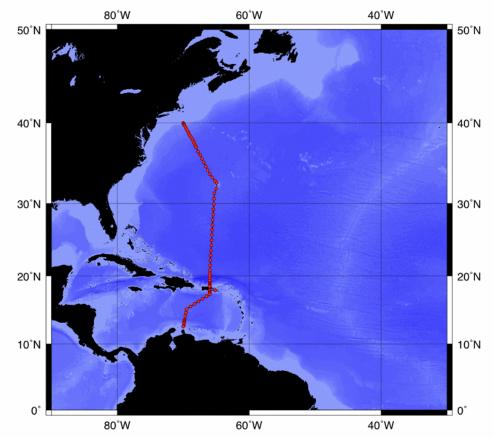
### **CRUISE REPORT: A22**

(Updated JUL 2012)



## Highlights

## **Cruise Summary Information**

WOCE Section Designation	A22
Expedition designation (ExpoCodes)	33AT20120324
Chief Scientists	Ruth Curry / WHOI
Dates	Sat Mar 24, 2012 - Tue Apr 17, 2012
Ship	R/V Atlantis
Ports of call	Woods Hole, Mass Bridgetown, Barbados
	40° 0.68' N
Geographic Boundaries	70° 0.38' W 64° 54.95' W
	12° 36' N
Stations	81
Floats and drifters deployed	0
Moorings deployed or recovered	0

### **Recent Contact Information:**

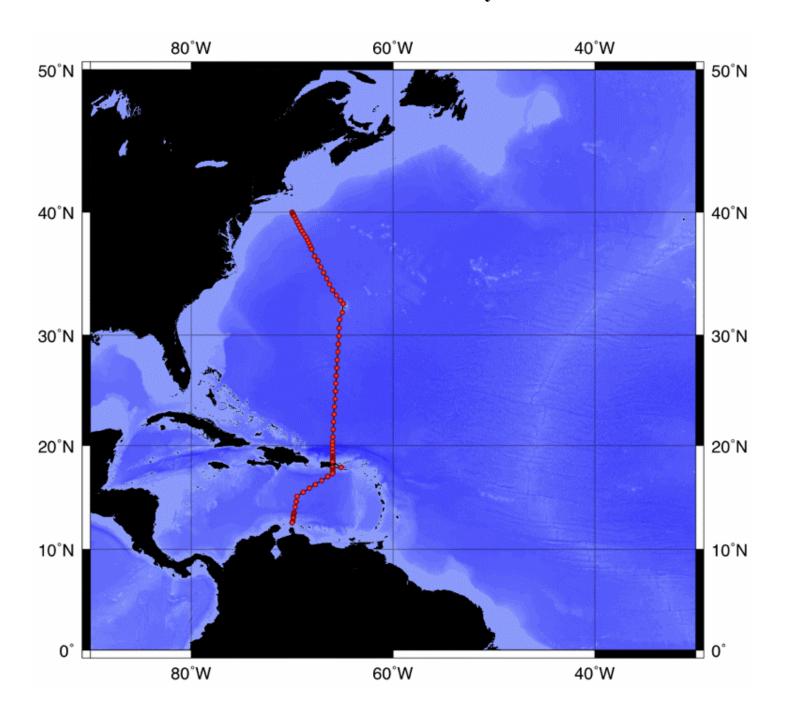
**Ruth Curry •** Woods Hole Oceanographic Institution 266 Woods Hole Rd. • MS# 21 • Woods Hole, MA 02543-1050 Phone: +1 508 289 2799 • Fax: +1 508 457 2181 • Email: rcurry@whoi.edu

## **Links To Select Topics**

Shaded sections are not relevant to this cruise or were not available when this report was compiled.

Cruise Summary Information	Hydrographic Measurements
Description of Scientific Program	CTD Data:
Geographic Boundaries	Acquisition
Cruise Track (Figure): PI CCHDO	Processing
Description of Stations	Calibration
Description of Parameters Sampled	Temperature Pressure
Bottle Depth Distributions (Figure)	Salinities Oxygens
Floats and Drifters Deployed	Bottle Data
Moorings Deployed or Recovered	Salinity
	Oxygen
Principal Investigators	Nutrients
Cruise Participants	Carbon System Parameters
	CFCs
Problems and Goals Not Achieved	Helium / Tritium
Other Incidents of Note	Radiocarbon
Underway Data Information	References
Navigation Bathymetry	
Acoustic Doppler Current Profiler (ADCP)	
Thermosalinograph	
XBT and/or XCTD	
Meteorological Observations	Acknowledgments
Atmospheric Chemistry Data	
Data Processing Notes	

# Station Track • A22 • 2012 • Curry • R/V Atlantis



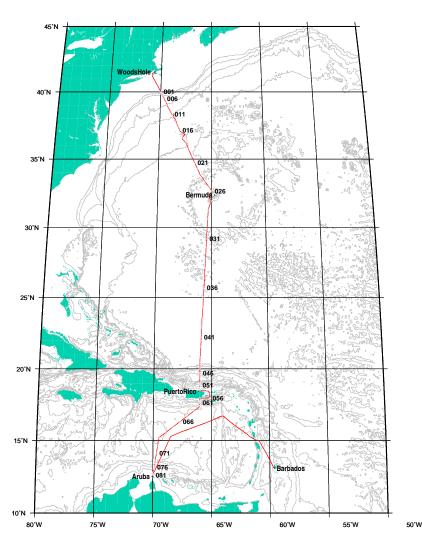
# US Global Ocean Carbon and Repeat Hydrography Program Section CLIVAR A22

RV Atlantis AT20

24 March 2012 - 17 April 2012

Woods Hole, Massachusetts - Bridgetown, Barbados

Chief Scientist: Dr. Ruth Curry Woods Hole Oceanographic Institution Co-Chief Scientist: Dr. Zoltán Szűts Max-Planck-Institut für Meteorologie



Cruise Report 17 April 2012

#### Narrative

#### **Summary**

**Section designation:** CLIVAR A22 **Expedition:** 33AT20120324

Chief Scientist: Ruth Curry, Woods Hole Oceanographic Institution

Ship: R/V Atlantis 20-01A

Ports: Woods Hole, MA - Bridgetown, Barbados

**Dates:** 24 March - 17 April 2012

A hydrographic survey consisting of CTDO (conductivity, temperature, pressure, oxygen), LADCP (lowered acoustic Doppler current profiler), rosette water samples, underway shipboard ADCP and total carbon dioxide (TCO2) measurements was conducted in the western North Atlantic Ocean and Caribbean Sea aboard the UNOLS vessel R/V Atlantis from 24 March - 17 April 2012. A total of 81 CTD/LADCP/rosette stations were occupied on a transect running roughly along meridian  $66^{\circ}$ W. CTD casts extended to within 10 meters of the seafloor and up to 36 water samples were collected throughout the water column on each upcast. Salinity and dissolved oxygen samples, drawn from each bottle on every cast, were analyzed and used to calibrate the CTD conductivity and oxygen sensors. Water samples were also analyzed on board the ship for nutrients (silicate, phosphate, nitrate, nitrite), total  $CO_2$  (TCO2), pH, total alkalinity, and transient tracers (CFCs,  $SF_6$  and  $CCl_4$ ). Additional water samples were collected and stored for analysis onshore: dissolved organic carbon (DOC),  $^3Helium$  / tritium,  $^{13}C$  /  $^{14}C$  and black carbon. Underway measurements included surface total  $CO_2$ , temperature, conductivity, dissolved oxygen, fluorescence, various meteorological parameters, and bathymetry.

#### **Cruise Narrative**

R/V Atlantis cruise 20-01A - a meridional transect through the western North Atlantic Ocean and Caribbean Sea, nominally along 66°W, between 40° - 12°N latitudes - was undertaken as one component of the ongoing US CLIVAR Carbon & Repeat Hydrography Program. This particular section, designated A22, had been occupied twice previously: in 1997 (R/V Knorr 151-4) and 2003 (R/V Knorr 173-2). A central objective of the program is an assessment of the changing physical properties of ocean water masses and circulation on the global scale, including heat, salt and carbon inventories, employing a network of hydrographic sections, to obtain a factual basis for evaluating the state of Earth's climate system. To this end, 81 full-depth CTD/LADCP/rosette casts were conducted at the locations shown in the Cruise Track map. The cruise track deviated from previous A22 occupations along its southern segment by a western jog around the Venezuelan exclusive economic zone (EEZ) ending at Aruba (near 12.6°N, 70.0°W) instead of Venezuela (11°N, 66°W). The conclusion of station work was followed by a 3-day transit to the port of Bridgetown, Barbados, from which a second CLIVAR section, A20 along 52°W, departed two days later.

As expected, weather conditions and temperatures ranged considerably over the meridional extent of the section (Figure 0). Beginning on the continental shelf south of New England (near 40°N), the first 5-6 days brought seasonally cold winds from the north. On the fifth day, we crossed the Gulf Stream north wall at Station 12, which was accompanied by a welcome 10°C rise in air/sea temperatures. Only once (29 March, Station 17) did winds and seas force a temporary halt (5-6 hours) to the otherwise round-the-clock CTD operations. Unsettled subtropical conditions persisted until we passed into the tropics on April 5, midway through the cruise. Winds generally remained under 10 kts for the remainder of the station work, then picked up again to a persistent 30+ kts for most of the transit to Barbados.

As a whole, the scientific equipment performed extremely well. Minor problems (replacement of a temperature sensor and a pump on the CTD package, and occasional repairs to Niskin bottles) were readily dealt with as they were encountered. The only significant issues - winch, wire-winding and weather difficulties - occurred at the start of the leg. The original cruise plan was to use the port-side traction winch, hydro-boom and drum equipped with .681 conducting wire, and the ROV hangar for shelter (of the package and samplers during transits between stations). On Station 2, the traction winch exhibited hydraulic problems which remained unresolved for the remainder of that leg. CTD operations were moved to the starboard deck and the 0.322" wire/drum/winch system - but at the expense of a secure shelter. The CTD package was tugged under an overhang area, aft of the main lab, and a tarp was rigged to provide some protection from wind. Until we reached the tropics, however, the ship had to remain hove-to on most stations while water sampling was conducted on deck. The only other significant time sink

arose from winding problems on the CTD wire/drum. As soon as possible (station 12), the CTD package was switched over to the ship's second drum/winch, which had been outfitted with a new spool of 0.322" wire before we left Woods Hole. Following this change, no further problems with the winch or wire ensued for the duration of the cruise.

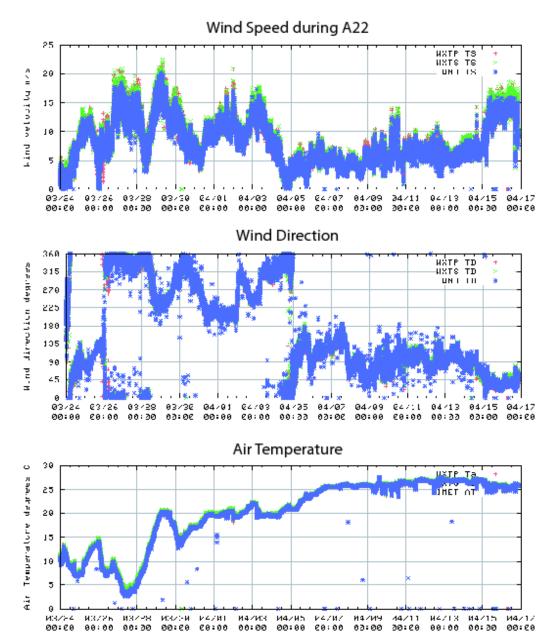


Figure 0 Time series of wind speed, direction and air temperature from the *Atlantis* shipboard meteorological sensors.

### Data Quality Assessment (refers to preliminary shipboard data only)

The overall data quality from Level 1 parameters measured on board the ship during A22 appears to be very good. Although minor difficulties developed with the equipment used to analyze bottle salinities and oxygen, these did not seriously compromise their calibration capabilities. There is no parameter whose overall quality of measurement does not appear to meet or exceed the Program's requirements and expectations. Details regarding calibration and quality control procedures are reported throughout section 1. Figures showing vertical sections of measured and derived properties plus profiles of properties vs. potential temperature are provided.

One Seabird CTDO instrument package was used throughout the cruise. The instrument was remarkably stable, and its drifts were small and easily corrected. Preliminary CTD conductivity data fit to the water sample data (expressed as salinity) shows overall agreement below 1500 db better than  $\pm 0.001$  PSS-78. Because of instabilities with the salinometer at the very end of the cruise, water samples for stations 77-81 were not analyzed immediately pending arrival of a replacement unit in port. With the possible exception of those few stations, it is highly unlikely that any post-cruise adjustments greater than 0.001 will be made to the preliminary CTD salinities. A preliminary fit of the SBE-43 dissolved oxygen sensor data to the water samples was performed for down-cast CTD oxygen values matched to up-cast water samples on density surfaces. The overall fit for A22 is excellent with differences of order 0.5  $\mu$ M/kg-1.

Shipboard analyses of bottle data also appear to be of very high quality. For salinity, oxygen and nutrients, the high degree of internal precision and consistency achieved over the cruise duration makes it unlikely that significant post-cruise changes will be made to the bottle values. It is possible that some quality code changes will occur during final post-cruise processing and evaluation.

### **Principal Findings and Features**

The A22 section crossed multiple boundary current regimes and sampled a variety of distinct water mass characteristics, some originating locally while others are transported meridionally over great distances. Compared to previous occupations, the northern end of the present section revealed a notable reduction of dissolved oxygen concentrations and increased vertical stratification (e.g. potential vorticity) in the sub-thermocline water masses of the DWBC and Gulf Stream recirculation regime. These changes reflect a decreased strength of buoyancy forcing over the last decade upstream in the subpolar basins where these water masses -- Labrador Sea Water (LSW) and Nordic Seas Overflow Waters (NSOW) -- are formed through the processes of deep convection, overflow and entrainment. The reduced ventilation is marked by the disappearance of a local oxygen maximum in the LSW layer (~1500-2500 meters depth) - a prominent feature of earlier sections.

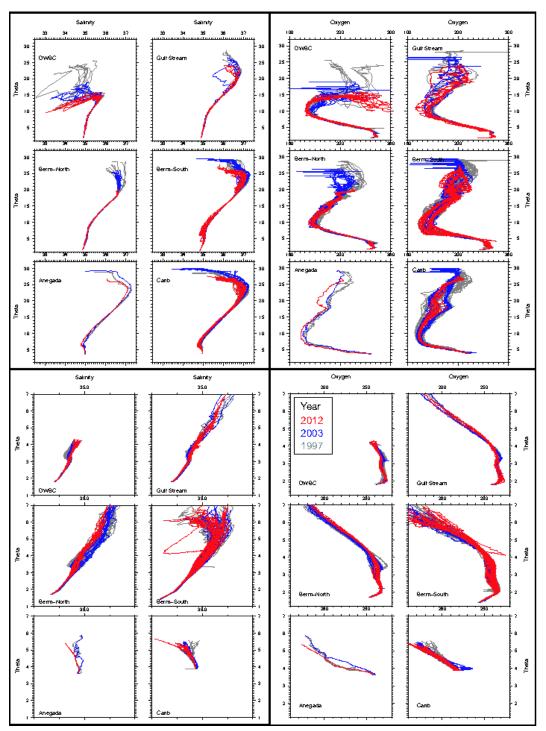
The timing of this occupation (March-April) provided a snapshot of winter-mixed layer formation in the subtropical gyre. On the offshore side of the Gulf Stream and extending southward to Bermuda (Stations 17 - 26), mixed layer depths approached 200 meters. These had not yet penetrated to the previous year's Eighteen Degree Water (EDW) - the two water masses were separated by a thinner layer of higher stratification (see potential vorticity section). Given the parade of storms that rolled off the eastern U.S. and blew up over the Gulf Stream during the cruise and after we had passed to the south, it is very likely that a healthy slug of EDW was formed locally this year at the northern end of A22.

The 2012 trackline purposely tracked up to the 3000 meter contour on the northwest flank of Bermuda Rise, and again from that contour, down the southwest flank to reveal the deep baroclinic flows banked against topography beneath 3000 meters (e.g. the potential density section). These flows originate in the Gulf Stream west of the Grand Banks and over steep topography along the Mid Atlantic Ridge where deep mixing sets the abyssal layers in motion. The resulting geostrophic flows become focused against Bermuda Rise and represent a pathway by which North Atlantic Deep Water density classes are transported through the interior western basin to subsequently join the DWBC flows in the vicinity of Cape Hatteras. The full extent of the uplift of deep isopycnals had not been captured in previous A22 sections.

At the southern end of the Atlantic part of the transect (Puerto Rico), the equatorward flowing DWBC again passed through the section, here from west to east. While the structure of the water column was very similar to both the 1997 and 2003 occupations, an eddy bearing very unusual water properties was encountered at Station 42, near 21.5°N, just north of the Puerto Rico Trench. The property anomalies - high oxygen and CFCs, low salinity and nutrients -- were particularly strong between 1000-1500 meters depth and pegged its origin to the circulation east of Newfoundland. The eddy structure and water mass signatures were remarkably intact for having journeyed so far.

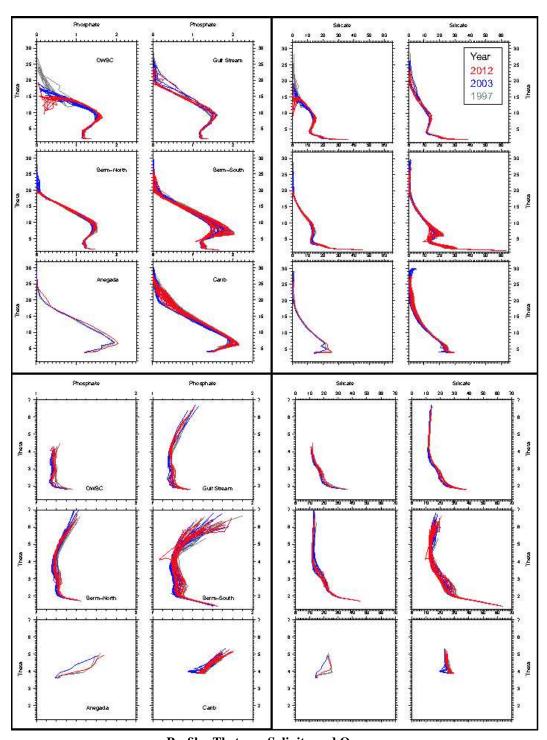
The section passed to the east of Puerto Rico and into the Caribbean where the water mass characteristics were very similar to previous years. A strong core of Antarctic Intermediate Waters (low oxygen, low salinity, high nutrients) was southward intensified along the section. A second, weaker core also flowed poleward along the boundary to the north of Puerto Rico. Below the sill depth of ~2000 meters, the Caribbean water column was very well mixed and weakly stratified, exhibiting characteristics of older (high inorganic carbon concentrations), poorly ventilated (low CFCs) water masses intermediate between northern and southern sources.

### Comparison Profiles A22 1997, 2003 and 2012



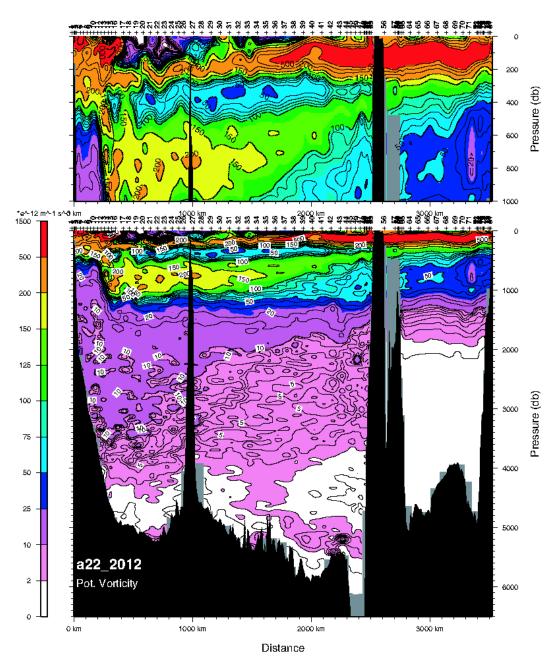
Profiles Theta vs. SiO3 and PO4

-5-

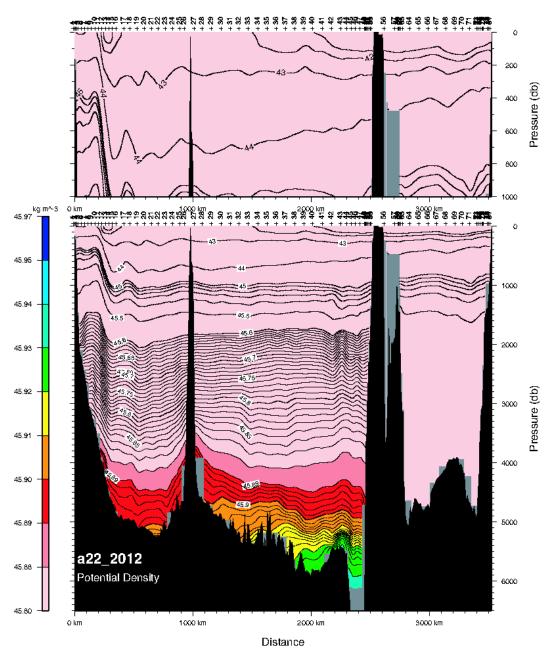


Profiles Theta vs. Salinity and Oxygen

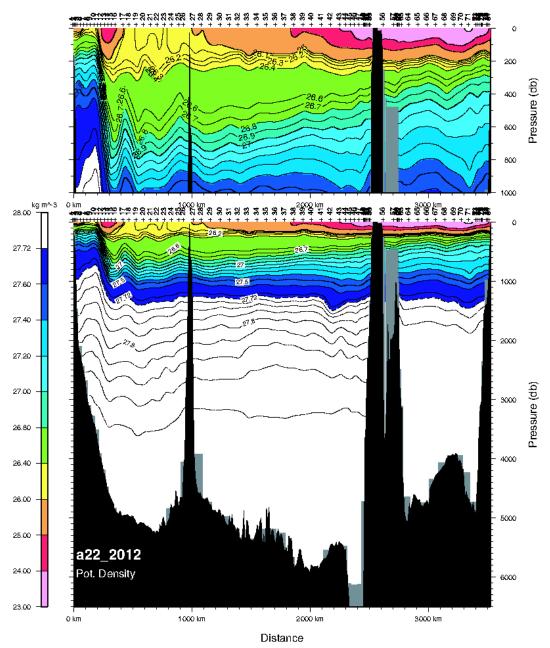
Sections of A22 2012



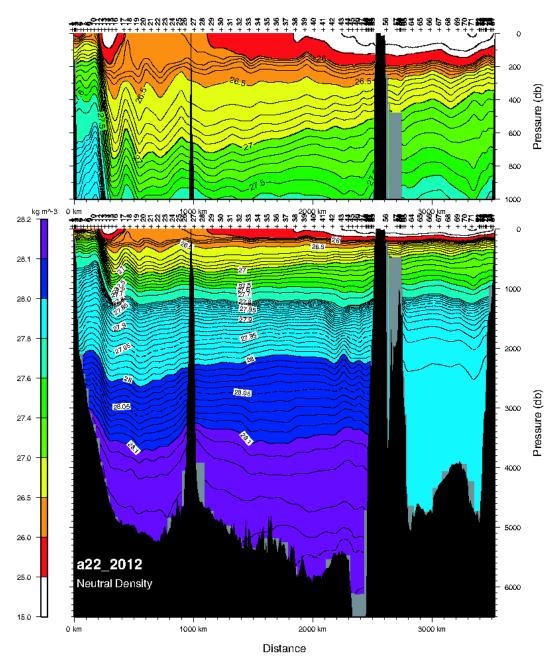
**Pressure vs. Potential Vorticity** 



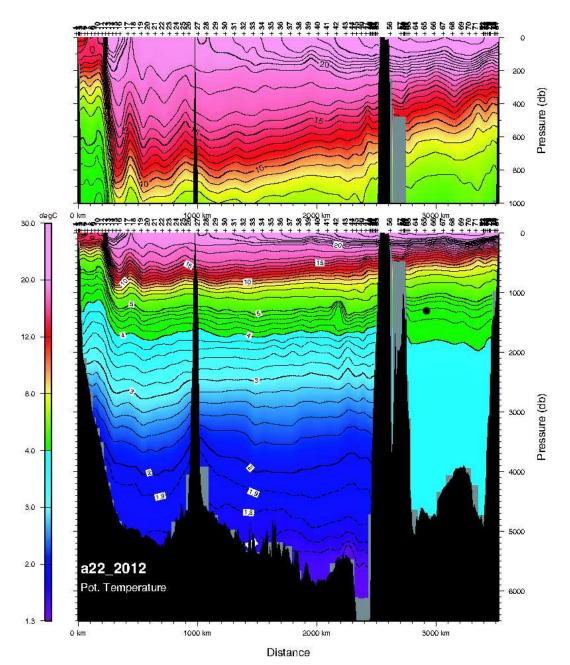
Pressure vs. Potential Density, Sigma 4



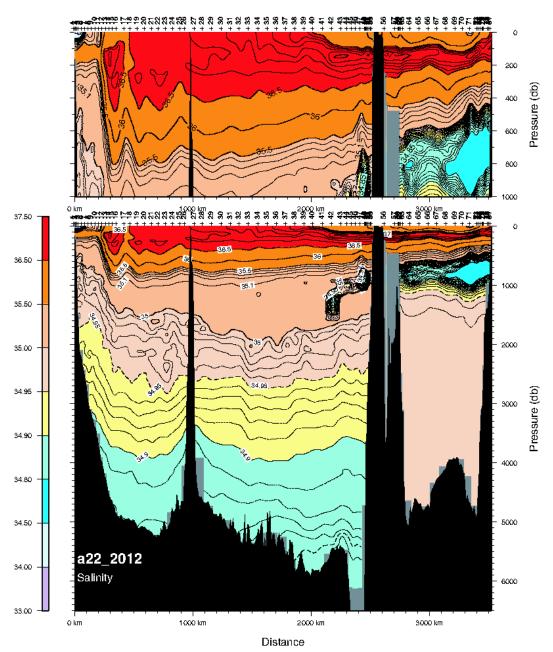
Pressure vs. Potential Density, Sigma 0



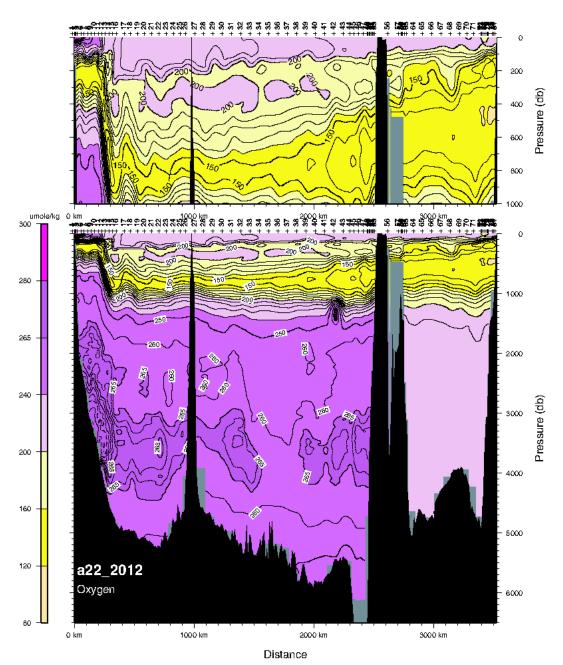
Pressure vs. Neutral Density



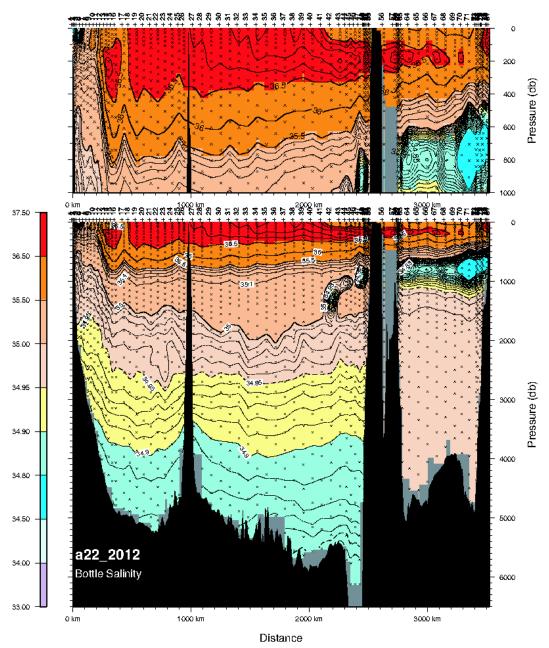
**Pressure vs. Potential Temperature** 



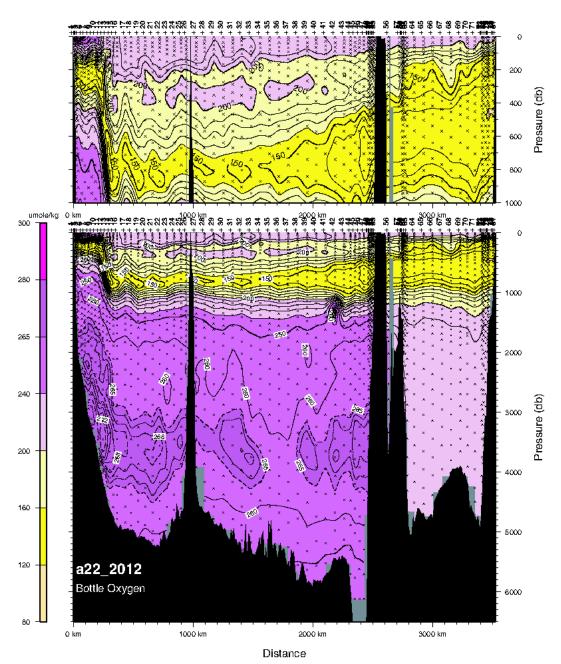
Pressure vs. Salinity



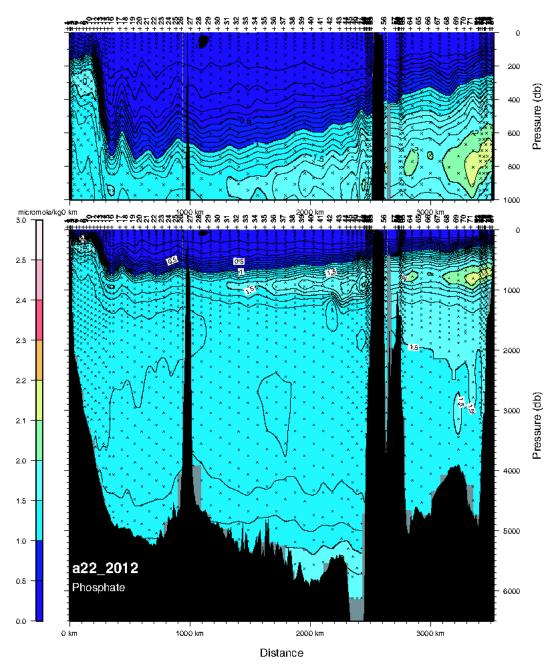
Pressure vs. CTD Oxygen



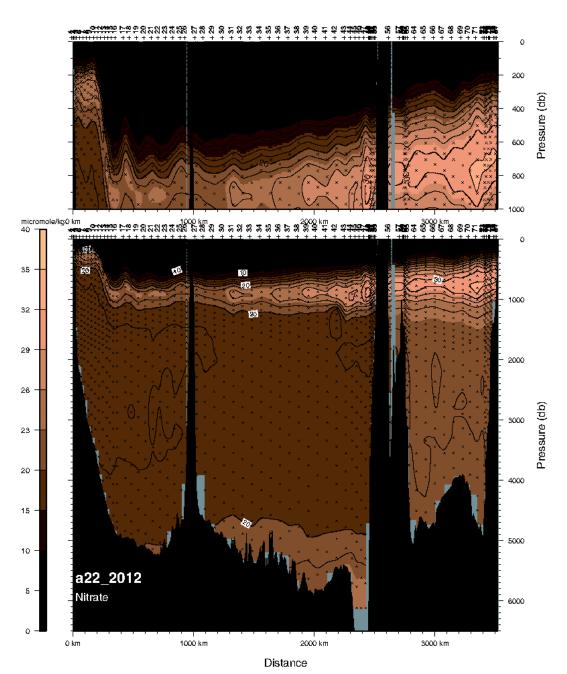
Pressure vs. Bottle Salinity



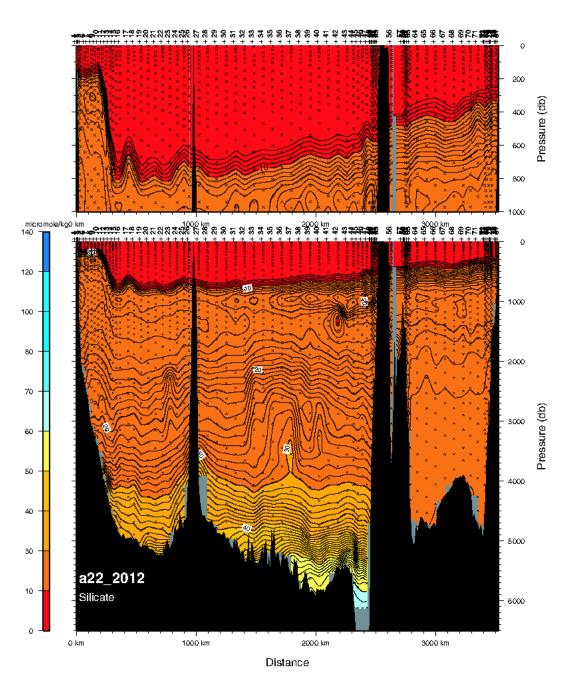
Pressure vs. Bottle Oxygen



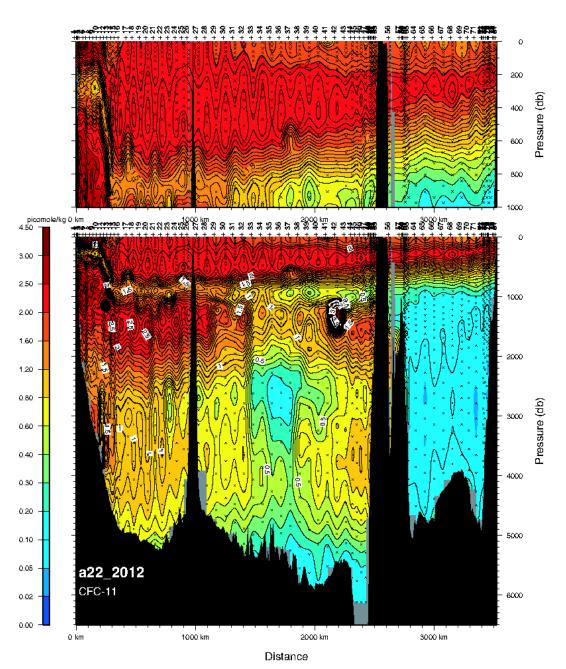
Pressure vs. Bottle Phosphate



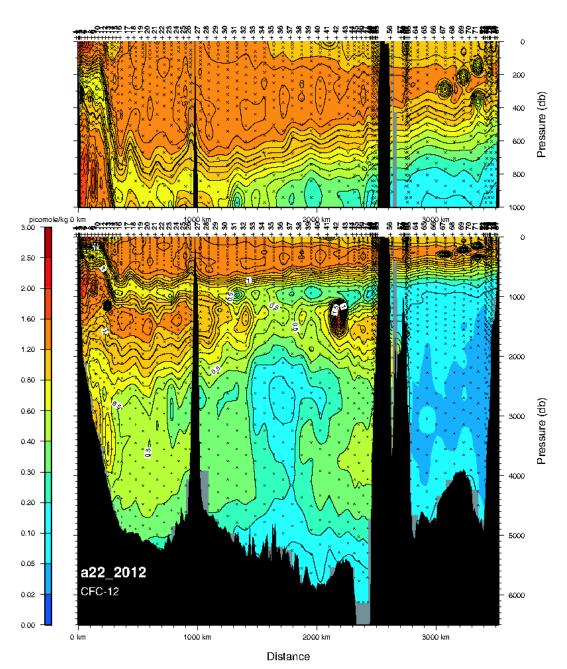
Pressure vs. Bottle Nitrate



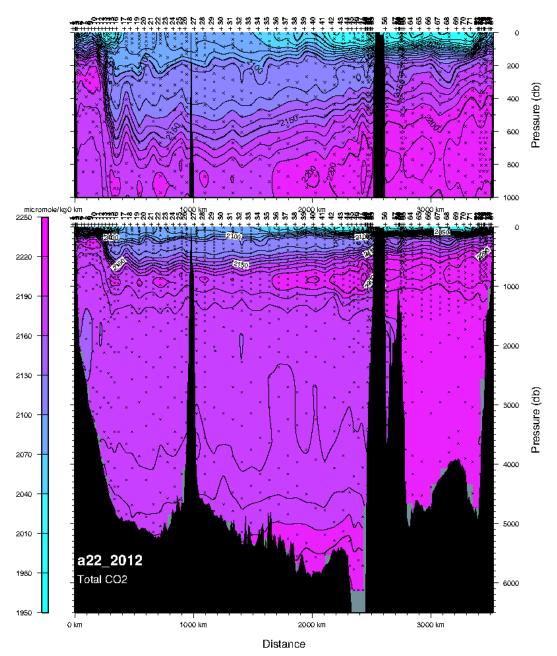
Pressure vs. Bottle Silicate



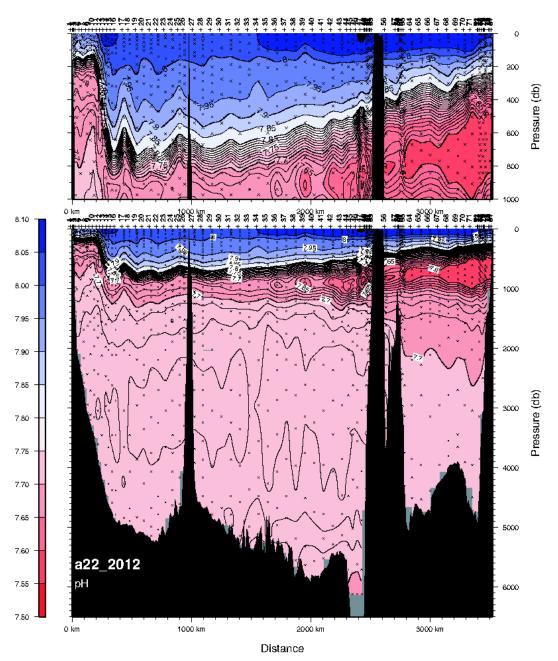
Pressure vs. CFC-11



Pressure vs. CFC-12



Pressure vs. Total  $CO_2$ 



Pressure vs. pH

## **Principal Programs of CLIVAR A22**

Program	Affiliation	Principal Investigator	email
CTDO/Rosette, Nutrients, O <sub>2</sub> , Salinity, Data Processing	UCSD/SIO	James H. Swift	jswift@ucsd.edu
ADCP/LADCP	UH	Eric Firing	efiring@soest.hawaii.edu
CFCs	LDEO	Bill Smethie	bsmeth@ldeo.columbia.edu
$SF_6$	UM/RSMAS	Rana Fine	rfine@rsmas.miami.edu
$^{3}$ He- $^{3}$ H	WHOI	Bill Jenkins	wjenkins@whoi.edu
CO <sub>2</sub> -DIC/Underway pCO <sub>2</sub>	NOAA/AOML	Rik Wannikhof	rik.wanninkhof@noaa.gov
CO <sub>2</sub> -DIC/Oliderway pcO <sub>2</sub>	NOAA/PMEL	Richard Feeley	richard.a.feeley@noaa.gov
Total Alkalinity, pH	UM/RSMAS	Frank Millero	fmillero@rsmas.miami.edu
Dissolved Organic Carbon (DOC)/ Total Dissolved Nitrogen (TDN)	UM/RSMAS	Dennis Hansell	dhansell@rsmas.miami.edu
Underway pCO <sub>2</sub> with underway T&S	NOAA/AOML	Rik Wanninkhof	Rik.Wanninkhof@noaa.gov
Carbon Isotopes <sup>13</sup> C/ <sup>14</sup> C-DIC	WHOI PU	Ann McNichol Robert Key	amcnichol@whoi.edu key@princeton.edu
Carbon Isotopes <sup>14</sup> C-DOC/ <sup>14</sup> C-Black C	UCI	Ellen Druffel	edruffel@uci.edu
Transmissometer	TAMU	Wilf Gardner	wgardner@tamu.edu
Surface Skin SST	UM/RSMAS	Peter Minnett	pminnett@rsmas.miami.edu

<sup>\*</sup> Affiliation abbreviations listed on page 24

## Shipboard Scientific Personnel on CLIVAR A22

Name	Affiliation	Shipboard Duties	Shore Email
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Hector Bustos-Serrano	UABC	pН	hbustos@uabc.edu.mx
Kevin Cahill	WHOI	$^{3}He/^{3}H$	kcahill@whoi.edu
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		Surface Skin SST	
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Jason Waters	UM/RSMAS	pH	jwaters@rsmas.miami.edu
Allison Heater	WHOI	SSSG Tech	sssg@atlantis.whoi.edu
Dave Sims	WHOI	SSSG Tech	sssg@atlantis.whoi.edu

<sup>\*</sup> Affiliation abbreviations are listed on page 24

**Ship's Crew Personnel on CLIVAR A22** 

Name	Shipboard Duties	Email
Allan Lunt	Captain	master@atlantis.whoi.edu
Peter Leonard	Chief Mate	chmate@atlantis.whoi.edu
Craig Dickson	Second Mate	secondmate@atlantis.whoi.edu
Rick Bean	Third Mate	thirdmate@atlantis.whoi.edu
Tim Logan	Communication Electronics Tech	comet@atlantis.whoi.edu
Patrick Hennessy	Bosun	bosun@atlantis.whoi.edu
Raul Martinez	Able-Bodied Seaman	
Jerry Graham	Able-Bodied Seaman	
Jim McGill	Able-Bodied Seaman	
Richard Barnes	Ordinary Seaman	
Leo Byckovas	Ordinary Seaman	
Jeff Little	Chief Engineer	cheng@atlantis.whoi.edu
Monica Hill	First Assistant Engineer	firsteng@atlantis.whoi.edu
Glenn Savage	Second Assistant Engineer	secondeng@atlantis.whoi.edu
Mike Spruill	Third Assistant Engineer	thirdeng@atlantis.whoi.edu
Richard Stairs	Oiler	
Matthew Slater	Oiler	
Nick Alexander	Oiler	
Leroy Walcott	Wiper	
Carl Wood	Steward	steward@atlantis.whoi.edu
Brendon Todd	Cook	
Cecile Hall	Mess Attendant	

	KEY to Institution Abbreviations
AOML	Atlantic Oceanographic and Meteorological Laboratory (NOAA)
LDEO	Lamont-Doherty Earth Observatory
MIT	Massachusetts Institute of Technology
MPIM	Max-Planck-Institut für Meteorologie
MWJ	Marine Works Japan Ltd.
NOAA	National Oceanic and Atmospheric Administration
ODF	Oceanographic Data Facility (SIO/STS)
PMEL	Pacific Marine Environmental Laboratory (NOAA)
PU	Princeton University
RSMAS	Rosenstiel School of Marine and Atmospheric Science (UM)
RT-E	Research Technicians - Electronics (SIO/STS)
SIO	Scripps Institution of Oceanography (UCSD)
SSSG	Shipboard Scientific Services Group (WHOI)
STS	Shipboard Technical Support (SIO)
TAMU	Texas A&M University
UABC	Universidad Autónoma de Baja California
UCI	University of California, Irvine
UCSD	University of California, San Diego
UH	University of Hawaii
UM	University of Miami
UW	University of Washington
WHOI	Woods Hole Oceanographic Institution

### Hydrographic/CTD Data, Salinity, Oxygen and Nutrients

Oceanographic Data Facility and Research Technicians Shipboard Technical Support/Scripps Institution of Oceanography La Jolla, CA 92093-0214

The CLIVAR A22 repeat hydrographic line was reoccupied for the US Global Ocean Carbon and Repeat Hydrography Program (sometimes referred to as "CLIVAR/CO2") during March-April 2012 from RV Atlantis during a survey consisting of CTD/rosette/LADCP stations and a variety of underway measurements. The ship departed Woods Hole, Massachusetts on 24 March 2012 and arrived Bridgetown, Barbados on 17 April 2012 (UTC dates).

A total of 81 stations were occupied with one CTD/rosette/LADCP cast completed at each. There were two aborted casts, one at Station 1 the other at Station 2. CTDO data and water samples were collected on each CTD/rosette/LADCP cast, usually to within 10 meters of the bottom. Water samples were measured on board as tabulated in the Bottle Sampling section.

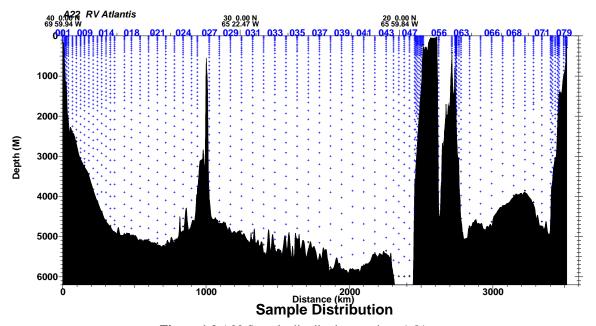
A sea-going science team gathered from 12 oceanographic institutions participated on the cruise. The programs and PIs, and the shipboard science team and their responsibilities, are listed in the Narrative section.

### **Description of Measurement Techniques**

### 1. CTD/Hydrographic Measurements Program

A total of 83 CTD/rosette/LADCP casts were made at 81 stations. Two of the 83 casts were aborted. Most casts were lowered to within 10m of the bottom.

Hydrographic measurements consisted of salinity, dissolved oxygen and nutrient water samples taken from each rosette cast. Pressure, temperature, conductivity/salinity, dissolved oxygen, and transmissometer data were recorded from CTD profiles. Current velocities were measured by the RDI workhorse ADCP. The distribution of samples are shown in the following figures.



**Figure 1.0** A22 Sample distribution, stations 1-81.

### 1.1. Water Sampling Package

Rosette/CTD/LADCP casts were performed with a package consisting of a 36-bottle rosette frame (SIO/STS), a 36-place carousel (SBE32) and 36 10.0L Bullister bottles (SIO/STS) with an absolute volume of 10.4L. Underwater electronic components consisted of a Sea-Bird Electronics SBE9plus CTD with dual pumps (SBE5), dual temperature (SBE3plus), reference temperature (SBE35RT) dual conductivity (SBE4C), dissolved oxygen (SBE43), transmissometer (WET Labs), altimeter (Simrad) and LADCP (RDI).

The CTD was mounted vertically in an SBE CTD cage attached to the bottom of the rosette frame and located to one side of the carousel. The SBE4C conductivity, SBE3plus temperature and SBE43 Dissolved oxygen sensors and their respective pumps and tubing were mounted vertically in the CTD cage, as recommended by SBE. Pump exhausts were attached to the CTD cage on the side opposite from the sensors and directed downward. The transmissometer was mounted horizontally near the bottom of the rosette frame. The altimeter was mounted on the inside of the bottom frame ring. The 150 KHz downward-looking Broadband LADCP (RDI) was mounted vertically on one side of the frame between the bottles and the CTD. Its battery pack was located on the opposite side of the frame, mounted on the bottom of the frame. Table 1.1.0 shows height of the sensors referenced to the bottom of the frame.

Instrument	Height in cm
Temperature/Conductivity Inlet	9
SBE35	9
Altimeter	2
Transmissometer	5
Pressure Sensor, inlet to capillary tube	17
Inner bottle midline	109
Outer bottle midline	113
LADCP face midline (bottom)	7
Zero tape on wire	280

Table 1.1.0 Heights referenced to bottom of rosette frame

The deck watch prepared the rosette 10-30 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 rosette was moved out from portside ROV hangar for stations 1 and 2 cast 1, under the portside squirt boom using cart and tracks. The rosette was moved out from the starboard quarterdeck to the deployment location under the starboard squirt-boom using cart and tracks for all other station casts. The CTD was powered-up and the data acquisition system started from the computer lab. The rosette was unstrapped from the cart. Tag lines were threaded through the rosette frame and syringes were removed from CTD intake ports. The winch operator was directed by the deck watch leader to raise the package. The squirt-boom and rosette were extended outboard and the package was quickly lowered into the water. Tag lines were removed and the package was lowered to 10 meters, until the console operator determined that the sensor pumps had turned on and the sensors were stable. The winch operator was then directed to bring the package back to the surface, at which time the wireout reading was re-zeroed before descent.

Most rosette casts were lowered to within 10 meters of the bottom, using the altimeter, winch wireout, CTD depth and echosounder depth to determine the distance.

For each up cast, the winch operator was directed to stop the winch at up to 36 pre-determined sampling depths. These standard depths were staggered every station using 3 sampling schemes. To insure package shed wake had dissipated, the CTD console operator waited 30 seconds prior to tripping sample bottles. An additional 10 seconds elapsed before moving to the next consecutive trip depth, to allow the SBE35RT time to take its readings. The deck watch leader directed the package to the surface for the last bottle trip.

Recovering the package at the end of the deployment was essentially the reverse of launching, with the additional use of poles and snap-hooks attached to tag lines and air-tuggers for controlled recovery. The rosette was secured on the cart and moved forward on the starboard quarter deck cover for sampling. The bottles and rosette were examined before samples were taken, and anything unusual was noted on the sample log.

Each bottle on the rosette had a unique serial number, independent of the bottle position on the rosette. Sampling for specific programs was outlined on sample log sheets prior to cast recovery or at the time of collection.

Routine CTD maintenance included soaking the conductivity and oxygen sensors with 1% Triton-X solution between casts to maintain sensor stability and eliminate accumulated bio-films. Rosette maintenance was performed on a regular basis. Valves and o-rings were inspected for leaks. The carousel was rinsed with fresh water as part of the routine maintenance.

#### 1.2. Underwater Electronics

The SBE9*plus* CTD supplied a standard SBE-format data stream at a data rate of 24 frames/second. The sensors and instruments used during CLIVAR A22, along with pre-cruise laboratory calibration information, are listed below in Table 1.2.0. Copies of the pre-cruise calibration sheets for various sensors are included in Appendix D.

Instrument/Sensor*	Mfr.§/Model	Serial Number	CTD Channel	Stations Used	Pre-Cruise C	Calibration Facility§
						• •
Carousel Water Sampler	SBE32 (36-place)	3216715-0187	n/a	1-81	n/a	n/a
Reference Temperature	SBE35	3528706-0035	n/a	1-81	16-Feb-2012	SIO/STS
CTD	SBE9plus SIO	09P39801-0796		1-81		
Pressure	Paroscientific Digiquartz 401K-105	796-98627	Freq.2	1-81	25 Oct 2011	SIO/STS
Primary Pump Circuit						
Temperature (T1a)	SBE3 <i>plus</i>	03P-4138	Freq.0	1-39	28 Oct 2011	SIO/STS
Temperature (T1b)	SBE3plus	03P-4924	Freq.0	40-81	24 Oct 2011	SIO/STS
Conductivity (C1)	SBE4C	04-3369	Freq.1	1-81	21 Feb 2012	SBE
Dissolved Oxygen†	SBE43	43-0614	Aux2/V2	1-56	18 Feb 2012	SBE
Pump	SBE5T	05-3334		1-5		
Pump	SBE5T	05-4374		6-81		
Secondary Pump Circuit						
Temperature (T2)	SBE3 <i>plus</i>	03P-4907	Freq.3	1-81	08 Feb 2012	SIO/STS
Conductivity (C2)	SBE4C	04-3399	Freq.4	1-81	21 Feb 2012	SBE
Pump	SBE5T	05-4160	rreq. i	1-81	211002012	SDL
Dissolved Oxygen†	SBE43	43-0614	Aux2/V2	57-81	18 Feb 2012	SBE
Diss.Oxygen Optode‡ Optode Temperature‡	RinkoIII ARO-CAV	084	Aux4/V6 Aux4/V7	1-47	21-Oct-2011	JFE Advantech
Transmissometer (TAMU)	WET Labs C-STAR	CST-327DR	Aux3/V4 Aux2/V3	1-16 17-81	30 Nov 2010	WET Labs
Altimeter (500m range)	Simrad 807	9711091	Aux1/V0	1-81		
			Aux2/V3	12-14		
Load Cell/Tension (WHOI)	3PSInc LP-5K-2000	A0512124	Aux3/V5	15-16		
			Aux3/V4	17-81		
LADCP Down (UH)	RDI Workhorse 150kHz	16283		1-81		
Deck Unit (in lab)	SBE11plus V2	11P21561-0518		1-81		

<sup>\*</sup> All sensors belong to SIO/STS/ODF, unless otherwise noted.

Table 1.2.0 CLIVAR A22 Rosette Underwater Electronics.

An SBE35RT reference temperature sensor was connected to the SBE32 carousel and recorded a temperature for each bottle closure. These temperatures were used as additional CTD calibration checks. The SBE35RT was utilized per the manufacturer's specifications and instructions, as described on the Sea-Bird Electronics website (http://www.seabird.com).

<sup>§</sup> SBE = Sea-Bird Electronics

<sup>†</sup> same SBE43 Oxygen sensor, shifted to secondary pump circuit after station 56

<sup>‡</sup> Experimental oxygen sensor, never gave any usable data. Removed after station 47

The SBE9*plus* CTD was connected to the SBE32 36-place carousel, providing for sea cable operation. A 0.681" fiber optic cable on the RV Atlantis's Markey DUTW-9-11 port-side winch was used during station 1 and station 2 cast 1. After a failure of the pump hydraulics during station 2, the starboard/forward Markey DESH-5 winch with an older wire was used for station 2 cast 2 through station 12. The Markey DESH-5 starboard/aft winch was used for all remaining casts. Both DESH-5 winches were outfitted with an 0.322" EM sea cable.

A new termination was done before the first use of each sea cable. Two inner conductors from the 0.681" fiber optic cable were used, one for power and signal, the other for ground (return). Only one conductor in the DESH-5 three-conductor wires was used for power and signal; the sea cable armor was used for ground. Power to the SBE9plus CTD and sensors, SBE32 carousel and Simrad altimeter was provided through the sea cable from the SIO/STS SBE11plus deck unit in the computer lab.

#### 1.3. Navigation and Bathymetry Data Acquisition

Navigation data were acquired at 1-second intervals from the ship's SeaNav 2050 GPS receiver by a Linux system beginning 24 March 2012 at 1600z, as the RV Atlantis left the dock in Woods Hole.

Centerbeam bathymetric data from the Kongsberg EM-122 multibeam echosounder system were available before arriving at the first station. Bottom depths associated with rosette casts were recorded on the Console Logs during deployments. A minor change in STS/ODF software was required to read in the serial data feed, but the program could not be re-compiled for several days. Starting 28 March 2012 at 0300z (during station 12), depth data were fed realtime into the STS acquisition system and merged with navigation data.

Depth data displayed by the ship were 6m deeper than the data from the feed. The 6m hull depth offset was added later to STS stored depth data for all events in the hydrographic database.

Corrected multibeam center depths are reported for each cast event in the WOCE and Exchange format files.

### 1.4. CTD Data Acquisition and Rosette Operation

The CTD data acquisition system consisted of an SBE-11*plus* (V2) deck unit and four networked generic PC workstations running CentOS-5.6 Linux. Each PC workstation was configured with a color graphics display, keyboard, trackball and DVD+RW drive. One system had a Comtrol Rocketport PCI multiple port serial controller providing 8 additional RS-232 ports. The systems were interconnected through the ship's network. These systems were available for real-time operational and CTD data displays, and provided for CTD and hydrographic data management.

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. Another of the workstations was designated the website and database server and maintained the hydrographic database for A22. Redundant backups were managed automatically.

CTD deployments were initiated by the console watch after the ship stopped on station. The acquisition program was started and the deck unit turned on at least 3 minutes prior to package deployment. The watch maintained a console operations log containing a description of each deployment, a record of every attempt to close a bottle and any relevant comments. The deployment and acquisition software presented a short dialog instructing the operator to turn on the deck unit, to 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 lowered it to 10 meters, or deeper in heavier seas. The CTD sensor pumps were configured with a 5-second start-up delay after detecting seawater conductivities. The console operator checked the CTD data for proper sensor operation and waited for sensors to stabilize, then instructed the winch operator to bring the package to the surface and descend to a specified target depth, based on CTD pressure available on the winch display.

The winch was controlled from the deck for the top 100m of each downcast, then handed over to the lab during a typically 10-15 second stop at ~100mwo (meters wire out). The CTD profiling rate was at most 30m/min to 200m and up to 60m/min deeper than 200m, depending on sea cable tension and sea state. As the package descended toward the target depth, the rate was reduced to 30m/min at 100m off the bottom, 20m/min at 50m off, and 10m/min at 20m off.

The progress of the deployment and CTD data quality were monitored through interactive graphics and operational displays. Bottle trip locations were transcribed onto the console and sample logs. The sample log was used later as an inventory of samples drawn from the bottles. The altimeter channel, CTD depth, winch wire-out and bathymetric depth were all monitored to determine the distance of the package from the bottom, allowing a safe approach to 8-10 meters.

Bottles were closed on the up-cast by operating an on-screen control. The expected CTD pressure was reported to the winch operator for every bottle trip. Bottles were tripped 30-40 seconds after the package stopped 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 ensure that stable CTD data were associated with the trip and to allow the SBE35RT temperature sensor to measure bottle trip temperature.

Winch controls were handed back from lab to deck after a bottle trip near 100mwo. The package was directed to the surface by the deck for the last bottle closure, then the package was brought on deck. The console operator terminated the data acquisition, turned off the deck unit and assisted with rosette sampling.

#### 1.5. CTD Data Processing

Shipboard CTD data processing was performed automatically during and after each deployment using SIO/STS CTD processing software v.5.1.6-1.

During acquisition, the raw CTD data were converted to engineering units, filtered, response-corrected, calibrated and decimated to a more manageable 0.5-second time series. Pre-cruise laboratory calibrations for pressure, temperature and conductivity were also 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 data associated with each rosette bottle. Both the raw 24 Hz data and the 0.5-second time series were stored for subsequent processing. During the deployment, the raw data were backed up to another Linux workstation.

At the completion of a deployment a sequence 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 generated from the down cast data. The pressure-series data were used by the web service for interactive plots, sections and CTD data distribution. Time-series data were also available for distribution through the website.

CTD data were routinely examined for sensor problems, calibration shifts and deployment or operational problems. The primary and secondary temperature sensors (SBE3*plus*) were compared to each other and to the SBE35 temperature sensor. CTD conductivity sensors (SBE4C) were compared to each other, then calibrated by examining differences between CTD and check sample conductivity values. CTD dissolved oxygen sensor data were calibrated to check sample data.

As bottle salinity and oxygen results became available, they were used to refine shipboard conductivity and oxygen sensor calibrations. Theta-Salinity and theta- $O_2$  comparisons were made between down and up casts as well as between groups of adjacent deployments.

A total of 83 casts were made using the 36-place CTD/LADCP rosette. Further elaboration of CTD procedures specific to this cruise are found in the next section.

### 1.6. CTD Acquisition and Data Processing Details

Secondary T/C sensors were used for all reported CTD data because:

- the same sensor pair was used through-out the cruise,
- there were no questions about flow obstruction in the secondary pump circuit,
- down/up data agreed better than primaries,
- there was less low-level noise in the data,
- T2C2 corrections were lower order and more consistent overall.

The following table identifies problems noted during specific casts (NOTE: mwo = meters of wire out on winch):

station	Comment
1/1	Start cruise with trawl winch (0.681-inch wire), aborted at 15m during sensor equilibration due to deck unit alarm: Dummy plug for bottom contact switch not installed.
1/2	Installed dummy plug for bottom contact switch on deck, then restarted as cast 2.
2/1	Aborted at 271mwo: winch problems, pay out/in speed has been limited to < 30 m/min so far.
2/2	Switch to starboard (aft) Markey winch with old 0.322-inch wire prior to cast 2.
2/2, 3-7, 10	Apparent obstruction in primary pump circuit near surface (approx. top 30 dbar), bad primary data. Secondary data used for TC, but CTDOXY was on primary circuit. Codes 3/4 added to near-surface problem CTDOXY data, typically deeper than when obstruction cleared due to slow CTDOXY sensor response. Primary pump 05-4374 changed to 05-4890 prior to sta 6 - no change in surface signal quality.
7	Upcast stopped at 2101mwo/2107 dbar pressure due to wire on winch looking suspicious. Lowered back to 2122mwo/2128.5 pressure to check: wire ok, resumed cast.
8	Upcast, after tripping bottle 20: 600mwo back down to 662m due to wire-wrapping issue. At 500m, back out to 530m for same issue. Source of wire-wrap problems is much further down the wire.
9	Winch readout reset itself at 3230mwo downcast (bottom bottle 37m deeper). Multiple wire wrap problems during upcast, winch back down 5-7m on most, some after bottles already tripped. 10m back out at 2635 dbar, 30m back down at 2614 dbar.
10	Stopped 4.5 minutes at winch change-over at 105 dbar downcast. Stopped at bottom to fix wire wrap problem. Stop at 822mwo, back down to 843m to fix spool; can't fix resume hoist. Spool wrapping wrong way at 114mwo upcast, winch op fixed. Winch display not showing in lab, okay at outside winch controls.
11	Change the primary TC duct (connector between T1 and C1 sensors) prior to sta 11. Winch reset itself on upcast between 807mwo and next bottle trip (~700m).
12	Shift to forward Markey winch with new 0.322 wire, add WHOI load cell to a/d 3 (same AUX as CTDOXY) prior to cast. Stopped 4.5 minutes at winch change-over at 105 dbar downcast to check O2 signal. Strange oxygen offsets/drops: approx. 500-1600 dbar down on sta.12, jumps back and forth. Substantial despiking (mostly raw CTDOXY offsets) required to salvage the CTDOXY signal: large sections of despiked CTDOXY were coded 3/questionable.
13	Strange oxygen offsets/drops: approx. 550?-1750 dbar down on sta.13, more "long" sections of drop. then more sections at 4300+ dbar down to bottom, and 3700-3430 dbar up. Substantial despiking (mostly raw CTDOXY offsets) required to salvage the CTDOXY signal: large sections of despiked CTDOXY were coded 3/questionable.
14	Strange oxygen offsets/drops: approx. 600-1300 dbar down, long offsets and/or noise; then not much after that. Substantial despiking (mostly raw CTDOXY offsets) required to salvage the CTDOXY signal: large sections of despiked CTDOXY were coded 3/questionable.
15	Shift load cell to a/d 5 prior to sta 15 (same AUX as trans); transm. noise and a few transm. dropouts during sta 15.
16	Extreme transm. problems: most of sta 16 transm. signal offset low. suspect load cell power cabling problem is affecting sensors on same AUX port. SSSG checked cable: resistance on pins 4/5 (ground) was low/not used on cable provided with sensor by WHOI, but these pins are used for

other sensors on Y cable.

station	Comment
17	Tagline problem: CTD down 5m and then back on-board before full-depth cast. Transm. shifted from a/d 4 to a/d 3 (same AUX as CTDOXY); load cell moved to a/d 4 before sta 17, on AUX by itself prior to sta 17. Transm. signal is ok now. Stopped at 3452 dbar on upcast to check cable wrap: looks good. Odd raw CTDOXY signal at surface (top 106 dbar coded 3/questionable), then drops dramatically after short ~100m winch-control handoff and looks ok.
23	6-minute delay while package still on deck: the winch needed to be reset.
29	New load cell cable made/installed prior to sta 29. Winch tension graphical display stopped working, but tension readout still updates: re-programming problem. Slowed package at 4214, bottle trip, waited until SSSG tech diagnosed the problem. Transm. signal noisier than previous casts, and slight drop at the bottom. Transm. windows cleaned after sampling finished.
30	Winch required a reset.
33	Rope knot on deployment, had to bring rosette back on deck. Surface bottle tripped 10 seconds early: large swells at surface.
35	High tension/slower winch: ~20m/min from bottom trip, ~30m/min from 4200m trip, ~40m/min from 3900m trip, ~30-45m/min from 3600m trip, 60m/min from 3300m trip to surface. Unusually large effect of shiproll on downcast data, much despiking required in areas where winch was slower.
38-39	T1/S/Sigma Theta have suspicious difference between down/up on stas 38-39, starting about 1200m.
40	Remove orig. T1a/03P-4138; install T1b/03P-4924 prior to sta 40.
41	winch payout reset itself to 0 at ~3900m on up cast.
48	remove RinkoIII O2/T sensors for testing prior to sta 48: not working yet during this cruise. Shift loadcell to AUX4/ad6 to test AUX4 in case this is part of Rinko problem.
57	SBE43 sensor shifted to secondary pump circuit (plumbing) prior to sta 57; no change in end cap connection.
62	10-minute delay in cast start: strap holding rosette stuck. Ship drifted while cast going down, slightly shallower than start. 8-minute stop at 2675mwo on upcast, between bottles 3 and 4: 6 modulo errors preceded ship switching to emergency generator, then 20 more with audible/visible deck unit alarm. Wait for ship power problem to be diagnosed before continuing cast. No additional missed frames the rest of the cast.
73	Return to surface (but not out of water) from 74 dbar downcast due to winch re-zeroing itself, plus large wire angle/current. Started from top of second yoyo for pressure-series data. Unable to hoist the winch from lab controls after the bottom trip. 5-minute delay to diagnose/fix problem. Problems after bottle 2 tripped (3853 dbar), quickly resolved; ship's engineers worked on electronics under winch controls in computer lab.
74	Winch monitor program failed at cast start, and wireout stopped streaming to the acquisition PC. Wireouts written from the winch box display, which still worked. SSSG traced the problem to the serial feed, fixed after cast.
79	Winch payout rezeroed itself at 160mwo on downcast. At ~115m on upcast, winch operator rezeroed. Winch rezeroed on its own twice more before cast finished.

## 1.7. CTD Sensor Laboratory Calibrations

Laboratory calibrations of the CTD pressure, temperature, conductivity and dissolved oxygen sensors were performed prior to CLIVAR A22. The sensors and calibration dates are listed in Table 1.2.0. Copies of the calibration sheets for Pressure, Temperature, Conductivity, and Dissolved Oxygen sensors, as well as factory and deck calibrations for the TAMU Transmissometer, are in Appendix D.

#### 1.8. CTD Shipboard Calibration Procedures

CTD #796 was used for all CTD/rosette/LADCP casts during A22. The CTD was deployed with all sensors and pumps aligned vertically, as recommended by SBE.

The SBE35RT Digital Reversing Thermometer (S/N 3528706-0035) served as an independent calibration check for T1 and T2 sensors. *In situ* salinity and dissolved  $O_2$  check samples collected during each cast were used to calibrate the conductivity and dissolved  $O_2$  sensors.

### 1.8.1. CTD Pressure

The Paroscientific Digiquartz pressure transducer (S/N 796-98627) was calibrated in October 2011 at the SIO/STS Calibration Facility. The calibration coefficients provided on the report were used to convert frequencies to pressure. The SIO/STS pressure calibration coefficients already incorporate the slope and offset term usually provided by Paroscientific.

The initial deck readings for pressure indicated a pressure offset was needed, typically because CTDs are calibrated horizontally but deployed vertically. An additional -1.0 dbar offset was applied during data acquisition/block-averaging starting for stations 1-17. A review during station 17 showed that -0.7 dbar was a better choice. Stations 1-17 were re-averaged with the lower offset, and the new offset was used for the remaining stations.

Residual pressure offsets (the difference between the first and last submerged pressures) varied from -0.34 to +0.23 dbar. Pre- and post-cast on-deck/out-of-water pressure offsets varied from +0.04 to +0.28 dbar before the casts, and -0.06 to +0.32 dbar after the casts.

#### **1.8.2.** CTD Temperature

Two SBE3*plus* primary temperature sensors (T1a: 03P-4138/stas 1-39 and T1b: 03P-4924/stas 40-81) and one secondary temperature sensor (T2: 03P-4907/stas 1-81) were used during A22. 03P-4138 was changed out after station 39 because of suspicious down/up cast differences in the higher-gradient region above 1000 dbar. Although these differences were also apparent in secondary sensors, the deep theta-salinity down/up plots for the primary sensors did not overlay as well as the secondaries.

Calibration coefficients derived from the pre-cruise calibrations, plus shipboard temperature corrections determined during the cruise, were applied to raw primary and secondary sensor data during each cast.

A single SBE35RT (3528706-0035) was used as a tertiary temperature check. It was located equidistant between T1 and T2 with the sensing element aligned in a plane with the T1 and T2 sensing elements. The SBE35RT Digital Reversing Thermometer is an internally-recording temperature sensor that operates independently of the CTD. It is triggered by the SBE32 carousel in response to a bottle closure. According to the manufacturer's specifications, the typical stability is  $0.001^{\circ}$ C/year. The SBE35RT on CLIVAR A22 was set to internally average over 5 sampling cycles (a total of 5.5 seconds).

Two independent metrics of calibration accuracy were examined. At each bottle closure, the primary and secondary temperature were compared with each other and with the SBE35RT temperatures.

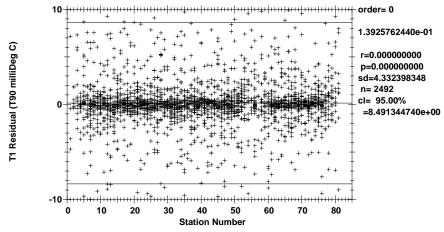
All 3 temperature sensors were first examined for drift with time, using the more stable SBE35RT at a smaller range of deeper trip levels (2000-3000 dbar). T1a and T2 required a time-based offset to account for drift. T1a drifted -0.0005 over 39 stations; T2 drifted -0.0013 over the first 40 stations, then only -0.0007 more until station 68, after which a drift was no longer apparent. T1b was stable enough to apply a single offset for all stations where it was used.

None of the sensors exhibited a temperature-dependent slope. However, T1a and T2 both had a small residual pressure dependence that required a first-order correction to pull deeper bottles in line with shallower bottles (about -0.001 °C correction for T1a and just +0.0002 °C for T2 at 6100 dbar).

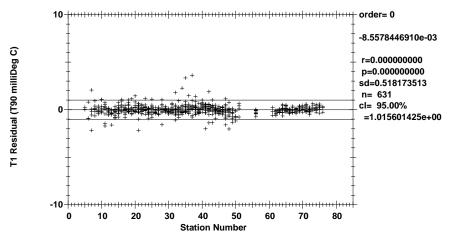
The final corrections for T2 temperature data reported on CLIVAR A22 are summarized in Appendix A. All corrections made to T2 temperatures had the form:

$$T2_{ITS90} = T2 + tp_1P + t_0$$

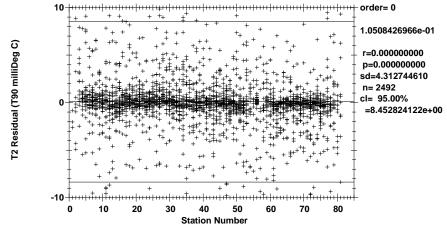
Residual temperature differences after correction are shown in figures 1.8.2.0 through 1.8.2.8.



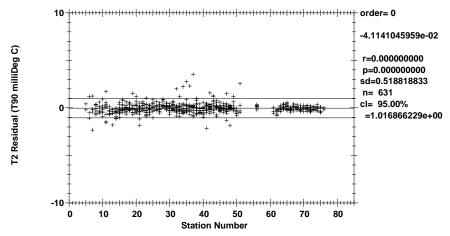
**Figure 1.8.2.0** SBE35RT-T1 by station  $(-0.01^{\circ}\text{C} \le T1 - T2 \le 0.01^{\circ}\text{C})$ .



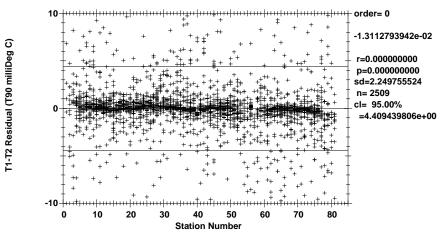
**Figure 1.8.2.1** Deep SBE35RT-T1 by station (Pressure >= 2000dbar).



**Figure 1.8.2.2** SBE35RT-T2 by station  $(-0.01^{\circ}\text{C} \le T1 - T2 \le 0.01^{\circ}\text{C})$ .



**Figure 1.8.2.3** Deep SBE35RT-T2 by station (Pressure >= 2000dbar).



**Figure 1.8.2.4** T1-T2 by station  $(-0.01^{\circ}\text{C} \le T1 - T2 \le 0.01^{\circ}\text{C})$ .

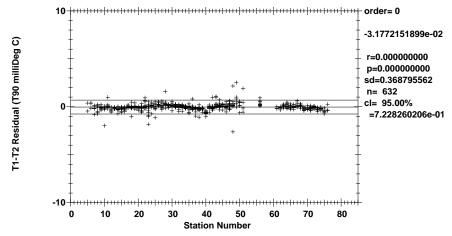
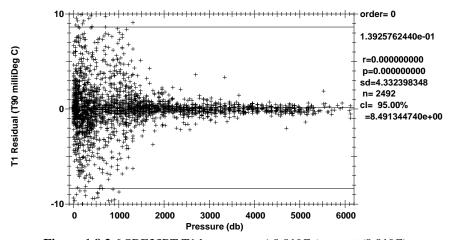
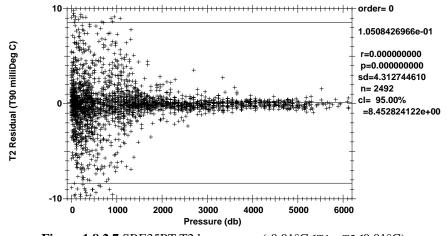


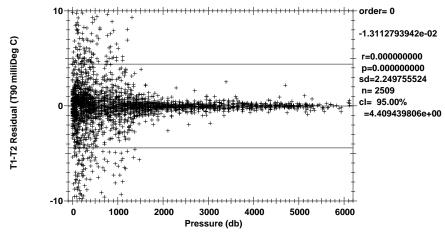
Figure 1.8.2.5 Deep T1-T2 by station (Pressure >= 2000dbar).



**Figure 1.8.2.6** SBE35RT-T1 by pressure  $(-0.01^{\circ}\text{C} \le T1 - T2 \le 0.01^{\circ}\text{C})$ .



**Figure 1.8.2.7** SBE35RT-T2 by pressure  $(-0.01^{\circ}\text{C} \le T1 - T2 \le 0.01^{\circ}\text{C})$ .



**Figure 1.8.2.8** T1-T2 by pressure  $(-0.01^{\circ}\text{C} \le T1 - T2 \le 0.01^{\circ}\text{C})$ .

The 95% confidence limits for the mean low-gradient differences are  $\pm 0.00845$ °C for SBE35RT-T2 and  $\pm 0.00441$ °C for T1-T2. The 95% confidence limit for deep temperature residuals (where pressure > 2000db) is  $\pm 0.00102$ °C for SBE35RT-T2 and  $\pm 0.00072$ °C for T1-T2.

## 1.8.3. CTD Conductivity

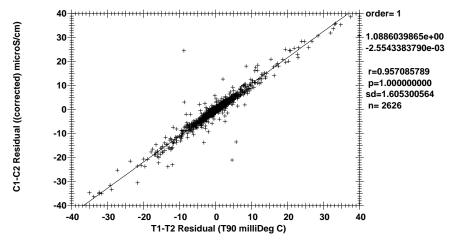
The same SBE4C primary (C1/04-3369) and secondary (C2/04-3399) conductivity sensors were used during all CLIVAR A22 casts. Secondary sensor data were used to report final CTD data because of apparent flow-obstruction issues in the primary pump system in the top 30 dbar of most of the first 10 stations, and because a single secondary temperature sensor was used through-out the cruise.

Calibration coefficients derived from the pre-cruise calibrations were applied to convert raw frequencies to conductivity. Shipboard conductivity corrections, determined during the cruise, were applied to primary and secondary conductivity data for each cast.

Corrections for both CTD temperature sensors were finalized before analyzing conductivity differences. Two independent metrics of calibration accuracy were examined. At each bottle closure, the primary and secondary conductivity were compared with each other. Each sensor was also compared to conductivity calculated from check sample salinities using CTD pressure and temperature.

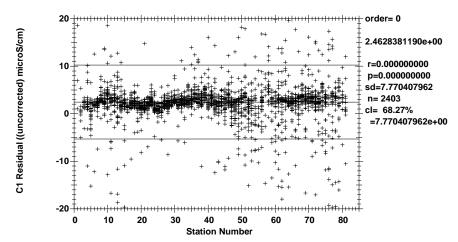
Stations 10, 24-27, 36, 39, 54, 57-58, and 73-81 were omitted from final conductivity fits due to various anomalies in bottle salinities, mostly attributable to standard dial changes and/or Autosal issues during this leg.

The differences between primary and secondary temperature sensors were used as filtering criteria for all conductivity fits to reduce the contamination of conductivity comparisons by package wake. The coherence of this relationship is shown in figure 1.8.3.0.

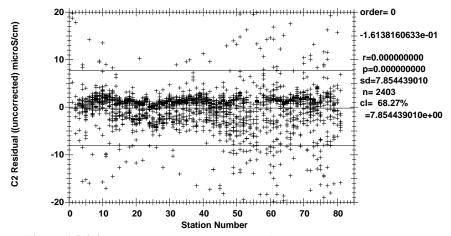


**Figure 1.8.3.0** Coherence of conductivity differences as a function of temperature differences.

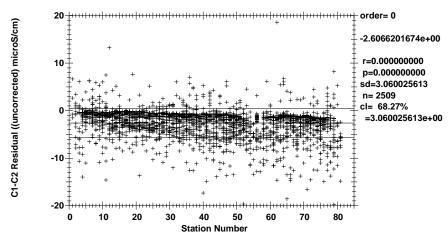
Uncorrected conductivity comparisons are shown in figures 1.8.3.1 through 1.8.3.3.



**Figure 1.8.3.1** Uncorrected  $C_{Bottle} - C1$  by station (-0.01°C $\leq T1 - T2 \leq 0.01$ °C).



**Figure 1.8.3.2** Uncorrected  $C_{Bottle}$  – C2 by station (-0.01°C $\leq$ T1-T2 $\leq$ 0.01°C).



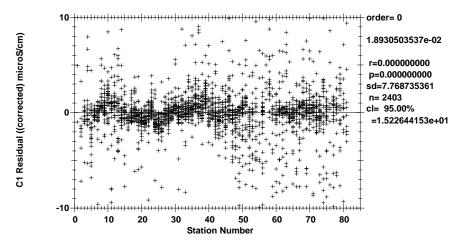
**Figure 1.8.3.3** Uncorrected C1 - C2 by station  $(-0.01^{\circ}\text{C} \le T1 - T2 \le 0.01^{\circ}\text{C})$ .

Offsets for each C sensor were evaluated for drift with time using  $C_{Bottle} - C_{CTD}$  differences from a deeper, limited pressure range (2000-3000 dbars). C1 offsets had a steady, slow shift with time; the total C1 drift from stations 1-81 was -0.0008 mS/cm. C2 displayed no significant drift with time; the offset calculated using stations 1-38 held through the rest of the leg.

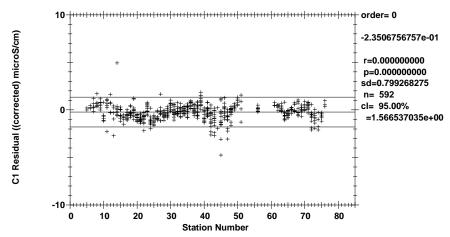
After conductivity offsets were applied to all casts, response to pressure was examined for each conductivity sensor. The pressure response was essentially linear for C1, requiring a -0.0005 mS/cm correction at the deepest pressures during the cruise. No pressure dependence was evident for C2 differences.

 $C_{Bottle} - C_{CTD}$  differences were then evaluated for response to temperature and/or conductivity, which typically shifts between pre- and post-cruise SBE laboratory calibrations. A comparison of the residual C1 differences showed an additional small conductivity-dependent slope was required. This correction lowered near-surface values by about -0.00056 mS/cm compared to the deepest data. C2 showed a strong first-order dependence on conductivity. Shallow C2 data were +0.00625 mS/cm compared to deep C2 data, so a conductivity-dependent slope was applied to correct the difference.

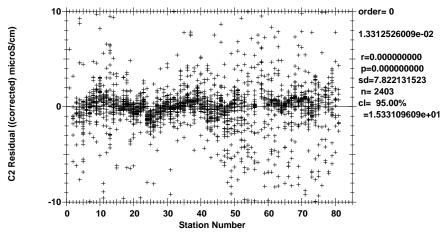
Deep Theta-S overlays showed that deep CTD data overlaid well for the data reported. The residual conductivity differences after correction are shown in figures 1.8.3.4 through 1.8.3.15.



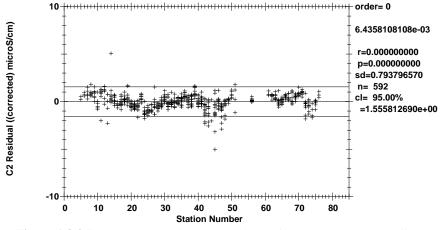
**Figure 1.8.3.4** Corrected  $C_{Bottle}$  – C1 by station (-0.01°C $\leq$ T1-T2 $\leq$ 0.01°C).



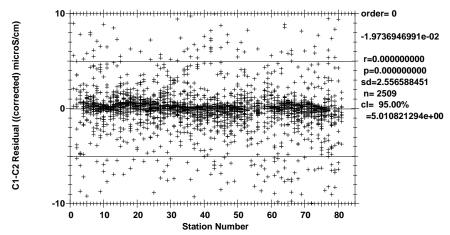
**Figure 1.8.3.5** Deep Corrected  $C_{Bottle}$  – C1 by station (Pressure >= 2000dbar).



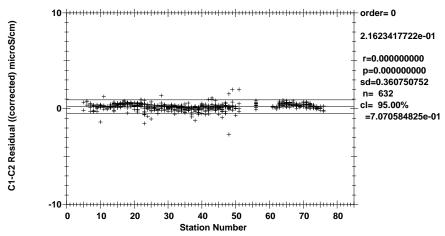
**Figure 1.8.3.6** Corrected  $C_{Bottle}$  – C2 by station (-0.01°C $\leq$ T1-T2 $\leq$ 0.01°C).



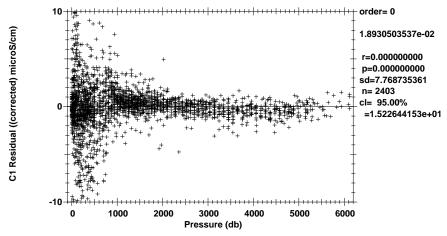
**Figure 1.8.3.7** Deep Corrected  $C_{Bottle}$  – C2 by station (Pressure >= 2000dbar).



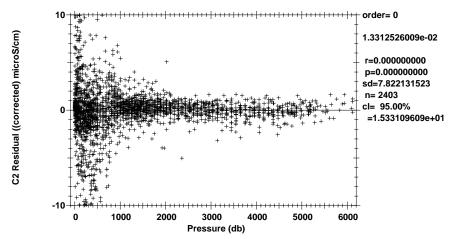
**Figure 1.8.3.8** Corrected C1 - C2 by station (-0.01°C $\leq$ T1-T2 $\leq$ 0.01°C).



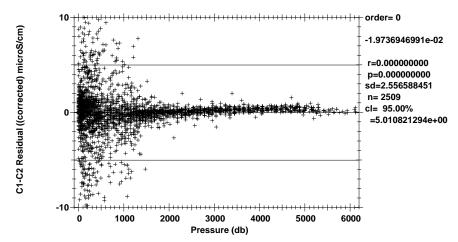
**Figure 1.8.3.9** Deep Corrected C1 - C2 by station (Pressure  $\geq 2000$ dbar).



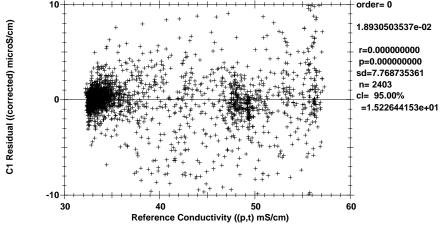
**Figure 1.8.3.10** Corrected  $C_{Bottle} - C1$  by pressure (-0.01°C $\leq$ T1-T2 $\leq$ 0.01°C).



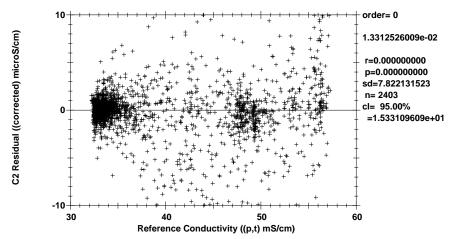
**Figure 1.8.3.11** Corrected  $C_{Bottle}$  – C2 by pressure (-0.01°C $\leq$ T1-T2 $\leq$ 0.01°C).



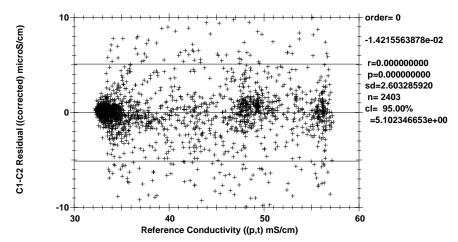
**Figure 1.8.3.12** Corrected C1 - C2 by pressure (-0.01°C≤T1-T2≤0.01°C).



**Figure 1.8.3.13** Corrected  $C_{Bottle}$  – C1 by conductivity (-0.01°C $\leq$ T1-T2 $\leq$ 0.01°C).



**Figure 1.8.3.14** Corrected  $C_{Bottle}$  – C2 by conductivity (-0.01°C $\leq$ T1-T2 $\leq$ 0.01°C).

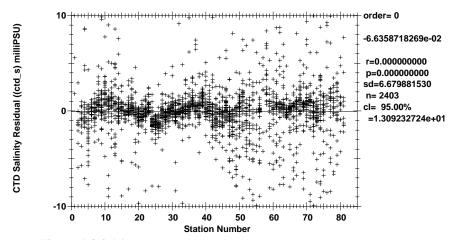


**Figure 1.8.3.15** Corrected C1 - C2 by conductivity  $(-0.01^{\circ}\text{C} \le \text{T}1 - \text{T}2 \le 0.01^{\circ}\text{C})$ .

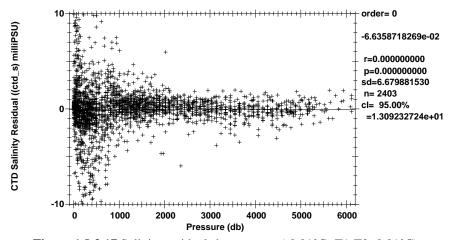
The final corrections for the secondary sensors used on CLIVAR A22 are summarized in Appendix A. Corrections made to C2 conductivity sensor had the form:

$$C2_{cor} = C2 + c_1C2 + c_0$$

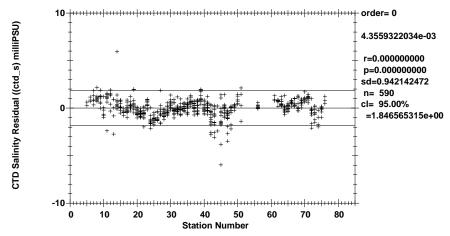
Salinity residuals after applying shipboard P/T/C corrections are summarized in figures 1.8.3.16 through 1.8.3.18. Only CTD and bottle salinity data with "acceptable" quality codes are included in the differences.



**Figure 1.8.3.16** Salinity residuals by station (-0.01°C≤T1-T2≤0.01°C).



**Figure 1.8.3.17** Salinity residuals by pressure (-0.01°C≤T1-T2≤0.01°C).



**Figure 1.8.3.18** Deep Salinity residuals by station (Pressure >= 2000dbar).

Figures 1.8.3.17 and 1.8.3.18 represent estimates of the salinity accuracy of CLIVAR A22. The 95% confidence limits are  $\pm 0.01309$  PSU relative to bottle salinities for all salinities, and  $\pm 0.00184$  PSU relative to bottle salinities for deep salinities, where T1-T2 is within  $\pm 0.01^{\circ}$ C.

## 1.8.4. CTD Dissolved Oxygen

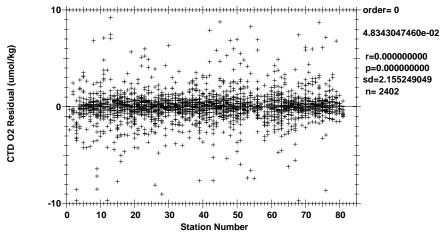
A single SBE43 dissolved  $O_2$  sensor (DO/43-0614) was used during CLIVAR A22. The sensor was plumbed into the primary T1/C1 pump circuit after C1. The  $O_2$  sensor was shifted to the secondary pump circuit before station 57, during the long run around Puerto Rico, after it was decided to use the secondary TC sensors for all reported data.

The DO sensor was calibrated to dissolved  $O_2$  bottle samples taken at bottle stops by matching the down cast CTD data to the up cast trip locations on isopycnal surfaces, then calculating CTD dissolved  $O_2$  using a DO sensor response model and minimizing the residual differences from the bottle samples. A non-linear least-squares fitting procedure was used to minimize the residuals and to determine sensor model coefficients, and was accomplished in three stages.

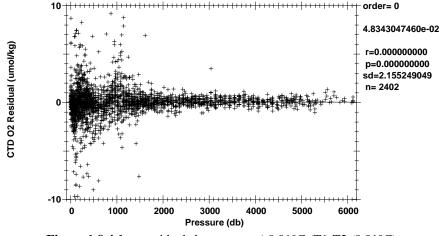
The time constants for the lagged terms in the model were first determined for the sensor. These time constants are sensor-specific but applicable to an entire cruise. Next, casts were fit individually to bottle sample data. Consecutive casts were compared on plots of Theta vs  $O_2$  to verify consistency.

At the end of the cruise, standard and blank values for bottle oxygen data were smoothed, and the bottle oxygen values were recalculated. The changes to bottle oxygen values were less than 0.01 ml/l for most stations before station 45, then as much as 0.017 ml/l for stations 62-68. CTD  $O_2$  data were re-calibrated to the smoothed bottle values after the leg.

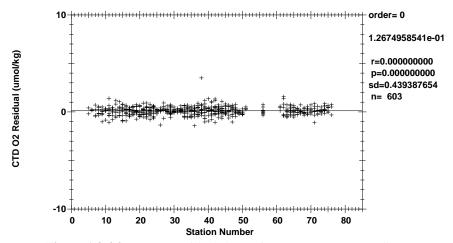
Final CTD dissolved  $O_2$  residuals are shown in figures 1.8.4.0-1.8.4.2.



**Figure 1.8.4.0**  $O_2$  residuals by station (-0.01°C $\leq$ T1-T2 $\leq$ 0.01°C).



**Figure 1.8.4.1**  $O_2$  residuals by pressure (-0.01°C $\leq$ T1-T2 $\leq$ 0.01°C).



**Figure 1.8.4.2** Deep  $O_2$  residuals by station (Pressure  $\geq$  2000dbar).

The standard deviations of 2.155  $\mu$ mol/kg for all oxygens and 0.439  $\mu$ mol/kg for deep oxygens are only presented as general indicators of goodness of fit. SIO/STS makes no claims regarding the precision or accuracy of CTD dissolved  $O_2$  data.

The general form of the SIO/STS DO sensor response model equation for Clark cells follows Brown and Morrison [Brow78], Millard [Mill82] and Owens & Millard [Owen85]. SIO/STS models DO sensor responses with lagged CTD data. *In situ* pressure and temperature are filtered to match the sensor responses. Time constants for the pressure response ( $\tau_p$ ), a slow ( $\tau_{Tf}$ ) and fast ( $\tau_{Ts}$ ) thermal response, package velocity ( $\tau_{dP}$ ), thermal diffusion ( $\tau_{dT}$ ) and pressure hysteresis ( $\tau_h$ ) are fitting parameters. Once determined for a given sensor, these time constants typically remain constant for a cruise. The thermal diffusion term is derived by low-pass filtering the difference between the fast response ( $T_s$ ) and slow response ( $T_t$ ) temperatures. This term is intended to correct non-linearities in sensor response introduced by inappropriate analog thermal compensation. Package velocity is approximated by low-pass filtering 1st-order pressure differences, and is intended to correct flow-dependent response. Dissolved  $O_2$  concentration is then calculated:

$$O_2ml/l = \left[C_1 \cdot V_{DO} \cdot e^{(C_2 \cdot \frac{P_h}{5000})} + C_3\right] \cdot f_{sat}(T, P) \cdot e^{(C_4 \cdot T_l + C_5 \cdot T_s + C_7 \cdot P_l + C_6 \cdot \frac{dO_c}{dt} + C_8 \cdot \frac{dP}{dt} + C_9 \cdot dT)}$$
(1.8.4.0)

where:

 $O_2 ml/l$  Dissolved  $O_2$  concentration in ml/l;

 $V_{DO}$  Raw sensor output;

 $C_1$  Sensor slope

 $C_2$  Hysteresis response coefficient

 $C_3$  Sensor offset

 $f_{sat}(T, P)$   $O_2$  saturation at T,P (ml/l); T in situ temperature (°C); P in situ pressure (decibars);

 $P_h$  Low-pass filtered hysteresis pressure (decibars);  $T_l$  Long-response low-pass filtered temperature (°C); Short-response low-pass filtered temperature (°C);

 $P_l$  Low-pass filtered pressure (decibars);

 $dO_c$ 

Sensor current gradient ( $\mu$ amps/sec);

dP

 $\frac{dt}{dt}$  Filtered package velocity (db/sec);

dT low-pass filtered thermal diffusion estimate  $(T_s - T_l)$ .

 $C_4 - C_9$  Response coefficients.

CTD  $O_2ml/l$  data are converted to  $\mu$ mol/kg units on demand.

#### 1.9. Bottle Sampling

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

- CFC-11, CFC-12, CFC-113, SF<sub>6</sub> and CCl<sub>4</sub>
- <sup>3</sup>He
- Dissolved O<sub>2</sub>
- Dissolved Inorganic Carbon (DIC)
- pH
- Total Alkalinity
- ${}^{13}C$  and  ${}^{14}C$ -DIC
- Dissolved Organic Carbon (DOC) and Total Dissolved Nitrogen (TDN)
- Tritium
- Nutrients
- 14*C*-DOC
- 14C-Black Carbon
- Salinity
- Millero Density

The correspondence between individual sample containers and the rosette bottle position (1-36) 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.

#### 1.10. Bottle Data Processing

Water samples collected and properties analyzed shipboard were centrally managed in a relational database (PostgreSQL 8.1.23) running on a Linux system. A web service (OpenACS 5.5.0 and AOLServer 4.5.1) 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).

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 Hydrographic Programme (WHP) [Joyc94].

Table 1.10.0 shows the number of samples drawn and the number of times each WHP sample quality flag was assigned for each basic hydrographic property:

Rosette Samples Stations 1- 81								
	Reported			WHP	Quality (	Codes		
	levels	1	2	3	4	5	7	9
Bottle	2651	0	2641	5	0	0	0	5
CTD Salt	2651	0	2651	0	0	0	0	0
CTD Oxy	2607	0	2543	16	48	19	0	25
Salinity	2607	0	2543	16	48	19	0	25
Oxygen	2640	0	2582	44	14	0	0	11
Silicate	2636	0	2586	18	32	9	0	6
Nitrate	2644	0	2638	2	4	0	0	7
Nitrite	2644	0	2639	1	4	0	0	7
Phosphate	2644	0	2639	1	4	0	0	7

**Table 1.10.0** Frequency of WHP quality flag assignments.

Additionally, data investigation comments are presented in Appendix C.

Various consistency checks and detailed examination of the data continued throughout the cruise. Chief Scientist, Ruth Curry, reviewed the data and compared it with historical data sets.

## 1.11. Salinity Analysis

## **Equipment and Techniques**

Two salinometers were used at different intervals for this cruise. One Guildline Autosal 8400B salinometer (S/N 65-740) and one 8400A (S/N 57-525) located in RV Atlantis's Hydro Lab were used for all salinity measurements. Both salinometers utilize National Instruments interface to decode Autosal data and communicate with windows based acquisition PC.

Samples were analyzed after they had equilibrated to laboratory temperature, usually within 4-18 hours after collection. The salinometers were standardized for each group of analysis (usually 1-2 casts, up to ~36 samples) using at least two fresh vials of standard seawater per group.

Salinometer measurements were aided by a computer using LabVIEW software developed by SIO/STS. A minor change to assist data processing was made during the expedition and LVASAL V1.33a was installed on the backup

acquisition computer and brought online. The software maintained an Autosal log of each salinometer run which included salinometer settings and air and bath temperatures. The air temperature was displayed and monitored via digital thermometer. The program guided the operator through the standardization procedure and making sample measurements. The analyst was prompted to change samples and flush the cells between readings.

Standardization procedures included flushing the cell at least 2 times with a fresh vial of Standard Seawater (SSW), setting the flow rate to a low value during the last fill, and monitoring the STD dial setting. If the STD dial changed by 10 units or more since the last salinometer run (or during standardization), another vial of SSW was opened and the standardization procedure repeated to verify the setting.

Samples were run using 2 flushes before the final fill. The computer determined the stability of a measurement and prompted for additional readings if there appeared to be drift. The operator could annotate the salinometer log, and would routinely add comments about cracked sample bottles, loose thimbles, salt crystals or anything unusual in the amount of sample in the bottle.

A system of fans were used to expedite equilibrating salinity samples. Cases of samples were placed on a frame with a fan attached to help bring them to room temperature. They were then removed and set on a shelf near the Autosal for storage for further equilibration. The next or current case to be run sat to the left of the Autosal, next to the standard seawater. The amount of time each case spent at each location varied depending on sample temperature and rate of analysis by the operator.

#### **Sampling and Data Processing**

A total of 2366 salinity samples were measurements were made. Autosal 65-740 was used for 463 samples and 1903 were analyzed on Autosal 57-525. 140 vials of standard seawater (IAPSO SSW) were used.

Salinity samples were drawn into 200 ml Kimax high-alumina borosilicate bottles, which were rinsed three times with the sample prior to filling. The bottles were sealed with custom-made plastic insert thimbles and kept closed with 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 equilibration times were logged for all casts. The samples were measured with an external thermometer by placing the probe against the salinity bottle for 2-3 minutes. When the temperature was close to the bath temperature, 1-2 degrees the samples for the cast were analyzed. 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 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 measured ratios. The corrected salinity data were then incorporated into the cruise database.

Data processing included double checking that the station, sample and box number had been correctly assigned, and reviewing the data and log files for operator comments. Discrete salinity data was compared to CTD salinities and were used for shipboard sensor calibration.

## **Laboratory Temperature**

The salinometer water bath temperature was maintained slightly higher than ambient laboratory air temperature at 24°C. The ambient air temperature varied from 21 to 24°C during the cruise.

#### Standards

IAPSO Standard Seawater Batches P-153 was used to standardize all stations.

#### **Analytical Problems**

Lack of stability of the Autosals required switching units while repairs were made. Table 1.11.0 tabulates the Stations which the units were employed.

Stations	<b>Guildline Autosal</b>
1-10a	65-740
10b-26	57-525
27	65-740
28-41	57-525
42-48a	65-740
48b-76	57-525
77-81	65-740

**Table 1.11.0** Autosal station reference

During analysis for station 6 cast 1, the check-heater light appeared solid for salinometer 65-740. Observation showed the forward heater lamp had burned out. Analysis was completed by running all samples slowly. Heat lamp was replaced after analysis was completed.

During analysis for station 9 cast 1 sample 1, 65-740 showed a decreasing trend. This was true for the following 5 samples. It appeared bath water was weeping into the cell at the upper arm end. Sample 6 also had a decreasing trend of the same magnitude. The run was aborted run without an ending SSW sample after six samples. The Autosal was removed from service until closer diagnosis of the problem and repairs could be made.

The WHOI spare Autosal number 10 (57-525) was set up. This is an unmodified Guildline 8400A with separate pumps. Autosal 57-525 pumps did not work upon start-up. On inspection it was found one pump turned very slowly, the second pump did not turning at all. Belts were loose to the point of falling off, bushings were frozen with congealed oil, leather washers were dry, and the flapper check valves were stuck shut. Suction filters were in good condition. As one pump had failed, the "flush" air line had been removed and the sample fill air line attached with only the marginally working pump. Both leather washers were cleaned and oiled, both flapper valves were blown out both flapper valves, cleaned pump bodies, removed and cleaned brass bushings, cleaned and descaled drive wheel axles, reassembled pumps, oiled bushings, installed pumps in housings and adjusted belt tension to normal fit. Pumps were back to near original specifications. Prior to analysis salinometer was checked with a stable temperature of 23.97.

Prior to analysis of station 27, unit 57-525 was replaced with 65-740. During analysis of sample 4 a decreasing trend was noticed with each measurement, this continued to sample 9. It appeared bath water was weeping into the cell at the upper arm end. The analysis was discontinued and 57-525 was once again employed.

Station 42 unit 65-740 was put back into service. After sample 2 on station 48 large step decreasing trends noted, 57-525 was put back into service.

Prior to station 74 cell coils looked dull and coated. IAPSO Standard readings were 40 units high. The cell was cleaned after the run was completed. Analysis of station 75 appeared to return standard normalized readings. After station 76 IAPSO standard readings had dropped by 10 units once again. Further analysis revealed a definite unstable data trend for stations 74-76.

## Results

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.

#### 1.12. Oxygen Analysis

#### **Equipment and Techniques**

Dissolved oxygen analyses were performed with an SIO/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 ODF PC software compiled in LabView. Thiosulfate was dispensed by a Titronic 110 Plus buret driver fitted with a 1.0 mL buret which was eventually changed to the Brickman Dosimat 765. The ODF method 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). Standard *KIO*<sub>3</sub> solutions prepared ashore were run daily (approximately every 2-4 stations), unless changes were made to the system or reagents. Reagent/distilled water blanks were also determined daily, or more often if a change in reagents required it to account for presence of oxidizing or reducing agents.

## **Sampling and Data Processing**

2645 samples were analyzed on A22. Samples were collected for dissolved oxygen analyses soon after the rosette was brought on board. Six different cases of 24 flasks each were rotated by station to minimize any potential flask calibration issues. Using a 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 an electronic resistance temperature detector (Omega<sup>TM</sup> HH370 RTD) embedded in the drawing tube. These temperatures were used to calculate  $\mu$ mol/kg concentrations, and as a diagnostic check of bottle integrity. Reagents ( $MnCl_2$  then NaI/NaOH) were added to fix the oxygen before stoppering. The flasks were shaken to assure thorough dispersion of the precipitate, once immediately after drawing, and then again after about 20 minutes. A water seal was applied to the rim of each bottle in between shakes.

The samples were analyzed within 1-2 hours of collection, and the data incorporated into the cruise database.

Thiosulfate normalities were calculated from each standardization and corrected to 20°C. The thiosulfate normalities and blanks were monitored for possible drifting or possible problems when new reagents were used. An average blank and thiosulfate normality were used to recalculate oxygen concentrations. The thiosulfate was changed between stations 31 and 32. The first set of averages were performed on Stations 1 through and including Station 32. The second set was done on Stations 32 through 71. The third set was from Stations 72 to 81 since the burette was changed. The difference between the original and "smoothed" data averaged 0.0%-0.1% over the course of the cruise.

Bottle oxygen data was reviewed ensuring proper station, cast, bottle number, flask, and draw temperature were entered properly. Comments made during analysis were reviewed. All anomalous actions were investigated and resolved. If an incorrect end point was encountered, the analyst re-examined raw data and the program recalculated a correct end point.

After the data was uploaded to the database, bottle oxygen was graphically compared with CTD oxygen and adjoining stations. Any points that appeared erroneous were reviewed and comments made regarding the final outcome of the investigation. These investigations and final data coding are reported in Appendix C.

#### **Volumetric Calibration**

Oxygen flask volumes were determined gravimetrically with degassed deionized water to determine flask volumes at ODF's chemistry laboratory. This was 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 and tested in 6 liter batches and bottled in sterile glass bottles at ODF's chemistry laboratory prior to the expedition. The normality of the liquid standard was determined by calculation from weight of powder temperature of solution and flask volume at 70°C. The standard was supplied by Alfa Aesar (lot B05N35) and has a reported purity of 99.4-100.4%. All other reagents were "reagent grade" and were tested for levels of oxidizing and reducing impurities prior to use.

#### **Analytical Problems**

A Schott Titronic 110 autoburet was used for the first 71 stations of A22. Towards the beginning of the expedition, the autotitration software would occasionally stall, causing the loss of a sample. The frequency of these stalls increased with time, until the third week when it was decided to return to the traditional Dosimat 765 unit. After the switch, no further errors of this kind occurred.

#### 1.13. Nutrient Analysis

## **Summary of Analysis**

2644 samples from 81 CTD stations.

The cruise started with new pump tubes; they were changed once after station 39. Three sets of Primary/Secondary standards were made up over the course of the cruise. The cadmium column efficiency was checked periodically and ranged between 98%-100%.

#### **Equipment and Techniques**

Nutrient analyses (phosphate, silicate, nitrate plus nitrite, and nitrite) were performed on a Seal Analytical continuous-flow AutoAnalyzer 3 (AA3). After each run, the charts were reviewed for any problems and final concentrations (in  $\mu$ M or micromoles per liter) were calculated using SEAL Analytical AACE 6.07 software.

The analytical methods used are described by Gordon *et al.* [Gord92], Hager *et al.* [Hage68] and Atlas *et al.* [Atla71]. The details of modification of analytical methods used for this cruise are also compatible with the methods described in the nutrient section of the GO-SHIP repeat hydrography manual [Hyde10].

### Nitrate/Nitrite Analysis

A modification of the Armstrong *et al.* [Arms67] procedure was used for the analysis of nitrate and nitrite. For nitrate analysis, a seawater sample was passed through a cadmium column where the nitrate was reduced to nitrite. This nitrite was then diazotized with sulfanilamide and coupled with N-(1-naphthyl)-ethylenediamine to form a red dye. The sample was then passed through a 10mm flowcell and absorbance measured at 540nm. The procedure was the same for the nitrite analysis but without the cadmium column.

## **REAGENTS**

## Sulfanilamide

Dissolve 10g sulfanilamide in 1.2N HCl and bring to 1 liter volume. Add 2 drops of 40% surfynol 465/485 surfactant. Store at room temperature in a dark poly bottle.

Note: 40% Surfynol 465/485 is 20% 465 plus 20% 485 in DIW.

N-(1-Naphthyl)-ethylenediamine dihydrochloride (N-1-N)

Dissolve 1g N-1-N in DIW, bring to 1 liter volume. Add 2 drops 40% surfynol 465/485 surfactant. Store at room temperature in a dark poly bottle. Discard if the solution turns dark reddish brown.

#### Imidazole Buffer

Dissolve 13.6g imidazole in  $^{\sim}3.8$  liters DIW. Stir for at least 30 minutes to completely dissolve. Add 60 ml of  $CuSO_4 + NH_4Cl$  mix (see below). Add 4 drops 40% Surfynol 465/485 surfactant. Let sit overnight before proceeding. Using a calibrated pH meter, adjust to pH of 7.83-7.85 with 10% (1.2N) HCl (about 20-30 ml of acid, depending on exact strength). Bring final solution to 4L with DIW. Store at room temperature.

 $NH_4Cl + CuSO_4$  mix

Dissolve 2g cupric sulfate in DIW, bring to 100 m1 volume (2%). Dissolve 250g ammonium chloride in DIW, bring to 1 liter volume. Add 5ml of 2% *CuSO*<sub>4</sub> solution to this *NH*<sub>4</sub>*Cl* stock. This should last many months.

## **Phosphate Analysis**

Ortho-Phosphate was analysed using a modification of the Bernhardt and Wilhelms [Bern67] method. Acidified ammonium molybdate was added to a seawater sample to produce phosphomolybdic acid, which was then reduced to phosphomolybdous acid (a blue compound) following the addition of dihydrazine sulfate. The sample was passed through a 10mm flowcell and absorbance measured at 820nm.

#### REAGENTS

## Ammonium Molybdate

 $H_2SO_4$  solution: Pour 420 ml of DIW into a 2 liter Ehrlenmeyer flask or beaker, place this flask or beaker into an ice bath. SLOWLY add 330 ml of concentrated  $H_2SO_4$ . This solution gets VERY HOT!! Cool in the ice bath. Make up as much as necessary in the above proportions.

Dissolve 27g ammonium molybdate in 250ml of DIW. Bring to 1 liter volume with the cooled sulfuric acid solution. Add 3 drops of 15% DDS surfactant. Store in a dark poly bottle.

#### Dihydrazine Sulfate

Dissolve 6.4g dihydrazine sulfate in DIW, bring to 1 liter volume and refrigerate.

#### Silicate Analysis

Silicate was analyzed using the technique of Armstrong *et al.* [Arms67]. Acidified 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. The sample was passed through a 10mm flowcell and measured at 660nm.

#### **REAGENTS**

## Tartaric Acid

Dissolve 200g tartaric acid in DW and bring to 1 liter volume. Store at room temperature in a poly bottle.

## Ammonium Molybdate

Dissolve 10.8g Ammonium Molybdate Tetrahydrate in 1000ml dilute  $H_2SO_4^*$ . \*(Dilute  $H_2SO_4 = 2.8$ ml concentrated  $H_2SO_4$  or 6.4ml of  $H_2SO_4$  diluted for  $PO_4$  moly per liter DW) (dissolve powder, then add  $H_2SO_4$ ) Add 3-5 drops 15% SDS surfactant per liter of solution.

#### Stannous Chloride stock (as needed)

Dissolve 40g of stannous chloride in 100 ml 5N HCl. Refrigerate in a poly bottle.

NOTE: Minimize oxygen introduction by swirling rather than shaking the solution. Discard if a white solution (oxychloride) forms.

working: (every 24 hours) Bring 5 ml of stannous chloride stock to 200 ml final volume with 1.2N HCl. Make up daily - refrigerate when not in use in a dark poly bottle.

## Sampling

Nutrient samples were drawn into 40 ml polypropylene screw-capped centrifuge tubes. The tubes and caps were cleaned with 10% HCl and rinsed 2-3 times with sample before filling. Samples were analyzed within 1-3 hours after sample collection, allowing sufficient time for all samples to reach room temperature. The centrifuge tubes fit directly onto the sampler.

#### Data collection and processing

Data collection and processing was done with the software (ACCE ver 6.07) provided with the instrument from Seal Analytical. After each run, the charts were reviewed for any problems during the run, any blank was subtracted, and

final concentrations ( $\mu$ M) were calculated, based on a linear curve fit. Once the run was reviewed and concentrations calculated a text file was created. That text file was reviewed for possible problems and then converted to another text file with only sample identifiers and nutrient concentrations that was merged with other bottle data.

#### Standards and Glassware calibration

Primary standards for silicate ( $Na_2SiF_6$ ), nitrate ( $KNO_3$ ), nitrite ( $NaNO_2$ ), and phosphate ( $KH_2PO_4$ ) were obtained from Johnson Matthey Chemical Co. and/or Fisher Scientific. The supplier reports purities of >98%, 99.999%, 97%, and 99.999 respectively.

All glass volumetric flasks and pipettes were gravimetrically calibrated prior to the cruise. The primary standards were dried and weighed out to 0.1 mg prior to the cruise. The exact weight was noted for future reference. When primary standards were made, the flask volume at 20°C, the weight of the powder, and the temperature of the solution were used to buoyancy correct the weight, calculate the exact concentration of the solution, and determine how much of the primary was needed for the desired concentrations of secondary standard. Primary and secondary standards were made up every 7-10 days. The new standards were compared to the old before use.

All the reagent solutions, primary and secondary standards were made with fresh distilled deionized water (DIW).

Standards used for the analysis were a combination of reference materials for nutrients in seawater (RMNS) and a dilution of the secondary standard. The RMNS preparation, verification, and suggested protocol for use of the material are described by Aoyama *et al.* [Aoya06] [Aoya07] [Aoya08] and Sato *et al.* [Sato10].

RMNS batches BS, BU, BT, and BD were used on this cruise. The high working standard was made up using the in house secondary standard and low nutrient seawater (LNSW). Surface water having low nutrient concentration was taken and filtered using 0.45 micrometer pore size membrane filter. This water was stored in 20 liter cubitainer within a cardboard box. The concentrations of nutrient of this water were measured carefully in Jul 2008. Standardizations were performed at the beginning of each group of samples. Two different batches of LNSW were used on the cruise. The first was used for stations 1-56 and a different batch of LNSW was used for stations 58-81. The concentration of the high working standard changed slightly with the new batch of LNSW.

Std.	N+N	PO4	SiO3	NO2	
BS	0.10	0.065	1.69	0.03	
BU	4.13	0.387	21.21	0.07	
BT	19.10	1.35	42.83	0.48	
BD	30.59	2.244	67.27	0.05	
Std5	46.54	3.650	91.64	1.51	sta 1-56
Std5	46 54	3 645	91 66	1 51	sta 57-81

**Table 1.13.0** CLIVAR A22 Concentration of RMNS and high standard ( $\mu$ M)

#### **Quality Control**

All data were reported in  $\mu$ M (micromoles/liter).  $NO_3$ ,  $PO_4$ , and  $NO_2$  were reported to two decimal places and  $SiO_3$  to one. Accuracy is based on the quality of the standards; the levels were:

Parameter	Accuracy (µM)
$NO_3$	0.05
$PO_4$	0.02
$SiO_3$	2-4
$NO_2$	0.05

Table 1.13.1 CLIVAR A22 Nutrient Accuracy

Precision numbers for the instrument were the same for  $NO_3$  and  $PO_4$  and a little better for  $SiO_3$  and  $NO_2$  (1 and 0.01 respectively).

The detection limits for the methods/instrumentation were:

Parameter	Detection Limits (µM)
$\overline{NO_3+NO_2}$	0.02
$PO_4$	0.02
$SiO_3$	0.5
$NO_2$	0.02

Table 1.13.2 CLIVAR A22 Nutrient Detection Limits

As is standard ODF practice, a deep calibration *check* sample was run with each set of samples and the data are tabulated below.

Parameter	Concentration ( $\mu$ M)
$NO_3$	17.20 +/- 0.04
$PO_4$	1.17 +/- 0.009
$SiO_3$	18.57 +/- 0.15

Table 1.13.3 CLIVAR A22 RMNS cruise-averaged data

## **Analytical Problems**

There were no major analytical problems. The calibration fits for all the nutrients were adjusted after noticing an offset in phosphate data between the 2003 and 2012 A22 occupations.

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Appendix A

CLIVAR A22: CTD Temperature and Conductivity Corrections Summary

	ITS-90 Temperatu		Conductivity Coefficients		
Sta/	corT = tp1*	corP + t0	corC = c1*	c + c0	
Cast	tp1	tO	c1	c0	
001/02	3.1700e-08	-0.001096	-2.08476e-04	0.008115	
002/02	3.1700e-08	-0.001013	-2.08476e-04	0.008115	
003/01	3.1700e-08	-0.001000	-2.08476e-04	0.008115	
004/01	3.1700e-08	-0.000988	-2.08476e-04	0.008115	
005/01	3.1700e-08	-0.000971	-2.08476e-04	0.008115	
006/01	3.1700e-08	-0.000951	-2.08476e-04	0.008115	
007/01	3.1700e-08	-0.000932	-2.08476e-04	0.008115	
008/01	3.1700e-08	-0.000909	-2.08476e-04	0.008115	
009/01	3.1700e-08	-0.000884	-2.08476e-04	0.008115	
010/01	3.1700e-08	-0.000848	-2.08476e-04	0.008115	
010/01	3.17000 00	0.000010	2.001700 01	0.000113	
011/01	3.1700e-08	-0.000817	-2.08476e-04	0.008115	
012/01	3.1700e-08	-0.000786	-2.08476e-04	0.008115	
013/01	3.1700e-08	-0.000755	-2.08476e-04	0.008115	
014/01	3.1700e-08	-0.000724	-2.08476e-04	0.008115	
015/01	3.1700e-08	-0.000698	-2.08476e-04	0.008115	
016/01	3.1700e-08	-0.000670	-2.08476e-04	0.008115	
017/01	3.1700e-08	-0.000601	-2.08476e-04	0.008115	
018/01	3.1700e-08	-0.000565	-2.08476e-04	0.008115	
019/01	3.1700e-08	-0.000534	-2.08476e-04	0.008115	
020/01	3.1700e-08	-0.000504	-2.08476e-04	0.008115	
021/01	3.1700e-08	-0.000474	-2.08476e-04	0.008115	
022/01	3.1700e-08	-0.000443	-2.08476e-04	0.008115	
023/01	3.1700e-08	-0.000412	-2.08476e-04	0.008115	
024/01	3.1700e-08	-0.000381	-2.08476e-04	0.008115	
025/01	3.1700e-08	-0.000353	-2.08476e-04	0.008115	
026/01	3.1700e-08	-0.000327	-2.08476e-04	0.008115	
027/01	3.1700e-08	-0.000327	-2.08476e-04	0.008115	
028/01	3.1700e-08	-0.000259	-2.08476e-04	0.008115	
029/01	3.1700e-08	-0.000224	-2.08476e-04	0.008115	
030/01	3.1700e-08	-0.000189	-2.08476e-04	0.008115	
030/01	3.17000 00	0.00010)	2.001700 01	0.000113	
031/01	3.1700e-08	-0.000155	-2.08476e-04	0.008115	
032/01	3.1700e-08	-0.000120	-2.08476e-04	0.008115	
033/01	3.1700e-08	-0.000084	-2.08476e-04	0.008115	
034/01	3.1700e-08	-0.000047	-2.08476e-04	0.008115	
035/01	3.1700e-08	-0.000012	-2.08476e-04	0.008115	
036/01	3.1700e-08	0.000030	-2.08476e-04	0.008115	
037/01	3.1700e-08	0.000064	-2.08476e-04	0.008115	
038/01	3.1700e-08	0.000100	-2.08476e-04	0.008115	
039/01	3.1700e-08	0.000136	-2.08476e-04	0.008115	
040/01	3.1700e-08	0.000172	-2.08476e-04	0.008115	
041/01	3.1700e-08	-0.000186	-2.08476e-04	0.008115	
042/01	3.1700e-08 3.1700e-08	-0.000130	-2.08476e-04	0.008115	
UT2/UI	J.1700C-00	0.00017/	2.00-700-04	0.000113	

	ITS-90 Temperatu		Conductivity C	
Sta/	corT = tp1*		corC = c1*	
Cast	tp1	tO	c1	c0
043/01	3.1700e-08	-0.000110	-2.08476e-04	0.008115
044/01	3.1700e-08	-0.000078	-2.08476e-04	0.008115
045/01	3.1700e-08	-0.000046	-2.08476e-04	0.008115
046/01	3.1700e-08	-0.000017	-2.08476e-04	0.008115
047/01	3.1700e-08	0.000017	-2.08476e-04	0.008115
048/01	3.1700e-08	0.000013	-2.08476e-04	0.008115
049/01	3.1700e-08	0.000069	-2.08476e-04	0.008115
050/01	3.1700e-08	0.00009	-2.08476e-04	0.008115
030/01	3.17006-08	0.000090	-2.064706-04	0.008113
051/01	3.1700e-08	0.000112	-2.08476e-04	0.008115
052/01	3.1700e-08	0.000129	-2.08476e-04	0.008115
053/01	3.1700e-08	0.000144	-2.08476e-04	0.008115
054/01	3.1700e-08	0.000157	-2.08476e-04	0.008115
055/01	3.1700e-08	0.000167	-2.08476e-04	0.008115
056/01	3.1700e-08	0.000203	-2.08476e-04	0.008115
057/01	3.1700e-08	0.000241	-2.08476e-04	0.008115
058/01	3.1700e-08	0.000250	-2.08476e-04	0.008115
059/01	3.1700e-08	0.000260	-2.08476e-04	0.008115
060/01	3.1700e-08	0.000273	-2.08476e-04	0.008115
061/01	3.1700e-08	0.000288	-2.08476e-04	0.008115
062/01	3.1700e-08	0.000306	-2.08476e-04	0.008115
063/01	3.1700e-08	0.000326	-2.08476e-04	0.008115
064/01	3.1700e-08	0.000357	-2.08476e-04	0.008115
065/01	3.1700e-08	0.000392	-2.08476e-04	0.008115
066/01	3.1700e-08	0.000429	-2.08476e-04	0.008115
067/01	3.1700e-08	0.000464	-2.08476e-04	0.008115
068/01	3.1700e-08	0.000499	-2.08476e-04	0.008115
069/01	3.1700e-08	0.000499	-2.08476e-04	0.008115
070/01	3.1700e-08	0.000499	-2.08476e-04	0.008115
071/01	3.1700e-08	0.000499	-2.08476e-04	0.008115
072/01	3.1700e-08	0.000499	-2.08476e-04	0.008115
073/01	3.1700e-08	0.000499	-2.08476e-04	0.008115
074/01	3.1700e-08	0.000499	-2.08476e-04	0.008115
075/01	3.1700e-08	0.000499	-2.08476e-04	0.008115
076/01	3.1700e-08	0.000499	-2.08476e-04	0.008115
077/01	3.1700e-08	0.000499	-2.08476e-04	0.008115
078/01	3.1700e-08	0.000499	-2.08476e-04	0.008115
079/01	3.1700e-08	0.000499	-2.08476e-04	0.008115
080/01	3.1700e-08	0.000499	-2.08476e-04	0.008115
081/01	3.1700e-08	0.000499	-2.08476e-04	0.008115

## Appendix B

## Summary of CLIVAR A22 CTD Oxygen Time Constants (time constants in seconds)

Pressure	Temperature		Temperature Pressure		O <sub>2</sub> Gradient	Velocity	Thermal
Hysteresis $(\tau_h)$	$\text{Long}(\tau_{Tl})$	$Short(\tau_{Ts})$	Gradient $(\tau_p)$	$( au_{og})$	$( au_{dP})$	Diffusion $(\tau_{dT})$	
50.0	300.0	4.0	0.50	8.00	200.00	300.0	

# **CLIVAR A22: Conversion Equation Coefficients for CTD Oxygen** (refer to Equation 1.8.4.0)

Sta/	$O_c$ Slope	Offset	$P_h$ coeff	$T_l$ coeff	$T_s$ coeff	$P_l$ coeff	$\frac{dO_c}{dt}$ coeff	$\frac{dP}{dt}$ coeff	$T_{dT}$ coeff
Cast	$(c_1)$	$(c_3)$	$(c_2)$	$(c_4)$	$(c_5)$	$(c_{6})$	$(c_7)$	$(c_8)$	$(c_{9})$
001/02	6.642e-04	-0.2448	-1.8400	5.212e-03	-1.762e-02	-1.158e-01	2.820e-03	-1.158e-01	1.047e-02
002/02	8.034e-04	-0.2422	3.4168	-2.263e-02	-8.080e-03	5.536e-02	1.441e-03	5.536e-02	1.397e-03
003/01	3.949e-04	-0.1604	-1.8875	2.991e-02	2.541e-03	-6.785e-02	2.586e-03	-6.785e-02	-2.328e-02
004/01	5.376e-04	-0.2191	-1.5090	1.622e-02	-1.032e-02	-4.067e-02	2.237e-03	-4.067e-02	3.515e-03
005/01	5.393e-04	-0.1994	-0.4073	1.593e-04	6.479e-03	-4.905e-03	2.795e-03	-4.905e-03	-1.132e-02
006/01	6.519e-04	-0.3291	1.6563	1.327e-02	-1.407e-02	1.844e-02	-4.520e-03	1.844e-02	1.340e-02
007/01	5.248e-04	-0.2377	3.8916	6.541e-03	5.073e-03	4.057e-02	1.320e-03	4.057e-02	-3.110e-03
008/01	6.446e-04	-0.2931	1.0297	1.327e-02	-1.743e-02	1.098e-02	6.621e-03	1.098e-02	8.420e-03
009/01	5.588e-04	-0.1983	-0.3408	-1.518e-02	1.798e-02	-1.283e-02	-6.638e-03	-1.283e-02	-1.676e-02
010/01	5.845e-04	-0.2076	0.5549	-6.587e-03	4.644e-03	2.543e-02	3.553e-03	2.543e-02	9.715e-04
011/01	5.734e-04	-0.1791	-0.1288	-2.393e-03	-2.075e-03	1.520e-04	-1.386e-03	1.520e-04	-4.564e-04
012/01	5.984e-04	-0.2469	-0.0528	1.525e-03	-6.083e-04	-6.380e-03	-4.691e-04	-6.380e-03	8.138e-04
013/01	5.865e-04	-0.2248	-0.0457	-7.871e-03	8.581e-03	-2.517e-03	-3.120e-04	-2.517e-03	-2.960e-03
014/01	5.631e-04	-0.2037	-0.2142	-7.642e-03	9.523e-03	-1.584e-02	-2.872e-03	-1.584e-02	-8.374e-03
015/01	5.676e-04	-0.2153	-0.1645	-3.316e-03	5.425e-03	-9.933e-03	4.065e-03	-9.933e-03	-4.889e-03
016/01	5.753e-04	-0.2345	-0.1532	-1.186e-03	3.113e-03	-1.103e-02	2.152e-03	-1.103e-02	-6.391e-03
017/01	5.815e-04	-0.2281	-0.0968	-4.255e-03	5.356e-03	-4.662e-03	-2.187e-03	-4.662e-03	-6.545e-03
018/01	5.843e-04	-0.2205	-0.1057	1.405e-03	-7.194e-04	-1.412e-02	-3.364e-03	-1.412e-02	5.856e-04
019/01	5.457e-04	-0.1785	-0.2546	-6.330e-03	8.641e-03	-1.583e-02	4.282e-04	-1.583e-02	-8.594e-03
020/01	5.841e-04	-0.2195	-0.1071	4.616e-04	5.877e-04	-7.168e-03	6.206e-03	-7.168e-03	-1.066e-04
021/01	5.604e-04	-0.1856	-0.2060	-2.592e-03	4.290e-03	-1.985e-02	1.776e-03	-1.985e-02	-4.818e-03
022/01	6.073e-04	-0.2593	-0.0210	3.002e-03	-3.049e-03	-1.270e-03	4.588e-04	-1.270e-03	1.229e-03
023/01	6.215e-04	-0.2836	-0.0326	7.060e-03	-6.814e-03	-1.541e-02	-4.079e-03	-1.541e-02	2.437e-03
024/01	5.770e-04	-0.2176	-0.1686	-1.668e-03	2.988e-03	-2.267e-02	5.513e-03	-2.267e-02	-5.717e-03
025/01	5.995e-04	-0.2387	-0.1036	4.072e-03	-4.162e-03	-1.395e-02	1.192e-03	-1.395e-02	2.164e-03
026/01	6.046e-04	-0.2528	-0.0754	5.358e-03	-5.103e-03	-7.404e-03	2.883e-03	-7.404e-03	3.209e-03
027/01	7.448e-04	-0.4388	0.6982	1.890e-02	-2.361e-02	5.354e-03	-3.894e-04	5.354e-03	1.539e-02
028/01	5.677e-04	-0.2120	-0.1722	-1.503e-03	3.311e-03	-1.179e-02	1.426e-03	-1.179e-02	-3.391e-03
029/01	5.803e-04	-0.2425	-0.1292	2.050e-03	-4.132e-04	-1.491e-02	-8.356e-04	-1.491e-02	-5.977e-03
030/01	5.790e-04	-0.2253	-0.1518	-1.671e-03	2.996e-03	-1.481e-02	8.281e-04	-1.481e-02	-3.489e-03
031/01	5.161e-04	-0.1043	-0.4482	-2.108e-02	2.385e-02	-1.855e-02	6.077e-04	-1.855e-02	-1.242e-02
032/01	6.241e-04	-0.2818	-0.0215	6.568e-03	-6.971e-03	-1.197e-02	-1.732e-03	-1.197e-02	1.837e-03
033/01	5.700e-04	-0.2094	-0.1466	-7.423e-03	9.500e-03	-7.522e-03	7.109e-03	-7.522e-03	-9.432e-03
034/01	6.097e-04	-0.2565	-0.0709	1.158e-03	-9.006e-04	-1.927e-02	-9.041e-04	-1.927e-02	-2.041e-03
035/01	5.940e-04	-0.2351	-0.0751	4.665e-04	-1.972e-04	-5.268e-03	-1.624e-05	-5.268e-03	-2.183e-04
036/01	6.050e-04	-0.2455	-0.0591	-2.220e-03	2.438e-03	-7.737e-03	2.220e-03	-7.737e-03	-1.476e-03

Sta/	$O_c$ Slope	Offset	$P_h$ coeff	$T_l$ coeff	$T_s$ coeff	$P_l$ coeff	$\frac{dO_c}{dt}$ coeff	$\frac{dP}{dt}$ coeff	$T_{dT}$ coeff
Cast	$(c_1)$	$(c_3)$	$(c_2)$	$(c_4)$	$(c_5)$	$(c_{6})$	$(c_7)$	$(c_8)$	$(c_{9})$
037/01	5.960e-04	-0.2318	-0.0711	-3.046e-03	3.290e-03	-9.082e-03	-1.217e-03	-9.082e-03	-2.500e-03
038/01	5.894e-04	-0.2241	-0.0754	-1.777e-03	2.270e-03	-6.374e-03	6.591e-03	-6.374e-03	-1.441e-03
039/01	5.799e-04	-0.2081	-0.1270	-1.023e-02	1.121e-02	-1.349e-02	7.165e-04	-1.349e-02	-1.155e-02
040/01	5.972e-04	-0.2230	-0.0880	-4.873e-03	4.842e-03	-1.164e-02	9.243e-04	-1.164e-02	-1.216e-03
041/01	6.030e-04	-0.2379	-0.0669	-4.746e-04	4.783e-04	-1.339e-02	1.707e-03	-1.339e-02	-8.161e-04
042/01	5.988e-04	-0.2409	-0.1065	8.253e-04	-4.436e-04	-1.524e-02	7.536e-04	-1.524e-02	-1.602e-03
043/01	6.131e-04	-0.2506	-0.0471	4.173e-03	-4.365e-03	-1.225e-02	-2.409e-03	-1.225e-02	5.186e-03
044/01	5.962e-04	-0.2377	-0.0611	-6.919e-03	7.333e-03	-9.207e-03	-4.140e-03	-9.207e-03	-6.448e-03
045/01	6.123e-04	-0.2453	-0.0607	-4.663e-04	-1.141e-04	-1.575e-02	4.695e-03	-1.575e-02	-2.767e-04
046/01	6.053e-04	-0.2309	-0.0370	-4.987e-03	4.674e-03	-8.153e-03	-1.251e-03	-8.153e-03	-9.248e-04
047/01	5.988e-04	-0.2351	-0.0640	-3.572e-04	2.408e-04	-6.832e-03	7.362e-05	-6.832e-03	3.573e-04
048/01	6.091e-04	-0.2391	-0.0242	5.777e-04	-1.264e-03	2.028e-03	2.624e-03	2.028e-03	4.997e-03
049/01	5.424e-04	-0.2024	-0.4397	-3.916e-03	7.303e-03	-2.151e-02	-2.002e-03	-2.151e-02	-1.090e-02
050/01	5.874e-04	-0.2264	-0.1444	-1.848e-03	2.539e-03	-4.929e-03	-1.007e-04	-4.929e-03	-2.246e-03
051/01	6.462e-04	-0.2894	0.4984	-1.469e-03	9.369e-05	7.334e-03	1.600e-05	7.334e-03	-4.420e-04
052/01	6.800e-04	-0.3162	1.0582	1.457e-03	-4.476e-03	1.028e-02	1.667e-03	1.028e-02	6.645e-03
053/01	6.172e-04	-0.3436	1.8013	4.988e-03	-2.265e-03	1.749e-02	-1.912e-04	1.749e-02	-4.357e-03
054/01	1.305e-03	-0.4242	0.6181	-1.905e-02	-1.131e-02	6.616e-02	-2.247e-03	6.616e-02	3.074e-02
055/01	4.768e-04	-0.1485	-1.2900	1.536e-03	5.287e-03	-4.643e-03	-1.450e-03	-4.643e-03	-2.402e-02
056/01	5.799e-04	-0.2016	-0.1106	-6.575e-03	7.012e-03	-5.650e-03	1.007e-03	-5.650e-03	-1.974e-03
057/01	4.446e-04	-0.0131	-2.7392	-4.282e-04	4.742e-03	-1.629e-02	1.302e-03	-1.629e-02	-2.815e-02
058/01	7.042e-04	-0.3953	1.9412	7.506e-03	-8.839e-03	-2.302e-02	1.392e-03	-2.302e-02	-8.596e-03
059/01	5.512e-04	-0.2265	-0.9362	-3.414e-03	7.440e-03	-6.389e-02	2.321e-03	-6.389e-02	-2.136e-02
060/01	7.470e-04	-0.3079	0.8010	-2.767e-04	-6.971e-03	2.378e-02	3.557e-03	2.378e-02	1.862e-02
061/01	6.403e-04	-0.2491	0.4444	-3.321e-03	1.166e-03	2.814e-03	1.601e-03	2.814e-03	5.290e-03
062/01	6.235e-04	-0.2744	1.1414	-1.780e-03	1.723e-03	1.897e-02	9.954e-04	1.897e-02	-1.302e-03
063/01	5.853e-04	-0.2416	-0.1827	-1.843e-03	3.831e-03	-1.386e-02	4.120e-03	-1.386e-02	-7.807e-03
064/01	5.737e-04	-0.1959	-0.0676	-6.374e-03	7.405e-03	6.091e-04	2.042e-03	6.091e-04	-1.524e-03
065/01	5.653e-04	-0.1960	-0.2058	-1.113e-02	1.308e-02	-1.371e-02	-6.072e-03	-1.371e-02	-1.001e-02
066/01	6.058e-04	-0.2414	-0.0153	-1.531e-04	3.664e-04	8.264e-04	-3.663e-04	8.264e-04	1.631e-03
067/01	6.003e-04	-0.2258	-0.0573	-1.284e-03	1.872e-03	-5.803e-03	-2.041e-03	-5.803e-03	2.618e-03
068/01	5.872e-04	-0.2298	-0.1921	-3.329e-03	4.343e-03	-1.128e-02	-2.297e-03	-1.128e-02	-3.229e-03
069/01	5.762e-04	-0.2080	-0.1232	-4.788e-03	6.109e-03	-2.954e-03	3.963e-03	-2.954e-03	-2.886e-03
070/01	5.980e-04	-0.2392	-0.0428	-2.163e-03	2.697e-03	4.681e-03	2.904e-03	4.681e-03	-2.398e-03
071/01	5.920e-04	-0.2296	-0.1134	-1.788e-03	2.429e-03	-7.441e-03	1.078e-03	-7.441e-03	-7.572e-04
072/01	5.858e-04	-0.2115	-0.0055	-4.615e-03	4.854e-03	-1.945e-03	-5.246e-03	-1.945e-03	8.465e-04
073/01	5.749e-04	-0.2188	-0.2200	-9.460e-03	1.123e-02	-1.228e-02	-4.721e-03	-1.228e-02	-1.143e-02
074/01	6.480e-04	-0.3024	1.2051	6.478e-03	-7.307e-03	1.817e-02	4.208e-03	1.817e-02	7.035e-03
075/01	6.422e-04	-0.3034	1.3200	4.102e-03	-4.214e-03	2.150e-02	3.701e-03	2.150e-02	2.501e-03
076/01	6.552e-04	-0.2975	0.4556	-4.107e-04	-8.647e-04	4.916e-03	3.520e-03	4.916e-03	-8.091e-04
077/01	6.471e-04	-0.2848	1.0507	2.420e-03	-3.838e-03	2.505e-02	3.758e-03	2.505e-02	7.071e-03
078/01	5.871e-04	-0.2207	-1.0264	-8.897e-03	1.001e-02	-4.135e-02	-3.298e-03	-4.135e-02	-1.079e-02
079/01	5.925e-04	-0.2134	-1.0264	-1.328e-02	1.369e-02	9.146e-03	-1.661e-03	9.146e-03	-9.215e-03
080/01	5.455e-04	-0.2131	0.8037	1.695e-03	2.624e-03	-1.996e-02	3.612e-04	-1.996e-02	-7.834e-03
081/01	2.886e-04	-0.1221	3.3148	2.545e-02	3.888e-03	-1.845e-01	2.998e-03	-1.845e-01	-4.318e-03

## Appendix C

## **CLIVAR A22: Bottle Quality Comments**

Comments from the Sample Logs and the results of STS/ODF's data investigations are included in this report. Units stated in these comments are degrees Celsius for temperature, Unless otherwise noted, milliliters per liter for oxygen and micromoles per liter for Silicate, Nitrate, Nitrite, and Phosphate. The sample number is the cast number times 100 plus the bottle number. Investigation of data may include comparison of bottle salinity and oxygen data with CTD data, review of data plots of the station profile and adjoining stations, and re-reading of charts (i.e. nutrients).

Station	Sample	Quality		
/Cast	No.	Property	Code	Comment
1/2	201	bottle	2	Cast 1 was aborted during equilibration process. Dummy plug was left off the bottom contact switch port resulting in an deck unit alarm.
1/2	202	o2	2	Saw bubble in flask before re-shaking. Oxygen as well as salinity and nutrients are acceptable.
1/2	204	o2	2	Left thio tip out, acid left in sample longer than normal while restarting run. Oxygen is a little low. Oxygen as well as salinity and nutrients are acceptable.
1/2	208	o2	2	Oxygen sample was run before any chemicals were added. Oxygen as well as salinity and nutrients are acceptable.
2/2	201	bottle	2	Cast 1 was aborted at ~270m, winch problem.
2/2	204	salt	2	Decreasing trend in salinity measurement, probable contamination. Salinity is slightly low, within accuracy of the measurement. Salinity as will as oxygen and nutrients are acceptable.
2/2	212	o2	5	Oxygen sample was lost during analysis.
2/2	213	reft	3	SBE35RT, CTDT1, CTDT2 all disagree; very unstable SBE35RT reading in a gradient. Code questionable.
2/2	217	po4	2	Appears the nutrients were mis-drawn from 16. Data are acceptable, leave as is. Subsequent stations show a feature. Analyst: Could be mis-drawn, no problem with the run or peaks.
2/2	219	reft	3	SBE35RT +0.07/+0.10 vs CTDT1/CTDT2; very unstable SBE35RT reading. Code questionable.
3/1	101	o2	2	Oxygen run stopped and then restarted, did not affect the sample.
3/1	114	reft	3	SBE35RT, CTDT1, CTDT2 all disagree; very unstable SBE35RT reading in a gradient. Code questionable.
3/1	116	o2	2	Oxygen run stopped and then restarted, did not affect the sample.
3/1	116	salt	2	3 attempts for a good salinity reading. Salinity as well as oxygen and nutrients are acceptable.
3/1	120	bottle	9	Bottle was knocked open on recovery, drained before sampling, no water for sampling.
3/1	120	reft	3	SBE35RT -0.02/-0.06 vs CTDT1/CTDT2; very unstable SBE35RT reading. Code questionable.
3/1	122	salt	2	Bottle salinity is low compared with CTD, agrees with adjoining stations at the surface. 3 attempts for a good salinity reading. Bottle salinity as well as the oxygen and nutrients are acceptable.
4/1	104	salt	2	3 attempts for a good salinity reading. Salinity as well as oxygen and nutrients are acceptable.
4/1	107	salt	2	3 attempts for a good salinity reading. First reading was more appropriate, corrected data file. Salinity as well as oxygen and nutrients are acceptable.

Station /Cast	Sample No.	Quality Property	Code	Comment
4/1	113	reft	3	SBE35RT -0.02/-0.025 vs CTDT1/CTDT2; unstable SBE35RT reading. Code
4/1	119	reft	3	questionable.  SBE35RT, CTDT1, CTDT2 all disagree; very unstable SBE35RT reading in a gradient. Code questionable.
4/1	120	salt	2	Extra salinity sample in position 36, it appears to have been drawn from bottle 20, corrected the raw data file. Data are acceptable. 4 attempts for a good salinity reading. Salinity as well as oxygen and nutrients are acceptable.
4/1	125	po4	2	Appears the nutrients were mis-drawn from 26, PO4 0.1 high and SiO3 1.0 high, do not see this in NO3 or salinity and oxygen. This feature is seen in subsequent stations. Data are acceptable. Analyst: Peaks look good.
5/1	102	salt	2	4 attempts for a good salinity reading. Thimble partially came out with cap. Possible contamination. Salinity is within specification and is acceptable as well as oxygen and nutrients.
5/1	108	salt	2	Bottle salinity is high compared with CTD and adjoining stations. 4 attempts for a good salinity reading. Thimble partially came out with cap. Possible contamination. Additional reading resolved salinity discrepancy. Salinity as well as oxygen and nutrients are acceptable.
5/1	109	bottle	2	CFC sampler reported that vent not closed, small leak when spigot opened. CFC did not sample. Oxygen and nutrients are acceptable.
5/1	116	salt	2	4 attempts for a good salinity reading. Salinity as well as oxygen and nutrients are acceptable.
5/1	118	bottle	9	O-ring cap leak, bottom end cap askew. No samples were taken.
5/1	121	salt	2	3 attempts for a good salinity reading. Additional readings resolved salinity discrepancy. Salinity as well as oxygen and nutrients are acceptable.
5/1	123	salt	2	3 attempts for a good salinity reading. Salinity as well as oxygen and nutrients are acceptable.
5/1	128	salt	2	Bottle salinity is low compared with CTD agrees as surface sample with adjoining stations. Salinity as well as oxygen and nutrients are acceptable.
5/1	130	po4	2	PO4 appears high, feature also seen in NO3 and O2, SiO3 does not show this. Trend seen in subsequent stations heading toward the Gulf Stream. Analyst: Data are acceptable.
5/1	131	o2	3	Noisy oxygen endpoint fixed. Measurement still appears questionable.
5/1	131	salt	2	Bottle salinity is low compared with CTD agrees as surface sample with adjoining stations. Salinity as well as oxygen and nutrients are acceptable.
6/1	115	o2	5	Oxygen appears to have been mis-drawn sample 15-18. 15 appears to have been drawn from 16, 16 from 17, 17 from 18 and 18 a duplicate with 19. Switched these levels. Code oxygen as lost.
6/1	116	no2	9	, c
6/1	116	no3	9	
6/1	116	o2	2	Oxygen appears to have been mis-drawn sample 15-18. 15 appears to have been drawn from 16, 16 from 17, 17 from 18 and 18 a duplicate with 19. Switched these levels.
6/1	116	po4	9	Nutrient tube was found empty, must have been a sampling error.
6/1	116	sio3	9	
6/1	117	o2	2	Oxygen appears to have been mis-drawn sample 15-18. 15 appears to have been drawn from 16, 16 from 17, 17 from 18 and 18 a duplicate with 19. Switched these levels.
6/1	118	bottle	3	Leaking from bottom end cap when top vent is opened, same as last station. O-ring changed out.
6/1	118	no2	9	-
6/1	118	no3	9	

Station /Cast	Sample No.	Quality Property	Code	Comment
6/1	118	o2	4	Oxygen appears to have been drawn from bottle 19. Sampler indicates there may have been a sampling error, appears bottle 15 was drawn from 16, 16 from 17, 17 from 18 and 18 was drawn from 19. Will leave the recorded value for 19 as is. Code Oxygen bad, salinity and nutrients not drawn.
6/1	118	po4	9	Nutrients were not drawn, bottle ran out of water.
6/1	118	salt	9	Salinity was not drawn, bottle ran out of water.
6/1	118	sio3	9	
6/1	121	salt	2	3 attempts for a good salinity reading. Salinity as well as oxygen and nutrients are acceptable.
6/1	124	salt	2	3 attempts for a good salinity reading. Check heater light signal came on; forward bulb burned out. Heater continues to cycle, on duty is approximately 90%. Salinity as well as oxygen and nutrients are acceptable.
6/1	126	reft	3	SBE35RT -0.03/-0.065 vs CTDT1/CTDT2; very unstable SBE35RT reading. Code questionable.
6/1	127	reft	3	SBE35RT -0.02/-0.06 vs CTDT1/CTDT2; very unstable SBE35RT reading. Code questionable.
7/1	102	bottle	2	Salinity and nutrient samples taken, water used for nutrient checks.
7/1	115	salt	2	3 attempts for a good salinity reading. Salinity as well as oxygen and nutrients are acceptable.
7/1	132	salt	2	Bottle salinity is low compared with CTD agrees with adjoining stations for a shallow profile. There is fluctuation in the CTD profile at the bottle trip. Salinity as well as oxygen and nutrients are acceptable.
7/1	134	o2	5	Error during analysis, O2 sample lost.
7/1	134	salt	2	Bottle salinity is low compared with CTD agrees with adjoining stations for a shallow profile. There is fluctuation in the CTD profile at the bottle trip. Salinity as well as oxygen and nutrients are acceptable.
7/1	135	bottle	2	Leaking at bottom, reported by DIC sampler. Oxygen as a surface sample is acceptable as well as salinity and nutrients.
8/1	101	bottle	2	Package lowered 60m after tripping bottle 20, winch problems. Bottles appear okay except for 19.
8/1	102	bottle	2	Package lowered 60m after tripping bottle 20, winch problems. Bottles appear okay except for 19.
8/1	103	bottle	2	Package lowered 60m after tripping bottle 20, winch problems. Bottles appear okay except for 19.
8/1	104	bottle	2	Package lowered 60m after tripping bottle 20, winch problems. Bottles appear okay except for 19.
8/1	105	bottle	2	Package lowered 60m after tripping bottle 20, winch problems. Bottles appear okay except for 19.
8/1	106	bottle	2	Package lowered 60m after tripping bottle 20, winch problems. Bottles appear okay except for 19.
8/1	107	bottle	2	Package lowered 60m after tripping bottle 20, winch problems. Bottles appear okay except for 19.
8/1	108	bottle	2	Package lowered 60m after tripping bottle 20, winch problems. Bottles appear okay except for 19.
8/1	109	bottle	2	Package lowered 60m after tripping bottle 20, winch problems. Bottles appear okay except for 19.
8/1	110	bottle	2	Package lowered 60m after tripping bottle 20, winch problems. Bottles appear okay except for 19.
8/1	111	bottle	2	Package lowered 60m after tripping bottle 20, winch problems. Bottles appear okay except for 19.

Station /Cast	Sample No.	Quality Property	Code	Comment
8/1	112	bottle	2	Package lowered 60m after tripping bottle 20, winch problems. Bottles appear okay except for 19.
8/1	113	bottle	2	Package lowered 60m after tripping bottle 20, winch problems. Bottles appear okay except for 19.
8/1	114	bottle	2	Package lowered 60m after tripping bottle 20, winch problems. Bottles appear okay except for 19.
8/1	115	bottle	2	Package lowered 60m after tripping bottle 20, winch problems. Bottles appear okay except for 19.
8/1	116	bottle	2	Package lowered 60m after tripping bottle 20, winch problems. Bottles appear okay except for 19.
8/1	117	bottle	2	Package lowered 60m after tripping bottle 20, winch problems. Bottles appear okay except for 19.
8/1	118	bottle	2	Package lowered 60m after tripping bottle 20, winch problems. Bottles appear okay except for 19.
8/1	119	bottle	3	Bottle appears to have leaked, caused by lowering of the package. PO4 low, NO2 low, SiO3 does agree with adjoining stations, O2 is high.
8/1	119	no2	4	
8/1	119	no3	4	
8/1	119	o2	4	O2 high, ~0.2 ml/l. No analytical problems noted, the bottle leaked. Code oxygen bad.
8/1	119	po4	4	
8/1	119	salt	4	Salinity low compared with adjoining stations.
8/1	119	sio3	4	· · · · ·
8/1	120	bottle	2	Package lowered 60m after tripping bottle 20, winch problems. Bottles appear okay except for 19.
8/1	124	reft	3	SBE35RT +0.04/+0.025 vs CTDT1/CTDT2; very unstable SBE35RT reading in a gradient. Code questionable.
8/1	128	reft	3	SBE35RT -0.045 vs CTDT; in a gradient. Code questionable.
8/1	131	salt	4	Bottle salinity is low compared with CTD and adjoining stations. No analytical problems noted, sample was run very quickly. Could have been mis-drawn from 33. Code salinity bad, oxygen and nutrients are acceptable.
8/1	135	bottle	2	Leak from bottom, bottom o-ring missing, replaced after sampling. Salinity, oxygen and nutrients are acceptable.
9/1	127	salt	5	Salinity sample bottle was empty. Code salinity lost, sampler error.
9/1	134	reft	3	SBE35RT -0.05 vs CTDT; very unstable SBE35RT reading. Code questionable.
9/1	134	salt	2	3 attempts for a good salinity reading. Salinity thimble came off with cap. Salinity is a little high compared with CTD changing area, acceptable as shallow sample with adjoining station. Salinity as well as oxygen and nutrients are acceptable.
10/1	104	salt	2	4 attempts for a good salinity reading. Salinity as well as oxygen and nutrients are acceptable.
10/1	105	salt	2	4 attempts for a good salinity reading. Salinity as well as oxygen and nutrients are acceptable.
10/1	106	salt	4	Bottle salinity is low compared with CTD and adjoining stations. 4 attempts for a good salinity reading. Additional readings did not resolve salinity discrepancy. Code salinity bad, oxygen and nutrients are acceptable. Backup salinometer was employed after this sample.
10/1	108	salt	2	3 attempts for a good salinity reading. Salinity as well as oxygen and nutrients are acceptable.
10/1	109	bottle	2	Could only rinse salinity bottle once, low on water. Minimal sampling on this bottle. Salinity as well as oxygen and nutrients are acceptable.

Station /Cast	Sample No.	Quality Property	Code	Comment
10/1	110	salt	2	3 attempts for a good salinity reading. Salinity as well as oxygen and nutrients are
10/1	120	salt	2	acceptable. Salinity bottle has a broken lip, bottle retired after analysis performed. Salinity as
10/1	129	reft	3	well as oxygen and nutrients are acceptable. SBE35RT -0.035/-0.04 vs CTDT1/CTDT2; unstable SBE35RT reading. Code
				questionable.
10/1	130	reft	3	SBE35RT -0.03/-0.05 vs CTDT1/CTDT2; unstable SBE35RT reading. Code questionable.
10/1	131	reft	3	SBE35RT -0.08/-0.07 vs CTDT1/CTDT2; unstable SBE35RT reading. Code questionable.
10/1	132	salt	2	4 attempts for a good salinity reading. Salinity as well as oxygen and nutrients are acceptable.
10/1	134	salt	2	Bottle salinity is high compared with CTD and adjoining stations. Variation at trip in CTD, salinity agrees with shallow region adjoining stations. Salinity as well as oxygen and nutrients are acceptable.
10/1	135	o2	2	Oxygen endpoint not believable. Measurement likely bad. Compared with adjoining stations and CTD, oxygen is acceptable.
11/1	105	salt	5	Salinity bottles are full after station 15. Salinometer had a problem and the spare was not equilibrated to complete the analysis and free bottles. Bottles 5, 9 and 15 were requested to be pulled for subsequent station, 16, 11 was pulled instead of 15. Code salinity lost.
11/1	109	salt	5	Code salinity lost, see bottle 5 explanation.
11/1	110	salt	4	Bottle salinity is high compared with CTD and adjoining stations. Additional readings did not resolve salinity discrepancy. If this were a mis-draw it would have to come from bottle 13. Code salinity bad, oxygen and nutrients are acceptable.
11/1	111	salt	5	Code salinity lost, see bottle 5 explanation.
11/1	135	reft	3	SBE35RT -0.07 vs CTDT; unstable SBE35RT reading. Code questionable.
11/1	135	salt	2	3 attempts for a good salinity reading. Salinity as well as oxygen and nutrients are acceptable.
12/1	103	salt	5	Salinity bottles are full after station 15. Salinometer had a problem and the spare was not equilibrated to complete the analysis and free bottles until Station 17. Bottles 5, 9 and 15 were requested to be pulled for subsequent station, 16, 11 was pulled instead of 15. Code salinity lost.
12/1	106	salt	4	Bottle salinity is high compared with CTD and adjoining stations. 3 attempts for a good salinity reading. Additional readings do not resolve salinity discrepancy, could be a mis-draw with 7. Code salinity bad, oxygen and nutrients are acceptable.
12/1	107	salt	5	Code salinity lost, see bottle 3 explanation.
12/1	110	salt	5	Code salinity lost, see bottle 3 explanation.
12/1	132	salt	2	Bottle salinity is low compared with CTD, acceptable for a shallow maximum sample with variation in the water column. Salinity as well as oxygen and nutrients are acceptable.
12/1	134	salt	2	Bottle salinity is low compared with CTD, acceptable for a shallow sample with variation in the water column. Salinity as well as oxygen and nutrients are acceptable.
13/1	101	salt	2	Larger than normal drift, suspect and adjust the beginning bad SSW vial. Salinity agreement much better with adjoining stations and CTD, although there was a lot of noise in the run.
13/1	104	salt	5	Salinity bottles are full after station 15. Salinometer had a problem and the spare was not equilibrated to complete the analysis and free bottles. Bottles 5, 9 and 15 were requested to be pulled for subsequent station, 16, 11 was pulled instead of 15. Code salinity lost.

Station /Cast	Sample No.	Quality Property	Code	Comment
13/1	106	salt	3	Salinity low compared with adjoining stations and CTD. Code salinity questionable,
13/1	100	Suit	5	oxygen and nutrients are acceptable.
13/1	108	salt	5	Code salinity lost, see bottle 4 explanation.
13/1	110	salt	3	Bottle salinity is low compared with CTD and adjoining stations. Suspect Black
13/1	110	san	3	Carbon sampling only left dregs. Code salinity questionable, oxygen and nutrients
				are acceptable.
13/1	111	salt	2	3 attempts for a good salinity reading. Additional readings resolved salinity
13/1	111	Suit	2	discrepancy. Salinity, oxygen and nutrients are acceptable.
13/1	112	salt	2	03 attempts for a good salinity reading. Additional readings did not resolved salinity
13/1	112	Suit	_	discrepancy. Throughout the run there were noisy values, this is within measurement
				specs. Salinity, oxygen and nutrients are acceptable.
13/1	113	salt	5	Code salinity lost, see bottle 4 explanation.
13/1	119	salt	4	Bottle salinity is low compared with CTD and adjoining stations. Salinity appears to
13/1	11)	san	-	have been mis-drawn from 18. Code salinity bad.
13/1	121	salt	2	Bottle salinity is low compared with CTD and adjoining stations. 3 attempts for a
13/1	121	san	2	good salinity reading. Additional readings did not resolve salinity discrepancy.
				Salinity as well as oxygen and nutrients are acceptable.
13/1	125	salt	2	5 attempts for a good salinity reading. Erratic readings, possible contamination.
13/1	123	sait	2	
				Additional readings did not resolve salinity discrepancy. Salinity as well as oxygen and nutrients are acceptable.
12/1	128	reft	3	•
13/1	128	ren	3	SBE35RT +0.035/+0.04 vs CTDT1/CTDT2; unstable SBE35RT reading in a
12/1	120	14	2	gradient. Code questionable.
13/1	130	salt	2	5 attempts for a good salinity reading. Erratic readings, possible contamination.
				Additional readings did not resolve salinity discrepancy. Salinity as well as oxygen
10/1	101	C.	2	and nutrients are acceptable.
13/1	131	reft	3	SBE35RT +0.06 vs CTDT; somewhat unstable SBE35RT reading. Code
10/1	100			questionable.
13/1	132	reft	3	SBE35RT -0.025/-0.03 vs CTDT1/CTDT2; unstable SBE35RT reading in a high
		_	_	gradient. Code questionable.
14/1	103	salt	5	Salinity bottles are full after station 15. Salinometer had a problem and the spare was
				not equilibrated to complete the analysis and free bottles. Bottles 5, 9 and 15 were
				requested to be pulled for subsequent station, 16, 11 was pulled instead of 15. Code
		_	_	salinity lost.
14/1	104	o2	3	Noisy endpoint for O2. May be slightly high, 0.03, compared with CTD and
				adjoining stations. Code O2 questionable, salinity and nutrients are acceptable.
14/1	105	bottle	2	Feature seen in oxygen, higher, and the nutrients, lower, which is not seen in salinity
				Data are acceptable.
14/1	109	salt	5	Code salinity lost, see bottle 3 explanation.
14/1	110	ctds	2	CTDS feature is real, seen in TS and O2, for both primary and secondary sensors.
				Code acceptable.
14/1	110	salt	2	Bottle salinity is high compared with CTD agrees with adjoining stations. Feature
				seen in CTD that must not have been captured by the bottle. Salinity as well as
				oxygen and nutrients are acceptable.
14/1	112	salt	5	Code salinity lost, see bottle 3 explanation.
14/1	115	salt	4	Bottle salinity is low compared with CTD and adjoining stations. Sample very fresh
				could have been sampled from another station, 1-11. Code salinity bad.
14/1	121	o2	4	Bad endpoint for O2 (None). O2 is slightly high compared with CTD and adjoining
				station. Code O2 bad.
14/1	128	o2	2	O2 program froze. Restarted, no problem with the sample.
14/1	132	reft	3	Somewhat unstable SBE35RT reading in gradient. Code questionable.

Station /Cast	Sample No.	Quality Property	Code	Comment
15/1	118	salt	4	Bottle salinity is high compared with CTD and adjoining stations. Thimble came
				with cap. Code salinity bad, oxygen and nutrients are acceptable.
15/1	128	salt	5	Marked as sampled, salt bottle was empty. Code salinity lost.
15/1	134	reft	3	SBE35RT +0.03/+0.025 vs CTDT1/CTDT2; somewhat unstable SBE35RT reading in a high gradient. Code questionable.
16/1	101	salt	2	Not all salinities were drawn on this station. Backup salinometer was brought into service and needed to equilibrate before using, all salinity bottles were employed. Salinity bottle were pulled from Stations 11, 12, 13 and 14 to provide salinity for levels sampled for carbon and some deep checks for CTD calibrations.
16/1	110	o2	2	Accidentally added 2 stir bars during O2 analysis, had to extract and rinse. Oxygen as well as salinity and nutrients are acceptable.
16/1	134	bottle	2	Vent was open when started to sample. Oxygen as well as salinity and nutrients are acceptable.
16/1	135	bottle	2	Vent was open when started to sample. Oxygen as well as salinity and nutrients are acceptable.
16/1	136	bottle	2	Vent was open when started to sample. Oxygen as well as salinity and nutrients are acceptable.
17/1	105	salt	4	Bottle salinity is high compared with CTD and adjoining stations. 3 attempts for a good salinity reading. Additional readings did not resolve salinity discrepancy. Code salinity bad, oxygen and nutrients are acceptable.
18/1	111	reft	3	deep SBE35RT +0.003 vs CTDT1/CTDT2; unstable SBE35RT reading. Code questionable.
18/1	117	salt	2	Bottle salinity is high compared with CTD and adjoining stations. 3 attempts for a good salinity reading. Thimble came out with cap, possible contamination. First reading resolved salinity discrepancy. Salinity as well as oxygen and nutrients are acceptable.
18/1	134	salt	2	3 attempts for a good salinity reading. Thimble came out with cap, possible contamination. Salinity, gradient and within data specification, as well as oxygen and nutrients are acceptable.
19/1	108	o2	2	Sample was over-titrated and back-titrated. This is the over-titrated run due to a very poor curve. Oxygen as well as salinity and nutrients are acceptable.
19/1	116	salt	2	3 attempts for a good salinity reading. Salinity as well as oxygen and nutrients are acceptable.
19/1	121	reft	3	SBE35RT +0.065/+0.035 vs CTDT1/CTDT2; somewhat unstable SBE35RT reading in a gradient. Code questionable.
20/1	114	salt	2	3 attempts for a good salinity reading. Salinity is slightly high, additional readings do not resolve salinity discrepancy. Salinity as well as oxygen and nutrients are acceptable.
20/1	116	salt	2	3 attempts for a good salinity reading. Salinity is acceptable with two reading agreement. Salinity as well as oxygen and nutrients are acceptable.
20/1	119	o2	2	O2 titration error. Oxygen agrees with adjoining station and reasonable in gradient. Oxygen as well as salinity and nutrients are acceptable.
20/1	131	salt	2	3 attempts for a good salinity reading. Salinity is acceptable with two reading agreement. Salinity as well as oxygen and nutrients are acceptable.
21/1	124	o2	2	Sample was over-titrated and back-titrated. Missed O2 Endpoint. Oxygen is acceptable.
21/1	124	salt	2	Bottle salinity is high compared with CTD, gradient area, acceptable agreement. Salinity as well as oxygen and nutrients are acceptable
22/1	113	salt	2	3 attempts for a good salinity reading. Thimble came out with cap, possible contamination. Additional reading resolved salinity discrepancy. Salinity as well as oxygen and nutrients.

Station /Cast	Sample No.	Quality Property	Code	Comment
22/1	115	o2	2	Sample was over-titrated and back-titrated, original curve bad. This didn't look much better. Original titration fits the station profile, corrected the file. Oxygen as well as
22/1	121	salt	2	salinity and nutrients are acceptable.  3 attempts for a good salinity reading. Salinometer had a momentary freeze of temperature control circuit bath temperature went low on first reading. Salinity as
22/1	122	reft	3	well as oxygen and nutrients are acceptable. SBE35RT +0.05/+0.06 vs CTDT1/CTDT2; unstable SBE35RT reading. Code questionable.
22/1	122	salt	2	Bottle salinity is high compared with CTD, gradient area. Salinity as well as oxygen and nutrients are acceptable.
22/1	135	o2	2	Sample was over-titrated and back-titrated. Looks much better. Oxygen as well as salinity and nutrients are acceptable.
23/1	101	salt	2	Bubbles in rinse discharge. Autosal cell cleaned prior to use. Salinity for cast are slightly low, well within measurement specifications.
23/1	110	o2	2	Dissolved sample sat for a while due to a needed computer reboot. Feature in O2 both bottle and CTD, same feature seen in salinity and nutrients.
23/1	123	o2	2	Oxygen endpoint a bit high, agrees with adjoining stations. Oxygen as well as salinity and nutrients are acceptable.
24/1	107	o2	2	Program froze. Restarted before titrating sample. Oxygen agrees with CTD and adjoining stations and is acceptable as are salinity and nutrients.
24/1	121	reft	3	SBE35RT +0.025/+0.035 vs CTDT1/CTDT2; very unstable SBE35RT reading in a gradient. Code questionable.
24/1	127	o2	2	Noisy, bad O2 endpoint. Oxygen agrees with CTD and adjoining stations and is acceptable as are salinity and nutrients.
25/1	122	salt	2	Bottle salinity is high compared with CTD, agrees as well in gradient area. Salinity, oxygen and nutrients are acceptable.
25/1	123	reft	3	SBE35RT -0.02/-0.035 vs CTDT1/CTDT2; somewhat unstable SBE35RT reading in a gradient. Code questionable.
25/1	123	salt	2	Bottle salinity is low compared with CTD, agrees as well in gradient area. Salinity, oxygen and nutrients are acceptable.
25/1	130	salt	2	Salinity computer shut off inexplicably. No other programs were running. No data transfer in progress. Unknown failure. Salinity as well as oxygen and nutrients are acceptable.
26/1	107	o2	5	Forgot to add acid. Oxygen sample lost.
26/1	108	o2	2	Sample was over-titrated and back-titrated, did over-titration after 0.139ml thio added to sample. system went into low o2 mode and was running too slowing. Oxygen is slightly low, will attempt to recalculate. O2 vs. SiO3 relationship low. Code oxygen questionable, salinity and nutrients are acceptable.
26/1	113	salt	5	Salinity error found empty before analysis, sampling error. Code salinity lost.
26/1	124	o2	2	Ran as niskin flask 1328 & temp 6.5, actually flask 1687 & temp 16.4. O2 data files corrected, oxygen is acceptable. Oxygen as well as salinity and nutrients are acceptable.
27/1	101	salt	2	3 attempts for a good salinity reading. Additional readings resolved salinity discrepancy. Salinity as well as oxygen and nutrients are acceptable.
27/1	105	salt	2	3 attempts for a good salinity reading. Salinity is within measurement specification and is acceptable as well as oxygen and nutrients.
27/1	107	salt	2	4 attempts for a good salinity reading, resolved salinity discrepancy. Salinity as well as oxygen and nutrients are acceptable.
27/1	108	salt	2	5 attempts for a good salinity reading. Salinity is acceptable with chosen readings. Salinity, oxygen and nutrients are acceptable.

1	_	Quality		
/Cast	No.	Property	Code	Comment
27/1	112	salt	2	4 attempts for a good salinity reading. Additional readings did not resolve salinity discrepancy. Salinity is within measurement specification and is acceptable as well as oxygen and nutrients.
27/1	125	o2	5	Software froze mid-titration. O2 sample lost.
27/1	135	o2	2	Oxygen flask 1544 broke, replaced with 1089.
28/1	108	o2	2	Stopper from 1311. O2 endpoint good but volume questionable. Oxygen is
28/1	122	salt	2	acceptable.  Bottle salinity is low compared with CTD agrees with adjoining gradient area stations with a strong difference between the down and up cast. No analytical problems noted. Salinity as well as oxygen and nutrients are acceptable.
29/1	109	salt	2	Salinity bottle had no water in it when first sampled indicating it may have been a new bottle. Salinity, oxygen and nutrients are acceptable.
29/1	113	reft	3	deep SBE35RT -0.007 vs CTDT1/CTDT2; very unstable SBE35RT reading. Code questionable.
29/1	122	o2	2	Sample was over-titrated and back-titrated, similar curve as before. Oxygen is acceptable. Oxygen, salinity and nutrients are acceptable.
29/1	122	reft	3	SBE35RT -0.75/-0.06 vs CTDT1/CTDT2; very unstable SBE35RT reading. Code questionable.
30/1	119	po4	2	PO4, NO3 and SiO3 appears high compared with adjoining stations. This is not seen in O2, salinity is slightly low. All within accuracy, nutrients as well as salinity and oxygen are acceptable. Analyst: Run looks good. Value seems ok on overlay plot with Stations 28-32.
30/1	130	reft	2	Winch restarted a few seconds before SBE35RT reading done, value looks ok.
31/1	101	o2	3	Oxygen high compared with CTD and adjoining stations, samples 1-7. Analysts not certain what caused this, suspect sampling exposure to high winds with no protection. Code oxygen questionable, salinity and nutrients are acceptable.
31/1	102	o2	3	Oxygen high compared with CTD and adjoining stations, samples 1-7. Analysts not certain what caused this, suspect sampling exposure to high winds with no protection. Code oxygen questionable, salinity and nutrients are acceptable.
31/1	102	salt	2	3 attempts for a good salinity reading. Thimble came off with cap. Additional readings resolved salinity discrepancy. Salinity as well as oxygen and nutrients are acceptable.
31/1	103	o2	3	Oxygen high compared with CTD and adjoining stations, samples 1-7. Analysts not certain what caused this, suspect sampling exposure to high winds with no protection. Code oxygen questionable, salinity and nutrients are acceptable.
31/1	104	o2	5	System froze. O2 sample lost. Salinity and nutrients are acceptable.
31/1	105	o2	3	Oxygen high compared with CTD and adjoining stations. Not certain what caused this however sampling was exposed to wind, suspect that is the cause of the high oxygen. Code oxygen questionable, salinity and nutrients are acceptable.
31/1	106	o2	3	Oxygen high compared with CTD and adjoining stations. Not certain what caused this however sampling was exposed to wind, suspect that is the cause of the high oxygen. Code oxygen questionable, salinity and nutrients are acceptable.
31/1	106	salt	2	3 attempts for a good salinity reading. Thimble came off with cap. Additional readings resolved salinity discrepancy. Salinity as well as oxygen and nutrients are acceptable.
31/1	107	o2	4	O2 value too high. Likely system/operator error. Salinity and nutrients are acceptable.
31/1	112	o2	4	Overshot O2 endpoint. Code O2 bad. Salinity and nutrients are acceptable.
31/1	113	sio3	3	SiO3 appears low compared with adjoining stations, did not show in other properties. Analyst: SiO3 peak is low in the run, real but questionable data. Code SiO3 questionable, other nutrients, salinity and oxygen are acceptable.

Station /Cast	Sample No.	Quality Property	Code	Comment
31/1	118	o2	3	Oxygen high compared with CTD and adjoining stations. Not certain what caused this however sampling was exposed to wind, suspect that is the cause of the high oxygen. Code oxygen questionable, salinity and nutrients are acceptable.
31/1	127	o2	3	Oxygen high compared with CTD and adjoining stations. Not certain what caused this however sampling was exposed to wind, suspect that is the cause of the high
31/1	135	02	3	oxygen. Code oxygen questionable, salinity and nutrients are acceptable. Oxygen high compared with CTD and adjoining stations. Not certain what caused the O2 problems on this station, however, sampling was exposed to wind, suspect that is the cause of the high oxygen. Code oxygen questionable. This bottle was found to have a leaking/tripping problem on Station 33. The O2 draw temperature does not reflect that problem. Reviewed previous stations specifically for bottle 35 and did not see a mis-tripping problem.
32/1	124	reft	3	SBE35RT +0.035/+0.045 vs CTDT1/CTDT2; somewhat unstable SBE35RT reading in a gradient. Code questionable.
32/1	125	o2	2	Oxygen may have lost thio, possibly bad. Oxygen agrees with adjoining stations and is acceptable.
33/1	105	salt	2	3 attempts for a good salinity reading. Two good readings averaged properly. Salinity as well as oxygen and nutrients are acceptable.
33/1	120	o2	2	Noisy endpoint. Oxygen as well as salinity and nutrients are acceptable.
33/1	126	o2	2	Lost part of sample after adding reagent. Oxygen as well as salinity and nutrients are acceptable.
33/1	135	bottle	3	Oxygen draw temperature colder than adjoining bottles, could be a mis-trip. Nutrients are high, oxygen is low, bottle in fact tripped early. On Station 34, spring changed out. Code bottle 3, samples bad. This bottle was found to have a leaking/tripping problem on Station 33. The O2 draw temperature indicates the bottl tripped shallower.
33/1	135	no2	4	••
33/1	135	no3	4	
33/1	135	o2	4	
33/1	135	po4	4	
33/1	135	salt	4	Salt bottle value low, niskin problem, code bad.
33/1	135	sio3	4	
34/1	126	bottle	9	Lanyard hooked on recovery-no water.
34/1	135	bottle	3	O2 draw temperature indicates a problem with the bottle tripping. Interconnect lanyard not repaired properly from Station 6 and repaired after Station 7. Bottom cap started shutting prematurely, repaired after this cast.
34/1	135	no2	4	
34/1	135	no3	4	
34/1	135	o2	4	Oxygen low, bottle problem. Code oxygen bad.
34/1	135	po4	4	Nutrients high, bottle problem. Code PO4, NO3, NO2, SiO3 bad.
34/1	135	salt	4	Salt bottle value low, niskin problem, code bad.
34/1	135	sio3	4	
35/1	101	bottle	2	Ship speed reduced to ~2kn for sampling.
35/1	124	reft	3	SBE35RT +0.08/+0.10 vs CTDT1/CTDT2; very unstable SBE35RT reading in a gradient. Code questionable.
35/1	125	salt	2	Bottle salinity is high compared with CTD, gradient area. Salinity as well as oxygen and nutrients are acceptable.
35/1	134	salt	2	3 attempts for a good salinity reading. First reading resolved slight salinity discrepancy. Salinity as well as oxygen and nutrients are acceptable.
36/1	118	o2	3	Same random slow titration problem, has not as yet affected the O2 sample. O2 low. Code O2 questionable, salinity and nutrients are acceptable.

Station /Cast	Sample No.	Quality Property	Code	Comment
37/1	113	salt o2	5	Salinity sample lost, operator error, forgot to take the reading after flushing.
37/1	122		4 2	Oxygen is high, suspect sampling error. Code O2 bad. Oxygen flask switched, Sample Log was followed during analysis and O2 is
37/1	125	o2		acceptable.
38/1	103	bottle	2	Difficult to open spigot/nozzle, 3, 12, 16, 23,26. Bottle maintenance prior to the next station, cleaning the pins.
39/1	105	salt	2	3 attempts for a good salinity reading. Readings resolved salinity discrepancy. Salinity is acceptable as well as oxygen and nutrients.
39/1	106	salt	3	Bottle salinity is high compared with CTD and adjoining stations. No analytical problems noted. Code salinity questionable, oxygen and nutrients are acceptable.
39/1	111	salt	3	3 attempts for a good salinity reading. Thimble came off with cap. Salinity high compared with CTD and adjoining stations. There is a feature in the nutrients, highe vs. adjoining stations, oxygen agrees with CTDO.
40/1	106	salt	2	3 attempts for a good salinity reading. Readings produced a good salinity value. Salinity as well as oxygen and nutrients are acceptable.
40/1	113	salt	5	Salinity sample lost, operator error, forgot to take the reading after flushing.
40/1	124	reft	3	SBE35RT +0.035/+0.045 vs CTDT1/CTDT2; somewhat unstable SBE35RT reading in a gradient. Code questionable.
40/1	127	bottle	2	Spigot is difficult to open. After the cast, the pin was found bent, so it was replaced.
40/1	134	reft	3	SBE35RT -0.03/-0.045 vs CTDT1/CTDT2; somewhat unstable SBE35RT reading. Code questionable.
40/1	135	salt	2	Bottle salinity is low compared with CTD, gradient area. Salinity as well as oxygen and nutrients are acceptable.
41/1	105	02	4	Endpoint was overshot on first run, and accidentally hit "Finish Sample". Added standard & re-ran sample in "low o2" mode. Obtained good endpoint. O2 high, need to be recalculated for back-titration. O2 slightly high could not save the sample. Code O2 bad.
41/1	118	o2	2	Sample was over-titrated and back-titrated. Endpoint was overshot. Good endpoint achieved. Oxygen agrees with adjoining stations.
41/1	124	bottle	9	Spigots/nozzle were hit during recovery, no water.
41/1	126	bottle	9	Spigots/nozzle were hit during recovery, no water.
41/1	136	salt	2	3 attempts for a good salinity reading. Readings chosen by the program are acceptable. Salinity as well as oxygen and nutrients are acceptable.
42/1	104	salt	2	Salinity bottle thimble came off with cap. Salinity slightly low compared with CTD and adjoining stations. Within measurement specifications, salinity as well as oxygen and nutrients are acceptable.
42/1	109	salt	2	3 attempts for a good salinity reading. Additional reading resolves low salinity discrepancy. Salinity as well as oxygen and nutrients are acceptable.
42/1	117	o2	2	O2 17-21 O2 draw temperature probe was reading 13.x, sampler went back after sampling bottle 22 to get the temperature from the spigot.
42/1	119	salt	2	3 attempts for a good salinity reading. Additional reading resolves low salinity discrepancy.
42/1	125	reft	3	SBE35RT +0.035/+0.045 vs CTDT1/CTDT2; very unstable SBE35RT reading in a
43/1	101	salt	2	gradient. Code questionable.  4 attempts for a good salinity reading. Salinity as well as oxygen and nutrients are acceptable.
43/1	104	salt	2	3 attempts for a good salinity reading. Agrees with Station 44, within the measurement specifications, although not within accuracy of other stations. Salinity
43/1	105	salt	2	as well as oxygen and nutrients are acceptable.  3 attempts for a good salinity reading. Additional reading resolved salinity difference. Salinity as well as oxygen and nutrients are acceptable.

Station /Cast	Sample No.	Quality Property	Code	Comment
43/1	119	salt	2	Bottle salinity is low compared with CTD, gradient, agrees with adjoining station, CTD is showing more features than the bottle. Salinity as well as oxygen and nutrients are acceptable.
43/1	123	salt	2	Bottle salinity is low compared with CTD, gradient, agrees with adjoining station for the gradient. Salinity as well as oxygen and nutrients are acceptable.
44/1	102	salt	3	Bottle salinity is low compared with CTD and adjoining stations. Salinometer problem, code salinity questionable, oxygen and nutrients are acceptable.
44/1	103	salt	3	Bottle salinity is low compared with CTD and adjoining stations. Salinometer problem, code salinity questionable, oxygen and nutrients are acceptable.
44/1	104	salt	3	Bottle salinity is low compared with CTD and adjoining stations. Salinometer problem, code salinity questionable, oxygen and nutrients are acceptable.
44/1	105	salt	3	Bottle salinity is low compared with CTD and adjoining stations. Salinometer problem, code salinity questionable, oxygen and nutrients are acceptable.
44/1	106	o2	2	Oxygen sample was over-titrated and back-titrated. No endpoint, original curve was bad, and was advised to overtitrate.
44/1	106	salt	3	Bottle salinity is low compared with CTD and adjoining stations. Salinometer problem, code salinity questionable, oxygen and nutrients are acceptable.
44/1	107	salt	3	Bottle salinity is low compared with CTD and adjoining stations. Salinometer problem, code salinity questionable, oxygen and nutrients are acceptable.
44/1	108	salt	3	Bottle salinity is low compared with CTD and adjoining stations. Salinometer problem, code salinity questionable, oxygen and nutrients are acceptable.
44/1	109	salt	3	Bottle salinity is low compared with CTD and adjoining stations. 4 attempts for a good salinity reading. Additional readings did not resolve salinity discrepancy. Salinometer problem, code salinity questionable, oxygen and nutrients are acceptable.
44/1	110	salt	3	4 attempts for a good salinity reading. Additional readings did not resolve salinity discrepancy, possibility is that cell was not flushed well enough after the last sample. Salinometer problem, code salinity questionable, oxygen and nutrients are acceptable.
44/1	111	02	4	Oxygen sample was over-titrated and back-titrated, endpoint looks better. Oxygen is high. Code O2 bad.
44/1	111	salt	3	Bottle salinity is low compared with CTD and adjoining stations. Salinometer problem, code salinity questionable, oxygen coded bad, nutrients are acceptable.
44/1	112	salt	3	Bottle salinity is low compared with CTD and adjoining stations. Salinometer problem, code salinity questionable, oxygen and nutrients are acceptable.
44/1	119	salt	2	04 attempts for a good salinity reading. Additional readings did not resolve slight salinity discrepancy. Salinity within measurement specifications and acceptable as are oxygen and nutrients.
44/1	131	o2	4	Oxygen high compared with adjoining stations. Suspect sampling error. Code O2 bad.
45/1	101	salt	2	5 attempts for a good salinity reading. Additional readings did not resolve slight low salinity discrepancy. Agrees with Station 46. Salinity as well as oxygen and nutrients are acceptable.
45/1	106	salt	2	3 attempts for a good salinity reading. Additional reading resolved salinity difference. Agrees with Station 46. Salinity as well as oxygen and nutrients are acceptable.
45/1	108	salt	2	4 attempts for a good salinity reading. Agrees with Stations 43 and 46. Within accuracy of measurement, salinity as well as oxygen and nutrients are acceptable.

Station /Cast	Sample No.		Code	Comment
45/1	109	salt	2	4 attempts for a good salinity reading. Additional readings did not resolve slight low salinity discrepancy. Salinity is a little low compared with Stations 43 and 46 agrees with 44. Within accuracy of the measurement, salinity as well as oxygen and nutrients are acceptable.
45/1	112	salt	2	Bottle salinity is low compared with CTD, agrees with adjoining stations. 4 attempts for a good salinity reading. Additional readings did not resolve salinity discrepancy. Salinity as well as oxygen and nutrients are acceptable.
45/1	118	salt	2	System crashed after 18, manually recorded conductivity reading. Salinity as well as oxygen and nutrients are acceptable.
46/1	105	o2	3	System didn't refill and number didn't reset though ready light was on. Subtracted value from previous value. Questionable measurement. Oxygen is slightly high, 0.02, compared to CTDO and adjoining station.
46/1	132	reft	3	SBE35RT -0.03 vs CTDT; in a gradient. Code questionable.
47/1	106	salt	2	3 attempts for a good salinity reading. Additional reading resolved salinity discrepancy. Salinity as well as oxygen and nutrients are acceptable.
47/1	108	salt	2	5 attempts for a good salinity reading. Salinity as well as oxygen and nutrients are acceptable.
47/1	111	salt	2	Bottle salinity is high compared with CTD and adjoining stations. Appeared that 11 and 12 were swapped. Corrected the sample number and the agreement is good for both 12 and 11. Salinity as well as oxygen and nutrients are acceptable.
47/1	112	salt	2	Bottle salinity is low compared with CTD and adjoining stations. Appeared that 11 and 12 were swapped. Corrected the sample number and the agreement is good for both 12 and 11. Salinity as well as oxygen and nutrients are acceptable.
47/1	113	salt	2	5 attempts for a good salinity reading. Salinity as well as oxygen and nutrients are acceptable.
47/1	118	o2	2	Endpoint mostly overshot. Possibly still acceptable. O2/SiO3 relationship is reasonable. Oxygen as well as salinity and nutrients are acceptable.
47/1	118	salt	2	3 attempts for a good salinity reading. Additional reading resolved salinity discrepancy. Salinity as well as oxygen and nutrients are acceptable.
48/1	102	salt	2	Bottle salinity is low compared with CTD and adjoining stations. First reading resolved salinity discrepancy, still a little low but within the measurement specification. Salinity as well as oxygen and nutrients are acceptable.
48/1	103	salt	2	Bottle salinity is low compared with CTD and adjoining stations. 4 attempts for a good salinity reading. First reading resolved salinity discrepancy. Salinity as well as oxygen and nutrients are acceptable.
48/1	108	salt	2	Nutrients tube was empty, analyst took sample from salinity bottle. Nutrients as well as salinity and oxygen are acceptable.
48/1	114	o2	2	One drop lost from O2 sample after acid added. O2/SiO3 relationship is reasonable. Oxygen is acceptable.
48/1	130	salt	4	Bottle salinity is low compared with CTD and adjoining stations. Mis-draw or operator error, appears it was drawn from bottle 29. Code salinity bad, oxygen and nutrients are acceptable.
48/1	133	salt	2	Bottle salinity is high compared with CTD is acceptable for gradient. Salinity as well as oxygen and nutrients are acceptable.
49/1	102	salt	4	Bottle salinity is high compared with CTD and adjoining stations. 3 attempts for a good salinity reading. Appears as a mis-draw or it could be operator error. Code salinity bad.
49/1	106	salt	2	3 attempts for a good salinity reading. Thimble came out with cap. Additional readings resolved salinity discrepancy. Salinity as well as oxygen and nutrients are acceptable.

Station /Cast	Sample No.	Quality Property	Code	Comment
49/1	108	salt	4	Bottle salinity is high compared with CTD and adjoining stations. 4 attempts for a good salinity reading. Thimble came out with cap. Probable contamination.  Additional readings did not resolve the high salinity. Appears as a mis-draw or it
49/1	113	salt	4	could be operator error. Code salinity bad, oxygen and nutrients are acceptable.  Bottle salinity is high compared with CTD and adjoining stations. 4 attempts for a good salinity reading. Salinity bottle thimble came out with cap, readings erratic.  Additional readings did not resolve salinity discrepancy. Appears as a mis-draw or it
49/1	118	salt	2	could be operator error. Code salinity bad.  Bottle salinity is high compared with CTD agrees with adjoining stations. Salinity as well as oxygen and nutrients are acceptable.
49/1	132	salt	2	Bottle salinity is high compared with CTD, gradient area agrees with adjoining stations. Salinity as well as oxygen and nutrients are acceptable
50/1	101	bottle	2	Pins on cart bent-did sampling at rosette recovery/launching site.
50/1	122	salt	2	3 attempts for a good salinity reading. Thimble came out with cap, possible contamination. Salinity as well as oxygen and nutrients are acceptable.
50/1	135	salt	2	3 attempts for a good salinity reading. Thimble came out with cap, possible contamination. Additional reading did not resolve salinity difference. Agrees with adjoining stations, slightly low compared with Station 47. Salinity as well as oxygen and nutrients are acceptable.
51/1	101	bottle	2	Vent was not closed. See oxygen comment. Salinity and nutrients are acceptable.
51/1	101	02	4	Overshot endpoint. Stopper mismatched as well. Code oxygen bad.
51/1	101	salt	2	Salinity samples 1 and 2 were switched, mis-drawn. Corrected file. Salinity as well as nutrients are acceptable.
51/1	102	bottle	2	Vent was not closed. Salinity oxygen and nutrients are acceptable.
51/1	103	salt	2	3 attempts for a good salinity reading. Additional reading resolved salinity discrepancy. Salinity as well as oxygen and nutrients are acceptable.
51/1	111	o2	4	Overshot endpoint. Code oxygen bad. Salinity and nutrients are acceptable.
51/1	118	o2	2	Sample was over-titrated and back-titrated. Oxygen is acceptable.
51/1	118	salt	2	Bottle salinity is high compared with CTD gradient agrees with adjoining stations. Salinity as well as oxygen and nutrients are acceptable.
51/1	119	salt	2	Bottle salinity is low compared with CTD, gradient agrees with adjoining stations. Salinity as well as oxygen and nutrients are acceptable.
51/1	121	salt	2	5 attempts for a good salinity reading. Additional reading resolved salinity discrepancy. Bung and sample tube not cleaned before this sample. Erratic readings. Gradient, salinity as well as oxygen and nutrients are acceptable.
51/1	122	salt	2	3 attempts for a good salinity reading. Program chosen readings are acceptable. Gradient, salinity as well as oxygen and nutrients are acceptable.
51/1	129	o2	2	Sample was over-titrated and back-titrated. Oxygen slightly low compared with adjoining stations, although it does look okay with SiO3/O2 relationship and CTDO.
51/1	130	salt	2	Bottle salinity is high compared with CTD, gradient agrees with adjoining stations. Salinity as well as oxygen and nutrients are acceptable.
52/1	101	o2	2	O2 "wake-up" sample not run, deep oxygen is acceptable.
52/1	110	salt	3	3 attempts for a good salinity reading. Additional readings do not resolve the salinity discrepancy. Code salinity questionable.
52/1	111	salt	2	3 attempts for a good salinity reading. Additional readings do not resolve the slight salinity discrepancy. Salinity is within the measurement specification and acceptable.
52/1	113	salt	2	3 attempts for a good salinity reading. Program chose the two good readings, salinity is acceptable.
52/1	114	salt	2	3 attempts for a good salinity reading. Additional readings do not resolve the slight salinity discrepancy. Salinity is within the measurement specification and acceptable.

Station /Cast	Sample No.	Quality Property	Code	Comment
52/1	116	salt	2	3 attempts for a good salinity reading. Additional readings do not resolve the slight salinity discrepancy. Salinity is within the measurement specification and acceptable.
52/1	118	salt	2	3 attempts for a good salinity reading. Additional readings do not resolve the slight salinity discrepancy. Salinity is within the measurement specification and acceptable.
52/1	122	salt	2	3 attempts for a good salinity reading. Additional readings do not resolve the slight salinity discrepancy. Salinity is within the measurement specification and acceptable.
52/1	129	salt	2	Bottle salinity is high compared with CTD, agrees with adjoining stations, gradient. Salinity as well as oxygen and nutrients are acceptable.
53/1	117	salt	4	Bottle salinity is high compared with CTD and adjoining stations. Salinity appears to have been mis-drawn from bottle 19 or operator error on analysis. Code salinity bad, oxygen and nutrients are acceptable.
54/1	102	salt	2	3 attempts for a good salinity reading. Additional reading resulted in a higher, acceptable salinity. Salinity as well as oxygen and nutrients are acceptable.
54/1	103	o2	3	Sample was over-titrated and back-titrated. Over-titration value came out slightly low, original value was high with CTDO and on SiO3/O2 relationship. Code O2 questionable.
54/1	105	salt	2	3 attempts for a good salinity reading. Program chose the correct two readings. Salinity as well as oxygen and nutrients are acceptable.
54/1	108	salt	2	3 attempts for a good salinity reading. Additional reading resulted in a higher, acceptable salinity. Salinity as well as oxygen and nutrients are acceptable.
54/1	110	salt	2	Bottle salinity is low compared with CTD and adjoining stations. 3 attempts for a good salinity reading. Analyst originally ran sample 9 as 10, sample 10 was analyzed, computer did not update with the correct value. Corrected raw data file. Salinity as well as oxygen and nutrients are acceptable.
54/1	111	salt	2	3 attempts for a good salinity reading. Additional reading resulted in a higher, acceptable salinity. Salinity as well as oxygen and nutrients are acceptable.
54/1	113	salt	2	3 attempts for a good salinity reading. Additional reading resulted in a higher, acceptable salinity. Salinity as well as oxygen and nutrients are acceptable.
55/1	106	salt	2	3 attempts for a good salinity reading. Additional reading would make the salinity higher. Salinity, gradient, as well as oxygen and nutrients are acceptable.
56/1	125	o2	5	System froze. O2 sample lost.
56/1	130	salt	2	3 attempts for a good salinity reading. Program chose the appropriate readings. Salinity as well as oxygen and nutrients are acceptable.
57/1	101	reft	3	SBE35RT 0.70/0.15 vs CTDT1/CTDT2; very unstable SBE35RT reading. Code questionable.
57/1	105	salt	2	3 attempts for a good salinity reading. Additional reading resolved salinity discrepancy. Salinity as well as oxygen and nutrients are acceptable.
57/1	106	salt	2	3 attempts for a good salinity reading. Additional reading resolved salinity discrepancy. Salinity as well as oxygen and nutrients are acceptable.
58/1	102	salt	2	Bottle salinity is high compared with CTD and adjoining stations. 4 attempts for a good salinity reading. Additional reading resolved the salinity discrepancy. Salinity as well as oxygen and nutrients are acceptable.
58/1	105	salt	2	3 attempts for a good salinity reading. Additional reading would have made the value higher. Salinity as well as oxygen and nutrients are acceptable.
58/1	106	salt	2	3 attempts for a good salinity reading. Program chose the appropriate reading. Salinity as well as oxygen and nutrients are acceptable.
58/1	108	salt	2	3 attempts for a good salinity reading. Additional reading resolved the salinity discrepancy. Salinity as well as oxygen and nutrients are acceptable.
58/1	109	salt	2	3 attempts for a good salinity reading. Program chose the appropriate reading. Salinity as well as oxygen and nutrients are acceptable.

Station /Cast	Sample No.	Quality Property	Code	Comment
58/1	118	salt	2	Bottle salinity is high compared with CTD, agrees with adjoining stations in
58/1	122	salt	2	gradient. Salinity as well as oxygen and nutrients are acceptable.  4 attempts for a good salinity reading. Additional reading resolved the salinity
				discrepancy. Salinity as well as oxygen and nutrients are acceptable.
60/1	124	bottle	2	Valve was found open. Oxygen as well as salinity and nutrients are acceptable.
60/1	125	bottle	2	Valve was found open. Oxygen as well as salinity and nutrients are acceptable.
60/1	126	salt	2	Bottle salinity is high compared with CTD, agrees with adjoining station for gradient. Salinity, oxygen and nutrients are acceptable.
61/1	118	salt	2	Bottle salinity is low compared with CTD, gradient appears acceptable as are oxygen and nutrients.
62/1	105	salt	2	3 attempts for a good salinity reading. Program chose the appropriate readings. Salinity as well as oxygen and nutrients are acceptable.
62/1	106	salt	4	Bottle salinity is high compared with CTD and adjoining stations. 3 attempts for a good salinity reading. Additional reading would result in a higher salinity. Code
				salinity bad, oxygen and nutrients are acceptable.
62/1	132	salt	2	Bottle salinity is high compared with CTD, gradient and is acceptable as are oxygen and nutrients.
63/1	110	salt	2	3 attempts for a good salinity reading. Program chose appropriate value. Salinity as well as oxygen and nutrients are acceptable.
63/1	123	salt	2	Bottle salinity is low compared with CTD, gradient, structure in CTD trace. Salinity
64/1	103	o2	2	as well as oxygen and nutrients are acceptable.
64/1 64/1	110	salt	2 2	Sample was overtitrated and backtitrated. Overshot endpoint. Oxygen is acceptable. Bottle salinity is high compared with CTD and adjoining stations. 3 attempts for a
04/1	110	sait	2	good salinity reading. First reading resolved salinity discrepancy. Salinity as well as oxygen and nutrients are acceptable.
64/1	120	o2	4	Sampling error. Code Oxygen bad.
64/1	122	o2	4	Sample was overtitrated and backtitrated. Overshot endpoint. Code Oxygen bad.
64/1	130	salt	2	3 attempts for a good salinity reading. Program chose the appropriate reading. Salinity as well as oxygen and nutrients are acceptable.
66/1	109	02	2	Draw temperature missed writing down, temperature for kg conversion should be okay. Oxygen as well as salinity and nutrients are acceptable.
67/1	111	salt	2	3 attempts for a good salinity reading. Program chose appropriate readings. Salinity as well as oxygen and nutrients are acceptable.
67/1	113	o2	2	Sample was overtitrated and backtitrated, overshot endpoint. Oxygen slightly low, good SiO3/O2 relationship, gradient, appears acceptable.
67/1	117	bottle	3	Bottle appears to have mis-tripped, draw temperature too warm. Nutrients and oxygen are low and indicate a mis-trip.
67/1	117	no2	4	oxygen are low and indicate a mis-trip.
67/1	117	no3	4	
67/1	117	02	4	Oxygen confirms mis-trip, code bad.
67/1	117	po4	4	Nutrients indicate a mis-trip, code bad.
67/1	117	salt	4	Salinity high compared to adjoining stations profiles and CTD, mis-trip, code bad.
67/1	117	sio3	4	zamento promos una erz, mas urp, code oud.
67/1	131	salt	5	Bottle salinity is low compared with CTD and adjoining stations. Salinity analyst
			-	stated that a sample was missed, suspect from the data that is was 30. Reassigned sample numbers and corrected files. Salinity is lost.
67/1	132	o2	5	O2 system froze, sample lost.
68/1	124	salt	5	Salinity operator stated she missed a sample. Salinity lost.
68/1	130	salt	4	3 attempts for a good salinity reading. Additional reading would result in lower salinity. Code salinity bad.

Station /Cast	Sample No.	Quality Property	Code	Comment
68/1	136	o2	3	Oxygen is high compared with adjoining stations, SiO3/O2 relationship and CTDO. No analytical problems noted. SiO3 is a little low, following other nutrients and acceptable. Code oxygen questionable.
69/1	101	o2	3	Oxygen high does not agree with CTDO or adjoining stations. No analytical notes indicating a problem. Code oxygen questionable, salinity and nutrients are acceptable.
69/1	103	o2	3	Oxygen high does not agree with CTDO or adjoining stations. No analytical notes indicating a problem. Code oxygen questionable, salinity and nutrients are acceptable.
69/1	111	o2	3	Oxygen high does not agree with CTDO or adjoining stations. No analytical notes indicating a problem. Code oxygen questionable, salinity and nutrients are acceptable.
69/1	127	o2	2	Missed recording O2 draw temperature, taken after sampling, conversion to kg units is acceptable.
69/1	127	salt	2	Bottle salinity is low compared with CTD, agrees with adjoining stations for gradient. Salinity, oxygen and nutrients are acceptable.
69/1	133	o2	3	Oxygen value high as reported by CTD operator. Also appears slightly high on SiO3/O2 relationship. No analytical problems noted. Code oxygen questionable.
70/1	105	o2	4	Oxygen high does not agree with CTDO or adjoining stations.
70/1	108	o2	4	Oxygen high does not agree with CTDO or adjoining stations.
70/1	111	salt	2	Salinity thimble came out with cap. This may have cause the slightly high salinity, just within measurement specifications. Salinity as well as oxygen and nutrients are acceptable.
70/1	113	salt	2	Salinity thimble came out with cap. This may have cause the slightly high salinity, within measurement specifications. Salinity as well as oxygen and nutrients are acceptable.
71/1	101	bottle	2	Bottle ran out of water for salinity. There were 3 parameters, DIC, Alkalinity and 13C/14C taking duplicates. This totals 8.45L and should have been enough water. Bottle o-rings checked prior to Station 73.
71/1	101	o2	4	Sampling error. Ran out of reagents.
71/1	102	o2	2	Oxygen appears a little low, could also have been part of the sampling error.
71/1	104	o2	4	Oxygen high does not agree with CTDO or adjoining stations.
71/1	107	o2	4	Oxygen high does not agree with CTDO or adjoining stations.
71/1	109	o2	4	Oxygen low. Analyst noted large debris in sample during analysis.
71/1	132	salt	2	Bottle salinity is high compared with CTD, gradient agreement with adjoining stations. Salinity as well as oxygen and nutrients are acceptable.
71/1	133	o2	4	Oxygen high, does not have good SiO3/O2 relationship, agreement with adjoining stations or CTDO.
71/1	135	o2	4	Oxygen high, does not have good SiO3/O2 relationship, agreement with adjoining stations or CTDO.
71/1	135	salt	2	Bottle salinity is low compared with CTD, gradient agreement with adjoining stations. Salinity as well as oxygen and nutrients are acceptable.
72/1	101	o2	4	Oxygen high, along with 3, 5, 8, 11 and 36, uncertain of the cause.
72/1	101	salt	2	Salinity run had a large drift. Analyst could not obtain a good ending Standard
				Seawater value. Suspect salinometer was the problem. Salinity is within measurement specifications and has a reasonable agreement with the CTD and adjoining stations.
72/1	103	o2	4	Oxygen high. Code O2 bad.
72/1	105	o2	4	Opened flask too soon before running. Oxygen high. Code O2 bad.
72/1	108	o2	4	Oxygen high. Code O2 bad.
72/1	111	o2	4	Oxygen high. Code O2 bad.

Station /Cast	Sample No.		Code	Comment
72/1	117	o2	5	Oxygen sample lost, was mistakenly drawn from 18, 18=19, 19=20 and 20 drawn from 21.
72/1	118	o2	2	Oxygen were drawn off on level, corrected data file and oxygen is acceptable.
72/1	119	o2	2	Oxygen were drawn off on level, corrected data file and oxygen is acceptable.
72/1	120	o2	2	Oxygen sampler suspected he drew from bottle 20 with flask intended for 21, redrew from 21.
72/1	136	o2	4	Oxygen high. Code O2 bad.
73/1	101	salt	2	Salinity run had a large drift. Suspect salinometer was the problem. Salinity is within measurement specifications and has a reasonable agreement with the CTD and adjoining stations. Salinometer retired after Station 76 run.
73/1	133	salt	2	Bottle salinity is high compared with CTD, variation in CTD profile, gradient, agrees with adjoining stations. Salinity as well as oxygen and nutrients are acceptable.
74/1	104	salt	4	Bottle salinity is low compared with CTD and adjoining stations. Salinometer had an issue very obvious with this station. It was taken off-line after Station 76. Code
74/1	105	salt	4	salinity bad, oxygen and nutrients are acceptable. Bottle salinity is low compared with CTD and adjoining stations. Salinometer had an
				issue very obvious with this station. It was taken off-line after Station 76. Code
				salinity bad, oxygen and nutrients are acceptable.
74/1	106	salt	4	Bottle salinity is low compared with CTD and adjoining stations. Salinometer had an issue very obvious with this station. It was taken off-line after Station 76. Code salinity had anyword and putrious are acceptable.
74/1	107	salt	4	salinity bad, oxygen and nutrients are acceptable.  Bottle salinity is low compared with CTD and adjoining stations. Salinometer had an issue very obvious with this station. It was taken off-line after Station 76. Code
74/1	108	salt	4	salinity bad, oxygen and nutrients are acceptable.  Bottle salinity is low compared with CTD and adjoining stations. Salinometer had an issue very obvious with this station. It was taken off-line after Station 76. Code
7.4/1	100	2	2	salinity bad, oxygen and nutrients are acceptable.
74/1	109	o2	2	Oxygen flask was chipped, used flask 1640 instead of
75/1	114	salt	4	Bottle salinity is low compared with CTD and adjoining stations. Salinometer had an issue very obvious with this station. It was taken off-line after Station 76. Code salinity bad, oxygen and nutrients are acceptable.
75/1	115	salt	4	Bottle salinity is low compared with CTD and adjoining stations. Salinometer had an issue very obvious with this station. It was taken off-line after Station 76. Code salinity bad, oxygen and nutrients are acceptable.
75/1	116	salt	4	Bottle salinity is low compared with CTD and adjoining stations. Salinometer had an issue very obvious with this station. It was taken off-line after Station 76. Code salinity bad, oxygen and nutrients are acceptable.
75/1	117	salt	4	Bottle salinity is low compared with CTD and adjoining stations. Salinometer had an issue very obvious with this station. It was taken off-line after Station 76. Code salinity bad, oxygen and nutrients are acceptable.
75/1	118	salt	4	Bottle salinity is low compared with CTD and adjoining stations. Salinometer had an issue very obvious with this station. It was taken off-line after Station 76. Code salinity bad, oxygen and nutrients are acceptable.
75/1	119	salt	4	Bottle salinity is low compared with CTD and adjoining stations. Salinometer had an issue very obvious with this station. It was taken off-line after Station 76. Code salinity bad, oxygen and nutrients are acceptable.
75/1	120	salt	4	Bottle salinity is low compared with CTD and adjoining stations. Salinometer had an issue very obvious with this station. It was taken off-line after Station 76. Code salinity bad, oxygen and nutrients are acceptable.

Station /Cast	Sample No.	Quality Property	Code	Comment
75/1	121	salt	4	Bottle salinity is low compared with CTD and adjoining stations. Salinometer had an issue very obvious with this station. It was taken off-line after Station 76. Code salinity bad, oxygen and nutrients are acceptable.
75/1	122	salt	4	Bottle salinity is low compared with CTD and adjoining stations. Salinometer had an issue very obvious with this station. It was taken off-line after Station 76. Code
75/1	128	o2	2	salinity bad, oxygen and nutrients are acceptable.  Analyst made the comment fix. SiO3/O2 relationship is good. Oxygen is acceptable.
76/1	104	salt	4	Bottle salinity is low compared with CTD and adjoining stations. Salinometer had an issue very obvious starting with Station 74. It was taken off-line after Station 76.
76/1	105	salt	4	Code salinity bad, oxygen and nutrients are acceptable.  Bottle salinity is low compared with CTD and adjoining stations. Salinometer had an issue very obvious starting with Station 74. It was taken off-line after Station 76. Code salinity bad, oxygen and nutrients are acceptable.
76/1	106	salt	4	Bottle salinity bad, oxygen and nutriens are acceptable.  Bottle salinity is low compared with CTD and adjoining stations. Salinometer had an issue very obvious starting with Station 74. It was taken off-line after Station 76. Code salinity bad, oxygen and nutrients are acceptable.
76/1	107	salt	4	Bottle salinity is low compared with CTD and adjoining stations. Salinometer had an issue very obvious starting with Station 74. It was taken off-line after Station 76. Code salinity bad, oxygen and nutrients are acceptable.
76/1	108	salt	4	Bottle salinity is low compared with CTD and adjoining stations. Salinometer had an issue very obvious starting with Station 74. It was taken off-line after Station 76. Code salinity bad, oxygen and nutrients are acceptable.
76/1	109	salt	4	Bottle salinity is low compared with CTD and adjoining stations. Salinometer had an issue very obvious starting with Station 74. It was taken off-line after Station 76. Code salinity bad, oxygen and nutrients are acceptable.
76/1	110	salt	4	Bottle salinity is low compared with CTD and adjoining stations. Salinometer had an issue very obvious starting with Station 74. It was taken off-line after Station 76. Code salinity bad, oxygen and nutrients are acceptable.
76/1	111	salt	4	Bottle salinity is low compared with CTD and adjoining stations. Salinometer had an issue very obvious starting with Station 74. It was taken off-line after Station 76. Code salinity bad, oxygen and nutrients are acceptable.
76/1	112	salt	4	Bottle salinity is low compared with CTD and adjoining stations. Salinometer had an issue very obvious starting with Station 74. It was taken off-line after Station 76. Code salinity bad, oxygen and nutrients are acceptable.
76/1	113	salt	4	Bottle salinity is low compared with CTD and adjoining stations. Salinometer had an issue very obvious starting with Station 74. It was taken off-line after Station 76. Code salinity bad, oxygen and nutrients are acceptable.
76/1	114	salt	4	Bottle salinity is low compared with CTD and adjoining stations. Salinometer had an issue very obvious starting with Station 74. It was taken off-line after Station 76. Code salinity bad, oxygen and nutrients are acceptable.
76/1	115	salt	4	Bottle salinity is low compared with CTD and adjoining stations. Salinometer had an issue very obvious starting with Station 74. It was taken off-line after Station 76. Code salinity bad, oxygen and nutrients are acceptable.
76/1	116	salt	4	Bottle salinity is low compared with CTD and adjoining stations. Salinometer had an issue very obvious starting with Station 74. It was taken off-line after Station 76. Code salinity bad, oxygen and nutrients are acceptable.
76/1	117	salt	4	Bottle salinity is low compared with CTD and adjoining stations. Salinometer had an issue very obvious starting with Station 74. It was taken off-line after Station 76. Code salinity bad, oxygen and nutrients are acceptable.

Station	Sample	Quality		
/Cast	No.	Property	Code	Comment
76/1	118	salt	4	Bottle salinity is low compared with CTD and adjoining stations. Salinometer had an issue very obvious starting with Station 74. It was taken off-line after Station 76. Code salinity bad, oxygen and nutrients are acceptable.
77/1	102	o2	4	Debris in sample. Endpoint looks okay. Oxygen high compared with adjoining stations and CTD.
77/1	103	o2	4	Oxygen high compared with adjoining stations and CTDO. No analytical problem noted. Code oxygen questionable.
77/1	127	salt	2	Bottle salinity is high compared with CTD, agrees with salinity max bottle values for adjoining stations, variation in CTD profile at bottle trip. Salinity as well as oxygen and nutrients are acceptable.
78/1	122	salt	2	Bottle salinity is high compared with CTD, agrees with salinity max bottle values for adjoining stations, as is 21. Salinity as well as oxygen and nutrients are acceptable.
79/1	115	no2	3	
79/1	115	no3	3	
79/1	115	po4	3	Nutrients low and appear to have been drawn from 16. NO3 and NO2 do not have this same agreement with 16, so they are even lower. No similar feature is seen in oxygen or salinity. Code nutrients questionable, salinity and oxygen acceptable.
79/1	115	sio3	3	
79/1	121	salt	2	Bottle salinity is high compared with CTD, agrees with salinity gradient bottle values for adjoining stations. Salinity as well as oxygen and nutrients are acceptable.

### Appendix D

## **CLIVAR A22: Pre-Cruise Sensor Laboratory Calibrations**

CTD 796 Sensors - Table of Contents					
CTD	Manufacturer	Serial	Station	Appendix D Page	
Sensor	and Model No.	Number	Number	(Un-Numbered)	
PRESS (Pressure)	Digiquartz 401K-105	0796	1-81	1	
T1 (Primary Temperature)	SBE3plus	03-4138	1-39	4	
T1 (Primary Temperature)	SBE3plus	03-4924	40-81	5	
C1 (Primary Conductivity)	SBE4C	04-3369	1-81	6	
O2 (Dissolved Oxygen)	SBE43	43-0614	1-81	7	
T2 (Secondary Temperature)	SBE3plus	03-4907	1-81	8	
C2 (Secondary Conductivity)	SBE4C	04-3399	1-81	9	
REFT (Reference Temperature)	SBE35	35-0035	1-81	10	
TRANS (Transmissometer)	WET Labs C-Star	CST-327DR	1-81	11	
RINKO (Optical O2 & Temp.)	RinkoIII ARO-CAV	084	1-47	13	

## **Pressure Calibration Report STS/ODF Calibration Facility**

SENSOR SERIAL NUMBER: 0796 CALIBRATION DATE: 25-OCT-2011 Mfg: SEABIRD Model: 09P CTD Prs s/n:

C1= -4.967252E+4
C2= 8.659237E-1
C3= 9.895243E-3
D1= 3.845316E-2
D2= 0.000000E+0
T1= 2.989468E+1
T2= -1.252866E-4
T3= 3.487851E-6
T4= 1.015145E-8
T5= 0.000000E+0
AD590M= 1.28520E-2
AD590B= -8.71454E+0
Slope = 1.00000000E+0
Offset = 0.00000000E+0

Calibration Standard: Mfg: RUSKA Model: 2400 s/n: 34336

t0=t1+t2\*td+t3\*td\*td+t4\*td\*td\*td

w = 1-t0\*t0\*f\*f

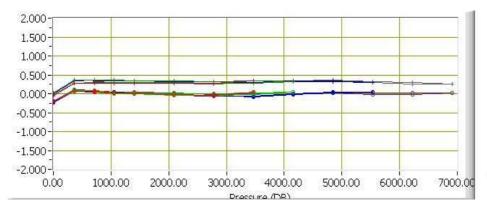
Pressure = (0.6894759\*((c1+c2\*td+c3\*td\*td)\*w\*(1-(d1+d2\*td)\*w)-14.7)

SBE9		SBE9	Ruska-SBE9	Ruska-Sl	BE9	
Freq	Ruska	New_Coefs	Prev_Coefs	New_Coe:	fs Tprs	Bath_Temp
33456.613	0.18	0.40	-0.03	-0.22	27.21	27.394
33634.161	364.98	364.91	0.28	0.06	27.26	27.396
33800.830	709.16	709.11	0.28	0.04	27.28	27.398
33966.550	1053.33	1053.31	0.28	0.02	27.31	27.399
34131.382	1397.59	1397.59	0.27	-0.00	27.34	27.402
34458.276	2086.07	2086.10	0.28	-0.02	27.38	27.402
34781.631	2774.62	2774.65	0.28	-0.04	27.39	27.403
35101.523	3463.25	3463.21	0.34	0.03	27.41	27.402
34781.631	2774.62	2774.66	0.27	-0.04	27.44	27.403
34458.266	2086.07	2086.09	0.29	-0.01	27.45	27.403
34131.368	1397.59	1397.58	0.28	0.01	27.46	27.403
33966.535	1053.33	1053.31	0.28	0.02	27.49	27.404
33800.804	709.16	709.10	0.30	0.06	27.49	27.403
33634.124	364.98	364.89	0.31	0.09	27.52	27.404
33457.116	0.18	0.40	0.03	-0.22	16.38	15.944
33634.609	364.98	364.89	0.36	0.09	16.38	15.944
33801.228	709.16	709.08	0.37	0.08	16.38	15.944
33966.921	1053.33	1053.30	0.34	0.03	16.39	15.944
34131.706	1397.59	1397.57	0.33	0.02	16.39	15.944
34458.512	2086.07	2086.07	0.34	0.01	16.39	15.944
34781.784	2774.62	2774.62	0.33	-0.00	16.39	15.944
35101.618	3463.25	3463.23	0.33	0.01	16.39	15.944
35418.115	4151.95	4151.91	0.32	0.03	16.39	15.944
35101.639	3463.25	3463.28	0.29	-0.03	16.39	15.944
34781.805	2774.62	2774.67	0.28	-0.05	16.39	15.944

# **Pressure Calibration Report STS/ODF Calibration Facility**

34458.534	2086.07	2086.11	0.29	-0.04	16.38	15.944
34131.719	1397.59	1397.60	0.31	-0.01	16.37	15.944
33966.937	1053.33	1053.33	0.30	-0.00	16.37	15.944
33801.249	709.16	709.12	0.33	0.04	16.37	15.944
33634.619	364.98	364.91	0.34	0.07	16.37	15.944
33456.684	0.18	0.41	0.01	-0.23	6.75	7.107
33634.143	364.98	364.90	0.34	0.07	6.78	7.107
33800.733	709.16	709.10	0.35	0.06	6.84	7.106
33966.374	1053.33	1053.28	0.36	0.05	6.86	7.106
34131.133	1397.59	1397.57	0.35	0.03	6.89	7.106
		2086.09	0.33			7.106
34457.884	2086.07			-0.02	6.91	
34781.092	2774.61	2774.65	0.32	-0.04	6.94	7.106
35100.886	3463.24	3463.32	0.28	-0.07	6.96	7.106
35417.299	4151.94	4151.96	0.32	-0.02	6.96	7.106
35730.475	4840.70	4840.68	0.33	0.02	6.99	7.106
36040.493	5529.51	5529.46	0.31	0.04	7.02	7.106
35730.468	4840.70	4840.65	0.35	0.04	7.02	7.106
35417.298	4151.94	4151.94	0.34	0.01	7.04	7.105
35100.886	3463.24	3463.30	0.30	-0.05	7.04	7.106
34781.105	2774.61	2774.65	0.33	-0.03	7.07	7.106
34457.910	2086.07	2086.11	0.32	-0.04	7.09	7.106
34131.159	1397.59	1397.58	0.34	0.01	7.12	7.106
33966.403	1053.33	1053.29	0.35	0.04	7.12	7.106
33800.763	709.16	709.10	0.35	0.06	7.14	7.106
33634.164	364.98	364.88	0.37	0.10	7.14	7.106
33455.693	0.18	0.37	-0.06	-0.19	-1.40	-1.286
33633.127	364.98	364.87	0.27	0.10	-1.38	-1.286
33799.694	709.16	709.08	0.28	0.08	-1.35	-1.287
33965.315	1053.33	1053.28	0.28	0.05	-1.32	-1.287
34130.038	1397.59	1397.55	0.29	0.03	-1.30	-1.287
34456.724	2086.07	2086.05	0.33	0.03	-1.25	-1.287
34779.895	2774.62	2774.64	0.31	-0.02	-1.21	-1.286
35099.609	3463.25	3463.25	0.34	-0.01	-1.20	-1.287
35415.997	4151.95	4151.96	0.34	-0.01	-1.20	-1.287
35729.123	4840.70	4840.68	0.34	0.02	-1.20	-1.287
36039.105	5529.51	5529.50				
36346.008			0.33	0.02	-1.14	-1.287
	6218.40	6218.39	0.29	0.02	-1.14	-1.287
36649.907	6907.34	6907.32	0.25	0.02	-1.12	-1.287
36346.028	6218.40	6218.43	0.25	-0.02	-1.12	-1.287
36039.121	5529.51	5529.53	0.30	-0.01	-1.12	-1.287
35729.144	4840.70	4840.69	0.35	0.01	-1.09	-1.287
35416.021	4151.95	4151.96	0.33	-0.02	-1.09	-1.287
35099.656	3463.25	3463.30	0.29	-0.06	-1.07	-1.286
34779.943	2774.62	2774.69	0.26	-0.07	-1.07	-1.286
34456.784	2086.07	2086.11	0.27	-0.04	-1.07	-1.286
34130.089	1397.59	1397.58	0.27	0.01	-1.07	-1.286
33965.364	1053.33	1053.29	0.28	0.04	-1.04	-1.287
33799.741	709.16	709.08	0.29	0.08	-1.04	-1.287
33633.177	364.98	364.87	0.28	0.11	-1.04	-1.287
33455.732	0.18	0.34	-0.02	-0.16	-1.04	-1.287

## **Pressure Calibration Report STS/ODF Calibration Facility**



28-Apr-10-27.4	1
New-27,4	1
28-Apr-10-15.9	1
New-15.9	1
28-Apr-10-7.1	1
New-7.1	1
28-Apr-101.3	1
New1.3	1

# Temperature Calibration Report STS/ODF Calibration Facility

SENSOR SERIAL NUMBER: 4138 CALIBRATION DATE: 08-Feb-2012

Mfg: SEABIRD Model: 03
Previous cal: 28-Oct-11
Calibration Tech: CAL

ITS-90_COEFFICIENTS	IPTS-68_COEFFICIENTS ITS-T90	
g = 4.40196965E-3	a = 4.40218263E-3	
h = 6.50785137E-4	b = 6.51002176E-4	
i = 2.34740143E-5	c = 2.35072239E-5	
j = 2.07164188E-6	d = 2.07319338E-6	
f0 = 1000.0	Slope = 1.0	Offset = 0.0

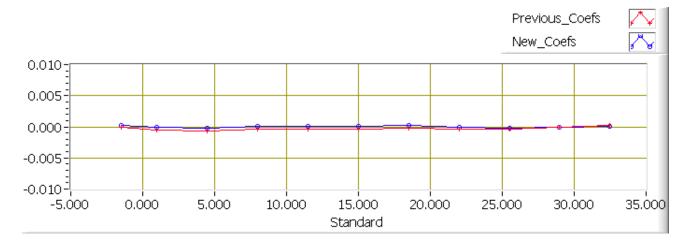
Calibration Standard: Mfg: ASL Model: F18 s/n: 245-5149

Temperature ITS-90 =  $1/{g+h[ln(f0/f)]+i[ln2(f0/f)]+j[ln3(f0/f)]} - 273.15$  (°C)

Temperature IPTS-68 =  $1/{a+b[ln(f0/f)]+c[ln2(f0/f)]+d[ln3(f0/f)]}$  - 273.15 (°C)

T68 = 1.00024 \* T90 (-2 to -35 Deg C)

SBE3 Freq	SPRT ITS-T90	SBE3 ITS-T90	SPRT-SBE3 OLD Coefs	SPRT-SBE3 NEW Coefs
3159.1317	-1.5052	-1.5054	-0.00011	0.00020
3339.6169	0.9939	0.9941	-0.00053	-0.00015
3604.7404	4.4942	4.4945	-0.00073	-0.00029
3884.7082	7.9958	7.9957	-0.00034	0.00014
4179.8774	11.4971	11.4970	-0.00042	0.00007
4489.8717	14.9903	14.9902	-0.00038	0.00009
4816.6825	18.4935	18.4933	-0.00025	0.00017
5159.4414	21.9927	21.9928	-0.00041	-0.00007
5519.1133	25.4947	25.4949	-0.00043	-0.00020
5895.3695	28.9933	28.9933	-0.00014	-0.00004
6289.1081	32.4937	32.4936	0.00016	0.00011



# Temperature Calibration Report STS/ODF Calibration Facility

SENSOR SERIAL NUMBER: 4924 CALIBRATION DATE: 10-Feb-2012

Mfg: SEABIRD Model: 03
Previous cal: 24-Oct-11
Calibration Tech: CAL

ITS-90_COEFFICIENTS	IPTS-68_COEFFICIENTS ITS-T90	
g = 4.32850794E-3	a = 4.32869684E-3	
h = 6.33103361E-4	b = 6.33309185E-4	
i = 1.98816686E-5	c = 1.99127639E-5	
j = 1.63362653E-6	d = 1.63497710E-6	
f0 = 1000.0	Slope = 1.0	Offset = 0.0

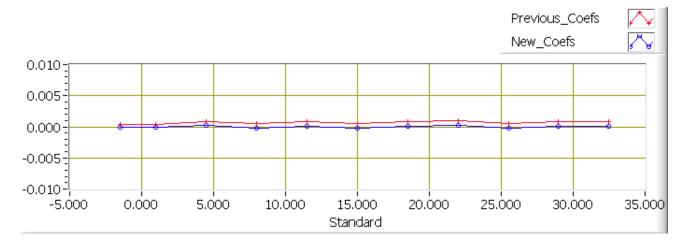
Calibration Standard: Mfg: ASL Model: F18 s/n: 245-5149

Temperature ITS-90 =  $1/{g+h[ln(f0/f)]+i[ln2(f0/f)]+j[ln3(f0/f)]} - 273.15$  (°C)

Temperature IPTS-68 =  $1/{a+b[ln(f0/f)]+c[ln2(f0/f)]+d[ln3(f0/f)]} - 273.15$  (°C)

T68 = 1.00024 \* T90 (-2 to -35 Deg C)

SPRT-SBE3 NEW Coefs	SPRT-SBE3 OLD Coefs	SBE3 ITS-T90	SPRT ITS-T90	SBE3
INEW_COEIS	OLD_Coels	113-190	113-190	Freq_
-0.00000	0.00042	-1.5071	-1.5071	2869.5251
-0.00007	0.00045	0.9937	0.9936	3035.9032
0.00023	0.00085	4.4947	4.4949	3280.3812
-0.00022	0.00048	7.9964	7.9962	3538.7458
0.00014	0.00088	11.4981	11.4982	3811.3185
-0.00024	0.00052	14.9912	14.9910	4097.7655
0.00012	0.00088	18.4940	18.4941	4399.9336
0.00020	0.00096	21.9932	21.9934	4717.0819
-0.00019	0.00058	25.4945	25.4943	5050.0467
0.00002	0.00079	28.9934	28.9934	5398.7301
0.00002	0.00080	32.4945	32.4945	5763.9048



## Sea-Bird Electronics, Inc.

### 13431 NE 20th Street, Bellevue, WA 98005-2010 USA

Phone: (+1) 425-643-9866 Fax (+1) 425-643-9954 Email: seabird@seabird.com

### SENSOR SERIAL NUMBER: 3369 CALIBRATION DATE: 21-Feb-12

## SBE4 CONDUCTIVITY CALIBRATION DATA PSS 1978: C(35,15,0) = 4.2914 Seimens/meter

### **GHIJ COEFFICIENTS**

g	=	-1.06925850e+001	
h	=	1.62141377e+000	
i	=	-2.92127126e-003	
j	=	3.29098643e-004	
CF	ے در	ar = -9.5700e - 0.08	(no

$$CPcor = -9.5700e-008$$
 (nominal)  
 $CTcor = 3.2500e-006$  (nominal)

### **ABCDM COEFFICIENTS**

a = 6.89638781e-007
b = 1.61372298e+000
c = -1.06769768e+001
d = -7.85663411e-005
m = 6.3

CPcor = -9.5700e-008 (nominal)

BATH TEMP (ITS-90)	BATH SAL (PSU)	BATH COND (Siemens/m)	INST FREO (kHz)	INST COND (Siemens/m)	RESIDUAL (Siemens/m)
0.0000	0.0000	0.00000	2.57223	0.00000	0.00000
-0.9984	34.8995	2.81079	4.90152	2.81077	-0.00001
1.0001	34.8994	2.98240	5.00872	2.98242	0.00002
15.0001	34.8998	4.28078	5.75483	4.28076	-0.00002
18.5001	34.8989	4.62815	5.93845	4.62817	0.00001
29.0001	34.8977	5.71416	6.47859	5.71417	0.00001
32.5001	34.8922	6.08774	6.65412	6.08773	-0.00001

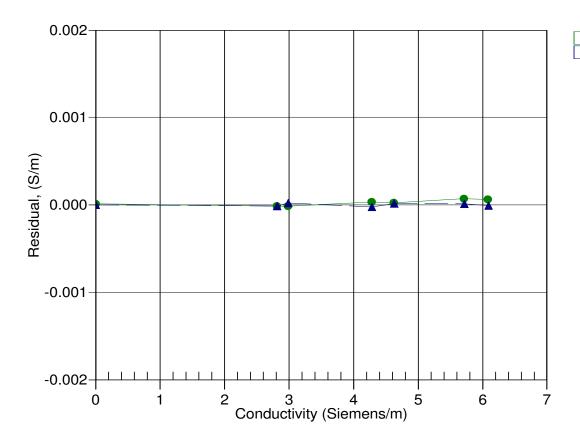
Conductivity =  $(g + hf^2 + if^3 + jf^4)/10(1 + \delta t + \epsilon p)$  Siemens/meter

Conductivity =  $(af^{m} + bf^{2} + c + dt) / [10 (1 + \varepsilon p) Siemens/meter$ 

 $t = temperature[°C)]; p = pressure[decibars]; \delta = CTcor; \epsilon = CPcor;$ 

Residual = (instrument conductivity - bath conductivity) using g, h, i, j coefficients

Date, Slope Correction



• 14-Sep-11 0.9999925 • 21-Feb-12 1.0000000

## Sea-Bird Electronics, Inc.

### 13431 NE 20th Street, Bellevue, WA 98005-2010 USA

Phone: (+1) 425-643-9866 Fax (+1) 425-643-9954 Email: seabird@seabird.com

### SENSOR SERIAL NUMBER: 0614 CALIBRATION DATE: 18-Feb-12

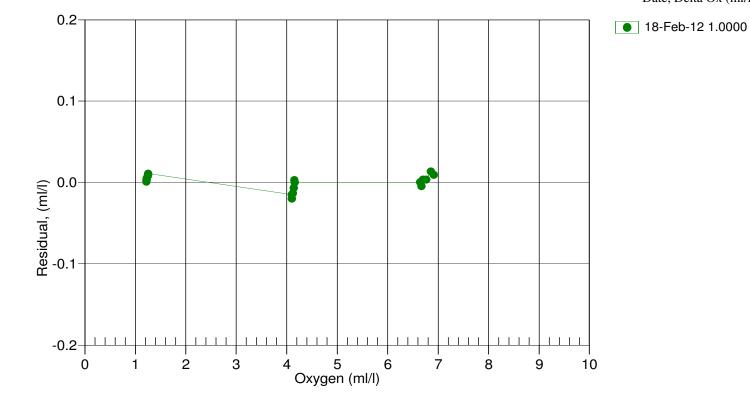
### SBE 43 OXYGEN CALIBRATION DATA

COEFFICIENTS	A = -3.3775e - 003	NOMINAL DYNAMIC COEFFICIENTS
Soc = 0.4835	B = 1.2081e-004	D1 = 1.92634e-4 $H1 = -3.30000e-2$
Voffset = -0.5013	C = -1.8327e - 006	D2 = -4.64803e-2 $H2 = 5.00000e+3$
Tau20 = 2.48	E  nominal = 0.036	H3 = 1.45000e+3

BATH OX	BATH TEMP	BATH SAL	INSTRUMENT	INSTRUMENT	RESIDUAL
(ml/l)	ITS-90	PSU	OUTPUT(VOLTS)	OXYGEN(ml/l)	(ml/l)
1.22	2.00	0.05	0.764	1.22	0.00
1.23	6.00	0.05	0.798	1.23	0.00
1.23	12.00	0.05	0.849	1.23	0.01
1.24	20.00	0.04	0.921	1.25	0.01
1.25	26.00	0.04	0.979	1.26	0.01
1.26	30.00	0.05	1.019	1.27	0.01
4.10	6.00	0.05	1.488	4.09	-0.02
4.10	2.00	0.05	1.380	4.08	-0.02
4.12	12.00	0.05	1.659	4.11	-0.01
4.14	20.00	0.04	1.893	4.13	-0.01
4.15	30.00	0.05	2.196	4.15	0.00
4.16	26.00	0.04	2.076	4.16	-0.00
6.64	26.00	0.05	3.019	6.65	0.00
6.67	30.00	0.05	3.222	6.66	-0.00
6.69	20.00	0.04	2.756	6.70	0.00
6.76	12.00	0.05	2.408	6.77	0.00
6.85	6.00	0.05	2.159	6.87	0.01
6.91	2.00	0.05	1.990	6.92	0.01

Oxygen (ml/l) = Soc \* (V + Voffset) \*  $(1.0 + A * T + B * T^2 + C * T^3) * OxSol(T,S) * exp(E * P / K)$ V = voltage output from SBE43, T = temperature [deg C], S = salinity [PSU] K = temperature [deg K] OxSol(T,S) = oxygen saturation [ml/l], P = pressure [dbar], Residual = instrument oxygen - bath oxygen

Date, Delta Ox (ml/l)



# Temperature Calibration Report STS/ODF Calibration Facility

SENSOR SERIAL NUMBER: 4907 CALIBRATION DATE: 08-Feb-2012

Mfg: SEABIRD Model: 03
Previous cal: 24-Oct-11
Calibration Tech: CAL

ITS-90_COEFFICIENTS	IPTS-68_COEFFICIENTS ITS-T90	
g = 4.34511554E-3	a = 4.34530983E-3	
h = 6.37076838E-4	b = 6.37285168E-4	
i = 2.09177953E-5	c = 2.09494275E-5	
j = 1.75265860E-6	d = 1.75407135E-6	
f0 = 1000.0	Slope = 1.0	Offset = 0.0

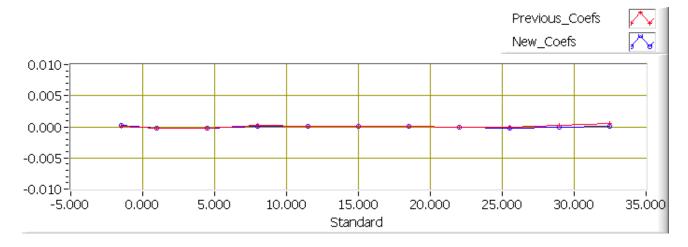
Calibration Standard: Mfg: ASL Model: F18 s/n: 245-5149

Temperature ITS-90 =  $1/{g+h[ln(f0/f)]+i[ln2(f0/f)]+j[ln3(f0/f)]} - 273.15$  (°C)

Temperature IPTS-68 =  $1/{a+b[ln(f0/f)]+c[ln2(f0/f)]+d[ln3(f0/f)]} - 273.15$  (°C)

T68 = 1.00024 \* T90 (-2 to -35 Deg C)

SBE3 Freq	SPRT ITS-T90	SBE3 ITS-T90	SPRT-SBE3 OLD Coefs	SPRT-SBE3 NEW Coefs
2934.7645	-1.5052	-1.5054	0.00007	0.00019
3104.4010	0.9939	0.9941	-0.00018	-0.00016
3353.7376	4.4942	4.4945	-0.00021	-0.00027
3617.2191	7.9958	7.9956	0.00022	0.00015
3895.1951	11.4971	11.4970	0.00012	0.00008
4187.3291	14.9903	14.9902	0.00007	0.00006
4495.5142	18.4935	18.4934	0.00008	0.00009
4818.9334	21.9927	21.9927	-0.00005	-0.00005
5158.5360	25.4947	25.4949	-0.00010	-0.00016
5514.0269	28.9933	28.9933	0.00017	-0.00002
5886.2702	32.4937	32.4936	0.00050	0.00008



## Sea-Bird Electronics, Inc.

### 13431 NE 20th Street, Bellevue, WA 98005-2010 USA

Phone: (+1) 425-643-9866 Fax (+1) 425-643-9954 Email: seabird@seabird.com

### SENSOR SERIAL NUMBER: 3399 CALIBRATION DATE: 21-Feb-12

### SBE4 CONDUCTIVITY CALIBRATION DATA PSS 1978: C(35,15,0) = 4.2914 Seimens/meter

### **GHIJ COEFFICIENTS**

g = -1.01511715e+001	
h = 1.53536729e+000	
i = -2.28594877e - 003	
j = 2.63108407e-004	
CPcor = -9.5700e-008	(nomina

al) CTcor = 3.2500e-006 (nominal)

### **ABCDM COEFFICIENTS**

a = 1.06291609e - 006b = 1.52937173e+000c = -1.01389439e+001d = -7.94633515e-005

m = 6.0

CPcor = -9.5700e-008 (nominal)

BATH TEMP (ITS-90)	BATH SAL (PSU)	BATH COND (Siemens/m)	INST FREO (kHz)	INST COND (Siemens/m)	RESIDUAL (Siemens/m)
0.0000	0.0000	0.00000	2.57477	0.00000	0.00000
-0.9984	34.8995	2.81079	4.99973	2.81077	-0.00001
1.0001	34.8994	2.98240	5.11060	2.98242	0.00002
15.0001	34.8998	4.28078	5.88148	4.28075	-0.00003
18.5001	34.8989	4.62815	6.07103	4.62817	0.00002
29.0001	34.8977	5.71416	6.62833	5.71417	0.00001
32.5001	34.8922	6.08774	6.80936	6.08773	-0.00001

Conductivity =  $(g + hf^2 + if^3 + jf^4)/10(1 + \delta t + \epsilon p)$  Siemens/meter

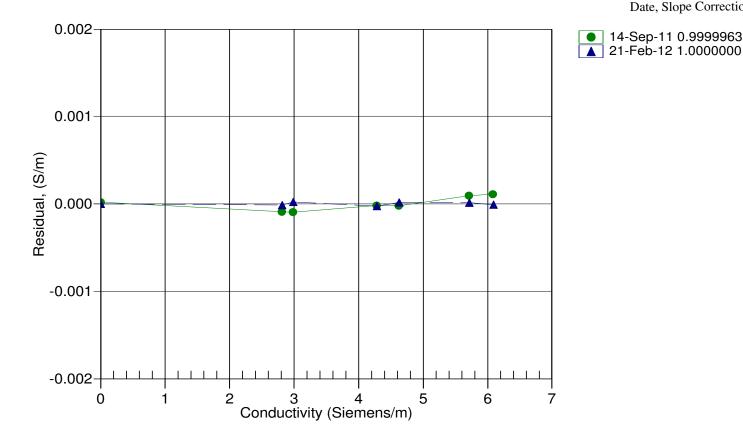
Conductivity =  $(af^{m} + bf^{2} + c + dt) / [10 (1 + \varepsilon p)]$  Siemens/meter

t = temperature[°C); p = pressure[decibars];  $\delta = CTcor$ ;  $\epsilon = CPcor$ ;

Residual = (instrument conductivity - bath conductivity) using g, h, i, j coefficients

Date, Slope Correction

14-Sep-11 0.9999963



## Temperature Calibration Report STS/ODF Calibration Facility

SENSOR SERIAL NUMBER: 0035 CALIBRATION DATE: 16-Feb-2012

Mfg: SEABIRD Model: 35
Previous cal: 27-Oct-11
Calibration Tech: CAL

### **ITS-90 COEFFICIENTS**

a0 = 3.491354356E-3

a1 = -8.999088258E-4

a2 = 1.472396592E-4

a3 = -8.336052929E-6

a4 = 1.820067296E-7

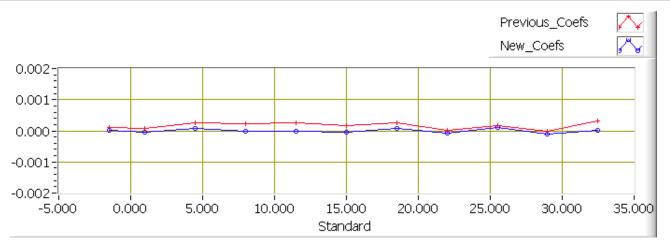
Slope = 1.000000 Offset = 0.000000

Calibration Standard: Mfg: ASL Model: F18 s/n: 245-5149

Calibration Standard: Mfg: ASL Model: F18 s/n: 245-5149

Temperature ITS-90 =  $1/{a0+a1[ln(f)]+a2[ln2(f)]+a3[ln3(f)]+a4[ln4(f)]} - 273.15$  (°C)

SBE35 Count	SPRT ITS-T90	SBE35 ITS-T90	SPRT-SBE35 OLD Coefs	SPRT-SBE35 NEW Coefs
659024.3000	-1.5058	-1.5058	0.00011	0.00001
590655.1500	0.9937	0.9938	0.00007	-0.00005
507831.3000	4.4948	4.4947	0.00026	0.00007
437794.8000	7.9964	7.9964	0.00023	-0.00002
378443.5750	11.4979	11.4979	0.00026	-0.00001
328132.9000	14.9908	14.9909	0.00018	-0.00006
285158.1500	18.4934	18.4933	0.00026	0.00009
248511.1500	21.9909	21.9910	0.00001	-0.00009
217094.7750	25.4936	25.4935	0.00016	0.00012
190156.6750	28.9927	28.9928	-0.00002	-0.00010
166962.4250	32.4946	32.4946	0.00032	0.00003



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(541) 929-5650 Fax (541) 929-5277 www.wetlabs.com

### **C-Star Calibration**

Date	November 30, 2010	S/N#	CST-327DR	Pathlength 25 cm
			Analog meter	
$V_d$			0.059 V	
$V_{air}$			4.752 V	
$\mathbf{V}_{ref}$			4.660 V	
Temp	erature of calibration wa	ter		21.3 °C
Ambie	ent temperature during ca	alibration		21.5 °C

Relationship of transmittance (Tr) to beam attenuation coefficient (c), and pathlength (x, in meters):  $Tr = e^{-cx}$ 

To determine beam transmittance:  $Tr = (V_{sig} - V_{dark}) / (V_{ref} - V_{dark})$ 

To determine beam attenuation coefficient: c = -1/x \* In (Tr)

 $V_{d}$ Meter output with the beam blocked. This is the offset.

 $V_{air}$ Meter output in air with a clear beam path.

Meter output with clean water in the path.

Temperature of calibration water: temperature of clean water used to obtain V<sub>ref</sub>.

Ambient temperature: meter temperature in air during the calibration.

Measured signal output of meter.  $V_{sig}$ 

Revision L 6/9/09

## Transmissometer Air Calibration M&B Calculator Wilf Gardner / Mary Jo Richardson Texas A&M

CST-	327-DR Factory Cal S	heet Info	Air Cal Date	AVG I	28-Mar-12 Deck/Lab Re	adings
Air Reading	4.752			4.649		
Water Reading	4.66			N/A		
Blocked Reading	0.059			0.059		
Air Temp.	12.875	12.884	12.997	13.088	13.134	13.168
M B	20.044 -1.183		Air Te	emp. Ave	erage	13.024
CST-	327-DR Factory Cal S	heet Info	Air Cal Date	AVG I	14-Apr-12 Deck/Lab Re	adings
Air Reading	4.752			4.611		
Water Reading	4.66			N/A		
Blocked Reading	0.059			0.06		
Air Temp.	29.342	29.365	29.329	29.380	29.452	29.432

Air Temp. Average

29.383

20.216

-1.213

M

В

## **CALIBRATION SHEET**

Name : RINKO-Ⅲ

Model : ARO-CAV

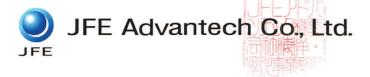
Serial No. :

84

Parameter

Temperature

Dissolved Oxygen



Ocean and River Instruments Division

Kobe Sales Department

7-2-3 Ibukidai-higashi, Nishi-ku, Kobe 651-2242, Japan.

TEL:+81-78-997-8686 FAX:+81-78997-8609 URL: http://www.jfe-advantech.co.jp/eng/

### **Temperature**

MODEL

: ARO-CAV

SERIAL

: 84

DATE

: October 21, 2011

Loaction

: Calibration office of manfacture department at Kobe

Method

: The instrument is calibrated in a constant temperature water tank.

5 outputs in n-value corresponding to 5 water temperature ranging from

3 to 31 degrees C are computed by least square method.

(To make the tank temperature constant, water is stirred. The reference

temperature is measured by a thermometer)

Reference

: Platinum thermometer (certified by JCSS)

Temperature : Temperature ( $^{\circ}$ C) = A+B×N+C×N<sup>2</sup>+D×N<sup>3</sup>

A = -5.556716E+00

B = 1.6795156E+01

C = -2.237491E+00

D = 4.7879874E-01

Reference	Output	Calculated	Error
[°C]	[V]	[℃]	$[^{\circ}C]$
3.631	0.58729	3.632	0.001
10.020	1.03908	10.016	-0.004
17.495	1.59640	17.501	0.006
24.058	2.08353	24.054	-0.004
31.330	2.59532	31.331	0.001

Criteria for

: 1. The errors in above form must be within ±0.02°C

acceptability

2. After writing the calibration coefficients into instrument,

one point check at any temperature must agree with the accuracy

declared by the instrument.

Output Check:

Reference	Calculated	Error
l°C1	[°C]	[°C]
22.696	22.704	0.008

Judgement

: Good

Calibration group,

Manufacture department at Kobe

JFE Advantech Co., LTD

### **Dissolved Oxygen**

MODEL

: ARO-CAV

SERIAL

: 84

DATE

: October 21, 2011

Loaction

: Calibration office of manfacture department at Kobe

Method

2 points calibration of span and zero is carried out with 100% saturation water and nigrogen gas. Calibration should be done after making the instruments accustomed in the water and keeping saturation with air-

bubbling. Outputs in saturated water and nitr

Film No=	160004A		
A =	-44.0512	E =	0.0052
B =	141.534	F =	0.00
C =	-0.09589	G =	0.00
D =	0.0123	H =	1.00

Results

Temperature at calibration[°C]	25
Air pressure at calibration[hPa]	1003.2
Air saturation at calibration[%]	99.0

	Span output [%]	zero output [%]	Span Error [%]	Zero Error [%]
1st	99.5	-0.1	0.5	-0.1
2nd	99.4	-0.1	0.4	-0.1
3rd	99.5	-0.1	0.5	-0.1

Judgement

: Good

Calibration group,

Appuracture department at Koho

Manufacture department at Kobe

JFE Advantech Co., LTD



#### **LADCP**

ADCP/LADCP PI: Eric Firing, Unversity of Hawaii

Cruise Participant: Sarah Eggleston

A University of Hawaii (UH) system was used to collect Lowered Acoustic Doppler Current Profiler (LADCP) data. Preliminary processing was completed during the cruise using a Lamont-Doherty Earth Observatory (LDEO) LADCP software.

### **LADCP System Setup**

One 36-bottle CTD rosette was used during the whole cruise. On deck, the rosette was moved into and out of the hangar atop a plywood platform mounted on two tracks. Initially installed on the port side of the ship, operations were switched to the starboard side of the ship after the port winch failed during station 2, cast 1.

One WH150-kHz LADCP (serial number 16283), was secured to the rosette, facing downward, along with an oil-filled 58V rechargeable lead-acid battery pack. The installation on deck consisted of a Lenovo T41 laptop computer for data acquisition and a Lenovo R52 laptop for data processing, as well as an American Reliance Inc. (AMREL) battery charger/power supply. The LADCP heads and battery pack were mounted inside the 36-bottle rosette frame and connected using a custom designed, potted star cable assembly. The head was placed looking downward underneath the bottles at approximately the same height as the CTD instruments. The battery pack and LADCP were mounted on opposite sides of the rosette frame center to avoid unequal balancing.

The power supply and data transfer was handled independently from any CTD connections. While on deck, the instrument communication was set up by means of a network of RS-232 and USB cables, using LDEO LADCP software for data processing (using version IX\_6beta) in Matlab [Thur08]. Additional scripts, authored by Prof. Eric Firing and the group at the University of Hawaii, were written for Python and used for instrument control and data transmission. The command file used in communication with the LADCP is shown below:

CR1

WM15

TC2

TB 00:00:02.20

TE 00:00:01.00

TP 00:00.00

WN40

WS0800

WT1600

WF1600

WV330

EZ0011101

EX00100

CF11101

LZ30,230

CL<sub>0</sub>

The LADCP and CTD acquisition computer clocks both used NTP to stay in sync with the ship clock and to assure that the absolute time recorded by the CTD and LADCP be the same.

### **LADCP Operation and Data Processing**

Upon arrival at each station, the LADCP heads were switched on for data acquisition using the LADCP software. Communication between the computer and the instrument was then terminated, the power cable was disconnected, and all connections were sealed with dummy plugs. After each cast, the data and the power supply cable was rinsed with fresh water and reconnected to the computer and battery charger; the data acquisition was terminated; the battery was charged; and the data was downloaded using the LADCP software. It took about 45 minutes to download the data and approximately 60 minutes to fully recharge the battery.

Within 10 hours after each cast, the data were preliminarily processed, combining CTD, GPS, and shipboard ADCP data with the data from the LADCP, thus producing both shear and inverse solutions for the absolute velocities. The preliminary processing produced velocity profiles, rosette frame angular movements, and velocity ascii and Matlab files. Plots (velocity profiles from each cast and transects showing the values of U and V along the course of the cruise) were put on a website that was made available to all computers on the local network.

### **Problems**

Prior to station 1, while the LADCP operator was training the opposite watch stander, the first communication problem between the acquisition computer and the instrument occurred. The problem manifested itself as an inability to communicate with the instrument; when the "Wakeup" or "Deployment initialization" commands were sent to the instrument, a timeout error was returned (typically after a long delay). The error message is copied below. It ultimately became clear that the problem was with the USB-to-serial cable (the one installed used a Prolific chip). However, after restarting both the computer (multiple times) and the LADCP (by unplugging the cable from the instrument for approximately 1 minute) and restarting with no cables connected to the computer, the communication proceded normally. Alternatively, it was possible to communicate with the instrument using /dev/ttyUSB1 instead of /dev/ttyUSB0; the easiest way to accomplish this was by using a 2-port USB-to-serial cable (using an FTDI chip) and plgging the power/communication cable of the LADCP into port 1 on the converter.

A small variation on this problem arose after downloading and saving the data from stations 68 and 71. After the data had been saved, the same timeout error appeared. However, this did not affect further communication with the instrument after the error box was dismissed.

At the beginning of station 81 (the final station), the same communication error appeared as during the initial instrument testing. The opposite watch stander was on watch and did not solve the problem or awaken the main LADCP operator, so the instrument was not collecting data when the rosette was deployed.

Between stations 40 and 41, the LADCP was repositioned on the rosette, as it appeared to have gradually slid downward from its initial position at a rate of approximately 0.5-1 mm a day. It was raised approximately 5cm, to ensure that the heads would not come in contact with the plywood platform that the rosette rested upon on deck.

Due to the pressure limitations of the LADCP and other instruments on the rosette, the package was lowered only to 6000m above the Puerto Rico Trench (stations 45-47).

Error message received (USB-to-serial cable communication error):

```
<type 'exceptions.TypeError'> Exception in Tk callback
Function: <bound method terminal.ask_send_setup of <uhdas.serial.rditerm.terminal instance at
0x9ce5f2c>> (type: <type 'instancemethod'>)
Args: ()
Traceback (innermost last):
File "/usr/lib/python2.6/dist-packages/Pmw/Pmw_1_3/lib/PmwBase.py", line 1747, in __call__
return apply(self.func, args)
File "/home/currents/programs/uhdas/serial/rditerm.py", line 248, in ask_send_setup
if os.path.exists(self.cmd_filename):
File "/usr/lib/python2.6/genericpath.py", line 18, in exists
st = os.stat(path)
<type 'exceptions.TypeError'>: coercing to Unicode: need string or buffer, tuple found
```

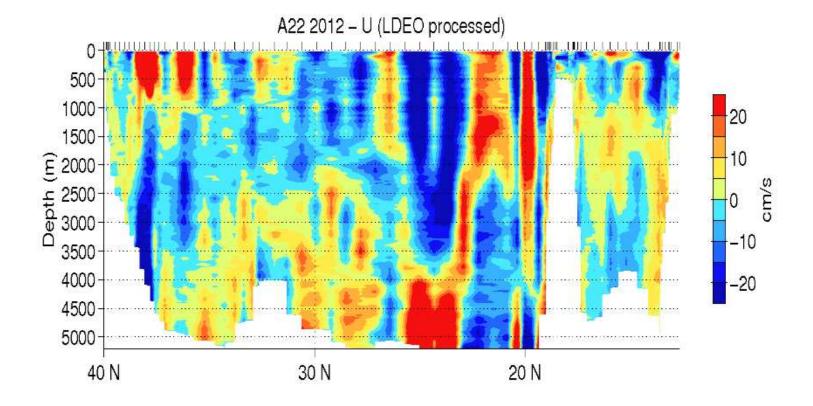
### **Preliminary results**

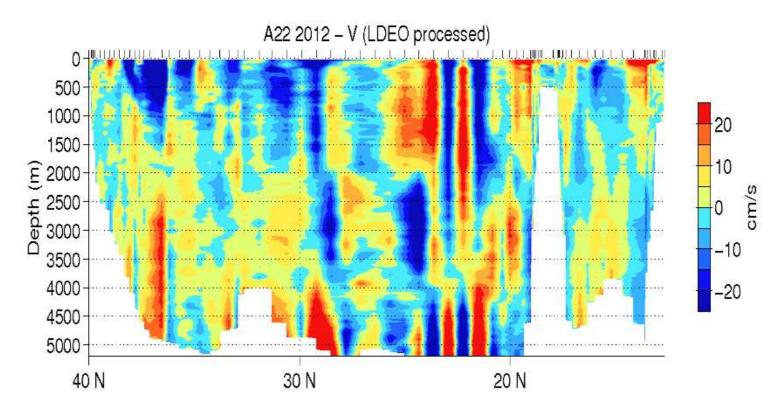
The latitude-depth section measured at stations 1-80 of zonal (U) and meridional (V) velocity is shown in the attached file (U\_V\_depth\_lat\_section\_LDEO.ps). Several notables features were observed:

- the Gulf Stream, 38.3-37.6N (stations 11 and 14), with an eastward-flowing current of approximately 2m/s at the surface
- possible presence of an eddy at 21.5N (station 42) at a depth of 1200m, flowing eastward at approximately 25cm/s; this was also noted as anomolies in chemical data, particularly SF6
- a strong north-westerly flow in the top 100m off the coast of Aruba (stations 71-80) of 0.5-1m/s

### References

Thurnherr, A. M., How To Process LADCP Data With the LDEO Software (last updated for version IX.5) July 9, 2008.





CLIVAR/CO2 A22 R/V Atlantis cruise at20 2012/03/18-2012/04/23 PI: Eric Firing, University of Hawaii Julia Hummon

### **Shipboard Acoustic Doppler Current Profiler**

The R/V Atlantis has a permenantly-mounted 75kHz acoustic Doppler current profiler ("ADCP", Teledyne R.D.Instruments) for measuring ocean velocity. During the cruise prior to A22, an additional higher frequency ADCP (300kHz Workhorse) was installed, and remained on the ship for the A22/A20 CLIVAR cruises.

Specialized software developed at the University of Hawaii has been installed on this ship for the purpose of ADCP acquisition, processing, and figure generation during each cruise. The acquisition system ("UHDAS", University of Hawaii Data Acquisition System) is an Open Sources suite, written in C and Python. UHDAS acquires data from the ADCPs, gyro heading (for reliability), Phins heading (for increased accuracy), and GPS positions from various sensors. An additional Phins is also logged.

Single-ping data are converted from beam to earth coordinates using known transducer angles and gyro heading, and are corrected by the average phins-gyro difference over the duration of the averaging interval.

Groups of single-ping ocean velocity estimates must be edited averaged to decrease measurement noise. These groups commonly comprise 5 minutes) or 2 minutes for WH300). Bad pings must be removed prior to averaging. UHDAS uses a CODAS (Common Oceanographic Data Access System) database for storage and retrieval of averaged data. Various post-processing steps can be administered to the database after a cruise is over, but the at-sea data should be acceptable for preliminary work.

UHDAS provides access to regularly-updated figures and data over the ship's network via samba share and nfs export, as well as through the web interface. The web site has regularly-updated figures showing the last 5-minute ocean velocity profile with signal return strength, and hourly contour and vector plots of the last 3 days of ocean velocity.

The LADCP data processing uses recent shipboard velocities as one of the constraints. Shipboard Doppler sonar work on this cruise

During the cruise, the Ocean Surveyor was run in "interleaved" pinging mode, where it can sample in broadband mode (higher resolution, reduced range) and in narrowband mode (coarser resolution, increased depth range) with alternating pings. These are processed into two separate datasets.

#### **Data quality**

Typical ADCP data quality issues are

- clock errors
- heading correction
- data loss or compromise:
  - data loss due to bad weather, bubbles, etc
  - data compromise due to deep scattering layers
  - depth penetration

#### clock

The ADCP computer was synced to the network time server during the cruise. This worked fine; times are in UTC; decimal days for processed ADCP data are zero-based, i.e. 2012/01/01 12:00:00 is 0.500000

#### heading

Gyro headings were corrected using the Phins. Heading correction is critical to minimize cross-track errors induced by errors in heading. A one degree heading heading error results in a 10cm/s cross-track error in shipboard ADCP data if the ship is travelling at 12kts.

### data loss or compromise:

ADCP system and data were monitored remotely during the cruise. Nothing was seen during the cruise that points to data loss

or compromise. Additional bottom editing will probably be necessary in the water near Puerto Rico, as odd artifacts appeared at depth in the remote monitoring plots.

### Overview

All in all, the instrument, ancillary devices, and acquisition system performed well.

### references:

UHDAS+CODAS Documentation http://currents.soest.hawaii.edu/docs/adcp\_doc/index.html

### 6 Chlorofluorocarbon (CFC) and Sulfur Hexafluoride (SF6) Measurements

PI: William Smethie, LDEO

Cruise Participants: Eugene Gorman, LDEO

Thomas Custer, University of Hawaii

Samples for the analysis of dissolved CFC-11, CFC-12, CFC-113 and SF6 were collected from approximately 1300 of the Niskin water samples collected during the expedition. When taken, water samples for CFC analysis were the first samples drawn from the 10-liter bottles. Care was taken to coordinate the sampling of CFCs with other samples to minimize the time between the initial opening of each bottle and the completion of sample drawing. In most cases, dissolved oxygen, alkalinity and dissolved inorganic carbon samples were collected within several minutes of the initial opening of each bottle. To minimize contact with air, the CFC samples were collected from the Niskin bottle petcock using PVC tubing flushed of air bubbles and filled into a 500-ml glass bottle. The glass bottle was placed into a plastic overflow container and filled from the bottom. The overflow water filled the container to a depth greater than the height of the glass bottle. The stopper was held in the overflow container or briefly in the sample stream to be rinsed. When the overflow container was filled, it (and the glass bottle) were lowered to remove the PVC tubing and the glass bottle was stoppered under water. A plastic cap was snapped on to hold the stopper in place. Samples were analyzed within 12 hours of sample collection and the temperature of the water bath noted immediately prior to analysis.

For atmospheric sampling, a 200 cm3 gas-tight, glass syringe was used to collect samples from the bow of the ship. Samples were injected directly into a calibrated sample loop and then sent to the traps and then columns of the analytical instrumentation. Average atmospheric concentrations determined during the cruise were 240 parts per trillion (ppt) for CFC-11, 235 ppt for CFC-12, 75 ppt for CFC-113, and 7.7 ppt for SF6.

Concentrations of CFC-11, CFC-12, CFC-113, and SF6 in air samples, seawater and gas standards were measured by shipboard electron capture gas chromatography (EC-GC). Samples were introduced into the GC-EC via a dual purge and trap system. CFCs were purged from ~20 mL water samples while SF6 was purged from a larger ~350 mL volume using UHP nitrogen. Samples were purged using flows of approximately 60-80 mL min-1 for CFCs and 80-90 mL min-1 for SF6. Purge gas was passed through a magnesium perchlorate dryer prior to reaching traps constructed from ~3 inches of 1/16 inch stainless steel tubing containing either Carbograph 1AC (for CFCs) or Carboxen 1000 (for SF6). Traps were held at approximately -80 C (CFCs) and -60 C (SF6) using a liquid CO2 cooling (Scientific Instrument Services, Inc.) for the 5 minute duration of trapping. Following collection, the traps are isolated and flash-heated by direct resistance to ~120 C (for CFCs) and ~150 C (for SF6) to desorb collected chemicals for further separation and detection.

Separation of SF6 was accomplished using a both a packed precolumn (~3' long) and analytical column (~6' long) containing 80/100 mesh molecular sieve 5A and held at 100 C. The precolumn was switched out and backflushed after 2 minutes to prevent N2O from entering the main column and prevent background chemicals from increasing the detector baseline. CFCs were separated using a series of three packed columns: a Porosil B precolumn (~ 4 feet), a carbograph 1AC analytical column (~ 6 feet), and a short column (~5 cm) containing 80/100

mesh molecular sieve 5A. Following release from the trap, the short column containing molecular sieves was switched out of the system and backflushed immediately following exit of CFC 12 (~1.8 min) to remove potential interference of nearby SF6 and N2O. The precolumn was switched out after 2 min and backflushed following exit of CFC-113. This prevented buildup of chemicals on the column that could increase the system background.

The analytical system was calibrated frequently using standard gases of known CFC and SF6 compositions. Gas sample loops of known volume were thoroughly flushed with standard gas and injected into the system. Loops equilibrated with atmosphere and the temperature and pressure was recorded so that the amount of gas injected could be calculated. The procedures used to transfer the standard gas to the trap, precolumns, main chromatographic columns and EC detector were similar to those used for analyzing water samples. Two different sizes of gas sample loops were used. Multiple injections of these loop volumes could be made to allow the system to be calibrated over a relatively wide range of concentrations. Air samples and system blanks (injections of loops of CFC-free gas) were injected and analyzed in a similar manner. The typical analysis time for samples was ~11.0 min.

Concentrations of the CFCs in air, seawater samples and gas standards are reported relative to the SIO98 calibration scale (Cunnold, et. al., 2000). Concentrations in air and standard gas are reported in units of mole fraction CFC in dry gas, and are typically in the parts per trillion (ppt) range. Dissolved CFC concentrations are given in units of picomoles per kilogram seawater (pmol kg-1), and SF6 in femtomoles per kilogram seawater (fmol kg-1). CFC concentrations in air and seawater samples were determined by fitting their chromatographic peak areas to multipoint calibration curves, generated by injecting multiple sample loops of gas from a working standard (cylinder 35060 for CFC-11: 591.03 ppt, CFC-12: 443.6 ppt, CFC 113: 249.6and SF6: 2.6 ppt) into the analytical instrument. Full-range calibration curves were run three times during the cruise. Single injections of a fixed volume of standard gas at one atmosphere were run much more frequently to monitor short-term changes in detector sensitivity. The SF6 peak was often on a small bump on the baseline, resulting in a large dependence of the peak area on the choice of endpoints for integration. Estimated accuracy is +/-2%. Precision for CFC-12, CFC-11, CFC-113 and SF6 was less than 1%. Estimated limit of detection is 1 fmol kg-1 for CFC-11, 3 fmol kg-1 for CFC-12 and 0.05 fmol kg-1 for SF6.

The efficiency of the purging process was evaluated periodically by re-stripping water samples and comparing the residual concentrations to initial values. No SF6 was detected in the restripped sample. The determination of a blank due to sampling and analysis of CFC-free waters was hampered by the apparent lack of CFC-free waters.

## **Analytical Difficulties**

Analytical difficulties were minimal over the course of this the first leg of the cruise. Occasionally glass bottles were dropped, caps found loose, or the stripping chamber was overfilled due to user error. CFC-12 was often not trapped as the liquid CO2 supply from a given tank ran out and the cooling traps did not reach the required temperature to hold this chemical effectively. Early in the analysis period, a batch of old magnesium perchlorate was

used that caused a blockage of the purging flow through the sample. This was corrected by using fresh magnesium perchlorate for the remainder of the cruise.

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#### CFC-11, CFC-12, CFC-113, CCl<sub>4</sub> and SF<sub>6</sub>

Cruise Participants: Jim Happell
Andrew Reed

## **Sample Collection**

All samples were collected from depth using 10.4 liter Niskin bottles. None of the Niskin bottles used showed a CFC contamination throughout the cruise. All bottles in use remained inside the CTD hanger between casts.

Sampling was conducted first at each station, according to WOCE protocol. This avoids contamination by air introduced at the top of the Niskin bottle as water was being removed. A water sample was collected from the Niskin bottle petcock using viton tubing to fill a 300 ml BOD bottle. The viton tubing was flushed of air bubbles. The BOD bottle was placed into a plastic overflow container. Water was allowed to fill BOD bottle from the bottom into the overflow container. The stopper was held in the overflow container to be rinsed. Once water started to flow out of the overflow container the overflow container/BOD bottle was moved down so the viton tubing came out and the bottle was stoppered under water while still in the overflow container. A plastic cap was snapped on to hold the stopper in place. One duplicate sample was taken on most stations from random Niskin bottles. Air samples, pumped into the system using an Air Cadet pump from a Dekoron air intake hose mounted high on the foremast were run when time permitted. Air measurements are used as a check on accuracy.

## **Equipment and technique**

CFC-11, CFC-12, CFC-113, CCl<sub>4</sub> and SF<sub>6</sub> were measured on 40 stations (odd stations 3 through 81) for a total of 1291 samples. Even stations and station 1 were sampled and analyzed by the LDEO CFC group. Analyses were performed on a gas chromatograph (GC) equipped with an electron capture detector (ECD). Samples were introduced into the GC-EDC via a purge and dual trap system. 202 ml water samples were purged with nitrogen and the compounds of interest were trapped on a main Porapack N/Carboxen 1000 trap held at ~ -15°C with a Vortec Tube cooler. After the sample had been purged and trapped for 6 minutes at 250ml/min flow, the gas stream was stripped of any water vapor via a magnesium perchlorate trap prior to transfer to the main trap. The main trap was isolated and heated by direct resistance to 150°C. The desorbed contents of the main trap were back-flushed and transferred, with helium gas, over a short period of time, to a small volume focus trap in order to improve chromatographic peak shape. The focus trap was Porapak N and is held at  $\sim$  -15  $^{\circ}$ C with a Vortec Tube cooler. The focus trap was flash heated by direct resistance to 180 °C to release the compounds of interest onto the analytical pre-columns. The first precolumn was a 5 cm length of 1/16" tubing packed with 80/100 mesh molecular sieve 5A. This column was used to hold back N<sub>2</sub>O and keep it from entering the main column. The second pre-column was the first 5 meters of a 60 m Gaspro capillary column with the main column consisting of the remaining 55 meters.

The analytical pre-columns were held in-line with the main analytical column for the first 35 seconds of the chromatographic run. After 35 seconds, all of the compounds of interest were on the main column and the pre-column was switched out of line and backflushed with a relatively high flow of nitrogen gas. This prevented later eluting compounds from building up on the analytical column, eventually eluting and causing the detector baseline signal to increase.

The samples were stored at room temperature and analyzed within 12 hours of collection. Every 12 to 18 measurements were followed by a purge blank and a standard. The surface sample was held after measurement and was sent through the process in order to "restrip" it to determine the efficiency of the purging process.

#### **Calibration**

A gas phase standard, 35060, was used for calibration. The concentrations of the compounds in this standard are reported on the SIO 2005 absolute calibration scale. 5 calibration curves were run over the course of the cruise. Estimated accuracy is  $\pm$ -2%. Precision for CFC-12, CFC-11, and SF<sub>6</sub> was less than 2%. Estimated limit of detection is 1 fmol/kg for CFC-11 and CCl<sub>4</sub>, 3 fmol/kg for CFC-12 and CFC-113, and 0.4 fmol/kg for SF<sub>6</sub>

#### **Helium and Tritium**

PI: William Jenkins

Cruise Participant: Kevin Cahill

Helium and Tritium samples were collected roughly once per day at 16 stations during A22.

## **Helium Sampling**

24 helium samples were drawn at 12 of the stations and 8-16 niskins were sampled at 4 of the shallower stations. Although all 36 niskins were not sampled, depths were chosen to obtain an accurate cross-section of the entire water column. A duplicate was taken at every other station when 24 bottles were sampled. Helium samples were taken in custom-made stainless steel cylinders and sealed with rotating plug valves at either end. The sample cylinders were leak-checked and backfilled with N2 prior to the cruise. Samples were drawn using tygon tubing connected to the niskin bottle at one end and the cylinder at the other. Cylinders are thumped with a bat while being flushed with water from the niskin to remove bubbles from the sample. After flushing roughly 1 liter of water through them, the plug valves are closed. Due to the nature of the o-ring seals on the sample vessels, they must be extracted within 24 hours. Eight samples at a time were extracted using our At Sea Extraction line in the Bio-Analytical Lab. The stainless steel sample cylinders are attached to the vacuum manifold and pumped down to less than 2e-7 Torr using a diffusion pump for a minimum of 1 hour to check for leaks. The sections are then isolated from the vacuum manifold and introduced to the reservoir cans which are heated to >80C for roughly 10 minutes. Glass bulbs are attached to the sections and immersed in ice water during the extraction process. After 10 minutes each bulb is flame sealed and packed for shipment back to WHOI. The extraction cans and sections are cleaned with distilled water and isopropanol, then dried between each extraction. Prior to the cruise, all vacuum components were cleaned, serviced and checked for leaks. The glass bulbs are baked to 640C for 6 hours and cooled slowly in an oven receiving a steady flow of nitrogen. 368 helium samples were taken, but 1 was lost due to glass cracking during the flame-sealing. This includes 20 samples and their duplicates taken solely for sampling technique comparisons as well as 6 regular duplicates. Helium samples will be analyzed using a mass spectrometer at WHOI.

The air conditioning problems that cropped up during the middle of the cruise put a strain on the -130C cold trap and water-cooled vacuum pump, but the engineers were able to supply additional cooling for our lab and did not appear to have affected the helium extractions.

## **Tritium Sampling**

Tritium samples were drawn from the same stations and bottles as those sampled for helium, with the exception of the duplicates. A duplicate was taken on stations where we drew 24 samples and where no helium duplicate was being taken. Tritium samples were taken using tygon tubing to fill 1 liter glass jugs. The jugs were baked in an oven, backfilled with argon, and the caps were taped shut prior to the cruise. While filling, the jugs are place on the deck and filled to about 2 inches from the top of the bottle, being

careful not to spill the argon. Caps were replaced and taped shut with electrical tape before being packed for shipment back to WHOI. 328 tritium samples were taken, including 6 duplicates. Tritium samples will be degassed in the lab at WHOI and stored for a minimum of 6 months before mass spectrometer analysis. No issues were encountered while taking tritium samples.

## **Dissolved Inorganic Carbon (DIC)**

PI: Richard Feely, NOAA/PMEL

Rik Wanninkhof, NOAA/AOML

Cruise Participants: Dana Greeley, NOAA/PMEL

Bob Castle, NOAA/AOML

The DIC analytical equipment (DICE) was designed based upon the original SOMMA systems (Johnson, 1985, '87, '92, '93). These new systems have improved on the original design by use of more modern National Instruments electronics and other available technology. These 2 DICE systems (PMEL-1 and PMEL-2) were set up in a seagoing container modified for use as a shipboard laboratory on the aft working deck of the R/V Atlantis. In the coulometric analysis of DIC, all carbonate species are converted to  $CO_2$  (gas) by addition of excess hydrogen to the seawater sample. The evolved  $CO_2$  gas is carried into the titration cell of the coulometer, where it reacts quantitatively with a proprietary reagent based on ethanolamine to generate hydrogen ions. These are subsequently titrated with coulometrically generated OH-.  $CO_2$  is thus measured by integrating the total charge required to achieve this. (Dickson, et al 2007).

Each coulometer was calibrated by injecting aliquots of pure CO<sub>2</sub> (99.995%) by means of an 8-port valve outfitted with two calibrated sample loops of different sizes (~1ml and ~2ml) (Wilke et al., 1993). The instruments were each separately calibrated at the beginning of each ctd station with a minimum of two sets of the gas loop injections. A total of 290 sets of loops were run on each system during this cruise.

Secondary standards were run throughout the cruise (at least one per station) on each analytical system. These standards are Certified Reference Materials (CRMs), consisting of poisoned, filtered, and UV irradiated seawater supplied by Dr. A. Dickson of Scripps Institution of Oceanography (SIO). Their accuracy is determined manometrically on land in San Diego. DIC data reported to the database have been corrected to the batch 117 CRM value. The reported CRM value for this batch is 2009.99 µmol/kg. The average measured values (in µmol/kg during this cruise) were 2010.36 for PMEL-1 and 2010.47 for PMEL-2.

The DIC water samples were drawn from Niskin-type bottles into cleaned, pre-combusted 300mL borosilicate glass bottles using silicon tubing. Bottles were rinsed once and filled from the bottom, overflowing by at least one-half volume. Care was taken not to entrain any bubbles. The tube was pinched off and withdrawn, creating a 5mL headspace, and 0.125mL of 50% saturated HgCl2 solution was added as a preservative. The sample bottles were sealed with glass stoppers lightly covered with Apiezon-L grease, and were stored in a 20°C water bath for a minimum of 20 minutes to bring them to temperature prior to analysis.

Over 1,800 samples were analyzed for discrete DIC. Greater than 10% of these samples were taken as replicates as a check of our precision. These replicate samples were typically taken from the surface, oxygen minimum, and bottom bottles. The replicate samples were interspersed throughout the station analysis for quality assurance and integrity of the coulometer cell solutions and no systematic differences between the replicates were observed. The absolute average difference from the mean of these replicates is 0.8 µmol/kg.

The DIC data reported at sea is to be considered preliminary until a further shoreside analysis is undertaken.

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## **Discrete Total Alkalinity analyses**

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Cruise Participants: Carmen Rodriguez¹and Tammy LaBerge¹

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## Introduction

We participated in the North Atlantic cruise (A22N) during the spring of 2012, which was part of the Global Ocean Repeat Hydrographic Study. The cruise was carried out from late March to the middle of April. This leg of the cruise was from the Woods Hole Oceanographic Institution, Woods Hole, MA (41.523°N; 70.672°W) to Bridgetown, Barbados (13.096°N; 59.608°W), and took place aboard the WHOI's RV Atlantis. We analyzed a total of 1589 seawater samples from 81 stations and approximately 90 bottles of Certified Reference Material. The stations occupied during the cruise are given in Table I. The major objective of this cruise was to retrace the same cruise that happened 9 years ago, and see the changes that had occurred in the carbonate system of the water. Our group was involved in the determination of total alkalinity (TA) using potentiometric techniques, and pH using spectrophotometric techniques (Hector Bustos-Serrano and Jason Waters). This report summarizes the measurements made by our TA group during the cruise.

Table I Stations Surveyed

Station	Latitude	Longitude	Depth	Distance	CumDist	MARCH
	N	W	(m)	(nm)	(nm)	
1	40.012	70.007	158	0	0	25
2	39.898	69.930	701	7.66	7.66	
3	39.858	69.933	1143	2.4	10.07	26
4	39.792	69.852	1296	5.49	15.56	
5	39.702	69.802	2092	5.87	21.43	
6	39.475	69.642	2436	15.48	36.91	
7	39.258	69.490	2696	14.79	51.7	
8	39.017	69.332	3074	16.26	67.96	
9	38.792	69.183	3269	15.18	83.14	27
10	38.558	69.027	3493	15.81	98.95	
11	38.330	68.862	3819	15.74	114.69	
12	38.090	68.700	4122	16.29	130.98	
13	37.852	68.533	4377	16.33	147.31	28
14	37.622	68.373	4619	15.75	163.06	
15	37.382	68.215	4730	16.25	179.32	
16	37.138	68.060	4896	16.37	195.69	29
17	36.658	67.742	4958	32.6	228.29	
18	36.190	67.450	4962	31.43	259.72	30
19	35.712	67.162	5087	31.93	291.66	
20	35.228	66.872	5104	32.28	323.94	
21	34.738	66.582	5208	32.68	356.62	
22	34.258	66.292	5233	32.17	388.79	31
23	33.785	65.993	5140	32.04	420.84	
24	33.358	65.597	4871	32.38	453.22	
25	32.933	65.200	4681	32.37	485.59	APRIL
26	32.648	64.937	3963	21.65	507.24	1
27	31.905	65.045	3951	44.94	552.18	
28	31.310	65.290	4682	37.83	590.01	
29	30.610	65.340	4837	42.08	632.09	2
30	29.910	65.380	4957	42.05	674.15	
31	29.210	65.430	5103	42.08	716.23	
32	28.520	65.480	5399	41.49	757.72	3
33	27.820	65.520	5276	42.06	799.78	
34	27.120	65.570	5139	42.09	841.86	
35	26.420	65.620	5097	42.09	883.95	4
36	25.720	65.660	5318	42.06	926.01	
37	25.020	65.710	5422	42.09	968.1	
38	24.320	65.750	5815	42.06	1010.16	5
39	23.620	65.800	5854	42.09	1052.25	

40	22.930	65.840	5828	41.46	1093.71	
10	22.550	05.010	5020	11.10	1000.71	
Station	Latitude	Longitude	Depth	Distance	CumDist	April
Station	N	W	(m)	(nm)	(nm)	119111
41	22.230	65.890	5739	42.09	1135.81	6
42	21.530	65.930	5445	42.06	1177.87	
43	20.830	65.980	5428	42.1	1219.97	
44	20.360	66.000	5995	28.22	1248.19	7
45	20.023	65.998	7532	20.2	1268.39	
46	19.687	65.998	7430	20	1288.39	
47	19.355	66.002	7727	19.9	1308.3	
48	19.027	66.007	3873	19.7	1328	8
49	18.978	66.003	3707	2.91	1330.91	
50	18.912	66.000	3031	4	1334.91	
51	18.837	66.002	2485	4.5	1339.41	
52	18.752	66.003	1957	5.1	1344.51	
53	18.653	66.000	1473	5.91	1350.42	
54	18.578	65.997	1059	4.5	1354.93	9
55	18.497	66.002	270	4.9	1359.83	
56	17.958	65.133	4527	59.1	1418.93	
57	17.938	65.998	442	49.39	1468.33	
58	17.733	66.000	997	12.3	1480.63	
59	17.700	66.000	1455	1	1481.63	
60	17.667	66.000	1953	1	1482.63	10
61	17.630	66.000	2485	2	1484.63	
62	17.493	66.002	3131	8.2	1492.83	
63	17.362	65.997	4591	7.9	1500.73	
64	17.068	66.473	4734	32.5	1533.23	
65	16.697	67.080	4687	41.36	1574.59	11
66	16.323	67.687	4776	41.48	1616.07	
67	15.950	68.292	4246	41.45	1657.52	
68	15.577	68.895	4003	41.42	1698.93	12
69	15.200	69.500	3901	41.67	1740.6	
70	14.668	69.598	4199	32.41	1773.01	
71	14.138	69.698	4741	32.33	1805.34	
72	13.607	69.797	4394	32.41	1837.75	13
73	13.563	69.803	3959	2.63	1840.38	
74	13.473	69.822	3476	5.51	1845.89	
75	13.342	69.845	3079	8.01	1853.9	
76	13.208	69.870	2467	8.14	1862.04	
77	13.163	69.878	2095	2.74	1864.78	
78	13.077	69.893	1466	5.27	1870.05	14
79	12.810	69.943	1028	16.27	1886.32	

80	12.678	69.968	728	8.04	1894.35	
81	12.633	69.977	210	2.74	1897.1	

#### Methods

Samples were collected at every station. A full cast consisted of 36 Niskin bottles. Depending on cast depth, the number of Niskin sampled varied. Bottles were chosen to match what DIC was sampling. After two full rinses, samples were collected in 250 mL Pyrex borosilicate bottles. A head space of  $\sim$ 5 mL was removed from the glass bottle and immediately 0.06mL of a saturated HgCl<sub>2</sub>solution was added to each sample. The samples were capped with a glass stopper in a Teflon sleeve. All samples were equilibrated at 20°C with a Thermo Scientific NESLAB7 water bath.

Dr. Dickson's CRM Batch 117 was used to determine the accuracy of the analysis.

According to the cast time and analysis capabilities, one, two or three duplicates were also analyzed. The duplicates were taken from bottom, intermediate and surface waters. Through the cruise approximately 200 duplicates were analyzed.

We used an open cell titration according to Dickson et al., (2007).

This data should be considered as preliminary since the correction for the difference between the CRMs stated and measured values has yet to be applied. In addition, the HgCl<sub>2</sub> correction has also not applied.

Titration system The titration system (see Figure 1, page 6) used to determine TA consisted of a Metrohm 765 Dosimattitrator and a Methrom electrode connected to an Agilent 34970A Data Acquisition/Switch Unit that is controlled by a personal computer developed by Dr. Andrew Dickson's group at SIO according to (Millero*et al.*, 1993). The seawater sample in the water jacketed open cell was controlled to a constant temperature of 20 0.1 C with a Neslab RTE7 constant temperature bath. The glass water jacketed open cell used is shown in Figure 2 (page 7). Figure 3 (page 8) shows the results of total alkalinity obtained during this cruise.

Samples of volume  $92.873 \pm 0.021$  ml were prepared using a volumetric pipette and a system of relay valves and air pumps, controlled by a laptop using LabVIEW 2001. The temperature of the samples at time of dispensing was taken automatically by a computer using a Measurement Specialties 4600 thermometer, to convert this volume to mass for analysis.

Samples were analyzed using an open beaker titration procedure using two thermostated beakers; one sample being titrated while the second was being prepared and equilibrating to the system temperature of 20 °C. The titration is controlled programmatically using National Instrument's Labwindows/CVI environment. After an initial aliquot of approximately 2.2 mL of standardized hydrochloric acid ( $\sim 0.1$  M HCl in  $\sim 0.6$  M NaCl solution), the sample was stirred for approximately 5 minutes to remove liberated carbon dioxide. The stir time has been minimized by bubbling air into the sample. After equilibration, 19 aliquots of 0.04 mL HCl were added. The data within the pH range of 3.5 to 3.0 were processed using a non-linear least squares fit from which the alkalinity value of the sample was calculated. This procedure was performed automatically by a laptop running LabVIEW.

*Electrodes* The electrode used to measure the emf of the sample during a titration consisted of a Metrohm glass combination electrode.

Standard acids The HCl used throughout the cruise were made, standardized, and stored in  $500 \text{ cm}^3$  glass bottles in the laboratory for use at sea. The 0.1 M HCl solutions were made from 1 M Mallinckrodt standard solutions in 0.6 M NaCl to yield an ionic strength equivalent to that of average seawater (0.7 M). The acid was standardized using a coulometric technique.

*Evaluation of the Carbonate Parameters* The total alkalinity of seawater was evaluated from the proton balance at the alkalinity equivalence point, pH<sub>equiv</sub>= 4.5, according to the exact definition of total alkalinity (Dickson, 1981)

$$TA = [HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] + [OH^-] + [HPO_4^{2-}] + 2[PO_4^{3-}] + [SiO(OH)_3^-] - [H^+] - [HSO_4^-] - [HF] - [H_3PO_4]$$
(1)

At any point of the titration, the total alkalinity of seawater can be calculated from the equation

$$(V_0 \text{ TA - VN})/(V_0 + V) = [HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] + [OH^-] + [HPO_4^{2-}] + 2[PO_4^{3-}] + [SiO(OH)_3^-] - [H^+] - [HSO_4^-] - [HF] - [H_3PO_4]$$
(2)

where  $V_0$  is the volume of the cell, N is the normality of the acid titrant, and V is the volume of acid added. In the calculation all the volumes are converted to mass using the known densities of the solutions. A computer program has been developed in Labwindows/CVI to calculate the carbonate parameters ( $pH_{SW}$ ,  $E^*$ , TA,  $TCO_2$ , and  $pK_1$ ) in seawater solutions. The program minimizes the sum of squares of residuals by adjusting the parameters  $E^*$ , TA,  $TCO_2$  and  $pK_1$ . The program is based on equation (2) and assumes that nutrients such as phosphate, silicate and ammonia are negligible. This assumption is valid only for surface waters. Neglecting the concentration of nutrients in the seawater sample does not affect the accuracy of TA, but does affect the carbonate alkalinity. The program requires as input the concentration of acid, volume of the cell, salinity, temperature, measured emf (E) and volume of HCl ( $V_{HCl}$ ). To obtain a reliable TA from a full titration at least 25 data points should be collected (9 data points between pH 3.0 to 4.5). The precision of the fit is better than 0.4  $\square$  mol kg<sup>-1</sup> when pK<sub>1</sub> is allowed to vary and 1.5  $\square$ mol kg<sup>-1</sup>when pK<sub>1</sub> is fixed.

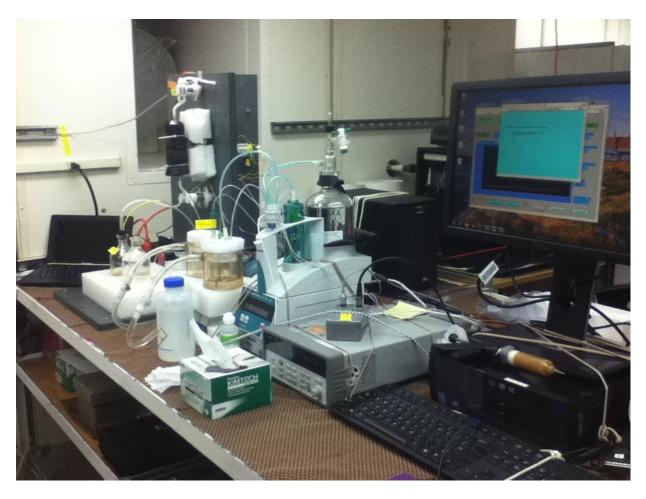


Figure 1: TA system including the Dosimat and emf Meter used during A20/22 Leg1 Cruise



Figure 2: Volume delivery system and titration cells

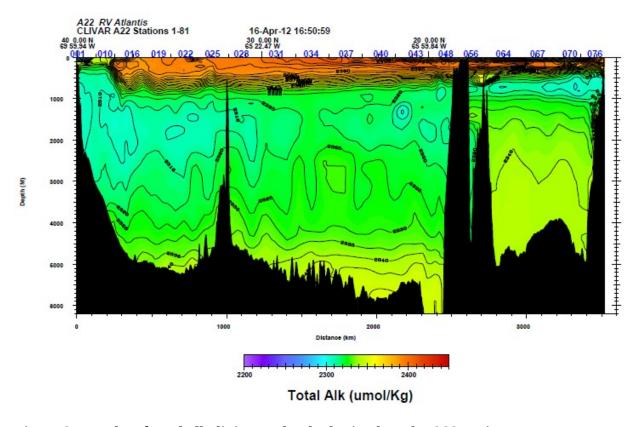


Figure 3: Results of total alkalinity vs. depth obtained on the A22 cruise.

## **Internal Consistency of Data**

The carbonate system is characterized by four parameters: total alkalinity, total carbon dioxide, partial pressure of carbon dioxide (pCO<sub>2</sub>) and pH. Knowing two of these parameters, one can calculate the other two. If more than two parameters are known, a comparison of calculated and measured values will tell if the measured value is internally consistent with the two used in the calculation. We will examine the internal consistency of our pH and TA measurements and the SOMMA values of  $TCO_2$ . The " $CO_2$ sys.bas" basic program written by Ernie Lewis and Doug Wallace and modified by Denis Pierrot to run in Excel will be used to make these calculations. We will use the carbonic acid constants of Millero*et al.*, (2006) for all calculations, as well as the constant of Dickson (1990) for bisulfate all on the seawater pH scale. We will examine an input of pH and TA to calculate  $TCO_2$ , pH and  $TCO_2$  to calculate TA and  $TCO_2$  to calculate pH.

Once the data has been proven to be accurate and precise, as well as internally consistent, a comparison of the 1997, 2003 and 2012 cruises will be made.

#### References

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- Dickson, A.G., 1990. Thermodynamics of the dissociation of boric acid in synthetic seawater from 273.15 to 318.15K, *Deep-Sea Res.*, <u>37</u>,755-766.
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## Discrete pH Analyses

PI: Dr. Frank Millero

Cruise Participants: Hector Bustos-Serrano and Jason Waters

### Sampling

Samples were collected in 250 mL borosilicate glass bottles with butyl rubber stoppers held in place using aluminum crimp caps. Each bottle was rinsed a minimum of 2 times, allowing approximately half the volume to overflow, and thermostated to 25°C before analysis. At Station 66, the sample bottles were switched to 250 mL borosilicate glass bottles with a ground glass stopper. The ground glass stopper was separated from the ground glass seal of the borosilicate bottle using a Teflon separator. Duplicate samples were taken in the 2 bottle types and agree to 0.0003 +/- 0.0010 (n=7), indicating there should be discernable offset between samples taken with the 2 bottle types. Three duplicates were collected from each station. Samples were collected from the same Niskin bottles as total alkalinity or dissolved inorganic carbon in order to completely characterize the carbon system. All data should be considered preliminary.

#### **Analysis**

pH (Î mol/kg *H2O*) on the total scale was measured using an Agilent 8453 spectrophotometer according to the methods outlined by Clayton and Byrne (1993). A Thermo NESLAB RTE-7 water bath maintained spectrophotometric cell temperature at 25.0°C. A 10cm flow through cell was filled automatically using a Kloehn 3v syringe pump. The sulfonephthalein indicator m-cresol purple (mCp) was also injected automatically by the syringe pump into the spectrophotometric cells, and the absorbance of light was measured at two different wavelengths (434 nm, 578 nm). The baseline was subtracted from these wavelengths, determined by averaging the absorbances from 730-735nm. The samples were run with the tungsten lamp only. The blank spectrum and absorbance spectrum were measured 6 times in rapid succession and then averaged. The ratios of absorbances at the different wavelengths were input and used to calculate pH on the total scales, incorporating temperature and salinity into the equations. Salinity data were obtained from the conductivity sensor on the CTD. These data were later corroborated by shipboard measurements. Temperature of the samples was measured immediately after spectrophotometric measurements using a YSI 4600 thermometer.

## Reagents

The mCp indicator dye made to a concentration of 2.0mM in 100ml batches as needed. A total of 3 batches were used during the cruise. The pH of the first two batches were adjusted to  $\sim$ 7.9 (NBS) by the addition of  $\sim$ 0.1N HCl. The indicator was provided by Dr. Robert Byrne of the University of South Florida, and was purified using HPLC (Liu et al., 2007; Yao et al., 2011).

#### Standardization

The precision of the data can be accessed from measurements of duplicate samples, certified reference material

(CRM) Batch 117 (Dr. Andrew Dickson, UCSD), and TRIS buffer Batch 10 (Dr. Andrew Dickson, UCSD). CRMs were measured approximately every third station. There were 12 bottles of TRIS buffer measured periodically throughout the cruise.

#### **Data Processing**

Addition of the indicator affects the pH of the sample and the degree to which pH is affected is a function of the differences between the pH of the seawater and indicator. Therefore, a correction is applied for each batch of dye. To determine this correction 2 samples from each station where measured twice. Once with a normal amount of indicator and once with double the amount of the indicator. The  $\Delta R/\Delta A_{\rm iso}$  versus the average of the ratio (R) is then plotted and fitted with a linear equation; where  $A_{\rm iso}$  is the absorbance as the isosbestic point (488nm). From this fitted equation the slope and intercept (b and a respectively) are determined by:

$$\Delta R/\Delta A_{iso} = bR + a \tag{1}$$

From this the corrected ratio (R') can be determined by:

$$R' = R - A_{iso}(bR + a)$$
 (2)

Preliminary data has not been corrected for the perturbation.

#### **Problems**

Very few problems occurred during the cruise. During the first 10 stations duplicates were very poor due to bubbles in the cell. Allowing the cell to soak in reagent grade water between stations helped reduce bubble formation.

#### References

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## **Dissolved Organic Carbon and Total Dissolved Nitrogen**

PI: Dennis Hansell

Participants: Silvia Gremes-Cordero and Alysha Coppola

The goal of the group is to obtain Dissolved Organic Carbon (DOC) and Total Dissolved Nitrogen (TDN) along the Atlantic A22 line, in order to better understand the cycle of carbon in the ocean, both in time and spatial scales.

DOC samples were obtained approximately every other station from station 5. Depending on the station 20-36 Niskin bottles were sampled (1305 samples). At the top 250m of the water column, inline filtering was performed, using GF/F glass fiber filters that were previously cleaned with 10% HCl solution and rinsed with the Mili-Q water available on board. Filtering is conducted to avoid the inclusion of particles (present in the upper 250 m of the water column) in the samples. High density polyethylene 60 ml bottles were rinsed 3 times before the sampling, and posteriorly frozen at -20 C° in the walk-in freezer. Frozen samples will be shipping back to University of Miami at the end of the cruises

TDN samples will be analyzed for the upper 200 m from the same samples.

fCO<sub>2</sub> (underway)

Robert Castle, AOML PI: Rik Wanninkhof, AOML

An automated underway fCO<sub>2</sub> measurement system was installed in the Hydro Lab of the R/V Atlantis for the A22 cruise. The system is a model 8050 built by General Oceanics (GO). The final data will be available on AOML's web page (<a href="http://www.aoml.noaa.gov/ocd/gcc">http://www.aoml.noaa.gov/ocd/gcc</a>).

Early instrument designs are discussed in Wanninkhof and Thoning (1993)) and in Feely et al. (1998). The current design as well as the data processing procedure is detailed in Pierrot et al. (2009).

Seawater continuously flows through a closed, water-jacketed equilibration chamber at approximately 1 liter/minute. A spiral nozzle creates a conical spray that enhances the gas exchange with the enclosed gaseous headspace. During "water" analyses this overlying headspace is pushed through an infrared analyzer (Licor model 6262) and returned to the equilibrator. During air analyses, outside air is pulled from an inlet on the forward mast and pushed through the analyzer. The pressure and temperature inside the equilibrator are constantly being measured. With knowledge of the seasurface temperature and salinity, along with all the parameters measured by the system, one can calculate the fugacity of CO<sub>2</sub> in the seawater and the atmosphere above it.

To ensure the accuracy of analyzer output, four standard gases are analyzed approximately every 3.25 hours. These standards (serial numbers JB03284 [287.45 ppm], JA02646 [463.00 ppm], JB02140 [356.84 ppm], and JB03268 [384.14 ppm]) were purchased from Scott-Marrin and calibrated using gases from NOAA/ESRL in Boulder, CO and primary reference standards from the laboratory of Dr. Charles Keeling, which are directly traceable to the WMO scale. In addition, approximately every 26 hours, the zero and span of the Licor are set using ultrapure (CO<sub>2</sub>-free) air for the zero and the 463 ppm standard for the span. After the standards five air analyses and 66 water analyses are done. With continuous operation, the system provides approximately 460 water analyses per day. The system operated continuously during the cruise except for a period on April 4 from 05:23 to 17:23 when the water flow failed. During this time only air measurements are good. Preliminary examinations of the data show good analyses but final fugacity values will require some time due to the volume of the data.

#### References:

Wanninkhof, R., and K. Thoning (1993), "Measurement of fugacity of CO2 in surface water using continuous and discrete sampling methods." Mar. Chem., 44, 189-205.

Feely, R.A., R. Wanninkhof, H.B. Milburn, C.E. Cosca, M. Stapp, and P.P. Murphy (1998), "A new automated underway system for making high precision pCO2 measurements onboard research ships." Analytica Chim. Acta, 377, 185-191.

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for autonomous underway pCO2 measuring systems and data reduction routines." Deep -Sea Res II, 56, 512-522.

## <sup>13</sup>C/<sup>14</sup>C – DIC Isotopes

PI: Ann McNichol, Woods Hole Oceanographic Institution Robert Key, Princeton University

Cruise Participant: Silvia Gremes-Cordero, RSMAS, University of Miami

<sup>13</sup>C/<sup>14</sup>C water samples were drawn routinely from the Rosette casts, every 5 stations approximately. In total, 12 stations were sampled (117 samples) and duplicates were obtained in four different stations (26, 71, 73, 75). In some of the sampled stations, 16 Niskin were sampled in the upper 1000m, and in the rest 32 bottles were sampled, in the lower and upper 1000m.

Samples were collected in 500 ml glass stoppered bottles. First, the stopper was removed from the dry flask and placed aside. Using silicone tubing, the flasks were rinsed well with the water from the Niskin bottle. While keeping the tubing near the bottom of the flask, the flask was filled and allowed to overflow about half its volume. Once the sample was taken, a small amount ( $\sim$ 30 cc) of water was removed to create a headspace and  $\sim$ 1.2  $\mu$ l of 50% saturated mercuric chloride solution was added.

After all samples were collected from a station, the neck of each flask was carefully dried using Kimwipes. The stopper, previously lubricated with Apiezon grease, was inserted into the bottle. The stopper was examined to insure that the grease formed a smooth and continuous film between the flask and bottle. A rubber band was wrapped over the bottle to secure the stopper.

The samples will be analyzed at the National Ocean Sciences AMS lab in Woods Hole, MA using published techniques.

#### Reference:

McNichol, A., Quay. P. D., Gagnon, A. R., Burton, J. R., "Collection and Measurement of Carbon Isotopes in Seawater DIC", *WHP Operations and Methods-March 2009*.

# Radiocarbon ( $\Delta^{14}$ C) measurements of Marine Dissolved Organic Carbon and Black Carbon

PI: Ellen R. M. Druffel, University of California Irvine Cruise Participant: Alysha Coppola, University of California Irvine, graduate student

### **Project Goal**

DOC  $\Delta^{14}$ C profiles in the North Atlantic will establish a better understanding of the timescale of DOC cycling. Black carbon  $\Delta^{14}$ C measurements will quantify the concentration of BC in the surface and deep Atlantic Ocean.

## **Preparations**

Two DOC  $\Delta^{14}$ C profiles were collected at 14 depths along the cruise transit line. Samples depths coincided with Alkalinity, DIC  $^{14}$ C (Ann McNichol) and [DOC] samples taken from the same niskins. At depths above 400m, water was filtered using a custom made stainless steel filter holder.

Dissolved Organic Carbon samples were collected using 1-L amber boston round bottom bottles with Teflon lined caps. The glass bottles were previously cleaned with soap and water, soaked in 10% HCl, rinsed with DI water, then baked at 550°C for two hours. The caps were washed in soap and water, flushed with 10% HCl, rinsed with DI, then airdried. The stainless steel filter holder was cleaned with soap and water, flushed with 10% HCl, rinsed with DIC, the air-dried. Filters were baked at 550°C for two hours, and placed in a pyrex petri dish covered in baked out aluminum foil to keep clean.

Water samples for Black Carbon (BC) analysis were collected in 1 gallon glass jugs. The jugs, filters, Teflon, and caps used were cleaned in the same manner as described above for DOC preparations. Samples in the mixed layer and at depth were collected.

No samples were processed aboard the Atlantis. All samples were frozen at -20°C in freezers, which were then sent back to the Druffel Lab.

#### **DOC** and **BC** $\Delta^{14}$ **C** methods:

In the Druffel Lab at UC Irvine, bulk DOC will be oxidized using a 1220-W ultra violet Hg-arc light source modified for a 900 ml volume and lower blank technique (Beaupre et al., 2007). Following the production of  $CO_2$ , aliquots are taken for  $\Delta^{13}C$  and  $\Delta^{14}C$  analysis.

Black carbon will be concentrated from water samples using a modified solid phase extraction (de Jesus, 2008). The Benzene Polycarboxlic Acid (BPCA) method is used to isolate BC in marine DOC (Ziolkwski and Druffel, 2009; Brodowski et al., 2005). Methylated BPCAs will be quantified and isolated using our Hewlett Packard 6890 PCGC with FID.

Radiocarbon measurements for DOC and BC samples are reported as 14C in per mil (Stuiver and Polach, 1977) and are corrected for extraneous carbon introduced during sample processing. Stable carbon isotope measurements will be performed on splits of the  $CO_2$  at the UCI Keck Carbon Cycle AMS Laboratory. Carbon dioxide will be quantified manometrically, reduced to graphite using iron powder as a catalyst with  $H_2$  as a reductant.

#### References

Beaupre, S.R., Druffel, E.R.M. and Griffin, S., 2007. A low blank photochemical extraction system for concentration and isotopic analyses of marine dissolved organic carbon. Limnology and Oceanography: Methods, 5:174-184.

Brodowski, A., Rodionov, A., Haumaier, L., Gaser, B. and Amelung, W., 2005. Revised black carbon assessment using benzene polycarboxylic acids. Organic Geochemistry. 1299-1300 pp.

De Jesus, Roman (2008), Natural abundance radiocarbon studies of dissolved organic carbon (DOC) in the marine environment. Doctoral Thesis, U.C. San Diego, pp. 83

Ziolkowski, L., 2009. Radiocarbon of Black Carbon in Marine Dissolved Organic Carbon. Doctoral Thesis, U.C. Irvine, Irvine, 117 pp.

Ziolkowski, L., Druffel, E. 2010. Quantification of Extraneous Carbon during Compound Specific Radiocarbon Analysis of Black Carbon. Anal. Chem, 81, 10158-10161.

## **Summary of Transmissometer Sampling Procedure**

PI: W.D. Gardner, Texas A&M Department of Oceanography
Mary Jo Richardson, Texas A&M Department of Oceanography
Cruise Participants: Robert Palomares, Courtney Schatzman, Kristin Sanborn SIO/STS

## TRANSMISSOMETER:

Instrument: WetLabs C-Star Transmissometer 327DR

#### AIR CALIBRATION:

- Calibrated the transmissometer in the lab at beginning and end of the cruise with a pigtail cable attachment to CTD.
- Wash and dried the windows with Kimwipes and distilled water.
- Compare the output voltage with the Factory Calibration data.
- Recorded the final values for unblocked and blocked voltages on the TRANSMISSOMETER CALIBRATION/CAST LOG. In most cases recorded the approximate air temperature as well.

#### **OPERATION:**

- windows. Block the light path in the center of the instrument with your fingers or a paper towel and measure the output voltage. Took reading of the output (voltage or counts) through the CTD and record the value on the "TRANSMISSOMETER CALIBRATION/CAST LOG". If the new value is substantially different, wash the windows with slightly soapy water or alcohol and rinsed with fresh water, then wipe dry. Checked output voltage again for stable readings then ceased drying the transmissometer windows; typically employing one or two, wipes with Kimwipes, of each window. This was done before cast, at the beginning and end of the cruise as well as every 20 casts. Temperature disequilibrium and condensation on windows will cause erratic readings.
- Washed the windows before every cast. Rinsed both windows with a distilled water bottle that contains 2-3 drops of liquid soap. This was the last thing before the CTD went in the water.
- Rinse instrument with fresh water at end of cruise.

Date	Blocked Value Vd	Unblocked Value Vair	Air T (°C)	Remarks
11/30/11	0.059	4.752	21.5	
		4.660	21.3	Factory Calibration
2/23/11	0.056	4.707		
3/12/11	0.056	4.673	5.8	
3/22/11	0.056	4.675	6.0	
4/04/11	0.056	4.652	5.8	
4/14/11	0.057	4.666	7.2	
4/19/11	0.059	4.665	8.3	
4/20/11	0.059	4.690	20	

## Sea surface skin temperature group

PI: Peter Minnett, University of Miami, RSMAS

Cruise Participant: Silvia Gremes Cordero, University of Miami, RSMAS

Sea surface temperature, cloud coverage and water vapor content in the air column were obtained continuously with the instrumentation described below.

The data were regularly downloaded into an external hard drive every 2-3 days. Sporadic shutdown of the instruments were related to solvable technical problems. Gaps in data recording never exceeded a 2 day period during the whole A22 leg.

#### M-AERI

Our main piece of equipment is the M-AERI (Marine-Atmosphere Emitted Radiance Interferometer – see Minnett et al., 2001). It consists in 2 main components: an external unit that is mounted on the deck of the ship, and an electronics rack that is installed inside the vessel (in the Main Lab, in our case), the two being linked by an umbilical bundle of about 5 cm diameter and 60 m in length. The external unit comprises the Fourier Transform infrared (FTIR) interferometer assembly, is a bulky piece of equipment which sits on a table that mounts on the railing where it can view the surface of the sea ahead of the bow wave, at an angle of about 55° to the vertical (Figure 1). Maintenance of the equipment requires a daily cleaning of the mirror with O-water, acetone and alcohol.



Figure 1. The M-AERI mounted on the R/V Atlantis

The system operates at an output rate of 1 complex spectrum (interferogram) per second. It runs continuously under computer control, except for a brief period beginning at 0:00 UTC, when the computer reboots and start the new files.

#### **Microwave Radiometer**

We set up a Microwave Radiometer where it has a clear view from zenith to the horizon. It measures atmospheric water content. The instrument mounts conveniently on the stand shown in the photo (Figure 2), but can be adapted to mount without the stand if there is a more suitable location. Power for this instrument is provided via cables into the Lab. Power requirements for the radiometer are 120 V A/C, 1 amp. The instrument also has an air blower fan which requires 120 V A/C, 1000 watts, 4 amps.

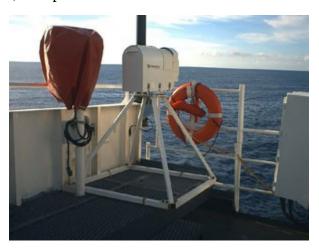


Figure 2. Microwave radiometer on flying bridge of the USCGC Polar Sea.

## The sky camera

The sky camera system is mounted in an unobstructed area for the best possible view of the dome of the sky, such as on the bridge top (Figure 3). All of the mounting structure is provided by us, there are no additional requirements from the ship. Power is supplied from to the Lab where the images are acquired by a laptop computer 120 V A/C, 50 watts.

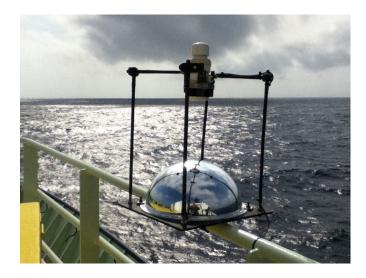


Figure 3. The sky camera mounted on the R/V Atlantis

#### Students at Sea

The NSF physical oceanography grant for the US Global Ocean Carbon and Repeat Hydrography Program supports participation of physical oceanography and CFC students on program cruises. Below are statements from the student participants on A22 (Atlantis).

*Isabela LeBras (Woods Hole Oceanographic Institution)* 

II came on this cruise to get a taste of observational work in oceanography. I wanted to get a better idea of what it entailed, what life at sea was like, and if I was well suited to it. I was working with the data from a previous occupation and it seemed like a good way to learn about the ocean from the source. Its Caribbean destination was certainly also a draw.

I didn't have very clear expectations, and at first I was a little surprised at how tedious many of my tasks were. I am used to being challenged intellectually as a student, but here were a new set of challenges. I gained a new appreciation for the hard work that goes into the data I use. As time wore on, I adapted to the routine and felt camaraderie develop with my shipmates. I also learned about the ocean in a way that I will not likely forget. Staring at profiles for long periods of time and toying with interpretations certainly builds good intuition. As the profiles progressed into sections, the development and advection of water masses made more sense as well. And there is no better way to appreciate the strength of the Gulf Stream and the depth of the Puerto Rico Trench than to experience them first hand.

Sam Billheimer (Unversity of California, San Diego, Scripps Institution of Oceanography)

The data from this cruise are interesting and relevant to my research, but this is certainly unnecessary for an engaging learning experience, even if one's interests are far from understanding changes in large scale physical oceanographic properties and the carbon system. In the classroom, or when reading Lynne Talley's superbly well written and informative textbook, Descriptive Physical Oceanography, it is easy to overlook the thought and hard work that go into the planning and execution of a hydrographic section. Although the work is extremely monotonous and the at-sea time is long, the experience is rewarding because you get hands-on experience with operating the instrumentation and get to learn first-hand the importance of a well thought out sampling plan for representing the extraordinarily vast ocean at relatively few locations. Working on a project using data from the cruise was an excellent way to motivate myself to understand the stream of important processes that data must go through, from birth at the CTD or niskin bottle to a state of maturity as a carefully QC'd array within a .mat or netcdf file. It's important to know that the subtleties of this process have the potential to significantly affect the overall outcome of the analysis.

I would especially like to thank Ruth Curry for welcoming me on board, taking the time to give helpful, thorough explanations of the hydrographic results, and for her encouragement and advice on my research project. I would also like to thank my adviser, Lynne Talley, for suggesting my participation. Finally, I'd like to acknowledge the NSF Ocean Sciences grant for the US Global Ocean Carbon and Repeat Hydrography Program for supporting my participation.

## Sam Potter (Princeton University)

The cruise was a great experience. As someone who works with models the chance to see how oceanographic data is collected was very rewarding. Before the cruise I had no concept of the amount of effort required to obtain high quality data: from physical samples to calibrate the CTD instruments to constant water sample processing by multiple teams of scientists to the poring over of data by individuals to search for errors generated by humans, instruments and random chance. I enjoyed making a small contribution to the massive team effort of A22. There are many difficulties I now realize oceanographic research cruises must constantly overcome: the twelve hour shifts and exhaustion, constant mechanical and instrumental failures, living on a boat for weeks (or months!) at a time, poor weather and seasickness (not fun), and both the boredom of watching a rosette fall to the ocean bottom for hours at a time with the very quick segue to the stress of needing to finish sampling one station so as to be able to jump to the next as quickly as possible.

In addition to the data collection side of things I also learned a lot of oceanography. As the cruise progressed we were able to use salinity, oxygen, and CFCs (among other variables) to identify water masses from the Labrador Sea, the Arctic Ocean, and the Antarctic Ocean. The collected data was also able to show strong eddy activity, and it is likely that we found evidence of a still coherent sub-thermocline eddy that had traveled south from Newfoundland all the way to a latitude south of Florida. As a side project I looked over the preliminary current velocity data from the acoustic doppler profiler (ADCP) from both the ship (SADCP) and the instrument package (LADCP). Using this data I was able to pick out the Gulf Stream and below that the deep western boundary current carrying cold water from the far north to the south. I was able to see the southward transport of NADW as far south as Puerto Rico. Boundary currents along the northern edge of Puerto Rico and South America were also evident, carrying warm waters to the north and west. A significant portion of the velocity data seemed to be dominated by eddy activity.

Andrew Reed (University of Washington)
Graduate Student, Chemical Oceanography
School of Oceanography

The primary purpose of participating on the CLIVAR A22 repeat hydrographic section was to gain ship experience in sampling CFCs. An added goal was to become further integrated into the relatively small CFC-tracer community within oceanography, and learn the limitations of the different machines utilized in the field. Since each CFC machine, while using the same basic principals to isolate and analyze CFCs and SF6, are constructed differently, they reflect the inherent measurement errors and biases due to different methods of trapping and series of columns and pre-columns. These biases are consequently reflected in the data analysis and conclusions that can be drawn from the observations, and thus represent an important constraint on the application of the tracer data.

Though the CFC data obtained on this hydrographic section will likely not be utilized by me in my graduate studies, gaining the experience of CFC analysis outside of the laboratory will prepare me for future cruises where I will be collecting data relevant to my area of study, the Southern Ocean Meridional Overturning. Additionally, the draw of the Caribbean and the final

port-of-call in Barbados were an additional incentive for participation. Participation on the CLIVAR A22 line also provided me an intellectual shift from the office, data analysis, and my Master's defense work, to the more adventuresome and exciting observational side of the field.

## **CCHDO Data Processing Notes**

	Contact	Data Type	Action	Summary			
2012-04-19	Kristin Sanborn	BTL/SUM	Submitted	PRELIMINARY, NOT to go online			
	Some bottle data parameters are considered preliminary and should be resolved by the on shore						
	labs. Submission of a22_hy1.csv, a22.sea, a22.sum and a22_33AT20120324_ct1.zip and Cruise						
	Report will be sul	Report will be submitted in 5 different submission sessions.					
2012-04-30	Kristin Sanborn	HYD/SEA/SUM	Submitted	Preliminary			
	Data should be la	beled as Preliminary	until all Project PI's	inform you otherwise.			
2012-04-30	Carolina Berys	HYD/SEA/SUM	Website Updated	Available under 'Files as received'			
	File a22_hy1.csv	containing BTL data	, submitted by Kristi	in Sanborn on 2012-04-30, available			
	under 'Files as rec	eived', unprocessed	by CCHDO.				
	File a22.sum containing WOCE SUM file, submitted by Kristin Sanborn on 2012-04-30, available under 'Files as received', unprocessed by CCHDO.						
		•	_	ristin Sanborn on 2012-04-30, available			
2012-04-30		•	_	ristin Sanborn on 2012-04-30, available to go online			
2012-04-30	under 'Files as rec	ceived', unprocessed CrsRpt	by CCHDO.				
2012-04-30	under 'Files as rec Kristin Sanborn	ceived', unprocessed CrsRpt	by CCHDO.				
	under 'Files as rec <i>Kristin Sanborn</i> prelim., pdf & txt	ceived', unprocessed CrsRpt formats,	by CCHDO. Submitted	to go online			
2012-04-30	under 'Files as rec Kristin Sanborn prelim., pdf & txt Carolina Berys	ceived', unprocessed CrsRpt formats, CrsRpt	by CCHDO. Submitted Website Updated	to go online  Available under 'Files as received'			
2012-04-30 2012-06-26	under 'Files as rec Kristin Sanborn prelim., pdf & txt Carolina Berys M. Johnson	ceived', unprocessed CrsRpt formats, CrsRpt CrsRpt CrsRpt Crs Rpt	by CCHDO. Submitted Website Updated Submitted	to go online  Available under 'Files as received'  Updates 4/30/12 submission			
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