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Notes

Spectrophotometric determination of dissolved oxygen in water

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A simple, rapid and sensitive spectrophotometric method has been developed for the determination of dissolved oxygen (DO) in river water samples. The method is based on the reaction of dissolved oxygen with manganous sulphate in alkaline iodide-azide solution and the liberation of iodine by manganese dioxide. The liberated iodine bleaches the violet colour of azure B which is measured at 644 nm. The decrease in absorbance is directly proportional to dissolved oxygen concentration and obeys Beer's law in the range 0.2-1.4 μgmL^{-1}. The molar absorptivity, Sandell's sensitivity, detection limit and quantitation limit of the method were found to be 5.86×10^4 $Lmol^{-1}$ cm^{-1}, 3.66×10^{-3} $\mu g/cm^2$, 0.030 and 0.090 μgmL^{-1}, respectively.

Keywords: Dissolved oxygen determination, spectrophotometry, azure B
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Accurate data on concentrations of dissolved oxygen (DO) in water are essential for documenting changes to the environment caused by natural phenomena and human activities. Sources of DO in water include atmospheric reaeration and photosynthetic activities of aquatic plants. Many chemical and biological reactions in ground water and surface water depend directly or indirectly on the amount of oxygen present. Dissolved oxygen is necessary in aquatic systems for the survival and growth of many aquatic organisms.

Dissolved oxygen measurement is the most important single test that environmental engineers use. A number of different approaches have been devised to determine dissolved oxygen, including various kinds of electrodes, but researchers[1,2] needing high level of accuracy and precision, still relay on the titrimetric method of Winkler. Many versions of original Winkler's titration[3-7] are possible. The main disadvantage is the equipment cost and also the time involved is considerably high. Polarographic methods using dropping mercury electrodes or the rotatory electrode have not been always reliable because impurities in the test solutions can cause electrode poisoning and other interferences. Many modifications of the Winkler's dissolved oxygen method by spectrophotometric methods have been proposed[8,9]. Several other methods[10-15] are available for the determination of DO in water. Some spectrophotometric methods for the determination of dissolved oxygen have been reported with some chromogenic reagents, such as aurocyanide complex with gold sol[16], argentocyanide complex with silver sol[17], indigo carmine[18], 4,7-dihydroxy-1,10-phenanthroline[19], and tris(4,7-dihydroxy-1,10-phenanthroline) iron (II)[20].

In the present investigation a rapid, sensitive and selective method is reported for the determination of dissolved oxygen with a new reagent azure B. The proposed method is based on the liberation of iodine in acidic medium equivalent to the amount of oxygen present. The liberated iodine bleaches the violet colour of azure B, which is measured at 644 nm. The developed method has been successfully employed to determine dissolved oxygen in various river water samples.

Experimental Procedure

A Secomam Anthelie NUA 022 UV-Visible spectrophotometer with 1cm quartz cell was used for the absorbance measurements and a WTW pH 330, pH meter was used.

Reagents

All chemicals used were of analytical reagent grade or chemically pure grade. Standard potassium iodate solution (1000 μgmL^{-1}) was prepared by dissolving desired amount of the KI crystals in distilled water and was standardized using sodium thiosulphate solution[21]. 2M, HCl and 2 % KI were used. A (0.1 %) solution of azure B was prepared by dissolving 0.1g azure B in 25 mL methanol and made up to 100 mL with distilled water. Manganous sulphate solution was prepared by dissolving 364 g $MnSO_4$ H_2O in distilled water filtered and diluted to 1000 mL and alkali-

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iodide-azide solution was prepared by dissolving 700 g KOH, 150 g KI and 10 g sodium azide in distilled water and the contents were made up to 1000 mL.

Method

Aliquots of the stock solution containing 1.78 to 10.69 μgmL^{-1} of potassium iodate were pipetted out into a series of 10 mL standard flasks. To each of these was added 1 mL of potassium iodide followed by 1 mL of 2 M hydrochloric acid. The mixture was gently shaken until the appearance of yellow colour, indicating the liberation of iodine. To this system was added 0.5 mL of 0.1 % azure B solution. The contents were diluted to 10 mL with distilled water. The absorbance of the solution was measured at 600 nm against the corresponding reagent blank.

Determination of dissolved oxygen in river water samples

All the samples (both spectrophotometric and titrimetric) were fixed with manganous sulphate, alkaline iodide-azide solution, and acid according to Winkler's procedure[22] and the resulting solution is diluted 40 times. 5 mL of this fixed sample was pipetted out into 10 mL flask and the liberated iodine was determined spectrophotometrically using azure B as per the above method. The dissolved oxygen was then found out from the calibration curve generated using potassium iodate as,

$$1\ \mu gmL^{-1}\ DO = 8.91\ \mu gmL^{-1}\ of\ KIO_3$$

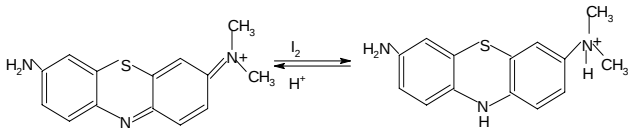
The dissolved oxygen concentration was obtained in parallel by titration with standard sodium thiosulphate, as in the standard Winkler's procedure (Table 1).

Results and Discussion

Oxygen converts Mn^{2+} to Mn^{4+} under alkaline conditions and that manganese in the +4 state of valance is capable of oxidizing I^- to I_2 under acidic conditions. Thus, the amount of I_2 released, is equivalent to the oxygen dissolved in the water. The liberated iodine bleaches the violet colour of azure B having an absorption maximum at 644 nm to colourless leucoform of azure B as given below.

$$Mn^{2+} + 2OH^- \rightarrow Mn(OH)_2$$
$$Mn^{2+} + 2OH^- + ½\ O_2 \rightarrow MnO_2 + H_2O$$
$$Mn(OH)_2 + ½\ O_2 \rightarrow MnO_2 + H_2O$$
$$MnO_2 + 2I^- + 4\ H^+ \rightarrow Mn^{2+} + I_2 + 2\ H_2O$$

$$KIO_3 + 5\ KI + 6\ HCl \rightarrow 3\ I_2 + 3\ H_2O + 6\ KCl$$



Azure B (Violet) Azure B(Leuco form)

Potassium iodate with potassium iodide in acid medium liberates iodine which bleaches the violet colour of azure B having an absorption maximum at 644 nm.

Effect of iodide concentration and acidity

The effect of iodide concentration and acidity on the colour development was studied with 1.0 μgmL^{-1} of potassium iodate. The oxidation of iodide to iodine was effective in the pH range 1.0 to 1.5, which could be maintained by adding 1 mL of 2M hydrochloric acid in a final volume of 10 mL. The liberation of iodine from KI in the acid medium was quantitative. The appearance of yellow colour indicates the liberation of iodine. It was found that 1-1.4 mL of 2 M HCl and 1 mL of 2 % potassium iodide were sufficient for the liberation of iodine from iodide by potassium iodate. The liberated iodine bleaches the violet colour of azure B to the colourless leucoform.

Table 1—Determination of dissolved oxygen in river water samples

Sample	Proposed method		Reference method		[c]*F*-test	[b]*t*-test
	DO μgmL^{-1} [a]found*	Standard deviation	DO $\mu g\ mL^{-1}$ [a]found*	Standard deviation		
RW1	6.20	0.02	6.18	0.013	2.36	1.87
RW2	4.26	0.02	4.24	0.011	3.30	0.69
RW3	5.58	0.021	5.56	0.012	2.77	1.92
RW4	5.43	0.025	5.42	0.011	5.16	0.82

[a] Dissolved oxygen concentration expressed in μgmL^{-1}
[b] Tabulated *t*-value for 8 degrees of freedom at p (0.95) is 2.78
[c] Tabulated *F*-value for (4,4) degree of freedom at p (0.95) is 6.39.

Effect of reagent concentrations

0.5 mL of 0.1 % azure B was used for the decolourization. A time of 1-2 min was necessary for the decolourization process to occur; an optimum time of 2 min was fixed for this process. The bleached colour was found to be stable over 5 h.

Analytical data

Beer's law was obeyed in the range of 0.2 to 1.0 μg mL^{-1}. The molar absorptivity and Sandell's sensitivity for the coloured system was found to be 5.86×10^{4} $Lmol^{-1}cm^{-1}$ and 3.66×10^{-3} μg cm^{-2} respectively. The detection limit (D_L = 3.3σ /S) and quantitation limit (Q_L = 10σ /*S*) (where σ is the standard deviation of the reagent blank (n=5) and S is the slope of the calibration curve) for the dissolved oxygen determination were found to be 0.030 μgmL^{-1} and 0.090 μgmL^{-1}, respectively.

Effect of diverse ions

Chloride, nitrite, hydrogen peroxide, various oxidants such as CrO_4^{2-}, Fe^{3+}, Ce^{4+} were found to interfere. Some of these ions could be masked by the addition of an appropriate amount of EDTA solution. The effect of Fe(III) can be nullified using sodium fluoride as a masking agent. The tolerance limits given in Table 2 are those that cause no more than 2% changes in the absorbance.

Application

Proposed method for the determination of dissolved oxygen in water was carried out for same river water samples. The water sample fixed for DO by the Winkler's procedure was directly used for the spectrophotometric measurements by the proposed method. The DO was obtained in parallel by titration with standard thiosulpate as in the Winkler's procedure. The results are given in Table 1.

Conclusion

The proposed method for the determination of dissolved oxygen is simple, rapid, sensitive, precise and has the advantage of enabling a wide range of determinations without the need for extraction or heating. The method is useful for the determination of DO in river water samples. The time taken by the spectrophotometric method is very less compared to that required to perform Winkler's titrimetry.

Table 2—Effect of diverse ions on the determination of dissolved oxygen (1.0 μgmL^{-1})

Foreign ion	Tolerance limit (μgmL^{-1})
Na^{+}, Ba^{2+}, F^{-}, CO_3^{2-}, Br^{-}, EDTA	1000
PO_4^{3-}, SO_4^{2-}, NO_3^{-}, WO_4^{2-}, Ca^{2+}, Ag^{+}, TeO_4^{2-}, Sr^{2+}, Th^{4+}, Sb^{5+}, citrate, tartrate	500
Al^{3+}, Cd^{2+}, Zn^{2+}, Be^{2+}, Hg^{2+}, Bi^{3+}, Cr^{3+}, Tl^{+}	100
Ni^{2+}, Pb^{2+}, Co^{2+}, AsO_4^{3-}, Cd^{2+}, Sb^{3+}	50
VO_4^{3-}, Fe^{3+}, Cu^{2+}, Mn^{2+}, Ce^{4+}	25*

*Masked with masking agents

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