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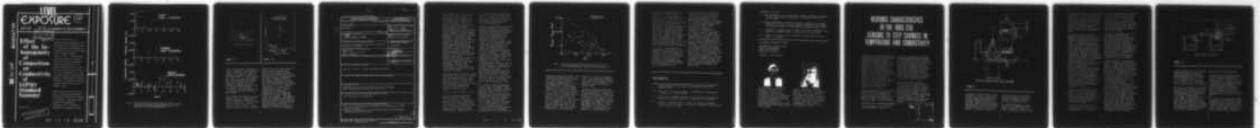
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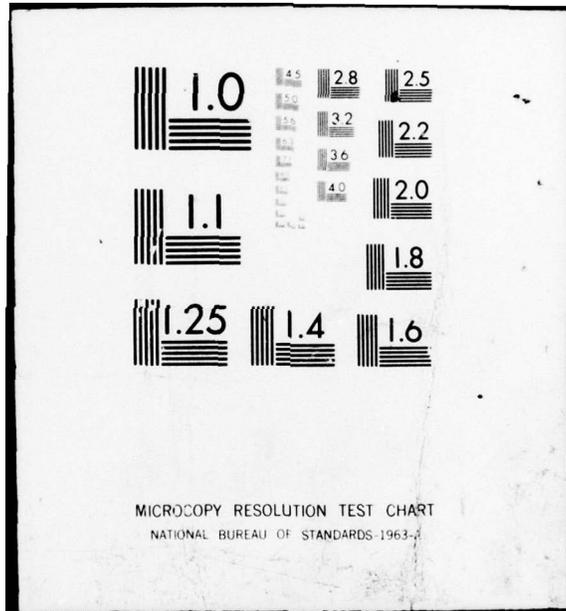
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Effect of the Inhomogeneity of Composition on Conductivity of IAPSO Standard Seawater

For more than 70 years the standard generally adopted for the determination of salinity has been the International Association for the Physical Sciences of the Ocean (IAPSO) standard seawater (UNESCO,¹ 1978). This standard is prepared from North Atlantic surface water and is supplied in sealed glass ampoules by the Standard Seawater Service. Each batch is certified in chlorinity (Cl ‰) as determined by a high precision weight titration method employing potentiometric end-point detection. The standard deviation is about 0.0003 ‰ in Cl ‰ (UNESCO, 1978).

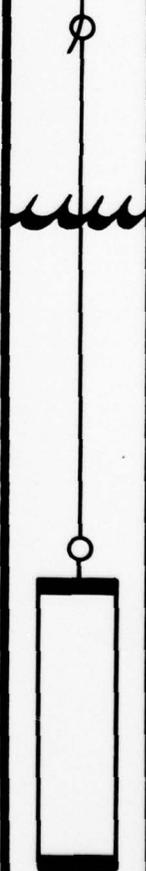
More recently, salinity has been widely determined by measurement of electrical conductivity instead of chlorinity. The usual method consists of calibrating a salinometer with a standard by trimming the instrument to read

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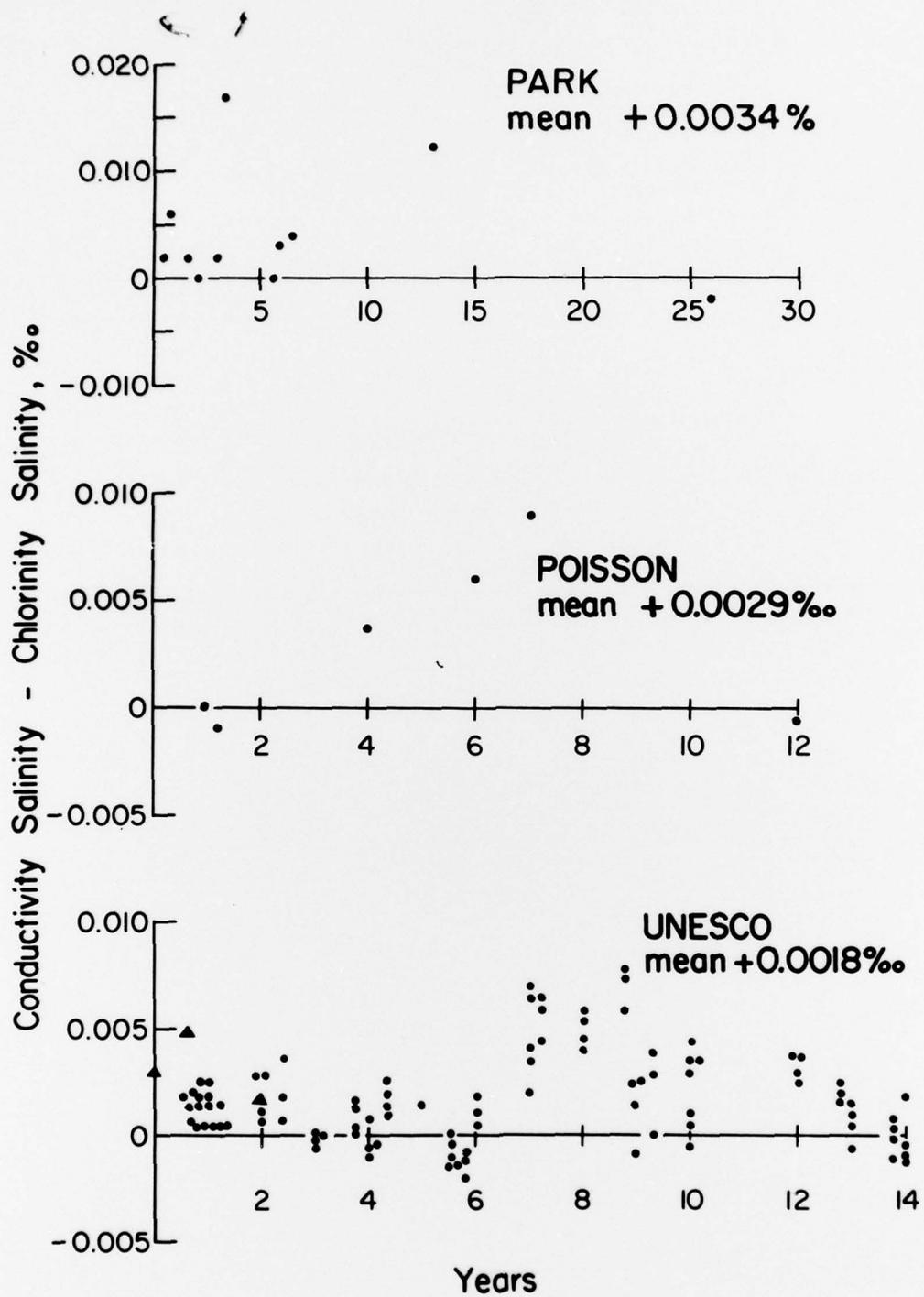


FIGURE 1. Differences between salinity values determined by conductivity measurements of various workers and values computed from certified chlorinities versus the ages of the IAPSO standard seawaters at the time of the measurements. Triangles are data measured at OSU.

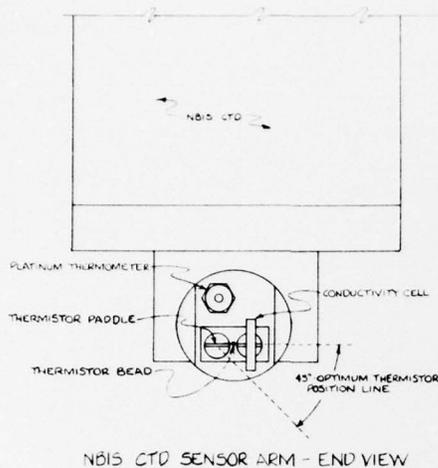


FIGURE 3.

tests were conducted to determine the "cosine response" of the thermistor sensor. Data from those tests are presented in Figure 4. When the thermistor paddle is angled down by 45° , there is a $\pm 15^\circ$ arc through which the thermistor time constant shows little variation (13 msec). Drop tests conducted with the thermistor assembly adjusted to the -45° position were extremely encouraging. The time constant for this position on three drop tests was 48 msec.

The original 8 mm conductivity cell supplied with the CTD was replaced with a 30 mm cell. Because of spatial limitations, the replacement cell was mounted at an angle of about 30° to the vertical. Time constant dependence on the flushing

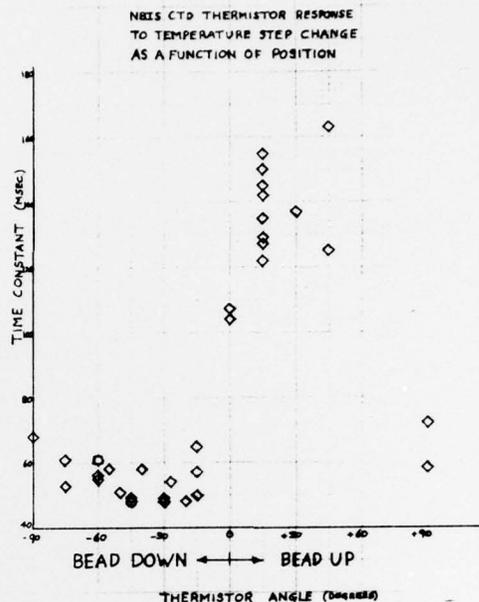


FIGURE 4.

length of the cell could result in time constant variations as a function of the angle of attack. Time constant determination for the conductivity cell was made employing the same techniques previously described. Seawater at 34.5 ‰ was circulated through the sensor tube and the CTD/fixture was dropped into a bath at 35 ‰. Because conductivity is a function of temperature as well as salinity, it is desirable to reduce the degradation of the conductivity gradient due to heat conduction across the interface. An attempt to adjust the temperature differential across the shutter to near zero was abandoned due to a faulty auxiliary bath temperature controller. A temperature gradient of about 0.3°C existed at the time of the drops.

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the conductance ratio corresponding to the salinity (S ‰) of the standard. Most workers use the IAPSO standard seawater (SSW) to calibrate their salinometers (Lewis and Perkin, 1978). In doing so, they have to assume that the S/Cl and Cl/conductivity relationships are the same for all batches of the SSW. This may not be correct because the SSW now appears to have a somewhat variable chemical composition. The SSW has only been certified in chlorinity and the precautions which have been taken to control its composition during the preparation and storage are no longer adequate for present-day instruments. Measurably different values of titration alkalinity (TA) and total CO₂ (TCO₂) have been reported (Brewer and Bradshaw,³ 1975; Millero, *et al.*,⁴ 1976) for different batches of SSW, and the conductivities measured relative to a given batch have been shown to vary when normalized to the same chlorinity. This may cause considerable confusion when intercomparison of different data sets are made--especially for deep, "blue water" studies.

Park⁵ (1964) made a comparison of the conductivity salinities of 11 batches of SSW (from 1937 to 1962), using batch P37 (1962) as the reference standard (Cl ‰ = 19.369). He then subtracted these salinity values from the values computed from certified chlorinity for the respective batches, using:

$$S \text{ ‰} = 1.805 \times Cl \text{ ‰} + 0.030$$

The salinity differences Park obtained (Figure 1) range from -0.002 ‰ to 0.017 ‰ with a mean of +0.0034 ‰. (Batch P18 contained white suspended material in its ampoule and is excluded when taking the mean. Batch P29 may also be faulty (Mantyla, private communication).) Poisson,⁶ in 1975,

also showed that the conductivity salinities (relative to P64 (1973) Cl ‰ = 19.378) of some batches were higher by as much as 0.009 ‰ than those calculated from the certified chlorinities.

Millero, Chetirkin and Culkin⁷ (1977), and others (UNESCO, 1978), made further measurements on the relative conductivities (relative to P64) of 26 samples of SSW (from 1962 to 1975). The differences in the conductivity salinity and the chlorinity salinity (S ‰ = 1.80655 Cl ‰) range from -0.0015 ‰ to 0.0075 ‰ and have a mean conductivity salinity that is 0.0018 ‰ higher than the P64 sample used as the reference. A plot of the differences versus age is shown on Figure 1. We suspect, as have others (UNESCO, 1978), that chemical reactions have altered the compositions of some, or all, batches of the SSW and caused their conductivities to vary. It has been known for years that TA and TCO₂ affect the conductivity of seawater; however, TA and TCO₂ in the SSW have never been systematically analyzed, although Park (1964) measured differing pH's among his SSW batches, implying changes in TA or TCO₂. Also, a few scattered reports do indicate that the TA and TCO₂ in the SSW are higher than the open-ocean values.

The results of the pH measurements by Park (1964), and UNESCO (1978), indicate that the values for SSW are generally lower than those of the open-ocean waters (~8.1). The magnitude of the pH decrease varies systematically with the increase in conductivity (Figure 2), but not with the age, suggesting that various amounts of CO₂ were formed in the sealed ampoules. Millero, *et al.*, reported that the pH increases slightly when the ampoule is left open to the atmosphere, indicating the loss of CO₂ from the

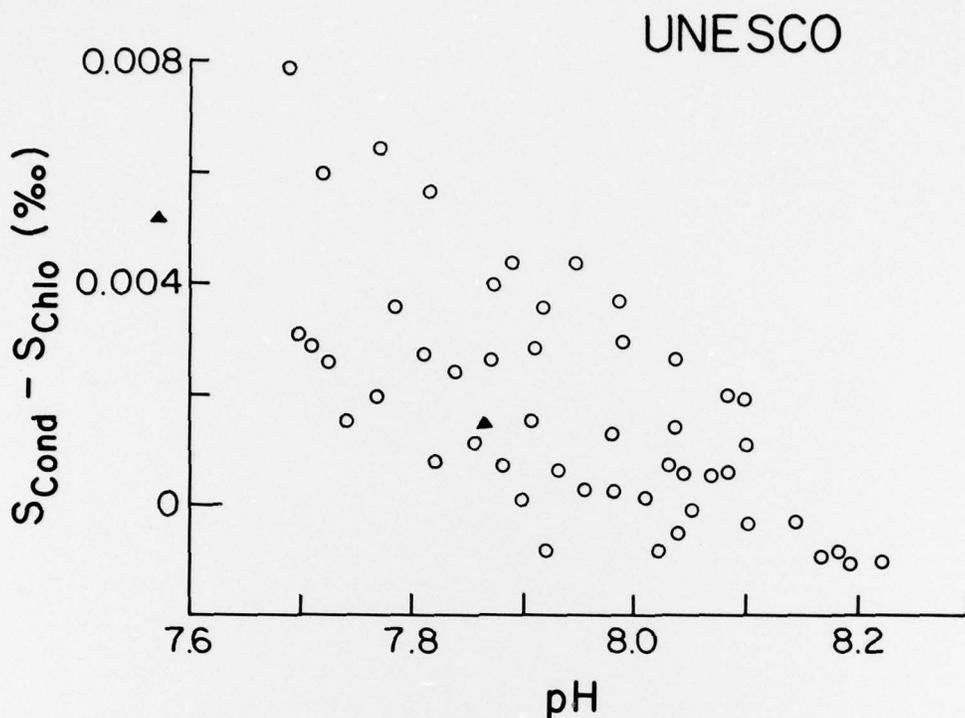


FIGURE 2. Differences between salinity values determined by conductivity measurements and values computed from certified chlorinities versus the pH of the IAPSO standard seawaters. Triangles are values determined at OSU.

apparently supersaturated SSW. (This occurred even though the preparation of the SSW involves warming to 27°C and re-equilibrating with the atmosphere (Johnston,⁸ 1969). Brewer and Bradshaw (1975) found that batch P61 (1972) of IAPSO standard seawater has a TA of 2.411 meg/kg and TCO_2 of 2.238 mmole/kg. Millero, *et al.*, (1976) also determined the TA and TCO_2 for a different batch of SSW (P63, 1973) and reported the values of 2.332 meg/kg and 2.226 mmole/kg, respectively. These values are all higher than the values of the North Atlantic surface waters whence the SSW comes (TA = 2.299 meg/kg, TCO_2 = 2.107 mmole/kg when normalized to 35 ‰ salinity,

according to Brewer and Bradshaw, 1975). The causes and consequences of the higher TA and TCO_2 values in SSW, and of the discrepancy in the measured values, have not been studied before.

The mean differences between SSW and the North Atlantic surface water are approximately 0.073 meg/kg for TA and 0.126 mmole/kg for TCO_2 when normalized to a salinity of 35 ‰. An increase of 0.073 meg/kg in TA increases the conductivity salinity and density by 0.00061 ‰ and 4.0 ppm (Brewer and Bradshaw, 1975), respectively, with no change in chlorinity. An increase of 0.126 mmole/kg in TCO_2 increases the

conductivity salinity and density by 0.0039 ‰ and 1.7 ppm, respectively, with no change in chlorinity. The combined result is an increase of 0.0045 ‰ in conductivity salinity and 5.7 ppm in density at the same chlorinity. In other words, the values of the conductivity salinity and density of the SSW are, respectively, 0.0045 ‰ and 5.7 ppm higher than those of the source water at the same chlorinity. (These values would be as much as 0.0049 ‰ and 8 ppm if Brewer and Bradshaw's TA and TC₂ values for SSW were used.) The density discrepancy would be 2.4 ppm if we compared with SSW and its source water at the same conductivity.

Since some of the SSW batches are apparently supersaturated in CO₂, a potential problem concerning the calibration of the salinometers is presented. The loss of the excess CO₂ upon opening the ampoules probably is time-dependent and relatively irreproducible, making the calibration of the conductivity bridge time-dependent and

correspondingly less reproducible. The only way to avoid the problem seems to be to produce SSW which does not form excess CO₂. The UNESCO/ICES/SCOR/IAPSO Joint Panel of Oceanographic Tables and Standards has recently decided (UNESCO, 1978) to certify the IAPSO standard seawater according to its conductivity in addition to chlorinity. This might not solve the problem unless we understand what happens to the seawater during preparation and storage. We must either have the ability to correct for the errors in conductivity and density caused by the composition change or we must find a way to stop the change. In either case, the basic knowledge about what happens to SSW between collection from the open ocean to point and time of use must be known. In the meantime, the least that should be done by all when using salinometers is to record the SSW batch numbers, publish this information with the data sets, and hope that baseline corrections can soon be made when comparing the various sets.

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RESPONSE CHARACTERISTICS OF THE NBIS CTD SENSORS TO STEP CHANGES IN TEMPERATURE AND CONDUCTIVITY

Differences in the dynamic response characteristics of the sensors on a CTD system can result in data dispersion (salinity spiking) when the sensor outputs are used in the computation of salinity values. To evaluate the effectiveness of a Weiner filter design developed at NAVOCEANO¹ for use with the NBIS² Mark III CTD system, to minimize the significance of salinity spiking, it became necessary to measure the response characteristics of the temperature and conductivity sensors. This article describes the method developed to measure these characteristics and reports the measured time constants.

Response characteristics of the NBIS CTD temperature and conductivity sensors have been determined by imposing actual step changes in the water environment and recording the resultant output. Initial attempts

to impose a temperature step change to the temperature sensor consisted of air-to-water drop tests in which the CTD was allowed to free-fall from air at ambient temperature into a temperature-controlled water bath at some lower temperature. The major operational problem associated with this method was achieving stable ambient conditions prior to a drop. Data resulting from the air-to-water tests showed considerable scatter, often greater than 200 percent.

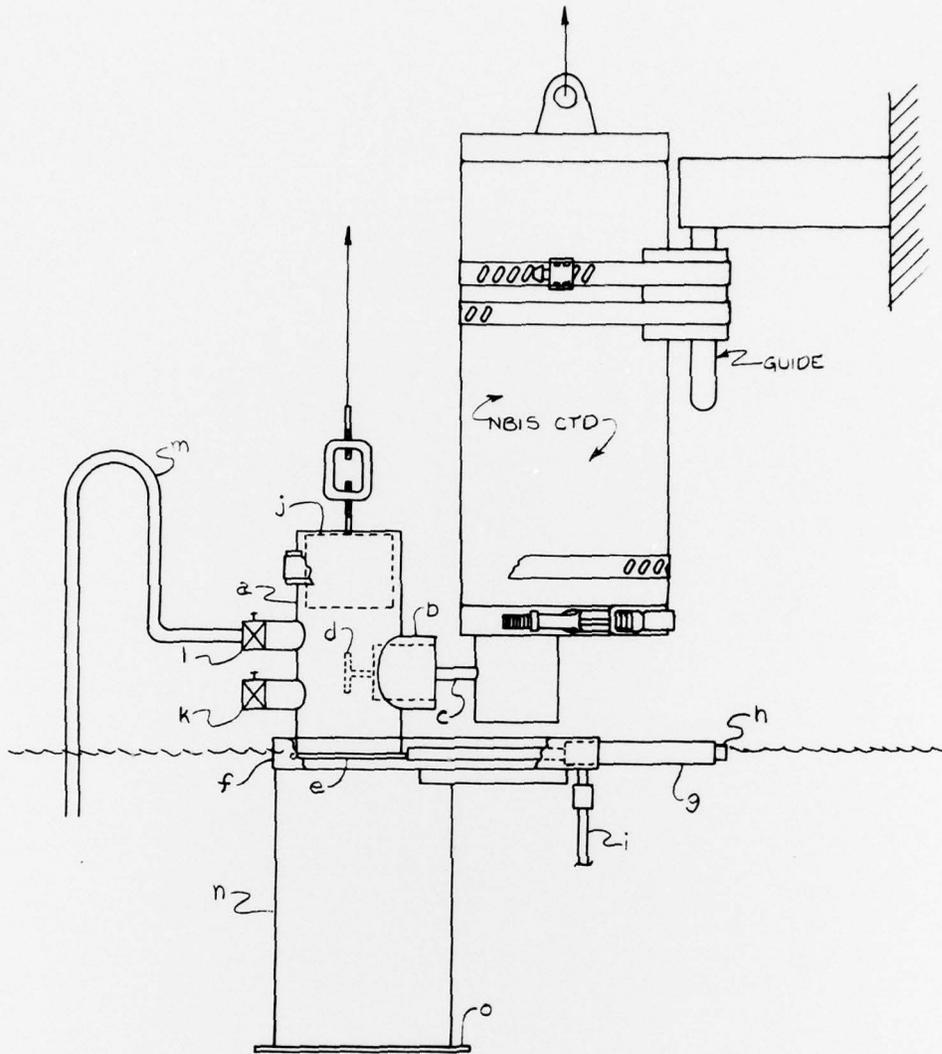
The next step was to create a sufficiently sharp water-to-water step temperature change so that the transit time of the sensor through the interface was short compared to one sensor time constant. It was decided that a reasonable design goal for the thickness of the temperature gradient would be 1 cm or the distance traveled by the temperature sensor in 10 msec when moving at 1 m/sec.

¹U.S. Naval Oceanographic Office (NAVOCEANO)

²Neil Brown Instrument Systems (NBIS)

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WATER TO WATER DROP TEST FIXTURE

FIGURE 1.

To eliminate turbulent mixing at the interface, a fixture incorporating a rigid shutter to separate the two different temperature fluids was designed. Shutter retraction speed was made constant and relatively slow (approximately 8 mm/sec) to prevent turbulent mixing in the wake of the shutter. Dye tracers, emitted at

the trailing edge of the shutter, verified a minimum of turbulent mixing (approximately 2-mm thick) caused by the shutter motion.

The fixture, designed to create a water-to-water temperature step change, is shown in Figure 1 as it would be attached to the CTD in the

drop test configuration. The fixture consists of a 3-inch-inside-diameter sensor tube (a) which has an O-ring sealed port (b), the center line of which is 5.7 cm above the lower end of the sensor tube. The CTD sensor arm (c) is inserted into the port such that the thermistor and conductivity cell (d) are positioned on the center line of the sensor tube.

The water-to-water interface is maintained at the lower end of the sensor tube by means of a glass shutter (e) which rides in a set of guides (f) affixed to the sensor tube. The shutter seals against an O-ring located on the lower end of the sensor tube. Glass was chosen as the shutter material because of its high rigidity and low thermal conductance. Shutter retraction is accomplished by means of a pneumatic cylinder (g) attached to the shutter. Prior to a drop test, the shutter is manually moved from its fully retracted position to close off the sensor tube end, and, in doing so, water is drawn into the non-pressurized end of the shutter actuation cylinder through a small orifice (h) located at the end of the shutter actuation cylinder. Constant shutter velocity during retraction is thus maintained as water is forced out of the orifice. Shutter retraction velocity is controlled by adjusting the air pressure at the shutter actuation cylinder inlet (i).

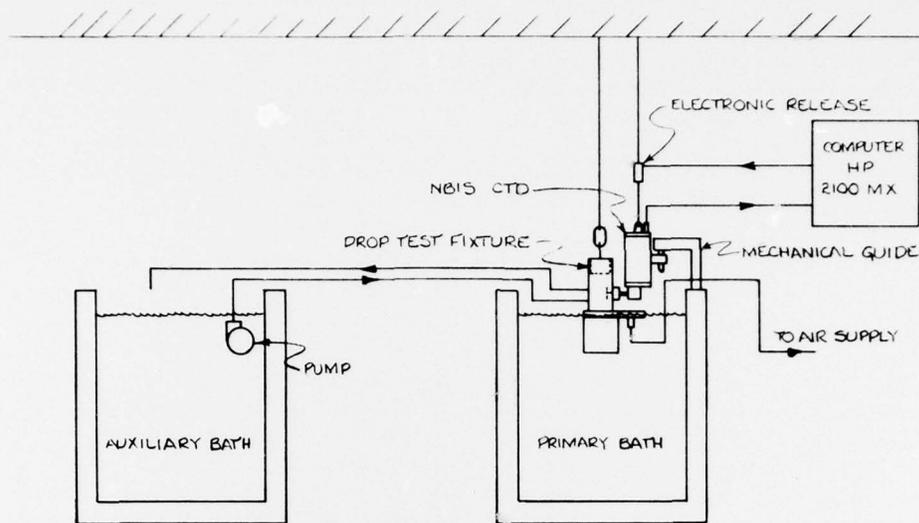
Mounted in the upper end of the sensor tube is an O-ring sealed piston (j) which is positioned to provide a 4-inch stroke before clearing the upper end of the tube. The piston is suspended from an overhead monorail by means of a cable and turnbuckle.

A constant-temperature water is created within the sensor tube by pumping water from an adjacent

temperature-controlled bath through the sensor tube via supply (k) and return (l) ports in the tube wall. Shutoff valves on the supply and return ports are provided to seal the sensor tube prior to a drop test. Quick-disconnects on the supply and return hoses at the sensor tube end permit rapid removal of the hoses prior to a drop test.

A pressure equalization line (m) is attached to the return port quick-disconnect after removal of the return line and just prior to shutter retraction; the free end protrudes below the bath water surface. With the return valve open, the piston position is adjusted to eliminate the pressure differential across the shutter, thus preventing water inflow to, or outflow from, the sensor tube at the time of shutter retraction and consequent contamination of the interface.

A baffle tube (n), approximately 8 inches in diameter and 12 inches in length, is positioned concentrically about the lower end of the sensor tube such that surface waves in the bath will not disturb the interface. In addition, the lower end of the baffle tube is sealed off to prevent similar disturbance caused by bath circulation currents. This is accomplished by covering the lower end of the baffle with a 1/8-inch-thick foam sheet (o); the sheet is held in position by its positive buoyancy. Cross cuts in the sheet permit flow through the sheet as the CTD drops into the bath. Because the piston remains fixed in space when the CTD/fixture free-falls into the bath, the water in the sensor tube also remains fixed as long as the piston effects a seal within the sensor tube. Thus, the CTD sensors will literally drop through the interface created at the shutter end of the sensor tube. Interface velocity past the sensors was measured to be 0.7 m/sec.



DROP TEST FACILITY

FIGURE 2.

Crude measurements of the temperature gradient were made by passing a thermistor through the interface. Such measurements indicate a mixed layer of approximately 1.3 cm to 1.9 cm thickness. This represents the worst case as the thermistor motion causes mixing of the interface.

The overall configuration of the drop test facility is shown in Figure 2. Primary and auxiliary baths are each 1-m diameter by 2.5-m deep and will control water temperatures to $\pm .002^\circ\text{C}/\text{day}$ over the range of -2°C to 40°C . Water is pumped from the auxiliary bath, through the sensor tube, and returned to the auxiliary bath. The auxiliary bath is normally controlled at a temperature such that the temperature in the sensor tube will be 0.5°C higher than the

temperature of the primary bath.

The CTD/fixture is suspended from an electronic release mechanism which can be activated manually or by computer control. A mechanical guide is attached to the temperature bath to provide pre-drop stability to the CTD/fixture assembly and also to prevent rotation of the assembly about a horizontal axis due to friction caused by the piston while the assembly is free-falling into the bath.

As a result of comparing air-to-water and water-to-water temperature sensor response curves, the position of the thermistor paddle (Figure 3) relative to the lowering axis of the CTD was found to significantly influence the sensor response times. Subsequent