PROGRESS REPORT

442418-23600

U.S.P.H.S. FR-7006-04 BIOMEDICAL SUPPORT

POLLUTION DETECTION AND MONITORING IN THE MARINE ENVIRONMENT BY ELECTROCHEMICAL MEANS

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POLLUTION DETECTION AND MONITORING IN THE MARINE ENVIRONMENT BY ELECTROCHEMICAL MEANS

The purpose of this study is to utilize in combination oxygen and sulfide electrodes to measure the range of values of O_2 and $S^=$ in marine and estuarine environments. The two principle areas of research were
(1) suitability tests of commercially available electrodes, and
(2) design of an appropriate tow vehicle to house the electrode array.

SULFIDE ELECTRODE

The response of the Beckman 39610 sulfide electrode in an estuarine environment was tested in an experiment using a bay model with San Francisco Bay water and bottom mud. Two liters of Bay mud with the included organism were placed in a glass container, then covered with one liter of Bay water (salinity 25%). The glass container was covered with a Plexiglas disk with port cut in it to permit insertion of the sulfide, pH, calomel, and platinum solution ground electrodes. The voltages of the sulfide-calomel and pH-calomel pairs were read with a Wilde-Rodgers electrochemical meter (Wilde and Rodgers, 1970). Temperature was measured to $0.1^{o}C$ with a thermistor network.

Two types of models were studied simulating

(1) a stagnant basin where the oxygen content is reduced by the organic content of the sediment and by the action of sulfate reducing bacteria operating in sea water (container sealed from exchange with the atmosphere); and

(2) a well mixed tidal estuary with gradual oxidation of organic matter (the overlying water was aerated with a commercial aquarium bubbler); results indicate for

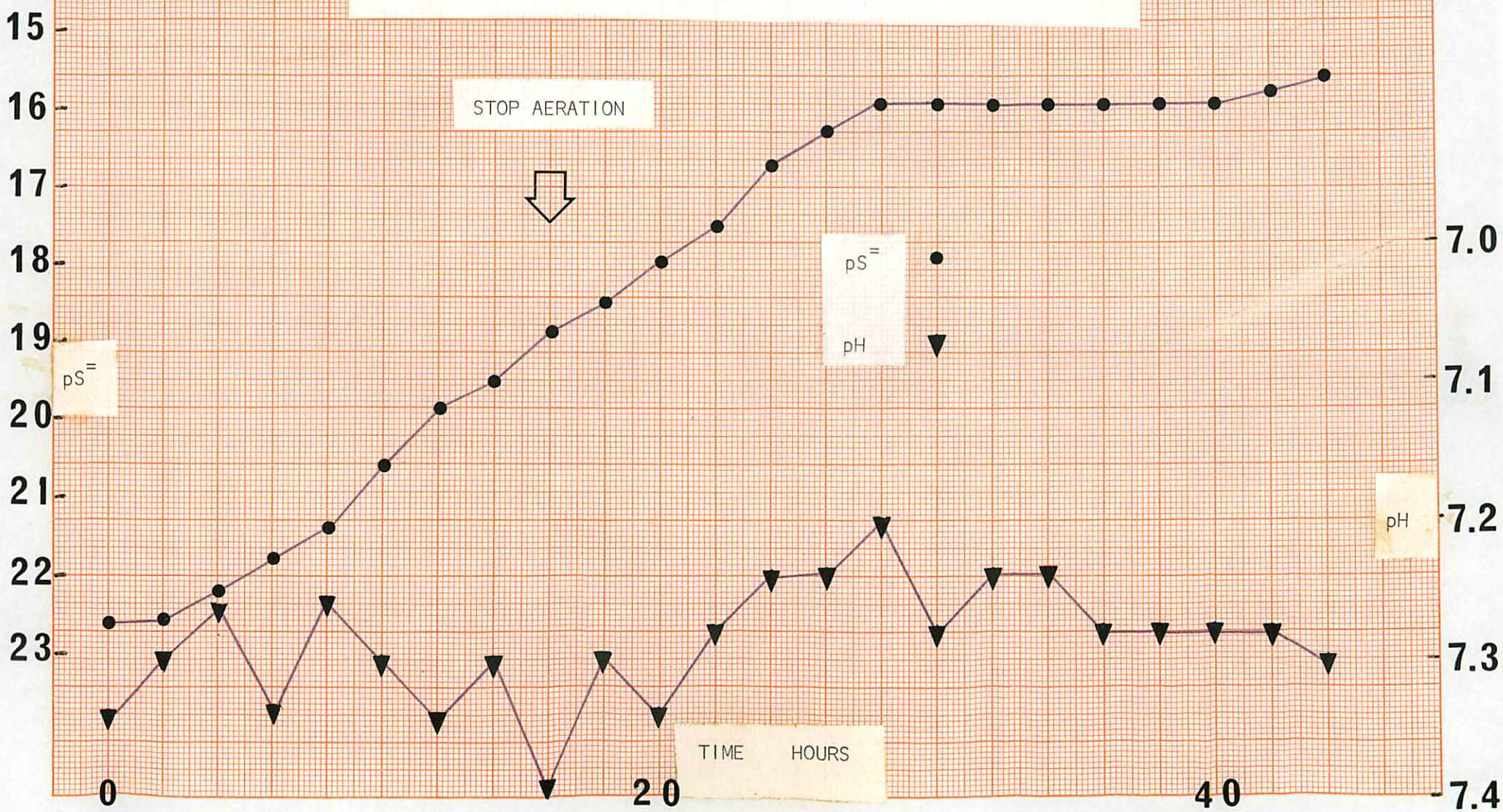
   (a) anaerobic Bay mud equilibrium
   $ps^=$ about 15 at pH = 7.3 (Figure 1)

   (b) in oxygenated Bay mud equilibrium from initial anaerobic condition to
   $ps^=$ about 23 at pH = 7.2 in about 90 minutes

FIGURE ONE

STARTING CONDITION: OVERLYING WATER MIXED AND OXYGENATED

ELECTRODE DEPTH IN SEDIMENT - 3 CENTIMETERS



These relationships are based on

$pS^{=} = pH_2S + pK_3 - 2pH$

where pK_3 = -Log of the equilibrium constant for the reactions

$H_2S \rightleftarrows H^+ + HS^-$ and $HS^- \rightleftarrows H^+ + S^{=}$.

Calibration tests in Na_2S + NaCl solutions of the sulfide electrode showed

(a) an acceptably linear quasi-Nernstian slope of 28 mv/$pS^{=}$ unit, from $pS^{=}$ values of 1 to 19

(b) fast response, and

(c) freedom from interference from HS^- and H_2S at pH values from 1.1 to 12.6

Comments: Commercially available solid state sulfide electrodes can be used in the marine environment. They will be most useful in anaerobic conditions where the oxygen is nonexistant or very low.

OXYGEN SENSOR

Membrane polarographic oxygen sensors

(1) lead electrode (Weston-Stack D.O. analyzer).

(2) platinum electrode blood (Goldstick, 1966), and

(3) gold electrode (Martek D.O.A.)

were tested in the following calibration solutions:

(1) air,

(2) aerated sea water,

(3) deoxygenated sea water (yeast), and

(4) reduced sea water (mixed with iron filings).

The test results were disappointing for in situ towed monitoring because

(1) equilibrium valves were attained slowly,

(2) reproducibility was low, on the order of 5 to 15% in aerated sea water, and

(3) membranes were fragile and difficult to change.

Slow response time, unfortunately, is inherent in electrodes such as the oxygen type which depends on diffusion of a gas through the membrane and the

underlying internal solution. The rate of response is a function of the ΔO_2 between the new and the previous solutions which is on the order of 2.0 mg/ℓ/minute.

Low precision is a difficult problem because it not only affects interpretation of the data but also makes calibration over wide ranges of oxygen concentration unreliable. Apparently low precision is caused in part by reactivity of the metal electrode as precision was

(1) from best to worst using platinum, gold, and lead electrodes, and
(2) best in solutions of low oxygen content and worst in aerated sea water.

Comments: Preliminary tests with the martek gold electrode with a teflon membrane suggest this electrode might be acceptable for in situ monitoring in areas of gradual oxygen concentration change and towing the sensor at slow speeds (5 knots maximum). Tests of this type of electrode are continuing as it was only received at the end of June.

MONITORING VEHICLE

Once acceptable electrodes have been found, immediately it will be possible to monitor

(a) a surface field by simply trailing the electrode from a moving vessel, and
(b) at a station profile by lowering the electrodes from a stationary vessel.

However, it would be convenient to have the added flexibility of continuous monitoring along

(a) a plane of constant depth from the surface to examine planar phenomenon such as mixing from a point source as a sewer outfall; and
(b) at constant depth from the bottom to examine contour following processes such as tidal mising.

Accordingly, concurrently with the electrode studies a towed monitoring is being constructed with the following specifications:

Speed	4 knots
Operating Depth	Surface to 100 feet
Bottom Contouring	10 to 50 feet above bottom
Length	5 feet
Wing Span	4 feet
Material	Plexiglass and fiberglass
Weight in Air with Electronic Package	110 pounds
Bouyancy	2 pounds
Towing Cable	1/8" stainless steel
Cable Length	200 to 400 feet

The basic configuration of the vehicle is that of an air plane with forward fixed wings and rear movable elevators. The elevators will be able to assume two positions that correspond to (1) diving, and (2) surfacing. The vehicle will travel by porpoising along a preset path with oscillations of one foot. The material used in the construction will be non-metallic to avoid generation of stray fields due to corrosion which may influence the output of the sensors.

The depth control system provides for two modes:

(a) constant depth, and

(b) bottom contouring at a fixed distance from the bottom.

In the constant depth mode, the depth is measured with a pressure sensor. In the bottom contouring mode the distance from the bottom is measured with an echo sounder mounted in the vehicle. For each mode the actual depth value is compared with a preset value. The sign of the difference determines whether the elevators are moved into diving or surfacing positions.

Comments: Hydrodynamic tests of the vehicle have been completed (Richards, 1970) (see Fig. 2,3,4 for pictures of the full scale hydraulic model) so that proper tracking and towing characteristics have been achieved. The next step is construction of the plexiglass working vehicle.

FIGURE TWO

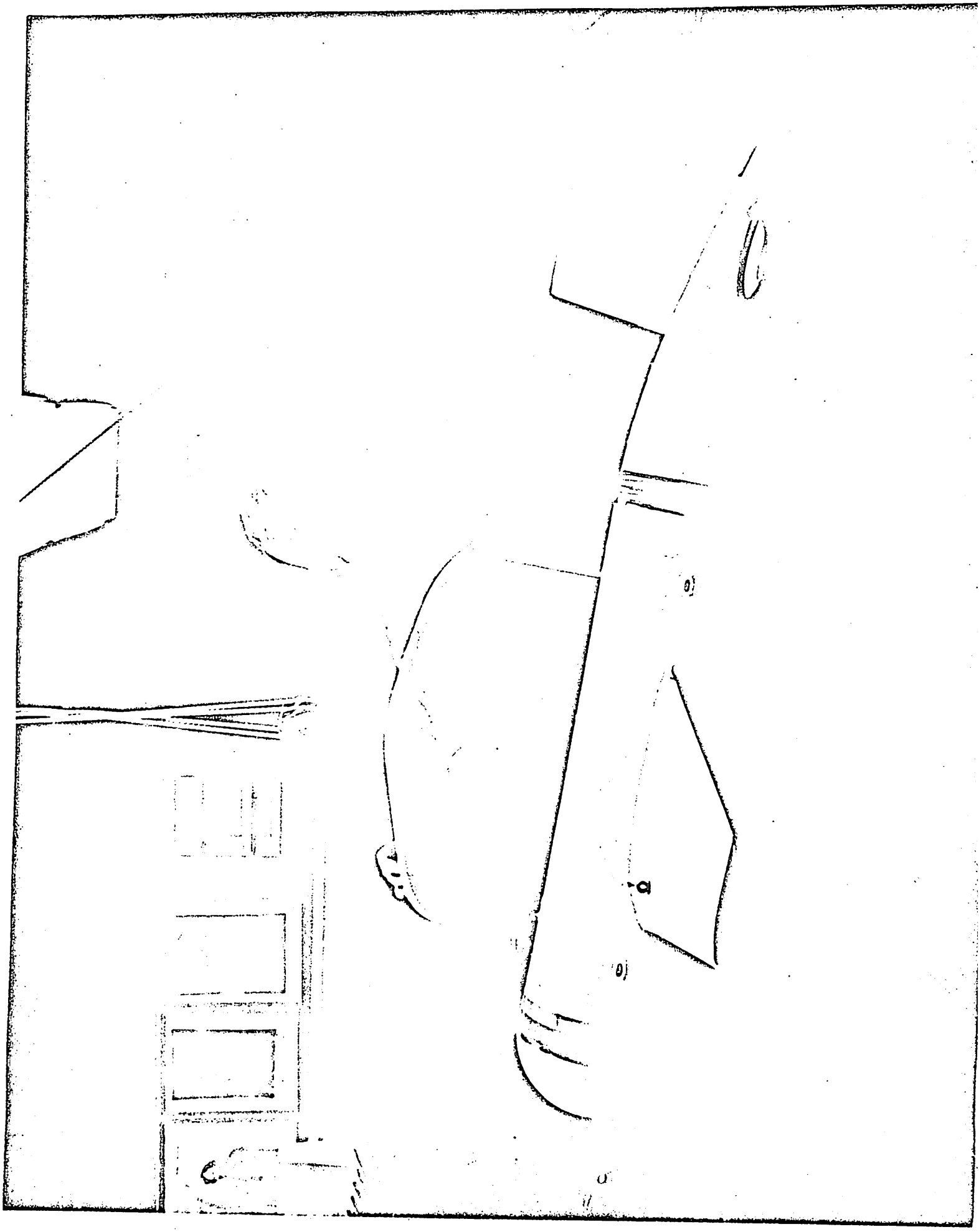


FIGURE THREE

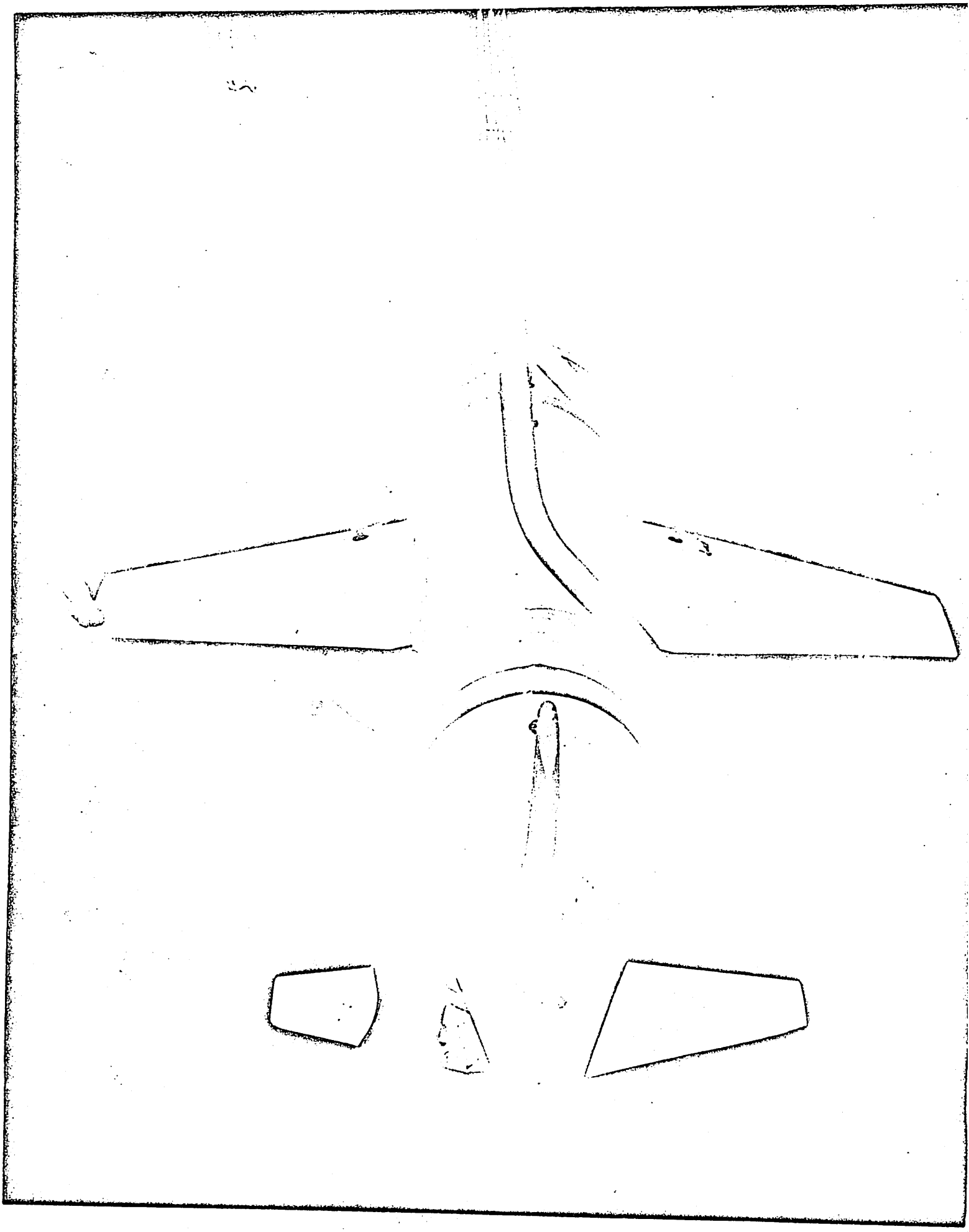
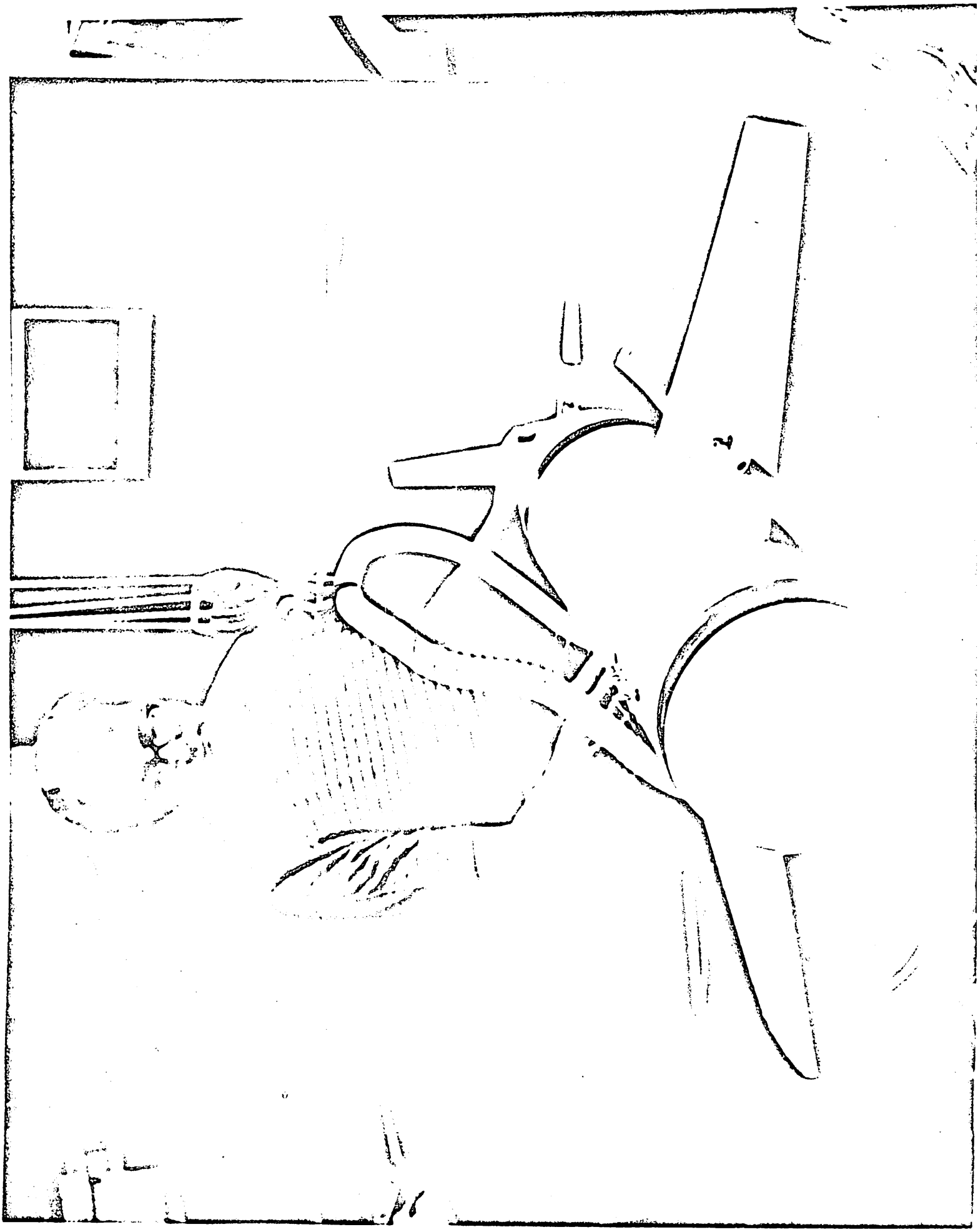


FIGURE FOUR



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APPENDIX A

Preliminary Electrochemical Study of Bacterial Sulfate Reduction in San Francisco Bay Sediments

Ugo - Conti

Abstract

San Francisco Bay mud was used in the laboratory to test the feasibility of in situ electrochemical measurements of pH and sulfide activity in marine sediments. Four experiments were made.

1) The early diagenesis of the mud from an oxidized to a reduced condition is marked by an increase in sulfide concentration and a decrease of pH. Temperature rise appears to decrease both $pS^{=}$ and pH.
2) If a reduced sediment is brought in contact with an excess of aerated water, a very rapid increase in pH and $pS^{=}$ is detected.
3) Aeration of overlaying water produces oxidation of reduced sediments only in a very thin layer at the mud-water interface. The reduction of the oxidized sediments is clearly shown in anaerobic conditions by the increase of sulfide concentration.
4) Measurements of $As^{=}$ in the vertical mud column show high $As^{=}$ in the black surface layer and in the organic rich bottom layer.

Preliminary Electrochemical Study of Bacterial Sulfate Reduction In San Francisco Bay Sediments

Introduction:

Purpose of this study is to check the feasibility of electrochemical measurements of ion activities in soft marine sediments. Sulfide and pH electrodes are used for measuring the early variation of $S^{=}$ and H^{+} ion activities caused in the sediment by the presence of large quantities of organic material.

In the natural environment, the major chemical changes with respect to pH^{+} and $pS^{=}$ take place in a narrow zone immediately below the sediment-water interface. (Berner, 1963). This is an equilibrium situation.

The limited time involved in the present study does not allow a comprehensive analysis of the problem. Thus, only the rapid changes involved in the beginning of anaerobic condition are taken into consideration.

Experimental Procedure

The sediment used for this experiment was surface mud from the San Francisco Bay. This mud contained a number of living organisms. Although an animal count was not made on this particular sample, an estimate can be made from available data on sediment samples taken in the general area. (Storrs and others, 1966).

In fact, it can be assumed that from 100 to 200 animals were

present in the sediment used in this study.

The exact location where the smaple was taken is 37°49'30"N and 121°20'40 W. At the depth of 5 meters.

The collecting of the sample and subsequent storing changed the original distribution of animals. In order to achieve a homogeneous distribution of organic material. The sample was thoroughly mixed before starting the experiment. Several animals were still alive and few of them succeeded in changing to a more suitable living position before dying.

About 2 liters of sediments were added to a glass container about 4 liters in capacity. One liter of estuarine water (salinity = 25°/oo) was added on top of the sediment. The glass container was covered with a plexiglass disk with holes for the insertion of the electrodes.

The measurement of pH and $Es^{=}$ (potential of the sulfide electrode) were made with a Wilde-Rodgers Electrochemical Meter (Wilde, Rodgers, 1970).

pH was measured with a glass electrode (Beckman #39610); the reference electrode was a saturated calomel electrode; the solution ground was a platinum electrode.

The calibrations of the pH and sulfide electrodes were not available at the time of this writing. In this paper only the electrodes voltages will be reported.

The temperature was measured with a laboratory made comp-

ensated thermistor with linear response.

The temperature, pH and $Es^{=}$ were recorded on a esterline angus chart recorder by scanning the electrodes and temperature probe at 10 seconds intervals with a digitec 10 points scanner.

The pH and sulfide electrodes were set very close to each other in order to minimize the influence of inhomogeneity on measurements and the system of the two electrodes could move vertically through the sediment.

A series of tests in different experimental conditions were made during a period of 10 days.

1) After the mud was stirred and had settled down for about two days without aeration of the overlaying water, it could be observed that several animals were still alive and there were no signs of anaerobic formations on the surface and in the mud in contact with the glass walls.

   At this point, 40 grams of lean ground fresh meat were injected at the bottom of the sediment.

   Then, the pH and sulfide electrodes were inserted in the mud above the organic deposit, 3cm. Below the mud-water interface. No oxygen was provided to the overlaying water.

   A recording of pH, $Es^{=}$ and temperature was then started and carried out for 60 hours. After about 16 hours, anaerobic activity started to be evident in the form of black spots around bits of organic material on the surface and inside the sediment.

By this time, no macroscopic life could be observed. The results of the recording are shown in Figure 1.

2) After experiment #1, an air supply was introduced in the water through the plexiglass cover.

In order to accomplish this, the pH, sulfide electrode assembly had to be removed from the former position.

It was later found that a pit had formed around the electrodes and oxygenated water was coming in contact with anaerobic sediments at the tip of the electrodes.

pH and sulfide were recorded for a period of 90 minutes with continuous aeration of the overlaying water.

The results of this test are shown in Figure 2.

3) The sediment was carefully mixed, the electrode assembly inserted 3cm below the mud-water interface and the glass container vibrated to avoid formation of a pit around the electrodes.

It was observed that the meat particles were more homogeneously distributed, although a higher concentration was left at the bottom of the container.

Some of the particles came to the surface of the mud. They were generally of a gray color and the mud attached to them was black.

The water was thoroughly aerated by bubbling air through a porous stone.

Within a few hours, the black mud present at the surface of the sediment changed color toward green and brownish.

The aeration was stopped after 16 hours from the start.

The pH and $Es^{=}$ were recorded for a period of 44 hours, the results are shown in Figure 3.

4). Three days after the end of experiment #3, a solid layer of black mud was found on top of the sediment. The average thickness of this layer was about 1cm.

It was assumed that the bottom of the glass container was still enriched in organic material.

The electrode assembly was inserted carefully in the mud and readings of pH and sulfide were taken at discrete depths. The results are shown in Figure 4.

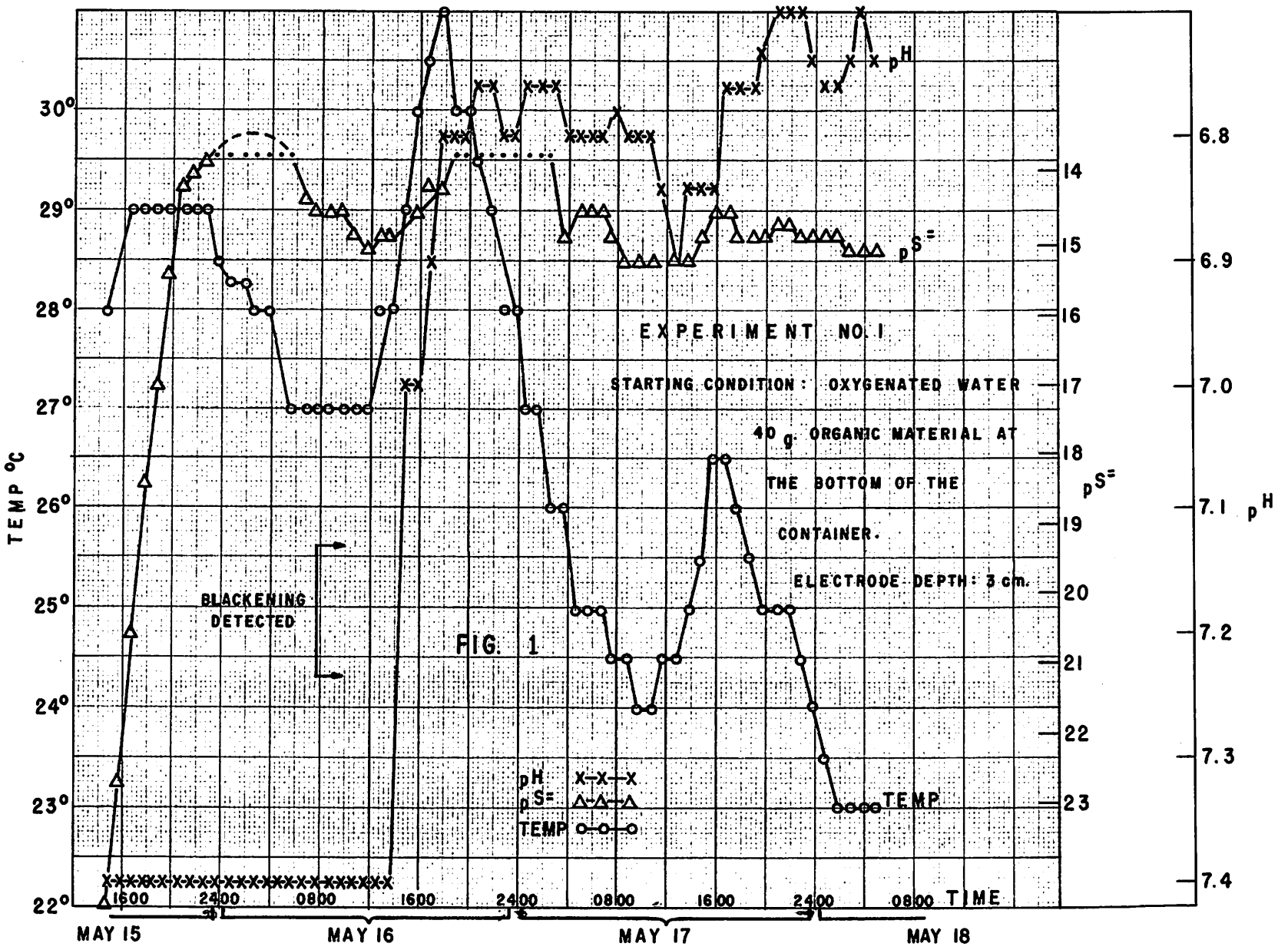

EXPERIMENT NO. I
STARTING CONDITION: OXYGENATED WATER
40 g. ORGANIC MATERIAL AT
THE BOTTOM OF THE
CONTAINER.
ELECTRODE DEPTH: 3 cm.
BLACKENING
DETECTED
pH X—X—X
pS= △—△—△
TEMP o—o—o
TEMP °C
30°
29°
28°
27°
26°
25°
24°
23°
22°
pS=
14
15
16
17
18
19
20
21
22
23
pH
6.8
6.9
7.0
7.1
7.2
7.3
7.4
TEMP
1600
2400
0800
1600
2400
0800
1600
2400
0800
TIME
MAY 15
MAY 16
MAY 17
MAY 18

FIG. 1

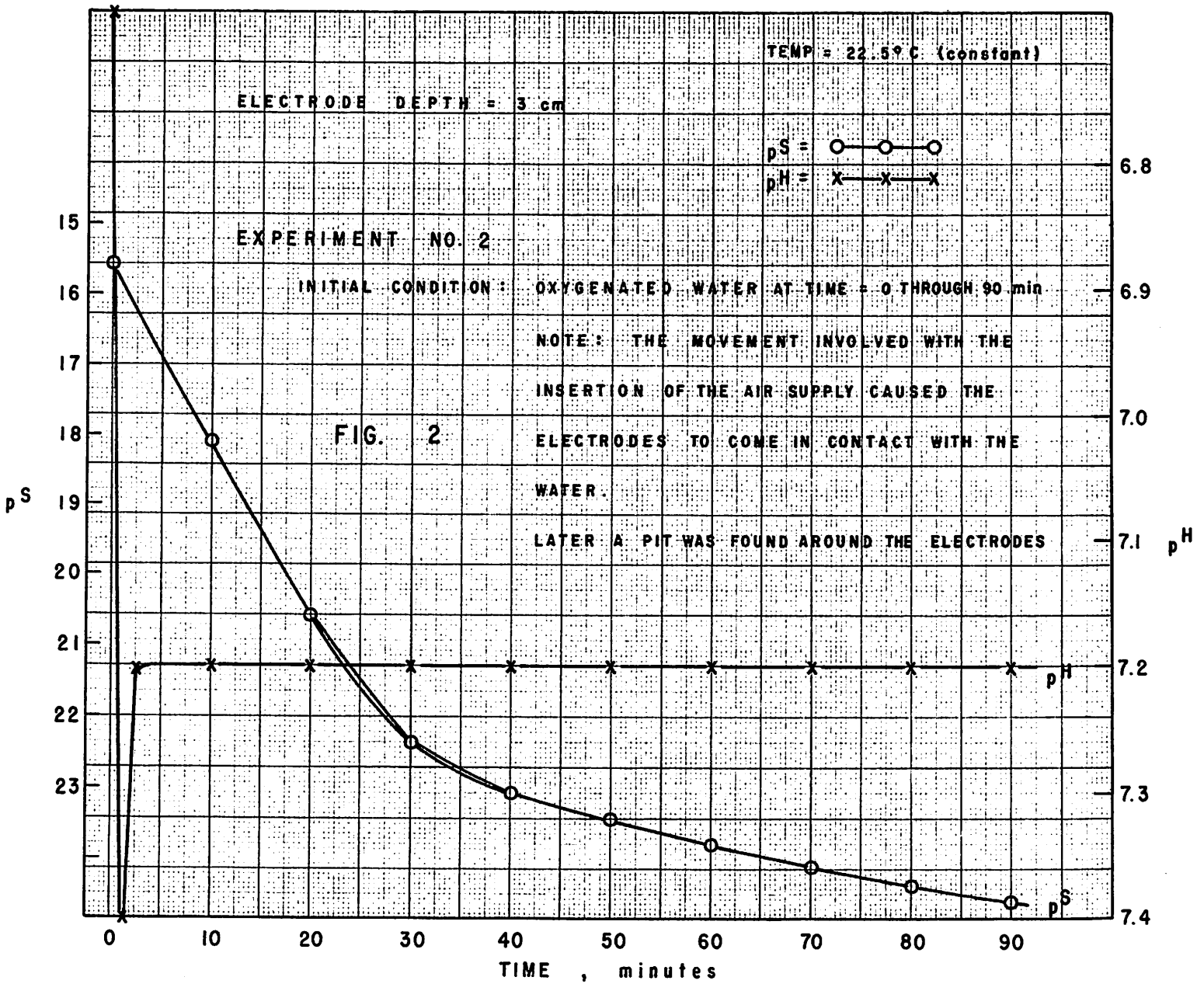
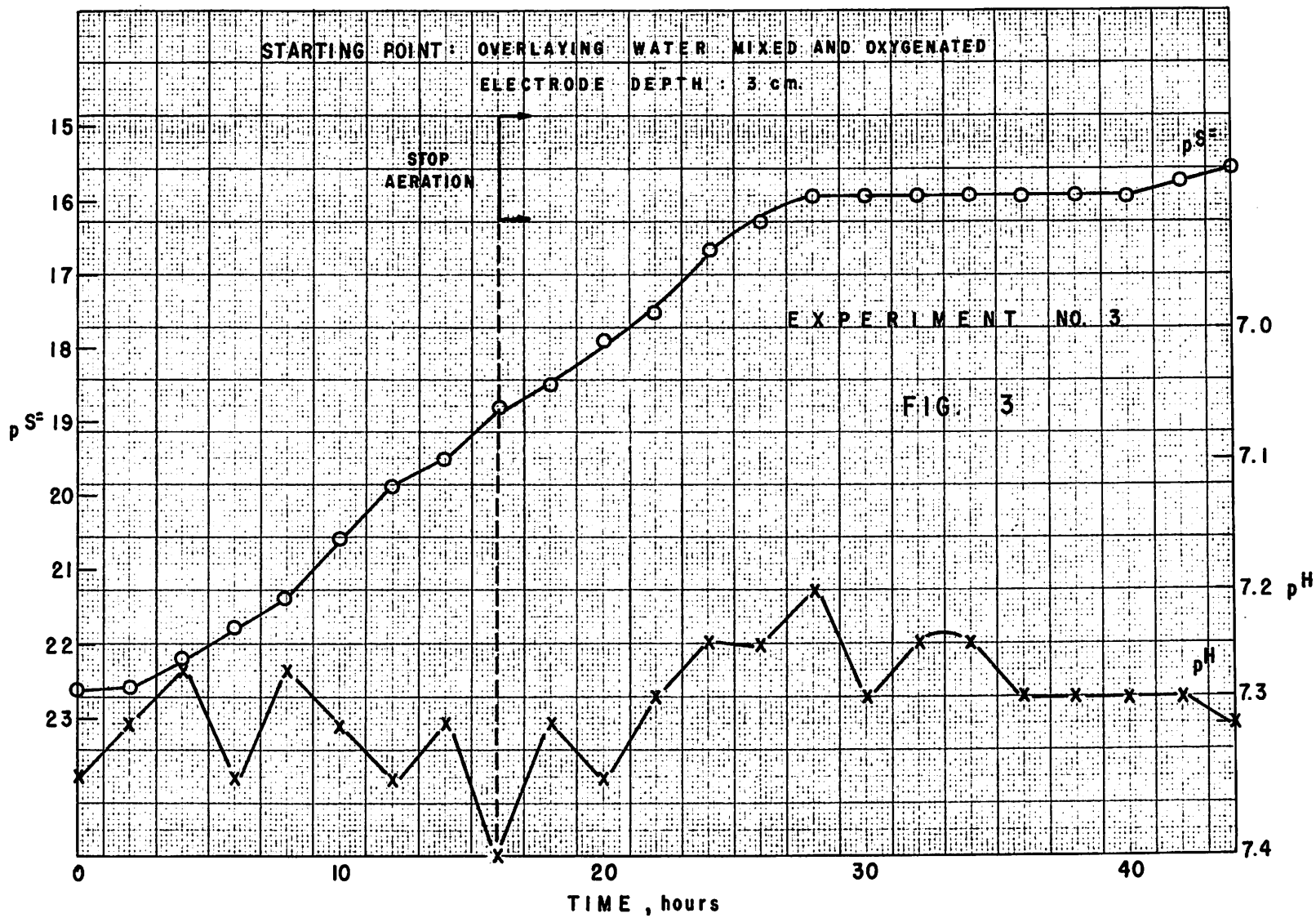

TEMP = 22.5° C (constant)
ELECTRODE DEPTH = 3 cm
pS = O—O—O
pH = X—X—X
EXPERIMENT NO. 2
INITIAL CONDITION: OXYGENATED WATER AT TIME = 0 THROUGH 90 min
NOTE: THE MOVEMENT INVOLVED WITH THE INSERTION OF THE AIR SUPPLY CAUSED THE ELECTRODES TO COME IN CONTACT WITH THE WATER.
LATER A PIT WAS FOUND AROUND THE ELECTRODES
pS
15
16
17
18
19
20
21
22
23
pH
6.8
6.9
7.0
7.1
7.2
7.3
7.4
pH
pS
0
10
20
30
40
50
60
70
80
90
TIME , minutes

FIG. 2


STARTING POINT: OVERLAYING WATER MIXED AND OXYGENATED
ELECTRODE DEPTH: 3 cm.
STOP AERATION
EXPERIMENT NO. 3
FIG. 3
p S=
p H
TIME, hours
15
16
17
18
19
20
21
22
23
7.0
7.1
7.2
7.3
7.4
0
10
20
30
40

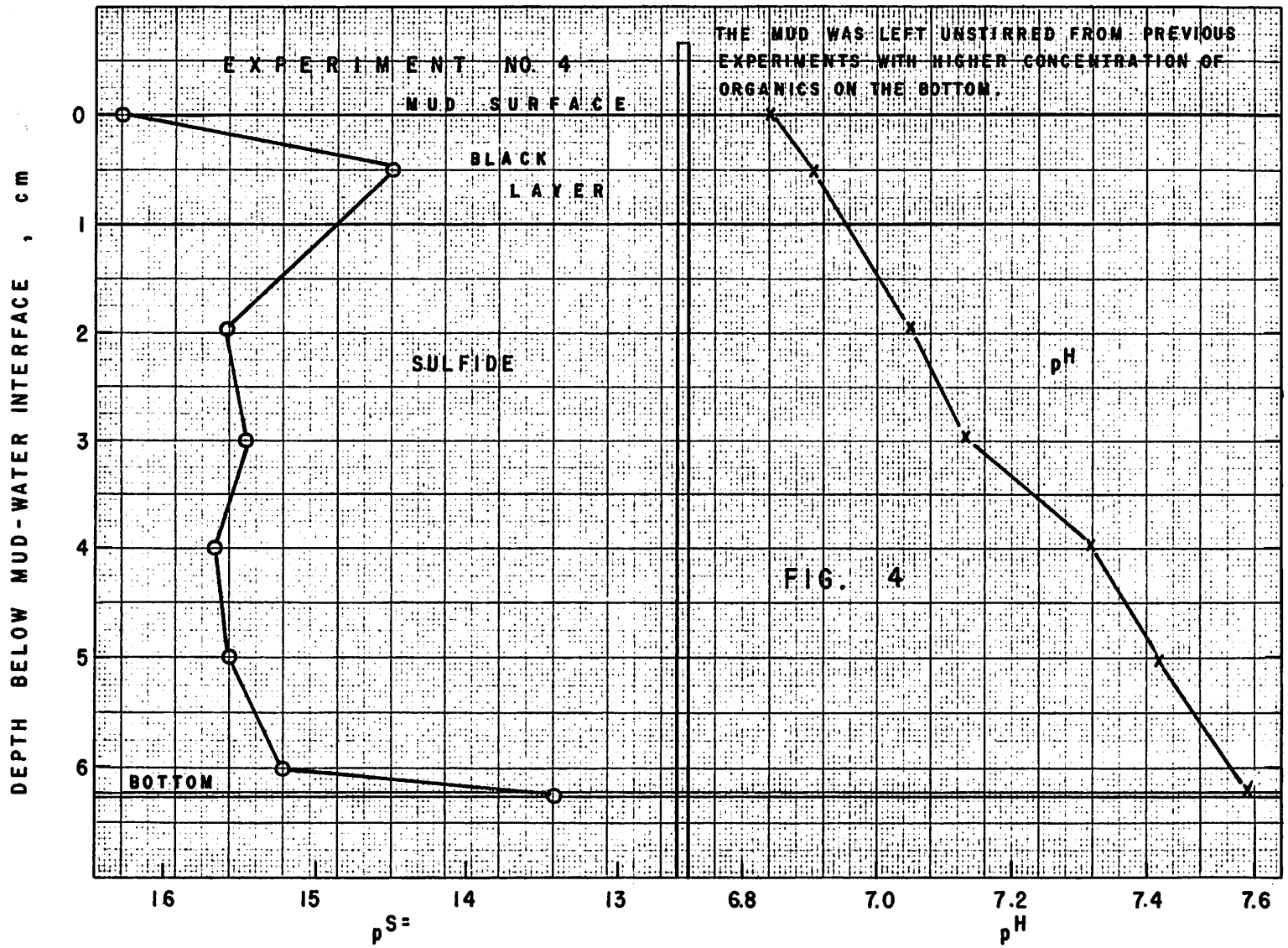

EXPERIMENT NO. 4
MUD SURFACE
BLACK LAYER
SULFIDE
BOTTOM
THE MUD WAS LEFT UNSTIRRED FROM PREVIOUS EXPERIMENTS WITH HIGHER CONCENTRATION OF ORGANICS ON THE BOTTOM.
pH
DEPTH BELOW MUD-WATER INTERFACE , cm
0
1
2
3
4
5
6
16
15
14
13
6.8
7.0
7.2
7.4
7.6
pS=
pH

FIG. 4