Many different aspects of the determination of dissolved oxygen
by controlled potential coulometry were investigated to find a means
of measuring the oxygen content of natural waters. Rapid
sampling techniques, simplicity of operation, and rugged structural
features were stressed. Cells were designed to operate by either
internal electrolysis or external potential control. A type of steel
flow cell of optimum geometry was designed, and measured oxygen
in flow streams with 3% accuracy. Periodic sampling was found to
be superior to flow analysis, and the flow cell operated by a method
of periodic entrapment of sample yielded the most promising results.
0.2% reproducibility was obtained for samples which contained one
to five ppm dissolved oxygen, and 1% reproducibility for samples
below one ppm. The error in the analysis could not be distinguished
from the two percent error in the Winkler titration which was used
to determine the standards. Other sample entrapment cells of a
different design and with different cathode materials were studied. Two vibrating electrode cells were investigated and found to give no better results than those cells which permit oxygen reduction in quiet solutions.

Mercury, gold, platinum, nichrome, stainless steel, and brass were tested as cathode materials. The polarographic and coulometric behavior of dissolved oxygen reduced in cathodes of these materials is described.

The investigation of mercury as a cathode material led to the development of an empirical method that relies on the rapid reduction of oxygen on a mercury-electrolyte interface. In one case, 0.5% reproducibility was obtained for individual samples determined at the rate of one every 15 seconds. The utility of these devices, although the current efficiency is low, is pointed out as their potential use as flow stream monitors.

The entire work yielded information based on new approaches for the development of ocean-going devices which will measure dissolved oxygen concentrations by controlled potential coulometry to a better degree of accuracy than the existing methods. Design theory and cell construction is presented for devices that operate where rapidity of successive determinations is more important than absolute accuracy.
COULOMETRIC DETERMINATION
OF DISSOLVED OXYGEN

by

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# TABLE OF CONTENTS

**INTRODUCTION** ................................................. 1

**ELECTROANALYTICAL CHEMISTRY OF DISSOLVED OXYGEN** 6

- Voltammetry .................................................. 7
- Coulometry .................................................. 15

**EXPERIMENTAL** ................................................

- Construction of the Circuit for Controlled Potential Coulometry .... 17
- Cell Studies and Electrode Designs .......................... 21
  - Reference Electrodes .................................... 21
  - Cells Using Various Cathodes ............................ 26

**INTERFACE ELECTROLYSIS** .................................... 58

- The Unstirred Mercury Cathode Cell ......................... 58
- The Mercury Torus Cell ....................................... 75

**CONCLUSIONS** ................................................ 88

**BIBLIOGRAPHY** ................................................. 93

**APPENDIX I** .................................................. 97

**APPENDIX II** .................................................. 109
<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>Polarogram of Molecular Oxygen in Sea Water</td>
<td>9</td>
</tr>
<tr>
<td>II</td>
<td>Schematic Diagram of the Simple Controlled Potential Coulometer</td>
<td>18</td>
</tr>
<tr>
<td>III</td>
<td>Diagram of the Potential Source</td>
<td>20</td>
</tr>
<tr>
<td>IV</td>
<td>Recorder Range and Zeroing Circuit</td>
<td>22</td>
</tr>
<tr>
<td>V</td>
<td>Representation of Reference Potentials</td>
<td>25</td>
</tr>
<tr>
<td>VI</td>
<td>Gold Screen Cathode Cell Assembly</td>
<td>28</td>
</tr>
<tr>
<td>VII</td>
<td>Diffusion Current of Oxygen on the Large Gold Cathode</td>
<td>30</td>
</tr>
<tr>
<td>VIII</td>
<td>Diagram of the 16&quot; Flow Cell</td>
<td>33</td>
</tr>
<tr>
<td>IX</td>
<td>Diagram of the 28&quot; Flow Cell</td>
<td>33</td>
</tr>
<tr>
<td>X</td>
<td>Voltage Scan with the Steel Cell</td>
<td>34</td>
</tr>
<tr>
<td>XI</td>
<td>Response of the Flow Cell</td>
<td>36</td>
</tr>
<tr>
<td>XII</td>
<td>Assembly of the Brass Flow Cell</td>
<td>40</td>
</tr>
<tr>
<td>XIII</td>
<td>Variation in Current vs. Time for the Steel Cell</td>
<td>46</td>
</tr>
<tr>
<td>XIV</td>
<td>Schematic of the Platinum Sandwich Cell</td>
<td>48</td>
</tr>
<tr>
<td>XV</td>
<td>Platinum Vibrating Electrode Short Circuit Electrolysis Cell</td>
<td>52</td>
</tr>
<tr>
<td>XVI</td>
<td>Vibrating Nichrome Wire Coulometric Cell</td>
<td>55</td>
</tr>
<tr>
<td>XVII</td>
<td>Response of the Vibrating Nichrome</td>
<td>57</td>
</tr>
<tr>
<td>XVIII</td>
<td>Interface Electrolysis Cell</td>
<td>61</td>
</tr>
<tr>
<td>XIX</td>
<td>Waves from Metering Pumped Samples</td>
<td>68</td>
</tr>
<tr>
<td>XX</td>
<td>Wave of a Metering Pumped Sample with Decreased Injection Time</td>
<td>69</td>
</tr>
</tbody>
</table>
LIST OF FIGURES (Cont'd)

XXI Wave of an Excessively Concentrated Sample 70
XXII Variation in Current vs. Time of Oxygen and Cadmium Samples 71
XXIII Final Design of the Mercury Torus Cell 77
XXIV Filtering Circuit 79
XXV Response of the Torus Cell 82

Appendices

I-A Polarograms with the Lead Electrode 99
II-A Polarograms with the Nichrome Wire Electrode 101
III-A Polarograms with the Nichrome Electrode 104
IV-A Graph of Results with the Nichrome Electrode 105
V-A Reduction of Oxygen on a Stainless Steel Microelectrode 108
I-B Schematic Diagram of Syringe Drive 111
II-B Schematic Diagram of Stopcock Drive 112
## LIST OF TABLES

<table>
<thead>
<tr>
<th>I</th>
<th>Results from the Flow Cell</th>
<th>38</th>
</tr>
</thead>
<tbody>
<tr>
<td>II</td>
<td>Results of the Entrapment Cell</td>
<td>43</td>
</tr>
<tr>
<td>III</td>
<td>Results from the Unstirred Mercury Cathode Cell</td>
<td>72</td>
</tr>
<tr>
<td>IV</td>
<td>Results from the Torus Cell</td>
<td>83</td>
</tr>
</tbody>
</table>
COULOMETRIC DETERMINATION
OF DISSOLVED OXYGEN

INTRODUCTION

For over half a century molecular oxygen dissolved in environmental waters, lakes, streams, or seas, has been analyzed by the Winkler wet-chemical procedure or some modification of it. Water samples obtained at depth in Nansen bottles from hydrographic casts in the ocean or from flow samples piped in from rivers are treated and titrated with standard reagents. Although this method is precise, it is subject to the following disadvantages: Accuracy is seldom better than two percent. Corrosive chemicals and fragile glassware must be stocked. Often pint-sized samples are needed. Each analysis requires several minutes. The analyst is required to perform titrations under conditions ranging from fatigue, seasickness and stormy weather to darkness, dampness and bad temper. An instrument automatically telemetering data from a remote chemical transducer to a ship based or land based data storage unit would obviate these difficulties. Construction of such a device presents immensely complex problems. Only certain phases have been met with success. Strangely enough, the present routine method has no predecessor. That it has no real successor speaks remarkably well for the 70 year old work of L. W. Winkler.

The enormous, world-wide quantity of controversial Winkler
oxygen data on dissolved oxygen distribution constantly are being being amassed. Winkler titrations are a convenience consistent with the casting method of sampling. The Winkler method will be replaced only with a great deal of energy on a global scale. In spite of this the various oceanographic and pollution laboratories under full realization of the disadvantages of the Winkler method now sponsor programs for the investigation and development of other oxygen methods. Because the acoustical behavior of wave transmission is influenced somewhat by the microstructure of the dissolved oxygen distribution, the United States Government has promoted effort in oxygen analysis research for the field of undersea communications and the conduct of antisubmarine warfare as well as in general oceanography.

In the past decade attempts have been made to perform the analysis of dissolved oxygen at the natural source as an in situ determination an Ort und Stelle. Various methods based on one or the other of the unique physical or chemical properties of molecular oxygen have been utilized. The advent of gas chromatography gave rise to the invention of sensitive methods for all the dissolved atmospheric gases. The peculiar paramagnetic behavior of molecular oxygen has led to the construction of successful devices based on this property. For these procedures as well as for others, however, the oxygen must be stripped from its dissolved state and transferred to the gas
phase before analysis is possible, and therefore they are not partic-
ularly promising for deep-sea studies. The lowering of a so-called
dissolved oxygen probe from the deck of a ship into a remote, sub-
merged environment has been more or less successfully accom-
plished. Since these probes are largely based on some voltam-
metric or polarographic process in which an electric current is
read out and correlated with oxygen tension, their success largely
depends upon the care in calibration needed to cope with the influ-
ence of extraneous variables on the current readings. These probes
are most suitable for differential analysis, such as the tracking of
oxygen concentration changes due to photosynthetic activity.

Since the beginning of this century, various authors have re-
ported values for the solubility of the permanent gases in sea water
and distilled water. Most of the values vary by ± 1% with some var-
iation up to 4%. The need for an accurate laboratory method to pro-
duce a reliable set of solubility data is obvious, since standards pre-
pared from air or oxygen saturated solutions are useful for calibrat-
ing field instruments. Recent work by other investigators is helping
to alleviate the problem.

The original motives of this investigation might well have been
concerned with attacking the solubility problem. However, the per-
fection of a precise laboratory device would have been an entire
project by itself. Therefore, because of the oceanographic need, it
was decided to investigate existing methods for an approach from which could be produced a rapid and more accurate in situ instrument. Efforts were directed toward that goal.

Operation of a device based on an electrochemical property, specifically the reduction of a molecular oxygen on the surface of a cathode in an electrochemical cell is suitable. The oxygen can be reduced at applied potentials less negative than those potentials which would reduce most of the other impurities or heavy metal ions existing in the aqueous media of streams or oceans. Copper, bismuth, antimony, lead and tin interfere but usually to a negligible degree. The current produced by the reduction of oxygen is the basis of the polarographic procedures now being used. Conductometric methods and catalytic electrolyses were also possibilities.

Of the existing methods, controlled potential coulometry was chosen (1) because of the inherent accuracy and flexibility of this method, (2) because the need for adding reagents is eliminated, and (3) because the final readout corresponds to the mass of dissolved oxygen in a definite volume of sample rather than an intrinsic concentration in the environment of the probe. These criteria apply to laboratory coulometric devices. Ideally, the in situ instrument must meet seven other criteria which require that (1) there be rapid sampling and analysis to enable the construction of oxygen vs. depth profiles, (2) the operation of sample input be mechanically
controlled, (3) no part of the operation of the cell involves the gaseous phase, (4) there be simplicity in all mechanical operations consistent with the capabilities of remotized engineering, (5) the cost be minimized if expended materials be used, (6) the physical nature of the probe be rugged and not require maintainance between samplings, and (7) the output signal is capable of being telemetered.

These additional criteria which define long-range goals place severe limitations on existing coulometric methods. Any new approach must be evaluated according to how many of the criteria can be met to a satisfactory degree.

The first of the sections in the thesis presents a review of electrochemical methods. The construction of the coulometer circuit is described in the next section. The following sections deal with the presentation of the development of the coulometric devices cataloged according to their mechanical nature. To meet some of the criteria, rather radical innovations in current theories of coulometric cell methodology had to be introduced. In general the form for the presentation of each approach is (1) principle to be developed, (2) description and operation of the final cell model, (3) analytical results, and (4) discussion and evaluation. Often a method yielded results which were useful for applications other than the original purpose.
ELECTROANALYTICAL CHEMISTRY OF DISSOLVED OXYGEN

Wet chemical methods for the determination of dissolved oxygen including recent modifications in the Winkler titration have been summarized in the bibliography of an article by Roskom and Langen (33). Their paper describes the compleximetric titration where ferrous ion is oxidized by molecular oxygen to ferric ion. Titrating the ferric ion at a pH of 7.5 with EDTA using salicylic acid as indicator yields a quantitative value for the oxygen. This method eliminates the elaborate precautions needed in polluted waters and the rather unstable thiosulfate titrant of the Winkler procedure.

Richards (32) has reported on oxygen in the oceans and summarized data on the distribution of oxygen in the various water masses throughout the world. He treated the physical and biological processes that are responsible for the depletion and renewal of oxygen in surface waters, and the circulation processes which alone replenish at depths. Oxygen distribution was related to other non-conservative properties as well as to depth, temperature, and salinity.

The search to determine a reliable set of data for the solubility coefficients and saturation values of atmospheric gases in waters at various salinities and temperature has spawned several approaches by different methods. The most recent work was performed by
Douglas (10) using a microgasometric technique. Douglas summarizes the methods and values of previous investigators.

**Voltammetry**

The electrochemical breakdown of water for the liberation of hydrogen and oxygen has been practiced since Faraday's time. The electrochemical analysis of oxygen, however, is based on the reverse process. Dissolved oxygen reacts with hydrogen ions or water molecules to form either hydrogen peroxide or hydroxyl ions. The analytical possibilities were seen as a naturally occurring result of the early experiments in the beginnings of polarography. Diffusion current waves for the reduction of dissolved molecular oxygen at the surface of a mercury drop were first encountered by Heyrovsky (17) and his co-workers during their initial studies of the dropping mercury electrode. The electrolyte solutions under investigation happened to contain dissolved atmospheric gases. Kolthoff and Lingane (24, p. 552-558) report in their section on oxygen various characteristics of the behavior of the reduction on mercury and with solid electrodes. In air saturated dilute aqueous solutions the oxygen concentration is of the order of $3 \times 10^{-4}$ moles per liter or eight parts per million. When such a solution is analyzed with a dropping mercury electrode, a diffusion current wave results as a linearly increasing negative potential is applied
between the electrode and reference half-cell. Two plateaus occur on the wave because the reduction follows a two-step mechanism. The first wave shows the reduction to hydrogen peroxide:

\[
O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \text{ (acid medium)} \quad (1)
\]

\[
O_2 + 2H_2O + 2e^- \rightarrow H_2O_2 + 2OH^- \text{ (neutral or alkaline medium)} \quad (2)
\]

As shown by the polarogram in Figure I, the reaction responsible for the first plateau occurs as the applied electromotive force vs. the saturated calomel reference crosses the zero volts axis and becomes increasingly negative. The electrolysis current becomes limited by the rate of diffusion of oxygen molecules to the surface of the mercury drop. The current levels off from -0.3 volts to -0.6 volts. Potentials more negative than -0.6 volts provide a driving force sufficient to initiate the reaction responsible for the second plateau:

\[
H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O \text{ (acid medium)} \quad (3)
\]

\[
H_2O_2 + 2e^- \rightarrow 2OH^- \text{ (alkaline medium)} \quad (4)
\]

The second plateau can extend from -1.1 to -1.8 volts. At higher potentials the decomposition of the solvent, \( H_2O \), masks the effects of further oxygen reduction. Either hydrogen ion is liberated as hydrogen gas in acid solutions or cations of the alkali metal group are reduced to metal and amalgamate in the drop, resulting in an excessively high current. If the medium has been purged of
Figure 1. Polarogram of Molecular Oxygen in Sea Water
molecular oxygen by bubbling prepurified nitrogen gas through it for 10 to 20 minutes, the polarographic traces contain no wave for oxygen as shown by curve 2 of Figure I. The current from this procedure is the base or residual current.

Reduction potentials for the $\text{O}_2$-$\text{H}_2\text{O}_2$ or $\text{O}_2$-$\text{OH}^-$ couples cannot be determined experimentally because the electrodes used for their measurement assume no definite equilibrium potential. The dissolved oxygen reduction fits neither this criterion for thermodynamic reversibility nor the criterion set up for polarographic systems; namely that a reversible reaction shows a rapidly rising current between the voltage at which the reaction occurs and the voltage at which the current becomes limited and the plateau is seen. The midpoint of this rise is the half-wave potential $E_{1/2}$ and is designated for the first step and second step in various media. The first step is slightly irreversible and the second step more so as seen by the slower rise of current preceding the second plateau in the polarogram. Irreversibility is more pronounced in chloride media of ionic strengths comparable to that of seawater than in dilute solutions—a characteristic which causes trouble in coulometric applications. Kern (22) has studied the mechanism and found that $E_{1/2}$ is constant for the first-step reduction in dilute solutions whose pH varies from 1 to 10. At pH's greater than 11 the reaction becomes reversible. The proposed mechanism from
equation (1) predicts a shift of 0.059 volts per unit change of pH since hydrogen ion is a reactant. A constant $E_1$ means that a reaction not involving hydrogen is the rate determining process, and the formation of $O_2^{-n}$ was suggested. No author as yet has confirmed a satisfactory mechanism. Meites (28, p. 50) lists half wave potentials for oxygen in various media and states that the values are -0.05 volts and -0.9 volts in most common supporting electrolytes.

A large number of voltammetric devices have been developed based on this polarographic behavior. Designs differ widely for specific applications. Some selected ones will be described in the following pages, beginning with dropping mercury electrode systems. Modifications are necessary because DME cells cannot yield reliable data when they are subjected to physical shock and vibration. Karchmer and Tyler have described a portable oxygen analyzer with a rapid dropping mercury electrode (20). A capillary tube projects horizontally into the side of a closed container with a sample inlet stopcock in the side opposite and a sampllet outlet stopcock at the top. Mercury drops from the capillary tube through the sample solution to a pool at the bottom which is the anode. Current readings for a sample are taken at constant applied voltage selected somewhere on the plateau of one of the waves in the polarogram. Sodium sulfite is added to another sample to destroy the dissolved oxygen and then the residual current is read. The difference is a function of the
concentration of dissolved oxygen obtained from previous calibration. The instrument is carried to ground-water locations, and it is typical of field devices in general. Briggs, Dyke and Knowles developed the wide-bore DME for long-period recording of dissolved oxygen concentration (5). Briggs and Viney have pursued the problem of compensation for the temperature coefficient of output current and have presented a final report of the elaborate circuitry required to maintain adequate compensation by his experience (6).

Larcher and Czuba describe a DME for the determination of oxygen in gases with automatic recording of results (25). A primitive but classic application of the DME to the waters of the sea was undertaken by Føyyn. A DME capillary was placed inside a zinc tube which acts as an anode when the electrode leads were short-circuited through a recording galvanometer. Lowering the cell on a cable gave a continuous record of oxygen concentration vs. depth. The accuracy was severely limited by difficulties in calibration (14).

Reasonably successful devices have been developed by using solid microelectrodes. The diffusion controlled reduction of dissolved oxygen can be maintained on the surfaces on silver, platinum, gold, or several other solid metals and graphite. The applied EMF range is less, however, because the overvoltage for hydrogen ion reduction is not as great for solid electrodes as for mercury. In neutral solutions hydrogen gas may be evolved around -1.0 volt vs.
SCE on platinum electrodes. The range is extended a few tenths of a volt for gold. Larger electrode surfaces increase the sensitivity of these devices but the accumulation of surface coatings may drastically inhibit their behavior.

Ingols (18) has written on his experience with solid platinum electrodes in the determination of dissolved oxygen in rivers influenced by pollution. Armstrong, Heemstra and Kincheloe devised a solid electrode amperometric instrument for measuring oxygen in oil field brines (1). Eckenfelder and Burris in a symposium report with 17 references have analyzed various polarographic oxygen methods (11).

Pioneering efforts in Europe in the development of the solid electrode galvanic cell have been led by Tödt (39). Extensive studies were made initially with the electrochemical characteristics of the types of cells that contain a gold amalgam microelectrode surface which becomes a cathodic half-cell when short-circuited through a galvanometer with a zinc anode. The current displayed on the galvanometer is proportional to dissolved oxygen concentration when the cell is immersed in sea or lake water. The progressive calibration required due to the influence of physical and chemical conditions of the medium is discussed in a book (38) which compiles the results of many investigations with various galvanic cell systems. Fresh, saline, biological, brewery and gaseous media were studied. The
relations among polarographic current, temperature, salinity, and oxygen content were determined with a rapid DME by Grasshoff (15).

A number of special liquid or gas phase oxygen detectors and analyzers have been described or patented. From the work of Hersch (16) an oxygen cell with a silver cathode and lead anode has been used by Phillips (31) as a detector in gas chromatography.

Recently the most dramatic scientific and commercial results have been attained following the invention of the membrane electrode. The property of oxygen to diffuse selectively through polymerized organic membranes lead to the in vivo determination of oxygen in blood in 1940. The pioneering work by Clark is developed in a recent article (4). The polarographic behavior of a number of gases with a membrane electrode was investigated by Sawyer, George, and Rhodes (35). Waves were observed for $\text{O}_2$, $\text{Cl}_2$, $\text{Br}_2$, $\text{SO}_2$, $\text{NO}_2$, NO, CO and HCN but not for $\text{N}_2$, $\text{H}_2$, or $\text{H}_2\text{S}$. Interest in membrane probes in natural waters was generated by the work of Carrit and Kanwisher (8). The membrane was stretched over a Pt. indicator electrode, trapping a thin layer of 0.5 N KOH electrolyte which made solution contact with the $\text{Ag}_2\text{O}$-Ag reference half-cell. Thermistor compensation for the severe temperature dependence of the cell was successful over a several degree temperature range. The gold, cadmium membrane cell was examined by Ryan-Neville (34). The most versatile membrane probe was developed by Mancy,
Okun and Reilley (27). The electrodes consisted of a silver button inside a lead ring with KOH electrolyte trapped between the electrodes and the polyethylene membrane. The current generated at steady state depends upon the rate of mass transfer across the membrane and the kinetics of the overall electrochemical process within the galvanic cell. An extensive theoretical treatment of permeability and diffusion through membranes was given. Applications in fresh, brackish, polluted and saline waters were discussed.

An improved cell based on the Mancy, Okun, and Reilley design has been developed by Mackereth (26). He has expanded the dimensions of the electrode surfaces so that the output current is of the order of hundreds of microamperes and was stable over a period of many months of continuous operation. By his design the sensitivity is increased from 1.05 ma./ppmO₂ to 22 ma./ppmO₂ and is more suitable for use as a probe in deep water bodies.

Coulometry

An internal electrolysis-coulometric method for determination of small quantities of oxygen has been reported by Knapp (23). In this method cupric ions are formed from the reaction of sample oxygen with cuprous ammonium chloride and subsequently electroreduced. Although small samples (0.2 to 10 ml.) are used, the reduction requires about ten minutes for completion. The cell efficiency was
22%, but consistent results were obtained.

Significant contributions have been made by Eckfeldt in the coulometry of oxygen in flowing streams by a process which he has designated as "derivative coulometry" (12). In one case (13) the solution flows through a small gold cathode chamber connected to a silver, silver chloride reference. In the other case the cathode chamber consists of a number of packed silver spheres biased with respect to a cadmium secondary electrode and silver, silver chloride reference. This cell responded to drastic changes of oxygen concentration in the flow stream in one minute or less, but it was claimed that good results could not be obtained in high chloride media.
EXPERIMENTAL

Construction of the Circuit for Controlled Potential Coulometry

In the initial stages of this work the most versatile coulometers were being constructed from operational amplifiers providing automatic potential control and current integration. However, it was felt that a simpler and more manual instrument would be satisfactory since there were no intentions to design cells yielding very small currents or requiring excellent potential control. Shipboard or field operation dictates the utilization of unsophisticated electronic systems wherever possible. Uncomplicated, two-electrode coulometers require only a potential source and current readout device.

A vacuum tube voltmeter (VTVM) was satisfactory to check the potential across the cell electrodes. Electrolysis current flowing through the cell from the external applied electromotive force was monitored with a 2.5 millivolt or 10 millivolt recorder by attaching leads to a dropping resistor inserted in the circuit. The schematic diagram for this assembly is shown in Figure II.

The applied emf was made variable so the cell potential could be arbitrarily selected. A potentiometer attached to battery leads provides a convenient source, however the source impedance must be kept low so that relatively high current may flow in the cell.
Reference half-cell (anode)

Applied EMF

Dropping Resistor $R_D$

VTVM

Strip Chart Recorder

Working electrode (cathode)

Stirrer

Cell

Figure II. Schematic Diagram of the Simple Controlled Potential Coulometer.
circuit without dropping the source voltage. By attaching two 100 \( \Omega \), 1 turn potentiometers to the leads of four 1.5 volt telephone dry cells in parallel, a low impedance source was made which could be varied from 0 to -1.5 volts. As one potentiometer center tap was turned toward either extremity, the other center tap control automatically became a rough adjust knob, and the first a fine adjust knob. The details of this modification are shown in Figure III. A power switch was added. Caution must be used in that the center taps must not be set at opposite extremes.

A variable range circuit was set up for the current readout by making the dropping resistor selective. Across \( R_D \) will flow a current which preliminary investigations show to be as large as 10 ma. For a 2.5 millivolt full scale reading \( R_d \) must be a 0.25 \( \Omega \) precision resistor. Across the switch center poles were attached jacks for connection with a decade resistance box to select 0.1 \( \Omega \) to 1000\( \Omega \). Thus the decade box could be used in parallel with either the 0.1\( \Omega \) or 0.4 \( \Omega \) resistor, allowing selection of almost any value of \( R_d \) from 0.05 to 1000\( \Omega \). For instance, at the lower ranges using the decade in parallel with the 0.4\( \Omega \) resistor, one could select \( R_d \) as 0.133, 0.171, 0.200, 0.222, ... 0.3999\( \Omega \). In Figure IV this circuit is attached to a recorder zeroing circuit. One of the recorder leads was biased either positive or negative by attaching it to a 50\( \Omega \) potentiometer in series with the supply side of \( R_D \). The positive leads
Figure III. Diagram of the Potential Source.
of two batteries (back to back mode) were attached to the center tap. To each negative lead one side of a resistor, \( R_x \) was attached. The opposite side of one \( R_x \) connected with one of the potentiometer leads and the second \( R_x \) was connected to the other lead. It was found that for a few microvolts bias \( R_x \) is 1 Megohm, for a few millivolts bias \( R_x \) is 10 K, and for biases approaching a volt \( R_x \) is 1 to 200Ω.

A Simpson Model 311 VTVM was used to check all potentials. All the described circuits were incorporated in a shielded chassis and banana jack sockets were used to accommodate the cell and recorder leads. The potentiostat supplied a constant voltage when cell currents were in the milliampere range. A drop in voltage of 2% occurred if the cell current rose to 10 milliamperes. The potential control was sufficient for most investigations.

Cell Studies and Electrode Designs

Reference Electrodes

In situations where both reference electrode and working anode have been combined to serve the same function, massive electrodes must be constructed. The term reference anode thus applies. For the various cells studied, where controlled potential coulometric cells were used, half-cells containing large calomel electrodes or large silver, silver chloride types of electrodes were used
Figure IV. Recorder Range and Zeroing Circuit.
extensively as reference anodes. Typically a calomel half-cell consists of a mercury, mercurous chloride (saturated), one normal potassium chloride system. Saturated sodium chloride rather than saturated potassium chloride was used in some half-cells because the variation of half-cell potential with temperature was less. For short circuit electrolysis applications, initially zinc, zinc chloride or zinc chloride and acetate systems looked promising. However, the magnitude of their potential vs. the $H_2, H^+$ half-cell is larger than 0.7 volts and thus provides a driving electromotive force which is too large for a single step, two electron reduction of oxygen, causing some four electron reduction and electrolysis involving different reactions. Various Cu, Cd, and Co electrodes were unsuccessful. A trial and error search for a more suitable anode gave rise to a peculiar system comprised of a lead electrode which was immersed in a saturated NaCl solution also saturated with lead chloride to which sufficient acetic acid was added to lower the pH to 4.0. The presence of the acetate anion appeared to complex and stabilise the dissolved plumbous ions so that the surface of the lead was kept fairly clean and insoluble compounds which were likely to adhere to the surface were not permitted to form. The reduction potential of this electrode system was 0.385 volts vs. SCE.

The disadvantage of the silver, silver chloride system when mercury was used as the cathode appeared to be caused by the
migration of silver ions into the electrolyte above the cathode and subsequent reduction of the silver ions into the mercury. A small amount of silver amalgam could be tolerated, but after long standing or use the pool became fouled. Using a mercury, calomel, sodium chloride (saturated) anode alleviated this problem because any mercurous ions migrating to the cathode chamber are spontaneously reduced to mercury. The response of the massive calomel cell was not nearly so rapid. Equilibrium was hard to attain after any event involving many millicoulombs of reducible substance in the cathode substrate. Silver wire anodized in 1N HCl was used to prepare small Ag, AgCl electrodes. Larger electrodes required the thermal-electrolytic preparation described by Bates (3, p. 205-207). To a 2/3 normal AgNO₃ solution, some 4 normal solution of NaOH was added dropwise until a brown suspension of Ag₂O appeared. One-half of a platinum cylinder cut laterally was coated repeatedly with the Ag₂O. After each coating the cylinder was heated to 450° in a muffle furnace ultimately leaving a thick coating of solid silver. By anodizing the cylinder in HCl, an Ag, AgCl electrode was obtained.

In short circuit analysis the lead, lead chloride, acetic acid system seemed to be ideal. The potential is sufficient to supply an electromotive force of proper magnitude to allow a 99% reduction of the oxygen present in the cathode. If half-cell potentials are represented on a one-dimensional graph as in Figure V, the
Figure V. Representation of Reference Potentials, Volts vs. NHE.
magnitude of desired applied voltage becomes evident. Used as a driving electrode for short-circuit electrolysis, the reduction of \( O_2 \) occurs on the plateau of the first wave at a potential below the half-wave potential of most interfering cations. The potentials on the adjoining polarogram in Figure V based on an SCE reference are compared to those based on a normal hydrogen electrode reference scale. Electrode systems such as Zn, Zn\(^{++}\) and those of higher values operate beyond the decomposition potential of the second wave and thus are unsuitable. Also shown on the scale are a number of other reference half-cell values that were used at various times.

Cells using Various Cathodes

The following parts of this section are presented according to the form in the introduction. In order to facilitate comparisons, a topical outline is given in order to catalog the variety of cell systems studied:

Types of Electrochemical Cells Employed for Coulometric Investigation

A. Solid Stationary Electrodes

1. Solution in motion ................................... 27
   a. Stirred solution, gold cathode .................. 27
   b. Flow cells ..................................... 31
      (1) Stainless steel .............................. 32
      (2) Brass ...................................... 32

2. Solution stationary, entrapment cells
   a. Stainless steel ................................. 41
   b. Platinum ...................................... 47
   c. Nichrome ...................................... 47
B. Electrodes in Motion

1. Solid vibrating coulometric cells
   (1) Platinum
   (2) Nichrome
2. Solid vibrating polarographic studies - see appendix I

Solid Stationary Electrodes

Solution in Motion

Stirring type in which the gold electrode was used

Solid stationary electrodes were the first to be investigated because mechanical problems with them were minimal. The principle to be developed with the following cell was (1) to check the feasibility of the coulometric method for determining dissolved oxygen in general and (2) to test the operation of a standard, laboratory type cell which had been modified to be an air tight system. Oxygen was expected to be quantitatively reduced on the gold surface.

The diagram of the assembly of this cell is shown in Figure VI. A 500 ml. Berzelius beaker was fitted with sidearms and used to contain the 5 cm. long, gold plated platinum screen cathode and stirring rod assembly. The beaker was filled with deaerated 1N KCl solution. One sidearm consisted of a platinum flag in 1N KCl to form the counter electrode (anode) and the other contained a saturated calomel reference electrode in 1N KCl. This particular three electrode system was connected to the department's multipurpose...
Figure VI. Gold Screen Cathode Cell Assembly
coulometer constructed from Philbrick operational amplifiers (36). A definite volume of air saturated 1N KCl was injected. Reduction of oxygen in the sample gave rise to an advance of the pen on a strip-chart recorder which recorded the integral of the current flowing through the cell and the time during which the electrolysis had been taking place, which represents the number of coulombs obtained from reducing all the molecular oxygen in the sample. A scan of applied voltage vs. current flowing through the cell was made with the stirrer off to get a rough idea of the magnitude of the diffusion current as different voltages were applied. The first plateau tends to be obscure on large electrodes as the results show in the graph in Figure VII.

The result of the electrolysis was such that for a sample from which 25.2 coulombs could be expected, 24 coulombs were obtained after the reduction had proceeded for 20 minutes.

Since the reduction proceeds so slowly, any utility the cell might have in this study is obviated. The results of the voltage scan show the range of voltage along the plateau which can be applied to attempt quantitative reduction on the large solid cathode. Electrolysis on the gold surface is feasible, but a much more efficient design is needed.
Figure VII. Diffusion Current of Oxygen on the Large Gold Cathode.
Flow Cells

Flow cells were designed for an investigation of the nature of dissolved \( \text{O}_2 \) electrolysis on the surface of a solid electrode in extremely confined spaces. The idea is to eliminate the need for stirring, vibration, or motion which would require cumbersome mechanical devices. The improvement sought could best be met by keeping the electrode surface to electrolyte volume ratio as large as possible.

The Stainless Steel Flow Cell

The final model was designed to be a rugged yet inexpensive cell. Stainless steel was used as a cathode. The polarographic behavior of molecular oxygen on steel as described in the appendix demonstrates the formation of a diffusion current plateau at -0.6 to -0.9 volts vs. SCE. The steel was a welded and drawn type 304, annealed and pickled, ASTM A 269-59, manufactured by Pacific Tube Company. A 3/16 inch diameter tube sold normally for gas chromatography columns was fashioned into the cathode.

In order to improve the surface to volume ratio and prevent channeling the cross section of the cell chamber must be thin and flat. Sixteen inches of this tubing was compressed with a hammer around an alarm clock spring 1/4 inch wide and 1/64 inch thick so that the cross sectional internal area was minimal and moreover,
so that any dissolved species in the entire channel was at a minimum distance from the steel surface. At various intervals along the tube the edge was ground out to expose the channel and to provide contact with the anode chamber. A Tygon tube was stretched over the steel tube and perforated with needle holes above the area where the slots appeared. Anodized silver wire was wrapped around the Tygon tube and this assembly was placed in a 3/4" I. D. Tygon tube which formed the outer covering of the anode chamber. The cell is shown in Figure VIII.

A second cell 28 inches long with smaller cross-sectional geometry was constructed and bent in the form of a circle as shown in Figure IX. This shape would minimize solution motion induced by pitching and rolling of a ship. Perforated skin diving suit neoprene was cemented around the outside of the tube for porous material. Although both cells display the same electrochemical behavior, the longer of the two was more efficient. Reduction of oxygen at applied potentials between -0.6 and -1.0 volts vs. Ag, AgCl(sat.) is possible as shown by the scan in Figure X. For this analysis, air saturated in 1NNaCl was allowed to flow through the steel chamber at a constant rate of 3.2 ml./min. The flow rate was faster than that for normal operation so there would be less depletion of the oxygen on the cathode surface and a diffusion controlled reduction could be maintained. The graph was obtained by noting the cell
Figure VIII. Diagram of the 16" Flow Cell.

Figure IX. Diagram of the 28" Flow Cell.
Figure X. Voltage Scan with the Steel Cell.
current for each stepwise increase of applied voltage.

The rate of response of the cell is somewhat dependent on the size of the current measuring resistor in the circuit. Resistances greater than 10Ω produced tailing of the current wave when the flow was stopped. For the 16 inch cell as shown in Figure XI, flow rates of 0.5 ml./min. or less give linear response without severe tailing. As oxygen containing electrolyte entered the cell containing solution which had been previously electrolyzed free of oxygen, the current rose to an equilibrium level within a few tenths of a minute. After the flow was stopped the current decayed to the initial value within two minutes.

In normal controlled potential coulometric analyses the mass of electrolyzed substance is related by Faraday's Law to the quantity of electricity Q obtained from the integral of the electrolysis current i_t from the beginning of each electrolysis to the time that is required for the current to decay to zero.

\[ \int_{\text{o}}^{\text{t}} i_t \, dt = Q = n F \, N^O \]  

(5)

where:

- n is the number of equivalents of substance per mole.
- \( F \) is the value for one Faraday of electricity, 96,497 coulombs per g-equivalent.
- \( N^O \) is the total number of moles of electrolyzed substance in the cell volume. However, analytical results were
Rd = 2 Ω

Flow = 1.09 ml./min.

Figure XI. Response of the Flow Cell.
conveniently obtained from the flow cell by the relationship between the
electrolysis current and oxygen concentration at flow rates slow
even to allow 100% reduction of the sample in the duration the
sample passes through the channel. The electrolysis current, \( i \), is
the value obtained by subtracting the decayed current value for the
previous sample from the cell current. The relationship is:

\[ i = nF \frac{RC}{Y} \]  

(6)

where: \( n = 4 \) gram-equivalents/mole

\( F = 96,497 \) coulombs/g-equivalent

\( R \) = Flow rate in ml/\( \text{sec} \)

\( C \) = Oxygen concentration, moles/ml.

Equation 6 is derived by equating \( \frac{dN}{dt} \), the instantaneous rate
that a number of moles of sample being electrolyzed to the flow
rate \( R \) and the molar concentration \( C \).

\[ \frac{dN}{dt} = RC \frac{dt}{y} \]

\[ nF \frac{dN}{y} = nF \frac{RCdt}{y} \]

\[ \frac{dQ}{dt} = nF \frac{dN}{y \ dt} = nF \frac{RC}{y} = i \]  

(7)

In Table I the oxygen concentration in the flow stream is compared
with that concentration found by the electrolysis current and equa-
tion (6).
Table I. Results from the Flow Cell

<table>
<thead>
<tr>
<th>Initial oxygen concentration, moles/ml.</th>
<th>Flow rate ml./min.</th>
<th>Oxygen concentration found, moles/ml.</th>
<th>Percent error</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.48x10^-7</td>
<td>0.51</td>
<td>2.34x10^-7</td>
<td>5.6</td>
</tr>
<tr>
<td>2.48x10^-7</td>
<td>0.51</td>
<td>2.35x10^-7</td>
<td>5.5</td>
</tr>
<tr>
<td>2.48x10^-7</td>
<td>0.51</td>
<td>2.34x10^-7</td>
<td>5.6</td>
</tr>
<tr>
<td>2.02x10^-7</td>
<td>0.51</td>
<td>1.95x10^-7</td>
<td>3.5</td>
</tr>
<tr>
<td>2.02x10^-7</td>
<td>0.51</td>
<td>1.94x10^-7</td>
<td>4.0</td>
</tr>
<tr>
<td>1.95x10^-7</td>
<td>1.09</td>
<td>1.19x10^-7</td>
<td>39.0</td>
</tr>
</tbody>
</table>

Since the initial oxygen concentration was known with an uncertainty of three percent, the data appear to be better than they actually are. As expected, the current efficiency of the cell falls off drastically with increased flow rate. For any given sample concentration at a constant flow rate the electrolysis current could be reproduced between interruptions in the sample flow with a variability of less than 1%. However, the reproducibility from sample to sample of various oxygen concentrations was not nearly as good.

The utility of the device of a flow cell is dependent upon the ability to maintain a constant, slow flow rate and constant efficiency throughout the range of oxygen concentrations. It was felt that continued effort would achieve this but was not warranted since the cell
demonstrated much better behavior when operated in a different manner which required no flow control. Thus the evaluation of the cell characteristics according to the criteria for in situ devices is deferred to the following section dealing with the method of periodic entrapment of sample.

The final design of the flow cell was accomplished by constructing and testing some primitive devices. Brass was first used as cathode material because it is an easily machineable metal and because of the results of work reported by Meites on the current-potential characteristics of oxygen on brass (28, p. 199). The primary purpose of initial investigations was to determine the magnitude of the current for varying flow rates. The first apparatus consisted of a piece of 5/8" or 15 cm. I. D. brass stock tubing 15 inches long whose inside was sandpapered to a rough finish to make up the cathode. The anode chamber was formed by inserting a piece of 13. 5 mm. O. D. Tygon tubing which had been perforated with a needle many times to allow solution contact through the fine holes. The inside of the Tygon contained a coil of anodized silver wire along its length and was filled with saturated KCl. The ends were fitted with special plugs to allow sample entry and exit. The cell volume was 18 cc. and was reduced to 3. 5 cc. when a perforated 13 mm. glass tube was inserted in the Tygon tube, Figure XII.

Air-saturated 1N KCl solutions were electrolyzed at one volt applied potential vs. Ag, Ag Cl, KCl (IN) half cell at flow rates of a few
Figure XII. Assembly of the Brass Flow Cell.
ml./min. The electrolysis currents were a few milliamperes in magnitude which could be conveniently displayed. Observed low current efficiencies demonstrated that channeling takes place and the cell volume was too large. Current efficiency decreased rapidly with repeated application. Brass is not a satisfactory cathode material in chloride media without persistent cleaning. The disadvantages of this design led to the improved design of the flow cell. It was noted that the Tygon tubing reseals when the needle is withdrawn. A small crack remains which traps a thin layer of solution when the tube is filled with anolyte. Internal resistance measurements show this tubing to perform excellently as a "fritted material substitute."

Solution Stationary, Entrapment Cells

**Stainless Steel Cathode**

In keeping with the principle that a high cathode surface area to solution volume ratio produces rapid response, studies were undertaken on the behavior of cells in which the sample is trapped in an extremely confined space. The nature of the design is such that any oxygen molecule in the sample must be only a minimal distance from the cathode surface. This principle is maintained with the stainless steel flow cell. Further, the need for control of mechanics having to do with the motion of solution is eliminated. With both
electrode and solution stationary, the mechanism for reduction is
d Controlled by diffusion processes alone. The best working model
of the cells studied turned out to be the flow cell.

By flushing the flow cell, sample is trapped in the cathode
channel. With the switch on, the current rose to a maximum value
immediately, and then decayed to a small base value. Since the
channel always traps a constant volume, several samples containing
the same molecular oxygen concentration should and did yield identi-
tical displays of the variation of current with time. The areas under
the displays were also identical as shown by Table II.

The analytical results obtained by electrolyzing samples of
various dissolved oxygen concentrations are compared with results
obtained by Winkler titration on more of the same samples. These
are reported in Table II. The area defined by the zero oxygen con-
centration display and the sample peak was determined as a number
of coulombs, and related to parts per million or mg./Kg. of O₂ by
the following relation:

\[
\text{ppmO}_2 = \frac{Q}{V_c} \times \frac{MW}{n} \times 10^3 \frac{ml}{l} \times 10^3 \frac{mg}{g} \times \frac{1}{\rho} \times \frac{1}{F_y}
\]

(8)

where:

\[
Q = \text{Number of coulombs}
\]

\[
V_c = \text{Cell volume in milliliters}
\]

\[
F_y = 96,497 \text{ coulombs per g-equivalent}
\]
MW = Molecular weight of oxygen, 32g./g-mole.

\( n = \) Number of electrons transferred per molecule or 4 g-eqivalents per gram mole.

\( \rho = \) Density of solution in kilograms per liter

Table II. Results of the Entrapment Cell

<table>
<thead>
<tr>
<th>( O_2 ) Concentration by Titration, ppm</th>
<th>( O_2 ) Concentration by Electrolysis, ppm</th>
<th>Percent Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.08</td>
<td>5.90</td>
<td>2.96</td>
</tr>
<tr>
<td>4.85</td>
<td>4.79</td>
<td>1.44</td>
</tr>
<tr>
<td>3.92</td>
<td>3.88</td>
<td>1.02</td>
</tr>
<tr>
<td>2.20</td>
<td>2.19</td>
<td>0.90</td>
</tr>
<tr>
<td>1.66</td>
<td>1.66</td>
<td>0.00</td>
</tr>
<tr>
<td>1.05</td>
<td>1.09</td>
<td>-3.80</td>
</tr>
<tr>
<td>0.78</td>
<td>0.83</td>
<td>-6.40</td>
</tr>
<tr>
<td>0.55</td>
<td>0.65</td>
<td>-18.2</td>
</tr>
<tr>
<td>0.19</td>
<td>0.29</td>
<td>-47.4</td>
</tr>
</tbody>
</table>
The reported results were obtained with the 28 inch cell with $1\,\text{M NaCl}$ solutions. Since the samples were not prepared by air saturation, Winkler titrations had to be performed. The percent difference column is a measure of the deviation from the titration results. The three percent difference for 6.08 ppm decreases to zero percent difference for 1.05 ppm and increases to a high degree for lower values. However, because of the inherent inaccuracy of the Winkler method it is difficult to tell whether or not this trend is a real cell characteristic. It is not an unreasonable result that the current efficiency decreases for the higher concentrated solutions, and increases above 100% for the very low concentrations. Some factor in the behavior of the external electronics might cause this trend. In spite of the lack of faith in the Winkler results, it can be concluded that the utility of the method comes from the fact that the reproducibility with which a sample of a given concentration could be analyzed repetitively was excellent. The values differ among themselves by about $1\%$ for the lower values and $0.2\%$ for those above 1 ppm.

The cell design fulfills many of the criteria for an in situ device. The response is fairly rapid, the mechanics are simple and inexpensive, the structure is rugged. However, the one overriding disadvantage is the difficulty in maintenance. After about 20 analyses the surface of the channel becomes coated and the response
becomes slower. With repeated use the current efficiency decreases and succeeding results become meaningless. Some description of the cell methodology of the final model follows.

The volumes of the cells were determined several ways. The volume to fill or drain each cell was measured, the volume of standard HCl solution flushed from a filled cell was determined titrimetrically, and also the volume was backcalculated by the number of millicoulombs yielded from an air saturated solution at a given temperature. The 16 inch chamber held 2.18 ml, and displayed the rather broad and slow current decay shown in Figure XIII as curve (4). The sharp current decay for the 28 inch chamber which held 0.441 ml is shown as curves (1), (2) and (3). These curves are for zero, 1.80 and 6.04 ppm O₂ respectively in 1N NaCl. Curve (4) is from a sample of ocean water containing 4.97 ppm O₂.

The samples of varying oxygen concentrations for Table II were prepared in a four foot long, 1-1/4 inches diameter glass tube by bubbling air or nitrogen through a glass frit in the bottom of the tube and through the KCl or NaCl solution therein. Samples were withdrawn simultaneously from a stopcock near the frit to both flush the cell and fill oxygen bottles for the Winkler titration.

Cleaning of the poisoned electrode could not be accomplished by flushing with dilute sulfuric acid. Stronger cleaning agents or acids cannot be applied without draining and disassembling the anode
Figure XIII. Variation in Current vs. Time for the Steel Cell.
chamber. The fouling of the cathode of the 16" cell negated the data obtained when the cell was operated on shipboard on an ocean cruise.

The rapidity of response of stationary solution electrolysis as well as the feasibility of internal electrolysis was established by the following preliminary investigations.

Platinum Cathode

The cathode consisted of a quarter dollar size button of platinum mesh sandwiched between the inverted bottom of a porous Coor's ware cup and a polyethylene disc cover. The solution containing dissolved oxygen was trapped in the interstices of the mesh where O₂ molecules could diffuse rapidly to the platinum wire surface. The polyethylene and glass cylinders comprising the anode chamber were joined by a standard taper joint as shown in Figure XIV to facilitate cleaning and filling.

The lead leaf immersed in chloride and acetate solution was used as the driving anode. Several layers of gauze were placed in the cathode chamber to increase the volume and signal height, but tailing became severe after more than four layers were used.

Nichrome Wire Electrode

Nichrome as a cathode material was compared to platinum.
Figure XIV. Schematic of the Platinum Sandwich Cell.
Since no gauze was available, a flat spiral was wound as shown in the top of Figure XIV. The electrode terminals of the cell were shorted across the precision resistor R and connected to a strip chart recorder. The well-formed spike of about one milliampere in height was formed, then the current decayed to the base line in a few minutes. The platinum electrode displayed a higher peak because the surface area was greater. Enough data was taken to demonstrate (1) that the stationary solution electrolysis could be driven by internal electrolysis, (2) that at least 90% current efficiency could be consistently maintained and (3) that the nichrome wire cathode would give results comparable to platinum. The main disadvantage in design was the awkwardness in sample dispensing and flushing.

In general, the design based on stationary solution entrapment cells with solid electrodes holds real promise for the in situ determination. With a noble metal as the cathode material, with an assembly which can be easily cleaned, and with an automatic calibrated readout attachment no difficulty is foreseen in obtaining much better accuracy than the Winkler method. The mechanical dimensions should be comparable to those of the 28" steel cell, with perhaps one entire narrow edge of the channel exposed to the porous material. Since the engineering difficulties in accomplishing these changes were difficult to surmount, other systems concurrently
being investigated were pursued in case an equally promising method could be found without the inherent difficulties of this one.

**Electrodes in Motion**

**Vibrating Electrodes**

A large electrode surface area to solution volume ratio can be maintained in a cell if the space inside the cell chamber is almost entirely occupied by electrode material. Rapid response is then expected if the electrode is set in motion. Vibration of electrodes was considered a feasible approach since more drastic design problems occur with the rotation of confined electrodes and no better results are anticipated. Vibrating drives are simple to construct and a simple mechanism can oscillate a large or heavy electrode if necessary.

Vibrating polarographic electrodes have been used extensively as a means of setting solid microelectrodes in motion. As reported in the section on polarography in Appendix I, vibrating electrodes were used to test the behavior of oxygen on the metal surfaces of electrodes proposed for coulometry.

**Coulometric Cells**

The results from two cells designed on the basis of the above
considerations show that certain disadvantages exist with this method. The data obtained were not accurate enough to warrant further development since no design change could be conceived which would yield a superior device. Although vigorous vibration tends to clean the electrode surfaces and enhance the oxygen electrolysis current by mixing, problems with gas intrusion and sample flushing override the advantages. It is felt that with the proper design, a successful in situ vibrating electrode cell might yet be accomplished by someone in the future. For this reason the details of the operation of the two cells are presented.

Platinum Electrode

A simple system was constructed to test the efficiency of a vibrating platinum cathode in a short circuit coulometry system. Enough platinum wire screen was rolled into a loose cylinder to occupy 0.8 ml. of a 2 ml. sintered glass filtering crucible as shown in Figure XV. The anode was made from a strip of zinc foil immersed in a 1 N ZnCl$_2$-80% saturated KCl solution. The half-cell potential of the anode was sufficient to drive spontaneously a four-electron oxygen reduction in 1N KCl catholyte. Reduction current was initiated and measured by shorting the external electrode terminals across an 0.400 ohm precision measuring resistor connected in parallel with a 2.5 millivolt strip chart recorder. The
Figure XV. Platinum Vibrating Electrode Short Circuit Electrolysis Cell.
cathode chamber was capped with a polyethylene disc through which protruded a platinum rod to connect the screen to the Vibro Tool. A water trap cup extended above the capping disc to prevent the penetration of atmospheric oxygen along the platinum shaft.

Air saturated 1N KCl solutions were analyzed, producing well-shaped current vs. time displays with initial peak currents of approximately 5 milliamperes in height at room temperature. Manual integration showed that the area under the peak agrees with the number of coulombs predicted for each sample within ten percent. Six or seven minutes were required for the electrolysis current to decay to a negligible value. The pumping action of the reciprocal motion caused some loss of sample. Since the reaction system appeared promising, a more sophisticated cell design was pursued. A similar three-dimensional platinum screen electrode design with stirred solution has just been developed by Dayton Carrit and E. Green (7) to give values for the solubility of dissolved oxygen in seawater and various chloride media, using an operational amplifier coulometer (36).

Nichrome Wire Electrode

A vibrating electrode cell was constructed which alleviated the problem of atmospheric penetration. The inside was hollowed out of a polyethylene cylinder two inches in diameter and 1 3/8 inches long. The cavity was essentially filled with a cylinder of
nichrome wire made by winding eight feet 1/32 inch wire on the end of a glass capillary tube. The final cell volume was 12.5 cc. A wire sealed in the capillary tube provided electrode contact. Vibration of the rod in the closed chamber caused severe bubble formation, and the pumping action of the electrode forced solution out of the connection. Sufficient freedom for the solution to oscillate was provided for by maintaining some kind of flexibility with the chamber. A 1/8 inch thick Tygon membrane was cemented to the rod at the top of the cell and clamped to the rim of the chamber with a cup inverted over the rod and tightened with an aluminum face plate. The back was sealed with another Tygon membrane. Figure XVI shows the assembly. Further freedom was maintained by means of the capillary coil at the top of the chamber. Solution which ordinarily would be forced through the seals was allowed to oscillate in the coil and yet be protected from atmospheric intrusion.

The glass anode chamber was welded to the side of the polyethylene cell as shown. A fritted disc made from the bottom of a porous Leco cup was sealed to the side of the cavity. Flushing and sample entry was arranged for by means of the dual stopcock at the bottom of the cell and the capillary tube at the inner end.

The anode chamber was filled with $\text{PbCl}_2$-$\text{KCl}$-$\text{HC}_2\text{H}_3\text{O}_2$ anolyte and a clean lead leaf was used as the anode. The electrodes were connected across a 5 ohm resistor in parallel with a 2.5
Figure XVI. Vibrating Nichrome Wire Coulometric Cell.
millivolt recorder to show the response of the short circuit analysis. The display obtained from the nichrome wire cell had a peculiar shape. An initial current spike was displayed which rapidly fell and the current increased again and slowly decayed to the base value as shown in Figure XVII. The unusual wave is probably partly a recorder characteristic and partly due to the vibration. If more than a 600 stroke per minute vibration rate is used, bubbles appear in the cell and the second rise is very pronounced. The base current from oxygen free solutions decayed without the second rise. After six to ten minutes the base line continued to drop slowly, making the last stages of electrolysis difficult to determine. Accurate values for the oxygen concentration determined by the area under the current vs. time displays could be obtained only if a base line was run for each sample. Thus integrated values from an in situ cell based on this design would not be dependable. Other approaches showed more promise. For future development a long, thin cell chamber and electrode which could be easily flushed might be considered.
Figure XVII. Response of the Vibrating Nichrome Wire Cell.
INTERFACE ELECTROLYSIS

Mercury cathodes are superior in many respects to solid metal electrodes. The advantage of mercury as a cathode material is that it can be conveniently replaced, that the surface can be continually renewed, and that oxygen is rapidly reduced on the surface. A disadvantage is that the electrode material is fluid. Cells using mercury must be protected from physical shock, vibration, and acceleration, otherwise erratic behavior results.

Because of the advantages of mercury it was hoped initially to find some means of confining and operating a mercury cathode in such a way that the effects of physical disturbances would be minimized. This improvement was not to be realized. However, the investigation led to the development of a method, which offers such promise for laboratory or land-based monitoring of streams, that the analysis was studied extensively. The method has utility because of the speed at which samples can be analyzed. Since the electrolysis occurs at special solution-mercury boundaries, the method has been designated "Interface Electrolysis."

The Unstirred Mercury Cathode Cell

The nature of mercury placed in a glass vessel and covered with a pool of aqueous salt solution is such that the solution will
penetrate in the space between the glass-mercury interface. At the very least, this solution collects in random pockets and droplets rather than forming a continuous layer, severing contact with the mother supply. When certain metal ions such as Li\(^{+}\), Na\(^{+}\), K\(^{+}\), Ca\(^{++}\), Mg\(^{++}\) and NH\(_{4}\)\(^{+}\) are discharged from the solution at the interface by electrolytic reduction, extraordinary changes take place at the contact line of mercury, electrolyte and glass. Johnston and Ubberlohde (19) have described this "wedge effect" at amalgam/electrolyte surfaces. Mercury surface tension is drastically reduced and between the resulting amalgam and the glass surface a wedge of electrolyte 0.01 to 0.001 mm thick will penetrate vertically for several centimeters. The wedge is formed only when the mercury was made cathodic by applying potentials to the Hg|Electrolyte|Pt cells. Ag\(^{+}\), Zn\(^{++}\), Cd\(^{++}\) and many other cations do not exhibit this behavior.

The existence of a thin wedge of solution between a mercury electrode and a glass surface should permit very rapid reduction of any electroactive species in that solution. However, the electrolytical conditions which must be imposed to create the natural establishment of the wedge are not compatible with the coulometric determination of dissolved oxygen. Therefore, it was proposed that an artificially produced wedge be maintained at the interface by means of a flowing stream of electrolyte. If the artificial wedge
effect or "interface effect" is to show any useful voltammetric behavior, it would do so with a reversible system, e.g. cadmium ion reduced to cadmium amalgam. Sample solutions of cadmium can be prepared accurately. Therefore cadmium was used in place of oxygen in many cases.

Design

The cell used to investigate the interfacial behavior was developed by immersing a capillary tube through the catholyte into the mercury pool and allowing sample solution to flow from the capillary end up along the tube to the connecting electrolyte above. The artificial wedge is maintained in the interface between the mercury and the glass tube. Without flow of sample, the natural wetting action of the solution will trap some electrolyte in the interface, generally in tiny isolated pockets without electrical continuity. The assembly is shown in the diagram in Figure XVIII. The reference electrode is connected electrolytically to the electrolyte by means of a frit, and connected externally through a scanning polarograph to the mercury pool. The voltammetric behavior of the interface then can be studied. The stream of sample solution during its passage through the interface has electrical continuity with the electrolyte once the stream reaches the top of the mercury chamber and merges with the electrolyte chamber above. The sample flowing through this interface
Figure XVIII. Interface Electrolysis Cell.
comprises a microcoulometric system.

The concentric tube which surrounds the sample inlet capillary tube constricts the mercury in the upper part of the cathode compartment into an annular shape. When the two tubes are perfectly parallel the annular body of mercury rises to the top of the outer tube as the mercury chamber is filled and spills out. But if the two tubes are cocked slightly with respect to their mutual vertical axis, some mercury in the upper part of the tube spills out. Only then is a stable and reproducible shape obtained. A diagram of this characteristic shape is shown in Figure XVIII.

The chambers were made from the upper and lower halves of an eight inch test tube. The top edge of the lower half was drawn in and sealed to a short piece of 6 mm. I.D. tubing to form the mercury chamber. Another length of this tube was connected to the top of the lower chamber with a piece of Tygon tubing to give the system flexibility. The capillary containing the sample stream could be inserted through these tubes into the neck of the mercury pool below. To the mercury chamber was fitted a sidearm to adjust the level. The mercury chamber was attached to the electrolyte chamber with a piece of 3/4" I.D. Tygon tubing. The top of the cell was fitted with a rubber stopper which held a capillary tube for overflow, a small plastic tube to fill and drain the electrolyte, and the sample inlet tube to which was attached a 3-way stopcock for flow control.
Mercury overflow from the filling of the pool chamber fell harmlessly to the bottom of the electrolyte chamber and could be drained away with the plastic tube.

Now upon the flow of sample, solution leaves the tip of the capillary and wells up the side in the wedge interface toward the neck of the outer tube. The mercury electrolyte interface which it finally contacts is that spade-shaped annular ring which is highest at its thickest point just after overflow. The area of this exposed ring is minimized. The tip of the capillary was broken to prevent any bubbles in the stream from remaining on the bottom of the tube.

Several experiments were performed with prepared solutions of known amounts of cadmium dissolved in saturated NaCl. By connecting the reference anode and the cathode terminals to a conventional recording polarograph the cell currents that resulted from increasing negative applied potentials were displayed on the strip chart.

**Results**

In the first experiments cadmium containing solutions were run through the capillary by gravity flow. In succeeding ones, small volumes of sample were injected into the capillary tube at short regular intervals.

**Experiment A.** The outlet of a Model 403 Beckman metering
pump with manual selection of flow rates from zero to 20 milliliters per minute was attached to the cell stopcock. Several stock solutions of Cd$^{++}$ were made available at the inlet. The pump injected one sample at three second intervals at a total flow rate of 0.2 milliliters per minute. Voltage scans were run on sample concentrations of zero, 0.000718 F and 0.001436 F Cd$^{II}$ solutions.

Experiment B. A Beckman metering pump with a zero to 0.2 milliliter per minute flow rate range was used to deliver samples. The pump injected one sample every 15 seconds, and voltage scans were run on 0.000718 F and 0.002872 Cd$^{II}$ solutions.

Experiment C. The special motor drive syringe sample dispenser described in Appendix II was used to deliver cadmium and oxygen solutions of various concentrations at controlled sample volume, rate of delivery of each sample, and interval between deliveries.

The samples fed by gravity flow produced current waves which were flat and rose in magnitude after the applied voltage reached -0.7 volt. The current from higher concentrated samples rose faster. For example, at 0.35 ml. solution per minute, the currents increased 5.25 $\mu$A per $10^{-5}$ moles/liter. Results from Experiment A are shown in Figure XIX. Until the applied potential reaches -0.7 volt the current envelopes are identical. The current envelope rises proportionally higher when the Cd$^{II}$ concentration is
doubled. From Experiment B the cell currents are displayed in Figure XX and Figure XXI. In both runs the peaks tend to level off when the applied voltage increases beyond -0.85 volt. Experiment C gave rise to the current displays shown in Figure XXII as typical results from many samples run. The data were treated by converting the area under the current displays to moles per liter for the cadmium samples and parts per million for oxygen samples. The results from a series of runs are shown in Table III.

The series of experiments led to the establishment of an analytical method based on the reaction of electrolytic species in the tiny volume of the artificial wedge. The gravity flow studies showed that reduction was taking place. Since the current rose somewhat with increasing voltage, diffusion controlled reduction was not being realized in the interface. A slow enough flow rate to attain this could not be stably produced by gravity feed operation.

For Experiment A, the metering pump was substituted in place of the gravity feed system in order to obtain better control over slow flow rates. Continuous current waves were no longer displayed. The fine structure of the waves responds to the mechanical action of the metering pump. Each current increase spike demonstrates the injection of solution for a moment. The mercury rises between the outer constricting tube and the capillary tube to accommodate the increase in liquid volume in the mercury compartment. As the
pump ceases to inject solution the current immediately falls to the normal base current level as before the injection. Then as the pump prepares to inject another quantity of sample, it draws a small amount of mercury into the sample tube, lowering the mercury level in the constricting tube and decreasing the base current below normal level. The indrawn solution is held and the base current rises toward equilibrium value near the normal level. The next portion of sample is injected, causing another characteristic rise. This cycle is repeated once every three seconds or 20 times per minute.

The wave characteristics are not unlike those of the DME. Mercury is continually oscillated in and out of the sample tube which tends to mix and renew mercury at the interface. Fresh sample can be reduced and demonstrate a current level not influenced from the electrochemical history of the past sample. The frequency of the spikes is a function of the pump. It was found that decreasing the flow rate only decreases spike and wave height. Were the flow rate at each injection and the total flow rate slow enough to allow complete reduction of the species left in the wedge, each spike would return to the base line.

In Experiment B, a sample every 15 seconds allowed more time for electrolysis of the cadmium after each injection and better current efficiency. The peak currents are limited by diffusion rate
to a constant magnitude for voltages greater than the half wave potential as shown in Figure XXI. The envelope of the wave is polarographic in nature for more concentrated samples as shown by Figure XX.

In Experiment C, the specially developed automatic syringe sample dispenser provided small enough sample volumes to allow depletion of the electrolytic species in the wedge once the flow is stopped. Displays are shown in Figure XXII. The CdII samples were 0.3 millimolar and the oxygen peaks were for samples of 2 ppm. The base current spike is expected as a consequence of disturbing or charging the interfacial layer.

The cell design was developed from a single compartment cell. Initial data showed the overriding effect of the mercury pool. Current from the voltage scan rose mostly due to the reduction on the mercury pool surface. A series of caps with loose holes bored in the center to allow the capillary tube to penetrate into the mercury were floated on the pool surface. Electrolysis in the wedge became dominant once the pool area exposed was reduced an estimated 99%. Containing the mercury in a separate compartment, minimized the pool effect.

The saturated NaCl electrolyte media was investigated because it is convenient not to need to purge oxygen from every sample for polarographic analysis. It was shown that only a few parts
Figure XIX. Waves from Metering Pumped Samples
Flow Rate = 0.457 ml/min.

Figure XX. Wave of a Metering Pumped Sample with Decreased Injection Time.
Flow Rate = 0.457 ml/min.

0.002872 F Cd$^{II}$

Applied Potential, volts

Current, $\mu$a

Figure XXI. Wave of an Excessively Concentrated Sample
Figure XXII. Variation in Current vs. Time of Oxygen and Cadmium Samples.
Table III. Results from the Unstirred Mercury Cathode Cell

<table>
<thead>
<tr>
<th>Initial cadmium concentration, moles per liter</th>
<th>Cadmium concentration found, moles per liter</th>
<th>Cell Efficiency, percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2.73 \times 10^{-4}$</td>
<td>$0.557 \times 10^{-4}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$0.560 \times 10^{-4}$</td>
<td>20.2</td>
</tr>
<tr>
<td></td>
<td>$0.557 \times 10^{-4}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$0.552 \times 10^{-4}$</td>
<td></td>
</tr>
<tr>
<td>$5.46 \times 10^{-4}$</td>
<td>$1.13 \times 10^{-4}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$1.09 \times 10^{-4}$</td>
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<tr>
<td></td>
<td>$1.11 \times 10^{-4}$</td>
<td>19.6</td>
</tr>
<tr>
<td></td>
<td>$1.11 \times 10^{-4}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$1.08 \times 10^{-4}$</td>
<td></td>
</tr>
<tr>
<td>$1.37 \times 10^{-4}$</td>
<td>$0.283 \times 10^{-4}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$0.281 \times 10^{-4}$</td>
<td>20.5</td>
</tr>
<tr>
<td></td>
<td>$0.280 \times 10^{-4}$</td>
<td></td>
</tr>
<tr>
<td>$0.546 \times 10^{-4}$</td>
<td>$0.114 \times 10^{-4}$</td>
<td>20.9</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Initial oxygen concentration, ppm</th>
<th>Oxygen concentration found, ppm</th>
<th>Cell efficiency, percent</th>
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</thead>
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<tr>
<td>6.2</td>
<td>1.08</td>
<td>17.6</td>
</tr>
<tr>
<td></td>
<td>1.09</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.08</td>
<td></td>
</tr>
<tr>
<td>3.1</td>
<td>0.565</td>
<td>18.2</td>
</tr>
<tr>
<td></td>
<td>0.562</td>
<td></td>
</tr>
</tbody>
</table>
per billion molecular oxygen dissolve in saturated sodium chloride solution. A conventional H-cell with D. M. E. was filled with saturated NaCl solution and polarograms were run at the highest sensitivity of 0.1µa/mm. The solution purged of oxygen with prepurified nitrogen showed only 0.2µa less diffusion current than the solution shaken with air. This drop was less than the experimental error. Cell design without a purging mechanism is simplified greatly. A polarogram of $5.32 \times 10^{-3}$ MCd$^{++}$ in saturated NaCl vs. SCE was run. The half wave potential is -0.704 volts. In the literature half-wave potentials for cadmium in high chloride media range from -0.6 to -0.7 volt, approaching 0.7 volt for one normal solutions.

Since some of the electroactive species always flows past the mercury before it can be reduced and is lost to the connecting electrolyte, absolute accuracy cannot be obtained and the method is empirical. Changing the camwheel to give slower sample injection increases the cell efficiency. But at an injection speed one-fifth of that used for Experiment C, the wedge cannot be maintained and the leading edge of the current spike displays erratic oscillations.

High current efficiency is not necessary for the analytical operation of the cell. The precision of the determinations shown in Table III for sample concentrations of a few tenths of a millimole per liter approaches one percent. The method is useful so long as the relative standard deviation in the cell efficiencies remains
low. Knapp (29) reports that his coulometric device operates at a fixed current efficiency of 22.8% at ten minutes per determination. In this case sample volumes of a few hundredths of a milliliter can be analyzed in 30 to 60 seconds.

In general, the major disadvantage of the entire system is lack of stability with respect to physical shock and vibration. Probably no amount of cell engineering will alleviate this limitation. The cell could be operated for several hours with frequent sampling without cleaning the chambers or replacing the solution and mercury. Optimization of capillary geometry, flow rate, and sample volume would produce a more accurate device. With proper standardization and automatic integration it is submitted that the cell and sampling system will make an effective microsample stream analyzer for reducible ions. In particular, oxygen solutions in a flow stream lend themselves to convenient periodic calibration by switching an occasional injection through a deareator or air saturator upstream of the sample inlet.

To further pursue the behavior of the mercury interface, and to create a system more physically stable with an even faster response, the system with the cathode in motion was investigated in the following pages.
The Mercury Torus Cell

A type of cell utilizing the dynamic behavior of the mercury-electrolyte interface has been designed. It was postulated that sample solution introduced at the interface of a rapidly flowing stream of electrolyte and mercury would be distributed in a fine layer and the contained electrolyte would be reduced immediately on the rapidly moving cathode surface. The apparatus developed to test the above postulate was called the mercury torus cell. Basically, the idea was to hollow out an annular ring inside a polyethylene cylinder which could be filled partly with mercury and partly with electrolyte solution. The cylinder was spun around its central vertical axis to set the mercury and anolyte in rapid motion. A stationary sample inlet tube protruding through the electrolyte and into the mercury caused the interface to bifurcate around the tip of the tube and roll past the tube in laminar overturning waves forming a thin, dynamic, reactive layer. In this layer reduction was found to be extremely rapid, and the mercury surface was continuously renewed. The pattern of the interfacial behavior is shown in the inset in Figure XXV.

The behavior of the cell is such that an expected large and noisy base current is displayed when the cell is connected to the potential source and set in rotation. The mercury rises against
the top and outside of the annular space forming a stable torroid.

Either by bubbling 1N NaCl or KCl with nitrogen or by using saturated NaCl as the electrolyte the base current level is established. A slight oxygen penetration or impurities in the electrolyte do not seriously interfere but only raise the total base current level. When solution containing oxygen is pumped in or drawn from a buret by gravity flow, the current immediately rises to a maximum value and decays within a few seconds to the base value as the oxygen is electrolyzed along the moving interface.

Design

Design and assembly of the final cell is shown in Figure XXIII. The detailed geometry of that cell evolved as a consequence of the shortcomings of four previous models that were tested. The polyethylene cylindrical blocks A, C, and D form the body of the cell and are rotated around their central vertical axis by attaching the bottom of D to a plate which sets on the top of a rotating shaft (not shown). The stationary sample tube holder (an 8" test tube) was clamped to remain in the center of the cell block and provide a close fitting space through which excess electrolyte can flow up to the vacuum. Since the space is narrow, penetration of atmospheric oxygen is minimized.

As the cell is rotated the mercury takes on a characteristic
Figure XXIII. Final Design of the Mercury Torus Cell.
toroidal shape and this torus E spins past the stationary sample inlet tube. Electrolytic contact is made through the electrolyte layer G and the porous polyethylene cylinders B to the anode chamber hollowed out of the block C. The silver, silver chloride reference anode terminal connects the silver wire through the external cell circuit to the platinum wire contact of the cathode chamber. The annular hollow was machined out of the inside of the polyethylene block D to give a shape to the outer edge of the torus of mercury which is smooth and fairly symmetrical. Then the interfacial area tends to remain constant and recover quickly from the spreading effect caused by the encounter of the torus with the sample inlet tube. The hollow was turned in the polyethylene cylinder with an L-shaped tool with a disc-shaped blade on the end.

The cell was operated with the same circuit used for solid electrode coulometry. Cell currents were recorded with a Bausch and Lomb V. O. M. -5 strip chart recorder which has a fast pen response. The cyclic noise filtering circuit drawn in Figure XXIV was placed between the recorder and the current measuring resistors. Electrode contacts sealed in the sides of the chambers were connected to a commutator beneath. A brass ring and wire commutator was found to be noisy and was replaced with a specially designed mercury commutator cup machined from polyethylene.

The rotation rate was monitored with an oscilloscope. A
Figure XXIV. Filtering Circuit.
stationary clock spring blade mounted close to the cell shaft was
connected to a 1.5 volt battery in series with a 1 megohm resistor
and the oscilloscope input. The oscilloscope ground terminal
was connected to the cell framework and contact with the stationary
blade was established with a rotating blade attached to the shaft. A
voltage peak was displayed for each revolution.

Samples were injected with the zero to two ml./min. Beckman
metering pump. The total volume of sample for each injection was
0.5 ml. since an overall flow rate of 2 ml./min. was used. Thus
the pump delivered an injection of sample at 15-second intervals.

The spinning rate is not too critical between 100 and 300 r.p.m.
and was optimum at 240 r.p.m. Above 300 r.p.m. turbulence forms
at the interface creating spurious current peaks. Below 100 r.p.m.
the base line undulates and displays more random noise. The best
results were obtained when the level of mercury was slightly above
the half-full mark. Excessive amounts of mercury swamped the in-
let tube such that the laminar layer disappeared. The best condi-
tions were obtained with the half-full level of mercury and the sam-
ple inlet intruding about 3/8" into the side of the mercury torus.

Several hundred analyses were run at three oxygen concentra-
tion levels from a stock solution of 5.96±0.05 ppm. The absolute
value of the stock air saturated 1N NaCl could not be known accur-
ately but fractional concentrations of the stock could be accurately
prepared by careful dilution of the stock with saturated NaCl.

Results

When the samples are injected, a current is obtained due to the electrolysis of the oxygen. The unfiltered display of this current shows a noisy, rounded wave. The displays of two consecutive waves are shown in Figure XXV. The filtered display adjoins the first two. Injection of saturated NaCl gave no detectable change in the base current value, and could be taken as a zero oxygen concentration sample. A tabulation of results is given in Table IV.

As a sample solution squirts onto the mercury layer it remains in contact with the surface long enough for a constant fraction to be electrolyzed. Since the noise is not random and the base current shows no peak, the area under the wave represents a known fraction of the original sample. Since the speed of injection of each sample was fixed by the pump mechanism and could not be varied, much lower than optimum cell efficiencies were obtained. Because no other pump mechanism on hand delivered the proper volume of samples at the fast 15-second interval its use in the system to obtain the reported data is justified in spite of the low cell efficiency. The cathode chamber held 35 ml. mercury and 35 ml anolyte. These volumes are large compared to a sample volume so a high base
Figure XXV. Response of the Torus Cell.
Table IV. Results from the Torus Cell

<table>
<thead>
<tr>
<th>Concentration found for 5.96 ppm samples, ppm</th>
<th>Concentration found for 2.98 ppm samples, ppm</th>
<th>Concentration found for 1.192 ppm samples, ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.539</td>
<td>0.272</td>
<td>0.109</td>
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<tr>
<td>0.539</td>
<td>0.272</td>
<td>0.109</td>
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<tr>
<td>0.538</td>
<td>0.272</td>
<td>0.109</td>
</tr>
<tr>
<td>0.538</td>
<td>0.272</td>
<td>0.107</td>
</tr>
<tr>
<td>0.536</td>
<td>0.268</td>
<td>0.106</td>
</tr>
<tr>
<td>0.539</td>
<td>0.269</td>
<td>0.109</td>
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<tr>
<td>0.536</td>
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<tr>
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<tr>
<td>0.538</td>
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<td>0.109</td>
</tr>
<tr>
<td>0.539</td>
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<td>0.106</td>
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<tr>
<td>0.539</td>
<td>0.272</td>
<td>0.109</td>
</tr>
<tr>
<td>0.538</td>
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<td>0.109</td>
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<tr>
<td>0.539</td>
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<tr>
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</tr>
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<td></td>
<td>0.272</td>
<td></td>
</tr>
</tbody>
</table>

9.05% Cell Efficiency 9.11% Cell Efficiency 9.16% Cell Efficiency
current is observed, two to three times the height of the peak. The output current must be filtered to eliminate the oscillations which occur as the result of cyclic noise of frequencies which are a function of the rate of rotation. The display of this noise was greatly decreased by the attachment of an R-C network between the current measuring resistor and the recorder. The network first tried was a quadruple parallel-T RC filter (21) whose circuit component values were chosen to damp the first and second harmonics of 0.6 cycles per second noise. The nature of the noise was such that this type of filter was only partially successful, however desirable the high D.C. pass characteristic of the parallel-T configuration.

A situation analogous to setting the mercury in motion by rotation of the container is to stir the pool. Mercury was spun against the sample inlet tube since simply injecting the sample into the electrolyte as in normal mercury pool electrolysis would require long reaction times. Results from this method were impressively poor. None of the apparent dynamic interfacial characteristics were observed. At slow speeds of rotation sample climbs immediately to the top of the pool and undergoes almost no reduction. At greater speeds the pool breaks up into tiny droplets, each coated with electrolyte and having no electrical continuity with the cathode terminal. This phenomenon is particularly marked when the mercury has been in contact with Tygon and polyethylene. The dissolution of traces of
organic materials into mercury causes it to froth at high speeds. Cells with spherical and cylindrical shaped pools were investigated.

The base current slowly drifts upward because of the presence of diluted, unreacted sample. The anolyte either had to be replenished after each 20 samples, or new anolyte had to be continually flushed through.

The first cell was made from a polyethylene cylinder three inches in diameter. The anode chamber was placed below the torus chamber. The whole assembly was spun on an axial rod so the stationary sample holder had to be in the shape of an annular ring.

Several design changes were attempted in order to increase the signal to base current and minimize noise. Since the first cell had been constructed with the anode chamber beneath the cathode, the second was designed with the anode chamber forming the inner side of the annular hollow. The third contained both stationary anode and a sample inlet tube inside the torus area. The fourth contained the anode above the cathode chamber with the sample inlet tube intruding into the spinning cylinder of mercury rather than a torus. In each of these designs the cathode chamber progressively was enlarged to give higher signals. All either showed slight improvement or presented new problems. The fifth and final design proved workable and was considered optimum within the limitations of the system for the data on Table III.
On the basis of the data, 0.5% precision could be claimed for the analysis. The reproducibility for the analysis approached 0.4% for the 5.96 ppm sample and 1% for the 1.192 ppm sample. However, an overall accuracy of no better than 1% is estimated because the amount of mercury, flow rate, rotation speed and base current variability were not controlled accurately enough from experiment to experiment.

The outstanding advantage of the mercury torus cell is the rate of sample analysis. Successive determinations at 15-second intervals with one percent accuracy is a decided improvement. Unfortunately, the mechanics involved in the operational aspects of the cell are complex and adjustments must be made within often narrow limits.

Peak currents can range around a milliampere without amplification; peak height and area vary with sample size, sample flow rate and sample concentration. Since the introduction of sample disturbs the interface layer and current response is affected by the filtering network, 100% current efficiency could not be demonstrated by relating sample concentration to absolute peak area. A large percentage of sample is lost to the electrolyte before it contacts the mercury surface, however, slower injection times tend to reduce this tendency. With the described variable conditions controlled, peak area is directly proportional to concentration of reducible
species. This method is useful where desire for rapid analyses with calibration supersedes the need for perfect current efficiency yielding theoretically treatable data. Current amplification and tiny sample volumes might yield one to ten-second analyses. Automatic determination of peak area would increase the accuracy and lend utility to the method.
CONCLUSIONS

The study of the coulometric determination of dissolved oxygen has been approached along several avenues. New information on cell operation, cell materials, cell design theory and cell methodology was yielded as a result of the research conducted to fulfill the original goals. For coulometric cells capable of underwater operation, the criteria of 1) rapid sampling, 2) provision for sample input, 3) elimination of gaseous phase problems, 4) simple mechanical operation, 5) minimal cost of expended materials, 6) maintenance free rugged probes, and 7) output signal telemetry capability had been set as a means of evaluating the developed cell systems.

In terms of rapid sampling, success was met with all the cell systems studied. The rate at which individual determinations can be made with the torus cell is five to ten times faster than the rate for existing methods, and can be compared to the 60 to 100 seconds sample analysis times obtained by Bard (2) with his method for high speed coulometry. Determinations of oxygen made in quiet solutions required only a few minutes for complete reduction. Mechanical operations are ideally simple because the sample input pump needs only an on-off control at the entry port. The major cost would be the outlay for the gold or goldplated cathode, however this is a
permanent item. The cell is rugged and would require only periodic chemical or mechanical cleaning to maintain it.

Shipboard operation with the channel cell would compete favorably with the wet chemical methods. Samples collected from the casts which were formerly titrated could be injected in the cell. With a third electrode system contacting the interior of the channel at various points, accurate potential control and coulombic readout is achieved with a common coulometer (36). A solid state operational amplifier network would replace the vacuum tube components to convert the instrument for permanent marine usage.

Operated as a flow cell, the 28 inch steel channel device gives results comparable to those obtained by Eckfeldt (13). His most accurate flow cell (12) with a cathode comprised of silver beads does not operate satisfactorily with high chloride electrolytes. The channel cell has twice the surface area to solution volume ratio compared to his gold channel device, and this cell is considered optimum in physical dimensions. Narrower channels would be difficult to flush. In any case, periodic sampling is considered superior to the flow system.

It was most unfortunate that no way could be found to contain mercury as a physically stable cathode for underwater analysis. The proposed utility of the mercury cells as stream monitors has been submitted. Bard achieved high current efficiency with ideally
electrolizable ions rapidly mixed in an open system where dissolved gases do not have to be protected from escape or intrusion. The torus cell must work with oxygen in a nonideal media. Any future application will be made with his excellent data handling system.

Since there is no air spaces in either electrolyte or cathode chamber, a program could be set up to continuously replace electrolyte. To periodically replace the mercury, the determinations occasionally would have to be interrupted. With these modifications, long time operation with minimal maintainence is proposed if proper readout instrumentation were installed.

The advantage of the unstirred mercury system compared with the torus is that it is simple to construct and operate. A stream which this device might be monitoring could be sampled for the tiny 0.03 ml. samples each minute. In either case, higher current efficiencies would be an immediate goal.

Finally, future plans have been made as a result of the entire research project, since no coulometric system investigated could claim much better than one percent accuracy if used in an under-water operation. Further effort is being directed toward the construction of a cell which perhaps combines the merits of both amperometric membrane and coulometric procedures. The limitations imposed upon membrane electrodes would be alleviated if some sort of in situ standardization were possible. Basically, a large
membrane can be covered at selected intervals by a relay driven piston in the casing. Oxygen diffuses from the thin layer of sea water trapped by the face of the piston through the membrane to the cathode surface. The cell current produced by the ambient oxygen reduction will decay and the base current level can be determined. If current efficiency is very high, the possibility of operation independent of water temperature exists.

At any time a periodic electrolysis is possible if the cover is designed so the volume of trapped sea water is constant. The cell is flushed when the piston is released and the cell circuit is off. Then the piston is moved in and the cell circuit activated, initiating electrolysis of the oxygen molecules moving through the membrane. The mechanics of this device are simple. At the present time a prototype of the large platinum membrane electrode shows a sensitivity of 13 µ amperes per ppm, 13 times greater than the sensitivity of most polarographic probes. It is possible the cell may operate best if it were permanently in the electrolysis mode.

Only the platinum screen entrapment cell had inconvenient sample input. Problems with bubbling and gaseous phase phenomena were not important with any cells except the vibrating cathode cells. This disadvantage might be solved by underwater operation. The requirement of simple mechanical operation presents no
disadvantage in the case of the channel and unstirred mercury cathode cells. Critical limitations are set on the torus cell by this requirement, restricting it to land-based operation. None of the cells are expensive outside of the cost of labor. All of the solid electrode cells were rugged, but this demand negates the use of the mercury cells in situ.

That the final output signal can be telemetered is the subject of concurrent work on this project by other investigators. Success is anticipated in the attempt to transmit low level D.C. voltages from underwater transducers.

Cathode materials have been evaluated by the results of polarographic studies and coulometric applications. In general the materials can be listed in the order of the best to the worst electrochemical behavior for oxygen reduction as mercury, gold, platinum, nichrome, stainless steel, German silver, brass and lead. No reports have been found in the literature for nichrome and stainless steel, although nickel has been investigated (38).

Of all the cell systems studied, the design of the steel channel electrode comes nearest to meeting the criteria.
BIBLIOGRAPHY


APPENDICES
APPENDIX I

Polarographic Studies with Vibrating Solid Electrodes

To determine the behavior of molecular oxygen on solid metal surfaces, oxygen reduction was investigated on the surface of a number of vibrating solid cathodes. Into a standard H-cell was immersed a 2 mm. capillary tube in which a small section of metal had been sealed in on end. The upper end was connected to a Burgess "Vibro Tool" and vibrated as an estimated frequency of 1250 strokes per minute. In some instances it was deemed desirable to control the rate of vibration. An offset rod was chucked in a variable speed stirring motor and connected to the electrode shaft with a ring bearing. This device was used later for vibrating coulometric electrodes.

Platinum and Gold Electrodes

Rotating platinum and gold microelectrodes have been used for the quantitative determination of dissolved oxygen for many years. Hydrogen overvoltage is so much less for these electrodes than for mercury that they are limited to operation at negative applied potentials less than about one volt vs. SCE. Several other metal surfaces were studied and the polarographic behavior of oxygen on these is reported in the following section.
Lead Electrode

One expects lead to form oxide coatings on its surface when exposed to seawater. Surface effects should tend to negate the formation of any reversible oxygen waves on a lead microelectrode. An investigation of the behavior of this electrode seemed warranted by the results of Strnad (37), who reported pronounced catalytic effects of plumbous ions on oxygen waves.

The lead microelectrode was constructed by setting molten lead in the flared end of a 2 mm. capillary tube. The melt ran down the capillary to meet a copper wire introduced from the other end to make external electrode contact. Since the lead button in the flare contracts upon cooling, epoxy resin was used to seal the glass-lead interface. The button was sheared off to expose a 1/16 inch diameter surface.

Figure I-A shows the diffusion current wave obtained in 1NKC1 as the electrode was vibrated at 800 strokes per minute. From the first run was recorded several small plateaus, but obviously the reduction occurs too irreversibly to allow a constant diffusion current at any point on the wave. As shown by run 2, the magnitude of successive current waves decreases. Surface contamination was visibly seen to grow on the electrode in spite of negative potential applied. Utilization of the catalytic effect must necessarily involve
Figure I-A. Polarograms with the Lead Electrode.
a more sophisticated system in which the sample would require pre-
treatment and reagent addition. The extremely high base current
would have to be depressed.

Nichrome Wire Electrode

Waves from dissolved oxygen on the surface of nichrome wire
are well-formed and reproducible for the first two-electron reduc-
tion. As shown from Figure II-A, a plateau occurs from -0.2 to
-0.4 volt vs. SCE. The second plateau which should form at a
slightly more negative voltage than -0.6 volt does not level off to
the same slope as the first plateau. Hydrogen overvoltage on the
nichrome surface is so much lower than on mercury that evolution
begins after -0.75 volt and is quite pronounced at -0.85 volt.
Curve (1) in Figure II-A was developed in 0.95 N KCl saturated
with air at 28°C. The electrode was vibrated at 800 strokes per
second. Curve (2) is a projection of the constant diffusion current
displayed when the scan mechanism was held constant, at -0.4 volt.
Irreversible electrodes tend to show a decreasing current when this
is done. Curve (3) is the surprisingly low and flat base current
wave. The KCl solution was purged of oxygen by bubbling pre-
purified nitrogen through the solution for 20 minutes.

The microelectrode consisted of a 21 gauge nichrome wire
protruding 0.5 mm. from the end of a 1 mm. capillary tube. Epoxy
Figure II-A. Polarograms with the Nichrome Wire Electrode.
resin sealed the wire-glass interface. A second electrode was fashioned similarly with a 1 mm. extension of the wire from the glass. An attempt to take quantitative data by measuring the diffusion current resulting from dissolved oxygen solution less than 100% saturated was made with this electrode. The greater wire surface gives greater sensitivity.

The difficulty of introducing partially saturated solution into a cell exposed to the atmosphere was overcome by preparing each sample solution in the H-cell compartment by dilution. A polyethylene stopper with three holes was capped with a flexible 1/8 inch thick Tygon membrane. Since the membrane fits tightly around the glass electrode tube, contact with the atmosphere was diminished yet the electrode would still vibrate. In one of the other holes a 1 mm. capillary tube exit was fitted flush with the bottom of the stopper. In the third hole the capillary extension from the bottom of a separatory funnel was pushed through the stopper far enough to extend just above the bottom of the cell compartment. By filling the cell from the separatory funnel until solution was extruded from the exit tube and the flexible membrane around the electrode, all gaseous spaces were eliminated. The first sample was 100% air saturated 0.95N KCl. The polarographic wave from this sample is shown as curve (1) in Figure III-A. Next the solution in the funnel was purged of nitrogen by bubbling. By adding 8.60 ml. of this solution
to the 30.1 ml. cell compartment, 8.60 ml. of air saturated solution was displaced. Hopefully the oxygen-free solution entering the bottom of the cell did not mix with the displaced solution. The resulting solution is considered to be $100 \left( \frac{30.1 - 8.60}{30.1} \right)$ or 71.5% saturated when mixed by switching on the vibrator. A polarogram of the sample is shown as curve (2). By repeating the above procedure but displacing 14.0 ml. of air-saturated solution a $100 \left( \frac{30.1 - 14.0}{30.1} \right)$ or 53.4% saturated solution was analyzed, and shown as curve (3). The results are shown on the graph in Figure IV-A. If the method is quantitative then the diffusion current height minus the base current height should be a linear function of percent saturation. The results show this is true to within 1%. A potential of -0.4 volt was chosen since it corresponds to the estimated working potential of the PbCl$_2$-HC$_2$H$_3$O$_2$ anode in coulometry. The base current was estimated at 1 microampere from Figure II-A. The second wave for oxygen reduction appearing at potentials more negative than -0.5 volt, is more clearly defined in the diluted samples. Curve (4) shows the dissolved oxygen wave for a seawater sample. The current sensitivity was one-half the value used on the previous runs. It was observed that the wave was identical in shape with those run in KCl solution.
Figure III-A. Polarograms with the Nichrome Electrode.
Figure IV-A. Graph of Results with Nichrome Electrode.
Stainless Steel Electrode

Excellent waves were produced by oxygen reduction on the stainless steel microelectrode. Better results for the four-electron reduction were obtained compared with the nichrome electrode. A broad, flat plateau was exhibited between -0.5 and -1.0 volt vs. SCE, as shown by the polarogram in Figure V-A. Artificial sea water was used as the medium.

Other Metal Electrodes

A tough nickle-silver alloy marketed as German silver was investigated. A German silver microelectrode operating in 1N KCl solution displayed diffusion currents similar to those from the nichrome electrode. Hydrogen overvoltage is extended a few tenths of a volt, since the rise in the wave for hydrogen did not appear until the scan had reached 1 volt vs. SCE. However, the surface of the alloy becomes coated and discolored after one scan and the polarograms were not reproducible. The electrode did not appear to be suitable in high-chloride media.

Brass was not suitable. In 1N NaCl the brass microelectrode turns dark brown after a few tenths of a volt is applied. The oxygen waves nevertheless are displayed, though quite slowly rising at the beginning of the two-electron and four-electron reduction. The
plateaus do not level off. Again poor waves are shown by a system in which the electrode surface cannot resist spontaneous attack by the medium.
Figure V-A. Reduction of O₂ on a Stainless Steel Microelectrode.
APPENDIX II

The Automatic Syringe Sample Dispenser

The assembly shown in Figure I-B was constructed in order to have a sample dispenser which will automatically fill and dispense a pre-selected volume of sample solution. The rate of delivery of sample is entirely dependent on the shape of the cam wheel and the frequency at which samples are delivered is dependent upon the speed of the motor. If the cam tapers outward sharply from its narrower radius the rate of delivery will be fast. By driving the plunger all the way in at each interval the dead volume in the syringe is eliminated.

Delivery is checked by a motor-driven rotating stopcock developed at Oregon State University (30). The stopcock must rotate 180° to fill the syringe and 180° to inject sample. A schematic of the driving mechanism is shown in Figure II-B. $S_1$ is depressed activating a relay which starts the motor to rotate the stopcock shaft at 24 rpm. After 90° rotation, cam 1 opens $S_4$ and the relay falls into the locking slot. However, the depression of $S_2$ by cam 2 is functional when $S_3$ is closed for 180° operation. After each 180° traverse the rotation again may be initiated by pulsing $S_1$. Switching contacts were placed on the camwheel of the syringe drive to correlate the stopcock rotation with syringe movements. Contact
bars shown in the diagram in Figure 1-B replaced the S₁ manual switch. The offset on the camwheel injected the sample during the delivery phase, and a spring caused the syringe to refill during the filling phase. The stopcock is rotated at the beginning of each phase, and injects a small sample during the cleaning phase to clear the capillary of old sample if concentrations vary greatly in the sample stream. This action causes blips between peaks on the strip chart. A one rpm motor was used for one minute spacing and an 0.25 ml syringe for the small samples. Either of these parts can be changed.
Figure I-B. Schematic Diagram of Syringe Drive.
Figure II-B. Schematic Diagram of Stopcock Drive.