SEA LAB

New Bedford Public Schools
New Bedford, Massachusetts

Analysis Of The Water Properties Extending From The Acushnet River At The Coggeshall Street Bridge To The Outer New Bedford Harbor

Summer, 1980

NEW BEDFORD PUBLIC SCHOOLS

OCEANOGRAPHIC EDUCATIONAL CENTER

SEA LAB

ANALYSIS OF THE WATER PROPERTIES EXTENDING FROM THE ACUSHNET RIVER AT THE COGGESHALL STREET BRIDGE TO THE OUTER NEW BEDFORD HARBOR

SUMMER 1980

ANALYSIS OF THE WATER PROPERTIES EXTENDING FROM THE ACUSHNET RIVER AT THE COGGESHALL STREET BRIDGE TO THE OUTER NEW BEDFORD HARBOR

STUDENTS

Keith Ainsworth
Jesse Bastos
Thomas Gardner
Patricia Gifford
Aubrey Hazner
Christopher Mello
Kevin Mello
Christopher Norton
Nicole Picard
Brian Richard
Deborah Sheehan
John Ventura
Nancy Walsh
Christopher Wolkowicz

INSTRUCTORS

Howard Smith
Ronald Souza

AUGUST, 1980

Class of 1980

ACKNOWLEDGEMENTS

We at Sea Lab wish to acknowledge the following for their support in making this project possible:

New Bedford School Committee for funding the program.

Arthur Dutra, Sea Lab Director, for his support and encouragement.

Sea Lab Keel, Inc, the parent-teacher organization, for its fund raising efforts.

Massachusetts Institute of Technology, Sea Grant Program Staff.

Crew of the R/V Edgerton.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

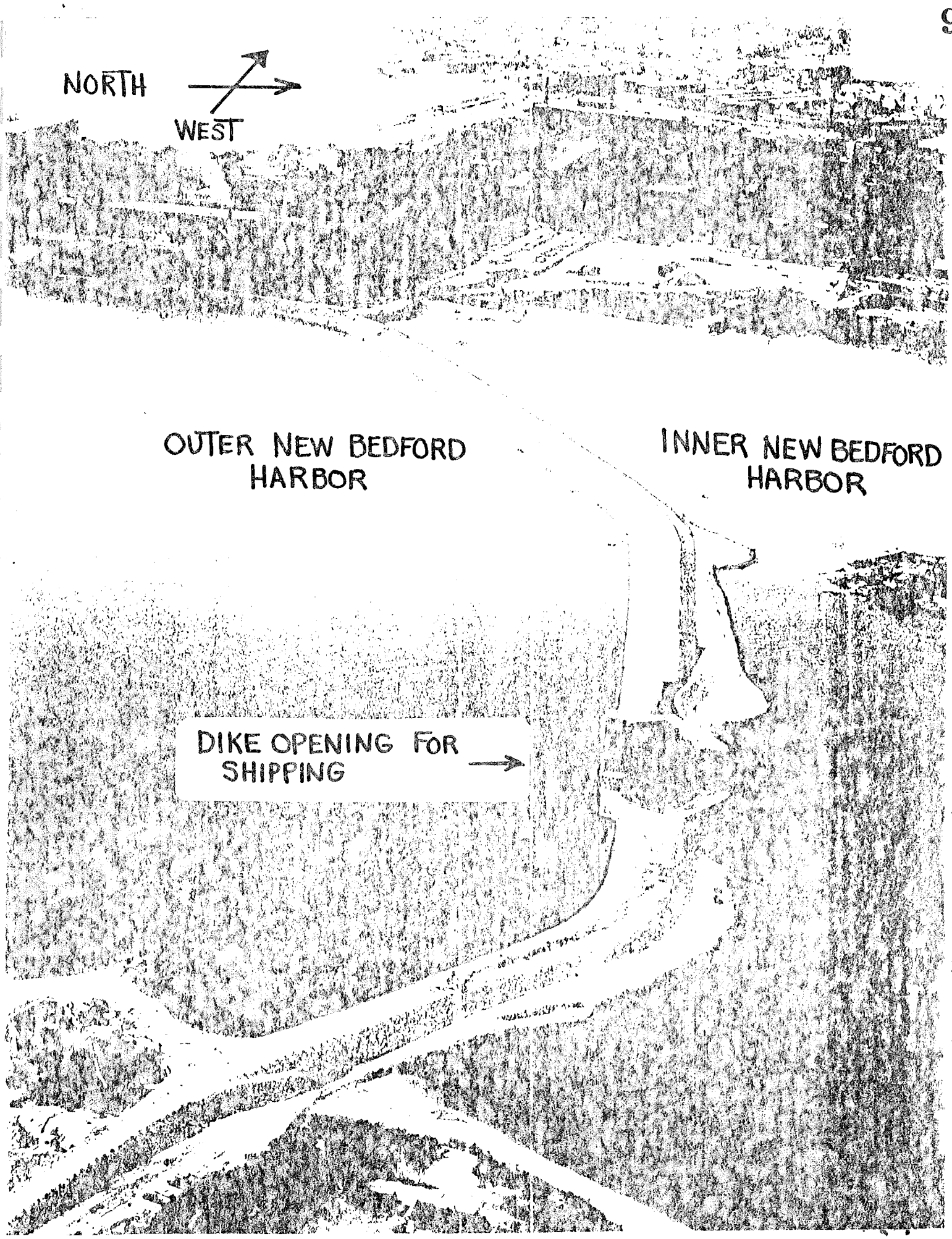
INTRODUCTION

Each summer, the ninth grade class at Sea Lab in New Bedford, involves itself in a project analyzing the local waters surrounding Fort Rodman, New Bedford, Massachusetts. The 1979 project involved itself with analyzing the waters composing what is known as New Bedford's outer harbor. The outer harbor extends outward from the hurricane dike in a southerly direction as shown in Figure 1. The intent of the 1979 report was to show that the inner and outer harbor could be differentiated from each other and thus constitute two distinct bodies of water. The hypothesis of two bodies of water was confirmed and can be seen quite clearly when the graph depicting the water's density vs. horizontal distance from the dike is examined. (See Figure 2) Rather than replicate the 1979 project study, it was established that a study of the inner harbor and a limited portion of the outer harbor should be the undertaking of the 1980 ninth grade project. The establishment of hydrographic stations ranging from the inner harbor, through the dike opening, to the outer harbor would establish a complete picture of how the hurricane dike acts in maintaining two distinct bodies of water.

New Bedford harbor, which borders Fort Rodman on the easterly side, is divided into two sections; an inner harbor and an outer harbor. A hurricane dike was built in 1965 to offer protection to the southern end of New Bedford from high tides and wave destruction during severe storms. (See Figure 1) Entrance into New Bedford's inner harbor from Buzzard's Bay is accomplished by means of a deep water channel which cuts through the dike at its only opening. A movable set of doors is provided at this location so that the inner and outer harbor can be sealed off from each other. (See Figure 3) The inner harbor can be thought of as a semi-closed body of water with one opening to the outer harbor and Buzzards Bay at is southern end and fresh water from the Acushnet River entering at its northern end. Industry and fishing piers surround the inner harbor. The outer harbor discharges into Buzzard's Bay and is bordered on its westerly side by various light industries. The interaction of the two water masses, inner and outer harbor water, will be the basis of this year's study.

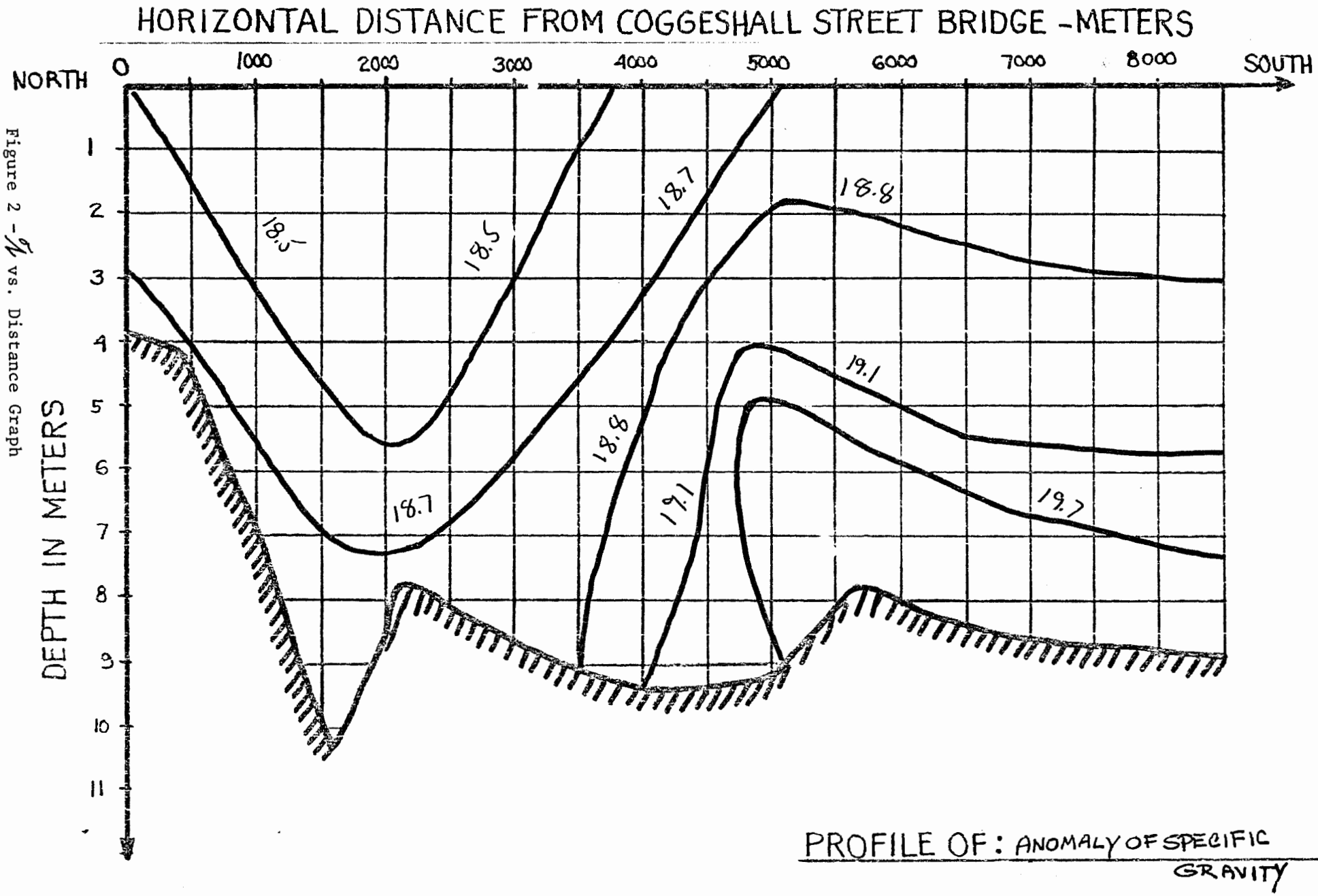
Tabulated data depicting water properties in a water column at various horizontal station locations is indispensable to oceanographers. Profiling is a method of presenting data which an oceanographer can use to illustrate regions in a body of water which have identical values of a particular variable which is being studied, that is, salinity, temperature, etc. At a given station, one locates a specific value for the variable being studied in the vertical water column. The value of the variable may be an actually measured value or one interpolated from the known data. The process is repeated for the variable under study at the next horizontal station location and a point or points in this water column having the same value as found at the previous station identified. One then connects these points of equal value for the quantity being studied with a smooth curve. When this process is extended for all the stations in the study, one has a curve showing regions of constant value of the variable being studied for the vertical section of water under examination. In a similar fashion, lines for other constant values of the variable can be constructed.

The shape of these contour lines, lines of constant variable value, provide a powerful interpretive tool for the oceanographer. For instance, if the lines are close together, the variable changes abruptly as one goes from one point in a water column to another point in the same water column. The greatest changes in the variable occur when one moves in a direction perpendicular to the contour lines. Conversely, if the contour lines are widely separated, the variable changes gradually within a given water column and movements parallel to the contour lines produce no changes in the variable being studied. The shape of the line aids in defining a given body of water or the interaction of differing bodies of water such as found in a costal estuary. Chemical and biological processes operating in the study area can also be identified.



Courtesy of Milton Silva, Standard-Times

Figure 1 - Aerial Photo Of New Bedford's Inner and Outer Harbor



PROFILE OF: ANOMALY OF SPECIFIC GRAVITY

Figure 2 - η vs. Distance Graph

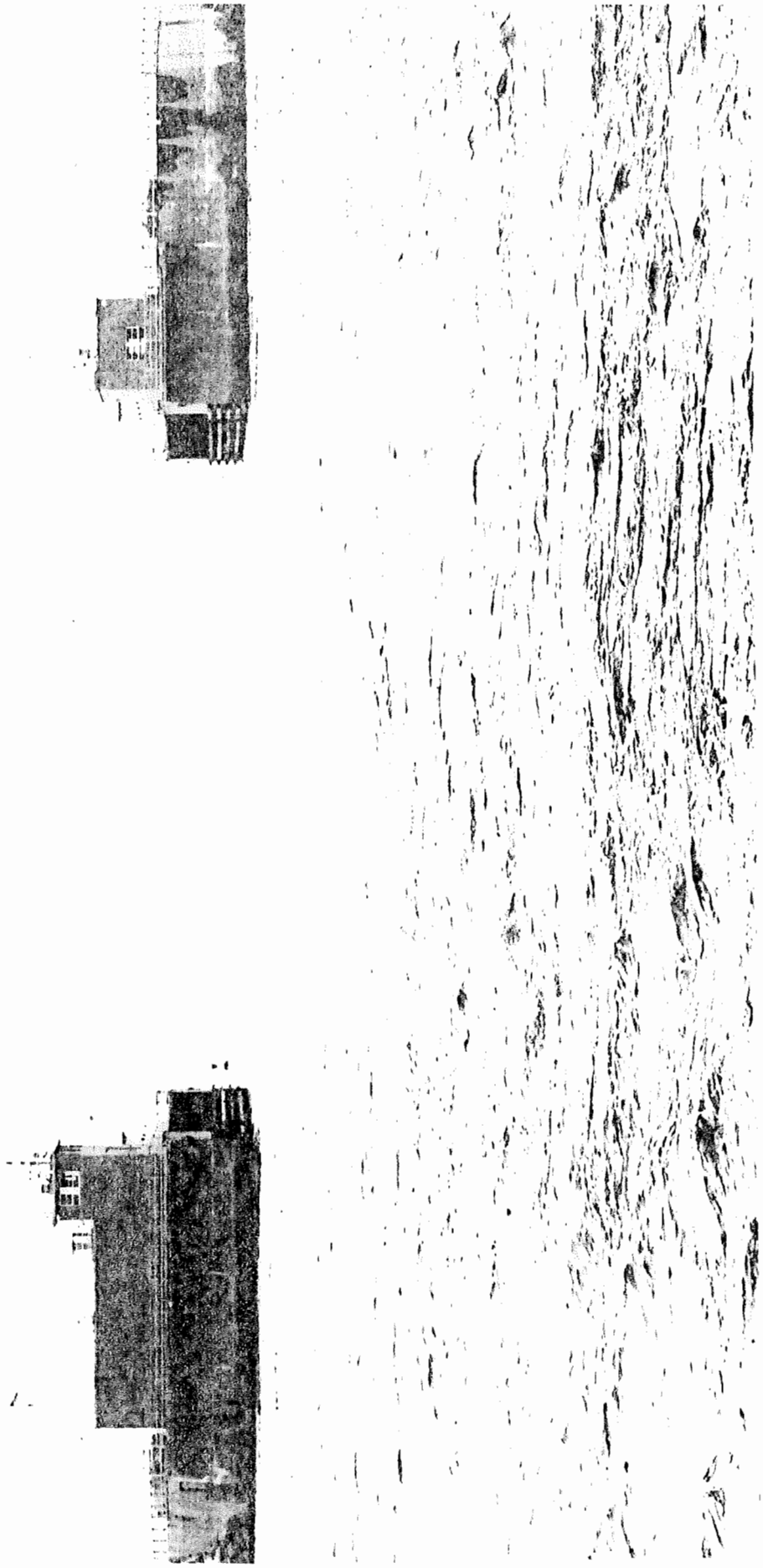


Figure 3 - Movable Set of Doors Separating Inner and Outer Harbor

INSTRUMENTATION

Bausch & Lomb Spectronic 20
Bausch & Lomb Analytical Systems Division, Rochester, NY

Thermometer - Temperature -20°C to 260°C

pH Paper - Range 0-14

Modified LaMotte Sampling Bottle

Slow Fill Collection Bottle
Sea Lab Oceanographic School, New Bedford, MA

Sand Piper Digital Depth Sounder

YSI Model 33 SCT Meter (Salinity, Conductivity and Temperature)
Yellow Springs Instrument Company, Inc., Yellow Springs, OH

YSI Model S1-B Oxygen Meter
Yellow Springs Instrument Company, Inc., Yellow Springs, OH

Corning Model S pH Meter
Corning Scientific Instruments, Medford, MA

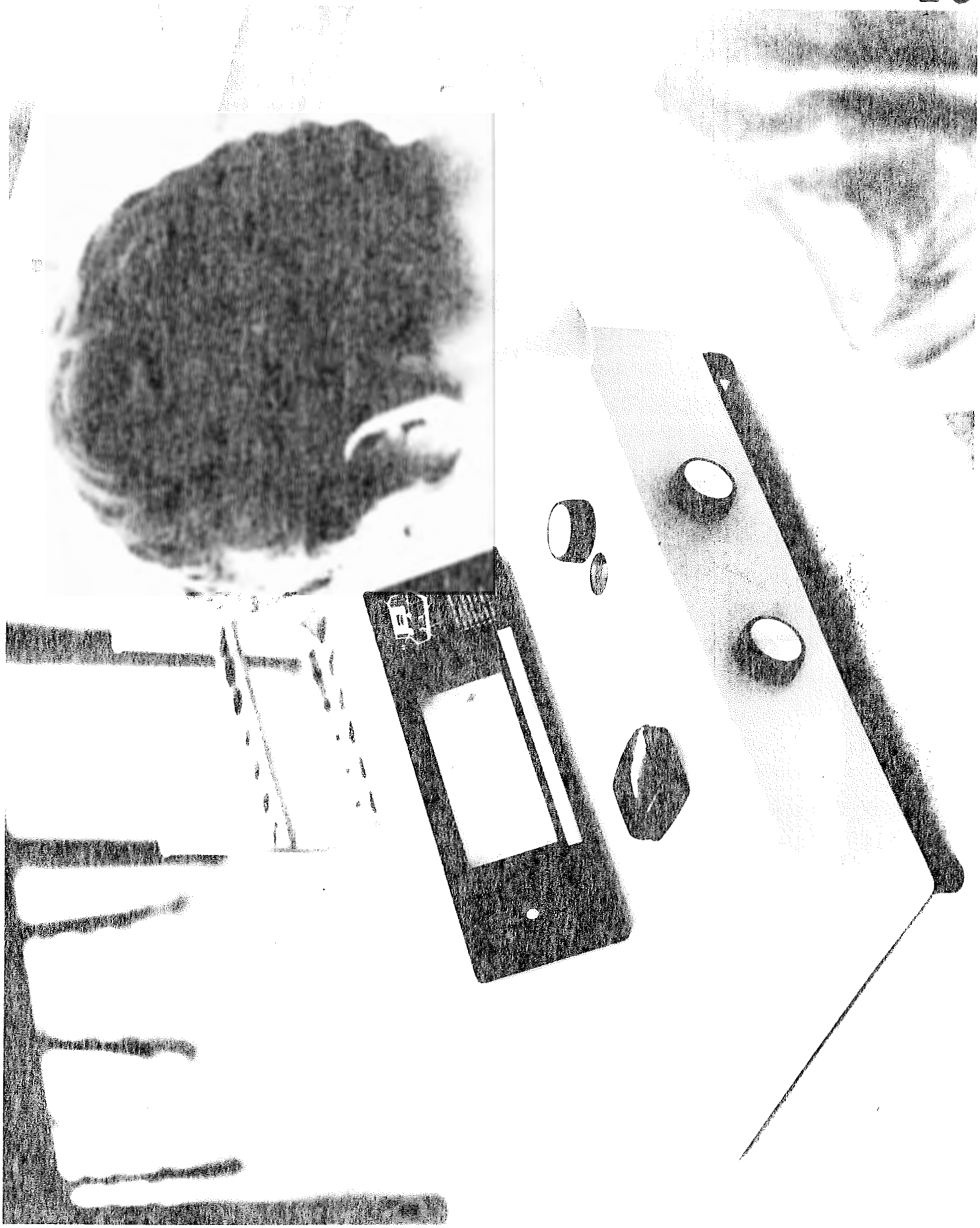


Figure 4 - Bausch & Lomb Spectronic 20

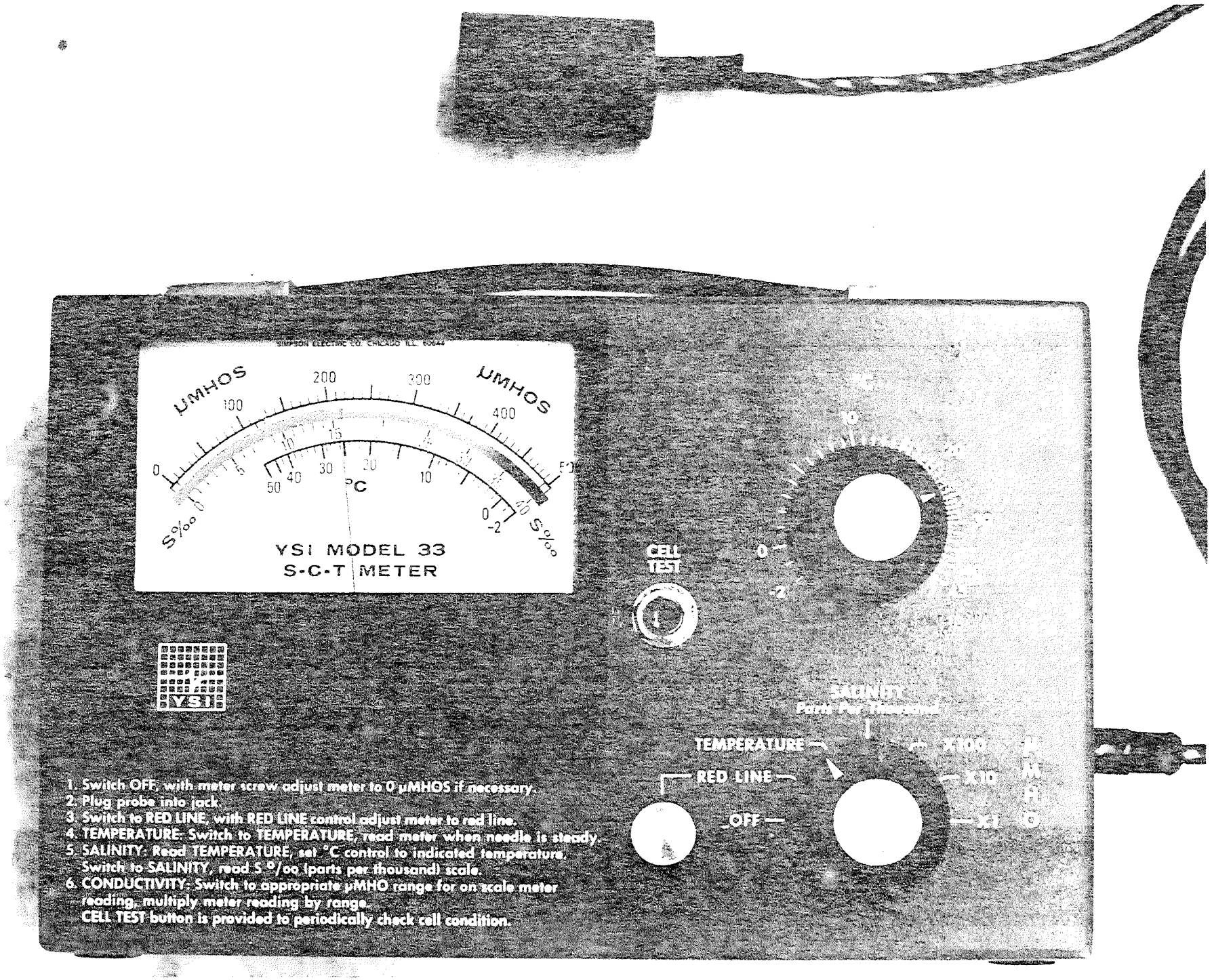


Figure 5 - YSI Salinometer

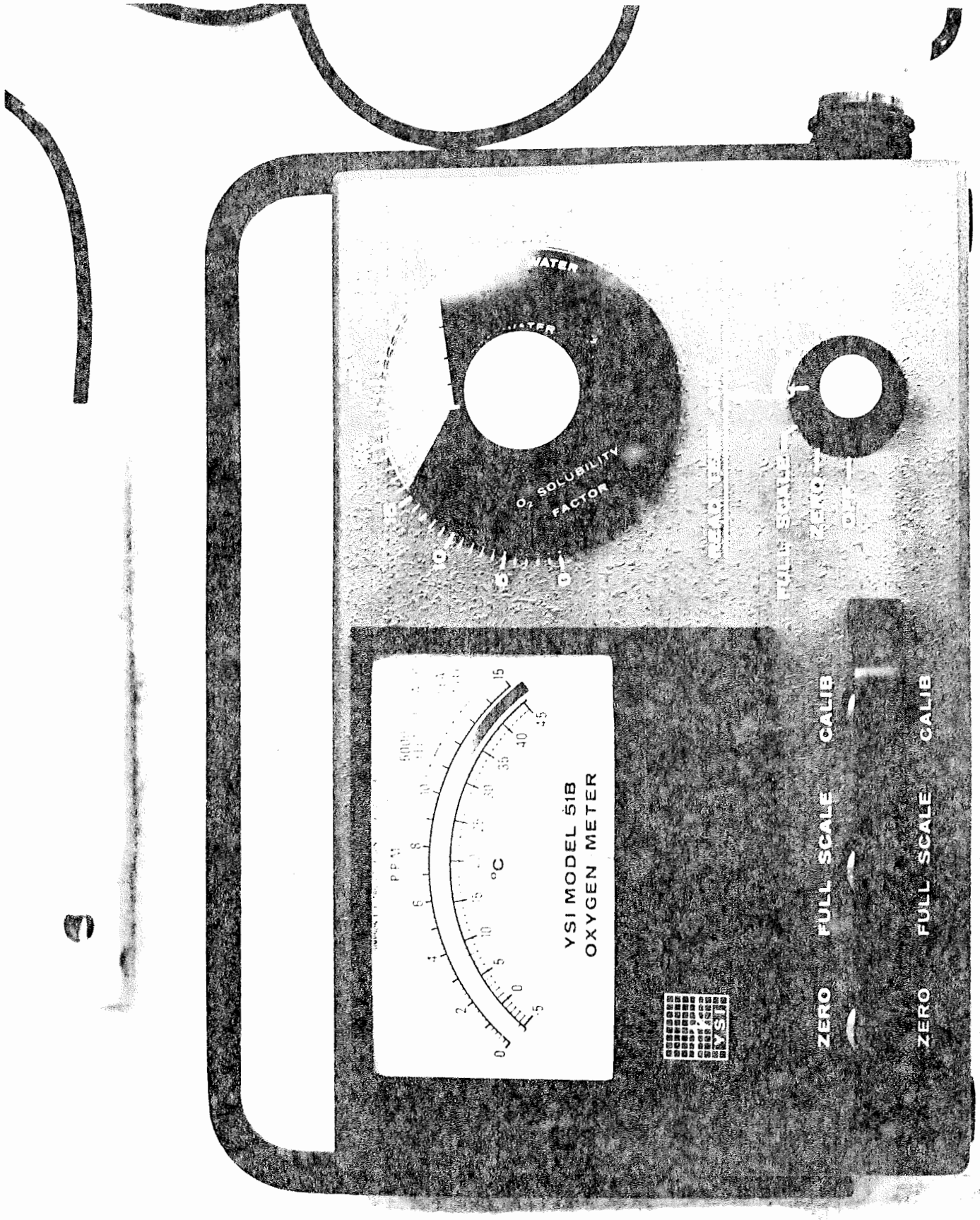


Figure 6 - YSI Dissolved Oxygen Meter

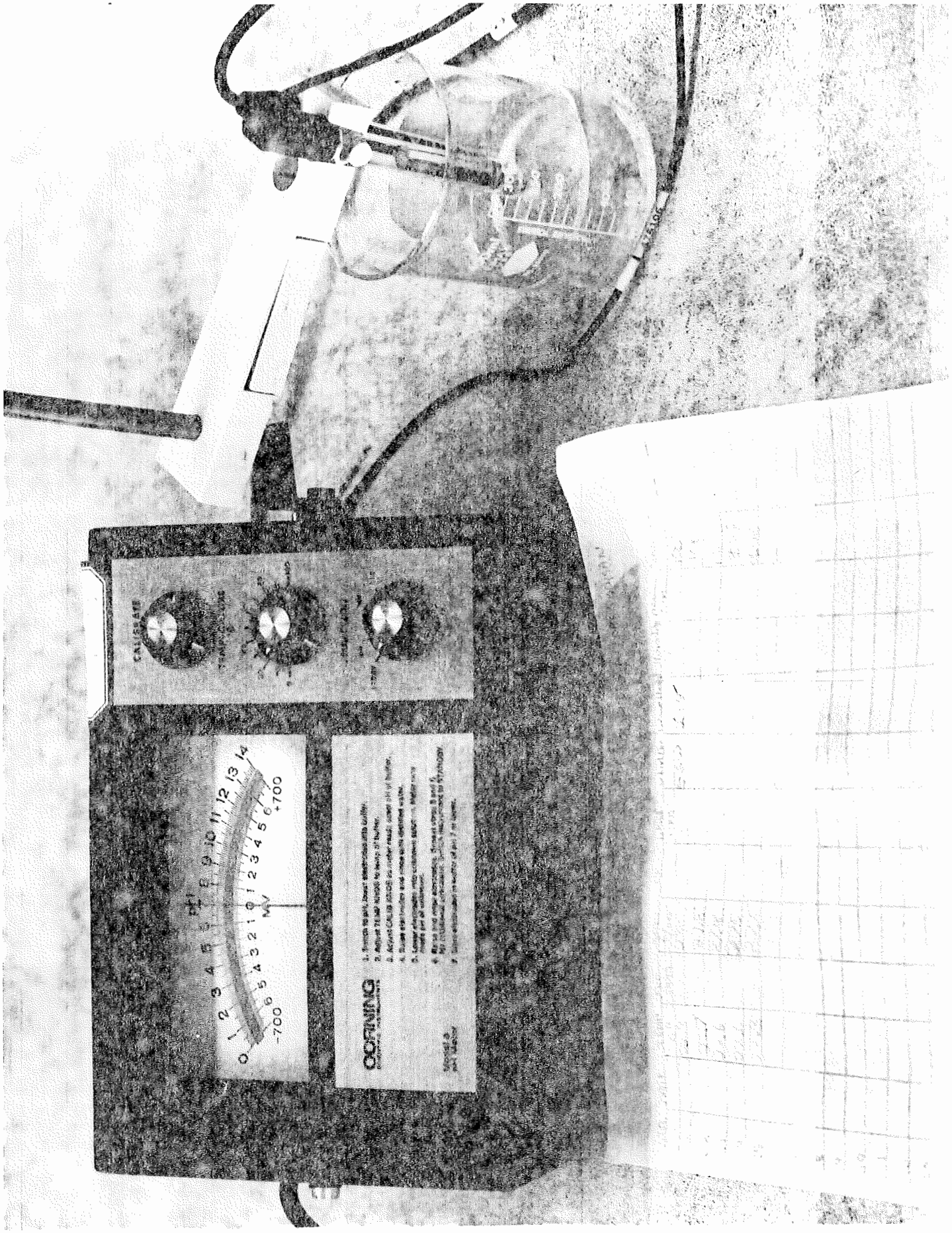


Figure 7 - Corning pH Meter

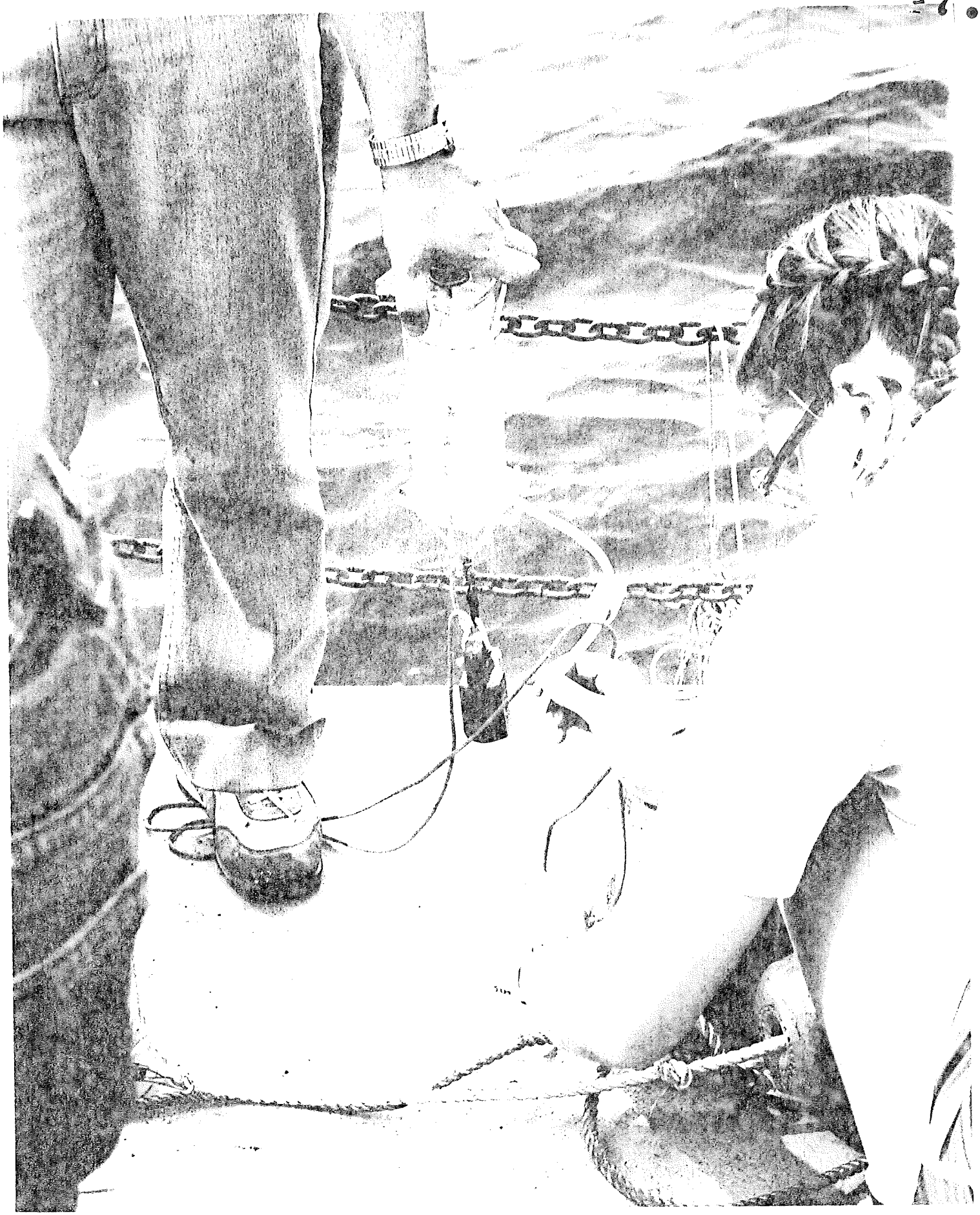


Figure 8 - Modified LaMotte Sampling Bottle

Figure 9 - Sea Lab Constructed Sampling Bottle

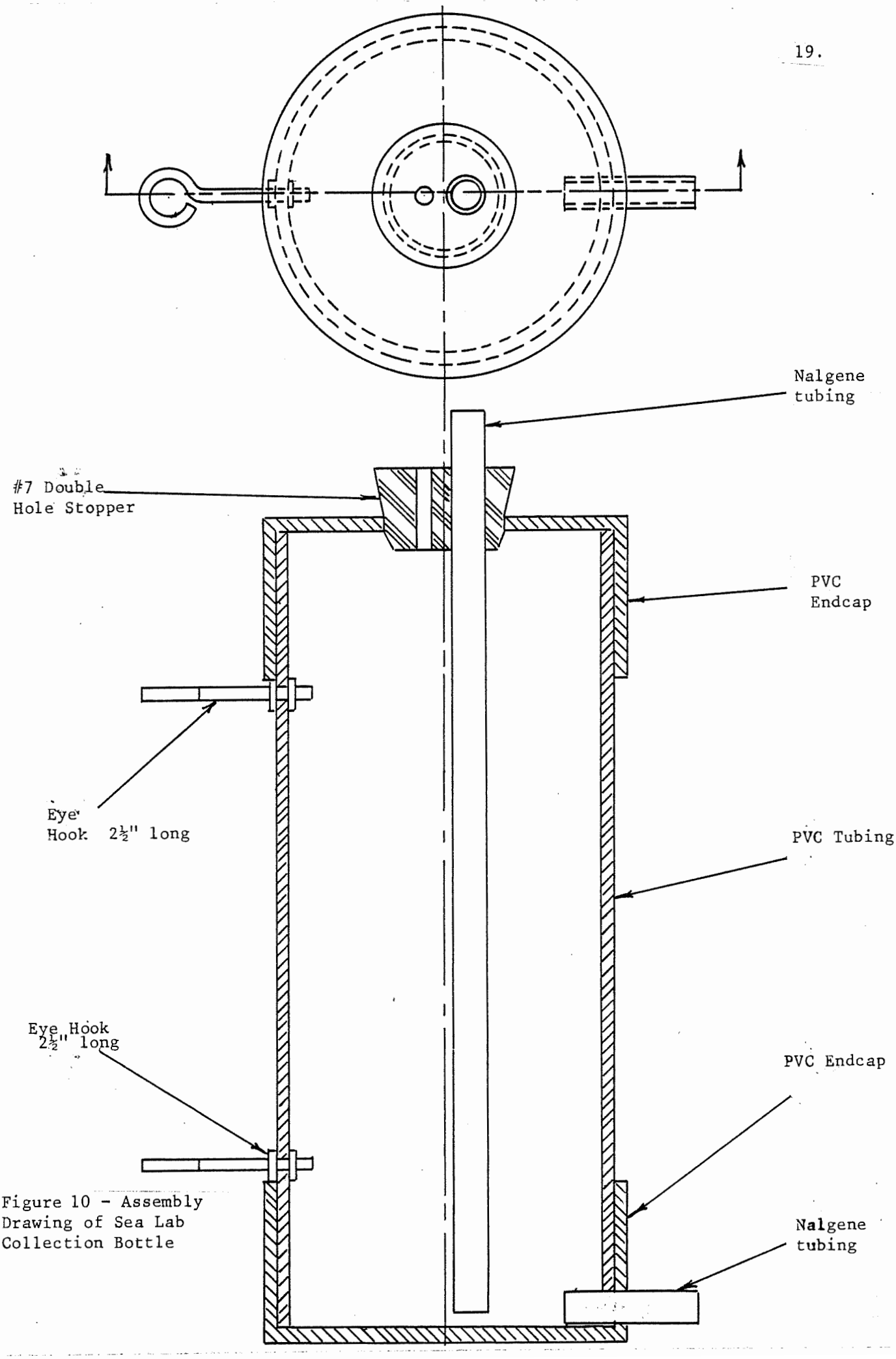


Figure 10 - Assembly Drawing of Sea Lab Collection Bottle

PROCEDURES

Dissolved Oxygen:	Winkler Method, by titration with Sodium Thiosulfate Standard Methods - 12th Edition, p. 4
Nitrate:	Brucine Method using Bausch & Lomb Spectronic 20 Spectrophotometer Standard Methods - 12th Edition, p. 405
pH:	pH Paper
Phosphates:	Ascorbic Acid Method using Bausch & Lomb Spectronic 20 Spectrophotometer
Salinity:	Mohr Titration
Temperature:	Thermometer with a range of 20°C to 260°C

Standard Method For The Examination Of Water, Sewage And Industrial Waste, 12th Edition, American Public Health Association, Baltimore, MD

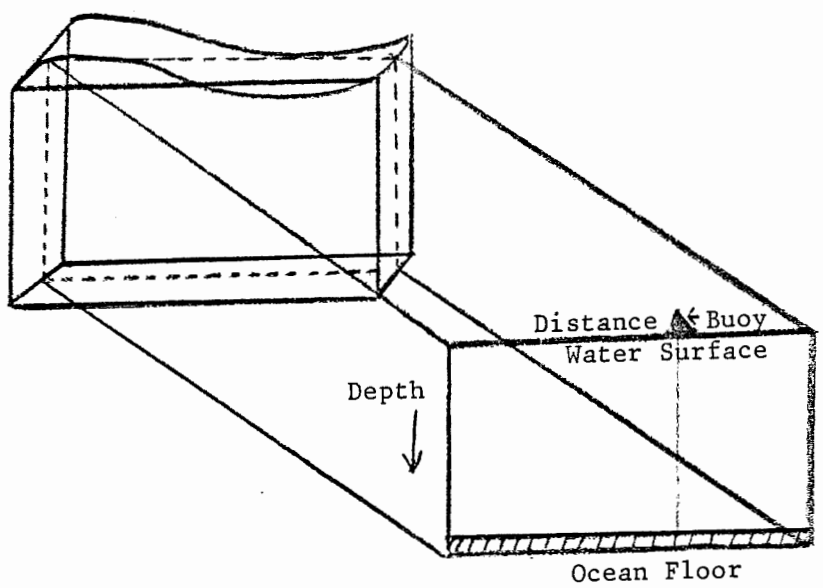
ORDER AND LOCATION OF STATIONS

During the summer of 1979, a series of hydrographic stations was chosen so that these exact locations could be located in the future. Since the buoys in the harbor provided this permanency, a series of nine stations was chosen extending from the New Bedford Hurricane Dike, southward, using the buoys as markers. In the summer of 1980, a similar study was conducted. Eight hydrographic stations were chosen; four stations in the outer harbor and four stations in the inner harbor. (See Figure 11) Again, buoys provided permanent markings. These buoys can be easily identified using navigational charts. Although these buoys are not equidistant from one another, they do provide a reasonable north-south horizontal course at relative distances apart.

These eight stations were so chosen to provide information regarding the intrusion of the Acushnet River into the inner and outer New Bedford harbors. The New Bedford Hurricane Dike virtually separates the inner and outer harbors, except for the area in which the movable doors operate.

At each hydrographic station, a digital depth sounder was used to measure depth. These readings were used to draw the topography of the inner and outer harbors. Using these readings of depth along with the horizontal distances, vertical profiles were constructed. (See Figure 12) These profiles were then used to graph different water properties. (D.O., salinity, temperature, etc.)

These profiles illustrate the cross section of the inner and outer harbors. This is similar to taking a volume of water and observing it laterally, as one does when observing a fish tank. (See figure below)



If a comparison of researched data is desired in the future, a comprehensive study can easily be conducted. This report provides concise information on station location that could be replicated exactly and at any desirable time.

New Bedford Harbor Channel

Phosphate-Nitrate Surface Samples

0 0.2 0.4 0.6 p.p.m.

1 cm. = .2 part per million

Map Scale:

0 1000 2000

1 inch = 1000 yds.

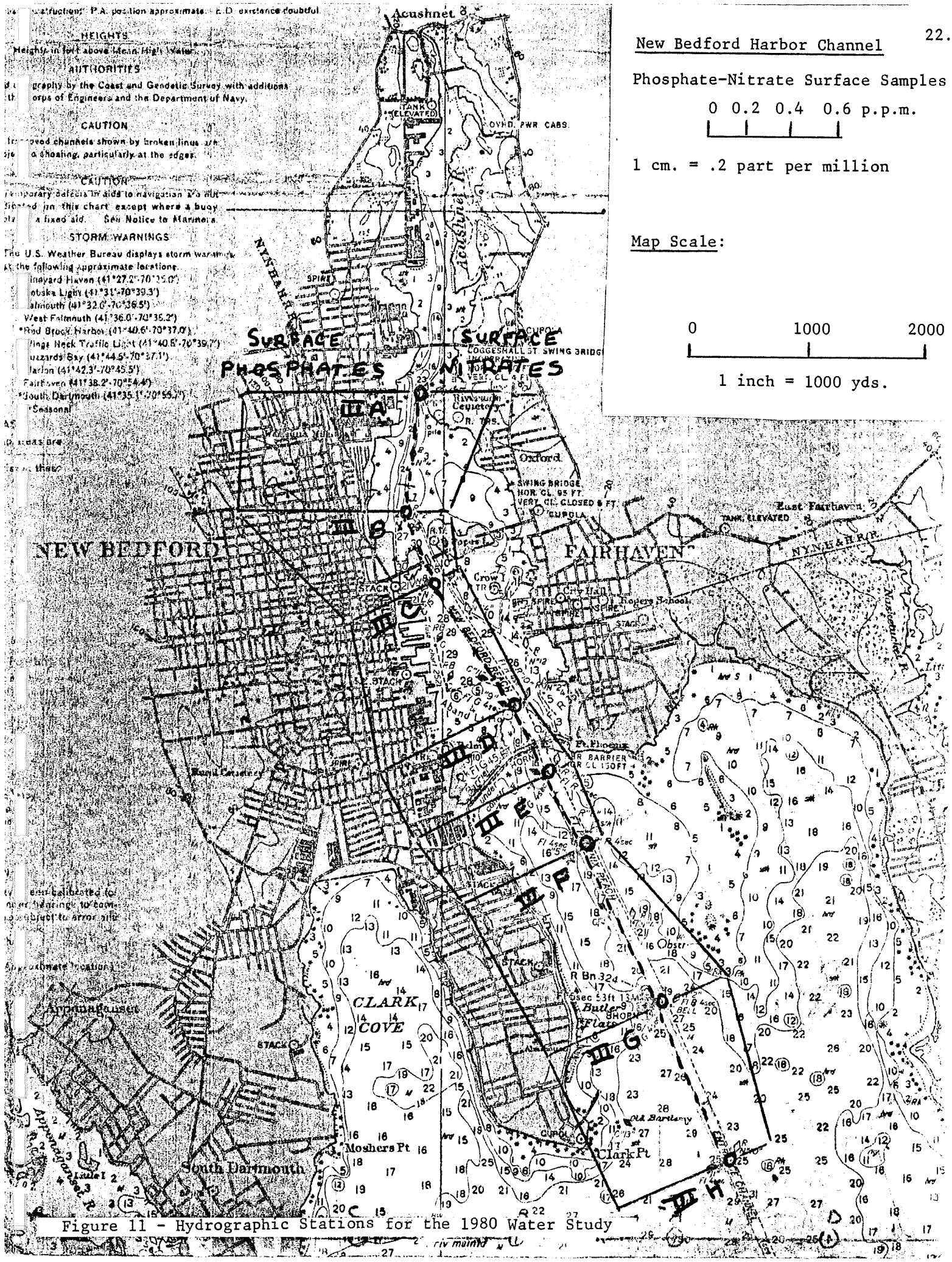


Figure 11 - Hydrographic Stations for the 1980 Water Study

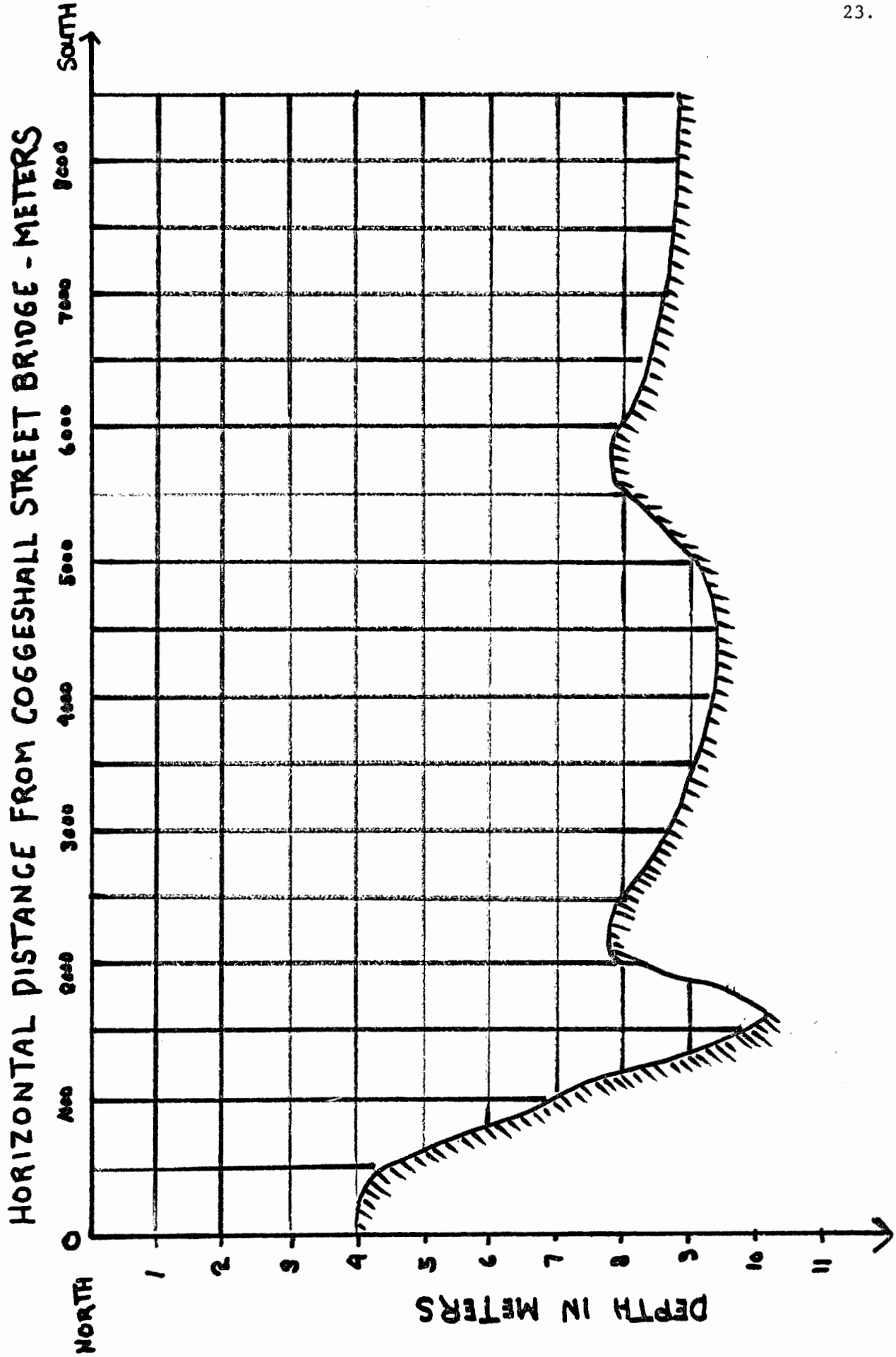


Figure 12 - Vertical Profile of Hydrographic Stations

from the collection bottle must be immersed into the water contained in the BOD bottle so the sample would not be altered when the water is transfered. The BOD bottles were allowed to overflow in order to assure that there would be no air in the bottles. Stoppers were then placed in the BOD bottles and they were brought back to the vessel's laboratory where the titration took place. (See Figure 20) Like the Mohr Method, the D.O. titration (Winkler Method) is a direct titration, except sodium thiosulfate is used in place of silver nitrate. Once the titration was complete, the number of ml of sodium thiosulfate used was recorded. This was a direct reading in p.p.m. of dissolved oxygen. For example, if the water sample required 6.8 ml of sodium thiosulfate to complete the titration, then the sample contained 6.8 p.p.m. of dissolved oxygen.

The pH of the collected water samples was measured by using pH paper. This is a colorimetric determination. Approximately 25 ml of water was drawn from each collection bottle and put into a test tube. (See Figure 21) The pH paper was put into the test tube and then matched to the colorimetric scale. The data was then recorded and tabulated for each water sample for future reference. (See Tables 1.0 - 1.3)

Using these data sheets, temperature, salinity and dissolved oxygen were then visually represented. Profiles were constructed showing isolines.

The two most important micronutrients, phosphates and nitrates, were determined by colorimetric methods using a Spectronic 20. (See Tables 2.0 and 2.1) As water samples were brought aboard, 30 ml samples were drawn for testing micronutrients. These water samples were labled, catalogued and then refrigerated so further tests could be conducted in the lab. Since the chemical analysis for determining both phosphates and nitrates was a tedious procedure, only bottom and surface samples were tested. Phosphates were determined by the Ascorbic Acid Method and nitrates by the Brucine Method. (See Tables 3 and 4) Known concentrations of phosphorus and nitrogen were treated with suitable reagents. From this, unknown water samples from each station were matched. Graphic techniques of profiling were again employed depicting isolines, which will be discussed later.

Appendix C contains the procedures for determining dissolved oxygen, Winkler titration; salinity, Mohr titration; phospahtes, Ascorbic Acid Method and nitrates, Brucine Method.

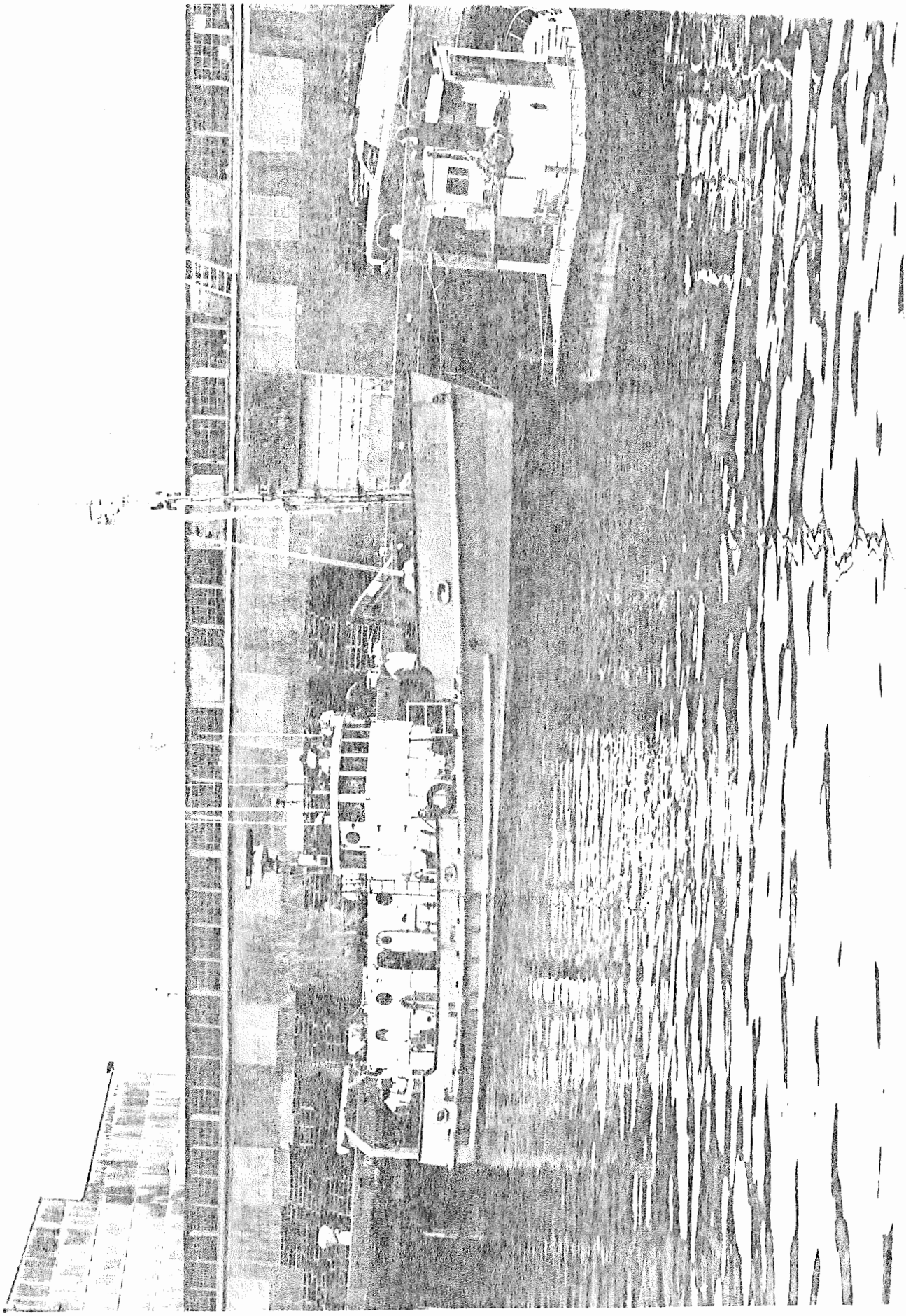


Figure 13 - Research Vessel Edgerton

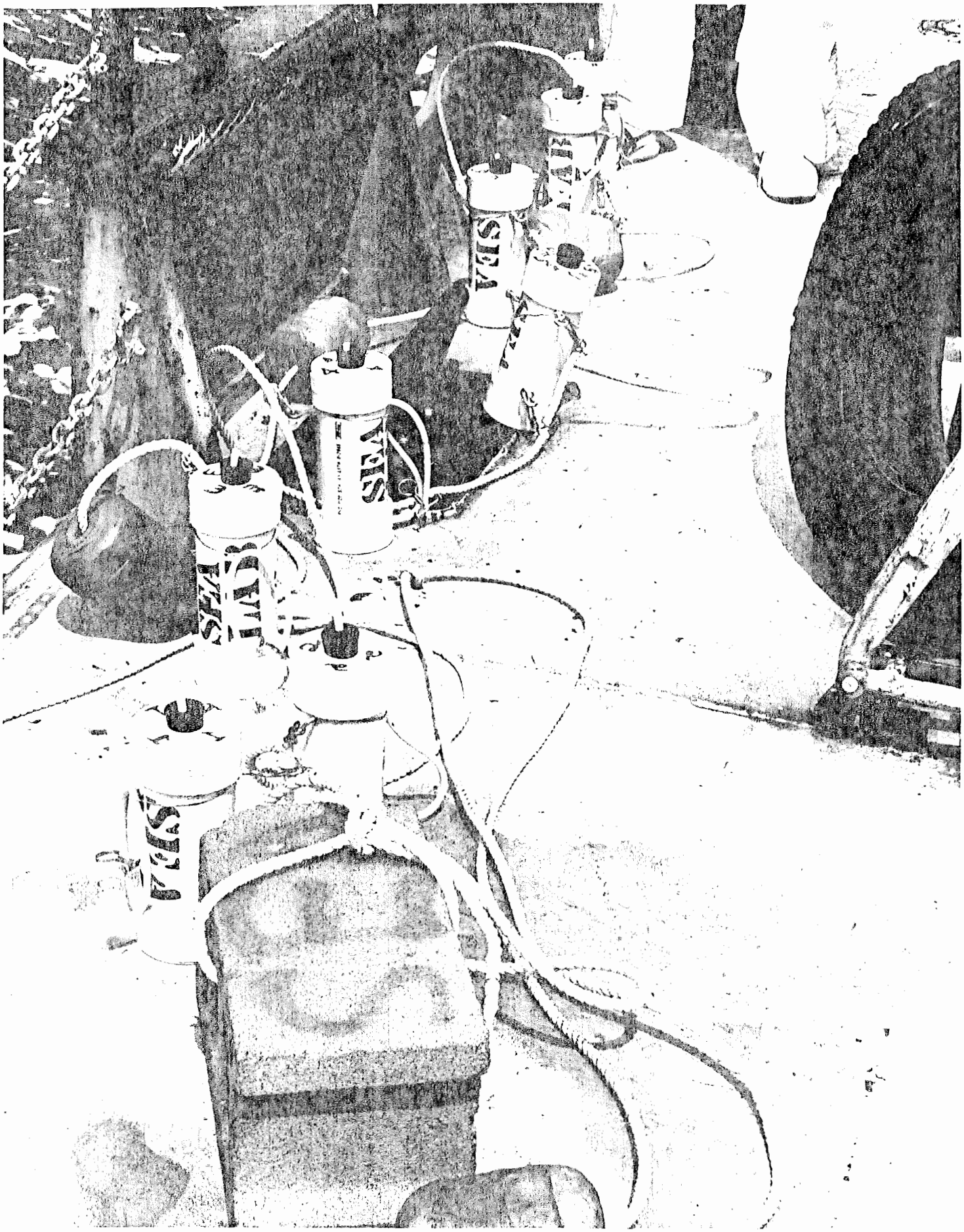


Figure 14 - Collection Bottles Comprising Sampling Tree

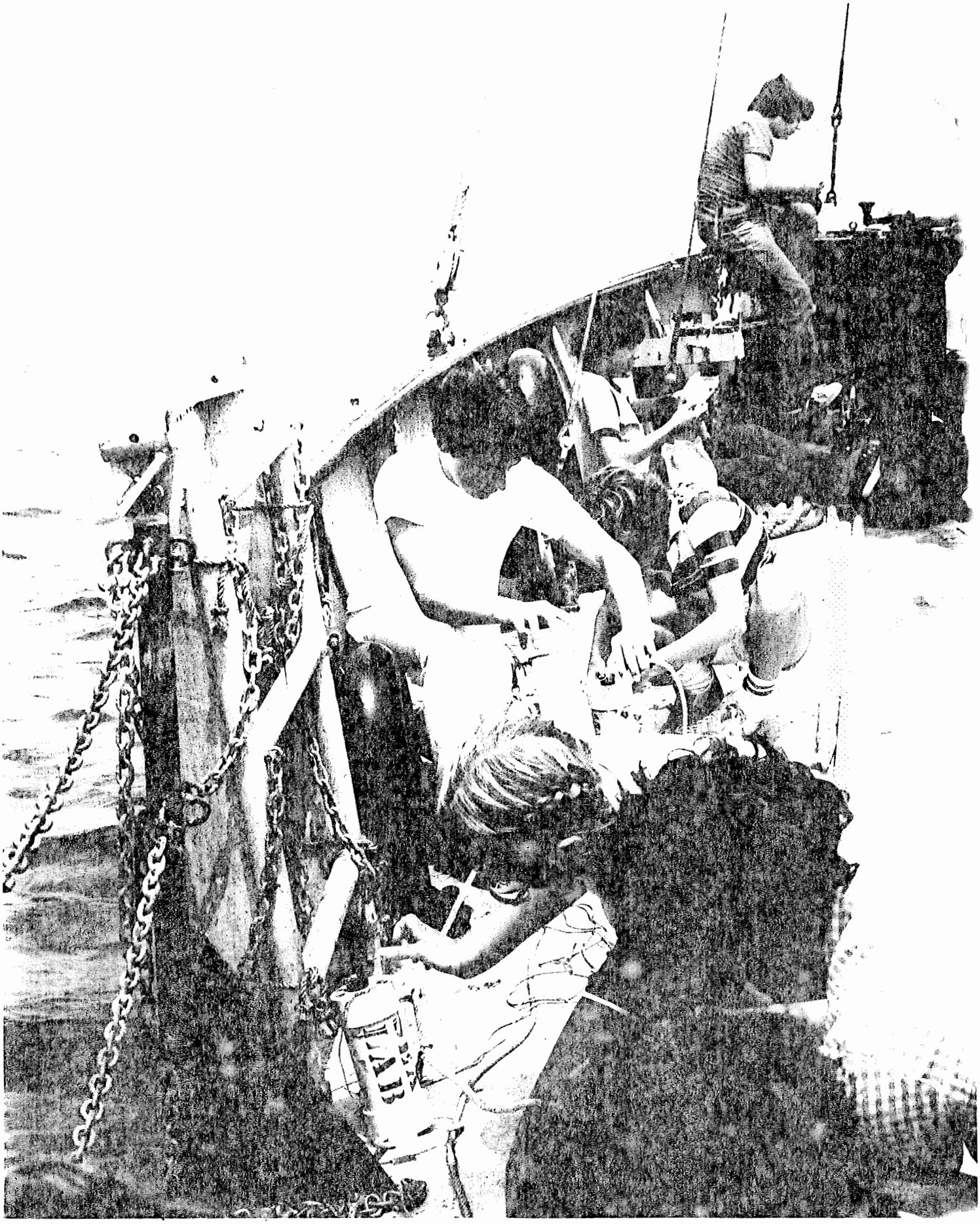


Figure 16 - Collecting and Recording Data

Figure 17 - Reading Temperature for Water Sample

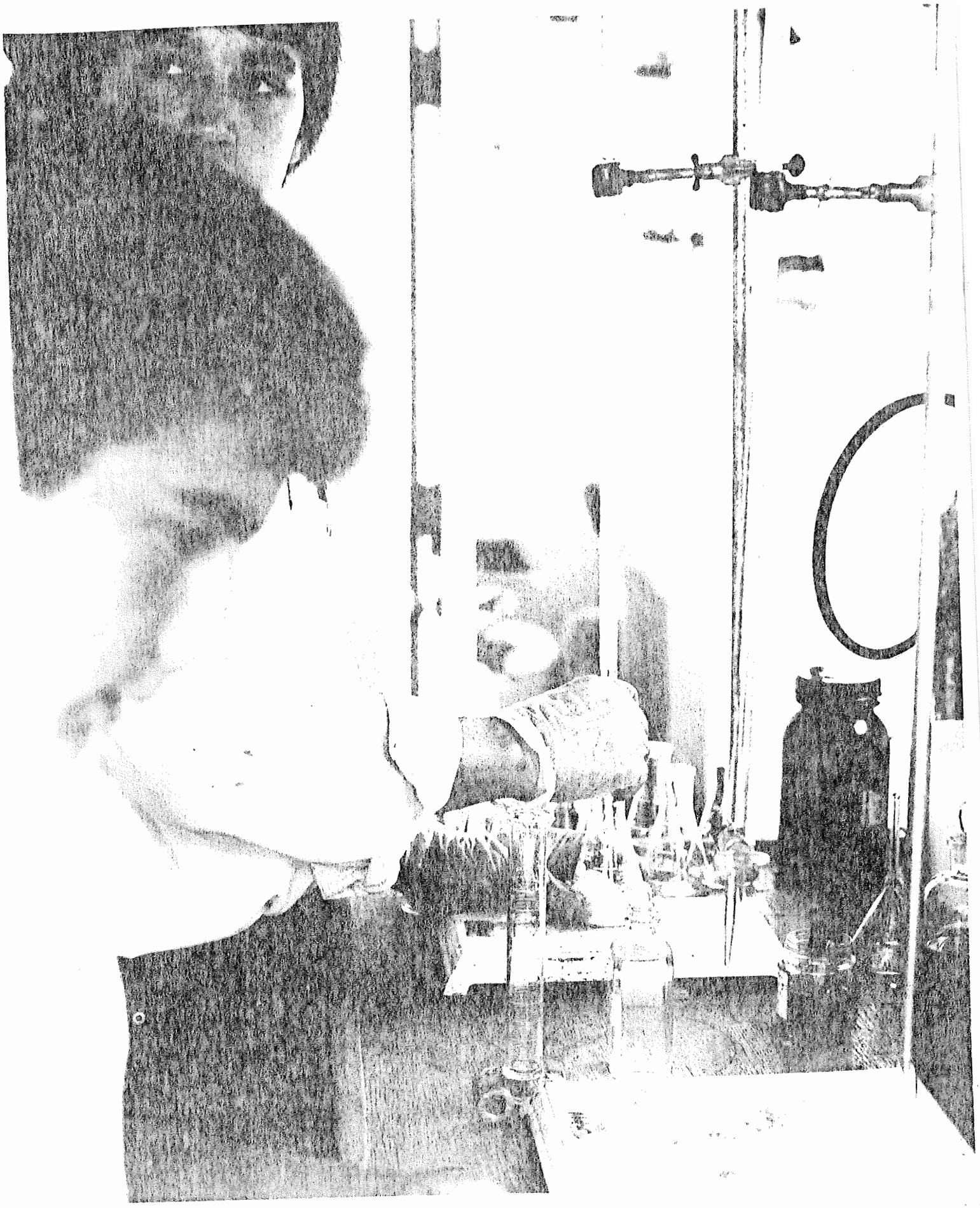


Figure 18 - Mohr Titration - R/V Edgerton Laboratory

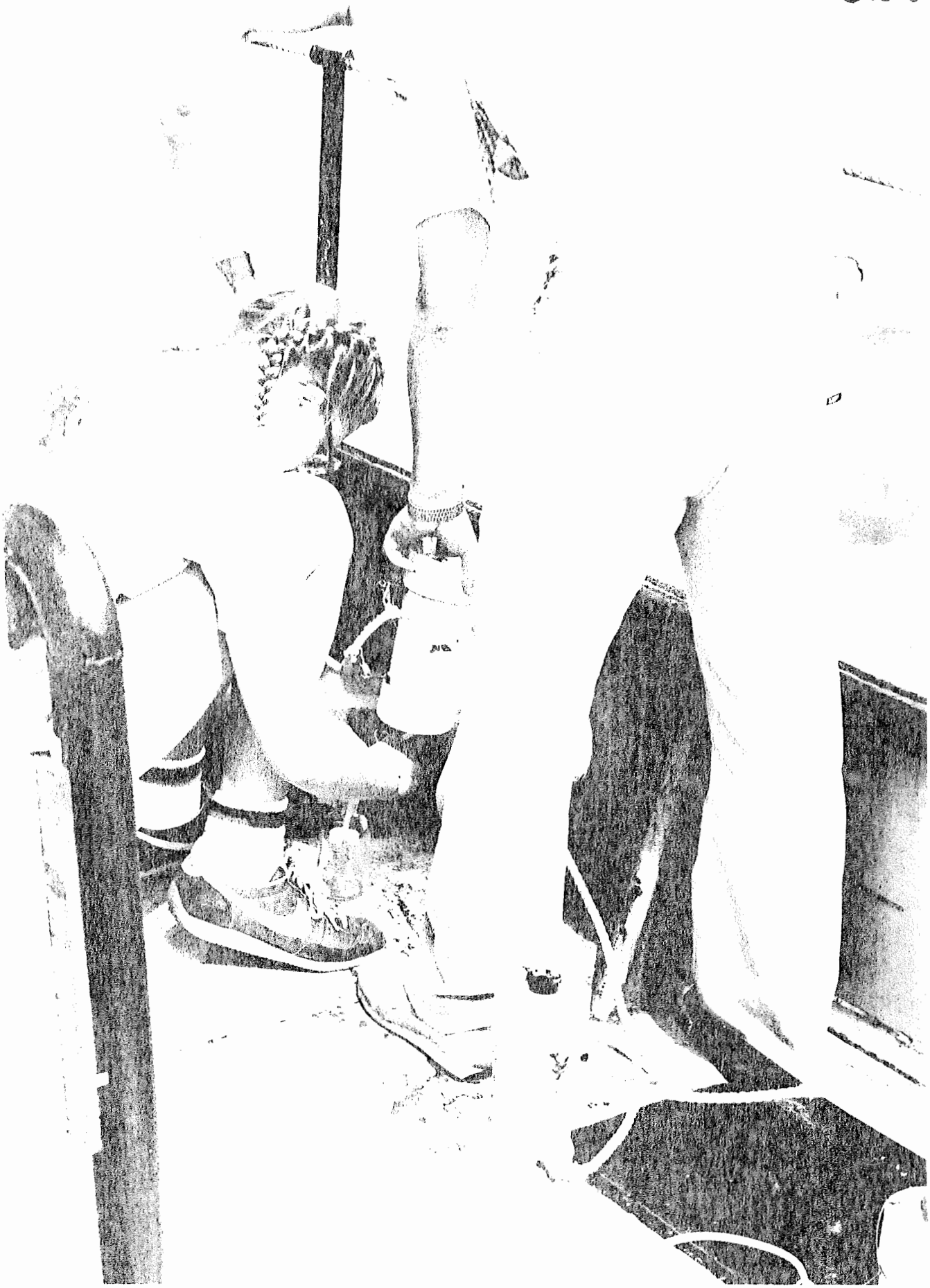


Figure 19 - Collecting Water Samples for Testing D.O.

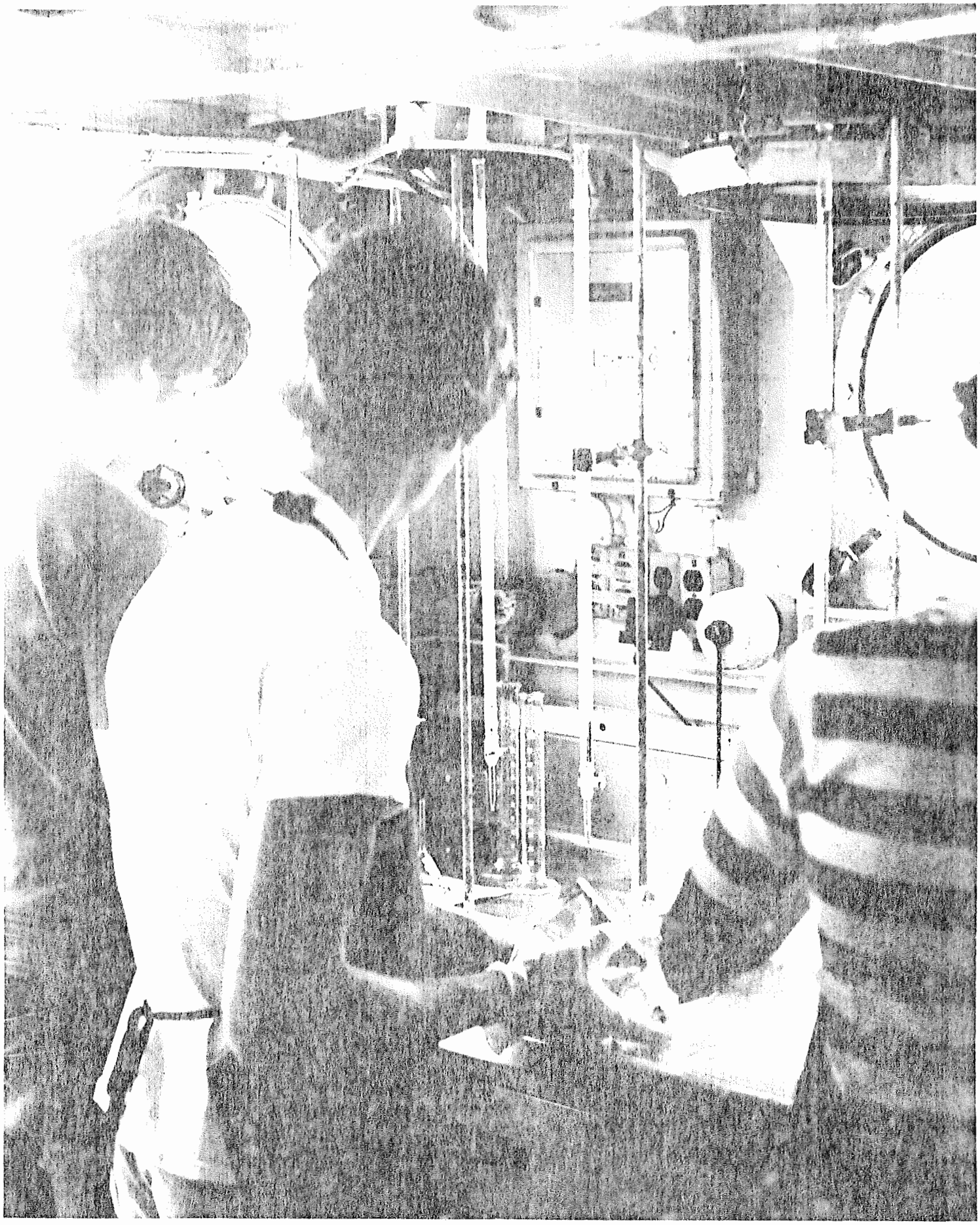


Figure 20 - Winkler Titration - R/V Edgerton Laboratory

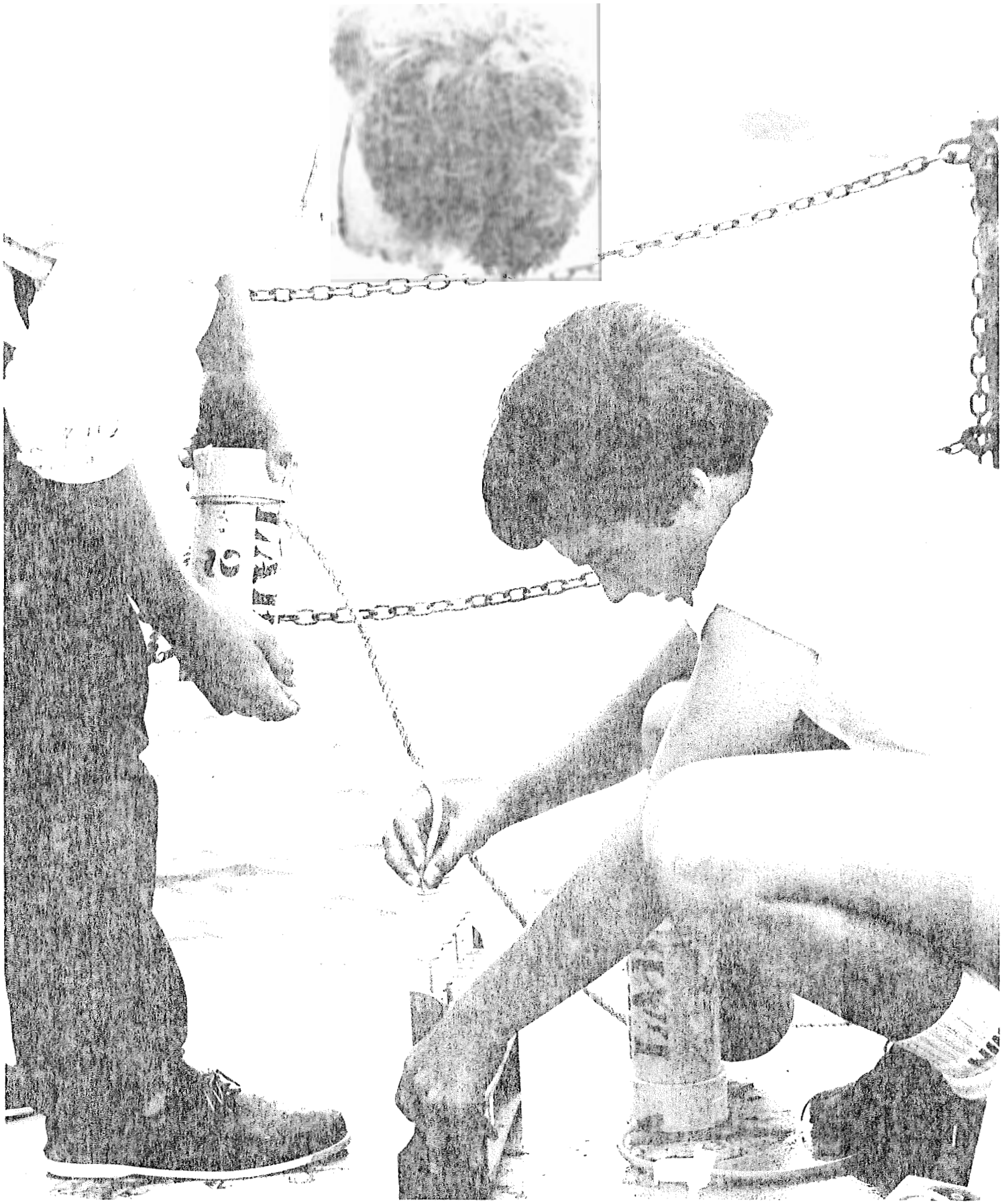


Figure 21 - Collecting Water Samples for pH

Station	Distance from Dike (Meters)	Bottle	Depth (Meters)	Temp. °C	Salinity ‰	S.G. Anomoly	Dissolved Oxygen (PPM)	% Saturation D.O.
IA	466 M	1	4.3	26°	29.5	18.8	3.5	50%
		2	3.3	26°	29.2	18.75	4.0	57%
		3	2.3	26°	29.8	19.15	4.0	58%
		4	1.3	25.9°	29.0	19.0	3.8	54%
		5	0.3	26°	28.9	18.5	3.7	53%
		6						
		7						
		8						
		Surface						
IB	1563 M	1	10.4	25°	27.2	17.5	4.5	62.5%
		2	9.4	25°	27.8	17.8	4.2	59.1%
		3	8.4	25°	26.0	16.8	3.9	55.7%
		4	7.4	25°	28.8	18.8	4.9	69.0%
		5	6.4	25°	24.1	15.2	4.6	63.0%
		6	5.4	25°	28.0	18.2	5.1	71.0%
		7	4.4	25.5°	23.9	14.8	3.8	53.4%
		8	3.4	26°	27.9	17.8	5.0	71.4%
		Surface	0	26°	27.2	17.2	4.6	64.7%

Table 1.0

Station	Distance from Dike (Meters)	Bottle	Depth (Meters)	Temp. °C	Salinity ‰	S.G. Anomoly	Dissolved Oxygen (PPM)	% Saturation D.O.
IC	2184 M	1	8.8	25.5°	29.3	18.8	5.2	74.8%
		2	7.8	25.2°	30.0	19.4	5.3	72.9%
		3	6.8	26°	29.5	18.7	6.3	90.6%
		4	5.8	26°	29.8	18.9	4.2	60.9%
		5	4.8	26°	29.8	18.9	4.5	64.7%
		6	3.8	26°	29.6	18.85	4.5	64.7%
		7	2.8	26°	29.7	18.89	5.2	74.8%
		8	1.8	26.1°	29.2	18.7	6.7	96.4%
		Surface	0	26°	29.8	18.9	6.2	89.9%
ID	3555 M	1	9.1	26°	29.2	18.7	6.7	96.4%
		2	8.1	25.9°	30.1	19.5	5.3	76.2%
		3	7.1	25.9°	30.0	18.4	6.1	87.7%
		4	6.1	25.9°	30.0	18.4	4.7	67.6%
		5	5.1	26°	29.0	18.3	5.2	74.8%
		6	4.1	26°	29.9	19.2	5.5	79.7%
		7	3.1	26°	29.9	19.2	6.3	91.3%
		8	2.1	26°	29.8	19.1	5.9	85.5%
		Surface	0	25.8°	28.9	18.6	6.7	95.7%

Table 1.1

Station	Distance from Dike (Meters)	Bottle	Depth (Meters)	Temp. °C	Salinity ‰	S.G. Anomoly	Dissolved Oxygen (PPM)	% Saturation D.O.
I E		1	9.45	25.1°	27.3	17.7	6.4	87.6%
		2	8.45	25°	29.8	19.4	6.1	87.1%
		3	7.45	–	–	–	6.2	–
		4	6.45	25°	29.6	19.2	6.1	85.9%
		5	5.45	25.1°	30.0	19.5	6.0	85.7%
		6	4.45	25°	29.0	18.8	6.5	90.2%
		7	3.95	25.1°	27.2	17.5	5.8	79.4%
		8	2.45	25.7°	20.7	12.4	5.4	72.0%
		surface	0	25.9°	24.7	15.6	4.8	65.7%
I F		1	9.10	25°	29.9	19.4	6.4	90.7%
		2	8.10	25°	30.0	19.7	5.9	83.6%
		3	7.10	25°	30.1	19.6	6.0	85.0%
		4	6.10	25°	30.0	19.7	6.2	88.0%
		5	5.10	25°	30.0	19.7	5.9	84.0%
		6	4.10	25°	30.0	19.7	6.1	87.0%
		7	3.10	25.2°	29.3	19.0	6.2	89.0%
		8	2.10	25.1°	29.9	19.6	6.1	86.0%
		surface	0	25.1°	29.0	18.8	5.7	81.0%

Table 1.2

Station	Distance from Dike (Meters)	Bottle	Depth (Meters)	Temp. °C	Salinity ‰	S.G. Anomoly	Dissolved Oxygen (PPM)	% Saturation D.O.
IG		1	8.5	24.1°	30.0	19.75	10.3	14.4%
		2	7.5	24.2°	30.6	19.97	7.4	103%
		3	6.5	24.5°	28.9	18.88	6.3	88.3%
		4	5.5	24.7°	29.7	19.17	7.7	100%
		5	4.5	24.7°	28.1	18.21	4.2	58.4%
		6	3.5	24.6°	28.0	18.08	6.9	95.8%
		7	2.5	24.9°	29.9	19.39	7.1	101.17%
		8	1.5	24.7°	30.9	20.19	7.6	108.5%
		surface	0	23.8°	29.9	19.21	7.0	96.1%
IH		1	8.8	23.9°	29.2	19.09	6.6	92.9%
		2	7.8	24°	26.4	17.10	7.1	95.9%
		3	6.8	—	—	—	7.1	—
		4	5.8	24.3°	29.0	19.05	7.5	104.7%
		5	4.8	24.3°	27.3	17.87	7.6	104.8%
		6	3.8	24.7°	29.8	19.30	6.8	86.1%
		7	2.8	24.5°	28.4	18.45	7.7	105.9%
		8	1.8	24.7°	29.0	18.95	5.8	80.5%
		surface	0	24.3°	27.3	17.87	7.1	98.6%

Table 1.3

Calculations for Nitrates

Station	Sample	Absorbance Value (Spec 20)	Value - Calibrated Curve	Nitrates (μg)
IA	surface	.085	.078	.345
	bottom	.080	.074	.327
IB	surface	.050	.046	.222
	bottom	.060	.055	.243
IC	surface	.028	.026	.117
	bottom	.005	.004	.017
ID	surface	.005	.004	.017
	bottom	.001	.0005	.002
IE	surface	.020	.017	.077
	bottom	.110	.102	.454
IF	surface	.010	.008	.037
	bottom	.020	.017	.077
IG	surface	.075	.069	.305
	bottom	.055	.050	.221
IH	surface	.050	.045	.199
	bottom	.065	.060	.265

Table 2.0

Calculations for Phosphates

Station	Sample	Absorbance Value (Spec 20)	Value - Calibrated Curve	Phosphates (PPM)
IA	surface	.100	.265	.795
	bottom	.065	.180	.550
IB	surface	.090	.248	.758
	bottom	.090	.248	.758
IC	surface	.050	.140	.428
	bottom	.075	.207	.633
ID	surface	.065	.180	.550
	bottom	.055	.154	.471
IE	surface	.080	.220	.673
	bottom	.070	.195	.596
IF	surface	.070	.195	.596
	bottom	.110	.270	.826
IG	surface	.065	.180	.550
	bottom	.035	.095	.293
IH	surface	.065	.180	.795
	bottom	.095	.260	.550

Table 2.1

Table for Standard Phosphorus Samples

PPM	Absorbance
.375	.2
.750	.285
1.250	.490
1.750	.600

Table 3.0

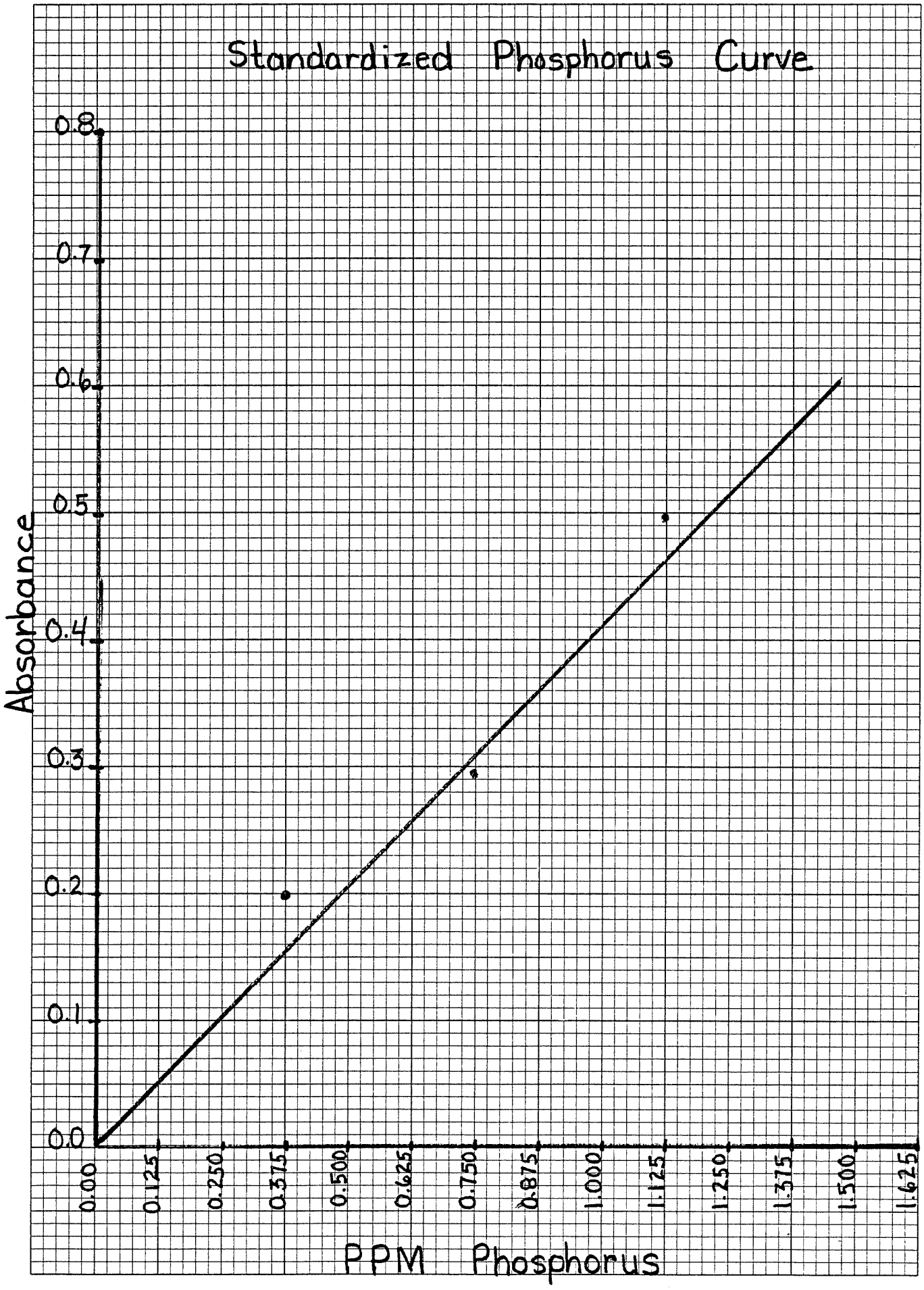


Figure 22 - Standard Phosphorus Curve

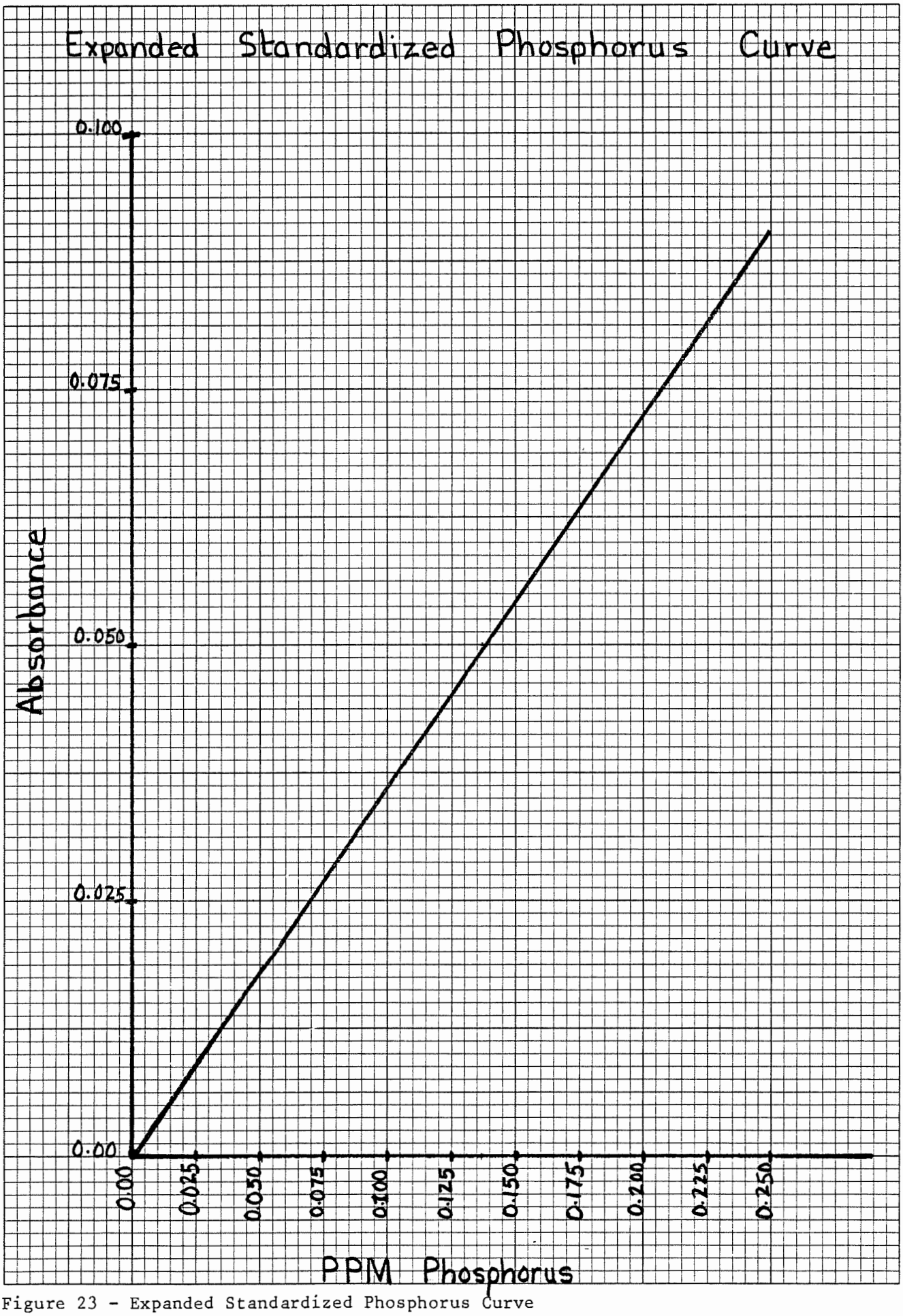


Figure 23 - Expanded Standardized Phosphorus Curve

Table for Standard Nitrogen Samples

Micrograms-N	Absorbance
.1	.37
.2	.51
.3	.64
.4	.71
.5	.84
.6	.97
.7	.86
.8	1.09

Table 4.0

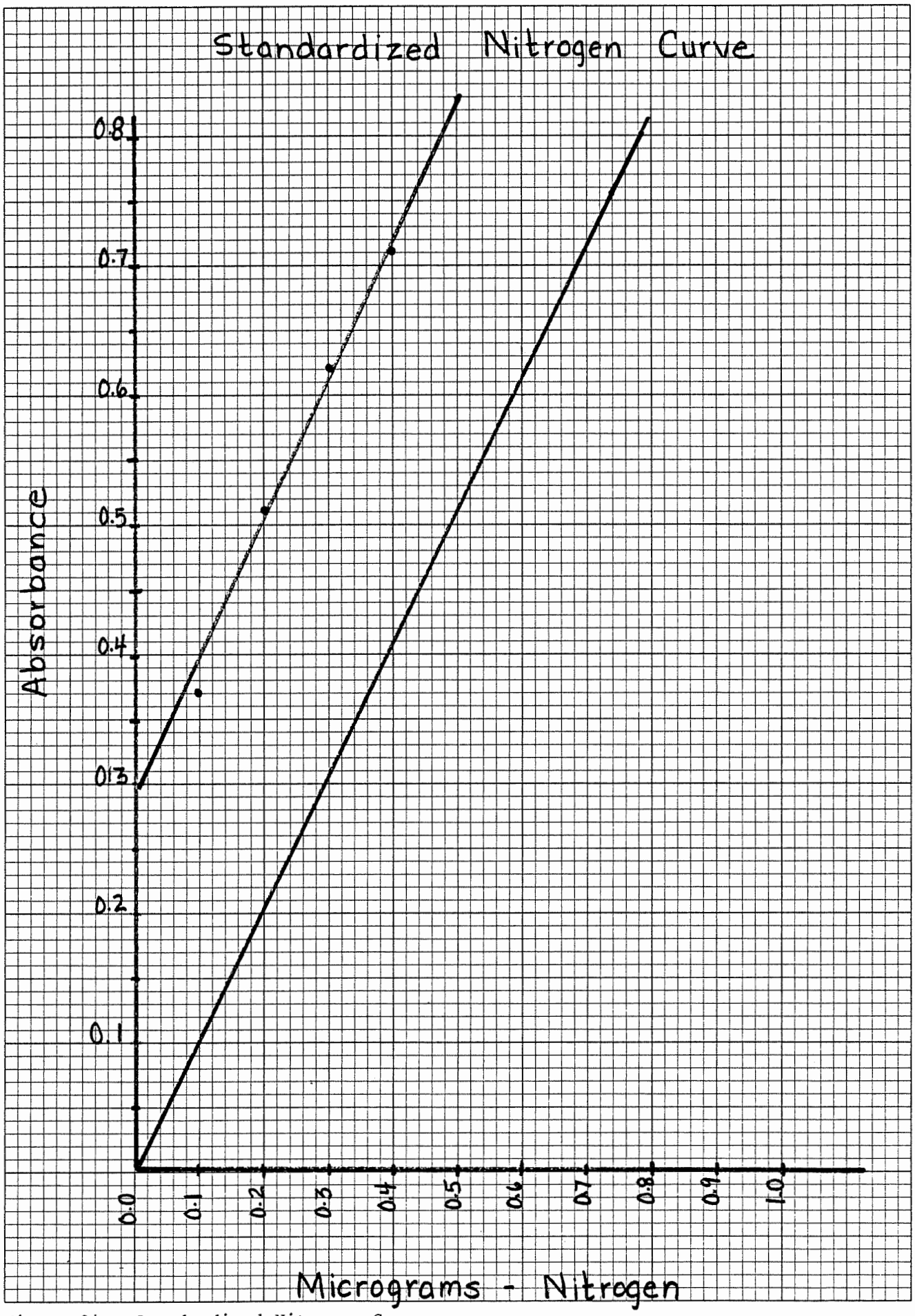


Figure 24 - Standardized Nitrogen Curve

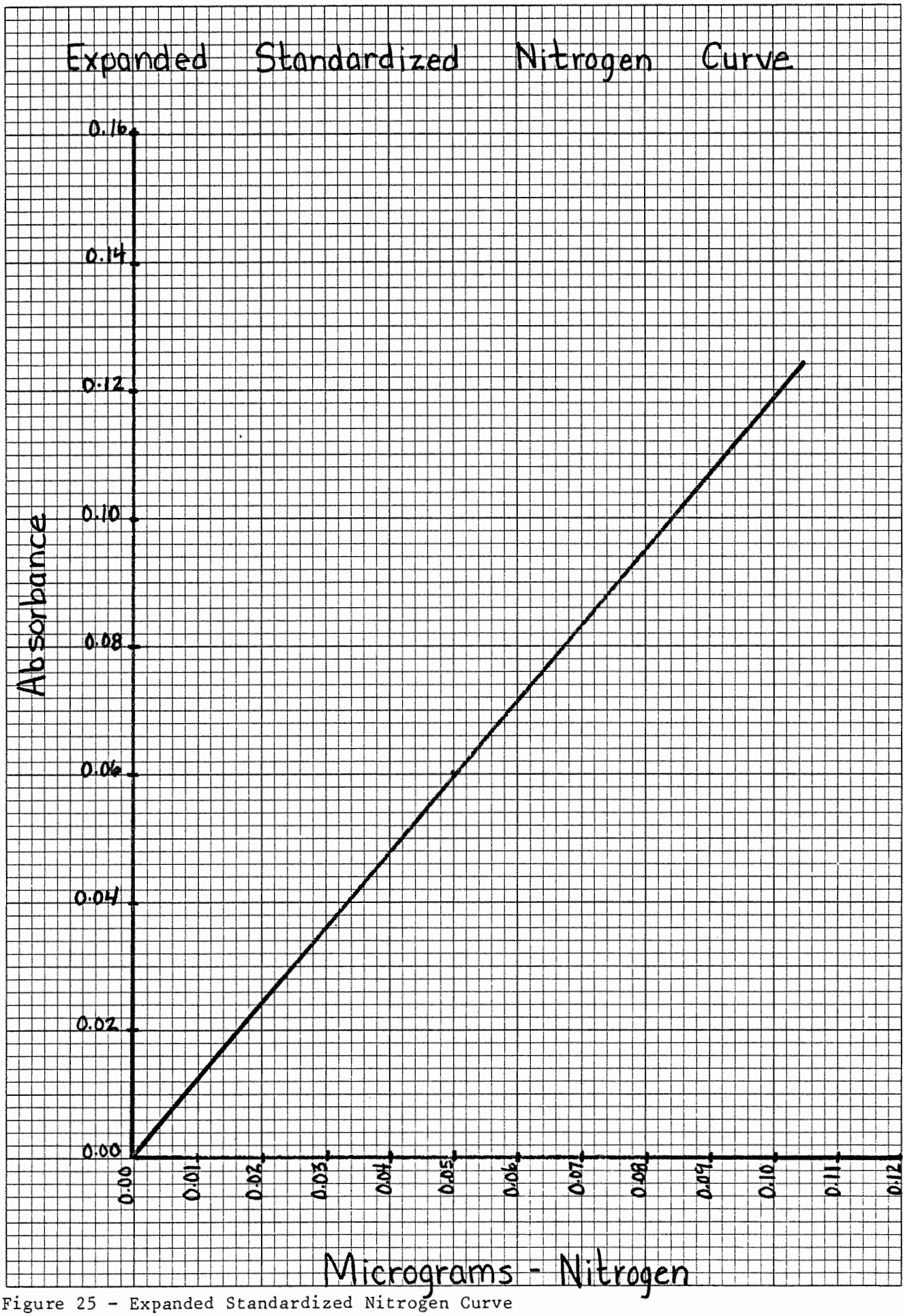


Figure 25 - Expanded Standardized Nitrogen Curve

DISCUSSION

Analizing the New Bedford harbor extending from the Coggeshall Street Bridge to the outer harbor offers the physical oceanographer a variety of water properties to study. A series of eight hydrographic stations was chosen extending in a south-easterly direction. Two stations were chosen in the inner harbor and the remaining six were located in the outer harbor. The study was conducted to illustrate: 1) the effect of fresh water intrusion on the harbor, 2) the effect of the hurricane dike on the water quality in the inner and outer harbors and 3) the improvement of water quality as one moves away from the inner harbor.

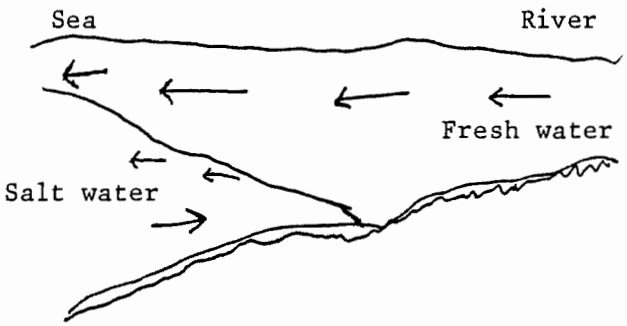
A number of water properties would be analyzed at each hydrographic station. Tests were to be conducted for dissolved oxygen, salinity, density, temperature and micronutrients (phosphates and nitrates). This data was to be tabulated and then visually represented by vertical profiles. Isolines for each parrameter would be represented in separate profiles and then compared with other parameters. The influence that one property had on another was then discussed and evaluated.

The density of seawater depends primarily on three factors: 1) temperature, 2) salinity and 3) pressure. Since temperature and salinity have the greatest effect on water, a Sea Water Density Anomaly as a function of temperature and salinity was constructed. (See Figure 26) The specific gravity of water at temperature t_0 is usually expressed in terms of either specific gravity anomaly (specific gravity - 1), or σ_t (specific gravity - 1) X 1000. Using the Sea Water Density Anomaly, it can be observed as temperature increases, density decreases. For every σ = 1, the water temperature is affected approximately by 3.5°C. It can also be noted that with increasing salinity, the density of sea water will also be increased. The lines with the greatest slope are the temperature lines, indicating that temperature has a greater effect upon sea water density than does salinity. The density values for each water sample were calculated with the use of a graph. The implications of the calculated values will be discussed later in this report.

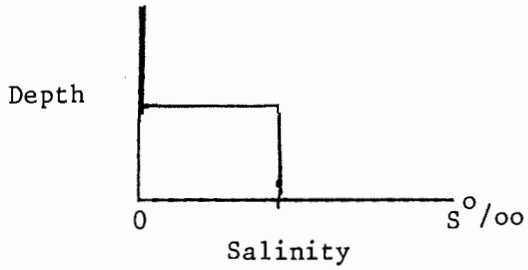
One of the easiest properties to measure, as well as being one of the most important, is water temperature. Observing water temperature enables an oceanographer to identify different bodies of water. Figure 27 depicts isotherms for the designated area of study. It can be noted as one moves in a southerly direction, the water gets colder. This indicates that as one approaches open, unprotected waters, the temperature decreases. The temperature changes 2°C in a 3000 meter span. This volume of water lies wihin the hurricane dike, and is therefore protected and stagnant water. Since temperature has the greates effect on sea water density, the two profiles, when compared, look quite similar. (See Figure 28) It can be observed that warmer water illustrates lower density and colder water illustrates greater density. It is also important to note that at about 2500 meters, there seems to be a dip in both profiles. If one consults a navigation chart, it will be discovered that this occurs in the exact location of the hurricane dike. The isotherms also indicate temperature gradients as one moves into the outer harbor; surface layers being warmer than the bottom layers. This may indicate that the only factor influencing the water's temprature at these locations is solar radiation.

One can conclude that the hurricane dike maintains the water's temperature in the inner harbor since the temperature variations are not as great as those in open waters. The temperature profile will be used later in the report to examine the effect of temperature on the other water properties.

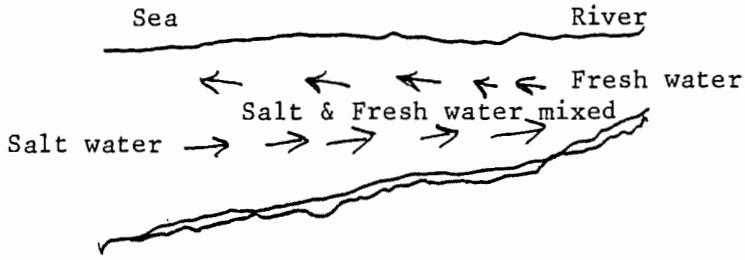
Since the New Bedford harbor has fresh water intrusion, the salinity of the harbor is an important property to study. Fresh water from a river can enter salt water in two basic fashions: 1) as a salt wedge and 2) partially mixed water. If fresh water enters the salt water and is not mixed, a wedge is formed. (See illustration on following page.)



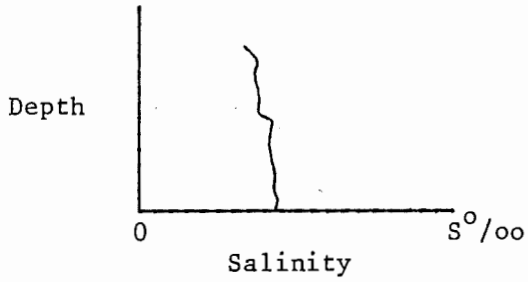
It can be observed that the denser water is at a greater depth. A depth vs. salinity graph can be illustrated as shown below:



One will note that there is a distinction between fresh and saline water. Two distinct bodies of water can be identified. If the fresh water is partially mixed with the salt water, the salinity will be consistent in a water column.



The graph of the water column below illustrates salinity at various depths in a partially mixed body of water.



The graph shows a slight increase in salinity at greater depths, due to the water's saline density. From the profile showing the water's salinity (See Figure 29) it appears that the less saline water is moving over the more saline water. Since the salinity of the surface water only differs by approximately 1°/oo (part per thousand), it can be assumed that the water is partially mixed. The mixing of water occurs in two directions: 1) horizontal and 2) vertical. The major causes for horizontal mixing are tides, currents and winds. In the New Bedford harbor, the change in tides can be attributed to the mixing of horizontal waters. Lower salinities can be found between 0 and 2000 meters, which can be accounted for by the fresh water river and the dike, which acts as a barrier. Vertical mixing is caused by wind action or by the friction of currents flowing over one another or the bottom. From the profile in Figure 30, it can be observed that the topography of the harbor is highly

irregular, and therefore causes the water to mix. Although the temperature profile indicates different temperature gradients which inhibit vertical mixing, the temperature differential from surface to bottom is only $2^{o}C$.

Besides its importance to the biological activity, dissolved oxygen also aids an oceanographer in identifying different bodies of water. Solubilities of gases in sea water are functions of temperature, salinity and pressure. Figure 31 illustrates the effect that chlorinity (Salinity = 1.8050 · Chlorinity +0.03) and temperature has on the maximum dossolved oxygen in seawater. The solubility of oxygen increases with a decrease in salinity. If one examines only the magnitude of the slopes of lines of constant salinity and compares it to the slope of lines of constant temperature, one can observe that oxygen's solubility is more sensitive to temperature changes than to salinity changes.

Figure 30 illustrates isolines and the constant values of dissolved oxygen. There are two major factors that influence the concentration of dissolved gasses in sea water: surface factors and internal factors. Surface factors which affect the amount of dissolved oxygen are water temperature and salinity. From observing the isotherms in the temperature profile (Figure 28), it is evident that the warmer water has higher values of dissolved oxygen. Between 0 and 2000 meters, the dissolved oxygen counts are extremely low, ranging from 3.5 p.p.m. to 4.9 p.p.m. It is also evident that in the colder water of the outer harbor, the values of the dissolved oxygen are much higher. As stated previously, the solubility of dissolved oxygen is more sensitive to temperature, just as the temperature and dissolved oxygen profile indicates.

Dissolved oxygen may also be represented in terms of percent saturation. Figure 32 depicts isolines generated by comparing the actual amount of dissolved oxygen values to the maximum saturation values. In this profile, it is evident that the colder water in the outer harbor has the highest values of percent saturation.

Elements such as carbon, hydrogen, and oxygen play a vital role in the biological processes which take place in the oceans. Other elements such as nitrogen and phosphorus play vital roles as micronutrients in the building of protiens, and in the supply and storage of energy within living organisms. By determining the amounts of nitrogen and phosphorus in a water sample, one can make inferences concerning the life processes operating in, or capable of being sustained in the study area. One may also be able to pinpoint possible sources of pollution which may introduce high values of nitrogen and phosphorus compounds into a given water mass.

In sea water of average salinity ($35^{o}/oo$ pH 8.0) at $20^{o}C$, 87% of the phosphates occur as HPO_4^{-2}, 12% as PO_4^{-3} and 1% as H_2PO_4. The distribution of phosphorus is controled by biological and physical agencies. (see phosphorus cycle in appendix C) Since the phosphorus cycle is not a completely closed cycle, portions undergo changes and are converted into minerals such as opartite - $Ca_5(PO_4)_3(OH_1F)$. The cycle is balanced by phosphorus entering the seas by weathering rocks and land runoffs.

The principle forms of nitrogen in sea water are the nitrate ions, nitrite ions and ammonia. The nitrogen cycle (see nitrogen cycle in appendix C), like the phosphorus cycle, is controlled by physical and biological factors. The nitrogen cycle is similar to the phosphorus cycle, and is not a closed system. Nitrogen enters the sea's water by rivers and rainfall. Free nitrogen dissolved in sea water from the atmosphere plays a minor role, as only a few bacterial organisms are capable of utilizing it directly in this form. Certain bacteria and algae present in the ocean and soils have the capability of bringing free nitrogen into inorganic nitrogen compounds known as nitrates. Nitrates are assimilated by phytoplankton into plant portions which, in turn, are either eaten by aquatic animals for producing animal proteins or decay into another nitrogen compound known as ammonia. The ammonia compounds are acted upon by bacterial action and produce an intermediate nitrogen compound known as nitrite which, in turn, is oxidized by bacteria to the nitrate form again. This is a simplification

of the nitrogen cycle, which is fundamental to all life. Nitrates are the form in which nitrogen can be utilized by phytoplankton, which will be the micrnutrient studied.

Phosphates (PO_4^{-3}) and nitrates (NO_3) are the two micronutrients which will be analyzed and computed by the photometric method. Figures 33 and 34 illustrate the various findings of phosphates and nitrates at the water's surface and bottom. At the southern end of the study area, it can be observed that there is an increase in phosphates in surface and bottom samples. One can speculate that the sewerage outfall is responsible for the influx in micronutrients. It is also evident that at station E, there is an extremely high count of nitrates. This can be attributed to the industrial wastes of the surrounding factories.

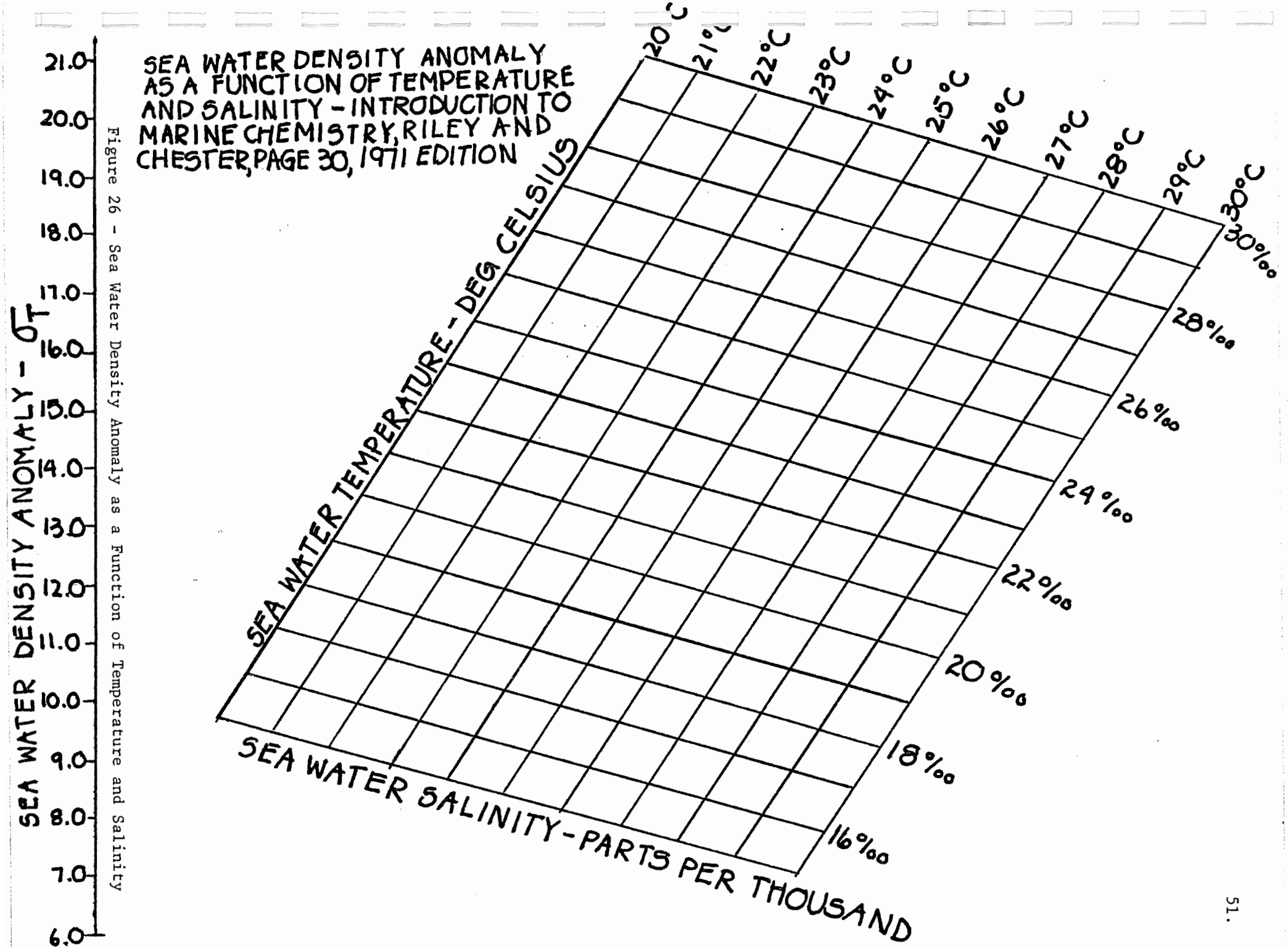


Figure 26 - Sea Water Density Anomaly as a Function of Temperature and Salinity

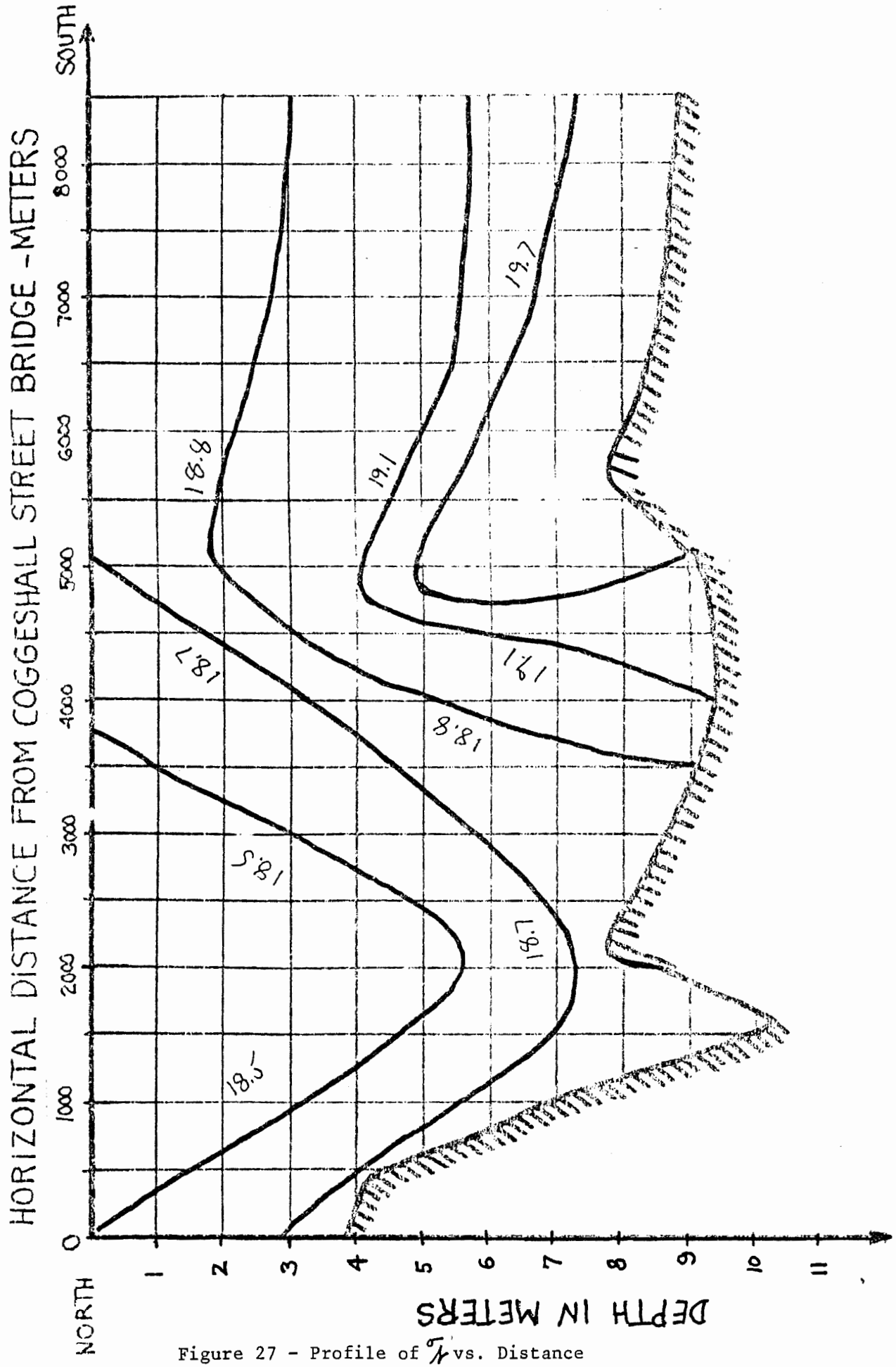


Figure 27 - Profile of σ_t vs. Distance

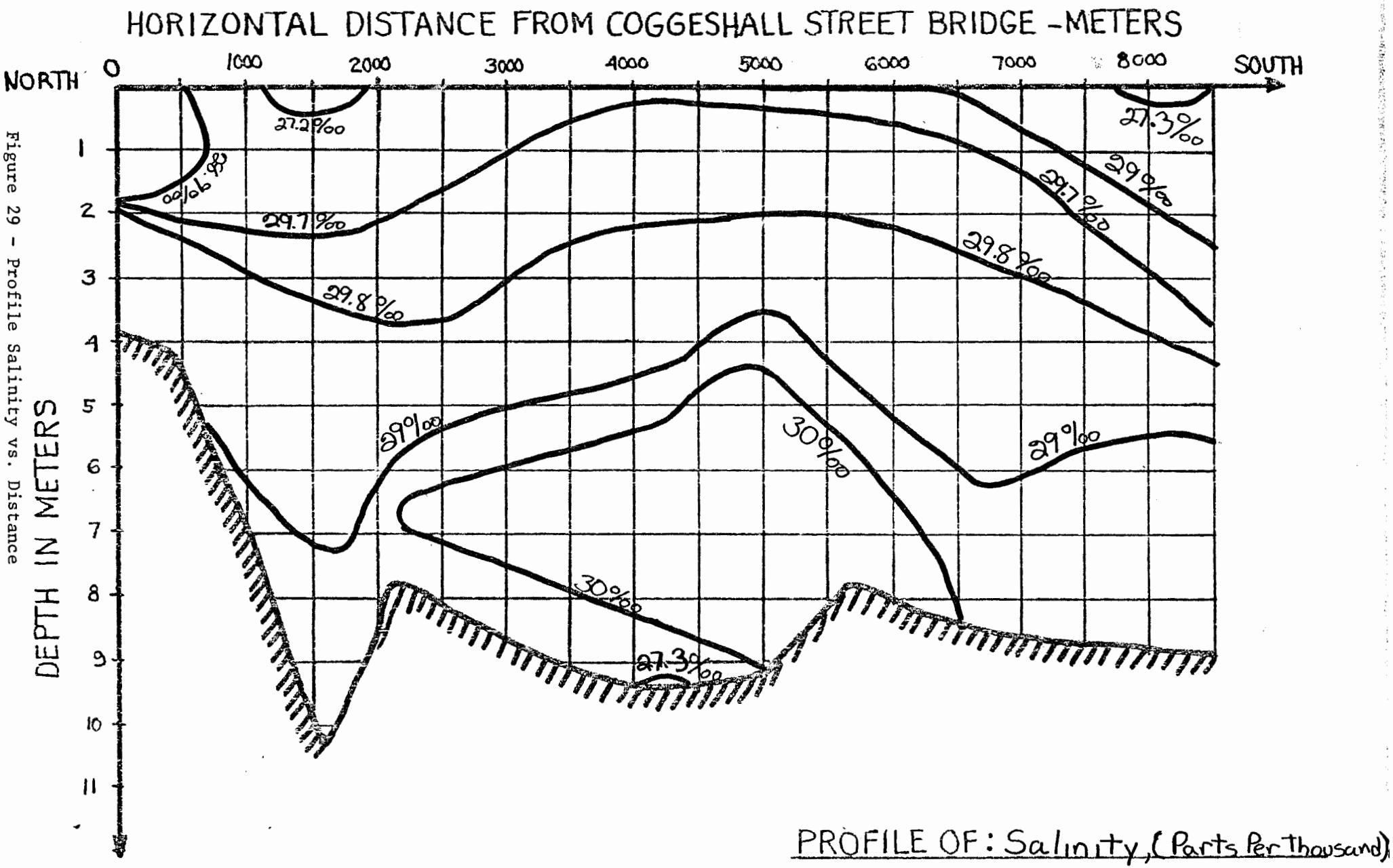


Figure 29 - Profile Salinity vs. Distance

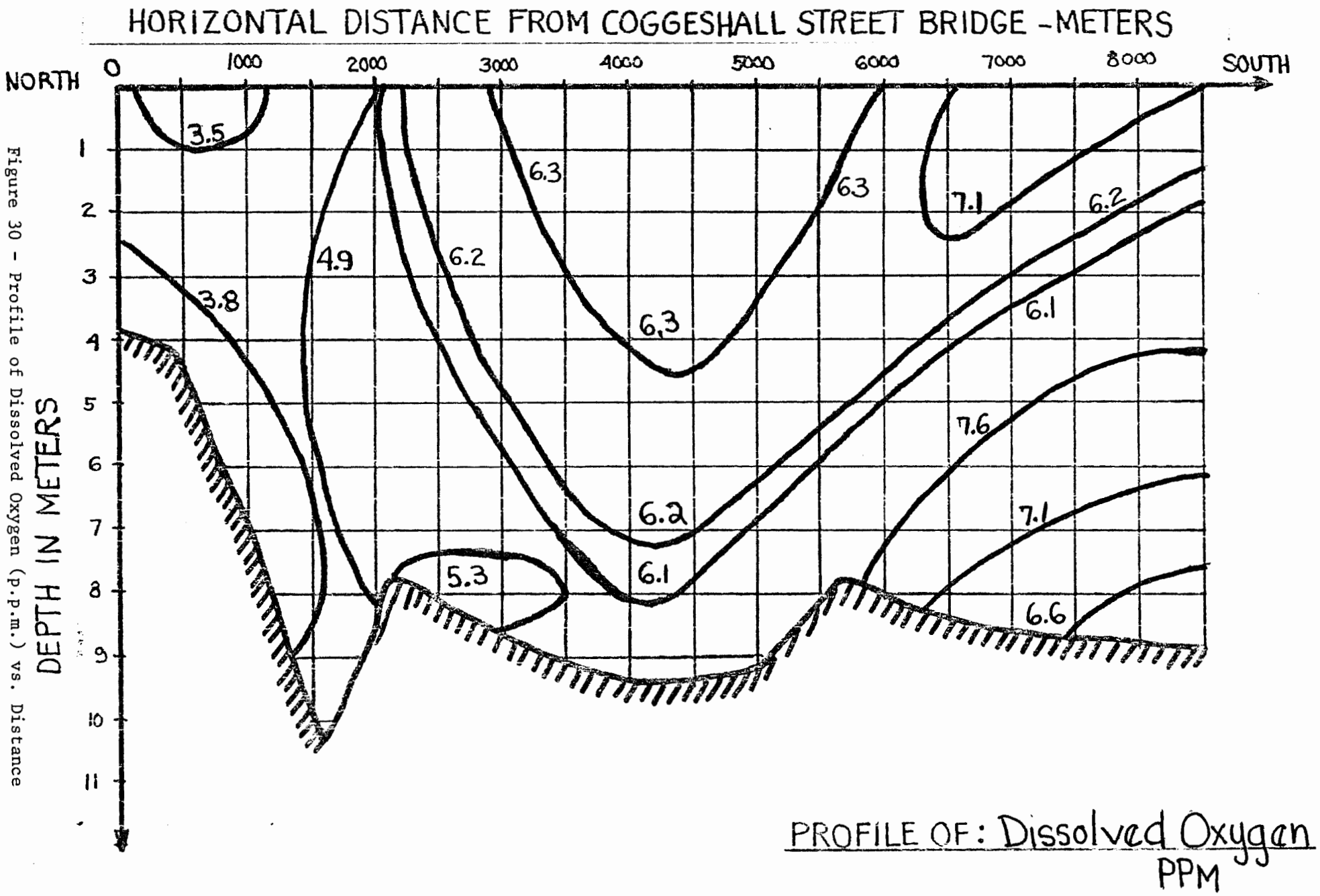


Figure 30 - Profile of Dissolved Oxygen (p.p.m.) vs. Distance

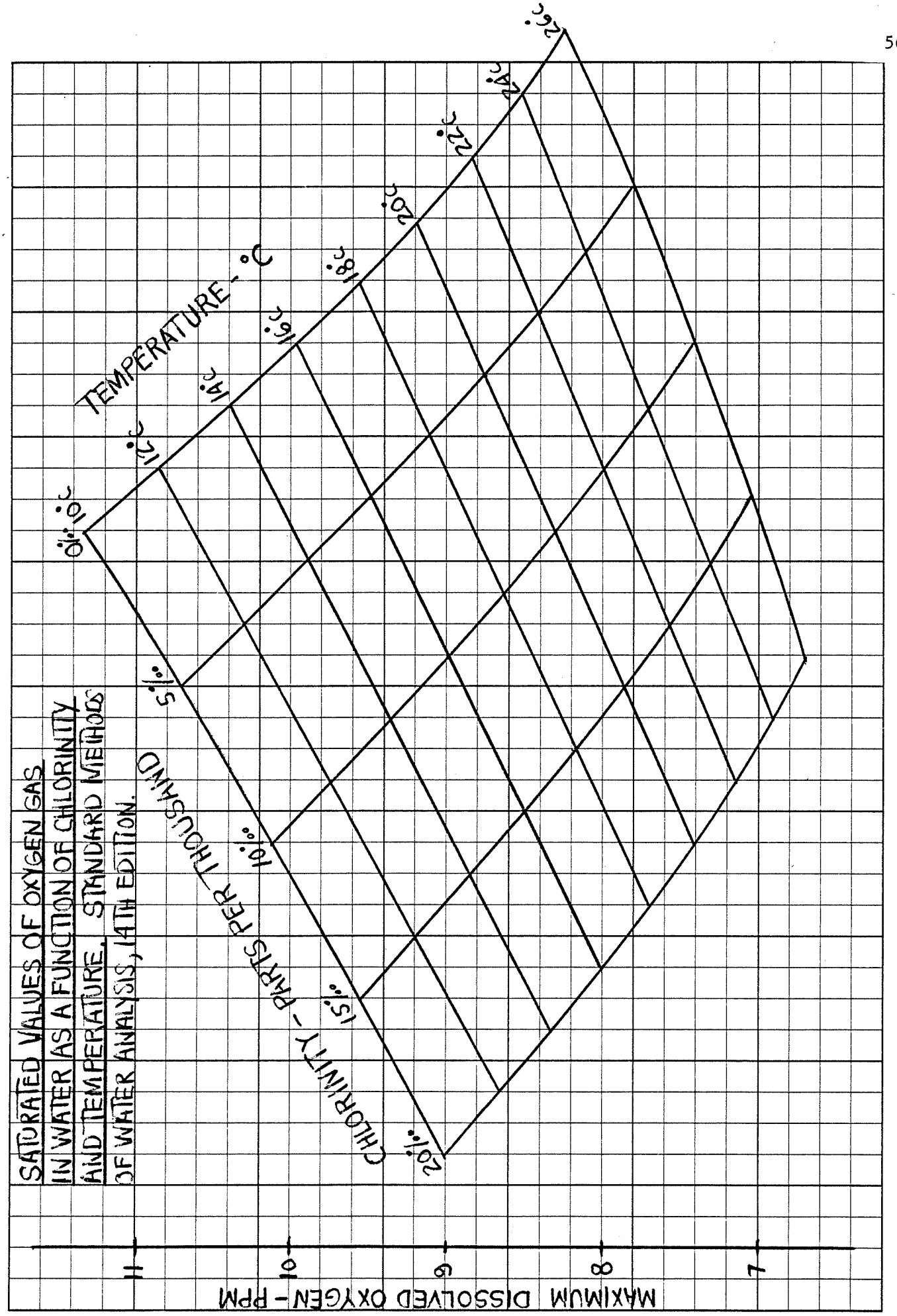


Figure 31 - Maximum Dissolved Oxygen in Water as a Function of Temp. & Chlorinity

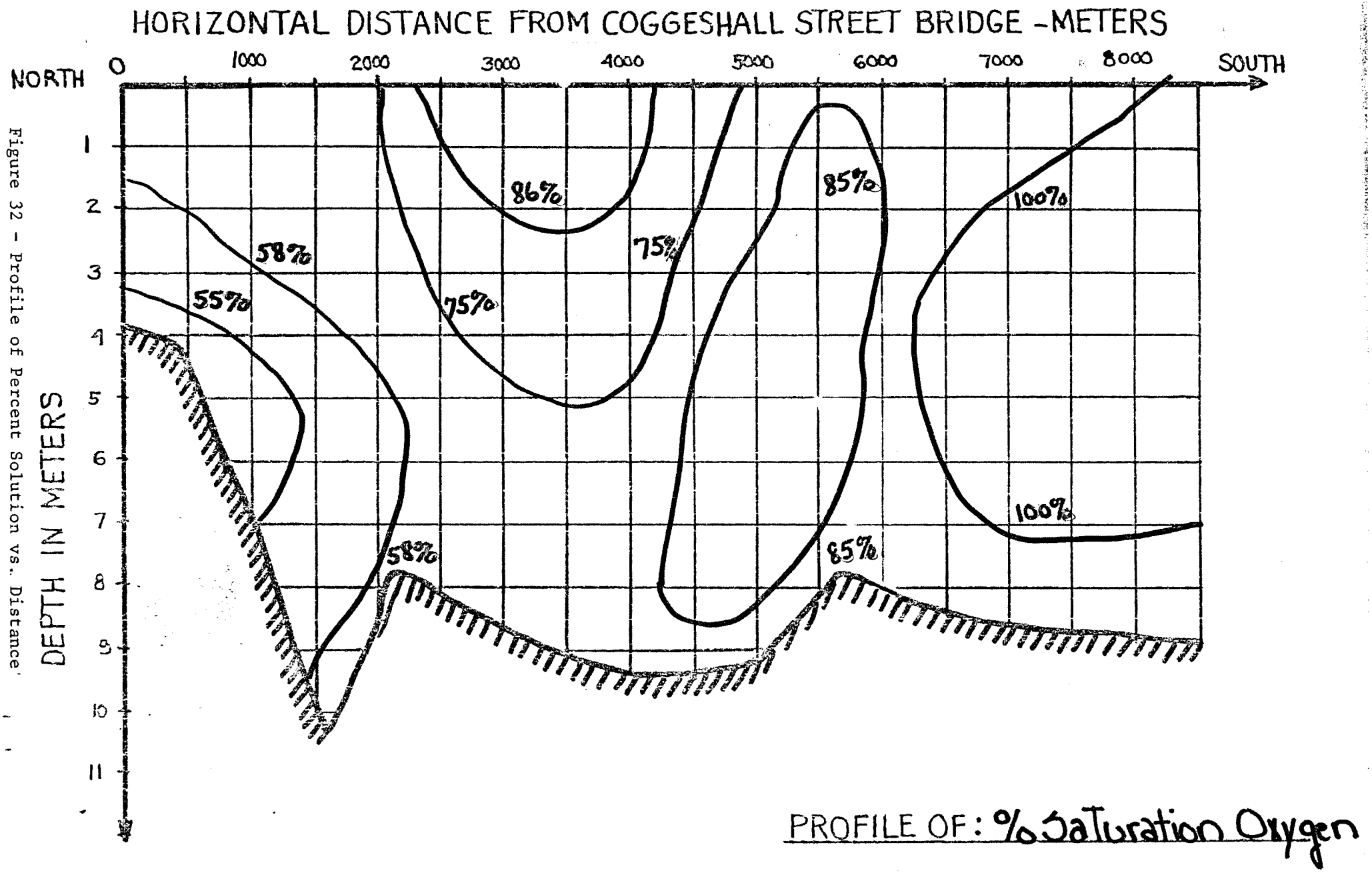


Figure 32 - Profile of Percent Solution vs. Distance

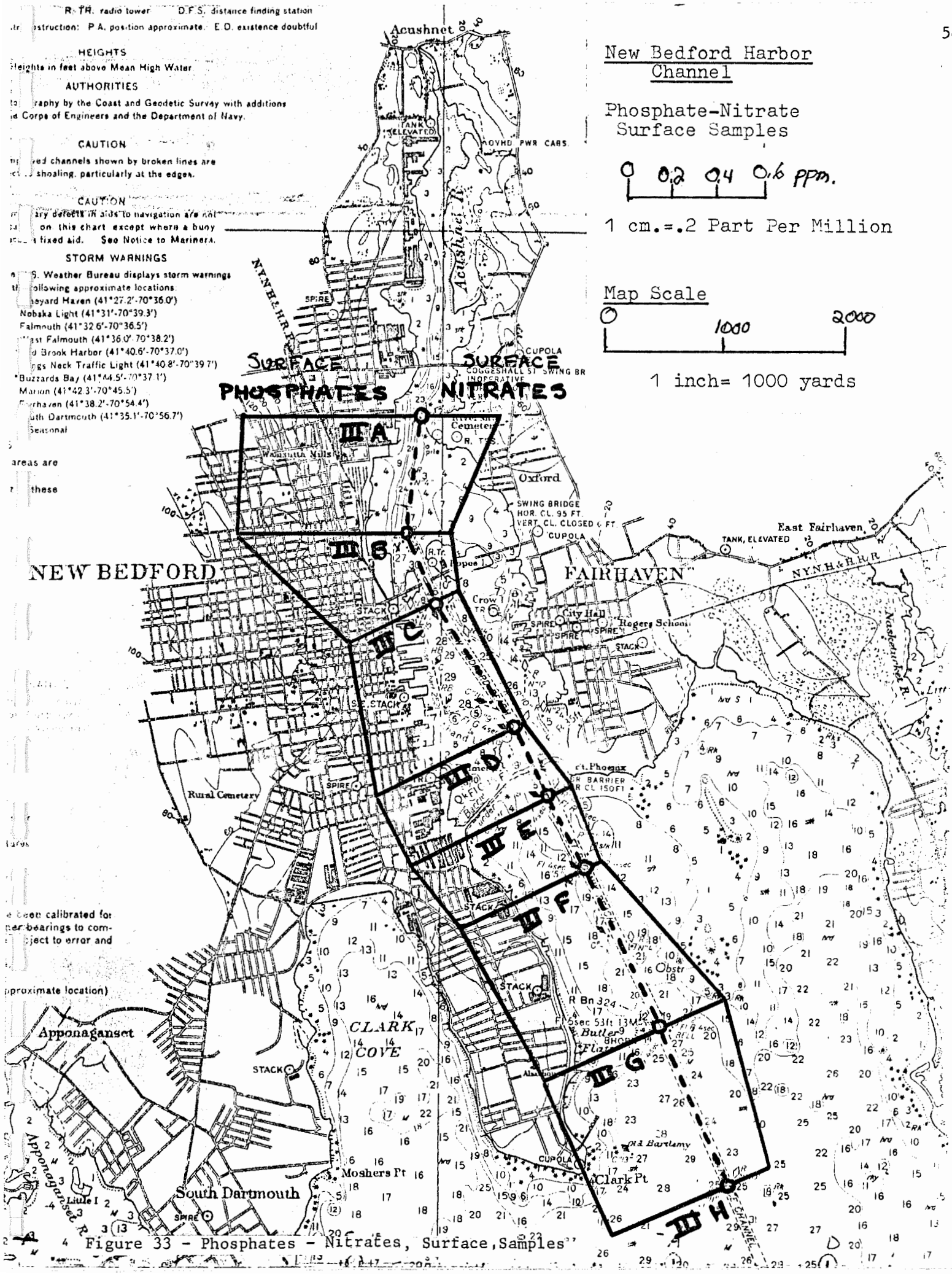


Figure 33 - Phosphates - Nitrates, Surface, Samples

New Bedford Harbor
Channel

Phosphate-Nitrate
Bottom Samples

0 0.2 0.4 0.6 ppm.

1 cm=.2 Part per Million

Map Scale

0 1000 2000

1 inch= 1000 yards

Phosphates
Bottom

Nitrates
Bottom

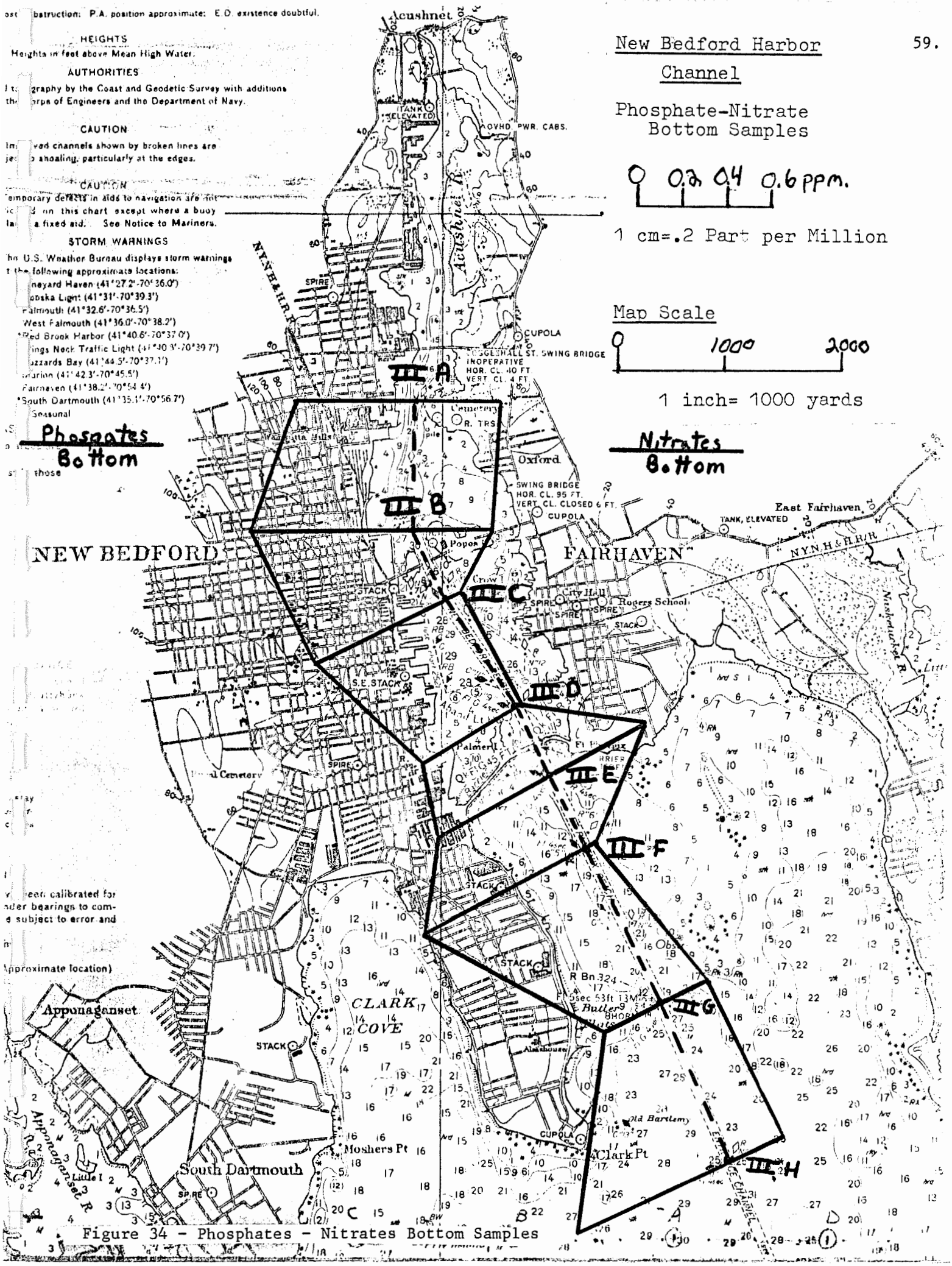


Figure 34 - Phosphates - Nitrates Bottom Samples

RECOMMENDATIONS

For future reference, and as a guideline for other classes at Sea Lab, this class wishes to make the following recommendations:

1. Perform the same water analysis and make a comparison on a yearly basis to evaluate the harbor's water quality.

2. Perform a quantative study on the effect of the fresh water intrusion on the biological activity in the harbor.

3. Study the topography extending from the first hydrographic station to the last hydrographic station.

4. Analyze the profiles constructed on a yearly basis.

5. Measure the content of various metals, such as copper, lead, nickle, etc. at each hydrographic station.

6. Measure various parameters, such as salinity and dissolved oxygen up the Acushnet River, to examine the effect of salt water on the river.

7. At each hydrographic station, obtain and test core sample.

8. Measure the rainfall during the summer and analyze the effect it has on the salinity of the harbor.

9. Analyze the rainfall for acidity and study the effect it has on the water's pH.

APPENDIX A - KEY TERMS

Absorbance:	A measure of the amount of light removed from a beam of light of known intensity and wavelength, after passing through a solution of known concentration, absorbing substance and test cell thickness.
Blank Reagent:	A sample to be used in conjunction with the Spectronic 20 and made with distilled water and all reagents to be used in a particular colorimetric test.
BOD Bottle:	Biochemical Oxygen Demand Bottle - used for collection of water samples for measuring dissolved oxygen present in a water sample.
Calibrate Curve:	That which is used to determine or mark the capacity or the graduation of various water parameters.
Contour Lines:	A line on a chart connecting points of equal value above or below a reference value, can protray temperature, salinity or other water properties.
Dissolved Oxygen:	Molecular oxygen in a solution with water, the amount of which is dependent on temperature, salinity and preasure, usually measured in parts per million (p.p.m.).
Estuary:	A semi-enclosed coastal body of water in which the ocean water is diluted by lower salinity water usually from a river or similar source.
Hydrographic Station:	A predetermined location in which a series of vertical water samples are collected.
Isotherm:	A line connecting points of equal temperature in a given body of water.
Microgram:	One millionth of a gram.
Micronutrient:	An organic or inorganic chemical compound used by phytoplankton or other organisms in primary production. Nitrates and phosphates are important micronutrients.
Nansen Bottle:	A device used by oceanographers to obtain subsurface samples of seawater.
Nitrate Ion (NO_3-1):	A micronutrient, formed by nitrogen fixing organisms and the action of bacteria on ammonia.
Phosphate Ion (PO_4-3):	A micronutrient which enters the water by sewage effluents, agrigultural runnoff, animal waste and decaying plants and animals.
p.p.m.:	Parts Per Million by weight.

Reagent: A pure substance which acts chemically in a known fashion, and as such, is used in chemical reactions to test or measure other chemical substances.

Sampling Tree: A series of collection bottles positioned at fixed depths for a given hydrographic station.

Saturation Percent: A comparison of the amount of gas dissolved in water sample to the maximum amount of the gas which can be dissolved at a given temperature, salinity and pressure of the water sample.

Specific Gravity: The ratio of the density of a substance to the density of the standard reference at specified conditions of temperature and pressure.

Stock Solution: A series of solutions containing known concentrations of a chemical species.

Titrate: The process by which the capacity of a solution of unknown concentration to combine with one of known concentration is measured.

Appendix B

Research Vessel Edgerton

Scientists working in the seas today are crossing the frontiers of knowledge. And sophisticated research vessels, like the Woods Hole Oceanographic Institution's *Alvin*, are aiding them in exploring the ocean floor at depths of 16,000 feet. But smaller research vessels, that are economical and flexible, are also needed to help us better understand the shallower waters in the coastal zone and on the continental shelves.

At MIT, the *R/V Edgerton*, a 65-foot, 90-ton ship, provides such a working platform for scientists and engineers. Managed by the Sea Grant Program, the *Edgerton*, since its christening in 1976, has taken hundreds of researchers to sea for a variety of oceanographic and engineering studies. The vessel is diesel powered with AC/DC redundancy for scientific instrumentation and ship's service. An A-frame aft and a telescoping crane forward are served by a free-fall, fast retrieval oceanographic winch located topside. Deck workspace and a lab will accommodate a research team of ten. Sea Grant's Massachusetts Marine Liaison Office manages the operation and charter of the vessel which is available to scientists and engineers from MIT, other universities, and industry.

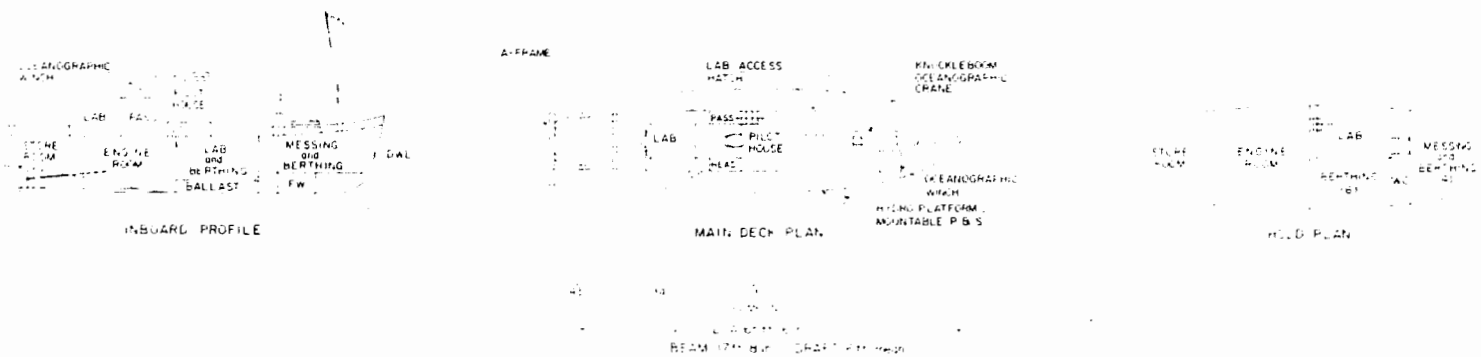


Figure 35 - Layout of the R/V Edgerton

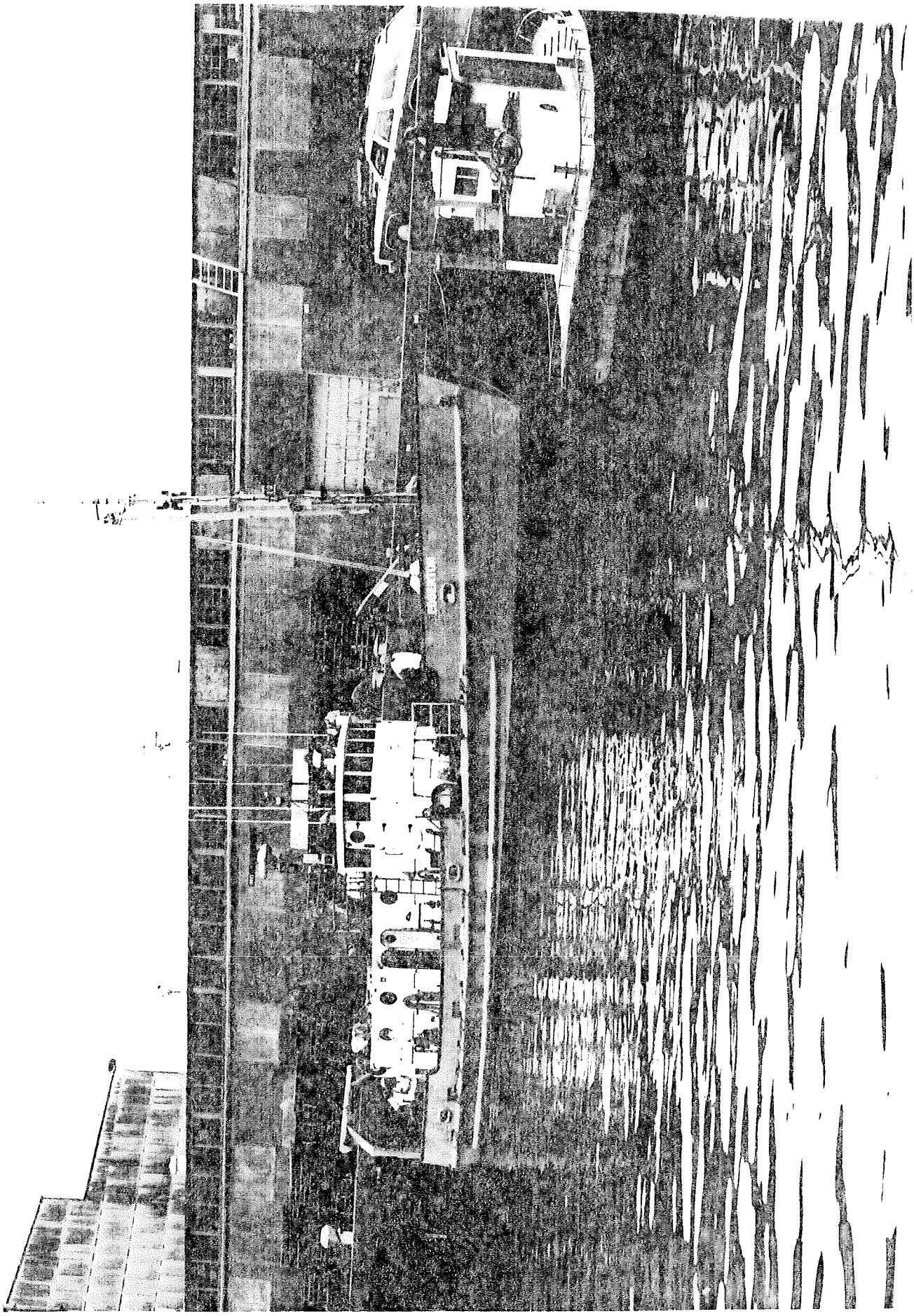


Figure 36 - Research Vessel Edgerton At State Pier, New Bedford

Appendix C

DISSOLVED OXYGEN (DO)

(Standard Methods, 12th Ed., p. 405)

DISSOLVED OXYGEN

Dissolved oxygen represents the amount of oxygen dissolved in water. DO is usually represented in parts per million (p.p.m.) and range from 7 p.p.m. to 14 p.p.m. DO is a very important parameter to measure because all aquatic organisms depend on it.

INTERFERENCE

In determining DO, various materials such as iron salts, suspended particles, and various metals cause interferences.

APPARATUS

1. Buret. graduated at 0.1 ml.
2. Three hundred ml glass-stoppered BOD bottles.
3. Wide-mouth Erlermeyer flask, 250 ml.
4. Ten ml measuring pipet.

REAGENTS

1. Manganous sulfate solution.
   Dissolved manganous sulfate crystals ($MnSO_4$-H_2O) in 80 to 120 ml distilled water. Filter through filter paper; then add distilled water to the filtered liquid to make a 200 ml volume.

2. Alkaline iodine-sodium azide solution.
   Dissolve 100 g sodium hydroxide (NaOH) in 100 to 120 ml distilled water; dissolve 30 g potassium iodide (KI) in 20 to 60 ml distilled water in a separate container. Exercise caution. Make solutions in a water cooled earthenware container, stirring constantly. Add the chemicals to the distilled water cautiously. Avoid breathing the fumes and bodily contact with the solution. Heat is produced when the water is added and the solution is very caustic.

   Mix both solutions when they are cool.

   Dissolve 2 g sodium azide (NaN_3) in 8 ml of distilled water. Exercise caution again. This solution is poisonous.

   Add the sodium azide solution with constant stirring to the cooled solution of alkaline iodide; then add distilled water to the mixture to make 200 ml.

3. Sulfuric acid.
   Use concentrated reagent-grade acid (H_2SO_4). Handle carefully, since this material will burn hands and clothes. Rinse affected area with tap water to prevent injury.

4. Sodium thiosulfate solution.
   Dissolve exactly 6.205 g sodium thiosulfate crystals ($Na_2S_2O_3$-$5H_2O$) in freshly boiled and cooled water, and make up to 1 liter. For preservation, add 0.4 g or 1 pellet of sodium hydroxide (NaOH).

5. Starch solution.
   Make a thin paste of 6 g of potato starch in a small quantity of distilled water. Pour this paste into one liter of boiling, distilled water, allow to boil for a few minutes, then settle overnight. Remove the clear supernatant and save; discard the rest. For preservation, add two drops of toluene ($C_6H_5CH_3$).

PROCEDURE

1. Completely fill a 300 ml BOD bottle with the sample to be analyzed by syphoning the sample slowly into the bottle and allowing it to overflow for a period to displace the volume of the bottle two or three times. Be sure no air is entrapped. (Note that samples for DO taken from streams or lakes should be taken in a special DO sampler available in most supply houses.)

2. By holding the tip of the pipet below the surface of the liquid, add two ml manganous sulfate solution and two ml alkaline iodide-sodium azide solution.

3. Replace stopper, avoiding trapped air bubbles, and shake well by gentle inversion. Repeat shaking after floc has settled halfway. Allow floc to settle again.

4. Remove stopper and add two ml of concentrated sulfuric acid. Hold pipet above the surface of the liquid. Mix until now floc is visible. Allow to stand for at least five minutes, but not in direct sunlight. The solution can stand safely for two hours in this condition.

5. Withdraw 203 ml of the solution in the Erlenmeyer flask and titrate with sodium thiosulfate solution until the yellow color almost disappears. (Note that since the standard BOD or DO bottle contains very close to 300 ml, it is simple to pour out 97 ml into a graduate and to titrate the remaining 203 ml of solution directly in the BOD bottle, thus eliminating two operations.

6. Add one ml starch solution and continue titration until the blue color just disappears.

7. Record the ml of thiosulfate used. Disregard any return of the blue color.

8. The amount of thiosulfate used equals the mg/l of dissolved oxygen.

SALINITY OF SEAWATER

Salinity is defined as the weight in grams of the dissolved inorganic matter in 1 kg of seawater after all bromide and iodide have been replaced by the equivalent amount of chloride, and all carbonates converted to oxide. The average salinity of ocean water is $35^{o}/oo$ (parts per thousand).

It was discovered by Knudsen in 1899 that there was a linear relationship between the salinity and precipitable halide concentration. Mohr titration is a method in which the halide is titrated with silver nitrate.

$$S^{o}/oo = 0.03 + 1.8050\ Cl\ ^{o}/oo$$

From the volume of silver nitrate ($AgNO_3$) used, the salinity can be determined by using the simplified Knudson tables (See Table I).

Apparatus: 50 ml burette
10 ml pipette
2 - 125 ml Erlenmeyer flask
2 - Glass stirring rods.

Reagents:

1. Standard seawater samples (See table recipe for artificial seawater)
2. Silver Nitrate (.2185 M) Add 37.11 g of silver nitrate ($AgNO_3$) to 1000 ml of water. Be sure the water is chloride free.
3. Potassium Chormate. Add 20 g of potassium chromate (K_2CrO_4) to 250 ml of distilled water.

Procedure:

Properly fill the burette with $AgNO_3$ and remove the drop on the tip of the burette with a piece of filter paper. Add 10.00 ml of the seawater to the 125 ml flask, about 10 ml of distilled water, and 5 drops of the K_2CrO_4 solution.

The burette stopcock is opened so the the $AgNO_3$ is added in a fine stream. At all times, stir the solution. When the red color of the Ag_2CrO_4 becomes fairly persistent, add the $AgNO_3$ dropwise with vigoruous stirring. The vigorus stirring is needed to break the precipitate and thus assure complete titration.

The dropwise addition is continued until a faint but definite red color persists in the liquid. Stop the titration and stir vigorously for 15 seconds. Any occluded Cl^- ions will dissolve and turn the solution back to a yellow color. Small fractions of $AgNO_3$ drops are then added until the liquid has a faint red-orange color. At this point, stop and wait about 30 seconds for the $AgNO_3$ solution in the burette to settle to a constant reading.

Take the final reading on the burette. Every titration that is done should be timed so that the exact same time interval occurs from the original addtion of the $AgNO_3$ to the final reading. This interval should be around 3 minutes.

Calculations:

Define:

$$f = \frac{\text{chlorinity of standard seawater}}{\tfrac{1}{2}\text{ direct titration of standard seawater as read from burette}}$$

$$dml = f \circ \frac{\text{direct titration of unknown samples}}{2}$$

Use the Knudsen table (see table) to find the salinity from the calculated dml.

RECIPES FOR ARTIFICIAL SEAWATER
19.00% Chlorinity

From McClendon, Gauls, and Mulholland (1917)

NaCl	20.726 g	N_3BO_3	0.088 g
$MgCl_2$	2.260	Na_2SLO_3	0.0024
$MgSD_4$	3.248	$Na_2Sl_4O_9$	0.0015
$CaCl_2$	1.153	N_3PO_4	0.0002
KCl	0.721	Al_2Cl_6	0.013
$NaKCO_3$	0.198	NH_3	0.002
NaBr	0.058	$LiNO_3$	0.0013

Add water to make a total weight of 1000 g

From Subov (1941)

NaCl	26.518 g	$CaCl_2$	0.725 g
$MgCl_2$	2.447	$NaHCO_3$	0.202
$MgSO_4$	3.305	NaBr	0.083

Add water to make a total weight of 1000 g

From Lyman & Flemming (1940)

NaCl	23.476 g	$NaHCO_3$	0.192 g
$MgCl_2$	4.981	KBr	0.096
Na_2SO_4	3.917	H_3BO_3	0.026
$CaCl_2$	1.102	$SrCl_2$	0.024
KCl	0.664	NaF	0.003

Add water to make a total weight of 1000 g

From Kalle (1945)

NaCl	28.014 g	$CaCO_3$	0.1221 g
$MgCl_2$	3.812	KBr	0.1013
$MgSO_4$	1.752	$SrSO_4$	0.024
$CaSO_4$	1.283	H_3BO_3	0.0277
K_2SO_4	0.8163		

Add water to make a total weight of 1000 g

From Kester, Dusdall, Conners, & Pytkowicz (1967)

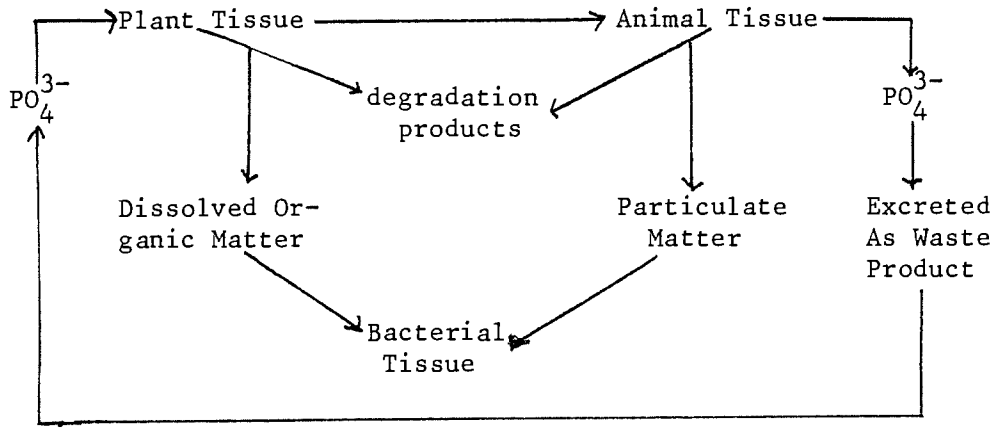
NaCl	23.926 g	H_3BO_3	0.026
Na_2SO_4	4.008	NaF	0.003
KCl	0.677	53.27 ml of a 1.0 M $MgCl_2$ solution	
$NaHCO_3$	0.196	10.33 ml of a 1.0 M $CaCl_2$ solution	
KBr	0.098	0.90 ml of a 0.1 M SrO_2 solution	

Table 5.0 - Recipes for Artificial Seawater

PHOSPHORUS

Phosphorus in the ocean occurs in various forms. In seawater of average salinity (35%) (pH 8) at 20°C, 87% of the phosphates occur as HPO_4^{2-}, 12% as PO_4^{3-}, and 1% as $H_2PO_4^-$.

The distribution of the various forms of phosphorus are controlled by biological agencies. The process in which phosphorus regenerates is called the phosphorus cycle. (See below.)



PHOSPHORUS CYCLE

APPARATUS

1. Colorimetric equipment.
   Spetrophotometer (Spectronic 20), with infared phototube for use at 880 my, producing a light path of.5 cm or larger.

2. Acid-washed glassware.
   All glassware should be washed with hot diluted hydrochloric acid (HCl) and rinsed with distilled water. Commercial detergent should be avoided because many contain phosphates. If hydrochloric acid is not available, fill all glassware with concentrated sulfuric acid (H_2SO_4) and let stand for 24 hours.

REAGENTS

a. Alcohol, ethyl (95%) or isopropyl.

b. Sulfuric acid (5N). Dilute 70 ml concentrated H_2SO_4 with distilled water to 500 ml.

c. Antimony potassium tartrate. Dissolve 4.3808 g of antimony pottassium tartrate in 200 ml of distilled water. Store in dark bottle at 4°C.

d. Amonium molylidate solution. Dissolve 20 g (NH_4), $Mo_7\ O_{24}\ 4H_2O$ in 500 ml of distilled water. Store in plastic bottle at 4°C.

e. Ascorbic acid: Dissolve 1.76 g ascorbic acid in 100 ml of distilled water. The solution is stable for about a week if stored at $4^{o}C$.

f. Combined reagent: Mix the above reagents in the following proportion for 100 ml combined reagent: 50 ml 5N sulfuric acid, 5 ml antimony potassium tartrate, 5 ml ammonium molybdate solution, and 30 ml ascorbic acid solution. Allow all reagents to reach room temperature before they are mixed, and mix in the order given. If turbidity forms in the combined reagent after the addition of the antimony potassium tartrate or ammonium molybdate, shake the combined reagent and let it stand for a few minutes until the turbidity dissappears before proceeding. The reagent is stable for at least 1 week if stored at $4^{o}C$.

g. Stock phosphate solution: Dissolve in distilled water 219.5 mg anhydrous potassium phosphate (dibasic) KH_2PO_4, and dilute to 1000 ml; 1.00 ml = 50.0 mg FO_4-P.

h. Standard phosphate solution: Dilute 50.0 ml stock phosphate solution to 1000 ml with distilled water to form a solution containing 2.5 ug P per 1.00 ml.

PROCEDURE

1. Treatment of sample: Pipet 20.0 ml clear sample into a clean, dry test tube or a 125 ml exlenmeyer flask. Add 1 ml ethyl or isopropyl alcohol. Mix thoroughly. Because curves prepared with ethyl alcohol are slightly different from those prepared with isopropyl alcohol, use the same alcohol in treating samples and standards. Add 1 ml combined reagent. Mix thoroughly and allow to stand 10 minutes for color development before reading in a specrophotometer at a wavelength of 880 my or a filter photometer equipped with a red color filter.

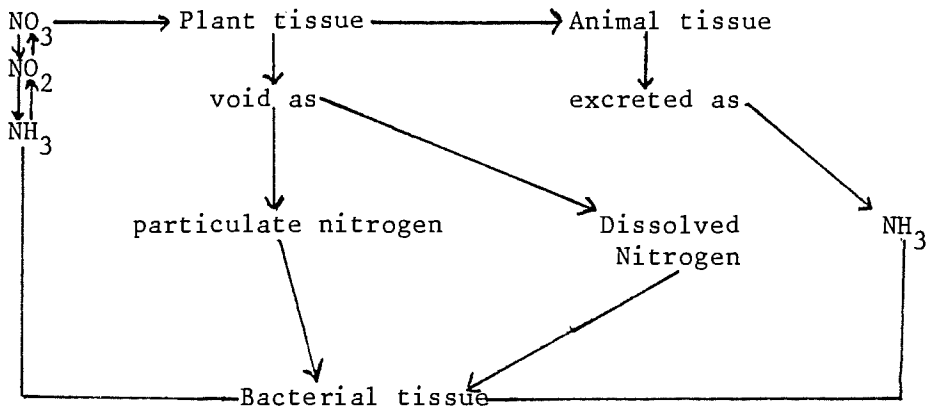
2. Correction for turbidity or interfering color: Prepare a blank by adding all the reagents except ascorbic acid and antimony potassium tartrate to the sample. Subtract the absorbance of the blank from the absorbance of each of the unknown samples.

3. Preparation of calibration curve: Use a distilled water blank with the combined reagent to make the photometric readings for the calibration curve. Plot absorbance vs. phosphate concentration which should form a strait line passing through the origin. Test at least one phosphate standard with each set of samples.

NITROGEN - NITRATE

Nitrogen exists in three principle forms: 1) Nitrate ion (1-500 mg NO_3^- - N/1); 2) Nitrate ion (c.1-SO mg NO_2^--N/1); 3) Ammonia (c.1-50 mg NH_3-N/1).

The process in which nitrogen is regenerated is called the nitrogen cycle (See diagram below.)



NITROGEN CYCLE

Apparatus

1. Colorimetric equipment: Spectrophotometer (Sepectronic 20) for use at 410 my and light path of 1 in.
2. Safety pipets
3. Boiling water bath
4. Test tubes (2.5 cm X 15 cm)

Reagents

a. Stock Nitrate - dissolve 721.8 mg of KNO_3 into 1000 ml of water. This is 100 mg 1/N.

b. Dilute 10.00 ml to 1000 ml of water.

c. Dissolve 1 g Brucine in 70 ml of hot distilled water. Add 3 ml of concentrated HCL - cool - add water to make 100 ml. Caution: Brucine is toxic.

d. Add 50 ml concentrated sulfuric acid (H_2SO_4) to 125 ml of water. Keep tightly stopped.

e. Dissolve 300 g NaCl to 100 ml of water.

Procedure

1. Treatment of sample: Take 1.00 to 10.00 ml of stock nitrate and dilute with 10 ml of water.
2. Each 10.0 ml sample (or aliquot diluted to 10 ml) place in cool water bath. Add 2 ml NaCl, swirl by hand and add 10 ml of H_2SO_4 solution - swirl. Add .5 ml Brucine, swirl, place in well boiled temperature bath. After exactly 20 minutes, immerse into cold water. Dry test tubes and read standard and samples against reagent blanks at 410 my.

3. Prepare Calibrate Curve: Plot absorbance vs. nitrogen concentration, which should form a straight line through the origin.

$$Mg/l\ NO_3 = mg/lNitrat\ N \times 4.43$$