

formed in the charcoal column from the reaction of oxygen with the charcoal. The furnace temperature must remain steady if baseline fluctuations are to be avoided. A  $40 \times 0.65$ -cm MS 5A column placed after the charcoal column and in the GC oven was satisfactory in sharpening the carbon monoxide peak and gave better separation of the three gas peaks for optimum electronic integration of their areas.

Oxygen can be quantitatively adsorbed from gas systems containing this gas mixed with nitrogen and argon without perturbing the nitrogen and argon determinations obtained by GC. Oxygen values from this gas mixture can be obtained as well as those for nitrogen and argon by passing the gases

through hot charcoal and recording the peak areas of argon, nitrogen, and carbon monoxide.

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## Use of a BOD oxygen probe for estimating primary productivity<sup>1</sup>

### ABSTRACT

The accuracy of a BOD oxygen probe for field measurements of primary production by the light and dark bottle oxygen technique is analyzed. A figure is presented with which to estimate the number of replicate bottles needed to obtain a given accuracy in estimating photosynthetic rates.

When estimating pelagic photosynthesis by measuring the difference in dissolved oxygen concentration (DOC) between light and dark bottles, one usually spends a large amount of time fixing and titrating samples. In an effort to lessen the time needed for such experiments, we used the oxygen probe method (Carritt and Kanwisher 1959).

### METHODS

Primary production was studied at the Jackson Hole Biological Research Station (Moran, Wyoming) during summer 1971. A self-stirring BOD probe (Yellow Springs

Instr. Co. No. 5420) with 0.001 inch (0.25 mm) thick membranes was used to measure DOC. A 6-V car battery and a 110-V a-c inverter powered the probe stirrer so that measurements could be made immediately in the boat.

Water samples were taken from various depths with a plastic Van Dorn sampler, and subsamples were placed in a series of 300-ml light and dark BOD bottles. Dissolved oxygen was then measured in each bottle both before and after a 6-hr in situ incubation. A single water sample was divided into six subsamples: DOC was measured in three of them by Winkler titration (Amer. Public Health Ass. 1971), and the remaining three were used to calibrate the oxygen probe.

We found it essential to avoid air bubbles on the membrane surface because this significantly increases the DOC readings. No method was devised to correct for air bubbles released by oversaturation of the water during incubation. We found it unnecessary to correct for oxygen consumed by the probe cathode.

Calibration of the probe by the Winkler titration was necessary at the time we collected data because we had no information on the proportion of oxygen in the atmo-

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sphere. When such information is available, atmospheric calibration may be preferable.

#### RESULTS AND DISCUSSION

Although no experiments were conducted during violent weather, samples were processed in the boat under conditions varying from calm to windy prestorm. The data discussed below were thus collected under ideal to nonideal field situations and are presented as an example of the type of accuracy attainable.

Preparation time at the beginning of each experiment was 1.4 min per bottle, and the time required to measure DOC at the end of each incubation was 0.6 min per bottle. Preparation time includes sampling at a given depth, filling the BOD bottles, measuring DOC in each bottle, and setting the bottles at the incubation depths. The light bottle change in DOC for seven photosynthesis vs. depth experiments ranged from -0.40 to +0.90 ppm and the dark bottle change +0.05 to -0.70 ppm. The ambient DOC was 7-10 ppm.

Using the oxygen meter (YSI model 54), we found it necessary to round off the oxygen reading to the nearest 0.05 ppm because of the close spacing of divisions on the meter face. Although high sensitivity membranes are available, measurements at the high range (5-10 ppm) remain limited by the meter's readability.

It is possible to measure both initial and final DOC in each bottle with the oxygen probe, and we could reduce variability by pairing the two readings from each bottle rather than using averages of initial and final readings from all bottles. Table 1 gives an example of the field data.

A one-way analysis of variance was used to estimate experimental error. Light bottle variance was 0.012831 ppm<sup>2</sup> with 53 df, and dark bottle variance was 0.009831 ppm<sup>2</sup> with 54 df. A Bartlett's test indicated no significant difference between light and dark bottle variances. A variance of 0.010960 ppm<sup>2</sup> with 49 df was obtained in the laboratory with slightly undersaturated distilled water samples at room temperature. Thus, the accuracy obtainable in the

Table 1. An example of data obtained by the use of the BOD oxygen probe to measure differences in dissolved oxygen (ppm) as an estimate of primary production

| Light bottles     |       |        | Dark bottles |       |        |
|-------------------|-------|--------|--------------|-------|--------|
| initial           | final | change | initial      | final | change |
| Sample depth, 1 m |       |        |              |       |        |
| 8.05              | 8.25  | 0.20   | 7.95         | 7.90  | -0.05  |
| 8.05              | 8.25  | 0.20   | 7.90         | 7.90  | 0.00   |
| 8.05              | 8.40  | 0.35   | 7.95         | 7.90  | -0.05  |
| Sample depth, 2 m |       |        |              |       |        |
| 8.10              | 8.50  | 0.40   | 8.00         | 7.90  | -0.10  |
| 8.20              | 8.60  | 0.40   | 8.00         | 7.95  | -0.05  |
| 8.10              | 8.50  | 0.40   | 7.90         | 7.95  | 0.05   |

field is comparable to that obtainable in the lab.

The variance of estimated gross photosynthesis equals the light bottle plus the dark bottle variances. This summed variance was used to construct Fig. 1, which shows the probabilities that the true gross photosynthetic rate will be within the confidence belt surrounding the mean photosynthetic rate calculated from the change in DOC. Photosynthetic rate is in units of change in DOC in parts per million. The numbers above Fig. 1 indicate the confidence belt as milligrams of carbon per liter. The ratio of oxygen molecules liberated per carbon dioxide molecules assimilated (PQ ratio) is assumed to be 1.2.

Figure 1 is used to estimate the number of replications necessary to obtain a given confidence belt. For example, if one wishes to estimate gross photosynthesis with an accuracy of  $\pm 0.07$  ppm ( $\pm 0.05$  ml O<sub>2</sub> liter<sup>-1</sup>) at a probability of 0.80, the required number of light and dark bottle replications is four. Thus to estimate gross photosynthesis at eight depths with this accuracy, 32 light bottle and 32 dark bottle replicates are necessary. This would necessitate 90

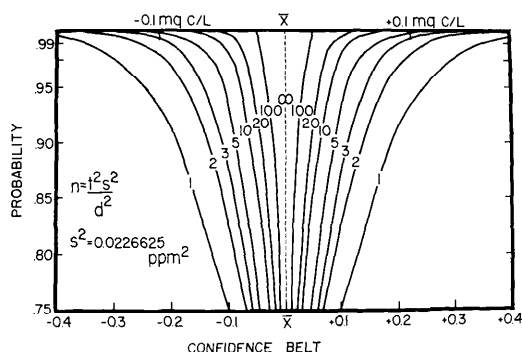


Fig. 1. Probability that the true gross photosynthetic rate will be within the confidence belt ( $\pm d$ ) surrounding the mean gross photosynthetic rate ( $\bar{X}$ ). Numbers on curves indicate number of replicates ( $n$ ). The confidence belt is given as deviations from the mean in parts per million dissolved oxygen. Numbers above figure give the confidence belt as deviations from the mean in milligrams carbon per liter assuming a photosynthetic quotient of 1.2.  $t$  is the value of "Student's"  $t$  with 53 df at an alpha level of  $1 - p$ .

min preparation time and 38 min to make the DOC measurements at the end of the incubation.

According to Strickland (1960), oxygen probe measurement of changes in DOC appears to have a higher variability than the Winkler method. He suggested a standard deviation of 0.034 ppm (0.024 ml  $O_2$  liter $^{-1}$ ) for a Winkler measurement of the difference in DOC between light and dark bottles under ideal conditions, and a variance of 0.00118 ppm $^2$  (0.05 times the oxygen probe variance). It would take 20 oxygen probe replicates to duplicate this accuracy.

However, Carritt and Carpenter (1966) report results for Winkler measurements of saturated seawater samples which would indicate an average Winkler variance three times larger than that we obtained with the oxygen probe. In many cases the oxygen

probe may have an accuracy approaching, if not surpassing, the accuracy of the Winkler method for the following reasons. First, Strickland's ideal conditions seldom, if ever, occur for Winkler determinations. Second, the Winkler method is susceptible to chemical interference, whereas the oxygen probe is much less sensitive to such problems (Amer. Public Health Ass. 1971). Third, although initial variation among samples will add to the variability of the Winkler method, the oxygen probe can detect variation in initial conditions because its measurement technique does not destroy the sample.

The BOD oxygen probe is a rapid, convenient instrument when used to estimate primary production, and its accuracy in certain cases may be comparable to that of the Winkler method.

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