CTD Calibration Report for R/V Oceanus 401-1 prepared by Margaret Cook Woods Hole Oceanographic Institution

I.1 Cruise Summary

Ship: R/V Oceanus 401-1 Project Name: Site W Dates: 28 April 2004 – 07 May 2004 Ports: Woods Hole – Woods Hole

18 CTD stations Rosette salts and dissolved oxygen

I.2 Digital data files included as part of this distribution:

320C401.doc This document in MS-Word format.

32OC401.SEA This file follows WOCE specifications for bottle data. Salt and oxygen quality words have been entered.

32OC401.SUM The SUM file contains the CTD station information using WOCE format.

*.*CTD* One 2db averaged file per station following the WOCE format specification for CTD profiles. All CTD salt and oxygen has been calibrated to the bottle salt and oxygen. CTD temperature are based on pre-cruise calibrations. CTD pressure are based on pre-cruise calibrations.

II. Finalized Description of Measurements

II.1 CTD Measurements

18 casts were made using a SeaBird 911plus CTD measuring pressure, temperature, conductivity, and oxygen current. For each cast, water samples were collected at discrete intervals and analyzed for salinity and dissolved oxygen – primarily for the purpose of calibrating the CTD sensors. All casts were full water column.

II.1.a Difficulties Encountered

CTD stations 1-18 were not collected in chronologicial order. The CTD operations schedule was adjusted to allow mooring operations to occur during daylight hours and calm weather conditions.

CTD stations were collected in the following order :

[12, 11, 9, 8, 7, 6, 5, 4, 3, 2, 1, 10, 13, 14, 15, 16, 17, 18] This order defines a transect incrementing from station 1 at the continental shelf to station 18 at the furthest extent southeast on the site W line.

(Note: tIn he ship's log stations are numbered chronologically and sequentially 1:18)

The secondary conductivity cell (S/N 2362) intermittently behaved badly below 1000 db after the collection of station 11. It was replaced by conductivity cell (S/N 2707) before station 10. Primary conductivity (S/N 2147) and primary temperature (S/N 4148) were used to calibrate the entire cruise since both perfomed well and without incident.

- There are no water sample salinities for station 8 as bottles were inadvertently reused before being analyzed.
- ∠ All water sample oxyens for station 5 are clearly bad.

II.1.b Equipment Configuration

A SeaBird 911plus CTD was used throughout the cruise. It was provided with a Digiquartz with TC pressure transducer S/N 69685, two temperature sensors S/N 4148 and S/N 2271, two conductivity sensors S/N 2147 and S/N 2362, and one SBE43 oxygen sensor S/N 0264. Calibrations for all CTD sensors were performed by the manufacturer before the cruise. The CTD was also provided with a Wetlab ECO-AFL/FL flourometer (S/N 013), a Chelsea/Seatech/Wetlab Cstar transmissometer (S/N 537DR), an OBS Seapoint Turbidity meter (S/N 1661), and an altimeter (S/N 639).

Primary conductivity sensor S/N 2362 was used for the entire cruise.

Secondary conductivity sensor S/N 2362 deteriorated during the first part of the cruise and was replaced by conductivity sensor S/N 2707. Stations 1 through 9, 11 and 12 (which occurred during the first part of the cruise) were collected with secondary conductivity sensor S/N 2362. Stations 10 and 13 through 18 (which occurred during the latter part of the cruise) were collected with secondary conductivity sensor S/N 2707.

The pylon was controlled through a dedicated personal computer using SeaBird's software SEASOFT.

A rosette frame was provided for the cruise. The frame held 24 4-liter bottles produced at WHOI.

II.1.c Acquisition and Processing Methods

Data from the CTD were acquired at 24 hz. The CTD data were acquired by an SBE Model 11 plus CTD Deck Unit providing demodulated data to a personal computer running SeaBird software. SEASAVE version 5.30b CTD acquisition software (SeaBird) provided graphical data to the screen. Bottom approach was controlled by real time altimeter data and ship provided ocean depth information.

After each station, the CTD data was run through SeaBird data conversion software listed in Table 2. The data was first-differenced, lag corrected, pressure sorted and centered into 2 decibar bins for final data quality control and analysis, including fitting to water sample salinity and oxygen results. WHOI post-processing software after Millard and Yang, 1993.

| SeaBird Module | Description (SeaBird, 2001) |
|----------------|--|
| DATCNV | Convert the raw data to pressure, temperature, conductivity, and dissolved oxygen current. |

Table 2. SeaBird Processing Software

| ROSSUM | Reads in a .ROS file created by DATCNV and writes out a summary of |
|----------------|---|
| | the bottle data to a file with a .BTL extension. |
| ALIGNCTD | Advance conductivity approximately 0.073 seconds relative to |
| | pressure. |
| WILDEDIT | Checks for and marks and 'wild' data points: first pass 2.0 standard |
| | deviations; second pass 20 standard deviations. |
| CELLTM | Conductivity cell thermal mass correction alpha = 0.03 and 1/beta = |
| | 7.0. |
| FILTER | Low pass filter conductivity with a time constant of approximately 0.03 |
| | seconds. Filter pressure with a time constant of 0.15 seconds to |
| | increase pressure resolution for LOOPEDIT. |
| LOOPEDIT | Mark scans where the CTD is moving less than the minimum velocity |
| | (0.1 m/s) or traveling backwards due to ship roll. |
| DERIVE oxy.cfg | Compute oxygen from oxygen current, temperature, and pressure. |
| BINAVG | Average data into the 2 dbar pressure bins. |
| DERIVE sal.cfg | Compute salinity. |
| STRIP | Extract columns of data from .CNV files. |
| TRANS | Change .CNV file format from ASCII to binary. |
| SPLIT | Split .CNV file into upcast and downcast files. |

II.1.d Summary of manufacture CTD Calibrations

All sensors were calibrated by the manufacturer. A listing of sensors and calibration dates are presented in Table 3.

| I doite of believe | Cumbration Dutest | <u>.</u> | · · · · · · · · · · · · · · · · · · · |
|--------------------|-------------------|-------------------------|---------------------------------------|
| Sensor Number | Sensor Type | Manufacturer | Calibration Dates |
| 69685 | pressure | Paroscientific/Sea-Bird | 18 Dec 2002 |
| 4148 | temperature | Sea-Bird | 10 Jan 2004 |
| 2271 | temperature | Sea-Bird | 18 Oct 2003 |
| 2147 | conductivity | Sea-Bird | 01 Nov 2003 |
| 2362 | conductivity | Sea-Bird | 01 Nov 2003 |
| 2707 | conductivity | Sea-Bird | 27 Feb 2003 |
| 0264 | SBE43 dissolved | Sea-Bird | 04 Mar 2004 |
| | oxygen | | |

Table 3. Sensor Calibration Dates.

II.1.e Summary of CTD Calibrations

PRESSURE CALIBRATION

The pressure bias of the CTD at the sea surface was monitored at the beginning of each station to make sure there was no significant drift in the calibration.

CONDUCTIVITY CALIBRATION

Basic fitting procedure:

The CTD primary conductivity sensor data was fit to the water sample conductivity. All stations (except station 8 which had no rosette water sample salinity data) were grouped together in chronological order to find the best fit. The group was fit for slope and bias. A linear pressure term (modified beta) was applied to conductivity slopes using a least-squares minimization of CTD and bottle conductivity differences. The function minimized was:

$$BC - m * CC - b - \beta * CP$$

| where | BC | - bottle conductivity [mS/cm] |
|-------|----|--|
| | CC | - pre-cruise calibrated CTD conductivity [mS/cm] |
| | CP | - CTD pressure [dbar] |
| | m | - conductivity slope |
| | b | - conductivity bias [mS/cm] |
| | ? | - linear pressure term [mS/cm/dbar] |

The slope term is a polynomial function of the station numberbased upon chronological station collection order. The polynomial function which provided the lowest standard deviation for a group of samples along with the corresponding bias were determined for each station grouping. A series of fits were made, each fit removing outliers having a residual greater than three standard deviations. This procedure was repeated with the remaining bottle values until no more outliers occurred. The best fit coefficients for each station grouping are presented in Table 4a for sensor 2147. Fits to primary conductivity and temperature were applied to the final data.

The final conductivity, FC [mS/cm] is:

$$FC = m * CC + b + \beta * CP$$

Data Quality

Calibrated, the overall standard deviation of the CTD and the water sample differences for S/N2147 was .0008932. Fits to the two secondary conductivity sensors were not used because the quality of the primary sensor data was excellent and that of the first of the two secondary conductivity sensors was so poor.

| Table 4a. | Best Fit | Conductivity | Coefficients for | Conductivity | ^v S/N 2147 |
|-----------|----------|--------------|-------------------------|--------------|-----------------------|
|-----------|----------|--------------|-------------------------|--------------|-----------------------|

| | | • | | | | |
|----------|------|-------|---------|-------|------|------|
| Stations | #pts | total | std dev | Slope | Bias | Beta |
| | used | #pts | (mS/cm) | | | |
| | | | | | | |

| Fit as a group in | 260 | 324 | 0.0037 | | | |
|----------------------|-----|-----|--------|------------|-------------|----------------|
| chronological order | | | | | | |
| [12 11 9:1 10 13:18] |] | | | | | |
| 1 | | | | 1.00018641 | -0.00805375 | 2.44516274e-07 |
| 2 | | | | 1.00018332 | -0.00805375 | 2.44516274e-07 |
| 3 | | | | 1.00018007 | -0.00805375 | 2.44516274e-07 |
| 4 | | | | 1.00017665 | -0.00805375 | 2.44516274e-07 |
| 5 | | | | 1.00017306 | -0.00805375 | 2.44516274e-07 |
| 6 | | | | 1.00016930 | -0.00805375 | 2.44516274e-07 |
| 7 | | | | 1.00016537 | -0.00805375 | 2.44516274e-07 |
| 8 | | | | 1.00016128 | -0.00805375 | 2.44516274e-07 |
| 9 | | | | 1.00015701 | -0.00805375 | 2.44516274e-07 |
| 10 | | | | 1.00018932 | -0.00805375 | 2.44516274e-07 |
| 11 | | | | 1.00015258 | -0.00805375 | 2.44516274e-07 |
| 12 | | | | 1.00014798 | -000.805375 | 2.44516274e-07 |
| 13 | | | | 1.00019207 | -0.00805375 | 2.44516274e-07 |
| 14 | | | | 1.00019465 | -0.00805375 | 2.44516274e-07 |
| 15 | | | | 1.00019706 | -0.00805375 | 2.44516274e-07 |
| 16 | | | | 1.00019930 | -0.00805375 | 2.44516274e-07 |
| 17 | | | | 1.00020137 | -0.00805375 | 2.44516274e-07 |
| 18 | | | | 1.00020328 | -0.00805375 | 2.44516274e-07 |

OXYGEN CALIBRATION

Basic fitting procedure

The CTD oxygen sensor variables were fit to water sample oxygen data to determine the six parameters of the oxygen algorithm (Millard and Yang, 1993). The oxygen calibration was performed after temperature and conductivity calibrations due to its weak dependence on the CTD pressure, temperature, and conductivity (salinity). A FORTRAN program oxfitmrx.exe

developed by Millard and Yang (1993) was encorporated into matlab routines by Millard (2004) for use in processing ctd oxygens using matlab. Matlab mfiles created by Jane Dunworth were used for determining the oxygen calibration coefficients using Millard's routines. The program uses the following algorithm developed by Owens and Millard (1985) for converting oxygen sensor current and temperature measurements with the time rate of change of oxygen current measurements to oxygen concentration. The weight was set to 0 as the new SBE43 oxygen sensor temperature is not measured and is assumed to be the same as the in situ temperature. The lag was set to 0 as per manufacturer recommendation.

$$Oxm = \left[slope * \left(Oc + lag * \frac{dOc}{dt}\right) + bias\right] * Oxsat * \exp\left(tcor * \left[T + wt * \left(T_o - T\right)\right] + pcor * P\right)\right]$$

| where | Oxm | - oxygen concentration [ml/l] |
|-------|-------|--|
| | Oc | - oxygen current [uA/s] |
| | Oxsat | - oxygen saturation [] |
| | Р | - CTD pressure [dbar] |
| | Т | - CTD temperature [°C] |
| | To | - oxygen sensor temperature [°C] |
| | S | - salinity [PSS-78, psu] |
| | slope | - oxygen current slope [] |
| | lag | - oxygen sensor lag [s] |
| | bias | - oxygen current bias [] |
| | tcor | - membrane temperature correction [] |
| | wt | - weight, membrane temperature sensitivity adjustment [] |
| | pcor | - correction for hydrostatic pressure effects |
| | | |

Data Quality

CTD oxygen calibrations were revisited in May/June 2007 following an in depth analysis by Ruth Curry of rosette oxygen data quality for all Line W cruises to date. Quality words were reset for rosette oxygen data before performing new residual fits to the data. Stations which did not already show adequate correlation between theta/oxygen CTD and rosette data, were refit to the more closely quality controlled rosette data. Many stations were fit independently

Stations were calibrated in seven separate groups (A through G) as indicated in the oxygen coefficients table (see Table 5). A station/time dependent fit for BI, SL, Pcor and Tcor was done to station groups A, C, D, and E. Groups B,F and G represent fits to individual stations for BI, SL, Pcor and Tcor. Calibrated, the overall standard deviation of the CTD and water samples differences for all data was 0.0321. The standard deviations for each independent fitting group are noted in the table below.

| Table 5. | Best Fit | Coefficients | for | Oxvgen | Sensor | 0264. |
|----------|-----------------|--------------|-----|--------|--------|-------|
|----------|-----------------|--------------|-----|--------|--------|-------|

| Group | A: | [12 11 9 8 7 6 5 4] | sta/time dependent | fit | std=0.0203 |
|-------|----|----------------------|--------------------|-----|------------|
| Group | в: | [3] BI SL PCOR TCOR | individual station | fit | std=0.135 |
| Group | C: | [2 1 10 13] | sta/time dependent | fit | std=0.109 |
| Group | D: | [13:15] | sta/time dependent | fit | std=0.0231 |
| Group | E: | [16:17] | sta/time dependent | fit | std=0.0871 |
| Group | F: | [18] BI SL PCOR TCOR | individual station | fit | std=0.046 |
| Group | G: | [10] BI SL PCOR TCOR | individual station | fit | std=0.0311 |

| | Bias | slope | tcor pcor | sta # |
|---|---------------|--------------|---------------------------|------------|
| А | -0.5304297605 | 0.3862195576 | 0.000141659164811 0.0004 | 637777 12 |
| А | -0.5302381191 | 0.3862195576 | 0.000141659164811 0.0004 | 637777 11 |
| А | -0.5295006911 | 0.3862195576 | 0.000141659164811 0.0004 | 637777 9 |
| А | -0.5293521953 | 0.3862195576 | 0.000141659164811 0.0004 | 637777 8 |
| А | -0.5292294802 | 0.3862195576 | 0.000141659164811 0.0004 | 637777 7 |
| А | -0.5291134868 | 0.3862195576 | 0.000141659164811 0.0004 | 637777 6 |
| А | -0.5287593416 | 0.3862195576 | 0.000141659164811 0.0004 | 637777 5 |
| А | -0.5286674425 | 0.3862195576 | 0.000141659164811 0.0004 | 637777 4 |
| В | -0.6549716997 | 0.5669571047 | -8.75379995133e-005 -0.02 | 51268494 3 |
| С | -0.5558918752 | 0.3843763149 | 0.000144837080016 0.0015 | 172586 2 |
| С | -0.5554355137 | 0.3843763149 | 0.000144837080016 0.0015 | 172586 1 |
| D | -0.5621846928 | 0.3867198910 | 0.000146325734404 0.0022 | 797623 13 |
| D | -0.5601887303 | 0.3867198910 | 0.000146325734404 0.0022 | 797623 14 |
| D | -0.5584429049 | 0.3867198910 | 0.000146325734404 0.0022 | 797623 15 |
| Е | -0.5518973580 | 0.3868852019 | 0.000144956018125 0.0019 | 164599 16 |
| Е | -0.5518973580 | 0.3868852019 | 0.000144956018125 0.0019 | 164599 17 |
| F | -0.5518973580 | 0.3868852019 | 0.000144956018125 0.0019 | 164599 18 |
| G | -0.5805123648 | 0.3882186095 | 0.000150153150939 0.0020 | 631686 10 |

Note: CTD oxygen data for station 3 was interpolated to rosette data between 796 and 900db and flagged as bad deeper than 900db.

II.1.f Other notable data acquisition/processing issues

At-sea logs were kept for CTD data acquisition. They include anything of note regarding each station: equipment changes, instrument behavior, equipment or operational problems.

II.2 Salinity and Dissolved Oxygen Measurements contributed by Dave Wellwood

II.2.a Summary

Water samples were collected from every bottle during this cruise for the determination of salinity and dissolved oxygen. The primary purpose of these measurements were to accurately calibrate the sensors on the CTD.

II.2.b Salinity

Water was collected in 200 ml glass bottles. The bottles were rinsed twice, and then filled to the neck. Samples were transferred to the shore based laboratory for analysis. Samples were analyzed at sea within 24 hrs of collection. After the samples reached the lab temperature of 22°C, they were analyzed for salinity using a Guildline Autosal Model 8400B salinometer (WHOI #11, serial #59210). The salinometer was standardized once a day using IAPSO Standard Seawater Batch P-143 (dated 26 Feb 2003). The Autosal worked flawlessly and showed virtually no drift during the entire analysis. Conductivity readings were logged automatically to a computer, salinity was calculated and merged with the CTD data, and finally used to update the CTD calibrations. Accuracies of salinity measurements were ± 0.002 psu.

II.2.c. Dissolved Oxygen

Measurements were made using a modified Winkler technique similar to that described by Strickland and Parsons (1972). Each seawater sample was collected in a 150 ml brown glass Tincture bottle. When reagents were added to the sample, iodine was liberated which is proportional to the dissolved oxygen in the sample. Samples were analyzed within 24 hours of collection. A carefully measured 50-ml aliquot was collected from the prepared oxygen sample and titrated for total iodine content. Titration was automated using a PC controller and a Metrohm Model 665 Dosimat buret. The titration endpoint was determined amperometrically using a dual plate platinum electrode, with a resolution better than 0.001 ml. Accuracy was about 0.02 ml/l, with a standard deviation of replicate samples of 0.005. This technique is described more thoroughly by Knapp et al (1990). Calculated oxygen was merged with the CTD data, and used to update the CTD calibrations. Standardization of the sodium thiosulphate titrant was performed before analysis. The titration apparatus worked flawlessly, and no unusual problems were noted.

III. References

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