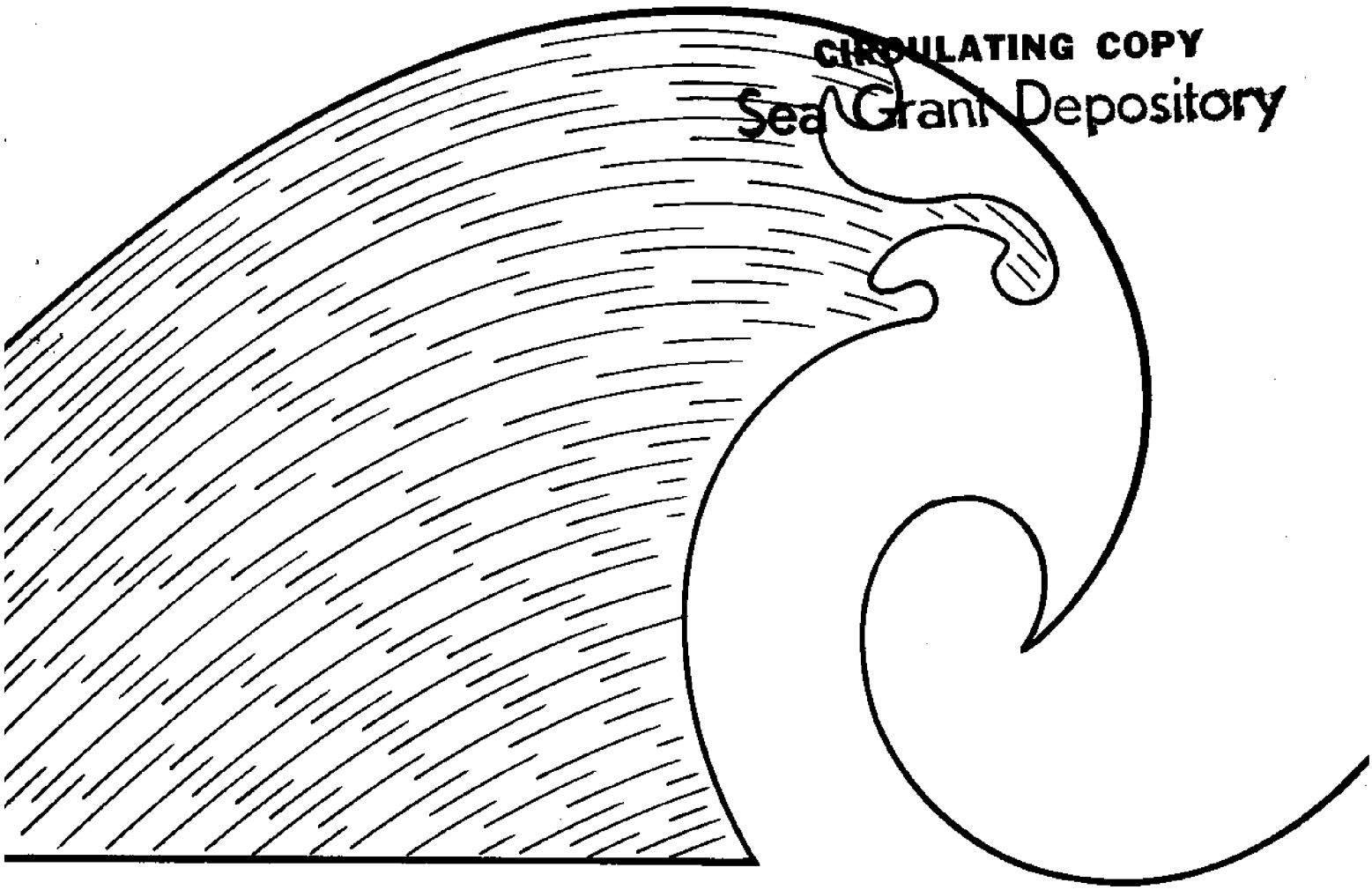

DEPARTMENT OF OCEAN ENGINEERING

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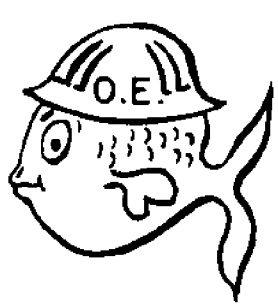
Memorandum Number 9M

ELECTROCHEMICAL SHIPBOARD WATER SAMPLING SYSTEM

BY
CHARLES CANNON

15 SEPTEMBER 1970



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by

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Under

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by

Department of Ocean Engineering

University of Rhode Island

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ELECTROCHEMICAL SHIPBOARD WATERSAMPLING SYSTEM

1.0 General

The primary objective of this project has been to build a water quality monitoring system capable of continuous, in situ gathering of data in Narragansett Bay. Such a system must necessarily be ship-mounted and be constructed for much less than the cost of commercially available systems. Our present equipment is capable of measuring dissolved oxygen, temperature, chloride ion concentration, and pH. This is (or will be) accomplished by electrodes placed in a sample stream on the suction side of a small pump, which draws water from the Bay thru a ½" teflon hose. More specifics later. The voltages generated by these electrodes in the flowing salt water electrolyte are conditioned and fed to a 12 channel recorder. Ideally, then, as the ISLANDER steams from grid point to grid point in the Bay, continuous recording of the above parameters will be produced.

2.0 Electrode Calibration

Each electrode's output (measured in millivolts) varies significantly with such things as temperature, flow rate, and secondary parameters (i.e. Cl^- concentration for dissolved O_2 electrodes) as well as with the parameters they are intended to measure. So calibration is no simple affair. First, absolute values must be found, relating the amount of the unknown in solution to the voltage output of the electrode under constant conditions. Then, with a constant amount of unknown, the other parameter (temperature flow rates), must be varied, to get cross curves of output.

To accomplish these controlled conditions, a glass-teflon flow loop was built, with a removable test section accommodating up to six electrodes. A one HP, 1750 rpm variable flow epoxy pump moves the fluid around the glass

loop at any speed required, and a small Freon-22 compressor unit is used to cool the sea water thru a ½" teflon coated copper heat exchanger tube. Temperatures as low as 2^{o} C have been reached. A flowmeter at the discharge side of the pump measures flow rate and its calibration curve as shown in Figure 1. A bubbler system was also installed by which means dissolved O_2 level can be increased. Total loop volume is 8200 ml.

2.1 Chloride Electrodes - Much time was spent on the flow loop in trying to calibrate the Cl^- electrode. First, a plot was made of electrode output (using a Orion model 94-17 Cl electrode and Orion model 401 pH meter) versus absolute chloride concentration. See Figure 2. The bottom line is for pure Na Cl solution of various chlorinities and constant temperature. The upper solid line represents the output of deep sea water successively diluted, also at a constant temperature. The dashed line is Narragansett Bay water, (Beavertail) whose original Cl $^{o}/_{oo}$ was determined by assuming that its undiluted output would be equal to that of deep sea water at the same salinity. Further output values were gotten by successive dilution.

With baselines such as in Figure 2, it remained to determine the millivolt - Cl $^{o}/_{oo}$ -- temperature surface. First, runs were made with solution of pure Na Cl at Cl $^{o}/_{oo}$ of 20 $^{o}/_{oo}$, 15 $^{o}/_{oo}$, and 10 $^{o}/_{oo}$. A sample of the kind of results obtained is given in Figure 3. The vertical lines indicate the amount of noise observed at the meter, and the small numbers beside the data points refer to the indicated flow rate. This figure is fairly typical of the data obtained for all the Na Cl runs. No apparent repeatable variation due to flow rate was observed, but day to day deviation of as much as $\pm$ .5 m were seen, and, refering back to Figure 2, this would mean an error of $\pm$ 0.3 $^{o}/_{oo}$ Cl.

A second set of runs was made using an artificial seawater solution. Typical data is plotted in Figure 4. These runs produced a much greater scatter, with some obvious flow rate effects.

2.2 Oxygen Electrodes - The O_2 electrode used is a YSI model 5450 membrane-covered polarographic probe with a temperature compensating thermistor, and the meter is a YSI model 54 portable type. The temperature readout was checked in a constant temperature bath and is accurate to approximately $\pm$ 7 C. Circuitry is available to print this temperature output at the recorder.

The O_2 probe was checked for flow rate variations during the set of runs made with artificial seawater. Readings tended to increase with increased flow, approximately 0.5 ppm increase from "apparent" flow rates increase of 5 to 20. Readings did not seem to level off at maximum flow rate (which, however, was slower than in the normal test section due to an unusually large x-section used for the O_2 probe).

Calibration is achieved by exposing the membrane to air and setting the meter for the known ppm O_2 in air at the given temperature and pressure. This method must be checked by using a Winkler analysis on a water sample, however.

2.3 pH Electrode - The pH electrode, an instrumentation labs silver-silver clhoride glass electrode, has not yet been checked for temperature or flow rate variation. It was planned to do this by making up large batches of buffer solutions (pH = 6.01, 6.86, 9.18) and running temperature of flow rate tests right in the flow loop.

3.0 Shipboard Loop

The shipboard flow loop consists of a 50' of ½" rubber covered teflon intake hose, six 1" Ø glass tee sections, a 12 volt, ½ HP jabsea pump, a ½"

glass flow meter, and section of plastic hose for overboard discharge. This system, as tested, delivers about 1.25 gpm (due to high friction losses in teflon hose) which gives a flow velocity of .5 ft/sec. thru the 1" test section. This is fine from the standpoint of electrode spacing (6") and recorder sampling rate (1 sec) but somewhat slow from a ship operations point of view. A ½" Ø plastic test section can be used which gives a flow velocity of 2.1 ft/sec., but which suffers from air leaks.

4.0 Electronics

The instrumentation of this system is not yet finalized, due to noise problems and possible electrode interference. At the heart of the system is a Leeds & Northrup 12 point recorder. Each channel relay is paired with an additional relay which selects among the probe outputs. From these probe relays, a common line runs to a high impedance pre-amplifier, then back to a common line in the recorder, where the proper signal is selected by the recorder relays and then printed out.

It was felt that the probe relays may have been causing some of the noise encountered, but many variations in wiring, grounding, etc. have as yet not been entirely successful in eliminating this problem.

Five back EMF sources were built, with range and sensitivity adjusting potentiometers and turns counting dials adjusted to read directly in C, ppm, or millivolts as the case may be. These are placed in series with the electrode outputs, in order to condition the output for the $\pm$ 5 mV scale on the recorder.

All the electronics equipment is battery powered and self contained, except the recorder amplifier, which requires 120 v, 60 cycle AC power.

5.0 Work Remaining

There is much work yet to be done before this system can produce meaningful data for the Bay Watch Program. The noise must be eliminated from the recording system, both in the lab and on board ISLANDER. All electrodes ought to be more carefully calibrated in the flow loop, using the recorder and pre-amplifier rather than trying to pick off points by band reduction of calibration data into useable tables or graphs might well be done with the aid of a computer. Electrode interference effects, where present, must be eliminated.

The electrical components have not yet been to sea, and unforeseen problems may arise there. Thought must be given to proper installation of the recorder, attendent electrical equipment, and flow system.

When the basic equipment is installed and working, an operational procedure must be worked out for collecting and reducing the data because there will be lots of it. Additional sensors might later be added, such as a relay electrode, metallic ion electrode, a conductivity cell, and temperature and pressure sensors at the sampler intake.