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A NEW SYRINGE METHOD FOR DETERMINATION OF DISSOLVED OXYGEN IN SMALL SAMPLES

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ABSTRACT

A new syringe method for determination of dissolved oxygen in 1.5ml samples is presented. The new method is compared to the Winkler method and to a membrane electrode with a BOD attachment; no significant differences were found between the three methods. Several possible uses for the new method are proposed.

INTRODUCTION

Dissolved oxygen (DO) concentration in natural and industrial waters is an important indicator of water quality. Respiration of aquatic organisms is dependent on DO concentrations; metabolic breakdown of organic materials (both natural and man-made) is also dependent on DO concentrations.

The classic technique for measuring DO is the iodometric Winkler method, (Winkler, 1888 in Standard Methods, 1981). This titration however, requires large water samples (300ml), and much glassware. Recently, the use of membrane electrodes has increased, becoming an acceptable alternative to the Winkler method. However, electrodes may not be convenient for intermittent use since they require frequent recalibration; in addition they are expensive to purchase and maintain.

Many papers cite micro-Winkler methods that use samples of 10ml to 60ml; for a review see Burke (1962). One micro-Winkler method we found used a 1.5ml sample and powdered reagents available in a commercial colorimetric kit (Gill 1981). However we could not duplicate the method and obtain comparable results among this proposed micro-Winkler method, the Winkler method, and the BOD probe method. The proportions suggested do not reflect logical scaling down of reagents relative to the standard Winkler method. In addition, the stated weights of the powdered reagents do not agree with our measurements; we found the weights to be off by several orders of magnitude.

Hence, this paper presents a new version of the Winkler method that is

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specifically designed for small samples (1.5ml). Our new method lends itself to biological research because it uses simple, inexpensive equipment and it is easy to prepare and titrate samples. The method is compared to the azide modification of the Winkler method Standard Methods (1981) and to a membrane electrode with a BOD attachment.

MATERIALS AND METHODS

The water samples were obtained from several sources to insure a wide range of DO values. Low range samples (0.4ppm to 2.0ppm) were obtained from a concurrent experiment that entailed measuring bivalve respiration rates in air tight, water-filled containers. Medium range samples (4.0ppm to 5.0ppm) and high range samples (7.5ppm to 10.0ppm) were obtained from tap water flowing slowly and vigorously, respectively. The samples were collected in 300ml glass BOD bottles, overflowing the neck to insure complete removal of all air bubbles. All DO measurements were taken immediately after the samples were collected to minimize changes in temperature and the possibility of outgassing.

A dissolved oxygen meter (Yellow Springs Instrument Co. INC., model 54) with a BOD probe attachment (model 5420A) was used on most samples to take the first DO reading inside the bottle. Then, two or three measurements were taken with the syringe method and averaged to give one reading. The Winkler method was used on the water remaining in the bottle to yield a third reading. All solution preparations used in the Winkler and syringe methods and the techniques of the Winkler Method followed Standard Methods (1981).

The syringe method was performed by submerging the needle tip (23 G) of a 2.5ml glass syringe beneath the surface of the sample in the BOD bottle, using a new needle for each sample. Between 1.5 and 2.0ml of water was drawn into the syringe, and the sample volume was brought to exactly 1.5ml. One minum of manganous sulfate and one minum of alkalide iodide azide solution were drawn into the syringe from inverted stoppered vials. The syringe was slowly shaken to insure complete mixing, allowed to stand in a test tube holder until the resulting flocculant settled, then reshaken. One minum of concentrated sulfuric acid was drawn into the syringe from a teflon coated septum top vial; the syringe was shaken again and when the floc had dissolved, exactly 1.0ml of the solution was expelled into a vial to be titrated. The titrant, 0.025N sodium thiosulfate, was diluted 10x with deionized water (1 part titrant to 9 parts water). The diluted titrant was drawn into a 0.5ml glass syringe and the solution was titrated to a pale straw color. Three drops of starch indicator were added and titration continued. The end point was reached when the solution was clear. Dissolved oxygen values were calculated from the relationship:

0.1ml titrant = 0.01ppm oxygen

The data were analyzed using the General Linear Model Procedure (PROC GLM) for two-way analysis of variance, SAS Institute (1979).

RESULTS

The dissolved oxygen values obtained for the ten different samples by the three techniques are presented in Table I. Two-way analysis of variance revealed no significant difference between the 3 techniques ($F = 0.98$, $P = 0.58$).

DISCUSSION

Our syringe method proves to be an accurate technique for measuring DO. The entire analysis takes less then 5 minutes per sample. All the reagents used in this method can be stored in small vials with serum stoppers; it requires far less glassware than the Winkler method, and hence, it can be transported in a small kit for field studies. This syringe method is much less expensive than a DO probe and DO meter. The small sample size is conducive to laboratory respiration bioassays and to measuring micro-stratification of DO in small bodies of water. Hence, the syringe technique is accurate, quick, and convenient for measuring dissolved oxygen.

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Table 1. Dissolved Oxygen Readings for Ten Water Samples Using 3 Techniques

Sample Number	Syringe Method[a]	Winkler Method[a]	Probe Method[a]
1	0.7	0.9	*
2	0.4	0.8	*
3	0.5	0.9	*
4	0.6	0.7	*
5	1.8	1.9	2.1
6	4.7	4.8	4.9
7	4.3	4.3	4.3
8	7.5	7.6	7.8
9	7.7	8.0	8.1
10	9.7	9.6	9.9

[a]measured in parts per million (ppm)
*test not performed