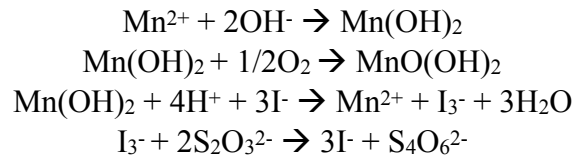


## SIO/STS/ODF OXYGEN ANALYSIS

### The Chemistry

This system is called an oxygen titrator; in fact it is an iodine titrator, employing what has been a very standard procedure for the quantitative analysis of iodine for many years. Oxygen in a water sample cannot be stored because of its involvement in biological cycles and chemical reactions. Therefore, as soon as the sample is drawn, reagents are added so that the oxygen is used as an oxidizing agent to change manganese ions quantitatively from the +2 state to +4 in a basic (alkaline) medium. This is a stable condition for the manganese, and the samples may be kept for days, with proper precautions, or even weeks under very carefully controlled conditions, before finally running the analyses. When the sample is acidified in the presence of iodide ions, the +4 manganese has sufficient oxidizing potential to oxidize iodide (-1) to free iodine, which is then titrated by the addition of a known concentration of thiosulfate until all iodine is exhausted.

The relevant chemical reactions occurring in the solution are:



The concentration of the thiosulfate, and the amount needed to react with the iodine, are then used in the calculation of the amount of oxygen that was originally present. A precisely known oxidizing agent,  $\text{KIO}_3$ , long used as a primary standard, is used to produce a known amount of iodine so that we can determine the exact strength or concentration of the thiosulfate solution. This process is known as standardization of the thiosulfate: stoichiometrically,  $\text{IO}_3^- + 8\text{I}^- + 6\text{H}^+ \rightarrow 3\text{I}_3^- + 3\text{H}_2\text{O}$

The experimental measurement using this technique thus essentially determines the ratio between the concentration of iodate in a standard solution and the concentration of oxygen in the sample using thiosulfate as a transfer standard. We use a similar process to determine a “blank”, the quantity of contaminants in the reagents, or even in the distilled or deionized water used in the procedure, that is capable of participating in the series of reactions, thereby acting to artificially increase or decrease the amount of oxygen calculated to be present. The blank, while generally not large, can be an order of magnitude greater than the precision of the measurement, and must therefore be determined.

### General Description

The function of the SIO oxygen titrator is little different in principle from the basic Winkler titration as modified by Carpenter (1965). Rather than using the visible color of

the iodine-starch complex as an indicator of the endpoint, it uses the very strong absorption of ultra-violet light by tri-iodide ion centered at 350 nm wavelength. Since this absorption band is rather wide, and 365 nm UV sources and filters are easily obtained, it is the latter wavelength that is actually used in the system.

The concept of using UV as a measure of titration progress is not new, and numerous descriptions of UV-based oxygen titrators may be found in the literature. While most are concerned with accurate volume measurement, it is not really volume with which we are concerned, rather the mass of reagent delivered. Therefore, since aqueous solutions change density substantially with changes of temperature, the temperature as well as the volume must be measured in order to calculate the mass of dispensed reagent.

The function of the titrator is to add reagent as rapidly as possible to the flask without overshooting the endpoint, to slow to a rate that permits complete mixing and reaction immediately before and through the endpoint, to determine the exact endpoint as closely as necessary to reach the design goals, and to apply via the computer algorithm and hardware those small and tedious corrections which have historically been omitted, but which may result in a significant error if neglected.

### **Reagents**

It is assumed that the user is familiar with dissolved oxygen analyses and has read the Culberson (1991) section on dissolved oxygen in the WOCE Operations Manual.

Water used in the preparation of reagents and standards is assumed to be distilled or deionized water of very high purity. Do not store DI water for long periods, stored water has been found to contain NO<sub>2</sub> or other contamination, which may react as an oxidizing or reducing agent and thereby affect the results of oxygen analyses. See the section on blanks.

Reagents other than KIO<sub>3</sub> standard may be made to volume in an Erlenmeyer flask calibrated using a volumetric flask. Standards are ALWAYS made up in a calibrated volumetric flask.

The first 3 of the reagents below are best made in 2-4 liter quantities to last an entire leg of an expedition. This avoids breaks in the reagent blank record, which may result from changing reagents in mid-leg. ODF stores oxygen reagents (other than KIO<sub>3</sub> standards) in 4-liter brown glass bottles which hold enough for most cruise legs, and, in the case of the NaOH/NaI reagent, prevents photochemical reactions. The reagent dispenser bottles, normally 1-liter Wheaton bottles with Wheaton or Brinkmann 1 mL dispensers, are refilled from these larger containers.

*Manganese Chloride (MnCl<sub>2</sub>x4H<sub>2</sub>O, 3 M)*

MnCl<sub>2</sub> is carried dry in pre-weighed 500 g quantities. Dilute to 833 mL.

*Sodium Hydroxide-Sodium Iodide (NaOH, 8 M + NaI, 4 M)*

Pre-weighed quantities carried aboard ship are: NaI, 500 g; NaOH, 267 g. The sodium iodide is dissolved first, in  $\frac{1}{2}$  to  $\frac{2}{3}$  of the final volume of water in an appropriate size Erlenmeyer flask. The flask volume should permit the solution to be swirled or mixed easily while in a sink or ice-bath for cooling, as it will become quite hot during the addition of NaOH. Add NaOH in small amounts to avoid excess heating. After the solution has cooled dilute to the final volume of 833 mL.

*Sulfuric Acid (H<sub>2</sub>SO<sub>4</sub>, 5 M)*

Concentrated sulfuric acid is normally carried aboard ship in 2.5 L bottles. Store in appropriate spaces. Add 280 mL of the concentrated acid, a small amount at a time, to about 750 mL of distilled water for each liter of dilute acid desired.

*NEVER ADD WATER TO CONCENTRATED ACID.*

Cool in an ice-bath to avoid high temperatures.

*Sodium Thiosulfate (Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>·5H<sub>2</sub>O, approximately 0.22 N)*

SIO practice is to make the reagent with 55 g/L of distilled water. With more dilute thiosulfate, the buret will exceed its 1 mL volume at 6-7 mL/L oxygen concentration. The more concentrated reagent permits a wider range of oxygen analyses without a buret fill. Thiosulfate is made in 1-2 L quantities by diluting the pre-weighed 55 g pellets in a 1-2 L Erlenmeyer flask.

Normal ODF practice is to make this reagent at least 1 day before it is needed. The results seem more stable after the first day or two.

*Potassium Iodate Standard (KIO<sub>3</sub>, approximately 0.012-0.013 N)*

ODF practice is to make up ashore 6L batches of ~0.012N KIO<sub>3</sub> standard using a 6L calibrated volumetric flask.

## **References**

Carpenter, J. H., "The Chesapeake Bay Institute technique for the Winkler dissolved oxygen method," *Limnology and Oceanography*, 10, pp. 141-143 (1965).

Culberson, C. H., Knapp, G., Stalcup, M., Williams, R. T., and Zemlyak, F., "A comparison of methods for the determination of dissolved oxygen in seawater," Report WHPO 91-2, WOCE Hydrographic Programme Office (Aug 1991).