

## Nansen-Bottle Stations at the Woods Hole Oceanographic Institution

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### Abstract

Nansen-bottle stations were occupied by ships and personnel of the Woods Hole Oceanographic Institution from 1931 to about 1981. Most of these data are in archives, but using them intelligently to depict the state of the ocean and to assess time changes in it requires knowing how the observations were made, what accuracies can be assigned to them, and generally how to approach them. This report describes the evolving methods on Woods Hole stations for measuring temperature, depth of observation, salinity, and dissolved-oxygen concentration, and for determining station position. Accuracies generally improved over time, although estimates from the early years are sparse, and even later there is indefiniteness. Analytical error is to be distinguished from sloppy sample collection and other blunders. The routine for carrying out Nansen-bottle stations, from the late 1950s through the 1970s, is reviewed.

### 1. INTRODUCTION

Hydrographic stations have been a prominent part of the research enterprise at the Woods Hole Oceanographic Institution throughout its history. They were done with Nansen bottles and reversing thermometers from the first cruise of the R.V. *Atlantis* in 1931 to the late 1970s. The last transoceanic Nansen-bottle section, in the tradition of the *Meteor* and IGY sections, was occupied in 1976, in the South Indian Ocean. After that Nansen bottles were still used to supplement CTD work until 1981, when they were entirely supplanted by the now superior CTDs. WHOI ships can be documented as having occupied about 14,000 Nansen-bottle stations; a few hundred more have probably escaped the records. And of course WHOI observers made stations from other ships as well.

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I was introduced to Nansen-bottle stations in 1955, and stayed with them until their demise. Two colleagues have suggested (several times) that I should write a detailed account of how they were done at WHOI, partly for the sake of recorded history, partly for the sake of newcomers trying to exploit the vast data archives who have no idea how the old observations were made or what significance to give to them. The undertaking seems especially worthwhile in light of today's concerns about climate variation, and scientists' endeavors to find out whether, where, and by how much the ocean has changed over the years.

This report is my attempt to do that. I have worked from my own memory and from references and documentation I knew and learned about, and could track down. Several times I wished I could ask someone about something, and I was reminded again that there is hardly anyone left whom I can consult about those years. I have made a few mentions of practices at the Scripps Institution of Oceanography, to the extent that I know about them, for comparison. I should like to have said something about how stations were made at other oceanographic laboratories as well, but I know too little to do it. Experienced veterans from some of those institutions could provide a useful service by doing so — before the memory is lost.

The next five sections discuss the determinations of station position, temperature, observation depth, salinity, and dissolved-oxygen concentration. The last section comprises some remarks about the making of the stations at Woods Hole.

In Sections 2-6 I have emphasized estimates of the accuracy of the measurements, because I think that these are probably of the most use to people trying to use these data now. However, that discussion is only about instrumental and analytical uncertainty. There is other uncertainty in archived data from most laboratories due not to “experimental error” in the strict sense, but (discussed at the end of Section 7) to what may better be called “blunders”: mis-tripped Nansen bottles, contaminated water samples, mis-drawn samples. Good watercatchers conscientiously scrutinized their data and threw out the evident junk so as not to mislead users. But sometimes a formalist pedant insisted on reporting all his “observations”, no matter how blatant a blunder; sometimes a flimsy observer dodged his moral responsibility to criticize his results; and sometimes an investigator lacked the fortitude to acknowledge flawed work. It would be fatuous to propose error bars for blunders; the best one can do is to recognize that some have slipped into the archives, and advise “Reader beware!”.

## 2. NAVIGATION

Station data are not of much use unless one knows where the observations were made. Before the Second World War positions far from land were obtained entirely by celestial navigation and dead-reckoning. Retired captain David Casiles estimated to me that in good observing conditions the accuracy of celestial fixes was “somewhat better” than one nautical mile; Backus and Worthington (1965) considered it to be 0.5 miles. The accuracy of positions dead-reckoned between them was certainly less. Only a few celestial fixes could be taken per day, and none at all under cloudy skies – as in the Gulf Stream region.

Sometime in the late 1940s Martin Pollak asked Fritz Fuglister for one of his recent temperature sections across the Gulf Stream. He complained that Fritz’s position plot (Loran based) was an irregular line, and didn’t he have a section along a nice straight line such as Columbus Iselin used to make? Fritz laughed, and told him that Iselin never knew where he was in the Gulf Stream, that he would get a fix under a clear sky somewhere on one side of the Stream, and another when the sky cleared on the other side, and dead-reckon his station positions between them.

After the war shore-based radio navigation systems (Loran-A off eastern North America, Decca off western Europe) provided positions any time of day or night. Loran-A was accurate to about 1 km within 1000 km of eastern North America; later developments (e.g., Loran-C) were good to 0.1 km. But the spatial coverage of these systems was severely restricted.

In the early 1960s the U.S. Navy placed satellites in five polar orbits, primarily to provide positional information to ballistic-missile submarines (the TRANSIT system). These gave fixes accurate to 0.2 km, globally, and independent of weather. The method involved measuring gradual changes in Doppler-shifted frequencies as a satellite passed by, and so required several minutes to get a fix; if the satellite passed very low on the horizon, too little time might be available. Because the orbits were polar, the number of possible fixes per day depended on latitude – perhaps half a dozen in low and middle latitudes, perhaps a dozen or more in high latitudes. But since hydrographic stations usually took several hours to make, it was usually possible to get one good satellite fix during the course of the work.

Oceanographers who know only the Global Positioning System, which since the late 1980s has provided fixes anywhere, anytime, to 10 m or so, have little idea how keenly their forebears sought and treasured good navigational information.

### 3. TEMPERATURE

Temperatures on hydrographic casts were measured with protected reversing thermometers attached to the Nansen bottles (e.g., Sverdrup et al., 1942, pp 349-351). Those at WHOI in the 1930s were mostly manufactured by Richter and Wiese (Berlin), and were of the ranges: -3 to 8°C, 3 to 13°C, -2 to 25°C, and 10 to 30°C (Iselin, 1936). There seem to have been a few as well by the original producer, Negretti and Zambra (London). Limited comparisons among readings of thermometers showed that corrected (see below) temperatures “seldom have an error greater than .03°, while the average error is undoubtedly considerably less” (Iselin, 1936).

From the 1950s (at the latest) the thermometers used were of the ranges: -2 to 30°C, -2 to 15°C, -2 to 8°C, and (from 1961) -2 to 6°C. Richter and Wiese was still the preferred manufacturer at WHOI, but thermometers were also bought from Kahl Scientific Instruments (El Cajon, California), GM Manufacturing, Kessler, two Japanese firms (Yoshino and Watanabe), Gohla (Kiel), and perhaps other companies. At Scripps Kahl was the preferred supplier, partly because of proximity.

These thermometers were read to one-tenth of the smallest graduation interval, and so, for the ranges listed immediately above, to  $\pm 0.01^\circ\text{C}$ ,  $\pm 0.01^\circ\text{C}$ ,  $\pm 0.005^\circ\text{C}$ , and  $\pm 0.002^\circ\text{C}$ , respectively. In my experience W. Gerrish Metcalf was the supreme watercatcher at WHOI; his opinion (Metcalf et al., 1973) was that corrected temperatures from thermometers of the first two ranges were accurate to  $\pm 0.02^\circ\text{C}$ , and of the last two, to  $\pm 0.01^\circ\text{C}$ . Some WHOI observers thought that the Richter and Wiese thermometers of range -2 to 6°C were better than that. Barrett (1967) made many repeated reversals of various pairings of some of these, and found mean differences in readings between pair members ranging from 0.001 to 0.009°C; his estimated standard errors of a single measurement from one thermometer ranged from  $\pm 0.002^\circ\text{C}$  to  $\pm 0.006^\circ\text{C}$ . For Scripps measurements in the 1950s, Wooster and Taft (1958) estimated the error of a single reading as about  $\pm 0.02^\circ\text{C}$ . Walter Bryan, who did the thermometer calibrations at Scripps in the 1960s and 1970s, told me that he had compared results from some Kahl thermometers of the range -2 to 6°C, and thought the best of them to be accurate to  $\pm 0.004^\circ\text{C}$ .

The length of the separated mercury column in the reversed thermometer changed when subjected to the difference between *in situ* temperature at reversal and laboratory temperature at time of reading, so a correction  $\Delta T$  had to be subtracted from the read temperature  $T'$  to obtain

the true *in situ* temperature  $T_w$ . Each reversing ("main") thermometer was therefore accompanied by a smaller, auxiliary thermometer inside its glass shell to show the laboratory temperature  $t$  at reading time. Observers at WHOI used an approximation to the Schumacher formula (1923; printed incorrectly by Sverdrup et al., 1942, p. 350) for  $\Delta T$ :

$$\Delta T = \frac{(T' - t)(T' + V_0)}{K - 100} + I$$

where  $V_0$  is the volume of the small bulb plus the capillary up to the  $0^\circ\text{C}$  graduation (specified in  $^\circ\text{C}$ );  $K^{-1}$  is the cubical expansion coefficient for mercury minus that of the thermometer glass, the numerical value of  $K$  typically being 6100; and  $I$  is an index correction for calibration adjustments. The error in  $\Delta T$  from making this approximation was only a few tenths of one per cent; values of  $\Delta T$  were typically a few tenths of a degree.

During the 1930s and 1940s the  $\Delta T$ -values were calculated by slide rule. By the time of the IGY (International Geophysical Year, 1957-58) graphs for each thermometer were being constructed on which isopleths of  $\Delta T$  were plotted against coordinates ( $T'$ ,  $t$ ). Determining  $\Delta T$ 's became rapid, easy, and accurate. An example of such a graph is included as Appendix A. When computers started going to sea in the early 1960s, programs were written for the  $\Delta T$ -calculations, but since these required entering  $T'$ ,  $t$ , and thermometer number for each calculation, the graphical method was often quicker.

From the early 1950s Geoffrey G. Whitney, Jr., calibrated and maintained the WHOI thermometers (Whitney, 1976, 1979). He acquired a national reputation for the thoroughness, accuracy, and rapidity of his work, and other institutions sent him their thermometers for calibration as well. For each thermometer purchased he checked the manufacturer's value of  $V_0$  (often in error), and the accuracy of the temperature graduations on both the main and auxiliary thermometers (corrections for which went into the value of  $I$ ). For the unprotected thermometers (see Section 4) he also measured the pressure factor  $Q$  in his pressure tank. He then issued a "Statement of Examination" for each thermometer; an example is attached as Appendix B. He re-measured the ice points of all the thermometers annually; changes in these also went into the index correction  $I$ . (Over time Whitney came to the opinion that ice points did not drift gradually but changed abruptly on release of accumulated internal stress.) He maintained a running card file of the history of each thermometer, copies of which went to sea with the thermometers;

examples of two cards from this file, for a protected and an unprotected thermometer, are attached as Appendix C.

Rather late in the Nansen-bottle years it was discovered that some of the protected thermometers were not fully “protected” against the pressure after all – a possibility that had been raised by Folsom et al. (1959). So Whitney began measuring pressure sensitivities as well on the thermometers of range -2 to 6°C, the ones expected to be used at great depths. The effect was absent from many of them, was often small when found, but could be as large as 0.03°C per kilometer (Whitney, 1976). Since it was a nuisance in making the temperature corrections, observers tended to avoid using such thermometers when so identified. Some manufacturers (e.g., Kahl, Gohla) redesigned their thermometers to eliminate the effect.

#### 4. DEPTH OF OBSERVATION

Depths of observations on WHOI Nansen-bottle stations were always determined with paired protected and unprotected (glass shell open at one end) reversing thermometers – a practice strongly urged by Iselin (1936) from early on. Although protected reversing thermometers were first produced in 1874, the use of unprotected thermometers for determining depth of bottle reversal was not developed until the first decade of the twentieth century (Perlewitz, 1908). But even as late as 1936 Iselin could state that it “has only recently become general practice”. The International Ice Patrol, for example, did not start using unprotected thermometers until the early 1930s (Smith et al., 1937).

Before then the depths of water samples were estimated from amount of line or wire payed out, with some adjustment for the angle of the wire from the vertical at the ship. These estimates could be very good in gentle conditions, but when strong winds and surface currents drove the ship away from the wire, and especially when the ship maneuvered on the wire to keep it within reach or to achieve some depth for the cast, they could be wildly off. Clearly, when trying to use old data to detect long-term changes in the ocean, it is crucial to know how the observation depths were figured, so as to be able to judge the credibility of (say) an old temperature-depth curve.

The unprotected thermometers were commonly of the ranges -2 to 30°C and -2 to 60°C but also -2 to 45°C and 35 to 60°C. Their readings, like those from protected thermometers, had to be corrected for the difference between laboratory temperature and water temperature to obtain

the value at reversal  $T_u$ . WHOI watercatchers used one of Schumacher's (1923) approximate formulas, printed (correctly) by Sverdrup et al. (1942, p. 351). Keyte (1965) reviewed the derivations of the exact formulas for both types of  $\Delta T$  and of the various approximations made to them; the precision of thermometer readings did not warrant adopting any of them in preference to the simpler, less exact versions used at WHOI.

Pressure factors  $Q$  were stated for the thermometers as the increase in height of the mercury column (reported in  $^{\circ}\text{C}$ ) for an increase in applied pressure of  $1 \text{ kg cm}^{-2}$ . The manufacturer's value was only nominal, so Whitney (1976) measured it for each thermometer at two pressures,  $100 \text{ kg cm}^{-2}$ , and  $200, 300, 400$ , or even  $500 \text{ kg cm}^{-2}$ . The pressure unit,  $1 \text{ kg cm}^{-2}$ , is (happily) obsolete; it equals  $980.665 \times 10^3 \text{ dynes cm}^{-2}$ , as referred to sea-level gravity at Lat.  $45^{\circ}$ . Numerical values of  $Q$  are roughly  $0.1$ . With the hydrostatic approximation and assumption of the same constant gravity value,  $980.665 \text{ cm s}^{-2}$ , the depth in meters  $D$  at thermometer reversal is  $D = 10(T_u - T_w)/(Q\rho_m)$  where  $\rho_m$  (in  $\text{g cm}^{-3}$ ) is the mean density of the water column above the Nansen bottle, and the factor  $10$  follows from the mixture of units. Wüst (1933) found that for these calculations the horizontal variations in  $\rho_m$  in the Atlantic could be disregarded, and that the horizontally averaged values of  $\rho_m$  as a function of depth were sufficient. From early on WHOI watercatchers used his (1933)  $\rho_m$  table for the Atlantic to make their depth calculations.

Since the depth formula includes depth implicitly through  $\rho_m$  (and slightly through  $Q$ ), it was implemented by first calculating, for each thermometer, the values of  $(T_u - T_w)$  corresponding to a fairly dense series of depths  $D$  spanning the full ocean. Anomalies  $\Delta D \equiv D - 100(T_u - T_w)$  were plotted (and connected) on graphs according to these values of  $(T_u - T_w)$ , for each thermometer. It was then a simple matter to find on the graph the proper value of  $\Delta D$  corresponding to an observed value of  $(T_u - T_w)$  and add that to  $100(T_u - T_w)$  to obtain the observation depth  $D$ .

Wüst (1933) estimated that the mean error of thermometric depth calculations was  $\pm 5 \text{ m}$  at depths shallower than  $1000 \text{ m}$ , and  $\pm 0.5\%$  at greater depths. This assessment was cited by oceanographers as gospel for years after, without, so far as I know, being re-examined. Eventually Whitney (1957) investigated thoroughly the possible instrumental and reading errors entering the calculation, and he concluded that below  $1000 \text{ m}$  the accuracy of the determinations

was indeed usually  $\pm 0.5\%$ , and was often  $\pm 0.2\%$ . The spread was broad enough to cover meridional variations in gravity as well as the horizontal variations in  $\rho_m$  in the Atlantic (neither was included in Whitney's error assessment). When WHOI oceanographers entered the Indian and Pacific Oceans in the 1960s, they took their Atlantic-based  $\Delta D$  graphs with them, but their resulting errors in depth calculations did not breach Wüst's and Whitney's limits: various mean densities given by Reid (1961), for example, suggest that  $\rho_m$  ought to be only 0.05% (roughly) lower in the Pacific than in the Atlantic. Even the deep waters of the Mediterranean and Red Seas are only about 0.2% denser than that at similar levels in the Atlantic (while much saltier, they are both also much warmer).

To improve the raw thermometric depths, "depth factors" were calculated as thermometric depth divided by wire out. These were plotted against wire out and a smooth curve drawn (either by eye or with French curves) through the field of points to produce "corrected depth factors"; from these, "corrected depths" were calculated. It was the custom at WHOI to mark with asterisks those corrected depths that did not differ from the raw thermometric depths by more than the Wüst-Whitney limits. Depths of Nansen bottles not equipped with unprotected thermometers were determined by reading off a corrected depth factor for the amount of wire out, and multiplying that by the wire out. Depth-factor curves could be wildly contorted for stations made with variable maneuvering on the wire (in the Gulf Stream, say) so the uncertainty in these interpolated depths was greater than for those determined in more congenial conditions.

Instead of calculating depth factors, Scripps oceanographers plotted the difference between wire out and raw thermometric depth ("L-Z") against wire out, and drew smooth curves through these data sets to even out the depth estimates.

## 5. SALINITY

Salinities were determined from water samples drawn from the Nansen bottles. Until the mid-1950s the method of analysis was titration for chlorinity (Cl, expressed as parts per thousand by weight) and calculation of salinity (S) by the Knudsen formula,  $S=1.805 Cl + 0.03$ . [Wallace (1974) gave a thorough account of the basis and historical development of the chlorinity-salinity method and of the formula]. Chlorinities may have been measured to three decimal places, but they were not thought accurate to better than two, and so were reported to only two decimal



places. In principle, then, the corresponding salinities were accurate at best to  $\pm 0.02\%$  and titration salinities were reported to only two decimal places.

Samples were usually sealed at sea and returned to a temperature-controlled laboratory ashore in Woods Hole for analysis. The risk of evaporation during transit was always of concern, and various procedures (in addition to prompt analysis) were tried to minimize it. For example, at one time or another (for reasons not known to me) the tops of the freshly filled and capped sample bottles either were or were not dipped in melted paraffin as a sealant. Each sample was customarily (not quite always) titrated three times (Iselin, 1936) and the results averaged. Undoubtedly the averaging improved the accuracy of these values: in a temperature/salinity plot for the deep Sargasso Sea (Iselin, 1936, Fig. 25) the *total spread* in salinity values (not standard deviation) at a given temperature is only  $\pm 0.02\%$ .

Titration in the shore laboratory were better controlled and more comfortably done than those at sea, which were required on long cruises far from home such as the Meteor Expedition in the Atlantic (1925-27) and the Discovery Investigations in the Southern Ocean (1930s). Work at sea was not necessarily inferior, however: in some regional potential-temperature/salinity plots from these two sets of cruises, the standard deviation of the salinity was only  $\pm 0.01\%$  (Cox, 1963). Those expeditions were probably rare, though, because L. Valentine Worthington's (1981) experience was that few of the sea-going titrators "could justifiably claim an accuracy of better than  $\pm 0.03\%$ ." In their careful analysis of shipboard Scripps titrations in the 1950s, Wooster and Taft (1958) calculated an upper bound on confidence limits of  $\pm 0.036\%$ .

Attempts to determine salinity by measuring the electrical conductivity of water samples began at the end of the nineteenth century (Smed, 2002), but the first practical sea-going salinometer was designed by Wenner in the 1920s (Wenner et al., 1930) for use by the International Ice Patrol. While its precision of measurement increased to  $\pm 0.005\%$ , Ice Patrol salinities were still reported to just two decimal places, apparently because the Wenner bridge was calibrated with titrated salinities.

The instrument was awkward to use and not always reliable, so only after Schleicher and Bradshaw (1956) substantially modernized and improved it did salinometers come into use at WHOI. The first cruise with one was by Val Worthington in 1954, and their use was well established by the time of the IGY cruises (1957-58). The salinometer made it possible to process samples quickly at sea, within a few hours of collection, thus reducing the risk of

evaporation, and letting the investigators see how they were doing. More important was the measurement improvement. Schleicher and Bradshaw (1956) estimated a formal accuracy (maximum deviation from the true value) of  $\pm 0.01\text{‰}$ , and a formal precision (maximum deviation from the average value) of  $\pm 0.008\text{‰}$ . However, even their reported early field tests indicated narrower limits, and the potential-temperature/salinity plot for the IGY stations in the western North Atlantic had a one-standard-deviation breadth at great depth of only  $\pm 0.003\text{‰}$  (Worthington and Metcalf, 1961).

Around 1959 the old titration laboratory at WHOI was shut down. It was replaced by a Schleicher-Bradshaw laboratory salinometer, whose operator processed any samples not analyzed at sea on WHOI cruises, as well as samples sent to WHOI from other institutions. WHOI samples, for salinometer analysis both at sea and ashore, were drawn into 120-ml flint glass bottles having screw caps fitted with poly-seal cones to preserve sample integrity. (Unfortunately, at least one laboratory operator was sometimes slack, and neglected processing so long that samples were noticeably degraded anyway.)

Commercial salinometers were developed in the 1960s, and WHOI purchased its first Guildline Autosal unit in 1971. These salinometers are listed by the manufacturer as accurate to  $\pm 0.003\text{‰}$  relative to the standard seawater employed to calibrate a course of measurements. Since they are more stable, easier to use, and less demanding of expertise than the Schleicher-Bradshaw models, the Autosals replaced them at WHOI. Knapp and Stalcup (1987) found that with strict temperature control imposed on their operation, accuracies of  $\pm 0.001\text{‰}$  (relative to the standard) could be achieved. [Inaccuracy in standard seawater salinities was another potential source of error. For batches prepared in the 1960s and 1970s the range in difference between measured values and those inferred from the batch labels was  $\pm 0.005\text{‰}$ ; since then, it has been close to  $\pm 0.001\text{‰}$  (Kawano et al., 2006).]

## 6. DISSOLVED-OXYGEN CONCENTRATION

The concentration of dissolved oxygen in water samples was (and is) determined by the Winkler method, in which reagents are added to an unaerated water sample to generate an amount of dissolved iodine equivalent to the original amount of oxygen. The treated sample is then titrated with sodium thiosulphate for the amount of iodine, and a standard sample of precisely known normality is also titrated to determine exactly the normality of the thiosulphate

solution. The traditional units of oxygen concentration are ml/l, meaning milliliters of oxygen gas at 0°C and 1 atmosphere pressure (an "amount of substance" unit) per liter of seawater.

I know very little about oxygen work before the late 1950s; accuracy estimates are hard to find. Winkler (1888) himself seemed to be able to repeat results to within a few hundredths of a unit in his laboratory. Thompson and Robinson (1939) thought the volume of the titer could be determined to  $\pm 0.02$  ml, which translates to an error in oxygen concentration of about  $\pm 0.02$  ml/l. This may have been the basis for the assertion by Jacobsen et al. (1950) that the method was accurate to 0.02 ml/l for nearly saturated samples. That figure, however, is not to be confused with the accuracy of shipboard analyses of Nansen-bottle samples (see below).

WHOI oxygens during the IGY were not first-rate: quite scattered, and low by about 5% overall. For this reason Fuglister (1960), regretfully, did not include oxygen concentration in his IGY atlas. There were at least two causes for this disappointment. During the IGY (and apparently as far back as the 1930s) WHOI analysts used a potassium dichromate solution for their standard (Worthington, 1976, p. 54), even though Thompson and Robinson (1939) had cautioned that it reacted slowly with the iodide reagent, and could generate erroneously low determinations. [Later, Carpenter (1965b) identified unavoidable contamination in the reaction with dichromate as well.] It was replaced in May 1959 with potassium bi-iodate; that produced credibly higher results (Worthington, 1976, p. 54), it had been recommended by Thompson and Robinson (1939), and it has been used at Woods Hole ever since. [Carritt and Carpenter (1966) subsequently preferred potassium iodate for the standard; that was adopted by Scripps and the GEOSECS program.]

Another problem was discovered in the brass Nansen-bottles themselves, some of them new in the IGY. On Metcalf's Crawford Cruise 22, at Station 420, 3 October 1958, the hydrographic winch broke down with a cast in the water. It took 12 hours of manual winch operation to retrieve all the Nansen bottles. The oxygen concentrations obtained from them were several tenths of a ml/l lower than those from neighboring stations (Worthington, 1982), and the oxygen loss was attributed to oxidation on the brass walls of the bottles, especially the newer ones. Since oxidation could have been degrading samples trapped in Nansen bottles even for normal amounts of time (1-2 hours), the insides of all WHOI Nansen bottles were immediately thereafter coated with a Teflon lining to prevent it. [Worthington (1982) had additional thoughts on ways to corrupt oxygen samples.]

Oxygen analysis benefited further after the IGY through entrusting Nathaniel Corwin to provide carefully prepared, filtered reagents for WHOI cruises. Corwin's reagents were so clean that analysts only occasionally needed to run blanks, because they were always nearly zero.

WHOI titrations were (and are) done by the "aliquot method". The oxygen sample is drawn, bubble-free, into a 150-ml bottle, the reagents are added, and after the reactions are finished a 50.0 ml aliquot sub-sample is taken from the iodine solution and titrated (Knapp and Stalcup, 1987; Knapp et al., 1989). Scripps analysts thought some iodine volatilized during the transfer of the aliquot sample, so they used (and use) the "whole-bottle method" instead (Carpenter, 1965b). The sample is drawn from the Nansen (or Niskin) bottle into a 125-ml Erlenmeyer flask of precisely measured volume, the reagents are added, the reactions run their course, and the sample is titrated directly in the flask. Knapp et al. (1991) found in an extended experiment that iodine is indeed lost in the aliquot transfer, but by only 0.01-0.03 ml/l in oxygen equivalent; and since the normality of the thiosulphate solution is determined by titrating an aliquot sample of standard solution in exactly the same way, a corresponding loss occurs, so the two errors cancel. They therefore concluded that the whole-bottle method "is not to be preferred" to the aliquot method. Field comparisons of WHOI and Scripps titrations (Saunders, 1986) support their conclusion.

Estimates of the quality of oxygen determinations were more numerous and varied in the 1960s and 1970s than earlier. While Carpenter (1965a) demonstrated a potential accuracy for the Winkler method of 0.1%, Carritt and Carpenter (1966) seemed close to despair regarding actual practice: "It seems likely that the  $\pm 0.05$  ml  $O_2$ /l frequently quoted as the accuracy to be associated with oxygen values obtained with the Winkler procedure is actually the precision or repeatability that can be achieved by a good analyst during the replication of certain standardization procedures. We have found no way of estimating the absolute accuracy of data now in the literature." Strickland and Parsons (1968) determined the precision of a single measurement in ideal laboratory conditions to be  $\pm 0.03$  ml/l; and they thought it likely to be  $\pm 0.06$  ml/l for shipboard analyses. Consistent with that assessment, Worthington (1982) made a potential-temperature/oxygen plot of data he had collected in 1976 in a small region of apparently homogeneous Antarctic Bottom Water, and he found a standard deviation for his oxygen values of  $\pm 0.04$  ml/l. Perhaps this figure is a good measure of the accuracy of the

technique when applied at sea by an expert in those years (though even that is relative to a standardization procedure).

In the early 1970s Marvel Stalcup pioneered the use of an electrode to determine titration end-points. These "amperometric" determinations were less demanding of the analyst than the traditional visual ones, and they eliminated any subjectivity. Other analysts were slow to take up the new technique, but eventually it caught on.

Later, when Nansen bottles had become obsolete but water samples were collected as much as ever from Niskin bottles on CTD stations, Stalcup and his colleagues made two other major improvements to the analytical process (Knapp and Stalcup, 1987; Knapp et al., 1989, 1990). They automated and computerized the entire procedure, so as to speed it up and require less attention and expertise from the analyst. Second, they moved their analytical work into portable, temperature-controlled laboratories. Quite apart from the convenience of these vans, the temperature control reduced the scatter in the oxygen values somewhat, apparently by eliminating changes induced by temperature variation in the volume of the automatic pipette used to draw the aliquot sample. (Construction of these laboratories had been motivated in the first place by a demonstrated need to have temperature control during salinometer runs.) With these improved conditions they estimated the accuracy of the analyses (Knapp et al., 1989, 1990) to be  $\pm 0.02$  ml/l, with precision of 0.005 ml/l. So, it seems unlikely that the general accuracy of the work in preceding decades could have been quite that good.

Some concern was raised that in the Winkler procedure applied to samples of very low concentration contamination of the samples and reagents by contact with the atmosphere gives results that are erroneously high by roughly 0.1 ml/l (Broenkow and Cline, 1969). Yet, for example, on some stations made in the nearly anoxic layer of the northern Arabian Sea in August 1987, during Charles Darwin Cruise 25, the WHOI (Winkler) analyst made many determinations of less than 0.1 ml/l, three of 0.01 ml/l, and even two of 0.00 ml/l. One must suppose that very low concentrations do not necessarily threaten the Winkler method.

Although titrations are inherently "per volume" measurements, many physical oceanographers have been persuaded by GEOSECS chemists to report oxygen concentrations in units of micromoles of oxygen per kilogram of seawater (neither molarity nor molality!). Conversion from ml/l requires the molar volume of oxygen (22.39 l), and the density of the seawater appropriate to the measured volume of seawater. With the aliquot method this is

straightforward, because the aliquot sub-sample is drawn at the laboratory temperature. For a temperature of 20°C, and a sample salinity of 35‰, say, the sub-sample density is 1.0248 g cm<sup>-3</sup>, so  $\mu\text{mol/kg}$  equals 43.58 times ml/l. (Varying the sample salinity by  $\pm 1\%$ , or the laboratory temperature by  $\pm 3^\circ\text{C}$ , affects the coefficient by slightly less than 0.1%). For the whole-bottle method, however, the measured volume is that of the Erlenmeyer flask, and is therefore that of the water sample at the time and temperature at which it was drawn. Since the sampler walls conduct heat, the draw-temperature is nearly always greater than the *in situ* temperature, by as a little as 1°C or so for 10-l Niskin bottles, but, as observed by Worthington (1982), up to 16°C for brass Nansen bottles. Without a measurement of draw-temperature, the appropriate sample density, and therefore the conversion factor, may be uncertain by 0.3%. But titrations are only now approaching this level of accuracy (the one-tenth decimal place in WOCE-reported oxygens is spurious), so a constant conversion factor (e.g. 43.58), especially for the old Nansen-bottle data, is still useable.

## 7. STATION PRACTICE

Cruises by WHOI ships have always been identified in a numerical sequence for each ship (so Atlantis II 93 means the 93rd cruise of the R.V. *Atlantis II*). Segments between two consecutive ports of an extended voyage could be specified by legs (as AII 93 Leg 10). Station numbers were also designated by a numerical sequence running through the entire history of a ship (so Crawford Sta. 819 means the 819th Nansen-bottle station occupied by the R.V. *Crawford* during its time at WHOI). A slight exception was the numbering of *Atlantis* stations, which began with 1001 (so Atlantis Sta. 5922 means the 4922nd station by the R.V. *Atlantis*). The sailing orders to the ships' captains always included the number of the first station to be occupied during a cruise.

The working data for a station were entered on a single log sheet, which went through only minor typographical modification from Atlantis Cruise 6 in February 1932. Appendix D is a copy of one, divided into two pages. The column headings are self-explanatory from the accounts of the previous sections, except perhaps for: "frame no.", the number on the Nansen bottle; "wire out", the amount of wire out at that Nansen bottle when the cast was down; and "meter wheel", the reading of the meter wheel attached to the sheave (through which the hydrographic wire ran from the winch) when that Nansen bottle was clamped onto the wire.

"Meter wheel" plus "wire out" equals constant, the total amount of wire put out for the cast, less the distance from deck to sea surface. The two unlabeled columns to the right of "sal." could be filled with other data, such as oxygen concentration or potential temperature, or sigma-t. By the late 1950s a few entries were already relics (e.g., "Secchi disc", "bottom sample no.").

The final accepted observations were transcribed by hand in pen-and-ink onto parchment-like Reduced Data Cards. These were easily photo-copied, were very durable, and were the permanent, formal record of the observations until they were replaced by computer files. The WHOI Nansen-bottle data were published in the *Bulletin Hydrographique* of the Conseil International pour l'Exploration de la Mer, until the *Bulletin* was discontinued following observation year 1956. During the later years of the *Bulletin* each data point was inspected – and possibly sent back to the originator for re-checking – by the editor, the formidable Jens Smed. After the *Bulletin* was superseded by the *ICES Oceanographic Data Lists*, WHOI data were sent to the U.S. National Oceanographic Data Center.

The following remarks about station practice have to do with the way things were done at WHOI after the mid-1950s. I was not witness to earlier practice, and there is no one I can ask about it.

Deep stations usually consisted of two lowerings, with up to 19 Nansen bottles on the shallow cast and up to 11 on the deep cast. Sampling for the shallow cast was generally standardized for a particular cruise; it was done first, so that while it was down the watchstanders could plan the sampling for the deep cast, which often depended on bottom depth. The shallow cast typically took one hour, the deep cast 2 ½ hours. WHOI stations rarely comprised more than 30 depths sampled in all, mainly because there were only 30 lines on the log sheet (Appendix D). When Scripps observers made deep stations, they often did two casts of 18 bottles each. This habit, petrified as doctrine, was the main reason why the CTD rosettes for the U.S. WOCE Hydrographic Program were constructed to hold 36 Niskin bottles.

The thermometer frames on WHOI Nansen bottles could hold two thermometers. In addition to one protected thermometer, every other bottle below 200 m (usually) carried an unprotected thermometer. Often additional protected thermometers were placed in the intervening frames, for back-up, or to compare thermometer performances. At Scripps, in contrast, the bottles all bore three-thermometer frames, and each frame was usually filled with

two protected thermometers and (below 100 m) one unprotected. (When WHOI lost a cast, it was a disaster; when Scripps lost one, it was a financial catastrophe.)

When a cast was down (i.e., lowered to its full depth), 5-10 minutes was allowed for the thermometers to equilibrate with the surrounding water. Then a brass messenger was dropped down the wire to strike and open the upper catch on the first bottle so that the bottle reversed (reversing its thermometer as well) and closed. The messenger then struck a lever on top of the clamp securing the bottle to the wire, so as to release a second messenger hung just below the clamp. This descended, tripped the next bottle in the series, and so on. The speed of messenger descent was figured at 200 m/minute, and after a suitably calculated time interval, the cast was raised. For a deep cast with the top bottle at 2000 m depth, say, no time was wasted on thermometer equilibration because it took 10 minutes for the messenger to reach the first bottle. For each cast the times of “start”, “down”, “messenger drop”, “start up”, and “in” were recorded on the log sheet (Appendix D).

For a full-depth station it was a challenge to guess how much extra wire to let out (beyond bottom depth) in order to put the deepest bottle close to, or on, the ocean floor, but not to overshoot and pile up a rat’s nest of tangled wire and bottles on the bottom. “Mud in bottom bottle” (without mishap) was a notation of success on the log sheet. By the late 1960s “pingers”, originally devised by Harold Edgerton to position cameras over the bottom, were being attached to the hydrographic wire just below the deepest Nansen bottle, to register approach to the bottom. Both the direct signal from the pinger and its bottom return were displayed on the depth recorder, so the observers could watch their cast descend, and stop the winch just before the pinger grounded. Pingers made for surer station-keeping, but they took away some of the adventure.

The platform on which the watchstander stood to hang and retrieve the Nansen bottles was a wooden grating projecting from the ship, with thigh-high posts mounted on the outboard corners and a chain running from the ship's rail around the tops of the posts for support and security. Occasionally the ship would roll into an approaching wave and flood the platform up to the observer's ankles. Sometimes he would get more adventure than he sought when the flood reached his knees. Scripps observers worked in a "bucket" and stayed drier.



When a cast was coming up, a watchstander waited by the ship's rail to look for the arriving bottles, and alert the winch operator when to slow down. The Nansen-bottles were usually painted yellow in order to be easily visible in the water.

Not all casts were successful. The upper catch on one Nansen bottle might be too stiff for the blow of the descending messenger to open it. Or some bumptious creature might wrap itself around the hydro wire and stop a messenger. Or, more rarely, hard steaming on the wire might set it vibrating so much as to slow a messenger to ineffectiveness in tripping the bottles. Or, when a cast was on the way down, a messenger might let go of its Nansen bottle unasked and trip all the deeper bottles prematurely; that kind of misfortune would usually be recognized by the watchstanders as they glanced at the thermometers when retrieving the bottles. On all these occasions the cast had to be repeated.

As the Nansen bottles were brought aboard they were racked in the wet laboratory, and the samples immediately drawn: oxygen first, as the most vulnerable, then salinity (three rinses for the sample bottles), and any others (e.g., nutrients). It took (and still does take) some practice to learn to draw an oxygen sample without bubbling air into it. Good watercatchers would blow away any water around the petcock on a Nansen bottle to keep clinging surface water from dripping into the salinity sample. On well organized stations all the sample-bottle numbers were matched to their Nansen-bottle numbers, and the sample bottles were distributed appropriately in the tray below the Nansen bottles beforehand, in order to make it as difficult as possible for an absent-minded or distracted watchstander to draw a sample from the wrong Nansen bottle. The sample bottle numbers were recorded at the right-hand end of the log sheet.

After the thermometers had equilibrated to the laboratory temperature, one watchstander read them (both main and auxiliary) with the help of a magnifying eyepiece and a flashlight to a second watchstander, who recorded his readings on the log sheet. The second then check-read the first; if their two values differed by more than the precision of the thermometers (usually), they discussed the matter, re-examined the thermometer, and came to an agreement on the reading. (At Scripps both readers' readings were recorded and averaged.)

In early years the Nansen bottles were then drained and left as they were in the rack until the next station, to be inverted then on the hydro wire. But during the IGY Gerry Metcalf and Val Worthington began the practice of inverting them in the laboratory after draining them. This promoted faster bottle-hanging, and, more beneficially, it allowed the observers to check well

beforehand that the mercury columns in the inverted thermometers had fallen into place, and to do so in a well lighted laboratory rather than on the hydro wire, perhaps in the dark with a flashlight. Gerry Metcalf was fiercely economical with stopped-ship time, and this new procedure allowed him to clamp the first Nansen bottle onto the hydro wire and send it down almost before the ship was hove to. (Scripps observers could not adopt this practice because they had modified their Nansen bottles to make premature messenger release impossible, and that design required inversion on the wire.)

Responsible watercatchers scrutinized their data for soundness. The upper catch on a Nansen bottle might shake loose, and the bottle pretrip on the way down; this failure would be marked by spurious thermometer readings and misplaced water-property values. Slight leaking in the valves or petcock of a Nansen bottle could contaminate the water inside as the cast was raised; or sloppy sample drawing and handling on deck could also contaminate samples. Despite all bookkeeping precautions a dreamy watchstander might still draw a sample from a wrong Nansen bottle. Occasionally a bad salinity could be detected by an apparent instability in the water column. A common (and still excellent) practice was to plot, as they became available during the course of a cruise, the cumulative salinity and oxygen values against potential temperature, so as to highlight dubious outliers (and to point, perhaps, to a Nansen bottle needing maintenance). Obviously bungled measurements ("blunders") were deleted from the records; suspect values not stark enough to be discarded with confidence were merely marked questionable.

Fritz Fuglister thought that investigators issuing sets of station data ought to be obliged to sign them, both to encourage them to check their observations thoroughly, and to let future users know the repute of the originator. This never happened. Nevertheless, it is still helpful in trying to sniff out the quality of some station data to know who collected them: individual, institution, or country.

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