

### 4.3 Oxygen sampling

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Leg 1 D285



Dissolved oxygen samples were drawn from Niskin bottles on each stainless CTD cast, bar those taken for thorium samples, and analysed using the Winkler whole bottle titration method. One duplicate sample was drawn on each cast from a randomly selected Niskin bottle after all other samples had been taken.

Samples were drawn through short pieces of silicone tubing into clear, pre-calibrated (approximately 100ml) wide-necked glass bottles. The temperature of each sample was taken using a handheld temperature probe immediately prior to fixing on deck with 1ml manganous chloride and 1ml sodium hydroxide. These chemicals were dispensed using Anachem dispensers, which were periodically rinsed throughout the cruise. The temperature at fixing of each of the samples was later used to calculate any temperature dependent changes in the volume of the sample bottles. After fixing, the lid of the sample bottles was inserted, taking care to ensure that no air bubbles were introduced, and the bottles shaken thoroughly. The samples were then taken to the CT (controlled temperature) laboratory, whereupon they were shaken once more, and then stored for later analysis. All reagents were prepared after Dickson (1994).

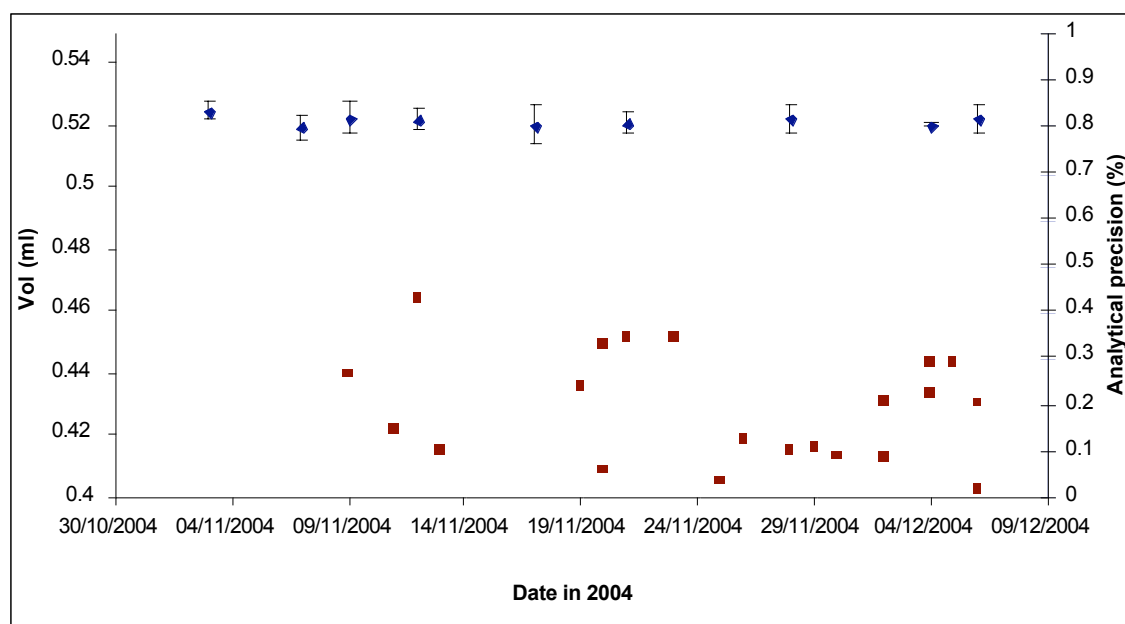
Analysis of the samples started at a minimum of one hour after the collection of the samples. The SIS Winkler whole bottle titration method with spectrophotometric endpoint was used for analysis. Immediately prior to titration, each sample was acidified with 1ml of sulphuric acid (using an Anachem dispenser) in order to dissolve the precipitate and stirred with a magnetic stir bar.

The user variable parameters in the SIS supplied software, (parameters screen in the options menu), were determined by trial and error at the start of the cruise and applied throughout. The following values were used: Stepsize 10, Wait time, 10, Fast delay, 3, Slow delay 3, Fast factor 0.5. This parameter set resulted in titration times of less than four minutes.

One batches of sodium thiosulphate solution ( $25\text{gL}^{-1}$ ) was made up at the start of the cruise. As the thiosulphate solution is unstable, it was standardised by titrating it against 5ml of certified standard 0.01N solution of potassium iodate. This was done every 5-7 days; the volume of thiosulphate required to titrate 5ml of this standard was then used in calculations of oxygen concentration in an MS Excel spreadsheet following the equations of Dickson (1994). Figure 1 shows the volume of thiosulphate required to titrate the reference iodate solution on each day a calibration was performed. The reagent blank was evaluated at the start of the cruise and was found to be  $1.0 \times 10^{-3}$  ml. This value was applied to all calculations undertaken.

The duplicate samples drawn at each station were compared and the percentage difference between them is also shown in figure 1, for a sample size of 22 pairs of duplicates. The mean percentage difference between duplicate samples is 0.2% and improved with time consistent with more experienced operators. Precision is weakly correlated with Niskin

number with low Niskin numbers having the poorest precision. This is consistent with ingassing of oxygen into undersaturated samples on deck once the niskin tap was undone.



**Fig. 4.2.** Volume of sodium thiosulphate used to titrate 5mls of certified standard of potassium iodate over the duration of the cruise (blue diamonds), error bars are the standard deviation of five replicate samples. Also shown is the time course of analytical precision evaluated from the duplicate samples (brown squares).

#### Leg 2 D286

A new batch of thiosulphate was prepared in Port Elizabeth. This was standardised on three occasions during the cruise. The individual volumes, together with the mean, standard deviation and relative standard deviation, of thiosulphate required to titrate 5ml of 0.01N KIO<sub>3</sub> on each of the determinations is shown below. The replication was good and the thiosulphate did not appear to degrade with time.

Date	Thiovol1	Thiovol2	Thiovol3	Thiovol4	Thiovol5	Mean thiovol	Stdev thiovol	RSD
	ml	ml	ml	ml	ml	ml	ml	%
20/12/2004	0.4613	0.468	0.4679	0.4665	0.4677	0.4663	0.0028	0.6108
31/12/2004	0.4626	0.4637	0.4632	0.4652	0.4629	0.4635	0.0010	0.2208
16/1/2005	0.4592	0.4656	0.4649	0.4669	0.4677	0.4649	0.0033	0.7200

#### Duplicates

One bottle per cast was duplicated. The results of the analyses of these duplicates are shown below. The mean difference between duplicates was 1.3 umol/l which equates to 0.5% of the mean oxygen concentration in the duplicate bottles analysed.

Cast	Niskin	Conc 1 umol/l	Conc 2 umol/l	Difference umol/l	Difference/ Mean %
15549	23	250.4	250.3	0.08	0.03
15553	12	296.2	294.5	1.73	0.59
15556	1	212.2	213.4	1.17	0.55
15557	9	194.5	194.0	0.53	0.27
15562	7	187.6	186.1	1.56	0.83
15565	23	318.4	316.9	1.42	0.45
15570	3	270.7	271.5	0.71	0.26
15573	13	222.3	222.3	0.06	0.03
15582	14	236.6	235.2	1.43	0.61
15584	14	265.3	263.7	1.58	0.60
15585	21	292.9	288.4	4.48	1.54
15586	14	305.4	305.5	0.1	0.03
15587	6	201.6	201.3	0.28	0.14
15596	14	227.1	228.1	0.99	0.44
15606	10	179.9	179.6	0.24	0.13
15614	2	201.5	199.4	2.05	1.02
15620	8	292.5	293.1	0.65	0.22
15623	4	286.9	287.4	0.51	0.18
15628	20	307.8	313.6	5.8	1.87
15632	15	301.4	300.7	0.74	0.25
Mean				1.3	0.50

#### 4.4 CTD calibration

Raymond Pollard

##### Salinity calibration for stainless CTD

Four separate conductivity cells potentially needed calibration, two each on the titanium and stainless CTDs. Salinities were mostly within a few ppm of salinometer derived values so calibrations were applied only to salinity, not conductivity. On most stainless CTD casts four to eight calibration samples were drawn, trying to use depths where vertical salinity gradients were weak. Comparisons of bottle values (botsal) with sensor 1 (sal1 - mounted on the tail) and sensor 2 (sal2 - mounted within the frame) suggested that sal1 should be reduced by 0.002. After this correction, salinity differences are shown in Table 4.2

**Table 4.2 Salinity calibration statistics**

Difference	no. in sample	outliers omitted	mean	standard deviation
botsal - sal1	184	24	0.0009	0.0022
botsal - sal2	177	31	0.0001	0.0018
sal1 - sal2	633	5	-0.0004	0.0014

Note that the standard deviation of within-cast scatter for sal1-sal2 is less than for botsal-sal1 or botsal-sal2, suggesting that the bottle samples have wider scatter than the instruments, probably because of sampling errors. Fig. 4.3a shows the offsets after correction against pressure for the primary salinity sensor. There is a suggestion that the offset should be further corrected by 0.001 at the surface down to  $-0.001$  at 4000m. However, the scatter in Fig. 4.3b against cast convinced us not to do this. The large positive offsets at the end are the result of a poor calibration for one box of samples, because of rising temperature in the salinometer room. Also there are few sample values deeper than 3500 dbar.

The cast to cast offsets in sal1-sal2 (Fig. 4.3c) are caused by changes in the secondary sensor sal2. As this is mounted within the frame, it is subject to offsets resulting from water trapped by the frame, so is not used except as backup, and so has not been calibrated. However, after the first few casts, sal1-sal2 remains close to zero for nearly all casts and depths, confirming that no calibration beyond the  $-0.002$  offset in sal1 is justified. Overall, we estimate that the 0.002 standard deviation given in the table is an upper limit to the accuracy of sal1, much of this being errors in the bottle values.

#### Salinity calibration for titanium CTD

To minimize potential iron contamination, no salinity samples were drawn from the titanium CTD. However, TiCTD casts were almost always associated with ssCTD casts close by in space and time at the major iron and productivity stations. We therefore attempted cross-calibration by comparing adjacent casts. The casts were merged on pressure, or potential temperature. Density cannot be used, as any error in salinity will affect density. Potential temperature proved the more useful parameter on which to merge, as internal waves can offset profiles at all depths. Above 2200 dbar, the difference in the primary salinity sensors was not stable at the 0.001 level, varying by typically  $\pm 0.002$  as the pressure difference varied. Below 2200 dbar however, there was less than 0.001 variation with depth, and comparative values are given in Table 4.3

By eye, we conclude that the titanium CTD primary salinity is correct at the 0.001 level. Plots of the primary-secondary salinities indicated that sal1-sal2 had similar standard deviation to the ssCTD (Table 4.2) and a mean of 0.006. Thus sal2 is too low by 0.006. This correction was not made.

**Table 4.3 Cross calibration of titanium to stainless rosette salinities and oxygens**

SsCTD	TiCTD	ss-tiSal for p > 2200 dbar		ss-tiOxy for p > 2200 dbar		
		mean	std devn	mean	std devn	correction
15490	15491	-0.0007	0.0005	23.6	0.3	+24
15494	15496	~-0.0005		~23.5		+24
15500	15499	max press 305 dbar				+24
15504	15502	-0.0003	0.0004	23.7	0.3	+24
15507	15511	0.0001	0.0019	28.2	0.9	+28
15518	15516	max press 507 dbar				+30
15525	15524	max press 500 dbar				+30
15525	15526	-0.0004	0.0010	29.9	0.4	+30
15532	15534	max press 1000 dbar				+30
15538	15537	0.0005	0.0003	30.1	0.2	+30
15544	15543	0.0000	0.0004	28.0	0.3	+28

Oxygen calibration for stainless CTD

On the ssCTD oxygen samples were drawn for calibration at most depths. After chemical analysis, the bottle oxygen values were converted from  $\mu\text{Mol/l}$  to  $\mu\text{Mol/kg}$  using the fixing temperature. Fig. 4.4a shows the scatter plot of (bottle oxygen – CTD oxygen) plotted against CTD oxygen. The mean and standard deviation of bot-CTDOxy for all values in the range  $-5$  to  $20 \mu\text{Mol/kg}$  was  $5.9 \pm 2.9 \mu\text{Mol/kg}$ . Linear regression suggested a correction to the CTD oxygen values oxygen (corrected) =  $1.7 + 1.01626 * \text{oxygen } \mu\text{Mol/kg}$  and this has been made in Fig. 4.4b. This reduced mean, but the standard deviation only marginally, to  $0.2 \pm 2.6 \mu\text{Mol/kg}$ . On reexamination, the slope has probably been overestimated because of the high outliers at high oxygen values, and post-cruise recalibration could slightly improve the calibration. Similarly, plotting the corrected oxygen differences against station number (Fig. 4.4c) indicates station to station changes of order  $\pm 2 \mu\text{Mol/kg}$ . Nevertheless, overall the CTD oxygens are remarkably good, with errors of order 2 in 200, or 1%.

Oxygen calibration for titanium CTD

Even more than for salinity, drawing oxygen samples from the titanium rosette would pose a serious contamination risk to the iron sampling, so cross calibration was attempted as for salinity as summarized in Table 4.3. No variation of oxygen calibration with depth could be determined because of variations of up to  $5 \mu\text{Mol/kg}$  with pressure difference and pressure for pressures less than 2200 dbar, though there was some evidence for such drift. Below 2200 dbar, Table 4.3 shows differences ranging from 23.6 to  $30.1 \mu\text{Mol/kg}$ , although the cast to cast differences in the stainless CTD values (corrected as above) may contribute. The offset corrections shown in the last column of Table 4.3 have been made to all data files for each cast.

Fluorimeter calibration

None was done during the cruise.