A Spectrophotometric Modification of the Winkler Method for Measurement of Dissolved Oxygen

Francis J. Nowaczyk Jr.,[1] Roger L. Schnaare,[1,2] Clyde M. Ofner III,[1] and Rodney J. Wigent[1]

Received October 14, 1991; accepted July 23, 1992

KEY WORDS: Winkler method; nonionic surfactant; spectrophotometry; oxygen measurement; oleth 10; polyoxethylene 10 oleyl ether.

INTRODUCTION

The method generally considered to be the most reliable for measurement of oxygen solubility is still the method reported by Winkler in 1888 (1–3), in which iodine is generated in proportion to oxygen in the sample and titrated with either thiosulfate or phenylarsine oxide.

We have found that the end point is more difficult to determine in surfactant solutions. The starch indicator does not produce detectable color in some surfactant solutions containing iodine, preventing a visual end point. Potentiometric end-point determination is possible, but the presence of surfactant reduces the redox potential of the system (4) as well as the slope of the titration curve at the point of inflection, making the end-point determination more difficult.

We have developed a modification of the Winkler method utilizing spectrophotometric properties of iodine in the presence of surfactant. In 1959 Ross and Olivier demonstrated the formation of a colored iodine–micelle complex allowing the spectrophotometric determination of the CMC of nonionic surfactants (5); this complex was shown to obey Beer's law (4). In our modification, the iodine generated in the Winkler method is measured spectrophotometrically in the presence of excess surfactant, facilitating oxygen measurement in samples where titration is difficult. The purpose of this study is to compare this spectrophotometric modification of the Winkler method to the standard Winkler titration.

MATERIALS AND METHODS

Materials

Oleth 10 (polyoxethylene 10 oleyl ether; Sigma Chemical Co., St. Louis, MO) was assumed to have an average molecular weight of 709.1 and used without further purification. All other chemicals were reagent grade or better. All solutions were prepared with water purified with a Nanopure filter system (Barnstead, Dubuque, IA).

Sample Solution Selection, Preparation, and Equilibration

Water and sodium chloride solutions were chosen as samples to provide a basis for comparison of methods because of the availability of published oxygen solubilities. The concentrations of sodium chloride were 0.154, 0.50, 1.00, and 2.00 *M*. Oleth 10 was chosen as an example of a surfactant which poses the problems to titration described above. Five oleth 10 solutions were prepared, ranging from 3.12×10^{-5} to 7.00×10^{-2} *M*. All solutions were stirred in a water bath at 37°C for 24 hr to equilibrate with the atmosphere prior to sampling. Oxygen activity and temperature of each solution were measured using the YSI Model 5750 oxygen electrode with the YSI Model 58 dissolved oxygen meter (YSI Incorporated, Yellow Springs, OH).

Winkler Method: Winkler Samples and Blanks

Winkler blanks were prepared as described in ASTM D888-87 (3) with the following alterations.

1. Alkaline sodium iodide solution was 0.75% in sodium azide as described by Toledo *et al.* (6) and added to each vessel to make the concentration of iodide 1.5×10^{-2} *M*.
2. Manganese sulfate solution was added to each vessel to make the concentration 7.5×10^{-2} *M*.

For clarity, "Winkler blanks" are those solutions where the order of the addition of manganese sulfate and sulfuric acid is reversed. No $Mn(OH)_2$ is formed in acidic solution, so no iodine is generated in the presence of oxygen. Aliquots (50 mL) of the Winkler samples and blanks were titrated potentiometrically with 0.01 *N* standardized sodium thiosulfate solution using a Fisher 825MP pH meter equipped with a platinum wire electrode and a calomel reference electrode (Fisher Scientific, Pittsburgh, PA).

Spectrophotometric Modification

Standard Curve. A standard curve of absorbance at 365 nm as a function of iodine concentration was generated for each different concentration of surfactant and electrolyte sample. Each 50-mL standard contained 5 mL of freshly prepared Winkler blank, 5 mL of a 10% oleth 10 solution, and an aliquot of iodine solution to give an iodine concentration of 6, 8, 10, 12, or 16 ppm I_2, corresponding to an oxygen concentration range of 3.78 to 10.09 ppm. The absorbance of each standard was read against a blank containing, in each 50 mL, 5 mL of the same Winkler blank as used for the standards and 5 mL of a 10% oleth 10 solution.

The data were regressed by the method of least squares, and 95% confidence intervals for the slopes and intercepts were calculated (7). An analysis of covariance to detect differences of the slopes and intercepts was done as described by Snedecor and Cochran (8) for the standard curves in sodium chloride solutions, and another for those in oleth 10 solutions.

Samples. Each sample to be measured for absorbance contained 5 mL of Winkler sample and 5 mL of 10% oleth 10 in each 50 mL. The absorbance was read against a blank freshly prepared as described above.

---

[1] Department of Pharmaceutics, Philadelphia College of Pharmacy and Science, 600 South Forty-Third Street, Philadelphia, Pennsylvania 19104-4495.

[2] To whom correspondence should be addressed.

0724-8741/93/0200-0305$07.00/0

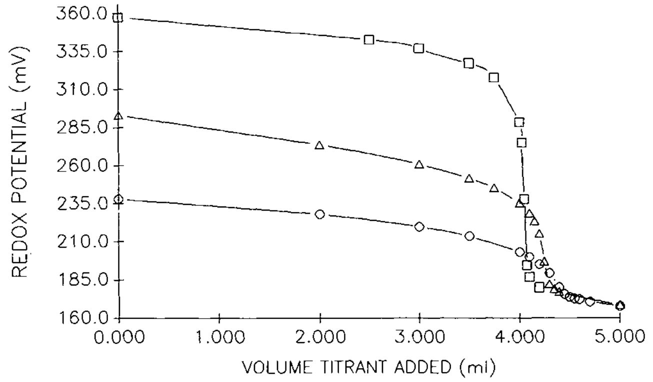

Fig. 1. Effect of surfactant concentration on potentiometric Winkler titration. Redox potential as a function of sodium thiosulfate added to 3.117 × 10^{-5} *M* (□), 4.767 × 10^{-3} *M* (△), and 0.070 *M* (○) oleth 10.

Normalization of Data

The data were normalized to 1 atm and 37.0°C by multiplying the experimentally determined oxygen concentration by the ratio of the theoretical oxygen concentration in water at 1 atm and 37.0°C to the theoretical oxygen concentration in water at the experimental temperature and pressure. This correction was never more than 2% of the measured value.

RESULTS AND DISCUSSION

As Fig. 1 illustrates, an increase in surfactant concentration reduces the redox potential of the system and decreases the slope at the point of inflection in the titration curve. These phenomena make determination of the end point more difficult. Typically we found that in a Winkler titration of a water sample, the potential drops about 60 mV after the addition of 0.025 mL of titrant. In the titration of a 0.070 *M* oleth 10 sample the potential drops about 3 mV at the end point with the same amount of titrant, making endpoint determination more difficult.

In initial experiments with the Winkler titration it was found that control of I^- concentration and pH was crucial. Under acidic conditions I^- is oxidized to I_2 in the presence of oxygen. If either H^+ of I^- is in great excess, I_2 formed from this side reaction increases the total I_2 concentration in excess of the I_2 generated from the O_2 in the sample. When iodine generated from water or sodium chloride solutions was analyzed in the absence of surfactant, the side reaction generated I_2 faster in the blank than in the samples due to the difference in I^- concentration, which led to decreasing absorbance in the samples. This difference in I^- concentration is unavoidable, because I^- is consumed in the samples in proportion to O_2 concentration. Dilution of the samples slowed the generation of excess I_2, but the absorbance readings became low, reducing the precision and accuracy of the assay. In order to use dilution to slow the side-reaction formation of excess I_2, the absorbance must be amplified.

It has been shown that absorbance of iodine solubilized by surfactant can be as much as nine times greater than that of aqueous iodine solutions of the same concentration (4). By diluting the samples after the formation of I_2 and adding a surfactant such as oleth 10, the generation of I_2 was slowed and the absorbance amplified, allowing the spectrophotometric determination of iodine in the Winkler method. Here it is convenient to note for the sake of clarity that oleth 10 was chosen as the "amplifying" surfactant because we knew that it solubilized iodine well to form clear solution, and it was the surfactant under examination when the titration problems were encountered.

All standard curves were linear and had correlation coefficients of 0.998 or better, in agreement with Durand *et al.* (4). The slopes and intercepts for the curves from sodium chloride solutions appear to be randomly distributed around 9.013 × 10^{-2} and 5.890 × 10^{-2}, respectively. The slopes were found to be not significantly different at the 95% confidence level (analysis of covariance), however, the intercepts were found to be significantly different. The same conclusions are reached for the oleth 10 solutions. Thus a standard curve must be generated for each type of solution to be measured for oxygen concentration.

The accuracy of the spectrophotometric modification of the Winkler method for measurement of dissolved oxygen

Table I. Comparison of Methods of Oxygen Measurement in Sample Solutions at 37°C and 1 atm

Sample composition	Oxygen solubility (ppm)			
	Spectrophotometric	Titration	Electrode	Theory
NaCl				
0.00 *M*	6.93 (0.16)[a]	6.82 (0.05)	6.35	6.69
0.15 *M*	6.38 (0.09)	6.55 (0.11)	6.53	6.37
0.50 *M*	5.93 (0.08)	6.08 (0.16)	6.42	5.72
1.00 *M*	5.17 (0.14)	5.15 (0.03)	6.45	4.89
2.00 *M*	3.95 (0.16)	4.03 (0.15)	6.36	3.58
Oleth 10				
3.12 × 10^{-5} *M*	7.15 (0.12)	6.90 (0.15)	6.49	
4.94 × 10^{-4} *M*	7.12 (0.12)	6.86 (0.20)	6.40	
4.77 × 10^{-3} *M*	7.22 (0.12)	7.18 (0.11)	6.38	
3.50 × 10^{-2} *M*	7.49 (0.12)	7.45 (0.34)	6.38	
7.00 × 10^{-2} *M*	7.72 (0.15)	7.59 (0.06)	6.35	

[a] Ninety-five percent confidence interval in parentheses.

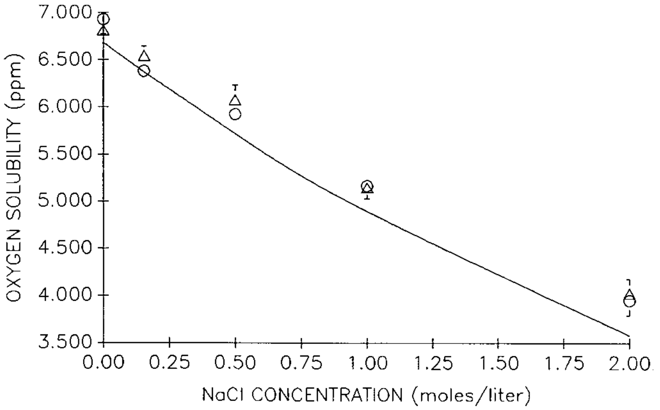

Fig. 2. Effect of NaCl concentration on oxygen solubility in aqueous solutions. The solid curve represents solubilities calculated as suggested by Cramer (10). The spectrophotometric method (○) is compared to titration (△). Error bars represent 95% confidence intervals.

was compared to that of the Winkler titration, the oxygen electrode, and published data (9,10) in water and sodium chloride solutions (Table I). The concentration of oxygen in solution decreased with increasing salt concentration as measured both spectrophotometrically and by titration (Fig. 2). The spectrophotometric results were generally closer to the literature values obtained manometrically (10) than those obtained by titration, however, the spectrophotometric results were not significantly different (Student's *t* test, 95% level) from those obtained by titration (with the exception of the oxygen concentration in 0.154 *M* sodium chloride).

All spectrophotometric and titration results (with the exception of 0.154 *M* sodium chloride) were found to be significantly different at the 95% confidence level from the theoretical values predicted by Cramer (10). As expected, the measurements made with the oxygen electrode did not vary because of equivalent activities.

The results of oxygen measurement in surfactant solutions cannot be compared to literature values, as publication of such data is limited. It has been demonstrated that oxygen concentration increases with increasing surfactant concentration (11), and our results illustrate the same trend (Fig. 3). The oxygen solubilities in oleth 10 solutions measured by spectrophotometric modification are not significantly different from those measured by titration at the 95% confidence level as determined by a *t* test. These results indicate that the accuracy of the spectrophotometric method is not significantly different from the accuracy of the titrimetric method.

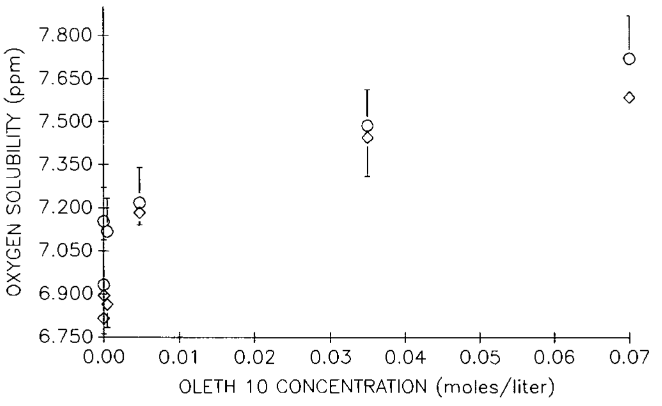

Fig. 3. Effect of oleth 10 concentration on oxygen solubility in aqueous solutions. Comparison of spectrophotometric method (○) to titration (◇). Error bars represent 95% confidence intervals.

Relative standard deviations (RSDs) can be used as a basis for comparing precision (12). The RSDs of oxygen measurements in sodium chloride solutions by the spectrophotometric modification of the Winkler method ranged from 0.16 to 2.88%, while those determined by Winkler titration ranged from 0.24 to 1.51%; those in oleth 10 solutions by spectrophotometric modification, from 0.63 to 1.42%, and those by Winkler titration, from 0.32 to 1.84%. Given these ranges, the precision of both methods is acceptable.

CONCLUSION

The precision and accuracy of spectrophotometric determination of iodine in the Winkler method are as good as those found titrimetrically. This alternative to traditional titration allows for measurement of oxygen in surfactant solutions for which titration was difficult and may be applied to electrolyte solutions as well if titration is not desirable.

ACKNOWLEDGMENT

This work was supported by a predoctoral fellowship from the Pharmaceutical Manufacturers Association.

NOMENCLATURE

C_{O_2}	Concentration as ppm oxygen
V_{tb}	Volume of titrant (sodium thiosulfate) added at the titrimetric end point in the blank
V_{ts}	Volume of titrant (sodium thiosulfate) added at the titrimetric end point in the sample
C_t	Molar concentration of the titrant
V_s	Volume of the sample titrated
A	Absorbance of the sample
b	Intercept of the standard curve
m	Slope of the standard curve

REFERENCES

1. L. W. Winkler. The determination of dissolved oxygen in water. *Ber. Deut. Chem. Ges.* **21**:2843 (1888).
2. M. L. Hitchman. *Measurement of Dissolved Oxygen,* John Wiley & Sons, New York, 1978, pp. 160–169.
3. American Society for Testing and Materials. Standard test methods for dissolved oxygen in water D888-87. In *Annual Book of ASTM Standards 1991. Vol. 11.01. Water and Environmental Technology,* ASTM, Philadelphia, 1991, pp. 522–533.
4. J. S. Durand, M. W. Kabbani, and L. M. Polo. A spectrophotometric study of iodine solutions in the presence of non-ionic surfactants. *An. Quim. Ser. B* **83**:186–189 (1987).
5. S. Ross and J. P. Olivier. A new method for the determination of critical micelle concentrations of un-ionized association colloids in aqueous or in non-aqueous solution. *J. Phys. Chem.* **63**:1671–1674 (1959).

6. A. P. P. Toledo, J. F. Carvalho, E. S. Miazaki, and J. A. Souza. Determination of dissolved oxygen: A comparison of some already proposed modifications of the Winkler method. *Int. J. Environ. Stud.* 16:219–221 (1981).
7. G. W. Snedecor and W. G. Cochran. *Statistical Methods*, Iowa State University Press, Ames, 1971, pp. 135–170.
8. G. W. Snedecor and W. G. Cochran. *Statistical Methods*, Iowa State University Press, Ames, 1971, pp. 432–436.
9. R. Battino (ed.), *Solubility Data Series, Vol. 7. Oxygen and Ozone*, Pergamon Press, New York, 1981, pp. 1–69.
10. S. Cramer. The solubility of oxygen in brines from 0 to 300°C. *Ind. Eng. Chem. Process Des. Dev.* 19:300–305 (1980).
11. I. B. C. Matheson and A. D. King, Jr. Solubility of gases in micellar solutions. *J. Colloid Interface Sci.* 66:464–469 (1978).
12. J. C. Miller and J. N. Miller. *Statistics for Analytical Chemistry*, 2nd ed., Halstead Press, New York, 1988, p. 35.