The 2008 North Atlantic Bloom Experiment

Calibration Report #20

Winkler titration of rosette (Niskin bottle) and underway samples for oxygen sensor calibration during North Atlantic Bloom Experiment 2008 (NAB2008)

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Methods

During R/V Knorr voyage KN 193-03 (Reykjavik–Reykjavik, 1-22 May 2008), 326 water samples (including replicates) from 131 Niskin bottles spread over 33 stations were collected into BOD flasks. This represents about 13 % of the total of 1004 individual sampling depths and 21 % of the total of 155 stations occupied. In addition 140 samples were drawn at regular intervals from the pumped surface seawater system.

The BOD flasks were analysed by whole-flask Winkler titration with photometric endpoint detection using a custom-built automatic titrator. Methodology and reagent concentrations (8 mol dm^{-3} NaOH / 4 mol dm^{-3} NaI, 3 mol dm^{-3} $MnCl_2$, 5 mol dm^{-3} H_2SO_4) followed WOCE recommendations [*Culberson*, 1991; *Dickson*, 1996]. The conically shaped BOD flasks were equipped with ground glass stoppers and a water seal around the neck to prevent evaporation of the seal and leakage. Their volumes were determined gravimetrically and corrected to the sample temperature from the CTD .BTL file. A thiosulphate concentration of 0.2 mol dm^{-3} was used, standardised by iodometry against a KIO_3 solution (2.336 mmol dm^{-3}). The KIO_3 standard was prepared gravimetrically at UEA using a potassium iodate certified reference material (Fluka, 60386) with an assay of (99.90±0.06) %. The KIO_3 standard was shipped to Reykjavik as a solution. A single batch of 500 cm^3 thiosulphate solution was sufficient to titrate all blanks, standards and samples. For the blanks, 0.1 cm^3 KIO_3 solution were dispensed using an Eppendorf pipette. For the standards, about 1 cm^3 KIO_3 were dispensed using an automated dispenser with 0.001 cm^3 display resolution. Typical titration volumes were between 0.7 and 0.9 cm^3 thiosulphate solution. The endpoint was determined to within 0.0001 cm^3 burette resolution.

Results

The reagent blank was determined with distilled water on two different days and found to be (0.0033±0.0019) cm^3 (n = 4) on 2 May 2008 and (0.0019±0.0013) cm^3 (n = 6) on 7 May 2008. Since both values were statistically indistinguishable and since the same set of reagents was used for the whole cruise, we used the overall average of (0.0025±0.0016) cm^3 as reagent blank. The oxygen content of the reagents was assumed to be 76 nmol and corrected for [*Dickson*, 1996]

The thiosulphate concentration was determined on 11 days spread over the cruise with typical 6 replicates. The initial result (based on a KIO_3 concentration of 2.336 mmol dm^{-3}) showed an apparent decrease of the concentration of the thiosulphate solution from 0.2018 to 0.2014 mol dm^{-3}, equivalent to 0.18 % (Fig. 1a). Though small, this behaviour was against our experience that the thiosulphate solution tends to be stable or if it changes, it tends to increase in strength with time (for unknown reasons).

We therefore compared the concentration of the KIO_3 solution remaining after the cruise against a set of fresh KIO_3 solutions, prepared gravimetrically from the same KIO_3 reference material. We found that the KIO_3 solution remaining after the cruise had a concentration of

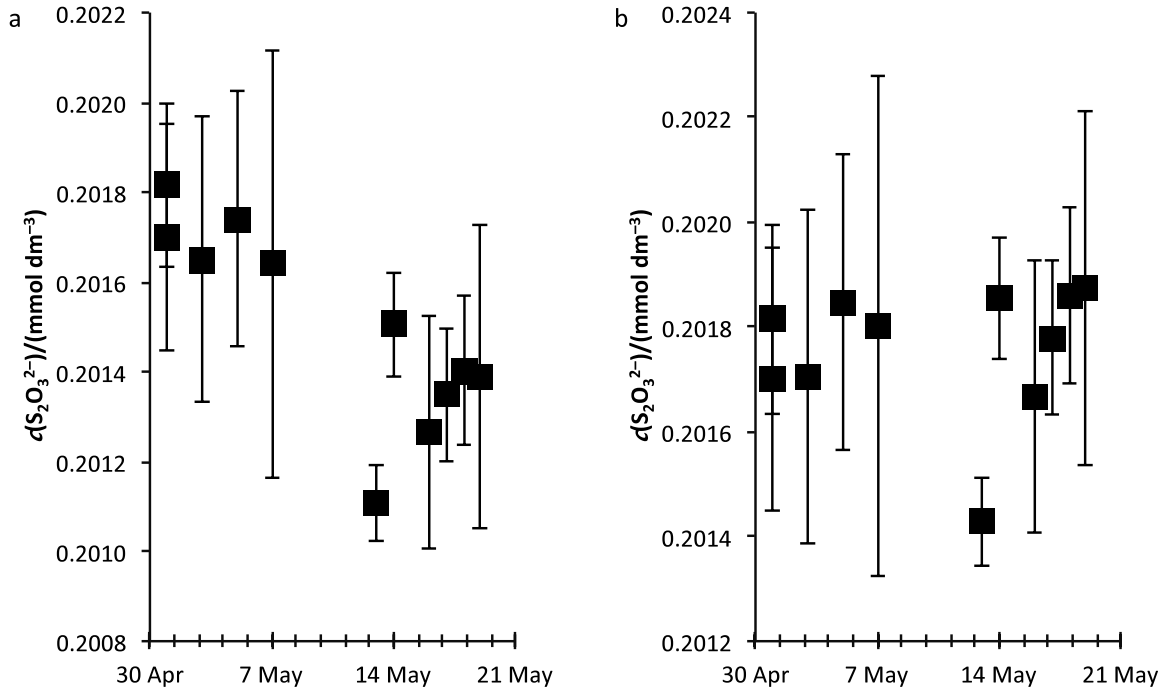

Fig. 1. a) Thiosulphate concentration based on initial gravimetric KIO_3 concentration of 2.336 mmol dm^{-3}. b) Thiosulphate concentration, corrected for linear increase of the KIO3 concentration from 2.336 mmol dm^{-3} (pre-cruise) to 2.342 mmol dm^{-3} (post-cruise).

2.342 mmol dm^{-3} and therefore apparently had gained in strength by 0.24 %. This explained the apparent decrease of the thiosulphate concentration. Assuming that the change in KIO_3 concentration occurred linearly with time, the inferred thiosulphate concentrations are stable during the cruise (Fig. 1b). We decided to use the arithmetic average of all standard titrations and adopted a thiosulphate concentration of (0.2018±0.0001) mol dm^{-3} for the titration of all unknown samples.

The unknown samples were determined in triplicate and duplicate. This was very helpful to remove obvious outliers. After outlier removal, the average standard deviation for the replicates was 0.28 µmol kg^{-1} (minimum 0.01 µmol kg^{-1}, maximum 1.6 µmol kg^{-1}), corresponding to a relative precision of 0.10 %. The concentrations ranged from 192 to 316 µmol kg^{-1}.

References:

Culberson, C. H. (1991), Dissolved oxygen, in *WOCE Operations Manual - Part 3.1.3: WHP Operations and Methods. WHP Office Report WHPO 91-1. WOCE Report No. 68/91. Revision 1*, edited, Woods Hole, Massachusetts, USA.

Dickson, A. (1996), Determination of dissolved oxygen in sea water by Winkler titration. Version 1.01, in *WOCE Operations Manual - Part 3.1.3: WHP Operations and Methods. WHP Office Report WHPO 91-1. WOCE Report No. 68/91. Revision 1*, edited, Woods Hole, Massachusetts, USA.