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스펙트로포토메터를 이용한 해수의 pH 측정 연구

A Study on the Spectrophotometric
Determination of Seawater pH

1996. 2

한국해양연구소

제 출 문

한국해양연구소장 귀하:

본 보고서를 “스펙트로포토미터를 이용한 해수의 pH 측정에 관한 연구” 사업의 최종보고서로 제출합니다.

1996. 2

한국해양연구소

연구책임자: 이 동섭

요약문

I. 제목

스펙트로포토메터를 이용한 해수의 pH 측정에 관한 연구

II. 연구개발의 목적 및 중요성

- 미국 에너지성이 발간한 “Handbook of Methods for the Analysis of the Various Parameters of the Carbon Dioxide System in Sea Water” 에 제시된 스펙트로포토메터를 이용한 해수의 pH 측정 방법 (SOP 7)을 현장에 적용 가능한 수준으로 숙지함
- 새 측정법의 정밀도를 활용할 연구 활용 범위에 대하여 논함
- 80년대 후반 염료와 스펙트로포토메터를 이용하여 매우 향상된 정밀도와 정확도로 pH를 측정하는 방법이 개발됨에 따라 pH를 활용하는 연구가 활발해지고 있음
- 수소이온 활동도 (pH)는 해수에 존재하는 각종 화학물질이 어떠한 화합물 또는 이온으로 존재하는가를 결정짓는 결정적인 인자로서 해양화학의 궁극적인 연구 목표의 하나인 화학종의 분포를 이해하는데 크게 기여함
- 해수의 수소이온 활동도는 해수에 녹아 있는 이산화탄소의 거동과 밀접하게 관련된 인자로서 정확한 pH 값의 측정은 지구온난화와 관련된 이산화탄소의 지구 규모 수지를 이해하는데 큰 도움을 줄 수 있음

III. 연구개발의 내용 및 범위

- 표준측정방법 SOP 7(DOE, 1994)의 기술 확보
- 기술적인 know-how 이전
- 현장 실측
- 해양학에서 pH 인자의 이용에 대한 토의

IV. 연구개발 결과 및 활용에 관한 건의

- 신 측정방법은 종래의 전극을 이용한 방법에 비해 정밀도가 10 배 이상 뛰어나고, 후일 자료의 보정 또한 가능하므로 향후 모든 해수의 pH의 측정을 위해서는 스펙트로포토메터에 의한 측정방법이 권장됨
- 자료의 정밀도와 정확도를 확보하기 위해서는 100 mm의 광투과거리를 가진 diode array 방식의 스펙트로포토메터의 사용이 권장됨
- 가능한 현장에서의 측정이 권고되나 실험실로 옮겨와 측정코자 할 경우는 반드시 SOP 7 (DOE, 1994)에 실려 있는 방법과 순서에 준하여 시료를 채취 보관하여야함
- 현행 방법에 광섬유 기술을 접목시키면 무인자동측정이 가능해져 환경감시용으로 활용이 기대되며 pH의 광범위한 측정 수요로 보아 산업적인 효과도 기대됨.

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1 | Introduction

In the 19th centuries many prominent chemists had undertaken analyses of inorganic natural substances. One important motivation was the search for unknown chemical elements to fulfill the gaps in the periodic table of elements, which was then being developed. Hundreds of samples of ores, lava then natural waters were analyzed. This leads J. H. van't Hoff to study the sequence of precipitates that form as seawater evaporates. From all these efforts it becomes clear by the end of century that seawater cannot be produced by the partial evaporation of river water. At the end of that route lie only closed-basin lakes such as the Dead Sea and Great Salt Lake, which are highly alkaline compared with oceans.

The processes controlling the composition of seawater were at an impasse until 1950's when Lars Gunnar Sillén of the Royal Institute of Technology in Stockholm showed that composition of seawater is dictated by thermodynamic equilibria of acid-base and oxidation-reduction. He asked what controlled the pH, or free hydrogen ion concentration of the ocean and why pH of the ocean lied consistently between 7.5 and 8 being quite close to acid-base neutrality. Subsequently Frederick T. Mackenzie and Robert M. Garrels of Northwestern University translated Sillén's rather abstract answer into geologic terms.

In short, what happens in the oceans is the reverse weathering process on land. Rocks are an aluminum silicate lattice in which cations are embedded. Chemical weathering is viewed as cation exchange process between hydrogen ion (proton) in rain and other cations in rocks. Rain is an acid solution because carbon dioxide in the atmosphere dissolves in water to make carbonic acid (H_2CO_3). During weathering, rain gives up hydrogen ion, leaving bicarbonate (HCO_3^{2-}) behind; thus rain water becomes alkaline. The hydrogen ions substitute the place of cations in the lattice, freeing them into solution.

This disrupts the lattice, transforming into disordered clay minerals such as kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$), which are easily eroded.

If only the weathering process took place, carbon dioxide in the atmosphere will be consumed up in about 4,000 years and seawater would have been more alkaline. Clearly there must be a reaction that converts bicarbonate back into carbon dioxide. Mackenzie and Garrels noted that the ratio of cations to hydrogen ion is about 1.2×10^3 in average continental waters, whereas that of the seawater is 6×10^7 , four orders of magnitude higher. Thus when aluminum silicate rich in hydrogen ion meets seawater of hydrogen ion depleted, the reactions that made them should reverse. Clays rich in cations should form; hydrogen ions released combine with bicarbonate to make water and carbon dioxide (Fig. 1).

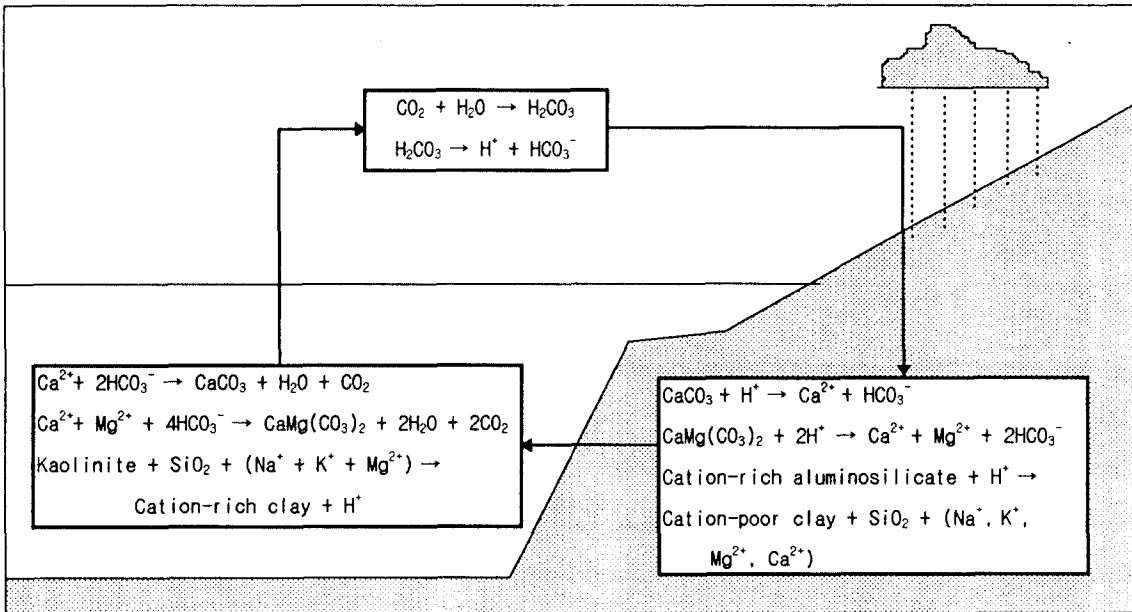


Figure 1. Chemical balance between the atmosphere, the continents and the ocean hypothesized by Lars Gunnar Sillén and worked out in detail by Frederick T. Mackenzie and Robert M. Garrels. Chemical weathering on land should reverse in the ocean to meet the chemical balance.

From a chemical point of view, the oceans are a large chemical reactor with multiple feeds and outputs. The chemical processes occurring within the ocean reactors are kinetically controlled driven largely by organisms, however, thermodynamic equilibria may also be inferred as Sillén first envisioned.

Most salts can dissociate into ions to some extents in seawater. Many ions in solution are in a free state, for example Na^+ and Cl^- . Sometimes we have ion pairs, however, e. g. $\text{Mg}^{2+} + \text{SO}_4^{2-} = \text{Mg}(\text{H}_2\text{O})_2\text{SO}_4^0$, a neutral species is present. If a pairing is made stronger than simple electrostatic nature, we call complex as seen in weak acids HCO_3^- or H_2CO_3 . Chemical equilibrium concept helps us to assess the forms of chemical species.

Historically, the importance of speciation was first recognized in understanding the acid-base properties of seawater. pH significantly influences chemical reactions involving the formation, dissociation, and alteration of various universal phases important in the geochemical cycling of the elements. pH reflects biological processes such as photosynthesis, respiration, denitrification, and sulfate reduction. pH influences biomolecule's ability to associate with cations. Natural waters are either weak acid or weak alkaline solutions, which in most cases allows coexistence of variety of chemical forms. For these reasons, pH regulation on speciation of major cations and anions in seawater is a key to understand the chemical behavior of the ocean. pH is called a master variable in understanding the speciation of constituents in seawater and its accurate and precise measurement are critical to quantitative characterizations of many aspects of ocean chemistry.

Earliest determination of seawater pH was made with colorimetric indicators. Subsequently potentiometric measurement becomes popular as the hydrogen ion-selective glass electrodes proven to be more convenient and precise. By 1970's pH measurement was made routinely on board ship, however, intrinsic problems such as drift and low precision limit the application of pH data. Consequently pH data contributed little in understanding the ocean chemistry. For the time being, oceanic pH

measurement is considered as obsolete by marine chemists, measured only infrequently.

In late 1980's Robert H. Byrne and colleagues in University of South Florida made every effort to develop a dye techniques to measure hydrogen ion concentration in seawater. The results turn out to be a huge success and soon recognized by marine chemist as an ideal substitute for messy glass electrodes. New techniques utilizing protonation/deprotonation of sulphonephthalein indicator showed extraordinary precision on the order of ± 0.0004 pH unit (Clayton and Byrne, 1993) with potential accuracy about ± 0.002 pH unit (Dickson, 1993). Andrew G. Dickson of Scripps Institution of Oceanography expects a revival in the popularity of pH measurements and renewed understanding of the importance of this parameter in interpreting acid-base processes in seawater. Overall, with this new level of precision and accuracy, pH now has a potential to become a parameter of characterizing the processes of controlling CO₂ concentrations in the ocean such as gas exchange, biological uptake and regeneration, and mixing etc.

The concentration of a primary greenhouse gas, CO₂ in the atmosphere has been increasing since the Industrial Revolution by fossil fuel burning and deforestation. We now know that only a fraction of CO₂ released by human is augmented in atmosphere. About 2/3 of CO₂ released is expected to be taken up in the ocean. However, precise amount and pathways are not known yet clearly.

Once CO₂ is dissolved in seawater, it dissociate into 4 chemical species (aqueous CO₂, H₂CO₃, HCO₃⁻, CO₃²⁻) that ocean has about 55 times more carbon than the atmosphere. Unfortunately we cannot measure directly the concentration of CO₂ species in seawater. They can only be inferred indirectly from 4 directly measurable parameters; total hydrogen ion concentration (pH), total dissolved inorganic carbon, total alkalinity, and partial pressure of gaseous CO₂. Theoretically any two of four parameter are enough for precise

characterization of the oceanic CO₂ system. However, it should be noted that comparison of measured and inferred values often fall into inconsistency due to error and sensitivity inherent to each measurement technique. Though redundant, measurements of three parameters including partial pressure of CO₂ are recommended currently for precise description of oceanic CO₂ system.

The aim of the study is to transfer a newly developed spectrophotometric pH measurement technique from proper US institution. We targeted pH, firstly, spectrophotometric pH measurement is simple, precise and cost-effective, and secondly wider area of applications such as biology and physics of the ocean.

Following two chapters deals theoretical background of pH and spectrophotometry, details of spectrophotometric measurement procedures (chapter 2), results of field measurement and discussion on the feasible applications of improved pH data in the future studies (chapter 3).

2 | Spectrophotometric Seawater pH Determination

2.1 Working definition of seawater pH

pH is defined originally as a measure of hydrogen ion concentration of a chemical system, however, it can not be determined exactly by electrometric methods. Instead working definition of pH is used as a measure of hydrogen ion activity responsible for electron motive force in the galvanic cell. At present the most reliable way to determine pH of seawater is to use H₂, Pt/AgCl, Ag electrode. Recently this cell has been used to develop a pH scale using seawater buffers and to determine the proton concentration in seawater (Dickson, 1990 cited in Millero et al., 1993).

The pH on the NBS (National Bureau of Standard) scale is given by the activity of hydrogen ion:

$$\text{pH}_{\text{NBS}} = -\log a_{\text{H}} = -\log (f_{\text{H}}[\text{H}^+]) \quad (1)$$

where, a_{H} is the activity of proton and f_{H} is the factor related to the calibration of the electrode used with NBS buffers. This scale uses dilute NBS buffers to define the pH or activity of proton, a_{H} . Although it is useful in dilute natural waters such as rivers and lakes, it is not recommended for use with seawater.

A pH scale based on the hydrogen ion concentration is more practical for oceanographic application. Three scales which are dependent on different buffer system are proposed. The free ion scale is defined as $\text{pH} = -\log [\text{H}^+]$ but not used for seawater. Two scales have been suggested using the total hydrogen ion scale and the seawater scale.

The total hydrogen ion scale defined by Hansson (1973) also accounts for HSO₄⁻:

$$\text{pH}_{\text{T}} = -\log ([\text{H}^+] + [\text{HSO}_4^-]) \quad (2)$$

The seawater scale includes both sulfate and fluoride ions and defined as:

$$\text{pH}_{\text{SWS}} = -\log ([\text{H}^+] + [\text{HSO}_4^-] + [\text{HF}^-]) \quad (3)$$

The two scales are related as:

$$[H^{+sws}]/[H^{+T}] = (1 + K_{H_2SO_4}[SO_4^{2-}] + K_{HF}[F^{-}]) / (1 + K_{H_2SO_4}[SO_4^{2-}]) \quad (4)$$

where, $K_{H_2SO_4}$ and K_{HF} are the dissociation constant of bisulfate ion and fluoride ion in seawater, respectively:

$$K_{SO_4} = \frac{[H^{+}][SO_4^{2-}]}{[HSO_4^{-}]}, \quad K_{HF} = \frac{[H^{+}][F^{-}]}{[HF]}$$

For conversion of these two pH scales, following expression is used:

$$pH_T = pH_{sws} - \log \left\{ \frac{(1 + [SO_4^{2-}]/K_{H_2SO_4})}{(1 + [SO_4^{2-}]/K_{H_2SO_4} + [F^{-}]/K_{HF})} \right\} \quad (5)$$

or by using eqn. (4):

$$pH_{sws} = pH_T - \log([H^{+sws}]/[H^{+T}]) - \log(1 - 1.005 \times 10^{-3} S) \quad (6)$$

Two units are commonly used and they cause confusion: molarity ($\text{mol}\cdot\text{kg}\cdot\text{H}_2\text{O}^{-1}$) and oceanographer's preferred unit of $\text{mol}\cdot\text{kg}\cdot\text{SW}^{-1}$. These two units are related by (Dickson, 1993):

$$pH(\text{mol}\cdot\text{kg}\cdot\text{SW}^{-1}) = pH(\text{mol}\cdot\text{kg}\cdot\text{H}_2\text{O}^{-1}) - \log(1 - 0.00106 S) \quad (7)$$

where, S is the salinity. Since different scales and units are used it is recommended that data are accompanied with scale and unit.

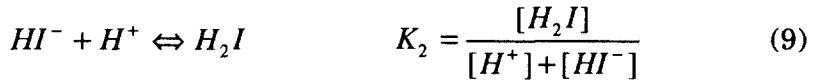
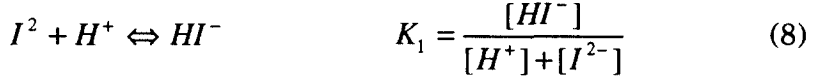
2.2 Theoretical background

Spectrophotometric determination of seawater pH first proposed by Baldo et al. (1985 cited in Breland and Byrne, 1989). The feasibility of spectrophotometric techniques has been probed further by Bob Byrne's group: calibrated against the total pH scale (Clayton and Byrne, 1993) and proven to be reliable enough for seawater CO_2 system study (Dickson, 1994). Owing to Byrne and his colleagues, simple, fast and precise measurement of seawater pH is made possible using spectrophotometer and pH sensitive dyes.

Although seawater consists of myriad of chemical compounds, relatively constant ration among major constituents and very low concentration of reactive trace elements pauses little problem using pH indicator dyes Baldo et

al. (1985 cited in Clayton and Byrne, 1993). Several dyes of sulfonephthalein indicators have suitable pK values close to seawater pH ranges.

All sulfonephthalein indicator exist in three forms: H_2I , HI^- , and I^{2-} with distinctive spectral absorption characteristics. The most popular pH dye, *m*-cresol purple (*m*CP) looks pink as H_2I , yellow as HI^- , and purple as I^{2-} . The chemical equilibria among sulfonephthalein species are described as follows:



where, [] denotes concentration. Total indicator concentration, $I_T = [I^{2-}] + [HI^-] + [H_2I]$, can be expressed in terms of K 's:

$$I_T = [I^{2-}](1 + K_1[H^+] + K_1K_2[H^+]^2) \quad (10)$$

The absorbance (A) at given wavelength due to *m*CP species is described by:

$$A = (\epsilon_I[I^{2-}] + \epsilon_{HI}[HI^-] + \epsilon_{H_2I}[H_2I]) b \quad (11)$$

where, ϵ_X is the molar absorptivity of species X at given wavelength, and b is the optical pathlength in cm. Eqn. 11 is rearranged using eqns. 8 & 9 as:

$$A/b = [I^{2-}] (\epsilon_I + \epsilon_{HI} K_1 [H^+] + \epsilon_{H_2I} K_1 K_2 [H^+]^2) \quad (12)$$

Dividing eqn. 12 by eqn. 10, and introducing new variable $a = A/(b I_T)$

$$a = \frac{\epsilon_I + \epsilon_{HI} K_1 [H^+] + \epsilon_{H_2I} K_1 K_2 [H^+]^2}{1 + K_1 [H^+] + K_1 K_2 [H^+]^2} \quad (13)$$

At low pH, when $[I^{2-}]$ is low enough to neglect, eqn. 13 is simplified to:

$$a = \frac{\epsilon_I + \epsilon_{H_2I} K_2 [H^+]}{1 + K_2 [H^+]} \quad (14)$$

On the contrary at high pH, $[H_2I]$ is low enough, then eqn. 13 is simplified to:

$$a = \frac{\epsilon_I + \epsilon_{HI} K_1 [H^+]}{1 + K_1 [H^+]} \quad (15)$$

Typical natural seawater has a pH range of about 7.4 to 8.4, in this case $[H_2I]/I_T$ is approximately 10^{-7} . Therefore eqn. 15 is appropriate to describe the absorbance of *mCP*. Using eqn. 15 at two different wavelengths of λ_1 and λ_2 , and introducing the ratio of A_{λ_1} and A_{λ_2} :

$$R = A_{\lambda_2} / A_{\lambda_1} = \frac{\epsilon_{I,\lambda_2} + \epsilon_{HI,\lambda_2} K_1 [H^+]}{\epsilon_{I,\lambda_1} + \epsilon_{HI,\lambda_1} K_1 [H^+]} \quad (16)$$

manipulating eqn. 16 yields:

$$\text{pH} = \log K_1 + \log \left(\frac{R - e_1}{e_2 - R e_3} \right) \quad (17)$$

where, $\text{pH} = -\log[H^+]$, $e_1 = \epsilon_{HI,\lambda_2}/\epsilon_{HI,\lambda_2}$, $e_2 = \epsilon_{I,\lambda_2}/\epsilon_{I,\lambda_2}$, $e_3 = \epsilon_{I,\lambda_1}/\epsilon_{HI,\lambda_1}$.

Clayton and Byrne (1993) did intensive calibration on spectrophotometric determination of seawater pH using *mCP*. The wavelengths of maximum absorption of three *mCP* species are:

$\lambda_0 = 529$ nm; maximum absorption wavelength of ϵ_{H_2I}

$\lambda_1 = 434$ nm; maximum absorption wavelength of ϵ_{HI}

$\lambda_2 = 578$ nm; maximum absorption wavelength of ϵ_I

Through intensive laboratory experiments with artificial seawater, Clayton and Byrne (1993) reported values of $e_1 = 0.0069_1$, $e_2 = 2.222_0$, $e_3 = 0.133_1$ and the dependence of K_{IT} ($\text{mol}\cdot\text{kg}\cdot\text{soln}^{-1}$) on salinity (S) and temperature (T) is described as:

$$\log K_{IT} = 1245.69/T + 3.8275 + (2.11 \times 10^{-3})(35-S) \quad (18)$$

over the temperature range $293 \leq T \leq 303$, and salinity $30 \leq S \leq 37$. pH ($\text{mol}\cdot\text{kg}\cdot\text{soln}^{-1}$) on the total hydrogen ion scale is then expressed as:

$$\text{pH}_{T(\text{sw})} = 1245.69/T + 3.8275 + (2.11 \times 10^{-3})(35-S) + \log \left(\frac{R - 0.0069_1}{2.222_0 - R 0.133_1} \right) \quad (19)$$

For natural seawaters, absorption at λ_0 is insignificant that absorbance ratio at λ_1 (434 nm) and λ_2 (578 nm) are utilized as $R = A_{578}/A_{434}$.

Injection of dye inevitably perturbs the sample pH slightly. To a samples of seawater about 30 ml volume, a injection of 80 μ l mCP solution changes pH less than 0.005 pH unit. Clayton and Byrne (1993) recommended to use a linear correction curve:

$$R = R_m + (A + B R_m) V \quad (20)$$

where, R_m is the measured absorbance ratio, V is the volume of mCP injected to sample, and A and B are the constants. With proper corrections, Clayton and Byrne (1993) reported the analytical precision is approximately 0.0004 pH unit.

2.3 Analytical procedures

This method is based on the procedures by Clayton and Byrne (1993) that utilizes the pH sensitive sulfonephthalein dye, m-cresol purple, and dissociate according to seawater pH. Absorption peaks of the dye are measured either by conventional UV-VIS or extended VIS spectrophotometer. This is a simple, fast and precise technique armed with much higher precision over conventional method using commercial electrodes. When spectrophotometer with PC control port is used routine measurement task can be facilitated by software originally developed by Millero's group in University of Miami.

A. Capability

Applicable range: oceanic seawater with pH 7.6 to 9.2

temperature: 293 - 303 K (20-30°C)

salinity: 30 - 37 ppt

Precision: 0.0004 pH unit

B. Outline of method

pH sensitive mCP is injected to seawater sample. Dye dissociates into chemical species according to a pH of solution in a moment. Maximum absorption peaks of two chemical species are measured at 578nm and 434 nm

by spectrophotometer. The ratio of peaks along with temperature and salinity of seawater samples used to calculate the pH in total scale.

C. Special apparatus and equipment.

Spectrophotometer: UV-VIS or extended VIS band, longpath cell (10 cm) holder mounted, diode-array type with PC communication port is recommended.

Flexible drawing tube: approximately 40 cm long, sized to fit snugly over cell port. Silicon rubber is suitable for this

Micropipette: for use dye injection. capacity- 100 μ l with adjustable volume. narrow PTFE tip is to be used.

Refrigerated thermocirculator: $25 \pm 0.05^\circ\text{C}$

Thermostated compartment: custom made that can hold 12 cells at once without getting them wet

D. Sampling procedure and sample storage

Collection of water at sea from Niskin bottle or other suitable sampler must be done soon after opening the sampler. It is recommended to take the sample before much water (less than half the bottle) has been removed from sampler to minimize the gas exchange with the head space. Generally trace gas sample has the highest priority. In any case, taking sample as soon as possible (within 10 minutes) reduces contamination. High quality borosilicate bottles are prepared with precombustion at $450\text{-}550^\circ\text{C}$ followed by rinse with deionized water. Chemical cleaning using a detergent is also fine when rinsed carefully.

Bottle is rinsed twice with 30 to 50 cm^3 of sample, so as to remove any traces of previous sample. The bottle is filled from the bottom using a silicon tube which extends from the Niskin drain to the bottom of bottle. To avoid bubbling, silicon tube is soaked for one day prior to use in clean water. The water is overflowed by at least a half, and preferably a full bottle volume.

A head space of 1% of the bottle volume is left to allow for water expansion without leakage. This can be done by removing excess water using a plastic pipette with a bulb. Mercuric chloride is then added to poison the sample. The recommended minimum amount is 0.02% by volume of a saturated aqueous solution.

Careful sealing of bottle is critical for long term storage of sample. Firstly wipe out the water in the neck and stopper with tissue. Grease the stopper with 4 vertical strips of Apiezon-L grease, each strip extending 2/3 of the way from top toward bottom of the ground portion of the stopper. This provides a path for air to escape when the stopper is inserted into the neck of the bottle. Insert the stopper completely, and twist the stopper to ensure a good seal. The clip or other positive pressure closure should then be secured. The bottle is shaken to disperse the mercuric chloride solution.

The samples should be stored in a cool, dark location. Refrigeration is preferred, however, avoid freezing. The following information must be recorded in the sampling log book at the time of sampling.

- Time and date of sampling
- Name of person who took the sample
- Location: an unambiguous designation of station, cast, water sampler number
- Container designation: a number or symbol unique to the sample container
- Comments: additional information, problems with sample collection, etc.

Some duplicate sampling is recommended both from the same water sampler, and from two samplers tripped together at the same depth to assess the quality of the sampling procedures.

E. Reagents

2.0 mM *m*-cresol purple indicator solution: Dissolve *m*-cresol in deionized water (191.2 mg of Sigma™ *m*-cresol purple (C₂₁H₁₈O₅S, FW: 382.4) in 250 ml of deionized water). pH should be adjusted as close as to the expected pH of sample using 1N HCl or NaOH. For general use pH 7.9 ± 0.1 is recommended. This implies that absorbance ratio (A₅₇₈/A₄₃₄) of *m*-cresol about 1.6. pH adjustment reduces the pH perturbation by injection of indicator solution to sample. Filter indicator solution with 0.45µm Millipore™ membrane filter. Since indicator solution is susceptible to atmospheric contamination, storage of indicator solution in a collapsible container or syringe is recommended to minimize atmospheric CO₂ contact. Checking absorbance ratio (A₅₇₈/A₄₃₄) prior to use is strongly recommended (Clayton and Byrne, 1993)

F. Measurement procedure

1. Set thermocirculator temperature to 25°C.
2. Take sample directly from seawater bottle or from sample storage bottle to longpath (10 cm) spectrophotometer cell using silicon tubing. Overflow more than 2 times volumes of cell and fill up to neck. Minimize air contact and bubbling during transfer of sample as described in sampling procedure and storage. Place teflon stopper gently and twist close.
3. Place cells in a thermocirculator and kept for more than 20 minutes.
4. Measure sample blank (unless you have dual beam spectrophotometer) from spectrophotometer.
5. Take out cell and inject exactly 80µl of 2.0mM *m*-cresol purple indicator solution, place stopper then shake gently about 20 times.
6. Put cell back to spectrophotometer and measure absorbance at 730, 578, 434 nm 10 times per sample. Steps 4 to 6 should be done normally within 10 minutes to avoid temperature change.

G. Calculation

1. Calibrate measured absorbance ratio (A_{578}/A_{434}) according to your correction curve (eqn. 20) you have determined
2. Mean and standard error calculated in step F-6 are used for calculation of pH as described in eqn. 19

PC-BASIC program developed for use with Hewlett-Packard diode-array model 8452A UV-VIS spectrophotometer may be used directly or modified for other spectrophotometers (Appendix I). Calculation, quality assurance procedures are imbedded in software. Details about calculation and quality assurance should be referred to DOE (1994).

3 | Results and Discussion

3.1 Field procedures for the measurement of seawater pH

Water sampling and hydrographic measurements were conducted on board the R/V Onnuri in the southwestern part of the East Sea between April 13 to 17, 1995 (Fig. 2 and Table 1) as a part of the “Study on the Oceanic Atlas in the Adjacent Seas to Korea - Southwest of the East Sea”. A total of 15 duplicate samples consisting of five surface water samples and 2 depth profile samples were collected using CTD-rosette with 24 x 10 liter Niskin bottles by method described in previous sampling and storage section. One set of samples were sent to Prof. F. J. Millero’s laboratory, Rosenstiel School of Marine and Atmospheric Science, University of Miami for the determination of total alkalinity and total CO₂ (Table 1).

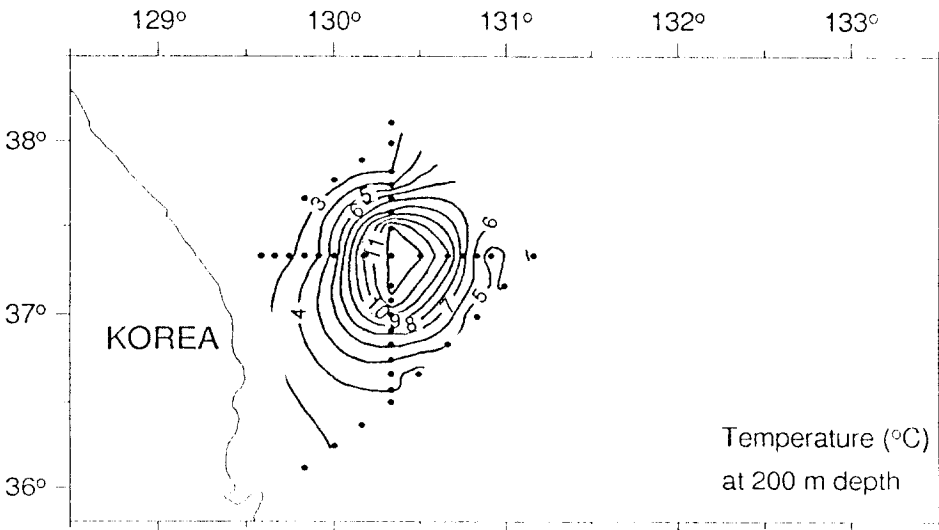


Figure 2. Temperature distribution at 200m depth; dots represent the hydrographic stations visited for the April 1995 cruise.

Table 1. Data from seawater samples collected off the southwestern East Sea during April '95 cruise.

Location		Depth (m)	T (°C)	S (‰)	pH _{sws}	T _{alk}	Total CO ₂
Latitude	Longitude						
35.60N	128.40E	0	14.68	34.57	8.0158	2290.7	1993.5
36.08N	129.50E	0	13.48	34.59	7.9889	2296.2	2018.7
36.30N	130.00E	0	12.25	34.54	7.9857	2293.4	2009.2
37.60N	130.20E	0	12.22	34.49	7.9774	2295.5	2015.9
37.20N	129.35E	0	12.67	34.58	7.9836	2292.6	2011.7
37.20N	130.20E	0	11.60	34.51	7.9535	2287.3	2028.5
		50	11.32	34.50	7.9427	2291.3	2037.2
		100	11.23	34.50	7.9359	2285.6	2032.9
		500	0.68	34.10	7.4835	2269.9	2209.3
		1000	0.28	34.10	7.4655	2280.0	2227.9
37.20N	131.10E	0	12.64	34.62	7.9670	2289.8	2008.6
		100	11.30	34.54	7.8710	2283.9	2062.9
		300	1.40	34.09	7.5706	2270.3	2172.4

3.2 Results of the measurement of seawater pH

Seawater pH was measured in the laboratory using a Hewlett-Packard diode-array UV-VIS spectrophotometer (model 8452A) with 2.0 mM *m*-cresol purple indicator prepared as described in Clayton and Byrne (1993). All absorbance were measured at 25°C using thermocirculator. For presentation, seawater scale is used (mol·kg-seawater⁻¹) throughout the report.

The reported precision of 0.0004 pH unit should be observed as is, however, the absolute accuracy is not guaranteed owing to lack of facilities to check. We simply expect the accuracy of our experiment is on the order of 0.01 pH unit (*cf.* Dickson, 1993 estimate 0.002).

The precision of pH measurements can be inferred usually from duplicate sample analysis from same water bottle and double trip sample analysis that

compares results of simultaneously fired water samples at a given depth. In our field experiments, double trip sampling was not possible due to a sampling scheme. Replicate samples were sent to CO₂ laboratory of Seoul National University for comparison, however, data are not released yet.

The pH of natural waters frequently measured at a fixed temperature (e. g. 25°C) and it is sometimes desirable to know the pH as is. The most reliable way to calculate the effect of temperature on pH is to use the value at a fixed temperature with another carbonate parameter such as total alkalinity or total CO₂. These experimental parameters can be used to determine the pH at another temperature from thermodynamic relationships. If only the pH is determined, one can estimate pH at another temperature from thermodynamic equations for waters at a fixed total alkalinity and total CO₂.

Millero (1995) used thermodynamic constants of Roy et al (1993, cited in Millero 1995) to generate values of pH_{sws} for waters of fixed total alkalinity and total CO₂ (TA/TCC₂ = 1.0 to 1.2) from 0 to 40°C and S = 30 to 40. Values of pH_{sws} appear to be a linear function of temperature, however, a quadratic fit is needed to fit the pH down to ± 0.001. The values of pH_{sws} are not very sensitive to salinity and the ratio of TA/TCO₂. pH_{sws} of seawater ranging from 0 to 40°C, S= 30 to 40, and pH from 7.5 to 8.5 have been fitted to quadratic equation by Millero (1995) as:

$$pH_t = pH_{25} + A + BT + CT^2 \quad (21)$$

$$A = -2.6462 - 0.0011019 S + 4.9319 \times 10^{-6} S^2 + 5.1872 X - 2.1586 X^2$$

$$B = 0.10265 - 0.20322 X + 0.084431 X^2 + 3.1618 \times 10^{-5} S$$

$$C = 4.4525 \times 10^{-5}$$

where, T, S denotes temperature and salinity, and X = TA/TCO₂. Millero discussed this translation accompanied by a typical standard error of 0.003 in pH unit. Data listed in Table 1 are qualified for using equation 21 that translates observed pH values to those at in situ temperature.

Spectrophotometer-determined pH of surface seawaters are plotted both as measured at 25°C and after conversion to an in situ temperature value using equation 21 (Fig. 3). Although measured values showed a good linear relationship with surface temperature ($n=7$, $r^2=0.80$), corrected to in situ temperature data exhibit no such trend ($r^2 < 0.1$). Despite the small area surface temperature of the study area varies over 3 degrees due mainly to the propagation of northward warm current into the system. Lack of defined relationship of pH with surface temperature attribute to a dynamic changes caused by current, mixing, eddy, etc. characteristics of the region prevent thermodynamic equilibrium requiring longer time than the time scale of physical perturbations.

Biological production can also affect surface seawater pH to a certain degree. Nonetheless the effect of a primary productivity on pH was not explored in depth in this pilot study. Primary reason for that is lack of a handy high precision primary production measurement techniques. Complicated situation arises from the fact that from a chemical point of view, what matters to seawater pH is not a biomass that can be inferred rather rigorously from chlorophyll concentrations but a primary productivity which unfortunately we don't have handy measurement techniques as chlorophyll.

To construct a relationship between pH change and chlorophyll concentration, it seems we need a fair number of time series data sets. For that purpose we need to monitor at least, four parameters simultaneously; pH, temperature, chlorophyll, and nutrients. Also it should be mentioned that we don't have a such instrument at hand.

Currently biological uptake of CO₂ in seawater can be traced more precisely with pCO₂ change than pH change. One line of group seeks to develop an autonomous pCO₂ measurement system for mooring applications whereas others look at the autonomous pH logger which seems much cheaper and easier to develop compared to a sophisticate pCO₂ system.

Temperature vs. pH at surface

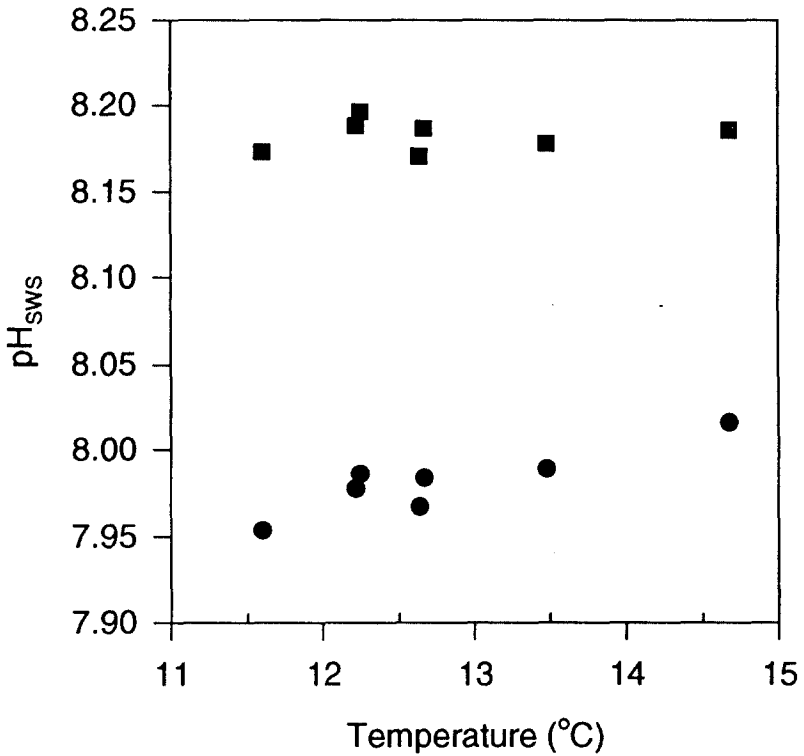


Figure 3. Relationship between sea surface temperature and pH_{sws} (in seawater scale) measured in the East Sea Eddy Cruise Apr.1995; circles represent measured values at 25°C and squares for in situ temperature corrected values.

Two vertical profiles of pH were obtained during the East Sea Eddy Cruise. For comparison, one was obtained near the center of eddy (Fig. 4) and the other at outer edge of the eddy (Fig. 5). At both sites pH showed a general pattern of decrement with depth. Because the number of data at the edge of eddy was limited due to sample leakage and broken bottles by accident, depth to depth comparison was not possible as intended. When vertical profile of central eddy site is compared to that of outer edge, development of thick surface mixed layer is seen clearly from both temperature and pH profiles.

Temperature-pH diagrams (Figs. 4c and 5c) reveal quite distinct nature of the two stations. T-pH diagram of the central station points out the possibility of linear relationship, however, that of the outer edge station suggests the curvilinear relationship. At present, description of seawater carbonic system focused on the effect of a meso-scale eddy is not published that only first order estimates were attempted here.

The shape of T-pH diagram, i.e. degree of linearity, seems to reflect the relative dominance between thermodynamic equilibria and kinetic control of the carbonic system. It can be viewed that with an enhanced mixing by rotating eddy, possible kinetic disequilibria driven by primary producers were masked out and resulted in a more or less linear relationship. On the other hand, where physical mixing is weak as in the case of summer stratification, local disequilibria are developed typically in the surface waters due mostly to biological and photochemical processes. Slow mixing and kinetic disturbance renders T-pH relationship more complicate resulting in a departure from simple linear relationship.

Since surface temperature of eddy was different (colder in our case, Table 1) from adjacent waters, biological activities are expected to be quite different too. Different shape of pH profiles (Figs. 4c and 5c) might be an indication of different physicochemical or biological processes took place.

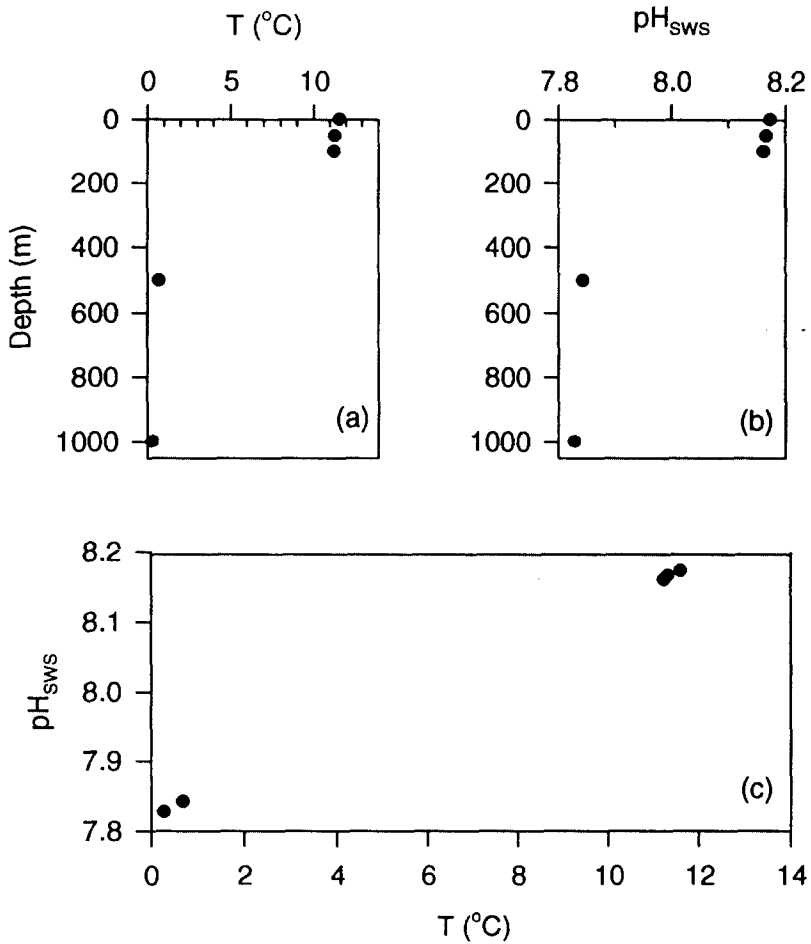


Figure 4. Depth profiles of (a) temperature, and (b) pH_{sWS} (seawater scale at in situ temperature), and (c) temperature vs. pH_{sWS} near the center of eddy (37.20N, 130.20E) in Apr. 1995.

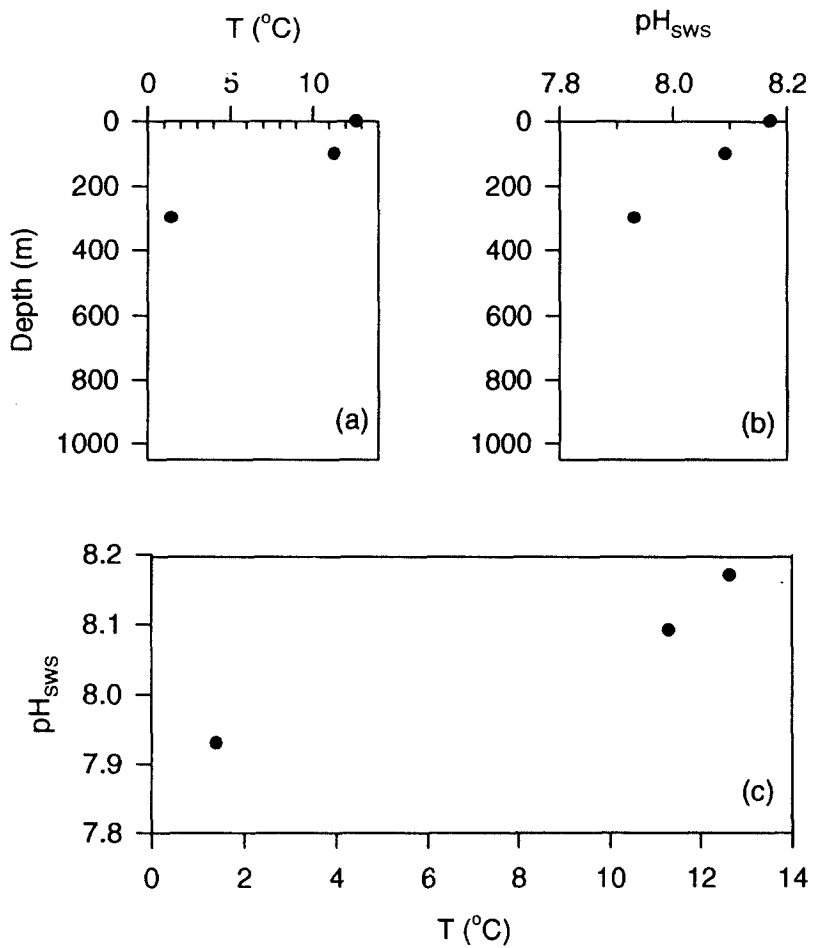


Figure 5. Depth profiles of (a) temperature, and (b) pH_{sws} (seawater scale at in situ temperature), and (c) temperature vs. pH_{sws} near the edge of eddy (37.20N,131.10E) in Apr. 1995.

3.3 Discussions

The prime reason why we measure the pH resides in that all chemical and physical processes, including biologically mediated ones, are governed by thermodynamic and kinetic principles where pH along with pE, temperature, and ionic strength of natural waters plays key roles in determining the composition of chemicals in aqueous system. Thermodynamic principles dictate equilibrium reactions and indicate the direction of spontaneous reactions at given conditions.

Under natural conditions, elements or compounds often found in various chemical and physical states, for example, H₂O as vapor, water, or ice depending on temperature and pressure, also known to exist as ionized to OH⁻ and H₃O⁺ in solution. Of specific environmental concerns, trace metals in aqueous system seldom exist as free ions, but as complexes bonded to variety of organic, inorganic and hydrated ligands which affect mobility, reactivity and solubility of compounds.

In reality, what we see in nature is far different from the composition and distribution of elements dictated by chemical equilibrium. Under current conditions most stable form of nitrogen is nitrate, however, 80% of nitrogen in the atmosphere consists of gaseous nitrogen (N₂). Such discrepancy is caused due in part to the fact that the spontaneous reactions do not always reach quickly and partly to the organisms which actively mediate the chemical reactions at the expense of energy. Potential and stored energy is released as chemical reactions proceed toward equilibrium state. Organisms are evolved to exploit the free energy from spontaneous but slow processes with their sophisticated biological catalysts.

Over the past 200 years since the industrial revolution, human mobilized a huge amount of chemicals at the surface of the earth which inevitably have disturbed the natural environmental balances. Two aspects of the perturbation have been recognized as serious; toxic effects on ecosystem and global climate changes. Until recently the former has been of primary concerns

where as the latter received growing concern these years. With regard to anthropogenic impacts on environment, trace metals and carbon are the major target elements. Understanding the cycling of these elements is essential to cope with environmental issues. The importance of pH in the oceanic water body, viewed frequently as carbonate buffer system, has already been discussed in introduction with respect to the global warming anticipated in the next century.

In aqueous systems major route of elements transportation is via waterways. During a long journey of elements from land to ocean, they faced drastic changes in terms of thermodynamic master variables of pH, pE, ionic strength and to a less degree temperature. As briefly mentioned earlier in introduction, most radical changes occurs in estuary where river water and seawater mixes. Transition metals bound to refractory organic materials, sediments and clay minerals abound in fresh water are displaced by alkali and alkaline earth metals or inorganic ligands abound in seawater. Two major variables of pH and ionic strength changed within water body and pE changes abruptly in the bottom sediments.

Most transition metals discharged into fresh water are bound to humic or fulvic acid, where as metal ions in marine environments generally precipitate as hydroxides, carbonates and sulfides or are bound to soils and sediments. Adsorption of metals onto sediments is generally fast. The adsorption of metals into clay minerals is dominated by pH, with the clay acting as an ion exchange resin. pH change (from 7.x to 8.x) as well as salinity change at estuary play critical role in removal of metal ions such as aluminum, iron, manganese and lead from land. The importance of pH is well illustrated by example of spontaneous oxidation reaction of ferrous ion (Fe^{2+}) to ferric ion (Fe^{3+}). Reaction halftime of this uncatalyzed reaction at pH below 4 is over 3 years, whereas that at about pH 7.5 is order of minutes (Stumm and Morgan, 1981).

Due to complexity of nature and human perturbation, myriad forms of chemical exist in natural waters. So far most of our knowledge comes from the laboratory experiments in the context of thermodynamic point of view. The activities of small organisms, especially microbes, are so intense that they do profound influence on the concentration of elements in the atmosphere, aquatic, and terrestrial environments (Lovelock, 1979) via kinetic control. When vast amount of CO₂ is removed by photosynthesis in summer, pH can go up from 7.2 to 9.2. Cadmium and zinc complexes are very sensitive to changes of pH in this region (Folsom and Wood, 1986). Since photosynthesis assimilates not only bicarbonate but nitrate, ammonia and phosphate, this affects the seawater alkalinity.

Despite the importance of pH in chemical reactions occur in estuarine environment in situ pH data were seldom utilized due to low resolution of potentiometric techniques and intrinsic problem associated with instability of electrode near the seawater pH of around 8. With the advent of precise pH measurement technique, revival of pH determination by spectrophotometer is expected in many fields of oceanography.

As discussed above pH is a rather simple property, however, interlinked with various physical, chemical and biological processes. Since pH variation is pronounced in estuary despite small space-time dimension, spectrophotometric pH measurement for the study of estuarine processes seems inevitable and rewarding when jointly measured with parameters of interest such as salinity, temperature, oxygen, nutrients, and concentration of target chemicals, etc.

Despite the growing popularity, to date papers utilizing the enhanced resolution of a spectrophotometric pH measurement technique are scarce (Feely et al., 1994; Bellerby et al., 1995; Millero et al., 1995) due mostly to a recent development.

Eastern equatorial Pacific supplies approximately 1-2 giga tons of carbon annually as CO₂ to the atmosphere and is the largest single natural source of carbon to atmosphere. Feely et al. (1994) reported that tropical instability

waves with periods of 15 to 20 days and zonal wave length of 700-800 km exert profound impacts on the variability of temperature and nutrients which controls CO₂ exchange. He and his colleagues surveys the CO₂ system parameters with other environmental factors and presented well defined wave like zonal fluctuations of temperature and CO₂ parameters. A very good correlation of pH with temperature is evidenced in the range from 8.036 to 8.102 which can only be made possible with the improved precision of spectrophotometric determination of pH. Clayton et al. (1995) observed similar wave-like fluctuations of CO₂ parameters induced by tropical instability waves in the equatorial Pacific.

Application of spectrophotometric determination of seawater pH in the field of biological production was attempted by Bellerby et al (1995). Their study was focused on the response of pH and *p*CO₂ to water mass changes and chlorophyll concentration. They concluded from Southern Ocean survey that no single parameter controlled the CO₂ system. Over majority of cruise track hydrographic condition was responsible for the observed distribution with the exception of high chlorophyll patches, where both pH and *p*CO₂ were well explained by the chlorophyll concentrations in the surface waters. pH in regions of containing more than 1 mg-chl. a·m⁻³ showed a strong relationship with chlorophyll a content ($r^2 = 0.86$, $n=80$). They also reported that pH and *p*CO₂ were fine enough to reveal a significant mesoscale variability in CO₂ system of surface waters.

It is, however, worthy of mentioning that correlation of pH with chlorophyll is currently poorer than when *p*CO₂ is used instead. This no doubt reflects the lower precision of the pH measurement techniques (precision of 0.005 pH unit is equivalent to 1.2% error, whereas those of *p*CO₂ is 0.5%). A desirable precision would be 0.001 pH unit which can be easily achievable when reliable instrumentation is adopted (*cf.* Clayton and Byrne, 1993).

Since chlorophyll content is a proxy of primary production, the result of Bellerby and colleagues deserve to test a new possibility that once the

relationship between primary production and pH is established, primary production can be estimated indirectly with simple pH measurements in productive coastal waters. Measurement of pH is easier than that of productivity by all means including remote sensing of chlorophyll which is not translated rigorously to primary production. Monitoring of pH can be routinely adopted to ship-of-opportunity and unmanned platforms such as data buoys and submersibles. An *in situ* photometric technique has already been developed for nitrate (Johnson et al., 1989), and although extension of pH would require multiple wavelength measurements, such a development should be technically feasible.

Utilizing the precision of spectrophotometric pH measurement techniques, Millero and his colleagues tested the 'iron hypothesis' of late John Martin near the Galapagos Islands (Millero et al., 1995 submitted). This is one of places so called high-nitrate, low chlorophyll (HNLC) waters where iron deficiency is hypothesized as responsible for slow growth of phytoplankton despite the plentiful nitrate supplied by upwelling of deep nutrient rich waters. They performed mesoscale iron-enrichment experiment and monitored the CO₂ pull down effect. Though result was somewhat less exciting regarding the removal of carbon, ability of pH and other parameters tracing CO₂ system change caused by iron spiking was unambiguously manifested. The result clearly demonstrates the applicability of pH measurement for the evaluating the degree of artificial perturbation in chemical system of natural waters.

Ideas of exploiting seawater pH are not necessarily restricted by the precision of determination. Most striking idea is formulated by Brewer et al. (1995); improving the understanding of sound absorption of seawater by refined pH measurement. Sounds of below 1 kHz frequencies are absorbed by seawater as a function of pH. Overall accuracy of sound absorption coefficient of 15% requires precision of pH of 0.05 unit whereas spectrophotometric determination offers enhanced precision down to 0.002 pH unit. Obverse approach is also attempted by Jin and Worcester (1989, cited therein). They

examine the possibility of deducing pH from acoustic signals. Both kind of studies will contribute a lot to the understanding of ocean in a global context.

Recently upwelled seawater is characterized by low pH because not much bicarbonate ions are taken up by photosynthetic algae. In compiling extensive survey data historically available to the Peruvian upwelling system, Copin-Montégut and Raimbault (1994)'s review included the pH data. Treatment of pH data by authors clearly demonstrates why once flourished pH measurements were put obsolete. With the precision offered by commercial electrodes, due to their inferior precision, data can only be used to check the consistency of pCO₂ measurements which have much superior precision over pH.

Chinese oceanographers are among the few who consistently treat seawater pH as important environmental parameters. Since they relied on the potentiometric techniques with conventional electrodes precision of the measurements is on the order of 0.01 pH unit. With this precision, as seen in other cases, quantitative description of chemical behaviors of elements seldom meets requested standards of international scientific journals. Recently Tian et al. (1993) studied the chemical nature of Changjiang plume fronts. They surveyed the area with finer grid than previous ones and showed that sharp nutrient fronts exist and geographical variation in nutrients concentrations, pH and biological production in narrow frontal band are tightly linked to each other. Just outside the plume front, authors found enhanced primary production resulted in raised pH. This points out the usefulness of monitoring seawater pH in estuary, plume and front. Since CO₂ system adjustment induced by physical perturbation such as seasonal warming and cooling, salinity diffusion takes relatively longer time (order of couple of months) compared to biological production (order of days) routine measurement of pH with other environmental factors such as temperature, salinity and nutrients can provides valuable information on high frequency variation.

Currently pH measurements are made most frequently for the study of oceanic CO₂ system. The commonly measured parameters used to study the CO₂ system are pH, TA (total alkalinity), TCO₂ (total inorganic carbon), and fCO₂ (fugacity of CO₂ as a proxy of partial pressure of CO₂ gas). Interestingly our famous Korean chemist Park (cited in Millero, 1995) was the first to point out that at least a pair of those 4 parameters is needed to characterized the carbonate system. Although pH can be measured very preciously (0.0004 pH unit), claimed accuracy (0.002 pH unit) is still under debate and relatively unsatisfactory (Table 2 and 3). This is the reason why pH is currently not a favored parameter for CO₂ system study. pH is often used to check the internal consistency of CO₂ system inferred from other parameters.

Table 2. Estimates of the analytical precision and accuracy of measured pH, TA, TCO₂ and pCO₂ (after Millero, 1995).

Analysis	Precision	Accuracy	Reference
pH (spectrophotometric)	± 0.0004	± 0.002	Clayton and Byrne (1993)
TA (potentiometric)	± 2 μmol·kg ⁻¹	± 4 μmol·kg ⁻¹	Millero et al. (1993)
TCO ₂ (coulometric)	± 1 μmol·kg ⁻¹	± 2 μmol·kg ⁻¹	Johnson et al. (1993)
fCO ₂ (infrared)	± 0.5 μatm	± 2 μatm	Wannikhof and Thoning (1993)

Table 3. Estimated probable errors in the calculated parameters of carbonic system using various input pairs (after Millero, 1995).

Input pairs	ΔpH	ΔTA	ΔTCO ₂	ΔfCO ₂
pH-TA	-	-	± 3.8	± 2.1
pH-TCO ₂	-	± 2.7	-	± 1.8
pH-fCO ₂	-	± 21	± 18	-
fCO ₂ - TCO ₂	± 0.0025	± 3.8	-	-
fCO ₂ -TA	± 0.0026	-	± 3.2	-
TA- TCO ₂	± 0.0062	-	-	± 5.7

Errors of pH inferred from other parameters are only slightly higher than that of direct measurement that pH can be calculated rather rigorously. On the other hand, estimated annual increment of $p\text{CO}_2$ is rather small, about $2 \mu\text{mol}\cdot\text{kg}^{-1}$ which necessitates the direct measurement of $p\text{CO}_2$. Since coulometric measurement of total inorganic carbon is accurate and inference from other parameters are not satisfactory, direct measurement is also recommended. Considering errors in experiments and thermodynamic calculations, Millero (1995) recommend the best two parameters for the study of CO_2 system in natural waters are $f\text{CO}_2$ and TCO_2 which are more directly related to the carbonate system.

From this study, a spectrophotometric determination of pH was proven to be precise and accurate enough with amenable uncertainty inherent to thermodynamic characteristics of dye. It is manifest that this is an easy and fast way of determining seawater pH. At present, the accuracy of spectrophotometric pH determination is not readily assessed, however, this uncertainty does not hinder from using spectrophotometric pH techniques since data can be corrected later flawlessly. The uncertainty arises from the dissociation characteristics of dye (*m*-cresol purple) in medium. Future refinement of K_s in this field of study can simply adopted for update or revision of spectrophotometric pH data. This merit along with high precision comprises unique advantage over potentiometric method which lacks revision. To ensure the high precision and accuracy diode-array spectrophotometer with 100 mm light path is recommended. Such instrumentation also handles more samples per time.

Next task in spectrophotometric technique will be the development of autonomous data gathering for use with drifters, mooring buoys etc. As stated before, photometric determination of other chemicals, especially nutrients, are under development plug in of pH detection unit can cause with minimal

charge. Recently Ocean Optics, Inc. (Dunedin, Florida) offers a miniature fiber-optic spectrophotometer. This company announced that the idea for this instrument was born when his partner, a marine biologist Michael Morris, was asked by the US Department of Energy to adapt a phenol red (now m-cresol purple is more popular dye) fiber-optic pH measuring system for use as a free-floating oceanographic pH sensor (Weiss, 1995). One of the most fascinating feature of pH measurement is tracing CO₂ system change. Because pH measurement is the simplest procedure compared to other three CO₂ system parameters, pH measurement will flourish in the near future.

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Appendix

'Qbasic PROGRAM to measure pH using m-CRESOL PURPLE dye on HP8452A'

'The original program is written in Professor F. J. Millero's lab in the University of Miami'

'Note that 52setup.bas is a program exclusively for use with HP8452 and a property of HP.'

'One who wishes to use other computer controllable spectrophotometers should use' 'appropriate software comparable to 52setup.bas.'

'Note that several commands such as measure and blank are activated by 52setup.bas'

'Beware that data file directory is specified as C:\pH\data in the following line.'

'One must have the directory before the execution of program, otherwise it will report error.'

'Initializing ...

```
$INCLUDE: '52SETUP.BAS'
```

```
CLS
```

```
INPUT "Enter Station Code"; STN$
```

```
FIL$ = "C:\pH\data\" + STN$ + ".pH"
```

```
INPUT "Enter number of samples for this station"; II%
```

```
FOR JJ% = 1 TO II%           'start spectrophotometric measurements'
```

```
    INPUT "Enter sample depth"; SPL
```

```
    INPUT "Enter salinity?"; S
```

```
    PRINT ""
```

```
        PRINT "Insert Blank, then press any key" 'start blank reading'
```

```
        WHILE INKEY$ = "": WEND
```

```
        blank                               'stop blank reading/adjust base line'
```

```
    PRINT "Insert sample, then press any key" 'start sample reading'
```

```
    WHILE INKEY$ = "": WEND
```

```
        WAVEMODE = 1
```

```
        NUMWAVES = 3
```

```

WAVELIST(1) = 434
WAVELIST(2) = 578
WAVELIST(3) = 730
measure
PRINT USING "wavelengths      #####      #####      #####"; RAW(1, 1); RAW(2,
          1); RAW(3, 1)
PRINT
A = 0: B = 0: C = 0: ASD = 0: BSD = 0: CSD = 0
FOR I% = 1 TO 10                                'reading sample 10 times'
  KILLTIME 1                                    'wait mode'
  measure
  AB(1, I%) = RAW(1, 2): AB(2, I%) = RAW(2, 2): AB(3, I%) = RAW(3, 2)
  PRINT USING "                #.####      #.####      #.####"; RAW(1, 2);
          RAW(2, 2); RAW(3, 2)
  A = RAW(1, 2) + A
  B = RAW(2, 2) + B
  C = RAW(3, 2) + C
NEXT I%                                          'stop sample reading & spectrophotometer operation'
'statistical operation for mean & standard deviation'
AM = A / 10
BM = B / 10
CM = C / 10
FOR I = 1 TO 10
  ASD = (AM - AB(1, I)) ^ 2 + ASD
  BSD = (BM - AB(2, I)) ^ 2 + BSD
  CSD = (CM - AB(3, I)) ^ 2 + CSD
NEXT I
ASDF = SQR(ASD / 9)
BSDF = SQR(BSD / 9)
CSDF = SQR(CSD / 9)
PRINT                                          ' start reporting statistics'
PRINT USING "averages      #.####      #.####      #.####"; AM; BM; CM

```

```

PRINT
PRINT USING "std. dev.      #.####      #.####      #.####"; ASDF; BSDF; CSDF
PRINT ""                  'end reporting'
'initializing data conversion'
  R = (BM - CM) / (AM - CM)
  REM
  REM SET ANALYSIS TEMP TO 25C
  REM
  T = 298.15
  PHT = -216.404 / T + 35.913 - 10.9913 * LOG(T) / LOG(10) + .00211 * (35 - S) + (LOG((R
    - .00691) / (2.222 - (.1331 * R))) / LOG(10))      'pH in total scale'
  PRINT

'Conversion of pH total scale to seawater scale in mol/kg-seawater'
  LNKHF = -1590.2 / T + 12.641 - 1.525 * ((.7223 * S / 35) ^ .5)
  KHF = EXP(LNKHF)
  ST = (.14 / 96.06) * (S / 1.80655)
  FT = (.000067 / 18.9984) * (S / 1.80655)
  LNKO = -4276.1 / T + 141.328 - 23.093 * LOG(T)
  LNKHSO4 = LNKO + (-2103.7 / T + 48.915 - 7.2345 * LOG(T)) * S ^ (.5) + (755.8 / T -
    16.3268 + 2.42784 * LOG(T)) * S + (-9.118 / T) * S ^ (1.5) + .836 * S * S / T
  KS = 1 / EXP(LNKHSO4)
  PHSWM = PHT - (LOG(1 + KS * ST + KHF * FT) / LOG(10)) + (LOG(1 + KS * ST) /
    LOG(10))
  PHSWS = PHSWM - (LOG(1 - .001005 * S) / LOG(10))
'final reporting'
PRINT "RATIO-r      pH(Total)      pH(SWS)"
PRINT
PRINT USING "#.#####      #.####      #.####"; R; PHT; PHSWS

'saving file to disk'
  OPEN FIL$ FOR APPEND AS #2

```

```
PRINT #2, USING "#####  ##.#####  ##.#####  ##.#####  ##.#####  
##.#####  ##.#####"; SPL; AM; BM; CM; R; PHT; PHSWS
```

```
CLOSE #2
```

```
NEXT JJ%
```

```
'end of program'
```