

Shipboard Techniques for Oceanographic Observations

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Moss Landing Marine Laboratories

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Abstract

This report gives the details of water sampling methods and chemical analyses used during MLML participation in the EOS MODIS investigations. It is intended to be used as a reference manual for those engaged in shipboard work.

Acknowledgements

This work is supported by Grant NA17ECO198 from the National Oceanic and Atmospheric Administration to William Broenkow. We appreciate the help of Craig Hunter (MLML) for preparing the section on TSM and POC and performing those analyses. Charles Trees (Center for Hydrologic Optics and Remote Sensing) provided the pigment and dissolved organic matter data.

CTD and Hydrographic Casts

The following outlines the sequence of events for making a CTD or Niskin bottle cast.

Alert the ship's bridge that you wish to make a CTD cast. Check with the chief scientist to determine if the ship is on station, and determine water depth from the PDR. NEVER ASSUME a water depth. When in areas of large bathymetric relief monitor depth constantly during the cast.

Two scientists and a ship's winch operator will make the CTD or hydro cast. The lead scientist has the responsibility for the safe handling of the CTD during launch and recovery and must insure that profile data are complete, that calibration samples are properly placed, calibration samples are correctly taken, and that the CTD or bottles are safely stowed. The second scientist must check all aspects of the CTD launch and recovery will operate the A-frame controls.

Prepare the Station Log with Cruise Name, Vessel, Station Name and Number, Date, Observers Names, CTD sequential cast number, Latitude and Longitude. When recording start and finish times specify the Time Zone (+8 for PST, +10 for HST, +0 for GMT, etc).

Ready the subsampling bottles for dissolved oxygen, salinity, TSM, pigments, nutrients, etc and record on the Field Log. Always use sampling bottles in numerical sequence, top-down order. This reduces the likelihood of confusion. If using reversing thermometers, record their serial numbers on the field log.

Cock all Niskin bottles and set the carousel lanyards. Reverse all thermometers and confirm that their mercury has reversed. Check all bottles to see that the air vents and stopcocks are closed. For a Niskin cast place, a messenger on each bottle except that at the bottom.

When doing a Niskin bottle cast, determine the sample depth and record on Field Log. Then determine

the meter wheel readings such that the first (and deepest) Niskin bottle is placed on the wire with the meter wheel reading 0. The final meter wheel reading is equal to the surface-most depth plus the working height above the sea surface (usually 2 to 4 m). Do this simple procedure carefully to avoid much confusion later about the depth at which the bottles tripped.

Just prior to the CTD cast turn on the deck unit and power up the instrument. Clean the transmissometer end windows with Kimwipes and alcohol until constant readings (approximately 85.5% transmission) are obtained. This requires coordination between the person on deck and the CTD cast operator. Check to readout from the CTD and note on the field log the value from the pressure transducer while the CTD is on deck. Repeat this process when the cast is retrieved. Remove the stopper on the CTD ducted inlet. FAILURE to do so will damage the oxygen electrode.

Launch the CTD. The two scientists will guide the CTD/Carousel over the side in cooperation with the winchman. This may be a dangerous procedure. NEVER allow the CTD to swing freely. If seas are rough, use a tag line on the top of the Carousel frame to minimize swing. Remove the tag line when the instrument enters the water.

Soak the CTD at the surface for several minutes to temperature equilibrate sensors. During this time observe readouts from all sensors to insure their proper operation. Proceed with the cast. While doing a CTD cast monitor the winch speed. The ducted flow past the thermometer and conductivity sensor must match the descent rate of 30 m/min. The CTD operator must monitor the cast continuously and be aware of the changing bottom depth. The second scientist can use this time to make the surface observations.

In making a Niskin bottle cast, put the hydrographic wire over the side and lower the weight to 10 meters. Ask the winchman to zero the meter wheel. Place the bottles on the wire using the bottom-most (the right-hand bottle in the bottle rack) bottle first. Check stopcock, air vent, then reverse the thermometers, cock the bottles and attach a messenger to the release mechanism and snap on the hydro wire (except on the bottom bottle). Before lowering the bottle check that all lanyards are correctly fixed, stopcocks are closed, and mercury in thermometers has reversed. Repeat this for each sample bottle.

When the Niskin cast has reached the deepest sampling depth, record the "DOWN" time and give the bottles 5 minutes to flush and for the reversing thermometers to equilibrate. At this time make the surface observations:

Surface Observations

Secchi Depth Find the disappearance depth when lowering, again when raising the disk. Record the average of the two readings in meters.

Munsell Color Secchi disk height of its diameter of the color of the sea. Record the Munsell color of the sea.

Wind Direction Remember to account for ship's heading; record in degrees true.

Wave Height Estimate the height of highest 1/3 of the waves; record in feet

Wave Period Time the passage of ten waves; record in seconds

Wave Direction Estimate direction of major sea or swell; record in degrees true

Barometric Pressure Read from ship's barometer; record in millibars

Cloud Cover Report as percent of sky covered; Cover record in percent

Cloud Type Use cloud chart to identify cloud type (ie. Cir)

Add comments for any unusual conditions or problems. It is particularly important when reducing data to account for exceptional circumstances. Human memory is usually insufficient.

Retrieve Cast

When doing a CTD cast, determine the calibration depths to trip Niskin bottles from the downcast profiles. Choose well-mixed layers so that conditions are not changing while the bottles flush. Establish criteria for bottle sampling. Water samples are taken to two reasons: first to characterize water column features; second to provide calibration values for CTD optical sensors. For example, 5 bottles might be used to obtain water for TSM and pigment analyses to characterize particle and beam attenuation maxima. Samples to calibrate CTD sensors should be tripped over the entire range of variability, from surface to bottom to evaluate pressure dependency; at several positions within the thermocline to calibrate temperature transducer and especially to evaluate oxygen sensor response, and throughout the oxygen minimum. For remote sensing work, the surface layer is the most important, and water samples in the photic zone have precedence for TSM, POC, DOM, and plant pigments.

When sampling strategy has been determined, retrieve the cast. No useful CTD data are acquired on the upcast, but profiling should be enabled to navigate to features of interest for bottle sampling. Stop at the desired sample depth and allow 30 seconds or more for bottle flushing before tripping the bottles. If reversing thermometers are used, complete equilibration requires 5 minutes. During CTD calibration, record the values of each CTD channel at each calibration depth on the field log. The SeaBird Carousel bottles are tripped manually and the CTD data are logged in the computer by pressing F5??. Keep a running log of water sample depths, so that all features of interest are adequately sampled during the course of several CTD profiles. When the cast has been retrieved inform the Chief Scientist so that other operations can proceed.

Air Temperature Carefully swing the sling psychrometer on the windward side of the ship for two minutes. Read and record the wet and dry bulb temperatures to 0.1° C.

Fathometer Depth Obtain this from the PDR or ask the bridge; record in m.

Wind Speed Obtain this from the ships anemometer, average out gusts; record in knots.

Water Sampling

Before the cast is made, the volumes of subsamples are determined by consultation with the chief scientist and members of the science party. In some cases sufficient water can be obtained only by tripping two or more water samplers at each depth. The figures below indicate volumes including rinses required. Samples are generally drawn from Niskin bottles in the following order:

Dissolved Oxygen 300 ml. Always draw oxygen samples first. Draw the water into an iodine determination flask as explained in the Winkler Oxygen section below and fix the oxygen with Winkler reagents #1 and #2.

Salinity 250 ml. Salinity is the most precise measurement we make. Rinse the salinity bottle three times with 25 ml rinses. Fill the bottle to the shoulder and tightly stopper the bottle. Evaporation can occur in loosely capped bottles. Do not leave the salinity bottles outside in sunlight.

Fluorometric Pigments 300-500 ml. Rinse the bottle twice. Fill to the shoulder. Pigment water samples cannot be stored, they will be filtered and analysed aboard ship.

HPLC Pigments 2 liters. Rinse twice and fill completely. The entire sample is filtered aboard ship and frozen in liquid nitrogen for analysis ashore.

Particulate Absorption 1 liter. Rinse twice; samples are filtered through 0.7 μm GFF glass fiber filters and analysed fresh.

Phycocrythrin filtered 350 ml. Rinse twice; sample water is filtered through 0.4 μm Nucleopore polyester filters.

DOM 125 ml. Rinse twice; Dissolved Organic Matter samples are filtered through a Sterrivex 0.2 μm filters and analysed aboard ship.

TSM 5 liters. Large volumes of water are required for Total Suspended Matter analyses. In offshore oligotrophic waters take 5 liter samples. Draw the water directly into the filtration bottles. If larger samples are required, two Niskin bottles may need to be tripped at each sample depth.

POC/PON 1 liter Particulate Organic Carbon and Nitrogen analyses. Sampling technique requires avoidance of sources of organic matter, including dust, dirt and smoke. The bottle top must be covered with a plastic glove at all times.

Nutrients 500 ml Nutrient samples are filled to the shoulder of twice rinsed polyethylene bottles. These samples should be filtered through glass fiber filters and frozen for later analysis. Water from the POC analysis can be used for nutrient analyses.

Reading the reversing thermometers is the last operation, because the thermometers retain their readings and must come to thermal equilibrium with air temperature before being read. Read the protected and unprotected thermometers in Niskin bottle order, from left to right: Left (protected) thermometer number, main temperature to 0.01°C, auxiliary thermometer to 0.1°C; repeat for Middle (protected) and Right (unprotected) thermometers. One observer will read and another will record. Avoid parallax and use a hand lens and flashlight. Repeat the process by exchanging reader and recorder. Readings are recorded on sequential lines on the field log.

Before leaving the station securely tie down the CTD/Carousel. Rinse the CTD, Carousel and bottles with fresh water. Rinse salt water from the tygon CTD duct and it with deionized water containing PhotoFlo wetting solution. The solution must fill the conductivity cell and cover the oxygen electrode. Rinse and dry the transmissometer windows, replace the protective caps on the transmissometer windows. Rinse and dry the fluorometer windows. Recharge batteries as may be required.

Dissolved Oxygen Analysis by Winkler Titration

This method is Carpenter's modification of the classic 1888 Winkler method (J. Carpenter, 1965 Limnology and Oceanography 1: 141-143).

Winkler titrations are done on batches of water samples that have been drawn from Niskin bottles on CTD or hydrographic casts. Since much of the effort is with the standardization procedure, it is efficient to titrate 12 or more samples at a time. Immediately after the samples have been drawn into iodine determination flasks they are "pickled" with Winkler Reagents 1 and 2. These treated samples may be stored in a cool, dark location for up several days before they are analysed by titration.

The titration procedure is: 1) to determine the normality of the thiosulfate titrant (see Standards, below); 2) to determine the concentration of reductants or oxidants in Winkler Reagents 1 and 2 (see Reagent Blank, below); 3) and to determine the concentration of dissolved oxygen in samples (see Sample Drawing and Titration below).

Standards

1. Thoroughly rinse 125 ml iodine determination flask with deionized water; Fill 3/4 full with deionized water; Add 1" magnetic stirring bar rinsed with deionized water.
2. Add 5.00 ml 0.02 N (or 10.00 ml of 0.01 N) Bi-iodate standard using a volumetric pipette; stir
3. Add 1.00 ml Sulfuric Acid Solution (Reagent 3); stir
4. Add 1.00 ml NaOH-NaI Solution (Reagent 2); stir
5. While stirring, titrate with Sodium Thiosulfate to a pale yellow color; Add 0.5 ml Starch Indicator; Complete titration to the endpoint (change from blue to colorless); Record burette reading to 0.01 ml as R_{std} . This value should be about 5 ml.
6. Repeat steps 1-5 twice or until R_{std} readings agree within 0.02 ml.

Reagent Blanks

1. Thoroughly rinse sample flask with deionized water; Fill 2/3 with deionized water; Add 1" clean stirring bar.
2. Add 5.00 ml of Bi-iodate standard from a volumetric pipette; stir
3. Add 1.0 ml Sulfuric Acid Solution (Reagent 3); stir
4. Add 1.0 ml NaOH-NaI Solution (Reagent 2); stir
5. Add 1.0 ml $MnCl_2$ Solution (Reagent 1); stir
6. Add 0.5 ml Starch Indicator;
7. While stirring, titrate with Sodium Thiosulfate to the colorless endpoint; Record burette reading to 0.01 ml

as R_1 .

8. Add 5.00 ml more of the Bi-iodate Standard to the same flask; Rezero the burette and titrate to the endpoint again; Record burette reading to 0.01 ml as R_2
9. Repeat steps 1-7 twice more. The reagent blank $R_{blk} = R_1 - R_2$.

Sample Drawing

Drawing samples without changing the oxygen concentration is the single most important aspect of accurate dissolved oxygen analyses. Such errors generally lead to anomalously high concentrations.

1. Attach a 20 cm piece of clean tygon tubing to the Niskin Bottle stopcock; Open the vent valve at the top of the Niskin Bottle; Hold the tubing vertically; open the stopcock and flush water through the tubing pushing all air bubbles up and out of the tubing;
2. With the vertical tubing filled with water, place an inverted iodine determination flask over the tubing, and rinse the flask. Then rotate the flask upright and continuously flush the tubing. Carefully fill the flask from the bottom up, avoiding bubbles. Overfill it with two volumes of water. While sample water is still flowing, withdraw the tube so that the reservoir above the stopper is completely filled with water.
3. Carefully add 1.0 ml of $MnCl_2$ (Winkler Reagent 1). Its high density causes it to sink to the bottom of the flask. Do not yet insert the stopper. Do not forcefully inject the reagent, let it flow down the side of the flask. Do not mix.
4. Carefully add 1.0 ml of NaOH-NaI (Winkler Reagent 2). It also should sink to the bottom of the flask. Carefully insert the glass stopper. Avoid trapping air bubbles below the stopper. Secure the stopper and mix thoroughly. When all samples from the cast have been drawn, use a squeeze bottle to fill the rim above the stopper with deionized water. This will make an effective seal which prevents atmospheric oxygen from leaking inside. Treated samples may be stored for several days before titrating. Samples must be stored in a cool, dark location.

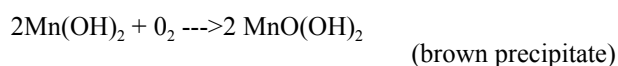
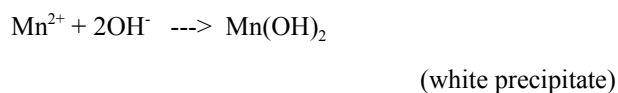
Sample Titration

1. Arrange samples by station and by increasing depth within the station. Pour off water from the wide neck above the stopper on the iodine determination flask. Atmospheric oxygen can react with the precipitate, thus titrations should not be done until the precipitate has settled to bottom.
2. Remove stopper with a twisting, pulling motion. Add 1" clean magnetic stirring bar.
3. Quickly add 1.0 ml Sulfuric Acid (Reagent 3). Stir until the precipitate dissolves.

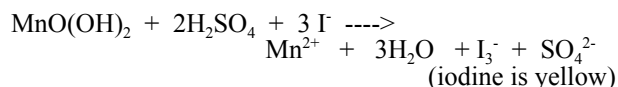
- Titrate to pale yellow color with Sodium Thiosulfate. Add 0.5 ml Starch Indicator. Complete titration to the endpoint (blue to colorless). Note that it takes a few seconds to thoroughly mix the thiosulfate throughout the bottle. Note that complete mixing of the titrant throughout the flask takes a few seconds. Avoid over-titrating. Record the final burette reading to 0.01 ml as R_{Sam} . NOTE: Set aside a sample following titration. In time the blue starch-iodine color might return. This is due to air oxidation when the pH is too low. If the blue color returns quickly, reduce the volume of Winkler Reagent 3 delivered by the pipette.

Chemistry

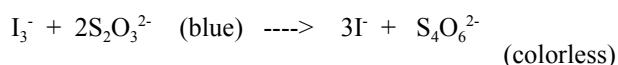
Following addition of Winkler Reagents 1 and 2:



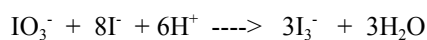
Following addition of Winkler Reagent 3:



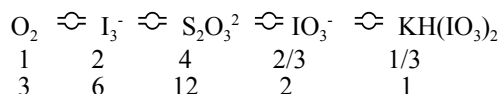
Titrate with sodium thiosulfate with starch indicator:



Bi-iodate standard in acid forms precise amount of iodine for standard titration:



Chemical equivalences:



This explains why 0.01 N Bi-iodate is figured at 1/12 of its molecular weight so that we weigh out 0.325 g in making a liter of standard: $1/12 \times 1/100 \times 389.93 = 0.3249$ g/liter.

Sources of Error

- Sample drawing. Aeration of sample and failure to rinse flask.
- Volatility of I_2 : Leads to apparent decrease in concentration. Avoid by complexing I_2 with iodide (I^-) and by avoiding heat.
- Air oxidation of iodide: Leads to apparent increase in concentration. Avoid by maintaining correct $1 < \text{pH} < 2$.
- Contaminants: Several oxidants or reductants may

cause problems. Nitrite leads to an apparent increase in oxygen concentration, hydrogen sulfide to an apparent decrease.

- Photochemical oxidation of iodide leads to apparently high concentrations of oxygen. Avoid by working with acidified samples away from direct sunlight.

Reagents

Winkler Reagent 1.

Dissolve 300 g $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (Manganous Chloride; molecular weight 197.91) in deionized water. Dilute to 500 ml in a volumetric flask. Mix well and store in a glass or polyethylene bottle. This solution is stable indefinitely.

Winkler Reagent 2.

Dissolve 160 g NaOH (Sodium Hydroxide molecular weight 40.00) in about 300 ml of deionized water. This is a fairly warm reaction. Add 300 g NaI (Sodium Iodide molecular weight 149.89) to this solution while it is still warm and mix until it is completely dissolved. Dilute to 500 ml in a volumetric flask. Mix well and store in a clean plastic bottle. Sodium hydroxide is very caustic and will fuse glass syringes. Immediately rinse all spills with fresh water, handle carefully. Clean repipettor if it will not be used for several days.

Winkler Reagent 3.

Slowly add 140 ml of concentrated Sulfuric Acid (36 N) to about 300 ml of deionized water. This is a strongly exothermic reaction. Mix carefully and allow solution to cool. When cool, transfer the acid solution to a Pyrex graduated cylinder then dilute to 500 ml. Store in a clean glass bottle. Sulfuric acid is very caustic, immediately rinse all spills with fresh or salt water, handle carefully. This solution is stable indefinitely.

Starch Indicator.

Dissolve 1 g of soluble starch in 100 ml of boiling deionized water. This solution is stable for only 1 week. When endpoint becomes brownish rather than a sharp blue, make new indicator.

Potassium Bi-Iodate Standard.

Dry at room temperature for 1 hour in dessicator. Dissolve exactly 0.325 g of $\text{KH}(\text{IO}_3)_2$ (molecular weight 389.912) in deionized water and dilute to 1000 ml. This makes a 0.0100 N solution. When using a 5 ml pipette, make a 0.02 N solution. The solution is stable indefinitely when stored properly. This solution is not caustic.

Sodium Thiosulfate Titrant.

Dissolve 5 g $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ (molecular weight 248.18) in deionized water and dilute to 1000 ml. This solution is not stable and must be standardized relative to Bi-Iodate for each analysis session. This solution is not caustic.

Calculations

$$F_{STD} = \frac{V_{IO3} N_{IO3} \frac{22.39 \times 1000}{4}}{(R_{STD} - R_{BLK})}$$

$$O_2 (ml/l) = F_{std} \frac{(R_{sam} - R_{blk})}{(V_{bot} - 2)} - 0.02$$

V_{IO3} is the volume of Bi-Iodate standard (usually 5.00 or 10.00 ml). N_{IO3} is the normality of the Bi-Iodate standard (usually 0.01 or 0.02 N). 4 is the number of moles of Sodium Thiosulfate equivalent to 1 mole of Oxygen. The normality of the Bi-Iodate is 1/12 its molecular weight and is figured relative to Sodium Thiosulfate. 22.39 l (STP) is equivalent to 1 mole of O_2 . 0.02 is a correction factor to account for the slight amount of oxygen dissolved in reagents 1 and 2

Units used in above calculations are ml (STP)/liter. The modern unit is umoles/kg and is obtained by multiplying ml/liter by $1000/22.39 \times 1.025 = 43.57$. 1.025 approximates seawater density. The precise density should be used, if known.

Bottle Volumes

The volume of each sample flask must be individually determined. Bottles are washed with detergent and rinsed with deionized water. After drying in an oven and cooled to room temperature they are weighed to ± 0.01 g. Fill each bottle with deionized water at a known and stable temperature $\pm 1^\circ C$. Put the stoppers in the flasks while avoiding bubbles. Carefully dry water from the sides and stopper area of the bottles, then weigh to ± 0.01 g. Calculate the volume in ml as the difference in the bottle weights filled and empty divided by the water density. Water density is calculated as a function of temperature from IES-80 using MLHPL calculator function DENSITY(S,T,P), with S = 0 psu and P = 0 dbar.

Bottle #	Vol (ml)	Bottle #	Vol (ml)
500	135.10	501	134.52
502	134.10	503	132.95
504	132.05	505	134.73
506	135.36	507	135.24
508	130.41	509	134.64
510	134.52	511	135.84
512	136.00	513	134.39
514	134.75	515	133.30
516	137.10	517	135.61
518	135.88	519	133.25
520	134.84	521	134.77
522	131.67	523	135.03

Salinity Determination by MiniSal Salinometer

The determination of salinity is done by measuring the electrical conductivity ratio of seawater relative to standard water. The modern Standard Water is a precisely prepared ampule of potassium chloride (32.4356 g KCl/kg solution). The MiniSal measures the conductivity ratio directly by use of two cells: one containing standard water, the other containing sample water. Because Standard Water prepared by the National Institute of Oceanography in England is expensive, a secondary standard should be used in place of the standard. This should be seawater with a salinity of very nearly 35 psu ± 0.01 .

An electrical current is passed through both the reference and sample cells. The voltage across each cell is inversely proportional to the electrical conductivity of each cell and directly proportional to the cell constant of each cell (K_1 and K_2). The ratio of these voltages is determined electronically, and this voltage ratio is proportional to the conductivity ratio, R_1 . During calibration the ratio K_2/K_1 is stored in microprocessor memory and is called Cell Constant A.

$$R_T \times A = \frac{V_s}{V_r} = \frac{K_2 C(s,t,0)}{K_1 C(kcl,t,0)}$$

Because temperature changes electrical conductivity, temperature must be measured. This is done in a clever way by the MiniSal. By measuring the conductivity of standard water relative to a very precise fixed resistor which represents another constant $K_3 C(kcl,15,0)$ (that is the conductivity of Standard water at $15^\circ C$). The value of K_2/K_3 is called B and is stored in microprocessor memory. When doing the B calibration the temperature of the water bath is measured to $0.1^\circ C$.

$$r_T \times B = \frac{V_s}{V_r} = \frac{K_2 C(kcl,15,0)}{K_3 C(kcl,t,0)}$$

When conductivity is measured with conductivity ratios near 1, errors in the measurement of temperature are not large. For example, the maximum temperature error in the measurement of temperature occurs at $R_T = 0.5$. Here a $1^\circ C$ error will cause a 0.007 psu error. However both the sample and standard water must be at the same temperature within $0.001^\circ C$. This is done by the stainless heat exchanger and the stirred water bath.

Setup

The MINISAL requires a 2 minute warm-up to achieve precision of ± 0.003 psu. Instrument calibration using Standard Water (or substandard water that has been recently calibrated with Standard Water) is recommended for each analysis session, though experience may show calibration is not always required. Instrument drift should be checked by repeated determination of the salinity of a single sample over the course of a session.

Open, level and secure the salinometer. Squeeze bulbs, tubing bottle holders and a ring-stand are shipped in the carrying case. Be sure to rinse the squeeze bulbs following use to keep check valves in good condition.

Attach the sample bottle holder to the top of the instrument (or the provided ring-stand and plastic flask holders for Standard Water ampules) so that the sample water level is 20 cm above the top of the MiniSal Dewar. Siphon action controls sample flow.

Attach 19 gauge Teflon tubing to the *Sample* and *Standard* inlet ports. Be careful not to pinch or puncture the tubing and to slide the tubing securely over the ports. Fill the temperature stabilizing Dewar with 1.5 liters of clean water at ambient temperature. Water cooler or warmer than ambient temperature may require 30 minutes to achieve temperature stability. Dirty water may cause algal growth. The water level should cover the top of the cells to provide a clear view of the electrodes.

Connect the squeeze bulbs to the clear plastic drain tubes from each cell. Insert the long Tygon drain tubing into the exit side of the bulbs.

Water will drain from the cells at 2 liters/hour or less. Arrange a catch bucket under the squeeze bulbs to avoid a conductive ground path that produces noisy instrument response and erroneous salinity readings.

Filling and Flushing

Water flow to the standard and sample cells is initiated by siphon action from the squeeze bulbs and is maintained by gravity flow. The siphon must be re-started if flow is interrupted. Sample and standard water levels must be at least 20 cm above the top of the Dewar flask.

Filling

To start the flow for either the standard or sample water, place the appropriate Teflon inlet tube into the water container.

- Squeeze the bulb;
- Cover the Fill and Flush holes;
- Release the bulb, creating suction;

After water fills the cell and is visible in the outlet tube, uncover the Fill and Flush holes in that order; Flow will be maintained by gravity.

Flushing

To flush water from either the standard or sample cells:

- Squeeze the bulb;
- Cover only the Flush hole;
- Release the bulb, creating suction;

After cell is flushed, uncover the Flush hole.

Hints

Filling is required when flow is interrupted, as between samples. Filling and flushing may introduce bubbles, and if stable readings are not observed after a few seconds it may be necessary to flush and refill the sample cell. Periodically check to see that the electrodes are completely covered by sample and standard.

Power flushing (by covering both the *Fill* and *Flush* holes) will speed salinometer response between samples having large (1.5 S) salinity differences. The power flush should be followed by a normal flush covering only the *Flush* hole.

STABI Menu System

Six routines are provided by the MINISAL firmware operating system to provide calibration and instrument setup functions.

- 1: Salinity Measurement
- 2: Temperature or *B* Calibration
- 3: Bottle Number Input
- 4: Conductivity or *A* Calibration
- 5: Interface Format Selection
- 6: Interface Parameter Setup

The STABI functions are initiated by pressing and holding the # key while in the normal salinity measuring mode. When the *STABI* prompt appears, press the numeric code 1-6 to select the appropriate function.

Data Entry

Date, time and calibration values are entered via the numeric keypad. The # key is used as an "Enter" or "Return" key to signify completion of data entry. The * key acts as a reset key allowing the user to correct or change numeric entries. Normally data are entered by pressing the numeric keys followed by #.

Note that input data can be corrected by automatic display wrap around. If mistakes are made during data entry, continue pressing numeric keys in the desired sequence followed by #.

Startup and Calibration

The instrument may be operated through internal battery power alone or with the AC power supply. Sufficient battery voltage is indicated when the LED below the AC power jack glows yellow. Red indicates low battery voltage and the AC power supply is required. If erratic readings are observed while using the AC power supply, unplug it to avoid possible ground loop problems.

Before salinity analyses are made, MiniSal operation is checked and the conductivity cell may be calibrated against Standard Water or substandard water of known conductivity ratio.

Turn the instrument ON. *MiniSal* should appear briefly on the display followed by the date display. If this is not the case, press the *Reset* button. Next turn the stirrer on.

Following *Reset*, the current date settings will be displayed in the form *D YYMMDD*. Press # to retain the date as displayed or enter the correct date followed by #. Time will be displayed in the form *H HHMMSS*. Press # to retain the time as displayed or enter the correct time followed by #. The clock is stopped during time and date setting.

Calibration

The MINISAL should be calibrated with each batch of samples. At the beginning of each cruise the 35 psu substandard water must be calibrated against Standard Water. During lengthy cruises the substandard should be standardized periodically with Standard Water. When calibrating, start the flow of standard or substandard water in both the standard and sample conductivity cells. Place the fill tube of both cells in the same standard water bottle or flask. Wipe the tubing dry to avoid contaminating the Standard Water.

Following the time display, The *K* value indicating the conductivity ratio of Standard Seawater will be displayed in the form *K X.XXXXX*. If the correct value for the standard water in use is shown, press # to retain the current value, otherwise enter the correct value followed by #.

Note: We have found that if the MiniSal loses the entered *K* value this is a sign that batteries need to be recharged on AC power.

STBAI4: Cell Ratio or A Constant

A is the ratio of the standard and sample cell constants K_1 and K_2 . After the flow of standard water through standard and sample cells is established, press and hold the 0 key. The display will alternately display conductivity ratio and temperature readings as *C X.XXXXX* and *T X.XXXXX*.

When accurate calibration is achieved, the conductivity ratio *C* displayed must equal the known value of *K*. To change the conductivity calibration, press and hold the # key until *STBAI* is displayed.

Press the 4 key and release. When *STABI4* is displayed, press #. The current value of the **A** constant will be displayed. Recalibration is accomplished by resetting the **A** value, which is automatically done by pressing and releasing the # key. The new value of **A** should agree closely with the value on the Constant Plate near the Dewar. A change in **A** indicates the cells require cleaning or the cells have changed. Record the cell constant, **A**, in the MiniSal calibration log and on the data sheet.

To exit the *A Constant* routine, press and hold #

Press and hold the 0 key. The display will alternately display conductivity ratio and temperature readings as *C X.XXXXX*. *C X.XXXXX* should now agree with the known value of the standard's conductivity ratio. If it does not, repeat this procedure.

STBAI2: Temperature or B Constant

The **B** constant is used to convert the conductivity of standard water to temperature.

Check that the *K* value of the standard water has been entered correctly by pressing *Reset*, #, #. Insure that standard water is flowing through the standard cell.

Measure the temperature of water in the Dewar to 0.1 C accuracy. We use a calibrated Micronta digital thermometer.

Press and hold the 0 key until the display alternates between *C X.XXXXX* and *T X.XXXXX*. If the displayed temperature agrees with the measured value, temperature calibration is complete. Display the **B** value by *STABI2* procedure, press # followed by 2, and record the **B** value in the MiniSal log and on the data sheet.

To change the **B** constant, press and hold # until *STABI* appears. Select temperature calibration by pressing 2. When *STABI2* appears press #. The display will show *B X.XXXXX*. To reset **B**, press * and release. *T INPUT* will appear. Key in the known temperature (to 0.1 °C) followed by #. Remember the wrap-around feature which allows editing.

Check to see that temperature calibration is accurate. Press and hold # until *STABI* is displayed; press *I* followed by # to return to the salinity mode. Then press and hold 0 to display the *C* and *T* values.

STBAI1: Salinity Analysis

Salinity analysis of samples normally follows setup and calibration procedures described above.

To enter the analysis mode, press and hold the # key until *STBAI* is displayed. Press *I* followed by #. The display will show *S XX.XXXX*.

Remove the sample inlet tubing from the standard water bottle. Check the standard water path to make sure the flow is continuous.

Wipe water from sample inlet tubing to avoid contamination of sample water.

Fill the sample cell, flush it, and refill. Read and record salinity. Stable salinity values should be observed after 15 seconds. If erratic values are observed flush and refill. Inspect sample and standard cells for bubbles or cells incompletely filled to top of platinum electrodes.

We have found that the *S* readings slowly oscillate between high and low limits. We calibrate and read sample values by consistently recording only the high values.

Erratic readings are most-likely caused by dirty cells.

STBAI:3 Bottle Number Entry

To enter a sample bottle number, press and hold

the # key until *STBAI* is displayed. Press 3 followed by #. The display will show the last bottle number *B XXXXXX*. Enter the new bottle number followed by #. The bottle number is used to identify samples through the serial interface.

STBAI:5 Interface Format Selection

The serial interface is used to send data to an external printer or computer. The format for these data is selected using *STBAI* function 5. To select an output format, press and hold the # key until *STBAI* is displayed. Press 5 followed by #. The display will show the prompt *CORI.2*. Enter the desired format (0,1 or 2) followed by #.

Format 0 = Continuously outputs temperature and salinity values followed by system parameters every 24th line.

```
T21.2345 S34.4567 S34.4568 S34.4566 S34.4569
S34.4569 S34.4566
```

(above format is repeated for 24 lines)

```
89/04/20 09:51:05 B=76543 A0.86137 B0.76268
K1.00002
```

Format 1 = Controlled Output Mode 1 prints conductivity values. Data are output to the serial device when * is pressed. In mode 1 system parameters, conductivity ratio and temperature are output:

```
89/04/20 09:51:05 B=76543 C0.98765 T21.2345
A0.86137 B0.76268 K1.00002
```

Format 2 = Controlled Output Mode 2 prints salinity values. Data are output to the serial device when * is pressed. In mode 1 system parameters, conductivity ratio and temperature are output:

```
89/04/20 09:51:05 B=76543 S34.4567 T21.2345
A0.86137 B0.76268 K1.00002
```

STBAI:6 Interface Parameter Selection

Serial interface parameters are selected using *STBAI* function 6. To select this function, press and hold the # key until *STBAI* is displayed. Press 6 followed by #. The display will show prompt, *COMbps*, where the three digits *bps* indicate settings as follows

b = number of bits transmitted. Normally you will set this to either 7 or 8 depending on the capabilities of your printer or computer interface.

p = parity. 0 = No parity; 1 = Odd parity; 2 = Even parity

s = stop bits. 1 = 1 stop bit; 2 = 2 stop bits.

Example: *COM801* specifies 8 data bits, no parity, 1 stop bit.

TSM and POC/PON Sampling

Water should be collected in the appropriate size bottle to allow sufficient water to filter for both Total Suspended Matter (TSM) and Particulate Organic Carbon and Nitrogen (POC/PON) analyses. Location and depth of the euphotic zone will determine the volume needed. Generally, 2-4 liters for oceanic surface waters and 0.5-2 liters for coastal waters are required for TMS analyses. POC/PON requires 1 liter in oligotrophic surface waters. It is preferable to sample the same depth several times rather than using several bottle subsamples. During every cruise a set of replicate samples should be obtained to check sampling and analytical reproducibility. Every effort should be made, despite bottle size, to have the water well mixed before samples are drawn. The bottle dregs often contain a large portion of the particulate material and care must be taken to include these in the subsamples.

Total Suspended Material (TSM) Analysis

Preparation

The TSM setup is shown in the Figure 1 and photographs. Before water is filtered make sure all the connections are tight. A vacuum pump protector must be installed between the vacuum pump and effluent bottles to prevent water from backing up into the pump. Turn the pump on with all the manifold valves closed to check for leaks. At the same time set the vacuum pump to 7 psi. If the vacuum goes over 7 psi cells may lyse and the effluent bottles collapse. Therefore the vacuum pump

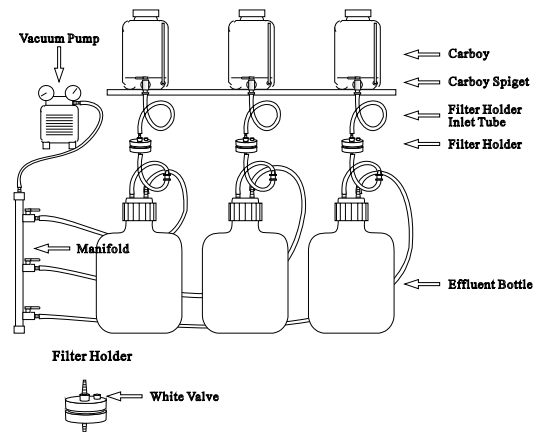


Figure 1.: TSM Filtration Setup

must be checked periodically.

Fill out the filtration and field logs, this relates the depth to the CTD bottle, sample carboys, and filter number (Fig. ??). The logs are also used when filling sample bottles on deck to coordinate sample collection. If any unusual event occurs that may affect the quality of the sample, such as touching the filter with your hands or tearing the filter, add appropriate comments in the filtration log. Label the filter container with the analysis name, cruise number (eg. L7 to designate the cruise name MOBY L7) followed by a sequential number (TSM L7 1,

TSM L7 2 . . .). The base of the filter container, not the lids, should be clearly labelled with a waterproof pen.

To save on station time, prepare the TSM filter holders by place a filter with tweezers in their holders before arriving on station. Use 47 mm, 0.45 um pore size Millipore membrane (MF) or Nuclepore polycarbonate filters. Filters are desiccated and tared to a constant weight, measured to tenths of a microgram and place in individual 47 mm filter container. Never touch the filters with your hands; always use tweezers. Rinse the carboys twice with 100 ml deionized water. This will save time and sample water. About every 10 samples a blank filter (which is just an unused TSM filter) should be folded, placed in plastic filter container, identified with a sequential filter number and placed in the drying oven.

Water Sampling

Some skill is required in knowing the volume required to determine TSM concentration to an accuracy of $\pm 1\%$. Water is collected directly from CTD bottles by filling 8 liter carboys. Rinsing is not necessary if the bottles have been rinsed previously with deionized water.

When filled to the brim, the carboys contain a precisely known volume. It is desirable to filter the entire carboy to avoid the need to measure the effluent volume. If the carboy is not filled completely, then the effluent must be measured with a graduated cylinder. Filtering 8 liters takes 2 to 3 hours. Filtering more water than required will waste time. Material that settles in the dregs will be lost if the entire volume is not filtered.

Filtration

Set the carboy in the TSM rack and attach the filter holder inlet tube to the carboy spigot (Fig. 1). If not already done, place a filter in the holder before you attach the tube. Open the spigot. If water does not flow you must open the white valve on the filter holder. This allows air to escape and water to flow. Once water is flowing, turn on the vacuum pump and open the manifold valve. The vacuum pump needs to be watched carefully, so that the pressure differential doesn't exceed 7 psi. Too high a vacuum causes the effluent bottles to collapse and cells to lyse. Filtering 8 liters requires 2 to 3 hours. When about 1 liter remains, stir the water in the carboy and tilt it so that all the water and the TMS dregs drain through the spigot.

After all the water has been filtered detach the inlet tube from the spigot and remove the filter holder top. Rinse the filter with two quick 10 ml deionized water rinses. When rinsing the 47 mm filters, use care not to splash material off the filter. We use a millipore filter (HA EP 047 OW) which has a hydrophobic (non-wetting) edge. This eliminates the need to rinse the edges and reduces the potential loss of material. Carefully remove the filter with tweezers and place in the filter container. Fold the filter and place in the filter container. Be careful not to squeeze material off the filter. If the filter tears or breaks off, save the torn material and add to filter container, note this in filtration log. If the effluent must be measured then determine the volume to plus or minus one percent (ie ± 50 ml in a 5 liter sample). The volume is recorded on the filtration log.

Filter Storage

Place the plastic filter container in the oven with its lid tilted a little to allow the filter to dry. When stacking filters in the oven be careful that the lids do not get mislaid. The oven temperature should be set to 60° C. A higher temperature may decompose some of the more volatile organic compounds and melt the filter container. The filters can be removed after 12 hours and the filter container placed back in the filter storage box. Place the filter box in a desiccated ziplock bag. Filters should preferably be dried and not frozen for storage. Only freeze filters if an oven is not available.

Details

- NEVER TOUCH the filters with your HANDS. Use tweezers.
- Rinse 47 mm filter holders with deionized water after each use.
- Dry filters before packing.
- When finished rinse all plastic ware with deionized water.
- Turn off the vacuum pump when not in use.

Examples from MOCE-1

Volume filtered:	2 to 5 liters until filters clog
Total Suspended Matter:	0.1 to 2 mg/l

Particulate Organic Carbon and Nitrogen Analysis

Setup

The POC/PON setup is shown in Fig. 2. Sample water is pressure filtered using compressed nitrogen applied at 5 to 7 psi. The pressure must be watched carefully, exceeding 7 psi can cause cell lysis and loss of material. Before sampling make sure all the connections are tight. Open the regulator to pressurize the manifold and check for leaks.

Fill out the filtration and field logs, to relate the depth to the CTD bottle, sample carboys, and filter number (Figs ? and ?). The logs are also used when filling sample bottles on deck to coordinate sample collection. Label the filter container with the analysis name, cruise number (L7 is from the cruise name MOBY L7) followed by a sequential number (POC/N L7 1, POC/N L7 2 ...). The petri dish lid and base, should be clearly labelled with a waterproof pen. About every 10 samples a blank, which is a clean ashed filter, should be included. Fold the blank and place in the oven with the other filters.

Filters are easily contaminated by touching them with your hands or the counter top. We use a 25 mm Whatman glass fiber GF/F having a nominal pore size of 0.7 μm . Prior to use these filters are pretreated by ashing in a muffle furnace at 500-510°C for at least 2 hours. After the ashing step, each filter is placed in an ashed aluminum lined petri dish. POC/PON bottles and anything associated with POC/PON filtration must be kept clean. Plastic gloves should cover the outlet tubes on the sample bottles, filter holders, tweezers, and valved caps when not in use. Wear gloves at all times, including filling the bottles. Cover any counter top you will be using with

heavy gauge aluminum foil. The foil provides a fairly clean working surface, but for the best work filtrations should be done in a laminar flow hood.

Water Sampling

The 4 liter bottles are filled directly from the CTD, reducing the risk of contamination. Rinse the bottle three times before filling. When filling the bottles cover the opening with a gloved hand to prevent contamination by engine exhaust and smoke. A quick rinse of the outside of the bottle when you are done filling washes off any contaminants. Fill the bottles as full as possible. TSM takes precedence on sample water so there may not be enough water to fill the bottle completely.

Filtration

To begin filtering attach the sample bottle to the manifold, with the valves closed. Run 100 ml of water through the outlet tube and stopcock to rinse the tube and flush out air. Connect the sample bottle outlet tube to the filter holder. Loosen the petri dish lid and set it near the filter holders. Open the stainless filter holder, take out the o-ring, and place it in a clean glove. Wet the filter holder with deionized water before placing the filter on holder.

Pick the filter up with tweezers, and place it carefully in the filter holder. Place the o-ring over the filter. Put the top housing back on the filter holder. Push down on the housing as the filter holder is tightened. If this procedure is not followed, the o-ring will twist as the housing is tightened and tear the filter.

Pressurize the sample bottle, make sure the pressure is not above 7 psi. The stainless filter holders will develop an air lock when first started. This is avoided by not completely tightening the filter holder and running water through the filter holder until bubbles no longer appear. If bubbles don't appear when the stopcock is open, the housing top may not be loose enough. If the pressure is applied too quickly, the o-ring may not seat correctly which results in leakage during filtering. When bubbles have stopped, tighten the filter holder. Begin filtering by opening the stopcock completely. If the filter holder begins leaking, stop; open the filter holder; reseal the o-ring and remove the air again. Once filtration begins place all equipment that needs to remain clean in gloves and close the petri dish. When the water level is low tilt the sample bottle to filter the dregs. Filtering 4 liters takes about one hour.

When filtration is finished, remove the filter, fold and placed in the petri dish. Care must be taken not to lose any material off the filter. The filter need not be rinsed to remove sea salts.

Storage

Place the filter in its filter container or petrie dish in the oven with the lid tilted. The oven used for drying must not be used for drying other organic material during this step, because contamination may occur. The oven temperature should be set to 60° C. A higher temperature may decompose some of the more volatile organic compounds and melt the filter container. The filters can be removed after 12 hours and the petri dish placed in the

filter box. Freeze filters if an oven is not available.

Details

- CLEANLINESS is essential in all water and filter handling.
- COVER bottle openings and tubing with plastic gloves.
- Rinse stainless filter holders after use with deionized water.
- Dry stainless filter holders after final use before packing.(place in the oven in separate

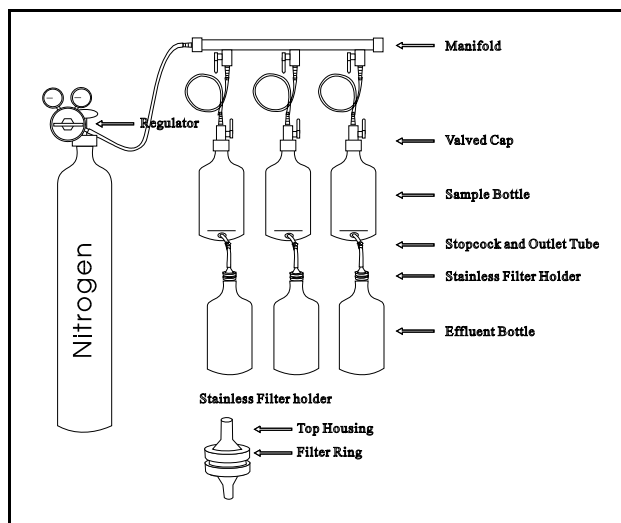


Figure 2: POC/PON Filtration Setup

- These holders will rust and get ugly, clean with wire brush as necessary.
- DO NOT let the filter with sample touch the top of the petri dish.
- TURN OFF COMPRESSED NITROGEN WHEN NOT IN USE.
- Don't use more than 7 psi.

Examples from MOCE-1

POC/PON	Filter 2-4 liters open ocean surface 4-8 liters below 150 m 10 liters below 500 m
Particulate Organic Carbon:	18 to 370 µg/l
Particulate Organic Nitrogen:	500-1000 µg/l bloom 3 to 50 µg/l
Organic Material:	50-100 µg/l bloom approximately 2 x POC

General Stuff:

Top-loading Balance have 1
 Ziplock Bags need 3 boxes
 Plastic Gloves have 2 boxes
 Kim Wipes have 4 boxes
 Aluminum Foil need 3 boxes
 Countertop Paper need 50 feet
 Tygon Tubing 1/4" have 50 ft
 Tygon Tubing 1/2" have 50 ft
 Tygon Tubing pressure have 10 ft
 Tubing straight connectors several
 Tubing Y connectors several sizes

Oxygen Titration Kit:

Oxygen Method in plastic
 Brinkman Titrator:
 Power Supply
 Dispenser Tip:
 Tubing for S₂O₃ bottle:
 Fiber Lamp: spare bulb
 Stirrer: have 2
 Stirring bars have 8

Glassware Box:

S₂O₃ 5-liter poly bottle
 KH(IO₃) 1-liter brown poly bottle have 1
 Winkler #1,2,3 brown glass bottles
 Starch bottle 100 ml
 Plastic dip rod
 Squeeze Bottle 500 ml have 1... need 3
 Glass burette 10 ml
 500 ml Volumetric (1 plastic 1 glass)
 1000 ml Volumetric (1 plastic 1 glass)
 100 ml Graduated Cylinder
 25 ml Graduated Cylinder have ?
 125 ml Erlenmeyer Flasks glass have 3
 125 ml Erlenmeyer Flasks polycarbonate have 6
 100 ml Beaker have 2
 500 ml Beaker have 3
 1000 ml Beaker have 3... need3

Chemical Box:

MnCl₂·4H₂O ?? g bottle have 2... need 2
 NaOH ?? g bottle have 2... need 2
 NaI ?? g bottle have 2... need 2
 H₂SO₄ concentrated have 2... need 2
 Na₂S₂O₄·5H₂O have 2... need 2
 Dry starch 100 gram bottle have 1... need 1

Preweighed Chemicals:

Winkler Reagent #1 to make 500 ml
 300 g MnCl₂·4H₂O have 2
 Winkler Reagent #2
 160 g NaOH have 2
 300 g NaI have 1... need 2
 Winkler Reagent #3
 180 ml H₂SO₄ to 500 ml have 0... need 2
 Na₂S₂O₄·5H₂O 10.0 g dry reagent have ?...need 3
 KH(IO₃) 0.325 g dry reagent have 0... need 5
 10 ml Glass Pipette have 0... need 2
 10 ml Glass graduated pipette have 0... need 2
 FinnPipette 5 ml pipette for standard have 2
 Eppendorf 1 ml pipette for #1,2,3 have 4

Oxygen Sample Bottle Box: have 24

Bottle Volumes in plastic: have 1... need 1

Salinity Kit:

MiniSal Salinometer: have 1
 MiniSal Instruction Book xerox original
 Aspirator Bulbs have 2... need 3
 Aspirator Valves have 2... need 8
 Glass File have 1... need 2
 Micronta Thermometer have 1... need 1
 Mercury Thermometer 0-35 C have 1... need 2
 Salinity Bottles (case of 24) have 2
 Standard Seawater (35 psu) have 9
 Standard Seawater (30 psu) have ?
 Bottle Rack for Salinometer have 1... need 1
 19-gauge Teflon tubing (roll) have 0... need 1
 Power Supply (12 v 500 ma) have 1... need 2
 Batteries (6 v 4 ah spare) have 6... need 2
 Clearing Solution (? type) have 0... need 1
 Secondary Standard 35 ppt (1 gal) have 1
 ParaFilm have 2... need 2

TSM Kit:

TSM Filter Rack with manifold
 TSM filter holders have 4
 Millepore Vacuum Pump have 1
 Gast Vacuum Pump have 1
 Vacuum Pump Repair Kit need 1
 Carboys have 3... need 4
 Preweighed TSM Filters have 100... need 100

POC/PON Kit:

POC/PON Filter Rack with manifold have 1... need 1
 Compressed Nitrogen have 1... need 1
 Regulator for nitrogen bottle have 1... need 1
 Nitrogen adapter

POC/PON Filtration Heads have 3... need 6
 5-liter Aspirator Sample Bottles have 3... need 4
 5-liter Poly Effluent Bottles have 3... need 4
 Tubing Valves have 3... need 8
 Tubing Stopcocks have 3... need 8
 Pressure Tubing (100 ft box) have 1... need 1
 5-gallon Jerry Cans have 7... need 7
 1000 ml Graduated Cylinder have 1
 Oven have 1
 Oven Thermometer have 1
 Mercury Thermometer 0-100 C have 0... need 1
 Pre-ashed Glass Fiber Filters have 100... need 100

CTD Components:

SeaBird SBE-9 CTD profiler
 SeaBird SBE-11 Deck Unit
 SeaBird SBE-7 Sea RAM
 SeaBird SBE-? Carousel
 Connectors
 Tygon Tubing

Water Sampling:

Niskin 8.5 liter GoFlow Bottles have 6... need 6
 MLML 20 liter Bottles have 0...need 6
 Messengers have 7... need 7
 Reversing Thermometers have 4... need 4
 Reversing Thermometer Correction Table

Bottle Repair Kit:

Nylon Lanyard

Spare Stopcocks
Spare Air Vents
Crimp Connectors
Crimp Tool
O-rings