A. Cruise Narrative: A05

A.1. Highlights

WHP Cruise Summary Information

Instructions: Click on headings below to locate primary reference or use navigation tools above. (Shaded headings were either not relevant to this cruise or not available when this report was assembled)

1.1.2. Cruise summary

Cruise track is shown in figure 1. Situation and date of stations are given i[n table I.](#page-5-0)

Sampling:

Water sampling included measurements of salinity both by CTD and bottle samples, CTD and bottle sample Oxygen determination, CTD temperature, nutrients (silicate, nitrate, nitrite and phosphate), CFC, pH, alkalinity, $CO₂$, particulate matter, chlorophyll pigments, C14. Al. ACDP.

Type and Number of stations:

During the cruise 118 CTD/rosette stations were occupied using a 24 bottle rosette equipped with 10 or 12 liter in GO water sampling bottles; 6 test stations were made between Cadiz and Las Palmas de G.C., 101 on the A-5 section and 11 on the Strait of Florida Section. For navigation and placement of stations, GPS and dynamic positioning were used.

1.1.3. List of Principal Investigators

1.1.4. Preliminary results

The ship departed from Cádiz on July 14, 1992 and 4 stations were made to test CTD and Rosette before arriving to Sta. Cruz de Tenerife on the 17th.

After the ship left Tenerife on the 18th and before arriving to L. Palmas the same day two more test stations were performed and the ADCP was checked.

During these stations several tests of a Falmouth Scientific Inst. CTD were also carried out.

The ship departed from L. Palmas in the early hours of the 20th to arrive to the first station of the section A-5 the same day. This section was finished, after 101 stations were made, at the Bahamas on August 14th. During the next day the Strait of Florida Section was completed and the cruise accomplished.

We carried 3 CTDs, 2 belonging to IEO and 1 to WHOI. They are EG&G NBIS MARK III instruments equipped with Sensor Medics dissolved oxygen sensors and titanium pressure sensor (Millard et al 1991). All were calibrated at the WHOI facilities before the cruise. Because the delays inflicted by the hurricane Andrew on the equipment shipment from Miami to Woods Hole the post-cruise calibration were not performed on the CTDs until December. The conductivity and oxygen sensors were also calibrated at sea using the analysis of the water samples collected at each station. The depths of the sampling were based on the classical standard ones although they were varied on a station by station basis according to participants need to sample a particular layer provided there was no impairment of the in situ calibration activities.

Table I

Water samples were collected from 10 or 12 liters PVC Niskin GO bottles mounted on a GO Rosette Sampler. All the water sample conductivity and oxygen measurements were made in a constant temperature laboratory soon after each cast was completed. Descriptions of analytical techniques, precision and accuracy are given later in this report. Additional samples were also collected for the analysis of the other parameters listed above, description of which are presented in other sections of this report.

According to the WOCE Implementation Plan this line was located at 24˚N. As two oceanographic sections had been made previously in 1957 and 1981) around 24.5˚N (Roemmich and Wunsch, 1985) we asked the WOCEIPO to move the WOCE section A5 to this latitude, which was agreed to. With respect to the station separations and because we were constrained by ship time, we decided to use the following judgment: the first 6 stations were located at the 50, 100, 150, 1500, 2000 and 2500 isobaths (about 18nm separation). From there to the 4000m depth (stl2) the separation was about 23nm. From station 12 to the eastern limits of the Mid Atlantic Ridge we separated the stations by 36nm. Across the Ridge the separation was 32nm. From its western limits to the 5000 isobath near the Bahamas, stations were separated again 36nm. Stations close to the Bahamas were separated by less than 30nm. The stations across the Straits of Florida were occupied every 5nm.

Near to Bahamas we deviated the heading of the section slightly from the original plan in order to cross the continental slope perpendicular to the direction of the isobaths and to obtain a clear crossing of the Deep Western Boundary Current.

The ADCP and a thermosalinograph recorded continuous during the whole cruise. Wind information was recorded every hour.

At the end of the cruise the ship was checked for Tritium and C14 contamination by the Tritium laboratory of the University of Miami.

Vertical profiles for T, S and $O₂$ together with a listing of this data for standard depths for each station are given in the Annex.

1.1.5. Incidences

During the test stations, there were problems with the rosette: several of the bottles were not triggered. The trouble had to do, probably, with too much friction on the bolts since this rosette had never been used before. After some lubrication the problem disappeared. There were some problems, during the test stations and some of the first stations of the A-5 section, with the portside winch. The oil of the hydraulic circuit became too hot causing the winch to lose power. After station 11 we switched to the other winch that worked from the stern.

On station 62, CTD # 1 stop sending conductivity data and it was replaced by CTD # 2 until station 74 when CTD# 1 was brought back, only for 7 stations since we started getting pressure spiking. From station 81 to 88 we used CTD #2 and from there on we used CTD# 1 after it was repaired on board.

On station 83 the wire was reterminated after cutting off 10 m of wire because of a faulty electrical contact. It was also reterminated after station 110 (in the Florida Strait) because of two-blocking the CTD on recovery at this station.

On station 61 the CTD hit the bottom because of a failure of the depth recorder.

The portable hydrophone-recording system for use with the pinger failed from the beginning and we were not able to repair it. We tried to use the EA500 SIMRAD echosounder of the ship, but there was not the necessary documentation on board so we could not effectively use the pinger at all. We decided to keep the CTD package between 50 or 100 m above the bottom when the floor was too rough and less that 50 m when it was flat.

The proposed Tritium and Helium survey by Dr. Z. Top could not be made since the equipment was lost during shipment from Miami and it never arrived to the ship.

1.1.6. List of Participants

1.1.7. Acronyms

2. MEASUREMENT TECHNIQUE AND CALIBRATIONS

2.1. CTD measurements

(R. Millard and M.J. Garcia)

2.1.1. Instrumentation, Calibrations and Standards

Two EG&G/NBIS Mark IIIb CTD underwater units each equipped with pressure, temperature, conductivity and polographic oxygen sensors were used throughout the cruise. The CTD instrument numbers are 1100 and 2326 and they belong to the Instituto Espanol de Oceanografia (IEO). Each CTD is configured identically with the same data scan length, variables, and scanning rate of 31.25 Hz. (A detailed description of the Mark IIIb CTD can be found in Brown and Morrison, 1978.) Both instruments were modified at Woods Hole Oce anographic Institution (WHOI) to add a titanium pressure sensor with a separately digitized resistive temperature device (RTD). A third EG&G/NBIS Mark IIIb CTD was provided by WHOI (WHOI instrument No. 8) but was not used during this expedition. A General Oceanics (GO) rosette fitted with 24 10 liters Niskin bottles was used with the CTD for collecting water samples. The GO rosette bottles are mounted approximately 0.5 m above the CTD sensors.

Titanium pressure sensors were manufactured by Paine Instrument and were installed with a separate pressure-temperature sensor in both CTDs prior to the cruise. The pressure data has a resolution of 0.1 decibars and an overall accuracy of $+ 2.0$ decibars for CTD# 1100 and + 5.0 decibars for CTD # 2326. The pre-cruise pressure calibration was used for CTD # 1100 while a combination of pre and post cruise pressure calibration was used to process CTD $#$ 2326. The Titanium pressure transducer processing methods follow Millard, et. al (1993). Pressure is calibrated across the pressure sensor's range in the laboratory before and after the cruise. These calibrations are carried out at both room temperature and at the ice point.

The temperature sensor is Rosemount platinum $# 171$. The fast response temperature thermistor normally employed in the Mark IIIb has been removed. The temperature resolution is 0.0005°C and the accuracy is better than \pm 0.0015°C (Millard & Yang (1993)) over the range 0 to 30.0°C. Temperature was calibrated in the laboratory before and after the cruise with the CTD instrument fully immersed as described by Millard & Yang (1993). A large (0.01 to 0.015° C) shift of temperature in the same direction was observed to occur with both CTD's 1100 and 2326. This shift was traced to a faulty pre-cruise laboratory temperature standardization. The conductivity sensor is a 3 centimeter alumina cell manufactured by EG&G/NBIS. The resolution of conductivity is 0.001 Ms/cm and the accuracy is directly tied to the water sample salinity accuracy discussed elsewhere in this report. The overall accuracy of the CTD conductivity calibrated to the rosette water bottle salinities is believed to be better than ± 0.0025 psu.

The CTD oxygen is measured with a polographic sensor manufactured by Sensormedics. The CTD oxygens are calibrated to shipboard Winkler oxygens.

2.1.2. CTD data collection and processing

The CTD data logging and processing was accomplished on two MSDOS PCs. The data logging was handled on an IBM compatible 80386 system with an 80387 math coprocessor. The EG&G data logging program CTDACQ was used to record down and up profiles, separately on disk together with a rosette bottle file. The CTD data was edited to flag spurious data using the EG&G program CTDPOST. The remainder of the CTD postprocessing was performed using the WHOI PC-based CTD processing system as described by Millard and Yang (1993). The post-processing was performed on an IBM compatible 80486 system with a 600 Mbyte optical disk (Sony SMO-C501) used for data archiving.

2.1.3. CTD calibration constants

The standard Alumina conductivity cell materials expansion factors: Alpha = -6.5 E-6, Beta $= 1.5$ E-8 were applied to CTD #1100 and CTD #2326. When the pre-cruise pressure calibration was applied to CTD 2326 data, a Beta $= -1.5$ E-8 was required to produce a salinity without a depth dependence; but a combination of pre/post-cruise pressure calibration allowed the use of the standard Beta value. The combined pressure calibration was used to process all CTD #2326 data because it produced CTD salinities free of depth dependence and yielded the pressure bias observed at sea.

2.1.3.1.Pre and post-cruise Laboratory calibrations polynomial coefficients

$$
Eng = E + Dr + Cr^2
$$

(where r is the measured raw CTD data value and Eng is the standard engineering unit of the variable).

The coefficients for each sensor are:

a) Pressure: (Loading/unloading)

CTD #1100

E= -1.075; D= .108604; C=0.593893 E-9 pre-cruise

CTD #2326

b) Temperature: (post-cruise)

CTD #1100 (2^{nd} order fit, stand. dev. = 0.00035) E= -0.4055 ; D= 0.499576 E -3 ; C= 0.13946 E -11 : Lag= 0.225 s

CTD #2326 (1st order fit, stand. dev. = 0.0006) $E= 0.0026$; D= 0.499889 E-3; Lag= 0.250 s

c) Conductivity:

For CTD #2326 and CTD #1100 conductivity calibrations the post-cruise temperatures were used. For CTD #2326 the data was pressure averaged again after the cruise using the combined pre/post-cruise pressure calibrations while CTD 1100 used the pre-cruise pressure calibration. The conductivity (salinity) calibration was examined closely at the change of instruments during the cruise (i.e. instrument swap outs at stations 62 – 63, 73 – 74, 80 – 81, 88 – 89) and no shifts were found that were not arguably due to oceanic variability.

CTD #1100

This CTD required some fine-tuning of conductivity slope calibrations. Bias, E= -0.0116 for all the stations

Stations 96, 97 and 98 salinities are low compared to the water samples, but we believe that water sample salinities are suspect for these stations.

CTD #2326

For this CTD, there is significant down-up hysteresis in one of the salinity sensors (P, T, or C: mostly likely Conductivity). The up-profile salinity is .005 - .007 fresher than the corresponding down-profile at a given potential temperature. Of course, at the bottom of the profile the salinity agrees but by 2.5°C (3500 dbars) on the 6000 dbar profiles a .005 psu discrepancy exists. A program was written to extract and create down-profile conductivity calibration data and we have to refit CTD # 2326 conductivities below 2500 dbars.

Stations $63 - 73$, bias; $E = 0.0083$

Final CTD data edit:

Two mean profiles were created. One for the West African Basin and a second for the North American Basin, by averaging all deep BIO Hésperides stations on pressure surfaces. These mean profiles have been used to screen the individual casts of each basin for question able temperature, salinity and oxygen data, comparing individual profiles to respective mean profile.

Two edit criteria were used to flag questionable data:

- Temperature, Salinity and Oxygen variations whose difference from the mean profile exceeding 5.5 standard deviations;
- Stability parameter exceeding –1.0E-5 per meter.

A list of stations with bad or questionable data at the surface is given below:

1. Stations with bad or too low surface salinities.

2. Stations with questionable surface salinities.

d) Oxygen

The oxygen parameters were adjusted as shown on tables II an[d III.](#page-15-0) The header abbreviations denote the following:

- STA= First and last station numbers of the group used for calibration.
- BIAS, SLOPE, PCOR, TCOR, WT, LAG and Edit factor are parameters of the fit as described by Millard and Yang (1993).
- STD DEV= Standard deviation of the fit after some outlying water sample observations are discarded.
- OBS= Number of water sample observations used for the calibration.

Table II Coefficients for Oxygen Calibrations

STN	BIAS	SLOPE	PCOR	TCOR	WT	LAG
$1 - 11$.029	.1104e-02	.1664e-03	$-2783e-1$.7510e+00	.7560e+01
12-14	.049	.1139e-02	.1461e-03	$-.2990e-1$.7500e+00	.7500e+01
15-19	.031		.1504e-03	$-0.2939e-1$.8219e+00	.4167e+01
15	"	.1129e-02		ϵ	ϵ	ϵ
16	"	.1156e-02	ϵ	\mathbf{G}	α	α
17	"	.1158e-02	α	α	α	α
18	"	.1170e-02	"	\mathbf{G}	\mathbf{G}	\mathbf{G}
19	"	.1182e-02	"	\mathbf{G}	\mathbf{G}	\mathbf{G}
$20 - 22$.024	.1197e-02	.1517e-03	$-0.3090e-1$.7408e+00	.7299e+01
23-31	.032	.1205e-02	.1491e-03	$-0.3033e-1$.7934e+00	.3211e+01
32-40	.024	.1228e-02	.1501e-03	$-0.2926e-1$.9210e+00	.7833e+01
41-43	.015	.1233e-02	.1553e-03	$-2998e-1$.7740e+00	.7000e+01
44-46	.006	.1229e-02	.1616e-03	$-0.3065e-1$.6702e+00	.1623e+02
47-50	.000	.1235e-02	.1673e-03	$-0.3092e-1$.5287e+00	.2187e+02
$51 - 55$.012	.1226e-02	.1590e-03	$-0.2953e-1$.8080e+00	.7340e+01
56-62	.032	.1216e-02	.1499e-03	$-0.2906e-1$.8221e+00	.1549e+02
63-71	-0.036	.1256e-02	.1683e-03	$-.3041e-1$.7448e+00	.4612e+01
70	ϵ	.1269e-02				
72-73	$-.047$.1338e-02	.1686e-03	$-.3241e-1$.6362e+00	.2927e+01
74-80	.027	.1201e-02	.1515e-03	$-2865e-1$.8869e+00	.1027e+02
81-83	-0.053	.1276e-02	.1788e-03	$-0.3177e-1$.6312e+00	.3351e+01
84-87	$-.030$.1284e-02	.1645e-03	$-.3047e-1$.8147e+00	.1998e+00
88	"	.1320e-02		"	ϵ	
89-101	.039	.1200e-02	.1459e-03	$-.2779e-1$.9109e+00	.1390e+02

Table III Statistics of Adjustments for Oxygen Calibrations

Notes to these tables

- Parameters obtained from stations 7 to 9 apply to stations 1 11.
- Stations 15 to 19 were fit fixing parameters of 15 21 except slope.
- Stations 32 to 39 calibrations applied to stations 32 to 40.
- Station 70 calibrated as group 63 71 except slope
- Station 88 calibrated as 84 87 except slope
- Station 89 to 101. Sta. 96 and 98 are excluded in setting calibration parameters. When they were included WT was negative.

[Figure 2 s](#page-30-0)hows the histograms for salinity and oxygen differences between CTD and bottle samples deeper than 2500 db.

The mean and standard error for the first one are 1.9 E-4 and 1.3 E-4 respectively. For oxygen, they are 1.1 E-4 and 2 E-3.

2.2. Salinity

(R. Molina)

For the salinity measurements the recommendations given in the training Course Notes (Ocean Scientific Int., Funchal, July 1991) were followed. The water sample salinities were measured with a Guildline Autosal Model 8400A salinometer. The manufacturer claims a precision of 0.0002 and an accuracy of 0.003 when the instrument is operated at a temperature between $+4^{\circ}$ and -2° C of ambient temperature. All the salinity measurements were made in a temperature controlled laboratory about 1˚ to 3˚C below that of the salinometer water bath.

Two different batches of standard water were used: batch P120 (April 6, 1992) with 50 ampoules and 20 ampoules from batch P117 (July 10, 1991). After the salinometer was standardised with water from the first batch, 8 samples from an ampoule of the second batch were measured, and the labelled value of 34.994 was obtained within 2x10⁻⁵. On the average, the salinometer was standardised every 31 samples.

Water samples were collected from the Niskin bottles in Ocean Scientific International glass bottles and the measurements were made within the 24 hours after the station was finished. In total 2294 samples were measured.

In determining the conductivity ratio, three measurements were made from every sample providing the differences were smaller than $2x10^{-5}$. If not, more measurements were made until three consecutive values exhibited differences smaller than $2x10^{-5}$.

Sta. Depth Bottle no. No. of Samples Standard dev. $50 \mid 2500 \mid 02, 3, 4, 5, 6, 7 \mid 6$ $\pm 3.6x10^{-4}$ $64 \mid 2532 \mid 6 \mid 8 \mid \pm 1.3x10^{-4}$ $72 \mid 249 \mid 16 \mid 8 \mid \pm 2.1 \times 10^{-4}$

In 3 stations, samples were replicated with the following results:

During one day when the air conditioning of the laboratory broke down, salinity measurements for stations 2 to 3 were made with the laboratory temperature 0.3˚C above the salinometer bath temperature.

2.3. Oxygen

(J. Escánez)

Oxygen determinations were carried out following the Winkler method and using the reagents prepared according to Carpenter (1965). We used the modified Carpenter's equation as given by Culberson et al (1991). The endpoint of titration was determined visually using starch as indicator.

Reagents were dispensed with all glass and Teflon dispensers "Dispensette" from Brand GMBH and Co. (0-2 ml capacity) with certified accuracy of \pm 0.6% and a coefficient of cariation of \pm 0.1%. The tips of the dispensers were lengthened up to 6 cm with thin plastic tubing to avoid the precipitation of manganese hydroxide in the neck of sample flasks.

Titration was done with a Metrohm Dosimat E.412 automatic burette using Potassium Iodate "pro.anlaysi" Merck (Lot N° 150 BZ 252853. Assay 99.95 - 100.05%) at a concentration of 0.0100 N.

Standards and blanks were dispensed with class "A" calibrated hand pipets with certified accuracy of \pm 0.02 ml for 10 ml pipets and \pm 0,006 ml for 1 ml pipets.

In total, 2338 samples were taken (Table IV). In order to assess good quality results, calibration sets were run through 7 stations. Inter-sample calibrations were run on 3 stations by taking 1 sample from 6 Niskin bottles triggered at the same depth, while on 4 stations intrasamples calibrations were performed taking 6 samples of 2 Niskin bottles triggered at the maximum and minimum $O₂$ layers respectively. Values are shown in Tables V an[d VI.](#page-18-0)

Table IV Distribution of Casts/Analysts

Table V Calibrations between Casts

Table VI Calibrations within Casts (Maximum and Minimum)

2.4. Nutrients

(A. Cruzado)

Analyses were performed on board with a four channel SKALAR segmented flow autoanalyzer. Samples were collected in 150 ml acid-rinsed polythene flasks directly from the Niskin bottles, following the protocol established by the WOCE Hydrographic Programme. Analyses were carried out immediately without any treatment of the samples. When necessary, samples were kept in the cold room (unfrozen and never for more than 10 hours) without additives.

The analytical techniques followed were those described by Whitledge et al. (1981) with minor modifications to adapt them to the particular conditions of the instrument used and concentration ranges observed. Primary standards were prepared at the beginning and in the middle of the cruise prepared every two days and preserved with some drops of chloroform in the fridge. Running standards were interleaved with unknown samples in order to provide a measure of analytical stability. Whenever changes in sensitivity (particularly in the case of nitrate) were noticed, these standards allowed for a correction to be applied.

All concentrations were referred to double distilled water prepared by reverse osmosis through milliRo, dionization through Milli-Q and distillation. No sea water sample has ever given a concentration negative with respect to this double distilled water. Phosphate analysis corrected for the change in absorbance due to the salinity effect. Surface seawater was used as carrier and, except for silicate, it always showed the minimum concentrations in the water column.

Silicate concentrations below the surface were often found to be lower than the surface values and very close to the values given by double distilled water. Replicate samples were analyzed at various depths both from the same and from different Niskin bottles. A comparison of all the primary and secondary standards used during the cruise is underway and may introduce some small corrections to the results. A statistical assessment of such analyses is being prepared. Some nutrient diagrams are shown in [figure 3.](#page-31-0)

Addendum to the Nutrients Report on A05

(A. Cruzado)

During the HE06 cruise (July/August 1992) along the WOCE line A-5, dissolved inorganic nutrients (orthophosphate, nitrate+nitrite, nitrite, and orthosilicate) were collected and analysed on board the R/V Hesperides using a continuous flow analyzer by Antonio Cruzado (Centro de Estudios Avanzados de Blanes, Spain) following methods adapted from Withledge et al. (1981). These methods were used in the fifth 1989/1990 ICES international inter-comparison exercise for nutrients in seawater (Aminot and Kirkwood, 1995). Three different quality control procedures were applied to the A5 nutrient data. First, spurious chemical data were flagged according to WOCE quality control codes. These are data values shown to be analytically incorrect ("Bad"). Second, the A5 chemical data were compared to the August 1992, Trident cruise on the RV Baldrige between Abaco Island, the Bermuda Rise and the Mid-Atlantic Ridge (Garcia, 1996). This provided a mean to compare the two cruises in the western basin only. Third, the A5 data were compared to historical oceanographic data collected since the GEOSECS program (Table 1). The long-term precision of the A5 chemical data was estimated following the method of Saunders (1986). Potential temperature (Fofonoff and Millard, 1983) was fitted to the nutrient data from the HE06 and AT109 cruises by linear least-squares for water with temperatures less than or equal to 1.8°C and 2.1°C in the western (45-75 W) and eastern (20-44 W) Atlantic basins, respectively (Garcia, 1996). The standard deviation of the measured values for each chemical variable from the expected values calculated from the coefficients of the regression lines for stations in the western and eastern basins are shown in Table 2. Chemical data points which deviated significantly (more than 5 SD from the mean) were flagged as questionable. No quality control was applied to the nitrite data.

Table 1 Historical data (1972-92) used in this work

Table 2 Estimates of precision (1 SD) of the AT109-II and HE06 chemical data. Numbers in parenthesis indicates the number of data points in the calculation described in the text above (Garcia, 1996).

2.5. CFC-11 and CFC-12

(W. Smethie)

The objective of the CFC measurement program on this cruise was to measure the distribution of CFC-11 and CFC-12 in the thermocline along 24˚N in the Atlantic and in recently ventilated components of North Atlantic Deep Water, including the Deep Western Boundary Current, spreading southward in the western North Atlantic.

The CFC measurements were made on board with a CFC analysis system interfaced to a gas chromatograph with an electron capture detector. This method is described in Smethie et al. (1988) and is similar to the Bullister and Weiss (1988) technique.

One difference for this cruise was the use of a Porasil B precolumn and a SP21000 main column instead of Porasil B for both columns. This combination allowed CFC-113 and carbon tetrachloride to be detected as well as CFC-11 and CFC-12. However carbon tetrachloride and CFC-113 were not measured on every station because of the longer analysis time required. The purpose of these measurements was to obtain preliminary information on the distribution of these substances in the ocean and they are not of the same quality as the CFC-11 and CFC-12 measurements.

Some problems were encountered. A set of new syringes had a low level CFC-11 contamination (0.02 – 0.04 pmol/kg). Blanks for these syringes were determined and monitored by analyzing zero CFC water from the deep eastern basin or by comparison to duplicate samples collected in old syringes which were not contaminated. These blanks decreased during the cruise. There was a high (20-30% of surface water concentration) and variable CFC-113 system blank and the Niskin bottles became severely contaminated with CFC-113 at station 75, probably due to a fire control exercise by ship's personnel, and remained contaminated for the remainder of the cruise.

The general sampling strategy was to sample every other station which resulted in approximately 60 nm spacing. Every station was sampled near the western boundary. Generally 10 or 11 samples were taken between the surface and 1000 m along the entire section. In the eastern basin the deep water contained no CFCs, but samples were

collected to determine Niskin bottle/sampling blanks and syringe blanks. In the western basin, CFCs were detected throughout the water column. Vertical spacing varied between 150 and 400 m with more closely spaced samples at about 1500 m and 3500-4000m to resolve CFC maxima at these levels. A section was also taken across Florida Strait with approximately 5 nm horizontal resolution and 50-100 m vertical resolution. A total of about 1100 water samples, not including duplicates, were analyzed.

In th[e figure 4, s](#page-32-0)hown are vertical profiles of preliminary shipboard values of F-11.

2.6. pH, Alkalinity, CO2

These measurements were carried on board by two independent groups.

2.6.1. CO2

(F. Millero)

The total alkalinity, TA, total carbonate, $TCO₂$ and pH were determined from titrations of seawater collected at 31 stations. The titrators were calibrated with Dickson standard before and during the cruise. The results agree to ± 7 µmol Kg-1. The pH was determined from the initial emf reading relative to TRIS buffers. The results for Dickson samples agree with laboratory spectroscopic measurements to ±0.005m ptl.

The values of the partial pressure of carbon dioxide, $pCO₂$, were calculated from the TA and $TCO₂$ are higher than the atmospheric values.

I[n figure 5 s](#page-29-0)ome preliminary results are shown.

2.6.2. pH and CO₂

(A.F. Ríos)

Direct pH measurements were made on the NBS scale for all stations (1 to 112 inclusive and at all levels, about 2400 samples total). The samples, kept in a 50 ml plastic bottles and perfectly closed, were introduced into a combined glass electrode associated to a thermocompensater. Measurements were referred to 15˚C according to the variation of pH with temperature (Pérez and Fraga, 1987a). The accuracy of measurement is 0.1% of the total inorganic carbon (Zirino, 1985), i.e. ±0.004 units, but in samples taken in very homogenous water columns it is possible to detect differences less than this value.

Alkalinity measurements were made by titration of about 250 ml of a seawater sample with HCl O, ¹³N, with potentiometric detection of the endpoint (Pérez and Fraga, 1987b). Stations 1 to 101 were sampled at all levels (about 2300 samples). Reproducibility was tested by sampling a 25 l storage bottle and was found to be less than 0.1%.

Total inorganic carbon and carbon dioxide pressure was determined indirectly from the pH and alkalinity according to methods described by Pérez and Fraga (1987b).

Some preliminary results are shown i[n figure 6.](#page-35-0)

2.7. Particulate Organic Matter

(A.F. Ríos)

Two liters of seawater at levels (10, 15, 50, 100, 200 and 400 m) on 25 stations were filtered through a glass fiber filter (Whatman GF/F of 25 mm diameter) in order to determine the particulate carbon and nitrogen using a 2400 Perkin Elmer Elemental Analyzer.

To determine particulate phosphorous, samples of one liter of seawater retained I filters (Millipore AAWPO2500) were taken at the same stations and levels as before. These samples will be oxydized with percloric-sulphuric acid (Ríos and Fraga, 1987) and later determination of phosphate will be carried out by the method described by Grasshoff et al. (1983).

Carbohydrates will be determined by the technique of Antron reagent (Rios, 1992) from samples of one liter of seawater retained in filters (Millipore AAWP02500) taken at these same stations and levels.

2.8. Calcium

(G. Rosón)

The 450 samples analyzed for this parameter were taken on 20 stations at all levels.

The method used for determining calcium is a volumetric titration of about 130 g of seawater with potentiometric detection of end point by calcium selective electrode, using EGTA (ethyle n eglycol-bis) (B- a mino eth yleter), N, N, N1, N1, tet ra a ce tic acid) as tit rant (0.18 M) and 25 ml of borax (0.1 M) as buffer (Rosón and Pérez, 1990; Rosón, 1992). The reproducibility of the method, made on a 25 I storage bottle, was 0.07% for 70 samples.

2.9. Carbon-14

(W. Smethie for W. Broecker)

Carbon-14 samples were collected in the thermocline at a few select stations. These samples will be analyzed by accelerator mass spectrometry. This is part of a larger program to collect samples over the entire North Atlantic from ships of opportunity during the next few years. The objective is to determine the distribution of bomb carbon-14 in the thermocline and compare this distribution to the distributions measured in 1981 on the TTO program and 1972 on the GEOSECS program. The evolving bomb carbon-14

distribution will be used to investigate circulation and mixing in the thermocline and uptake of carbon dioxide by the ocean.

Samples were collected at stations 13, 24, 35, 53, 66, 81, and 92. In general 8 samples were collected at each station, one in the surface mixed layer and seven at the following sigma-theta surfaces: 26.2, 26.4, 26.6, 26.8, 27.0, 27.2, and 27.4. Samples were also collected at stations 103 (one in the oxygen maximum) and 107 (six throughout the water column) in the Straits of Florida and at test station (ten samples) just west of the Strait of Gibraltar. A total of 71 samples were collected.

2.10. ADCP

(M. Garcia)

The ADCP model used was a RD-VMO 150. The selected sampling intervals were 180 s, 40 depth bins of 8 m length. The profiler was recording continuously during the whole cruise and the data was recorded on diskettes.

2.11. Thermosalinograph

(E. Alvárez)

During W.O.C. E. A-5 section, temperature and salinity were measured across the Atlantic O ce an surface using a Se a bird ther mo salin om eter (se rial numb er 626a). Data acquisition began on station number one and finished close to Miami harbor. The time step between each acquisition was three minutes. The obtained data were stored in groups of files, each group corresponding to one navigation day. Water conductivity was recorded from the third n avigation day on. Two electricity failures (during the second and fourth days) and at least one water flux stoppage (during the fourth day) interrupted the continuous time series.

2.12. Chlorophyll Pigments and Primary Production

Two kinds of analysis have been undertaken for pigment studies. One was based on spectrophotometric equations with readings of absorbances at 664, 645, 630 and 750 nm. In the other smaller volumes of seawater were used for analysis of chlorophyll and phaeopigments based on fluorescence readings before and after acidification of the sample.

2.12.1. Chlorophyll Pigments

(Z.R. Velásquez)

Water samples were taken at several depths (0-250m) on all stations of the WOCE A-5 section from NW Africa to the Bahamas.

The phytoplanktonic pigments were determined on board immediately after sampling by

the spectrophotometric technique described by Jeffrey and Humphrey (1975). About 3.3 liters of seawater were filtered under vacuum through 4.7 cm Whatman GF/F filters. After extraction during a minimum of 24 hours with 5 ml (90%) acetone in the dark at 0°C, the resulting suspension was centrifuged at 3000 rpm for 30 minutes.

The absorbances at 664, 645 and 630 nm, required for the computation of the concentrations of Chlorophyll A, B and C, were determined in the supernatant (5 ml), allowance being made for the eventual presence of turbidity by measuring also the absorbance at 750 nm. All absorbance measurements were done with a LBK spectrophotometer linked to a computer.

The following formula was used for the computation of the pigment concentration in the supernatant in μ g/l.

(Chlorophyll (µg/l) =OD* Vac / Vsw

OD (a) = 11.85*(D664-D750)-1.54* (D645-D750)-0.08*(D630-D750) OD (b) = 21.03*(D645-D750)-5.43* (D664-D750)-2.26*(D630-D750)
OD (c) = 24.52*(D645-D750)-1.67* (D664-D750)-7.66*(D645-D750) OD (c) = $24.52*(D645-D750)-1.67*$

where

 $Vac =$ volume of acetone (in ml);

 $Vsw =$ volume of seawater (in I);

Dxxx = optical density at wavelength xxx and 1 cm optical path

Pheopigments were determined by acidifying the extracts with two drops of 10% HCl and reading at the same wavelengths.

Samples of water at the same level were preserved with Lugol (Potassium Iodate/Iodine solution buffered with sodium acetate) for further phytoplankton analysis with an Olympus inverted microscope to which a computer/video digitizing system has been adapted.

2.12.2. Chlorophyll Pigments and Primary Production

(J. García-Braun)

Water samples were taken for pigment analysis at several depths (mainly, 0 - 200 m) on 90 stations for a total of 1152 analyses for chlorophyll and phaeophytin.

With respect to the pigment distribution in the water column, ours main objectives were: to obtain the vertical distribution of chlorophyll a, based on fluorescence readings, calibrated against spectrophotometer following SCOR-UNESCO (1966) and the vertical distribution of chlorophyll and phaeophytin, based on fluorescence readings, before and after acidification, according to equations by Lorenzen (1966); and to estimate the pigments

biomass including size classes, evaluating picoplankton less than 2 microns and populations bigger than 2 microns.

Two samples of 1 liter sea water for each depth were filtered through Whatman GF/F filters. Pigments were extracted in 10 ml of 90% acetone during about 12 hours in the dark at 0˚C. The fluorescence measurements (before and after acidification with two drops of 10% ClH) were used to calculate the pigments according with the following equations:

Chlorophyll a = 11.64 e_{663} - 2. 16 e_{645} + 10 e_{630}

where e_{663} , e_{645} and e_{630} are the absorbances at 663, 645 and 630 nm after substration of the absorbance at 750 nm, using 1 cm spectrophotometer cell. If the obtained value is multiplied by the extract volume in ml and divided by the volume of seawater filtered in liters, the amount of chlorophyll a in mg/m3 is obtained.

The equation proposed by SCOR-UNESCO (1966) was used to calibrate the Fluorometer Turner Design in which all the readings of Fluorescence were made during the cruise. Concentrations of chlorophyll a and phaeophytin a were also calculated following the equations given by Lorenzen (1966).

2.12.2.1. Primary Production

(J. García-Braun)

Water samples for primary production experiments were taken at several depths in the photic zone, representing approximately 100%, 25%, 10% and 1% of surface light. The standard C14 method proposed by Steeman Nielsen (1952) was used with some modifications. The incubations were done in incubators under artificial light during 2-3 hours. The selected stations (11 stations and 99 samples) were chosen in order to make the incubations in early hours during the morning.

For each depth, samples of 100 cc of seawater were inoculated with 4 μ Ci of C14 bicarbonate. After incubation one sample was passed through Nucleopore filter (2 micron pore size) and the other sample through Whatman GF/F filters. A separate sample was incubated in the dark in order to substract the incorporated radioactivity with respect to the light bottles. The filters were preserved in the deep freeze for future readings of counts per minute in a Liquid Scintillation Counter.

2.13. Aluminum

(M.D. Gelado and J.J. Hernández)

A voltametric method was used for aluminum determination during WOCE-AS Cruise.

The procedure is based on complexation of aluminum with 1,2-dihydroxyanthraquinone-3 suplhonic acid (DASA) and measurement of reduction current of this complex using high speed cathodic stripping voltametry (HSCSV). Reduced Al-DASA complex produces an intensity of faradaic current proportional to dissolved Al concentration. The free DASA ligand has a cathodic peak at - 0.63 V while Al-DASA peak is more negative at -1.1 V (Ag/ClAg).

Optimal experimental parameters include an accumulation potential of -0.95 V during 45 s, DASA concentration $2x10^{-6}$ M and staircase scan mode to 30 V/s speed. Samples are buffered at 7.1 pH using N, N1bis(2-hydroxyethyl)-2-aminoethane suphonic acid(BES). The method (Gelado-Caballero, 1992) is specially adapted for on board determinations. The electrochemical system has been designed to measure the instantaneous currents at short times with a low noise level (Hernandez-Brito et al., 1990). Thus, the analytical time required for each sample is substantially reduced, allowing an increase of the number of measurements in situ. A PAR303A electrochemical cell with hanging mercury drop electrode (HMDE) was connected to a specially made computer-controlled potentiostat.

The detection limit was 1.75 nM for 30 s adsorption time. The deviation was less than 3% for a 19 nM Al concentration based on repetitions for 7 seawater samples.

In total 1000 samples were taken in 52 stations. In most of the stations, except in those close to the African coast, maximum was detected at the surface layers. Below a minimum at intermediate depths the dissolved Al concentrations increased with depth.

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Station Number

Figure 2: The histograms for a) salinity and b) oxygen differences between CTD and bottle samples deeper than 2500 db.

Figure 3: Nutrients diagrams.

Figure 4: Vertical profiles of preliminary F-11 values at depths less than (a) and greater than (b) 1000m.

 $TCO₂$ (µmol/kg)

Figure 5a: Total carbonate according to the depth for all the stations in which it was measured.

Figure 5b: Calculated pressure of $CO₂$ throughout the passage of the cruise.

Figure 6b: Vertical distribution of the alkalinity and total carbon for station 47.

DQE of CTD data for the 6th cruise of the r/v "Hesperides", WOCE section A5 across **the North Mid-latitude Atlantic.**

(Eugene Morozov) 1995 MAY 02

Data quality of 2-db CTD temperature, salinity and oxygen 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.

Questionable data in *.hy2 file were marked in QUALT2 word.

The calibration of upcast CTDSAL and CTDOXY data seem to be worse than downcast data.

There were two data sets for WCT files. One for the eastern part of the section the (station numbers 49 and less) and the western part (stations 50-112). The data sets came different sources so I analyzed them separately.

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

Eastern part

Western part

Salinity and oxygen are examined separately because there were many problems with CTDOXY calibration.

Salinity

Oxygen

There are problems with calibration of CTD oxygen sensor for many of the stations. Some CTD casts contain data that are definitely bad and they are not flagged bad at all.

WHPO-SIO Data Processing Notes

