Dissolved oxygen profiles made with an in situ polarographic device reveal structure in the form of inversions and gradient changes in the 100-600 meter depth zone off Oregon. Inversions 10-70 meters thick are traced over distances of 40 miles in some cases and are bracketed by a distance of 8 miles in others. The horizontal extent of these features agrees with observations of similarly-sized temperature and salinity structure reported by Stommel and Federov (1967) and by Hamon (1967).

Oxygen maxima are correlated with changes in the vertical temperature gradient. Corresponding salinity minima are sometimes found. This relationship between properties is consistent with the formation of oxygen structure by a horizontal mixing process off Oregon. The existence of significant horizontal gradients in properties over distances of tens of miles favors the interleaving
of dissimilar waters along density surfaces. A quantitative example of the horizontal mixing process yields temperature gradient changes near oxygen maxima similar to those observed.

The in situ production of oxygen structure by layers of oxygen-consuming materials is considered unlikely in the size range studied. A transient state vertical model indicates that the consumption layers required for this mechanism are more intense than is consistent with recent biomass measurements.

Diffusion calculations are used to model the decay of oxygen maxima. Calculated lifetimes range from 2.6 days for features 15 meters thick to 48.1 days for features 60 meters thick. These are considered estimates of the time scales associated with the stratification process.
An Investigation of High Resolution Dissolved Oxygen Profiles off the Oregon Coast

by

Hewitt Webb Jeter

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to my parents

to Gerrie

to Ernst Føyn
# TABLE OF CONTENTS

I. INTRODUCTION 1

Objectives 1
The Waters Off Oregon 3
Areal Classifications 3
Meridional Exchange Processes 5
Vertical Classifications 6

II. A POLAROGRAPHIC OXYGEN PROFILING SYSTEM 9

Instrumentation 9
Sensors 9
System Description 11
Oxygen Sensor Interface 13
Data Reduction 14
Procedure 14
Establishing the Calibration Line 17
Spatial Resolution 20
Response Time 20
Response Distance 21
Evaluation of in situ Measurements 26
Methods 26
Data 27
Systematic Trends 27
Regression Analysis and Correlation 31
Paired Differences 34
Summary 37

III. LARGE-SCALE OXYGEN DISTRIBUTIONS 40

Variation Along the Continent 40
Variation Along the Oregon Coast 44
Variation on a Twenty-Mile Scale 47
T-O Diagrams 50
T-AOU Diagrams 55
S-O Diagrams 58
Discussion 58

IV. A DESCRIPTION OF MEDIUM-SCALE OXYGEN STRUCTURE 64

Spatial Extent 66
Twenty-mile Spacing 66
Close Interval Spacing 68
Temporal Changes
  February 1970 Series  75
  May 1970 Series  78
Temperature and Salinity Distributions  81
  Temperature Measurements  81
  Salinity Measurements  85
Summary  89

V. MODELS FOR THE GENERATION AND DECAY OF MEDIUM-SCALE OXYGEN STRUCTURE  90

A Horizontal Mixing Model  90
  Introduction  90
  Model Formulation  91
  Results  93
  Discussion  94

A Layered Consumption Model  96
  Introduction  96
  Governing Equation and Solution Form  97
  Initial and Boundary Conditions  98
  Results  101
  Discussion  106

Diffusive Decay Models  107
  Introduction  107
  Vertical Model Formulation  109
  Vertical Model Results and Discussion  111
  Horizontal Model Formulation  116
  Horizontal Model Results and Discussion  118

VI. SUMMARY AND CONCLUSION  121

BIBLIOGRAPHY  124

APPENDIX I  129

APPENDIX II  149
<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Water Mass Locations, and Oxygen Distribution on the 26.8 Sigma-t Surface</td>
<td>4</td>
</tr>
<tr>
<td>2.</td>
<td>Isentropic Analysis Diagram and Representative T-S Relationships</td>
<td>7</td>
</tr>
<tr>
<td>3.</td>
<td>Block Diagram of the Oxygen Probe System</td>
<td>12</td>
</tr>
<tr>
<td>4.</td>
<td>Signal Conditioning Circuit</td>
<td>15</td>
</tr>
<tr>
<td>5.</td>
<td>Constructing the in situ Calibration Line</td>
<td>18</td>
</tr>
<tr>
<td>6.</td>
<td>Response to Oxygen Level Changes at Varying Temperatures</td>
<td>22</td>
</tr>
<tr>
<td>7.</td>
<td>Response to Idealized Oxycline and Oxygen Maxima</td>
<td>24</td>
</tr>
<tr>
<td>8.</td>
<td>Fidelity in Representation of Small Oxygen Extrema</td>
<td>25</td>
</tr>
<tr>
<td>10.</td>
<td>Comparison of Oxygen Probe Profiles to Hydrographic Sampling: June 1971</td>
<td>29</td>
</tr>
<tr>
<td>11.</td>
<td>Relative Frequency Distributions of Paired Differences</td>
<td>36</td>
</tr>
<tr>
<td>12.</td>
<td>Oxygen Distribution on the 26.8 Sigma-t Surface</td>
<td>41</td>
</tr>
<tr>
<td>13.</td>
<td>Dissolved Oxygen and AOU Profiles at Stations Along the Continent</td>
<td>43</td>
</tr>
<tr>
<td>14.</td>
<td>Oxygen and AOU Profiles at Stations Along the Oregon Coast</td>
<td>45</td>
</tr>
<tr>
<td>15.</td>
<td>Stations Along the Oregon Coast (NORPAC 1955)</td>
<td>46</td>
</tr>
<tr>
<td>17.</td>
<td>Superimposed Profiles: June 1971</td>
<td>49</td>
</tr>
<tr>
<td>Figure</td>
<td>Description</td>
<td>Page</td>
</tr>
<tr>
<td>--------</td>
<td>-----------------------------------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>18.</td>
<td>T-O Diagram: March 1971</td>
<td>51</td>
</tr>
<tr>
<td>19.</td>
<td>T-O Diagram: June 1971</td>
<td>52</td>
</tr>
<tr>
<td>20.</td>
<td>T-AOU Diagram: March 1971</td>
<td>56</td>
</tr>
<tr>
<td>21.</td>
<td>T-AOU Diagram: June 1971</td>
<td>57</td>
</tr>
<tr>
<td>22.</td>
<td>S-O Diagram: March 1971</td>
<td>59</td>
</tr>
<tr>
<td>23.</td>
<td>S-O Diagram: June 1971</td>
<td>60</td>
</tr>
<tr>
<td>24.</td>
<td>Mixing Pattern Sketch for Conceptual Isentropic Model</td>
<td>63</td>
</tr>
<tr>
<td>25.</td>
<td>Station Chart</td>
<td>65</td>
</tr>
<tr>
<td>27.</td>
<td>Close-interval Stations: May 1970</td>
<td>69</td>
</tr>
<tr>
<td>28.</td>
<td>East-West Transect: May 1970</td>
<td>72</td>
</tr>
<tr>
<td>29.</td>
<td>West-East Transect: May 1970</td>
<td>73</td>
</tr>
<tr>
<td>30.</td>
<td>North-South Transect: May 1970</td>
<td>74</td>
</tr>
<tr>
<td>31.</td>
<td>Profile Series at Station F: February 1970</td>
<td>76</td>
</tr>
<tr>
<td>32.</td>
<td>CTD Profiles: February 1970</td>
<td>79</td>
</tr>
<tr>
<td>33.</td>
<td>Profile Series at Station M: May 1970</td>
<td>80</td>
</tr>
<tr>
<td>34.</td>
<td>Correspondence of Oxygen Inversions to Changes in the Vertical Temperature Gradient</td>
<td>83</td>
</tr>
<tr>
<td>35.</td>
<td>Oxygen Probe and Hydrographic Profiles: Station NH-65, September 1969</td>
<td>87</td>
</tr>
<tr>
<td>37.</td>
<td>Horizontal Mixing Model Construction</td>
<td>92</td>
</tr>
</tbody>
</table>
Figure

38. Steady State Oxygen and Consumption Rate Profiles 100
39. Calculated Effect of a Consumption Rate Peak: Case I 102
40. Calculated Effect of a Consumption Rate Peak: Case II 103
41. Calculated Effect of a Consumption Rate Peak: Case III 104
42. Calculated Decay of a Small Oxygen Maximum by Vertical Diffusion 112
43. Calculated Decay of an Intermediate-sized Oxygen Maximum by Vertical Diffusion 113
44. Calculated Decay of a Large Oxygen Maximum by Vertical Diffusion 114
45. Calculated Decay of a Lateral Oxygen Maximum by Horizontal Diffusion 119
46. Simplified Sketches of the Polarographic Cell 130
47. Polarization Plateau 132
48. Polarographic Cell Temperature Characteristics (Grasshoff, 1962), and Temperature Correction Schematic 134
49. Temperature Correction Curve, With Experimental Values 140
50. Cell Response to a Step Change in Dissolved Oxygen Concentration at 20 Degrees Centigrade 143
51. Polarographic Cell Response to Oxygen Level Transients at Four Temperatures 144

Plate

1. Polarographic Cell Affixed to Instrument Package 10
## LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>I.</td>
<td>Regression Analyses of Oxygen Probe Data on Winkler Titrations: Parameter Estimates (with 95% confidence limits)</td>
<td>32</td>
</tr>
<tr>
<td>II.</td>
<td>Partition of Overall Precision</td>
<td>38</td>
</tr>
<tr>
<td>III.</td>
<td>Isentropic Correlations Between Properties Using 20 Mile Station Separation</td>
<td>54</td>
</tr>
<tr>
<td>IV.</td>
<td>Characteristics of Several Medium Scale Oxygen Features</td>
<td>84</td>
</tr>
<tr>
<td>V.</td>
<td>Consumption Rate Parameters and Characteristics for Layered Consumption Model</td>
<td>105</td>
</tr>
<tr>
<td>VI.</td>
<td>Oceanic Structure Lifetime Estimates (Stommel and Federov, 1967)</td>
<td>108</td>
</tr>
<tr>
<td>VII.</td>
<td>Calculated Half-lives and Lifetimes of Oxygen Maxima Under Vertical Diffusive Decay</td>
<td>115</td>
</tr>
<tr>
<td>VIII.</td>
<td>Normalized Temperature Correction Slopes, With Fitted Values and Experimental Comparisons</td>
<td>138</td>
</tr>
<tr>
<td>IX.</td>
<td>Hydrographic and Oxygen Probe Data, March 1971</td>
<td>157</td>
</tr>
<tr>
<td>X.</td>
<td>Hydrographic and Oxygen Probe Data, June 1971</td>
<td>159</td>
</tr>
<tr>
<td>XI.</td>
<td>Results of Difference Analysis: Statistics and Parameter Estimates (with 95% Confidence Limits)</td>
<td>162</td>
</tr>
<tr>
<td>XII.</td>
<td>Comparisons of Overall Precision</td>
<td>166</td>
</tr>
</tbody>
</table>
AN INVESTIGATION OF HIGH RESOLUTION DISSOLVED OXYGEN PROFILES OFF THE OREGON COAST

CHAPTER I

INTRODUCTION

1. Objectives

The use of in situ (on site) profiling instruments has revealed variability in the distributions of oceanic properties on smaller scales than is found by routine hydrographic sampling. Continuous profiles of temperature and conductivity often show "structure" in the form of inversions and abrupt gradient changes. These features have received intensive observational and theoretical study in the last decade (Stommel and Federov, 1967; Turner, 1967; Tait and Howe, 1968; Stern, 1969; Simpson, 1971).

Small features have also been found in continuous dissolved oxygen profiles, but have not received as much attention. Føyn (1955, 1965) found inversions and gradient changes near the pycnocline in Norwegian fjords. Oxygen structure was also seen in continuous profiles made by Kanwisher (1959) and by Grasshoff (1962). In addition, recent tests of the Minos DOM Dissolved Oxygen Monitor by Beckman Instruments, INC. (1969), Carlson (1970), and by VanLandingham and Greene (1971) have shown considerable structure...
in both the Atlantic and Pacific oceans.

The purpose of this study is to examine details of the dissolved oxygen distribution in the waters overlying the continental slope and continental rise off Oregon. Profiles made with an in situ instrument are used to describe the oxygen structure in the "medium-scale" range, defined by Hamon (1967) to extend 10-100 meters in the vertical and tens of kilometers in the horizontal. The choice of this range is fixed by the spatial resolution of the oxygen profiling instrument. Although the variability of properties on this scale can be studied using closely-spaced hydrographic bottles (Cooper, 1967), the long sampling and analysis times necessary to locate and follow features of interest makes it impractical in most cases.

The emphasis of this work is to compare the medium-scale oxygen structure, and associated temperature and salinity measurements, with the overall distribution of properties along the western coast of North America. Since the interleaving of waters of dissimilar properties is considered one of the most probable mechanisms for generating medium-scale temperature and salinity structure (Stommel and Federov, 1967; Pingree, 1969; Simpson, 1971), a similar mechanism will be sought to explain the observed dissolved oxygen structure. The production of oxygen features by in situ non-conservative processes is also considered. Finally, the time scales over which the observed features persist are estimated and are
compared to those estimated by Stommel and Federov (1967) for medium-scale temperature and salinity structure.

2. The Waters off Oregon

Areal Classifications

This study is concerned with waters lying seaward of the continental shelf and below the zone of high oxygen, temperature and salinity gradients. The region between the 26.2 and 27.2 sigma-t (density) surfaces is of primary interest. Coastal upwelling off Oregon is believed to have principal influence above this zone (Mooers, Collins and Smith, 1972).

The Northeastern Pacific has been classified in several ways. On the basis of its temperature-salinity (T-S) relationship it has been designated part of the Transition Region in the overall classification of the North Pacific Ocean (Sverdrup, Johnson and Fleming, 1942). This region extends along the western coast of North America (Figure 1), and displays a T-S correlation intermediate between that of Subarctic Waters to the north and Equatorial Waters to the south. More recent classifications have been discussed by Dodimead, Favorite and Hirano (1963). The locus of a vertical isohaline of 34.0‰ divides a northern Subarctic region from a southern Subtropical region. This boundary is located at about 42° N over most of the North Pacific but turns southward as the
Figure 1. Water Mass Locations*, and Oxygen Distribution on the 26.8 Sigma-t Surface**

*Redrawn from Sverdrup, Johnson and Fleming (1942), p. 740
**From Reid (1965), p. 68
continent is approached, so that the previously-defined Transition Region is included in the Subarctic classification. Dodimead, Favorite and Hirano (1963) then subdivide the two principal regions into several "domains," designed to replace earlier water mass concepts.

Meridional Exchange Processes

The process of mixing between high and low latitude waters is important in this work. Tibby (1941) and Rosenberg (1962) studied the distributions of temperature and salinity adjacent to the continent by isentropic analysis. Simple mixing along surfaces of constant sigma-t is assumed. The T-S relationships found at stations C and B (Figure 1) were used to represent the high latitude and the low latitude source waters, respectively. These T-S diagrams are shown in Figure 2. For a given value of sigma-t, the Subarctic waters are characterized by relatively low salinity and temperature, while Equatorial waters display high salinity and temperature. Under the assumptions of isentropic analysis, the relative composition of water at any location adjacent to the continent may be derived by plotting the observed T-S relationship on Figure 2, and by reading off the mixture percentages at various density values. The T-S curves from three stations used by Rosenberg (1962) to represent the waters off California, Oregon, and Washington are drawn in
Figure 2.¹

Lateral exchange of the northern and southern waters is further implemented by a variety of meridional currents. A broad and slow equatorward flow, forming part of the general anticyclonic circulation of the North Pacific, is called the California Current. It is interrupted in winter by the narrower, poleward-flowing Davidson Current. Evidence for and against a northward-flowing California Undercurrent and California Countercurrent has been reviewed by Blanton (1968). Although poleward-flowing subsurface currents have been reported on the Oregon continental shelf (Collins et al., 1968; Collins and Pattullo, 1970) and in the shallow waters over the continental slope (Sakou and Neshyba, 1972), extensive drogue measurements 70 kilometers off the coast showed mean currents toward the south at all depths to 500 meters (Stevenson, Pattullo and Wyatt, 1969).

**Vertical Classifications**

The Northeast Pacific has been divided into various zones corresponding to conspicuous hydrographic features or physical processes. Dodimead, Favorite and Hirano (1963) designated an

¹Station 3 actually lies to the north of Washington.
Figure 2. Isentropic Analysis Diagram and Representative T-S Relationships
upper zone of seasonal influence (to about 150 meters), and a lower zone of a more permanent nature.

An Intermediate Water zone having widespread influence in the North Pacific has been studied in detail by Reid (1965). This water is formed at high latitudes, and flows on or near the 26.8 sigma-t surface under most of the central Pacific, where it is identified as a salinity minimum. This water is also a source of dissolved oxygen, an oxygen maximum sometimes being found near the salinity minimum. North Pacific Intermediate Water is generally traced to the subarctic boundary west of North America, where the salinity minimum disappears. The depth of the 26.8 sigma-t surface is at 500-700 meters in the central parts of the Pacific but rises to about 300 meters off Oregon. The distribution of properties on this surface has been plotted by Reid (1965). The dissolved oxygen distribution, which is pertinent to this study, is shown in Figure 1.

An intense oxygen minimum zone occurs over most of the Pacific Ocean. The depth of the oxygen minimum has been plotted by Weyl (1965) and appears near 800 m off Oregon. This zone may be a region of sluggish circulation between the overlying oxygenated waters and deeper waters of Antarctic origin (Weyl, 1965).
A POLAROGRAPHIC OXYGEN PROFILING SYSTEM

1. Instrumentation

Sensors

The in situ profiling system used in this work employs a membrane-covered polarographic cell as an oxygen sensor (Delta Scientific, model 110-1). The characteristics of this device were measured in the laboratory and are presented in Appendix I. Such cells respond to the partial pressure of oxygen rather than to oxygen concentration (Clark et al., 1953; Kanwisher, 1959). The partial pressure of a dissolved gas is directly proportional to its concentration in solution. The proportionality constant is a function of temperature, salinity, and pressure. Since concentration rather than partial pressure units are desired, an in situ calibration method is applied which permits readout in concentration units, compensating for the salinity and hydrostatic pressure effects.

The instrument package is pictured in Plate I. Brackets cut from one inch PVC stock and two stainless steel hose clamps hold the polarographic cell in place. A platinum resistance thermometer (Rosemount model 171 CE) is mounted beneath the oxygen sensor.
PLATE I  Polarographic Cell Affixed to Instrument Package
An MB/ALINCO 0-3000 psia strain gauge pressure transducer is mounted inside the same endcap, with a passage communicating to the outside. All sensors are bottom-most when the instrument is lowered.

In order to make the oxygen cell easily removable, electrical leads were replaced by pressure-tight Mecca (ser. M-16) fittings. Techniques developed for sealing the cell against electrical leakage to seawater ground are discussed in Appendix I.

System Description

A block diagram of the oxygen probe system is shown in Figure 3. Signals from the three sensors are scanned in succession, each two-second period including a reading of each. A digitizer then reduces each signal to a 12-bit binary number by a successive-approximation process. The fundamental design of the digital conversion and scanning system is presented by Albin (1968).

The binary data are transmitted serially to shipboard through a single-conductor armored cable. A Geodyne model 990 digital interface aboard ship serves to receive the data, as well as to provide a square wave clock signal which drives the digital circuitry in the probe. The unmodified binary data are stored on paper tape by a Tally model 420 perforator. Although this tape is the primary
Figure 3. Block Diagram of the Oxygen Probe System
data source, a program in the shipboard Digital PDP-8/S computer allows the raw data to be printed out in octal form by teletype during each cast. This information is used for monitoring the instrument's performance and for visualizing trends in the measured parameters.

Data are reduced by reading the punched tape into the computer, where it is interpreted through calibration and temperature-correction formulae. Values of depth (m), temperature (°C), and dissolved oxygen (ml/l) are printed out by teletype as the data tape is being read. The interpretation of temperature and depth information is by linear interpolation of the respective sensor signals between calibration values. The reduction of oxygen data follows the procedure of interpolation and temperature correction described in Section 2. The computer program allows new calibration data to be entered via teletype at any time.

**Oxygen Sensor Interface**

In order to use a polarographic cell, the supporting electrical system must supply a polarization potential to the electrodes, and provide a means for measuring the resulting current (Appendix I). When used for profiling, it is important that the current flow through the sensor is uninterrupted during measurement, since the cell requires several minutes to reach steady state after startup.

The data acquisition system used in this work requires sensor
output in the form of a voltage which varies continuously with the measured parameter between zero and 4.4 volts. As the polarographic cell output is in the form of a current (0-40 \( \mu \)a under most oceanic conditions), a signal conditioning circuit such as shown in Figure 4 is required. This circuit is advantageous in that it offers low impedance to the cell and has a low impedance output. The varying cell current, \( i \), is linearly converted to a voltage, \( E_0 \), according to the formula \( E_0 = i R_f \). The value of the feedback resistor \( R_f \) is chosen so that the maximum expected cell current is converted to the maximum voltage which the digitizing system is designed to measure. A value of 110 K is used in this work. Zero adjusting of the output is accomplished with the variable resistor shown wired between pins 1 and 5. The resistor \( R_f \) (50 K) prevents undesired oscillation of the amplifier.

2. Data Reduction

Procedure

The current passed by a membrane-covered polarographic cell is influenced by temperature, salinity, and hydrostatic pressure as well as by the dissolved oxygen content of the sample (Appendix I). In this work a direct measure of the cell current is transmitted to shipboard by the data acquisition system. Temperature effects are
Figure 4. Signal Conditioning Circuit
then corrected by computer, while pressure and salinity effects are approximately compensated by a method of *in situ* calibration.

Data reduction is accomplished in two stages. The procedure is an adaptation of that described by Grasshoff (1962). A calibration line is established at a fixed temperature $TC$. The telemetered cell currents are applied to the calibration line by interpolation to derive preliminary oxygen values $O_{TC}$. Final oxygen concentrations at the *in situ* temperatures $T$ are then computed from the formula

$$O_T = \frac{f(TC)}{f(T)} \cdot O_{TC}$$

where:

- $O_T =$ oxygen concentration at the sample temperature, $T$
- $O_{TC} =$ interpolated oxygen concentration from the calibration curve at temperature $TC$
- $f =$ generalized temperature correction function.

Equation 1 is derived from the polarographic cell characteristics in Appendix I. The empirical function $f$, also derived in the appendix, is given by

$$f(T) = A + BT + CT^2 + DT^3 + ET^4,$$
where: \[ A = 1.701968 \times 10^0 \]
\[ B = -9.277200 \times 10^{-2} \]
\[ C = 2.619997 \times 10^{-3} \]
\[ D = -3.598612 \times 10^{-5} \]
\[ E = 1.492265 \times 10^{-7} \].

Temperature correction is nominally six percent per degree (cell currents increase with increasing temperatures). One-third of this figure stems from the temperature coefficient of oxygen solubility in water, and the balance results from changes of the membrane diffusivity with temperature.

**Establishing the Calibration Line**

The oxygen probe system is calibrated against chemical analysis of two water samples, one taken at shallow depths (0-50 m), and the other at intermediate depths (200-1000 m). The samples are extracted from either a hydrographic cast or from electrically-tripped bottles attached to a CTD system. Casts for reference samples are taken as close in time as possible to the oxygen probe casts. Depth, temperature, and dissolved oxygen data are required from the two reference samples.

The method for constructing a calibration line from in situ data can be illustrated with reference to Figure 5. The dissolved oxygen analysis from the shallower reference bottle, \( O_s \), and the binary-coded polarographic cell current from the same depth or temperature surface, \( i_s \), establish point \( s \) on the diagram. The
calibration temperature $TC$ is chosen as the in situ temperature at this calibration point. In a similar way, the oxygen analysis and corresponding encoded cell current from the deep reference sample ($O_d$ and $i_d$) establish point $d$. Since the temperature at the deep sample, $T_d$, will in general differ from that of the shallow sample, $TC$, a line from $s$ to $d$ would not constitute a calibration line.

![Graph](image)

**Figure 5. Constructing the in situ Calibration Line.**

In order to complete the construction, a re-arrangement of Equation 1 is used to calculate $O_{dTC}$, the deep oxygen value corrected to temperature $TC$:

$$O_{dTC} = \frac{f(T_d)}{f(TC)} \cdot O_d.$$  \hspace{1cm} (3)
This formula is derived by solving Equation 1 for $O_{TC}$ and adding the subscript $d$ to denote the deep reference sample. The current reading $i_d$, together with $O_{dTC}$ then establish point $dTC$ in Figure 5. The straight line between point $s$ and point $dTC$ is then the in situ calibration line at temperature $TC$. In practice the equation of this line is stored in the computer, and preliminary oxygen values $O_{TC}$ are derived from telemetered cell currents $i$ by interpolation.

The choice of optimum depths for locating reference sample bottles is dependent upon the gross oxygen structure in the water column. It is desirable that the oxygen gradient be as small as possible in the chosen sites, so that the polarographic cell is in equilibrium with its environment. The sites should also differ considerably in oxygen concentration. Finally, the shallow and deep reference points should be sufficiently separated so that the in situ calibration line reflects salinity and pressure change in the water column. The oceanic mixed layer and various intermediate depths near 600 m meet the above requirements in waters off Oregon. The accuracy and precision of profiles made using calibration at these depths will be examined in Section 4.
3. Spatial Resolution

Response Time

When a polarographic cell is used for oceanic profiling, its response time limits the spatial resolution of measurement. Abrupt changes of oxygen content in the water column may be smoothed, and small features completely obscured, by a cell which has slow response. According to Carey and Teal (1965), response to changes in oxygen concentration is proportional to the square of membrane thickness and inversely proportional to membrane diffusivity.

Although membranes are currently available which are sufficiently tough for oceanographic use while having response times less than one second, their use may be barred in practice by lowering rate restrictions. Relative motion between the cell and the sample solution must be rapid enough to sweep away a boundary layer of oxygen-depleted water adjacent to the membrane. In the profiling configuration used, this motion is provided by the lowering rate. Since membranes having short response times require faster relative motion for reliable operation (Carey and Teal, 1965), the desired lowering rate provides a limitation on the choice of membrane. It is advisable to select a membrane having response slow enough that its use with normal winch speeds will not incur the risk
of poor data due to insufficient velocity. As the rolling motion of the ship can alternately add to and subtract from the probe's lowering speed, a significant margin should be left between the minimum permissible velocity and the anticipated lowering rate. The cell used in this work is lowered at near 0.5 meters per second, well above the approximately 5 centimeters per second minimum jogging speed recommended by the manufacturer for the 0.001 inch Teflon membrane used.

Transient response of the cell was measured at several temperatures in the laboratory. The procedures are discussed in Appendix I. Figure 6 shows the times required for the cell to achieve 63 percent and 97 percent response to step changes in oxygen content, as functions of temperature. The former percentage corresponds to the time constant (1 - 1/e response), and the latter is a convenient measure of "full response." Measurements of transient thermal behavior are similar (Appendix I).

Response Distance

The spatial resolution of in situ measurement is related to the cell response time through the instrument's lowering rate. A cell achieving 97 percent response in t seconds, if lowered through the water at R meters per second, will require a distance \( L = t \cdot R \) meters to record 97 percent of a step change in oxygen content in
Figure 6. Response to Oxygen Level Changes at Varying Temperatures
the water column (Figure 7, upper). If 97 percent is considered "full response," then it can be said that the amplitude of oxygen extrema or structure having characteristic thicknesses greater than or equal to $L$ will be faithfully reported by the instrument.

The utility of the response distance concept is illustrated by the rectangular maxima in Figure 7 (lower). Although the shape of an extremum of thickness $L$ may be largely distorted, the instrument still shows its presence and approximate amplitude. Features having thickness less than $L$ will be aliased both in amplitude and in shape, as suggested by the oxygen maximum of thickness $L/2$. In this case, only 83 percent of the feature's amplitude is recorded. The percentage of total amplitude attained is plotted for different fractions of $L$ in Figure 8, based on idealized rectangular extrema.

The cell used in this work is lowered at a nominal speed of 0.5 meters per second. Using the 97 percent response times shown in Figure 6, the range of $L$ is calculated as follows:

$$L_{20\%} = (0.5 \text{ m/sec}) (13.7 \text{ sec}) = 6.8 \text{ m}$$

$$L_{5\%} = (0.5 \text{ m/sec}) (25.0 \text{ sec}) = 12.5 \text{ m}.$$
Figure 7. Response to Idealized Oxycline and Oxygen Maxima
Figure 8. Fidelity in Representation of Small Oxygen Extrema
4. Evaluation of *in situ* Measurements

**Methods**

The accuracy of *in situ* oxygen measuring devices must be established by comparison of profiles to standard chemical analyses of samples drawn from the water column. Although tests can be performed under different conditions of salinity, temperature, and pressure in the laboratory, it is hazardous to extend such results to the oceanic environment where these factors vary simultaneously, and where other factors such as ship roll, winch speed, and electrical noise are operative. Establishing *in situ* comparisons presents several sampling problems, however. In all but one of the studies presented in this section (VanLandingham and Greene, 1971) hydrographic casts are taken shortly before or after making an *in situ* oxygen profile. Analysis of the samples drawn from the hydrographic bottles is then compared to the oxygen probe readings at the same depths. With this procedure it is unlikely that the waters sampled by the two methods are true replicates. Nevertheless, statistical analysis of a large number of such data can be used to characterize instrument accuracy and precision.
Data

Profiles made with the digital oxygen probe system were submitted to extensive comparisons with standard hydrographic sampling on two occasions. Stations NH-65, NH-85, and NH-105 off the Oregon Coast (Figure 25) were occupied in March 1971 and again in June 1971. Hydrographic casts using non-metallic NIO sample bottles were conducted in a routine manner on each station. Oxygen probe casts were taken soon afterwards, where the minimum time interval between releasing the messenger and lowering the probe was 22 minutes and the maximum interval was 55 minutes. Calibration of the oxygen probe system by the method described in Section 2 was effected at each station.

The results of modified Winkler analysis (Strickland and Parsons, 1965) for the March and June cruises are presented in Tables IX and X (Appendix II), along with oxygen probe readings at corresponding depths. Differences between the paired observations are also tabulated. The profiles are plotted side-by-side in Figures 9 and 10. Chemical analyses appear as circles, and oxygen measurements, read every five meters, appear as dots.

Systematic Trends

It is evident from Figures 9 and 10 that the greatest disparity
Figure 9. Comparison of Oxygen Probe Profiles to Hydrographic Sampling: March 1971
Figure 10. Comparison of Oxygen Probe Profiles to Hydrographic Sampling: June 1971
between the two methods occurs in the shallow seasonal oxycline. Differences of several tenths milliliter per liter are shown in Tables IX and X. As discussed in Section 3, the response of the polarographic cell is insufficient to allow equilibration with the environment in regions of extreme oxygen gradient. In addition, small errors in depth determinations cause anomalously large replication errors in such regions. Data from the seasonal oxycline are disregarded in the statistical analyses presented in this chapter since comparable oxygen gradients were not found in the waters used to test the Beckman Minos DOM system, and since the statistics are used in part to draw comparisons between the two instruments.

It is also evident in Figures 9 and 10, particularly in the June data, that oxygen probe readings are systematically higher than the Winkler analyses in mid-depths (between calibration points), and systematically lower outside this depth range. This trend is further shown in the tables of data where the algebraic sign in the difference column changes between the three depth zones. Failure of the cell to equilibrate with the environment may contribute to this systematic deviation, since negative differences are found when the probe is being lowered through a decreasing oxygen level and positive deviations occur when the oxygen concentration is rising. Relatively large discrepancies of this sort appear near the surface in the June data.
where the oxygen level rapidly increases with depth due to a sub-
surface maximum.

Further contributions to equilibration error near the ocean
surface arise from insufficient relative velocity. Since the probe
is held at rest at the surface before lowering, these readings are
expected to be anomalously low due to "stagnation" of the sensor.
This trend is evident in the data from both cruises.

Regression Analysis and Correlation

The results of simple linear regression analysis of the March
and June 1971 data are presented in Columns 3, 4, and 5 of Table I.
The oxygen probe readings are considered the dependent variable (y).
Also shown are the results of similar analyses of data obtained by
VanLandingham and Greene (1971), using the Beckman Minos DOM. 2
The latter study is fundamentally different, however, since sample
bottles were attached to the instrument itself, largely eliminating
replication error. Separate tabulation is shown omitting cast 3,
when the probe was allegedly lowered at insufficient speed.

The table shows point estimates of the regression line slopes
and intercepts and the standard deviation about the regression lines,

2Only "down-cast" data were analyzed, and all chemical
determinations which the authors concluded were erroneous (about
25 percent of the total) were discarded.
| Source                  | Sample Size | Regression Line Intercept | Regression Line Slope | Standard Dev. About Regression Line, S̄<sub>y|x</sub> | Correlation Coefficient r | Coeff. of Determination r² |
|------------------------|-------------|---------------------------|------------------------|-----------------------------------------------------|--------------------------|-----------------------------|
|                        | (1)         | (2)                       | (3)                    | (4)                                                 | (5)                      | (6)                         |
| Digital Oxygen Probe   | 42          | 0.067                     | 0.983                  | 0.071                                               | 0.9995                   | 0.9991                      |
| (March '71)            |             |                           |                       |                                                     |                          |                             |
| Digital Oxygen Probe   | 48          | 0.072                     | 0.970                  | 0.138                                               | 0.9979                   | 0.9959                      |
| (June '71)             |             |                           |                       |                                                     |                          |                             |
| Beckman Minos DOM      | 47          | 0.334                     | 0.900                  | 0.127                                               | 0.9743                   | 0.9493                      |
| (VanLandingham & Greene, 1971) |          |                           |                       |                                                     |                          |                             |
| " " "                   | 36          | 0.067                     | 0.983                  | 0.066                                               | 0.9945                   | 0.9890                      |
| (without cast 3)       |             |                           |                       |                                                     |                          |                             |
|                        |             |                           |                       |                                                     |                          |                             |

TABLE I. Regression Analyses of Oxygen Probe Data on Winkler Titrations: Parameter Estimates (with 95% confidence limits)
as calculated by the computer program SIMLIN (Yates, 1967). Symmetric 95 percent confidence intervals appear in parentheses, constructed by methods described in Wine (1964). In both tests of the digital oxygen probe the estimated intercept of the regression line is near 0.07 ml/l. This value is significantly different from zero at the five percent level. Similarly, the regression line slopes are both found to be significantly less than unity at the five percent level. These tests show that the in situ measurements are biased relative to the Winkler analyses, the former being greater at low concentrations and the bias decreasing algebraically with increasing oxygen concentration. This trend reflects the systematic error at shallow and intermediate depths where most comparison data were obtained. Values of $s_{y|x}$ will be discussed later, together with similar measures of precision.

Regression analysis of data obtained with the Beckman Minos DOM also yields positive intercepts and slopes less than unity. When all 47 samples are retained, the slope and intercept are significantly different from one and zero, respectively, at the five percent level. When the comparisons from cast 3 are deleted (the probe being lowered at insufficient speed), the calculated slope and intercept are not significantly different from these values. The broader confidence intervals obtained in tests of this instrument reflect the smaller range of oxygen concentrations used (3.33 to 4.47 ml/l, with one
observation at 5.85 ml/l, compared to a range of 0.35 to 6.81 ml/l in the case of the digital probe). Data covering a wide range of the measured parameter provide a better test of the instrument (Wine, 1964), and the resulting narrower confidence intervals assign more certainty to point estimates. It should be stated, however, that the Minos DOM was tested in waters having a larger total temperature variation (about 22°, compared to 5° in the March cruise and 11° in the June cruise).

Values entered in Columns 6 and 7 of Table I are point estimates of the correlation coefficient and its square, calculated as part of the SIMLIN execution. The values of \( r^2 \) are near unity in all cases, showing a high degree of linear dependence between in situ measurements and Winkler analyses (Wine, 1964). Less than one-half percent of the total variation in digital oxygen probe measurements is attributable to extraneous causes. The somewhat inferior values obtained from tests of the Minos DOM partly reflect the smaller range of oxygen concentrations used.

**Paired Differences**

Statistics based on the numerical difference between oxygen probe readings and corresponding chemical analyses are useful for characterizing instrument reliability. The effect of varying oxygen concentration level is canceled by the subtraction, leaving an overall
measure of the systematic and random relationships between the two methods. A statistical model equation developed in Appendix II permits the following evaluation of instrumental accuracy and precision.

Paired difference data resulting from the March and June 1971 tests are presented in Tables IX and X. The relative frequency distributions of these values are shown in Figure 11, grouped in classes of 0.05 ml/l. Also shown are the distributions resulting from two tests of the Beckman Minos DOM system (VanLandingham and Greene, 1971; Carlson, 1970). In the latter case, differences were read from a plot. It is evident that the digital oxygen probe displayed greater central tendency on the March cruise than on the June cruise. Similarly, a greater range of differences is observed in Carlson's evaluation of the Minos DOM than in VanLandingham and Greene's evaluation. 3

Statistical tests described in Appendix II show that neither the digital oxygen probe nor the Beckman Minos DOM system displays overall bias relative to Winkler analysis. The systematic error in various parts of the water column remains, as reflected in the results of regression analysis, Table I.

3Carlson's tests, like the tests of the digital probe, contain replication error due to hydrographic comparisons.
Figure 11. Relative Frequency Distributions of Paired Differences
The precision of in situ measurement is demonstrated in Table II, based on the analysis of variance in Appendix II. Only data from the June 1971 cruise is treated since it was found to be significantly poorer than the March data and since conservative estimates of precision are desired. The standard deviation of the paired differences \( s_d \) is a measure of the overall precision of measurement. It is comparable in magnitude to \( s_y|x' \), the dispersion about the regression line in Table I. The contributions to overall variance which stem from the variance of Winkler analysis \( (s_w^2) \), and from replication error \( (s_r^2) \), appear in Columns 3 and 4. The former was obtained from a shipboard intercomparison experiment conducted by Linnenbom, Swinnerton and Cheek (1965). The analysis of variance in Appendix II then yields the instrumental precision values in Column 5. These are estimates of the standard deviation of oxygen probe measurements alone.

**Summary**

The digital oxygen probe system used in this work shows no overall bias relative to Winkler analysis but displays systematic differences in various parts of the water column. The depth dependence of this bias is best visualized from Figure 10, and is reflected in the results of regression analysis, Table I.

The response time of the sensor contributes to the inaccuracy
TABLE II. Partition of Overall Precision (values in ml/l).

<table>
<thead>
<tr>
<th>Source</th>
<th>$s_d$</th>
<th>$s_w$</th>
<th>$s_r$</th>
<th>$s_p$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>(2)</td>
<td>(3)</td>
<td>(4)</td>
<td>(5)</td>
</tr>
<tr>
<td>Digital Oxygen Probe (June 1971)</td>
<td>0.152</td>
<td>0.046</td>
<td>0.120</td>
<td>0.081</td>
</tr>
<tr>
<td>VanLandingham and Greene, 1971</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Beckman Minos DOM</td>
<td>0.139</td>
<td>0.046</td>
<td>0.000</td>
<td>0.131</td>
</tr>
<tr>
<td>(VanLandingham and Greene, 1971)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Beckman Minos DOM (Carlson, 1970)</td>
<td>0.184</td>
<td>0.046</td>
<td>0.120</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(assumed same)</td>
</tr>
</tbody>
</table>
of in situ measurements, especially in regions of high oxygen gradient. The spatial resolution of measurement may be characterized by the vertical distance traversed by the probe before achieving 97 percent response to a step change in oxygen content. Estimates of this distance range from 7 meters at 20°C to 13 meters at 5°C, based on laboratory experiments.

In situ evaluations of instrument precision are complicated by replication error when comparing oxygen probe readings to the results of hydrographic casts. Rough analysis of variance yields a value of 0.08 ml/l for the standard deviation of oxygen probe measurements. This figure compares with 0.05 ml/l for shipboard Winkler analysis and is comparable to, or somewhat better than, the precision of the Beckman Minos DOM.
CHAPTER III

LARGE-SCALE OXYGEN DISTRIBUTIONS

The zone of interest in this work lies between the 26.2 and the 27.2 sigma-t surfaces. The former density value is found below the region of high temperature, oxygen, and salinity gradients where oxygen probe data are significantly aliased (Chapter II). The latter density value is found near 600 m off Oregon. Profiles in the zone of interest often reveal medium-scale oxygen structure and significant horizontal variation in oxygen concentration from station to station. Profiles below 600 m grade smoothly through the oxygen minimum (Figures 9, 10).

1. Variation Along the Continent

The oxygen distribution on the 26.8 sigma-t surface, lying in the center of the zone of interest, is shown in Figure 1. This distribution is reproduced in Figure 12 without the oceanographic boundaries. North Pacific Intermediate Water is an important source of dissolved oxygen and low salinity on this density surface (Reid, 1965). A tongue of high oxygen concentration, and related contours, extends eastward from the source region in the direction of the general anticyclonic circulation.
Figure 12. Oxygen Distribution on the 26.8 Sigma-t surface (Reid, 1965, p. 68)

Stations

B  NORPAC 36, 8° 51.5'N, 87° 01'W, 23 Nov. 1959
C  NORPAC 110-54, 52° 38'N, 161° 14'W, 4 Sept. 1955
1  NORPAC 74, 31° 37'N, 126° 19'W, 4 Sept. 1955
2  NORPAC 19, 43° 50'N, 130° 30'W, 17 Aug. 1955
3  NORPAC 110-64, 50° 54'N, 137° 37'W, 10 Sept. 1955
4  ARGO 21, 45° 52'N, 154° 43'W, 20 Jan. 1966
The variation of dissolved oxygen along the North American continent is illustrated in Figure 13. Stations B, C, 1, 2, 3 (Figure 12) are located at or near those used by Rosenberg (1962) to represent the temperature and salinity variations along the continent. Dissolved oxygen and apparent oxygen utilization (AOU)\(^4\) are plotted against sigma-t in the 26.2-27.2 zone. Comparison between profiles is most meaningful horizontally in Figure 13, since interchange and mixing of water along sigma-t surfaces involves a minimum change in entropy and potential energy (Sverdrup, Johnson and Fleming, 1942).

The trends of oxygen and AOU resemble those of temperature and salinity (Figure 2) in that the California, Oregon, and Washington profiles grade progressively away from an extremum at station B. The oxygen profiles differ, however, in that the subarctic station C does not represent another extremum. This profile is shown as a

\(^4\)The apparent oxygen utilization is a measure of the amount of oxygen consumed by oxidation and respiration processes since the parcel of water left the ocean surface. It is defined as follows:

\[ \text{AOU} = O_s - O \]

where:

- \(O\) = measured oxygen concentration
- \(O_s\) = solubility of oxygen at the \textbf{in situ} salinity and temperature

Values of \(O_s\) were calculated from the formula of Weiss (1970). In this work the concept is useful because the AOU calculation removes the influence of oxygen solubility, which can vary between source regions as a result of temperature and salinity differences.
Figure 13. Dissolved Oxygen and AOU Profiles at Stations Along the Continent
dashed line in Figure 13. The highest values of oxygen and the lowest values of AOU are found at station 4, located in the tongue extending from the North Pacific Intermediate Water source.

Since portions of the oxygen profiles at stations 1, 2, 3 contain higher concentrations than at station C, it is evident that the latter cannot be considered a source of high oxygen concentrations for mixing along the continent. North Pacific Intermediate Water does provide a source, and its properties must be included in the characteristics of Subarctic Water. Without specifying exact source locations, however, it can be stated that oxygen concentrations increase, and temperature, salinity and AOU decrease isentropically toward the north along the continent.

2. Variation Along the Oregon Coast

Dissolved oxygen and AOU are plotted against sigma-t for six stations near the Oregon Coast in Figure 14. The measurements were made on a single cruise over a period of nine days, at locations shown in Figure 15. The southernmost station (35) exhibits the lowest oxygen concentrations and highest AOU values over most of the 26.2-27.2 sigma-t range. Station 17, which is one of the two northernmost stations, exhibits the highest oxygen concentrations and lowest AOU values over half the range. The relationship between these stations follows the previously-discussed meridional trend of
Figure 14. Oxygen and AOU Profiles at Stations Along the Oregon Coast
Figure 15. Stations Along the Oregon Coast (NORPAC 1955)
properties along the continent. Measurements of temperature and salinity at these stations also follow the large-scale trends and are presented and discussed in Chapter V.

Other profiles in Figure 14 do not display systematic variation with latitude. Station 28, intermediate between 17 and 35, exhibits the lowest oxygen concentration of the group near \( \sigma_t = 26.2 \), and the highest near \( \sigma_t = 27.0 \). Station 34 shows higher oxygen concentrations than station 15, despite the latter being farther north. Adjacent stations differ by 1 ml/l in oxygen content in some cases. The significance of non-systematic spatial variation of oxygen is examined by correlations to conservative properties in the next station.

3. Variation on a Twenty-Mile Scale

Dissolved oxygen variations between stations separated by 20 miles can be illustrated by superimposing the previously-discussed profiles obtained in the March and June 1971 cruises, as shown in Figures 16 and 17. Only hydrographic data are plotted in the latter case to avoid confusion due to overlapping. In the 150-600 m depth zone there is a difference in oxygen content of as much as 0.6 ml/l between adjacent stations. It is important to note that oxygen concentration does not vary monotonically with distance offshore in the March cruise; at station NH-65 there is a minimum concentration, and station NH-85 shows a maximum concentration. The spatial
Figure 16. Superimposed Profiles; March 1971
Figure 17. Superimposed Profiles: June 1971
variation is quite different in the June cruise, where station NH-65 has the highest concentrations and stations NH-85 and NH-105 show a progressively decreasing trend.

The approach adopted in this section is to examine the correspondence of oxygen content to temperature and salinity along sigma-t surfaces in order to discern whether the lateral variability in oxygen is consistent with a process of isentropic mixing between northern and southern waters. Examination will be based solely upon closely-spaced hydrographic samples, as only these are simultaneous observations of temperature, salinity, and oxygen.

**T-O Diagrams**

Plots of temperature against oxygen concentration in the 150-600 m depth range appear together in Figure 18 for the March 1971 cruise and in Figure 19 for the June 1971 cruise. Data points are represented by circles, with error bars indicating the 0.046 ml/l standard deviation of shipboard Winkler analysis (Chapter II). Solid lines connect data points obtained at each station. Figures appearing near each datum are the two decimals of sigma-t. It is understood that these decimals are preceded by 26 for all points except the deepest (600 m), which is preceded by a 27.

Dashed lines between the T-O curves connect values of equal
Figure 18. T-O Diagram: March 1971
Figure 19. T-O Diagram: June 1971
Linear interpolation was used to determine the points of intersection in cases where identical sigma-t values do not appear at each station. Error bars of ± 0.046 ml/l are also applied to these intersections, giving a lower limit to the precision of interpolated oxygen values. These values are considered good estimates of the oxygen concentrations at intermediate density values, since the sample bottles were closely spaced in the region of interest.

The T-O plot resembles a scatter diagram in that it shows the correlation between properties. Temperature and oxygen are positively correlated at each station, i.e., relatively high values of oxygen are found at relatively high values of temperature. This reflects the usual trend off Oregon, that above the oxygen minimum both oxygen and temperature decrease with depth. By contrast, it is evident that oxygen and temperature are negatively correlated along surfaces of constant sigma-t in both cruises.

Most of the isentropes in Figures 18 and 19 can be drawn straight if the uncertainty in oxygen measurements, represented by the error bars, is taken into account. Correlation coefficients, separately calculated for each of the isentropes, are summarized in Table III. The values are grouped near minus one, showing strong linear dependence between oxygen and temperature.

\footnote{Such lines are hereafter called isentropes, following Blanton (1968).}
TABLE III. Isentropic Correlations Between Properties Using 20 mile Station Separation.

<table>
<thead>
<tr>
<th>Properties Correlated</th>
<th>Number of Correlations</th>
<th>percent having $r \geq 0.90$</th>
<th>percent having $r \geq 0.97$</th>
<th>percent having $r \leq -0.90$</th>
<th>percent having $r \leq -0.97$</th>
</tr>
</thead>
<tbody>
<tr>
<td>T-O</td>
<td>17</td>
<td>94</td>
<td>71</td>
<td>94</td>
<td>71</td>
</tr>
<tr>
<td>T-AOU</td>
<td>17</td>
<td>82</td>
<td>53</td>
<td>82</td>
<td>53</td>
</tr>
<tr>
<td>S-O</td>
<td>15</td>
<td>87</td>
<td>87</td>
<td>87</td>
<td>87</td>
</tr>
<tr>
<td>S-AOU</td>
<td>15</td>
<td>87</td>
<td>67</td>
<td>87</td>
<td>67</td>
</tr>
</tbody>
</table>
The T-O correlations in Figures 18 and 19 show that the isentropic oxygen variability is consistent between the two cruises, for high oxygen values are correlated with low temperatures despite the differing geographic variability. The negative correlation is not constrained by the temperature coefficient of oxygen solubility, for oxygen content is influenced heavily by non-conservative processes, and positive T-O correlations are often observed in the ocean (eg., at any single station in Figures 18 and 19). The influence of oxygen solubility will be subtracted presently from the observations when dealing with AOU.

**T-AOU Diagrams**

Temperature-AOU relationships for the March and June 1971 cruises are shown in Figures 20 and 21. Solid lines connect data from a single station, and dashed lines connect values of equal sigma-t. Error bars show the precision of oxygen measurement, although additional error might be ascribed to interpolation and to uncertainty in the oxygen solubility formula. 6

On both plots the temperature and AOU are positively correlated along sigma-t surfaces. As in the temperature-oxygen case, most isentropes could be drawn straight if the uncertainty of oxygen

6 The estimated accuracy of the oxygen solubility formula is ± 0.015 ml/l (Weiss, 1970).
Figure 20. T-AOU Diagram: March 1971
Figure 21. T-AOU Diagram: June 1971.
measurements is considered. Correlation coefficients are summarized in Table III, showing strong positive correlation.

**S-O Diagrams**

Plots of salinity against oxygen (Figures 22 and 23) follow the notation and interpolation conventions previously introduced. Values of salinity increase upward and values of oxygen increase to the right to retain the usual representation of positive and negative correlations. This convention places deep values near the top of the diagram, however, as indicated.

On all stations, taken separately, salinity and oxygen are negatively correlated. This is the usual trend in Oregon waters above the oxygen minimum. The S-O lines sometimes show a strong inflection resulting in a plateau near a sigma-t value of 26.8. This feature is best shown at station NH-85 in the March data. Salinity and oxygen are also negatively correlated isentropically (Table III). Similar plots of salinity against AOU have been constructed but are not included here since they are considered superfluous. Salinity and AOU are positively correlated isentropically (Table III).

**Discussion**

The preceding graphical analyses and correlation calculations show that the observed oxygen variability is directly linked to
Figure 22. S-O Diagram: March 1971
Figure 23. S-O Diagram: June 1971
variability in temperature and salinity. Oxygen is negatively corre-
related with temperature and salinity along sigma-t surfaces despite
differing trends in the geographic distributions of properties. AOU
is positively correlated with temperature and salinity in a similar
way.

A linear relationship between conservative oceanic properties
is consistent with simple mixing between two water "types" (Sverdrup,
Johnson and Fleming, 1942). Dissolved oxygen is a non-conservative
property, and in general does not vary linearly with temperature
and salinity in simple mixing situations (Munk, 1966). Oxygen be-
haves conservatively, however, when in situ consumption or produc-
tion processes do not have sufficient time to produce measurable
effects. The non-conservative nature of dissolved oxygen is not
expected to be evident over 20-mile intervals in the upper regions
of the ocean. Neither oxygen nor AOU is suitable for isentropic
analysis over distances used by Tibby (1941) and Rosenberg (1962),
however.

The observed correlations between oxygen, temperature, and
salinity do not contradict the hypothesis that the waters off Oregon
are an isentropic mixture of high and low latitude waters in the
density range considered. As northern waters are characterized

\footnote{An instance in which oxygen behaves conservatively is
reported by Menzel and Ryther (1968).}
by high oxygen concentrations and by low salinity, temperature and AOU relative to southern waters on corresponding isentropes (Figures 2, 13), mixtures of the two would produce the observed relationship between properties. A conceptual model is shown in Figure 24, where the geographic pattern of isentropic mixing is represented by arrows. The case portrayed yields an irregular lateral distribution of properties such as found on the March 1971 cruise. A relatively high proportion of northern water at station NH-85 accounts for the lateral oxygen maximum found there and for the corresponding temperature and salinity minima. In principle, the mixing pattern may be depth-dependent, yielding different lateral variability along separate isentropes. This model is essentially that of Tibby (1941), except that it operates on a smaller scale, includes oxygen with temperature and salinity, and does not specify unique source locations. A quantitative example based on this model is considered in Chapter V to account for medium-scale oxygen structure.
Figure 24. Mixing Pattern Sketch for Conceptual Isentropic Model
CHAPTER IV

A DESCRIPTION OF MEDIUM-SCALE OXYGEN STRUCTURE

Oxygen profiles off the Oregon Coast often reveal structure in the zone beneath the halocline to 600 meters. The results of several cruises are presented in this chapter to describe the spatial extent and temporal changes in these features. Stations appear in Figure 25. Measurements of temperature and salinity in the vicinity of oxygen structure are also presented. When dealing with inversions, a terminology similar to that of Roden (1964) is adopted:

1. The "intensity" of an inversion is expressed by the difference between oxygen concentrations at the maximum and at the first overlying minimum.

2. The "depth" of an inversion is that depth at which the maximum occurs.

3. The "thickness" of an inversion is measured from the minimum downward to the depth at which that oxygen value first reoccurs.
Figure 25. Station Chart
1. Spatial Extent

**Twenty-mile Spacing**

Profiles from stations J1, J2, and J3 (Figure 25) are plotted in Figure 26. The stations were occupied at 20 mile intervals in July 1970, approximately four hours apart. Lines between profiles are isotherms, drawn every tenth degree Centigrade.

A small oxygen maximum appears near 250 m in all three profiles, lying at nearly constant temperature values. The intensity of this maximum is less than 0.1 ml/l, and its thickness varies from about 11 meters at station J1 to 17 meters at station J2. At station J3 the feature appears to be divided into two parts. Similarly, a step-like oxygen feature near 190 m in profile J1 appears to have degenerated into several steps at station J2, where a significant temperature inversion is encountered. This latter feature is bounded by the 7.5 and the 7.2 degree isotherms on stations J1 and J2. Although station J3 does not show any steps in this temperature range, it is possible that the underlying composite structure is related. Isotherms are discussed further in Section 3.

Another oxygen maximum appears at 337 m in Profile J1. It has a thickness of 15 meters and an intensity near 0.05 ml/l. No counterpart of this maximum is evident at the other two stations.
Figure 26. Oxygen Probe Profiles at Stations J1, J2, J3: July 1970
These profiles suggest that some oxygen features having an intensity less than 0.1 ml/l can be traced over distances of 40 miles, although undergoing changes in shape, intensity, and thickness. In other cases a distance of 20 miles is enough to separate the occurrence of an inversion from a region where no trace of it appears. These observations agree in general with the horizontal persistence of medium-scale temperature and salinity structure. Hamon (1967) observed that inversions and lamina rarely show similarity over distances greater than 55 km (30 miles). Details of structure were persistent over distances of 5-10 km, however. Stommel and Fedorov (1967) found medium-scale temperature and salinity features in the main thermocline which extended greater than 10 miles in some cases, and less than 6 miles in others.

**Close-Interval Spacing**

A cruise in May 1970 was designed to map the extent of a small oxygen feature in detail. The sampling pattern was based on the results found on each station. Nine oxygen probe casts were made over a period of 24 hours in the vicinity of the moored spar buoy Totem I (Figure 27) on 12 and 13 May. No distinct oxygen features were found during this series. A course to the west was then set, taking oxygen probe casts at four-mile intervals. The time at which each station was occupied is indicated. At station 12 a significant
Figure 27. Close-interval Stations: May 1970
oxygen maximum was encountered at 152 meters depth, having a thickness of 22 m, and an intensity of 0.25 ml/1. This feature did not appear four miles farther west at station 13. Profiles from stations 10 through 13 are shown in Figure 28, with isotherms drawn at 0.1°C intervals.

In an attempt to relocate the feature, the ship's course was reversed along the same track. Stations 14 through 17 were taken at two mile intervals, yielding the profiles shown in Figure 29. An oxygen maximum was found at station 16, two miles east of station 12 and about six hours later in time. This feature exhibits nearly the same thickness and intensity as that previously found but is somewhat shallower (140 m) and has a greater oxygen concentration at the maximum (3.86 ml/1 vice 3.56 ml/1). The temperature at the oxygen maximum is 0.2°C higher than observed at Station 12, and a significant temperature inversion is apparent.

The maximum shown in Figures 28 and 29 appears to extend less than eight miles in the east-west direction. Weak maxima are discernible two miles to either side of the feature at station 16. A medium-scale temperature inversion observed by Stommel and Federov (1967), for comparison, was found at four stations over a five-mile interval, but not at further stations. A salinity minimum observed by Hamon (1967) changed shape measurably over 6 km
(3.2 miles), and disappeared in another 27 km (14 miles). 8

Stations 18-21 to the north were occupied to map the spatial extent in that direction. Some irregularities were found but no distinct oxygen maximum. Subsequent sampling at previous locations (stations 22 and 23) also yielded no results. Speculating that the feature had been transported by currents during the intervening seven hours, stations 24, 25 and 26 to the south were then taken. The profiles revealed a maximum six miles south of the last sighting, nine hours later (Figure 30). The depth and thickness of this inversion are similar to the previous one, but its intensity is about half as great (0.12 ml/l). Temperature and oxygen concentration near the maximum resemble those at station 12.

If it is assumed that the inversion at station 25 is the same as at station 12 or 16, southward currents of 0.4 and 0.7 knots, respectively, are required to transport the feature to its new location. Drogue current measurements at this depth, for comparison, often reveal a southward current of 0.2 knots (Stevenson, Pattullo and Wyatt, 1970).

The oxygen inversion appears to degenerate between stations 25 and 26 by losing the overlying minimum. This is different from

---

8 Temperature and salinity structure measuring 3-5 meters in the vertical has been found to extend over horizontal distances as short as 400-1000 meters (Cooper and Stommel, 1968).
Figure 28. East-West Transect: May 1970
Figure 29. West-East Transect: May 1970
Figure 30. North-South Transect: May 1970
the east-west transects where the maximum has greater concentrations than neighboring stations. The exact geometry of the feature (or features) remains unclear. Further attempts to relocate the phenomenon by close-interval stations (27-33) were unsuccessful.

2. Temporal Changes

February 1970 Series

Repetitive profiling was conducted over a 26-hour period in February 1970 at station F (Figure 25). All casts were taken within one mile of the moored spar buoy Totem I. A significant oxygen maximum was found near 300 m during the afternoon of 9 February, as shown by the first four profiles in Figure 31. The time of each cast is marked. Difficulties with a partly degenerated sensor were experienced on this day, with the result that no deeper data were collected.

The series was interrupted during the night of 9 February in order to refurbish the polarographic cell. When sampling was continued on the next day, a large oxygen maximum was again found near 300 m, and a smaller one was found at greater depth. Horizontal lines and shaded areas marked in Figure 31 indicate positions of sonic scattering layers, discussed in the next chapter.

The thickness of the shallower oxygen maximum varied between
Figure 31. Profile Series at Station F: February 1970
30 and 40 meters on 9 February and increased to 40-50 meters on the succeeding day. Its intensity is 0.1-0.25 ml/l. The deeper feature has a thickness of 25 meters and an intensity of 0.1 ml/l. Oxygen concentrations at the upper and lower maxima are 2.7 and 1.9 ml/l, respectively.

The depth of both inversions varied by about 20 meters during the sampling period. This movement is considered real, since positions of the probe were checked on each cast by observing its trace on a precision depth recorder. The depths of corresponding isotherms varied in the same way, the oxygen features remaining associated with nearly constant temperature values throughout the series (6.4° at the upper maximum and 5.2° at the lower). Similar vertical movements of medium-scale temperature and salinity structure have been reported by Stommel and Federov (1967), and were ascribed to internal wave activity.

The results of this series show that strong oxygen inversions may persist in one location for periods greater than 24 hours, although they may undergo changes in thickness, shape, and depth. Because of currents, however, it is unlikely that the same water was profiled during the entire period. The spatial extent and the temporal duration of features observed in this way are not clearly separable. If a current of 0.2 knots is assumed, observation of the shallower maximum for 26 hours at one location implies a
minimum extent of 13 miles. Since the profile series was terminated before the feature disappeared, no estimate of its actual extent can be made.

Several CTD casts were taken during the 26-hour period in order to confirm the temperature structure and to obtain salinity measurements. Reduced profiles from a cast at 0930 on 10 February are shown in Figure 32. The correspondence between these profiles and the oxygen features in Figure 31 is indicated by arrows, based on the temperature values which the oxygen features followed. This figure is discussed in Section 3.

May 1970 Series

A series of profiles was taken through a weak oxygen inversion at station M (Figure 25) on 15 May 1970. This feature was found at 320 m on the day after the close-interval search described in Section 1. It lies well below the previous phenomenon and is not considered related to it in any way.

Oxygen probe casts were made at half-hour intervals from 2053 to 2301 (Figure 33). The ship was allowed to drift, covering a distance of 0.6 miles toward the southeast in three hours. The oxygen inversion displayed a maximum intensity of 0.03 ml/l. It became distorted during the series, degenerating into a series of gradient changes. This series gives a measure of the persistence
Figure 32. CTD Profiles: February 1970
Figure 33. Profile Series at Station M: May 1970
of very weak oxygen features. The observed change may be either spatial or temporal in nature, as previously discussed. Estimates of decay rates due to diffusion processes are presented in Chapter V.

3. Temperature and Salinity Distributions

Temperature Measurements

The isotherms in Figures 26, 28, 29, 30 show the temperature distribution in the vicinity of small oxygen features. Values of temperature were derived from the transducer mounted on the oxygen probe.

A correspondence between thermal structure and oxygen structure is suggested at the small maximum near 340 m in the July cruise (profile J1, Figure 26). Isotherms are relatively closely spaced as the oxygen maximum is approached, and widely spaced underneath. This indicates a temperature gradient change within the maximum. Profiles J2 and J3 do not show any corresponding

9 It should be emphasized that oxygen features described in this work cannot be artifacts caused by the thermal characteristics of the oxygen sensor or by temperature correction. The uncorrected data, which is a direct measure of the polarographic cell current, were examined in each case. Cell currents increase as the oxygen maxima are approached, while temperatures are always decreasing. Since the thermal response of the cell is the reverse of this trend (Chapter II), the oxygen maxima must be considered real.
features, and the temperature gradient is found to be weaker and more uniform. The oxygen maxima near 250 m in Figure 26 display a similar isotherm pattern, although less pronounced.

Closely-spaced profiles of the May 1970 cruise suggest the same relationship between temperature and oxygen structure. The oxygen maximum at station 12 (Figure 28) is associated with a sharper temperature gradient, and gradient change, than neighboring stations where no maximum is found. The trend is still more pronounced at station 16 (Figure 29) where the oxygen maximum coincides with a temperature minimum. This case can be considered an extension of the previous one, since the temperature gradient here becomes not only less negative, but actually becomes positive. A temperature minimum also accompanies the deeper oxygen maximum in Figure 31, as shown by the CTD profile in Figure 32.

A correspondence between oxygen inversion intensity and temperature gradient change is indicated in the scatter diagram of Figure 34. Characteristics of the eleven oxygen features used are summarized in Table IV, coded by the profiles in which they occur. Only clearly identifiable single inversions are tabulated. Values in Column 5 were calculated by subtracting the temperature gradient averaged over several tenths of a degree above an oxygen maximum from that similarly calculated below it. The gradient change may be visualized by fitting straight line segments to the temperature profile
Figure 34. Correspondence of Oxygen Inversions to Changes in the Vertical Temperature Gradient
### TABLE IV. Characteristics of Several Medium-Scale Oxygen Features.

<table>
<thead>
<tr>
<th>Station</th>
<th>Depth (m)</th>
<th>Thickness (m)</th>
<th>Intensity (ml/l)</th>
<th>Temperature Gradient Change (°C/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M 12</td>
<td>152</td>
<td>22</td>
<td>0.25</td>
<td>0.069</td>
</tr>
<tr>
<td>M 15</td>
<td>145</td>
<td>10</td>
<td>0.02</td>
<td>0.021</td>
</tr>
<tr>
<td>M 16</td>
<td>140</td>
<td>22</td>
<td>0.20</td>
<td>0.054</td>
</tr>
<tr>
<td>M 17</td>
<td>158</td>
<td>17</td>
<td>0.03</td>
<td>0.028</td>
</tr>
<tr>
<td>M 24(a)</td>
<td>145</td>
<td>10</td>
<td>0.05</td>
<td>0.042</td>
</tr>
<tr>
<td>M 24(b)</td>
<td>203</td>
<td>9</td>
<td>0.02</td>
<td>0.009</td>
</tr>
<tr>
<td>M 25</td>
<td>141</td>
<td>17</td>
<td>0.12</td>
<td>0.023</td>
</tr>
<tr>
<td>J 1(a)</td>
<td>263</td>
<td>11</td>
<td>0.03</td>
<td>0.009</td>
</tr>
<tr>
<td>J 1(b)</td>
<td>337</td>
<td>15</td>
<td>0.04</td>
<td>0.013</td>
</tr>
<tr>
<td>J 2</td>
<td>255</td>
<td>17</td>
<td>0.06</td>
<td>0.005</td>
</tr>
<tr>
<td>F (b)</td>
<td>400</td>
<td>25</td>
<td>0.11</td>
<td>0.040</td>
</tr>
<tr>
<td>*S 1</td>
<td>300</td>
<td>70</td>
<td>0.45</td>
<td>0.015</td>
</tr>
<tr>
<td>*F (a)</td>
<td>300</td>
<td>45</td>
<td>0.20</td>
<td>0.010</td>
</tr>
</tbody>
</table>

*Large inversions with anomalously low temperature gradient change, excluded from Figure 34 (see p. 86, 95).
in Figure 32.

The scatter diagram shows a positive correlation between oxygen inversion intensity and temperature gradient change. A correlation coefficient of 0.83 is calculated for the eleven points. The significance of Figure 34 is discussed with models of oxygen structure in Chapter V.

Salinity Measurements

CTD casts were taken through several oxygen features during the sampling period. The results are illustrated in Figure 32. A scatter of about 0.03‰ in salinity is evident, attributed to the characteristics of the instrument (Geodyne, model 775-2). The calculated density profile shows corresponding scatter.

Salinity values remain constant or decrease slightly in Figure 32 as the shallower oxygen maximum is traversed, and increase beneath the feature. A sharp decrease is suggested in the vicinity of the deeper maximum, but the precision of measurement is insufficient to be certain. No density features are evident near either oxygen inversion. CTD casts through other oxygen features did not resolve salinity trends better than shown in this figure.

Precise salinity measurements were obtained near a medium-scale feature on one occasion, as shown in Figure 35. Hydrographic bottles were spaced five meters apart in order to confirm the in situ
profile. A weak but distinct decrease in salinity of 0.06‰ accompanied the oxygen maximum. As overall salinity profiles increase with depth off the Oregon Coast, this feature is likely to be a salinity minimum.

The oxygen inversion shown in Figure 35 was the largest observed in the sampling period. It has a thickness of 70 m and an intensity of 0.45 ml/l. It resembles maximum "A" in Figure 31, which was the second largest observed, in that it lies at nearly the same sigma-t value (26.75 and 26.77). The two features exhibit small temperature excursions (Figures 32, 35), but anomalously low overall temperature gradient change for their intensity (Table IV). These maxima are considered separately in Chapter V.

Inversion S1 was not found at stations S2, S3, S4 (Figure 25) occupied several hours later. Hydrographic profiles from the September 1969 cruise are superimposed in Figure 36. Although oxygen probe data are not available at the latter stations, it is evident that large horizontal concentration gradients accompany this large oxygen inversion.

10 The disparity between the observed depths of the oxygen maximum is considered real, and may be due to internal wave activity (Section 2). There was a time interval of one-half hour between the oxygen probe cast and the hydrographic cast.
Figure 35. Oxygen Probe and Hydrographic Profiles: Station NH-65, September 1969
Figure 36. Superimposed Oxygen Profiles: September 1969
4. Summary

The characteristics of several medium-scale oxygen features in the 100-600 m depth zone off Oregon are presented in Table IV, and in Figures 26, 28-36. They may be summarized as follows:

1. Dissolved oxygen profiles exhibit irregularities or "structure" in the form of abrupt gradient changes and inversions.

2. The vertical extent of oxygen features varies from the smallest which the probe can accurately resolve (about 10 meters) up to 70 meters.

3. The intensity of inversions varies from zero to 0.45 ml/l.

4. Oxygen structure appears to extend over distances of 40 miles in some cases, and less than eight miles in others.

5. Repetitive profiling at fixed locations reveals changes in the shape, intensity, thickness, and depth of oxygen features. In one case a significant maximum was observed over a 26-hour period.

6. Temperature gradient changes accompany oxygen maxima, as shown in Table IV and Figure 34.

7. A salinity decrease of 0.06‰ accompanied the largest oxygen maximum observed, as measured by a detailed hydrographic cast. Less precise CTD measurements sometimes suggest that salinity decreases near oxygen maxima.
CHAPTER V

MODELS FOR THE GENERATION AND DECAY OF MEDIUM-SCALE OXYGEN STRUCTURE

1. A Horizontal Mixing Model

Introduction

The horizontal mixing of dissimilar waters is considered a probable mechanism for the generation of medium-scale temperature and salinity structure. Pingree (1969), in a study of the deep waters off the western coast of France, writes:

Large horizontal variations do occur in temperature and salinity at the same potential density and depth on a small horizontal scale. A process which allows a horizontal exchange of water could introduce into the water column a water mass with a significantly different T-S character. If the water was made to move along its isopycnal surface into neighbouring regions, the horizontal mixing process would be in keeping with the phase and density variations.

(Pingree, 1969, p. 295)

A similar hypothesis is advanced by Simpson (1971) in a shallow-water study of the Irish Sea:

... the interleaving mechanism suggested by Stommel and Federov seems likely to be important in this case. The existence of marked horizontal gradients of temperature and salinity in the surrounding waters would favor the intrusion of well mixed water masses of appropriate density into the area of microstructure.

(Simpson, 1971, p. 319)

A quantitative example is considered in this section to estimate whether horizontal mixing is a probable cause of medium-scale
oxygen structure off Oregon. The example is based on the conceptual model introduced in Chapter III.

**Model Formulation**

Source profiles for generating medium-scale oxygen structure are arbitrarily chosen near the northern and southern borders of Oregon, at stations 17 and 35 (Figure 15). Observations of oxygen, temperature, and salinity from these stations are plotted against sigma-t in Figure 37. The relationship between properties in this case follows the general meridional trend (Chapter III) in that the northern station has higher values of oxygen, and lower values of salinity and temperature.

A hypothetical oxygen profile is drawn between the source oxygen profiles in Figure 37, incorporating two medium-scale maxima. The upper and lower features have intensities of 0.25 ml/l and 0.1 ml/l, respectively. Their thicknesses are 25 and 18 m, derived from a nominal vertical density gradient of 0.1 sigma-t/50 m.

Temperature and salinity profiles associated with the modeled oxygen maxima are calculated by assuming simple horizontal mixing between source profiles. On any sigma-t surface, the value of salinity (S) and temperature (T) is calculated from the given value of oxygen (O) by the proportion
Figure 37. Horizontal Mixing Model Construction
\[
\frac{S - S_{35}}{S_{17} - S_{35}} = \frac{T - T_{35}}{T_{17} - T_{35}} = \frac{O - O_{35}}{O_{17} - O_{35}},
\]

where the subscribed variables refer to the source profiles at stations 35 and 17.

**Results**

The calculated temperature and salinity profiles in Figure 37 show gradient changes accompanying the oxygen features. The deeper oxygen maximum, chosen to resemble F (b) in Figure 31, is associated with temperature structure similar to that observed in the corresponding CTD profile (Figure 32). The temperature gradient change calculated from the horizontal model is 0.04 °/m, also agreeing with that measured (Table IV, Figure 34). The shallower modeled oxygen inversion is associated with a temperature gradient change of 0.02 °/m, somewhat less than that observed for oxygen maxima of similar intensity (0.07 °/m at Feature M 12).

Calculated salinity features are both less than 0.05‰ in intensity. The deeper salinity decrease resembles that suggested by the CTD record near 400 m in Figure 32.
Discussion

The temperature gradient changes calculated from the model are of the same order of magnitude as those observed near oxygen inversions. This agreement supports the generation of medium-scale oxygen structure by a horizontal mixing mechanism. The corresponding salinity structure has intensity near the limit of the CTD resolution (0.03% scatter), so that rare observations of salinity trends near oxygen features are also consistent with the model.

The source profiles used in this example are not considered either permanent or unique. Considerable seasonal variation in the T-S properties off Oregon has been shown by Rosenberg (1962). The change in property distributions between the March and June 1971 cruises (Chapter III) illustrates this temporal variability. The results of these two cruises also show that considerable horizontal variations of properties can be found over distances as short as 20 miles. Consequently, the "source regions" for medium-scale structure can be separated by distances much shorter than between stations 17 and 35 in the model. The limited spatial extent of oxygen features is consistent with their generation on a scale of tens of miles.

A correlation of temperature gradient change to oxygen feature intensity (Figure 34) is in general agreement with the horizontal
mixing model. As the proportion of "northern water" in part of the water column is increased, progressively higher oxygen concentrations and lower temperatures result. These changes are manifested in the vertical by oxygen maxima and by temperature gradient changes (or minima) of increasing intensity. Because the characteristics of the sources are expected to change with depth and with time, however, scatter in the correlation is anticipated.

The two large oxygen maxima listed at the bottom of Table IV have comparatively low temperature gradient changes for their intensity. A definite salinity decrease was found in the case of feature S1, however, and a similar decrease near feature F(a) is suggested by the CTD profile in Figure 32. Under the horizontal mixing model this relationship would be produced by a relatively large proportion of water characterized by high oxygen content and by low salinity. These characteristics are found in North Pacific Intermediate Water, shown to be an important component of the northern waters at a sigma-t value of 26.8 (Chapter III). The influence of this Intermediate component is the probable cause of oxygen features near 300 m which have anomalously low temperature gradient changes.

11"Northern" here designates water characterized by relatively high oxygen content and by low salinity and temperature, regardless of its proximity or geographic relationship to waters of southern character.
2. A Layered Consumption Model

Introduction

The large-scale vertical distribution of oxygen has been modeled as a steady state balance between advective, diffusive, and non-conservative processes (Riley, 1951; Wyrtki, 1962; Munk, 1966). A transient state model is used in this section to estimate whether layers of oxygen-consuming materials would generate oxygen structure on a medium scale. Layering of detritus or biological organisms may represent sinks of this sort.

The calculations which follow are motivated by the observation of a sound-scattering layer near the large oxygen maximum in the February 1970 profile series (Figure 31). The hatched region designates a band of intense sound scattering at 12 kHz. Horizontal lines above and below show the boundaries of less intense sound scattering. Such layers are regarded as concentrations of sound-scattering organisms. They are often observed to migrate vertically, rising to shallow depths at night and descending during the day. Figure 31 suggests that a sufficiently strong concentration of organisms could diminish the oxygen concentration in a layer by respiration, indirectly causing the underlying maximum. This possibility was also suggested by Carlson (1970), although he found no oxygen structure when profiling through scattering layers with the Beckman Minos
DOM. It should be stated that an oxygen feature near the deep scattering layer (DSL) was only found on one cruise in this work.

**Governing Equation and Solution Form**

The case considered is a horizontally homogenous sink for dissolved oxygen, influenced by vertical eddy diffusion but not by advective processes. The governing one-dimensional equation, using a constant diffusion coefficient, is:

$$\frac{\partial c}{\partial t} = A_z \frac{\partial^2 c}{\partial z^2} - R_z(z),$$  

where:  
- $c$ = oxygen concentration  
- $t$ = time  
- $A_z$ = vertical diffusion coefficient  
- $z$ = depth  
- $R_z(z)$ = vertical consumption/distribution.

Features discussed in this work extend tens of meters in the vertical and are considered sufficiently large to be affected by turbulent processes. A constant eddy diffusion coefficient of 1 $\text{cm}^2/\text{sec}$ is assumed for all vertical calculations. This value is frequently calculated in the shallow regions of the main thermocline (Wyrtki, 1961; National Research Council, 1971).

Equation 5 is solved numerically using the explicit form
\begin{equation}
    c_{i,j+1} = c_{i,j} + r(c_{i-1,j} - 2c_{i,j} + c_{i+1,j}) \frac{R.(\Delta z)^2 r}{Az},
\end{equation}

where: $c =$ oxygen concentration

$i =$ grid index

$j =$ time step index

\begin{align*}
    r &= \frac{Az \Delta t}{(\Delta z)^2} \\
    \Delta t &= \text{time increment} \\
    \Delta z &= \text{grid point spacing} \\
    R &= \text{consumption rate.}
\end{align*}

Such computations yield accuracies within several percent for $r < 1/2$ (Gebhart, 1961; Smith, 1965). The procedure illustrated by Gebhart (1961) was adapted for computerized operation in this work, specifying $r = 1/3$.

Initial and Boundary Conditions

The layered consumption problem is approached by calculating the changes in oxygen profiles produced by hypothetical layers of oxygen-consuming material. An initial oxygen profile is chosen which is in equilibrium with a smooth consumption distribution (Figure 38), following a steady-state vertical model described by Wyrtki (1962). The consumption rate is expressed by
obtained from studies by Riley (1951) and Wyrtki (1962). Independent estimates of $R$ by enzyme assays yield similar results (Packard, 1969).

The initial oxygen profile in Figure 38 is given by

$$c(z) = -1.097 + 0.00119 z + 8.979 e^{-0.0035 z}. \quad (8)$$

Equation 8 is the steady state solution of $S$, using the consumption expression 7 and $A_z = 1 \text{ cm}^2/\text{sec}$. The boundary conditions specify a constant oxygen concentration of 6.5 ml/l at 50 m, and 2.0 ml/l at 2600 m. These values are considered fixed by contact with the atmosphere, and by deep advection, respectively.

The time-dependent model is produced by adding a bell-shaped peak to the exponential consumption profile, simulating the migration of an oxygen-consuming layer into the region near 300 m:

$$R(z) = (110 \times 10^{-10}) e^{-0.0035 z} + \frac{M}{(z-300)^2 + H^2}. \quad (9)$$

The parameters $M$ and $H$ can be varied to specify different thicknesses and intensities of the peak. Boundary conditions are the same as for the steady-state model.
Figure 38. Steady State Oxygen and Consumption Rate Profiles
Results

The numerical solution form 6 was first tested by performing 100 iterations on the steady state profiles. Grid points separated by 5 m were assigned initial oxygen values by equation 8 between 50 and 2600 m. The corresponding iteration interval is 0.962 days ($r = 1/3, \frac{A_z}{2} = 1 \text{cm}^2/\text{sec}$). Values of R at each grid point were assigned by equation 7. No changes in the initial oxygen concentrations, to three decimal places, were found after 100 iterations.

The effects of three consumption peaks were then calculated (Figures 39-41). Solid lines designate the initial oxygen profile between 100 and 500 meters. Points show the calculated departures from this profile after the indicated time intervals. Consumption rate distributions are inset on semi-logarithmic scales.

All consumption peaks were chosen to take significant effect between 250 and 350 m. The parameters and characteristics of each are summarized in Table V. The layer modeled in Case I has a peak consumption rate about 25 times that of the background exponential, and approximately doubles the total consumption rate in the water column to 700 m (Table V). The calculated oxygen profile shows a change after 96.2 days (Figure 39), but not enough to create a minimum-maximum pair. In Case II an oxygen inversion of low intensity is formed after 38.5 days, and a significant feature after
Figure 39. Calculated Effect of a Consumption Rate Peak: Case I
Figure 40. Calculated Effect of a Consumption Rate Peak: Case II
Figure 41. Calculated Effect of a Consumption Rate Peak: Case III
TABLE V. Consumption Rate Parameters and Characteristics for Layered Model.

<table>
<thead>
<tr>
<th>Source</th>
<th>M (ml-m^2/(1-sec))</th>
<th>H (m)</th>
<th>Consumption rate at 300 m (10^-9 ml/l/sec)</th>
<th>Total Consumption to 700 m (10^-6 ml-m/l-sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Background</td>
<td>--</td>
<td>--</td>
<td>3.85</td>
<td>2.9</td>
</tr>
<tr>
<td>exponential</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Peak I</td>
<td>10^-5</td>
<td>10</td>
<td>104^a</td>
<td>3.1^b</td>
</tr>
<tr>
<td>Peak II</td>
<td>10^-5</td>
<td>5</td>
<td>404^a</td>
<td>6.2^b</td>
</tr>
<tr>
<td>Peak III</td>
<td>10^-5</td>
<td>10/3</td>
<td>904^a</td>
<td>9.3^b</td>
</tr>
</tbody>
</table>

^a Exponential plus peak
^b Peak only
96.2 days. The layer modeled in this case has a peak consumption rate 100 times that of the background exponential, and it trebles the total consumption in the water column to 700 m. Case III, using still higher consumption, produces an oxygen inversion in less than 10 days.

Discussion

The preceding calculations indicate that very strong concentrations of oxygen-consuming material are necessary to produce significant effects on oxygen profiles over moderate time intervals. If the exponential consumption distribution (7) is representative of oceanic conditions, it would be impossible to generate the modeled peaks for lack of sufficient oxygen-consuming material in the water column. Expression 7 is far from certain, however, especially in the shallowest 100 meters. In addition, consumption rates are expected to vary widely between fertile coastal waters and relatively sterile open-ocean waters.

Despite the above uncertainty, available evidence indicates that the vertically migrating deep scattering layer off Oregon does not contain a sufficiently strong biomass concentration to produce oxygen structure over moderate time intervals. Multiple net tows sometimes yield relatively high catches in sound-scattering layers, but not consistently (Pearcy and Mesecar, 1970). At times when
high catches are made in the deeper layers (350-420 m), the biomass concentration is found to be only about 10 percent of that found in near-surface layers. The strong sound scattering properties of these layers may result from low concentrations of fishes with gas-filled swim bladders.

It should be pointed out that long-lived layers of oxygen-consuming materials are not expected to produce oxygen inversions in steady state. The process illustrated in Figures 40 and 41 cannot proceed for long periods of time without forming negative oxygen concentrations, which is clearly impossible. An oxygen maximum in the interior of the ocean can only be maintained in steady state by lateral advection/mixing processes or by in situ production, since a source must be provided to balance diffusive decay in the vertical. The latter process is not considered feasible below about 150 m, where low light levels exclude the net production of oxygen by photosynthesis.

3. Diffusive Decay Models

Introduction

Profile transects have been presented which illustrate the spatial scales associated with oxygen features off Oregon. The time scales associated with their generation and decay are also of
importance. Although the former is difficult to estimate, the decay of structure by diffusion can be calculated if several assumptions are made.

Stommel and Federov (1967) estimated the lifetime of temperature and salinity structure by the formula

$$T = \frac{h^2}{2 A_z},$$

(10)

where: $T =$ lifetime

$$h =$ characteristic half-thickness of the structure

$$A_z =$ vertical diffusion coefficient.

An eddy diffusion coefficient of $1 \text{ cm}^2/\text{sec}$ was used, yielding the lifetimes in Table VI. These values were considered equally applicable to temperature and salinity features because of the turbulent nature of the diffusion process. The same table may be used for dissolved oxygen structure if non-conservative processes are neglected.

### TABLE VI. Oceanic Structure Lifetime Estimates (Stommel and Federov, 1967).

<table>
<thead>
<tr>
<th>Half-thickness (h)</th>
<th>Lifetime (T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 cm</td>
<td>1 minute</td>
</tr>
<tr>
<td>1 meter</td>
<td>0.2 days (0.06 days)$^a$</td>
</tr>
<tr>
<td>10 meters</td>
<td>20 days (5.8 days)$^a$</td>
</tr>
</tbody>
</table>

$^a$ Values calculated by the author using the same formula.
Several examples of the decay of oxygen structure by vertical and horizontal diffusion are calculated in this section. A numerical solution of the diffusion equation is employed, using initial conditions based on oxygen probe data. The results are compared to those calculated by Formula 10.

**Vertical Model Formulation**

The decay of horizontally homogeneous oxygen maxima are treated first. Non-conservative processes are neglected since their transient-state effects are small (Section 2). Although advective processes could be effective in dissipating structure, they are omitted because conservative lifetime estimates similar to those of Stommel and Federov (1967) are desired. The governing one-dimensional equation is

\[
\frac{\partial c}{\partial t} = A \frac{\partial^2 c}{\partial z^2},
\]

where:

- \( c \) = oxygen concentration
- \( t \) = time
- \( A_z \) = vertical diffusion coefficient
- \( z \) = depth.

The solution form 6 is applicable if the non-conservative term is deleted:
\[ c_{i, j+1} = c_{i, j} + r(c_{L, j} - 2c_{i, j} + c_{i+1, j}) . \]  

(12)

Notation is the same as in equation 6.

Three sizes of oxygen inversions are considered. They represent relatively small features such as J1 (a), intermediate sizes such as M 12, and large sizes such as F (b) and S1 (Table IV). The initial profiles are simulated by the equation

\[ c(z) = \frac{-z}{150} + 3.9 + \frac{M}{(z-300)^2 + H^2} , \]  

(13)

where:  
\( c = \) oxygen concentration, ml/l  
\( z = \) depth, m  
\( M, H = \) peak parameters.

The first two terms in Equation 13 represent a linear background profile, approximating that generally found off the Oregon Coast in the 150-450 m depth zone (Figures 9, 10). The particular case chosen is station NH-65 of the March 1971 cruise. The third term adds a bell-shaped peak symmetric about 300 m. Values of \( M \) and \( H \) are varied to specify the thickness and intensity of the features. Portions of the initial profiles are plotted in Figures 42, 43, 44.

The values of \( M \) and \( H \) used in each case are shown in Table VII.

The boundary conditions in all calculations specify that the initial concentrations at depths of 150 and 450 meters remain fixed.
These points are well removed from the medium-scale features, and their concentration is assumed controlled by larger-scale processes. A grid point spacing of 2 m was chosen for the smaller two features (Figures 42, 43), and 5 m for the largest (Figure 44). The corresponding time increments are 0.154 and 0.962 days, respectively. These spacing adequately resolve the maxima while permitting significant advancement of the solution within 100 iterations.

**Vertical Model Results and Discussion**

Several representatives of the computed profiles are plotted in Figures 42-44. The number of time increments and corresponding values of real time are marked in each case. The oxygen maxima are found to disperse and become less intense with time, tending toward a linear final state described by the first two terms in Equation 13.

The time scale of the decay process can be simply represented by the elapsed time when the intensity of a maximum is reduced to half its initial value. The calculated half-lives, defined in this way, are presented in Table VII. Lifetimes are also shown, defined as the elapsed time when the intensity equals zero. They agree closely with those calculated by the formula of Stommel and Federov (Column 10).

The lifetimes vary from 2.6 to 48.1 days, depending upon the
Figure 42. Calculated Decay of a Small Oxygen Maximum by Vertical Diffusion
Figure 43. Calculated Decay of an Intermediate-sized Oxygen Maximum by Vertical Diffusion
Figure 44. Calculated Decay of a Large Oxygen Maximum by Vertical Diffusion
<table>
<thead>
<tr>
<th>Size</th>
<th>Intensity (ml/l)</th>
<th>Thickness (m)</th>
<th>H (m)</th>
<th>M (ml·m⁻²)</th>
<th>△x (m)</th>
<th>△t (day)</th>
<th>Half-life (days)</th>
<th>Lifetime (days)</th>
<th>Lifetime calculated by Formula 10 (days)</th>
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<tbody>
<tr>
<td>Small maximum</td>
<td>0.05</td>
<td>15</td>
<td>7</td>
<td>8.8</td>
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<td>0.154</td>
<td>0.77</td>
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<td>3.2</td>
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<tr>
<td>Intermediate maximum</td>
<td>0.17</td>
<td>25</td>
<td>9</td>
<td>29</td>
<td>2</td>
<td>0.154</td>
<td>1.85</td>
<td>8.6</td>
<td>9.0</td>
</tr>
<tr>
<td>Large maximum</td>
<td>0.37</td>
<td>60</td>
<td>23</td>
<td>450</td>
<td>5</td>
<td>0.962</td>
<td>11.5</td>
<td>48.1</td>
<td>52.1</td>
</tr>
</tbody>
</table>
size of the features. According to these estimates, oxygen structure is expected to persist longer than any profile series reported in the previous chapter. A change in intensity should be evident, however, if a small or intermediate-sized maximum is successfully traced over one or two days.

The intermediate-sized feature observed in the May 1970 cruise was tracked over a 15 hour period, although it is not certain that the same part of the feature was profiled in all cases. The intensity of the maximum was found to decrease in time (0.25, 0.20, 0.12 ml/l at stations 12, 16, 25), somewhat faster than expected from its estimated half life of 1.85 days under vertical diffusion.

Horizontal Model Formulation

The oxygen maximum encountered at stations 12 and 16 appeared to extend less than eight miles in an east-west direction (Figures 28, 29). It was found to be a maximum in the horizontal as well as in the vertical since it contains higher concentrations than the neighboring stations at corresponding depths or temperature surfaces. The single meridional transect (Figure 30) showed that it was not a horizontal maximum in that direction.

An estimate of this feature's half-life under horizontal diffusion can be simply made by considering it a ridge of high oxygen concentration, extending indefinitely in the north-south direction.
Equation 11 applies if the zonal coordinate \((x)\) is substituted for \(z\), and if a horizontal diffusion coefficient \(A_x\) is used. A constant value of \(10^6\) cm\(^2\)/sec is assigned to \(A_x\), as reported for small areas of the California Current in the 200-400 m depth zone (Sverdrup, Johnson and Fleming, 1942).

An initial condition for this problem is provided by the transects shown in Figures 28 and 29. The horizontal oxygen distribution at the maximum is shown in Figure 45, with scales shifted to make stations 12 and 16 coincide. Lateral oxygen gradients vary between 0.05 and 0.25 ml/l/mile as the feature is traversed, most values being between 0.1 and 0.2 ml/l/mile.

The observations plotted in Figure 45 are smoothly approximated by the relationship

\[
c(x) = \frac{4.8}{16 + (x - x_m)^2},
\]

where:

- \(c\) = oxygen concentration (ml/l)
- \(x\) = horizontal distance (miles)
- \(x_m\) = horizontal coordinate of the maximum.

A zero background level is used for convenience, since only gradients in the horizontal are relevant. The initial concentrations at distances 15 miles to either side of the maximum (offscale in Figure 45) are chosen to remain fixed. These boundaries are well removed
from the maximum, and are considered controlled by larger scale processes.

**Horizontal Model Results and Discussion**

The solution form (12) was applied using a grid spacing of 1/2 nautical miles. The corresponding time increment is 0.033 days ($r = 1/3, A_x = 10^6 \text{ cm}^2/\text{sec}$). Several examples of the calculated distributions are plotted in Figure 45.

The horizontal maximum was found to be reduced to half its original intensity in 2.1 days (63 iterations). This half-life is close to that previously calculated for vertical decay of the same feature (1.9 days). No estimate of lifetime is meaningful in this case, since the intensity approaches zero asymptotically in the absence of a background gradient.

The close agreement of the horizontal and vertical half-life calculations in this case may be coincidental. It is of interest, however, that the feature appears to be equally unstable with respect to diffusion in each direction, despite a difference in diffusion coefficients of six orders of magnitude. The effect of choosing different coefficients is easily calculated, since time scales vary inversely with values of $A$. If the diffusion coefficient is doubled, for example, the estimated half-life and lifetime are halved. Similar agreement
Figure 45. Calculated Decay of a Lateral Oxygen Maximum by Horizontal Diffusion
between horizontal and vertical calculations in the above case result as long as the ratio $A_x / A_z$ is maintained at $10^6$. 
CHAPTER VI

SUMMARY AND CONCLUSION

Medium-scale oxygen structure found in the 100-600 m depth zone off Oregon takes the form of inversions and gradient changes extending up to 70 meters in the vertical. The characteristics of several features are presented in Table IV.

The horizontal extent of oxygen structure agrees in general with that of medium-scale temperature and salinity structure observed by Stommel and Federov (1967) and by Hamon (1967). Inversions extend over distances of 40 miles in some cases, although undergoing changes in shape and size. Clearly identifiable maxima have been bracketed by distances of eight miles in other cases.

Temperature and salinity structure has been observed associated with dissolved oxygen structure. Temperature gradient changes are most evident. A correlation coefficient of 0.83 was calculated between the intensity of eleven oxygen inversions and the magnitude of associated temperature gradient changes. The largest oxygen inversion observed was accompanied by a salinity decrease of 0.06‰, as measured by a detailed hydrographic cast. Less precise CTD measurements sometimes suggest salinity decreases near oxygen maxima.
Two models for the generation of medium-scale oxygen structure have been considered. A horizontal mixing model based on the larger isentropic model of Tibby (1941) postulates the interleaving of dissimilar water masses along sigma-t surfaces. This model resembles that used by Pingree (1969) and by Simpson (1971) to interpret medium-scale temperature and salinity structure. The existence of large horizontal gradients in properties off the Oregon coast over distances as short as 20 miles favors this mechanism.

A quantitative example of horizontal mixing was worked using source profiles found at the northern and southern borders of Oregon. Temperature gradient changes resulted near the modeled oxygen maxima. The magnitude of these gradient changes agreed with those observed, supporting the horizontal mixing mechanism.

The in situ generation of medium-scale oxygen structure by layers of oxygen-consuming materials is unlikely. A transient state vertical model was considered in which consumption rate peaks were added to the exponential profiles calculated by Riley (1951) and by Wyrtki (1962). Consumption peaks several hundred times more intense than the background profile were required to produce medium-scale oxygen structure over periods less than ten days. Multiple net tows off Oregon do not indicate biomass layering of similar intensity (Pearcy and Mesecar, 1970).

Time scales associated with the decay of structure were
estimated by diffusion calculations. The results agree closely with those of Stommel and Federov (1967). Lifetimes of medium-scale structure are estimated at 2.6 days for features 15 meters in thickness to 48.1 days for features 60 meters in thickness, using an eddy diffusion coefficient of 1 cm$^2$/sec in the vertical.
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APPENDICES
APPENDIX I

CHARACTERISTICS AND USE OF A POLAROGRAPHIC CELL

The cell used in this study was manufactured by Delta Scientific Co., Lindenhurst, N. Y. (model 110-1). A simplified diagram appears in Figure 46. It is about six inches in length and 7/8 inches in diameter, with 5/16 inch diameter gold cathode. A rubber diaphragm equalizes the pressure between the environment and the electrolyte chamber, so that the cell may be used under hydrostatic pressure. Buffered KCl electrolyte and 0.001 inch thick Teflon membrane were supplied by the manufacturer. Modifications of the electrical leads used in this work are described in Chapter II.

Membrane-covered cells such as this one can be used in gas mixtures or in solutions, since oxygen diffuses through the membrane to the cathode in either case. When used in liquids, the probe must be moved relative to the fluid rapidly enough to ensure that a stagnant, oxygen-depleted layer will not develop adjacent to the membrane. Such a layer would constitute an additional diffusion barrier and influence the cell current. A relative velocity in excess of 0.05 meters per second is recommended by the manufacturer.
Figure 46. Simplified Sketches of the Polarographic Cell
1. Polarization Plateau

For operation of the cell, a potential source and a current-measuring circuit are connected in series with the electrodes as indicated in Figure 46. An example of the variation of cell current with applied voltage is shown in Figure 47. In this case the probe was operated in air at 18.6 degrees Centigrade. The applied potential region over which current varies only slightly is called the polarization plateau. When excited in this region, the cell current is limited by the rate of diffusion of oxygen to the cathode. As the rate of diffusion is the basis of measurement, membrane-covered cells are usually operated with a fixed potential in the polarization plateau region. Intermittent excitation is useful in some applications, however, as described by Lilley, Story, and Raible (1969).

Carey and Teal (1965) describe the variation of the polarization plateau under different conditions of electrolyte strength, membrane material, and membrane thickness. It was found that variations in temperature do not affect the position of the plateau region. The manufacturer of the cell used in this work recommends an 0.8 volt excitation. A fixed potential of 0.84 volts was used throughout this work.
Figure 47. Polarization Plateau
2. Thermal Characteristics

The following discussion applies to measurements taken in aqueous solutions at constant salinity and pressure. Grasshoff (1962), and Mancy, Okun and Reilley (1962) demonstrated that the current passed by a given cell at a fixed temperature varies linearly with dissolved oxygen concentration. At other fixed temperatures, the cell current also varies linearly with oxygen content, but with different constants of proportionality. This relationship is illustrated in Figure 48, redrawn from Grasshoff (1962) for temperatures between 2° and 30° Centigrade. The variation of slope with temperature results from changes in the membrane diffusivity and from the thermal coefficient of oxygen solubility in water.

Current-oxygen (i-o) plots, when derived from well-designed cells, show an intercept at the origin. Carey and Teal (1965) found that newly-constructed cells often show a non-zero intercept, probably resulting from the reduction of trace contaminants in the electrolyte. After operation for several hours, however, this "zero-error" was found to diminish to a negligible value.

If a polarographic cell is to be used to measure samples at constant temperature, it is possible to calibrate the instrument by measuring the current produced in one solution of known oxygen content. The straight line drawn between this point and the origin of
Figure 48. Polarographic Cell Temperature Characteristics (Grasshoff, 1962), and Temperature Correction Schematic
the i-o plot constitutes a calibration curve. In practice, it is advisable to use several measurements to establish the calibration line for greater certainty.

**Temperature Correction**

When the cell is to be used to measure the oxygen content under varying temperature conditions, it is desirable to use one calibration for all temperatures. Grasshoff (1962) tabulated the slopes, \( m_T \) (\( \mu A/ml/1 \)) of the cell performance curves for temperatures between 2° and 30° Centigrade. Choosing to establish calibration at 20°, a temperature correction factor \( F_T(20°) \) was defined by dividing the various slopes into the slope observed at 20°:

\[
F_T(20°) = \frac{m_{20°}}{m_T}.
\]  

(15)

It was asserted that the oxygen concentration read off the 20° calibration curve, when multiplied by \( F_T(20°) \) appropriate to the sample temperature, would yield the correct oxygen concentration of the sample.

The justification of this method of temperature correction can be explained with reference to the i-o schematic at the bottom of Figure 48. A given cell current, represented by a horizontal line, signifies different oxygen contents at each temperature (dotted abscissa values). This relationship can be expressed mathematically
if equations are written for each performance curve. The equation of the calibration line at temperature TC (20° in the case of Grasshoff) is:

\[ i = m_{TC} \cdot O_{TC} \]

For another temperature, T, the analogous equation is:

\[ i = m_{T} \cdot O_{T} \]

Equating the current in these expressions yields

\[ m_{TC} \cdot O_{TC} = m_{T} \cdot O_{T} \]

or

\[ O_{T} = \left( \frac{m_{TC}}{m_{T}} \right) \cdot O_{TC} \tag{16} \]

The slope ratio shown in parenthesis is the temperature correction factor defined in (15), if calibration is carried out at TC=20°. In practice, the cell current observed from the sample is applied to the calibration curve at temperature TC to derive a value \( O_{TC} \) (the oxygen content if the sample were at temperature TC). Multiplication by the slope ratio \( \frac{m_{TC}}{m_{T}} \) then gives \( O_{T} \), the actual oxygen content of the sample.
Generalized Temperature Correction

A method of \textit{in situ} calibration is used in this work (Chapter II) which necessitates calibration at any temperature found in the water column (including fractions of degrees). The temperature correction formula (16) can be used under these conditions if the i-o slope is written as a continuous function of temperature:

\[
\frac{m_T}{c} = f(T) .
\]  

(17)

The normalization constant \(c\) is used for convenience. Substituting this expression into 16 yields the generalized temperature correction formula used in this work (Chapter II):

\[
O_T = \frac{f(T_C)}{f(T)} \cdot O_{TC} .
\]  

(1)

The functional relationship 17 was obtained by fitting a fourth degree polynomial to a table of values supplied by the manufacturer of the polarographic cell used (Delta Scientific, undated). Temperature correction (slope) values, normalized\(^{12}\) by division by \(m_{10^\circ}\), are shown in Table VIII. Fitted values appear in Column 3, resulting from the polynomial given in Chapter II (Eqn. 2). Comparison

\(^{12}\)The normalization constant \(c\) (Eqn. 17) is chosen to be \(m_{10^\circ}\), with the result that \(f(10^\circ) = 1.\)
TABLE VIII. Normalized Temperature Correction Slopes, With Fitted Values and Experimental Comparisons.

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>Normalized Slope m/m$_{100}$</th>
<th>Fitted Value</th>
<th>Experimental Value</th>
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<tr>
<td>(1)</td>
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<td>(3)</td>
<td>(4)</td>
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values shown in Column 4 were derived from laboratory measurements of the current passed by a cell in a closed, stirred flask of seawater while temperatures were varied in a thermostated bath. A plot of \( f(T) \) appears in Figure 49.

3. Salinity and Hydrostatic Pressure Effects

Salinity

Membrane-covered polarographic cells respond to the partial pressure, or "tension," of oxygen in the sample rather than to oxygen concentration (Clark et al., 1953; Kanwisher, 1959; Mancy, Okun, and Reilley, 1962; Beckman Instruments Inc, 1969). Partial pressure is related to concentration through the gas solubility, according to Henry's law. Since concentration rather than partial pressure data are desired, salinity changes in the sample must be considered.

Kanwisher (1959) illustrates the effect as follows:

If an instrument is to be read in amount rather than in tension, it must be calibrated with a solution of the same gas solubility. Fortunately the salting out effect on gas solubility is not large. A change of 0 to 3.5 per cent salt decreases the oxygen solubility by only 20 per cent. (Kanwisher, 1959, p. 213)

A salinity change of 4% may be found in the water column off Oregon. The corresponding change in oxygen solubility is about 2.5 percent, providing an estimate of the error introduced by salinity changes. In applying the in situ calibration method, however, the
Figure 49. Temperature Correction Curve, With Experimental Values
oxygen probe data are made to correspond exactly to the chemical analyses at the deep and shallow calibration points (Chapter II). This method makes a two-point adjustment for the effects of salinity change in the water column. The systematic error found between calibration points, and below the deeper calibration point (Chapter II) includes salinity change error.

**Hydrostatic Pressure**

Hydrostatic pressure affects the diffusion characteristics of cell membranes, resulting in a decrease in the measured current (Chemical and Engineering News, 1964; Beckman Instruments Inc, 1969). Pressure changes in the water column are compensated by the in situ calibration method in this work. The effectiveness of this procedure is reflected in the overall instrument performance, Chapter II.

4. Transient Response

**Oxygen Level Transients**

The response of the Delta Scientific model 110-i cell was measured at several temperatures in the laboratory. A procedure described by Carritt and Kanwisher (1959) was used to provide step changes in oxygen concentration. The cell was quickly transferred
from a beaker of air-saturated water to a beaker in which oxygen was diminished by vigorous bubbling with nitrogen gas. Both beakers were 80 percent immersed in a thermostated bath and were allowed to equilibrate for a half hour before a run. Bubbling of nitrogen gas and air into the separate beakers was carried out during the equilibration and measurement periods.

An example of cell response to step changes in oxygen concentration is shown in Figure 50. A Varian (chassis Al) strip chart recorder was used to measure the cell current as a function of time. In this experiment, at 20°C, 63 percent of full response was achieved in 5.4 seconds, and 97 percent in 13.7 seconds. The results of similar experiments at different temperatures are shown graphically in Figure 51. The responses are found to be approximately logarithmic, as shown by extracting several values from the recordings and plotting them on semi-log scale. The variation of 63 percent and 97 percent response times with temperature is portrayed in Figure 6 (Chapter II).

**Thermal Transients**

Laboratory experiments were conducted to measure the thermal response of the Delta Scientific model 110-1 cell. The procedure

---

13 The full-scale response time of this recorder is about one-half second, comparable to the one-fourth second digitizing interval for the in situ oxygen probe system.
Figure 50. Cell Response to a Step Change in Dissolved Oxygen Concentration at 20 Degrees Centigrade
Figure 51. Polarographic Cell Response to Oxygen Level Transients at Four Temperatures
used was similar to that previously discussed, except that the two test beakers were immersed in separate thermostated baths, one at 20°C and the other at 10°C. In order to isolate the effect of temperature, both beakers were vigorously bubbled with air for one-half hour. Assuming equilibrium, both solutions contain the same partial pressure of oxygen under these conditions. When the cell was quickly transferred from the warmer to the colder solution, 97 percent response was achieved in 13 seconds.

The possible variation of thermal response time with oxygen level was studied by diluting the common bubbled gas mixture with nitrogen until the oxygen content was 76 percent atmospheric in one case, and 46 percent atmospheric in another case. The measured 97 percent response times under these conditions were 12 seconds and 16 seconds, respectively.

An experiment involving a step change in oxygen partial pressure and a simultaneous change in temperature from 20°C to 10°C was performed to simulate conditions which might be found in the seasonal pycnocline. Air was bubbled through the beaker at 20°C, while the beaker at 10°C was stripped by bubbling with nitrogen. The measured 97 percent response time in this case was 16 seconds.

The above tests give an estimate of thermal response to conditions which might be found in the ocean. No attempt was made to cover all combinations of temperature and oxygen ranges. The
results of these tests all show a 97 percent response time near 15
seconds for a temperature change from 20° to 10°. This figure is
close to the response for a step change in oxygen level alone at inter-
mediate value of 15° (See Figure 6). For purposes of deriving
approximate values for the response distance L, then, it may be
concluded that thermal response times are commensurate with oxygen
level response times and that values from Figure 6 may be used
alone. Conversely, it would not be profitable to attempt to improve
spatial resolution by compensating for thermal transients (either
electronically or by computer) since response to oxygen transients
is of comparable duration, and since temperature and oxygen gradi-
ents usually occur simultaneously in the ocean.

5. Sealing Techniques for in situ Use

The most important single consideration for using the cell
in situ is to insure that the electrolyte reservoir be completely sealed
from the surrounding seawater. As most data transmission systems
are electrically referenced to seawater ground, any minute leakage
constitutes an alternate current path to the measuring system and
generally causes the signal to be unreadable. Although the method
of fitting new membranes described by the manufacturer\(^\text{14}\) was

\(^{14}\text{Considerable practice is required to fit a membrane smoothly}
\text{without trapping a thin bubble of air adjacent to the cathode.}\)
followed (Delta Scientific Co, undated), it was found that the "o" ring seal is not sufficient to prevent leakage around the membrane. Reliable sealing is accomplished by omitting the plastic collar ahead of the "o" ring (Figure 46) and applying electrical splicing compound. Scotchfil Insulation Putty is stretched until thin and is wound directly onto the membrane material ahead of the "o" ring, starting at the edge of the convex front surface. The wrapping is continued over the rear collar and directly onto the cell body. Membranes sealed in this way have required no further servicing for more than 40 oceanographic casts and have retained their integrity for several successive cruises.

A simple electrical method was devised for testing the cell for leakages. One lead of an ohmmeter, set on the highest resistance scale, is connected to either of the polarographic cell leads. The cell is immersed gradually into a bucket of seawater, while repeatedly touching the water surface with the other ohmmeter lead. Any slight deflection of the meter needle indicates an electrical communication between the cell reservoir and the seawater. The location of the leak can be inferred from the mark of the water on the cell when deflection first begins. A totally sealed cell can be completely immersed without any needle deflection.

Leakages have been found at joints in the cell body itself, as well as around the membrane. These can be corrected by roughening
the area with a file and applying epoxy cement. Trace electrical leakages around the "o" rings which seal the electrolyte filling port and the pressure equalization diaphragm can be avoided by applying silicone grease. It is important that the electrolyte reservoir be filled until no large air bubbles remain, in order to prevent the diaphragm from rupturing when the cell is deeply submerged.
APPENDIX II

STATISTICAL METHODS AND DATA

1. Paired Difference Methods

Model Equation

The following treatment, although simple, is judged worthy of stating because it illuminates the general problem of assessing the reliability of in situ measurement in oceanography.

In order to interpret difference statistics it is instructive to account for the various factors which enter into each measurement. Since Winkler analysis is standard for determining the dissolved oxygen content of water, it can be assumed that the mean of many analyses of a given sample yields the true oxygen content. Any single determination, however, may contain a random measurement error \( \epsilon_w \), since the method is not absolutely precise. A model equation for Winkler analysis, then, can be written as

\[
X_w = O + \epsilon_w,
\]

(18)

where: \( X_w \) = Winkler analysis determination (ml/1)

\( O \) = oxygen content of the sample (ml/1)

\( \epsilon_w \) = random error (ml/1).
In the case of oxygen probe measurements, there may be a systematic error \( \gamma \) as well as a random error \( \varepsilon_p \). Accordingly, a simple model equation is

\[
X_p = O + \gamma + \varepsilon_p ,
\]

(19)

where \( X_p \) = oxygen probe reading

\( O \) = oxygen content of the sample

\( \gamma \) = bias

\( \varepsilon_p \) = random error.

Subtracting 19 from 18 eliminates the oxygen level, \( O \), and yields a model equation for the difference between paired observations:

\[
d = (X_w - X_p) = \gamma + \varepsilon_w + \varepsilon_p .
\]

(20)

This expression applies when both methods of measurement are performed on the same sample. The sign of \( \gamma \) is arbitrary, and the random terms \( \varepsilon \) assume positive and negative values.

In the present work, hydrographic casts and oxygen probe casts are made successively, and replication error is certain to occur. If the oxygen contents in model Equations 18 and 19 are subscripted to show that they differ, a replication term \( (O_w - O_p) \) would appear in the right-hand side of Equation 20. Since in any pair of observations it is equally likely that \( O_w \) exceeds \( O_p \) as the reverse, it is reasonable to take \( (O_w - O_p) \) as a random variable with
a mean of zero. Denoting this as the replication error, $\varepsilon_r$, the model equation for the present work becomes

$$d = \gamma + \varepsilon_r + \varepsilon_w + \varepsilon_p.$$  \hspace{1cm} (21)

If the three error terms are assumed to be normally distributed and mutually independent, then it follows that $d$ is a normal random variable with mean $\mu_d = \gamma$, and with variance

$$\sigma_d^2 = \sigma_r^2 + \sigma_w^2 + \sigma_p^2.$$ \hspace{1cm} (22)

**Test of Bias**

A number of paired observations can be used to test whether $\mu_d = 0$, i.e., whether the instrument readings differ systematically from Winkler analyses. For this purpose it is not necessary to specify the sources of error, but only to stipulate that $d$ is a normally distributed random variable. For $n$ pairs of observations, $d_i$, the sample mean

$$\bar{d} = \frac{\sum_{i=1}^{n} d_i}{n}$$

and standard deviation

$$s_d = \sqrt{\frac{\sum_{i=1}^{n} (d_i - \bar{d})^2}{n-1}}$$

are calculated, and used to compute the $t$ statistic

$$t = \frac{\bar{d} - \mu_d}{s_d / \sqrt{n}}.$$  \hspace{1cm} (23)

\[15\] The Chi-square test for normality (Wine, 1964) was applied separately to the distribution of $d$ resulting from the March and June 1971 cruises. In each case the hypothesis that the parent population is normal is not rejected at the 2.5% significance level.
In this expression $\mu_d$ is the value of the population mean under test (zero). The computed value of $t$ is compared to tabulated values having $(n-1)$ degrees of freedom, according to the desired significance level of the test, $\alpha$. If the absolute value of $t$ calculated is greater than the appropriate tabulated value, then the hypothesis that $\mu_d = 0$ is rejected, and the instrument is concluded to be biased (Wine, 1964, sect. 8.7).

Symmetric $(1-\alpha)$ confidence intervals for $\mu_d$ are given by

$$\bar{d} \pm t_{\alpha/2} \cdot \frac{s_d}{\sqrt{n}},$$

(24)

where $t$ is the tabulated value of $t$ having $(n-1)$ degrees of freedom. The hypothesis that $\mu_d = 0$ can be rejected at the $\alpha$ significance level if the symmetric $(1-\alpha)$ confidence interval for $\mu_d$ does not include zero.

**Overall Precision**

The standard deviation of many replicate determinations on a single sample is often used as a measure of analytical precision. This method is not directly applicable to *in situ* oceanic measurements because of the impossibility of making truly replicate observations. Aside from the dispersion about the regression line, previously mentioned, the dispersion of the difference random variable $d$ may be used to represent the overall precision of measurement.
The percentage of \( d \) values which lie within convenient limits, as reported by Carlson (1970) and by VanLandingham and Greene (1971), is a measure of this dispersion. The sample standard deviation, \( s_d \), is perhaps more useful, since it can be used to construct confidence intervals for the population standard deviation \( \sigma_d \), and to test hypotheses concerning the equality of variances. It must be assumed first that \( d \) is a normally-distributed random variable.

It is often desirable to compare the precision of two instruments or to test whether the precision of an instrument is significantly different in two tests. The corresponding hypothesis that two variances \( \sigma_1^2 \) and \( \sigma_2^2 \) are equal can be tested by forming the ratio of their respective sample variances, \( s_1^2 / s_2^2 \). This ratio is called the F statistic with \((n_1-1)\) and \((n_2-1)\) degrees of freedom where \( n_1 \) and \( n_2 \) are the two sample sizes. If this value of F exceeds the tabulated value for the significance level desired, the hypothesis that \( \sigma_1^2 = \sigma_2^2 \) is rejected.

A symmetric confidence interval for \( \sigma_d^2 \) may be constructed from the sample standard deviation by using the Chi-square distribution. The \((1-\alpha)\) confidence interval for \( \sigma_d^2 \) is

\[
\frac{(n-1) s_d^2}{\chi^2_{1-\alpha/2}} \leq \sigma_d^2 \leq \frac{(n-1) s_d^2}{\chi^2_{\alpha/2}},
\]

(25)
where the denominators are the tabulated values of Chi-square having (n-1) degrees of freedom.

**Partition of Overall Precision**

Measures of overall precision are useful for indicating the gross effects of substituting oxygen probe measurements for hydrographic sampling. Such measures underestimate the performance of the probe itself. According to Equation 22, the variance of \( d \) contains additive contributions from Winkler analysis, from replication error, and from the oxygen probe. In order to characterize the probe, it is desirable to subtract these contributions, leaving \( \sigma_p^2 \) alone.

Although an estimate of the Winkler analysis precision \( \sigma_w^2 \) can be derived by performing many analyses upon a single sample, the variance introduced by replication error, \( \sigma_r^2 \), cannot be evaluated directly. Its value might depend upon the time interval between hydrographic casts and *in situ* casts, upon any errors in depth determinations, and upon the character of the water sampled. Paired observations made in waters containing sharp oxygen gradients would be expected to contain more replication error than those made in more homogeneous water.

An indirect estimate of replication variance can be derived from the results of two tests performed on the Beckman Minos DOM
system. In one of these studies (VanLandingham and Greene, 1971) sample bottles were attached to the probe itself, so that the results do not contain replication error. Consequently, model Equation 20 applies to this study, and the term $\sigma_r^2$ should be omitted from Expression 22. In the other study (Carlson, 1970) comparisons were made to hydrographic casts, so that model Equation 21 and Expression 22 apply directly. Assuming that $\sigma_w^2$ and $\sigma_p^2$ are the same in both tests, the difference between the observed overall sample variances ($s_d^2$) is a point estimate of $\sigma_r^2$. This figure may be used with caution to represent the replication error in other experiments having similar time differences between hydrographic casts and oxygen probe casts.

Using the above methods to derive estimates of $\sigma_w^2$ and $\sigma_r^2$, it is possible to make rough estimates of instrumental precision ($\sigma_p^2$) for both the digital oxygen probe and the Beckman Minos DOM. In the latter case it is sufficient to deduct $s_w^2$ from the value of $s_d^2$ calculated from the data of VanLandingham and Greene (1971). In the case of the digital oxygen probe, $s_w^2$ and $s_r^2$ are both subtracted from the observed value of $s_d^2$. Figures obtained in this way should be interpreted only as approximations to the relative magnitudes of the various components of overall precision.
2. Paired Difference Results

Data

The oxygen probe system was compared to hydrographic sampling on two occasions, using the methods described in Chapter II. The results of modified Winkler analysis (Strickland and Parsons, 1965) for the March and June 1971 cruises are presented in Tables IX and X, respectively, along with oxygen probe readings at corresponding depths. Differences between the paired observations are also tabulated. Various statistics based on the observed differences (d) are presented in Table XI. The measures of dispersion introduced by Carlson (1970) are shown in columns 3 through 5. On the assumption that the differences stem from normal populations, 95 percent confidence intervals for $\mu_d$ and $\sigma_d$ are given in parenthesis below their respective point estimators $\bar{d}$ and $s_d$, as calculated by equations 24 and 25.

Bias Tests

It can be inferred directly from Table XI that in both the March and the June evaluations of the digital oxygen probe, the observed mean $\bar{d}$ is not significantly different from zero at the
### TABLE IX. Hydrographic and Oxygen Probe Data, March 1971

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<th>Temperature (°C)</th>
<th>Salinity (%)</th>
<th>$\sigma_t$</th>
<th>Winkler oxygen (ml/l)</th>
<th>AOU (ml/l)</th>
<th>Oxygen probe difference (6)-(8)</th>
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*Values excluded from statistical analysis because derived from the seasonal oxycline

**Values excluded from statistical analysis because used for in situ calibration
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### TABLE X. Hydrographic and Oxygen Probe Data, June 1971

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*Values excluded from statistical analysis because derived from the seasonal oxycline

**Values excluded from statistical analysis because used for in situ calibration
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<th>Salinity (%)</th>
<th>$\sigma_t$</th>
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<th>AOU (ml/l)</th>
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*Correlations significant at the .05 level.
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<th>AOU (ml/l)</th>
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**TABLE X.** Continued
TABLE XI. Results of Difference Analysis; Statistics and Parameter Estimates (with 95% confidence limits).

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<th>% d within 0.2 ml/l</th>
<th>% d within 0.3 ml/l</th>
<th>Sample Mean, d</th>
<th>Sample Standard Deviation, SD_d</th>
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<td>(.069, .107)</td>
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<td>Beckman Minos DOM</td>
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<td>91</td>
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<td>(Carlson,'70)</td>
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<td>(-0.022, -0.022)</td>
<td>(.054, .086)</td>
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*Based on grouped data extracted from plot
five percent level. The same test applied to the Minos DOM shows \( \bar{d} \) significantly greater than zero in the investigation of VanLandingham and Greene (1971), but this bias disappears when data from cast 3 are discounted. The grouped data of Carlson (1970) also does not contradict the hypothesis that \( \mu_d = 0 \) at the five percent significance level if two decimal places are retained.

It can be concluded that if \( d \) is treated as a normal random variable, neither the digital oxygen probe nor the Minos DOM is biased relative to Winkler analysis. This conclusion differs from the results of simple linear regression analysis previously shown. The discrepancy is explained by noting that regression analysis takes into account linear trends of the bias with oxygen concentration level, whereas the difference method does not.

**Overall Precision**

The standard deviations of the observed differences \( s_d \) shown in Table XI are measures of overall precision. As previously discussed, this figure generally contains contributions from Winkler analysis precision, instrumental precision, and replication error. In the study by VanLandingham and Greene (1971), replication error was avoided by the sampling method.

\[1^6\] The hypothesis \( \mu_d = 0 \), referred to the alternative \( \mu_d \neq 0 \), is not rejected at the five percent significance level.
In order to represent the overall precision of measurements, it is first necessary to decide whether the results of the March and June tests of the digital oxygen probe should be pooled or treated separately. Similarly, it must be decided whether or not to include the results of cast 3 in the study of VanLandingham and Greene. The applicable statistical test is the F test, which may be used to decide whether the observed variances could stem from the same population.

In the case of the digital probe, the ratio of sample variances for the June and March cruises is computed to be \((0.152)^2/(0.084)^2 = 3.29\). Since this value exceeds that of the appropriate F statistic at the five percent significance level, \(F_{(47,41)} = 1.66\), it is concluded that the variance in the June cruise stems from a different population. The greater temperature range in this cruise and the difficulty in applying the in situ calibration method because of the near-surface oxygen maximum may account for this significantly greater variance. In a similar way, the ratio of sample variances in the two subdivisions of VanLandingham and Greene's study is \((0.139)^2/(0.066)^2 = 4.45\), which lies well beyond the five percent level critical point, \(F_{(46,35)} = 1.71\). Consequently, it is decided that the inclusion of data from cast 3 has a significant effect.

Since the above tests show the two pairs of results to be internally incompatible, it is well to choose the less perfect figure
in each case to represent overall precision. The following reasons may be cited:

1. A user of the digital probe would be likely to be faced with *in situ* calibration in a region of high oxygen gradient, as in the June cruise.

2. A user of the Beckman Minos DOM would be likely to make velocity errors, as did VanLandingham and Greene.

3. The analyses are to be compared to that of Carlson (1970) who reports no special treatment of data.

4. Conservative estimates of precision are preferable, in general.

The results shown in the second, third, and fourth rows of Table XI are therefore chosen to represent the three studies.

The chosen values of $s_d$ are summarized in Table XII, arranged in order of magnitude. Also shown are the results of F tests performed in various combinations between them. The numbers in parentheses are values of the sample variance ratios and the corresponding critical values of F at the five percent significance level. In forming the variance ratios the larger value was always used in the numerator.

The only significant difference shown in Table XII occurs between the two tests of the Minos DOM. Although both studies were performed on the same make of instrument, the populations from which these two variance samples were drawn differ in that
one contains replication error and the other does not. The conclusion that the two population variances are unequal is, therefore, not unexpected.

Table XII. Comparisons of Overall Precision

| Source                      | Sample Size | $s_d$ (ml/1) | Results of F tests | $s_{y|x}$ from regression analysis (ml/1) |
|-----------------------------|-------------|--------------|--------------------|------------------------------------------|
| Beckman Minos DOM (VanLandingham & Greene, 1971) | 47           | 0.139        | not significant (1.19, 1.63)          | 0.127                                    |
| Digital Oxygen Probe (June 1971) | 48           | 0.152        | not significant (1.47, 1.50)          | 0.138                                    |
| Beckman Minos DOM (Carlson, 1970) | 199*         | 0.184*       | significant (1.74, 1.51)              |                                           |

* Based on grouped data extracted from plot.

The value of $s_d$ stemming from the digital oxygen probe lies between the two corresponding values derived from the Minos DOM. Since it also contains a contribution from replication error, it is more properly compared to the value derived by Carlson (1970). The point estimate of $s_d = 0.152$ is not significantly different from 0.184 at the five percent level, but it is significantly different at
the ten percent level. It may be concluded that the overall precision displayed by the digital oxygen probe is comparable to, or somewhat better than, that obtained by Carlson (1970) using the Beckman Minos DOM.

Values of $s_{y|x}$ entered in Table XII are only slightly lower than corresponding values of $s_{d'}$, showing that the two measures of overall precision are comparable.

**Partition of Overall Precision**

The additivity of variances for tests of the digital oxygen probe and for the study conducted by Carlson (1970) is expressed by Equation 22. For the study by VanLandingham and Greene (1971) the replication term $\sigma^2_r$ is omitted. Estimation of the magnitude of each variance component can be performed by subtraction of sample variances, as previously discussed.

Since oceanographic dissolved oxygen analyses are carried out aboard ship under often adverse conditions, the figure chosen to represent Winkler analysis precision should be based on these real conditions. Linnenbom, Swinnerton, and Cheek (1965) report a value of 0.046 ml/l as an estimate of $\sigma_w'$ based on a shipboard intercomparison experiment involving 94 samples. This figure will be used to represent Winkler analysis precision for all studies
reported in this work.\footnote{17}

An estimate of the instrumental precision of the Beckman Minos DOM can be made by subtracting the Winkler variance from the overall variance observed in the study of VanLandingham and Greene (1971):

\[
s_p^2 = s_d^2 - s_w^2 = (0.139)^2 - (0.046)^2 = 0.0173,
\]

or, \( s_p = 0.131 \text{ ml/l} \). A similar computation excluding cast 3 yields \( s = 0.047 \text{ ml/l} \), a precision comparable to that of the Winkler method itself. This latter figure cannot be considered a conservative estimate of instrumental precision, since it is based on selected data.

An estimate of replication error variance is found by subtracting the value of \( s_d^2 \) resulting from VanLandingham and Greene's study from that resulting from Carlson's study. Using the figure from Table XII:

\[
s_r^2 = (0.184)^2 - (0.139)^2 = 0.0144,
\]

or \( s_r = 0.120 \text{ ml/l} \).

Partition of overall precision in the case of the digital oxygen probe can be carried out by using the above value of \( s_r \), the previously-assigned value of \( s_w \), and the observed sample variance \( s_d^2 \) stemming from the cruise in June 1971. According to Equation 22:

\footnote{17 The precision of shipboard Winkler analysis at Oregon State University is comparable to this figure (Wyatt et al., 1971).}
\[ s_p^2 = s_d^2 - s_w^2 - s_r^2 \]
\[ = (0.152)^2 - (0.046)^2 - (0.120)^2 \]
\[ = 0.0065, \]
or, \( s_p = 0.081 \text{ ml/l}. \) The justification for extending the previously-derived value of \( s_r \) to the present analysis is the similarity of standard hydrographic procedures and the similarity of the time intervals between oxygen probe casts and hydrographic casts. If the differences in the character of the waters sampled are considered, a higher replication error would be expected in tests of the digital oxygen probe, since Oregon waters show greater total variation in oxygen concentration. Subtraction of a higher replication variance would result in a yet lower estimate of instrumental precision.

Results of the partition of overall variance are summarized in Table II (Chapter II). Values of \( s_r \) and \( s_p \) should be interpreted liberally but are useful for indicating the relative importance of the components of the variances observed.