

NOTES AND COMMENT

THE CHESAPEAKE BAY INSTITUTE TECHNIQUE FOR THE WINKLER DISSOLVED OXYGEN METHOD

A modified technique for the Winkler determination of dissolved oxygen has been used at the Chesapeake Bay Institute for several years. The modifications result in increased simplicity and speed and reduction in the errors due to manipulation. The unusual features of the technique are the elimination of the volumetric transfer of the final iodine solution and the reagent concentrations.

The sources of errors in the various techniques for the Winkler method are discussed in detail by Carpenter (1965) and by Carritt (1964), who also reports the results of an intercomparison experiment.

APPARATUS

Sample flasks—Erlenmeyer flasks of 125-ml nominal capacity (130–140 ml calibrated capacity) with full-length 19/38 ground-glass stoppers are used. Bottles may be substituted for the flasks, but more care is required to avoid trapping air bubbles. The stoppers should be rounded or tapered to avoid trapping air bubbles.

Reagent dispensers—Syringes with Chaney adapters are used for the viscous reagent solutions. Any rapid delivery automatic pipette may be substituted.

Microburette—A 1-ml total capacity burette is required. The most satisfactory burette appears to be the Gilmont micro-pipette-burette (Emil Greiner Co.) with digital counter readout. Filling the burette can be facilitated by attaching it to a capillary three-way stopcock that has a 100-ml reservoir and the delivery tip on its other two arms. The burette is mounted in a three-sided box with a white interior (Fig. 1). Lights and a magnetic stirrer are mounted in the box. Two 8-w fluorescent lamps, located at the forward vertical edges, give adequate illumination. The magnetic stirrer is mounted so that it can be swiveled

in the horizontal plane to permit positioning the sample flask under the burette with the delivery tip immersed in the sample. The pipettes for standardization and blank determination are hung on the wall of the box for convenience.

REAGENT SOLUTIONS

1) $MnCl_2 \cdot 4H_2O$	600 g/liter (3 M)
2) NaOH	320 g/liter (8 N)
NaI	600 g/liter (4 M)
3) H_2SO_4	280 ml concd H_2SO_4 /liter (10 N)
4) Starch	1% solution
5) $Na_2S_2O_3 \cdot H_2O$	35 g/liter (0.14 N)
6) KIO_3	0.3567 g/liter (0.01 N)

NOTES

1) Manganous sulfate may be substituted for the chloride. The chloride is suggested because of its solubility and its freedom from higher-valence manganese com-

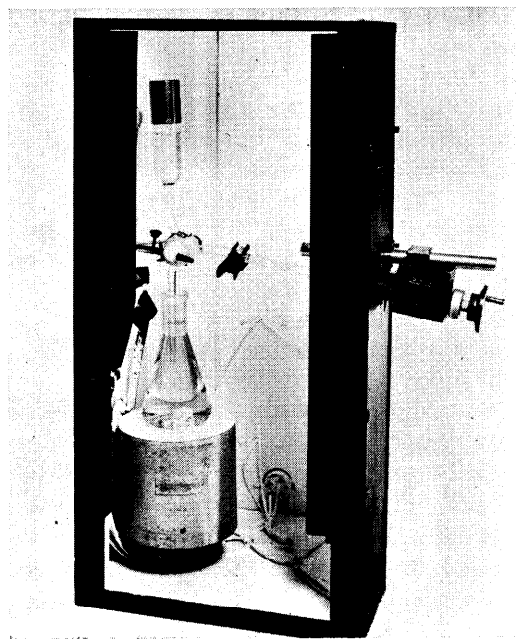


FIG. 1. Titration apparatus.

pounds in the commercial products examined.

2) The sodium hydroxide-sodium iodide reagent has the desirable features of the Pomeroy-Kirschman reagent without its excessive viscosity and tendency to crystallize. The hydroxide is adequate to precipitate all the manganese and to react with a bicarbonate alkalinity of 2×10^{-3} N (sea-water). The sodium iodide is sufficiently concentrated to decrease the amount of free iodine to 5% of the total iodine in air-saturated water samples. This increased complexing of iodine as the triiodide ion results in sharper end points and reduces volatilization losses. The oxygen content of the manganous chloride and the sodium hydroxide-sodium iodide solutions amounts to the addition of 0.018 ml/liter when 1 ml of each reagent is used in a 140-ml sample.

3) The strength of the sulfuric acid reagent is chosen so that the final solution will be pH 2. Greater acidity favors the air oxidation of iodide ions. The final pH must be less than 2.7 for the solution and reaction of the oxidized manganese. The errors in the volumes of the hydroxide and acid solutions should not be greater than 5% for proper pH control.

4) A variety of stable starch solutions has been proposed in the literature, but freshwater solutions are satisfactory and easily prepared. The starch should be discarded when any reddish tint of the starch-iodine complex is noted.

5) The 0.14 N sodium thiosulfate solution should be used for samples with a maximum dissolved oxygen concentration of 5.5 ml/liter. For more concentrated samples, the strength of the thiosulfate solution should be increased to avoid refilling the burette during titration.

6) While potassium iodate is suggested here, potassium biiodate appears to be an equally good iodine standard. The virtue of the iodate is its stability during drying (180C). Decomposition of the biiodate at temperatures above 100C can be observed, and it should be dried by vacuum desiccation. Potassium dichromate is not a satisfactory standard because it is impractical

to avoid air oxidation of iodide at the high acidities required for the reaction between dichromate and iodide ions.

PROCEDURE FOR SAMPLES

1) Collect the desired number of replicate samples in 125-ml glass-stopper Erlenmeyer flasks that have been calibrated "to contain" by weighing. Flasks having calibrated volumes of from 130 to 140 ml are suitable, and no effort should be made to pair flasks of equal volume. Fill and overflow by at least one bottle volume.

2) Add 1 ml of the manganous ion solution and 1 ml of the sodium iodide-sodium hydroxide solution with a syringe or other rapid delivery pipette and seat the stopper securely without trapping bubbles.

3) Disperse the precipitate uniformly throughout the bottle by shaking. Allow the precipitate to settle at least halfway to the bottom and repeat the shaking. Allow the precipitate to settle two-thirds of the way to the bottom.

4) Add 1.0 ml of the sulfuric acid, stopper, and mix thoroughly.

5) Place a magnetic stirring bar in the flask. Titrate with 0.14 N sodium thiosulfate from the microburette to a straw yellow color, add 0.5 ml of starch indicator solution and continue the titration to the complete disappearance of the blue complex.

STANDARDIZATION

Pipette 10 ml of 0.01 N potassium iodate into a clean sample flask and nearly fill with distilled water. Add 1.0 ml of the sulfuric acid reagent and 1 ml of the sodium iodide-sodium hydroxide reagent. Titrate the liberated iodine as for the sample. The sample flask must be carefully rinsed to avoid the presence of manganese ions, or a separate flask should be reserved for the standardization.

BLANK DETERMINATION

Pipette 1 ml of 0.01 N potassium iodate into a *clean* sample flask and nearly fill the flask with distilled water. Add 1.0 ml of

the sulfuric acid reagent, 1 ml of the sodium iodide-sodium hydroxide reagent, mix, and then add 1 ml of the manganous ion reagent. Titrate precisely to the end point.

Pipette a second 1 ml of 0.01 N potassium iodate into the final solution above. Titrate the liberated iodine.

The difference between the first and second titrations is the reagent and indicator blank. Manganese must be absent during the hydroxide addition.

The procedure may be repeated using sample water rather than distilled water to determine the blank due to sample constituents that liberate or react with iodine in acid solution. The method is unsuitable for grossly polluted samples.

Either positive or negative blanks may be found for the reagents.

CALCULATION OF RESULTS

The concentration of dissolved oxygen in the sample may be computed from the following equation:

$$DO = \frac{(R - R_{\text{blk}})V_{10_3} \cdot N_{10_3} \cdot E}{(R_{\text{std}} - R_{\text{blk}})(V_b - V_{\text{reg}})} - DO_{\text{reg}}$$

where

DO = dissolved oxygen (ml/liter)

R = sample titration burette reading

R_{blk} = difference between blank titrations burette readings

R_{std} = standardization burette reading

V_{10_3} = volume of KIO_3 standard (ml)

V_b = volume of sample bottle (ml)

V_{reg} = volume of sample displaced by reagents (ml)

N_{10_3} = normality of KIO_3 standard (equivalent/liter)

E = 5,598 ml O_2 /equivalent, and

DO_{reg} = oxygen added with reagents

For the procedure described,

$$DO = \frac{(R - R_{\text{blk}})559.8}{(R_{\text{std}} - R_{\text{blk}})(V_b - 2)} - 0.018$$

GENERAL COMMENTS

Titration of the whole sample has the following features:

1) Speed. Elimination of removing aliquots expedites the titration.

2) Precision estimate. Titration of duplicate aliquots safeguards against gross titration errors and permits the estimation of the precision of the aliquoting and titrating. However, the precision of the method must be based on repetition of the whole procedure. The normal variation in bottle size results in different titers for replicates, which eliminates the personal tendency to obtain the same result for aliquots.

3) Minimum volatilization error. Transfer of aliquots by graduated cylinder results in greater losses of iodine than does pipette transfer, suggesting that the common procedure of transfer of the whole sample to a titration vessel also results in serious iodine loss.

4) Convenience. The digital readout burette and absence of the transfer step make precise results possible even under adverse conditions.

5) Cost. The full-length ground-glass stoppers and flasks used are approximately twice as expensive as standard medium-stopper bottles. The burette used is from three to six times as expensive as an ordinary burette, but the cost of the glass parts is comparable to that of an ordinary burette.

6) Calculation. The volume of each bottle and stopper combination enters the calculation of the results, so a factor converting the burette to dissolved oxygen concentration cannot be used.

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REFERENCES

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