

Water Properties, CTD; and High Precision Digitizers

The equation of state of seawater, which relates the density to temperature, salinity, and pressure, has been determined with great care by laboratory methods. Of almost as great interest as the density (and more for water watchers) is the salinity. The direct determination of salinity is awkward. It is defined as the weight of solids in one kilogram of seawater when evaporated and all the carbonates converted to oxides, bromine and iodine converted to chlorine and all organic matter completely oxidized. (Forch, Knudsen, and Sorensen, 1902 from Sverdrup, Johnson, and Fleming.) Direct evaporation doesn't work because chlorides are lost. But a simpler indirect measure can be based on the constant composition of seawater (same ratios of ions everywhere, only the water content varies). This involves titrating the chloride (and other halogens) with silver nitrate and indicating with potassium chromate. The relation is

$$\text{Salinity} = 0.03 + 1.805 \times \text{Chlorinity.}$$

Even that is slow and awkward so an attempt was made to determine the salinity by electrical conductivity measurements. The comparison was made between conductivity of diluted standard seawater and full strength standard seawater at a common temperature. The relation was fairly linear even though seawater is more than a very dilute solution. Once the relations were worked out from measurements, it became possible to measure salinity by putting the unknown sample in a temperature bath and measuring the ratio of its conductivity to that of a known sample in the same temperature bath. Schleicher and Bradshaw did some of this work.

The next step was to determine the temperature coefficient and this permitted correcting the measurement without a temperature bath. The principal variable responsible for conductivity changes in seawater is temperature, not salinity, so the temperature had to be measured very accurately and the lab work done very carefully. All this permitted salinities to be run at sea from Nansen bottles, which improved accuracy somewhat because salt samples can sometimes spoil if kept too long. But the observations were from only a few points in the profile. Then Neil Brown added pressure measurements and made an in situ sampler, the STD. Schleicher and Bradshaw did the pressure effect on conductivity (by now a three variable problem) and Brown and Allentoft extended the conductivity ratio measurements. As an aside, it took Brown and Allentoft about a year to discover that they had an error from contamination of the diluted seawater samples by the glassware which had been cleaned with chromic acid and then exchanged ions from the glass for some time.

The STD was a new window on the ocean and immediately presented problems for interpretation by showing fine structure (called microstructure then, in the middle 1960's). The STD corrected the conductivity measurement with analog circuitry using temperature and pressure. Then computers began to go to sea and Brown realized a

better algorithm could be applied to raw conductivity, temperature, and pressure measurements by computer than by using the analog corrections. Furthermore the original data could always be reprocessed if the algorithm was improved. Finally the precision and accuracy of the measurement could be improved and the size of the sensors reduced to push the microstructure observations into the centimeter scale. It was the latter that drew Brown to WHOI in 1969 to develop the microprofiler.

Temperature can be measured to about 2 millidegrees with reversing thermometers and salinity can be relied upon to a few parts per million. To improve on this, Brown shot for resolution of salinity to 1 ppm which required resolution of temperature to 0.5 millidegree. Stability had to be very good to make calibrations to this standard meaningful. For standards work, the platinum thermometer is used and Brown chose that for the CTD. To minimize size and retain high stability with the conductivity measurement, Brown chose a ceramic, platinum and glass conductivity cell. For pressure he used a strain gauge bridge on a hollow cylinder.

Original plans to make his own thermometer, in a helium filled ceramic capillary tube, were discarded when it was discovered how hard the ceramic work was. Endless difficulties in glass to ceramic and glass to metal seals developed and overcoming these in the conductivity cell which had no voids was hard enough. A commercial platinum thermometer was chosen, Rosemont, with a time constant of 300 ms and a specified stability of 10 millidegrees in a year but in practice somewhat better.

The conductivity cell was a four electrode configuration to minimize electrode effects and had a symmetry that made it insensitive to local contamination of the electrodes. It was 3mm in diameter and 8mm long so it was hoped it would resolve centimeter scale structure. The 300 ms response time of the thermometer meant that for 1 cm resolution, descent rates of 1/2 cm/s would be required. This was a bitter result and Brown added a fast response thermistor to correct the temperature measurement at faster descent rates. Later he increased the size of the conductivity cell (the first one had a flushing length at speeds above 10 cm/s of about 3.5 cm despite its small size) and the new cell flushed in about 8 cm. With a thermistor response time of 30 ms, a 10 cm vertical resolution was possible at descent speeds of 50 cm/s or 30 meters per minute, a reasonable winch speed.

The requirement of resolving structure to 10 cm at a descent rate of 30 meters per minute meant a sample rate of 10 per second. (The original resolution target was higher and the first microprofiler had three channels running at 32 ms each in parallel.) The present CTD successively digitizes conductivity, pressure, and temperature at 32 ms each meaning it obtains a complete sample every 96 milliseconds which is fast enough.

The range in temperature is 30 degrees from freezing to the warmest surface water. For packing efficiency, straight binary integers are used and 2^{15} is 32,768. Thus a 16 bit measurement of temperature gives 0.5 millidegree resolution and 0 to 32.8 degree range. (For some work, a -2 degree lower end is needed and this has since been incorporated.) Conductivity varies over the same range because it tracks temperature. 16

bits generally permits salinities up to 38 ppt to be measured to 1 ppm precision. The depth range is 6500 meters (or a pressure range of 6500 decibars) for much of the ocean and with a digitizer capable of 16 bit resolution, this permits 10 cm depth resolution, again right on target for the resolution of the sensors. But to make a measurement to a part in 65 thousand and have it remain accurate and stable is not easy. Furthermore the conductivity measurement must be made at about 10 kHz because of electrode polarization.

In resistance bridges, the stability of ordinary precision resistors, RN60's, is 10 ppm/degree C. Vishay precision resistors are 1 ppm/degree C. The switches used to put the resistances in or out of the circuit have resistances of a few tens of ohms typically, although FET's are now available with on resistances of less than 0.2 ohms. The resistance of relays is typically 0.01 ohm but they require power to close and can only close in a about 1 millisecond. So Brown made his digitizer work from voltage sources rather than the more traditional resistances. In particular, the voltage sources were ratio transformers.

Transformers are voltage devices and are based on the voltage around a circuit depending on the change of flux through the circuit.

$$V = d\phi/dt.$$

In a transformer winding nearly all the circuit and essentially all the flux containing part is wrapped around the core of the transformer. Another winding around the same core has the same flux through it. By wrapping all the way around the core, the flux contained in the output circuit increments by integers times the flux through the core whenever a turn is added to the winding. The flux leakage in a toroid core is small, perhaps 10 ppm, determined by the geometry and the relative permeability of the core and air. Thus the EMF in the secondary is related to the voltage in the primary by the turns ratio of the secondary to the primary. Two things can wreck this, current in the secondary which causes a resistive voltage drop, and too low a frequency so that the core saturates and loses the leakage flux advantage.

In Brown's digitizer, there are three stages of ratio transformer, each having one primary winding and five sets of secondary windings in binary ratios. The precision of the divider effect of these ratios is determined by the counting of turns (only 32 for the secondary at the most, and 160 for the primary) so the precision is built in from the start. The windings are added in series with FET switches and a comparator determines if the total output of the sum of the windings is greater or less than the signal to be measured before deciding to add or delete a winding. At balance there is no current flowing in the windings.

The signal is produced by an impressed voltage across an essentially resistive sensor and this voltage is matched to a sample taken from one of the windings on the ratio transformer so the whole thing is independent of the exact voltage used to drive the ratio transformer, being only the ratio of the output voltage to that driving the sensors.

Where are the problems in this marvelous scheme? There are capacitive effects that couple voltages into the output windings and create errors. However they are out of phase with the proper magnetically coupled signals and drive voltages. Thus if the detector is carefully adjusted to be synchronously in phase with the driving voltage, it should reject all out-of-phase components. In practice these voltages can get to be so large that they saturate the comparator near balance and must be tuned out. The major components can be balanced out with trimpots during instrument checkout. The residual is variable and still troublesome.

Since the error signal is exactly in quadrature with the signal, it too can be detected but by a detector running synchronously in quadrature to the drive signal. The output of this detector can then be used to control a quadrature voltage to be added back to the signal in opposite sense to drive the effective resultant quadrature signal to zero. This works very well.

Improvements to further reduce the leakage flux in the ratio transformers and the quadrature error have permitted the technique to be used to advance the state of the art in laboratory standards and NBIS (Brown went commercial in 1974) is now making voltage standards used by NBS (no relation).

The CTD is now a standard oceanographic instrument and has replaced the Nansen cast as a hydrographic tool. The data is sent up conducting cable as a frequency-shift-keyed signal. It is recorded as an acoustic signal on tape and decoded and repacked in a deck unit and output to a computer for digital recording and preliminary processing. The algorithm is clumsy in that it sticks close to the actual relations derived from the laboratory data sets. These were derived by going from salinity to conductivity not the other way around. More seriously, dynamically one wants to know density and this is now computed as a second step when it could be done directly. Some of these things are being taken care of. This is characteristic of the second decade in the life of a successful instrument. But maybe a direct measurement of density is appropriate or of some other essential variable. Successful instruments tend to stop development at the same time that they stimulate an observational field.

Optical fluorescence is a valuable tool in the lab for phytoplankton identification. The flow cytometer measures the optical properties of single cells as they pass through a cuvette. In the lab, the stream of cells is concentrated into a fine column by flow focussing. In this technique, the cell containing flow is surrounded with a cell-free sheath of filtered water. Then both are accelerated by a constriction in the channel diameter and the cells are constrained to a column only about 10 μ in diameter. This region is illuminated by a laser (formerly another bright light) and the scattering at 90° is measured, the fluorescence at several wavelengths measured, and the responses categorized to define a specific phytoplankton. Big green fluorescing cells may be one type while small red fluorescing cells are another. This tool has opened up the study of nanoplankton and picoplankton at sea and now flow cytometers are taken to sea as well as used ashore to process samples taken at sea. A development is underway to put the

flow cytometer in the sea for tows and profiles.

The biggest problem foreseen for the in situ flow cytometer has been the fluid focussing requiring filtered water and precise pumping. For the in situ instrument, a coincidence requirement has been implemented that selects only cells on the flow axis and in the center for measurement. There is no sheath flow. Rather, two infrared beams focussed in the center of the flow, one slightly above the other, are used to select particles that by chance are in the center of the channel. Then the scattered light from a frequency doubled laser (blue/green) is measured and the fluorescence at two wavelengths. These are recorded and the other signals are ignored.