Standards and Laboratory Calibration

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1. Overview

This report is concerned with:

1. Standards for the measurement of physical and chemical variables envisaged in the WOCE Hydrographic Programme (WHP).
2. Procedures for the transfer of the standards to both continuously measured and discretely sampled variables (calibration) stating the accuracy to be routinely achieved.
3. Steps to be taken to ensure the harmonization of these standards and calibration procedures.

It is also divided into two sections which deal with: (a) the physical variables [the chemical variables, dissolved oxygen and nutrients], and (b) 'small volume' geochemical tracers. The chemical variables – dissolved oxygen and nutrients – are considered together with the sampling procedures in later sections of this report.

One of the aims of this document is to remind those readers already possessed of skill and experience in the measurement of oceanographic variables to the highest standards, as required in the WHP, of good laboratory practice; and to introduce the concept to those who wish to achieve these measurement standards. Good laboratory practice may be thought of as "a set of rules, operating procedures and practices … that are adequate to ensure the quality and integrity of data generated by a laboratory," (Vijverberg and Cofino, 1987).

Institutions committed to making measurements to the standards required by the WHP will be expected to be equipped in a manner which should become apparent in the pages of this report. This equipment and apparatus must be installed in a special laboratory or, at a minimum, a low-use area which is environmentally controlled. Laboratory personnel will need to be skilled in the operation of the equipment and its maintenance, and must keep good records. The aim of the standards/calibration laboratory is to furnish the user with calibrated equipment for use at sea. All relevant information including calibration history must be available at both the calibration facility and to the user. The widespread use of small personal computers and mini discs should make this relatively straightforward. In general, we are opposed to adjusting and trimming electronics components to achieve a pre-determined relation between instrument output and the variable being measured. Rather a correction procedure is to be applied to the data stream. There will be occasions when adjustments need to be made in order to ensure proper operation of the instrument, but these will lead to a discontinuous behavior in the calibration history, equivalent to the introduction of a new sensor.

1.1 Physical Variables

In the following paragraphs, we shall consider the physical variables pressure (p), temperature (T), and conductivity (salinity) ($C(S)$), defining their standards and the methods of calibration of sensors to measure these variables. In the context of the WHP, the instrument under consideration is the CTD. These same methods, however, will apply to any instruments measuring p, T, $C(S)$ to the highest achievable standards.

2. Standard of Pressure

Pressure has the dimensions of force per unit area. The SI unit is Pascal (Pa) or Newtons per square meter. 10^4 Pa = 1 decibar (or dbar) is the non-SI unit generally employed in oceanography. The standard of measurement of this physical variable is provided by the pressure balance, also known as the piston gauge and deadweight tester. The use of the pressure balance involves the manual placement of weights on the instrument together with an adjustment of the position of the piston. Although these operations are not readily automated, with care the reproducibility of measurement is very high. Commercially manufactured instruments should be purchased with a specified accuracy of better than ± 0.02% full-scale range (or of reading). If the full scale pressure is 6000 dbar, an error of ± 1.2 dbar results. This figure meets the specification of the WHP (Joyce, 1988).

The theory and operation of the pressure balance is described in the literature (Dadson *et al.*, 1982) and its specific application to oceanographic measurements made in an article by Banaszek (1985). The instrument manual is also an important reference. In order to achieve an accuracy of 0.02% the instrument must be carefully levelled in an air conditioned location, and a number of corrections made. The most important are: (1) correcting for the local value of the gravitational acceleration at the site of measurement; (2) correcting the effective piston area for changes due to temperature (usually small) and for changes due to pressure. This last correction (0.015 to 0.025%) probably limits the accuracy of the measurement. Corrections are also made for the weight of air displaced (0.015% typically) and for the head of hydraulic fluid between the pressure balance reference point and the pressure transducer under test (0.0–1.0 dbar). The pressure balance must be returned periodically to the manufacturer for recertification and overhaul, and we recommend that this interval should not exceed four years.

3. Calibration of Pressure Sensors

For calibration of a pressure sensor to operate to full oceanic depth, the pressure balance and the pressure sensor are connected *via* a stainless steel tube of specified diameter filled with specified hydraulic fluid (care should be taken to bleed all air from the line). Providing the sensor is appropriately constructed and fitted, it will be quite unresponsive to the slight compressional changes of the pressure case in which it is mounted when the entire instrument is subject to the pressure of full ocean depth. The pressure balance generates pressure above atmospheric (differential mode) but the CTD sensor measures pressure including the atmospheric component (absolute mode). The variations of atmospheric pressure near sea level are about ± 0.25 dbar so that atmospheric pressure during testing should be included with calibration data.

In the calibration of a pressure transducer, two difficulties present themselves: All sensors are temperature sensitive; and all suffer from hysteresis. For sensors widely in use in 1989, the temperature sensitivity is of the order 0.1 to 1.0 dbar/° C, and the hysteresis (a function of pressure range) is of order 2 to 8 dbar zero offset. Improvement in sensor design should reduce these problems in the near future. Thus, the calibration data for a pressure sensor will normally include readout for both increasing and decreasing pressure at 10 to 20 values, performed at both low and high temperatures (with the instrument immersed in a temperature controlled bath stable to ± 0.1°C).

Pressure sensors respond to temperature transients, such as step changes, in a different manner from their equilibrium response; laboratory measurements should be made to quantify the effect. An exponential decay model with a time constant chosen to fit the measurements may describe the temperature response with adequate accuracy and be suitable for field use.

A new pressure sensor may profitably be cycled through its operating range several tens of times before a calibration is attempted. The recalibration of a well-used sensor is normally performed on its first work cycle although the practice varies between labs. Cycling information, however, should appear with the calibration documentation.

The stability over time of high-quality pressure sensors is such that, providing a record is kept of the sensor reading at atmospheric pressure, annual calibrations should suffice. However, if other CTD sensor calibrations are performed more frequently, it is prudent to take advantage of the opportunity and shorten the intervals for pressure calibrations too.

4. Temperature Standard

The temperature given by the International Temperature Scale of 1990 (ITS-90) is the present best approximation to the thermodynamic temperature(T). The unit is the Kelvin, (K), defined as the fraction 1/273.16 of the thermodynamic temperature of the triple point of water. It is common practice to define the temperature according to the Celsius scale t with units °C and with t = T - 273.15. The International Temperature Scale of 1990 replaced the earlier scale of 1968 (IPTS-68) on January 1, 1990, and where it is necessary to distinguish between them, suffixes will be used.

In the range of interest to oceanographers ITS-90 is defined by certain fixed points and an interpolation procedure employing a platinum resistance thermometer (Comité consultatif de thermométrie, 1990). The following fixed points will be relevant to oceanographic work.

	$t_{90}/°C$	W_r
Triple point Hg	- 38.8344	0.844 142 11
Triple point H_2O	0.0100	1.000 000 00
Melting point gallium	29.7646	1.118 138 89
Freezing point indium	156.5985	1.609 801 85

The significance of W_r is described later in the text.

Secondary fixed points, the triple points of phenoxybenzene (near 26.86 °C) and ethylene carbonate (near 36.31 °C), may also be employed in some laboratories, and their temperatures will be certified by the National Standards Laboratories. Thus, the requirements for temperature standardization are: At least two triple point cells from the above list, high-quality platinum resistance thermometers with associated AC resistance bridge, standard resistors, and an interpolation procedure.

Temperatures are determined in terms of W, the ratio of the resistance $R(T_{90})$ at a temperature T_{90} and the resistance $R(273.16\text{ K})$ at the triple point of water. The ratio is written:

$$W(T_{90}) \;=\; R(T_{90})/R(273.16\text{ K}) = R(t_{90})/R(0.010^\circ\text{ C}).$$

(Note that the resistance $R(0°\text{C})$ used for the IPTS-68 scale is no longer employed.)

A platinum resistance thermometer that is acceptable for the definition of the temperature scale must be made from pure, strain-free, platinum and must satisfy at least one of the following two relations:

$$\text{At the melting point of gallium} \quad W \geq 1.11807$$

$$\text{At the melting point of mercury} \quad W \leq 0.844235$$

Construction of a thermometer used as a standard must allow its insertion into the fixed point cells – a feature which excludes most, if not all, CTD sensors used for oceanographic measurements to date. Thus, a laboratory transfer standard must be employed in order to calibrate the CTD sensor.

In order to understand how a transfer standard is calibrated and how temperature is determined from the measurement of its electrical resistance, the official texts introduce the expression 'reference function.' This is best thought of as the resistance-temperature characteristics of a high-quality, albeit fictional, instrument. For this fictional instrument, the ratio of the resistance at temperature T to the resistance at the triple point of water is designated W_r and is specified as a function of temperature.

In the range 13.8 to 273.16 K the relation between t_{90} and W_r is given by a polynomial of order 12; in the range 0°C to 961.78, the polynomial is only of order 9. In the oceanographic range $-2°$ to $+35°$C, the following expression reproduces the above relations with an accuracy of better than 0.1 mK.

$$t_{90} = 0.010015 + 250.7140(W_r - 1) + 9.71421(W_r - 1)^2$$

Calibration of the secondary standard involves relating W to W_r, that is relating the performance of the laboratory and exemplary thermometer.

The deviation of $W - W_r$ over the range of oceanographic interest is given by either a linear or a quadratic function, depending on the number of fixed points used in the calibration, *viz*:

$$W - W_r = a(W - 1) + b(W - 1)^2$$

If gallium and H_2O, or indium and H_2O are used, a will be specified and b set to zero. If mercury, gallium and H_2O are used, both a and b will be specified by the calibration. Determination of the temperature ITS-90 then involves measuring W, calculating W_r from the appropriate deviation function and then computing t_{90} from the quadratic expression above (providing the temperature so computed falls in the range $-2°$ to $+35$ °C). At this point it is appropriate to recall the approximate relationships between t_{68} and t_{90} in the same range, *viz:*

$$t_{90} = 0.99976\ t_{68} \quad \text{and} \quad t_{68} = 1.00024\ t_{90}$$

The error of this relation is less than 0.5 mK.

In the stagnant conditions of triple point cells the ohmic self-heating of the transfer standard must be kept to a minimum (< 1 mK); currents should probably not exceed 1 mA and a correction should be made. Manufacturers may quote a figure for self-heating but its determination by varying the current is relatively straightforward. The history of a secondary temperature standard is a vital component in assessing its performance: A slow drift with time is invariable, erratic jumps should disqualify its use.

The reproducibility of the temperature within the triple point cells mentioned in an earlier paragraph, in skilled hands, is approximately 0.5 mK. Thus, overall a transfer standard determines the ITS-90 to better than 1 mK in the range of oceanographic interest. We recommend that the calibration of the transfer standard be repeated at least once every six months and more frequently if the observed rate of drift exceeds 0.5 mK between calibrations.

5. Calibration of Temperature Sensors

Given the existence of a suitable secondary temperature transfer standard, the calibration of a CTD temperature sensor must be undertaken in a medium free of temporal and spatial temperature gradients with the two thermometers in close proximity. For oceanographic use, it is general to use water as the medium. A satisfactory calibration can probably only be achieved by total immersion of the instrument rather than by immersion of the sensor alone, although there is a measure of debate about this (Saunders, 1986). The requirement is thus for a well-regulated bath large enough to contain the CTD.

Despite the availability of suitable commercial units, descriptions of temperature calibration facilities are rare in the oceanographic literature; Lewis (1985) provides some useful guidance. Baths having volumes between 100 and 400 liters need to be stirred vigorously, moving the bath volume in the order of a minute or less; and yet temperature must be controlled to within 1 mK. The number of calibration values visited will lie in the range 5–10. High quality thermometers will, in general, have an output very nearly linear in temperature. At least five points will be needed to establish linearity and ten to establish any non-linear component, see examples in Chapter 3 of a report of SCOR[1] Working Group 51 (UNESCO, 1988). Particular problems of nonlinearity may arise near the zero of a signal and a change of its sign. It is recommended that an offset be introduced so that oceanographic measurements lie entirely in the region of positive signal. The accuracy of the temperature calibration of the CTD depends principally on the care with which each step is accomplished. A recent experiment with CTDs calibrated at laboratories in Europe and N. America and then intercompared at a common location (Kiel, FRG November 1988), provisionally suggests that the WOCE requirement of ± 0.002 °C (Joyce, 1988) is a realistic target. (The experiment was carried out under the auspices of SCOR –Working Group 77 - "Laboratory Tests related to basic physical measurements at sea.")

The frequency with which the calibration of a thermometer should be undertaken is a function of its use and quality. During WOCE, CTD instrumentation from the major institutions will rarely be in the laboratory; nevertheless a six-month calibration cycle would seem desirable at this stage. The interval might be extended if duplicate temperature sensors are installed in the CTD, a practice we recommend. Small step changes in calibration can then be detected and, utilising the conductivity measurement, the culprit probably established.

6. Conductivity Standard

The electrical conductivity (or inverse resistivity) has SI dimensions of Siemens per meter (Siemen = ohm^{-1}). The non-SI unit widely used in oceanography is mS.cm^{-1} (= 0.1 S m^{-1}). The conductivity of a sample of sea water is a function of the temperature, pressure and total salt content of the sample; to describe the latter property the concept of 'practical salinity' has been adopted (UNESCO, 1981). The importance of conductivity

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[1] Scientific Committee on Oceanic Research, a committee of the International Council of Scientific Unions

measurements in oceanography is solely in providing determinations of practical salinity (see the next section).

The standard of conductivity for oceanographic measurements is provided by that of a pure potassium chloride (KCl) solution in which the mass fraction of KCl is 32.4356 x 10^{-3}. Because it is impractical to prepare and distribute KCl on the scale required for standardization of all conductivity measurements, a secondary standard called IAPSO standard sea water fills the role. IAPSO standard sea water (SSW) is prepared from North Atlantic surface sea water by the Staff of Ocean Scientific International, Ltd. at the Institute of Oceanographic Sciences, Deacon Laboratory, Wormley, UK. The electrical properties of a sample are specified in terms of the ratio of the conductivity of the SSW sample to that of KCl of the prescribed concentration (above), both measured at a temperature of 15 °C, on the IPTS-68 scale, and at standard atmospheric pressure. Each sample of SSW is supplied in sealed glass ampoules (capacity *ca.* 280 cm^3) and is labelled with a conductivity ratio; the value is always very close to unity (0.99975 to 1.00007). At the time of bottling the variations in conductivity ratio within a batch and relative to recently prepared batches is only ± 0.0001 (Culkin, personal communication), which implies standardization of practical salinity to within ± 0.0003, well within the specification of the WOCE Hydrographic Programme (Joyce, 1988).

As a sample of standard sea water ages, physical and chemical changes take place and the conductivity ratio changes (Mantyla, 1980, 1987). Thus, even in 1989 when new procedures are being tested, which it is hoped will slow the aging process, a recent batch of SSW should be employed for calibration purposes.

The requirements of conductivity measurement are thus, SSW and a high precision conductivity ratio bridge, capable of an accuracy of at least 0.002 $mS.cm^{-1}$ in conductivity (equivalent to better than 0.003 in salinity) and resolution which is ten times better. One conductivity bridge of successful design (Dauphinee and Klein, 1975) invariably known as a bench salinometer, houses the conductivity cell in a stabilised water bath and brings the sample whose conductivity (salinity) is to be determined to the bath temperature by drawing it through an efficient heat exchanger. The measurement of the conductivity of some tens of samples is interspersed with samples of SSW and the constancy of the SSW value demonstrates the stability of the instrument and ensures high quality measurements. To achieve the desired precision this model switches ranges for 5% change in conductivity; a series of internal adjustments ensures that measurements at the top of a lower range and the bottom of the next highest range correspond exactly and these must be checked periodically.

7. Calibration of Conductivity Sensors

Conductivity of sea water is a function of pressure, temperature and practical salinity; in a closed system at near atmospheric pressure and with a salinity of 35.0, a range of temperatures from 0° to 25 °C generates conductivities that range from 29 to 53 $mS.cm^{-1}$. Alternatively, a series of baths at temperature 25 ° C and salinity varying between 18.0 and 36.5 yields a comparable range of conductivity. The latter procedure provides a much more rapid calibration of a conductivity sensor. Temperature must be measured to an accuracy of ± 0.002 °C, and the water must be circulated rapidly. Samples are drawn from each bath as each sensor calibration is performed and a conductivity measurement made employing SSW and a conductivity bridge (bench salinometer).

Few laboratories attempt this procedure, and there is much less experience of conductivity calibration to the accuracy required than for the variables pressure and temperature. Consequentially, there is little detailed information about the influence of walls and other obstacles which may influence the laboratory calibration but are not present in field measurements (proximity effect). Some conductive sensors have compact internal fields and exhibit almost no proximity effect; but generally, inductive sensors (and even some conductive ones) have external fields which extend several times the sensor dimensions and exhibit the proximity effect. In the latter case, transferring the laboratory calibration to the field is uncertain. Writing in 1990, at this time only a few experimentalists are convinced of the benefits of laboratory calibration of conductivity cells and the practice of field calibration is universal. Field calibration in skilled hands leads to an accuracy in conductivity measurement, equivalently to an accuracy of salinity measurement of ± 0.002, as required by the WOCE Hydrographic Programme.

8. Salinity (Practical)

The practical salinity of a sample of seawater is presently defined in terms of the ratio, k_{15}, of the electrical conductivity of the sample at a temperature of 15°C, measured on the IPTS-68 scale, and a pressure of one standard atmosphere to that of a potassium chloride (KCl) solution in which the mass fraction is 32.4356×10^{-3}, at the same temperature and pressure. A k_{15} of unity corresponds exactly to a practical salinity of 35.

The practical salinity of a sample of seawater is invariant under both pressure and temperature changes, but its electrical conductivity is not. Fofonoff and Millard (1983) have prepared an algorithm relating conductivity ratio and salinity that is valid in the temperature range -2 to 35 °C, in the pressure range 0 -10,000 dbar and the (derived) salinity range 2–42. The algorithm employs temperatures determined on the International Practical Temperature Scale of 1968, whereas during the WHP temperatures will be measured on the International Temperature Scale of 1990. Thus the conversion $t_{68} = 1.00024 t_{90}$ must be employed before the salinity is calculated. Without this step at a pressure of 0 dbar and salinity near 35, the following errors result:

t_{90} °C	0	5	10	20	30
Salinity error	0	.0013	.0024	.0041	.0053

(Employing t_{90} rather than t_{68} for a given conductivity leads to an overestimate of salinity.)

The algorithm is internationally approved and may not be substituted. Note that practical salinity is dimensionless and any previous nomenclature such as 42 x 10^{-3} or 42‰ has been discarded. The use of PSU for practical salinity units is also discouraged.

The procedures for the measurement of conductivity (including the use of standard seawater) are described in the preceding sections; from them salinity is derived as indicated above. The accuracy sought in the measurement of salinity in the WHP is 0.002 or approximately one part in 10^4.

9. Harmonization of Measurements in WHP

The major technical challenge within the WHP is for groups from differing nations to conduct measurements in the field consistently to the highest realizable accuracy. To ensure that biases between the measurements of such groups are made as small as possible, additional desirable steps are described in the following paragraphs. Again, attention is confined to the physical variables: pressure, temperature and salinity.

The primary source of uniformity for measurements depends on the accurate transfer to CTDs of the standards provided by the standards laboratories in the countries involved. However, there is a role for travelling or portable secondary standards in checking this transfer. Such equipment should preferably be capable of being hand carried, should have excellent long-term stability and be installed alongside the CTD during the CTD calibration. If suitable units can be found, shipment between calibration facilities could be coordinated by the WHP office according to the timing of WHP cruises. Frequent returns of these portable secondary standards to their homes for recalibration would be an essential element in the scheme. In the absence of experience, the equipment employed and the detailed procedures followed would need to be determined from the early results of such a programme.

There is a role, too, for CTD field intercomparison experiments. However, in this regard the working group possibly steps outside its terms of reference. Nevertheless, since such experiments measure the end-to-end effect of the procedures recommended in this document, we offer the following advice. Such CTD comparison trials will be cost effective only (a) if they are short; and (b) if measurements are made simultaneously by at least a pair of CTDs on any lowering. A combination of internally and externally recording CTDs is proposed or, through the use of multicore conducting cable, two or more externally recording CTDs. The latter procedure could only be used where the instruments and their signals were so different as to preclude all possibility of mutual interference. Such intercomparison experiments would also permit the dynamic responses of different instruments to be compared, as well as processing methodologies. These are areas of consideration of our companion work groups and will not be elaborated here.

The salinity measurements are, of course, already provided with a travelling secondary standard in the form of IAPSO standard sea water. Such standards have a practical salinity very close to 35 and provide the basis for field calibration of salinity measurements, as described in an earlier section. The working group proposes that the standard seawater service be asked to fabricate a special WOCE sample of known practical salinity. The salinity value would be unknown to the user but would be supplied to the WHP office; its value would be appropriate to deep/bottom water of the region where the cruise takes place. Measurements of these 'unknown' samples would be included every 5–10 stations and be performed between, rather than close to true standardization of the bench salinometer. By such measurements, both random and systematic salinity errors would be assessed for each cruise.

We believe that the combination of good laboratory practice and these recommendations for harmonization amongst calibration centres will ensure that the measurements of physical variables made in WOCE approach the accuracy sought and never yet achieved on a truly global basis.

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