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A modified Winkler's method for determination of dissolved oxygen concentration in water: Dependence of method accuracy on sample volume

Amritanshu Shriwastav [a,b,*], Guttapati Sudarsan [a], Purnendu Bose [a], Vinod Tare [a]

[a] Environmental Engineering and Management Program, Department of Civil Engineering, Indian Institute of Technology Kanpur, Kanpur 208 016, India
[b] Centre for Environmental Science and Engineering, Indian Institute of Technology Bombay, Mumbai 400 076, India[1]

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A B S T R A C T

A modification to the standard Winkler's method (WM) for measurement of dissolved oxygen (DO) concentration in aqueous samples enabled DO measurements in 1 mL sample volume. However, advanced statistical analysis indicated that the proposed method (PM) showed a small positive bias, giving results that were on average about 6% higher than corresponding values measured using the WM. In this study, DO measurements were carried out in sample volumes ranging from 2 mL to 10 mL using the PM. Statistical analysis of these results indicate that the bias reported in the PM could be eliminated (i.e., limited to a ± 2% range) using sample volumes of 7 mL or higher. Use of a larger sample volume also enables lowering the least count of the PM to 0.1 mg/L O_2 as compared to 0.25 mg/L O_2 reported previously.
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1. Introduction

Most reliable and universally accepted method for determination of dissolved oxygen (DO) concentration in aqueous samples is the Winkler's method (WM) [1,2], where oxygen is quantified in terms of equivalent iodine. However, a major drawback of WM is the requirement of a large sample volume of 200 mL [3]. Several alternative methods for DO measurement using a variety of measurement principles have been developed, viz. colorimetric, gas chromatographic, electrochemical and optical methods. Though popular under certain circumstances, all these methods have their own share of drawbacks [4–10] and WM remains the primary standard against which all other methods are compared. Several modifications to WM have been proposed to reduce the sample volume requirements. However, these "Micro Winkler" methods have not gained much popularity due to various complexities involved [11–15].

A modified Winkler's method was proposed for DO measurements in sample volumes of 1 mL [16]. This proposed method (PM) claimed to retain the accuracy and reliability of the standard WM. However, the least count of the PM was ~0.25 mg L^{-1} DO in comparison to ~0.1 mg L^{-1} DO of standard WM. It was further revealed through advanced statistical analysis, viz., Functional Relationship Estimation by Maximum Likelihood (FREML) [17], that the PM had a positive bias of ~6% (see Fig. 1) vis-à-vis the standard WM. This may be due to inherent difficulties in avoiding sample contamination with atmospheric oxygen when working with small sample volumes.

The objective of the present study was to analyze whether increasing the sample volume used in the PM can substantially eliminate the above bias, i.e., limit the bias to a ± 2% range. For this purpose, large number of DO measurements was performed in a variety of samples using both WM and PM. The sample size used for DO measurement by PM varied in the range of 2–10 mL.

2. Material and methods

All reagents used were of analytical reagent grade (>99% purity, Loba chemicals, India). De-ionized water (Milli-Q, Millipore, USA) was used for preparation of reagents and dilution of samples. The n-hexane used was of HPLC grade (>99% purity, Merck, India). All glassware used was made of borosilicate glass. $MnSO_4$ and alkali-azide-iodide solutions were prepared as per standard methods (Method No. 4500-O C) [1].

The basic method of DO measurement by PM remained the same as before [16]. Sample volumes of 2 mL to 10 mL were analyzed for DO concentrations as follows; 1 mL of n-hexane was

* Corresponding author.
E-mail address: amritan@iitb.ac.in (A. Shriwastav).
[1] Present address.

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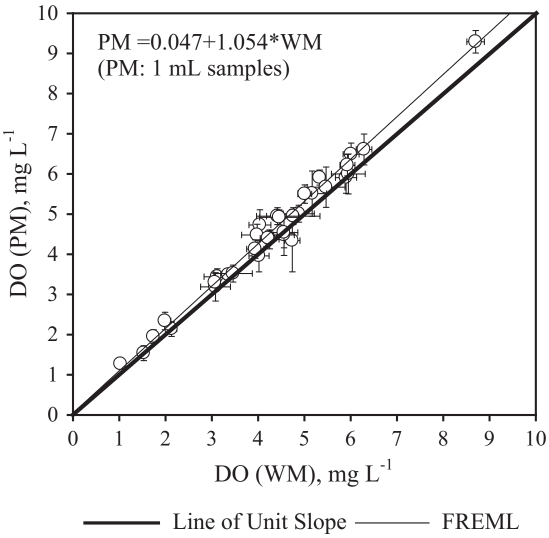

Fig. 1. Bias of proposed method for sample volume of 1 mL (Adapted from Shriwastav et al. [16]) (the error bars represent 95% confidence intervals).

Table 2
Strengths of $Na_2S_2O_3$ for different sample volumes and the least count of PM.

S. No.	Sample volume (mL)	Strength of $Na_2S_2O_3$ (N)	Least count of PM (mg L^{-1} of DO)
1	2	0.0025	0.100
2	3	0.0036	0.095
3	4	0.0050	0.100
4	5	0.0062	0.100
5	6	0.0071	0.095
6	7	0.0083	0.095
7	8	0.0100	0.100
8	9	0.0111	0.099
9	10	0.0125	0.100

taken in a 10 mL or 15 mL pipette, and the pipette was further filled with required volume of the water sample whose DO concentration was to be determined; mouth of the pipette was then placed below a 0.5 mL hexane layer in the 16-mL glass vial (Wheaton Science, USA) such that the sample was introduced below the hexane layer, thus avoiding any contact between the sample and the atmosphere. Required amounts of $MnSO_4$ and alkali-azide-iodide solutions were successively added using syringe to the sample placed below hexane layer. The amount of different reagents added for different sample volumes is given in Table 1. Precipitate

Table 1
Details of reagent requirement in PM.

S. No.	Sample volume	$MnSO_4$	Alkali-azide-iodide reagent	H_2SO_4	Starch	n-Hexane
1	2 mL	10 µL	10 µL	0.1 mL	1–2 drops	1.5 mL
2.	3 mL	15 µL	15 µL	0.1 mL	1–2 drops	1.5 mL
3	4 mL	20 µL	20 µL	0.1 mL	1–2 drops	1.5 mL
4	5 mL	25 µL	25 µL	0.1 mL	1–2 drops	1.5 mL
5	6 mL	30 µL	30 µL	0.1 mL	1–2 drops	1.5 mL
6	7 mL	35 µL	35 µL	0.1 mL	1–2 drops	1.5 mL
7	8 mL	40 µL	40 µL	0.1 mL	1–2 drops	1.5 mL
8	9 mL	45 µL	45 µL	0.1 mL	1–2 drops	1.5 mL
9	10 mL	50 µL	50 µL	0.1 mL	1–2 drops	1.5 mL

Table 3
Correction factor to account for untitrated iodine solution.

S. No.	Sample (mL)	$MnSO_4$ (mL)	Alkali-azide-iodide (mL)	H_2SO_4 (mL)	Total vol. (mL)	Volume titrated (mL)	Correction factor
1	2	0.01	0.01	0.1	2.12	2	1.060
2	3	0.015	0.015	0.1	3.13	3	1.043
3	4	0.02	0.02	0.1	4.14	4	1.035
4	5	0.025	0.025	0.1	5.15	5	1.030
5	6	0.03	0.03	0.1	6.16	6	1.027
6	7	0.035	0.035	0.1	7.17	7	1.024
7	8	0.04	0.04	0.1	8.18	8	1.022
8	9	0.045	0.045	0.1	9.19	9	1.021
9	10	0.05	0.05	0.1	10.2	10	1.020

Table 4
Sample details for DO measurement.

S. No.	Sample vol. (mL)	Sample details				Total no. of samples
		TW	GW	Diluted DWW	RW	
1.	2	4	1	2	8	15
2.	3	1	1	2	12	16
3.	4	2	3	2	8	15
4.	5	2	0	2	13	17
5.	6	3	2	2	6	13
6.	7	2	1	2	8	15
7.	8	3	1	2	9	15
8.	9	3	1	2	9	15
9.	10	1	2	3	9	15

TW: Tap Water; GW: Ground Water; Diluted DWW: Diluted Domestic Wastewater; RW: River Water.

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