

preliminary data report  
may 4,1995

## **A. Cruise Narrative**

### **A.1. Highlights**

A.1.a WOCE designation: AR7W

A.1.b EXPOCODE: 18DA90012\_1

A.1.c Chief Scientists: John Lazier  
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A.1.d Ship: CSS Dawson

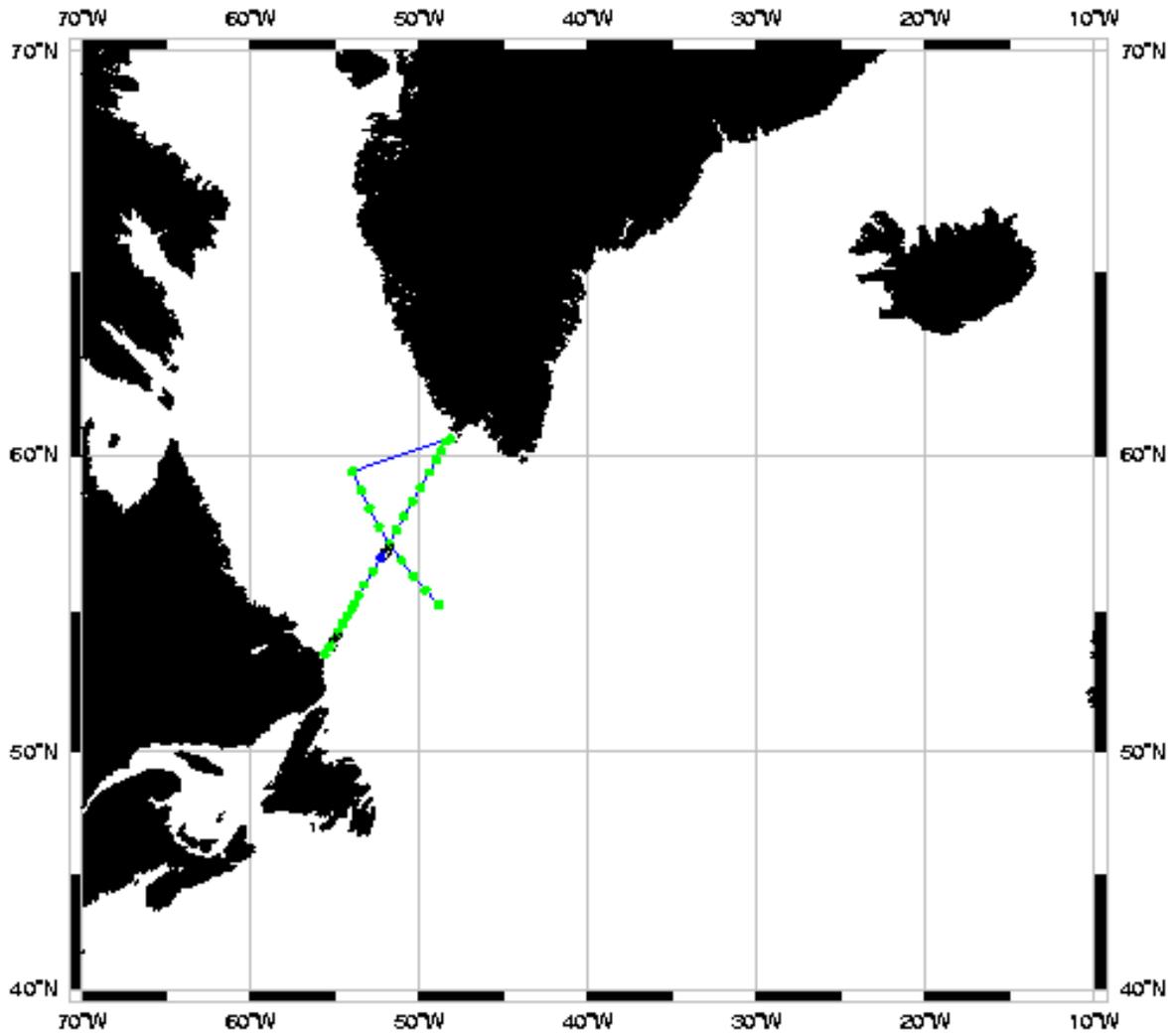
A.1.e Ports of Call:

A.1.f Cruise Dates: July 2 - 9, 1990

### **A.2 Cruise Summary**

A.2.a Geographic Boundaries

**Station locations for AR07WA : LAZIER**



A.2.b Total number of stations occupied

A.2.c Floats and drifters deployed

A.2.d Moorings deployed or recovered

### A.3 List of Principal Investigators

Table 2: List of Institutions

Abbreviation	Institution
BIO	Bedford Institute of Oceanography P.O. Box 1006 Dartmouth, N.S. Canada B2Y 4A2
BDR	BDR Research P.O. Box 652, Station M Halifax, N.S. Canada B3J 2T3

### A.4 Scientific Programme and Methods

The purpose of this cruise was to occupy the WOCE AR7/W repeat section across the Labrador Sea. This section has been selected for repeat observations because it is at or near the sources of three of the major water masses of the North Atlantic Ocean; the Labrador Sea Intermediate Water, the North Atlantic Deep Water and the Denmark Strait Overflow Water. All these water masses contain significant fractions of Arctic water which enters the North Atlantic principally over the sills in Davis Strait and between Greenland and Scotland. The characteristics and/or quantities of these overflowing waters vary over time because of changing meteorological and oceanographic conditions and these variations are reflected in the properties of the northern water masses.

Some significant variations have already been observed. For example, from 1967 to 1971 the summer-time salinity of the near surface water in the central Labrador Sea decreased by  $\sim 0.6$  ( $\sim 3$  times the annual range) because of an unusually large flow of fresh water out of the arctic. Over the intervening years this lower salinity water has mixed down to  $\sim 2000$  m via deep convection and lowered the salinity of the Labrador Sea Intermediate Water by  $\sim 0.07$ . As the density of the water remains roughly constant the drop in salinity has been accompanied by a drop in temperature of  $\sim 0.40^\circ\text{C}$ . The temperature and salinity of the Denmark Strait Overflow Water have also been observed to change significantly over the past 25 years.

By observing the properties of the three main water masses in the Labrador Sea once a year throughout the five year WOCE observing period we hope first to specify anomalous properties before they are advected into the main body of the Atlantic Ocean and second to identify, where possible, correlations between anomalous properties and changes in the meteorological/oceanographic conditions.

The first 9 stations constitute a short line up the middle of the Labrador Sea to help us position the WOCE AR7/W line (stations 10 to 31) and to get the instruments and staff in top working condition. One of the main criteria for the position of the line was that it pass through the slow cyclonic gyre which dominates the circulation in the central Labrador Sea. This gyre contains the source waters of the Labrador Sea Intermediate Water. The line was also placed to pass across Hamilton Bank on the southern Labrador shelf where a mooring programme has been conducted for a number of years.

There was a decrease in the later deep stations in the number of oxygen samples due to an unfortunate lack of the required chemicals.

Over the Greenland and Labrador shelves, sub-zero water of ~33 salinity flows in the West Greenland and Labrador Currents. Over the Greenland slope, indicated by the 40C isotherm and 34.90 salinity contours at 200-400 m, is a warm-saline remnant of the Irminger Current which becomes part of the East Greenland Current before it rounds Cape Farewell to become the West Greenland Current. In the central part of the section from roughly 200 m to 2000 m lies the Labrador Sea Intermediate Water obviously very homogeneous in its properties staying for the most part between 3.0 and 3.20 C and between 34.82 and 34.84 salinity. Below 2000 m to about 3200 m is the North Atlantic Deep Water identified by a salinity maximum and below, next to the bottom at a salinity of <34.90 is the Denmark Strait Overflow Water.

Preliminary comparisons with reversing thermometers indicate the CTD measured temperatures to within +/-0.005. Comparisons with salinity samples suggest the CTD values are low by ~0.005 from 0-2000m. Between 2000 and 4000 m there is a linear decrease such that the CTD measures low by 0.012 at 4000 m.

Computer Report (by Paul Dunphy) The MicroVAX II system performed well on this cruise. Loran C navigation data was logged non-stop throughout the cruise. There was one 20 minute period where we experienced several power failures and a small portion of this navigation data was lost. These data are not essential to the program and no attempt was made to retrieve it. In the past we have had no success recovering such data in files left open due to power loss.

Thirty-one CTD stations were logged successfully. We used the 1990 version of the PIPE processing software to do both real time and post acquisition analysis. Minor modifications were made to the directive files to tailor them to the scientific program. In addition to the usual PIPES (real time, plotting and processing), two other plotting PIPES were added for each down cast. This made a total of two logging processes and six analysis PIPES running at once. During this time other tasks such as editing and backing up data files were extremely slow. We attributed the degradation in speed to the smaller memory size on the DAWSON system (7 Mb).

Between stations we processed and plotted the CTD data a number of times using various primitive combinations. No errors were found.

The only serious concern was the performance of the TK-50 tape drive. Soon into the cruise it began reporting that it was losing the position of the tape. After several days of sporadic problems, it failed completely and would not mount or initialize tapes. Re-booting did not clear the problem. I considered reinstalling the operating system but it was on a TK-50 tape. I could not tell if it was a software or hardware problem.

Account and data backups were made on using the EXABYTE tape system. Both the EXABYTE and external disk performed flawlessly.

In summary, the computer presented few problems during the cruise. Both watch keepers had substantial experience both with the system and the CTD operation and this was a major factor in previous years, thanks to John O'Neill of the software shop for putting in the extra effort prior to our sailing.

A.5 Major Problems and Goals Not Achieved

A.6 Other Incidents of Note

A.7 List of Cruise Participants

Table 3: list of Cruise Participants

<b>Name</b>	<b>Responsibility</b>	<b>Institution*</b>
John Lazier	Sr. Scientist	BIO
Rick Boyce	Oxygens	BIO
Bruce Carson	CTD/Rosette	BIO
Paul Dunphy	Computer/Data	BIO
Bob Gershey	CFC & CCl4	BDR Research
Jennifer Hackett	Computer/Data	BIO
Mike Hingston	CFC	BDR Research
Marion Smith	Computer/Data	BIO
Frank Zemlyak	CFC & CO2	BIO

\*See Table 2 for list of Institutions

## **B. Underway Measurements**

B.1 Navigation and bathymetry

B.2 Acoustic Doppler Current Profiler (ADCP)

B.3 Thermosalinograph and underway dissolved oxygen, fluorometer, etc

B.4 XBT and XCTD

B.5 Meteorological observations

B.6 Atmospheric chemistry

## C. Hydrographic Measurements

### C.1 Measurements of Halocarbons and Total Inorganic Carbon (by F. Zemlyak, R.M. Gershey and M.P. Hingston)

#### Objectives

- (1) To test new instrumentation for the measurement of various halocarbons in sea water by a purge-and-trap gas chromatographic method.
- (2) To test a coulometric titrator for the measurement of total inorganic carbon in sea water.
- (3) To make measurements of the above chemical species in water samples collected from the Labrador Sea.

#### Background

The instrumentation mentioned above has been developed at the marine chemistry division of the Bedford Institute of Oceanography under a PERD funded program managed by P.Jones. The main objective of this program is to develop approaches to model the rate of transport of carbon dioxide gas from the atmosphere to the deep ocean. The flux of atmospheric CO<sub>2</sub> to the ocean can be estimated from measurements of alkalinity, total CO<sub>2</sub>, various transient tracers and a knowledge of the large scale convective transport of surface water to the deep ocean.

The first phase of this project has largely been concerned with the design and construction of instruments to measure these tracers and total inorganic carbon in sea water. The halocarbon system is a modification of a system used previously at BIO. The most important improvement in the new design is the capability to measure a larger suite of compounds including the chlorofluorocarbons (CFC-12, CFC-11, CFC-113), 1,1,1-trichloroethane and carbon-tetrachloride. In addition to these man-made compounds, the system may also be able to measure other volatile halocarbons that are produced by organisms in seawater, such as bromoform, methyl bromide, methyl iodide and other halogenated species.

The method used for the determination of total carbonate involves acidification of the sample with phosphoric acid, purging the evolved CO<sub>2</sub> from the sample with a stream of nitrogen and detection of the same with a coulometric detector. For the purposes of modelling the rate of CO<sub>2</sub> transport, total inorganic carbon must be measured with a precision of 1-2 parts per thousand. An automated system was tested on previous cruises and found to produce data with inadequate precision. This instrument was modified and brought on the present cruise for further testing.

## Work Done

Halocarbons: This cruise provided the first opportunity to test this newly developed method at sea. Several days were required to make the instrument operational and to purge the system of contamination. One of two chromatographic columns could not be adequately cleaned and was removed from the system. As a result, the ability to separate and measure CFC-12 was lost. However, the system as operated during the cruise was able to determine the concentrations of CFC-11, CFC-113, and carbon tetrachloride (CCl<sub>4</sub>). Water samples were taken from seventeen stations and depth profiles of the three compounds mentioned above were produced. In addition to these identified peaks, chromatograms of the sea water samples showed eight additional well-resolved peaks. Work will be done in the laboratory to identify these compounds. Likely candidates are 1,1,1-trichloroethane, and the bromine and iodine-containing compounds that are produced by algae.

Total inorganic carbon: At each station, water samples were taken for total inorganic carbon analysis from the same bottles as were the halocarbon samples. The instrument did not, however, produce results that were of consistently high quality. Two aspects of the system were found to be the major contributors to this problem. A leaking rotary valve contaminated samples with extraneous carbon dioxide and prevented accurate standardization. Secondly, the performance of the coulometer's titration cell appeared to degrade prematurely during use, apparently the result of interfering compounds entering through the gas stream.

Summary A new halocarbon measurement system was successfully setup and operated during the cruise. Profiles of CFC-11, CFC-113 and CCl<sub>4</sub> were obtained. These are the first measurements of CCl<sub>4</sub> profiles at sea by a purge-and-trap method. Testing of the automated system for the determination of total inorganic carbon revealed that data with adequate precision could be attained, but that this was not realized on a routine basis. Several problems with the instrument were identified as a result of our tests.

C.2 Oxygen Titrations (by Rick Boyce) The titration system was set up to attempt to standardize the thiosulphate solution (titrant). It was quickly discovered that the Metrohm 655 Dosimat was inoperative in the mode used with the PC computer. It was replaced with a spare and all was fine, for the time being. The thiosulphate solution was standardized and blanks run using both distilled water and seawater giving the following results:

Standard Titration Volumes	Blank Titration Volumes
1.767	0.008
1.766	0.013
1.769	0.012
1.761	0.010

All looked in readiness and the samples 73201 - 73220 from CTD #1 were sigma-t vs dissolved oxygen curve quite well.

During the next few days samples 73221 - 73340 from stations 2-6 were offset with respect to the historic curve. When the thiosulphate and blanks were rechecked, it was discovered that the standard had changed from an average of 1.766 to 1.880 (weaker). The blanks were OK. Recalculating the oxygens with this new value appeared to remove the offset for stations 2 - 6 but imposed an offset for station 1, which would be expected since station 1 looked OK with the original value for the standardization of the thiosulphate.

For samples 73341 - 73343, the PC 800 Colorimeter could not be adjusted Colorimeter had a LED segment missing which made it difficult to distinguish between the numbers 8 and 9.

For the first few stations the duplicates were quite good but afterwards they tended to get worse. At sample 73382, it was noticed that the piston assembly in the Dosimat had been leaking. It was changed and the system once again appeared to work properly, as did the duplicates.

At sample 73452, the remaining thiosulphate solution was saved and sealed in the original container. The second half of the solution was used for the remaining titrations. At this point, the standard iodate solution had been depleted making standardization of the second aliquote of thiosulphate impossible. At sample 73512, the thiosulphate solution was running low which resulted in the cutting back on the number of oxygen samples per cast. The oxygen samples for the last two stations were not run because of lack of titrant. What was left was sealed and stored to be restandardized back at BIO.

#### **D. Acknowledgements**

#### **E. References**

Unesco, 1983. International Oceanographic tables. Unesco Technical Papers in Marine Science, No. 44.

Unesco, 1991. Processing of Oceanographic Station Data, 1991. By JPOTSeditorial panel.

#### **F. WHPO Summary**

Several data files are associated with this report. They are the da9012.sum, da9012.hyd, da9012.csl and \*.wct files. The da9012.sum file contains a summary of the location, time, type of parameters sampled, and other pertinent information regarding each hydrographic station. The da9012.hyd file contains the bottle data. The \*.wct files are the ctd data for each station. The \*.wct files are zipped into one file called da9012wct.zip. The da9012.csl file is a listing of ctd and calculated values at standard levels.

The following is a description of how the standard levels and calculated values were derived for the da9012.csl file:

Salinity, Temperature and Pressure: These three values were smoothed from the individual CTD files over the N uniformly increasing pressure levels using the following binomial filter-

$$t(j) = 0.25t_i(j-1) + 0.5t_i(j) + 0.25t_i(j+1) \quad j=2 \dots N-1$$

When a pressure level is represented in the \*.csl file that is not contained within the ctd values, the value was linearly interpolated to the desired level after applying the binomial filtering.

Sigma-theta (SIG-TH: KG/M<sup>3</sup>), Sigma-2 (SIG-2: KG/M<sup>3</sup>), and Sigma-4 (SIG-4: KG/M<sup>3</sup>): These values are calculated using the practical salinity scale (PSS-78) and the international equation of state for seawater (EOS-80) as described in the Unesco publication 44 at reference pressures of the surface for SIG-TH; 2000 dbars for Sigma-2; and 4000 dbars for Sigma-4.

Gradient Potential Temperature (GRD-PT: C/DB 10<sup>-3</sup>) is calculated as the least squares slope between two levels, where the standard level is the center of the interval. The interval being the smallest of the two differences between the standard level and the two closest values. The slope is first determined using CTD temperature and then the adiabatic lapse rate is subtracted to obtain the gradient potential temperature. Equations and Fortran routines are described in Unesco publication 44.

Gradient Salinity (GRD-S: 1/DB 10<sup>-3</sup>) is calculated as the least squares slope between two levels, where the standard level is the center of the standard level and the two closest values. Equations and Fortran routines are described in Unesco publication 44.

Potential Vorticity (POT-V: 1/ms 10<sup>-11</sup>) is calculated as the vertical component ignoring contributions due to relative vorticity, i.e.  $p_v = fN^2/g$ , where f is the coriolis parameter, N is the buoyancy frequency (data expressed as radius/sec), and g is the local acceleration of gravity.

Buoyancy Frequency (B-V: cph) is calculated using the adiabatic leveling method, Fofonoff (1985) and Millard, Owens and Fofonoff (1990). Equations and Fortran routines are described in Unesco publication 44.

Potential Energy (PE: J/M<sup>2</sup>: 10<sup>-5</sup>) and Dynamic Height (DYN-HT: M) are calculated by integrating from 0 to the level of interest. Equations and Fortran routines are described in Unesco publication, Processing of Oceanographic station data.

Neutral Density (GAMMA-N: KG/M<sup>3</sup>) is calculated with the program GAMMA-N (Jackett and McDougall) version 1.3 Nov. 94.

## G. Data Quality Evaluations

DQE of CTD data for the 90012/1 1990 cruise of the r/v "Dawson", WOCE section A7W in the Northern Atlantic. Eugene Morozov Data quality of 2-db CTD temperature and salinity profiles and reference rosette samples were examined. Vertical distributions and theta-salinity curves were compared for individual stations using the data of up and down CTD casts and rosette probes. Data of several neighboring stations were compared. The data were compared with the 92/14 and 93/19 cruises of the r/v "Hudson" carried out in the same region. Questionable data in \*.hy2 file were marked in QUALT2 word. The CTD oxygen data were flagged not calibrated by originators. The latest information is that analysis is not yet received for all bottle oxygen data. The flag should be - 1. The differences between CTDOXY data and OXYGEN were so great that data need a more thorough analysis by the originators. Only minor remarks were made concerning the bottle OXYGEN data. CTDOXY data are unreasonably high and should be calibrated.

Listing of results from the comparison of salinity data. Only those stations and pressures are listed which have data remarks.

Stat.	Press.	Remarks
1	390 db	SALNTY is high 34.822 compared with upcast CTDSAL 34.815 and downcast CTDSAL 34.814 flag 4
	1960 db	SALNTY is low 34.865 compared with upcast CTDSAL 34.874 and downcast CTDSAL 34.883 flag 4
	3728 db	SALNTY is low 34.887 compared with upcast CTDSAL 34.889 and downcast CTDSAL 34.890, (this is the deepest level and there was no time lag between the bottle measurement and downcast CTD flag 3.
2	1991 db	SALNTY is low 34.902 compared with upcast CTDSAL 34.912 and downcast CTDSAL 34.910 flag 4
	3397 db	SALNTY is high 34.910 compared with upcast CTDSAL 34.904 and downcast CTDSAL 34.907 flag 3.
3	585 db	SALNTY is high 34.828 compared with upcast CTDSAL 34.819 and downcast CTDSAL 34.821 flag 4

Stat.	Press.	Remarks
3	2494 db	SALNTY is low 34.916 compared with upcast CTDSAL 34.926 and downcast CTDSAL 34.926 flag 4.
4	980 db	SALNTY is high 34.837 compared with upcast CTDSAL 34.830 and downcast CTDSAL 34.830 flag 4
	1240 db	SALNTY is high 34.834 compared with upcast CTDSAL 34.831 and downcast CTDSAL 34.828 flag 3.
11	201 db	SALNTY is low 34.391 compared with upcast CTDSAL 34.409. Downcast CTDSAL 34.192, is much lower which is probably associated with a high horizontal salinity gradient in coastal Greenland waters, flag 3 for SALNTY
	260 db	SALNTY is VERY high 34.898 compared with upcast CTDSAL 34.700 and downcast CTDSAL 34.648 no other idea but to flag both SALNTY and upcast CTDSAL bad flag 4.
13	3160 db	SALNTY is slightly low 34.881 compared with upcast CTDSAL 34.884 and downcast CTDSAL 34.885 flag 3.
14	3047 db	SALNTY is high 34.915 compared with upcast CTDSAL 34.903 and downcast CTDSAL 34.904 flag 4.
16	2777 db	SALNTY is high 34.939 compared with upcast CTDSAL 34.918 and downcast CTDSAL 34.922 flag 4.
20	3564 db	SALNTY is low 34.879 compared with upcast CTDSAL 34.883 and downcast CTDSAL 34.884 flag 3.
21	995 db	SALNTY is high 34.839 compared with upcast CTDSAL 34.827 and downcast CTDSAL 34.829 flag 4.

<b>Stat.</b>	<b>Press.</b>	<b>Remarks</b>
21	3545 db	SALNTY is low 34.878 compared with upcast CTDSAL 34.881 and downcast CTDSAL 34.881 (this is the deepest level and there was no time lag between the bottle measurement and downcast CTD, flag 3.
	24757 db	SALNTY is high 34.853 compared with upcast CTDSAL 34.834 and downcast CTDSAL 34.835 flag 4.

OXYGEN measurements from station 15, 1411 db and station 16, 506 db seem very low compared with neighboring levels and stations. There are no minimums on upcast and downcast CTDOXY measurements (though they are not calibrated). I consider these data questionable although the whole data set is not ready yet.