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Hydrografiska avd., Box 4031, 400 40 Göteborg

A FREE FALLING POLAROGRAPHIC
OXYGEN SENSOR

by

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Institute of Oceanography,
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August 1972

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Abstract

The properties of a flush-mounted, uncovered platinum cathode in polarographic oxygen determination are discussed. These properties are used in the design of a recording instrument. This instrument continuously measures relative oxygen saturation versus depth. Some results obtained with a prototype of the instrument are shown. Possible applications are in surveys of regions with large variations in oxygen concentration, where rapidity and high spatial resolution are more important than accuracy.

I Introduction

Due to the relationship to biological activities the concentration of dissolved oxygen in sea water is a parameter which is of interest in marine biology. With gross knowledge of the biological processes which change oxygen concentrations, it is possible to reconstruct the history of a water mass from the measured distribution of dissolved oxygen. This makes oxygen concentration a parameter of value in physical oceanography also.

The Winkler titration has become the standard method of determining oxygen concentration. In many applications in situ measurements that allow for continuous profiling are preferable. Polarography is one of the electrochemical methods which have been used for this purpose. The majority of commercially available polarographic instruments are of a kind with a semi-permeable membrane separating the electrodes from the water. This has the advantage that measurements become relatively insensitive to the velocity of the water, and that the electrodes are protected from chemical contamination. The main disadvantages are: the slow response which makes truly continuous measurements difficult, the temperature dependence of diffusion properties of the membrane which introduces large temperature corrections, and the need for frequent recalibration due to longtime drift. An instrument with fast response and facility of operation at sea would be of practical use.

In a review of the applications of polarographic methods to field measurement Odén (1962) proposed an electrode configuration with several small platinum cathodes dispersed over an insulated surface. The time constant for the response to a change in concentration in a stationary fluid would be proportional to the square of the electrode radius. By decreasing the radius the time constant can be made small, and by connecting many electrodes in parallel the measuring current can be kept sufficiently large. Odén further concludes that this fast response makes the electrode insensitive to velocities relative to the fluid. This should make it a good choice for an in situ instrument aimed at rapid surveys of oxygen concentrations.

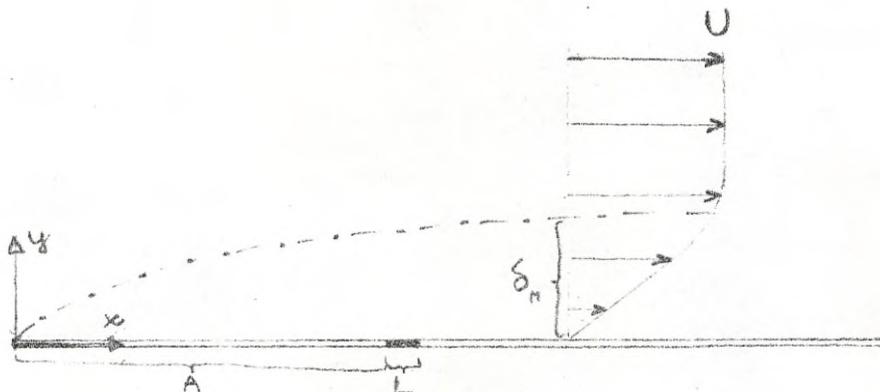
In testing an electrode of the kind discribed, it became clear that it was far from insensitive to velocity. A simple analysis confirmed that the measuring current was proportional to the square root of the velocity of the probe. In addition it was seen that the time constant was inversely proportional to the velocity, thus making the spatial resolution a constant, independent of velocity.

These properties were considered in the construction of an instrument which was essentially free falling. This disconnects the instrument from the motion of the ship, and with a high descent rate, the velocity variations can be kept small. With a pressure sensor on the instrument the polarographic current can be recorded directly versus depth on an X-Y recorder.

A prototype of the instrument was tested in the laboratory and at sea. The response to oxygen concentration was linear and the temperature coefficient was about $2\%/^{\circ}\text{C}$. Change in output due to salinity variations at constant oxygen concentration was approximately $0.5\ \text{\%}/\text{\%}$.

II The disperse electrode

A simple 2-dimensional model of the electrode arrangement is a thin plate moving in a plane parallel to itself with the velocity $-U$ relative to the undisturbed fluid. At a distance A from the leading edge of the plate is situated an electrode, with a width L in the direction of motion. A coordinate system is introduced with origin at the leading edge, and moving with the plate.



The velocities close to the plate are governed by the equations:

$$u \frac{\partial u}{\partial x} + v \frac{\partial u}{\partial y} = \nu \frac{\partial^2 u}{\partial y^2} \quad \text{--- (1)}$$

$$\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} = 0 \quad \text{--- (2)}$$

With the boundary conditions:

$$u = v = 0 \quad \text{at} \quad y = 0 \quad \text{and} \quad x \geq 0$$

$$u = U \quad \text{when} \quad y \rightarrow \infty$$

where u and v are the velocity components in the boundary layer, and ν is the kinematic viscosity.

If the flow is laminar then the solution to this Blasius boundary layer is well known and is given, for example, in Schlichting (1955).

If $u \frac{\partial u}{\partial x}$ is representative of the order of magnitude of the inertial terms in (1), and δ_m is the measure of thickness of the boundary layer, then at $x = A$ we obtain a balance:

$$\frac{U^2}{A} \sim \frac{\nu U}{\delta_m^2}$$

$$\delta_m \sim \left(\frac{\nu A}{U} \right)^{\frac{1}{2}}$$

Close to the plate u increases linearly with y and we can write:

$$u \sim \frac{U y}{\delta_m}$$

$$u \sim y U^{\frac{3}{2}} \nu^{-\frac{1}{2}} A^{-\frac{1}{2}}$$

and from (2)

$$v \sim y U A^{-1}$$

A criterion for the laminar solution to be valid is that the Reynolds number Re , based on the boundary layer thickness, be less than some critical value of the order 10^3 .

$$Re = \frac{U \delta_M}{\nu} \sim \left(\frac{U A}{\nu} \right)^{\frac{1}{2}}$$

The order of magnitude of Re for the present probe is 10^2 , so this analysis seems to be applicable.

If there are no gradients of temperature or salinity, then the distribution of dissolved oxygen in the vicinity of the electrode is given by the diffusion equation:

$$u \frac{\partial c}{\partial x} + v \frac{\partial c}{\partial y} = \kappa \frac{\partial^2 c}{\partial y^2} \quad \dots \quad (3)$$

As all the oxygen is reduced at the electrode surface we obtain the boundary conditions:

$$c = 0 \quad \text{at} \quad y = 0 \quad \text{and} \quad A \leq x \leq A+L$$

$$c = C \quad \text{when} \quad y \rightarrow \infty$$

where c is the local concentration, C the concentration of oxygen in the ambient fluid and κ is the diffusivity.

Suppose the term $u \frac{\partial c}{\partial x}$ is at least as large as $v \frac{\partial c}{\partial y}$ and label the thickness of the diffusion boundary layer δ_D . In a distance a from the upstream edge of the electrode the balance between horizontal advection and vertical diffusion is given by

$$\frac{\delta_D U C}{\delta_M a} \sim \kappa \frac{C}{\delta_D^2}$$

$$\delta_D \sim U^{-\frac{1}{2}} A^{\frac{1}{6}} a^{\frac{1}{2}} \nu^{\frac{1}{6}} x^{\frac{1}{3}}$$

If $\delta_D \ll L$ the flux Q of oxygen to a square electrode with the area L^2 is given by

$$Q \sim x \frac{C}{\delta_D} L^2$$

The current supported by the flux Q is then given by

$$i \sim K U^{\frac{1}{2}} L^{\frac{5}{3}} A^{-\frac{1}{6}} x^{\frac{2}{3}} \nu^{-\frac{1}{6}} C \quad \dots \quad (4)$$

where K is Faradays constant multiplied with the number of electrons involved in the reduction; if the concentration is given as molality.

We can now check the hypothesis that the vertical advection does not dominate the process.

$$\frac{v \frac{\partial c}{\partial y}}{u \frac{\partial c}{\partial x}} \sim \frac{\delta_D U C}{A \delta_D} = \frac{L \delta_M}{A \delta_D} \sim \left(\frac{L}{A}\right)^{\frac{2}{3}} \left(\frac{\nu}{x}\right)^{\frac{1}{3}}$$

Now $\left(\frac{\nu}{x}\right)^{\frac{1}{3}} \approx 10$, so for $\left(\frac{L}{A}\right) \lesssim 10^{-2}$

the vertical advection could be neglected. If $\left(\frac{L}{A}\right)$ is significantly larger, then the horizontal advection can be neglected, and we get

$$\delta_D \sim U^{-\frac{1}{2}} A^{\frac{1}{2}} x^{\frac{1}{2}}$$

$$i \sim K U^{\frac{1}{2}} L^2 A^{-\frac{1}{2}} x^{\frac{1}{2}} C$$

It is also seen that $\delta_D \ll L$

$$\frac{\delta_D}{L} \sim \left(\frac{A \nu x^2}{U^3 L^4} \right)^{\frac{1}{2}}$$

with $U \approx 10^2$, $A \approx 1$ and $L \approx 10^{-2}$ in cgs units, which are the order of magnitude of the parameters of the present probe, this ratio is of order 10^{-2} .

Consider a sudden change in the oxygen concentration in the x-direction. This change in concentration will be felt at the electrode after a delay which is partly due to the dispersion in the Blasius layer and partly a delay in the diffusive boundary layer of the electrode.

In the Blasius layer, diffusion and horizontal and vertical advection will distort the front. The vertical advection and diffusion counteract and will be disregarded in comparison to horizontal advection. Thus at the level δ_D the front will be retarded a time τ_a , relative to the passage of the front in the ambient fluid, where

$$\tau_a \approx \frac{A}{u(\delta_D)} - \frac{A}{U}$$

However

$$\frac{u(\delta_D)}{U} \sim \left(\frac{L x}{A \nu} \right)^{\frac{1}{3}} \ll 1 \quad \text{if } L \leq A$$

therefore

$$\tau_a \approx \frac{A}{u(\delta_D)} \sim \left(\frac{A^4 \nu}{U^3 L x} \right)^{\frac{1}{3}}$$

The time constant of the diffusive sublayer is

$$\tau_d \sim \delta_D^2 x^{-1}$$

and

$$\frac{\tau_d}{\tau_a} \approx \frac{L}{A}$$

The actual probe can be approximated by a sum of model electrodes with different A . With the present design $L \ll A$. Furthermore if $B = A_{max} - A_{min}$ and $L \ll B$ we can then disregard τ_d and describe the response of the probe as a pure lag τ_L and a smoothing of the discontinuity with a characteristic time constant τ ; where

$$\tau_L \sim \left(\frac{A_{min}^4 v}{U^3 L \lambda} \right)^{\frac{1}{3}}$$

$$\tau \sim \left(\frac{B^4 v}{U^3 L \lambda} \right)^{\frac{1}{3}}$$

The maximum spatial resolution λ will be

$$\lambda = U \tau \sim \left(\frac{B^4 v}{L \lambda} \right)^{\frac{1}{3}}$$

substituting $L \approx 10^{-2}$ cm and $B \approx 2$ cm gives $\lambda \approx 100$ cm.

III Design of the instrument

The cathode in the prototype is a cylinder with electrodes at the surface, some distance from the rounded tip. The cylinder is oriented so as to move along its axis. The probe is made in the following way: a platinum wire is wound about a glass rod and a copper wire, soldered to the copper wire and cut at the opposite side of the rod. The copper wire is wound to a helix with the platinum bristles outwards. This arrangement is casted in epoxy, which is turned and polished to expose the tips of the platinum wires, see fig. 1 a.

The number of electrodes are chosen so as to give a measurable current. A single electrode with a diameter of 10^{-2} cm will, according to (4), give a current of the order of magnitude 10^{-7} A at a velocity of 100 cm/s and an oxygen concentration of 1 ppm. To obtain in this case

a current which is conveniently handled in an ordinary operational amplifier, approximately 100 electrodes in parallel are sufficient.

The anode is a silver-silverchloride electrode of the kind used in the GEK (van Arx 1962). A paste of silverchloride and silveroxide is smeared on to a silver gauze which is rolled on a silver wire and fired in a furnace to decompose the silveroxide to metallic silver. The silver wire is connected to the cable and partly embedded in epoxy in a protective pipe, as shown in fig. 1 b. The electrode is mounted with the tube pointing upwards. In this way the electrode can be kept immersed in water continuously by simply putting a cork in the opening when the instrument is stowed away.

The electrodes are mounted together with a strain gauge pressure transducer and a fast response glasscoated thermister on a sledge-like protecting structure, see fig. 2. The instrument is connected to the ship via a thin 8 conductor cable, which is paid out in excess during the descent, and is used to recover the instrument after the measurement.

The sensor must fall stably and with a constant speed. With the present design the terminal sinking rate is reached within a few meters and is determined by a balance between the drag force F and the net negative buoyance B .

$$F = D \rho A' U^2$$

$$B = (M - \rho V) g$$

where

D - drag coefficient

A' - projected area perpendicular to motion

M - mass of instrument

V - volume of instrument

ρ - density of water

this gives for the velocity

$$U = \left(\frac{[M - \rho V] g}{D \rho A'} \right)^{\frac{1}{2}}$$

U is determined by the sinking rate of the cable, which preferably should be somewhat larger than U to minimise influence from the trailing cable during the descent. This value of U can be obtained by varying A' or $M - \rho V$. It is desirable to make M large compared to ρV , as ρ will vary irregularly during a descent, hence G will be large and A' has to be increased. This was done by putting a cone of wire net at the upper end of the cage. The shape and position tends to reduce oscillations, and the permeability decreases vortex shedding. The stability is further increased by an incompressible float inside the cone, giving a strong static righting moment to the structure.

The schematic circuit diagram in fig. 3 shows the principle of the polarographic current measurement. The voltage E^* across the electrodes is compared to the fixed voltage E . By the action of the operational amplifier a current i , such that $E^* = E$, is fed through the water loop. The same current flows through the feedback resistors, and the output voltage is strictly proportional to the polarographic current. The voltage E is taken from a mercury battery over a voltage divider. By replacing the electrodes with a fixed resistor, E can be monitored and if necessary adjusted. A value of 0.8 V was chosen for E .

The temperature measuring circuit is an unbalanced Wheatstone-bridge with a Fenwal GB32SMM1 thermistor as one arm of the bridge. The other resistances are chosen so as to give minimum nonlinearity (Petrén 1972). The residual nonlinearity and calibration uncertainty is less than 0.1 deg in the interval 0 - 20 °C.

The range of the Bell & Howell pressure transducer used is 0 - 150 psi; equivalent to approximately 100 m depth. The maximum error due to nonlinearity and hysteresis corresponds to less than 0.5 m and the resolution is essentially infinite.

All recordings were made on a battery powered Minigore X-Y-T recorder, with a relative error of approximately 1 %.

IV Laboratory testing

The properties of the electrodes were studied in a calibration tank shown in fig. 4. The volume of water in the tank was 30 l, and it was sealed off from the air by a thick layer of hollow epoxy spheres of a diameter of 3 mm. This had the advantage that the water level could be varied and instruments inserted freely. It also showed a good insulation to gas diffusion, almost oxygen free water could be kept for days without appreciable change in concentration.

Oxygen concentration was varied by bubbling nitrogen or air through the water. Temperature could be changed by pumping hot or cold water through a coil of copper tubing. The water was continuously circulated by a propeller.

In the tank was placed a small calibration tunnel for the oxygen electrode. Water was circulated through a duct via an impeller pump and a waterflow meter. A number of finemeshed nets were placed at the entrance of the duct to smooth eddies produced by the inlet. The electrode was centered in the duct, and the velocity of the water passing it was kept constant by monitoring the flow with the flow meter. Watersamples could be taken via a three-way valve on the tubing of the pump.

Oxygen concentration was determined by Winkler titration. Generally, single samples were taken and the random error in the measurements was probably not larger than 0.05 ppm. Systematic absolute errors, which may be considerably larger, are of no consequence in the interpretation of the results.

The results of a calibration run with temperature and velocity kept constant are given in fig. 5 and tab. 1. It is seen that the polarographic current is linear with change in concentration of dissolved oxygen. All deviations but one are less than what is explainable by the quoted uncertainty in the titration alone. The residual current at zero concentration is in this case 1.6 % of the current at 10 ppm, this varied somewhat in other calibrations.

The flux of oxygen is proportional to the gradient of chemical potential of the dissolved oxygen. As the chemical potential depends on

salinity and temperature, this means that α in equation (3) is a function of salinity and temperature, and hence that i will vary with changes of temperature or salinity at constant concentrations. The fact that a difference in chemical potential is the driving force of diffusion is expressed by Henry's law. The partial pressure of a gas in solution, and the relative saturation, are defined by this law. These will, if substituted for concentration in the diffusion equation, give a less variable diffusion coefficient. Besides α , viscosity is a function of salinity and temperature in the expression for i .

The temperature dependence was measured by continuously heating the water and recording current versus temperature on the X - Y recorder. The mean of a number of runs was taken and the resulting temperature coefficient is given in fig. 6. There was a considerable spread in the individual recording for temperature above approximately 15 °C. This may have been caused by a local decrease in oxygen concentration when the water was subjected to a pressure drop in the pump and the concentration approached saturation at the increased temperature. No changes in concentration were noted in the samples, however these were taken before passing the pump.

The salinity coefficient was determined by dilution of the sea water in the tank with distilled water of the same temperature and oxygen content. One series of measurements were made, and the results are presented in fig. 6. There was a small difference in oxygen concentration between the sea water and the distilled water. This introduced a correction of the same order of magnitude as the measured current changes. Hence the accuracy of the determination was rather low.

As can be seen from fig. 6 the polarographic current is essentially a measure of the partial pressure of oxygen. The only significant differences between measured coefficients and what should be expected from the change in partial pressure is the temperature dependence at low temperature, here the deviations are larger than the spread in the measurements.

By towing the instrument at different speeds in a large tank the velocity dependence was studied. As can be seen from fig. 7 the output is proportional to the square root of the velocity.

When the voltage across the electrodes is switched on there follows a period during which the current changes rapidly as the cathode becomes polarised. This is completed in less than 5 minutes, and after this the current drift is low; shorttime variations are less than 1 %/hour. Longtime drift depends essentially on changes at the cathode surface. The hydroxyl ions produced by the reduction of oxygen will increase the pH locally, and calcium carbonate might precipitate. Other chemical reactions and direct contamination will change the effective surface area, and hence the polarographic current. This long-time drift can be large especially if the electrode is allowed to become dry between measurements.

V Field testing

Fig. 8 shows a recording of temperature and polarographic current made in the Gullmarfjord. Values of oxygen partial pressures obtained from a simultaneous hydrographic cast are fitted to the recording with a linear relation between partial pressure and instrument output. Two successive recordings at the same station in the Skagerack is shown in fig. 9. Here salinity data are missing, so comparison is made to the oxygen concentration. The temperature variations are small, and the distribution of relative oxygen saturation is probably not much different from that of oxygen concentration.

The main features of the oxygen distributions as obtained from discrete water samples are recognisable in the recordings, but there is a considerable amount of noise superimposed, giving an uncertainty of approximately 5 %. This noise is probably due to small oscillations of the instrument, changing the angle of attack of the cathode, and producing fluctuations in the boundary layer velocity. In order to study these oscillations a pendulum with a stylus making a trace on the glass slide of a modified bathythermograph was mounted on the instrument (Brooke and Mason 1969). The amplitude of the oscillations proved to be small, 1 degree or less, but the typical periods are similar to those in the oxygen measurements. By recording pressure versus time the vertical velocity of the instrument could be computed. The local mean velocity over depth intervals of 5 m were determined at a number of drops. The maximum deviation was approximately 5 % of the total mean velocity. If the velocity is averaged over larger intervals of depth the variability is less. In terms of variability in the calibration

coefficient this means a maximum error of 1 - 2 %, depending on the relative importance of the current at zero velocity to the actual current.

VI Discussion

As far as the limited results from use at sea have shown, this instrument has a low accuracy in the order 10 %. The relatively stable and linear behavior of the electrodes in the laboratory give some hope that this can be improved. The main source of error seems to be the oscillations of the cathode. It is obvious that boundary layers of other shapes, for example a cone or a wedge, are less sensitive to changes in angle of attack. Electrodes of this kind will be tried in the future. The longtime drift can be corrected for by sampling water from the mixed layer at some of the stations occupied. Occasional cleaning with an acid or polishing of the platinum cathode is recommendable especially if the instrument has been used in anoxic water. If the instrument is kept submerged and running between stations it is ready for immediate use, as it is necessary to allow it to polarise for at least 5 minutes before measurements are taken.

The main advantage is the simplicity and rapidity of measurement. Total station time for a continuous ^u recording down to 100 m depth is less than 5 minutes.

Without corrections the instrument essentially measures relative saturation of dissolved oxygen. If salinity variations are small a simple voltage divider with the thermistor probe as variable part can be used to make an approximate conversion to oxygen concentration.

Acknowledgements

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Grasshoff, K.,: Untersuchungen über die Sauerstoffbestimmung im Meer-
wasser. Kieler Meeresforschungen,
1) 1962: Band XVIII, 42-50.
2) 1962: Band XVIII, 151-160.
3) 1963: Band XIX, 8-15.

Table 1.

Percent deviation of polarographic current
from linear regression line.

Oxygen concentration ppm	Current deviation %
6.70	0.3
5.62	0.4
5.56	-0.5
4.57	-0.1
3.93	-0.9
3.68	1.4
3.01	0.8
2.04	-0.5
1.35	-2.0
0.00	17.8

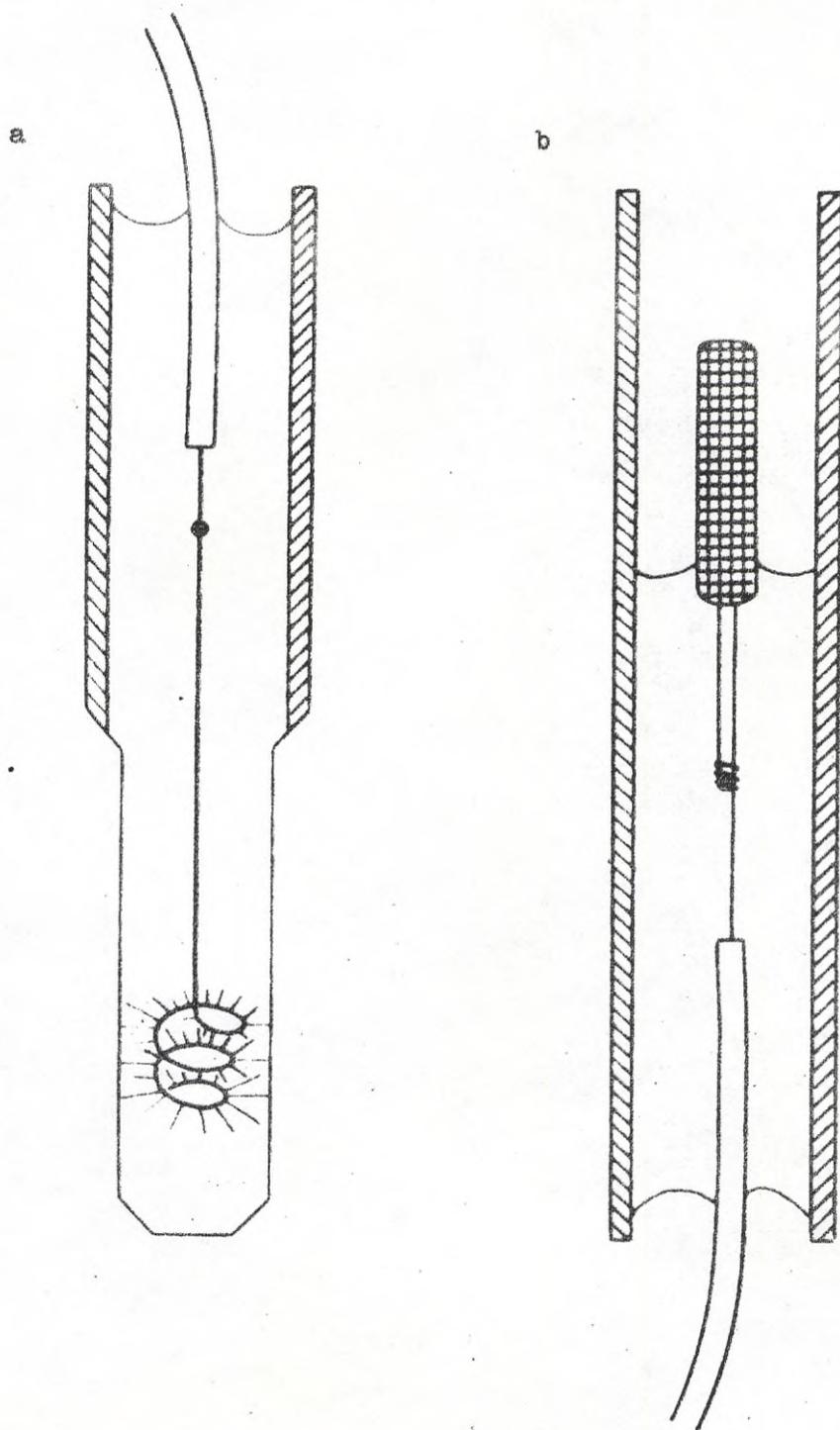
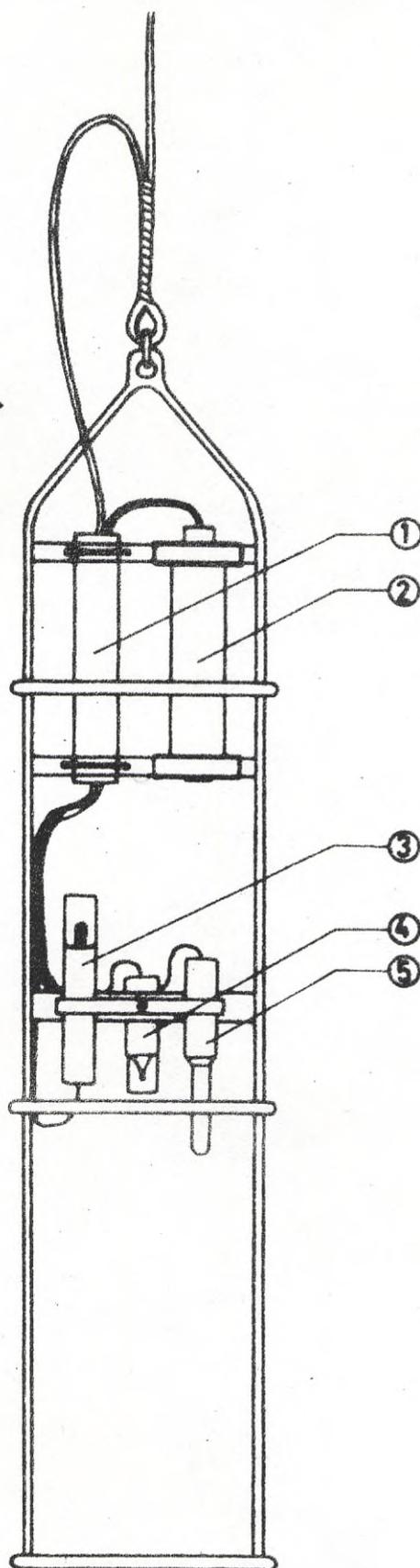


Fig 1 a/ the platinum electrode
b/ the silver-silverchloride electrode

Fig 2 Underwater unit

- 1 - cable connector
- 2 - pressure transducer
- 3 - anode
- 4 - thermistor
- 5 - cathode



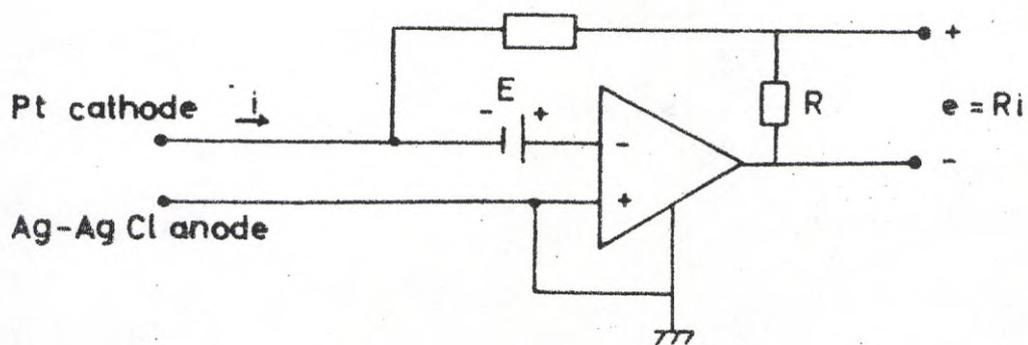


Fig 3 Schematic diagram of the polarographic current measuring circuit.

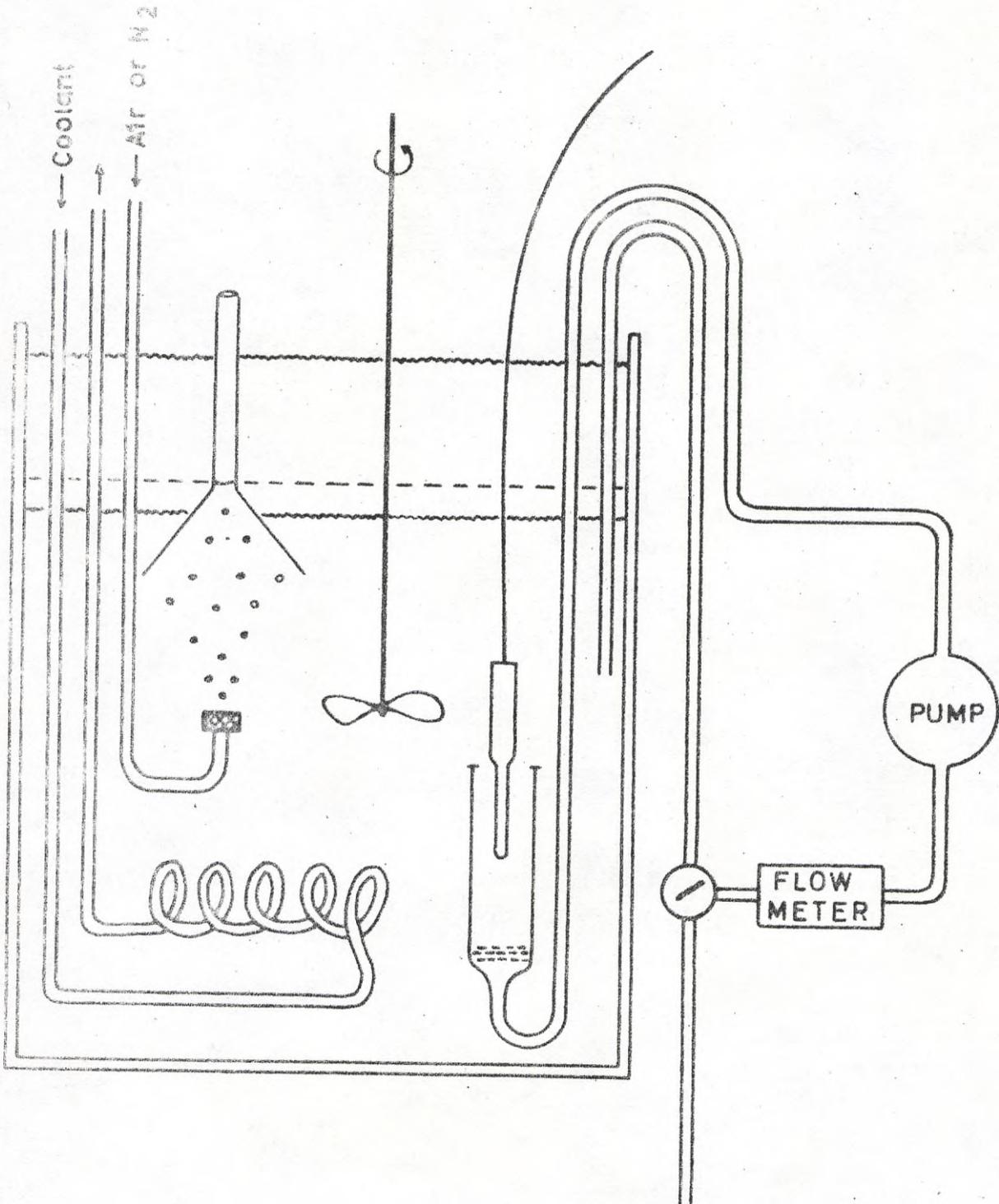


Fig 4 The calibration tank.

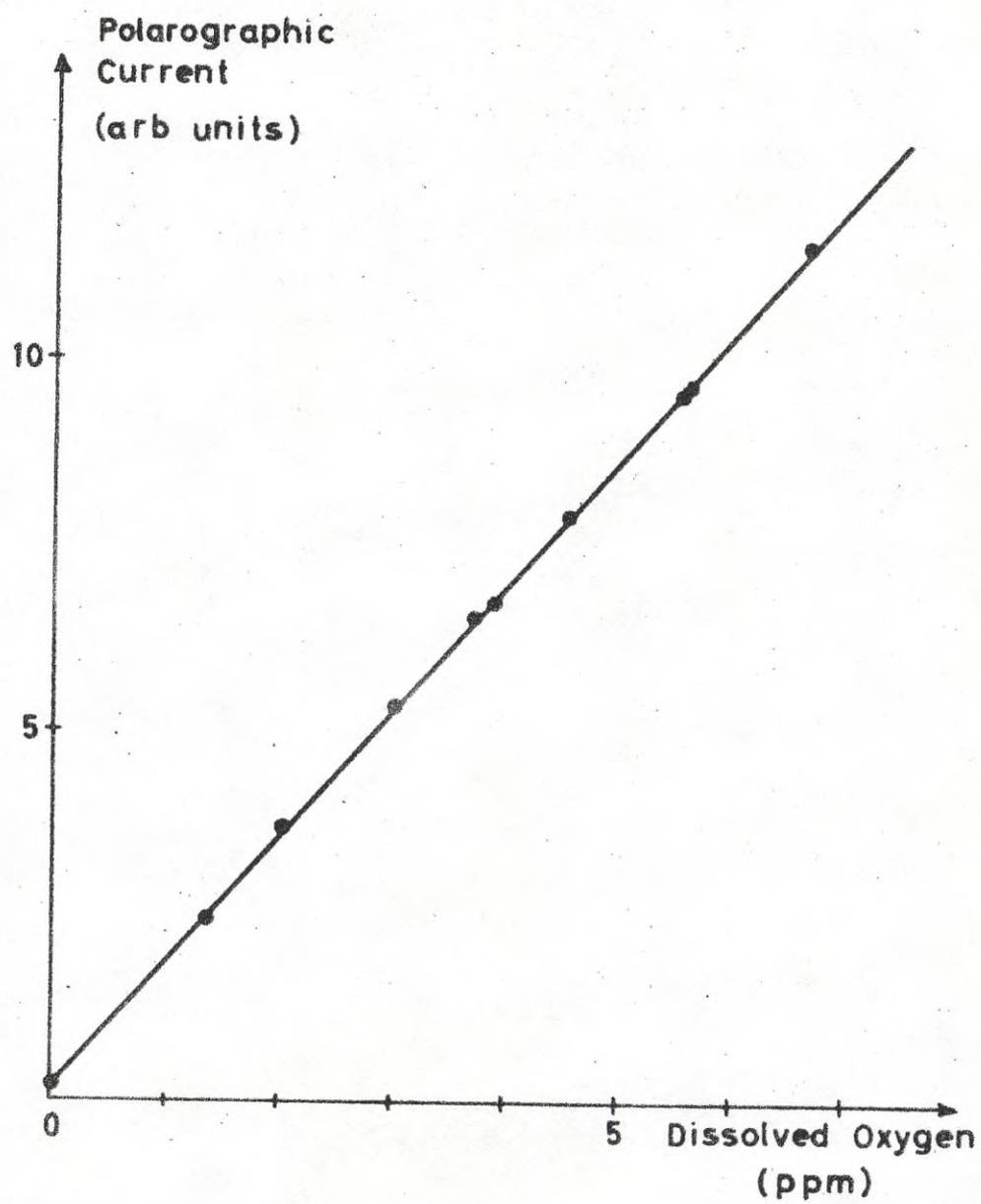


Fig 5 Calibration curve of the electrode.

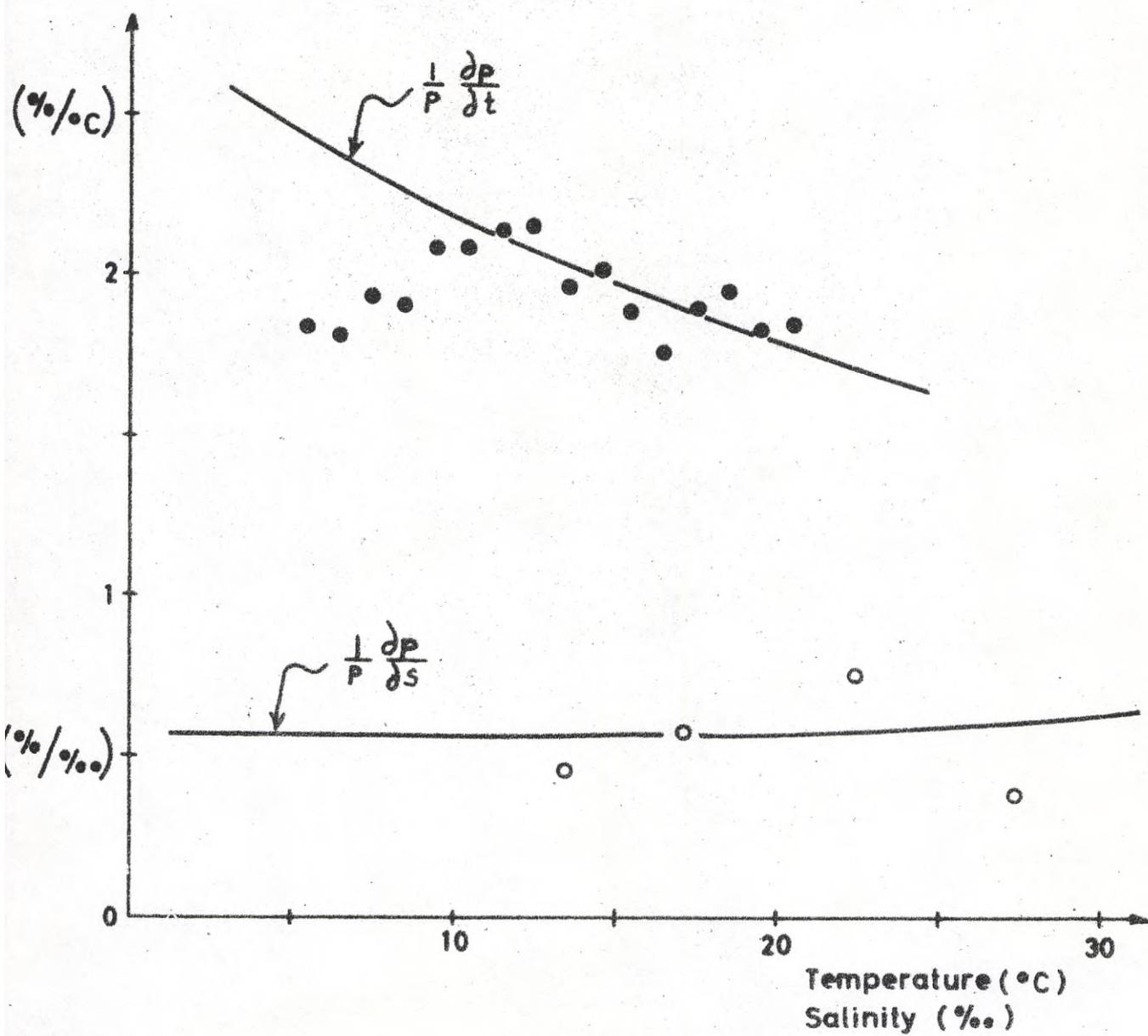


Fig 6 Temperature coefficient versus temperature (filled circles) and salinity coefficient versus salinity (open circles). The curves show the change of partial pressure of oxygen due to temperature and salinity.

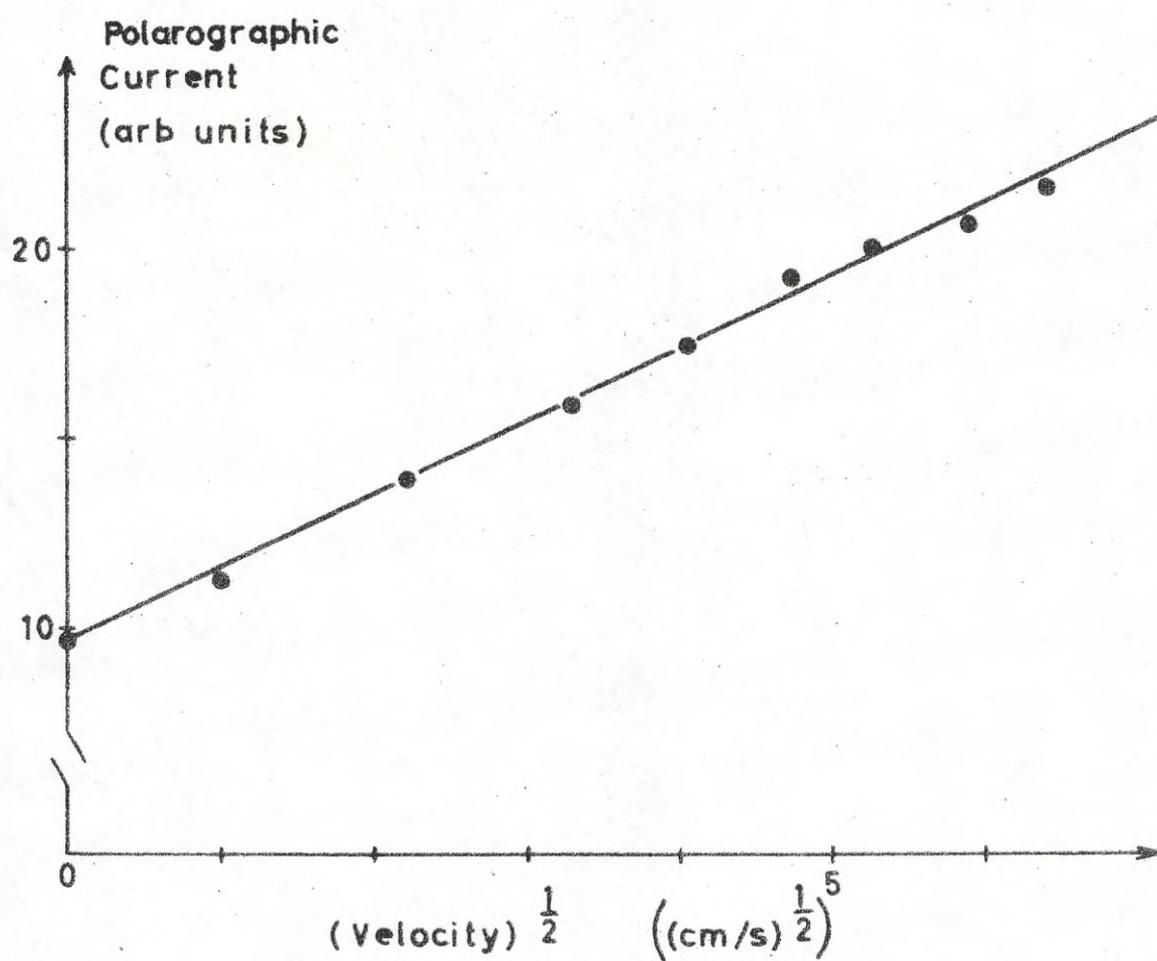


Fig 7 The polarographic current at constant oxygen concentration versus square root of the velocity of the electrode.

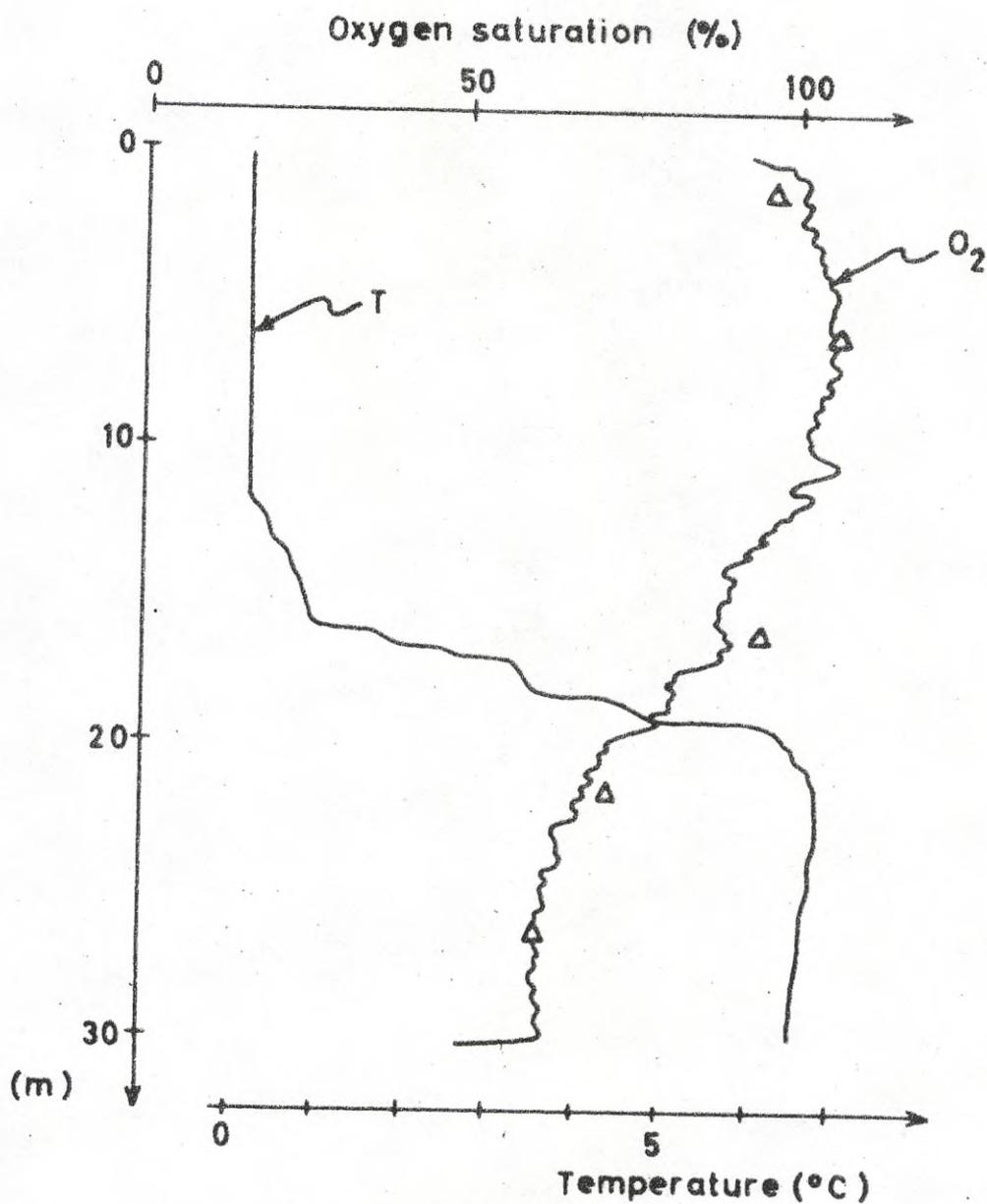


Fig 8 Recordings of temperature and polarographic current versus depth. Triangles show relative oxygen saturation determined by a hydrographic cast, Bornö March 1972.

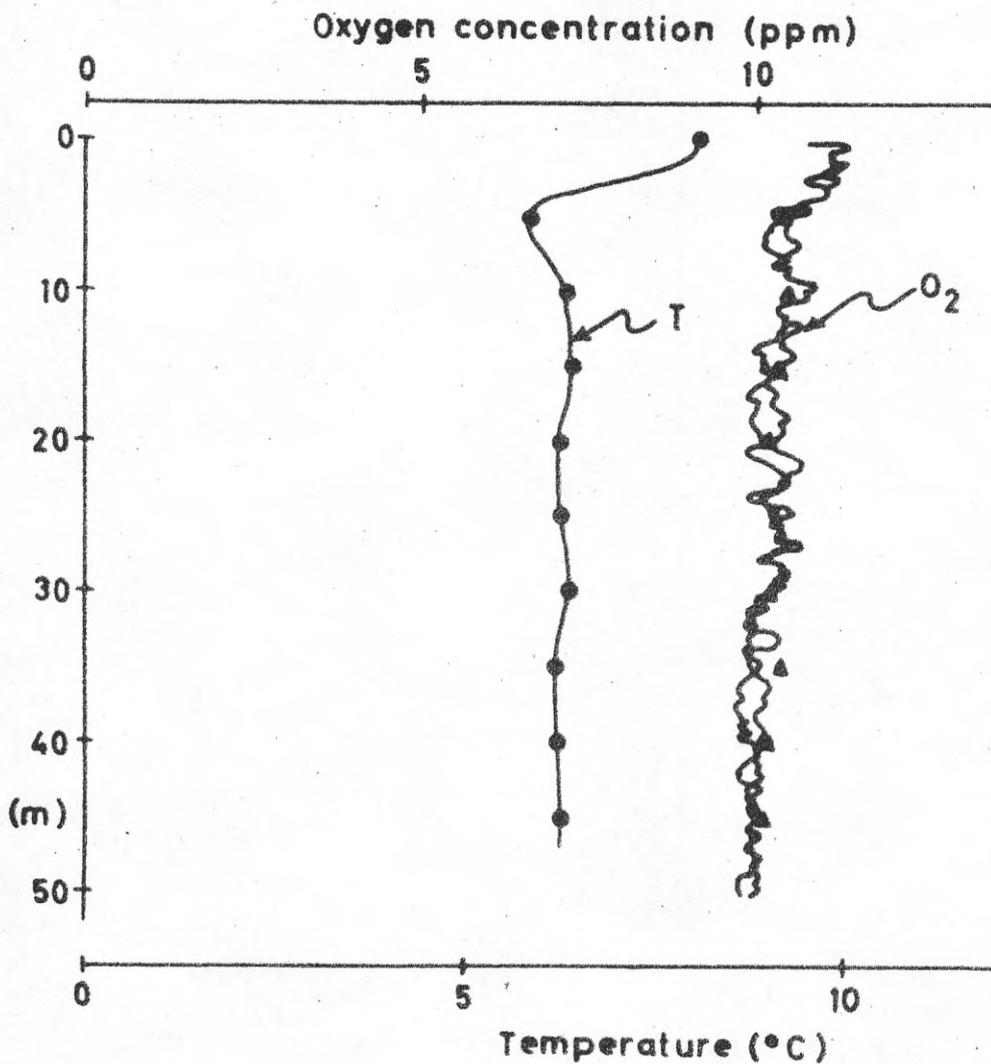


Fig 9 Repeated recordings of polarographic current obtained at the same station. Temperature (dots) and oxygen concentration (triangles) from hydrographic cast. "Skagerak" 57° 50' N 10° 25' E May 1972.

