

## Measurement of the apparent pH of seawater with a combination microelectrode<sup>1</sup>

**Abstract**—A method for precisely measuring the apparent pH of seawater, using a microelectrode and a specially designed cell, is described. The cell requires a 25-ml sample, reaches equilibrium in 6 min or less, and its precision in routine use at sea was  $\pm 0.0026$  pH units.

Although the "apparent" (Park 1968) pH of seawater is measured routinely, precision is generally poor because many electrode systems fail to achieve constant junction and asymmetry potentials during a series of determinations, CO<sub>2</sub> is exchanged with the atmosphere, and often temperature is not constant. Commonly, precise pH measurements have been regarded as the province of skilled specialists (Pytkowicz et al. 1966; Park 1966; Culberson and Pytkowicz 1970; Takahashi et al. 1970) and are not included with the customary hydrographic determinations, even though much chemical and biological information can be obtained from pH-alkalinity-O<sub>2</sub> (AOU) data.

During the course of a 3-year study of the O<sub>2</sub>-minimum zone in the eastern tropical Pacific Ocean, I used a microelectrode with a specially designed cell and developed a technique which gave highly reproducible pH values in routine use at sea.

I wish to thank R. S. Keir and S. Yamamoto for their contributions to this project.

An Orion model 801 digital pH meter and a No. 476055 Corning combination microelectrode with Ag/AgCl reference (with ceramic junction) were used.

The pH cell (Fig. 1) resembles a water-jacketed volumetric flask. There are four openings: the first accommodates the electrode, which is tightly seated by a piece of surgical rubber tubing; the second juts out into a nipple and seats a rubber septum. The two remaining ports are the overflow, through a 1-mm capillary, and the cell drainage, both ports equipped with Teflon

stopcocks. The volume of the cell is about 25 ml.

Before use, the electrode is kept in deionized water or buffer solution. All measurements are made at constant temperature and with stirred solutions. Seawater samples are collected with 50-ml glass syringes from septum-fitted PVC hydrographic bottles; the syringe cannulas are then capped with a rubber stopper and the samples are stored under water until analysis. This procedure is similar to that used by C. Culberson (*see* Takahashi et al. 1970) except that the samples are brought to constant temperature in the cell at the time of analysis. Before determination of seawater samples, the electrode response is calibrated with buffers at pH 4 and 7. Equilibrium is assumed when the rate of change of the cell potential is 0.1 mV 10 min<sup>-1</sup>. Beckman buffers numbered 14054 (pH = 4.008 at 25°C), 135229 (pH = 7.413 at 25°C), and 3007 (pH = 7.00 at 25°C) were used. The pH 7.00 buffer was treated as 7.000 for calculation. The linearity of the electrode response between pH 4 and 9 was often checked at 25°C in the laboratory and at sea with the pH = 4.008 buffer and a pH = 9.18 buffer (Beckman No. 14049). Figure 2 combines two such calibrations made at sea during the MINOX II expedition.

Following calibration, a seawater sample is injected into the cell, left for about 15 min, and discarded. A fresh seawater sample is then slowly injected into the cell and allowed to overflow through the capillary. The stopcock is closed, the sample equilibrated for about 6 min, and the cell potential recorded. The sample generally reaches thermal and chemical equilibrium with the electrode after 6 min; samples that have been stored at the temperature of analysis require less time. The remaining samples are processed in the same manner. The cell is then rinsed and filled with deionized water or dilute buffer.

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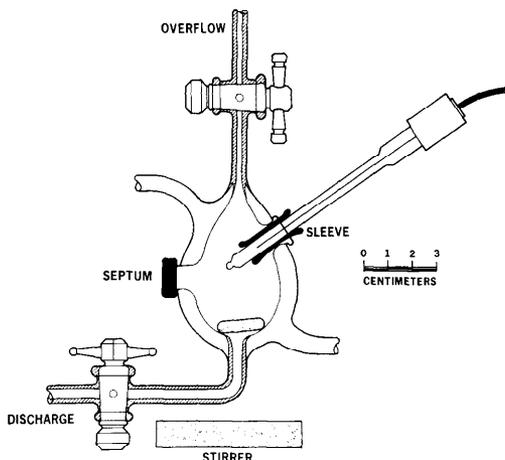


Fig. 1. Cell for the measurement of pH with a combination microelectrode.

The apparent pH can be calculated from the following:

$$\text{pH} = \frac{(E_{\text{cell}} - E_7)/(B_7 - B_4)}{(E_7 - E_4)} + B_7,$$

where  $E_{\text{cell}}$  = cell response with seawater;  $E_4$ ,  $E_7$  = cell response with pH 4 and 7 buffers; and  $B_7$ ,  $B_4$  = the standardized values of the buffer solutions, e.g. 7.413 and 4.008 at 25°C.

Measurements should be made on the millivolt scale against an internal reference. Use of the calibration knob to set the instrument to the buffer pH, and restandardizations during analysis, are discouraged. Buffer pH readings are not reproducible after the electrode has been exposed to seawater, since sea salts absorbed into the reference junction cause the reference potential to vary from its value in dilute media. Thus, the buffer potential cannot be reproduced until the sea salts have been rinsed out of the ceramic frit. For this system, the effect of sea salts on the asymmetry potential cannot be separated from their effect on the junction.

The calculated pH of stirred samples was 0.01 pH units greater than that for unstirred samples, because the pH 7 buffer gave values 0.3 mV higher (less negative) when stirred, while seawater samples in general gave values 0.3 mV more negative when

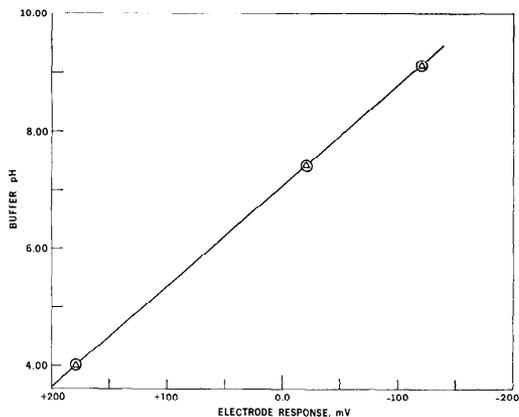


Fig. 2. Calibration of the microelectrode at 25°C at sea in the eastern tropical Pacific Ocean. Circles—3 March 1972; Triangles—11 March 1972.

stirred. The steady state junction potential after the electrode is transferred from buffer to seawater is achieved much more rapidly when the seawater is stirred. This observation is consistent with the view that the junction is acting as a "constrained diffusion boundary" (McInnes 1961). The effect of stirring was tested by storing replicate samples of seawater at  $25.00 \pm 0.02^\circ\text{C}$  and then measuring the pH at the same temperature under stirred and unstirred conditions. The cell potential was first observed for 6 min without stirring and then stirred for an additional 6 min. Unstirred samples reach the steady state pH value in about 1 h. The first stirred sample reaches an apparent steady state within 12 min, but this value is not reproducible. The second and following samples reach the steady state pH value within 2 min and are reproducible. Once the electrode has equilibrated, unstirred pH values are within 0.01 pH units of the stirred values.

Successively drawn and analyzed samples gave nearly identical pH values; for example, four samples of surface water analyzed aboard the RV *Alpha Helix* were within 0.002 pH units. However, a better measure of the precision of the method under field conditions was obtained during the MINOX III expedition of the Naval Undersea Center to the eastern tropical Pacific Ocean. In a series of casts, three

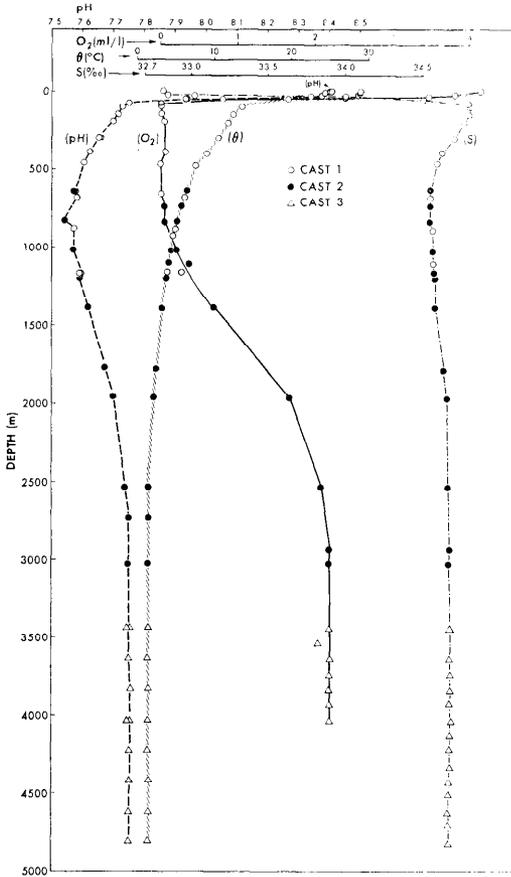


Fig. 3. pH at 25°C, dissolved oxygen ( $O_2$ ), potential temperature ( $\theta$ ), and salinity ( $S$ ) at 17°53'N and 103°55'W during 21–23 October 1973.

duplicate samples were drawn from the PVC hydrographic bottles and the pH was measured at 25°C in random order with another 15 samples from the cast. Forty replicate determinations were made over a period of about 3 weeks. All of the samples were measured within 7 h of surfacing. For all replicates, the average deviation from the individual mean was 0.0026 pH units, and 87% of the replicate pairs were within 0.004 pH units of the individual mean. This result compares favorably with the expected error of 0.003 pH units reported by Pytkowicz et al. (1966) for laboratory work and by Culberson (see Takahashi et al. 1970) for field determinations.

Another estimate of the day to day reliability and usefulness of pH measurements in routine hydrographic work is presented in Fig. 3. A station north of Acapulco was occupied for 2 days. Three casts were made; the electrode was recalibrated before each cast and pH measured along with other routine hydrographic determinations. For each cast, pH values overlapped and were within experimental error.

The pH vs. depth curve is also of interest because of the great difference in pH between the surface and the  $O_2$ -low zone. The high surface pH values are due to photosynthesis and loss of  $CO_2$  from the warmer surface layer. From 100 to 800 m the pH curve is shaped exactly like the potential temperature profile: this is because at essentially zero  $O_2$ , the pH profile reflects the amount of  $O_2$  available, which at constant salinity is directly related to the temperature of the water. A small pH minimum exists at 800 m; I do not know whether this is an artifact or whether it implies an additional source of oxygen.

Finally, the original oxygen data indicated two minima below 4,000 m. These might have been accepted as representative of natural phenomena. However, the lack of agreement between the pH and  $O_2$  suggested experimental errors, and discussions with the technician who made the  $O_2$  determinations confirmed this. The faulty data were therefore not included in the figure.

These results are of a precision similar to that obtained by Culberson (see Takahashi et al. 1970). The techniques differ in methodology and in the electrodes used. Before every series of measurements the reference junction is returned to its value in dilute solution, giving consistently reproducible numbers. The other option—maintaining a junction saturated with sea salts—was not adopted because a drift of potential was observed when the electrodes were transferred from seawater back to the buffer. Use of the combination microelectrode in conjunction with a thermostatically controlled, sealed cell permits close control

of experimental variables and precise measurements. The results of this work, and those of Culberson (*see* Takahashi et al. 1970), show that precise, routine field determinations of the apparent pH of seawater are attainable.

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## An evaluation of sediment trap methodology

*Abstract*—Five sediment traps with collecting areas ranging from 8 to 1,465 cm<sup>2</sup> collected the same amount of material, as measured by dry weight, ash weight, and phosphorus content, on a unit area basis. Variances from different size traps were not significantly different. These results are presented as further illustration that traps are a meaningful technique for measuring sedimentation in certain lakes.

Sediment traps afford a unique method of measuring the downward movement of materials within a lentic environment; they enable us to estimate loss of materials from the trophogenic zone or accumulation of materials in the sediments. However, despite their apparent utility sediment traps have not received the general acceptance that might be expected. One factor leading to the reluctance to use this method in quantitative studies is the suspicion that the rate of sediment accumulation in a trap does not necessarily equal that in a lake. Kleerekoper (1952) and Golterman (1973) have suggested that, by decreasing turbulence, sediment traps increase the sedimentation rate in their vicinity. Although the suggested effect is not supported by results

from studies of rain collectors (Bruce and Clark 1969), concern over the effects of turbulence seems justified.

One approach to evaluating the influence of turbulence on catching efficiency is to measure the catch per unit area for sediment traps with different collecting areas. The rationale for this type of experiment is that the effect of turbulence should be correlated with size of trap aperture: that is, if traps increase turbulence the catch per unit area should increase with increasing diameter, since larger traps would have a larger portion of their collecting area sufficiently distant from the circumference to minimize the effect of the turbulence which is presumably enhanced by the trap sides.

To date, five studies have dealt with the effect of trap size on catch. As Table 1 shows, these studies have resulted in contradictory conclusions. In addition, certain aspects of these studies limit their value. Pennington (1974) has shown that funnel traps are not suitable collectors and therefore studies based on this design must be discounted. Examination of the remaining data in Table 1 reveals that the trap size ranges used have all been rather narrow,