**DISSOLVED OXYGEN ANALYSIS**

**PIs**

Susan Becker

Todd Martz

**Technician**

Zac Anderson

**1. Equipment and Techniques**

Dissolved oxygen analyses were performed with an SIO/ODF-designed automated oxygen titrator using photometric end-point detection based on the absorption of 365 nm wavelength ultra-violet light. The titration of the samples and the data logging were controlled by PC LabView software. Sodium thiosulfate was dispensed by a Brinkmann Dosimat 665 burette driver fitted with a 1.0 mL burette. ODF used a whole-bottle modified Winkler titration following the technique of Carpenter (Carpenter, 1965)with modifications by Culberson (Culberson, 1991), but with higher concentrations of potassium iodate standard (approximately 0.012N), and sodium thiosulfate solution (approximately 55 g/L). Pre-made liquid potassium iodate standards were run every day of station work (approximately every 2-4 stations), and/or if changes were made to the system or reagents. Reagent/distilled water blanks were determined with every standardization or more often if a change in reagents required it, to account for presence of oxidizing or reducing agents.

**2. Sampling and Data Processing**

A total of 671 oxygen samples were collected and measured from 53 CTD casts out of a total of 73. Samples were collected for dissolved oxygen analyses soon after the rosette was brought on board, and were the first sample drawn. Nominal 125 mL volume-calibrated iodine flasks were rinsed 3 times with minimal agitation using a silicone drawing tube, then filled with the tube at the bottom of the flask and allowed to overflow for at least 3 flask volumes to ensure no air bubbles remained within the sample. The sample drawing temperatures were measured with an electronic resistance temperature detector (RTD) embedded in the drawing tube. These temperatures are essential to calculate dissolved oxygen concentrations in umol/kg, and were used as a quick diagnostic check of bottle integrity. Pickling reagents (MnCl2 followed by NaI/NaOH solution) were added in excess (1 mL of each) to fix the dissolved oxygen before stoppering. The flasks were checked again for bubble contamination following reagent addition before shaking thoroughly (10-12 inversions) to assure thorough dispersion of the precipitate. Samples were shaken again after about 30-40 minutes.

Samples were analyzed within 2-18 hours of collection, and within 0-4 hours of standardization of the sodium thiosulfate.Sodium thiosulfate normalities were calculated for each standardization and corrected to 20°C. The corrected normalities and blanks were plotted versus time and were reviewed for irregularities that would suggest a possible problem. Sodium thiosulfate normality remained remarkably stable throughout the cruise (0.2249 – 0.2251 N). Blanks were also stable and close to zero (-0.00018 – 0.00019 mL). As such, no correction for drift was necessary for any of the data.

Data were compared to CTD bottle files to allow for QC at a basic level. Bottle fire data were crudely corrected, with any clear outlying dissolved oxygen samples flagged as 3 (suspect data) or 4 (bad data) appropriately.

**3. Volumetric Calibration**

Oxygen flask volumes were determined gravimetrically with degassed deionized water to determine flask volumes at ODF’s chemistry laboratory. This is done once before using flasks for the first time and periodically thereafter when a suspect volume is detected. The volumetric flasks used in preparing iodate standards were volume-calibrated by the same method, as was the 10 mL Dosimat burette used to dispense standard iodate solution.

**4. Standards**

Liquid potassium iodate standards were prepared in 6-liter batches and bottled in sterile glass bottles at ODF’s chemistry laboratory prior to the expedition. The normality of the liquid standard was determined by calculation from weight. The standard was supplied by Alfa Aesar and has a reported purity of 99.4-100.4%. All other reagents were “reagent grade” and were tested for levels of oxidizing and reducing impurities prior to use.

**5. Narrative**

Setup occurred in Cape Town, South Africa from 2020-01-22 to 2020-01-25, the date of departure. The oxygen analysis rig was setup and secured on the starboard bench in the hydrolab of the R/V Thomas G. Thompson. Initial reagent batches (2 L each of MnCl2, NaI/NaOH and H2SO4, and 1 L of sodium thiosulfate) were made in port. Temperature sensors for the sodium thiosulfate and iodate standard burettes disagreed on initial setup (difference > 1.5°C), so were calibrated using an 8-point calibration spanning 20-27°C and a linear regression against voltage applied to correct the slope and offset. Before departure an initial sodium thiosulfate standardization was carried out to check the oxygen rig was fully functioning, and to provide a timepoint to check thiosulfate normality drift before any samples were taken and analyzed.

Station sampling and analysis went very well, with only a few samples lost at the sampling stage due to duplicate niskin bottles already having been cracked when the occasionally leaking bottle was discovered. No samples were lost at the analysis stage as the oxygen titrator worked well for the duration of the cruise.

Halfway through sampling the second cast it became apparent the temperature probe imbedded in the drawing tube was not responding to changes in water temperature. Draw temperatures were inferred by calculating a second order regression of in-situ CTD bottle temperature against draw temperature for CTD casts 3-5, and the model coefficients applied to CTD data from casts 1 and 2. This method was checked against later casts and found to have a precision of 0.5 °C or better. The temperature probe again malfunctioned during the sampling of one bottle during cast 3. The inferred draw temperatures have been given a flag 3 (suspect data) but should be adequate for conversion of dissolved oxygen from mL/L to µmol/kg. After changing the temperature probe there were no further issues.

On the second leg (Durban – Mauritius) additional “trip and fly” CTD casts were carried out for increased spatial CTD data resolution and additional DIC, alkalinity and nutrient measurements. These were not sampled for dissolved oxygen as sensors would not have stabilized enough for effective CTD sensor calibration. Replicate oxygen samples taken from duplicate bottom-depth niskin bottles on three deep CTD casts showed excellent agreement (+/- 0.002 mL/L).