### Dissolved Oxygen

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Oxygen samples were analyzed at sea using an automated Winkler titration system (Metrohm Dosimat model 665, a UV light source and detector with a 365 nm filter controlled by LVO2\_876 software designed and constructed by Scripps Institution of Oceanography) with modifications based on Carpenter (1965) and adhering to WOCE protocols (Culberson 1991). A depth profile down to 1000m was collected at all 11 stations during the North Pacific leg between Victoria and Dutch Harbor. In addition, 7 loop samples were collected for calibration of the underway oxygen optode. For further analysis details than those described below, see document QF2017-93OXY.xls.

#### Pre-cruise preparation

All cruise preparation was performed by Kenny Scozzafava (DFO-IOS)

##### Reagents and Standards

All reagents and standards were prepared in Extran- and acid-washed glassware and plastic ware according to the protocols outlined in the Scripps Institute of Oceanography (SIO) Oxygen Titration Manual Version 10-Apr-2003 (updated in July 2010 by Nina Nemcek). Reagents (manganous chloride, MnCl2; alkaline iodide, NaI/NaOH; and sulfuric acid, H2SO4), titrant (sodium thiosulfate, which will be referred as Thio) and potassium iodate (KIO3) standards were prepared using chemicals of the highest purity available. The chemical batches were prepared at IOS within the last year. Reagents and Thio were made in 4000 mL glassware and the standards were prepared in 2000 mL Class A volumetric flasks. KIO3 standard normalities were calculated with the Scripps Institute of Oceanography (SIO) program io3norm.exe using the temperature of the solutions, volume of the flask and weight of standard added.

##### Equipment Calibrations

Bottle top dispensers, Dosimat burettes and oxygen sampling flasks are all calibrated on a routine basis in the lab by Kenny Scozzafava. For details see previous years’ reports.

#### Sampling

Samples were collected in ~140 mL calibrated ground glass stoppered iodine flasks. Seawater temperatures at time of sampling were measured with a digital probe thermometer (Fisher Scientific) potted into one arm of a Y-connector with sampling tubing attached to the other two arms (one to the Niskin spigot and one into flask). The samples were immediately fixed with 1.0 mL of MnCl2 and 1.0 mL of NaI/NaOH, the stopper was inserted and flask shaken vigorously to mix the contents and fix dissolved oxygen. Samples were then allowed to partially settle before being re-shaken and water-sealed (usually immediately following conclusion of all water sampling). Samples were left on deck in the rosette shack prior to analysis within 24 hr of collection. All sampling and analysis at sea was performed by Nina Nemcek.

#### Analysis at sea

All samples were analyzed by Nina Nemcek on the Scripps Institution of Oceanography (SIO) Winkler-based UV titration kit A:

* Scripps software **LVO2 v 2.34** running on laptop with Windows 10 operating system.
* System controller laptop with a USB to RS232 converter (KEYSPAN).
* 2 Brinkmann (Metrohm) 665 Dosimats, one with a handheld keyboard and a 10 mL calibrated burette for the KIO3 standard, and the other with a software-controlled 1mL burette for thiosulfate.
* Pencil UV lamp (Spectronics Corp.) with mount and power supply.
* UV100BQ photodiode detector equipped with a 365 nm filter.
* Mini stirrer with a water bath sample holder mounted on top (VWR).
* 2 Platinum Resistance Thermometers (PRT) to monitor solution temperatures.
* An analogue to digital converter to convert voltages from the detector and the 2 PRTs to a digital signal.

##### Thiosulphate Calibration

Standards and blanks were run twice at the start of the cruise to confirm stability of Thio normality and were run every two days after that just prior to sample analysis. A dedicated Dosimat was used to accurately dispense either 1.00 mL of KIO3 for blanks or 10.00 mL of KIO3 for standards. Blanks and standards were always prepared in ultrapure deionized water brought out in a carboy from IOS. Blanks and standards were run in sets of 4 with the criteria that 3 out of 4 titers had to agree to within 0.0003 (blank titer or standard titer in ml). Only once did a second set of standards need to be run to achieve this result. The temperature of both the standard and the thiosulfate were recorded by the program and used to correct the delivered mass of both reagents to 20°C in order to calculate the Thio normality.

Blanks were not rerun with every set of standards towards the end of the cruise as the same bottles of reagent were used throughout and all previous titers were stable. Running blanks with every set of standards is a waste of time and resources and has the potential to introduce random error to the dataset. Unfortunately, the SIO program does not automatically calculate Thio normality using the blank values from the previous standardization so this value was calculated manually to confirm its stability.

##### Analytical Procedure

Prior to analysis each day, the UV light source and stir plate were turned on and allowed to warm up and stabilize for 20-30 min and the water bath was cleaned and drained to ensure good light transmission. The Dosimat lines were checked thoroughly for bubbles and purged as needed and the bottle top dispensers were flushed.

Bottle files containing sample numbers, flask IDs and draw temperatures were prepared for each cast. Following system prep described above, the sample run was started. Sample flasks were inspected for bubbles, the water seal was removed from atop the stopper, and 1.0 mL of sulfuric acid and a stir bar were added to the flask which was then placed inside the water bath. The Thio burette dose tip was inserted into the flask and the titration initiated. Dissolved oxygen values were recorded on the rosette logs.

#### Precision and Accuracy

Of the 186 unique samples collected during the course of this survey, 23 were collected in duplicate. Of the replicated samples, the average was chosen as the final DO value. The precision of the dissolved oxygen replicate measurements was excellent, with a pooled standard deviation (*sp*) of 0.003 mL/L after the removal of 1 outlier, determined by the Chauvenet’s criterion. Oxygen values ranged from 0.247-7.204 ml/L.

#### Thio normality

One batch of Thio titrant (Batch #1603) and 1 batch of KIO3 standard (Batch #1702) was utilized during the course of the survey. Accuracy of KIO3 solutions had been confirmed in the lab prior to sailing so there was no need to change standard batches. Thio normality was stable throughout the cruise ranging from 0.24064-0.24068N falling well within the maximum acceptable range of 0.0005N. Furthermore, Thio normality values were within 0.0005N of values measured during last year’s cruise (2016-17) where a different bottle of the same batch was used.

#### Issues during sampling and analysis

There were no major issues with either sampling or analysis during this cruise. A few samples had to be over-titrated due to uneven titration curves and late endpoints. Over-titration improved the results for all samples. Flask #1119 seems to have a stopper that is too small for the flask as on two occasions it popped out during sample shaking. In one instance the sample was lost and on the second occasion the sample was re-drawn into a different flask and #1119 was pulled from rotation. The stopper on this flask should be changed and flask volume re-calibrated.