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## Electrochemical Instrumentation

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### GLOSSARY OF SYMBOLS

$a_x$	Ion activity (equation 1)
$B$	Constant (equation 7)
$E$	Electrode potential (equation 1)
$E^\ominus$	Standard electrode potential (equation 1)
$F$	Faraday (equation 1)
$I_B$	Input bias current (equation 2)
$I_T$	Current sensitivity of oxygen electrode (equation 5)
$J$	Constant (equation 5)
$K_0, K_F$	Constants (equations 4 and 5, respectively)
$R_{in}$	Amplifier input resistance (equation 2)
$R_0$	Constant (equation 7)
$R_p$	Internal resistance (Figure 2)
$R_s$	Variable resistance (Section 3.2.2)
$V_{in}$	Voltage input to amplifier (Figure 2)
$V_{os}$	Offset voltage (equation 2)
$V_{out}$	Voltage output from amplifier (Figure 2)
$V_p$	Polarization potential (Figure 5)
$\epsilon$	Maximum acceptable voltage error (equation 3)

## 3.1. INTRODUCTION

Marine electrochemistry, by definition, involves the application of electrochemical methods in marine studies. As such, experimental marine electrochemistry is often based on scientific principles and methods originally developed by 'land electrochemists'. Unfortunately, however, the direct application of conventional electrochemical instrumentation is seldom possible, especially when on-site or *in situ* studies are attempted. The complexity of sea water composition, the harsh marine environment, and the constant quest for more precise and accurate data pose special instrumentation challenges to the marine electrochemist. To meet these challenges, conventional electrochemical techniques have been refined and special instrumentation systems developed. Thus, a research programme in experimental marine electrochemistry often involves a considerable instrumentation effort.

This chapter is written with two aims in mind. First, it attempts to present a coherent outline of basic instrumentation concepts and techniques applicable to the solution of marine electrochemistry problems. The discussion is mainly concerned with problems related to on-site and in particular *in situ* instrumentation. A thorough discussion of general electrochemical instrumentation problems can be found, of course, in numerous review articles and texts (e.g. Sawyer, 1974). A second objective of this chapter is to present marine electrochemistry cells and electrodes in electronic engineering terms. This may assist engineers to better understand the special problems of marine electrochemistry and enable them to contribute to their solution.

An experimental marine electrochemistry system will usually encompass at least some of the units shown schematically in Figure 1. A sensor, probing the tested solution in the laboratory, on-site or *in situ*, produces an electrical signal. The signal may be either a self-generated response, such as the

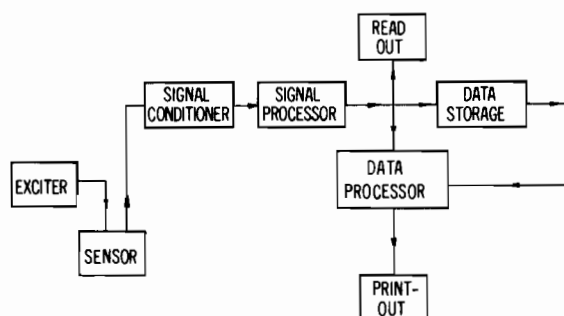


Figure 1. Schematic representation of a general configuration of a marine electrochemical instrumentation system

response of an ion-selective electrode, or an induced response dependent on some external excitation, as in the case of conductance measurements. The signal is then fed to a signal conditioner which transforms it to a high-level signal capable of driving a readout unit, a data transmitter, or a signal processor. The function of the last unit is to transform the raw signal to a more convenient form. This may involve signal amplification, linearization, or more sophisticated processing, such as automatic temperature compensation. The processed signal can then be read directly or stored for further processing. More elaborate data processing can then be done on-line or off-line by a digital computer.

In this chapter an attempt is made to review some of the instrumentation approaches taken by various investigators in the past in designing marine electrochemical studies. The discussion will follow the outline presented schematically in Figure 1. It is unfortunate, however, that many of the design details of the instrumentation used by marine electrochemists have not been reported in the scientific or technical literature. Extremely valuable experience has thus been lost and marine electrochemists often have to 're-invent the wheel' when designing an experiment. Consequently, many of the specific design details discussed in this chapter are examples of approaches taken by the author and his co-workers. An attempt is made, however, to generalize and to sort out and discuss the key problems that proved to be crucial to the success of the experiments.

### 3.2. SIGNAL CONDITIONERS AND EXCITERS

Apart from the electrochemical sensor itself, the signal conditioner (Figure 1) is the most important unit in determining the accuracy and precision of the electrochemical measurement. For this reason, great care must be taken when specifying the requirements for the signal conditioner. When considering the desired parameters, it is helpful to specify the parameters of the electrochemical sensor in electrical terms. This procedure is required because the parameters of commercially available signal conditioners are defined for electrical sources and loads. The relevant source parameters are signal range, internal resistance, frequency, bandwidth, and acceptable error range. The error is usually referred to the input of the signal conditioner, i.e. compared with the signal level of the sensor. Some of these considerations are discussed in conjunction with the specific examples given below.

#### 3.2.1. D.c. amplifiers (electrometers)

Marine potentiometric studies have mainly involved ion-selective electrodes (Whitfield, 1975). These electrochemical sensors consist of two electrodes, an ion-selective electrode and a reference electrode. The signal is

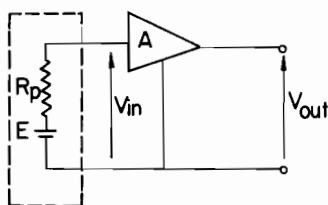


Figure 2. Schematic representation of an ion-selective electrode and signal conditioner. The electrode pair is represented by an equivalent circuit consisting of a voltage source  $E$  and an internal resistance  $R_p$ .

a potential established between the leads of the two electrodes. From an electrical engineering point of view the electrode pair can be described as a voltage source and an internal resistance (Figure 2). The voltage source  $E$  represents the total potential measured between the leads of the electrodes including the reference electrode potential and the potential of the inner reference electrode of the ion-selective electrode. The internal resistance  $R_p$  represents the total (d.c.) resistance seen between the electrode leads. The ideal response of an ion-selective electrode is described by the Nernst equation (Warner, 1972):

$$E = E^\ominus(P, T) + \frac{RT}{nF} \ln a_Y \quad (1)$$

where  $a_Y$  is the activity of the ion in the tested solution,  $P$  is pressure and  $R$ ,  $T$ ,  $F$ , and  $n$  have their usual significance.

Assuming that the response of the ion-selective electrode is near ideal,  $E$  (equation 1) is the open-circuit voltage of the cell. However, any amplifier will load the sensor to some degree and, as a result, the actual voltage  $V_{in}$  (Figure 2) at the input of the d.c. amplifier (electrometer) input will differ in magnitude from the open-circuit voltage  $E$ . This can readily be seen by considering the equivalent circuit of a practical amplifier (Burr Brown, 1971) shown schematically in Figure 3. As can easily be shown the actual voltage  $V_{in}$  at the amplifier's input is

$$V_{in} = (E + V_{os} + I_B R_p) \frac{R_{in}}{R_{in} + R_p} \quad (2)$$

where  $V_{os}$  is the input offset voltage of the amplifier,  $R_{in}$  is the amplifier's input resistance, and  $I_B$  is the input bias current.

It is thus evident that in order to minimize the errors introduced by the amplifier its parameters should obey the relationships

$$R_{in} \gg R_p; \quad I_B R_p < \varepsilon; \quad V_{os} < \varepsilon \quad (3)$$

where  $\varepsilon$  is the maximum acceptable voltage error at the input.

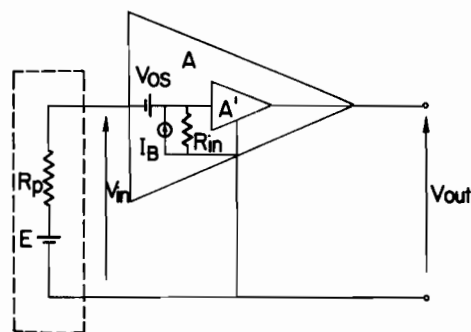


Figure 3. An equivalent circuit of the amplifier shown in Figure 2.  $V_{os}$  is the input offset voltage,  $I_B$  is the input bias current (represented by a current source),  $R_{in}$  is the input resistance, and  $A'$  is an ideal amplifier

The internal resistances of ion-selective electrodes span a relatively large range from a few thousand megohms ( $>10^9 \Omega$ ) for a glass electrode (Bates, 1964) to a few ohms for solid-state electrodes (Sensorex Inc., Irvine, Calif., USA). Furthermore, the internal resistance  $R_p$  is not constant and may depend strongly on temperature. The resistance of glass membrane electrodes increases markedly at low temperature (Bates, 1964), which dictates a very low value for  $I_B$  (equation 2) if large errors are to be avoided. On the other hand, a relatively large offset voltage  $V_{os}$  could be tolerated because it is compensated for during calibration (in fact it can be considered as part of  $E^\ominus$  in equation 1). However, the drift of  $V_{os}$  with respect to temperature and time must be kept small. Consequently, for situations where the temperature varies the conditions of equation 3 are modified to

$$\begin{aligned}
 R_{in} &\gg R_p \\
 I_B R_p &< \varepsilon \\
 \left| \int_{T_1}^{T_2} \frac{dV_{os}}{dT} \cdot \Delta T \right| &< \varepsilon \\
 \left| \int_{t_1}^{t_2} \frac{dV_{os}}{dt} \cdot \Delta t \right| &< \varepsilon
 \end{aligned}$$

where  $T$  is temperature,  $t$  is time and subscripts 1 and 2 signify the range of the experiment.

It is thus evident that the basic specifications of a d.c. amplifier (electrometer) for ion-selective electrodes are high input resistance, low input bias current, and low input offset voltage drift with temperature. Recent advances in electronic engineering have made possible the miniaturization of these types of amplifiers and have thus made practical the design of *in situ* instrumentation for ion-selective electrodes. Some of the design details of *in*

*situ* instrumentation, relevant to the subject matter discussed here, were reported by Ben-Yaakov and Kaplan (1968a,b, 1973), Wilde and Rodgers (1970), Conti and Wilde (1972), and Ben-Yaakov and Ruth (1974).

Wilde and co-workers used a Type 132A or a Type 1302 (Zeltex Inc., Concord, Calif., USA) amplifier as a signal conditioner for ion-selective electrodes. These are FET input operational amplifiers (Burr Brown, 1971) with the following specifications; input resistance,  $10^{12} \Omega$ ; input bias current,  $5 \times 10^{-11} \text{ A}$ ; and input offset voltage drift,  $20 \mu\text{V}^\circ\text{C}^{-1}$ .

Assuming that the internal resistance of the glass electrode was  $10^9 \Omega$ , the input voltage to the amplifier ( $V_{\text{in}}$  in Figures 2 and 3) is 0.99 of  $E$  (equation 1) and the internal voltage drop due to the internal resistance of the electrode and input bias current ( $I_{\text{B}}R_{\text{p}}$ ) is 50 mV. Assuming a  $20^\circ\text{C}$  temperature range, the input voltage drift with temperature is 0.4 mV. The major source of error is thus the internal voltage drop due to the input bias current. As stated by Wilde and Rodgers (1970), this voltage drop could be adjusted by a balancing potentiometer. Unfortunately, however, this procedure cannot correct for errors due to a change in the input bias current or in the internal resistance of the glass electrode due to a temperature drop. As already discussed, the expected resistance change is large (Bates, 1964) and one would therefore expect relatively large (and probably unacceptable) errors if the amplifier and sensor are subjected to a variable ambient temperature during the experiment.

In the *in situ* pH sensor assembly used by Ben-Yaakov and Ruth (1974), a d.c. amplifier of novel design was used, incorporating an FET transistor as its input stage. The FET transistor Type AD 832 (Analog Devices, Norwood, Mass., USA) had an input bias current of  $10^{-13} \text{ A}$  at room temperature (lower at low temperatures) and an input offset voltage drift of  $40 \mu\text{V}^\circ\text{C}^{-1}$ . The *in situ* glass electrode (Sensorex Inc., Irvine, Calif., USA) was fabricated from a low-resistance glass and had a large area to decrease further the internal resistance. The resistance of a typical electrode was less than  $10^7 \Omega$  at room temperature. Assuming again a  $20^\circ\text{C}$  temperature range and a ten-fold increase in the resistance of the glass electrode, the d.c. errors contributed by the input bias current and input offset voltage drift are  $[I_{\text{B}}R_{\text{p}}]$  0.01 mV and  $[(dV_{\text{os}}/dt) \cdot \Delta t]$  0.8 mV, respectively. The largest error was therefore contributed by the input voltage drift with temperature. Assuming an ideal response for the glass electrode, the corresponding pH error at  $4^\circ\text{C}$  would be approximately 0.8/50, i.e. about 0.016 pH unit. The actual experimental error was further reduced by measuring the input offset voltage of the amplifier at the *in situ* conditions (Ben-Yaakov and Kaplan, 1973). This was accomplished by adding two relays at the input of the d.c. amplifier (Figure 4), one in parallel to the input (A) and the other in series with the pH electrode lead (B). During pH measurements the contacts of relay A were open while those of relay B were closed. To measure the

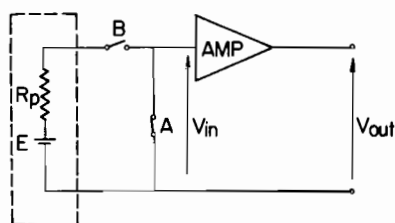


Figure 4. Relay arrangement for measuring the input offset voltage of amplifier AMP under *in situ* conditions. After Ben-Yaakov and Kaplan (1973)

amplifier's drift, the contacts of relay A were closed and those of B opened and the voltage at the amplifier's output was recorded. This voltage was later subtracted from the output voltage obtained during pH measurement (when relay A is open and B closed), resulting in an offset free value. The relays were special dry reed relays (Compac Inc., Series 10-1A-HIR) with an insulation resistance of  $10^{15} \Omega$ . This high resistance is required to prevent signal attenuation due to leakage to earth and across contacts when the relay contacts are open. These points will be further discussed below.

The specific examples given above illustrate some of the difficulties encountered when designing a signal conditioner for *in situ* ion-selective electrode studies. However, once the characteristics of the electrochemical sensor are defined in electronic engineering terms, electronic components are usually available off the shelf to meet the requirements set by the investigators. The selection of a specific amplifier to be used often involves a trade-off between a large number of parameters, such as electrical specifications, size, price, availability, reliability, power supply requirements, and power drain. Recent advances in electronic technology have made possible the manufacture of small and inexpensive high input impedance and low input bias current amplifiers. For example, modern microelectronic technology has made possible the fabrication of inexpensive monolithic operational amplifiers with a MOSFET (metal oxide field effect transistor) front end having a very low input bias current, e.g. RCA CA3130 with a typical input bias current of  $5 \times 10^{-12}$  A. The present price of these devices is less than one twentieth of the price of a device with similar electrical characteristics available a decade ago. It is thus evident that *in situ* marine electrochemical studies are in no way limited by the electronics. Furthermore, one can safely speculate that future *in situ* studies will be easier to design and less expensive, at least as far as electronic instrumentation is concerned.

### 3.2.2. *In situ* signal processing

Since the response of marine electrochemical sensors is, in general, a function of temperature and pressure, the ambient conditions must be

known for a proper interpretation of *in situ* measurements. As discussed by Brown (1968a), it is possible to transmit (or record) either the raw data or data that have been compensated for pressure and temperature effects.

In the latter approach, the output signals of the pressure and temperature transducers and the electrochemical sensor are combined so as to generate an electrical signal which can be directly calibrated in the appropriate physical units for the measured parameter. For example, conductivity, temperature, and pressure signals can be combined to produce a salinity signal (Brown, 1968b; see Chapter 5). This approach not only produces a signal that can be directly calibrated in the desired units, but may also considerably simplify the accuracy requirements of the telemetry (or recording) devices. Brown (1968a) has shown that, if conductivity, temperature and pressure are transmitted or recorded separately, the following accuracies must be maintained in order to retain an accuracy of 0.02‰ in salinity: conductivity, 0.025%; temperature, 0.033%; and depth, 0.4%. This estimate assumes a mean salinity of 35‰, a temperature range of 0–35°C, and a depth range of 0–6000 m. Since the oceanic salinity range is 30–40‰, 0.02‰ accuracy represents 0.05% of full-scale. Hence, the accuracy requirements of the data link are less stringent if the combined (salinity) signal is transmitted/recorded. These considerations and, of course, the convenience of handling signals which are directly calibrated in physical units has encouraged investigators to explore various methods for *in situ* compensation. Hamon (1956), Brown and Hamon (1961), and Brown (1968b) described methods for conductivity to salinity conversion and Briggs and Viney (1964) discussed a temperature-compensated electrode for oxygen measurements. The basic approach of *in situ* compensation will be discussed here in further detail by describing the method used by the author in the design of a temperature-compensated dissolved oxygen (DO) sensor (see also Chapter 9).

#### *Automatic temperature compensation of DO sensors*

Membrane-covered polarographic sensors (Clark *et al.*, 1953; Hoare, 1968) have been successfully applied in oceanographic and limnological studies (Van Landingham and Greene, 1971; Lambert *et al.*, 1973). These sensors are usually referred to as membrane-covered polarographic electrodes, although the method is clearly amperometry rather than polarography (see Chapter 2). Atwood *et al.* (1977) found that present technology and calibration procedures are inadequate to permit the use of polarographic oxygen electrodes for the determination of dissolved oxygen in discrete samples on board ship. They pointed out, however, that *in situ* oxygen probes are clearly useful since they give a continuous profile of dissolved oxygen *versus* depth. It was suggested that absolute calibration



could be accomplished by simultaneously collecting discrete samples and analysing them by Winkler titration (Carpenter, 1965).

A major source of error in the membrane-covered polarographic sensor is its extremely high sensitivity to temperature (about a 5% change in current sensitivity per degree Celsius). As discussed by Mancy *et al.* (1962), the sensor's current,  $I_T$ , as a function of concentration,  $c$ , and temperature,  $T$  (K), can be represented by

$$I_T = K_0 c e^{-J/T} \quad (4)$$

where  $J$  and  $K_0$  are constants for a particular sensor geometry and membrane (Pijanowski, 1975). The exponential temperature relationship is due to the temperature dependence of gas permeation through the thin plastic film which follows the activation energy relationship (Lebovits, 1966). Mancy *et al.* (1962) pointed out that a single fixed thermistor cannot offer adequate temperature compensation due to the variability in membrane permeability from one batch to another and due to possible variations in the degree of stretching during mounting. Nevertheless, in a number of applications where less accurate results are acceptable (Lambert *et al.*, 1973; Atwood *et al.*, 1977), automatic temperature compensation may be highly desirable.

Following the general diagram of Figure 1, temperature compensation can be accomplished by feeding the sensor's signal to a signal processing unit which multiplies the signal by the reciprocal of the temperature dependence function. For the case under consideration, the transfer function of the signal processing unit should follow the function  $f(T)$ :

$$f(T) = K_F e^{J/T} \quad (5)$$

where  $K_F$  and  $J$  are constants. As pointed out by Briggs and Viney (1964), this correction can be accomplished by incorporating a thermistor in a feedback loop as shown in Figure 5a. The output voltage of the amplifier

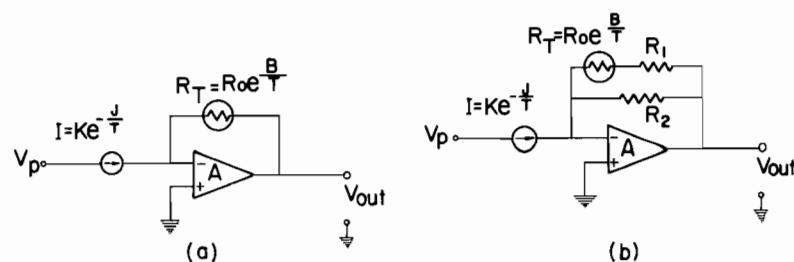


Figure 5. Schematic representation of an automatic temperature compensator for DO sensor. A is an operational amplifier,  $V_p$  is the polarization potential, and  $R_T$  is a thermistor. (a) Direct thermistor compensation; (b) improved compensator

will be (Burr Brown, 1971)

$$V_{\text{out}} = -R_T K_0 c e^{J/T} \quad (6)$$

where  $R_T$  is the thermistor resistance.

Fortunately, the temperature dependence of the thermistor's resistance is of the form (Fenwal, 1976)

$$R_T = R_0 e^{B/T} \quad (7)$$

where  $R_0$  and  $B$  are constants. Substituting  $R_T$  in equation 6 we obtain

$$V_0 = -K_0 c e^{(B-J)/T} \quad (8)$$

If  $B$  is now chosen to be equal in magnitude to  $J$ ,  $V_0$  will be independent of temperature. However, good compensation can be achieved only if one is successful in finding a commercial thermistor with the desired  $B$  value. If such a thermistor is not commercially available one can still obtain good temperature compensation by replacing the single thermistor by a network (Figure 5). A method for selecting the resistors  $R_1$  and  $R_2$  in the network was described by Hamon (1956) and is based on a three-point fit. This approach is demonstrated in Figure 6, which summarizes experimental

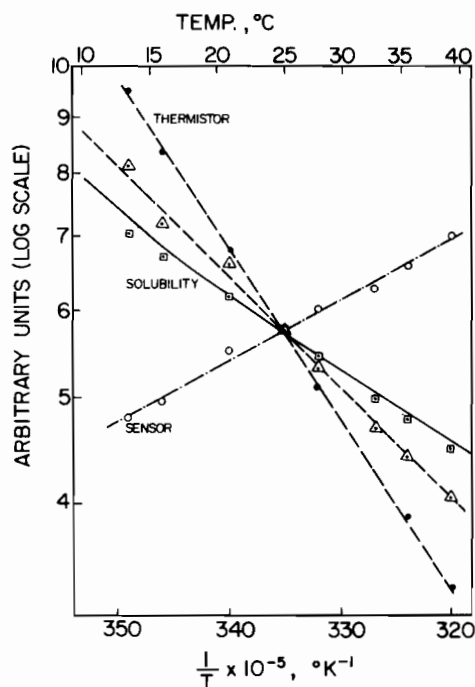


Figure 6. The response of an uncompensated DO sensor (open circles), after direct thermistor compensation (triangles), and after improved compensation (squares). The solid line represents the solubility of  $O_2$  in water and the broken line the resistance of the thermistor (YSI 4006)

results for a specific DO sensor (Model S4022, MBK Instruments and Controls Ltd., Beer Sheva, Israel).

As pointed out by Mancy *et al.* (1962), the response of a membrane-covered polarographic sensor is sensitive to salinity. This stems from the fact that the sensor responds to the activity (i.e. to the partial pressure) of  $O_2$  rather than to its concentration. Hence, if the sensor's output is to be calibrated in concentration units one has to take into consideration the activity coefficient of molecular oxygen in solution, that is, the salt effect on the solubility of oxygen at a constant partial pressure of oxygen. Although automatic salinity compensation is theoretically possible, it would be complicated to achieve, especially if universal compensation is attempted. The salt effect is a function of the ionic composition of the salt and hence every solution would require a special compensation scheme. Compensation for sea water and diluted sea water (estuaries) can be accomplished by taking advantage of the fixed relative chemical composition of the world oceans (Chapter 1).

Manual salinity compensation for DO measurements in sea water and diluted sea water can be easily accomplished by feeding the sensor's signal to a variable gain amplifier, as shown schematically in Figure 7. A is an operational amplifier,  $R_{in}$  and  $R_1$  are fixed resistors and  $R_s$  is a variable resistor. The overall gain of the amplifier is

$$\frac{V_{out}}{V_{in}} = -\frac{R_s + R_1}{R_{in}}$$

The scale of  $R_s$  could now be marked in salinity units to give the appropriate overall gain. This compensation scheme (which can be found on a number of commercially available instruments) could be made accurate for a given salinity for one temperature. The salt effect, in general, is temperature dependent, whereas the compensation scheme of Figure 7 assumes a constant salinity dependence. For sea water, the solubility  $c$  [in ml(STP)  $dm^{-3}$ ] can be expressed as (Weiss, 1970)

$$\begin{aligned} \ln c = & A_1 + A_2(100/T) + A_3 \ln (T/100) + A_4(T/100)^2 \\ & + S[B_1 + B_2(T/100) + B_3(T/100)^2] \end{aligned}$$

where the  $A_s$  and  $B_s$  are experimentally determined constants (Appendix,

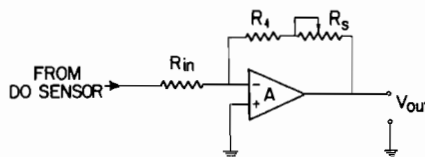


Figure 7. Salinity compensator for DO sensor. The  $R_s$  scale is marked in salinity units

Table X) and  $S$  is the salinity (‰). It is evident that, due to the cross-term factors, a temperature-independent salinity compensation is only a first-order approximation. This could be overcome by providing  $R_s$  with a different salinity scale for each temperature (Figure 7).

The purpose of the foregoing discussion was to illustrate some of the instrumentation problems that need to be handled when attempting to compensate the output of marine electrochemical sensors. High-precision electroanalytical studies should be conducted at constant temperature and pressure. Such ideal conditions may be realized in the analytical laboratory, but seldom on-site and practically never *in situ*. When variable conditions are encountered one has to weigh the pros and cons of automatic signal compensation. To date, salinometers are the only commercially available instruments which truly accomplish high-precision compensation for temperature and pressure (Brown, 1968b). This has been possible simply because modern conductivity cells are remarkably linear and stable (see Chapter 5). Indeed, the stability of the sensor is the single most important factor when considering automatic signal compensation. Efforts to develop a high-precision compensator are warranted only when it is possible to achieve a high overall accuracy. In other cases, such as the DO sensor, a less accurate compensation scheme may be acceptable because the sensor itself is subject to many errors. The constant improvement in reliability and stability of electrochemical sensors for marine studies will eventually justify comprehensive studies of various automatic compensation schemes to suit particular applications.

### 3.3. EARTHING, SHIELDING, AND INSULATING

Special attention must be paid to the electrical earthing of *in situ* marine electrochemical instrumentation to avoid spurious errors due to noise and electrical leakage. The problem is especially severe when line transmission is used between a submersible unit and a surface unit. As an example of the problems that may arise, consider an *in situ* pH sensor housed in a pressure housing and linked to the surface via a coaxial cable (Figure 8). In conventional designs of pH meters, the reference electrode lead (point E in Figure 8) is the ground of the electronic circuitry. To provide efficient shielding of electrical noise it is desirable to earth the case, i.e. to provide a galvanic path between the case and the electronic earth. However, direct connection of point E (Figure 8) to the case is not possible as it would short out the reference electrode (via  $E_R$ , sea water and  $E_H$  in Figure 8). An alternative approach would be to connect a relatively large capacitor (say  $1 \mu\text{F}$ ) between the case and point E so as to earth the case with respect to a.c. signals but to block the d.c. path. If this approach is selected then utmost caution must be exercised to avoid electrical leakage between any part of

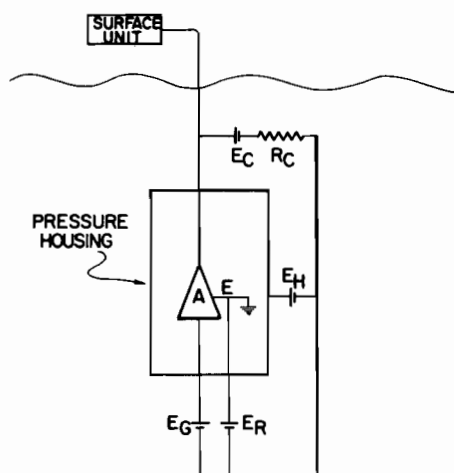


Figure 8. Electrical equivalent circuit of an *in situ* pH meter. A is an amplifier,  $E_G$  represents the glass electrode,  $E_R$  the reference electrode,  $E_H$  the casing to sea water half-cell,  $R_C$  the cable leakage to sea water, and  $E_C$  the cable to sea water half-cell. The heavy line signifies conductance via sea water

the electrical system and sea water. Any path such as wire-to-sea water leakage ( $R_C$  in Figure 8) will load the reference electrode and may cause large errors due to polarization. The same precautions must be taken with respect to the surface unit. It is thus evident that a straightforward approach in which the electrical cable has a galvanic path to the electrochemical cell is not recommended as, sooner or later, it will cause spurious errors.

Two approaches have been used in the past to overcome the problem of possible polarization of the reference electrode due to cable leakage. One approach is based on transformer coupling and a second on the use of a differential amplifier. The latter will be discussed below in connection with the design of the UCLA Deep Sea Probe.

The transformer coupling approach has been used by Ben-Yaakov and Kaplan (1968b) in the design of an *in situ* probe which measured temperature, pH, and depth (pressure). The probe included the sensors, signal conditioners (but no signal processing), a voltage to frequency converter (to be discussed later) and a battery pack. The data were transmitted to the surface via a two-conductor cable, which was also used to relay electrical commands from the surface to the *in situ* unit and for mechanical support. The signals were time multiplexed by a stepping relay and the frequency signals were sent one at a time to the surface. The command to advance the stepping relay was sent from the surface so that the operator on board ship could select any one of the probe's channels. The operator could also send a command to short out the electrometer input and thus measure the voltage

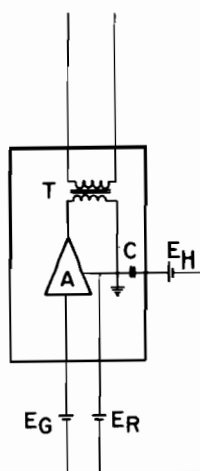


Figure 9. Earthing arrangement in the *in situ* pH probe of Ben-Yaakov and Kaplan (1968b). The reference electrode was earthed and the housing was a.c. earthed via capacitor C. The inner electronics were galvanically insulated from the cable by the transformer T

offset of the d.c. amplifier under *in situ* conditions (see Section 3.2.1). To avoid the problem of possible polarization of the reference electrode due to cable leakage, a transformer coupling was used to insulate (in the galvanic sense) the inner electronics circuitry from the cable-sea water system. As shown schematically in Figure 9, the reference electrode was earthed and the stainless steel pressure housing was a.c. earthed via capacitor C. A transformer was then used to insulate galvanically the electrical cable-sea water system from the probe's electronics. Hence, even if the cable developed a leakage to sea water (which it did), the probe's electronics and hence the reference electrode had no galvanic path to sea water, owing to the insulation between the primary and secondary windings of the transformer. It is obvious that this scheme can be used only if the signal is converted to a form which can be transmitted via transformers. In the particular design of Ben-Yaakov and Kaplan (1968b) frequency modulation was used, i.e. the analog signal was represented by a pulse train whose frequency was linearly proportional to the analog signal (Ben-Yaakov, 1968). A transformer was therefore an adequate coupling device for the converted signal. The general problems of data modulation will be discussed below in detail.

To improve further the electrical shielding and earthing in an *in situ* marine electrochemical probe, Ben-Yaakov and Ruth (1974) used a differential amplifier for the signal conditioner of a pH-reference electrode pair. In this case the electronics earth is connected directly to the pressure

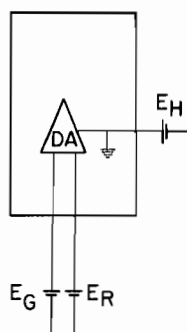


Figure 10. Earthing arrangement in the *in situ* probe described by Ben-Yaakov and Ruth (1974). DA is a differential amplifier having two high-impedance, low-current inputs

housing (Figure 10). This arrangement not only improves electrostatic shielding but also eliminates possible polarization of the reference electrode due to leakage. However, when using differential amplifiers one must pay special attention to the problem of common mode input voltage (Burr Brown, 1971). The common mode input voltage is defined as the voltage between the inputs of the differential amplifier and its earth. This voltage must be kept within a given range for proper operation. As can be seen in Figure 10, the common mode input voltage of the differential amplifier is a function of the potential of the housing–sea water half-cell ( $E_H$ ). It was found that this potential will normally be below 1 V, which is acceptable for practical amplifiers. However, when the probe is not completely immersed, the galvanic path between the electrodes and the electronic earth is lost even if the electrodes are soaked in a buffer held in a beaker. This breaks the path of the amplifier's input bias current, however small, and will cause a malfunction of the differential amplifier. Hence, calibration of the pH electrode when the probe is not completely immersed could be performed only after providing a galvanic path between the probe's housing and the buffer solution. This was usually accomplished by connecting an electrical wire to the housing and immersing its bare end in the buffer.

An additional problem that requires considerable attention when designing *in situ* marine electrochemical instrumentation is the problem of d.c. insulation to prevent electrical leakage. This problem is especially important when high resistance electrodes, such as glass electrodes, are used.

*In situ* marine electrochemical instrumentation is prone to surface leakage problems due to the humid and salty air on board ship. Whenever the housing is opened, for battery replacement, etc., the electronics circuitry is exposed to the ambient corrosive atmosphere. Special precautions must therefore be taken in the selection of components and their layout when

designing the electronics of an *in situ* probe which incorporates high-resistance electrodes. This dictates the use of PTFE-insulated wires and cables, PTFE-insulated stand-offs, guard techniques for shielded cable, and the application of silicone grease to all critical surfaces. These are standard techniques which have proved to be helpful in preventing signal attenuation due to poor insulation and surface leakage.

Another problem area is lead penetration to the high-pressure housing. To provide proper insulation, the wire-to-body resistance of the feedthroughs must be at least two (but preferably three or four) orders of magnitude higher than the internal resistance of the sensor under the worst operating conditions. For low to moderate resistance glass electrodes (*ca.*  $10^8 \Omega$ ) the wire-to-body resistance of the feedthrough should be at least  $10^{11} \Omega$ . Ben-Yaakov and Kaplan (1968a) have described the design of a high-pressure, high-resistance feedthrough that was found to function satisfactorily to an ocean depth of 6000 m.

The inlet was built around a Swagelok (Crawford Fitting Co., Solon, Ohio, USA) Type 201-A-OR stainless-steel pipe fitting and consisted of a platinum wire sealed into glass and cemented with epoxy to the pipe fitting (see also Chapter 6).

### 3.4. *IN SITU* DATA ACQUISITION

Three methods have been used in the past for the acquisition of data from *in situ* marine electrochemical probes: direct reading by a diver, line transmission and *in situ* recording. Direct reading by a diver (Conti and Wilde, 1972) is practical only for shallow water studies and for very small volumes of data. The use of line transmission enables the on-board operator to look at the data in real time. This may have an advantage if an attempt is made to locate special features, for example when probing the sediment-water interface (Whitfield, 1971). For deep sea studies, line transmission is possible only if the research vessel is equipped with the proper equipment, i.e. an electrical cable winch. Another possible approach is the use of expendable probes which are lowered by a very thin electrical wire (Jeter *et al.*, 1972). This approach, however, is clearly applicable only to very special marine electrochemical sensors intended for routine use, which will make possible high-volume, low-cost production.

Design details of marine electrochemical *in situ* probes employing line transmission have been given by Hamon (1956) and Ben-Yaakov and Kaplan (1968b). In both cases frequency modulation—rather than direct transmission of analog signals—was employed. The latter is not practical owing to unpredictable cable attenuation which introduces large errors when cables longer than a few hundred metres are used. Also, as discussed earlier,



direct transmission of analog signals may cause polarization of the reference electrode for certain earthing schemes. It is thus evident that frequency modulation has a distinct advantage over direct analog transmission.

Hamon (1956) and Hamon and Brown (1958) described an *in situ* salinometer which incorporated an FM (frequency-modulated) oscillator. The conductivity bridge and a thermistor were part of the oscillator so that the frequency of oscillation was a linear function of salinity. In subsequent studies, Brown (1968b) developed a very precise FM subcarrier oscillator whose frequency is a linear function of salinity corrected not only for temperature but also for *in situ* pressure. A different approach was taken by Ben-Yaakov and Kaplan (1968b). They first obtained an analog signal and then converted it to a proportional signal using a linear analog-to-frequency converter (Ben-Yaakov, 1968). This approach is readily applicable to electrochemical sensors such as ion-selective electrodes, whereas integration of the sensor into the oscillator circuit is adaptable only to sensors that can be incorporated into a transfer-function type network.

If several parameters are measured by an *in situ* probe, data can still be sent along a single transmission channel by using time multiplexing or frequency multiplexing. When using time multiplexing (Ben-Yaakov and Kaplan, 1968b) only one data channel is available at a time. While this simplifies the shipboard electronics it may require more time for data collection. Frequency multiplexing, on the other hand, requires more elaborate shipboard electronics but is faster as all channels are transmitted simultaneously.

A more advanced system for transmission of electrochemical data from an *in situ* probe has been described by Brown (1974). The system used pulse code modulation (PCM), which has several advantages over frequency modulation. Here the information is already coded in a digital form so it can be directly displayed on digital readouts, fed to a digital computer, or stored on digital tapes and other digital storage devices. Using standard digital techniques one can scan the data at a very high rate, if required. The system described by Brown (1974) made a complete high resolution scan (16 bits) of three sensors within 30 ms.

Apart from transmitting the data themselves, the transmission line can also be used to test the performance and even calibrate the probe *in situ*. The *in situ* probe described by Ben-Yaakov and Kaplan (1968b) included several self-check data channels. Apart from checking the battery voltage and the stability of the voltage regulator, the system was capable of performing a calibration of the analog-to-frequency converter. This was achieved by recording the output frequency of the converter when it was fed by two highly stable voltages. The entire calibration curve could then be drawn by passing a straight line between the two points, taking advantage of

the good linearity of the analog-to-frequency converter (Ben-Yaakov, 1968). Another calibration that could be performed *in situ* was the determination of the input offset voltage of the electrometer, by shorting its input with a high insulation resistance reed relay. The frequency reading for the shorted input was later subtracted from the frequency reading of the pH electrode signal, thereby obtaining a drift-free measurement.

When an electrical cable is not available, *in situ* recording must be employed. Ben-Yaakov and Kaplan (1971b) described an *in situ* marine electrochemical probe which included a magnetic tape recorder. The *in situ* recorder was designed around an entertainment-type tape recorder using a novel, digital recording technique (Ben-Yaakov, 1968b). Based on the original design and experience gained in many cruises, the recording system was redesigned using a specially constructed two-channel digital tape deck and associated electronics. Details of the newer design are given in Section 3.5.

The amount of data collected by a multi-parameter *in situ* probe can be too large to handle manually. For example, the *in situ* probe described by Ben-Yaakov and Kaplan (1971b) and Ben-Yaakov (1970) recorded data at a rate of 1 channel per 5 s and had a capacity of 8 h of continuous operation. The total number of data points per tape reel therefore exceeded 11 000 data points or 22 000 numbers, as each datum was recorded twice to increase reliability by redundancy. It is obvious that this amount of data could not be handled manually, especially since extensive data reduction was required (Ben-Yaakov, 1970). The system described by Ben-Yaakov and Kaplan (1968b) and Ben-Yaakov (1970) used a two-step data reduction scheme. First the magnetic tape was read into a PDP-8/L minicomputer which was used to prepare an edited perforated paper tape. The paper tape was then read back into the minicomputer and the data were processed by a FOCAL program. The processed data were finally printed out in a tabular form by a teletype which was also used as a plotter to present some of the data in a graphical form. A more sophisticated data reduction scheme was employed in the newer instrumentation system described in Section 3.5.

An important feature of the system described by Ben-Yaakov and Kaplan (1970) is the possibility of looking at the raw data as soon as the deep sea probe was brought back on board ship. From a practical point of view this feature is essential considering the vulnerability of oceanographic instruments and the very high cost of shiptime operation. The option of looking at the data as soon as the probe is recovered enables the investigator to base his operational decisions on the quality of the data obtained. Ideally, one should have the tools to process the data on board ship. The 'poor man's' solution would be to print out part of the raw data on a slow digital printer as soon as the probe returns from its journey.

As more marine electrochemical sensors are developed and refined, the

need for reliable *in situ* data acquisition systems will increase. A number of companies are at present involved in the field of data acquisition and one can safely assume that a large variety of reliable systems will be commercially available in the future. It is also probably safe to assume that one will be able to adapt some of these systems to *in situ* marine electrochemical studies.

### 3.5. A DESIGN EXAMPLE: UCLA DEEP SEA PROBE

The deep sea probe described in this section was developed during an oceanographic research programme conducted at UCLA in collaboration with Professor I. R. Kaplan. The engineering activity of the programme was initiated in 1967 and was aimed at the development of a high-pressure pH electrode and associated electronic circuitry for *in situ* oceanographic studies (Ben-Yaakov and Kaplan, 1968a-c). Subsequently an *in situ* recorder was incorporated in the system and it was used to study the carbonate system in the oceans (Ben-Yaakov and Kaplan, 1971a,b). The field experience gained with the instrumentation system was then used to design the Deep Sea Probe (DSP) and associated surface units described here. Actual construction of the new system was completed in late 1972. The probe was then used in a number of studies to a maximum depth of 6000 m. A modified version of the probe was constructed for the GEOSECS programme and used in a number of GEOSECS profiles.

The UCLA system is composed of two major subsystems, the DSP and a data reader (DR). The function of the probe is to sample the input signal from *in situ* sensors, to digitize the signals, to record the data on a magnetic tape cassette, and/or to feed the digitized information to a telemetry line. The function of the DR is to read out the information recorded on the magnetic tape by the *in situ* probe. However, the DR can also be used to monitor the function of the probe. That is, when the DR is interconnected to the probe, it will read out and display the information recorded by the probe. Furthermore, the DR is capable of controlling, through the interconnecting lines, the function of the probe. This feature enables one to check out completely the operation of the DSP just before lowering it into the ocean.

The information read off the magnetic tape by the DR is displayed on a LED display and is also available through the pins of an output connector. The information retrieved is then fed to a PDP-8/L minicomputer or transferred to a multitrack computer-compatible magnetic tape for further data processing.

#### 3.5.1. Deep Sea Probe

The DSP consists of sensors, signal conditioners, analog multiplexer and digitizer, and a digital cassette recorder. A general view of the DSP with the

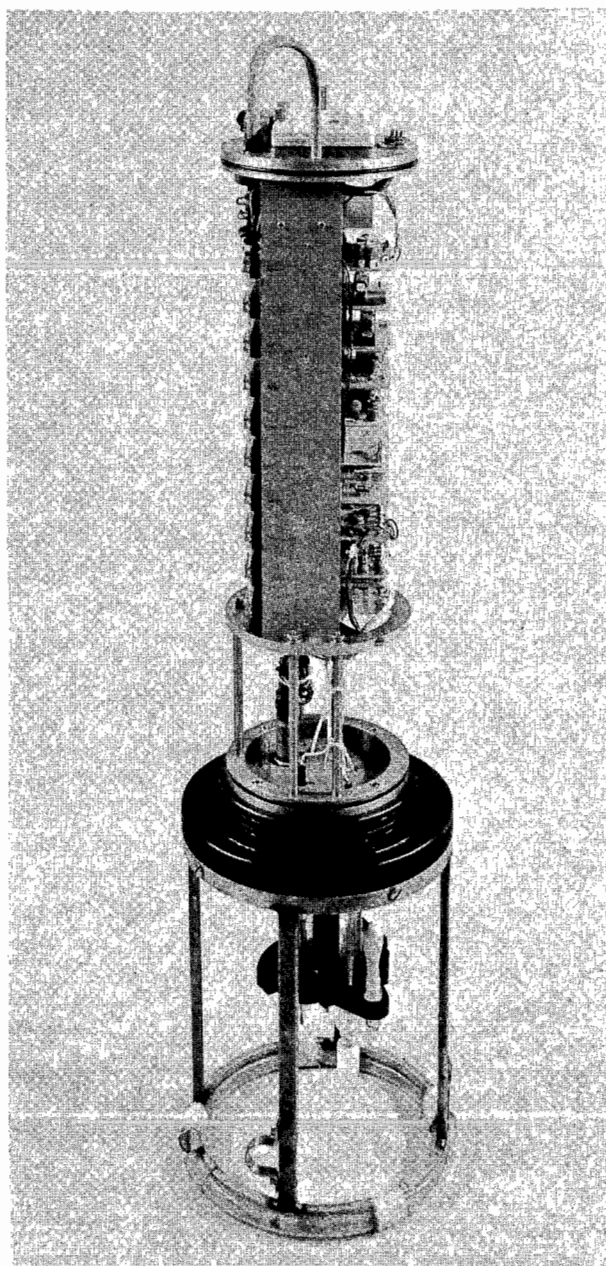


Figure 11. The UCLA Deep Sea Probe with pressure housing removed. The sensors are located at the bottom and the digital cassette deck is at the top

pressure housing removed is given in Figure 11. The sensors are located at the bottom and the digital magnetic cassette deck is at the top. As can be seen, the electronics are constructed on square printed circuit boards of about  $10 \times 10$  cm.

The data acquisition system of the DSP was designed to record up to 16 channels of data on a standard cassette (Figure 12). The system accepts analog or digital inputs and records digital information on the magnetic tape cassette. Analog signals are digitized by an integrating digitizer.

By setting self-contained printed circuit switches, the data acquisition can be programmed to operate in one of three modes: (i) continuous operation; (ii) on/off mode; and (iii) a single scan mode. When in standby condition all subassemblies except the clock are turned off, thereby reducing the current drain to an extremely low value ( $50 \mu\text{A}$ ).

Digitization is accomplished by an integrating bi-polar analogue-to-digital (A/D) converter. The relatively long integration period (approximately 0.5 s) ensures reliable conversion even of noisy signals. The digitized data are recorded serially in a true digital form on a standard (Philips) cassette. Two-channel recording provides high reliability and independence of tape speed. A total of 16 bits are recorded for each channel including synchronization and sign bits. A separate synchronization signal is recorded at the beginning of each scan. Tape movement is controlled by a single gearhead motor driving the take-up reel of the cassette. No capstan or pressure rollers are used.

In the original design, the DSP incorporated the following sensors: a thermistor, a pressure transducer, a reference electrode, and three pH electrodes. A single differential high-impedance amplifier (Ben-Yaakov and Ruth, 1974), was used to service the three glass electrodes. Connection of the electrodes to the amplifier were made via high insulation type dry reed relays. A fourth relay was used for checking the input offset voltage of the amplifier.

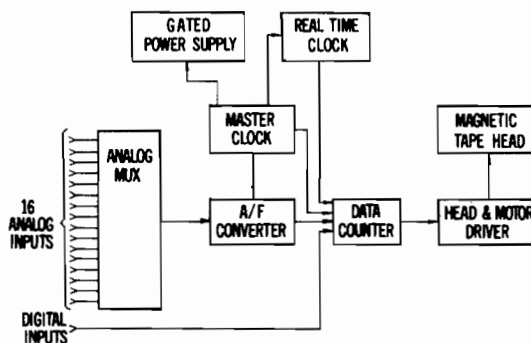


Figure 12. Block diagram of the data acquisition portion of the UCLA Deep Sea Probe

In most of the studies the DSP was used as an autonomous unit and lowered by a regular hydrographic cable. In a number of studies the DSP was used to conduct *in situ* experiments for periods of more than 10 h. During all this time data were continuously recorded on the cassette *in situ*. To facilitate operation with an electrical cable and thus permit examination of the collected data in real time, an interface unit was developed. The interface unit uses an optical coupler to avoid the problem of earth loops and possible polarization of the reference electrode (see Section 3.3).

### 3.5.2. Data reduction

Two methods have been used to process the data of the DSP: (a) direct processing by a minicomputer and (b) translation to an IBM compatible digital magnetic tape and reduction by the computer facility at UCLA (Figure 13). The first method was found to be satisfactory for moderate data loads. It has the advantage of in-house operation and is the least expensive, neglecting the original expense of acquiring the minicomputer. Unfortunately, data reduction by a minicomputer is a slow process and is not suitable for handling large masses of data. The bottleneck of the operation is the teletype (ASR 33) used as an output device. This problem was overcome by developing a hardware–software package that facilitates processing by a large computer installation.

A procedure was developed to transfer the data from the cassette to a 7-track IBM compatible format. The transfer of the data from the cassette to the 7-track tape was carried out by the minicomputer under the control of a program written in SYMBOLIC language. The program reads the data from the DR, codes it to IBM format, and transmits it to the 7-track recorder. The program also arranges the data in files and initiates record and file gap formats. Once transferred to the 7-track recorder the data were

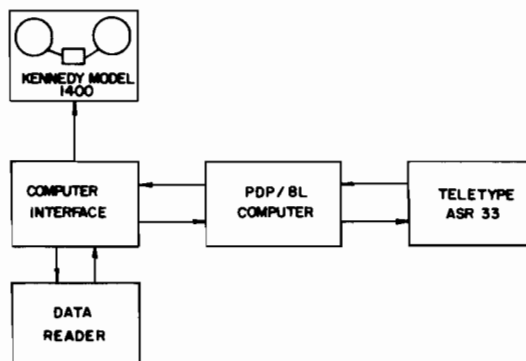


Figure 13. Block diagram of the data reduction system of the UCLA Deep Sea Probe

available in a format that could be handled by a large computer installation. Final data reduction was achieved by a FORTRAN IV program.

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