



# Preliminary Cruise Report 5 October 2005

Data Submitted by:

Shipboard Technical Support/Oceanographic Data Facility Kristin M. Sanborn, Teresa Kacena, Dan G. Schuller Shipboard Technical Support/Shipboard Electronics Group Carl Mattson, Scott Hiller, Bob Green Shipboard Technical Support/Computing Resources Frank Delahoyde Scripps Institution of Oceanography La Jolla, Ca. 92093-0214

## Summary

A hydrographic survey consisting of LADCP/CTD/rosette sections, underway shipboard ADCP, XCTD profiling, float and drifter deployments in the southeast Pacific was carried out August to October 2005. The R/V Knorr departed Punta Arenas, Chile on 21 August 2005. A total of 135 LADCP/CTD/rosette stations were occupied, 399 XCTDs were launched, 13 ARGO floats and 20 surface drifters were deployed from 23 August - 5 October. Water samples (up to 24), LADCP, and CTD data were collected on each cast in most cases to within 10 meters of the bottom. Salinity, dissolved oxygen and nutrient samples were analyzed for up to 24 water samples from each cast of the principal LADCP/CTD/rosette program. Water samples were also measured for CO2 and CFCs, and underway surface pCO2, N2O, temperature, conductivity, oxygen, and meteorological measurements were made. The cruise ended in Puerto Montt, Chile on 6 October 2005.

#### Introduction

Antarctic Intermediate Water (AAIW) is a low salinity water mass that fills most of the southern hemisphere and the tropical oceans at about 800 to 1000 m depth. As the densest of the circumpolar Subantarctic Mode Waters (SAMW), AAIW is formed as a thick, outcropping mixed layer in the southeastern Pacific just north of the Subantarctic Front (SAF). SAMW and AAIW formation have a major impact on the oceanic sink for anthropogenic CO2, whose largest uncertainty is at intermediate depths. The goal of Knorr cruise 182-07 was to characterize the wintertime AAIW formation processes. A follow-on summer hydrographic survey of the AAIW outcropping region and the fronts that bound it is scheduled for January to March 2006.

A sea-going science team gathered from three oceanographic institutions participated on the cruise. Several other science programs were supported with no dedicated cruise participant. The science team and their responsibilities are listed below.

ffiliation	email
ffiliation	email
CSD/SIO	tchereskin@ucsd.edu
CSD/SIO/STS	cmattson@ucsd.edu
CSD/SIO/STS	scott@odf.ucsd.edu
CSD/SIO/STS	bobg@odf.ucsd.edu
CSD/SIO/STS	fdelahoyde@ucsd.edu
CSD/SIO/STS	ksanborn@ucsd.edu
CSD/SIO/STS	dan@odf.ucsd.edu
CSD/SIO/STS	teresa@odf.ucsd.edu
CSD/SIO	sescher@ucsd.edu
CSD/SIO	jafghan@ucsd.edu
CSD/SIO	jafghan@ucsd.edu
CSD/SIO	ganderson@ucsd.edu
CSD/SIO	brcarter@ucsd.edu
CSD/SIO	jholte@ucsd.edu
CSD/SIO	ylenn@ucsd.edu
CSD/SIO	brcarter@ucsd.edu
CSD/SIO	jholte@ucsd.edu
CSD/SIO	ylenn@ucsd.edu
SMAS	jhappell@rsmas.miami.edu
SMAS	fleece@eritter.net
. Concepcion	mauricio@profc.udec.cl
J. Concepcion	victor@profc.udec.cl
J. Concepcion	eduardo@dgeo.udec.cl
/HOI	sssg@knorr.whoi.edu
	SD/SIO SD/SIO SD/SIO SD/SIO SD/SIO SD/SIO SMAS Concepcion Concepcion Concepcion HOI

#### Personnel

Scientific Personnel AAIW 2005

Analysis	Institution	Principal Investigator	
CTDO/S/O <sub>2</sub> /Nutrients	UCSD/SIO	Lynne Talley	Italley@ucsd.edu
		James H. Swift	jswift@ucsd.edu
Transmissometer	TAMU	Wilf Gardner	wgardner@tamu.edu
CO <sub>2</sub> -Alkalinity	UCSD/SIO	Andrew Dickson	adickson@ucsd.edu
CO <sub>2</sub> -DIC	UCSD/SIO	Andrew Dickson	adickson@ucsd.edu
CFCs	RSMAS-UMiami	Rana Fine	rfine@rsmas.miami.edu
ADCP/LADCP	UCSD/SIO	Teresa Chereskin	tchereskin@ucsd.edu
ARGO Floats	UCSD/SIO	Dean Roemmich	droemmich@ucsd.edu
CTD/XCTD/satellite data	UC	Samuel Hormazabal	sam@profc.udec.cl
Underway pCO <sub>2</sub>	UC	Osvaldo Ulloa	oulloa@profc.udec.cl
		Samuel Hormazabal	lfarias@profc.udec.clk
pCO <sub>2</sub> drifter	MBARI	Francisco Chavez	chfr@mbari.org

## **Principal Programs**

Principal Programs of AAIW 2005

## **Cruise Narrative**

The Knorr departed Punta Arenas, Chile on 21 August 2005 at 0900 local. Almost immediately we hove to for repairs on the starboard steering, which was not functioning when we left the dock. The repairs took about 8 hours during which time the various groups finished testing equipment and tying down gear. We also took the opportunity to deploy a shallow test cast in the Straits of Magellan. The other serious problem that was discovered in Punta Arenas was that the wire on both winches had only one good conductor. We used the starboard one for the duration of the survey. The condition of the wire influenced our choice of a 24-place over a 36-place rosette and dictated conservative wire speeds for this cruise. Another major factor influencing wire speed was wire tension, especially during times when we had several sets of large swells coming from multiple directions.

During AAIW, CTD stations at roughly 50 km spacing were supplemented by XCTD sampling every 15 to 20 km. Generally, three XCTDs were launched between CTD stations. Additionally, two intensive surveys were carried out in regions of deep mixed layers, steaming a diamond pattern centered on the main AAIW track, with dense XCTD sampling throughout and CTD stations at the corners. The first intensive survey began after CTD station 9, triggered by deep mixed layers (400 m) observed at stations 6 and 7. We turned back and steamed a diamond pattern centered on station 7, with CTD stations 8, 10, 6, and 11 located at the corners. The second intensive survey was triggered by crossing the Subantarctic Front (station 14). We turned back to survey the deep mixed layers north of the front. We again steamed a diamond pattern, centered on station 13, with CTD stations 14, 15, 12, and 16 at the corners. Surface drifters were deployed at the corners of the intensive surveys, accounting for 8 of our 20 deployments.

In total we made 6 crossings of the Subantarctic Front (SAF) and 2 crossings of the Polar Front (PF). Microwave SST images made for our region by Lynne Talley and downloaded from the internet were very helpful in tracking the fronts. Based on a 1980 cruise by McCartney, we anticipated that the first pair of SAF crossings along 77W and 79W, nearest to Drake Passage, would have the deepest mixed layers. In fact, we found equally deep mixed layers on the second pair of SAF crossings, located near/on the 89W meridian. The 89W PF crossing was our furthest south, to 62S.

The third pair of SAF crossings was our furthest west, meant to measure the SAMW upstream condition. ARGO floats supplied by Dean Roemmich (SIO) were deployed at predetermined sites, with the first deployments made along this section of our track. It was also along this portion of our survey that we encountered our heaviest seas and winds. The steaming speed fell below 9kts and our wire speed was often limited to 20 m/s for the upper 1500 m. From station 62 to 69, our station spacing was increased from 50 km to 100 km in order to keep on schedule, and the density of XCTDs was increased to compensate. However, strong and gusty winds (above 50 kts) were often the cause of XCTD cast failure along the westward line from station 62 to station 70. Finally, at station 70, conditions were deemed

unsafe for deployment and we have to for 24 hours until winds and seas abated. Sea cable reterminations were required after several of these stations to remove wire kinks caused by snap loading of the wire by ship roll/heave.

Our weather improved from stations 77 to 92, but from 92 to 100 we again encountered high winds and swell as we continued east towards the Chilean coast. However, we maintained 50 km station spacing, closer at the coast. From the coast, we transited back to pick up our line northward along 89W. The 89W line repeats the 1980 McCartney cruise line, as does our final eastward segment to the coast along 45S. On our final eastward segment we replaced 3 stations with XCTD casts, because of time constraints.

Science operations halted at 1000 local on 5 October 2005 to begin the 26 hour steam to Puerto Montt, which required making rendezvous with pilot boats at two locations for our final transit through Chilean coastal waters.

The science parties and the officers and crew of the Knorr are to be commended for their hard work and careful measurements. A CDROM of preliminary data obtained within the Chilean EEZ was produced and given to the Chilean observer/participating scientist, Eduardo Navarro.

#### **Description of Measurement Techniques**

#### 1. CTD/Hydrographic Measurements Program

The basic CTD/hydrographic measurements consisted of salinity, dissolved oxygen and nutrient measurements made from water samples taken on CTD/rosette casts, plus pressure, temperature, salinity, dissolved oxygen and transmissometer from CTD profiles. A total of 136 CTD/rosette casts were made usually to within 10 meters of the bottom. No major problems were encountered during the operation. The distribution of samples is illustrated in figure 1.0 - 1.8.



Figure 1.0 Sample distribution, stations 1-21.



Figure 1.1 Sample distribution, stations 21-33.



Figure 1.2 Sample distribution, stations 33-44.



Figure 1.3 Sample distribution, stations 44-62.



Figure 1.4 Sample distribution, stations 62-70.







Figure 1.6 Sample distribution, stations 77-109.



200 300 400 500 600 700 800 Distance (km) Figure 1.8 Sample distribution, stations 118-136.

900

1000

1100

## 1.1. Water Sampling Package

100

6000 <sup>-</sup>0

LADCP/CTD/rosette casts were performed with a package consisting of a 24-bottle rosette frame (ODF), a 24-place pylon (SBE32) and 24 10-liter Bullister bottles (ODF). Underwater electronic components consisted of a Sea-Bird Electronics (SBE) 9*plus* CTD (ODF #796) with dual pumps, dual temperature (SBE3*plus*), dual conductivity (SBE4), dissolved oxygen (SBE43) and transmissometer (Wetlabs C-Star); an SBE35RT Digital Reversing Thermometer, an RDI LADCP (Broadband 150khz) and a Simrad altimeter.

The CTD was mounted vertically in an SBE CTD frame attached to the bottom center of the rosette frame. The SBE4 conductivity and SBE3*plus* temperature sensors and their respective pumps were mounted vertically as recommended by SBE. Pump exhausts were attached to inside corners of the CTD cage and directed downward. The entire cage assembly was then mounted on the bottom ring of the

rosette frame, offset from center to accommodate the pylon, and also secured to frame struts at the top. The SBE35RT temperature sensor was mounted vertically and equidistant between the T1 and T2 intakes. The transmissometer was mounted horizontally along the rosette frame adjacent to the CTD. The altimeter was mounted on the outside of the bottom frame ring. The LADCP was vertically mounted inside the bottle rings on the opposite side of the frame from the CTD. The locations of bottles 16, 17 and 18 were adjusted to accommodate the LADCP.

The rosette system was suspended from a UNOLS-standard three-conductor 0.322" electro-mechanical sea cable. The R/V Knorr's starboard-side Markey winch was used for all casts. It was discovered at the beginning of the cruise that the two sea cables on board had only a single functional conductor each. Sea cable reterminations were made prior to casts 22/1, 70/1, 71/1, 73/1 and 110/1. Cast 75/1 was aborted at 212m on the downcast due to sea conditions.

The deck watch prepared the rosette 10-20 minutes prior to each cast. The bottles were cocked and all valves, vents and lanyards were checked for proper orientation. Once stopped on station, the LADCP was turned on and the rosette moved into position under the starboard-side squirt boom using an airpowered cart and tracks. The CTD was powered-up and the data acquisition system in the main lab started when directed by the deck watch leader. Tag lines were threaded through the rosette frame, and syringes were removed from the CTD intake ports. The winch operator was directed by the deck watch leader to raise the package, the boom and rosette were extended outboard and the package quickly lowered into the water. The tag lines were removed and the package was lowered to 10 meters, by which time the sensor pumps had turned on. The winch operator was then directed to bring the package back to the surface (0 winch wireout) and to begin descent. The entry procedure was frequently modified as dictated by weather and sea conditions and for many casts no attempt was made to return close to the surface prior to descent.

Each rosette cast was usually lowered to within 10 meters of the bottom, using the altimeter to determine a safe distance.

On the up cast the winch operator was directed to stop at each bottle trip depth. The CTD console operator waited 30 seconds before tripping a bottle to insure the package wake had dissipated and the bottles were flushed, then an additional 10 seconds after receiving the trip confirmation to allow the SBE35RT temperature sensor time to make a measurement. The winch operator was then directed to proceed to the next bottle stop.

Sea conditions were sufficiently poor toward the end of several casts that no stops were made shallower than 200m. In these cases, the rosette was hauled at a constant rate (20m/min) and the remaining bottles closed "on-the-fly". These bottles have a quality code of "4" (did not trip correctly) associated with them and are well-documented.

Standard sampling depths were used throughout AAIW 2005, depending on the overall water depth (table 1.1.0). These standard depths were staggered every other station.

Recovering the package at the end of the deployment was essentially the reverse of launching, with the additional use of poles and snap-hooks to attach tag lines, and air-tuggers on the tag lines for added safety and stability. The rosette was moved into the forward hangar for sampling. The bottles and rosette were examined before samples were taken, and anything unusual noted on the sample log.

Each bottle on the rosette had a unique serial number. This bottle identification was maintained independently of the bottle position on the rosette, which was used for sample identification. Six bottles were replaced on this cruise, and various parts of bottles were occasionally changed or repaired.

Routine CTD maintenance included soaking the conductivity and DO sensors in fresh water between casts to maintain sensor stability. Rosette maintenance was performed on a regular basis. O-rings were changed as necessary and bottle maintenance was performed each day to insure proper closure and sealing. Valves were inspected for leaks and repaired or replaced as needed.

(1)	top bottle within sight of the surface
(2)	bottom bottle within 10 meters of bottom
(3)	0-about 500 meters: spacing no greater than 50-60 meters
(4)	500-800 meters: spacing no greater than 100 meters
(5)	800-1200 meters: spacing no greater than 200 meters
(6)	1200-2000 meters: spacing no greater than 350 meters
(7)	2000-bottom: spacing no greater than 500 meters
(8)	bottom of SAMW: resolve the property break with one
	bottle above and one below if the layer is obvious (within
	50 meters of break)
(9)	AAIW if obvious salinity minimum (north of SAF): try to hit
	the minimum
(General)	Stagger the sampling so that sample depths are not
	exactly the same from one to the next.

 Table 1.1.0 AAIW 2005 water sampling guidelines.

## 1.2. Underwater Electronics Packages

CTD data were collected with a SBE9*plus* CTD (ODF #769). This instrument provided pressure, dual temperature (SBE3), dual conductivity (SBE4), dissolved oxygen (SBE43), transmissometer (Wetlabs SeaStar) and altimeter (Simrad 807 or 1007) channels. The CTD supplied a standard SBE-format data stream at a data rate of 24 frames/second (fps).

Sea-Bird SBE32 24-place Carousel Water Sampler	S/N 3223219-0320
Sea-Bird SBE35RT Digital Reversing Thermometer	S/N 35-0034
Sea-Bird SBE9 <i>plus</i> CTD	S/N 09P39801-0796
Paroscientific Digiquartz Pressure Sensor	S/N 98627
Sea-Bird SBE3 <i>plus</i> Temperature Sensor	S/N 03P-4486 (Primary)
Sea-Bird SBE3 <i>plus</i> Temperature Sensor	S/N 03P-4476 (Secondary)
Sea-Bird SBE4C Conductivity Sensor	S/N 04-3023 (Primary)
Sea-Bird SBE4C Conductivity Sensor	S/N 04-3002 (Secondary, 1/1-72/1)
Sea-Bird SBE4C Conductivity Sensor	S/N 04-2319 (Secondary, 73/1-136/1)
Sea-Bird SBE43 DO Sensor	S/N 43-0872 (1/1-32/1, 35/1)
Sea-Bird SBE43 DO Sensor	S/N 43-0185 (33/1-34/1, 36/1, 37/1-136/1)
Wetlabs Sea-Star Transmissometer	S/N 327DR (owned by TAMU)
Roll and Pitch Sensor	S/N SBE13-475
Accelerometer Sensor	S/N SBE13-471
Simrad 807 Altimeter	S/N 9711090
Simrad 1007 Altimeter	S/N 20174
RDI Broadband 150khz LADCP S	S/N 1394
LADCP Battery Pack	

 Table 1.2.0 AAIW 2005
 Rosette Underwater Electronics.

The CTD was outfitted with dual pumps. Primary temperature, conductivity and dissolved oxygen were plumbed on one pump circuit and secondary temperature and conductivity on the other. The sensors were deployed vertically. The primary temperature and conductivity sensors (T1 #03P-4486 and C1 #04-3023) were used for reported CTD temperatures and conductivities on all casts. The secondary temperature and conductivity sensors were used for calibration checks.

The SBE9*plus* CTD and SBE35RT temperature sensor were both connected to the SBE32 24-place pylon providing for single-conductor sea cable operation. The sea cable armor was used for ground (return). Power to the SBE9*plus* CTD (and sensors), SBE32 pylon, SBE35RT and Simrad 807 altimeter was provided through the sea cable from the SBE11*plus* deck unit in the main lab.

Navigation data were acquired at 1-second intervals from the ship's C-Nav GPS receiver by one of the Linux workstations beginning August 21. Data from the ship's Knudsen 320B/R Echosounder (12 KHz transducer) were also acquired and merged with the navigation. The Knudsen bathymetry data were noisy and subject to washing out when the seas were choppy or the ship's bow thruster engaged.

Bathymetric data from the ship's multibeam echosounder system (Seabeam 2000) were also logged and archived independently.

# 1.4. CTD Data Acquisition and Rosette Operation

The CTD data acquisition system consisted of an SBE-11*plus* (V2) deck unit and three networked generic PC workstations running Fedora Core Linux. Each PC workstation was configured with a color graphics display, keyboard, trackball and DVD+RW drives. One of the three systems also had 8 additional RS-232 ports via a Comtrol Rocketport PCI serial controller. The systems were connected through a 100BaseTX ethernet switch, which was also connected to the ship's network. These systems were available for real-time operational and CTD data displays, and provided for CTD and hydrographic data management and backup.

One of the workstations was designated the CTD console and was connected to the CTD deck unit via RS-232. The CTD console provided an interface and operational displays for controlling and monitoring a CTD deployment and closing bottles on the rosette.

CTD deployments were initiated by the console watch after the ship had stopped on station. The watch maintained a console operations log containing a description of each deployment, a record of every attempt to close a bottle and any pertinent comments. The deployment and acquisition software presented a short dialog instructing the operator to turn on the deck unit, examine the on screen CTD data displays and to notify the deck watch that this was accomplished.

Once the deck watch had deployed the rosette, the winch operator would begin the descent. When permitted by sea conditions, the rosette was lowered to 10 meters, raised back to the surface then lowered for the descent. This procedure was adopted to allow the immersion-activated sensor pumps time to start and flush the sensors.

Profiling rates were frequently dictated by sea conditions but never exceeded 60m/minute.

The progress of the deployment and CTD data quality were monitored through interactive graphics and operational displays. Bottle trip locations were decided and transcribed on the console and sample logs. The sample log would later be used as an inventory of samples drawn from bottles.

The combination of altimeter distance, CTD depth, winch wire-out and echo-sounder depth provided reliable, precise control of package distance from the bottom and allowed routine approaches to within 10 meters.

Bottles were closed on the up cast by operating an on-screen control. The winch operator was given a target wire-out for the bottle stop, proceeded to that depth and stopped. Bottles were tripped at least 30 seconds after stopping to allow the rosette wake to dissipate and the bottles to flush. The winch operator was instructed to proceed to the next bottle stop at least 10 seconds after closing bottles to allow the SBE35RT calibration temperature sensor time to make a measurement.

After the last bottle was tripped, the console watch directed the deck watch to bring the rosette on deck. Once on deck, the console watch terminated the data acquisition, turned off the deck unit and assisted with rosette sampling.

# 1.5. CTD Data Processing

The shipboard CTD data acquisition was the first stage in shipboard processing. The raw CTD data were converted to engineering units, filtered, response-corrected, calibrated and decimated to a more manageable 0.5 second time-series. The laboratory calibrations for pressure, temperature and conductivity were applied at this time. The 0.5 second time-series data were used for real-time graphics during deployments, and were the source for CTD pressure and temperature associated with each rosette bottle. Both the raw 24hz data and the 0.5 second time-series were stored for subsequent processing

## steps.

At the completion of a deployment a series of processing steps were performed automatically. The 0.5 second time-series data were checked for consistency, clean sensor response and calibration shifts. A 2 decibar pressure-series was then generated from the up cast. The up cast data were selected because of missing near-surface down cast data in many of the deployments due to sea conditions. Both the 2 decibar pressure-series and 0.5 second time-series data were then made available for downloading, plotting and reporting on the shipboard cruise website.

CTD data were routinely examined for sensor problems, calibration shifts and deployment or operational problems. The primary and secondary temperature sensors (SBE 3) were compared to each other and to the SBE35 temperature sensor. CTD conductivity sensors (SBE 4) were compared and calibrated by examining differences between CTD and check-sample conductivity values. The CTD dissolved oxygen sensor data were calibrated to check-sample data. Additional deep TS and theta- $O_2$  comparisons were made between down and up casts as well as with adjacent deployments. Vertical sections were made of the various properties derived from sensor data and checked for consistency.

A total of 136 casts were made (including 1 aborted cast). The 24-place 10-liter rosette and CTD #796 were used on all casts.

## 1.6. CTD Sensor Laboratory Calibrations

Laboratory calibrations of the CTD pressure, temperature, conductivity, dissolved oxygen and the SBE35RT Digital Reversing Thermometer sensors were performed prior to AAIW 2005. The calibration dates are listed in table 1.6.0.

Sensor	S/N	Calibration Date	Calibration Facility
Paroscientific Digiquartz Pressure	98627	7-July-05	SIO/ODF
Sea-Bird SBE3plus T1 Temperature	03P-4486	7-July-05	SIO/ODF
Sea-Bird SBE3plus T2 Temperature	03P-4476	7-July-05	SIO/ODF
Sea-Bird SBE4C C1 Conductivity	04-3023	14-July-05	SBE
Sea-Bird SBE4C C2 Conductivity	04-3002	14-July-05	SBE
Sea-Bird SBE4C C2 Conductivity	04-2319	04-March-05	SBE
Sea-Bird SBE43 Dissolved Oxygen	43-872	N/A	SBE
Sea-Bird SBE43 Dissolved Oxygen	43-848	N/A	SBE
Sea-Bird SBE35RT Digital Reversing Thermometer	35-0034	18-May-05	SIO/ODF

Table 1.6.0 AAIW 2005 CTD sensor laboratory calibrations.

## 1.7. CTD Shipboard Calibration Procedures

CTD #796 was used for all AAIW 2005 casts. The CTD was deployed with all sensors and pumps aligned vertically, as recommended by SBE. The primary temperature and conductivity sensors (T1 & C1) were used for all reported CTD data on all casts. The secondary temperature and conductivity sensors (T2 & C2) served as calibration checks for the primary sensors. The SBE35RT Digital Reversing Thermometer (S/N 35-0034) served as an independent calibration check. *In-situ* salinity and dissolved  $O_2$  check samples collected during each cast were used to calibrate the conductivity and dissolved  $O_2$  sensors.

## 1.7.1. CTD Pressure

The Paroscientific Digiquartz pressure transducer (S/N 98627) was calibrated in July 2005 at the SIO/STS Calibration Facility. Calibration coefficients derived from the calibration were applied to raw pressures during each cast. Residual pressure offsets (the difference between the first and last submerged pressures) were examined to check for calibration shifts. All were < 0.5db, and the sensor exhibited < 0.2 db offset shift over the period of use. No additional adjustments were made to the calculated pressures.

### 1.7.2. CTD Temperature

A single primary temperature sensor (SBE 3, S/N 03P-4486) and secondary temperature sensor (SBE 3, S/N 03P-4476) served the entire cruise. Calibration coefficients derived from the pre-cruise calibrations were applied to raw primary and secondary temperatures during each cast.

Two independent metrics of calibration accuracy were examined. The primary and secondary temperatures were compared at each rosette trip, and the SBE35RT temperatures were compared to primary and secondary temperatures at each rosette trip.

Calibration accuracy was first examined by tabulating T1-T2 over a range of pressures (bottle trip locations) for each cast. These comparisons are summarized in figure 1.7.2.0.





The SBE35RT Digital Reversing Thermometer is an internally-recording temperature sensor that operates independently of the CTD. It is triggered by the SBE32 pylon in response to a bottle trip. According to the Manufacturer's specifications the typical stability is 0.001°C/year. The differences between the SBE35RT and T1 (primary CTD temperature) are summarized in figure 1.7.2.1, and between the SBE35RT and T2 (secondary CTD temperature) in figure 1.7.2.2.





Figure 1.7.2.1 SBE35RT-T2 by station, p>2000db.

The SBE35RT used on AAIW 2005 was calibrated in May 2005 at which time it was reported to have < -0.0002°C correction over the entire operating range. The sensor was used for a 40-day cruise prior to AAIW 2005 during which it exhibited a -0.00082 °C offset relative to the CTD sensors. Evidently the SBE35RT began to drift significantly on 67/1. Examining casts 1/1-66/1, the mean differences are -0.0017988°C for SBE35RT-T1 and -0.0020826°C for SBE35RT-T2. Since T1 and T2 had been calibrated more recently (July 2005) than the SBE35RT, had not been used prior to AAIW 2005 since calibration and had a mean calibrated difference of -0.00023°C the SBE35RT differences were only used to check for calibration shifts. No additional corrections were applied to either T1 or T2 temperatures.

Post-cruise calibrations for all the temperature sensors are pending.

## 1.7.3. CTD Conductivity

A single primary conductivity sensor (SBE 4, S/N 04-3023) and two secondary conductivity sensors (SBE 4, S/N 04-3002 1/1-72/1, S/N 04-2319 73/1-136/1) served the entire cruise. Conductivity sensor calibration coefficients derived from the pre-cruise calibrations were applied to raw primary and secondary conductivities.

Comparisons between the primary and secondary sensors and between each of the sensors to check sample conductivities (conductivity calculated from bottle salinities) were used to derive conductivity corrections. None of the sensors showed any appreciable conductivity slope. The second C2 sensor used (04-2319) showed a slight (9.65e-8mS/cm/db) pressure slope. C1 was determined to have a slight drift amounting to a +0.0021 mS/cm offset change over the cruise. This drift correction was actually applied in 5 separate groupings as determined by secondary sensor and bottle conductivity differences. C2 #3002 had a constant offset of -0.0012mS/cm relative to corrected C1. C2 #2319 had a constant offset of -0.00012mS/cm for casts 73/1-109/1, and +0.00066mS/cm for 110/1-136/1 relative to corrected C1.

The comparison of the primary and secondary conductivity sensors by station, after applying shipboard corrections, is summarized in figure 1.7.3.0.



Figure 1.7.3.0 C1 and C2 conductivity differences by cast, p>2000db.

Salinity residuals after applying shipboard T1/C1 corrections are summarized in figures 1.7.3.1 through 1.7.3.3.



Figure 1.7.3.1 salinity residuals by pressure, all pressures.



Figure 1.7.3.2 salinity residuals by cast, all pressures.



Figure 1.7.3.3 salinity residuals by cast, p>2000db.

Figure 1.7.3.3 represents an estimate of the deep salinity accuracy on AAIW 2005. The 95% confidence limit is  $\pm 0.0018$  PSU relative to the bottle salts.

## 1.7.4. CTD Dissolved Oxygen

Two SBE43 dissolved  $O_2$  (DO) sensor were used during this cruise: S/N 43-0872 (1/1-32/1, 34/1-35/1) and 43-0848 (33/1, 36/1-136/1). The sensor was plumbed into the primary T1/C1 pump circuit after C1. Sensor 0872 was replaced prior to 33/1 because of diminishing sensor response. Problems with the sensor cable on 33/1 rendered the DO data unusable, and 0872 was returned to service for two more casts.

The DO sensors were calibrated to dissolved  $O_2$  check samples at bottle stops by calculating CTD dissolved  $O_2$  then minimizing the residuals using a non-linear least-squares fitting procedure. The fitting procedure determined the calibration coefficients for the sensor model conversion equation, and was accomplished in stages. The time constants for the exponential terms in the model were first determined for each sensor. These time constants are sensor-specific but applicable to an entire cruise. Next, casts were fit individually to check sample data. The resulting calibration coefficients were then smoothed and held constant during a refit to determine sensor slope and offset.

Standard and blank values for bottle oxygen data were smoothed and the bottle oxygen recalculated prior to the final fitting of CTD oxygen.

The residuals are shown in figures 1.7.4.0-1.7.4.2.





The standard deviations of 0.97 uM/kg for all oxygens and 0.74 uM/kg for deep oxygens are only presented as general indicators of goodness of fit. ODF makes no claims regarding the precision or

#### accuracy of CTD dissolved O2 data.

The general form of the ODF  $O_2$  conversion equation for Clark cells follows Brown and Morrison [Brow78] and Millard [Mill82], [Owen85]. ODF models membrane and sensor temperatures with lagged CTD temperatures and a lagged thermal gradient. *In-situ* pressure and temperature are filtered to match the sensor response. Time-constants for the pressure response  $\tau_p$ , two temperature responses  $\tau_{Ts}$  and  $\tau_{Tf}$ , and thermal gradient response  $\tau_{dT}$  are fitting parameters. The thermal gradient term is derived by low-pass filtering the difference between the fast response ( $T_f$ ) and slow response ( $T_s$ ) temperatures. This term is SBE43-specific and corrects a non-linearity introduced by analog thermal compensation in the sensor. The  $O_c$  gradient,  $dO_c/dt$ , is approximated by low-pass filtering 1st-order  $O_c$  differences. This gradient term attempts to correct for reduction of species other than  $O_2$  at the sensor cathode. The time-constant for this filter,  $\tau_{og}$ , is a fitting parameter. Dissolved  $O_2$  concentration is then calculated:

$$O_{2m//l} = [c_1 O_c + c_2] \cdot f_{sat}(S, T, P) \cdot e^{(c_3 P_l + c_4 T_l + c_5 T_s + c_6 \frac{dO_c}{dt} + c_7 dT)}$$
(1.7.4.0)

where:

O <sub>2ml/l</sub>	= Dissolved O <sub>2</sub> concentration in ml/l;
O <sub>c</sub>	= Sensor current (µamps);
$f_{sat}(S,T,P)$	= $O_2$ saturation concentration at S,T,P (ml/l);
S	= Salinity at O <sub>2</sub> response-time (PSUs);
Т	= Temperature at O <sub>2</sub> response-time (°C);
Ρ	= Pressure at O <sub>2</sub> response-time (decibars);
Pı	= Low-pass filtered pressure (decibars);
$T_f$	= Fast low-pass filtered temperature (°C);
T <sub>s</sub>	= Slow low-pass filtered temperature (°C);
$\frac{dO_c}{dt}$	= Sensor current gradient (µamps/secs);
dŤ	= low-pass filtered thermal gradient $(T_f - T_s)$ .

## 1.8. Bottle Sampling

At the end of each rosette deployment water samples were drawn from the bottles in the following order:

- CFCs
- O<sub>2</sub>
- Dissolved Inorganic Carbon (DIC)
- Total Alkalinity
- Nutrients
- Salinity
- Nitrous Oxide

The correspondence between individual sample containers and the rosette bottle position (1-24) from which the sample was drawn was recorded on the sample log for the cast. This log also included any comments or anomalous conditions noted about the rosette and bottles. One member of the sampling team was designated the *sample cop*, whose sole responsibility was to maintain this log and insure that sampling progressed in the proper drawing order.

Normal sampling practice included opening the drain valve and then the air vent on the bottle, indicating an air leak if water escaped. This observation together with other diagnostic comments (e.g., "lanyard caught in lid", "valve left open") that might later prove useful in determining sample integrity were routinely noted on the sample log. Drawing oxygen samples also involved taking the sample draw temperature from the bottle. The temperature was noted on the sample log and was sometimes useful in determining leaking or mis-tripped bottles.

Once individual samples had been drawn and properly prepared, they were distributed for analysis. Oxygen, nutrient and salinity analyses were performed on computer-assisted (PC) analytical equipment networked to the data processing computer for centralized data management.

## 1.9. Bottle Data Processing

Water samples collected and properties analyzed shipboard were managed centrally in a relational database (PostgreSQL-8.0.3) run on one of the Linux workstations. A web service (OpenAcs-5.1.5 and AOLServer-4.0.10) front-end provided ship-wide access to CTD and water sample data. Web-based facilities included on-demand arbitrary property-property plots and vertical sections as well as data uploads and downloads.

The Sample Log (and any diagnostic comments) was entered into the database once sampling was completed. Quality flags associated with sampled properties were set to indicate that the property had been sampled, and sample container identifications were noted where applicable (e.g., oxygen flask number). Each Sample Log was also scanned and made available as a JPEG file on the website.

Analytical results were provided on a regular basis by the various analytical groups and incorporated into the database. These results included a quality code associated with each measured value and followed the coding scheme developed for the World Ocean Circulation Experiment (WOCE) Hydrographic Programme (WHP) [Joyc94].

Sea conditions were sufficiently poor at the end of several deployments that no bottle stops were made shallower than 200m. In these cases, the rosette was hauled at a constant rate (20m/min) and the remaining bottles closed "on-the-fly". These bottles have a quality code of "4" (did not trip correctly) associated with them and are well-documented.

Various consistency checks and detailed examination of the data continued throughout the cruise. The individual sample comments are included in Appendix A.

## 1.10. Salinity Analysis

## **Equipment and Techniques**

Two Guildline Autosal Model 8400A salinometers (S/N 57-526 & S/N 53-503), located in the 01 lab, were used for all salinity measurements. The salinometers were modified by ODF to contain an interface for computer-aided measurement. The water bath temperatures were set and maintained at a value near the laboratory air temperature. They were set to 21°C for stations 1-92 and 118-124 analyses, then switched to 24°C for stations 92-117 and 121-134.

The salinity analyses were performed after samples had equilibrated to laboratory temperature, usually within 8-26 hours after collection. The salinometers were standardized for each group of analyses (usually 1-2 casts, up to ~48 samples) using at least two fresh vials of standard seawater per group. Salinometer measurements were made by computer, where the analyst was prompted by software to change samples and flush.

## Sampling and Data Processing

3114 salinity measurements were made and approximately 280 vials of standard water (SSW) were used.

Salinity samples were drawn into 200 ml Kimax high-alumina borosilicate bottles, which were rinsed three times with sample prior to filling. The bottles were sealed with custom-made plastic insert thimbles and Nalgene screw caps. This assembly provides very low container dissolution and sample evaporation. Prior to sample collection, inserts were inspected for proper fit and loose inserts replaced to insure an airtight seal. The draw time and equilibration time were logged for all casts. Laboratory temperatures were logged at the beginning and end of each run.

PSS-78 salinity [UNES81] was calculated for each sample from the measured conductivity ratios. The difference (if any) between the initial vial of standard water and the next one run as an unknown was applied as a linear function of elapsed run time to the data. The corrected salinity data were then incorporated into the cruise database. Temperature control was somewhat problematic and a few runs were rendered unusable for calibration purposes because of a lack of temperature stability. The estimated accuracy of bottle salinities run at sea is usually better than  $\pm 0.002$  PSU relative to the particular standard seawater batch used. The 95% confidence limit for residual differences between the bottle salinities and calibrated CTD salinity relative to SSW batch P-145 was  $\pm 0.0037$  PSU for all

### Laboratory Temperature

The temperature in the salinometer laboratory varied from 17.0 to 24.0°C, during the cruise. The air temperature during any particular run varied from -7 to +4.5°C.

#### Standards

IAPSO Standard Seawater (SSW) Batch P-145 was used to standardize for stations 1-122 salinity measurements and IAPSO Standard Seawater Batch P144 was used to standardize for stations 123-134.

#### 1.11. Oxygen Analysis

#### **Equipment and Techniques**

Dissolved oxygen analyses were performed with an ODF-designed automated oxygen titrator using photometric end-point detection based on the absorption of 365nm wavelength ultra-violet light. The titration of the samples and the data logging were controlled by PC software. Thiosulfate was dispensed by a Dosimat 665 buret driver fitted with a 1.0 ml buret. ODF used a whole-bottle modified-Winkler titration following the technique of Carpenter [Carp65] with modifications by Culberson *et al.* [Culb91], but with higher concentrations of potassium iodate standard (~0.012N) and thiosulfate solution (~55 gm/l). Pre-made liquid potassium iodate standards were run once a day approximately every 4 stations, unless changes were made to system or reagents. Reagent/distilled water blanks were determined every day or more often if a change in reagents required it to account for presence of oxidizing or reducing agents. The auto-titrator performed well.

#### Sampling and Data Processing

3126 oxygen measurements were made. Samples were collected for dissolved oxygen analyses soon after the rosette was brought on board. Using a Tygon and silicone drawing tube, nominal 125ml volume-calibrated iodine flasks were rinsed 3 times with minimal agitation, then filled and allowed to overflow for at least 3 flask volumes. The sample drawing temperatures were measured with a small platinum resistance thermometer embedded in the drawing tube. These temperatures were used to calculate uM/kg concentrations, and as a diagnostic check of bottle integrity. Reagents were added to fix the oxygen before stoppering. The flasks were shaken twice (10-12 inversions) to assure thorough dispersion of the precipitate, once immediately after drawing, and then again after about 20 minutes.

The samples were analyzed within 1-12 hours of collection, and the data incorporated into the cruise database.

Thiosulfate normalities were calculated from each standardization and corrected to 20°C. The 20°C normalities and the blanks were plotted versus time and were reviewed for possible problems.

The blanks and thiosulfate normalities for each batch of thiosulfate were smoothed (linear fits) in three groups during the cruise and the oxygen values recalculated.

A noisy endpoint was occasionally acquired during the analyses, usually due to small waterbath contaminations. These endpoints were checked and recalculated using STS/ODF designed software.

## Volumetric Calibration

Oxygen flask volumes were determined gravimetrically with degassed deionized water to determine flask volumes at STS/ODF's chemistry laboratory. This is done once before using flasks for the first time and periodically thereafter when a suspect volume is detected. The volumetric flasks used in preparing standards were volume-calibrated by the same method, as was the 10 ml Dosimat buret used to dispense standard iodate solution.

## Standards

Liquid potassium iodate standards were prepared in 6 liter batches and bottled in sterile glass bottles at STS/ODF's chemistry laboratory prior to the expedition. The normality of the liquid standard was determined at ODF by calculation from weight. Two standard batches were used during AAIW 2005. Potassium iodate was obtained from Acros Chemical Co. and was reported by the supplier to be 98% pure. The second standard was supplied by Alfa Aesar and has a reported purity of 99.4-100.4%. Tests at ODF indicate no difference between these 2 batches. All other reagents were "reagent grade" and were tested for levels of oxidizing and reducing impurities prior to use.

## 1.12. Nutrient Analysis

## **Equipment and Techniques**

Nutrient analyses (phosphate, silicate, nitrate and nitrite) were performed on an ODF-modified 4-channel Technicon AutoAnalyzer II, generally within one to two hour after sample collection. Occasionally samples were refrigerated up to 4 hours at ~4°C. All samples were brought to room temperature prior to analysis.

The methods used are described by Gordon *et al.* [Gord92]. The analog outputs from each of the four colorimeter channels were digitized and logged automatically by computer (PC) at 2-second intervals.

Silicate was analyzed using the technique of Armstrong *et al.* [Arms67]. An acidic solution of ammonium molybdate was added to a seawater sample to produce silicomolybdic acid which was then reduced to silicomolybdous acid (a blue compound) following the addition of stannous chloride. Tartaric acid was also added to impede  $PO_4$  color development. The sample was passed through a 15mm flowcell and the absorbence measured at 660nm.

A modification of the Armstrong *et al.* [Arms67] procedure was used for the analysis of nitrate and nitrite. For the nitrate analysis, the seawater sample was passed through a cadmium reduction column where nitrate was quantitatively reduced to nitrite. Sulfanilamide was introduced to the sample stream followed by N-(1-naphthyl)ethylenediamine dihydrochloride which coupled to form a red azo dye. The stream was then passed through a 15mm flowcell and the absorbence measured at 540nm. The same technique was employed for nitrite analysis, except the cadmium column was bypassed, and a 50mm flowcell was used for measurement.

Phosphate was analyzed using a modification of the Bernhardt and Wilhelms [Bern67] technique. An acidic solution of ammonium molybdate was added to the sample to produce phosphomolybdic acid, then reduced to phosphomolybdous acid (a blue compound) following the addition of dihydrazine sulfate. The reaction product was heated to ~55°C to enhance color development, then passed through a 50mm flowcell and the absorbence measured at 820nm.

Explicit corrections for *carryover* in nutrient analyses are not made. In a typical AutoAnalyzer system, sample to sample carryover is ~ 1-2% of the concentration difference between samples. This effect is minimized by running samples in order of increasing depth such that concentration differences between samples are minimized. The initial surface samples could be run twice or a low nutrient sea water sample run ahead of the surface sample since these samples generally follow standard peaks.

## Sampling and Data Processing

3126 nutrient samples were analyzed.

Nutrient samples were drawn into 45 ml polypropylene, screw-capped "oak-ridge type" centrifuge tubes. The tubes were cleaned with 10% HCl and rinsed with sample 2-3 times before filling. Standardizations were performed at the beginning and end of each group of analyses (typically one cast, up to 36 samples) with an intermediate concentration mixed nutrient standard prepared prior to each run from a secondary standard in a low-nutrient seawater matrix. The secondary standards were prepared aboard ship by dilution from primary standard solutions. Dry standards were pre-weighed at the laboratory at ODF, and transported to the vessel for dilution to the primary standard. Sets of 7 different standard concentrations were analyzed periodically to determine any deviation from linearity as a function of absorbence for each nutrient analysis. A correction for non-linearity was applied to the final nutrient concentrations when

necessary. A correction for the difference in refractive indices of pure distilled water and seawater was periodically determined and applied where necessary. In addition, a "deep seawater" high nutrient concentration check sample was run with each station as an additional check on data quality. The pump tubing was changed 3 times.

After each group of samples was analyzed, the raw data file was processed to produce another file of response factors, baseline values, and absorbences. Computer-produced absorbence readings were checked for accuracy against values taken from a strip chart recording. The data were then added to the cruise database.

Nutrients, reported in micromoles per kilogram, were converted from micromoles per liter by dividing by sample density calculated at 1 atm pressure (0 db), *in situ* salinity, and a per-analysis measured laboratory temperature.

Some stations showed small yet significant concentrations of NO2 deeper than expected (i.e. ~0.01 uM below the thermocline). These stations were carefully reviewed and included in the final data report. It should be noted, however, that 0.01 uM is at the detection limit of the autoanalyzer system.

## Standards

Primary standards for silicate ( $Na_2SiF_6$ ) and nitrite ( $NaNO_2$ ) were obtained from Johnson Matthey Chemical Co.; the supplier reported purities of >98% and 97%, respectively. Primary standards for nitrate ( $KNO_3$ ) and phosphate ( $KH_2PO_4$ ) were obtained from Fisher Chemical Co.; the supplier reported purities of 99.999% and 99.999%, respectively. The efficiency of the cadmium column used for nitrate was monitored throughout the cruise and ranged from 99-100%.

No major problems were encountered with the measurements. The temperature of the laboratory used for the analyses ranged from  $21.6^{\circ}$ C to  $25.8^{\circ}$ C, but was relatively constant during any one station (±1.5°C).

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# Appendix A: Individual Sample Comments

# Appendix A

This appendix contains remarks for samples and bottles having a quality code of other than "2" (no problem noted).

Individual Sample Comments