WHP Cruise Summary Information

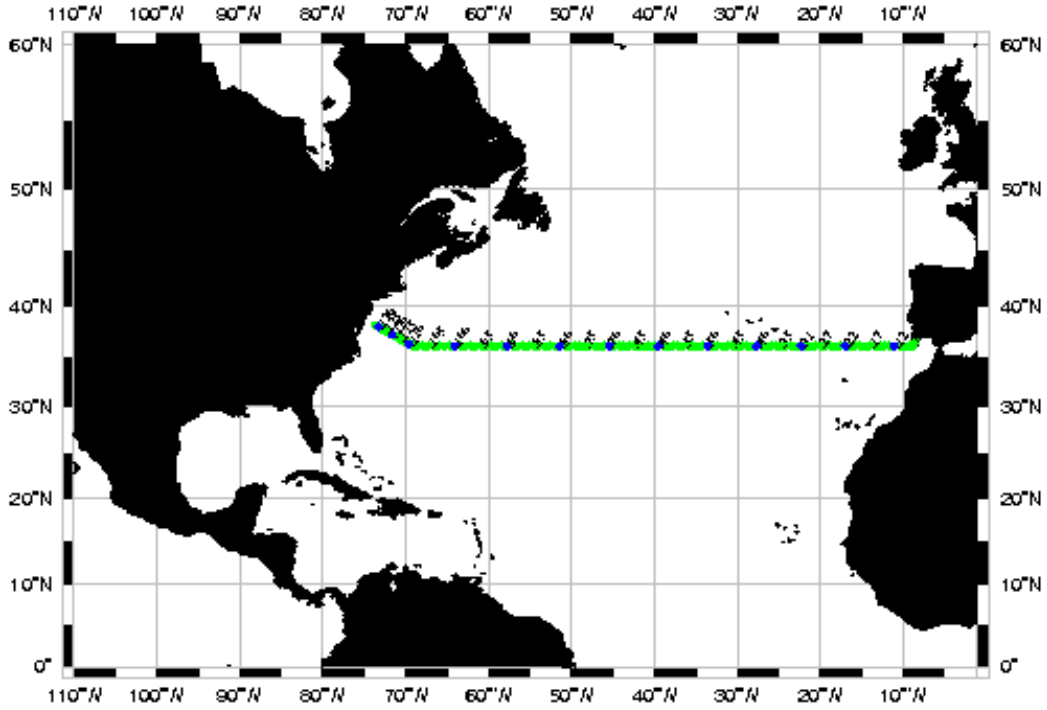
WOCE section designation	A03
Expedition designation (EXPOCODE)	RUCT40_1
Chief Scientist(s) and their affiliation	Vladimir Tereschenkov, SOI
Dates	1993.09.11 – 1993.09.21
Ship	PROF. MULTANOVSKIY
Ports of call	St. Petersburg to Hamburg to Woods Hole
Number of stations	133
Geographic boundaries of the stations	38°14.36''N 08°31.58''W 73°40.36''W 36°11.06''N
Floats and drifters deployed	none
Moorings deployed or recovered	none
Contributing Authors (In order of appearance)	S. Dobroluybov Ev. Yakushev S. Borodkin V. Konnov

WHP Cruise and Data Information

Instructions: Click on items below to locate primary reference(s) or use navigation tools above.

Cruise Summary Information	Hydrographic Measurements
	CTD - general
	CTD - pressure
	CTD - temperature
Cruise track (figure)	CTD - conductivity/salinity
Description of stations	
Description of parameters sampled	
	Salinity
	Oxygen
	Nutrients
Principal Investigators for all measurements	
Cruise Participants	
Problems and goals not achieved	
	Other parameters

Station locations for a03



(Produced from .SUM files by WHPO)

C.1 Cruise Narrative

C.1.1 Highlights

Expedition Designation:
"Professor Multanovskiy" Cruise 40

Chief Scientist:
Vladimir Tereschenkov, SOI

Ship:
R/V Professor Multanovskiy

Ports of Call:
St.Petersburg-Hamburg-Woods Hole-Hamburg-St.Petersburg

Cruise Date:
September 11,1993 - November 21,1993

C.1.2 Cruise Summary

Cruise Track

The cruise track and station location are shown.

Sampling Accomplished

Water sampling on the cruise included measurements of salinity both by CTD and water bottle samples, bottle sample oxygen determination, CTD and DSRT temperature, CTD and UDSRT pressure, nutrients (silicate, nitrate, nitrite and phosphate).

Type and Number of Stations

During the occupation of A3 section a total of 133 CTD/rosette stations were occupied using 24-bottle rosettes. 98 XBT stations were occupied on a track along 48°N.

C.1.3 List of Principal Investigators

The principal investigators for all the parameters measured on the cruise are listed in Table C.1

Table C.1 Principal Investigators for All Measurements

Name	Responsibility	Affiliation
V. Tereschenkov	CTD	SOI
U. Reva	-"-	SOI
S. Dobroluybov	S	MSU
V. Konnov	nutrients	IORAN
Ev. Yakushev	-"-	IORAN
S. Borodkin	oxygen	IORAN
Ev. Yakushev	-"-	IORAN

C.1.4 Preliminary results

The ship departed from St. Petersburg on September 11, 1993. On September 15-17 the ship made a stop at Hamburg. During this stay some problems concerned with scientific equipment and supplies were solved due to generous assistance of oceanographers from BSH. On 21 of September two stations were occupied near 45°N 8.5°W location to test the CTD/rosette system and to define the quality of the sampling bottles and the operating state of the ship boarded equipment. The first station on A3 section was occupied on September 24. The whole section was completed in 32 days with total of 133 stations occupied. Space resolution between the stations varied from 29 n. miles in the open ocean to 8 n. miles in the boundary regions. On each station a CTD/rosette cast was carried out, that extended as close to the bottom as it was possible, considering the bottom detection uncertainties. On the up cast up to 24 water samples were taken. After the rosette was brought on board, water samples were drawn in the following order: oxygen, nutrients, and salinity. The chemical analyses were routinely conducted soon after the samples were collected.

Two CTD/rosette systems were used in the cruise for the seawater temperature and conductivity profiling and water sampling collection purposes:

- EG&G NBIS Mark-III CTD together with the GO Rosette equipped with 24 1.7l GO Niskin bottles
- "Hydrozond-6000" CTD together with 24 position rosette with 1l PVC bottles (manufactured by Central Construction Bureau of Hydromet Instruments, Russia).

Water temperature and pressure were also measured by mercury Deep-Sea Reversing Thermometers (protected and unprotected, respectively). The conductivity of the bottle water samples was determined using Guildline Laboratory Autosal 8400A and than transformed to salinity according to equation of the Practical Salinity Scale of 1978 (UNESCO, 1981). The dissolved oxygen analyses were carried out using Winkler method. The silicate and nitrate plus nitrites analyses were performed using AKEA Flowcomp 1500 auto analyzer, phosphate was determined using KFK-3. Details of calibrations, methods, techniques and accuracies are documented below.

During the ships movement along the A3 line continuous depth recording has been conducted using ELAG echo sounder. On October 27-30 the ship made a call to Woods Hole for the refill. There is a pleasant and productive communications with WHOI people had occurred. After that "Professor Multanovskiy" occupied an XBT section similar to A2 line. Total of 98 Sippican T-7 probes were dropped at synoptical space resolution. On November 14-17 the ship visited Hamburg, where the XBT data and some scientific equipment were passed to scientist from BSH and the results of the first view data analyses have been discussed.

On November 21 ORV "Professor Multanovkiy" returned to St. Petersburg.

C.1.5 Problems

During an occupation of station 31 (Sept. 30 1993) the Niel Brown Mark-III CTD underwater unit together with the GO Rosette slipped off the cable and was lost. After that the backup instruments were used. The problems arise since that moment were all connected with the unstable performance off the "Hydrozond-6000" sensors. Nevertheless the natural desire to get the best of the data caused the departure of the post-cruise data processing procedure from the scheduled routine. That is why the final version of the CTD data is still not available.

C.1.6 List of Cruise Participants

The cruise participants are listed in Table C.2.

Table C.2 Cruise Participants

Name	Responsibility	Affiliation
V.Tereschenkov	Chief Scientist	SOI
A.Sokov	CTD, Rev. Instrum.	SOI
S.Pisarev	CTD	SOI
U.Reva	CTD	SOI
A.Andreev	CTD	SOI
S.Grigoriev	Software	SOI
S.Dobroluybov	Salinity	MSU
V.Konnov	nutrients	IO-RAN
Yu.Konnova	nutrients	IO-RAN
Ev.Yakushev	Salts,oxygen	IO-RAN
S.Borodkin	oxygen	IO-RAN
V.Bulanov	Hardware	VNIIRO
S.Yunovidov	Hardware	AARI
A.Tarasov	Watch Stander	AARI
A.Nikankin	Watch Stander	AARI

C.2 Measurement Techniques and Calibration

C.2.1. Salinity Analyses

S. Dobroluybov
(Moscow State University).

Equipment and Technique

The water sample salinity were measured with a Guildline Autosal Model 8400A salinometer N54403 that was standardized daily (usually twice) with IAPSO Standard Sea Water Batch 115. The last calibration of the salinometer was carried out by Guildline representation on May 1991. All measurements, initial quality control and shipboard data-processing were performed by S. Dobroliubov (Moscow State University). A total of 3094 water samples from 132 stations (mean value - more than 23 samples per each) were analyzed for salinity including 80 replicates.

Sampling procedure

Salinity samples were collected strictly according to WHP Manual (Stalcup, 1991). BSH silicate-glass sample bottles with a capacity of 200 ml and separate cones for sealing the caps were thoroughly rinsed three times, filled to the shoulders, dried and moved to the laboratory with controlled temperature. Time lag between sampling and analysis usually varied from 4 to 20 hours, but sometimes it was decreased to 2-3 hours by immersing the sample bottles to the water bath. The number of samples exceeded analyzed ones on 520 bottles transported to BSH, Hamburg for Autosal intercalibration purposes.

Sample measurements

Salinometer laboratory was the best temperature controlled room onboard though this control wasn't automatic. Nevertheless attempts to maintain the constant temperature during the section operation (24.09-25.10.1993) were successful with one exception 12.10 when air conditioning was remounted. Laboratory temperature during salinometer operation ranged mainly between 26.0 and 27.3˚C with mean value 26.8˚C and standard deviation 0.5˚C.

The published accuracy of the 8400A salinometer according to Operating Manual is 0.003 psu. But if measurements are made in a laboratory with quasi-constant temperature (+1˚C) it should be possible to reach the precision better than 0.001 psu. All the procedures to attain highest accuracy described in the Operating Manual (section 6.5) were performed. Only twice the shift between the two daily standardizations exceeded 0.001 psu at the time of lowest and highest laboratory temperatures. Mean difference between standartizations was 0.0004 psu. This shifts linearly interpolated between the first and the last sample readings.

All the samples were measured with Autosal bath temperature 27˚C. The salinometer readings were inverted to salinity in accordance with Guildline Operational Manual formula and Practical Salinity Scale-1978.

Data quality control

Control operations contained four parts. The first one - Autosal calibration control that performed weekly with a simple suppression switch check described by Stalcup (1987). This check showed absence of any discontinuities. Full calibration procedure was not completed during the cruise.

Another type of data control consisted of replicate analysis. 21 pairs of samples were collected from the same 1.8l Niskin bottles at different stations. Module mean difference between the salinities of these pairs was 0.0007 psu with standard deviation 0.0006 psu. The same procedure was promoted with Gydrozond 1.2l bottles. 59 replicates were collected including two calibration casts and its analysis revealed module mean salinity difference of 0.0009 psu with standard deviation 0.0007 psu. From this point of view the difference in measurement accuracy with both types of bottles was considered to be statistically indistinguishable.

The third type of quality control included plotting scatter potential temperature-salinity diagrams and comparisons with historical data from International Geophysical Year and Long Lines 36˚N sections. All measurements sharply deviated from the subsequent climatic mean deepwater trend were assigned low quality flags.

In order to intercalibrate salinity measurements 520 sample bottles were collected and carried to BSH, Hamburg. These samples were randomly distributed below 2000 m. Such procedures allow checking Autosal calibration by indirect method.

References

Guildline Instruments, 1984. Operating and Technical Manual for ‘Autosal' Laboratory Salinometer Model 8400 A.

Stalcup M.C.,1991. Salinity Measurements. WHP Operations and Manuals. WOCE Office.

C.2.2. Oxygen Analysis

Ev. Yakushev and S. Borodkin
(P.P. Shirshov Institute of Oceanology Russian Academy of Science)

The dissolved oxygen analysis was performed by analysts from P.P. Shirshov Institute of Oceanology, Moscow (IORAN) following the Winkler method. The procedures for the calibration of volumetric glassware, for the preparation of reagents and for water sampling was similar to corresponding IORAN technique (Chernyakova, 1991). The procedure for calculations of oxygen concentrations based on whole bottle formulas considering the oxygen pickling temperature presented in WHPO publication (Culberson, 1991). The parallel measurements of the oxygen concentrations with reagents prepared by Culberson

and Chernyakova technique hadn't shown the significant differences. Therefore the IORAN technique of reagent preparation was accepted. The sampling procedure hadn't differences in both modifications.

Equipment and Technique

Reagents

The manganese chloride reagent was prepared by dissolving 500 g of analytical grade $MnCl_2 \cdot 4H_2O$ in 600 ml of distilled water. This solution was filtered through the paper filter and made up to 1 liter. The alkaline iodate reagent was prepared by dissolving 700 g of analytical grade KOH in 700 ml of distilled water. If necessary, the solution was filtered. 300 grams of KI were separately dissolved in 450 ml of distilled water. Both solutions were mixed together. The solutions of $MnCl_2$ and KOH/KI reagents were stored in the laboratory. Small portions of these reagents were added before the stations to the plastic bottles were taken on deck. The sulfuric acid (20%) solution was prepared by adding of one volume of analytical grade H_2SO_4 (density 1.84 g/cm3) to four volumes of distilled water. 0.02N sodium thiosulfate was prepared by dissolving of 25.0 g of $Na_2S_2O_3 \cdot 5H_2O$ in 5 liter of fresh prepared distilled water. The starch solution (0.5 %) was prepared by adding 0.5 g of soluble starch to 100 ml of boiling distilled water. Then the solution was boiled for a minute. The reagent blank was determined according to the following procedure. Two ml of sulfuric acid, 1 ml of KI/KOH and 1 ml of manganese chloride solutions were added to 96 ml of distilled water and thoroughly stirred after each addition. After the addition of 1 ml of starch solution a blue color didn't appear in all cases during the cruise. The titration was not necessary, and the value of blank accepted was equal to 0.

Instruments

The oxygen flasks with capacity between 90-140 ml were weight calibrated with accuracy of 0.01 ml in IORAN hydrochemical laboratory (Moscow). A 10 ml weight calibrated automatic burette with scale division every 0.02 ml was used to dispense the thiosulfate. The burette constant errors changed in different ranges from 0.63 ml to 9.54 ml from -0.01 ml to + 0.04 ml. A weight calibrated 10 ml pipette (exact volume 10.00 ml) was used to dispense the potassium iodate solution during standardization. The 1 ml plastic automatic reagent dispensers for KI/KOH and $MnCl_2$ solutions were calibrated by dispensing 1ml ten times into 10 ml graduated cylinder. The calibration checked during the work several times. A magnetic stirrer was used to thoroughly mix the sample during titration.

Sampling Procedure

A six-inch piece of tygon tubing slipped over the outlet valve of the water sampler was used as the drawing tube. The oxygen flasks were rinsed three times with sample water prior to filling. The flasks were overflowed at approximately 3 bottle volumes of sample water. The $MnCl_2$ and KOH/KaI reagents were added immediately after sampling with the dispensers. The stoppers were carefully placed in the bottles to avoid the introduction of the air bubbles. The flasks were carefully shaken (at least 15 energetic turns) and were

stored in the laboratory while the precipitate settled on the bottom (about 30 minutes). The temperature of the collected water was measured using a digital thermometer connected to the tygon tubing used for the nutrient sampling just when the oxygen flask was pickling. The precipitate dissolved when 2 ml of sulfuric acid solution had been added. A magnet was placed in the flask and the flask was placed on a magnetic stirrer.

The titration provided using 10-ml automatic burette. The sample was titrated with the thiosulfate solution until it became a light straw color. 1 ml of starch added as an indicator and titration continued up to elimination of the blue solution.

Calculations of Oxygen Concentrations

The procedure of calculations of the oxygen concentrations followed one described by Culberon (Culberson, 1991). A corresponding Turbo C program had been written during the cruise. The oxygen pickling temperature and the AUTOSAL salinity determination results were used for the conversion of volumetric to weight concentrations.

Table C.3 Duplicate Samples Collected on Multanovskiy Cruise 40. Samples were collected from single Niskin bottles. The differences between the oxygen measurements made on these duplicate samples are shown. The standard deviation of the oxygen differences is 0.9 umol/kg (0.0005 ml/l).

Station Number	Flask Number	Oxy. Diff.		Station Number	Flask Number	Oxy. Diff.	
		ml/l	umol/kg			ml/l	umol/kg
4	43,17	0.03	1.2	69	1,10	0.00	0.1
4	15,18	0.04	1.8	69	3,12	0.01	0.6
4	16,19	0.00	0.2	69	24,13	0.01	0.4
9	10,46	0.02	0.8	69	5,14	0.02	0.7
10	19,46	0.02	1.0	69	6,16	0.04	1.8
10	20,47	0.02	0.6	69	8,17	0.05	2.4
15	23,24	0.04	1.5	69	9,18	0.01	0.1
16	23,24	0.03	1.1	72	19, 1	0.01	0.2
19	17,46	0.06	2.7	72	20, 2	0.01	0.2
19	16,47	0.03	1.6	76	22,23	0.05	1.9
32	15, 1	0.01	0.3	77	19,13	0.00	0.1
33	20, 1	0.02	1.1	77	20, 1	0.00	0.1
35	19, 1	0.01	0.3	80	19, 1	0.01	0.7
36	18, 1	0.03	1.4	80	9,10	0.02	1.1
39	20, 1	0.03	1.2	81	19, 1	0.00	0.2
40	20, 1	0.00	0.2	81	20, 2	0.01	0.1
41	18, 1	0.02	1.0	84	20, 1	0.01	0.3
44	23, 1	0.02	1.1	85	19, 1	0.00	0.3
45	20, 1	0.01	0.6	88	19, 1	0.01	0.5
49	21, 1	0.02	0.9	88	20, 2	0.00	0.1
50	10,22	0.02	0.8	89	19, 1	0.02	1.0
50	8,21	0.02	1.0	92	10, 1	0.01	0.4

Station Number	Flask Number	Oxy. Diff.		Station Number	Flask Number	Oxy. Diff.	
		ml/l	umol/kg			ml/l	umol/kg
51	10,23	0.03	1.6	95	19, 1	0.01	0.3
54	20, 2	0.01	0.5	98	19, 2	0.01	0.2
54	19, 1	0.01	0.2	98	20, 1	0.01	0.3
54	21,24	0.00	0.1	98	1, 1	0.00	0.0
55	19, 1	0.02	1.1	101	19, 1	0.00	0.2
58	5,12	0.04	1.9	101	20, 2	0.01	0.4
59	19, 2	0.00	0.1	101	21, 3	0.03	1.2
62	8,16	0.03	1.3	105	19, 1	0.04	1.7
62	7,15	0.00	0.2	105	20, 2	0.00	0.1
62	6,14	0.06	2.4	108	19, 1	0.02	0.9
62	5,13	0.01	0.4	108	20, 2	0.00	0.0
62	24,12	0.03	1.2	113	19, 1	0.03	0.9
62	2,10	0.02	0.6	113	20, 2	0.01	0.4
62	1, 9	0.02	1.1	114	19, 1	0.01	0.6
63	19, 1	0.02	0.7	114	20, 2	0.02	0.6
63	20, 2	0.00	0.1	119	19, 1	0.00	0.1
66	19, 1	0.00	0.1	119	20, 2	0.01	0.5
66	20, 2	0.01	0.2	120	19, 1	0.01	0.3

Calibrations and Standards

The potassium iodate standard solution (0.020 N) was prepared using 0.7134 g of twice crystallized dried at 105˚C analytical grade KIO_3 weighted in the IORAN Laboratory of hydrochemistry (Moscow). This KIO_3 was dissolved and making up to 1 liter with distilled water using in 1-liter glass volumetric flask. The solution was stored in a glass bottle with ground glass stopper in the refrigerator. For calibration it was prepared a solution by adding of 10.00 ml of potassium iodate standard solution with weight calibrated 10 ml pipette to approximately 80-100 ml of distilled water in an oxygen flask. Two ml of sulfuric acid, 1 ml of KI/KOH and 1 ml of manganese chloride solutions were consequently added and the solution thoroughly stirred after each addition. Then the solution was titrated with thiosulfate using automatic burette. The difference between three-four parallel titer determination was during the cruise less then 0.02 ml. The thiosulfate titer checked during the cruise every second day. The replicate dissolved oxygen samples were collected from the single 1 liter Niskin bottles during the cruise every day and titrated to asses the precision of the dissolved oxygen measurements. Table C.3 shows these results.

The standard deviations of the two tests was 0.918 umol/kg (0.0005 ml/l) indicated the precision was about 0.4%. On the first station of the voyage the Culberson and Chernyakova reagent preparing modifications were parallel used. The differences in reagent solution concentrations are shown in Table C.3. The soviet made REACHEM reagents used in the solution's preparation. 22 measurements collected from separate Niskin bottles tripped at the same depth indicated that a difference less then 0.05 ml/l. A very short range didn't allow calculation of the deviation.

Comparison with Historical Data

To check accuracy we compared our results with the data of Atlantis-2 cruise (1981). The present data set agrees with the old within our reproducibility. The maximum oxygen concentrations (greater than 6.5 ml/l) were observed in bottom layer of the western part (latitude 73˚W) of the section. The minimum oxygen concentrations (less than 3.3 ml/l) were observed in the oxygen minima layer in the western part of the section. The obtained now picture was more sharp than in 1981 because the water samples were collected not in standard levels but in the hydrophysical extremum levels which depth determined before the sampling by the temperature and salinity soundings.

C.2.3 Nutrient Analyses

Ev. Yakushev and V. Konnov
(P.P. Shirshov Institute of Oceanology Russian Academy of Science)

Equipment and Technique

The nutrient analyses were performed by a team of analysts from P.P. Shirshov Institute of Oceanology (Moscow) and Arctic and Antarctic Research Institute (S-Petersburg) using an ACE AutoAnalyzer model and KFK-3 photoelectric photometer. The methods for silicate acid, nitrates plus nitrite and nitrite were those given in AKEA manual (DATEX AKEA, 1978). The method for phosphate was an adaptation of Murphy-Riley method for photometers (Modern Methods, 1992). The Photometer KFK-3 (Photoelectric Photometer, 1992) was made by the Optico Mechanical Plant in Sergiev Posad (ZOMZ). KFK-3 provides measurements in spectral diapason from 315 to 990 nm with absolute error no greater than 0.15%. The 100 mm cuvets were used to analyze both phosphate and nitrite.

Sampling Procedure

Sampling for nutrients followed that for dissolved oxygen on average 15-30 minutes after the casts were on deck. Samples were drawn into 500 cm^3 high-density polyethylene, narrow mouse, screw-capped bottles. Then they were immediately drawn into 50 ml Nessler cylinders (for phosphate and nitrite analyses) and introduced into the AKEA sampler (for silicate acid and nitrate plus nitrite analyses) by pouring into 4 cm^3 polysteren cups which fit the AKEA sampler tray. The 500 cm^3 bottles, 50 ml Nessler cylinders and 4 cm^3 cups were rinsed three times prior to filling. Analyses routinely were begun within 5-15 minutes after the 500 cm^3 bottles were filled and completed within additional hour and a half.

Procedure of analyses

Phosphates

A method based on the Koroleff (Koroleff, 1972) proposals was used. The produced color intensity is measured with KFK at 885 nm in a 100 mm cell.

Reagents.

REACHEM reagents were used:

Molybdate reagent

Ammonium heptamolybdate (a.g.)	15.0 g
Distilled water, q.s.	500.0 ml

Sulphuric Acid

Sulphuric acid 5 N

Antimonyl Potassium Tartrate

Antimonyl potassium tartrate	0.34 g
Distilled water, q.s.	250.0 ml

Ascorbic Acid

Ascorbic Acid	5.4 g
Distilled water, q.s.	100.0 ml

Calibration and Standards

Stock standard 10 000 mkg-at P /l was prepared by dissolving of salt (1.3609 g KH_2PO_4) in a 1000 ml volumetric flask and diluting to volume. The salt was re-crystallized, dried at 110oC and weighted in the IORAN Laboratory of hydrochemistry (Moscow).

Silicate

The silicate method for AKEA utilized the method introduced by Grasshoff based on the formation of B - 1:12 silico-molybdic acid and its partial reduction to a blue heteropoly acid. The color intensity was measured at 880 nm with a 20nm flow cell.

Reagents.

MERCK reagents were used.

Molybdate reagent:

Ammonium heptamolybdate (a.g.)	10.0 g
Sulphuric acid 5 N	40.0 ml
Distilled water, silicate-free q.s.	1000.0 ml

Complexing Composition:

Oxalic acid (a.g.)	7.0 g
Sulphuric acid, conc.	50.0 ml
Distilled water, silicate-free q.s.	1000.0 ml

Reducing Reagent:

Metol (p-methylaminophenol sulphate)	10.0 mg
Anhydrous sodium sulphite	12.0 g
Distilled water, silicate-free q.s.	1000.0 ml
Wetting Agent LEVOR I	0.25 ml

Wash Solution:

Sodium chloride (a.g.)	20.0 g
Distilled water q.s.	1000.ml

Calibration and Standards

Stock standard 10 000 mkg-at Si /l was prepared by dissolving of salt (0.950 g Na_2SiF_4) in a 500 ml volumetric flask and diluting to volume. The salt was re-crystallized, dried over concentrated sulfuric acid and weighted in the IORAN Laboratory of hydrochemistry (Moscow).

Working solutions, containing 1 mkg-at Si/ml were prepared with the 0.5 ml glass weight calibrated pipett and 500 ml weight calibrated flask. The solutions were prepared in distilled water. The apparent silicate contents were corrected for a salt error, which was determined separately in the beginning and the end of the cruise, and consisted percent.

Nitrates plus Nitrites

The nitrate method for AKEA utilizes the method introduced by Wood, Armstrong and Richards whereby nitrate is reduced to nitrite by a copper cadmium reductor column. The nitrite is converted to a reddish-purple azo-dye by using sulfanilamide and N-1-naphthylethylendiamine dihydrochloride for the diazotisation. The produced color intensity is measured at 520 nm in a 20 mm flowcell.

Reagents

MERCK reagents were used.

Ammonium Chloride Buffer Solution:

Ammonium chloride	10 g
Distilled water q.s.	1000 ml
Concentrated ammonia solution	
Triton X-100, 15 % solution	1.0 ml

Sulfanilamide:

Sulfanilamide	5 g
37 % Hydrochloric acid	35 ml
Distilled water, q.s.	1000 ml

N-1-Naphthylethylendiamine Dihydrochloride:

N-1-Naphthylethylendiamine dihydrochloride	0.5 g
Distilled water, q.s.	1000 ml

Wash Solution:
Distilled water

Copper Cadmium Reductor Column:
Copper cadmium
Glass reductor column

Calibrations and Standards

Stock standard 10 000 mkg-at N /l was prepared by dissolving of salt (1.0110 g KNO_3) in a 1000 ml volumetric flask and diluting to volume. The salt was re-crystallized, dried at 110˚C and weighted in the IORAN Laboratory of hydrochemistry (Moscow).

Nitrites

Nitrite is converted to a reddish-purple azo-dye by using sulfanilamide and N-1-naphthylethylendiamine dihydrochloride for the diazotisation. The produced color intensity is measured with KFK at 543 nm in a 100 mm cell.

Reagents

REACHEM reagents were used.

Sulfanilac Acid:

Sulfanic acid	1 g
Acetic acid 12 %, q.s.	300 ml

Alpfa-Naphthylamin:

Alpha-naphthylamin	0.4 g
Acetic acid 12 %, q.s.	300 ml

Griss Solution:
Equal parts of Alpha-naphthylamin and sulfanic acid solutions.

Calibrations and Standards

Stock standard 10 000 mkg-at N /l was prepared by dissolving of salt (0.6910 g $NaNO_2$) in a 1000 ml volumetric flask and diluting to volume. The salt was dried at 110˚C and weighted in the IORAN Laboratory of hydrochemistry (Moscow).

Conversion of Volumetric to Weight Concentrations

The obtained values of phosphate, silicate, nitrate and nitrite were converted into weight concentrations. To calculate the seawater density there were used the salinity data obtained with AUTOSAL and temperature of seawater in the moment of the sample bottles filling (the same as at which oxygen samples were pickled). The same formulas as for the oxygen conversion were used (Culberson, 1991).

According to the recommendations of Gordon (Gordon et al, 1993) the temperature of the laboratory air should be used. But it doesn't appear to be optimal: for silicates analysis the + 50˚ bath is used while the nitrate+nitrite analysis is provided without a bath under the plastic cover (the similar for AKEA, TECHNIKON and ALPKEM). Additionally in our case phosphate and nitrites were measured using the 50-ml Nessler cylinders with relatively large volumes of water.

The temperature at which the samples were drawn had been accepted because water samples from bottles of relatively large volume (about 250 ml) were drawn into AKEA cups and Nessler cylinders very quickly (from 1-2 to 15-20 minutes). The difference between the water samples from deep (less then 10˚C) and surface (up to 27˚C) remained even in an hour, when the phosphate samples were taken into photo-colorimeter.

Nevertheless the nutrient laboratory temperature was measured and results are given in Table C.4. The row of temperature at which oxygen was pickled is given in the WHP massive as an additional row.

Table C.4 Nutrient laboratory temperatures for each station.

St.	Date	Time	T˚C	St.	Date	Time	T˚C	St.	Date	Time	T˚C
3	092393	2305	22	47	100593	1100	24	91	101693	1720	25
4	092493	0120	21	48	100593	1535	25	92	101693	2345	25
6	092493	0520	21	49	100593	1945	25	93	101793	0720	25
7	092493	0840	22	50	100693	0015	24	94	101793	1530	25
8	092493	1130	22	51	100693	0445	24	95	101793	2350	25
9	092493	1640	22	52	100693	0920	25	96	101893	0735	25
10	092493	2245	23	53	100693	1345	26	97	101893	1415	25
11	092593	0530	23	54	100693	2030	26	98	101893	2200	25
12	092593	1140	22	55	100793	0235	26	99	101993	0530	24
13	092593	1630	22	56	100793	0940	26	100	101993	1230	24
14	092593	2215	22	57	100793	1530	26	101	101993	2030	24
15	092693	0330	22	58	100793	2130	25	102	102093	0315	23

St.	Date	Time	T˚C	St.	Date	Time	T˚C	St.	Date	Time	T˚C
16	092693	0850	22	59	100893	0350	24	103	102093	0945	23
17	092693	1420	22	60	100893	0850	23	104	102093	1720	23
18	092693	1830	22	61	100893	1415	23	105	102193	0005	23
19	092693	2320	22	62	100893	1925	23	106	102193	1040	24
20	092793	0450	22	63	100993	0415	23	107	102193	1715	24
21	092793	1050	22	64	100993	1030	24	108	102293	0055	24
22	092793	1645	23	65	100993	1645	25	109	102293	0445	24
23	092793	2315	22	66	100993	2325	25	110	102293	0845	25
24	092893	0540	22	67	101093	0615	25	111	102293	1245	25
25	092893	1230	22	68	101093	1230	25	112	102293	1620	24
26	092893	2000	23	69	101093	1925	25	113	102293	2030	23
27	092993	0300	23	70	101193	0100	25	114	102393	0030	22
28	092993	0830	22	71	101193	1200	26	115	102393	0420	22
29	092993	1340	23	72	101193	1855	25	116	102393	0830	22
30	092993	2350	22	74	101293	0715	26	117	102393	1215	22
31	093093	2355	23	75	101293	1315	26	118	102393	1555	22
32	100193	1740	23	76	101293	1955	26	119	102393	2015	22
33	100293	0025	23	77	101393	0230	26	120	102493	0106	22
34	100293	1015	23	78	101393	0835	25	121	102493	0540	22
35	100293	1545	23	79	101393	1445	26	122	102493	0830	22
36	100293	2130	23	80	101393	1935	26	123	102493	1020	22
37	100393	0345	23	81	101493	0100	26	124	102493	1355	22
38	100393	0935	23	82	101493	0740	26	125	102493	1630	22
39	100393	1500	24	83	101493	1345	26	126	102493	1930	22
40	100393	2030	24	84	101493	2040	26	127	102493	2230	22
41	100493	0230	24	85	101593	0325	25	128	102593	0055	22
42	100493	0825	24	86	101593	0940	25	129	102593	0315	22
43	100493	1435	24	87	101593	1545	25	130	102593	0525	22
44	100493	2000	24	88	101593	2230	25	131	102593	0730	22
45	100593	0115	24	89	101693	0455	25	132	102593	0850	22
46	100593	0640	24	90	101693	1120	25	133	102593	1025	22

Comparison with WHOI Standard Solutions

In Woods Hole we checked our standard solutions with the WHOI ones. Dr. Zofia Molodzinska kindly presented the standard solutions taken into the analysis procedure. The WHOI phosphate standard appeared to be 4% higher than our standard. The difference between the nitrates solutions was about 3% (the WHOI standard was higher). The silicate standards haven't differed at all.

The differences for phosphates and nitrates were relatively large but correspond to the methods accuracy. It's a pity, the measurements were provided at sea after we left Woods Hole, so it was not possible to repeat them and to check the standard qualities.

Comparison with Historical Data

To check accuracy we compared our results with the data of Atlantis-II cruise (1981).

The present data of nitrates set agrees with the old within our reproducibility. The concentrations reached 20 umol/l in the bottom layers of western part and 22-24 umol/l in western part. The maximum concentration (29 umol/l) was found in the maximum layer at depth 935 m at latitude 71˚W. The minimum concentrations (0 umol/l) observed in the surface layers.

The phosphate fields also agreed with the old ones. The maximum concentrations were observed in bottom layer (1.4 umol/l in western part and 1.6 umol/l in eastern) and in the layer of maximum in the western part (1.7 umol/l). The minimum concentrations (0 umol/l) were observed in the surface layer.

The silicate concentrations were found some greater than in 1981. The maximum concentrations (greater than 50 umol/l) were observed in the bottom layer at the latitude 56˚W. The concentration in the maximum layer was 24 umol/l. The minimum values (less than 1 umol/l) were observed in the surface waters.

As for oxygen, the 1993 pattern was more contrast than 1981, because the water samples were collected not at standard levels but at the hydrophysical extremum levels which were determined during the temperature and salinity downcast soundings.

RV "Professor Multanovskiy" Leg 1
Sep 23 - Oct 25, 1993
Hamburg, Germany to Woods-Hole, USA
Chief Scientist V.Tereschenkov
State Oceanographic Institute, Moscow, Russia

1. CTD measurements

1.1 Chief scientist overview

The ship occupied total of 133 hydrographic stations along A3 (WHP-ID) section. Detailed information on stations' position can be found in 90CT40.sum file. The stations were occupied from the surface to the bottom with respect to the fact that the sounding instruments in use were not equipped with the altimeter. Thus precautions were taken to avoid the contact of the instrument with the bottom, what resulted in the absence of near bottom observations. The first 31 stations were carried out using the NBIS Mark-3B CTD system owned by the VNIIRO (Russian Fishery and Oceanography Institute, Moscow Russia). The rest of the stations were occupied with the Hydrozond-6000 CTD system, possessed by the AARI (Arctic and Antarctic Research Institute, St. Petersburg, Russia). The latter instrumentation was produced by Central Design Bureau of the Hydromet Instruments (Obninsk, Russia).

The switch of the CTD occurred due to unexpected loss of the NBIS CTD device, which sledded off the cable wire on the way up and drowned. The reasons of the accident were thoroughly investigated. The conclusion indicated the malfunctioning of the "frog-type" grasping mechanism and no operator fault.

In any case the following information will be concerned with both measuring systems.

1.2 CTD data collection and processing.

1.2.1 CTD data acquisition

Three channels (pressure, temperature, conductivity) were acquired by the NBIS Mark-B CTD at a data rate of 15.85 Hz and Hydrozond-6000 at a data rate of 4 Hz. The CTD signal was demodulated by a deck unit and output to an RS-232 bus interface. A 386DX IBM PC with a 120 Mb hard disk and 1 Mb RAM was used as the primary data collection device. The data from NBIS CTD has been logged in the computer using EG&G Oceansoft MkIII/SCTD Acquisition Software package.The data from Hydrozond-6000 was logged using a software package developed by SOI computer group. Each cast data were transferred to Phillips 386DX computer with 640 Mb hard disk and 8 Mb memory for further processing. A backup of all the data was stored on magnetic cartridge tape and magnetic diskettes.

1.2.2 CTD Laboratory Calibrations

The manufacturer's sensor specification is given in Table 1. The pre-cruise calibration was performed only for the NBIS Mark-3B CTD.

The laboratory calibration was performed by VNIIRO group, using EG&G Ocean Products calibration stand. All the standards have been certified by both the US and Russian National Standards Bureau. The post cruise calibration of the unit was impossible due to the loss of the instrument.

The Hydrozond-6000 sensors were not calibrated in the laboratory water bath at all. According to the routine adopted by the Russian Hydrometeorological Service the supervisor of the CTD owner AARI, only the scheduled check and correction of the resistant bridges of the measuring circuit were fulfilled two month prior to the cruise.

Table 1 Manufacturer CTD sensor specification.

Sensors	NBIS Mark - 3B		Hydrozond - 6000	
	resolution	accuracy	resolution	accuracy
Pressure, dbar |%	0.1	6.5	1	0.5%
Temperature, °C	0.0005	0.005	0.01	0.02
Conductivity, mS/cm	0.001	0.005	0.01	0.03

1.2.2.1 Pressure Transducer Calibration

NBIS CTD Paine Instruments pressure transducer was calibrated in a temperature controlled bath by comparison with the pressures generated by an EG&G Chandler Engineering 58-001J-T-1 piston pressure gage. The calibration tests showed the accuracy of the CTD sensor of ± 2 dbar in a pressure range 0-9000 psi with respect to the loading - unloading hysteresis.

1.2.2.2 PRT Temperature Calibration

The NBIS CTD Rosemount PRT temperature sensor was calibrated in a temperature controlled bath by comparison to a standard PRT used in EG&G Ocean Products calibration system. The latter was checked against the known water and diphenyl ether triple point cells. The calibration tests showed the agreement of the two sensors readings within ± 0.002°C.

1.2.3 Field calibration

As long as Hydrozond-6000 sensors were not calibrated at the laboratory, the at sea calibration was the only one applied to the sensors readings, based on the comparison with the bottled salinity and the pressure and temperature observations obtained by thermometric method using mercury DSRT and UDSRT. Same means were used to control the NBIS pressure and temperature sensor performance and to calibrate the NBIS CTD conductivity sensor.

The field calibration routine was performed by producing a polynomial fit of the CTD pressure, temperature and conductivity readings with the appropriate measurements of the onboard salinometer and reversing thermometers. The CTD values obtained by averaging the CTD sensors readings taken during 15 seconds before the bottles were fired and thermometer racks reversed. The bottles not equipped with the thermometer racks were kept at the sampling level for 30 seconds, otherwise they stayed unmoved for 3 minutes, the time interval adequate for thermometers to stabilize. All the data selected for calibration was subjected to 2.8 standard deviation rejection.

These procedures require an established level of confidence in the auxiliary observational tools.

1.2.3.1 DSRT and UDSRT

During the cruise the DSRT and UDSRT produced by Gohla Precision (Kiel, Germany) were implemented (see Table 2). The possibility to utilize the temperature and pressure values determined by these instruments for needs of CTD calibration is based on the research of Quadfasel, Verch and Langhof (1991).

One of the advantages of the mercury thermometers is their highly stable time behavior. The time drift of the measurements is shown to be only ± 1.4 mK/year.

Calibration of the Gohla Precision instruments is done with an accuracy of 0.001°C.

Table 2 Gohla Precision DSRT and UDSRT summary.

Instrument	Serial#	Range	Etching	Calibration date
DSRT	11459	-2+6	0.01	17.07.90
	11709	-2+6	0.01	17.01.92
	11818	-2+6	0.01	25.11.91
	11817	-2+6	0.01	25.11.91
	11816	-2+6	0.01	25.11.91
	11738	-2+16	0.02	16.01.92
	11739	-2+16	0.02	21.11.91
	11741	-2+16	0.02	21.11.91
	11835	-2+16	0.02	21.11.91
	11959	-2+35	0.1	19.11.91
	11960	-2+35	0.1	19.11.91
	11626	-2+35	0.1	09.11.90
	12067	-2+35	0.1	19.11.91
UDSRT	11519	+30+60	0.1	16.05.91
	11520	+30+60	0.1	16.05.91
	11521	+30+60	0.1	16.05.91
	11428	-1+35	0.1	30.05.90
	11427	-1+35	0.1	30.05.90
	11426	-1+35	0.1	30.05.91
	11492	-2+60	0.2	07.06.90
	11491	-2+60	0.2	07.06.90
	11695	-2+60	0.2	27.11.91

The manufacturer claims the accuracy of the thermometers to be 0.5 of the etching interval. But with the experienced observers we believe it to be 0.2 of the etching interval.

The field test of the thermometers was performed on a test station. All the thermometers were reversed on the same level within the homogeneously stratified water layer. The standard deviation of the high resolution DSRT was 0.005°C. These instruments were mainly used for calibration purposes. The scatter of the low-resolution thermometers was within ± 0.01°C. These DSRT were used in 1-2 racks put above the thermocline. Same tests were performed several times during the cruise with similar results.

At the first 31 station the pairs of DSRT were changed all the time. And in all cases the difference between the measured temperatures was less than the warranted accuracy. After that the combinations of the DSRT stayed permanent. The differences between the reading of the DSRT and UDSRT in the same rack didn't change with time confirming the time stability of the instruments. The variations between the pressure measurements carried out by different UDSRT agreed within 0.3% of the depth.

The thermometric measurements of pressure and temperature were supervised by A. Sokov (now at P.P. Shirshov Institute of Oceanology).

1.2.3.2 Bottle salinity

The water sample salinity were measured with a Guildline Autosal Model 8400A salinometer N54403 that was standardized daily (usually twice) with IAPSO Standard Sea Water Batch 115. The last calibration of the salinometer was carried out by Guildline representation on May 1991. All measurements, initial quality control and shipboard data-processing were performed by S.A. Dobroliubov (Moscow State University). A total of 3094 water samples from 132 stations (more than 23 samples per each) were analyzed for salinity including 80 replicates.

Salinity samples were collected strictly according to WHP Manual (Stalcup, 1991).

The published accuracy of the 8400A salinometer according to Operating Manual is 0.003 psu. But if measurements are made in a laboratory with quasi-constant temperature ±1°C (as in our case) it should be possible to reach the precision better than 0.001 psu. All the procedures to attain highest accuracy described in the Operating Manual (section 6.5) were performed. Mean difference between standardizations was 0.0004 psu. These shifts were linearly interpolated between the first and the last sample readings. The salinometer readings were inverted to salinity in accordance with Guildline Operational Manual formula and Practical Salinity Scale-1978.

Autosal calibration control was performed weekly with a simple suppression switch check described by Stalcup (1987). This check showed the absence of any discontinuities. Another data control included replicate analysis. 21 pair of samples were collected from the same 1.8l Niskin bottles at different stations. Module mean difference between the salinities of these pairs was 0.0007 psu with standard deviation 0.0006 psu. The same procedure was promoted with Hydrozond-6000 1.2l bottles. 59 replicates were collected including two calibration casts and its analysis revealed module mean salinity difference of 0.0009 psu with standard deviation 0.0007 psu. From this point of view the difference in measurements' accuracy with both types of bottles was considered to be statistically insignificant.

1.2.3.3 NBIS Mark-3B vs. thermometric pressure and temperature

Statistics of NBIS Mark-3B temperature and pressure comparison with DSRT (temperatures) and UDSRT (pressure) observations is presented in Table 3. The good agreement is a justification for DSRT and UDSRT measurements application to Hydrozond-6000 calibration.

1.2.3.4 Hydrozond-6000 pressure correction

The Hydrozond-6000 CTD uses three separate pressure sensors each working in a certain pressure range without any overlaps. The switch between the sensors occurs at prescribed pressure readings that are 320 and 1780. The switch between the sensors

was accompanied by a jump in pressure readings. So for each station these jumps were determined and eliminated by applying a local pressure offset to the preceding readings in order to ensure the continuous records.

The analyses of the initial pressure records also revealed consistent peculiarities in the sensor behavior. All the records had a noticeable "silence" zone. That is by reaching certain pressure (reading) 1000 and 3100 the readings didn't change for approximately 40 and 250 seconds consequently. To avoid this effect and maintain the gradual pressure change, the averaged pressure time increment was calculated for periods of 30 seconds before and after the "silence" zone. Than the difference between the time increment was linearly distributed for time interval corresponding to the constant pressure segment and used to model the real pressure behavior. The pressure offset that occurred at the end of the "silence" zone was applied to the preceding pressure readings.

1.2.3.5 Hydrozond-6000 pressure calibration

As long as all the bottle samples were drawn during the CTD up cast and without a lab pressure calibration we had to trip some bottles with the thermometers racks on the way down in order to determine the pressure loading calibration. This has been done during the occupation of three special pressure calibration stations and several times with one bottle fired on a downcast during the routine work. All together 39 observations were selected to perform the loading pressure calibration.

Fitting of (both loading and unloading) CTD and thermometric pressures was done by a third order polynomial.

Special attention was paid to the detected Hydrozond-6000 pressure hysteresis. To obtain the up cast pressure the following formula was used:

$$Pcor = Pmes - (ofs_d + (ofs_u-ofs_d)/Pmax*(Pmax-Pmes))$$

where: Pcor - corrected pressure
Pmes - measured pressure
Pmax - maximum downcast pressure
ofs_d - downcast pressure offset
ofs_u – up cast pressure offset

Summary of CTD and thermometric pressure comparison can be found in Table 4.

1.2.3.6 Hydrozond-6000 temperature calibration

The CTD temperatures were calibrated against the DSRT measurements using the 3-order polynomial. The time drift of the CTD sensor was detected and taken care of by applying a linear correction. Summary of CTD and thermometric temperature comparison can be found in Table 4.

1.2.3.7 NBIS Mark-3B and Hydrozond-6000 conductivity calibration

The Hydrozond-6000 CTD conductivity measurements were calibrated against the Autosal bottle conductivity measurements using the 3-order polynomial.

For NBIS Mark-3B the second order polynomial has been used. The both CTD conductivities were corrected for station and pressure dependence.

Summary of CTD and bottle salinities comparison can be found in Tables 3 and 4.

Table 3 Bottle vs. NBIS Mark-3B CTD statistical summary.

Parameter	pressure range (dbar)	Mean difference	Standard deviation	#values in mean
Pressure	all pressures	-0.07822	4.03609	23
	press < 1500	-0.95554	5.45300	9
	press > 1500	0.48477	2.89719	14
Temperature	all pressures	-0.00040	0.00577	26
	press < 1500	-0.00069	0.00664	12
	press > 1500	-0.00016	0.00514	14
Salinity	all pressures	-0.00022	0.00307	471
	press < 1500	0.00045	0.00377	220
	press > 1500	-0.00081	0.00213	251

Table 4 Bottle vs Hydrozond-6000 CTD statistical summary.

Parameter	pressure range (dbar)	Mean difference	Standard deviation	#values in mean
Pressure	all pressures	-0.45583	13.87512	120
	press < 1500	2.94694	9.30399	49
	press > 1500	-2.80423	15.94445	71
Temperature	all pressures	-0.00053	0.00943	103
	press < 1500	-0.00251	0.01110	28
	press > 1500	0.00021	0.00859	75
Salinity	all pressures	0.00036	0.00981	1756
	press < 1500	0.00050	0.00997	832
	press > 1500	0.00013	0.00966	924

1.3 CTD processing

1.3.1 NBIS Mark-3B processing

The NBIS Mark-3B station records were processed by procedures adopted in BSH, Germany.

- the pressure offset (on deck the pressure sensor readings) is subtracted from the record.
- starting cycles corresponding to time period of conductivity sensor adaptations to water conditions are eliminated from the record
- pressure records are smoothed by Bezier cubic splines in order to digitize pressure beyond the sensor resolution and to evaluate the package speed
- time lag correction is applied to pressure and conductivity due to inertion of the PRT sensor. The time lag was determined by deriving the least spiking salinity profile.
- cycles corresponding to CTD upward or extreme movements (less are than 0.4 dbar/sec and greater than 2.5 dbar/sec) are eliminated
- temperature and conductivity are twice subjected to median filter (window 31)
- temperature and conductivity are subjected to running mean filter (window 21)
- 2 dbar averaging is performed in accordance to the scheme suggested by R. Millard and Keqi Yang (1992).

1.3.2 Hydrozond-6000 processing

The routines applied to Hydrozond•6000 CTD data were based on traditional procedures of signal digital processing adopted for specific features of the measuring device.

The peculiarity of the Hydrozond-6000 is the three pressure sensors working at different pressure ranges. The sensors differ by sensitivity and as a consequence, they are characterized by different spectral structure of the "noise" and different "signal" to "noise" ratio. That instantly leads to a necessity of independent treatment of each sensor record and smooth merge of the records.

So, at the first stage the segments of the records corresponding to each sensor were detected. Within the each segment the spike 2.5 standard deviation control against the local second order polynomial was performed for all measured parameters.

The noise elimination was done by a running mean filter, with utilization of second order polynomial values as weights. The filter windows were 21,51,121 for consequent pressure sensor and 21 for both temperature and salinity sensors. Application of the polynomial has a good advantage compared to usual equal weighted running mean filters. It allows us to consider the evident temporal trends of parameters. To avoid the energy "alias-ing", that is common for the running mean filters, the second filter run has been done, with changed window, which was chosen as 3/4 of the initial.

This changes the frequency characteristic of the filter in such a manner, that now the extremes match the zeroes of a first run filter.

The rest of the processing was in an agreement with R. Millard and K. Yang (1992). 10 dbar averaging has been selected to maintain statistics within the averaging bin, considering the sampling rate of 4Hz.

1.4 General comments/problems

The temperatures measured by CTD are all in ITS-68.

On station 5, the sounding was performed with unremoved cover of the conductivity sensor. The station was repeated at the same location (station 6). At stations 23, 24, 25, 26, 27, 28, 29, 30, 31 artificial staircases were detected at depth 1200 – 2000 db. For these data digital smoothing polynomial filter of 2-order was applied.

On several stations conductivity sensor of Hydrozond-6000 didn't perform well. This was detected by TS relation analyses and comparison with historical data (RV Atlantic-II, 1981 and RV Chain, 1959). For these reasons data from stations 70 and 71 was rejected completely. Observations at station 55 in 981-1350 dbar layer were omitted, as well as the observations at station 69 in a layer from the surface to 3570 level. Near bottom records at stations 32, 38, 62, 84, 121 were eliminated due to same argumentation.

Some suspicions exist concerning the observations in 2000 – 2300 dbar layer of station 101, although the data is reported.

Special caution must be attributed to all the Hydrozond-6000 data in the deep layers. Some low-scale salinity variations were spotted in almost all the profiles. The origin of these fluctuations are still under consideration, so no corrections were applied to the data. Therefore it must be kept in mind that the data must be expertly treated in accordance with the specific individual research goals.

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