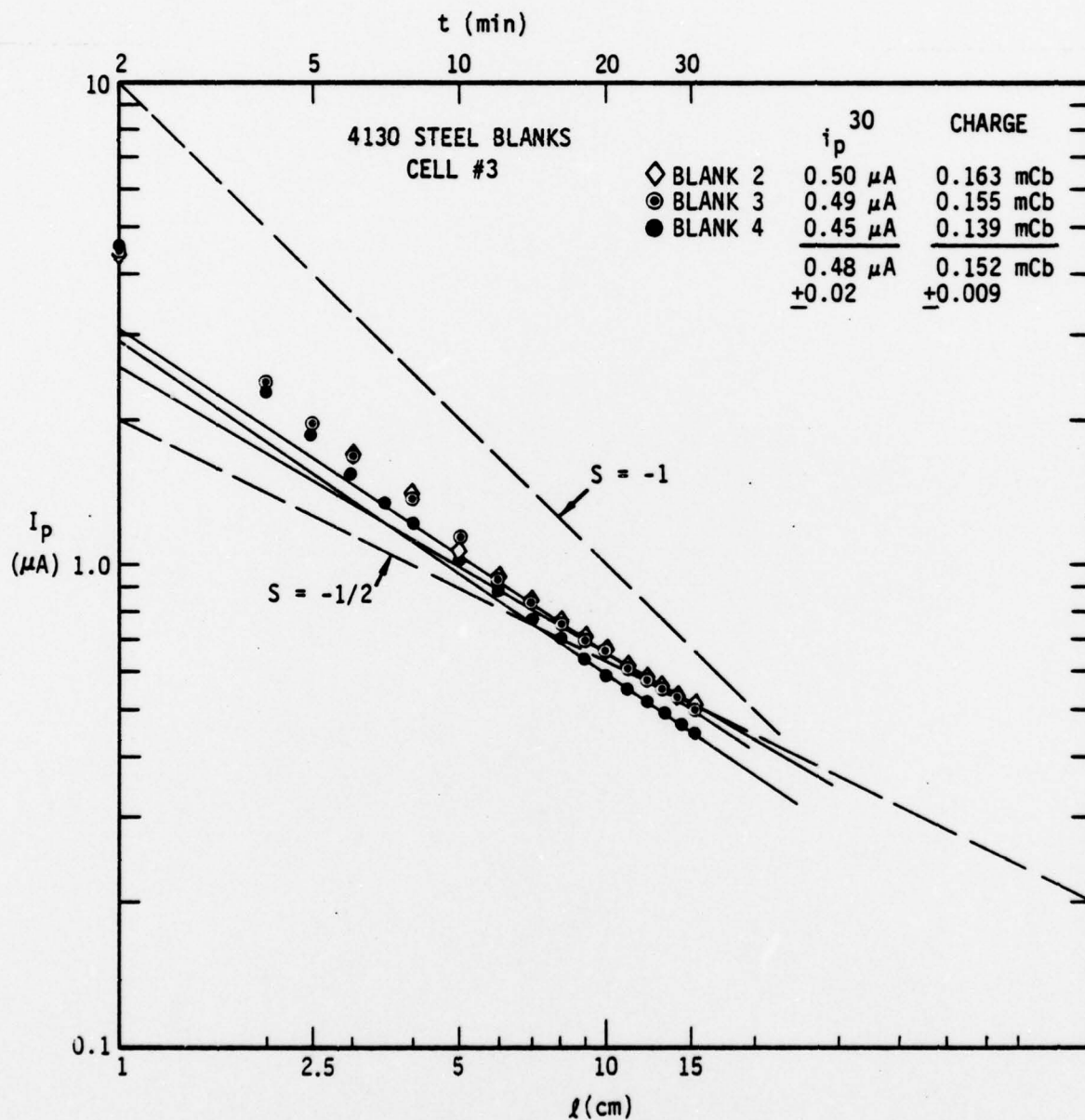


Figure 13c

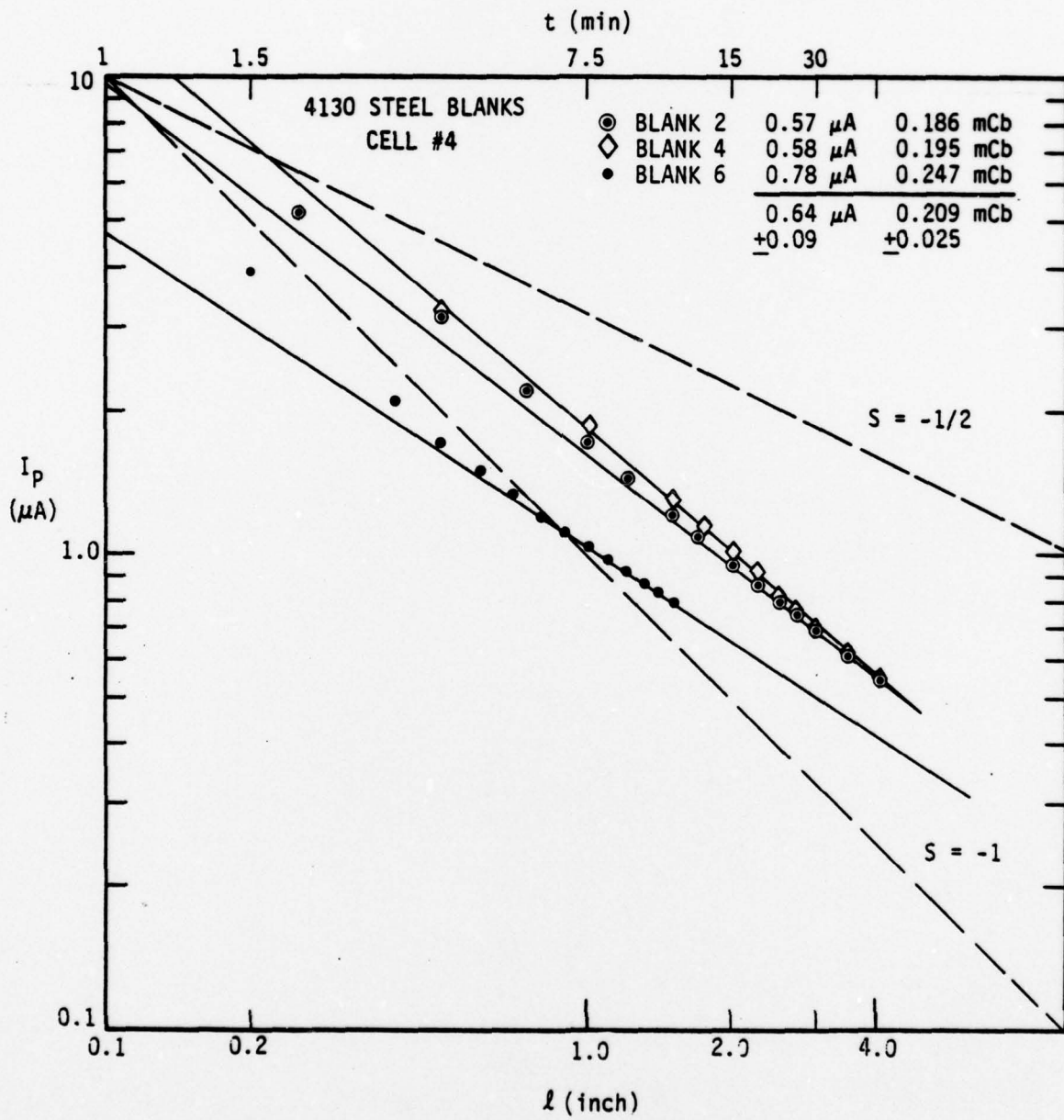


Figure 13d

Table VI Average Current and Charge for Four Test Cells

<u>Cell</u>	<u>n</u>	<u>i_p^{30} (μA)</u>	<u>Q (mCb)</u>
1	3	0.66 ± 0.09	0.214 ± 0.028
1a	2	0.53 ± 0.03	0.168 ± 0.007
3	3	0.48 ± 0.02	0.152 ± 0.009
4	3	0.64 ± 0.09	0.209 ± 0.025

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3. D. A. Berman, W. Beck and J. J. DeLuccia in "Hydrogen in Metals", I. M. Bernstein and W. W. Thompson, editors, ASM (1974), p. 595.
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A P P E N D I X

CIRCUIT DESCRIPTION

1. Analog Section

Cell current is converted to an analog voltage by operational amplifier 0A1 as shown in Fig. A1. This configuration, known as a current follower, provides very low resistance and high accuracy. Output voltage of 0A1 is equal to $-i_{\text{cell}} R_f$ where R_f is the feedback resistor (R1-R5). Capacitors C1-C5 reduce noise above a frequency of about 16 Hz. Amplifiers selected for this circuit contribute negligible errors due to offset current (10 pA), offset voltage (adjustable to <0.1 mV) and temperature coefficients of offsets. Diodes D1 and D2 provide limiting when the cell current exceeds full scale rating by about 30%. Cell circuit is closed through electronic switch ES1, a CMOS device with leakage current of <100 pA and on resistance of <50Ω.

Output of 0A1 is a negative voltage for normal operation of the barnacle cell; 0A2 inverts this voltage at unity gain to provide positive signal for the recorder output jacks. 0A2 also drives the analog meter and provides the signal for the analog to digital converter, described later.

The Ni/NiO reference electrode in the barnacle cell is connected to 0A3 which functions as a comparator. If the voltage between the reference electrode and the NiO/Ni cathode exceeds 100 mV, due to depletion of the cathode, the output of 0A3 swings negative and a light emitting diode LED2, is activated to warn the operator to check the cell. This monitoring occurs both before and during the measurement cycle. In addition, if the cell has inadequate amount of electrolyte, 0A3 will sense the resulting iR drop during

a measurement cycle and LED2 will be lighted. Threshold voltage for OA3 is set by potentiometer P6.

Integration of the cell current signal is accomplished by OA4 and timer T5. OA4 is connected as a typical analog integrator with C7 in the feedback loop. Output voltage of OA4 is $-V_{in} t/RC$ where V_{in} is the output of OA1 (equal to $-i_{cell} R_f$), R is the sum of P4 and R11, C is C7 and t is time in seconds. When the output of OA4 reaches the threshold of the zener (ZD1) stabilized reference voltage (4 V) connected to the comparator circuit in T5, a short pulse is produced by T5 which closes ES3 and ES4 discharging C7 in about five milliseconds. This same pulse is counted and drives the charge display, described later. From the above information, one pulse results from

$$V_o(OA4) = i_{cell} R_f t / RC$$

which can be solved for $i_{cell} t$, or charge, and numerical values substituted, giving

$$\text{charge/pulse} = i_{cell} t = (4V)(250-k\Omega)(1 \mu F) / R_f$$

or

$$\text{charge/pulse} = 1 \text{ Vs} / R_f .$$

If R_f is $1 \text{ M}\Omega$, then the required charge to produce one pulse is $1 \text{ Vs} / 10^6 \Omega$ or $1 \mu\text{C}$. An input current of $1 \mu\text{A}$ will produce one pulse per second at this current range.

Low voltage of the battery supply is indicated by LED1. As the battery supply decreases below 12.2 V, transistor Q6 is switched off and the current from R25 illuminates LED1.

2. Digital Current and Charge Section

Digital display of the cell current is provided by the A/D converter circuit in Fig. A2. Analog voltages from OA2 are converted to digital formats and the corresponding numbers appear on seven segment LED displays. DEC1 converts BCD to the equivalent seven segment code and each digit is illuminated in multiplex fashion through inverters I1-I5. This reduces battery power requirements. The A/D converter operates only during the time set on the Current Hold switches after Start is depressed. The last current value in the display is held at the moment that the Current Hold time elapses. This action is a result of the timer circuit, described later, acting on NAND gates NAN1 and NAN2. The current display is held indefinitely after the measurement cycle is completed and the Stop switch is depressed. It is lost if power is switched off, of course, or if the Start switch is depressed again. The A/D converter is calibrated by P7 which divides the reference voltage from RV.

Pulses from T5 of the integrator circuit are counted by DC1 during the Integration Time set on the thumb wheel switch. DC1 drives seven segment LED displays directly and multiplexes the digits through transistors Q1-Q4. DC1 is cleared to read all zeros when the Start switch is depressed. Readings are held indefinitely after the measurement cycle; loss of power or depressing the Start switch will change the display. The total capacity of DC1 is 9999 counts. There can only be a maximum charge display of 600 due to the design of the Integrator; the left-hand digit is used to establish the correct reading in millicoulombs for the most sensitive (200 nA) current range.

Decimal points for both digital displays are controlled by S2 of the current range switch. Diodes D10 and D11 are necessary to change from units of nanoamperes to microamperes.

During a measurement cycle, LED4 is driven on by I6 in response to logic from NAN3 and NAN4 which determine when both the Current Hold Time and the Integration Time have been completed.

3. Timing Section

All timing circuits are inactive until the Start switch is depressed. This switch changes the logic state of cross-coupled NOR gates 1 and 2 and transition is differentiated by C13 and R107 to produce a pulse which starts timers T1, T2 and T3, shown in Fig. A3. These timers control, respectively, the Recorder Delay Time, Current Hold Time and Integration Delay Time. Upon initiation of a measurement cycle, output pin 3 of the timer IC goes high (Ca. 5.5 V) and Capacitors C16, C17 and C18 are charged through resistor values set by the thumbwheel switches. When the capacitor voltage reaches the value set by the calibration potentiometer (P8, P9 and P10), the timing cycle is completed, the output goes low and the capacitor is discharged. Accuracy of the timers is not affected by battery voltage changes. Depressing Stop during a measurement cycle immediately inhibits the timing circuits. When power is switched on, C15 insures the initial logic state of NOR1 and NOR2.

The output of T1 is combined with the Start condition through NOR3 to close ES2 at the end of the Recorder Delay Time. Recorder Out jacks

are then active until the Stop switch is depressed. Recorder Strobe is also obtained from NOR3, but clamped by diode D6. This signal may be used to control the chart drive of the recorder through appropriate circuitry.

Time T2 controls the updating of the digital current display through NAN1. When the output of T2 is high after depressing Start, NAN2 passes the end of conversion pulse from pin 14 of the A/D converter to the display update control, pin 9. NAN2 inverts the signal pulse for required polarity. A shift in logic levels is provided by R111 and clamping diode D7. At the end of the Current Hold time, T2 output is low and the last conversion of the A/D converter is held in the display register. Depressing Stop followed by Start opens the logic gate for display updating. T2 also controls the Cycle On light through NOR4 and other logic.

Integration Delay is provided by T3. At the end of its timing cycle, the falling edge is differentiated by C14 and R109 to initiate the timing cycle of T4 which determines the Integration Time. T3 also contributes to control of Cycle On light and clears the output registers of the charge counter, CD1.

During Integration Time, the output of T4 is high which allows T5 to operate as described above. At the end of the timing period, the output is low, T5 is inhibited and C7 is held shorted by ES3 and ES4. R112 and D3 shift the logic level of the low state to that required by T5.

All of the timing circuits depend upon the stability of tantalum electrolytic capacitors for their accuracy and repeatability. The capacitors used were selected for low leakage (<10 nA) and low temperature coefficient ($\leq \pm 0.02\%/^{\circ}\text{C}$). After a long period of storage, they may be restored by cycling the instrument several times before measurements are made.

A timing diagram is given in Fig. A4 as a summary of circuit operation.

4. Instrument Calibration

Before attempting calibration, charge the battery for 15 hours or until the High Rate Charging light blinks every few seconds.

Required equipment includes a digital voltmeter with resolution of 0.1 mV; low voltage, adjustable power supply or mercury battery with 10 k, ten turn potentiometer; precision resistor, 100 k 1%; timing device such as a universal digital counter or electric clock with second hand; and small screw driver.

Remove the three mounting screws located on the edge of the instrument panel between the digital displays, near the Current Range Switch and between the Integration Delay and Integration Time thumbwheel switches. Carefully lift out the instrument from the case.

If only the timers are to be calibrated, the battery pack need not be removed. Otherwise remove the three screws holding the battery pack and carefully lift it free of the panel. Leads are long enough to allow the pack to be placed next to the panel.

Refer to Fig. A5 for component location.

a. Calibration of Timers: Switch instrument ON, set all timers to one minute and cycle several times by depressing Start button, Stop button after Cycle On light goes out, Start button again, etc.

Recorder Delay, timer T1, is calibrated by adjusting P8 which is accessible through the hole in the aluminum heat sink. If a digital counter is available, set it for interval time measurements and connect the input to the blue/white lead near pin 3 of T1. Set Recorder Delay to 1 min., depress

Start and note time interval. Adjust P8, clockwise to decrease delay, as necessary to bring delay in the range of 59.5 to 59.7 s. To repeat timing cycle, Stop switch must be depressed, then Start. Check delay at a setting of 10 min. If measured time exceeds 606 s, adjust P8. In general, at short times the timers should be set to have a slight negative error, but less than -1%, so that the inherent error at long times is not greater than +1%. If an electric clock is used, connect the DVM to Recorder Strobe jacks and note elapsed time at a setting of 10 min. from the moment of depressing Start until the Strobe rises to +6 V. Adjust P8 as necessary to bring measured time within the range 597-603 s.

Current Hold, timer T2, is calibrated by connecting the digital counter to end of R111 near pin 3 of T2. Set for 1 min. and note elapsed time after Start. Adjust P9 as necessary to bring measured time within 59.5 to 59.7 s. If an electric clock is used, set time for Current Hold to 10 min. and both Integration times to 1 min. Observe the Cycle On light to measure elapsed time and adjust P9 to bring within the range of 593 to 603 s.

Integration Delay, timer T3, is calibrated by connecting the digital counter to R108 near pin 3 of T3. Set for 1 min. and note elapsed time after Start. Adjust P10 as necessary to bring measured time within 59.5 to 59.7 s. If an electric clock is used, set time for Integration Delay to 10 min., Integration Time to 0 min. and Current Hold to 1 min. Observe Cycle On light to measure elapsed time and adjust P10 to bring within the range of 597 to 603 s.

Integration Time, timer T4, is calibrated by connecting the digital counter to R112 near pin 3 of T4. Set for 1 min. and note elapsed time after Start. Adjust P11 as necessary to bring measured time within 59.8 to 60.0 s. If an electric clock is used, set Integration Time for 5 min., Integration Delay for 0 min. and Current Hold for 1 min. Observe Cycle On light to measure elapsed time and adjust P10 to bring within the range of 298 to 302 s.

A typical set of timing measurements of the Current Hold time is shown below. Initially, the timer was calibrated in the 1 min. position using a Tektronix TM502 Universal Counter. Repeatability of measurements was typically $\pm 0.5\%$.

<u>Set Time</u>	<u>Measured Time</u>
1 min	59.63 s
2	119.68
5	299.27
10	600.5
30	1815.5

b. Calibration of Analog/Digital Section: Switch instrument ON and set Current Range to 20 μ A, Integration Delay and Current Hold to 30 min. Depress Start. Connect DVM to pole of S1 (white wire) and to common (negative terminal of current meter). Adjust P1 to bring output of OA1 to be 0 ± 0.1 mV. To zero OA2, adjust P2 so that the digital current display is 0.00 with the minus sign blinking. Now connect the DVM to the end of R20 near C7 and adjust P5 to zero OA4 to 0 ± 0.1 mV. If more than 30 min. elapses during these adjustments, depress Stop, then Start again.

To calibrate the digital current display and the current meter, connect one end of the 100 k 1% resistor to the red pin jack of the input cable. Connect the other end to a low voltage source (0-2 V) or the wiper of a 10 k, 10 turn pot powered by a mercury cell. Connect the white pin jack to the negative of the voltage source or mercury cell. Connect the DVM to the output of OA1 (white wire on S1) and common (negative terminal of current meter), depress Start. Adjust the voltage source (or 10 k potentiometer) until the DVM shows -1.000 V, then adjust P7 until the digital current meter reads 10.00. Adjust P3 until the analog current meter reads 100 when in a vertical position.

After these adjustments, the instrument is calibrated to be within $\pm 1\%$ of full scale on all current ranges and the zero readings will be within the same range.

Calibration of the integrator should not be made until all of the preceding steps have been completed. Set Integration Delay to 0 min., Integration Time to 5 min. and Current Range to 20 μ A. Use the same set-up for calibration of the digital current display. Depress Start, adjust the voltage source until the current display reads 10.00, then depress Stop. Upon depressing Start again, the charge display will increase at a rate of one count per second and should reach 300 at the end of 5 min. integration time. Adjust P4 if necessary so that the final count is within the range of 297 to 303 in subsequent measurements.

To adjust the comparator level at which the Check Cell LED is lighted, connect a low voltage source to the black jack of the input cable and the negative of the source to common (negative terminal of analog current meter) or to white jack. Depress Start and set voltage source to +100 mV, adjust P6 until Check Cell LED just glows.

Low Battery light threshold level may be set by monitoring the battery voltage with a voltmeter and adjusting P12 for a faint glow of the LED when voltage reaches 12.2. Alternatively, measure the voltage between battery plus terminal and the emitter of Q6 and set P12 for a reading of 11.7 V.

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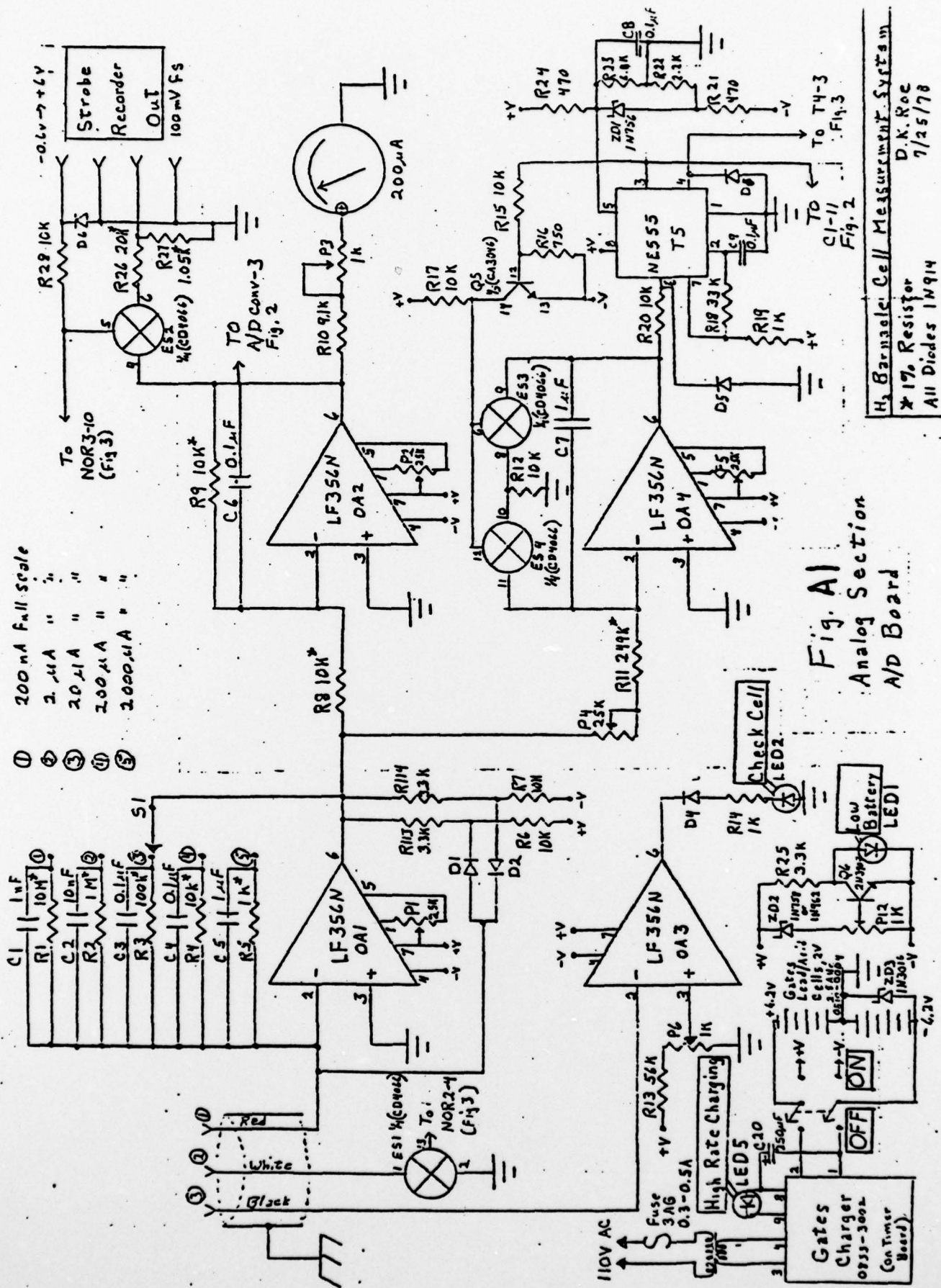


Fig. A1
Analog Section
A/D Board

H₂ Barnable Cell Measurement System
 * 170 Resistor
 All Diodes 1N914
 D.K. Roc
 7/25/78

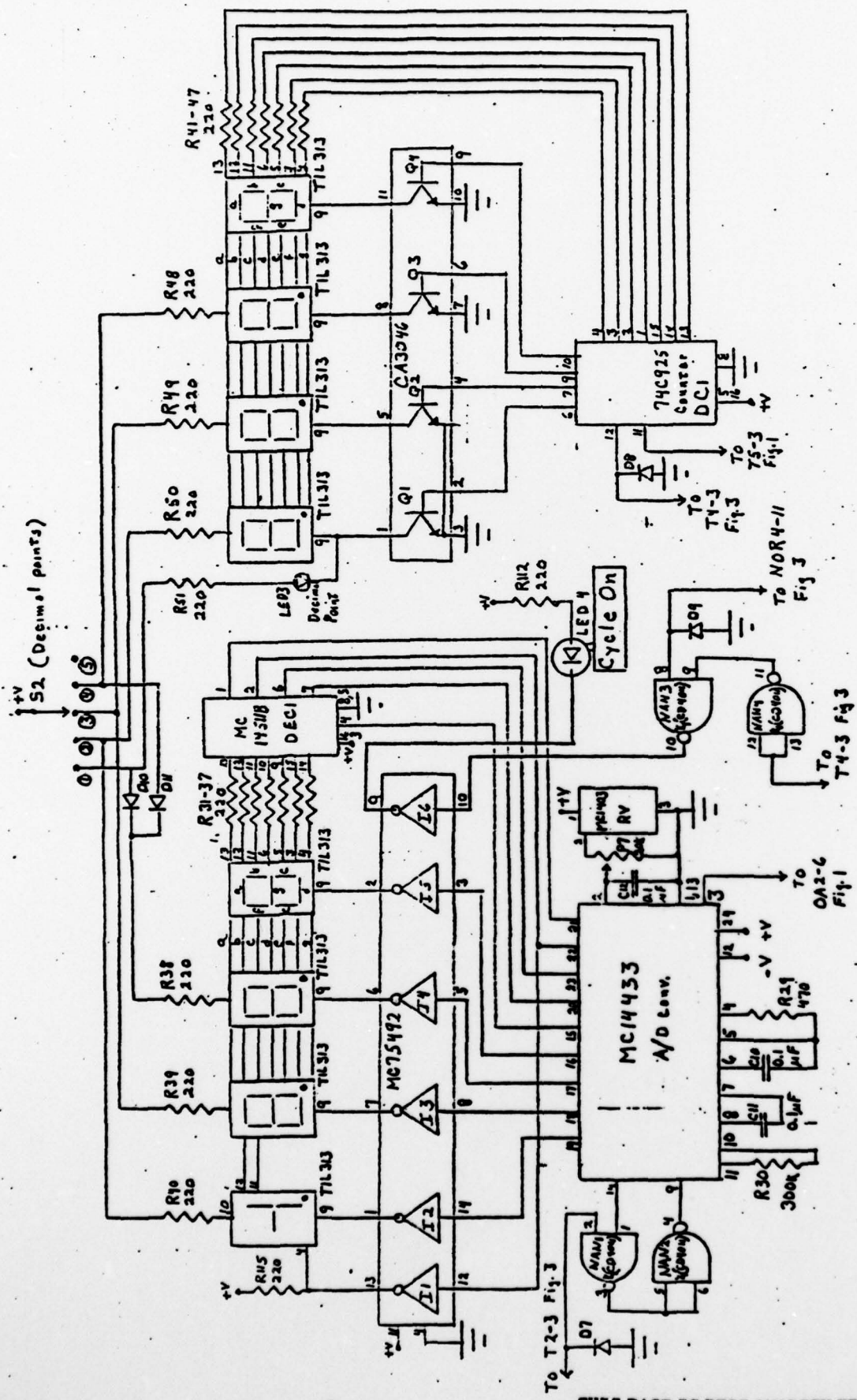
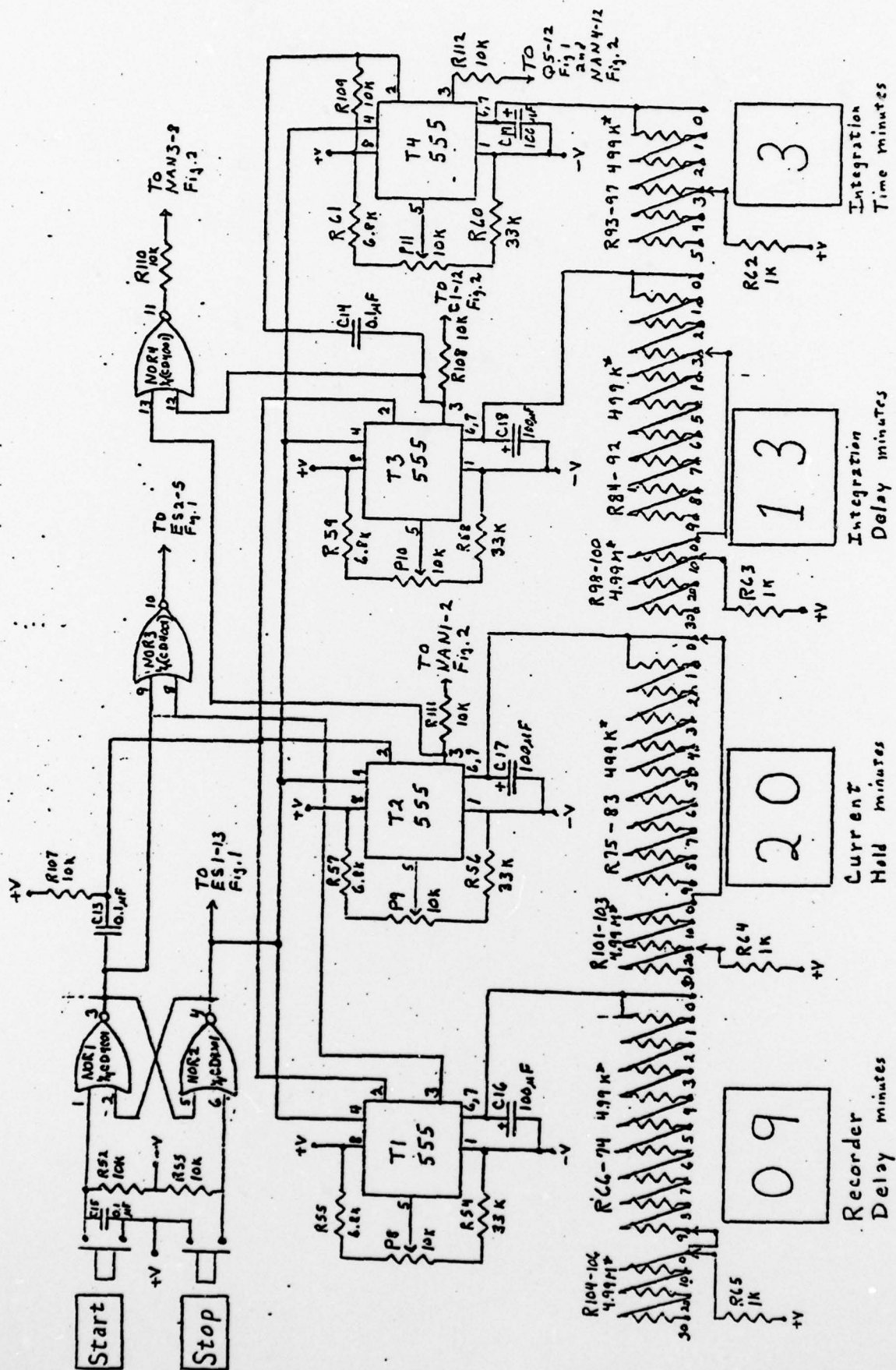


Fig. A2
 Digital Current and
 Charge Section - A/D Board

H₂ Barnable Cell Measurement System
 DK Roc
 7/25/78
 All diodes 1N914



H₂-Barnacle Cell Measurement System

DK Roc
7/25/78

Fig. A3
Timer Board

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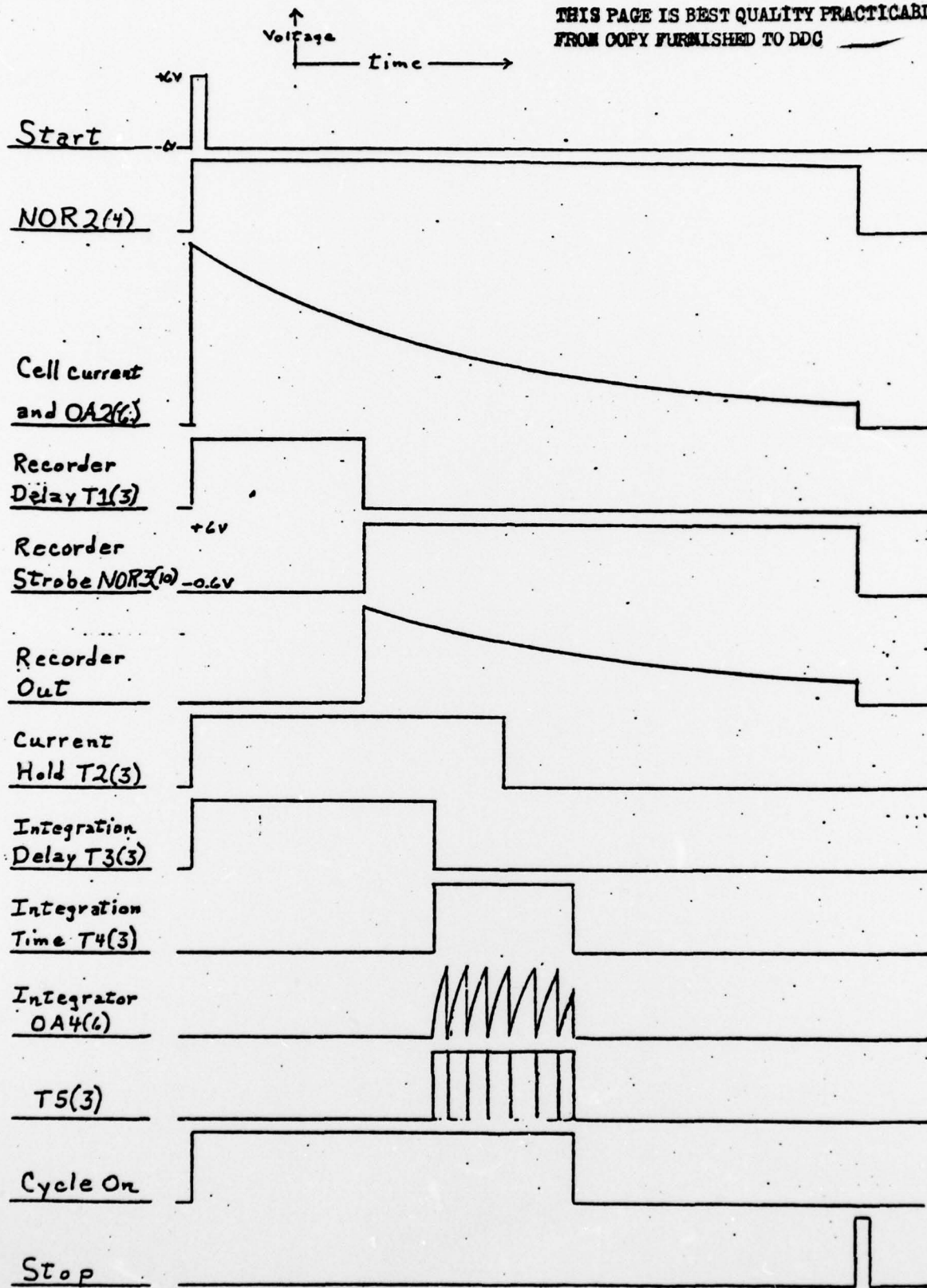


Fig. A4
Timing Diagram
H₂ Barnacle Cell Measurement
System

D.K. Roe
7/25/78

7 Segment LED
Displays on reverse side

Analog/Digital
Board

Note: CF indicates Filter
Capacitor; not shown
on circuit diagrams.

Heat Sink For Charger
(do not ground)
Charger module
and C20 below

Timer
Board

H₂ Gaseous Cell
Measurement
System
D.K. Roe
7/25/54

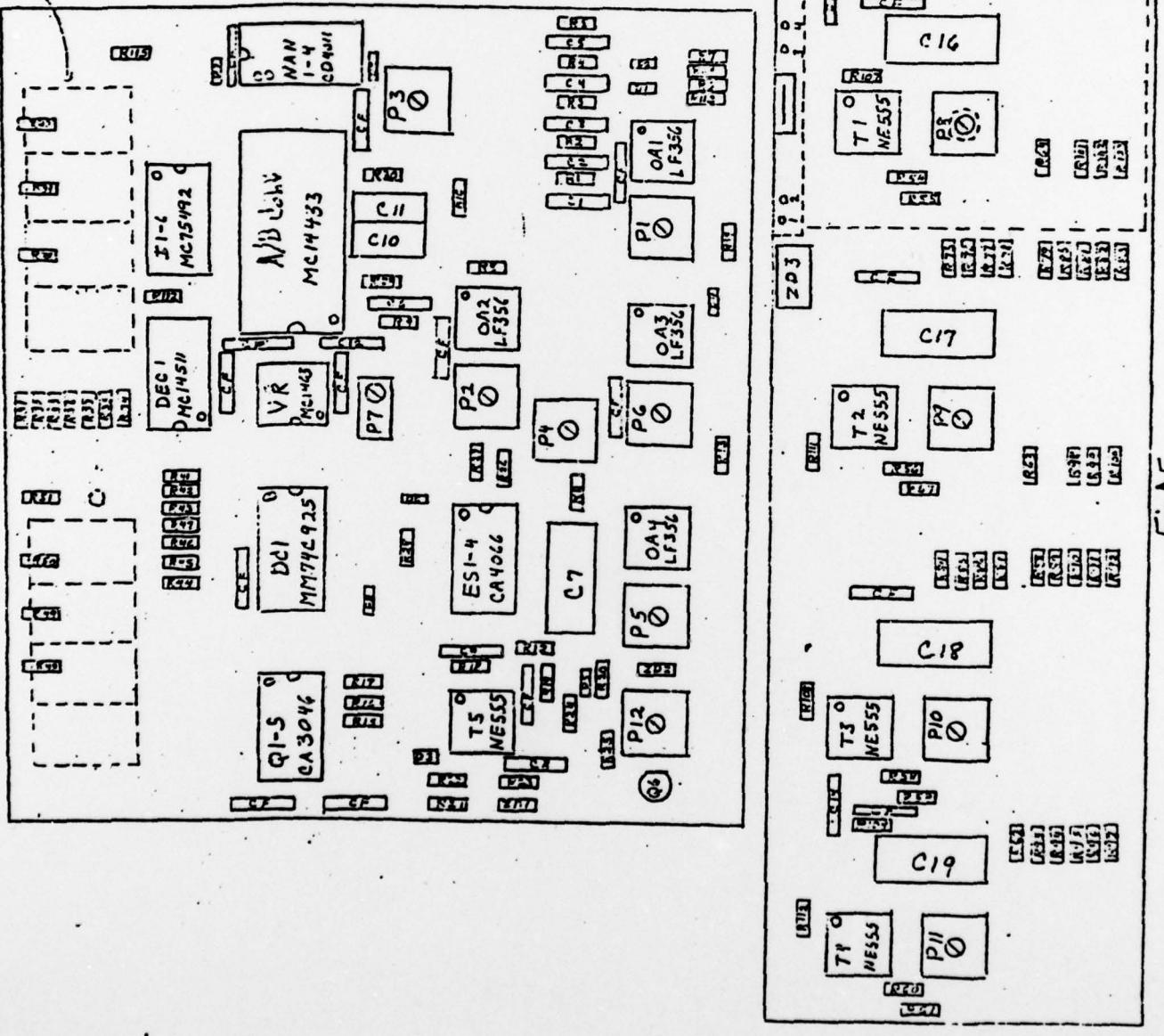


Fig A5
Printed Circuit Boards - Component Location

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