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A METHOD FOR THE DETERMINATION OF DISSOLVED OXYGEN IN WATER

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ABSTRACT

The analysis for dissolved oxygen in water from small volume systems has required some modification of the standard method. These changes consist mainly of an alteration in the method of obtaining a sample and a more sensitive means for determining the released iodine.

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INTRODUCTION

In order to analyze for dissolved oxygen in small volume systems, some modification of the ASTM method is required. A method has been developed which has proved so convenient and trouble-free that its use is suggested for more conventional systems.

DESCRIPTION OF APPARATUS

The ASTM sample bulb has been altered as shown in Figure 1. Helium gas is used to flush the system and to eliminate the need for large volumes of sample water. The regular stopcock system as used by the ASTM referee method is replaced by two-way stopcocks. This greatly simplifies the removal of reagents from the calibrated zone.

MANNER OF DETERMINING IODINE

In the proposed method, the main difference is in the manner of determining the released iodine. Up to that point the method is essentially the same as the regular ASTM referee method. A sample is obtained in the modified bulb after either helium flushing or sample water flushing. The sample is "fixed" as in the regular method using the reagents as given in the attached appendix. After the iodine is released by the addition of acid, an aliquot of the sample is transferred to a 250-ml separatory funnel and extracted for two minutes with 20 ml of toluene. The optical density of the toluene layer is obtained by means of a spectrophotometer at 500 microns. The oxygen concentration can now be read directly from a previously prepared standard curve. A reagent blank is determined on a similar sample by the addition of the reagents in the reverse order.

CONCLUSION

Although it is not necessary to use small samples in standard boiler water analysis, the speed with which this analysis can be performed is an advantage. In addition, the constant use of standard solutions is eliminated. The only requirement is that an accurate standard curve must be prepared, which then remains constant for one spectrophotometer. By this method, a sensitivity of 0.001 ppm can be obtained. The use of 100-ml samples and a reduction of the toluene volume to 10 ml has made it possible to analyze water containing a few parts per billion.

APPENDIX

THE ANALYSIS OF DISSOLVED OXYGEN IN BOILER WATER

Range: 0.04 to 0.4 ppm. Sensitivity: 0.004 ppm.

REAGENTS

1. Alkaline potassium iodide solution

   700 g KOH
   150 g KI. Dissolve separately and dilute to 1 liter.
   Store in a brown bottle.

2. Manganous sulfate solution

   480 g $MnSO_4 \cdot 4H_2O$ dissolved in water and diluted to 1 liter.

3. H_2SO_4 solution

   750 ml conc H_2SO_4. Pour slowly into 250 ml of water.
   Cool and dilute to 1 liter.

4. Standard iodine solution

   1.586 g resublimed iodine + 15 g KI
   Dilute to 1 liter

   or

   0.4454 g of KIO_3 + 15 g of KI + 5 ml of H_2SO_4
   Dilute to 1 liter

   Either of these solutions is equivalent to 0.1 mg oxygen/ml.

Make a careful dilution of 10 ml standard iodine solution to 1 liter.

1 ml = 1.0 μg oxygen

PREPARATION OF STANDARD CURVE

Transfer an aliquot of the dilute standard (1 ml = 1 μg oxygen) to a 250-ml separatory funnel. Add by pipet or burette exactly 20 ml of ACS reagent grade toluene. Stopper and vigorously shake the separatory for one to two minutes. Discard the lower layer (aqueous) and transfer the toluene layer to a spectrophotometer curvette (such as Lumetron colorimeter). Centrifuge the toluene layer and compare against a black of toluene. Plot the equivalent oxygen vs the reading of optical density. The line will be straight up to concentration of at least 1 μg oxygen per ml of toluene. A typical plot is shown in Figure 2.

FIXING THE SAMPLE

Mount the sample upright in a suitable support. Fill the calibrated stem with alkaline KI reagent solution. Adjust the solution to the zero mark by allowing the excess reagent to flow out through the open stopcock. Add 0.5 ml of the KI reagent to the sample, allowing an equal volume of sample to be displaced through the lower stopcock.

Rinse the calibrated stem, first with distilled water, then with manganous sulfate reagent solution. Adjust the volume as before and add 0.5 ml of the manganous reagent. Mix the precipitate thoroughly and allow the sample to stand one to two minutes for complete reaction.

Rinse the calibrated stem with water, and then with the sulfuric acid reagent. Add 0.5 ml of the sulfuric acid reagent to the thoroughly mixed sample. Rotate the sample bulb to dissolve the precipitate. Replace the sample bulb in the vertical support and discard 10 to 15 ml of the solution from the lower stopcock.

DETERMINATION OF IODINE

Withdraw a 50-ml portion and transfer to a 250-ml separatory funnel. Accurately transfer 20 ml of ACS reagent grade toluene to the funnel by means of a burette. Stopper and vigorously shake the funnel for one to two minutes. Discard the lower layer (aqueous) and transfer the toluene layer to a spectrophotometer tube. Centrifuge the sample to clear the toluene layer and compare at 500 microns against a blank of toluene. From the standard curve obtain the value of µg of oxygen. Should the optical density value be above 0.05, repeat the extraction with a 25-ml portion of the sample rather than a 50-ml portion. Alter the calculations accordingly.

CALCULATION

$$\text{ml sample} = 50 \times \frac{(\text{volume of tube} - \text{volume of reagents})}{(\text{volume of tube})}$$

μg of oxygen x ml of toluene/ml sample = ppm oxygen

A reagent blank should be determined each day by adding the reagents in the reverse order, and extracting as a regular sample.

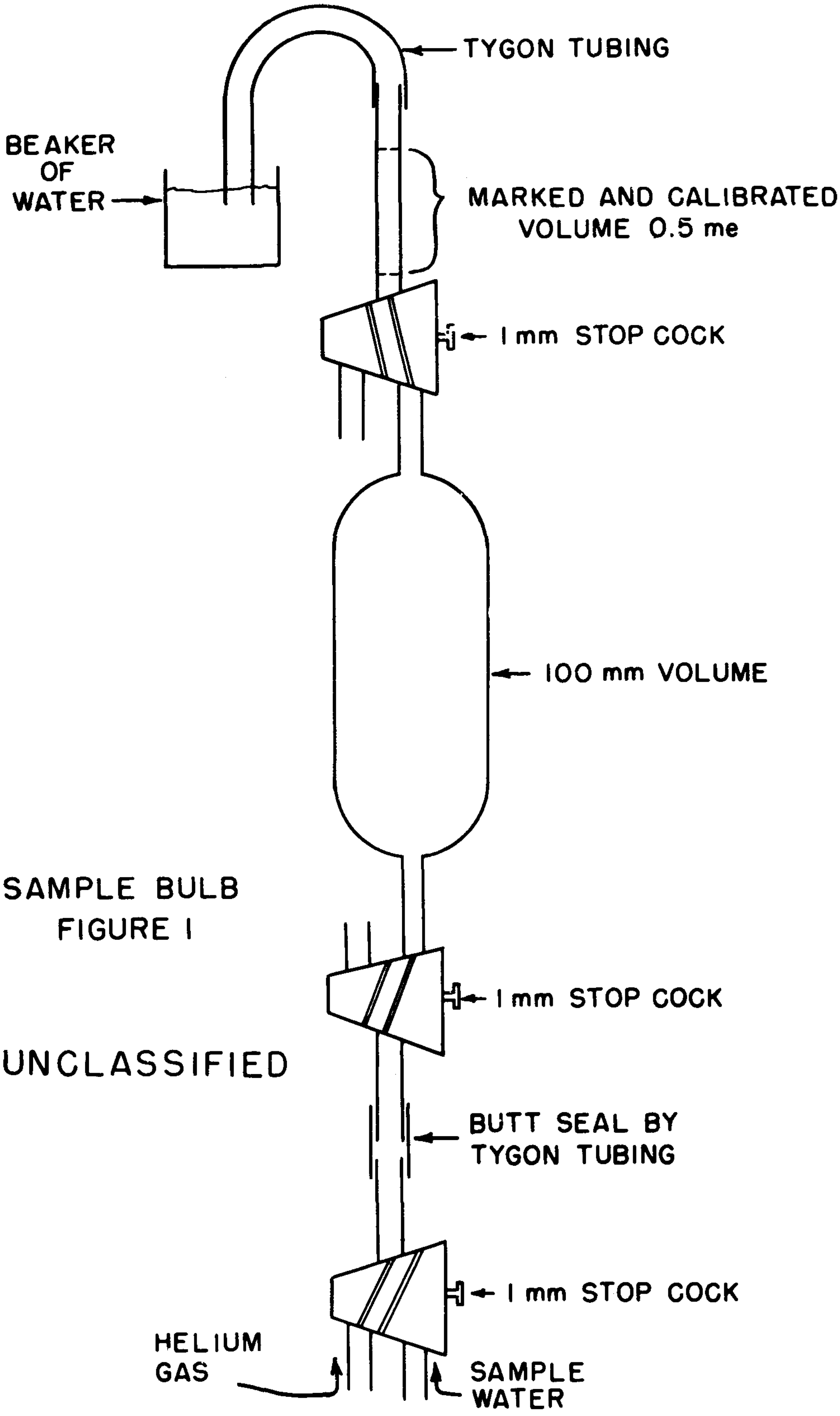

Fig. 1--Sample bulb.

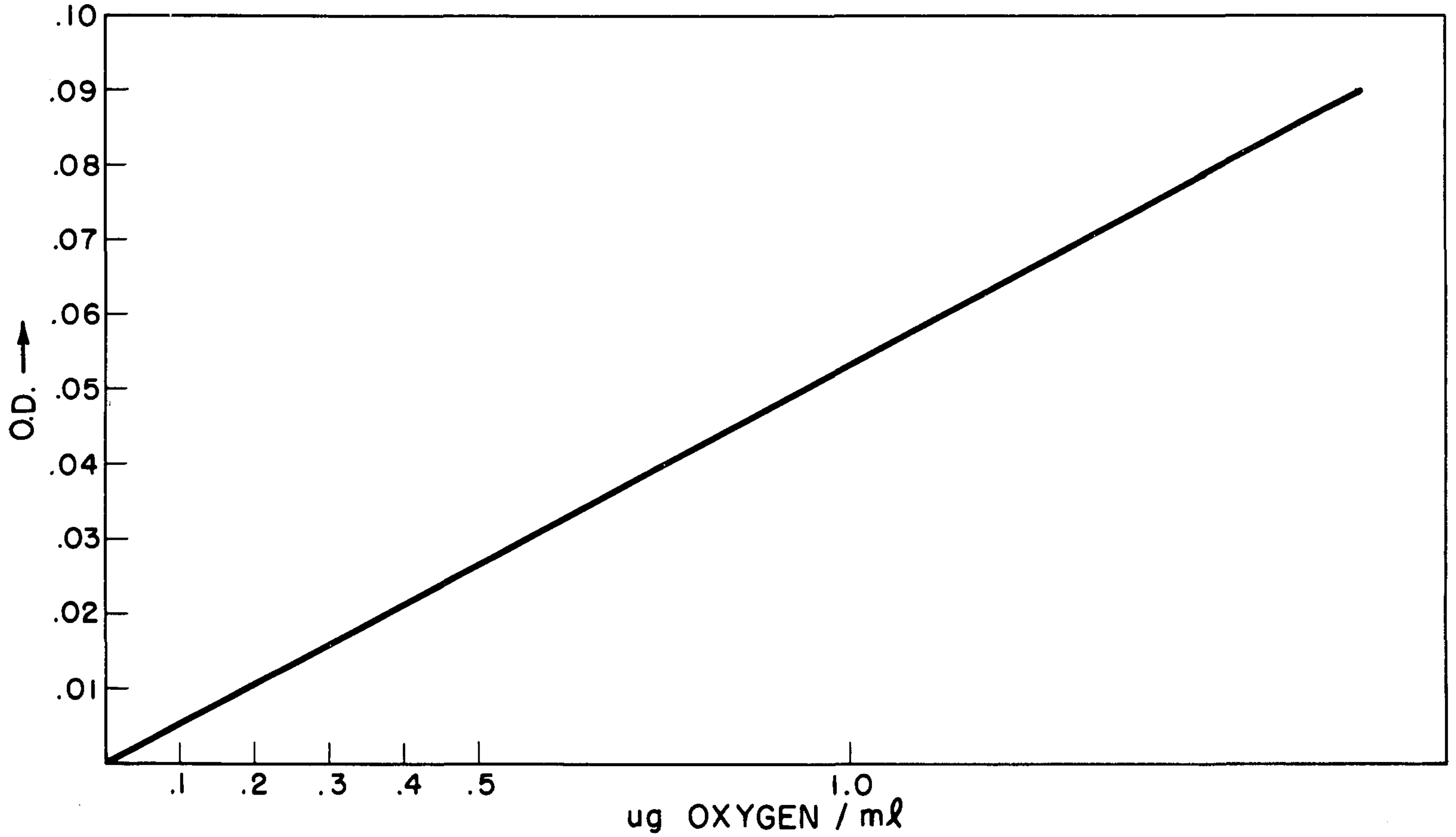

Fig. 2--Typical standard curve at 500 mμ.