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THE OXYMETER

by Ernst Føyn

The great importance in oceanographic research of using instruments which continuously register hydrographical properties when they are lowered through the sea was first demonstrated by the temperature registering instruments, the thermosonde by Mosby and the bathythermograph by Spilhaus. The amount of new information obtained with these instruments clearly indicated the value of also searching for methods of continuously registering other hydrographical properties.

About 10 years ago the Institute of Marine Biology at the University of Oslo succeeded in developing a simple instrument for registration of dissolved oxygen in sea water (Føyn, 1955). The apparatus continuously measures the amount of dissolved oxygen as it is lowered through the sea, and it was stated that the oxygen content in any depth could be determined with fairly good accuracy if a calibration curve was prepared. The latter is based on the registered values plus a few oxygen values obtained by ordinary technics, that is determination of the oxygen content in water-samples by the Winkler method.

The apparatus consists of a zinc electrode and a dropping mercury electrode, and was built in the laboratory from a zinc tube and a glass tube, the latter about 3 cm in diameter and 10 cm high, open at the upper end and closed with a rubber stopper, penetrated by a thin glass capillary at the lower end. The capillary was drawn out to a point. The glass tube was three-quarters filled with mercury and a few milliliter of carbon tetrachloride were added. The point

was then broken so that the mercury could drop out rapidly. The zinc tube was chosen so that it fitted closely around the glass tube.

The zinc metal was connected with the mercury through a 500 meter long plastic-covered electric cable and a microammeter on deck. When placed in water, this apparatus generated an electric current which was found to depend on the amount of dissolved oxygen in the water and could be measured with the microammeter. This apparatus is, therefore, principally different from the membrane-covered electrode, later introduced by Kanwisher (1959) and recently modified by Grasshoff (1962).

The zinc mercury electrode has been regularly in use at our institute since 1954. During this time experience has been gained in handling the apparatus and the obtained results. The apparatus itself has also been altered a little.

In the original arrangement the produced electric current was measured with an ordinary microammeter, full scale 100 microampere. With this equipment the oxymeter is very simple to build, and can be produced in any laboratory at a price of less than £ 30.

It has, however, been found desirable to try to evolve a recording microammeter which could draw the oxygen curves directly. A bolomat messystem from Fernsteuergeräte O.H.G., Berlin was modified for our purpose in the following way:

In the original recorder the watch which moves the paper with the time by electric pulses from an accumulator was replaced by an arrangement on the metre wheel which gives electric pulses by closing and opening a feather-contact twice for each time the wheel turns round. In this way the

paper is moved synchronously with the lowering of the apparatus, one millimeter per meter. The curve is drawn both when the instrument moves downward and upward. The two parts of the curve will then be mirror images of each other.

The electrodes themselves are still built and handled in essentially the same way as the original ones. Some small details have, however, been changed, in order to make the apparatus more practical for use. The zinc tube is now placed on an open foot with a holder for the cup for collecting the mercury which drops out.

The glass tube is open and, therefore, completely independent of the pressure when lowered. When the instrument is not in operation, it is recommended that the tube should be closed by means of a stopper, in order to prevent the mercury from dropping out. This precaution is taken because it has been found necessary to leave a certain level of mercury always in the tube to keep the capillary clean and dry.

Originally the oxymeter was fixed below the lead at the end of the hydrographic cable. This was found impracticable, especially when working near the bottom. Now the lead is placed below the oxymeter.

When lowering the apparatus in places with strong water currents, it has sometimes been found that the instrument tips over and stops working. Schram (not yet published), using the oxymeter in Øresund, where strong subsurface currents run, avoided this difficulty by placing the apparatus in an open container with a steering fin, fixed to the hydrographic cable in such a way that it was always kept in a vertical position. Fixed in this way, the oxymeter can even be used from a boat when it is moving at a slow speed. A speed between 1 and 2 knots can easily be tolerated.

The apparatus has been operated in Norwegian fjords from our 40 feet research vessel "Gunnar Knudsen" under all weather conditions.

With high waves small oscillations appeared on the curves. These do not disturb the measurements, as the mean values may be used for the evaluation. The apparatus has also been tested on a bad weather cruise with the Norwegian research ship "Helland Hansen". It was found possible to operate the instrument also under these extraordinarily bad conditions.

The apparatus has been used down to 300 meters, but there does not seem to be any limit except that given by the length of the cable and the amount of mercury in the container.

The apparatus is usually lowered at a speed of about 10 metres per minute except when very great variations per meter in the oxygen content appear. This might happen in the discontinuity layers. Then the pen on the recording instrument needs some more time to reach the right position, which may naturally be avoided by chosing a more rapid ammeter.

In order to determine the dependence on temperature of the apparatus, measurements were made in the laboratory both with the oxymeter and with oxygen analysis according to Winkler. The relation between the recorded microampere and the oxygen content of the water was found to be at 22°C, 11.4 micram/ml O_2 and at 2°C, 8.2 micram/ml O_2, or a variation of 1.5% per degree at this temperature level.

Grasshoff (1962), working with the membrane-covered electrode, reports similar measurements. He found with his electrode the following values: 22°C, 3.39 micram/ml O_2 and

2°C, 0.89 micram/ml O_2. It seems, therefore, that the electrode used by us is far more oxygen sensitive and much less temperature dependent than the membrane-covered one. On the other hand the stability of the oxygen electrode, when used over longer periods, is not as good as that reported for the membrane-covered one. Therefore, it is recommended to check the calibrations with one or two analyses per day.

In ordinary hydrographic water sampling it is, however, difficult and sometimes impossible to get representative samples from water levels where the hydrographical conditions change rapidly from meter to meter with the depth. Therefore, the calibration values should be chosen from those levels where the curve runs smoothly.

Preparation of a full calibration curve can then be made as in the following example from Bonnefjord.

Bonnefjord 14/8. 63

Bathythermograms and oxygen recordings taken. depth chosen

Metre	Temperature	O_2 ml per liter
0	19.0	6.68
20	3.49	4.05
50	5.83	2.03
70	6.62	3.00
140	6.62	2.90

Fig. 1 shows the oxymeter curve from Bonnefjorden 14/8. 62.

The calibration curve, which is drawn in, is based on the analytically obtained values and values from the oxygen curve in the above-cited depths.

All values ought to be adjusted to the same temperature by choosing this at 6°C. Corrections of the

three deeper depths are negligible. The 20 meter value should have the following correction:

$$\frac{32 \times 1.5 \times (6-3.5)}{100} = 0.78 \text{ microampere}$$

and the 0 meter value a negative correction:

$$\frac{67 \times 1.5 \times (6-19.0)}{100} = -13.1 \text{ microampere.}$$

The points fit well on a straight line, and the accuracy of the recorded values gives accordingly an accuracy of about 0.1 ml O_2 per liter, even if - as in this case - the whole analytical error is placed on the recorded values and the Winkler analyses are accepted as fully correct.

In Fig. 2 the two halves of a curve from inner Oslofjord are reproduced. The curve to the right is that obtained when lowering the apparatus, and that to the left when taking it up. The reproduce-ability of the measurements is demonstrated by the way the two curves follow each other down to the finest details. These curves demonstrate also the micro structure of the water masses.

It has been the purpose of this article to describe the oxymeter in its present form as well as to give a report on experience obtained and results gained during the work with this instrument. This may be of value since different instruments have different advantages and disadvantages under different conditions. It is necessary to know how the instruments work, in order to be able to choose the right one in each special case.

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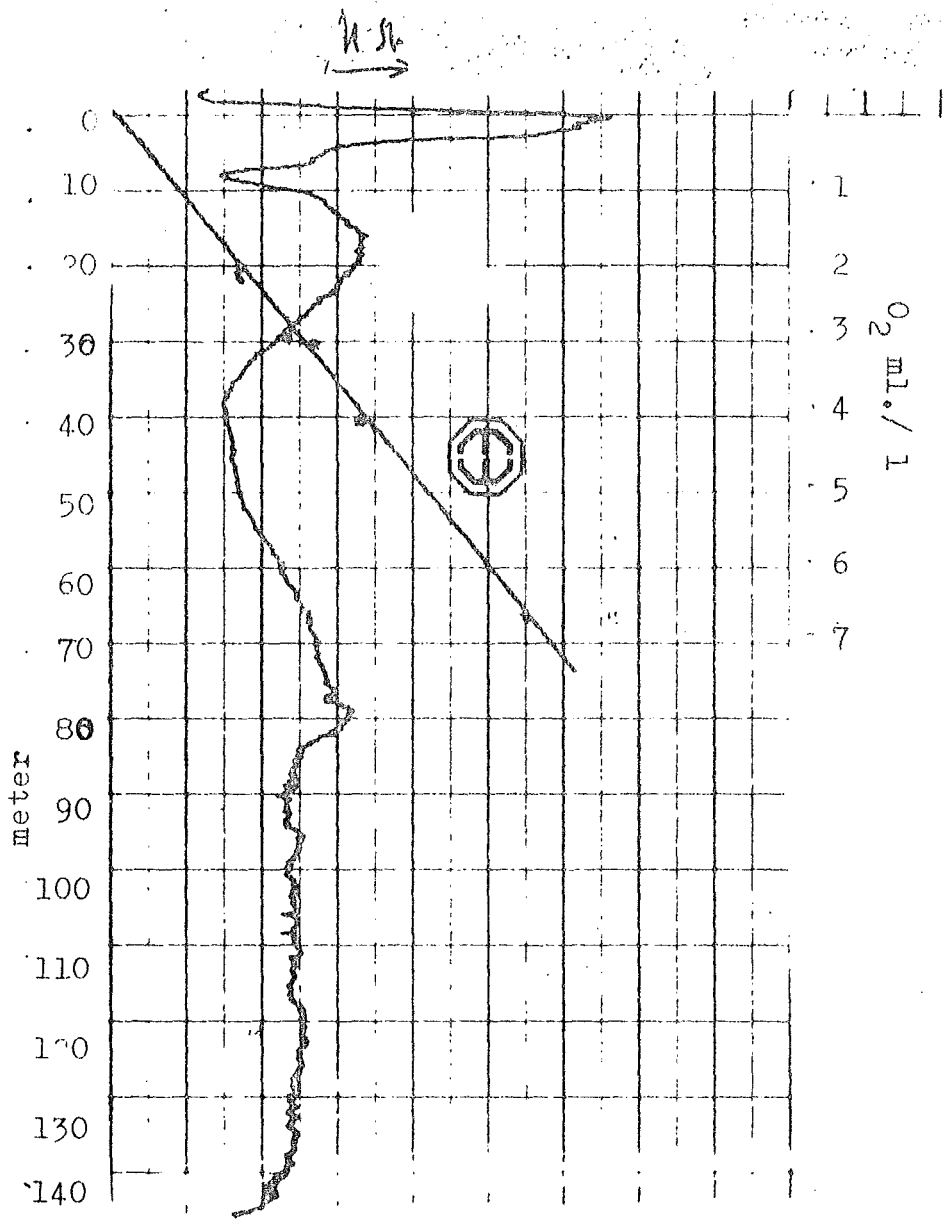
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40
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meter
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4
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6
7
O2 ml./ l

Fig. 1

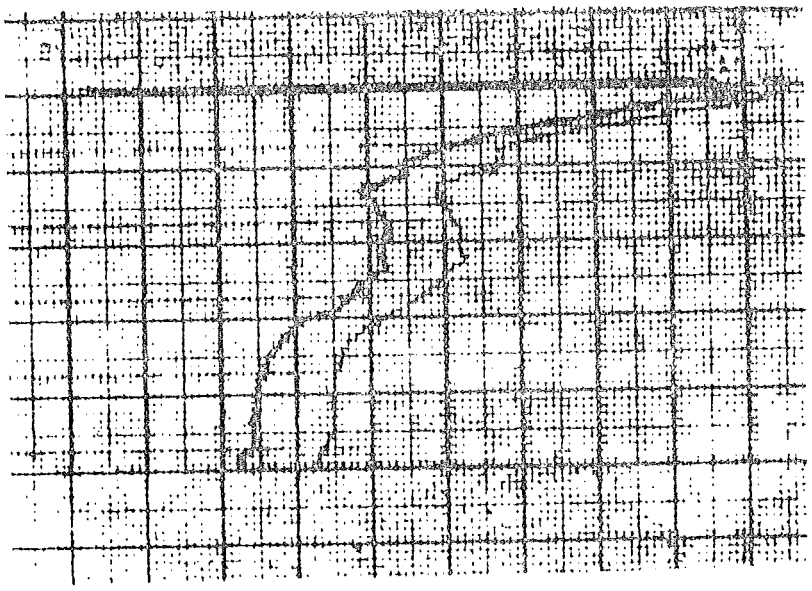

Fig. 2