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**Progress in the Measurement of Salinity and Oxygen
at the Woods Hole Oceanographic Institution**

by

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Technical Report

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Approved for Distribution:

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ERRATA

Page 5, first paragraph, second to last sentence should read:

Experience at sea has shown that best results are achieved when the laboratory temperature is maintained about 2° ($\pm 1^{\circ}$) lower than the water bath temperature.

Page 19, third paragraph, first sentence should read:

The reference equation presented by Saunders (1986) is valid only below a potential temperature of 2.6° C and does not describe these data.

ADDENDUM

To further support our claim of accuracy of salinity and oxygen measurements the following analysis was made of data collected in December-January, 1986-87 onboard the R.V. Charles Darwin in the Indian Ocean. Both the salinity and oxygen measurements were made in a constant temperature laboratory by personnel from N.E.R.C. and W.H.O.I.

Because of the large geographic variability in the distribution of salinity and oxygen, the data were divided into three sets, based on their geographic positions and interpolated onto three potential temperature surfaces. Stations 22-31 were made in the Arabian Basin, and Stations 32-78 and 79-113 were taken in the northern and southern halves, respectively, of the Somali Basin.

	No. of Points	SALT (ppt)		OXYGEN (ml/l)	
		Ave.	Std. Dev.	Ave.	Std. Dev.
Darwin 22-31					
1.8° C	6	34.7548	0.0012	3.342	0.029
Darwin 32-78					
1.8° C	23	34.7525	0.0018	3.399	0.048
1.2° C	13	34.7254	0.0013	4.012	0.030
1.0° C	10	34.7187	0.0012	4.217	0.035
Darwin 79-113					
1.8° C	15	34.7476	0.0025	3.532	0.063
1.2° C	13	34.7257	0.0011	4.044	0.038
1.0° C	9	34.7188	0.0019	4.269	0.053

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ABSTRACT

Improvements in the measurement of salinity and dissolved oxygen during the past few years at WHOI have increased the accuracy of salinity observations to ± 0.001 ppt and that of dissolved oxygen determinations to ± 0.04 ml/l. These improvements are attributable to the careful maintenance of the sample collection and analysis equipment, the construction of portable, sea going laboratories in which the temperature is constant to ± 1 degree C and the skillful use of an Autosal 8400-A salinometer and a Metrohm Titroprocessor by well trained technicians. An automated data logging system eliminates transcription errors and facilitates the timely calibration of the CTD sensors.

BACKGROUND

Salinity:

Before 1956 at the Woods Hole Oceanographic Institution (WHOI), salinities were determined by the Knudsen silver nitrate titration for the chloride ion. The salinity in ppt was determined by multiplying the chlorinity by 1.805 and adding 0.03. Standard sea water prepared by the Laboratoire Hydrographique (Copenhagen) was used to calibrate the chlorinity titrations and the accuracy of this technique was ± 0.023 ppt. The construction of a conductivity bridge for measuring the conductivity of sea water by Schleicher and Bradshaw (1956) not only increased the accuracy of salinity determinations to ± 0.005 ppt but also permitted the analyses to be made at sea soon after the water sample was collected. By 1961 experience at sea with this conductivity salinometer had shown that, when each of the five cells was individually calibrated with standard sea water by a skilled operator, the accuracy of the salinity measurement was ± 0.003 ppt. The first Guildline Autosal salinometer was purchased by WHOI in 1971. The four-arm cell in this instrument is inherently more stable than the two electrode cell in the Schleicher-Bradshaw salinometer. This factor, coupled with its ease of operation and the relatively low degree of expertise needed to obtain high quality salinity measurements has resulted in an industry-wide acceptance of the Autosal as the standard for salinity measurements. A concomitant increase in the general quality of salinity measurements has attended its international acceptance.

Oxygen:

Carritt and Carpenter (1966) point out that, after temperature and salinity, oxygen is the sea water parameter most often measured during oceanographic cruises. The classical Winkler titrimetric method or one of its many variants is the technique of choice though other methods such as gas chromatography, mass spectrometry, gasometry and the oxygen electrode have been employed. Systematic differences have been noted in dissolved oxygen concentrations within the same oceanographic regime during separate cruises and by different investigators. Although some of these differences have been identified and corrected (Worthington, unpublished) most are simply noted.

Worthington (1982) describes the serendipitous discovery of apparent oxygen consumption in water samples collected in uncoated, brass Nansen bottles during a hydrographic station by Metcalf in 1960. During a cruise in the South Atlantic the oceanographic winch broke down while making a 3000 m station. Hand cranking the winch took 12 hours to retrieve the wire and Nansen bottles. Comparison of the dissolved oxygen values from these samples with those from a nearby station showed oxygen losses as great as 1 ml/l. The interior of all WHOI Nansen bottles was coated with Teflon subsequent to this cruise. In 1977 Worthington (1982) compared oxygen samples collected with Teflon coated Nansen bottles to those collected in Polyvinyl Chloride (PVC) Niskin bottles. He found that for samples collected at potential temperatures less than 3 degrees C., the Niskin samples were higher by about 0.17 ml/l. He attributes this difference to degassing of the samples (collected in the thermally conductive, brass Nansen bottles) as they are warmed above their saturation temperature. Nansen samples collected at shallower depths and those collected in PVC Niskin bottles did not reach saturation temperature.

The modified Winkler titration used at WHOI has changed little over the past 30 years. The re-pipets presently used to dispense the $MnCl_2$ and $NaOH/NaI$ reagents are easier to use and are less likely to become contaminated than those used in the past. A Metrohm Titroprocessor, controlling a Dosimat reagent dispenser, has replaced the 10 ml automatic burette and eliminates errors in both reading the amount of thiosulphate dispensed and in determining the end point. The present microprocessor controlled titration system automatically measures the end point and transmits this information to a micro-computer where it is stored temporarily during various quality control procedures. The output from the Autosal salinometer is also transmitted directly to this computer. The temperature of both the samples and reagents are now held constant to ± 1 degree C in a temperature controlled laboratory. And finally, with the widespread use of the oxygen electrode (calibrated with Winkler titrations of discrete water samples) to continuously monitor the water column, we are learning more about the distribution and variability of dissolved oxygen in the ocean and are better able to assess the validity of the observations.

SALINITY MEASUREMENTS

Since 1976 the Guildline Autosal salinometer has been used both at sea and ashore to measure salinity at WHOI. The Autosal measures the conductivity of sea water with a four cell electrode (Dauphinee, 1975) within a range of 5 to 42 ppt equivalent salinity. This range can be modified by special order. The accuracy of these measurements is better than ± 0.003 ppt and the instrument has a stability of better than 0.002 ppt for 24 hours without restandardization. The maximum resolution is 0.0002 ppt equivalent salinity at 35 ppt. Starting with fresh water in the cell about 100 ml of sea water is needed for a measurement; half this volume is adequate when subsequent salinities differ by less than 3 ppt. The temperature controlled bath contains 16.8 liters of water (treated with algae inhibitor). The bath temperature is selectable from 18 to 33 degrees C in 3 degree C steps. The selected temperature must be within ± 4 to -2 degrees C of ambient. Experience at sea has shown that best results are achieved when the laboratory temperature is maintained about 2 degrees (± 1 degree) higher than the water bath temperature. Both the vials of standard water and the sea water samples are allowed to equilibrate at the laboratory temperature before they are analysed.

Several problems with the salinometers have occurred over the years and are discussed here to help others obtain the excellent measurements possible with the Guildline Autosal.

AUTOSAL PROBLEMS

Cell drain tube:

The Autosal service manual carefully points out the importance of ensuring that the cell drain tube is never permitted to become a ground path to the conductivity cell. If this should occur the conductivity ratio measurements are invalid. The drain tubing should be about 1 cm in diameter and only 15-20 cm long and the end should be suspended above the waste water receptacle so that it touches neither the water nor the container. This tubing must be short and of large enough diameter so that water does not collect in it. A long, small diameter tubing may fill with water and produce back-pressure in the cell which will not only increase the time needed to fill the cell but will act as an antenna for radio signals.

Conductivity cell:

The conductivity cell should always be filled with distilled water when it is not in use. If it is permitted to dry out, the electrodes and the inside of the glass cell may become contaminated.

When this occurs the electrical characteristic of the cell is changed and it will then drift rapidly towards its original state. Measurements made during this period are subject to large drift corrections. The cell is also generally difficult to fill after it has dried out. To clean a contaminated cell, it is best to disassemble it and thoroughly scrub it with a bottle brush and mild detergent. It should then be rinsed thoroughly with distilled water and reassembled. The use of a weak acid solution to clean the cell and electrodes may polarize the electrode and is not recommended.

Radio interference:

Radio transmissions can be a source of spurious salinometer readings. A research vessel's single side band transmitter is notorious for interfering with salinity measurements. A long, small diameter cell drain tube, filled with sea water, is a good antenna for receiving these radio signals and is a good reason for using a short discharge tube.

Air pumps:

Aquarium air pumps are used to force the sample through the heat exchanger and conductivity cell and to flush the cell. When operating at peak efficiency, they are just adequate for this task and must be routinely serviced to maintain maximum pressure. The leather cups in each pump are oiled at least twice a year, and the drive belt tension is adjusted for maximum RPM.

Cell drain fitting:

The cell drain fitting is located on the reverse side of the front panel of the salinometer and sometimes leaks. When a leak occurs, salt is deposited around the fitting and a ground path to the cell is created. This condition results in conductivity readings which change when one touches the salinometer case or when the drain tubing fills with salt water at the end of a filling cycle. The problem can be corrected by first thoroughly cleaning the fitting and surrounding area to remove encrusted salt and then applying a dielectric potting compound in the fitting around the tubing to make it watertight and electrically insulated from the case.

Filling tube:

The small diameter tubing leading from the sample bottle filling stopper to the heat exchanger and conductivity cell may rupture. When this occurs, salt water is sprayed over the electronic components within the cabinet with disastrous results. This type of failure has been corrected at WHOI by replacing the thin walled tubing supplied by Guildline with a thick walled Tygon tubing.

Heater lamps:

The bath temperature is precisely controlled by continuously cooling the water bath while two heater lamps are switched on and off by the temperature controlling circuit. The temperature of the bath will be maintained poorly if one lamp is not functioning. Unfortunately it is nearly impossible to see the front heater lamp and determine whether it is burned out. To solve this problem WHOI salinometers have

been equipped with test switches and indicator lamps which fail to light when the heater lamp filament is broken. These filaments are quite fragile and do not generally survive shipping so that several replacement lamps are included in the spare parts kit which accompanies the salinometers on cruises.

Thermistors:

The thermistors used to monitor the temperature within the bath sometimes fail. This failure can be complete so that the bath is either cooled or heated continuously, or it can be subtle so that the bath continues to maintain a temperature that may or may not be close to the correct value. An error of 0.050 degrees C in the bath temperature results in an error of 0.001 ppt in the calculated salinity. The condition of the thermistors should be periodically determined by following the test procedure described in the Autosal service manual. If one thermistor should fail, it is possible to operate the salinometer at reduced accuracy by setting the 'ck' switch to the good thermistor and allowing the bath to equilibrate at this new temperature setting. The salinometer must be recalibrated with standard water when this is done. The errors caused by operating the salinometer at temperatures greater than 4 or less than 2 degrees C from ambient are discussed later.

Discontinuity between suppression dial settings:

Mantyla (1986) has noted a discontinuity between suppression dial settings which may occur with the Autosal. Such discontinuities can be identified as follows. Fill the cell with a sample in which the double conductivity reading is near the upper limit of a suppression switch setting (1.9+9995). Increase the suppression number by one and note the new reading. If the sum of the second reading (2.0-0005) is not the same as the sum of the first reading, a discontinuity is present. Refer to the Autosal service manual for instructions describing the adjustment of the linearity in the suppression switch steps. At WHOI the alignment of the Autosals is checked regularly as is the absolute temperature of the water bath at those temperature settings normally employed during cruises.

Absolute salinity:

Beginning in 1986 all of the salinities measured at WHOI have been referenced to Standard Water batch number P96 as recommended by Mantyla (1986). All of the salinities measured with a batch of standard water are corrected by adding the difference between P96 and that batch.

Record keeping:

Complete records should be maintained of all the measurements, calibrations, standard water batch number, room temperature, bath temperature setting, zero reading and standby number. Such records are useful in identifying problems and determining their cause and can sometimes be used to correct erroneous data.

Salinity sample bottles:

The bottles used to collect salinity samples are 120 ml flint

glass bottles with screw caps equipped with poly-seal cones to prevent leakage. The poly-seal caps deteriorate with use and are generally replaced every 2-3 years. The interiors of the bottles react with salt water and bottles are replaced every 10 years or so. Plastic bottles should never be used nor should bottle caps which do not contain poly-seal inserts. The salinity of samples stored in such bottles has been shown to change with time. On several occasions frozen samples have been thawed and used to measure salinity. In each instance the scatter in the measurements has made the results useless.

Salinity sample collection:

Sample bottles and caps are rinsed three times with the sample water and then filled only to the shoulder of the bottle to allow for the expansion of cold samples. The bottles are kept in 'tote' boxes, each of which is labeled with a different letter of the alphabet. The bottles within the box are numbered consecutively 1-28. When salinity samples are collected from the 24 bottle Rosette, each sample is collected from its respective Niskin bottle so that salinity sample #1 is collected from Niskin bottle #1, etc. This procedure is also followed for all of the other samples drawn from the Niskin bottles in order to reduce the chance of assigning values to the wrong depth.

Lab temperature vs salinometer accuracy:

An intercomparison of the hydrographic data (Piola et. al., 1978) and CTD data from R/V Atlantis II cruise #107, Leg X was made to assess the accuracy of these shipboard salinity measurements. Figure 1 shows the cumulative changes in salinity needed to standardize the salinometer (ppt, solid line) and the average daily laboratory temperature (degrees C, dashed line) during the cruise. This figure clearly shows the correspondence between the lab temperature and salinometer calibration and illustrates the problems in achieving excellent salinity measurements in a typical shipboard laboratory in which the temperature varies widely. The results of this study provided the impetus to build portable laboratories in which the temperature could be held constant to within +/- 1 degree C.

Figure 2 shows plots of the difference between the water sample salinity values and the salinity derived from the calibrated conductivity, temperature and pressure data from the CTD for potential temperatures less than 6 degrees C. The lower plot illustrates the large scatter in the salinity data from Atlantis II cruise #107, leg X described above. The upper plot shows similar data from Endeavor cruise #128 during which all of the measurements were made in a temperature controlled, portable laboratory. CTD data are calibrated in groups of stations defined by the stability of the sensors and not on a station by station basis. Thus the curves in this figure present a good evaluation of the relative accuracy of the salinities measured during these cruises. Differences greater than 0.03 ppt are generally interpreted as denoting leaking bottles. The mean standard deviation for differences less than this is 0.0087 ppt for the Atlantis II data and 0.0046 ppt for the Endeavor data.

OXYGEN MEASUREMENTS

Technique:

Over the past 30 years at WHOI most dissolved oxygen measurements in sea water have been determined using the following modified Winkler titration. The oxygen samples are collected as soon as possible after the cast in brown glass Biochemical Oxygen Demand bottles with volumes of 150 ml (+/- 1 ml). Special care is taken to minimize aeration of the sample. One ml of $MnCl_2$ (3 molar) and one ml of $NaI-NaOH$ (8 normal) are added to the sample, the bottle is stoppered and vigorously shaken 10-15 times. The violent agitation of the sample is needed to reduce the size of the flocculent and thus increase its area to ensure that all the dissolved oxygen rapidly oxidizes an equivalent amount of divalent manganese. The samples are placed in the temperature controlled, portable laboratory, and, when the precipitate has settled to less than half the volume of the bottle, they are shaken a second time. After the precipitate has resettled, and immediately before the samples are titrated, one ml of 25% sulphuric acid is added to the sample, and it is shaken to completely dissolve the precipitate and liberate iodine equivalent to the dissolved oxygen contained in the sample. A 50.0 ml aliquot of the iodine solution is drawn with an automatic pipette. This sample is quickly titrated with 0.01N sodium thiosulphate until the blue starch color disappears. Recently the end point has been determined automatically using a Metrohm Titroprocessor with a platinum electrode. The normality of the sodium thiosulphate is determined by titration against a standard solution of 0.0100 N potassium biiodate. The reproducibility of this titration and the blank determination is generally better than +/- 0.02 ml. The normality of the thiosulphate and the reagent blanks are determined frequently during each cruise. The sodium thiosulphate reagent is pre-weighed and stored in vials to be mixed with 2 liters of distilled water as needed. All of the other reagents are pre-mixed in the shore based laboratory and taken to sea in 1 liter PVC bottles.

Oxygen supersaturation:

During a recent cruise in the tropical Pacific Ocean (R/V T. Thompson cruise WEPOC I, 1985), the accuracy of the WHOI oxygen measurements was questioned. Oxygen supersaturation of 10-20% was measured in samples collected above the thermocline, and it was believed that such supersaturation could not exist in the open ocean. The reagents were part of a larger batch mixed for this cruise and for another in the tropical Atlantic Ocean. Although the reagents remaining after the Pacific cruise were discarded, those from the Atlantic were returned to WHOI where careful measurements were made to assess their efficacy. No problems were found with these chemicals. The reagent dispensers, glassware, sample collection and titration technique and

the computer algorithm used to calculate dissolved oxygen were also examined and found to be the same as those employed at WHOI for the past several years. During the tropical Atlantic cruise oxygen values 10-18% supersaturated were also observed in samples collected above the thermocline.

Jenkins and Goldman (1985) have analysed hydrographic data from station 'S' near Bermuda for the period 1960-1980 and find that the subsurface oxygen maximum near 50m is of photosynthetic origin. They report supersaturation as great as .6 ml/l (about 10% supersaturated) with a strong seasonal periodicity and note that the highest supersaturation occurs during periods of minimum ventilation. The absence of wind induced mixing leads to the accumulation of photosynthetically produced oxygen and the creation of a shallow layer which is supersaturated with respect to oxygen. The super-saturation observed in the tropical Pacific and Atlantic may result from this mechanism.

Titroprocessor:

In 1985 a Metrohm model 672 Titroprocessor was purchased to control the modified Winkler titration used at WHOI. This equipment consists of a microprocessor which has been programmed to measure the electric potential of a platinum electrode and to control the dispensing of the thiosulphate reagent during the titration of the iodine solution. The proprietary program within the microprocessor continuously reads the electrode potential and the amount of reagent used in the titration. Depending upon parameters selected by the operator, the program adjusts the rate at which the reagent is dispensed from quite fast during the initial stages to very slow as the end point is approached. This pattern of dispensing thiosulphate closely mimics that employed by a skilled analyst but does so with greater precision and consistency. The equipment has been successfully used during several cruises in both the temperate and tropical Atlantic Ocean during which several thousand analyses were performed. Neither the collection and handling of the oxygen samples nor the preparation of the reagents has been changed from that employed at WHOI for the past 30 years. The only change with the new Titroprocessor based system is that the end point is now sensed electronically instead of relying upon an operator to determine the disappearance of the blue starch color. Intercomparisons between the Titroprocessor measured end point and the colorimetric end point determined by several experienced analysts shows that the former is about 0.02 ml greater than the visual end point. The Differences between repeatedly determined end points of prepared samples have a standard deviation of 0.005 ml/l. Only one problem has occurred with this system. During the first cruise on which it was used, the electrical characteristic of the electrode began to drift. This drift was not detected for several stations during which the Titroprocessor overshot the end point at each titration. Fortunately the amount of overshoot was predictable so that the data could be corrected.

Data handling:

The Titroprocessor prints out a complete record of each titration including:

1. Date and time
2. Program #
3. Identification #
4. Sample volume
5. Initial electrode voltage
6. Final electrode voltage
7. Volume of thiosulphate dispensed
8. Calculated oxygen, ml/l

These data are transmitted to a Commodore B-128 computer system for interim storage and various quality control procedures. When both the salinity and oxygen for a station have been analysed, the data are merged and plotted versus potential temperature and compared with nearby stations for quality control. When these procedures have been completed, the data are transmitted to a Micro-Vax computer used by the WHOI CTD group to calibrate the CTD salinity and oxygen measurements. The automatic data transfer from the salinometer and Titroprocessor to the computer eliminates hand entry of the data as a source of error and frees the operator of tedious paper work.

Accuracy:

In spite of the formidable problems in measuring the concentration of dissolved oxygen in sea water, it is heartening to note that a study by Saunders (1986) shows that the rms deviation in dissolved oxygen measurements below 3500 m during 6 cruises varied by only .05 to 1.3 percent. The data were collected in the northeastern Atlantic Ocean during 1980-81 by several different investigators. Four of the cruises were aboard WHOI research vessels where investigators used the modified Winkler technique described in this report (except without the Titroprocessor). The accuracy determined by Saunders compares well with the 0.1 % reported by Carpenter (1965) using a sophisticated photometric technique in a closely controlled experiment. Progress in measuring oxygen at WHOI since 1981 has improved both the resolution with which the titrant is measured and the repeatability of the endpoint determination. In addition to these improvements it has been noted that, since oxygen measurements have been made within the temperature controlled portable laboratory, the scatter of these observations has been reduced. Some of this scatter was caused by temperature induced changes in the volume of the automatic pipette used to collect the 50 ml aliquot. The constant temperature in our portable laboratory has eliminated this source of error and thus the accuracy of our present oxygen measurements should be better than that reported by Saunders.

IN SITU SAMPLING BOTTLES

Since 1971 WHOI has used a General Oceanics Rosette in situ sampling system to collect water samples during a CTD station. The primary purpose of this sampling program is to provide calibration samples for both the conductivity and oxygen sensors on the CTD and to collect sample water for other analyses. The underwater unit of the rosette contains a stepping motor which is advanced each time a button is pushed at the deck unit. A tripping mechanism, connected to the motor shaft, releases a lanyard attached to the end caps of each bottle. Closure of the end caps traps the sample water within the PVC body of the Niskin bottle. Each time the stepping motor advances, a confirmation signal is sent to the deck unit. A failure of the deck unit to indicate a confirmation is generally the first symptom of a salt water leak in the cables or connectors. Such a leak results in a high resistance short between the signal conductor and ground which attenuates the confirmation signal from the rosette. The mechanical components of the tripping mechanism are exposed to salt water corrosion, fouling and electrolysis. The reliability of the rosette is improved when it is rinsed with fresh water after each cast and is periodically sprayed with a lubricant during the cruise. Water may leak into the oil filled pressure case and cause corrosion and eventual failure of the bulkhead connector at the bottom of the case. Periodic removal and inspection of the oil sometimes reveals this problem before damage occurs. At the end of each cruise all parts of the rosette are thoroughly cleaned, lubricated and tested for proper operation.

The earlier versions of the Niskin bottles employed a breather valve assembly which relied upon a nylon to PVC seal to prevent leakage. In many of these bottles the threaded hole in the valve seat was not perpendicular to the seat so that when the breather valve was tightened a gap remained under one edge and caused a leak. This problem was solved by replacing faulty valve seats and installing soft, synthetic rubber washers on the breather valves to provide a good seal. Consultation with General Oceanics has resulted in a redesigned breather valve which uses an 'O' ring to seal the breather vent. Since this improved breather valve was introduced, leaking of this type is no longer a problem.

When new Niskin bottles are received from General Oceanics, they are disassembled, inspected and the 'O' rings are lightly greased with a high quality, silica free grease. The surgical rubber tubing used to close the end caps is retied to provide a firmer and more positive closure and the bottles are reassembled. Each bottle is then filled with water and the spigot, breather valve and end caps are closed. If water comes out of the spigot when it is opened, then air is entering the bottle through a leak which must be found and corrected. Some leaks are difficult to locate, especially those in the body of the bottle. Pumping air pressure into the bottle while it is submerged in a

water bath generally indicates the location of a leak by the stream of bubbles issuing from it.

It has been found that 'O' rings deteriorate with age and use. Regular replacement of the end cap 'O' rings after each cruise has greatly reduced the problems with 'leaky' bottles. Some sampling programs require the replacement of the surgical rubber tubing used to close the end cap with plastic-coated springs. To prevent abrasion of the end cap 'O' rings, the springs are installed using short loops of monofilament to attach them to the end caps.

The present widespread use of Conductivity- Temperature-Depth (CTD) instruments as a replacement for standard Nansen bottle hydrographic stations has enabled oceanographers to obtain almost continuous measurements of temperature, salinity and oxygen versus depth. However these data are only as accurate as the water sample data used to calibrate the CTD sensors. During a typical, deep oceanographic CTD station on a WHOI vessel, 24 water samples are obtained during the 'up' portion of the cast and are used to calibrate the CTD data collected during the 'down' part of the cast. The down cast CTD data is preferred for several reasons. The sensors are located on the bottom of the instrument and thus encounter relatively undisturbed water during descent while during ascent the sensors are in the wake of the CTD package. The signal from the CTD is interrupted each time a water sample bottle is tripped and the missing data from these interruptions cause problems during data processing. Interrupting the power to the CTD also affects the oxygen sensor and results in spurious oxygen data when the interior battery power is too low.

A few years ago there was some interest in developing the ability to collect water samples during the 'down' cast. It was hoped that collecting samples during this part of the station would ameliorate many of the problems encountered when calibrating CTD measurements recorded during the 'down' cast with water samples collected during the 'up' cast. Several 1.2 liter Niskin bottles were modified with rubber diaphragms to compensate for the change in volume caused by the increased pressure and decreased temperatures encountered after closing the bottle on the down cast. These bottles were tested at sea during two cruises, but the increased maintenance problems with the rubber diaphragms argued against adopting this design.

In order to minimize the contamination of water samples, they should be collected only during the up cast when they are subjected to decreasing pressures and increasing temperatures. Both of these factors increase the volume of the samples and tend to expel water from the bottles. The opposite is true of course if the samples are collected during the down cast when increasing pressure and decreasing temperature tend to force water into the bottle and contaminate the sample.

As presently configured the General Oceanics Rosette is bulky, awkward to use and is not as reliable as we would like. The dissimilar metals used in its construction result in rapid corrosion and the

fouling of components in the tripping mechanism may make it impossible to cock a bottle. Sometimes the Niskin bottles trip early, fail to trip or trip late and close at a shallower depth. The bottles can be tripped only sequentially, and neither the surgical rubber tubing used to close the Niskin bottles nor the rubber 'O' rings are compatible with the analysis of some components of sea water. The oceanographic community sorely needs a water sampler that addresses these shortcomings.

PORTABLE LABORATORIES

In 1983 the National Science Foundation provided funds to build a portable, sea-going laboratory in which the temperature could be controlled to within ± 1 degree C in the hope of increasing the accuracy of our salinity measurements. An insulated, cold storage type, shipping container (2.6 x 2.6 x 6.5 m) was purchased and modified to include the necessary benches, cabinets, sink etc. needed for the measurement of salinity and the analysis of dissolved oxygen. Space was also provided to maintain the electronic equipment used by the WHOI CTD Group. Although the interior of the container was extensively modified to meet these needs, the exterior was changed as little as possible. It was felt that the more closely the portable laboratory resembled externally a typical Sea-Land container the easier it would be to ship around the world. This expectation has been realized during several shipments to the Pacific, Indian and Atlantic Oceans. An additional incentive to the construction of the portable laboratory was the savings to be realized in the cost of shipping the CTD and hydrographic equipment to meet cruises in foreign ports. Shortly after the first portable laboratory returned from a successful cruise in the Pacific aboard the R/V T. Thompson, funds were obtained to construct an additional portable lab using \$20k of the \$46k air freight budget in a contract supporting a cruise to the South Atlantic. The cost of shipping the portable laboratory to South America and returning it from South Africa was \$6k. Thus the entire cost of building and shipping the portable laboratory was \$20k less than the budget for air freight. A third laboratory was constructed to accommodate a Pacific cruise during a period when the other labs were in use. Although we are missing a few pieces of equipment, we can now come close to supporting three major oceanographic cruises simultaneously.

Figures 3a and 3b are plan views of a portable laboratory showing the layout of the sink, benches and various features found useful during extended oceanographic cruises.

The portable hydrographic laboratories built at WHOI are constructed from 2.6 x 2.6 x 6.5 meter container vans originally used to transport frozen foods across the oceans. These containers are constructed with aluminum sheathing (alternately of fiberglass) over rigid steel end frames connected with steel beams. The floors are reinforced with 'I' beams every 60 cm to support the maximum design load of 22,000 kilograms. The only opening to the container is a large double door at one end which opens completely for easy access to the interior. This door is 8 cm thick with 8 closure cams and a large, thick rubber gasket which makes an air tight seal. The walls, ceiling and floor are about 8 cm thick with poured-in-place foam insulation which provides a high 'R' rating. Aluminum reinforcing beams are spaced on 60 cm centers within the walls and ceiling to provide rigidity. Each beam is attached only to the interior or exterior aluminum sheathing to

eliminate conduction of heat via this avenue. The rivets used to fasten the sheathing to the beams have plastic bodies to reduce heat conduction along these paths.

The construction of the walls precludes hanging shelves or equipment from them. The first step in the fabrication of each portable laboratory is to build an interior framework of steel channel along the walls and ceiling to make a sturdy interior framework to support shelves, cabinets, overhead light fixtures, etc. A 2 cm thick marine grade plywood floor is laid over the existing aluminum floor channels. A personnel door is installed near the corner at the double door end of the van where its hinge is supported by the steel framework at the corner of the lab. Steel clad insulated house doors with double glazed windows have been used though the galvanized hinges are replaced with ones of solid brass. The magnetic weather stripping on these doors makes them air tight. Three marine windows (about 18x32 cm) are set into walls at seated eye-height near the operator's chairs. These windows not only provide the occupants with a opportunity to view the horizon and alleviate eye strain but have also been useful to pass wires and cables into the lab for instrument repair.

Each lab is equipped with:

- 25 feet of bench space with almost continuous electric outlets.
- 27 feet of cabinets with a volume of 80 cubic feet.
- 16 drawers with a capacity of 40 cubic feet.
- One B-128 Commodore computer system.
- Two Guildline Autosal 8400-A Salinometers (with spare parts)
- One Metrohm Titroprocessor for oxygen analysis (with spare parts)
- A small refrigerator.
- A sink with drain and cold water faucet.
- Reagent bottle racks.
- Distilled water bottles and racks.
- Electronic repair equipment and CTD spare parts.
- Complete set of small tools.
- Sample bottle racks for all of the salinity and oxygen sample bottles.
- Expendable office supplies.
- Two salt water cooled heat exchangers, each 9000 BTUs cooling and 11000 BTUs reverse cycle heating.
- Three adjustable swivel chairs bolted to the floor.
- A 440v to 110v, 30 ampere transformer and circuit breaker box with four separate circuits.
- A ventilator for fresh air.
- External fittings for fresh, salt and waste water.
- Stuffing tubes for electrical power, communication and computer cables.
- The wall and ceiling are covered with plywood panelling.

A temperature recorder within the lab provides a permanent record of the interior temperature. An added bonus to this record is an indication on the chart of radio interference from the ship's transmitter. The long wire between the thermistor and the chart recorder acts like an antenna. The temperature measuring circuit amplifies and records this signal as large amplitude, short period fluctuations in the temperature record. The unique character of the signal provides graphic proof of this type interference and alerts the salinometer operator to cease analysis. The labs have been used from the tropics to 55 degrees North Latitude and the interior temperature was easily controlled to within +/- 1 degree C.

INTERCOMPARISON BETWEEN 1.2 AND 5.0 LITER NISKIN BOTTLES

An intercomparison of salinity and oxygen measurements was made between samples drawn from 1.2 and 5.0 liter Niskin bottles during R/V Knorr cruise # 118. This cruise took place in November 1985 and was part of the C-SALT experiment east of Barbados in the western tropical Atlantic Ocean. The large bottles were required to provide sufficient water to analyze dissolved Freon. These bottles were equipped with plastic coated springs instead of the surgical rubber tubing normally used to close the end caps. The end cap 'O' rings in the 5 liter bottles had been baked for some hours in a stream of inert gas to remove contaminants. Several of these 'O' rings were overcooked and became brittle and cracked. The cracks caused leaks which subsequently contaminated the samples. These samples have been excluded from the following discussion. The oxygen and salinity samples from the 5 liter Niskin bottles were drawn after the Freon samples were collected, generally 20-30 minutes after the station was over.

Fig. 4 shows potential temperature versus the differences between the dissolved oxygens and the salinities measured from samples drawn from the 1.2 and 5 liter bottles. The average difference between the oxygen values is -0.032 with a standard deviation of 0.065 . The average difference between the salinity samples is 0.004 ppt with a standard deviation of 0.0043 ppt. This compares with standard deviations of 0.039 ml/l and 0.0013 ppt measured during R/V Endeavor cruise # 128 when only 1.2 liter bottles were used (see next section). The scatter in the intercomparison measurements is larger than we normally experience with the 1.2 liter bottles and may be the price one pays when the standard sampling scheme is changed and the oxygen and salinity samples are the last to be drawn from the Niskin bottle. The greater scatter may also be the result of baking the end cap 'O' rings and causing leaks which only slightly contaminated the samples. Another factor which may be causing the large scatter is the limited experience we have in using and maintaining the 5 liter bottles. Additional data are needed to determine and eliminate the cause of the increased scatter.

ACCURACY

The accuracy of the salinity and dissolved oxygen data collected during WHOI cruises is clearly dependent on the skill and experience of the individual making the measurements. During the past 10 years the quality of the salinity and oxygen data from several cruises has been degraded by unskilled technicians. It is generally not possible to train individuals in a shore based laboratory and expect them to collect the highest quality data without supervision at sea. Several training cruises are generally needed to develop the skills and confidence to obtain the quality of the WHOI data described below.

Saunders (1986) has found that between 20-50 degrees North in the northeast Atlantic and at depths greater than 3000 db the theta-salinity relationship is remarkably uniform. He suggests that the accuracy of salinity measurements and dissolved oxygen determinations made by different laboratories can be compared if the observations are made within this area. In May 1986 the WHOI CTD group occupied 101 stations within this region during R/V Endeavor cruise #143. The 5 liter Niskin bottle rosette sampler used during this cruise was the same used during the Knorr-118 cruise described earlier. Twenty-seven stations reached 3000 db. Although these observations did not sample the water described by Saunders, the deep theta-salinity relationship observed during this cruise appears to be consistent enough to place an upper limit on the accuracy of the salinity and oxygen measurements. The 2.8 degree potential temperature surface was the coldest found at all of the stations and was chosen to assess the accuracy of these measurements.

2.8 degree potential temperature surface

	Average	Std. Dev.
Pressure	2754 db	60 db
Salinity	34.962 ppt	0.0044 ppt
Oxygen	5.83 ml/l	0.064 ml/l

The reference equation presented by Saunders (1986) is valid only below a potential temperature of 2.6 degrees C and does describe these data. However, the theta-salinity values from this cruise overlie the data presented in his Figure 2. The standard deviation of the salinity and oxygen measurements are larger than reported by Saunders for the greater than 3000 db water. This increased scatter may be caused by leaks in the 5 liter bottles such as seen during Knorr-118, or it may result from geographic variations in these parameters. In any event it is likely that the standard deviations in the salinity and oxygen measurements shown above contain variations due to factors other than analytical technique.

In 1985, during Endeavor cruise # 128, ninety-two CTD stations were occupied between 9-15 N, 53-59 W. Twenty-three of these stations

were deep enough to sample the water at a potential temperature of 2.5 degrees C, and sixteen of these stations recorded potential temperatures less than 1.8 degrees C. The following tables show the average salinity and dissolved oxygen and their standard deviations on the two potential temperature surfaces.

2.5 degree potential temperature surface

	Average	Std. Dev.
Salinity	34.993 ppt	0.0018 ppt
Oxygen	5.95 ml/1	0.066 ml/1

1.8 degree potential temperature surface

	Average	Std. Dev.
Salinity	34.884 ppt	0.0013 ppt
Oxygen	5.95 ml/1	0.039 ml/1

A least squares fit to the 114 potential temperature-salinity pairs between 2.1-3.0 degrees C has a standard deviation of 0.002 ppt. A similar fit to the data below a potential temperature of 2.0 degrees C also shows a standard deviation of 0.002 ppt. Plots of these differences and an intercomparison with CTD data suggest that geographic variability accounts for some of this variation.

The study described above indicates that the accuracy of the salinity and dissolved oxygen measurements presently made by experienced operators at WHOI is at least as good as that achieved during Endeavor-128 at a potential temperature of 1.8 degrees C or about +/-0.001 ppt and +/-0.04 ml/1. We agree with Saunders that intercomparisons of temperature, salinity and oxygen measurements by all oceanographic institutions are highly desirable. Such intercomparisons are especially important during multi-national, multi-institutional experiments such as the forthcoming World Ocean Circulation Experiment. The WHOI CTD group plans to continue to assess and improve the accuracy of its measurements as opportunity permits and welcomes suggestions to achieve this goal.

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Figure 3b. The plan view of a portable laboratory showing the shelves, cabinets, etc.

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A II-107 Leg 10

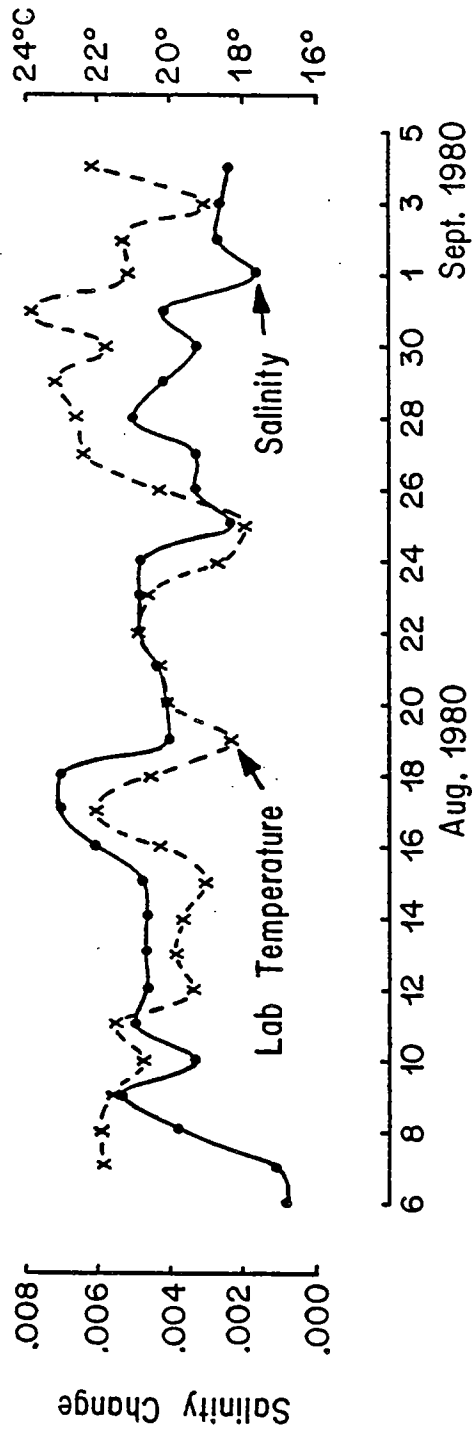


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SALINITY DIFFERENCE AT < 6°C

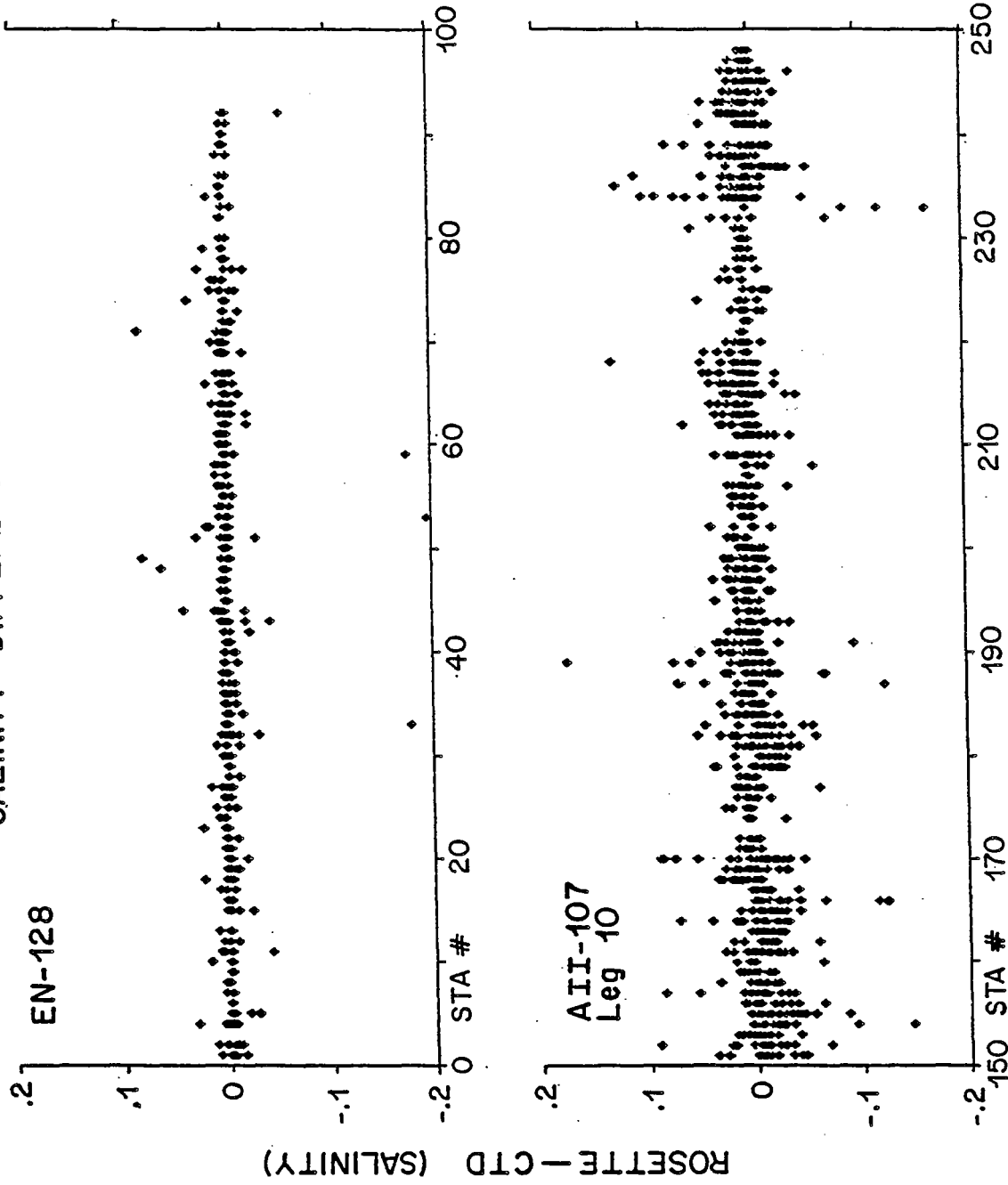


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Portable Laboratory
(Workbenches)

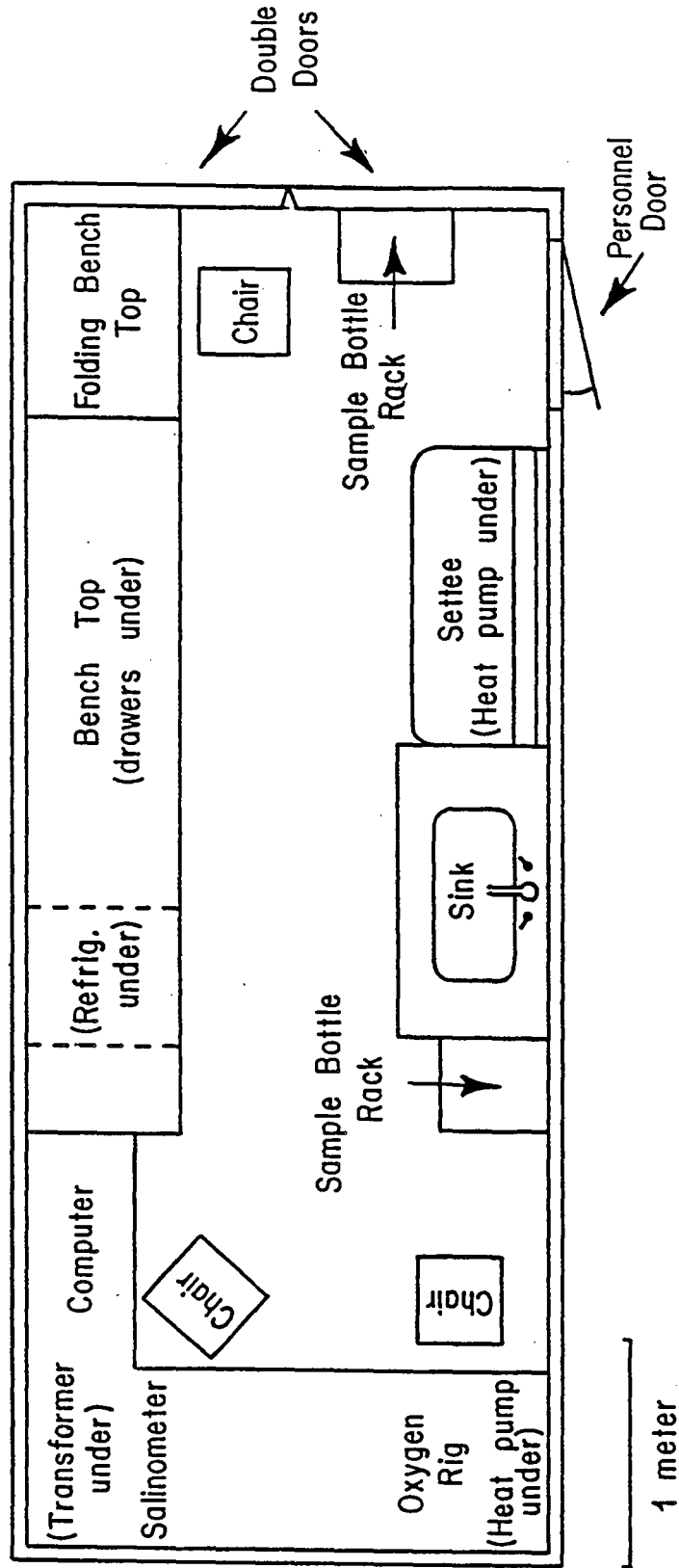


Figure 3a. The plan view of a portable laboratory built at WHOI showing the size and location of benches, chairs, etc.

Portable Laboratory
(Cabinets)

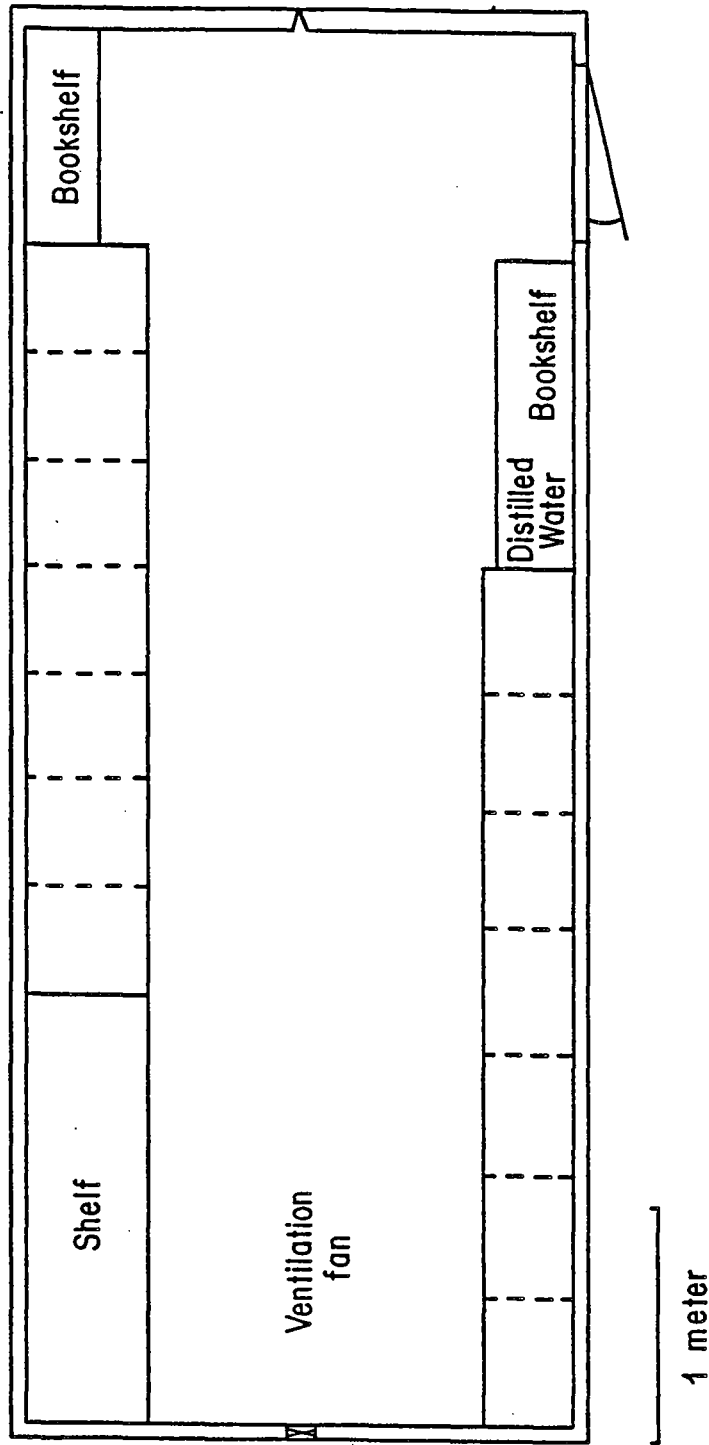


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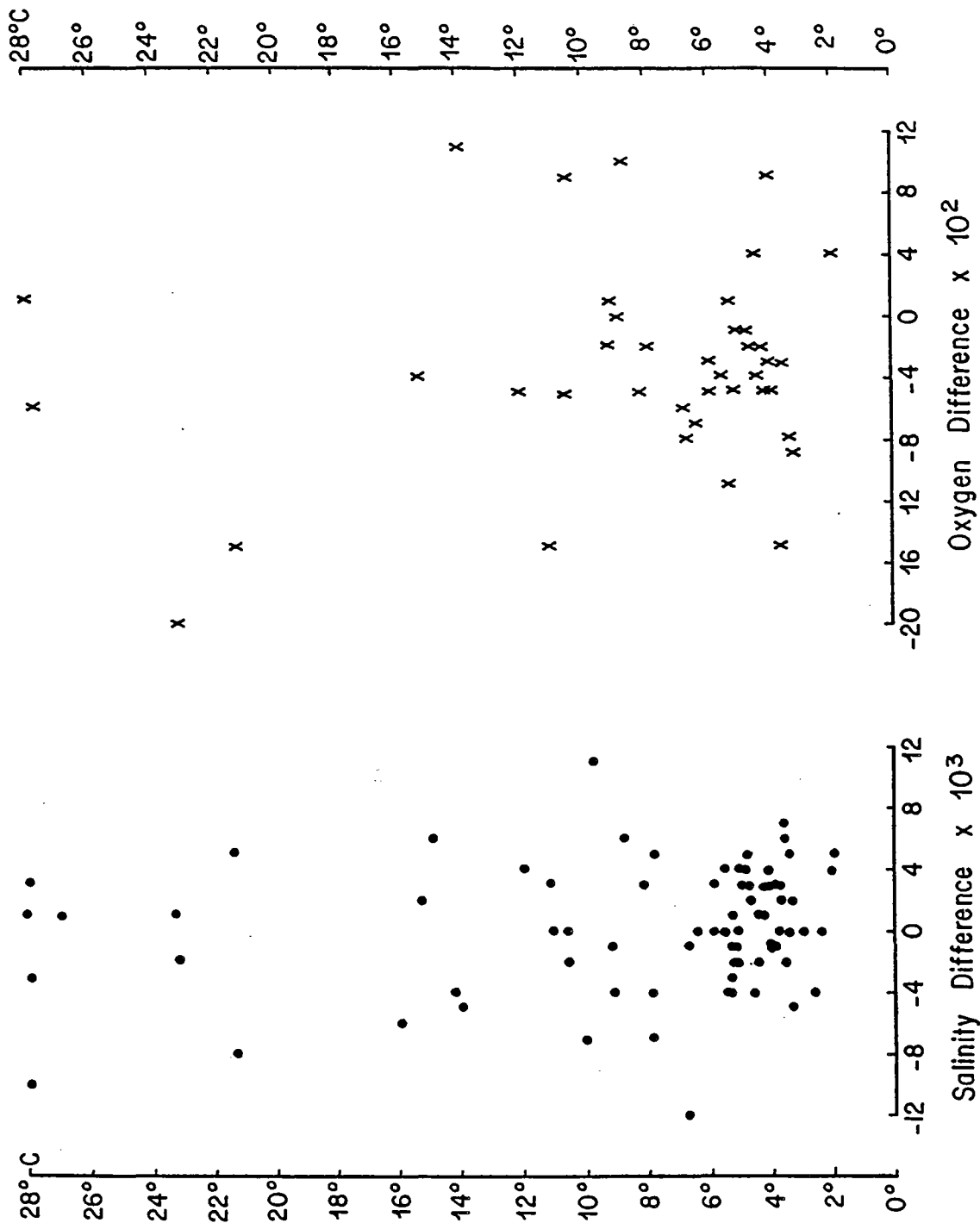


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