

DESIGN AND APPLICATION OF A DEEP SEA pH SENSOR

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ABSTRACT

A rugged, high pressure pH sensor was constructed and successfully applied to oceanographic studies at depth to 4000 meters. The sensor comprises an equilibrated glass electrode, an incrementally pressurized reference electrode and is incorporated in an in situ instrumentation system. The sensor was applied to studies related to the carbonate system in the ocean. A close relation between pH and dissolved O_2 as measured and the North Eastern Pacific appears to be near saturation with respect to calcium carbonate down to 3500 meters.

INTRODUCTION

Marine pH measurements have traditionally been made by bringing samples to the surface in collecting bottles and equilibrating them to a fixed temperature. However, since the PH of sea water is a non-conservative parameter, pH values determined on the surface are not equal to the in situ pH. The correct pH can be calculated by taking into account the temperature and pressure dependence of the apparent dissociation constants of carbonic acid (Ben-Yaakov, 1970a). In situ pH measurements, therefore, offer an attractive method to overcome some of the inherent inaccuracies of conventional pH measurements, due to uncertainty in temperature and pressure coefficients of the constants used to correct shipboard values, and possibly due to errors caused by CO_2 exchange while the samples are handled on board ship.

Direct measurements of pH were made 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's surface. Disteché (1959) built pressure-compensated glass and reference electrodes which were used to a depth of 2350 m from the French Bathyscaphe Archimede (Disteché, 1964). However, in the latter case, the

electrodes were not used as a remote sensor and no attempt was made to calibrate them and to translate the measured potentials into pH units.

This paper describes the design and application of a deep sea pH sensor developed at UCLA by the authors. As details of the design and results of specific studies made with the in situ system were given elsewhere (see reference list), an attempt will be made here to give an overview and to summarize our experience with the in situ pH sensor, which could be considered as a model for deep sea specific ion electrode measurements.

SENSOR CONSTRUCTION AND CALIBRATION

The glass membrane electrode can be used for in situ oceanic pH measurements because it maintains its sensitivity to pH at high hydrostatic pressure when both sides of the membrane are exposed to the same pressure (Disteche, 1959). Besides the basic requirement of pressure equilibration to avoid breakage of the delicate glass membrane, a practical design of an in situ pH electrode must, also ensure good electrical insulation of the electrodes output lead. The internal resistance of glass electrodes may reach 10^8 ohm (and even higher values at low temperatures) so that an insulation resistance of at least 10^{12} ohm must be achieved in order to prevent leakage attenuation. These requirements were met in the present design (Figure 1), by constructing the in situ glass electrode from two compartments; an outer silicone oil compartment and the internal solution compartment. The compartments are separated from each other, and from the ambient sea water, by flexible walls (Tygon^R tubing) which transmit the hydrostatic pressure to the inside of the pH sensitive glass bulb (Figure 1). Electrical insulation of the output signal is obtained by the silicone fluid compartment, which surrounds the output lead, and by a specially constructed high pressure feed-thru. This inlet is built around a stainless steel pipe fitting and consists of a platinum wire sealed into glass and cemented to the fitting with epoxy resin. The insulation resistance of this inlet is between 10^{12} and 10^{13} ohms.

The potential of the glass electrode is measured against a silver-silver chloride (Ag/AgCl) reference electrode with a leaky junction. This electrode (Figure 2) is also composed of two compartments; the upper silicone fluid compartment and the lower KCl filling solution

compartment. The electrolyte flow is controlled by a rubber bulb which is slightly inflated, thereby maintaining a hydrostatic pressure always higher than the ambient pressure. This ensures an outflow of the KCl solution through the nylon wick which serves as the liquid junction. The junction end of the reference electrode also serves as a filling port. Filling is accomplished by unscrewing the teflon cap and replacing it with a special cap connected to a syringe. The solution is forced in, the tubing which leads to the rubber bulb is temporarily clamped to prevent loss of solution, and the original cap is replaced.

The internal reversible electrodes (Ag/AgCl in 2.7 M KCl) of the glass and reference electrodes are symmetrical, so as to improve the thermal tracking of the two cells. The internal solution of the glass electrode is also made 0.1 N in HCl to obtain a reference pH which is practically independent of hydrostatic pressure (Harned and Owen, 1958). The asymmetry potential shift of electrode pairs was checked in a high pressure chamber (Ben-Yaakov, 1970b) and was typically found to be approximately 1 mv for a 10,000 psi pressure range. Since the error due to this shift is small, it is generally neglected when converting the output potential of the pH sensor to pH units.

Conversion of the output signals to pH units is accomplished by preparing a calibration curve for each electrode pair. The curve is obtained by recording the output potential of the electrode when placed in a temperature controlled phosphate buffer (6.86 at 21°C; Bates, 1964). The buffer is first cooled to 0°C, and then slowly warmed to room temperature while the output potential of the electrode pair is registered for a number of temperature points. This information, along with the buffer test data obtained on board ship prior to each ocean measurement, is later used in the computation. The calculation is made under the assumption that the slope of the pH electrode approximately follows the Nernst slope. This is periodically verified by a conventional two-buffer test.

IN SITU INSTRUMENTATION

The high internal resistance and the low DC output of the pH sensor demand in situ signal conditioning. Since analog transmission over long electrical cables may result in appreciable error due to attenuation along the line, we have used a frequency modulation technique to transmit the signals from the in situ assembly (Ben-

Yaakov and Kaplan, 1968b). A simplified block diagram of the probe is given in Figure 3. The output signal of the pH sensor is buffered and converted to a proportional frequency signal by a current to frequency converter (Ben-Yaakov, 1968a). The output signal is then either sent to the surface via an electrical cable (Ben-Yaakov and Kaplan, 1968b) or recorded by an in situ recorder (Ben-Yaakov, 1968b). A more detailed schematic diagram of the amplifier used to buffer the output signal of the pH sensor is given in Figure 4. The high input resistance is achieved by a commercially available electrometer type operational amplifier (Analog Devices Type 311J) which is connected as a non-inverting amplifier. The reference electrode is connected to the "ground" of the electronic circuit which is floating with respect to the case and connected to it by a by-pass capacitor (Cb). The DC drift of the operational amplifier is monitored by shorting relay B (Figure 4) and monitoring the output voltage of the amplifier. Relays A and B are special dry reed relays with an insulation resistance of 10^{15} ohms (Compac series 10-1A-HIR).

The overall resolution of the instrumentation system used in our in situ oceanic studies is ± 0.1 mv (Ben-Yaakov, 1970b). The overall accuracy of the measurements is estimated to be 0.1% after correcting for drifts. Corrections are facilitated by routinely monitoring in situ internal standards built into the circuit (Figure 3). Accuracies stated above apply to the measurements of the raw signals and not to the overall accuracy of in situ measurements. The latter depend not only on the accuracy of the electronic system but also on errors introduced by the pH electrodes, the precision of the calibration curve and the accuracy of the on board buffer standardization. It will be demonstrated below, that direct deep sea pH measurements with an overall reproducibility to within ± 0.02 pH units are feasible.

FINE DETAILS OF OCEANIC pH PROFILES

Typical shallow pH and temperature profiles for the ocean off southern California at a station approximately 32 km west of San Diego are shown in Figure 5. In general, the value of pH at the surface of the sea was near 8.3 and a maximum value was reached between 20 and 40 m below the surface. In general, the temperature and pH curves follow the same trend below the pH maximum. Interestingly, pH and temperature were found to vary linearly, approximately 0.1 pH unit per 1°C . This

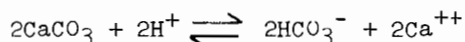
dependence is about 10 times larger than the pH temperature dependence of sea water with fixed composition. It was found (Ben-Yaakov and Kaplan, 1968c) that the pH drop is controlled by respiration and oxidation of organic carbon. These processes consume oxygen and produce CO₂ thereby lowering the pH of the waters.

The insert of Figure 3 demonstrates the ability of the *in situ* measuring assembly to follow the fine details of the pH profile. The magnitude of this subsurface maximum was found to vary with time of day, seasons, and location. Since the maximum is located within the euphotic zone, it is probably associated with consumption of CO₂ by photosynthesis (or primary production) on the one hand and to the rate of atmosphere water exchange and mixing on the other. This pH layering should be maintained whenever the latter rate is smaller than the former. It is suggested, therefore, that detailed pH profiles, especially if recorded diurnally, may be used to estimate primary production, if the photosynthetic compensation depth is below the well-mixed layer.

IN SITU CARBONATE SATUROMETRY

Apart from its application as a tool for mapping the pH in the ocean, the oceanographic pH sensor has also been used to perform *in situ* carbonate saturometer experiments (Ben-Yaakov and Kaplan, 1971a). These experiments are useful in testing the degree of saturation of a calcium carbonate in the ocean, and the information is important for understanding related phenomena such as the mechanism controlling the amount of CaCO₃ in marine sediments and the CO₂ and calcium cycles in nature.

The basic principle of the carbonate saturometer experiment is the measurement of the pH before and after a sample of sea water has been equilibrated with a solid phase of CaCO₃ (Weyl, 1961). A pH change will take place according to the reaction:



Hence, a pH increase indicates that the original sea water was undersaturated with respect to the carbonate mineral, whereas a pH decrease signifies supersaturated. The magnitude of the pH shift can be used to accurately calculate the degree of saturation (the ratio of ionic product) of the original sample (Ben-Yaakov and Kaplan, 1969).

The in situ carbonate saturometer (Figure 6) is composed of a high pressure glass electrode which is inserted in a plexiglass cup filled with coarse CaCO_3 (calcite or aragonite) and connected through a hose to a pump and a solenoid-operated valve. When the pump and valve are on, sea water is rapidly pumped through the cell to flush out any water present in the cell, and the pH electrode then registers the pH of the sea water. During the off period, the trapped sea water reacts with the CaCO_3 , moving toward equilibrium with the solid phase. The chemical reaction between the sea water and the carbonate mineral is monitored by the pH electrode, and this information is later used to calculate the degree of saturation of the sea water at the point of measurement. A typical output of the in situ carbonate saturometer is shown in Figure 7. The measurements were taken at a depth of 1200 m in the northeastern Pacific, 100 nautical miles west of San Diego. The horizontal axis of the figure is given in pH units (0.0125 pH units per dot), whereas the vertical axis represents running time (min.). The two plots correspond to the output of the saturometer electrode (O) and to the output of an auxillary pH electrode (*). Also marked on the figure are flushing periods (pump on) during which time the output of the two electrodes should be equal. The agreement between the two independent in situ pH determinations is ± 0.02 pH units.

The saturometer electrode output (*) shifted during equilibration toward higher pH values, which implies that the carbonate material (aragonite) was dissolving, and hence the Pacific is undersaturated with respect to aragonite at that station. The degree of saturation (IP/K'sp) for this measurement was calculated to be 0.7.

CONCLUSIONS

The results presented here demonstrate the feasibility of applying ion selective electrodes for in situ measurement in the oceanic environment. Judging from the results of our field experiments it would appear that the expected inaccuracy of in situ specific ion determination should be within ± 0.02 pIon units and perhaps can be improved to ± 0.01 pIon units. The corresponding concentration uncertainty for the error is about $\pm 3\%$ for univalent ions and 6% for divalent ions. As the range of variation of the major ion in sea water is much smaller than that band (Culkin, 1965), the accuracy of direct in situ determination of major ions in open

sea water is probably unacceptable. However, in situ specific ion electrode measurement could be useful in estuarine or lake studies, for determining activities of minor ions, and for performing specialized experiments such as carbonate saturometry.

ACKNOWLEDGMENTS

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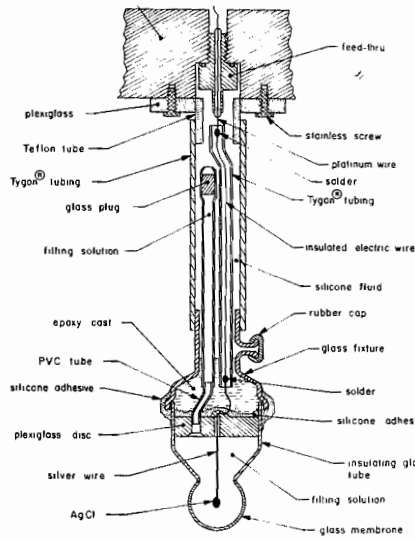


Figure 1: In situ pH electrode.

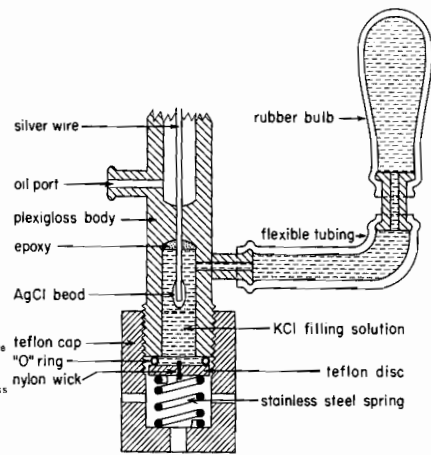


Figure 2: In situ reference electrode.

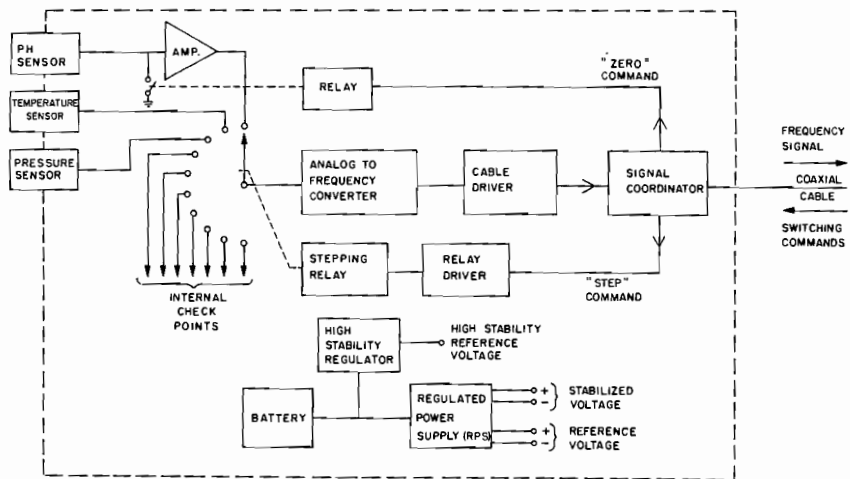


Figure 3: Block diagram of an oceanographic probe designed for in situ pH measurement.

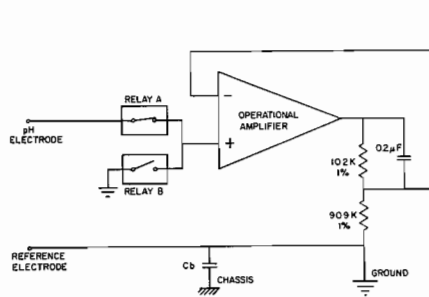


Figure 4: Buffer amplifier used in the probe described in Figure 3.

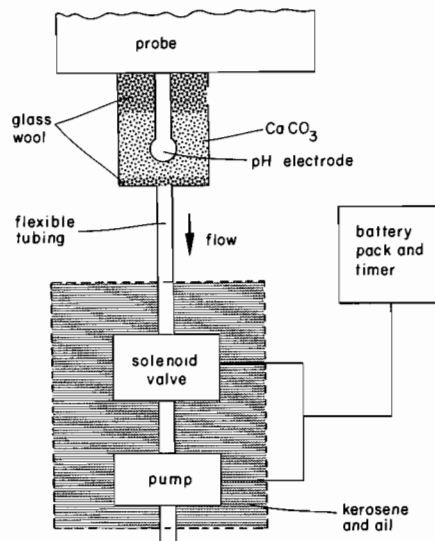


Figure 6: Block diagram of an in situ calcium carbonate saturometer.

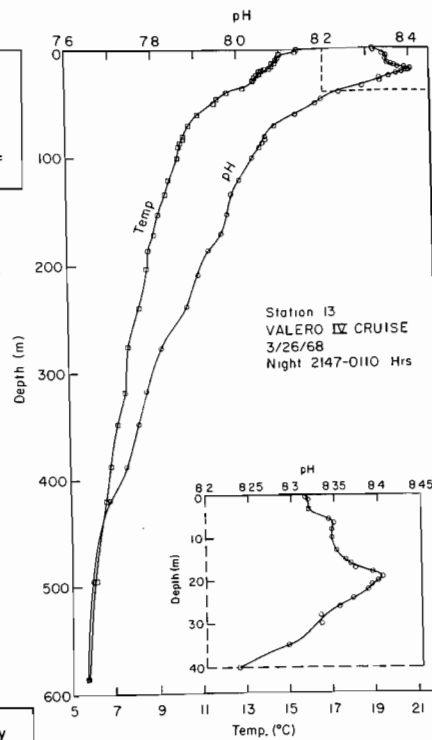


Figure 5: A pH profile measured on the continental borderland of Southern California with in situ probe.

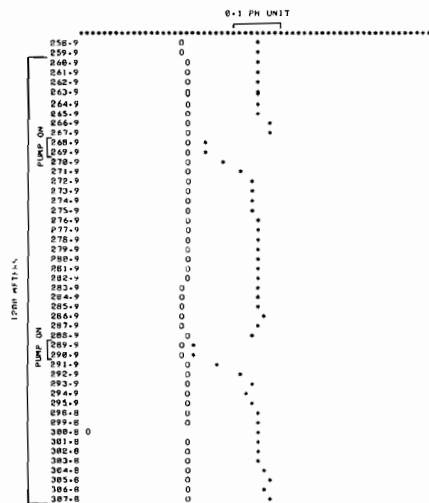


Figure 7: Results of in situ pH and carbonate saturation measurements.

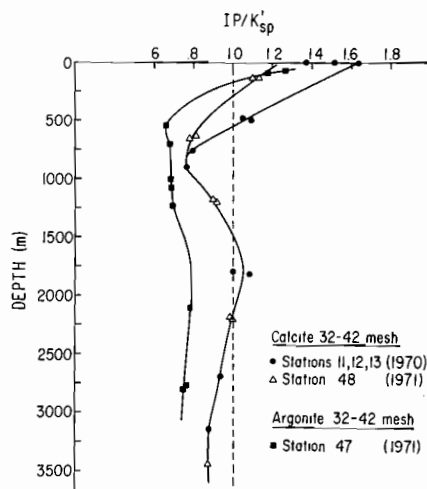


Figure 8: Calcite and aragonite saturation in North Eastern Pacific as determined by the in situ carbonate saturometer.

