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*p*H-TEMPERATURE PROFILES IN OCEAN AND LAKES
USING AN *IN SITU* PROBE

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pH-TEMPERATURE PROFILES IN OCEAN AND LAKES USING AN *IN SITU* PROBE¹

Measurements of pH have traditionally been made by bringing samples to the surface in collecting bottles and equilibrating them to a fixed temperature (Strickland and Parsons 1965). This method is tedious and may be erroneous, since gas exchange could occur during equilibration.

Direct measurement of pH has been accomplished by Manheim (1961) to a depth of 16 m in the Baltic Sea, using a robust glass electrode and a reference electrode floating at the water surface. Distéche (1959) built pressure-compensated glass and reference electrodes, which were used to depths of 2,350 m from the French bathyscaphe *Archimede* (Distéche 1964). In the latter case, the electrodes were not used as remote submersible probes nor has the author shown how the electropotential signal can be converted into real *in situ* pH units.

With the exception of the measurements of Park (1966) showing a typical deep-sea profile in the Pacific Ocean and possibly some profiles from the seas surrounding Japan (Akiyama et al. 1966) there are few reliable data available.

We wish to thank M. Goldhaber, S. Friedman, and E. Ruth for their assistance in calibrating the electrode and carrying out measurements at sea. We also wish to thank the University of Southern California, Hancock Foundation, for use of RV *Velero IV*, from which measurements were taken. The study was supported by Office of Naval Research Contract No. N00014-67-A-0111-004, NR 104-700.

TECHNIQUE

An oceanographic pH probe recently has been developed in our laboratory and tested to pressures of 150 kg/cm² (corresponding to 1.43 km ocean depth). A

description of the electrodes and electronic system is given elsewhere (Ben-Yaakov and Kaplan 1968*a, b*). In brief, the probe consists of four sensors (a transducer for pressure, a thermistor for temperature, a glass electrode, and a silver-silver chloride reference electrode with a liquid junction for pH). These sensors are exposed to the ambient pressure. They are connected to an electronic system housed above the sensors in a 10-cm-ID × 60-cm-long stainless steel tube. The signals and commands from the probe to a

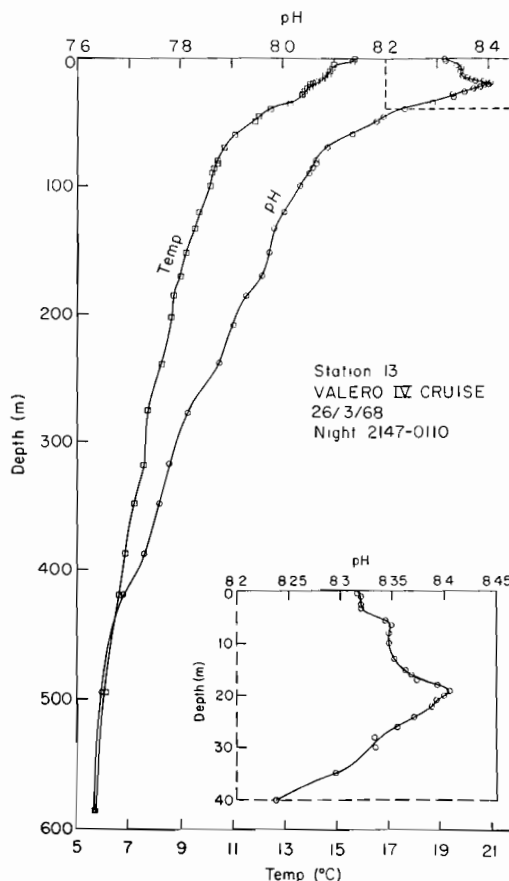
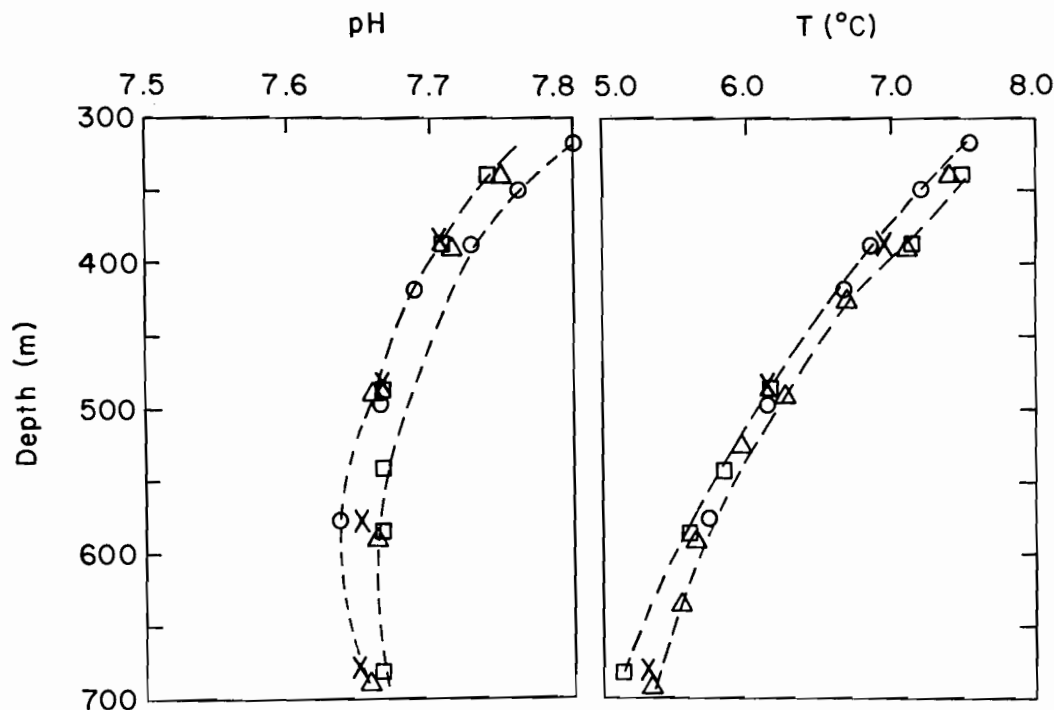


FIG. 1. Typical pH and temperature profile for a station taken off San Diego, California.

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○ Station 13, △ Station 14, □ Station 15, X Station 21

FIG. 2. Comparison of pH and temperature for five stations off southern California showing reproducibility in readings.

control unit on board ship are sent via a two-conductor cable. The output signal of the sensors is converted to an a-c signal whose frequency is linearly proportional to the amplitude of the signal. This method eliminates the errors due to attenuation and distortion of the transmission line.

The probe has been calibrated in the laboratory at various pressures (0–150 kg/

cm²) and temperatures (0–20°C) using a Tris buffer (described by Smith and Hood 1964) at pH 8 and a phosphate buffer at pH 7 (defined by the Bureau of Standards). Before and after each lowering, the electrodes are placed in a known buffer and the signal is recorded. Any shift from the laboratory calibration resulting from asymmetric potential shifts, etc., are, therefore, corrected for by taking into account the deviation from the curve calibrated in the laboratory.

The reproducibility of the electrode's measurement was found to be $\pm 0.01C$ for temperature and ± 0.02 units for pH . An example of this reproducibility has been found by measuring temperature and pH during both the ascent and descent (Ben-Yaakov and Kaplan 1968a). The response time for a pH change is insignificantly small when compared with the thermal time constant which is approximately one minute.

TABLE 1. Location of marine stations where measurements were made

Station No.	Date (1968)	N. lat	W. long	Sonic depth (m)
5	15 Mar	33°41'55"	118°19'25"	43
6	15 Mar	33°41'25"	118°19'32"	78
13	26 Mar	32°48'52"	117°44'57"	575
14	27 Mar	32°06'30"	118°18'15"	770
15	28 Mar	32°38'10"	118°07'00"	960
17	2 Apr	37°28'09"	122°03'40"	6
18	2 Apr	37°30'25"	122°07'18"	14.5
20	10 Apr	33°29'20"	118°22'50"	490

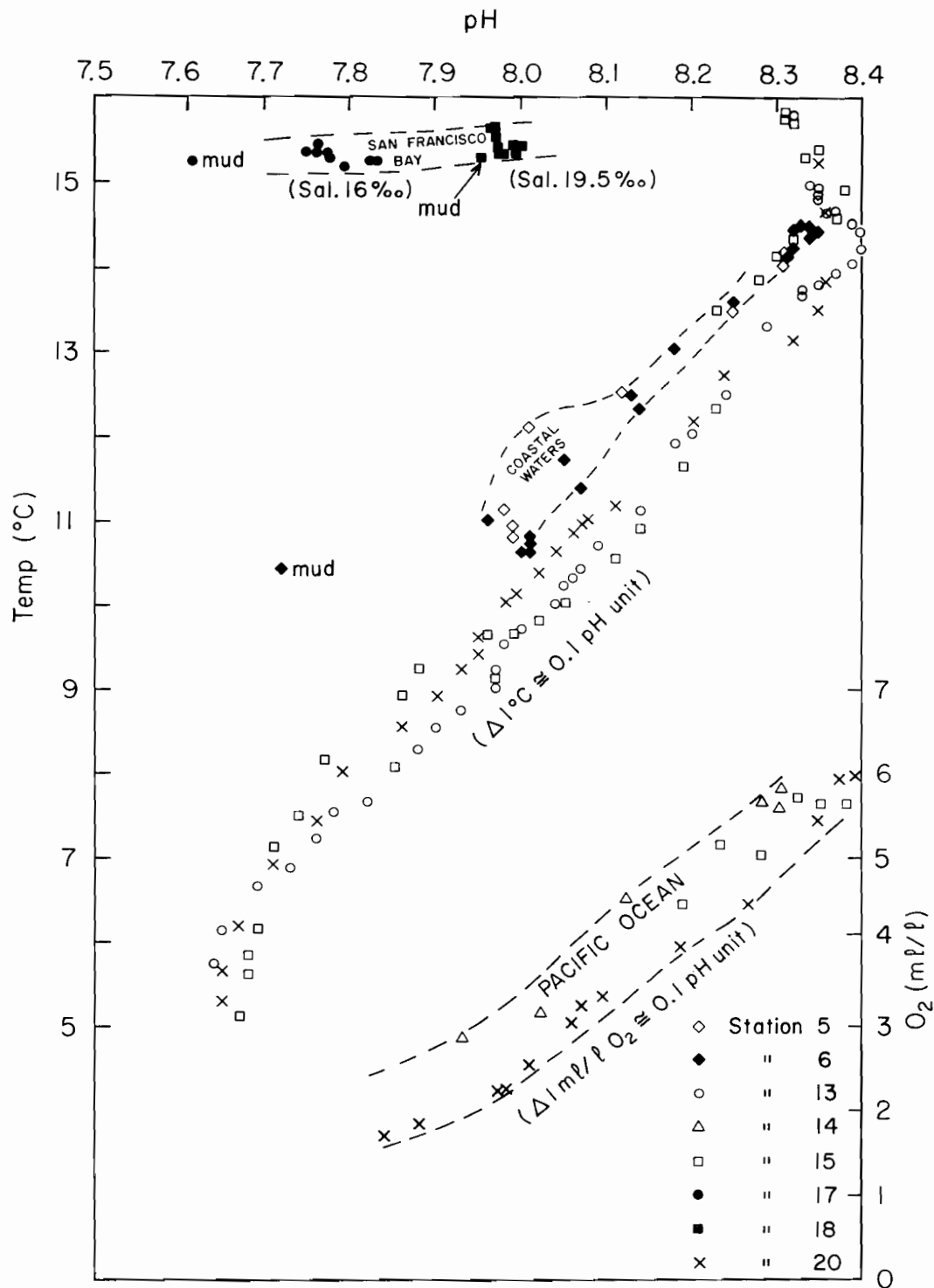


FIG. 3. Relationship between temperature, oxygen, and pH for several stations off southern California and for two shallow stations in San Francisco Bay.

Dissolved oxygen concentration was determined by sampling the water with plastic water samplers and analyzing the samples aboard ship with a polarographic electrode (Beckman type 39065). The measuring system was composed of a specially designed analyzing cell and associated electronic circuitry. This cell is a Plexiglas container (4.5 cm ID \times 10 cm long) in which an oxygen electrode and a thermistor probe are inserted. The electronic circuitry contains an operational amplifier (NEXUS type SQ10a) and an analog to frequency converter similar to the one incorporated in the pH probe.

The oxygen cell was calibrated in the laboratory by air-saturating water over the temperature range 5–30°C. The electrode's signal for air-saturated water is lower than the signal obtained when measuring air (gas) at the same atmospheric pressure and temperature. The ratio of the two signals depends on the rate of stirring and was 1.15 for the rate we used.

Before and after beginning a set of field measurements, we standardized the electrode by air (gas) so that the deterioration of the electrode's response with time could be taken into account when reducing the data. The overall accuracy of dissolved oxygen determination by this method is approximately $\pm 3\%$ of full scale (air-saturated solution).

MEASUREMENTS

The pH probe has been tested off the coast of southern California, in San Francisco Bay, and in two inland lakes—a saline evaporitic body (Salton Sea, Calif.) and a lake in the San Bernardino Mountains, at an elevation of approximately 2,700 m (Lake Arrowhead, Calif.). Table 1 shows the locations of the marine stations where pH-temperature profiles were measured.

A typical pH and temperature profile for the ocean off southern California at a station approximately 32 km west of San Diego is shown in Fig. 1. In general, values of pH at the surface of the sea were near 8.3 during March and April 1968, although at the end of September 1967,

values averaged 0.1 pH units lower. A maximum value between 8.3 and 8.4 was generally reached between 20 and 40 m below the surface. The magnitude of this maximum varied with depth, time of day, and location. In general, the temperature and pH curves followed the same general trend below the pH maximum. The insert in Fig. 1 demonstrates the ability of the probe to follow small changes in pH within the euphotic zone.

Four stations in southern California, all measured at about the same time (Table 1), are compared in Fig. 2. The similarity in temperature at each depth suggests that the water column was probably similar. At the same time, pH changed in the same uniform manner at each station, showing a maximum separation of about 0.03 pH units.

There is considerable interest in the cause of pH change in the ocean and the mechanism of buffering. Sillen (1961), Garrels (1965), and others believe that ion exchange processes involving silicate minerals and clays are of primary importance. Park (1965, 1966) has shown that pH changes closely follow changes in total dissolved carbon dioxide which is a function of the biological activity in the ocean. He has demonstrated an inverse relationship between dissolved carbon dioxide and oxygen. The ratio $\Delta O_2 : \Delta \Sigma CO_2$ appears to vary around 1.0 ± 0.2 . Oxygen and pH show a close similarity in their pattern of change with depth.

The relationship of pH to temperature and pH to oxygen for eight stations off southern California and pH-temperature relationships for two stations in San Francisco Bay are shown in Fig. 3. The latter stations are shallow (6 m and 14.5 m) and are influenced by inflow of freshwater. Their pH is lower than normal coastal seawater and the pH of the sediment is still lower than that of the overlying seawater.

This same relationship is observed in coastal waters, where the pH of the bottom sediment is lower than the overlying water by 0.3 pH units (Fig. 3). The upper near-

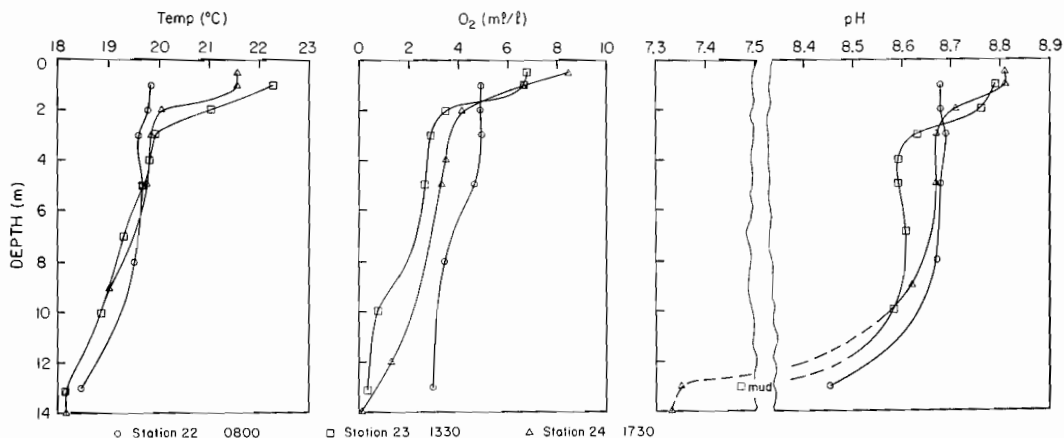


FIG. 4. Temperature, oxygen, and pH profiles in the Salton Sea, California.

shore waters generally show more variation than waters farther offshore. However, there is good direct agreement between decrease of temperature and pH. These appear to agree well with the correlation coefficients published by Akiyama et al. (1966) for the seas surrounding Japan. The general slope of the curve is $\approx 0.1 \text{ pH}/^\circ\text{C}$.

There is also good agreement between decrease in dissolved oxygen and decrease in pH. In Fig. 3, $\Delta\text{O}_2/\Delta\text{pH} = 10 \text{ ml liter}^{-1} (\text{pH unit})^{-1}$ for the values measured (down to 300 m). By applying the equations connecting carbonate alkalinity with pH (Skirrow 1965), $\Sigma\text{CO}_2 \approx \text{CA}(a_{\text{H}^+} + k'_2)/(a_{\text{H}^+} + 2k'_2)$, it is possible to show that between pH 7.7 and 8.2 the average for

$(\Delta\Sigma\text{CO}_2/\text{CA})/\Delta\text{pH} \approx 0.1/\text{pH unit}$. We did not make carbonate alkalinity measurements, but if we take an average carbonate alkalinity value of 0.0024 moles/liter (a common value for oceans) in this pH range, we obtain $\Delta\Sigma\text{CO}_2/\Delta\text{pH} \approx 5.4 \text{ ml liter}^{-1} (\text{pH unit})^{-1}$ and $\Delta\text{O}_2/\Delta\Sigma\text{CO}_2 \approx 1.85$. This value depends heavily on the carbonate alkalinity, which probably increases with depth (Park 1965) so that the ratio would decrease accordingly. Richards (1965) suggests that the ratio would be near 1.30 in the oceans.

The *in situ* pH probe was also used in measuring pH in two lakes. Fig. 4 shows values obtained in the Salton Sea at three different times on 11 April 1968. The values for morning show homogeneity in the surface waters indicating that a pre-dawn breeze had stirred the waters to a level of 3 or 4 m. There is excellent agreement between pH and oxygen, indicating their dependence on some common mechanism—undoubtedly photosynthesis and catabolism of the fixed carbon compounds. The sharp decrease in pH of the mud (to 7.35 and 7.48) is also noteworthy.

Two stations were measured in Lake Arrowhead on 22 March 1968 (Fig. 5). The waters here were less stratified in pH than the Salton Sea, and only a slight thermal stratification was evident. This is a mountain lake, so wind stirring is probably important.

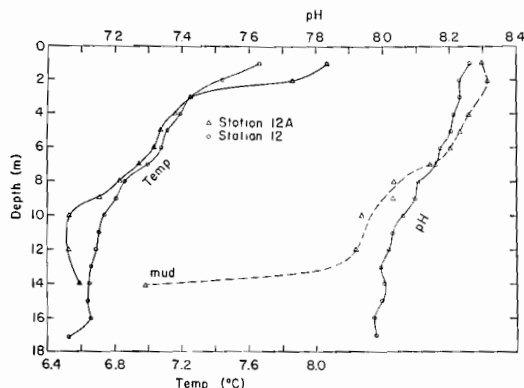


FIG. 5. Temperature and pH profiles in Lake Arrowhead, California.

CONCLUSION

We have described the successful application of an *in situ* pH meter developed here. The instrument has been used to a depth of 700 m by lowering it on the end of a two-conductor cable and recording the signal at the surface. A complete set of readings (pressure, temperature, and pH) at any one depth can be made in less than 5 min. The high precision of the pH measurement suggests that the instrument may serve a useful role in understanding the composition at the mud-water interface and in rapid detection of the depth of maximum productivity.

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