3 Hydrographic Measurement Techniques and Calibrations

3.1 CTD/O₂ Measurements

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(2) Winch arrangements

The CTD package was deployed by using 4.5 Ton Traction Winch System (Dynacon, Inc., Bryan, Texas, USA), which was installed on the R/V MIRAI in April 2001. The CTD Traction Winch System with the Heave Compensation Systems (Dynacon, Inc.) is designed to reduce cable stress resulting from load variation caused by wave or vessel motion. The system was operated passively by providing a nodding boom crane that moves up or down in response to line tension variations. Primary system components include a complete CTD Traction Winch System with up to 10 km of 9.53 mm armored cable (Ocean Cable and Communications Co., Yokohama, Kanagawa, Japan), a cable rocker and Electro-Hydraulic Power Unit, a nodding-boom crane assembly, two hydraulic cylinders and two hydraulic oil/nitrogen accumulators mounted within a single frame assembly. The system also contains related electronic hardware interface and a heave compensation computer control program.

(3) Overview of the equipment

The CTD system, SBE 911plus system (Sea-Bird Electronics, Inc., Bellevue, Washington, USA), is a real-time data system with the CTD data transmitted from a SBE 9plus underwater unit via a conducting cable to the SBE 11plus deck unit. The SBE 11plus deck unit is a rack-mountable interface which supplies DC power to underwater unit, decodes serial data stream, formats data under microprocessor control, and passes the data to a companion computer. The serial data from the underwater unit is sent to the deck unit in RS-232 NRZ format using a 34,560 Hz carrier-modulated differential-phase-shift-keying (DPSK) telemetry link. The deck unit decodes the serial data and sends them to a personal computer to display, at the same time, to storage in a disk file using SBE SEASOFT software.

The SBE 911plus system acquires data from primary, secondary and auxiliary sensors in the form of binary numbers corresponding to the frequency or the voltage outputs from those sensors at 24 samples per second. The calculations required to convert raw data to engineering units of the parameters are performed by the SBE SEASOFT in real-time. The same calculations can be carried out after the observation using data stored in a disk file.

The SBE 911plus system controls 36-position SBE 32 Carousel Water Sampler. The Carousel accepts 12-litre water sample bottles. Bottles are fired through the RS-232C modem connector on the back of the SBE 11plus deck unit while acquiring real time data. The 12-litre Niskin-X water sample bottle (General Oceanics, Inc., Miami, Florida, USA) is equipped externally with two stainless steel springs. The external springs are ideal for applications such as trace metal analysis because the inside of the sampler is free from contaminants from springs.

SBE’s temperature (SBE 3) and conductivity (SBE 4) sensor modules were used with the SBE 9plus
underwater unit fixed by a single clamp and "L" bracket to the lower end cap. The conductivity cell entrance is co-planar with the tip of the temperature sensor’s protective steel sheath. The pressure sensor is mounted in the main housing of the underwater unit and is ported to outside through the oil-filled plastic capillary tube. A compact, modular unit consisting of a centrifugal pump head and a brushless DC ball bearing motor contained in an aluminum underwater housing pump (SBE 5T) flushes water through sensor tubing at a constant rate independent of the CTD’s motion. Motor speed and pumping rate (3,000 rpm) remain nearly constant over the entire input voltage range of 12-18 volts DC. Flow speed of pumped water in standard TC duct is about 2.4 m/s. SBE’s dissolved oxygen sensor (SBE 43) was placed between the conductivity sensor module and the pump. Auxiliary sensors, Deep Ocean Standards Thermometer (SBE 35), altimeter (PSA-916T; Teledyne Benthos, Inc., North Falmous, Massachusetts, USA) and oxygen optode (Oxygen Optode 3830; Aanderaa Data Instruments AS, Bergen, Norway) were also used with the SBE 9plus underwater unit. The SBE 35 position in regard to the SBE 3 is shown in Figure 3.1.1.

It is known that the CTD temperature data is influenced by motion (pitching and rolling) of the CTD package. In order to reduce the motion of the CTD package, a heavy stainless frame (total weight of the CTD package without sea water in the bottles is about 1,000 kg) was used and an aluminum plate (54 × 90 cm) was attached to the frame (Figure 3.1.1).

[Summary of the system used in this cruise]

Deck unit:
SBE 11plus, S/N 0344

Under water unit:
SBE 9plus, S/N 79511 (Pressure sensor: S/N 0677)

Temperature sensor:
SBE 3, S/N 1464 (Leg.1: primary)

SBE 3plus, S/N 4216 (Leg.1: secondary, Leg.2, 3: primary)
SBE 3, S/N 1525 (Leg.2, 3: secondary)

Conductivity sensor:
SBE 4, S/N 1203 (Leg.1: primary)
SBE 4, S/N 2854 (Leg.1: secondary)
SBE 4, S/N 3124 (Leg.2: primary from 146_2 to 197_1)
SBE 4, S/N 3036 (Leg.2: secondary from 146_2 to 197_1)
SBE 4, S/N 2854 (Leg.2, 3: primary from X14_1 to TS_1)
SBE 4, S/N 3116 (Leg.2, 3: secondary from X14_1 to TS_1)

Oxygen sensor:
SBE 43, S/N 0391 (Leg.1: primary, Leg.2: primary from 146_2 to WC7)
SBE 43, S/N 0488 (Leg.1: secondary)
SBE 43, S/N 0390 (Leg.2, 3: primary from WC8 to TSI)
SBE 43, S/N 0394 (Leg.2: secondary from 146_2 to 283_1, Leg.3: secondary)
SBE 43, S/N 0205 (Leg.2: secondary from 285_1 to 351_2)
Oxygen Optode 3830, S/N 612 (Leg.1, 2, 3: pilot)

Pump:
SBE 5T, S/N 3293 (Leg.1: primary)
SBE 5T, S/N 3118 (Leg.1: secondary)
SBE 5T, S/N 0984 (Leg.2, 3: primary)
SBE 5T, S/N 2627 (Leg.2, 3: secondary)

Altimeter:
PSA-916T, S/N 1100 (Leg.1)
PSA-916T, S/N 1157 (Leg.2, 3)

Deep Ocean Standards Thermometer:
SBE 35, S/N 0022 (Leg.1, 2)
SBE 35, S/N 0045 (Leg.3)
Carousel Water Sampler:
SBE 32, S/N 0391 (Leg.1, 2, 3)
Water sample bottle:
12-litre Niskin-X (no Teflon coating)

Figure 3.1.1. The CTD package (right) and the SBE 35 position in regard to the SBE 3 temperature sensors (left).

(4) Pre-cruise calibration

(4.1) Pressure

The Paroscientific series 4000 Digiquartz high pressure transducer (Paroscientific, Inc., Redmond, Washington, USA) uses a quartz crystal resonator whose frequency of oscillation varies with pressure induced stress with 0.01 per million of resolution over the absolute pressure range of 0 to 15,000 psia (0 to 10,332 dbar). Also, a quartz crystal temperature signal is used to compensate for a wide range of temperature changes at the time of an observation. The pressure sensor (MODEL 415K-187) has a nominal accuracy of 0.015% FS (1.5 dbar), typical stability of 0.0015% FS/month (0.15 dbar/month), and resolution of 0.001% FS (0.1 dbar).

Pre-cruise sensor calibrations were performed at SBE, Inc. The following coefficients were used in the SEASOFT:

S/N 0677, 2 July 2002

\[ c_1 = -62072.94 \]
\[ c_2 = -1.176956 \]
\[ c_3 = 1.954420 \times 10^{-02} \]
\[ d_1 = 0.027386 \]
\[ d_2 = 0.0 \]
\[ t_1 = 30.05031 \]
\[ t_2 = -4.744833 \times 10^{-04} \]
\[ t_3 = 3.757590 \times 10^{-06} \]
\[ t_4 = 3.810700 \times 10^{-09} \]
\[ t_5 = 0.0 \]

Pressure coefficients are first formulated into

\[ c = c_1 + c_2 \times U + c_3 \times U^2 \]
\[ d = d_1 + d_2 \times U \]
\[ t = t_1 + t_2 \times U + t_3 \times U^2 + t_4 \times U^3 + t_5 \times U^4 \]
where U is temperature in degrees Celsius. The pressure temperature, U, is determined according to

\[ U (°C) = M \times (12 \text{ bit pressure temperature compensation word}) – B \]

The following coefficients were used in SEASOFT:

\[ S/N \ 0677 \]

\[ M = 0.0128041 \]
\[ B = -9.324136 \]

(in the underwater unit system configuration sheet dated on 22 February 2002)

Finally, pressure is computed as

\[ P (\text{psi}) = c \times \left[1 - \left(t_0^2/t^2\right)\right] \times \left(1 - d \times \left[1 - \left(t_0^2/t^2\right)\right]\right) \]

where t is pressure period (µsec). Since the pressure sensor measures the absolute value, it inherently includes atmospheric pressure (about 14.7 psi). SEASOFT subtracts 14.7 psi from computed pressure above automatically.

Pressure sensor calibrations against a dead-weight piston gauge (Model 480DA, S/N 23906; Bundenberg Gauge Co. Ltd., Irlam, Manchester, UK) are performed at JAMSTEC, Yokosuka, Kanagawa, Japan by Marine Works Japan. LTD (MWJ), Yokohama, Kanagawa, Japan, usually once in a year in order to monitor sensor time drift and linearity. The pressure sensor drift is known to be primarily an offset drift at all pressures rather than a change of span slope. The pressure sensor hysteresis is typically 0.2 dbar. The following coefficients for the sensor drift correction were also used in SEASOFT:

\[ S/N \ 0677, \ 8 \ September \ 2005 \]

\[ \text{slope} = 0.9998495 \]
\[ \text{offset} = -0.49595 \]

The drift-corrected pressure is computed as

\[ \text{Drift-corrected pressure (dbar)} = \text{slope} \times (\text{computed pressure in dbar}) + \text{offset} \]

Result of the pressure sensor calibration against the dead-weight piston gauge is shown in Figure 3.1.2. Time drift of the pressure sensor based on the offset and the slope of the calibrations is also shown in Figure 3.1.3.
(4.2) Temperature (SBE 3)

The temperature sensing element is a glass-coated thermistor bead in a stainless steel tube, providing a pressure-free measurement at depths up to 10,500 (6,800) meters by titanium (aluminum) housing. The sensor output frequency ranges from approximately 5 to 13 kHz corresponding to temperature from –5 to 35°C. The output frequency is inversely proportional to the square root of the thermistor resistance, which controls the output of a patented Wien Bridge circuit. The thermistor resistance is exponentially related to temperature. The SBE 3 thermometer has a nominal accuracy of 1 mK, typical stability of 0.2 mK/month, and resolution of 0.2 mK at 24 samples per second. The premium temperature sensor, SBE 3plus, is a more rigorously tested and calibrated version of standard temperature sensor (SBE 3). A sensor is designated as an SBE 3plus only after demonstrating drift of less than 1 mK during a six-month screening period. In addition, the time response is carefully measured and verified to be 0.065 ± 0.010 seconds.

Pre-cruise sensor calibrations were performed at SBE, Inc. The following coefficients were used in SEASOFT:

**S/N 1464 (Leg.1: primary), 14 September 2005**

- \( g = 4.84384166 \times 10^{-3} \)
- \( h = 6.80721378 \times 10^{-4} \)
- \( i = 2.69562893 \times 10^{-5} \)
- \( j = 2.12657768 \times 10^{-6} \)
- \( f_0 = 1000.000 \)

**S/N 4216 (Leg.1: secondary, Leg.2 and 3: primary), 20 September 2005**

- \( g = 4.35983643 \times 10^{-3} \)
- \( h = 6.46129037 \times 10^{-4} \)
- \( i = 2.28907910 \times 10^{-5} \)
- \( j = 1.94862979 \times 10^{-6} \)
- \( f_0 = 1000.000 \)

Temperature (ITS-90) is computed according to

\[
\text{Temperature (ITS-90)} = \frac{1}{g + h \times \ln(f_0 / f) + i \times \ln^2(f_0 / f) + j \times \ln^3(f_0 / f)} - 273.15
\]

where \( f \) is the instrument frequency (kHz).

Time drift of the SBE 3 temperature sensors based on the laboratory calibrations is shown in Figure 3.1.4.

Figure 3.1.4. Time drift of SBE 3 temperature sensors based on laboratory calibrations.
The flow-through conductivity sensing element is a glass tube (cell) with three platinum electrodes to provide in-situ measurements at depths up to 10,500 meters. The impedance between the center and the end electrodes is determined by the cell geometry and the specific conductance of the fluid within the cell. The conductivity cell composes a Wien Bridge circuit with other electric elements of which frequency output is approximately 3 to 12 kHz corresponding to conductivity of the fluid of 0 to 7 S/m. The SBE 4 has a nominal accuracy of 0.0003 S/m, typical stability of 0.0003 S/m/month, and resolution of 0.00004 S/m at 24 samples per second.

Pre-cruise sensor calibrations were performed at SBE, Inc. The following coefficients were used in SEASOFT:

S/N 1203 (Leg.1: primary), 15 September 2005

\[
g = -4.05182265e+00 \\
h = 4.93438395e-01 \\
i = 9.77451923e-05 \\
j = 2.18599851e-05 \\
CPcor = -9.57e-08 \text{ (nominal)} \\
CTcor = 3.25e-06 \text{ (nominal)}
\]

S/N 2834 (Leg.1: secondary, Leg.2: primary from X14_1 to 351_2, Leg.3: primary), 15 September 2005

\[
g = -1.02631821e+01 \\
h = 1.38692851e+00 \\
i = 9.77451923e-05 \\
j = 2.18599851e-05 \\
CPcor = -9.57e-08 \text{ (nominal)} \\
CTcor = 3.25e-06 \text{ (nominal)}
\]

S/N 3036 (Leg.2: secondary from 146_2 to 197_1), 23 September 2005

\[
g = -1.02631821e+01 \\
h = 1.38692851e+00 \\
i = 9.77451923e-05 \\
j = 2.18599851e-05 \\
CPcor = -9.57e-08 \text{ (nominal)} \\
CTcor = 3.25e-06 \text{ (nominal)}
\]

Conductivity of a fluid in the cell is expressed as:

\[
C (\text{S/m}) = \frac{g + h \times f^2 + i \times f^3 + j \times f^4}{10 \times (1 + CTcor \times t + CPcor \times p)}
\]

where \( f \) is the instrument frequency (kHz), \( t \) is the water temperature (°C) and \( p \) is the water pressure (dbar).

The value of conductivity at salinity of 35, temperature of 15°C (IPTS-68) and pressure of 0 dbar is 4.2914 S/m.
(4.4) Oxygen (SBE 43)

The SBE 43 oxygen sensor uses a Clark polarographic element to provide in-situ measurements at depths up to 7,000 meters. Calibration stability is improved by an order of magnitude, and pressure hysteresis is largely eliminated in the upper ocean (1,000 m) compared with the previous oxygen sensor (SBE 13). Continuous polarization eliminates wait-time for stabilization after power-up. Signal resolution is increased by on-board temperature compensation. The oxygen sensor is also included in the path of pumped sea water. The oxygen sensor determines dissolved oxygen concentration by counting the number of oxygen molecules per second (flux) that diffuse through a membrane, where the permeability of the membrane to oxygen is a function of temperature and ambient pressure. Computation of dissolved oxygen in engineering units is done in SEASOFT software. The range for dissolved oxygen is 120% of surface saturation in all natural waters, nominal accuracy is 2% of saturation, and typical stability is 2% per 1,000 hours.

Pre-cruise sensor calibrations were performed at SBE, Inc. The following coefficients were used in SEASOFT:

\[ \text{Oxygen (ml/l)} = \{\text{Soc} \times (v + \text{Offset})\} \times \exp(\text{TCor} \times t + \text{PCor} \times p) \times \text{Oxsat}(t, s) \]

\[ \text{Oxsat}(t, s) = \exp[A_1 + A_2 \times (100 / t) + A_3 \times \ln(t / 100) + A_4 \times (t / 100) + s \times \{B_1 + B_2 \times (t / 100) + B_3 \times (t / 100) \times (t / 100)] \]

where \( p \) is pressure in dbar, \( t \) is absolute temperature, and \( s \) is salinity in psu. Oxsat is oxygen saturation value minus the volume of oxygen gas (STP) absorbed from humidity-saturated air.
Serial number 0488 is used in SBE’s research for oxygen sensor membranes. This sensor has a membrane that is thicker than production SBE 43s. This thicker membrane will cause the sensor to respond more slowly than standard SBE 43s but it may be more stable. The field performance of this sensor is examined in the leg.1.

(4.5) Deep Ocean Standards Thermometer

Deep Ocean Standards Thermometer (SBE 35) is an accurate, ocean-range temperature sensor that can be standardized against Triple Point of Water and Gallium Melt Point cells and is also capable of measuring temperature in the ocean to depths of 6,800 m.

Temperature is determined by applying an AC excitation to reference resistances and an ultrastable aged thermistor with a drift rate of less than 0.001 °C/year. Each of the resulting outputs is digitized by a 20-bit A/D converter. The reference resistor is a hermetically sealed, temperature-controlled Vishay. The switches are mercury wetted reed relays with a stable contact resistance. AC excitation and ratiometric comparison using a common processing channel removes measurement errors due to parasitic thermocouples, offset voltages, leakage currents, and gain errors. Maximum power dissipated in the thermistor is 0.5 µwatts, and contributes less than 200 µK of overheat error.

The SBE 35 communicates via a standard RS-232 interface at 300 baud, 8 bits, no parity. The SBE 35 can be used with the SBE 32 Carousel Water Sampler and SBE 911plus CTD system. The SBE 35 makes a temperature measurement each time a bottle fire confirmation is received, and stores the value in EEPROM. Calibration coefficients stored in EEPROM allow the SBE 35 to transmit data in engineering units. Commands can be sent to SBE 35 to provide status display, data acquisition setup, data retrieval, and diagnostic test by using terminal software.

Following the methodology used for standards-grade platinum resistance thermometers (SPRT), calibration of the SBE 35 is accomplished in two steps. The first step is to characterize and capture the non-linear resistance vs temperature response of the sensor. The SBE 35 calibrations are performed at SBE, Inc., in a low-gradient temperature bath and against ITS-90 certified SPRTs maintained at Sea-Bird’s primary temperature metrology laboratory. The second step is frequent certification of the sensor by measurements in thermodynamic fixed-point cells. Triple point of water (TPW) and gallium melt point (GaMP) cells are appropriate for the SBE 35. The SBE 35 resolves temperature in the fixed-point cells to approximately 25 µK. Like SPRTs, the slow time drift of the SBE 35 is adjusted by a slope and offset correction to the basic non-linear calibration equation.

Pre-cruise sensor calibrations were performed at SBE, Inc. The following coefficients were stored in EEPROM:

S/N 0022 (Leg.1 and 2), 12 October 1999 (1st step: linearization)

\[ a_0 = 4.320725498e-3 \]
\[ a_1 = -1.189839279e-3 \]
\[ a_2 = 1.436299593e-3 \]
\[ a_3 = -1.032916769e-5 \]
\[ a_4 = 2.225491125e-7 \]

S/N 0045 (Leg.3), 27 October 2002 (1st step: linearization)

\[ a_0 = 5.84093815e-03 \]
\[ a_1 = -1.65329280e-03 \]
\[ a_2 = 2.37944937e-04 \]
\[ a_3 = -1.32611385e-05 \]
\[ a_4 = 2.83355203e-07 \]

Linearized temperature (ITS-90) is computed according to

Linearized temperature (ITS-90) =

\[ 1 / \left( a_0 + a_1 \times \ln(n) + a_2 \times \ln^2(n) + a_3 \times \ln^3(n) + a_4 \times \ln^4(n) \right) - 273.15 \]

where \( n \) is the instrument output. Then the SBE 35 is certified by measurements in thermodynamic fixed-point cells of the TPW (0.0100°C) and GaMP (29.7646°C). The slow time drift of the SBE 35 is adjusted by periodic recertification corrections.
Temperature (ITS-90) is calibrated according to

\[ \text{Temperature (ITS-90)} = \text{Slope} \times \text{Linearized temperature} + \text{Offset} \]

The SBE 35 has a time constant of 0.5 seconds. The time required per sample is \(1.1 \times \text{NCYCLES} + 2.7\) seconds. The 1.1 seconds is total time per an acquisition cycle. NCYCLES is the number of acquisition cycles per sample. The 2.7 seconds is required for converting the measured values to temperature and storing average in EEPROM. Root mean square (rms) temperature noise for a SBE 35 in a Triple Point of Water cell is typically expressed as \(82 / \text{NCYCLES}^{0.5}\) in \(\mu\text{K}\). In this cruise NCYCLES was set to 4 and the rms noise is estimated to be 0.04 mK.

When using the SBE 911 system with SBE 35, the deck unit receives incorrect signal from the underwater unit for confirmation of firing bottle #16. In order to correct the signal, a module (Yoshi Ver. 1; EMS Co. Ltd., Kobe, Hyogo, Japan) was used between the underwater unit and the deck unit.

Time drift of the SBE 35 based on the fixed point calibrations is shown in Figure 3.1.5.

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Figure 3.1.5. SBE35 time drift based on laboratory fixed point calibrations (triple point of water, TPW and gallium melt point, GaMP) performed by SBE, Inc.
(4.6) Altimeter

Benthos PSA-916T Sonar Altimeter (Teledyne Benthos, Inc.) determines the distance of the target from the unit by generating a narrow beam acoustic pulse and measuring the travel time for the pulse to bounce back from the target surface. The PSA-916T is the same as the standard PSA-916 Sonar Altimeter except it is housed in a corrosion-resistant titanium pressure case. It is O-ring-sealed and rated for operation in water depths up to 10,000 meters. In this unit, a 250 microseconds pulse at 200 kHz is transmitted 5 times in a second. The PSA-916T uses the nominal speed of sound of 1,500 m/s. Thus the unit itself, neglecting variations in the speed of sound, can be considered accurate to 5% or 0.1 meter, whichever is greater. In the PSA-916T the jitter of the detectors is approximately 5 microseconds or ± 0.4 cm total distance. Since the total travel time is divided by two, the jitter error is ±0.2 cm.

The following scale factors were used in SEASOFT:

\[
\text{S/N 1100, S/N 1157} \\
\text{FSVolt} \times 300 / \text{FSRange} = 15 \\
\text{Offset} = 0.0
\]

(4.7) Oxygen Optode

Oxygen Optode 3830 (Aanderaa Instruments AS) is based on the ability of selected substances to act as dynamic fluorescence quenchers. The fluorescent indicator is a special platinum porphyrine complex embedded in a gas permeable foil that is exposed to the surrounding water. A black optical isolation coating protects the complex from sunlight and fluorescent particles in the water. This sensing foil is attached to a sapphire window providing optical access for the measuring system from inside watertight titanium housing. The foil is excited by modulated blue light, and the phase of a returned red light is measured. By linearizing and temperature compensating, with an incorporated temperature sensor, the absolute O₂ concentration can be determined.

In order to use with the SBE 911plus CTD system, an analog adaptor (3966) is connected to the oxygen optode (3830). The analog adaptor is packed into titanium housing made by Alec Electronics Co. Ltd., Kobe, Hyogo, Japan (Figure 3.1.6). The sensor is designed to operate down to 6,000 meters and the titanium housing for the analog adaptor is designed to operate down to 7,000 meters. The range for dissolved oxygen is 120% of surface saturation in all natural waters, nominal accuracy is less than 5% of saturation, and setting time (68%) is shorter than 25 seconds.

The following scale factors were used in SEASOFT:

\[
\text{S/N 612} \\
\text{Phase shift (degrees)} = V_p \times 12 + 10 \\
\text{Temperature (°C)} = V_t \times 9 - 5
\]

where \(V_p\) and \(V_t\) are voltage output (V) of phase shift and temperature, respectively.

Each batch of sensing foils is delivered with calibration data describing the behavior with respect to oxygen concentration and temperature.

**Foil batch No. 4104 (S/N 612), 13 November 2004**

\[
\begin{align*}
\text{C0Coeff}_0 &= 3.199840e+3 \\
\text{C0Coeff}_1 &= -1.119634e+2 \\
\text{C0Coeff}_2 &= 2.408296 \\
\text{C0Coeff}_3 &= -2.248740e-2 \\
\text{C1Coeff}_0 &= -1.744936e+2 \\
\text{C1Coeff}_1 &= 5.462500 \\
\text{C1Coeff}_2 &= -1.244084e-1 \\
\text{C1Coeff}_3 &= 1.239153e-3 \\
\text{C2Coeff}_0 &= 3.941711 \\
\text{C2Coeff}_1 &= -1.086677e-1 \\
\text{C2Coeff}_2 &= 2.719394e-3 \\
\text{C2Coeff}_3 &= -2.906343e-5 \\
\text{C3Coeff}_0 &= -4.220910e-2 \\
\text{C3Coeff}_1 &= 1.018155e-3
\end{align*}
\]
C3Coef2 = –2.905609e–5
C3Coef3 = 3.306610e–7
C4Coef0 = 1.738870e–4
C4Coef1 = –3.637668e–6
C4Coef2 = 1.227403e–7
C4Coef3 = –1.468399e–9

Temperature dependent coefficients are calculated as follows.

\[ C_{0\text{Coef}} = C_{0\text{Coef}0} + C_{0\text{Coef}1} \times t + C_{0\text{Coef}2} \times t^2 + C_{0\text{Coef}3} \times t^3 \]
\[ C_{1\text{Coef}} = C_{1\text{Coef}0} + C_{1\text{Coef}1} \times t + C_{1\text{Coef}2} \times t^2 + C_{1\text{Coef}3} \times t^3 \]
\[ C_{2\text{Coef}} = C_{2\text{Coef}0} + C_{2\text{Coef}1} \times t + C_{2\text{Coef}2} \times t^2 + C_{2\text{Coef}3} \times t^3 \]
\[ C_{3\text{Coef}} = C_{3\text{Coef}0} + C_{3\text{Coef}1} \times t + C_{3\text{Coef}2} \times t^2 + C_{3\text{Coef}3} \times t^3 \]
\[ C_{4\text{Coef}} = C_{4\text{Coef}0} + C_{4\text{Coef}1} \times t + C_{4\text{Coef}2} \times t^2 + C_{4\text{Coef}3} \times t^3 \]

where \( t \) is temperature (°C). The oxygen concentration can be calculated by use of the following formula.

\[ O_2 (\mu\text{mol/l}) = C_{0\text{Coef}} + C_{1\text{Coef}} \times P + C_{2\text{Coef}} \times P^2 + C_{3\text{Coef}} \times P^3 + C_{4\text{Coef}} \times P^4 \]

where \( P \) is phase shift (degrees) measured by the Optode. In addition to the above mentioned coefficient, phase measurement is calibrated for individual sensor and foil variations by a two point calibration (one in air saturated water and one in a zero-oxygen solution).

\[ P = A + B \times P_b \]

where \( P \) is a calibrated phase shift (degrees) and \( P_b \) is a raw phase measurement. The coefficients \( A \) and \( B \) can be calculated by ordinary linear curve fitting and is delivered.

\[ S/N 612, 20 September 2005 \]
\[ A = –3.00536 \]
\[ B = 1.11847 \]

Outputs from the sensor are the raw phase shift (\( P_b \)) and temperature. The raw phase data was calibrated using above coefficients after data acquisition. The oxygen concentration was calculated using temperature data from the first responding CTD temperature sensor instead of temperature data from slow responding optode temperature sensor.

Since the sensing foil is only permeable to gas and not water, the optode can not sense the effect of salt dissolved in the water, hence the optode always measures as if immersed in fresh water. Therefore the oxygen concentration, \( \mu\text{mol/l} \), was multiplied by the following factor.

\[ \exp(S(B_0 + B_1 \times T_s + B_2 \times T_s^2 + B_3 \times T_s^3 + C_0 \times S^2)) \]

where \( S \) is salinity, \( T_s \) is scaled temperature (\( = \ln((298.15 - t)/(273.15 + t)) \)), \( t \) is temperature (°C),

\[ B_0 = –6.24097e–3 \]
\[ B_1 = –6.93498e–3 \]
\[ B_2 = –6.90358e–3 \]
\[ B_3 = –4.29155e–3 \]
\[ C_0 = –3.11680e–7 \]

The response of the sensing foil decreases to some extent with the ambient water pressure. Therefore the oxygen concentration was multiplied by the following factor.

\[ (1 + 0.03 \times P_r / 1000) \]

where \( P_r \) is pressure in dbar. This factor (0.03) is empirically determined and different from that in the user’s manual. (The factor was changed as 0.032 after analyzing the data obtained in this cruise.)

![Figure 3.1.6. Oxygen Optode (3830) with analog adaptor (3966). The analog adaptor is packed into titanium housing made by Alec Electronics Co., Ltd.](image)
(5) Data collection and processing

(5.1) Data collection

CTD measurements were made by using a SBE 9plus equipped with two pumped temperature-conductivity (TC) sensors. The TC pairs were monitored to check drift and shifts by examining the differences between the two pairs. A dissolved oxygen sensor was placed between the primary conductivity sensor module and the pump. Auxiliary sensors included Deep Ocean Standards Thermometer, altimeter and oxygen optode. The SBE 9plus was mounted horizontally in a 36-position carousel frame.

CTD system was powered on at least 30 minutes in advance of the data acquisition and was powered off at least two minutes after the operation in order to acquire pressure data on the ship’s deck.

The package was lowered into the water from the starboard side and held 10 m beneath the surface for about one minute in order to activate the pump. After the pump was activated, the package was lifted to the surface and lowered at a rate of 1.0 m/s to 200 m (or 300 m when significant wave height is high) then the package was stopped in order to operate the heave compensator of the crane. The package was lowered again at a rate of 1.2 m/s to the bottom. The position of the package relative to the bottom was monitored by the altimeter reading. Also the bottom depth was monitored by the SEABEAM multi-narrow beam sounder on board. For the up cast, the package was lifted at a rate of 1.1 m/s except for bottle firing stops. At each bottle firing stops, the bottle was fired after waiting from the stop for 30 seconds and the package was stayed at least 5 seconds for measurement of the Deep Ocean Standards Thermometer. At 200 m (or 300 m) from the surface, the package was stopped in order to stop the heave compensator of the crane.

Water samples were collected using a 36-bottle SBE 32 Carousel Water Sampler with 12-litre Nisken-X bottles. Before a cast taken water for CFCs, the 36-bottle frame and Niskin-X bottles were wiped with acetone.

The SBE 11plus deck unit received the data signal from the CTD. Digitized data were forwarded to a personal computer running the SEASAVE data acquisition software. Temperature, conductivity, salinity, oxygen and descent rate profiles were displayed in real-time with the package depth and altimeter reading. Differences in temperature, salinity and oxygen between primary and secondary sensor were also displayed in order to monitor the status of the sensors.

Data acquisition software

SEASAVE-Win32, version 5.27b

(5.2) Data collection problems

Leg.1:

At following stations, trigger of the bottle was not released. Therefore the latch assembly was replaced after the cast.

33_1 (#12), 51_1 (#28), 116_1 (#36)

At station 38_1, bottle #19 did not trip correctly. It was found by temperature reading at dissolved oxygen sampling. Therefore the latch assembly was replaced after the cast.

At station 51_1, bottle #26 was not fired by missed operation.

After station 51_1, bottle #15 was changed from S/N X12006 to S/N X12009 due to frequent leak.

At following stations, output from the sensor showed abnormal values.

94_1, secondary sensors, 32-96 dbar (down cast)

114_1, secondary conductivity, 1,192-2,546 dbar (down cast)

118_1, primary conductivity, 1,391-1,438 dbar (down cast)

Leg.2:

At following stations, trigger of the bottle was not released. Therefore the latch assembly was replaced after the cast.

X14_1 (#17), 201_1 (#17), 203_1 (#10), 217_2 (#28), 231_1 (#26), 322_1 (#18), 351_2 (#14)

At following stations, bottle did not trip correctly. It was found by temperature reading at dissolved oxygen sampling. Therefore the latch assembly was replaced after the cast.

WC5_1 (#8), 291_1 (#20), 351_2 (21)
At following stations, bottle did not trip correctly. It was found by sampled water analysis.

185_1 (#17): The latch assembly was replaced after station 195_1.
WC2_1 (#1): The latch assembly was replaced after station WC5_1.
357_1 (#17): The bottle tripped before firing the bottle.

At station 217_2, bottle #36 was not fired by missed operation.

At following stations, output from the sensor showed abnormal values.

146_2, secondary sensors
148_1, secondary sensors
WC7_1, primary sensors
328_1, primary sensors, 0-1,106 dbar (up cast), Jellyfish in primary TC duct

At station 239_1, the deck unit fuzed at 2,790 dbar of up cast. The system was re-started at the depth.

At station 347_1, system error occurred at 2,743-2,744 dbar of up cast by unknown reason.

For primary oxygen sensor S/N 0391, noise became large near surface (0-400 dbar) compared to the data obtained from the same sensor in leg 1. The sensor was bleached after stations 171_1, 209_1 and WC6_1. Noise became large again although it was improved after bleaching.

After station 197_1, the primary conductivity sensor was changed from S/N 3124 to S/N 2854, and the secondary conductivity sensor was also changed from S/N 3036 to S/N 3116, due to large time drift.

After station WC7_1, the primary oxygen sensor was changed from S/N 0391 to S/N 0390 due to shift and noise.

After station 283_1, the secondary oxygen sensor was changed from S/N 0394 to S/N 0205 due to small noise. But the noise was found in the secondary oxygen data after the sensor change as well. So the connecting cable for the secondary oxygen sensor after station 285_1. But the noise was found as well. At station 333_1, the connecting port was changed from AUX3 to AUX2 and the noise disappeared after that.

Leg.3:

At station 380_1, bottle #23 was not trip correctly. It was found by temperature reading at dissolved oxygen sampling. Therefore the latch assembly was replaced after the cast.

5.3) Data processing

SEASOFT consists of modular menu driven routines for acquisition, display, processing, and archiving of oceanographic data acquired with SBE equipment, and is designed to work with a compatible personal computer. Raw data are acquired from instruments and are stored as unmodified data. The conversion module DATCNV uses instrument configuration and calibration coefficients to create a converted engineering unit data file that is operated on by all SEASOFT post processing modules. Each SEASOFT module that modifies the converted data file adds proper information to the header of the converted file permitting tracking of how the various oceanographic parameters were obtained. The converted data is stored in rows and columns of ASCII numbers.

The following are the SEASOFT data processing module sequence and specifications used in the reduction of CTD data in this cruise.

Data processing software

SEASOFT-Win32, version 5.27b

DATCNV converted the raw data to scan number, pressure, depth, temperatures, conductivities, oxygen voltage, descent rate, altitude, and optode phase shift. DATCNV also extracted bottle information where scans were marked with the bottle confirm bit during acquisition. The duration was set to 4.4 seconds, and the offset was set to 0.0 seconds.

ROSSUM created a summary of the bottle data. The bottle position, date, and time were output as the first two columns. Scan number, pressure, depth, temperatures, conductivities, oxygen voltage, descent rate, altitude
and optode phase shift were averaged over 4.4 seconds. And salinity, potential temperature, density ($\sigma_\theta$) and oxygen were computed.

ALIGNCTD converted the time-sequence of conductivity and oxygen sensor outputs into the pressure sequence to ensure that all calculations were made using measurements from the same parcel of water. For a SBE 9plus CTD with the ducted temperature and conductivity sensors and a 3,000-rpm pump, the typical net advance of the conductivity relative to the temperature is 0.073 seconds. So, the SBE 11plus deck unit was set to advance the primary and the secondary conductivity for 1.73 scans ($1.75/24 = 0.073$ seconds). Oxygen data are also systematically delayed with respect to depth mainly because of the long time constant of the oxygen sensor and of an additional delay from the transit time of water in the pumped plumbing line. This delay was compensated by 6 seconds advancing oxygen sensor output (oxygen voltage) relative to the temperature. For the serial number 0488 that have thicker membrane than standard SBE 43s, the delay was compensated by 14 seconds. Oxygen optode data are also delayed by relatively slow response time of the sensor. The delay was compensated by 8 seconds advancing optode sensor output (phase shift and optode temperature) relative to the CTD temperature.

WILDEDIT marked extreme outliers in the data files. The first pass of WILDEDIT obtained an accurate estimate of the true standard deviation of the data. The data were read in blocks of 1,000 scans. Data greater than 10 standard deviations were flagged. The second pass computed a standard deviation over the same 1,000 scans excluding the flagged values. Values greater than 20 standard deviations were marked bad. This process was applied to all variables.

CELLTM used a recursive filter to remove conductivity cell thermal mass effects from the measured conductivity. Typical values used were thermal anomaly amplitude $\alpha = 0.03$ and the time constant $1/\beta = 7.0$.

FILTER performed a low pass filter on pressure with a time constant of 0.15 seconds. In order to produce zero phase lag (no time shift) the filter runs forward first then backwards.

SECTION selected a time span of data based on scan number in order to reduce a file size. The minimum number was set to be the start time when the CTD package was beneath the sea-surface after activation of the pump. The maximum number was set to be the end time when the package came up from the surface. Data for estimation of the CTD pressure drift were prepared before SECTION.

LOOPEDIT marked scans where the CTD was moving less than the minimum velocity of 0.0 m/s (traveling backwards due to ship roll).

DERIVE was used to compute oxygen.

BINAVG averaged the data into 1-dbar pressure bins. The center value of the first bin was set equal to the bin size. The bin minimum and maximum values are the center value plus and minus half the bin size. Scans with pressures greater than the minimum and less than or equal to the maximum were averaged. Scans were interpolated so that a data record exist every dbar.

DERIVE was re-used to compute salinity, potential temperature, and density ($\sigma_\theta$).

SPLIT was used to split data into the down cast and the up cast.

For stations from 146_2 to 331_1 in Leg.2, small noise was found in the secondary oxygen data because the sensor connected to the port of AUX3. Therefore the sensor output (voltage) was low-pass filtered with a time constant of 1 second at the same time of the low-pass filtering for the pressure data mentioned above. At following stations, the noise could not be removed completely from down cast profile data.

<table>
<thead>
<tr>
<th>Station</th>
<th>Depth Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>X14_1</td>
<td>5,650-5,800 dbar</td>
</tr>
<tr>
<td>201_1</td>
<td>5,600-5,760 dbar</td>
</tr>
<tr>
<td>203_1</td>
<td>5,710-5,850 dbar</td>
</tr>
<tr>
<td>205_1</td>
<td>5,760-5,820 dbar</td>
</tr>
<tr>
<td>207_1</td>
<td>5,660-5,860 dbar</td>
</tr>
<tr>
<td>213_1</td>
<td>5,840-5,880 dbar</td>
</tr>
<tr>
<td>215_1</td>
<td>5,750-5,920 dbar</td>
</tr>
<tr>
<td>217_1</td>
<td>5,730-5,880 dbar</td>
</tr>
</tbody>
</table>
Remaining spikes in salinity or oxygen data were manually eliminated from the raw data or the 1-dbar-averaged data. When number of data in the 1-dbar-pressure bin was less than 10, the data of the bin was not used. The data gap over 1-dbar was linearly interpolated with a quality flag of 6.

For the oxygen optode data, the delay due to the long time constant was compensated by 8 seconds using the software module ALIGNCTD mentioned above. However it was found that the delay was dependent on temperature. So the delay was compensated advancing optode sensor output relative to the CTD temperature as a following function of temperature.

\[
\begin{align*}
\text{align (sec)} &= 25 \times \exp(-0.13 \times t) \quad (\text{for } 0 \leq t \leq 16.3 ^\circ C) \\
\text{align (sec)} &= 25 \quad (\text{for } t < 0 ^\circ C) \\
\text{align (sec)} &= 3 \quad (\text{for } t > 16.3 ^\circ C)
\end{align*}
\]

where \( t \) is CTD temperature (°C).

(6) Post-cruise calibration

Post-cruise calibration is basically performed for each leg. However the cruise period of Leg.2 is longer than usual (53 days). So the data of Leg.2 is divided into two periods for the post-cruise calibration. In this section the two periods are called as Leg.2a (from station 146_2 to WC10_1) and Leg.2b (from station 217_2 to 351_2).

(6.1) Pressure

The CTD pressure sensor offset in the period of the cruise is estimated from the pressure readings on the ship deck. For best results the Paroscientific sensor has to be powered for at least 10 minutes before the operation and carefully temperature equilibrated. Therefore CTD system was powered on for 30 minutes in advance of the data acquisition (from S5_1, Leg.1). In order to get the calibration data for the pre- and post-cast pressure sensor drift, the CTD deck pressure is averaged over first and last one minute, respectively. Then the atmospheric pressure deviation from a standard atmospheric pressure (14.7 psi) is subtracted from the CTD deck pressure. The atmospheric pressure was measured at the captain deck (20 m high from the base line) and sub-sampled one-minute interval as a meteorological data. Time series of the CTD deck pressure is shown in from Figure 3.1.7 to Figure 3.1.10.

The CTD pressure sensor offset is estimated from the deck pressure obtained above. Mean of the pre- and the post-casts data over the whole period gave an estimation of the pressure sensor offset from the pre-cruise calibration. Mean residual pressure between the dead-weight piston gauge and the calibrated CTD data at 0 dbar of the pre-cruise calibration is subtracted from the mean deck pressure. Estimated offset of the pressure data is summarized in Table 3.1.1. The post-cruise correction of the pressure data is not deemed necessary for the pressure sensor.

<table>
<thead>
<tr>
<th>Leg</th>
<th>S/N</th>
<th>Mean deck Pressure (dbar)</th>
<th>Standard deviation (dbar)</th>
<th>Residual pressure (dbar)</th>
<th>Estimated offset (dbar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Leg.1</td>
<td>0677</td>
<td>-0.53</td>
<td>0.03</td>
<td>0.03</td>
<td>-0.56</td>
</tr>
<tr>
<td>Leg.2a</td>
<td>0677</td>
<td>-0.54</td>
<td>0.03</td>
<td>0.03</td>
<td>-0.57</td>
</tr>
<tr>
<td>Leg.2b</td>
<td>0677</td>
<td>-0.53</td>
<td>0.02</td>
<td>0.03</td>
<td>-0.56</td>
</tr>
<tr>
<td>Leg.3</td>
<td>0677</td>
<td>-0.49</td>
<td>0.02</td>
<td>0.03</td>
<td>-0.52</td>
</tr>
</tbody>
</table>
Figure 3.1.7. Time series of the CTD deck pressure for Leg.1. Pink dot indicates atmospheric pressure anomaly. Blue and green dots indicate pre- and post-cast deck pressures, respectively. Red dot indicates an average of the pre- and the post-cast deck pressures.

Figure 3.1.8. Same as Figure 3.1.7, but for Leg.2a.

Figure 3.1.9. Same as Figure 3.1.7, but for Leg.2b.

Figure 3.1.10. Same as Figure 3.1.7, but for Leg.3.
(6.2) Temperature

The CTD temperature sensors (SBE 3) were calibrated with the SBE 35 under the assumption that discrepancies between SBE 3 and SBE 35 data were due to pressure sensitivity, the viscous heating effect, and time drift of the SBE 3, according to a method by Uchida et al. (2007).

Post-cruise sensor calibrations for the SBE 35 were performed at SBE, Inc.

S/N 0022, 1 February 2006 (2nd step: fixed point calibration)
Slope = 1.000034
Offset = 0.000038

S/N 0045, 21 February 2006 (2nd step: fixed point calibration)
Slope = 1.000009
Offset = –0.001109

Offset of the SBE 35 (S/N 0022) data from the pre-cruise calibration is estimated to be 0.1 mK for temperature less than 4°C. So the post-cruise correction of the SBE 35 temperature data is not deemed necessary for the SBE 35.

The CTD temperature is calibrated as

\[ \text{Calibrated temperature} = T - (c_0 \times P + c_1 \times t + c_2) \]

where \( T \) is CTD temperature in °C, \( P \) is pressure in dbar, \( t \) is time in days from pre-cruise calibration date of CTD temperature and \( c_0, c_1, \) and \( c_2 \) are calibration coefficients. The best fit sets of coefficients are determined by minimizing the sum of absolute deviation from the SBE 35 data. The MATLAB® function FMINSEARCH is used to determine the sets.

The calibration is performed for the CTD data created by the software module ROSSUM. The deviation of CTD temperature from the SBE 35 temperature at depth shallower than 2,000 dbar is large for determining the coefficients with sufficient accuracy since the vertical temperature gradient is too large in the regions. So the coefficients are determined using the data for the depth deeper than 1,950 dbar. For Leg.3 the calibration coefficients determined for Leg.2b are used for the calibration because the maximum pressure of the CTD casts is shallower than 2,000 dbar in Leg.3.

Finally following temperature data are used for the data set in consideration for the data quality.

Leg.1: secondary (S/N 4216) except for 94_1 and 114_1
primary (S/N 1464) for 94_1 and 114_1

Leg.2: primary (S/N 4216) except for WC7_1 and 328_1
secondary (S/N 1525) for WC7_1 and 328_1

Leg.3: primary (S/N 4216)

The number of data used for the calibration and the mean absolute deviation from the SBE 35 are listed in Table 3.1.2 and the calibration coefficients are listed in Table 3.1.3. The results of the post-cruise calibration for the CTD temperature are summarized in Table 3.1.4 and shown in from Figure 3.1.11 to Figure 3.1.17.

Table 3.1.2. Number of data used for the calibration (pressure \( \geq 1,950 \) dbar) and mean absolute deviation (ADEV) between the CTD temperature and the SBE 35.

<table>
<thead>
<tr>
<th>Leg</th>
<th>S/N</th>
<th>Number of data</th>
<th>ADEV (mK)</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>Leg.1</td>
<td>1464</td>
<td>976</td>
<td>0.10</td>
<td>for 94_1, 114_1</td>
</tr>
<tr>
<td></td>
<td>4216</td>
<td>976</td>
<td>0.10</td>
<td></td>
</tr>
<tr>
<td>Leg.2a</td>
<td>4216</td>
<td>672</td>
<td>0.12</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1525</td>
<td>661</td>
<td>0.10</td>
<td>for WC7_1</td>
</tr>
<tr>
<td>Leg.2b</td>
<td>4216</td>
<td>1070</td>
<td>0.14</td>
<td>for 328_1</td>
</tr>
<tr>
<td></td>
<td>1525</td>
<td>1070</td>
<td>0.11</td>
<td></td>
</tr>
</tbody>
</table>
Table 3.1.3. Calibration coefficients for the CTD temperature sensors.

<table>
<thead>
<tr>
<th>Leg</th>
<th>S/N</th>
<th>$c_0$ (°C/bar)</th>
<th>$c_1$ (°C/day)</th>
<th>$c_2$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Leg.1</td>
<td>1464</td>
<td>−1.090e−7</td>
<td>1.3833e−5</td>
<td>−0.34e−3</td>
</tr>
<tr>
<td></td>
<td>4216</td>
<td>1.8917e−8</td>
<td>−4.1245e−6</td>
<td>0.35e−3</td>
</tr>
<tr>
<td>Leg.2a</td>
<td>4216</td>
<td>−3.9992e−9</td>
<td>−1.1221e−6</td>
<td>0.70e−3</td>
</tr>
<tr>
<td></td>
<td>1525</td>
<td>1.0202e−9</td>
<td>−5.4892e−6</td>
<td>0.84e−3</td>
</tr>
<tr>
<td>Leg.2b</td>
<td>4216</td>
<td>−7.2135e−9</td>
<td>1.0834e−5</td>
<td>−0.65e−3</td>
</tr>
<tr>
<td></td>
<td>1525</td>
<td>2.7008e−9</td>
<td>1.8342e−6</td>
<td>−0.07e−3</td>
</tr>
<tr>
<td>Leg.3</td>
<td>4216</td>
<td>Same as Leg.2b</td>
<td>Same as Leg.2b</td>
<td>Same as Leg.2b</td>
</tr>
</tbody>
</table>

Table 3.1.4. Difference between the CTD temperature and the SBE 35 after the post-cruise calibration. Mean and standard deviation (Sdev) are calculated for the data below and above 1,950 dbar. Number of data used (Num) is also shown.

<table>
<thead>
<tr>
<th>Leg</th>
<th>S/N</th>
<th>Pressure ≥ 1,950 dbar</th>
<th>Pressure &lt; 1,950 dbar</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Num</td>
<td>Mean (mK)</td>
</tr>
<tr>
<td>Leg.1</td>
<td>1464</td>
<td>976</td>
<td>−0.01</td>
</tr>
<tr>
<td></td>
<td>4216</td>
<td>976</td>
<td>−0.01</td>
</tr>
<tr>
<td>Leg.2a</td>
<td>4216</td>
<td>672</td>
<td>0.02</td>
</tr>
<tr>
<td></td>
<td>1525</td>
<td>661</td>
<td>−0.00</td>
</tr>
<tr>
<td>Leg.2b</td>
<td>4216</td>
<td>1070</td>
<td>−0.00</td>
</tr>
<tr>
<td></td>
<td>1525</td>
<td>1070</td>
<td>−0.01</td>
</tr>
<tr>
<td>Leg.3</td>
<td>4216</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

Figure 3.1.11. Difference between the CTD temperature (primary) and the SBE 35 for Leg.1. Blue and red dots indicate before and after the post-cruise calibration using the SBE 35 data, respectively. Top panel shows for $P ≥ 1950$ dbar. Lower two panels show histogram of the difference after the calibration.
Figure 3.1.12. Same as Figure 3.1.11, but for the secondary CTD temperature for Leg.1.

Figure 3.1.13. Same as Figure 3.1.11, but for the primary CTD temperature for Leg.2a.
Figure 3.1.14. Same as Figure 3.1.11, but for the secondary CTD temperature for Leg.2a.

Figure 3.1.15. Same as Figure 3.1.11, but for the primary CTD temperature for Leg.2b.
The discrepancy between the CTD salinity and the bottle salinity is considered to be a function of conductivity and pressure. The CTD salinity is calibrated as

\[
\text{Calibrated salinity} = S - (c_0 \times P + c_1 \times C + c_2 \times C \times P + c_3)
\]

(6.3) Salinity

The discrepancy between the CTD salinity and the bottle salinity is considered to be a function of conductivity and pressure. The CTD salinity is calibrated as

\[
\text{Calibrated salinity} = S - (c_0 \times P + c_1 \times C + c_2 \times C \times P + c_3)
\]
where $S$ is CTD salinity, $P$ is pressure in dbar, $C$ is conductivity in S/m and $c_0$, $c_1$, $c_2$ and $c_3$ are calibration coefficients. The best fit sets of coefficients are determined by minimizing the sum of absolute deviation with a weight from the bottle salinity data. The MATLAB® function FMINSEARCH is used to determine the sets. The weight is given as a function of vertical salinity gradient and pressure as

$$Weight = \min(4, \exp(\text{log}(4) \times Gr / \text{Grad}) \times \min(4, \exp(\text{log}(4) \times P^2 / PR^2)))$$

where Grad is vertical salinity gradient in PSU dbar$^{-1}$ and $P$ is pressure in dbar. Gr and PR are threshold of the salinity gradient (0.5 mPSU dbar$^{-1}$) and pressure (1,000 dbar), respectively. When salinity gradient is small (large) and pressure is large (small), the weight is large (small) at maximum (minimum) value of 16 (1). The salinity gradient is calculated using up-cast CTD salinity data. The up-cast CTD salinity data is low-pass filtered with a 3-point (weights are 1/4, 1/2, 1/4) triangle filter before the calculation.

Finally salinity data derived from following conductivity sensor are used for the data set in consideration for the data quality.

**Leg.1:** secondary (S/N 2854) except for 94_1 and 114_1

primary (S/N 1203) for 94_1 and 114_1

**Leg.2:** primary (S/N 3124 and S/N 2854) except for WC7_1 and 328_1

secondary (S/N 3116) for WC7_1 and 328_1

**Leg.3:** primary (S/N 2854)

The CTD data created by the software module ROSSUM are used after the post-cruise calibration for the CTD temperature.

The coefficients are determined for some groups of the CTD stations. The results of the post-cruise calibration for the CTD salinity are summarized in Table 3.1.5 and shown in from Figure 3.1.18 to Figure 3.1.21.

And the calibration coefficients and the number of the data used for the calibration are listed in Table 3.1.6.

<table>
<thead>
<tr>
<th>Leg</th>
<th>Pressure ≥ 950 dbar</th>
<th>Num</th>
<th>Mean (mPSU)</th>
<th>Sdev (mPSU)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Leg 1</td>
<td>1320</td>
<td>0.01</td>
<td>0.32</td>
<td>1002</td>
</tr>
<tr>
<td></td>
<td>920</td>
<td>-0.02</td>
<td>0.34</td>
<td>656</td>
</tr>
<tr>
<td></td>
<td>1422</td>
<td>-0.02</td>
<td>0.36</td>
<td>1025</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>-0.04</td>
<td>0.41</td>
<td>296</td>
</tr>
</tbody>
</table>

Table 3.1.5. Difference between the CTD salinity and the bottle salinity after the post-cruise calibration. Mean and standard deviation (Sdev) are calculated for the data below and above 950 dbar. Number of data used (Num) is also shown.

<table>
<thead>
<tr>
<th>Leg</th>
<th>Pressure &lt; 950 dbar</th>
<th>Num</th>
<th>Mean (mPSU)</th>
<th>Sdev (mPSU)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Leg 1</td>
<td>25</td>
<td>0.01</td>
<td>0.32</td>
<td>1002</td>
</tr>
<tr>
<td></td>
<td>920</td>
<td>-0.02</td>
<td>0.34</td>
<td>656</td>
</tr>
<tr>
<td></td>
<td>1422</td>
<td>-0.02</td>
<td>0.36</td>
<td>1025</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>-0.04</td>
<td>0.41</td>
<td>296</td>
</tr>
</tbody>
</table>

Table 3.1.6. Calibration coefficients for the CTD salinity. Number of data used (Num) is also shown.
Figure 3.1.18. Difference between the CTD salinity and the bottle salinity for Leg.1. Blue and red dots indicate before and after the post-cruise calibration using the bottle salinity data, respectively. Top panel shows for $P \geq 950 \text{ dbar}$. Lower two panels show histogram of the difference after the calibration.

Figure 3.1.19. Same as Figure 3.1.18, but for Leg.2a.
Figure 3.1.20. Same as Figure 3.1.18, but for Leg.2b.

Figure 3.1.21. Same as Figure 3.1.18, but for Leg.3. Top panel shows for full pressure range.
(6.4) Oxygen (SBE 43)

The CTD oxygen is calibrated using the oxygen model as

Calibrated oxygen (ml/l)

\[
= \{(Soc+dSoc) \times \{v+offset+doffset\} \times \exp\{(TCor+dTCor) \times t + (PCor+dPCor) \times p\}\} \\
\times Oxsat(t, s)
\]

where \(p\) is pressure in dbar, \(t\) is absolute temperature and \(s\) is salinity in psu. \(Oxsat\) is oxygen saturation value minus the volume of oxygen gas (STP) absorbed from humidity-saturated air. \(Soc, offset, TCor\) and \(PCor\) are the pre-cruise calibration coefficients and \(dSoc, doffset, dTCor\) and \(dPCor\) are calibration coefficients. The best fit sets of coefficients are determined by minimizing the sum of absolute deviation with a weight from the bottle oxygen data. The MATLAB® function \text{FMINSEARCH} is used to determine the sets. The weight is given as a function of vertical oxygen gradient and pressure as

\[
\text{Weight} = \min\{4, \exp(\log(4) \times \text{Gr} / \text{Grad})\} \times \min\{4, \exp(\log(4) \times \text{P}^2 / \text{PR}^2)\}
\]

where \(\text{Grad}\) is vertical oxygen gradient in \(\mu\text{mol kg}^{-1}\text{ dbar}^{-1}\), and \(\text{P}\) is pressure in dbar. \(\text{Gr}\) and \(\text{PR}\) are threshold of the oxygen gradient (0.3 \(\mu\text{mol kg}^{-1}\text{ dbar}^{-1}\)) and pressure (1,000 dbar), respectively. When oxygen gradient is small (large) and pressure is large (small), the weight is large (small) at maximum (minimum) value of 16 (1). The oxygen gradient is calculated using down-cast CTD oxygen data. The down-cast CTD oxygen data is low-pass filtered with a 3-point (weights are 1/4, 1/2, 1/4) triangle filter before the calculation.

Finally oxygen data derived from following oxygen sensor are used for the data set in consideration for the data quality.

Leg.1: primary (S/N 0391)  
Leg.2a: primary (S/N 0391) for 146_2 and 148_1  
Leg.2b: secondary (S/N 0394) from 150_1 to WC8_1  
Leg.3: primary (S/N 0390) from WC9_1 to 351_2  

Table 3.1.7. Difference between the CTD oxygen and the bottle oxygen after the post-cruise calibration. Mean and standard deviation (Sdev) are calculated for the data below and above 950 dbar. Number of data used (Num) is also shown.

<table>
<thead>
<tr>
<th>Leg</th>
<th>Pressure ≥ 950 dbar</th>
<th>Pressure &lt; 950 dbar</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Num</td>
<td>Mean (µmol/kg)</td>
</tr>
<tr>
<td>Leg.1</td>
<td>1325</td>
<td>–0.04</td>
</tr>
<tr>
<td>Leg.2a</td>
<td>925</td>
<td>0.04</td>
</tr>
<tr>
<td>Leg.2b</td>
<td>1419</td>
<td>–0.03</td>
</tr>
<tr>
<td>Leg.3</td>
<td>25</td>
<td>–0.10</td>
</tr>
</tbody>
</table>

The down-cast CTD data sampled at same density of the up-cast CTD data created by the software module ROSSUM are used after the post-cruise calibration for the CTD temperature and salinity.

The coefficients are basically determined for each station. Some stations, especially for shallow stations, are grouped for determining the calibration coefficients. The results of the post-cruise calibration for the CTD oxygen are summarized in Table 3.1.7 and shown in from Figure 3.1.22 to Figure 3.1.5.19. And the calibration coefficients and number of the data used for the calibration are listed in Table 3.1.8.
Figure 3.1.22. Difference between the CTD oxygen and the bottle oxygen for Leg.1. Blue and red dots indicate before and after the post-cruise calibration using the bottle oxygen data, respectively. Top panel shows for \( P \geq 950 \) dbar. Lower two panels show histogram of the difference after the calibration.

Figure 3.1.23. Same as Figure 3.1.22, but for Leg.2a.
Figure 3.1.24. Same as Figure 3.1.22, but for Leg.2b.

Figure 3.1.25. Same as Figure 3.1.22, but for Leg.3. Top panel shows for full pressure range.
Table 3.1.8. Calibration coefficients for the CTD oxygen. Number of data used (Num) is also shown.

<table>
<thead>
<tr>
<th>i</th>
<th>j</th>
<th>k</th>
<th>S</th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>d</th>
<th>e</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.8341531072-4</td>
<td>1.1575444678e-3</td>
<td>3.79130682e-2</td>
<td>-0.3816050863e-3</td>
<td>5.29e858833383</td>
<td>2.999967525e-5</td>
<td>5.979509750e-6</td>
<td>1.649534582e-7</td>
<td>1.649534582e-7</td>
</tr>
<tr>
<td>1.848163261e-4</td>
<td>3.330544263e-4</td>
<td>3.79130682e-2</td>
<td>-0.3816050863e-3</td>
<td>5.29e858833383</td>
<td>2.999967525e-5</td>
<td>5.979509750e-6</td>
<td>1.649534582e-7</td>
<td>1.649534582e-7</td>
</tr>
<tr>
<td>2.848163261e-4</td>
<td>3.330544263e-4</td>
<td>3.79130682e-2</td>
<td>-0.3816050863e-3</td>
<td>5.29e858833383</td>
<td>2.999967525e-5</td>
<td>5.979509750e-6</td>
<td>1.649534582e-7</td>
<td>1.649534582e-7</td>
</tr>
<tr>
<td>3.848163261e-4</td>
<td>3.330544263e-4</td>
<td>3.79130682e-2</td>
<td>-0.3816050863e-3</td>
<td>5.29e858833383</td>
<td>2.999967525e-5</td>
<td>5.979509750e-6</td>
<td>1.649534582e-7</td>
<td>1.649534582e-7</td>
</tr>
</tbody>
</table>

Table continued...
Oxygen optode

The optode oxygen is calibrated by the Stern-Volmer equation, according to a method by Uchida et al. (submitted manuscript):

\[
O_2 (\mu\text{mol/l}) = \left( \frac{\tau_0}{\tau} - 1 \right) / K_{sv}
\]

where \(\tau\) is decay time, \(\tau_0\) is decay time in the absence of oxygen and \(K_{sv}\) is Stern-Volmer constant. The \(\tau_0\) and the \(K_{sv}\) are assumed to be functions of temperature as follows.

\[
K_{sv} = C_{11} + C_{12} \times t + C_{13} \times t^2
\]

\[
\tau_0 = C_{21} + C_{22} \times t
\]

\[
\tau = C_{31} + C_{32} \times P_b
\]

where \(t\) is CTD temperature (°C) and \(P_b\) is raw phase measurement (deg). The calibration coefficients (\(C_{11}, C_{12}, C_{13}, C_{21}, C_{22}, C_{31}\) and \(C_{32}\)) are determined for post-cruise calibration. The best fit sets of coefficients are determined by minimizing the sum of absolute deviation from the bottle oxygen data. The FORTRAN subroutine DMINF1 of the Scientific Subroutine Library II (Fujitsu Ltd., Kanagawa, Japan) is used to determine the sets.

For compensation of the pressure response of the sensing foil, the oxygen concentration is multiplied by the following factor \(1 + 0.032 \times P_b / 1000\), where \(P_b\) is pressure in dbar.

The calibration is performed for the up-cast phase data created by the software module ROSSUM after the post-cruise calibration for the CTD temperature and salinity.

The calibration coefficients are determined for Leg.1 and Leg.2 to 3. The results of the post-cruise calibration for the optode oxygen are summarized in Table 3.1.3 and shown in from Figure 3.1.26 and Figure 3.1.5.21. And the number of data used for the calibration are listed in Table 3.1.10.3.

Table 3.1.9. Difference between the optode oxygen and the bottle oxygen after the post-cruise calibration. Mean and standard deviation (Sdev) are calculated for the data below and above 950 dbar. Number of data (Num) used is also shown.

<table>
<thead>
<tr>
<th>Leg</th>
<th>Pressure ≥ 950 dbar</th>
<th>Pressure &lt; 950 dbar</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Num</td>
<td>Mean (µmol/kg)</td>
</tr>
<tr>
<td>Leg.1</td>
<td>1319</td>
<td>0.11</td>
</tr>
<tr>
<td>Leg.2/3</td>
<td>2365</td>
<td>-0.01</td>
</tr>
</tbody>
</table>

(6.5) Oxygen optode

The optode oxygen is calibrated by the Stern-Volmer equation, according to a method by Uchida et al. (submitted manuscript):

\[O_2 (\mu\text{mol/l}) = (\tau_s / \tau - 1) / K_{sv}\]

where \(\tau\) is decay time, \(\tau_s\) is decay time in the absence of oxygen and \(K_{sv}\) is Stern-Volmer constant. The \(\tau\) and the \(K_{sv}\) are assumed to be functions of temperature as follows.

\[K_{sv} = C_{11} + C_{12} t + C_{13} t^2\]

\[\tau_s = C_{21} + C_{22} t\]

\[\tau = C_{31} + C_{32} P_b\]

where \(t\) is CTD temperature (°C) and \(P_b\) is raw phase measurement (deg). The calibration coefficients (\(C_{11}, C_{12}, C_{13}, C_{21}, C_{22}, C_{31}\) and \(C_{32}\)) are determined for post-cruise calibration. The best fit sets of coefficients are determined by minimizing the sum of absolute deviation from the bottle oxygen data. The FORTRAN subroutine DMINF1 of the Scientific Subroutine Library II (Fujitsu Ltd., Kanagawa, Japan) is used to determine the sets.

For compensation of the pressure response of the sensing foil, the oxygen concentration is multiplied by the following factor \(1 + 0.032 \times P_b / 1000\), where \(P_b\) is pressure in dbar.

The calibration is performed for the up-cast phase data created by the software module ROSSUM after the post-cruise calibration for the CTD temperature and salinity.

The calibration coefficients are determined for Leg.1 and Leg.2 to 3. The results of the post-cruise calibration for the optode oxygen are summarized in Table 3.1.9 and shown in from Figure 3.1.26 and Figure 3.1.5.21. And the number of data used for the calibration are listed in Table 3.1.10.3.

Table 3.1.9. Difference between the optode oxygen and the bottle oxygen after the post-cruise calibration. Mean and standard deviation (Sdev) are calculated for the data below and above 950 dbar. Number of data (Num) used is also shown.

<table>
<thead>
<tr>
<th>Leg</th>
<th>Pressure ≥ 950 dbar</th>
<th>Pressure &lt; 950 dbar</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Num</td>
<td>Mean (µmol/kg)</td>
</tr>
<tr>
<td>Leg.1</td>
<td>1319</td>
<td>0.11</td>
</tr>
<tr>
<td>Leg.2/3</td>
<td>2365</td>
<td>-0.01</td>
</tr>
</tbody>
</table>
Figure 3.1.26. Difference between the optode oxygen and the bottle oxygen for Leg.1. Blue and red dots indicate before and after the post-cruise calibration using the bottle oxygen data, respectively. Top panel shows for $P \geq 950$ dbar. Lower two panels show histogram of the difference after the calibration.

Figure 3.1.27. Same as Figure 3.1.26, but for Leg.2 and Leg.3.
Table 3.1.10. Calibration coefficients for the optode oxygen. Number of data used (Num) for the calibration and mean absolute deviation (ADEV) between the optode oxygen and the bottle oxygen are also shown.

<table>
<thead>
<tr>
<th>Leg</th>
<th>Num</th>
<th>ADEV</th>
<th>$C_{11}$</th>
<th>$C_{12}$</th>
<th>$C_{13}$</th>
<th>$C_{21}$</th>
<th>$C_{22}$</th>
<th>$C_{31}$</th>
<th>$C_{32}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2332</td>
<td>0.41</td>
<td>3.05627e-3</td>
<td>1.40559e-4</td>
<td>2.14264e-6</td>
<td>61.1209</td>
<td>9.86981e-2</td>
<td>-8.48263</td>
<td>1.10631</td>
</tr>
<tr>
<td>2/3</td>
<td>4369</td>
<td>0.45</td>
<td>2.85451e-3</td>
<td>1.30281e-4</td>
<td>2.00579e-6</td>
<td>61.6282</td>
<td>0.101157</td>
<td>-7.42425</td>
<td>1.11110</td>
</tr>
</tbody>
</table>

References


3.2 Bottle Salinity

September 7, 2007

(1) Personnel

Takeshi Kawano (JAMSTEC)
Fujio Kobayashi (MWJ)
Naoko Takahashi (MWJ)
Tatsuya Tanaka (MWJ)

(2) Objectives

Bottle salinities were measured to compare with CTD salinities for identifying leaking bottles and for calibrating CTD salinities.

(3) Instrument and Method

(3.1) Salinity Sample Collection

The bottles in which the salinity samples are collected and stored are 250 ml Phoenix brown glass bottles with screw caps. Each bottle was rinsed three times with sample water and was filled to the shoulder of the bottle. The caps were also thoroughly rinsed. Salinity samples were stored more than 12 hours in the same laboratory as where the salinity measurement was made.

(3.2) Instruments and Method

The salinity analysis was carried out on Guildline Autosal salinometer model 8400B (S/N 62556), which was modified by attaching an Ocean Science International peristaltic-type sample intake pump and two Guildline platinum thermometers model 9450. One thermometer monitored an ambient temperature and the other monitored a bath temperature. The resolution of the thermometers was 0.001 degrees C. The measurement system was almost same as Aoyama et al (2003). The salinometer was operated in an air-conditioned laboratory of the ship at a bath temperature of 24 degrees C.

An ambient temperature varied from approximately 19 degrees C to 24 degrees C, while a bath temperature was very stable and varied within +/- 0.002 degrees C on rare occasion. A measure of a double conductivity ratio of a sample is taken as a median of thirty-one reading. Data collection was started after 5 seconds and it took about 10 seconds to collect 31 readings by a personal computer. Data were sampled for the sixth and seventh filling of the cell for Leg.1 and the eighth and ninth filling for Leg.2 and Leg.3. In the case where the difference between the double conductivity ratio of this two fillings is smaller than 0.00002, the average value of the two double conductivity ratios is used to calculate the bottle salinity with the algorithm for practical salinity scale, 1978 (UNESCO, 1981). If the difference is greater than or equal to 0.00003, we measure another additional filling of the cell. In the case where the double conductivity ratio of the additional filling does not satisfy the criteria above, we measure two other fillings of the cell and the median of the double conductivity ratios of five fillings are used to calculate the bottle salinity.

The measurement was conducted for about 10 to 18 hours per day (typically from 3:00 to 17:00) and the cell was cleaned with ethanol or soap or both after the measurement of the day. We measured more than 8,000 samples in total.

(4) Preliminary Result

(4.1) Stand Seawater

Leg.1

Standardization control was set to 501 and all measurements were done by this setting. STNBY was 5517 ±0001 and ZERO was 0.00001 ±0.00001. We used IAPSO Standard Seawater batch P145 whose conductivity ratio was 0.99981 (double conductivity ratio is 1.99962) as the standard for salinity. We measured 117 bottles of P145 during routine measurement. There were 5 bad bottles which conductivities are extremely high. Data of these 5 bottles are not taken into consideration hereafter.

Figure 3.2.1 shows the history of double conductivity ratio of the Standard Seawater batch P145.
Figure 3.2.1. History of double conductivity ratio of P145 during Leg.1. X and Y axes represent time (Julian day) and double conductivity ratio, respectively.

Drifts were calculated by fitting data from P145 to the equation obtained by the least square method (solid lines). Correction for the double conductivity ratio of the sample was made to compensate for the drift (Figure 3.2.2). After correction, the average of double conductivity ratio became 1.99961 and the standard deviation was 0.000012, which is equivalent to 0.0002 in salinity. We added 0.00001 to the corrected measured double conductivity ratio.

Figure 3.2.2. History of double conductivity ratio of P145 during Leg.1. X and Y axes represent time (Julian day) and double conductivity ratio, respectively. (after correction)

Leg.2

Standardization control was set to 474 before WIPE (Wake Islands passage Flux Experiment). STNBY was 5498 ±0.0001 and ZERO was 0.00001 ±0.00001. We removed the conductivity cell and washed it thoroughly with soap. Then, standardization control was changed to 479. STNBY became 5501 ±0.0001 and ZERO was 0.00001 ±0.00001.

We used IAPSO Standard Seawater batch P145 whose conductivity ratio was 0.99981 (double conductivity ratio is 1.99962) as the standard for salinity. We measured 54 bottles of P145 during routine measurement before WIPE and 109 bottles after WIPE. There were 2 bad bottles whose conductivities were extremely high. Data of these 2 bottles are not taken into consideration hereafter.

Figure 3.2.3 shows the history of double conductivity ratio of the Standard Seawater batch P145. Drifts were calculated by fitting data from P145 to the equation obtained by the least square method (solid lines). Correction for the double conductivity ratio of the sample was made to compensate for the drift (Figure 3.2.4). After
correction, the average of double conductivity ratio became 1.99962 and the standard deviation was 0.00012 before WIPE and 0.00011 after WIPE, those are equivalent to 0.0002 in salinity. We added 0.000021 before WIPE and 0.000012 after WIPE to the corrected measured double conductivity ratio.

Leg.3

Standardization control was set to 484 and all the measurements were done by this setting. STNBY was 5505 ±0.001 and ZERO was 0.00001 ±0.00001. We used IAPSO Standard Seawater batch P145 whose conductivity ratio was 0.99981 (double conductivity ratio is 1.99962) as the standard for salinity. We measured 25 bottles of P145 during routine measurement.

Figure 3.2.5 shows the history of double conductivity ratio of the Standard Seawater batch P145. Drifts were calculated by fitting data from P145 to the equation obtained by the least square method (solid lines). Correction for the double conductivity ratio of the sample was made to compensate for the drift (Figure 3.2.6). After correction, the average of double conductivity ratio became 1.99962 and the standard deviation was 0.00014, which is equivalent to 0.0003 in salinity. We added 0.000004 to the corrected measured double conductivity ratio.
(4.2) Sub-Standard Seawater

We also used sub-standard seawater which was a deep-sea water filtered by pore size of 0.45 micrometer and was stored in a 20 liter cubitainer made of polyethylene and stirred for at least 24 hours before measuring. It was measured every six samples in order to check possible sudden drift of the salinometer. During the whole measurements, there was no detectable sudden drift of the salinometer.

(4.3) Replicate and Duplicate Samples

Leg.1

We took 435 pairs of replicate and 27 pairs of duplicate samples. Figure 3.2.7 (a) and (b) shows the histogram of the absolute difference between each pair the replicate samples and that of the duplicate samples, respectively. There were 2 bad measurements in the replicate samples. Particularly, one of the pair was extremely high (more than 0.01 in salinity). Excluding these bad measurements, the standard deviation of the absolute difference in 433 pairs of the replicate samples was 0.00017 in salinity and that in 27 pairs of the duplicate samples was 0.00032 in salinity.

Leg.2

We took 668 pairs of replicate and 20 pairs of duplicate samples. Figure 3.2.8 (a) and (b) shows the histogram of the absolute difference between each pair of the replicate samples and that of the duplicate samples, respectively. There were 3 questionable measurements in the replicate samples. Excluding these questionable measurements, the standard deviation of the absolute difference in 665 pairs of the replicate samples was 0.00017 in salinity and that in 20 pairs of the duplicate samples was 0.00025 in salinity.

Leg.3

We took 48 pairs of replicate and 3 pairs of duplicate samples. Figure 3.2.9 shows the histogram of the absolute difference between each pair of the replicate samples. There was one bad (miss-trip) sample for
duplicates. The standard deviation of the absolute difference of 48 pairs of the replicate samples was 0.00031 in salinity. The absolute differences in salinity between 2 duplicate samples were 0.00002 and 0.00007.

The results of replicate samples were averaged and flagged as 6 in the seafile.

Reference


Figure 3.2.7 (a). The histogram of the absolute difference between replicate samples in Leg.1.

Figure 3.2.7 (b). The histogram of the absolute samples between duplicate samples in Leg.1.
Figure 3.2.8 (a). The histogram of the absolute difference between replicate samples in Leg.2.

Figure 3.2.8 (b). The histogram of the absolute samples between duplicate samples in Leg.2.

Figure 3.2.9. The histogram of the absolute difference between replicate samples in Leg.3.
3.3 Bottle Oxygen

May 1, 2007

(1) Personnel

Yuichiro Kumamoto (JAMSTEC)
Ikuo Kaneko (JAMSTEC)
Takayoshi Seike (MWJ)
Keisuke Wataki (MWJ)
Kimiko Nishijima (MWJ)
Takuhei Shiozaki (MWJ)

(2) Objectives

Dissolved oxygen is one of significant tracers for ocean circulation study. Recent studies on the subarctic North Pacific indicated that dissolved oxygen concentration in intermediate layers decreased in basin wide scale during the past decades. The causes of the decrease, however, are still unclear. During MR05-05 Leg.1 (from 31-Oct-05 to 24-Nov-05), Leg.2 (from 27-Nov-05 to 17-Jan-06), and Leg.3 (from 20-Jan-06 to 30-Jan-06), we measured dissolved oxygen concentration from surface to bottom layers at all the hydrocast stations along around 24°N. These stations were the reoccupation of the WHP-P03 stations in 1985. Our purpose is to evaluate change of dissolved oxygen in the subtropical North Pacific between 1985 and 2005/2006.

(3) Reagents

Pickling Reagent I: Manganese chloride solution (3 M)
Pickling Reagent II: Sodium hydroxide (8 M) / sodium iodide solution (4 M)
Sulfuric acid solution (5 M)
Sodium thiosulfate (0.025 M)

Potassium iodate (0.001667 M)
CSK standard of potassium iodate: Lot ASE8281, Wako Pure Chemical Industries Ltd., 0.0100 N

(4) Instruments

Burette for sodium thiosulfate;
APB-510 manufactured by Kyoto Electronic Co. Ltd. / 10 cm³ of titration vessel
Burette for potassium iodate;
APB-410 manufactured by Kyoto Electronic Co. Ltd. / 20 cm³ of titration vessel
Detector; Automatic photometric titrator manufactured, Kimoto Electronic Co. Ltd.

(5) Seawater sampling

Following procedure is based on a determination method in the WHP Operations Manual (Dickson, 1996). Seawater samples were collected from Niskin sampler bottles attached to the CTD-system. Seawater for bottle oxygen measurement was transferred from the Niskin sampler bottle to a volume calibrated glass flask (ca. 100 cm³). Three times volume of the flask of seawater was overflowed. Sample temperature was measured by a thermometer during the overflowing. Then two reagent solutions (Reagent 1, II) of 0.5 cm³ each were added immediately into the sample flask and the stopper was inserted carefully into the flask. The sample flask was then shaken vigorously to mix the contents and to disperse the precipitate finely throughout. After the precipitate has settled at least halfway down the flask, the flask was shaken again vigorously to disperse the precipitate. The sample flasks containing pickled samples were stored in a laboratory until they were titrated.

(6) Sample measurement

At least two hours after the re-shaking, the pickled samples were measured on board. A magnetic stirrer bar and 1 cm³ sulfuric acid solution were added into the sample flask and stirring begun. Samples were titrated by sodium thiosulfate solution whose molarity was determined by potassium iodate solution (section 3.3.7).
Temperature of sodium thiosulfate during titration was recorded by a thermometer. We measured dissolved oxygen concentration using two sets of the titration apparatus, named DOT-1 and DOT-3. Dissolved oxygen concentration (µmol kg⁻¹) was calculated by the sample temperature during the sampling, CTD salinity, flask volume, and titrated volume of the sodium thiosulfate solution.

(7) Standardization

Concentration of sodium thiosulfate titrant (ca. 0.025 M) was determined by potassium iodate solution. Pure potassium iodate was dried in an oven at 130°C. 1.7835 g potassium iodate accurately weighed out was dissolved in deionized water and diluted to final volume of 5 dm³ in a calibrated volumetric flask (0.001667 M). 10 cm³ of the standard potassium iodate solution was added to a flask using a volume-calibrated dispenser. Then, 90 cm³ of deionized water, 1 cm³ of sulfuric acid solution, and 0.5 cm³ of pickling reagent solution II and I were added into the flask in order. Amount of titrated volume of sodium thiosulfate (usually 5 times measurements average) gave the molarity of the sodium thiosulfate titrant. Table 3.3.1 shows the result of the standardization during this cruise. Error (C.V.) of the standardization was 0.02±0.01%, ca. 0.05 µmol kg⁻¹.

(8) Determination of the blank

The oxygen in the pickling reagents I (0.5 cm³) and II (0.5 cm³) was assumed to be 3.8 x 10⁻⁸ mol (Murray et al., 1968). The blank from the presence of redox species apart from oxygen in the reagents (the pickling reagents I, II, and the sulfuric acid solution) was determined as follows. 1 cm³ and 2 cm³ of the standard potassium iodate solution were added to two flasks, respectively. Then 100 cm³ of deionized water, 1 cm³ of sulfuric acid solution, and 0.5 cm³ of pickling reagent solution II and I each were added into the two flasks in order. The blank was determined by difference between the two times of the first (1 cm³ of KIO₃) titrated volume of the sodium thiosulfate and the second (2 cm³ of KIO₃) one. The results of 3 times blank determinations were averaged (Table 3.3.1). The averaged blank of DOT-1 and DOT-3 during the whole legs were -0.009 and -0.005 cm³, respectively.
Table 3.3.1.  (continued)

<table>
<thead>
<tr>
<th>Date (UTC)</th>
<th>KIO₃ DOT-1 (cm³)</th>
<th>DOT-3 (cm³)</th>
<th>Samples (Stations)</th>
<th># bottle</th>
<th>Na₂S₂O₃ E.P. blank</th>
<th>Na₂S₂O₃ E.P. blank</th>
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<td>1.969</td>
</tr>
</tbody>
</table>

# Batch number of the KIO₃ standard solution.

(9) Reagent blank

The blank determined in section 3.3.8, pure water blank (Vₖᵦ₋ₖₒ) can be represented by equation 1,

\[ V_{dk,0} = V_{dk,oe} + V_{dk,reg} \]  

(1)

where

\[ V_{dk,oe} = \text{blank due to differences between the measured end-point and the equivalence point;} \]

\[ V_{dk,reg} = \text{blank due to oxidants or reductants in the reagent.} \]

Here, the reagent blank (Vₖᵦ₋ₖₒ) was determined by following procedure. 1 cm³ of the standard potassium iodate solution and 100 cm³ of deionized water were added to two flasks each. 1 cm³ of sulfuric acid solution, and 0.5 cm³ of pickling reagent solution II and I each were added into the first flask in order. Then, two times volume of the reagents (2 cm³ of sulfuric acid solution, and 1.0 cm³ of pickling reagent solution II and I each) was added to the second flask. The reagent blank was determined by difference between the first (2 cm³ of the total reagent volume added) titrated volume of the sodium thiosulfate and the second (4 cm³ of the total reagent volume added) one. We also carried out experiments for three and four times volume of the reagents. The results are shown in Figure 3.3.1

\[ V_{bk,reg} = \text{blank due to redox species apart from oxygen in the reagents.} \]

The relation between difference of the titrant (Na₂S₂O₃) volume and the volume of the reagents added

Figure 3.3.1. Blank (cm³) due to redox species apart from oxygen in the reagents.

\[ R^2 = 0.7918 \]
(\(V_{\text{reagent}}\)) is expressed by equation 2,

\[
\text{Difference of the titrant volume} = -0.0009 \ V_{\text{reagent}} \quad (2)
\]

There was no significant difference between the results of DOT-1 and DOT-3. \(V_{\text{blk, reg}}\) was estimated to be about -0.002 cm\(^3\), suggesting that about 0.01 µmol of reductants was contained in every 2 cm\(^3\) of the reagents added. In other words, the difference of the pure water blank (\(V_{\text{blk, pw}}\)) between DOT-1 and DOT-3, determined in the section 3.3.8, was due to the difference of the end-point blank (\(V_{\text{blk, ep}}\)) between the two titration apparatus (-0.007 and -0.003 cm\(^3\) for DOT-1 and DOT-3, respectively).

(10) Sample blank

Blank due to redox species other than oxygen in the sample (\(V_{\text{blk, spl}}\)) can be a potential source of measurement error. The total blank during the seawater measurement, the seawater blank (\(V_{\text{blk, sw}}\)) can be represented by equation 3,

\[
V_{\text{blk, sw}} = V_{\text{blk, spl}} + V_{\text{blk, dw}} \quad (3)
\]

If the pure water blank (\(V_{\text{blk, pw}}\)) that is determined in section 3.3.8 is identical both in pure water and in seawater, the difference between the seawater blank and the pure water one gives the sample blank (\(V_{\text{blk, spl}}\)).

Here, \(V_{\text{blk, dw}}\) was determined by following procedure. Seawater sample was collected in the volume calibrated glass flask (ca. 100 cm\(^3\)) without the pickling. Then 1 cm\(^3\) of the standard potassium iodate solution, 1 cm\(^3\) of sulfuric acid solution, and 0.5 cm\(^3\) of pickling reagent solution II and I each were added into the flask in order. Additionally a flask contained 1 cm\(^3\) of the standard potassium iodate solution, 100 cm\(^3\) of deionized water, 1 cm\(^3\) of sulfuric acid solution, and 0.5 cm\(^3\) of pickling reagent solution II and I was prepared. The difference of the titrant volumes of the seawater flask and the deionized water one gave the sample blank (\(V_{\text{blk, spl}}\)).

We measured vertical profiles of the sample blank at four stations (Table 3.3.2) using DOT-1 system. The sample blank ranged from 0.4 to 0.8 µmol kg\(^{-1}\) and its vertical and horizontal variations are small. Our results agree to reported values ranged from 0.4 to 0.8 µmol kg\(^{-1}\) (Culberson et al., 1991) and our previous results obtained in the western North Pacific, reoccupation of WHP-P10 in 2005. Ignorant of the blank sample will cause systematic errors in the oxygen calculations, but these errors are expected to be the same to all investigators and not to affect the comparison of results from different investigators (Culberson, 1994).

<table>
<thead>
<tr>
<th>Station: P03-006</th>
<th>Station: P03-031</th>
<th>Station: P03-136</th>
<th>Station: P03-215</th>
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<tr>
<td>CTD Pres.</td>
<td>CTD Pres.</td>
<td>CTD Pres.</td>
<td>CTD Pres.</td>
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<tr>
<td>dbar</td>
<td>Sample blank</td>
<td>dbar</td>
<td>Sample blank</td>
</tr>
<tr>
<td>µmol kg(^{-1})</td>
<td>µmol kg(^{-1})</td>
<td>µmol kg(^{-1})</td>
<td>µmol kg(^{-1})</td>
</tr>
<tr>
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<td>1867</td>
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<td>4459</td>
<td>0.72</td>
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(11) Replicate sample measurement

Replicate samples were taken from every CTD cast. Total amount of the replicate sample pairs in good measurement (flag=2) was 837. The standard deviation of the replicate measurement was 0.08 µmol kg\(^{-1}\) and there was no significant difference between DOT-1 and DOT-3 measurements. The standard deviation was calculated by a procedure (SOP23) in DOE (1994). The difference between the replicate sample pairs did not depend on sampling pressure (Figure 3.3.2) and measurement date (Figure 3.3.3). The standard deviations during
Leg.1, Leg.2, and Leg.3 were 0.083 (n=299) and 0.083 (n=493), and 0.085 \( \mu \text{mol kg}^{-1} \) (n=45), respectively. In the hydrographic data sheet, a mean of replicate sample pairs is shown with the flag 2.

![Figure 3.3.2. Differences in the replicate measurements against sampling pressure.](image)

(12) Duplicate sample measurement

We also collected seawater samples from two Niskin samplers that were collected at same depth (duplicate sampling). Total 50 pairs of the duplicate samples were taken in deep layers below 800 dbar during all the legs. The standard deviation of the total duplicate measurement was 0.10 \( \mu \text{mol kg}^{-1} \). We concluded that total measurement error of bottle oxygen was less than 0.10 \( \mu \text{mol kg}^{-1} \) during MR05-05 cruise.

![Figure 3.3.3. Differences in the replicate measurements against measurement date (Julian date).](image)

(13) CSK standard measurements

The CSK standard solution is commercial potassium iodate solution (0.0100 N) for analysis of oxygen in seawater. During the cruises, we measured concentration of the CSK standard solution (Lot ASE8281) against our KIO3 standard in order to confirm the accuracy of our oxygen measurement on board (Table 3.3.3). Error weighted means of DOT-1 and DOT-3 results were 0.009999±0.000005 and 0.010002±0.000006 normal (N) respectively, which indicates that there was no systematic difference between DOT-1 and DOT-3 measurements. The averaged value of the CSK standard solution was so close to the certified value (0.0100 N) that we did not correct sample measurements results using the CSK standard results. Additionally, we also measured the same lot (ASE8281) of the CSK standard solution during our previous cruise in 2005 (MR05-02). Results of the CSK measurements in the both cruises agreed well within the errors (less than 0.1%), suggesting that there was no systematic difference in the oxygen measurements between MR05-02 and MR05-05.
Table 3.3.3. Results of the CSK standard measurements.

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<th>DOT-2</th>
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</thead>
<tbody>
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<td>error (N)</td>
<td>Conc. (N)</td>
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Table 3.3.4. Summary of assigned quality control flags.

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<tr>
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</tr>
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<td>4</td>
<td>Bad (Faulty)</td>
</tr>
<tr>
<td>5</td>
<td>Not reported (missing)</td>
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<td></td>
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<td>6,717</td>
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</table>

(14) Quality control flag assignment

Quality flag values were assigned to oxygen measurements using the code defined in Table 0.2 of WHP Office Report WHP 91-1 Rev.2 section 4.5.2 (Joyce et al., 1994). Measurement flags of 2 (good), 3 (questionable), 4 (bad), and 5 (missing) have been assigned (Table 3.3.4). The replicate data (section 3.3-11) were averaged and flagged 2 if both of them were flagged 2. If either of them was flagged 3 or 4, a datum with "younger" flag was selected. Thus, we did not use flag of 6 (replicate measurements). For the choice between 2, 3, or 4, we basically followed a flagging procedure as listed below:

a. Bottle oxygen concentration and difference between bottle oxygen and CTD oxygen at the sampling were plotted against CTD pressure. Any points not lying on a generally smooth trend were noted.

b. Dissolved oxygen was then plotted against potential temperature or sigma-theta. If a datum deviated from a group of plots, it was flagged 3.

c. Vertical sections against pressure and potential density were drawn. If a datum was anomalous on the section plots, datum flag was degraded from 2 to 3, or from 3 to 4.

d. If the bottle flag was 4 (did not trip correctly), a datum was flagged 4 (bad). In the case of the bottle flag 3 (leaking) or 5 (unknown problem), a datum was flagged based on steps a, b, and c.

(15) Results

(15.1) Comparison at cross-stations during MR05-05

At stations of P03-146, 217, and 351, hydrocast sampling for dissolved oxygen was conducted two times at interval of about a week. Dissolved oxygen profiles of the two hydrocasts at the three cross-stations agreed well (Figure 3.3.4). In the layers deeper than 4,000 dbar, difference of dissolved oxygen between the two hydrocasts was calculated to be 0.20 µmol kg⁻¹ (standard deviation, n=24).

(15.2) Comparison at cross-stations of MR05-05 and MR05-02

During June of 2006, we also conducted another repeat cruise of WHP-P10, named MR05-02 cruise, along about 149°E in the western North Pacific. At the cross point of MR05-05 and MR05-02, we carried out two cross-stations at 24.5°N/149.4°E (MR05-02_P10-067 and MR05-05_P03-X10) and 24.2°N/149.0°E (MR05-02_P10-X03 and MR05-05_P03-275). Repeat measurements of dissolved oxygen at interval of about six months showed that dissolved oxygen decreased by 20 µmol kg⁻¹ in deep layers ranged from about 1,500 to 2,500 dbar (Figure 3.3.5). It should also be noted that oxygen concentration also decreased slightly (about 2 µmol kg⁻¹) in bottom water below 5,000 dbar at the both two cross-stations. As mentioned in section 3.3.15.1, the results at the cross-stations during MR05-05 cruise showed that the repeat measurements of dissolved oxygen in bottom water agreed within 0.2 µmol kg⁻¹. Additionally, using the CSK standard solution we ensured traceability of dissolved oxygen.
oxygen analyses during MR05-02 and MR05-05 cruises within about 0.1% correspondent to about 0.2 \( \mu \text{mol kg}^{-1} \) (section 3.3.13). These results indicate that total reproducibility of our oxygen measurement is about 0.2 \( \mu \text{mol kg}^{-1} \), suggesting that observed oxygen decreases of about 2 \( \mu \text{mol kg}^{-1} \) in the bottom water at the cross-stations are significant. The variability of oxygen concentration within six months in the deep and bottom waters implies that apparent decadal change of dissolved oxygen derived from repeat hydrography should be discussed carefully.

![Figure 3.3.4](image1.png)

Figure 3.3.4. Comparison of dissolved oxygen profiles between the first hydrocast (circles) and the second one (crosses) at the cross-stations of Stn. P03-146 (a), -217 (b), and -351 (c) during MR05-05 cruise.

![Figure 3.3.5](image2.png)

Figure 3.3.5. Comparison of dissolved oxygen profiles during MR05-02 and MR05-05 cruises at the cross-stations located at 24.5\(^\circ\)N/149.4\(^\circ\)E (a) and 24.2\(^\circ\)N/149.0\(^\circ\)E (b). Circles show data obtained at Stn. P03-X10 (a) and P03-275 (b) of MR05-05 cruise on December/12/2005. Crosses indicate data obtained at Stn. P10-067 (a) and P10-X03 (b) of MR05-02 cruise on June/10/2005.

(15.3) Comparison with WHP-P03 oxygen data in 1985

We compared our oxygen data and gridded data of WHP-P03 in 1985 and found that our oxygen data were slightly lower than those of WHP-P03. Below 2,000 m depth the difference in average is calculated in \(-2.2 \pm 1.7 \mu\text{mol kg}^{-1}\) (Figure 3.3.6). This "offset" value is closed to reported adjustments, about minus 3 \( \mu\text{mol kg}^{-1} \) for dissolved oxygen data of WHP-P03 (Johnson et al., 2001; Gouretski and Jancke, 2001). We here corrected oxygen data of WHP-P03 by the averaged offset value, 2.2 \( \mu\text{mol kg}^{-1} \).
Figure 3.3.6. Oxygen difference (2005/2006 data minus 1985 data, µmol kg\(^{-1}\)) against water depth. Closed circles denote mean of the differences with 1 sigma error at sampling layers.

Figure 3.3.7(a) shows distribution of oxygen difference (2005/2006 data minus 1985 data) against water depth. Below 1,000 m depth, there were not differences more than 5 µmol kg\(^{-1}\). The dispersion of the difference in the deep/bottom water (±1.7 µmol kg\(^{-1}\) for 1 sigma) was also independent from the sampling depths, suggesting that the dispersion was derived from analytical errors and the data gridding. The dispersion of 2 sigma (±3.4 µmol) and the offset correction of 2.2 µmol kg\(^{-1}\) imply that oxygen differences less than 5 µmol kg\(^{-1}\) between 1985 and 2005/06 is not significant. In the layers shallower than 1,000 m depth, we found some increases and decreases of dissolved oxygen. In order to focus on the shallow variations, the differences were plotted against water density (sigma theta) from 24.5 to 27.5 (approximately correspondent to layers from 200 to 1,200 m depth) in Figure 3.3.7(b).

Figure 3.3.7. Differences of dissolved oxygen (µmol kg\(^{-1}\)) between 2005/06 and 1985 (2005/2006 data minus 1985 data) against water depth (a) and water density, sigma-theta (b). Data of WHP-P03 in 1985 were corrected by the deep/bottom offset. Contour intervals are 5 µmol kg\(^{-1}\). Small dots indicate sampling layers of dissolved oxygen during MR05-06 in 2005/06.
We found a significant decrease of dissolved oxygen at the eastern end where oxygen concentration was relatively low. This decrease may be due to variability of local upwelling. Oxygen increase around 130°W to the International Date Line ranged from 25.0 to 26.2 sigma theta implies variation of mesoscale eddies. From 160°W to 160°E, around 26.8 sigma theta dissolved oxygen decreased, which is similar to the intermediate oxygen decrease in the subarctic regions in the North Pacific (Emerson et al., 2001; Watanabe et al., 2001). The decadal change along around 24°N, however, was smaller than that found in the subarctic North Pacific.

References
Gouretski, V.V. and K. Jancke (2001) Systematic errors as the causes for an apparent deep water property variability: global analysis of the WOCE and historical hydrographic data, Prog. Oceanogr., 48, 337-402.
3.4 Nutrients

July 19, 2007

(1) Personnel

Michio Aoyama (MRI / Japan Meteorological Agency, Principal Investigator)

Leg.1

Kenichiro Sato (MWJ)
Ayumi Takeuchi (MWJ)
Junji Matsushita (MWJ)

Leg.2

Junko Hamanaka (MWJ)
Ayumi Takeuchi (MWJ)
Kohei Miura (MWJ)

Leg.3

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Kohei Miura (MWJ)

(2) Objectives

The objectives of nutrients analyses during the R/V MIRAI MR0505 cruise along 24N line in the Western North Pacific are as follows:

- Describe the present status of nutrients concentration with excellent comparability.
- The determinants are nitrate, nitrite, phosphate and silicate (Although silicic acid is correct, we use silicate because a term of silicate is widely used in oceanographic community.)
- Study the temporal and spatial variation of nutrients based on the previous high quality experiments data of WOCE, GOESECS, IGY and so on.
- Study temporal and spatial variation of nitrate: phosphate ratio, so-called Redfield ratio.
- Obtain more accurate estimation of total amount of nitrate, phosphate and silicate in the interested area.
- Provide more accurate nutrients data for physical oceanographers to use as tracers for water mass movement.

(3) Equipment and techniques

(3.1) Analytical detail using TRAACS 800 systems (BRAN+LUEBBE)

The phosphate analysis is a modification of the procedure of Murphy and Riley (1962).

Molybdic acid is added to the seawater sample to form phosphomolybdic acid which is in turn reduced to phosphomolybdous acid using L-ascorbic acid as the reductant.

Nitrate + nitrite and nitrate are analyzed by according to the modification method of Grasshoff (1970).

The sample nitrate is reduced to nitrite in a cadmium tube inside of which is coated with metallic copper. The sample stream with its equivalent nitrite is treated with an acidic, sulfanilamide reagent and the nitrite forms nitrous acid which reacts with sulfanilamide to produce a diazonium ion. N1-Naphthylethylene-diamine added to the sample stream then couples with the diazonium ion to produce a red, azo dye. With reduction of the nitrate to nitrite, both nitrate and nitrite react and are measured; without reduction, only nitrite reacts. Thus, for the nitrite analysis, no reduction is performed and the alkaline buffer is not necessary. Nitrate is computed by difference.

The silicate method is analogous to that described for phosphate. The method used is essentially that of Grasshoff et al. (1983), wherein silicomolybdic acid is first formed from the silicic acid in the sample and added molybdic acid; then the silicomolybdic acid is reduced to silicomolybdous acid, or “molybdenum blue,” using ascorbic acid as the reductant.

The flow diagrams and regents for each parameter are shown in Figures 3.4.1-3.4.4.
Nitrate Reagents

Imidazole (buffer), 0.06 M (0.4% w/v)
Dissolve 4 g imidazole, C₃H₄N₂, in ca. 900 ml DIW; add 2 ml concentrated HCl; make up to 1,000 ml with DIW. After mixing, 1 ml Triton(R)X-100 (50% solution in ethanol) is added.

Sulfanilamide, 0.06 M (1% w/v) in 1.2 M HCl
Dissolve 10 g sulfanilamide, 4-NH₂C₆H₄SO₃H, in 1,000 ml of 1.2 M (10%) HCl. After mixing, 1 ml Triton(R)X-100 (50% solution in ethanol) is added.

N-1-Napthylethylene-diamine dihydrochloride, 0.004 M (0.1% w/v)
Dissolve 1 g NEDA, C₁₀H₇NHCH₂CH₂NH₂ · 2HCl, in 1,000 ml of DIW; containing 10 ml concentrated HCl. Stored in a dark bottle.

Nitrite Reagents

Sulfanilamide, 0.06 M (1% w/v) in 1.2 M HCl
Dissolve 10 g sulfanilamide, 4-NH₂C₆H₄SO₃H, in 1,000 ml of 1.2 M (10%) HCl. After mixing, 1 ml Triton(R)X-100 (50% solution in ethanol) is added.

N-1-Napthylethylene-diamine dihydrochloride, 0.004 M (0.1% w/v)
Dissolve 1 g NEDA, C₃H₇NHCH₂CH₂NH₂ · 2HCl, in 1,000 ml of DIW; containing 10 ml concentrated HCl. Stored in a dark bottle.
Silicic Acid Reagents

- Molybdic acid, 0.06 M (2% w/v)
  - Dissolve 15 g Disodium Molybdate(VI) Dihydrate, $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$, in 1,000 ml DIW containing 6 ml $\text{H}_2\text{SO}_4$.
  - After mixing, 20 ml sodium dodecyl sulphate (15% solution in water) is added.

- Oxalic acid, 0.6 M (5% w/v)
  - Dissolve 50 g Oxalic Acid Anhydrous, HOOC: COOH, in 1,000 ml of DIW.

- Ascorbic acid, 0.01 M (3% w/v)
  - Dissolve 2.5 g L (+)-Ascorbic Acid, C$_6$H$_8$O$_6$, in 100 ml of DIW. Stored in a dark bottle and freshly prepared before every measurement.

Phosphate Reagents

- Stock molybdate solution, 0.03 M (0.8% w/v)
  - Dissolve 8 g Disodium Molybdate(VI) Dihydrate, $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$, and 0.17 g Antimony Potassium Tartrate, C$_7$H$_7$K$_2$O$_7$Sb$_2$·3H$_2$O, in 1,000 ml of DIW containing 50 ml concentrated $\text{H}_2\text{SO}_4$.

- Mixed Reagent
  - Dissolve 0.8 g L (+)-Ascorbic Acid, C$_6$H$_8$O$_6$, in 100 ml of stock molybdate solution. After mixing, 2 ml sodium dodecyl sulphate (15% solution in water) is added. Stored in a dark bottle and freshly prepared before every measurement.

- PO$_4$ dilution
  - Dissolve Sodium Hydrate, NaCl, 10 g in ca. 900 ml, add 50 ml Acetone and 4 ml concentrated $\text{H}_2\text{SO}_4$, make
up to 1,000 ml. After mixing, 5 ml sodium dodecyl sulphate (15% solution in water) is added.

(3.2) Sampling procedures

Sampling of nutrients followed that of oxygen, trace gases and salinity. Samples were drawn into two of virgin 10 ml polyacrylates vials without sample drawing tubes. These were rinsed three times before filling and vials were capped immediately after the drawing. The vials are put into water bath at 25 +1 deg. C for 10 minutes before used to stabilize the temperature of samples.

No transfer was made and the vials were set an auto sampler tray directly. Samples were analyzed after collection, basically within 17 hours.

(3.3) Data processing

Raw data from TRAACS800 were treated as follows:

Check baseline shift.

Check the shape of each peak and the positions of the peak values taken, and then change the positions of the peak values taken if necessary.

Carryover correction and baseline drift correction were applied to peak heights of each sample followed by sensitivity correction.

Baseline correction and sensitivity correction were done basically by using liner regression.

Load pressure and salinity from CTD data to calculate density of seawater.

Calibration curves to get nutrients concentration were assumed second order equations.

(4) Nutrients standards

(4.1) In-house standards

(i) Volumetric Laboratory Ware

All volumetric glass- and plastic (PMP)-ware used were gravimetrically calibrated. Plastic volumetric flasks were gravimetrically calibrated at the temperature of use within 2-3 K.

Volumetric flasks

Volumetric flasks of Class quality (Class A) are used because their nominal tolerances are 0.05% or less over the size ranges that are likely to be used in this work. Class A flasks are made of borosilicate glass, and the standard solutions were transferred to plastic bottles as quickly as possible after they were made up to volume and well mixed in order to prevent excessive dissolution of silicic acid from the glass. High quality plastic (polymethylpentene, PMP or polypropylene) volumetric flasks were gravimetrically calibrated and used only within 3-4 K of the calibration temperature.

The computation of volume contained by glass flasks at various temperatures other than the calibration temperatures were done by using the coefficient of linear expansion of borosilicate crown glass.

Because of their larger temperature coefficients of cubical expansion and lack of tables constructed for these materials, the plastic volumetric flasks were gravimetrically calibrated over the temperature range of intended use and used at the temperature of calibration within 3-4 K. The weights obtained in the calibration weightings were corrected for the density of water and air buoyancy.

Pipettes and pipettors

All pipettes have nominal calibration tolerances of 0.1% or better. These were gravimetrically calibrated in order to verify and improve upon this nominal tolerance.

(ii) Reagents, general considerations

General Specifications

All reagents were of very high purity such as “Analytical Grade,” “Analyzed Reagent Grade” and others. In addition, assay of nitrite was determined according as JISK8019 and assays of nitrite salts were 98.9%. We use that value to adjust the weights taken.
For the silicate standards solution, we use commercial available silicon standard solution for atomic absorption spectrometry of 1,000 mg L\(^{-1}\). Since this solution is alkaline solution of 0.5 M KOH, an aliquot of 40 ml solution were diluted to 500 ml as B standard together with an aliquot of 20 ml of 1 M HCl. Then the pH of B standard for silicate prepared to be 6.9.

Ultra pure water

Ultra pure water (MilliQ water) freshly drawn was used for preparation of reagents, higher concentration standards and for measurement of reagent and system blanks.

Low-Nutrient Seawater (LNSW)

Surface water with low nutrient concentration was taken and filtered using 0.45 µm pore size membrane filter. This water is stored in 20 liter cubitainer with paper box. The concentrations of nutrient of this water were measured carefully in March 2005.

(iii) Concentrations of nutrients for A, B and C standards

Concentrations of nutrients for A, B and C standards are set as shown in Table 3.4.1. The C standard is prepared by according as recipes, as shown in Table 3.4.2. All volumetric laboratory tools were calibrated prior to the cruise as stated in chapter (i). Then the actual concentration of nutrients in each fresh standard was calculated based on the ambient, solution temperature and determined factors of volumetric laboratory wares.

Table 3.4.1. Nominal concentrations of nutrients for A, B and C standards.

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
<th>B'</th>
<th>C-1</th>
<th>C-2</th>
<th>C-3</th>
<th>C-4</th>
<th>C-5</th>
<th>C-6</th>
<th>C-7</th>
<th>C-8</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO(_3)(µM)</td>
<td>45000</td>
<td>900</td>
<td>900</td>
<td>0</td>
<td>BA</td>
<td>AY</td>
<td>AX</td>
<td>AV</td>
<td>BC</td>
<td>55.0</td>
<td>55.0</td>
</tr>
<tr>
<td>NO(_2)(µM)</td>
<td>4000</td>
<td>20</td>
<td>20</td>
<td>0</td>
<td>BA</td>
<td>AY</td>
<td>AX</td>
<td>AV</td>
<td>BC</td>
<td>1.2</td>
<td>1.2</td>
</tr>
<tr>
<td>SiO(_2)(µM)</td>
<td>36000</td>
<td>2880</td>
<td>3240</td>
<td>0</td>
<td>BA</td>
<td>AY</td>
<td>AX</td>
<td>AV</td>
<td>BC</td>
<td>172.8</td>
<td>194.4</td>
</tr>
<tr>
<td>PO(_4)(µM)</td>
<td>3000</td>
<td>60</td>
<td>60</td>
<td>0</td>
<td>BA</td>
<td>AY</td>
<td>AX</td>
<td>AV</td>
<td>BC</td>
<td>3.6</td>
<td>3.6</td>
</tr>
</tbody>
</table>

(iv) Renewal of in-house standard solutions

In-house standard solutions as stated in (iii) were renewed as shown in Table 3.4.3.

(4.2) Reference material of nutrients in seawater

To obtain more accurate and high quality nutrients data to achieve the objectives stated above, huge numbers of the bottles of the reference material of nutrients in seawater (hereafter RMNS) are prepared (Aoyama et al., submitted). In the previous world wide expeditions, such as WOCE cruises, higher reproducibility and precision of nutrients measurements were required (Joyce and Corry, 1994). Since no standards were available for the measurement of nutrients in seawater at that time, the requirements were described in term of reproducibility. The required reproducibility was 1%, 1-2%, 1-3% for nitrate, phosphate and silicate, respectively. Although nutrient data from the WOCE one-time survey was of unprecedented quality and coverage due to much care in sampling and measurements, the differences of nutrients concentration at crossover points are still found among the expeditions (Aoyama and Joyce, 1996, Mordy et al., 2000, Gouretski and Jancke, 2001).
Table 3.4.3. Timing of renewal of in-house standards.

<table>
<thead>
<tr>
<th>Standard</th>
<th>Substance</th>
<th>Renewal</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-1 Std. (NO₃)</td>
<td>maximum 1 month</td>
<td></td>
</tr>
<tr>
<td>A-2 Std. (NO₂)</td>
<td>maximum 1 month</td>
<td></td>
</tr>
<tr>
<td>A-3 Std. (SiO₂)</td>
<td>commercial prepared solution</td>
<td></td>
</tr>
<tr>
<td>A-4 Std. (PO₄)</td>
<td>maximum 1 month</td>
<td></td>
</tr>
<tr>
<td>B-1 Std. and B-1’ Std. (mixture of NO₃, SiO₂, PO₄)</td>
<td>8 days</td>
<td></td>
</tr>
<tr>
<td>B-2 Std. (NO₂)</td>
<td>8 days</td>
<td></td>
</tr>
<tr>
<td>C Std</td>
<td>Renewal</td>
<td></td>
</tr>
<tr>
<td>C-7~C-8 Std (mixture of B1 (B1’) and B2 Std.)</td>
<td>24 hours</td>
<td></td>
</tr>
<tr>
<td>Reduction estimation</td>
<td>Renewal</td>
<td></td>
</tr>
<tr>
<td>D-1 Std.</td>
<td>when A-1 renewed</td>
<td></td>
</tr>
<tr>
<td>43µM NO₃</td>
<td>when C-std renewed</td>
<td></td>
</tr>
<tr>
<td>47µM NO₂</td>
<td>when C-std renewed</td>
<td></td>
</tr>
</tbody>
</table>

For instance, the mean offset of nitrate concentration at deep waters was 0.5 µmol kg⁻¹ for 345 crossovers at the world oceans, though the maximum was 1.7 µmol kg⁻¹ (Gouretski and Jancke, 2001). At the 31 crossover points in the Pacific WHP one-time lines, the WOCE standard of reproducibility for nitrate of 1% was fulfilled at about half of the crossover points and the maximum difference was 7% at deeper layers below 1.6 deg. C in potential temperature (Aoyama and Joyce, 1996).

(i) RMNS preparation

RMNS preparation and homogeneity for previous lots

The study on reference material for nutrients in seawater (RMNS) on the seawater base has been carried out to establish traceability on nutrient analyses in seawater since 1994 in Japan. Autoclaving to produce RMNS has been studied (Aminot and Kerouel, 1991, 1995) and autoclaving was used to stabilize the samples for the 5th intercomparision exercise in 1992/1993 (Aminot and Kirkwood, 1995). Aminot and Kerouel (1995) concluded that nitrate and nitrite were extremely stable throughout their 27 months storage experiment with overall standard deviations lower than 0.3% (range 5-50 µmol l⁻¹) and 0.8% (range 0.5-5 µmol l⁻¹), respectively. For phosphate, slight increase by 0.02-0.07 µmol l⁻¹ per year was observed due to the leaching from the container glass. The main source of nutrient variation in seawater is believed to be microorganism activity, hence, production of RMNS depends on biological inactivation of samples. In this point of view, previous study showed that autoclaving to inactivate the biological activity is acceptable for RMNS preparation.

In the R/V MIRAI BEAGLE2003 cruise, which was an around the world cruise along ca. 30 deg. S and conducted in 2003 and 2004, RMNS was analyzed at about 500 stations. The results of BEAGLE2003 cruise will be available soon. (Databook of BEAGLE2003)

The seawater for RMNS production was sampled in the North Pacific Ocean at the depths of the surface where the nutrients are almost depleted and the depths of 1,500-2,000 meters where the nutrients concentrations reach its maximum. The seawater was gravity-filtered through a membrane filter with a pore size of 0.45 µm (Millipore HA). The latest procedure of autoclaving for RMNS preparation is that the seawater in a stainless steel container of 40 liters was autoclaved at 120 deg. C, for 2 hours, 2 times in two days. The filling procedure of autoclaved seawater basically remained the same throughout our study. After cooled at room
temperature in two days, polypropylene bottles of 100 ml capacity were filled with the autoclaved seawater of 90 ml through a membrane filter with a pore size of 0.2 µm (Millipore HA) at a clean bench in a clean room. The polypropylene caps were immediately and tightly screwed on and a label containing lot number and serial number of each bottle was attached on all of the bottles. Then the bottles were vacuum-sealed to avoid potential contamination from the environment.

RMNSs for this cruise

RMNS lots BC, AV, AX, AY and BA, which covers full range of nutrients concentrations in the western North Pacific were prepared as packages. These packages were renewed daily and analyzed every 2 runs on the same day. 250 bottles of RMNS lot AZ were prepared to use every analysis at every hydrographic station. These RMNS assignment were completely done based on random number. The RMNS bottles were stored at a room, REGENT STORE, where the temperature was maintained around 24-26 deg. C.

Assigned concentration for RMNSs

We assigned nutrients concentrations for RMNS lots BC, AV, AX, AY and BA as shown in Table 3.4.4.

(ii) The homogeneity of RMNSs

The homogeneity of lot BC and analytical precisions are shown in Table 3.4.4. These are for the assessment of the magnitude of homogeneity of the RMNS bottles, which were used during the cruise. As shown in Table 3.4.5, the homogeneity of RMNS lot BC for nitrate and silicate are the same magnitude of analytical precision derived from fresh raw seawater. The homogeneity for phosphate, however, exceeds the analytical precision at some extent.

<table>
<thead>
<tr>
<th></th>
<th>Nitrate</th>
<th>Phosphate</th>
<th>Silicate</th>
</tr>
</thead>
<tbody>
<tr>
<td>RMNS-BA</td>
<td>0.1 ± 0.0</td>
<td>0.06 ± 0.01</td>
<td>1.6 ± 0.1</td>
</tr>
<tr>
<td>RMNS-AY</td>
<td>5.6 ± 0.0</td>
<td>0.52 ± 0.01</td>
<td>30.1 ± 0.1</td>
</tr>
<tr>
<td>RMNS-AX</td>
<td>21.4 ± 0.1</td>
<td>1.61 ± 0.01</td>
<td>59.5 ± 0.1</td>
</tr>
<tr>
<td>RMNS-AV</td>
<td>33.4 ± 0.1</td>
<td>2.52 ± 0.01</td>
<td>157.9 ± 0.2</td>
</tr>
<tr>
<td>RMNS-BC</td>
<td>40.7 ± 0.1</td>
<td>2.78 ± 0.01</td>
<td>160.0 ± 0.2</td>
</tr>
<tr>
<td>RMNS-AZ</td>
<td>42.3 ± 0.1</td>
<td>3.02 ± 0.01</td>
<td>137.2 ± 0.2</td>
</tr>
</tbody>
</table>

Table 3.4.5. Homogeneity of lot BC and previous lots derived from simultaneous 30 samples measurements and analytical precision onboard R/V Mirai in May 2005.

<table>
<thead>
<tr>
<th></th>
<th>Nitrate</th>
<th>Phosphate</th>
<th>Silicate</th>
</tr>
</thead>
<tbody>
<tr>
<td>BC</td>
<td>0.22</td>
<td>0.32</td>
<td>0.19</td>
</tr>
<tr>
<td>(AH)</td>
<td>(0.39)</td>
<td>(0.83)</td>
<td>(0.13)</td>
</tr>
<tr>
<td>(K)</td>
<td>(0.3)</td>
<td>(1.0)</td>
<td>(0.2)</td>
</tr>
<tr>
<td>Precision</td>
<td>0.22</td>
<td>0.22</td>
<td>0.12</td>
</tr>
</tbody>
</table>

Note: N=30 x 2

(5) Quality control

(5.1) Precision of nutrients analyses during the cruise

Precision of nutrients analyses during the cruise was evaluated based on the 12 measurements, which are measured every 12 samples, during a run at the concentration evaluated n of C-7. We also the reproducibility based on the replicate analyses of five samples in each run. Summary of the precisions are shown in Table
3.4.6. As shown in Table 3.4.6 and Figures 3.4.5-3.4.7, the precisions for each parameter are generally good considering analytical precisions estimated from the simultaneous analyses of 60 samples in May 2005. The analytical precisions previously evaluated were 0.22% for phosphate, 0.22% for nitrate and 0.12% for silicate, respectively. During this cruise, analytical precisions were 0.08% for phosphate, 0.07% for nitrate and 0.08% for silicate in terms of median of precision, respectively. Therefore we can conclude that the analytical precisions for phosphate, nitrate and silicate throughout this cruise were maintained or better than those compared to the pre-cruise evaluations. The time series of precision are shown in Figures 3.4.5-3.4.7.

Table 3.4.6. Summary of precision based on the replicate analyses of 12 samples in each run throughout cruise.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>CV%</th>
<th>CV%</th>
<th>CV%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Median</td>
<td>0.070</td>
<td>0.070</td>
<td>0.090</td>
</tr>
<tr>
<td>Mean</td>
<td>0.076</td>
<td>0.072</td>
<td>0.087</td>
</tr>
<tr>
<td>Maximum</td>
<td>0.170</td>
<td>0.190</td>
<td>0.170</td>
</tr>
<tr>
<td>Minimum</td>
<td>0.030</td>
<td>0.030</td>
<td>0.020</td>
</tr>
<tr>
<td>N</td>
<td>277</td>
<td>277</td>
<td>277</td>
</tr>
</tbody>
</table>

Figure 3.4.5. Time series of precision of nitrate.
Figure 3.4.6. Time series of precision of phosphate.

Figure 3.4.7. Time series of precision of silicate.
(5.2) Carry-over

We can also summarize the magnitudes of carry-over throughout the cruise. These are small enough within acceptable levels as shown in Table 3.4.7.

Table 3.4.7. Summary of carry-over throughout cruise.

<table>
<thead>
<tr>
<th></th>
<th>Nitrate</th>
<th>Phosphate</th>
<th>Silicate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Median</td>
<td>0.21</td>
<td>0.20</td>
<td>0.24</td>
</tr>
<tr>
<td>Mean</td>
<td>0.21</td>
<td>0.20</td>
<td>0.23</td>
</tr>
<tr>
<td>Maximum</td>
<td>0.40</td>
<td>0.40</td>
<td>0.43</td>
</tr>
<tr>
<td>Minimum</td>
<td>0.01</td>
<td>0.00</td>
<td>0.05</td>
</tr>
<tr>
<td>N</td>
<td>277</td>
<td>277</td>
<td>277</td>
</tr>
</tbody>
</table>

(6) Evaluation of Z-scores of RMNSs

Since we used RMNSs throughout the cruise, we can evaluate the trueness of our analysis in terms of Z-score of RMNSs.

Z-score for each analysis of RMNS is defined as follows:

\[ Z_{\text{par}} = \text{ABS} \left( \frac{C_{\text{par}} - C_{\text{nominal}}}{P_{\text{par}}} \right) \]  

Where

- \( Z_{\text{par}} \) is Z-score for an analysis
- \( C_{\text{par}} \) is obtained concentration of a RMNS for interested parameter, nitrate, phosphate or silicate.
- \( C_{\text{nominal}} \) is assigned concentration of RMNS for interested parameter, nitrate, phosphate or silicate.
- \( P_{\text{par}} \) is analytical precision at the concentration of RMNS for interested parameter, nitrate, phosphate or silicate.

Averages of these Z-scores were obtained for three parameters, nitrate, phosphate and silicate based on Z-scores for 7 RMNSs used at each run and shown in Figure 3.4.8. Means of Z-score based on the Z-score of three parameters were also obtained and shown in Figure 3.4.9.

These Z-scores were less than 0.5 in general and indicating that our analyses were in excellent tracernessibility throughout the cruise.
Figure 3.4.8. Z-score of nitrate, silicate and phosphate.

Figure 3.4.9. Means of Z-score at the stations.
Problems/improvements occurred and solutions

Nothing occurred during the cruise.

Reference


