Dissolved Oxygen Analysis

1. Cruise Objectives

The objectives of the dissolved oxygen analysis were to provide a calibration for the oxygen sensor mounted on the frame of the CTD for cruise JC031, which undertook two transects within Drake Passage. For this, a Winkler titration was performed on a water sample taken from the Niskin bottles mounted on the CTD frame.

2. Methods

Dissolved oxygen samples were only taken from the CTD casts and they were the second samples to be drawn from the Niskin bottles after the CFC sampling. Every Niskin bottle that had been fired and was being sampled for other analysis was sampled for dissolved oxygen. The samples were drawn through short pieces of silicon tubing into clear, pre-calibrated, wide necked glass bottles. The temperature of the sample water at the time of sampling was measured using an electronic thermometer probe. The temperature would be used to calculate any temperature dependant changes in the sample bottle volumes. Each of these samples was fixed immediately using 1 ml of a 600g/l manganese chloride and 600g/l alkaline iodide solution. The samples were shaken thoroughly and then left to settle for 30 minutes before being shaken again. The samples were then left for a few hours before analysis.

The samples were analysed in the chemistry laboratory following the procedure outlined in Holley and Hydes (1994). The samples were acidified using 1ml of a 5M sulphuric acid solution immediately before titration and stirred using a magnetic stirrer. The Winkler whole bottle titration method with amperometric endpoint detection (Culberson and Huang, 1987), with equipment supplied by Metrohm, was used to determine the oxygen concentration. In total 1,557 samples were analysed for dissolved oxygen.

The normality of the sodium thiosulphate titrant was checked using a potassium iodate standard. This was done approximately daily throughout the cruise. Sodium thiosulphate standardisation was carried out by adding 5ml of 0.01N potassium iodate solution after the other reagents had been added to a CTD bottle water sample in reverse order. The sample was then titrated and the volume of sodium thiosulphate required was noted. This was repeated 5 times and the average amount of sodium thiosulphate required was calculated. This standardisation was then used in the calculation of the final dissolved oxygen calculation. The sodium thiosulphate was changed during the cruise. Figure 1 shows the average volume of sodium thiosulphate required to titrate the 5ml potassium iodate for both sets of sodium thiosulphate.

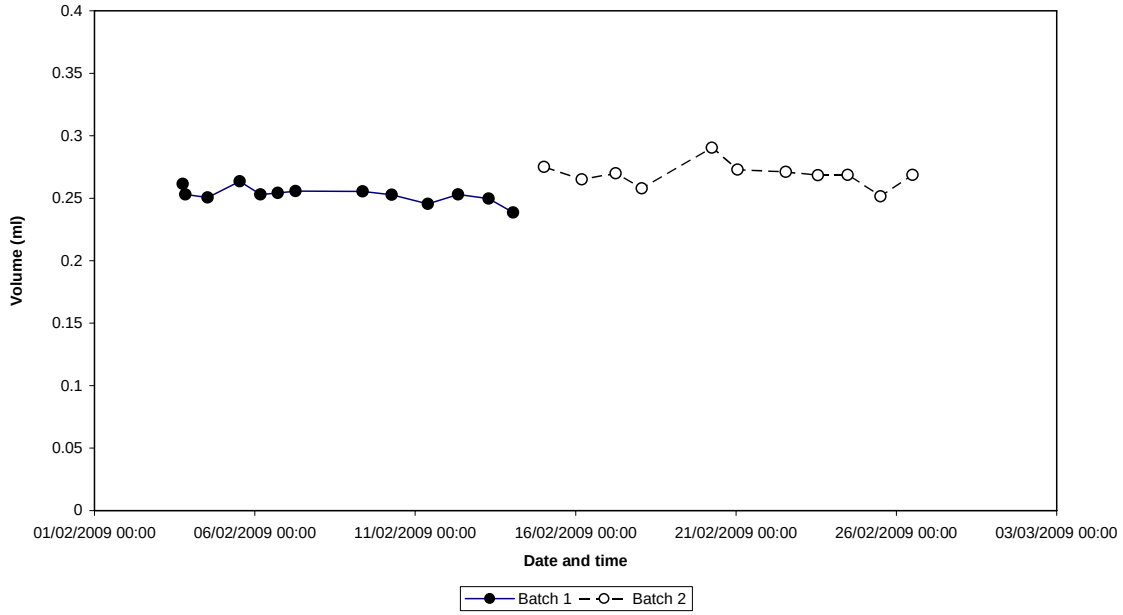

Figure 1: The volume of sodium thiosulphate required to titrate 5ml of a 0.01N potassium iodate solution. The values are relatively stable with time indicating that the sodium thiosulphate did not degrade over the course of the cruise.

A blank was also carried out to account for the oxygen in the reagents. The reagents were added in reverse order, as for the sodium thiosulphate standardisation, and then 1ml of the 0.01N potassium iodate standard was added. This was titrated and the volume of sodium thiosulphate required was noted. 1ml was again added to the same sample and it was titrated again. This was again repeated. The average of the second two volumes of sodium thiosulphate was subtracted from the first volume. This whole process was repeated three times in total and the average blank was taken and used in the calculation of the final dissolved oxygen calculation.

3. Dissolved oxygen measurements; further data quality control

Dissolved oxygen residuals (i.e. sensor data subtracted from measured values) plotted against station number (Figure 2) showed there was high variability between stations throughout the cruise. This prompted us to further quality control our measurements back at the NOCS.

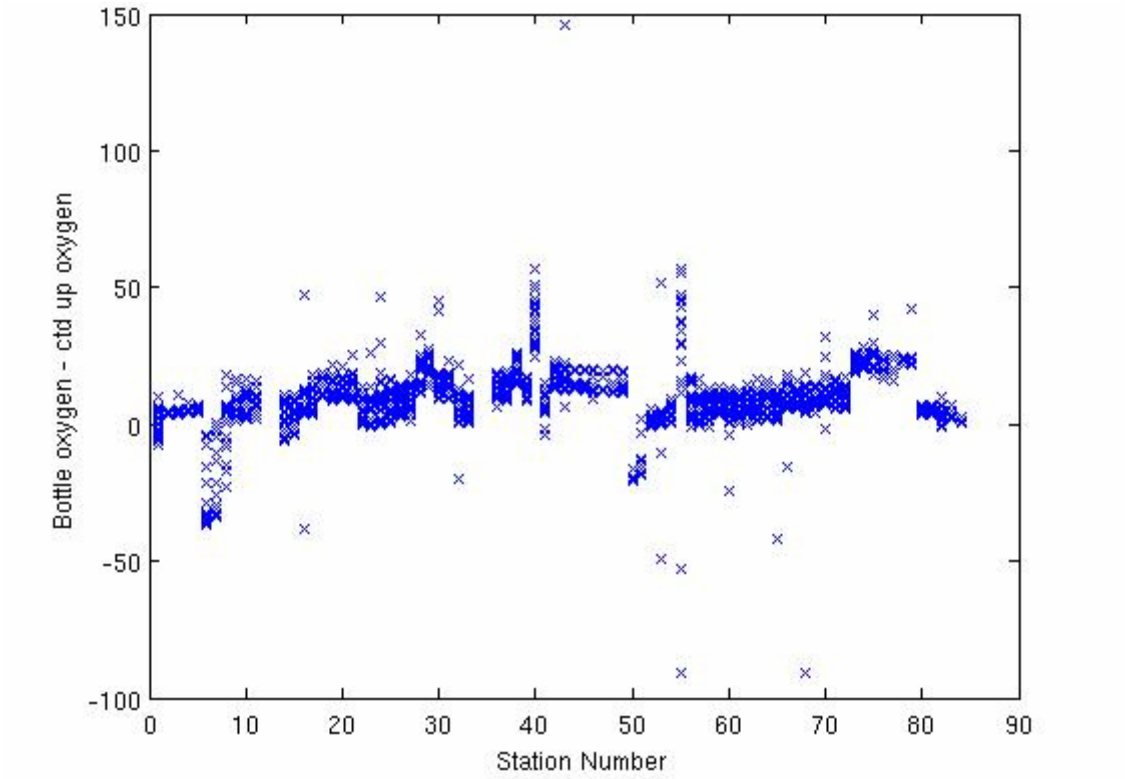

Figure 2: The oxygen residuals plotted against station number. There is no stable offset throughout the cruise. We believe this to be because of the thiosulphate and reagent calibrations undertaken during the cruise.

The first step taken was to check log sheets for consistency in the recorded titration values and calculation spreadsheets for consistency in input values. Typographic errors and outliers were found, and were corrected and removed accordingly. Dissolved oxygen concentrations were then recalculated. Variability of the residuals was reduced to some degree, but it was not satisfactory yet.

Measurements of dissolved oxygen involves addition of chemical reagents at different steps, most of which are controlled by means of automatic dispensers and automated titration burettes. However, the standardisation of the method involves manual additions using pipettes and this step is the most prone to introducing errors.

After further reviewing all log sheets, it became apparent the standardisation values were highly variable during the early stages of the cruise, but improved as the cruise progressed. We think the reason for this is that during this first set of calibrations, there were three different people doing the pipetting and two of them were new to oxygen analysis. Then measurements improved as they became more familiarised and confident with the technique. We thus decided the best way to proceed was to average out all standardisations for each batch of thiosulphate solution used during the cruise. Doing this very much improved the residuals consistency between stations. However, given that there were three different thiosulphate solutions used during the cruise, there were now three groups of data, with the residuals between stations being consistent within each

group. Having compared the residuals for these three thiosulphate solutions, dissolved oxygen concentrations for Stations 32 to 84, which were titrated with our third thiosulphate solution, produced the most consistent and minimum residuals and these were used to correct Stations 1-29.

All standardisation data for Stations 1-29 produced an average of 0.2528ml with a standard deviation of 0.0081. Due to the variability caused by the three operators the true standardisation value was considered to be within this range. By comparing the residuals values for Stations 32-84 with Stations 1-29, the standardisation volume required to negate the offset was 0.2555ml. This was well within the range of values obtained for the first batch of thiosulphate and this value was used to calculate oxygen concentrations for Stations 1-29. The residuals were again plotted and showed a much more stable offset, as would be expected (Figure 3).

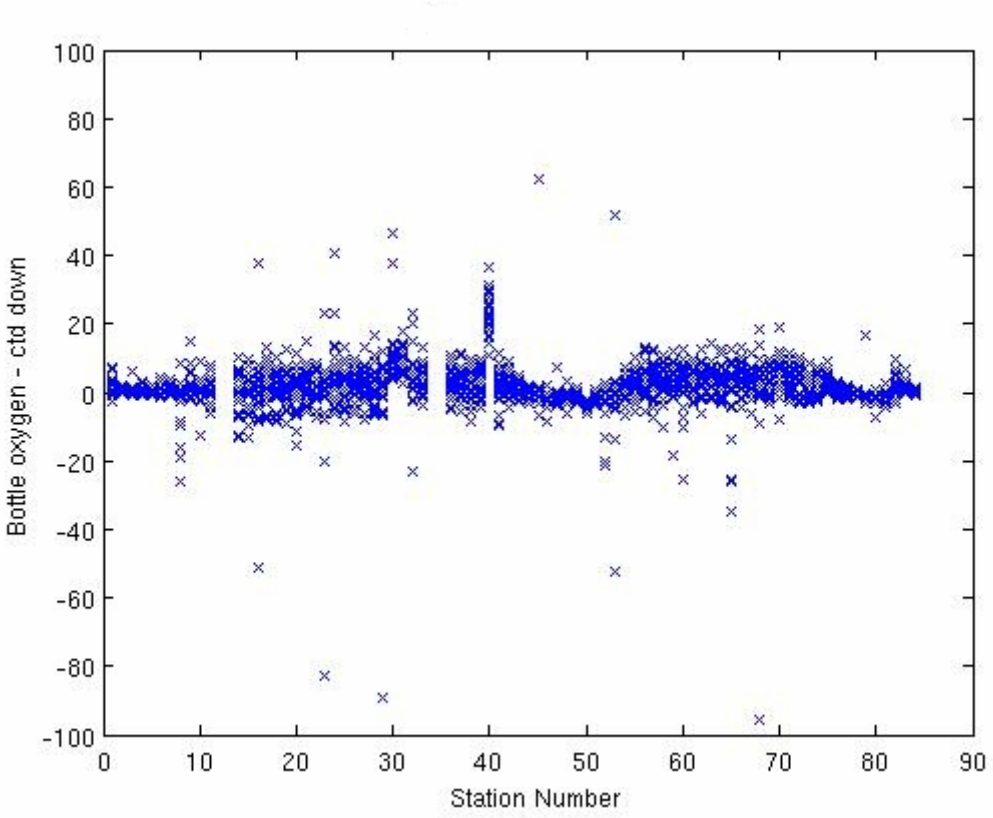

Figure 3: The oxygen residuals plotted against station number. There is now a stable offset across the cruise. The majority of data points are within a range of -5 and +10 but this plot does include all data points, even those that had been flagged as suspicious.

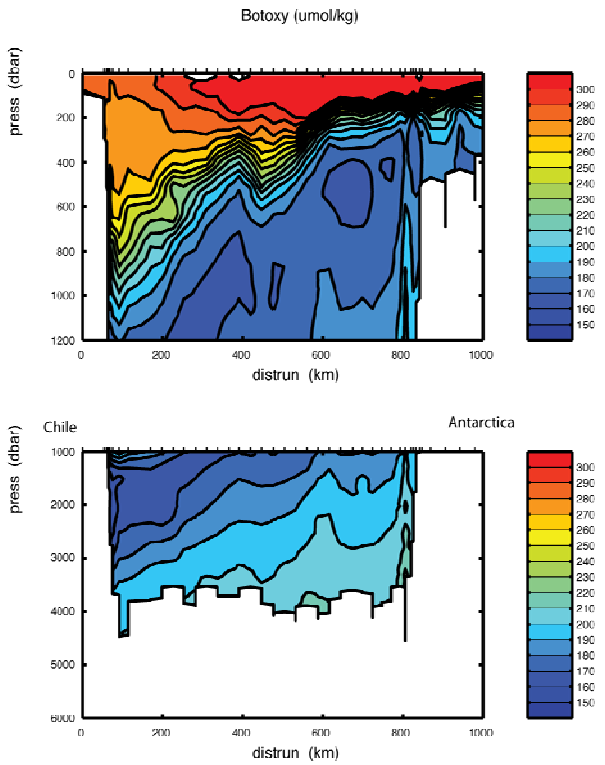

Figure 4: Contour plots for the parameters of bottle oxygen along section SR1

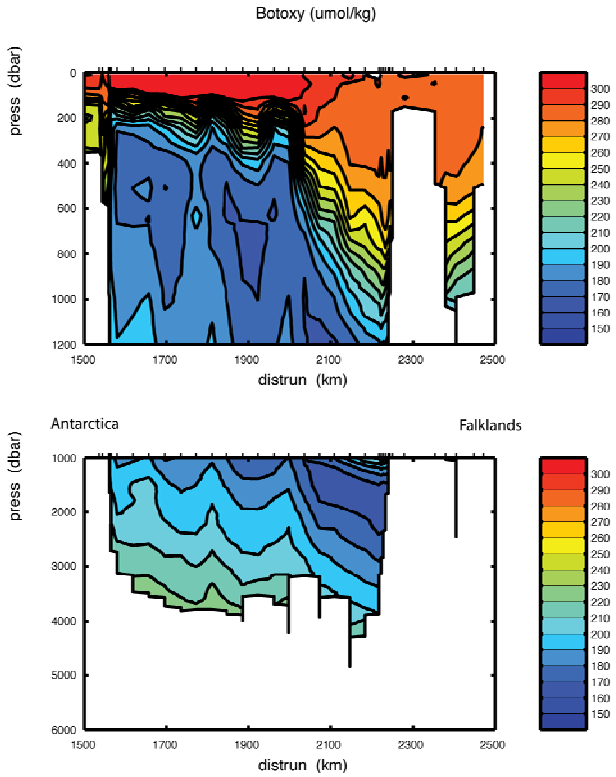

Figure 5: Contour plots for the parameters of bottle oxygen along section SR1b

4. References

Holley, S. E. and D. J. Hydes (1994). Procedures for the determination of dissolved oxygen in seawater, James Rennell Centre for Ocean Circulation: 1-38.

Culberson, C. H. and S. Huang (1987). Automated amperometric oxygen titration, Deep-Sea Research Part a-Oceanographic Research Papers 34(5-6): 875-880.