

High Pressure p_H Sensor for Oceanographic Applications*

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A high pressure p_H sensor has been developed and tested in the laboratory to a pressure of 150 kg/cm² and in the ocean to a depth of 270 m. The sensor is composed of specially designed glass membrane and reference electrodes. A pressure equalizing technique is used to prevent pressure gradients across the walls of the electrodes. Seawater buffer was used to calibrate the sensor for oceanographic application resulting in 0.02 p_H units reproducibility.

INTRODUCTION

It was demonstrated by Distéche¹ that a glass membrane electrode maintains its sensitivity to p_H at high hydrostatic pressure up to 1500 kg/cm². His experiments were carried out in the laboratory and at sea from the French Bathyscaphe *Archimede*.² A number of disadvantages limit the applicability of Distéche's assembly as an oceanographic and limnologic research tool, or as a practical sensor for continuous operation. His assembly is not portable in the true sense of the word. The complicated mechanical construction² requires careful transportation and handling. Since no salt bridge is used at the reference electrode, it is restricted to constant chloride activity solutions. Another drawback, also stated by Distéche, is that the electroplated Ag/AgCl electrodes—used both as a reference electrode and an internal reference in the glass electrode—have to be replaced after approximately one week of laboratory experiments. And finally, no method has been suggested by Distéche by which the measured electrochemical potentials can be converted to p_H reading at different temperatures.

The present p_H sensor was developed as part of an oceanographic *in situ* p_H meter,³ but its ruggedness and stability make it convenient for any high pressure measurements. It is composed of two electrodes, a silver-silver chloride reference electrode and a glass membrane electrode. In addition to the p_H sensor, a thermistor and a pressure transducer were incorporated to enable temperature and depth to be measured. The thermistor is a commercial glass probe (VECO, 32A1), and the depth sensor is a Bourdon tube-type potentiometric pressure transducer (Robinson-Halpern P61).

Figure 1 shows a photograph of the entire probe assembly.

REFERENCE ELECTRODE

Distéche^{2,4} and Culberson *et al.*⁵ have used electroplated silver-silver chloride reference electrodes for high pressure

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¹ A. Distéche, *Rev. Sci. Instr.* **30**, 474 (1959).

² A. Distéche, *Bull. Inst. Oceanog.* **64**, 1320 (1964).

³ S. Ben-Yaakov, "An Oceanographic *in situ* p_H Meter." Master Thesis, Department of Engineering, UCLA (1967).

⁴ A. Distéche, *J. Electrochem. Soc.* **109**, 1084 (1962).

⁵ C. Culberson, D. R. Kester, and R. M. Pytkowicz, *Science* **157**, 59 (1967).

measurements. We found that the thermally-coated "bead" type Ag/AgCl is far more stable and performs equally well under high pressure conditions. This electrode is prepared simply by dipping the tip of a cleaned silver wire into a melted AgCl solution under a nitrogen atmosphere.

The stability of the bead type electrode depends largely on the electrolyte solution in which the electrode is immersed. We have found two essential requirements for this solution. It has to be highly concentrated in chloride ions and it must be saturated with AgCl. At least 2 M of chloride ions are required, as a lower chloride ion concentration will result both in short and long term instability. The electrolyte solution used at present is 2.7 M KCl saturated in AgCl. Although saturated KCl can be used, 2.7 M KCl is preferred to prevent salt precipitation at low temperatures. Such a precipitation can change the concentration of the chloride ion, which will alter the electrode potential, and prevent the electrode from readily reaching equilibrium at a higher temperature.

Since both the bare silver wire and the AgCl bead are in contact with the solution, a layer of AgCl has to be formed on the silver wire to form an Ag/AgCl reversible electrode. It is evident from our experimental results that both high chloride ion concentration and a saturation in AgCl are essential requirements for the formation of this layer. Such a bead type electrode was found to be stable to within

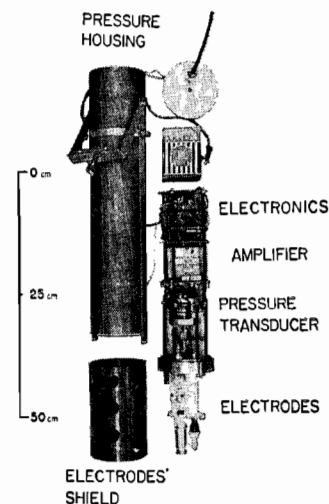


FIG. 1. The oceanographic p_H probe.

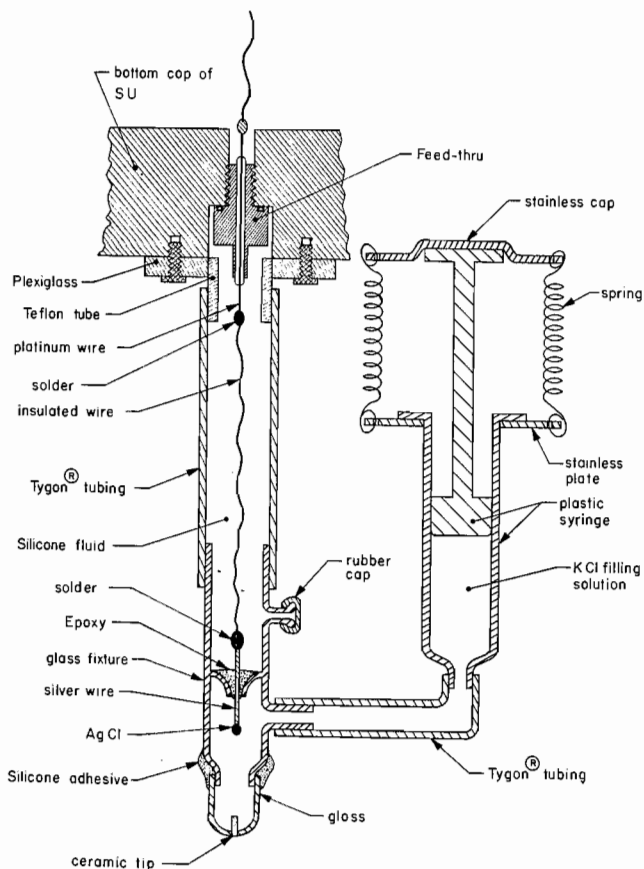


FIG. 2. Cross section of the reference electrode.

0.5 mV showing no deterioration even after months of operation.

Figure 2 is a cross section of the reference electrode attached to an oceanographic submerged unit (SU). It is composed of two compartments, the upper silicone fluid compartment, and the lower KCl filling solution compartment. The KCl solution is compressed by the spring-loaded syringe to maintain a hydrostatic pressure always higher than the outside pressure. This ensures an outflow of the KCl solution through the ceramic porous tip. The Ag/AgCl electrode enters the KCl compartment through an opening in the glass fixture and is sealed by epoxy cement. The ceramic tip is sealed or glued to a piece of glass tube and the whole unit is bonded to the main electrode body by a silicone adhesive (Dow Corning RTV 731).

The upper compartment is filled with Dow Corning 200 fluid of 1 cS viscosity. The silicone fluid has a volume resistivity of $1 \times 10^{16} \Omega\text{-cm}$ providing excellent insulation of the electric wire from sea water. A small opening in the electrode enables filling and draining the silicone fluid as necessary.

The silicone fluid compartment is partially constructed out of a flexible tubing (Fig. 2), which serves as a diaphragm equalizing the internal pressure to the external hydrostatic pressure. Hence, both the electrolytic and the

silicone fluid compartments are maintained at a hydrostatic pressure close to the external pressure. None of the electrode walls is thus exposed to a large pressure difference.

GLASS ELECTRODE

We have used Beckman's low resistance general purpose (GP) process electrode type 19500, which has an insignificant sodium error at the p_H of sea water. The insulating glass stem was cut 2 cm above the glass membrane bulb so as to separate the membrane from the electrode's body. This section was then used to build our glass electrode.

The glass electrode also consists of two compartments: a silicone fluid compartment and an electrolytic compartment. The sections are pressure-equalized by a flexible diaphragm which is realized by a 6 mm o.d. tubing extending into the silicone fluid compartment. Another flexible diaphragm equalizes the electrode pressure to the external hydrostatic pressure. Figure 3 is a cross section of a glass electrode attached to an oceanographic submerged unit (SU).

The reference and glass electrodes are mounted on an electrode holder by clamps around the external tubing. The other end of the Tygon tubing is slid over Teflon

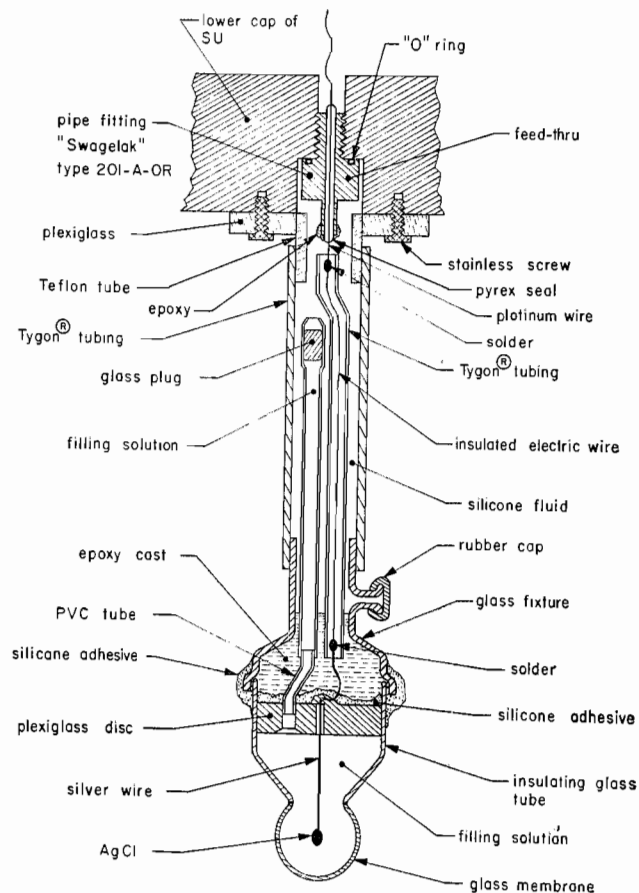
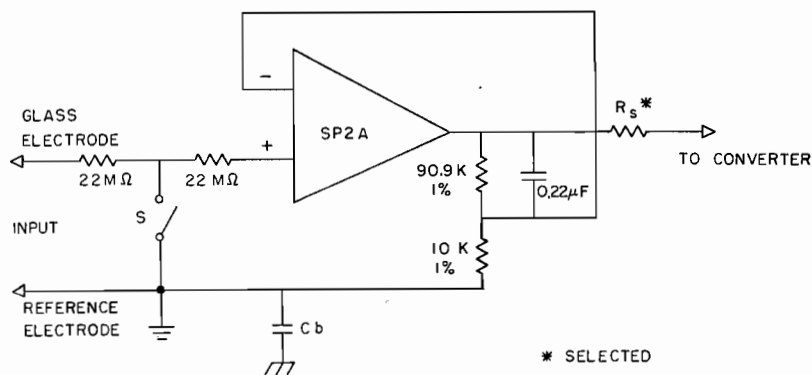


FIG. 3. Cross section of the glass electrode

FIG. 4. Electrometer amplifier using a Philbrick SP2A operational amplifier.



tubes which are pressed into the upper plate of the electrode holder (Figs. 2 and 3). A third clamp is used to mount the syringe. The electrode holder is made out of Plexiglas and attached by stainless steel screws to the bottom plate of the submerged unit.

ELECTRICAL INLET

The electrical inlets should be capable of withstanding high pressure and maintaining a high insulation resistance to the case. The last requirement is of particular importance for the glass electrode electrical inlet.

The inlet is built around a Swagelok (Crawford Fitting Co., Solon, Ohio) type 201-A-OR stainless steel pipe fitting (Fig. 3), and consists of a platinum wire sealed into glass and cemented with epoxy resin to the pipe fitting. The glass-to-platinum seal is prepared by heating the Pyrex tubing, with the platinum wire in it, until the glass starts to run and wets the platinum wire. The glass surface and the pipe fitting are then roughened by emery paper and cleaned by soaking them in warm concentrated KOH solution for 15 min, followed by an intensive washing and oven drying.

The seal is cemented to the fitting by Emerson & Comming Eccobond # 285 epoxy resin (catalyst no. 9) and cured at 110°C for 30 min. After cooling slowly to room temperature, the unit is soaked under vacuum (5–10 mm Hg) in silicone fluid (Dow Corning silicone fluid 200) for 30 min. This procedure markedly reduces surface leakage.

The insulation resistance of a well-prepared inlet is between 10^{12} and $10^{13} \Omega$ at room temperature.

SIGNAL CONDITIONING

We have used a commercial operational amplifier to achieve high input resistance and low input current. The amplifier used at present is a Philbrick type SP2A connected in the follower configuration (Fig. 4). The typical theoretical specifications of the amplifier in this connection

are:

Input resistance	$10^{13} \Omega$
Voltage gain	10.9
Input current	1 pA typical
Input current drift (0–25°C range)	10 pA typical
Input voltage drift (0–25°C range)	1 mV typical.

The input current drift can be neglected for a 10–20 MΩ internal resistance glass electrode. The input voltage offset is checked by closing switch S and measuring the output voltage. R_s is incorporated to match the amplifier signal to the following stage. We have used an analog to frequency converter to transmit the output signal along an oceanographic cable, and this signal was then read by a frequency counter. Since the information is contained—after the conversion—in the frequency rather than the amplitude of the signal, no error will result due to transmission attenuation or distortion. This procedure also increases markedly the resolution of the measurements and provides a digital reading.

TESTING AND CALIBRATION

Laboratory tests have been made on all the components both at atmospheric and higher pressures. As it was determined that pressure up to 150 kg/cm² does not affect the functioning of the sensor, all calibrations were therefore made only at atmospheric pressures. Asymmetry potential change due to pressure⁶ is approximately 0.6 mV at 150 kg/cm² which corresponds to 0.01 p_H units. This change should be measured and taken into account for very high accuracy applications.

Changes in the asymmetry potential of the glass electrode⁶ with time will cause a shift in the p_H sensor's output which should be taken into account when interpreting the measured data. The asymmetry potential change is determined by measuring a known standard solution prior to

⁶ R. G. Bates, "The Glass Electrode," in *Reference Electrode*, D. J. G. Ives and G. J. Janz, Eds. (Academic Press Inc., New York, 1961), pp. 231–269.

and after measurement of the test solution. This same standard solution was also used to measure the asymmetry potential during calibration of the sensor.

The operational definition⁷ of the p_H values relates the p_H of an unknown solution to a known p_H of a standard solution, and the emf of the two solutions. The unknown p_H can then be calculated according to Eq. (1),

$$p_{H_x} = p_{H_s} + K(E_x - E_s), \quad (1)$$

where p_{H_x} is the p_H of the test solution, p_{H_s} is the p_H of the standard solution, E_s is the electromotive force of the cell when in the standard solution, E_x is the electromotive force of the cell when in the test solution, and $K = \text{constant}$. For the hydrogen electrode,

$$I/K = S = RT/F \ln 10, \quad (2)$$

where S is the Nernst slope, F is the Faraday number, R is the gas constant, and T is the temperature in Kelvin degrees.

A glass membrane electrode does not exactly follow the theoretical slope of Eq. (2) and the sensitivity slope S should be replaced by the glass membrane sensitivity slope S_θ , which can be derived from measurements with two different standard solutions and with a glass electrode replacing the hydrogen electrode. This follows from Eq. (1),

$$p_{H_{s2}} = p_{H_{s1}} + (1/S_\theta)(E_{s2} - E_{s1}) \quad (3)$$

where $p_{H_{s1}}$ is the p_H value of standard solution no. 1, $p_{H_{s2}}$ is the p_H value of standard solution no. 2, E_{s1} is the electromotive force of standard solution no. 1 measured by the glass electrode, E_{s2} is the electromotive force of standard solution no. 2 measured by the glass electrode, and S_θ is the sensitivity slope of the glass electrode. S_θ can thus be calculated from Eq. (3),

$$S_\theta = (E_{s2} - E_{s1}) / (p_{H_{s2}} - p_{H_{s1}}). \quad (4)$$

S_θ is usually not constant over the entire p_H scale and thus the two standard solutions should be in the p_H vicinity (within 1 or 2 p_H units) of the test solution.

Equation (4) is valid only if all the measurements are performed at the same temperature. In oceanographic measurements, the p_H sensor has to measure p_H at a range of temperatures, requiring the sensor to be calibrated in such a manner as to enable conversion of the recorded data to real p_H values.

One method of calibration using a number of standard buffers was described by Fricke.⁸ This method is quite cumbersome, but yields a calibration curve over a relatively large range of p_H . We have found that one can use a much simpler method, the "one buffer calibration," which requires a p_H reference solution having a p_H within

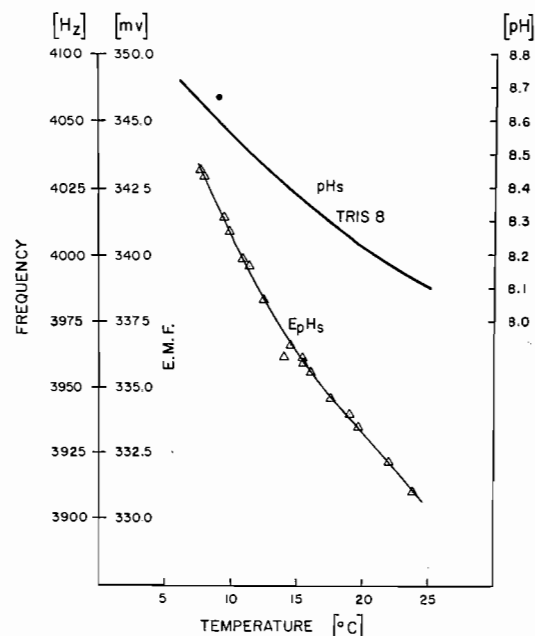


FIG. 5. One buffer calibration chart.

one unit of the test solution. It was determined that this method is applicable for calibration in the oceanographic range.

CALIBRATION WITH SEAWATER BUFFER

The response of glass membrane electrodes (S_θ) is usually⁸ within 1 to 2% of the theoretical slope (S). Suppose the standard buffer p_{H_s} used for calibration, is within 1 p_H unit from the test solution. Using Eq. (3), p_{H_x} can be calculated from E_x if E_s is known. A 1% error in S_θ will result in an approximately 0.01 p_H unit error in the calculated value of p_{H_x} . We have found that for the GP glass membrane electrode, S_θ is within 98% of the theoretical slope. S_θ can be easily calculated at room temperature by using two standard reference solutions, it can then be estimated for every temperature by extrapolating the $S_\theta(T)$ function. The error in this estimation was found to be less than $\pm 0.5\%$ for an electrode in "good condition," which is defined as an electrode with a slope S_θ , 1–1.5 mV smaller than the theoretical slope S at room temperature.

Smith and Hood⁹ have found that a tris salt, tris-(hydroxymethyl)aminomethane, can be used to buffer natural seawater in the range p_H 7– p_H 9. One buffer (designated as tris 8) was accurately measured by Smith and Hood over the 0–35°C range against NBS standards and was found to be stable to 0.01 p_H units over a period of 150 days. We have used this buffer for calibration of the p_H sensor in the oceanographic range.

⁹ W. H. Smith, and D. W. Hood, " p_H Measurements in the Ocean: A Seawater Secondary Buffer System," in *Ken Sugawara Festival Volume, Recent Researches in the Field of Hydrosphere, Atmosphere and Nuclear Geochemistry*, Y. Miyake and T. Koyama, Eds. (Maruzen Co., Tokyo, 1964), pp. 182–202.

⁷ R. G. Bates, *Am. Soc. Testing Mater. Publ. No. 190* (1959).

⁸ H. K. Fricke, *Beitrage zur Angewandten Glasforschung*, E. Scott, Ed. (Wissenschaftliche Verlag Stuttgart, 1959), p. 175.

The one buffer calibration procedure is as follows: a freshly prepared tris 8 buffer is cooled down to 0°C with the p_H sensor immersed in it, and the assembly is then allowed slowly to warm to room temperature. The output is recorded approximately every 1 C°, and the data used to draw a smooth curve. Figure 5 represents such a calibration. The upper trace is the p_H value of tris 8 as a function of temperature, and the lower trace is the sensor's output.

The same buffer used in the calibration procedure is also used to check asymmetry potential changes. This is done by inserting the p_H sensor in the tris 8 solution and recording the output frequency prior to lowering the probe into the ocean. The reading is compared to the calibration scale and the observed deviation is used to correct the measured values by subtracting or adding the difference.

RESULTS

The performance of the high pressure p_H sensor was found to be comparable to the performance of a good quality p_H glass electrode. The overall accuracy obtained by the one buffer calibration method was 0.02 p_H when the potential was measured to within 0.2 mV, the temperature to 0.1 C° and the test solution was within 1 p_H unit from the standard buffer. The response time for a p_H change is insignificantly small when compared to the thermal time constant, which is approximately 1 min.

The p_H sensor was field-tested on September 29, 1967. The *in situ* p_H of the ocean above the San Pedro Basin off Southern California was measured using a 300 m cable

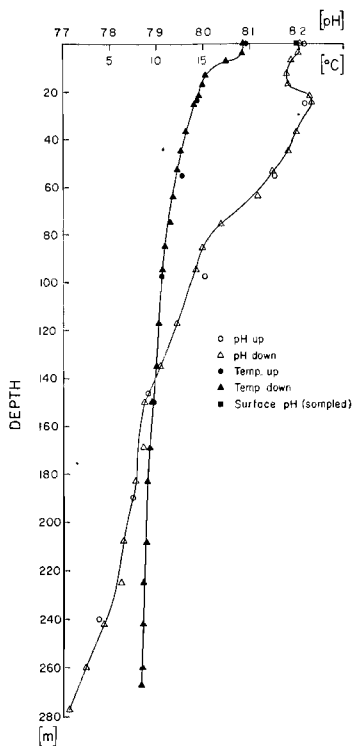


FIG. 6. Temperature and p_H vs depth as recorded at station I above the San Pedro Basin 3.5 km from shore off Southern California.

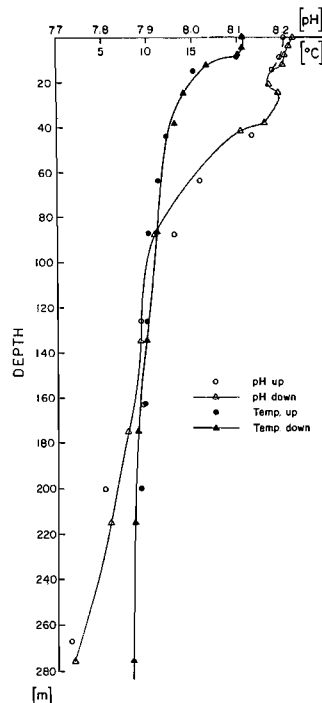


FIG. 7. Temperature and p_H vs depth as recorded at station II above the San Pedro Basin some 8.6 km from shore off Southern California.

which reached a maximum vertical ocean depth of 270 m. The measurements were performed aboard *Velero IV* (University of Southern California research vessel) at two stations 3.5 and 8.6 km from shore. The raw data were corrected for drifts and sensitivity change and the calculated values of the measured temperature and p_H were plotted against depth. Figures 6 and 7 are the resulting graphs of stations I and II, respectively.

We have arbitrarily connected the descending points by a smooth curve, which assists in following the general tendency of the measured phenomena. We do not have enough data to support the smooth plots and it is possible that some of the deviation from the smooth curves represents a real change in the measured component. Inconsistencies are in part due to the uncertainty of the depth measurements, which were made with a potentiometric type transducer having a 1% error of its full range (200 kg/cm²).

The descending and ascending p_H values of station I agree in general to within 0.02 p_H units. We do not have evidence that we have measured the same water body due to drift of the ship, and it is possible that these discrepancies are due to real change in p_H .

The descending and ascending sets of measurements at station II show a deviation of up to 1 C° in temperature and 0.045 p_H . Further, the deviation of the ascending temperature and p_H values is not always in the same direction. In view of the good agreement in station I, it seems that the deviations between ascending and descending points at station II are due to real differences in the water bodies. It should be noticed that station II measurement took

approximately 2 h and the average wind speed was 4.1 m/sec. Station I measurements took approximately $1\frac{1}{2}$ h with an average wind speed of 2.1 m/sec. Hence, the ship drifted a considerably greater distance at station II than at station I.

The surface p_H was measured aboard at station I, using an Orion type 401 portable p_H meter, by sampling the upper layer of the sea. The electrodes were standardized by a Beckman p_H 7 buffer after equalizing the buffer temperature with the sample temperature, and the measurement agrees to within 0.006 p_H units of the *in situ* surface measurement made with the *in situ* sensor.

The range of our p_H results is well within the oceanic p_H range that has been previously recorded. In a recent work, Park¹⁰ measured some 3000 p_H values in the north-eastern Pacific Ocean on samples collected at various

depths. The measured value was p_H 8.2– p_H 8.3 at the surface and approximately p_H 7.7 at a depth of 300 m. These values are close to our values: p_H 8.20 at the surface and p_H 7.73 at 270 m depth. Our values are also well within the range of previous p_H measurements along the coast of Southern California.¹¹

ACKNOWLEDGMENTS

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¹¹ Kenneth O. Emery, *The Sea Off Southern California* (John Wiley & Sons, Inc., New York, 1960), p. 265.

¹⁰ K. Park, *Science* 154, 1540 (1966).

