
IOS Institute of Ocean Sciences
 9860 West Saanich Road
 Sidney, B.C. Canada
 V8L 4B2

Taiwan National Sun Yet-sen University
 Kaohsiung, Taiwan

Camosun College Camosun College
 Victoria, B.C.

A.4 Scientific Programme and Methods

Our plans to intensify sampling and modify procedures for a WOCE one time survey in 1994 are progressing. The first measurements with a new Feon analyzer concentrated on assessing sample replicability and sources of contamination. Neither lab air nor Niskin bottles introduced serious contamination into deep ocean samples.

Warm, saline waters were present along the B.C. coast. Temperatures were elevated by about 2 C over long term averages, in the mixed layer between P1 and P6. As the mixed layer deepens, the temperature anomaly decreased to 1o C in the upper 100 m (station P26). Only in coastal waters was a decrease in NO3 + NO2 observed. In 1989, February concentrations were about 12 uM, whereas 1992 levels were 8 uM.

**

Warmer than usual surface waters were encountered in the entire region, the result of a warm water mass that Howard Freeland has tracked across the North Pacific for the past year. It is not clear if this is a feature of the current El Nino.

Measurements with a new Freon analyzer were made during this cruise, with promising results. Shipboard and Niskin bottle contamination was less of a problem than had been anticipated.

A.5. Major Problems and Goals not Achieved

The time allotted to the cruise was not sufficient to complete Line R.

Our primary CTD was not compatible with data accumulation software, so the back-up probe was used. This meant we could not use a 3 bottle Rosette that was interfaced with the main CTD.

A.6. Other incidents

None.

A.7. List of Cruise Participants

Table 4: List of Cruise Participants

Name	Responsibility	Affiliation
Frank Whitney	Nutrients	IOS
Keith Johnson	Total CO2	IOS
Shu Lun Wang	Total CO2	Taiwan
Wendy Richardson	Freons	IOS
Ron Bellegay	Water sampling	IOS
Bernard Minkley	T, S, O2, depth	IOS
Les Spearing	CTDs	IOS

Clayton Stark	student	Camosun College
Robert Millar	student	Camosun College

 *See Table 3 for list of Institution

C. Description of Measurement Techniques and Calibrations

C.1. Water sampling

The Tully has a sea water line (sea water Loop) that services its main laboratory. Near the Loop's intake, conductivity and temperature sensors are sampled every 2 minutes and data is logged on the ship's SAIL system. At each CTD station, samples were taken for salinity (to calibrate the conductivity cell) nutrients, chlorophyll a and total CO₂. This sampling is denoted L4M in the .SUM file to indicate a Loop sample nominally from 4 m depth.

Niskin samplers (a combination of 1.7 and 10 L) were used for all hydro casts. Water samples were collected in the order: Freons (10 L bottles only), O₂, TCO₂, nutrients and salinity. Freon samples were drawn into 100 mL glass syringes and then stored under sea water until samples were analyzed. Oxygen samples were immediately pickled with standard reagents (Carpenter, 1965) and the temperature of the sample recorded using a Guildline Model 2175A digital thermometer. TCO₂ samples were pickled with 200uL saturated HgCl₂ solution, and stored cool until coulometrically analyzed onboard. Salinity samples were drawn into borosilicate bottles for analysis onboard ship.

C.2. Hydro cast temperature and depth

Reversing thermometers were used to record temperature and provide correct depths on all hydro casts. Protected thermometers were used in pairs, and an average value recorded, unless a discrepancy greater than 0.04o C occurred. Then thermometers were cross checked with those that were known to be consistant. Unprotected thermometers were used to estimate the bottle depths.

C.3. Oxygen

The micro-Winkler procedure of Carpenter (1965) with a starch end-point titration was used. The sulfuric acid concentration was increased to 420 mL/L (from 320 mL/L) to improve the dissolution of the precipitate. This lowered the pH of titrated samples to 1.78 - 1.95, av = 1.84 (n=4) from a recommended pH of 2, which may increase air oxidation of iodide (Carpenter, 1965). Standards were prepared as outlined in WOCE Report 73/91. A probe colorimeter was tested for sensitivity to the starch endpoint. The use of 10 L Niskins for most of our sampling improved our oxygen results noticeably, since we could flush flasks more thoroughly. Duplicate samples agreed much better than in our last cruise (October 1991).

	Cruise 9105	Cruise 9201
Sp = (sum d ² /2k) ^{0.5}	1.09 uM/kg	0.57 uM/kg
k = no. of pairs	21	22
Range	10 to 280 uM/kg	10 to 300 uM/kg

 Sp is the pooled standard deviations of pairs.

Since sample temperatures were not measured at the time of pickling, CTDTMP (CTD temperature) was used to calculate sample densities. Sample warming between collection and pickling has subsequently been measured as less that 2 C (typically 0.2 to 0.5 C) which increases O₂ concentrations by less than 0.1 uM kg.

4. Nutrients

Samples were collected in 16 x 125 mm polystyrene test tubes (duplicate samples taken from each depth). With the exception of Loop samples and the first hydro cast at P26, all samples were analyzed within 3 h of collection. Loop and P26(1) samples were refrigerated for up to 1 day before analysis (JF1 to P41) or were frozen and analyzed within 2 weeks (P32 to J05). Standard solutions are routinely made at concentrations 100 to 250 times higher than the lowest standards used and are diluted daily for standardizations. These solutions are checked against commercial CSK Standards (WACO Pure Chemical Industries) to verify that no gross contaminations or errors have been made in their preparation. Their molarity is based on the accurate weights taken during preparation. Reagents that have been consistently used for 5 years or longer include KNO₃ (Primary Standard, Fisher), NaSiF₆ (Certified, Fisher) and KH₂PO₄ (Reagent ACS, MCB). Standards have proven to be stable for upto 6 months when preserved with 1 mL/L chloroform and stored in the dark.

An aging Technicon Autoanalyzer sampled a single test tube for NO₃ & NO₂, PO₄ and Si according to Technicon procedures.

NO₃ + NO₂ were reduced with Cd/Cu, then complexed with sulfanilamide and N-Naphthylethylene-diamine to form an azo dye (Technicon Method No. 158-71W/B). PO₄ produces a molybdenum blue complex in presence of acidic molybdate and ascorbic acid (Technicon Method No. 155-71W). Dissolved Si also forms a molybdenum blue complex and oxalic acid removes PO₄ interference (Technicon Method 186-72W). Occasional problems with this equipment caused some minor loss of data quality.

Lab temperatures were occasionally checked during each analytical run.

Station	Date	Temperature (C)
P04	Feb. 4	19.8 to 21.2
P12	Feb. 5	22.8 to 23.5
P16	Feb. 6	23.9 to 24.8
P20	Feb. 7	24.3 to 24.9
P26	Feb. 9	17.2 to 20.6

C.5. Salinity

A Guildline Model 8410 Portosal (SN 58,879) salinometer was used onboard ship to analyze all samples. IAPSO Standard Seawater was used for daily calibrations. Duplicate samples from 2000 to 3800 m, run in sequence, had a standard deviation Sp = 0.001 (k=9), confirming that sampling and analyses are precise, and that Niskin bottles did not leak (since a salinity gradient is evident in leaking bottles).

C.6. CTD

Guildline Model 8715 CTD (SN 58,483) outfitted with a 3000 db pressure sensor, temperature and salinity sensors was used exclusively after the early failure of the primary CTD which had been outfitted with 3 temperature channels. Profiles routinely reached 1500 m.

Guildline Instruments tested a prototype CTD to 3000 m (the limit of our cable) with good success.

C.7. Freons

Since many tests need to be completed before we can supply data of assured quality, we do not intend to submit Freon data from this cruise. However, I will outline our procedures in way of providing a progress report.

Glass syringes (100 mL) were rinsed then filled from the spigot of 10 L Niskin samplers, before other sampling was begun, and always within 1 h of sample bottles coming to the surface. Filled syringes were stored under sea water to reduce possible atmospheric contamination.

An analyzer designed after the system described in Bullister and Weiss (1988) was tested only briefly before going onboard ship. Consequently, most analyses at sea were intended to check the replicability of our sampling and contamination from ship's air and water samplers. Since many new 10 L Niskin bottles were being used without cleaning, it was feared that contamination would obscure intermediate water concentrations. However, deep water blanks (below 1000 m) proved that Freons from 400 to 600 m were detectable.

D. Acknowledgments

E. References

Bullister, J.L. and Weiss, R.F. 1988. Determinations of CCl₃F and CCl₂F₂ in seawater and air. *Deep-Sea Res.* 35: 839-853.

Carpenter, J.H. 1965. The Chesapeake Bay Institute technique for the Winkler dissolved oxygen method. *Limnol. Oceanogr.*, 10: 141-143.

Macdonald, R.W. and McLaughlin, F.A. 1982. The effect of storage by freezing on dissolved inorganic phosphate, nitrate and reactive silicate for samples from coastal and estuarine waters. *Water Res.* 1: 95-104.

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

Unesco, 1991. Processing of Oceanographic Station Data, 1991. By JPOTS editorial panel.

F. WHPO Summary

Several data files are associated with this report. They are the dd9201.sum, dd9201.hyd, dd9201.csl and *.wct files. The dd9201.sum file contains a summary of the location, time, type of parameters sampled, and other pertinent information regarding each hydrographic station. The dd9201.hyd file contains the bottle data. The *.wct files are the ctd data for each station. The *.wct files are zipped into one file called dd9201.wct.zip. The dd9201.csl file is a listing of ctd and calculated values at standard levels.

The following is a description of how the standard levels and calculated values were derived for the dd9201.csl file:

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

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

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

Sigma-theta(SIG-TH:KG/M3), Sigma-2 (SIG-2: KG/M3), and Sigma-4(SIG-4: KG/M3): These values are calculated using the practical salinity scale (PSS-78) and the international equation of state for seawater (EOS-80) as described in the Unesco publication 44 at reference pressures of the surface for SIG-TH; 2000 dbars for Sigma-2; and 4000 dbars for Sigma-4.

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

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

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

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

Potential Energy (PE: J/M2: 10-5) and Dynamic Height (DYN-HT: M) are calculated by integrating from 0 to the level of interest. Equations and Fortran routines are described in Unesco publication, Processing of Oceanographic station data.

Neutral Density (GAMMA-N: KG/M3) is calculated with the program GAMMA-N (Jackett and McDougall) version 1.3 Nov. 94.

G. Data Quality Evaluation□