Precise shipboard determination of dissolved oxygen (Winkler procedure) for productivity studies with a commercial system[1]

Abstract—An automatic system of dissolved oxygen titration based on a potentiometric end-point detector is described. The equipment is a simple commercial apparatus that can be used by a relatively unskilled operator. The C.V. of the oxygen measurement is 0.1%. The titration is quick (3–5 min) and suitable for field studies of phytoplankton production and related subjects.

Historically, oxygen has been a widely studied gas (Kester 1975) because it is of great interest to physicists studying the circulation of water masses in the deep ocean as well as to biologists examining oxygen variations due to biological processes. Since the introduction of the Winkler technique in 1888, modifications have been made to improve the precision and to automate the original method (Carritt and Carpenter 1966; Rual and Voituriez 1969; Williams and Jenkinson 1982). When electrochemical devices appeared, they had the advantage of providing a simple, fast method of measuring dissolved oxygen. These oxygen sensors—called oxygen electrodes or oxygen probes (membrane-covered polarographic detectors)—became successful because they allow direct measurement of dissolved oxygen in the environment without altering it chemically and also allow continuous monitoring of oxygen variations in space and in time. For these reasons CTD systems are often being fitted with such oxygen detectors. Despite much effort to overcome the main failure of the detecting system—the lack of precision (the common YSI oxymeter has a C.V. of 1%) and accuracy (Czaplewski and Parker 1973)—oxygen electrodes generally compare poorly with conventional Winkler titration (Atwood et al. 1977). Recently Langdon (1984) im-

proved the reproducibility and long-term stability of such a sensor, but the precision remains poorer than that given by the most sensitive Winkler titration procedures.

The well-known Winkler procedure is founded on quantitative oxidation of Mn(II) into Mn(III) in alkaline solution followed by oxidation of iodide by Mn(III) in acidified solution. The released iodine is titrated with a standard solution of sodium thiosulfate. Improvements aimed at reducing the errors of the Winkler method are the choice of reagent concentrations (Carritt and Carpenter 1966; Rual and Voituriez 1969) that limit the loss of iodine by volatization and replacement of visual colorimetry with an electrochemical or optical detector (Broenkow and Cline 1969; Talling 1973; Hartwig and Michael 1978; Williams and Jenkinson 1982) to determine the end-point of iodine-thiosulfate titration. Contrary to Strickland and Parsons (1968), the potentiometric, amperometric, or photometric detection of the end-point improves the precision of titration. Above all, it allows automation of the method, which means a gain of time and relief for the analyst subjected to an increasing number of routine shipboard measurements. Strickland and Parsons (1968) estimated a C.V. of 0.5% with the classical starch end-point, while Williams and Jenkinson (1982) claimed a C.V. in the range 0.03–0.1% on a routine basis with a photometric system controlled by microprocessor. According to Williams and Jenkinson (1982), photometric end-point detection seems to be the most precise: 0.01% or better. With an unmodified commercial apparatus (Metrohm) based on a potentiometric end-point detector, we get a C.V. of the titration of 0.1%. It is not a sophisticated system and is precise enough to enable the estimation of photosynthetic production of oxygen in tropical areas (Oudot 1984). That fact is very important
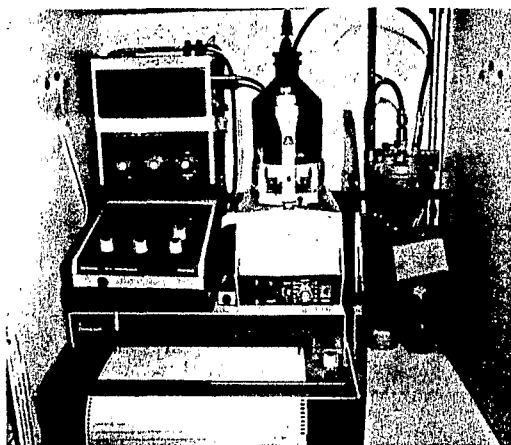
Fig. 1. The Metrohm titration system. Above left—digital 605 pH meter provided with a combined Pt electrode to measure the redox potential of the solution to be titrated; middle left—614 Impulsomat, to regulate the titration; below—625 Dosigraph to record the titration curve; center—655 Multidosimat automatic burette with a digital display of the delivered thiosulfate volume; right—649 magnetic stirrer to mix in thiosulfate added to the iodine solution in the titration vessel.
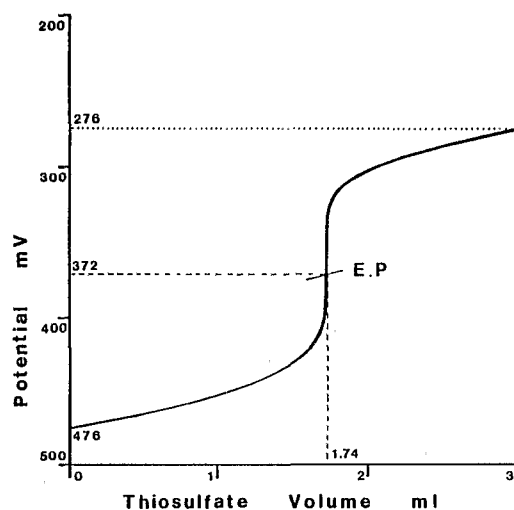

Fig. 2. Diagram of the output of the 625 Dosigraph: titration curve of iodine solution by thiosulfate solution for determining the equivalence point (E.P.) of the titration.

because the classical ^{14}C method for estimating primary production is suspected of underestimating gross production (Shulenberger and Reid 1981; Jenkins 1982), and high-precision oxygen determination is a powerful tool to estimate primary production (Oudot in prep.).

Titration of the iodine solution is performed with a Metrohm titration system consisting of the five major components shown in Fig. 1. Seawater is sampled into a 125-ml dark bottle. One-half milliliter of manganese-sulfate reagent and 0.5 ml of alkaline-iodine solution are added to the sample, and the stopper of the bottle is replaced, taking care not to trap air under it. The bottle is shaken vigorously and then allowed to stand until the manganese hydroxide precipitate has settled (at least 2 h). Then the stopper of the bottle is removed and 0.5 ml of concentrated sulfuric acid is added immediately. The bottle is restoppered with no air trapped inside and shaken so that all the precipitate dissolves. The iodine solution is titrated by transferring 50 ml of the acidified sample with a Kimax automatic-zeroing pipette (precision of 0.01%) into the titration vessel, which is provided with a

small magnetic stirring bar. The vessel is closed with a plastic cover that supports the Pt electrode and the pipette tip delivering the thiosulfate. The measuring electrode is a combined massive platinum electrode (P.N. 6.0415.000) for which the reference system is Ag/AgCl/3 M KCl. Calibration of the thiosulfate solution is with a standard solution of potassium iodate freshly prepared in the laboratory and checked against a CSK standard solution prepared by the Sagami Chemical Research Center (Japan).

The major component of the system is undoubtedly the 614 Impulsomat which regulates the addition of thiosulfate according to the difference between the potential of the solution measured by the 605 pH meter and the predetermined potential at the end of iodide-thiosulfate reaction. This latter potential is previously deduced from the recorder trace of the titration curve of an iodine solution by a thiosulfate solution (E.P. on Fig. 2). After a continuous initial addition of reagent, the amount depending on the quantity of iodine contained in the sample, the burette delivers automatic pulses of decreasing volume of thiosulfate as the end-point is approached. With a 5-ml (interchangeable) unit connected to the 655 Multidosimat burette, the last additions of reagent volume are quantities of 1 μl. When
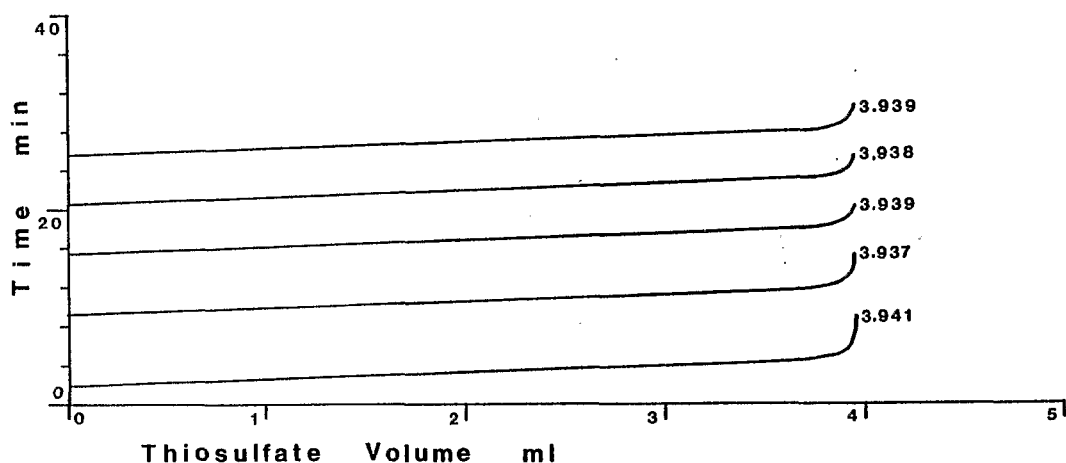
Fig. 3. Diagram of the output of the 625 Dosigraph: titrations of five replicates of a seawater sample.

the Impulsomat recognizes that the end-point is reached exactly, a pilot lamp lights. It indicates the end of the titration and allows reading of the final volume of added thiosulfate before automatic refilling of the burette for the next sample titration. It takes 3–5 min for a single analysis — the exact time depending on the initial oxygen concentration of the sample.

The 625 Dosigraph has two functions. One is to record the delivered thiosulfate volume as a function of time (Fig. 3) and to check the dynamics of the titration of an unknown sample (duration of the pulses and delay between the pulses) and so to judge the approach to the end-point. The other function, the main one, is to trace the redox titration curve of iodine by thiosulfate (Fig. 2) in order to determine the equivalence point at which the potential will be chosen as the reference value of the Impulsomat. In this latter mode (titration curve recording), the Impulsomat ensures a continuous scanning of the reference potential (a decrease in the present case) as a function of time for comparison with the potential (measured by the pH meter) of an iodine solution similar to the one being titrated. First, the reference value is set as the measured value of the solution potential (initial value is 476 mV on Fig. 2). When the titration is started, the scanning reveals a gap between the reference potential and the measured potential that is converted into pulsed additions of thiosul-

fate, constraining the measured potential to approach the reference potential. At the beginning of the titration (Fig. 2), the potential of the solution does not change very much for each addition of reagent, and the slope of the titration curve (potential as a function of reagent volume) is low. As the equivalence point nears, the reagent volume to be added so that the measured value of potential reaches the reference value becomes smaller and smaller; the slope of the curve becomes sharper and sharper, then the sign of the first derivative of the slope changes. This inflection point determines the value of the reference potential to be fixed on the Impulsomat as the end-point of titration.

As to precision, it is important to distinguish precision of titration of iodine by thiosulfate solution from precision of the determination of the dissolved oxygen concentration in the sample. The former precision is estimated at the time the thiosulfate solution is calibrated. In a flask filled with 250 ml of seawater, 1 ml of concentrated sulfuric acid, 1 ml of alkaline iodide solution, and 1 ml of manganous sulfate solution are added, with thorough mixing. Finally 50 ml of this mixed solution is withdrawn into the titration vessel and a certain volume of the standard iodate solution is put in the vessel to liberate a known quantity of iodine. Table 1 shows the results of various tests of replicate titrations of iodine liberated by a similar volume of iodate so-

Table 1. Replicate titrations of iodine liberated by 1–10 ml of standard potassium iodate solution. the concentrations of the solutions are: 0.1592 g KIO_3 liter^{-1} and 2.77 g $Na_2S_2O_3$, 5 H_2O liter^{-1}; 10 ml of the standard KIO_3 solution liberate the same quantity of iodine as 50 ml of seawater containing about 5 ml O_2 liter^{-1}.

| | KIO_3 volume (ml) | | | | | |
	1	2	3	4	5	10
$Na_2S_2O_3$ volume (ml)	0.409	0.815	1.230	1.639	2.024	3.941
	0.411	0.812	1.228	1.641	2.027	3.937
	0.413	0.810	1.227	1.641	2.025	3.939
	0.408	0.813	1.230	1.637	2.022	3.938
	0.409	0.812	1.225	1.639	2.025	3.939
Mean (ml)	0.410	0.812	1.228	1.639	2.025	3.939
SD (ml)	0.0020	0.0018	0.0021	0.0017	0.0018	0.0015
C.V. (%)	0.49	0.25	0.16	0.10	0.09	0.04

lution (varying from 1 to 10 ml). For comparison, the iodine quantity liberated by 10 ml of iodate solution is the same as is liberated by 50 ml of seawater containing about 5 ml of dissolved oxygen per liter. The standard deviation of the titration is relatively constant (0.002 ml) whatever the thiosulfate volume delivered by the burette. The C.V. of the iodine titration decreases as the iodate volume increases: for the range corresponding to the most common dissolved oxygen concentrations in the upper layers of the tropical ocean (5–2 ml O_2 liter^{-1}), the C.V. is in the range 0.04–0.1%.

The latter precision—the overall analytical precision of the determination of dissolved oxygen—is estimated by carrying out replicate analyses of single batches of seawater sampled with a 5-liter Niskin bottle. Table 2 shows the results for five replicates of three seawater samples. The SD of the titration (0.004 ml) is higher than the preceding one (0.002 ml) because it includes

all the successive errors of the determination of dissolved oxygen (sampling, formation of the manganese hydroxyde precipitate, dissolution of this precipitate, withdrawal of the iodine solution, and titration of the iodine solution). We conclude that manipulation of the sample, as well as detection of the end-point, limits the precision of the method. The C.V. is 0.10–0.12% for a dissolved oxygen concentration of about 3 ml liter^{-1}.

Without presenting results of application of this sensitive and automatic procedure of oxygen determination (Oudot in prep.), we would mention only that the precision is good enough to allow study of diurnal changes in oxygen concentration in oligotrophic waters. In conclusion, with the Metrohm titration system, it is very easy to routinely make precise measurements of oxygen concentration by the Winkler technique.

Claude Oudot
Robert Gerard
Pascal Morin

Institut Français de Recherche
  pour le Développement en
  Coopération (ORSTOM)
B.P. 1386
Dakar, Senegal

Itaf Gningue

Centre de Recherches
  Océanographiques
B.P. 2241
Dakar, Senegal

Table 2. Replicate determinations of dissolved oxygen concentrations (ml liter^{-1}) on three different samples of seawater.

| | Sample | | |
	1	2	3
1st replicate	3.223	2.526	3.193
2nd replicate	3.227	2.519	3.185
3rd replicate	3.217	2.529	3.192
4th replicate	3.224	2.526	3.191
5th replicate	3.225	2.258	3.193
Mean	3.223	2.256	3.191
SD	0.0038	0.0039	0.0033
C.V. (%)	0.12	0.15	0.10

References

ATWOOD, D. K., W. F. KINARD, M. J. BARCELONA, AND E. C. JOHNSON. 1977. Comparison of polarographic electrode and Winkler titration determinations of dissolved oxygen in oceanographic samples. Deep-Sea Res. **24:** 311–313.

BROENKOW, W. M., AND J. D. CLINE. 1969. Colorimetric determinations of dissolved oxygen at low concentrations. Limnol. Oceanogr. **14:** 450–454.

CARRITT, D. E., AND J. H. CARPENTER. 1966. Comparison and evaluation of currently employed modifications of the Winkler method for determining dissolved oxygen in sea water. A NASCO report. J. Mar. Res. **24:** 286–318.

CZAPLEWSKI, R. L., AND M. PARKER. 1973. Use of a BOD oxygen probe for estimating primary productivity. Limnol. Oceanogr. **18:** 152–154.

HARTWIG, E. O., AND J. A. MICHAEL. 1978. A sensitive photoelectric Winkler titrator for respiration measurements. Environ. Sci. Technol. **12:** 712–715.

JENKINS, W. J. 1982. Oxygen utilization rates in the North Atlantic subtropical gyre and primary production in oligotrophic systems. Nature **300:** 246–248.

KESTER, D. R. 1975. Dissolved gases other than CO_2, p. 498–556. *In* J. P. Riley and G. Skirrow [eds.], Chemical oceanography. Academic.

LANGDON, C. 1984. Dissolved oxygen monitoring system using a pulsed electrode: Design, performance, and evaluation. Deep-Sea Res. **31:** 1357–1367.

OUDOT, C. 1984. Echange physique d'oxygène et production primaire dans la couche homogène en zone équatoriale de l'Océan Atlantique est. Oceanogr. Trop. **19:** 95–109.

RUAL, P., AND B. VOITURIEZ. 1969. Modification et automatisation de la méthode de Winkler pour le dosage en mer de l'oxygène dissous. Initiations-Doc. Tech. ORSTOM 10. 27 p.

SHULENBERGER, E., AND J. L. REID. 1981. The Pacific shallow oxygen maximum, deep chlorophyll maximum, and primary productivity reconsidered. Deep-Sea Res. **28:** 901–919.

STRICKLAND, J. D., AND T. R. PARSONS. 1968. A practical handbook of seawater analysis. Bull. Fish. Res. Bd. Can. 167.

TALLING, J. F. 1973. The application of some electrochemical methods to the measurement of photosynthesis and respiration in fresh water. Freshwater Biol **3:** 335–362.

WILLIAMS, P. J. LEB., AND N. W. JENKINSON. 1982. A transportable microprocessor-controlled precise Winkler titration suitable for field station and shipboard use. Limnol. Oceanogr. **27:** 576–585.