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Development of a Portable, OCaPI, for the Measurement of pH and pCO_2 in the Seawater: A Key Issue for Monitoring Acidification in the Mediterranean

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Abstract

This development highlights the significant advantages of the portable instrument (UV-Vis spectrophotometer OCaPI) for the analysis of two parameters of the oceanic carbonate system. This method is characterized by its appreciable precision, its modest construction and operating costs, as well as its minimal ecological footprint due to the use of small sample volumes. The optimization of the spectrophotometer parameters (integration time, average scan, Boxcar) facilitated the precise study of the parameters of the oceanic carbonate system and contributed to monitoring ocean acidification. This instrument is a compact, space-saving device that is easy to transport at sea. Its ease of use and maintenance, combined with its optimal performance appreciated in the field, make it a preferred choice. This facility allows the global scientific community to monitor ocean acidification regularly and widely.

Keywords

Acidification, Mediterranean, Carbonate System, Seawater, OCaPI

1. Introduction

Today, in a world where atmospheric CO_2 levels remain high, it is more crucial than ever to accurately assess fluctuations in the ocean carbon cycle. This is particularly essential for measuring the influx of anthropogenic carbon and its impact on ocean acidification. It is therefore crucial to collect as much data as possible across the entire ocean, including adjacent seas. This is a global issue that can only be addressed if these efforts are easy to implement at low cost and as environmentally friendly as possible (Wang et al., 2007).

More than a decade ago, researchers proposed that spectrophotometric techniques are ideal for simultaneously measuring multiple properties at a relatively affordable cost. However, since this type of instrumentation is not yet commercially available, only a few specialists have managed to customize their own systems for marine applications (Wang et al., 2007).

Consequently, there is currently little ocean data derived from spectrophotometric measurements. However, over the past decade, pH assessment via spectrophotometry has seen advances; dyes are now purified, and formulas have been updated accordingly (Roche & Millero, 1998).

In light of the ongoing acidification of the oceans, many researchers, particularly those in the GOA-ON Network, are taking a special interest in accurate measurements of seawater pH. However, spectrophotometric pH measurements are significantly more accurate than potentiometric pH measurements (Dickson & Goyet, 1994).

Building on the prior research of many scientists, we demonstrate in this paper that it is possible to design a compact integrated system for assessing two of the four properties of the ocean system, to simplify the performance of accurate measurements at sea.

2. Materials and Methods

More than three decades ago, they introduced the concept of precise and accurate determination of pH measurements in seawater (Byrne et al., 1989). Currently, the most reliable and accurate method for determining ocean pH remains spectrophotometry, a widely recognized technique (Clayton & Byrne, 1993; Dickson & Goyet, 1994; Zhang & Byrne, 1996).

Since the other parameter (pCO_2) of the oceanic carbonate system can be derived from pH variations in various colored solutions, all these parameters can be calculated from a single pH measurement. Consequently, it is possible to measure these parameters using spectrophotometry (Roche & Millero, 1998; Bégovic, 2001; Louis, 2015; Wimart-Rousseau, 2021).

These methods are based on the following concept:

2.1. System Installation

This system uses two peristaltic pumps to feed seawater and dye into a mixer. After homogenization, the solution is fed into an 18-cm-long tube and then discharged into the sample waste. Light from a visible-light source is guided through an optical fiber, passes through the solution in the tube, and is directed toward the detector (**Figure 1**).

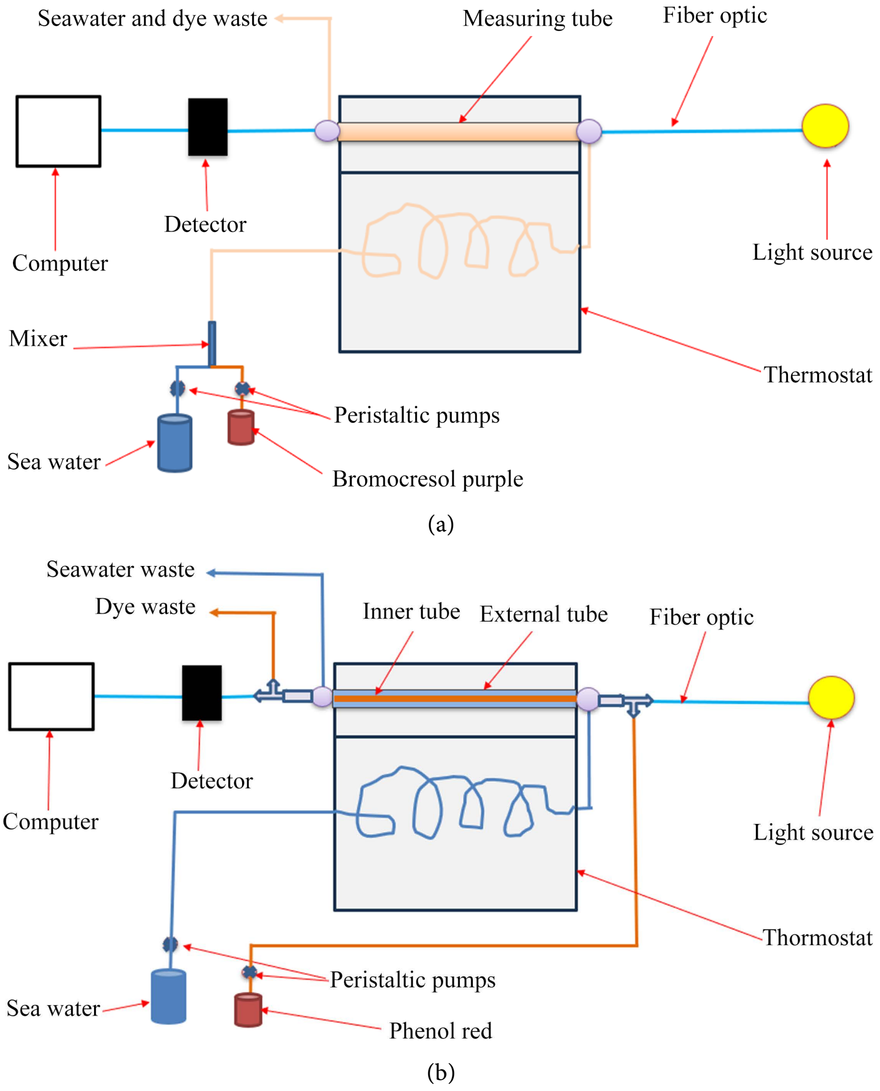

Figure 1. Diagram showing how the pH (a) and pCO_2 (b) measurement channels work.

After starting up and stabilizing the device, take three measurements of the reference intensities, followed by ten measurements of the transmitted intensities. Using Beer-Lambert's law, calculate the absorbance, then the pH of the seawater and the pCO_2 between the air and the sea.

2.2. Calculation of Parameters

In seawater ($7.5 < pH < 8.2$), several color indicators can be used to directly measure the pH of surface seawater. Thymol blue, phenol red, and bromocresol purple are frequently used (Wang et al., 2007; Clayton & Byrne, 1993; Dickson & Goyet, 1994).

We use bromocresol purple (BCP) here because the dye is now purified (reference) and the coefficients e_1, e_2, e_3 are correctly adjusted to the wavelengths $\lambda_1 = 434$ nm and $\lambda_2 = 578$ nm.

The pH is therefore expressed as follows:

$$\text{pH} = -\log\left(K_I \cdot e_2\right) + \log\left(\frac{R - e_1}{1 - R \cdot \dfrac{e_3}{e_2}}\right) \text{ and } -\log\left(K_I \cdot e_2\right) = a + \frac{b}{T} + c \cdot \ln\left(T\right) - d \cdot T \tag{1}$$

This equation was used to calculate pH for temperatures ranging from 5˚C to 35˚C and salinities ranging from 20 to 40.

For pH, bromocresol purple (BCP), with the formula $C_{21}H_{16}Br_2O_5S$, was used as a color indicator (Dickson & Millero, 1987).

As previously detailed (Wang et al., 2007): "For spectrophotometric measurements of pCO_2, the LCW internal standard solution consists of a Na_2CO_3 indicator solution with a constant total alkalinity. During equilibration, the pCO_2 in the sample water is equal to the pCO_2 of the internal solution".

The pH corresponds (Weiss, 1974; Goyet & Poisson, 1989; Rérolle et al., 2012):

$$\text{pCO}_2 = \frac{AT}{L} \text{ and } L = 2 \cdot K_0 \cdot K_1 \cdot K_2 \left[H^+\right]^{-2} + K_0 \cdot K_1 \left[H^+\right]^{-1} \tag{2}$$

We used phenol red as the indicator dye for this measurement, with $\lambda_1 = 434$ nm, $\lambda_2 = 558$ nm (Wang et al., 2007). This equation was used to calculate the pH for temperatures ranging from 10˚C to 30˚C (Rérolle et al., 2012).

As for pCO_2, the color indicator used is phenol red (Ph Red) with the formula $C_{19}H_{14}O_5S$ (Goyet & Poisson, 1989).

2.3. Determination of Values

After verifying the stability of the pH measurement and the carbon dioxide equilibrium time at the pCO_2 level, the measurements were performed as follows:

Motor 1 (seawater) was started at a speed of 600 to take 3 measurements after 3 minutes; then motors 1 and 2 (speeds 600 - 100, seawater-bromocresol purple) to take 10 measurements after 5 minutes under controlled temperature conditions. We obtained a pH of 8.0004 with a standard deviation of 0.002 pH units.

Engines 1 and 2 (speeds 600 - 600, seawater) were started to take 3 measurements after 10 minutes, then restarted but replacing the internal seawater with phenol red to take 10 measurements after 10 minutes. We obtained a pCO_2 of 403 ppm with a standard deviation of 2 ppm.

We used two USB4000 miniature fiber-optic spectrophotometers (Ocean Optics) to detect optical signals for pH and pCO_2. To prevent signal drift caused by temperature changes, the spectrophotometers are maintained at room temperature using a thermostat designed and built specifically for this purpose. In addition, the manufacturer provided built-in linearization coefficients to correct the linear behavior of the spectrophotometers. A simple household LED is used as the light source and serves both channels. Three ISMATECH multi-channel digital peristaltic pumps were used to regulate the flow of all solutions (water samples, colored solutions, standard solutions, and acid solution) within the system. Each pump can be equipped with up to four channels. For example, in our scenario, both channels are used to pass the water sample through each of the two optical cells to evaluate the two parameters of the oceanic carbonate system.

The cells are like those described previously (Wang et al., 2007). The optical pH cell consists of a standard PEEK tube through which the combined sample and dye solution flows. The other pCO_2 cell consists of a PEEK tube into which a Teflon AF 2400 LCW has been inserted. In the LCW, the optical fibers run from the light source to the spectrophotometer and are inserted at the ends. Two small O-rings in the PEEK connectors ensure their watertightness.

In November 2023, seawater samples were collected in the western Mediterranean. Sampling was conducted at depths ranging from 0 to 10 m. The environmental conditions observed included a temperature range of 13˚C to 18˚C and salinity ranging from 35 to 40 mg/L. Each sample was measured 10 times.

A Python program called "ocapi v.5" has been developed and fine-tuned to ensure continuous operation. It includes the following functions: Sleep, Pump speed, Pump off, and Readstore reference pH, which allow the motors to be turned on and off, and set the optimal wait time before taking measurements for both reference and transmitted intensities. It is programmed to collect pH and pCO_2 data in less than 15 minutes.

2.4. Validation of Results

To assess the metrological reliability of the OCaPI prototype in monitoring acidification in the Mediterranean Sea (winter), the data related to pH and pCO_2 were compared with the requirements of the GOA-ON program, climate level (**Table 1**).

Table 1. Comparison of OCaPI outputs with GOA-ON program requirements.

Parameter	OCaPI performance	GOA-ON climate threshold
pH	±0.002 (repeatability), bias < ±0.004	±0.002 - 0.005
pCO_2	σ = 2 ppm, bias < ±0.5%	<±1%

Optimization of the instrument parameters led to very high repeatability. The pH calibration covered the entire measurement spectrum (certified by the University of California, San Diego), while the $pC0_2$ calibration was performed using certified gases. Under operational conditions, the standard deviations observed in series of values show minimal random dispersion and meet the GOA-AN program criterion (accuracy level "climate").

Furthermore, the analysis of systematic biases relative to certified references (salinity and alkalinity matrices) revealed no significant drift exceeding ±0.004 for pH and ±0.5% for pCO_2. This confirms the accuracy of the OCaPI approach for monitoring ocean-atmosphere gradients in the Mediterranean.

3. Results and Discussion

The initial objective of the portable instrument (OCaPI) is to measure, with sufficient accuracy and simultaneously, two of the four parameters of the carbonate system: hydrogen ion concentration and carbon dioxide partial pressure.

Measuring pH in water is crucial for understanding carbonate chemistry and its impact on marine ecosystems. Rising carbon dioxide concentrations in the atmosphere lead to ocean acidification, altering chemical equilibria and threatening marine life, particularly calcifying organisms (Wang et al., 2007).

This device uses optical methods to reduce errors associated with traditional manual measurement techniques, enabling the acquisition of accurate data in real time.

Following the optimization of parameters related to both detector noise (improvement of the signal-to-noise ratio by increasing the scan-to-average and boxcar values) and dye input (addition of a mixer, pump speed), the device can currently measure the pH of seawater with an accuracy of 0.002 pH units.

The use of a thermostat made it possible to control the solution temperature during measurements and ensured the reproducibility of the results. Calibrated solutions were used to demonstrate the accuracy of the pH measurements as well.

OCaPI measurements are consistent with current Mediterranean winter values, where the sea still absorbs atmospheric CO_2. However, regional acidification is a concern: in the western Mediterranean, the pH is decreasing by 0.005 to 0.007 units per year, a rate 3 to 5 times faster than the global average for the open ocean.

For comprehensive monitoring, OCaPI will need to be expanded to cover the entire seasonal cycle, with a particular focus on summer when CO_2 absorption is highest.

Measurements of carbon dioxide partial pressure in the oceans are essential for understanding carbon dioxide exchange between the atmosphere and the ocean, as well as for assessing the impact of ocean acidification on marine ecosystems. Traditional measurement methods, often based on water samples collected manually and analyzed in the laboratory, face limitations in terms of timeliness and precision (Roche & Millero, 1998).

Furthermore, automation facilitates the collection of large amounts of data, enabling long-term analyses and monitoring across geographically diverse areas.

Integrating these measurements into global ocean monitoring networks allows for the mapping of pCO_2 variations on broader spatial and temporal scales, thereby providing crucial insights for researchers and environmental managers.

The results obtained from these measurements are also fundamental for better anticipating the effects of climate change on the carbon cycle. The availability of accurate and reliable data on ocean carbon parameters is essential for climate modeling as well as for the formulation of policies aimed at combating the effects of climate change.

4. Conclusion

The analysis of two of the four parameters of the ocean carbonate system using OCaPI offers numerous advantages over the systems currently in use, including guaranteed measurement accuracy, low cost of construction, maintenance, and sample analysis using a single, simple technology (spectrophotometry), and the use of small quantities of samples and reagents, minimal environmental impact, and a compact, lightweight system.

The spectrophotometer's measurement parameters, performed with the motors off, were optimized at integration times of 45.000 µs and 25.000 µs for pH and pCO_2, respectively, with a scan-to-average of 30 and a boxcar of 5. This was followed by the determination of measurement intervals, which are 3 minutes for reference measurements and 5 minutes for transmitted intensity measurements for pH, compared to 10 minutes for pCO_2 for all reference and transmitted intensity measurements. Optimizing these parameters allowed us to study the variation in seawater pH and the partial pressure of carbon dioxide between the atmosphere and the sea with standard deviations of 0.002 pH units and 2 ppm, respectively.

In addition, besides examining the two remaining elements (CT and AT) by system assembly or simulation via CO2SYS, coupled with deep-sea exploration, this offers the possibility of assessing ocean acidification and its consequences. This device, which is both compact and lightweight, is easily transportable to research vessels and can perform multiple people all over the world can use it. In addition, measurements can be taken anywhere, including in seawater and estuarine environments.

Conflicts of Interest

The authors declare no conflicts of interest.

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Abbreviations

OCaPI	Ocean Carbon Parameters Instrument
pH	Hydrogen ion concentration
pCO_2	Partial pressure of Carbon dioxide
CT	Total dissolved inorganic carbon
AT	Total alkalinity
BCP	Bromocresol Purple
Ph red	Phenol red
GOA-ON	Global Ocean Acidification Observing Network