Marine Chemistry 160 (2014) 75–81

Contents lists available at ScienceDirect

Marine Chemistry

journal homepage: www.elsevier.com/locate/marchem

Seawater pH measurements in the field: A DIY photometer with 0.01 unit pH accuracy ☆

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ARTICLE INFO

Article history:
Received 30 October 2013
Received in revised form 10 January 2014
Accepted 10 January 2014
Available online 22 January 2014

Keywords:
pH
Photometer
Seawater
LED

ABSTRACT

A portable light-emitting-diode (LED) photometer has been developed to provide low-cost seawater pH measurements. The benefits of the new system include a simple "do-it-yourself" construction design, a hundredfold reduction in cost relative to benchtop spectrophotometric systems, routine calibration-free operation in the field, and precision and accuracy well suited to applications such as education, coastal zone monitoring (including citizen science programs), and aquaculture and aquarium management. The photometer uses a high-sensitivity light-to-voltage integrated circuit as a detector, two LED light sources, and an open-source Arduino microcontroller for system control and data processing. Measurements are based on observations of absorbances of a pH-sensitive indicator. With meta-cresol purple, a sulfonephthalein indicator appropriate to natural seawater, the photometer system produces pH_T measurements within 0.01 units of state-of-the-art spectrophotometric measurements ($7.6 \le pH \le 8.2$, $30 \le S \le 36.2$, and $15\ °C \le t \le 30\ °C$) and has a pH precision of ± 0.002. Measurement accuracy is achieved with a one-time calibration that relates absorbance ratios measured by the broadband photometer (R_B) to absorbance ratios measured by a high-quality (narrowband) spectrophotometer (R_N). Calculation of R_N from R_B allows the use of published algorithms that yield seawater pH as a function of R_N, temperature, and salinity.

1. Introduction

Solution pH is a key variable used to describe the equilibrium and kinetics of chemical processes in oceanic and fresh waters (Stumm and Morgan, 1981; Zeebe and Wolf-Gladrow, 2001). The development of highly precise spectrophotometric pH methods has led to the increasing use of spectrophotometric procedures in marine CO_2-system characterizations (Byrne et al., 2002; Clayton and Byrne, 1993; Yao and Byrne, 1998). Because pH measurements based on sulfonephthalein indicators are highly reproducible and calibration-free, these methods obviate some of the disadvantages associated with the use of pH-sensitive glass electrodes (e.g., requirements for frequent calibration (Dickson, 1993)).

Spectrophotometric measurements of seawater pH (Byrne and Breland, 1989; Clayton and Byrne, 1993; Robert-Baldo et al., 1985) are based on observations of absorbance (A) contributions from distinctly colored acidic (HL^-) and basic (L^{2-}) forms of pH-sensitive indicator dyes (generally diprotic sulfonephthalein indicators) that are dissolved in seawater at low concentrations:

$$HL^- \Longleftrightarrow H^+ + L^{2-}. \quad (1)$$

Seawater pH on the total hydrogen ion concentration scale (Byrne and Breland, 1989; Byrne et al., 1988; Clayton and Byrne, 1993; Robert-Baldo et al., 1985) is obtained using Eq. (2):

$$pH_T = -\log\left(K_2^T e_2\right) + \log\left[(R - e_1)/(1 - R \cdot e_3/e_2)\right] \quad (2)$$

where K_2^T is the equilibrium constant for Eq. (1); R is the ratio of sulfonephthalein absorbances at λ_1 and λ_2, the wavelengths of maximum absorbance of the L^{2-} and HL^- forms of the indicator (i.e., $R = {}_{\lambda 2}A_{L^{2-}} / {}_{\lambda 1}A_{HL^-}$); and the e_i coefficients are ratios of indicator molar absorptivities (ε) at wavelengths λ_1 and λ_2:

$$e_1 = \frac{\lambda 2\varepsilon_{HL^-}}{\lambda 1\varepsilon_{HL^-}}; e_2 = \frac{\lambda 2\varepsilon_{L^{2-}}}{\lambda 1\varepsilon_{HL^-}}; e_3 = \frac{\lambda 1\varepsilon_{L^{2-}}}{\lambda 1\varepsilon_{HL^-}}. \quad (3)$$

Sulfonephthalein indicators (e.g., cresol red, bromocresol purple, thymol blue) have been used for high-precision measurements of pH, total alkalinity, and total dissolved inorganic carbon in seawater and freshwater (Byrne et al., 2002; Byrne and Breland, 1989; Clayton and Byrne, 1993; Hopkins et al., 2000; Robert-Baldo et al., 1985; Yao and

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http://dx.doi.org/10.1016/j.marchem.2014.01.005

Byrne, 1998; Yao and Byrne, 2001; Zhang and Byrne, 1996). The indicator meta-cresol purple (mCP) is often used because its ideal indicating range ($7.2 \leq pH_T \leq 8.1$) provides good coverage of the pH ranges typically encountered in a variety of saltwater environments (Byrne et al., 1988; Clayton and Byrne, 1993). Since indicator impurities can contribute to pH offsets as large as 0.018 pH units (Liu et al., 2011; Patsavas et al., 2013; Yao et al., 2007), procedures to purify commercially available indicator powders have been developed and the properties of some purified indicators, including mCP, have been reported (Liu et al., 2011; Patsavas et al., 2013). The precision of spectrophotometric pH measurements is on the order of ±0.0004 (Byrne et al., 1999; Clayton and Byrne, 1993; Liu et al., 2011), in accord with the requirements of open-ocean and laboratory studies of ocean acidification.

Solution pH also serves as an important water quality parameter in monitoring programs associated with coastal zone, aquaculture, and aquarium management. In these applications, the benchtop spectrophotometers used for high-precision open-ocean and laboratory work would be unnecessarily expensive and cumbersome, especially for fieldwork. In coastal waters, temporal and spatial variations of pH are much larger than those in the open ocean. For example, the average range of diel pH variation in Tampa Bay, Florida, can be as great as 0.22 (Yates et al., 2007). In the controlled environments of marine aquaria and especially aquaculture, pH measurement requirements are likewise less stringent than those in open ocean settings. For a saltwater aquarium, a pH range of 8.1–8.3 is acceptable (Blasiola, 2000). A typical aquaculture pond should have a pH range of 7–8 (Egna and Boyd, 1997).

In many operational settings, the use of pH test strips or consumer-level potentiometric probes is common. These methods offer the benefits of low cost and portability but have precisions on the order of 0.1–0.5 pH units. Few options have been available in the intermediate ranges of simplicity, accuracy, and precision.

Recently, technological innovations have paved the way for the development of new sensors to fill this intermediate niche at low cost. Light-emitting-diodes (LEDs), widely used in many spectrophotometric devices (Dasgupta et al., 1993; Gaião et al., 2008; Li et al., 2003; Ma et al., 2011; Veras et al., 2009; Vreman et al., 1998), are inexpensive, power-saving, compact, and sufficiently robust for field use. The combination of LED light sources, integrated optical detection circuits, and simple microcontrollers enables the development of sturdy, easy-to-use photometers that can provide pH field measurements of much higher accuracy and precision than pH electrodes but at roughly the same cost.

This paper describes the development of a portable microcontrolled LED photometer for spectrophotometric seawater pH measurements using meta-cresol purple (mCP). The instrument components are commercially available and the design is sufficiently simple that "do-it-yourself" (DIY) construction is possible. A one-time calibration method was also developed to improve the accuracy of the pH measurements. The performance of the photometer was evaluated by comparisons against the performance of a high-accuracy benchtop spectrophotometer in laboratory, shipboard, and aquarium settings.

2. Materials and methods

2.1. Reagents

The indicator mCP was purified from sodium salt (Alfa Aesar, Batch H11N06) according to the procedure of Patsavas et al. (2013). A 10 $mmol \cdot L^{-1}$ mCP stock solution in 0.7 $mol \cdot kg^{-1}$ NaCl was used for all measurements. The *R*-ratio of the stock solution was adjusted to 1.6 by an addition of 1 N HCl or 1 N NaOH (Sigma-Aldrich). Tris acidimetric SRM 723e (tris(hydroxymethyl)aminomethane) was obtained from the National Institute of Standards and Technology (NIST) for preparing the tris-buffered synthetic seawater (Dickson et al., 2007). High-purity salts (NaCl, KCl, and Na_2SO_4) were obtained from Sigma-Aldrich.

2.2. Characterization of purified mCP

The terms on the right side of Eq. (2) must be experimentally determined such that they are internally consistent. The equilibrium constant K_2^T is a function only of solution salinity, temperature, and pressure and is thus independent of the configuration of the optical instrumentation. In contrast, the molar absorptivity terms are generally a function not of solution chemistry but of instrument configuration. The values of the ε ratios (Eq. (3)) therefore depend on whether they are determined using a narrowband or broadband instrument (within the class of narrowband spectrophotometers—i.e., bandwidths on the order of 2 nm or less—instrumental differences are insignificant.).

In the original development of high-precision spectrophotometric methods for measuring seawater pH_T (Clayton and Byrne, 1993), Eqs. (4)–(7) were determined using monochromatic light (bandwidth ~1 nm) to assess the relative concentrations of the unprotonated and protonated (L^{2-} and HL^-) forms of indicator. Subsequent characterizations of purified indicator were likewise conducted using narrowband spectrophotometers. For purified mCP (Liu et al., 2011):

$$pH_T = -\log\left(K_2^T e_2\right) + \log\left[(R_N - e_1)/(1 - R_N \cdot e_3/e_2)\right] \quad (4)$$

where $R_N = {}_{578}A_L{}^{2-} / {}_{434}A_{HL}{}^{-}$ (this R_N is equivalent to the *R* of Eq. (3) of Liu et al.).

The corresponding (narrowband) e_i coefficients are a function of temperature (T) and salinity (S):

$$e_1 = -0.007762 + 4.5174 \times 10^{-5} T \quad (5)$$

$$e_3/e_2 = -0.020813 + 2.60262 \times 10^{-4} T + 1.0436 \times 10^{-4}(S - 35) \quad (6)$$

at a measurement pressure of 1 atm. The equilibrium constant term of Eq. (2) is given as:

$$-\log\left(K_2^T e_2\right) = a + \frac{b}{T} + c \ln T - dT \quad (7)$$

where

$$a = -246.64209 + 0.315971S + 2.8855 \times 10^{-4} S^2$$
$$b = 7229.23864 - 7.098137S - 0.057034S^2$$
$$c = 44.493382 - 0.052711S$$
$$d = 0.0781344.$$

This characterization is appropriate for $278.15 \leq T \leq 308.15$ K and $20 \leq S \leq 40$.

2.3. Instrumentation

Fig. 1 illustrates the structure of the DIY LED photometer (part list, circuit schematic, and source code can be found in supplementary material.). For the light source module, LED1 (MV5B60, Everlight) and LED2 (LTL1CHKGKNN, Lite-On) were used to generate light with outputs centered near 434 nm and 578 nm, the wavelengths of maximum absorbance of the acidic and basic forms of mCP. The emission spectra of both LEDs were measured with a USB-4000 spectrophotometer (Ocean Optics, Inc.). The detector module is based on a light-to-voltage optical converter TSL257 (TAOS Inc.), which combines a photodiode and a transimpedance amplifier on a single monolithic complementary metal–oxide–semiconductor (CMOS) integrated circuit. The system can be powered by either 4 AA batteries or 5V DC from a standard USB port. A 100 mL PYREX® (Corning Inc., USA) screw-cap round glass bottle seated within a foam nest serves as the sample bottle, reaction chamber, and optical cell (path length = 5.6 cm). The photometer measures 90 × 90 × 100 mm and weighs 370 g.

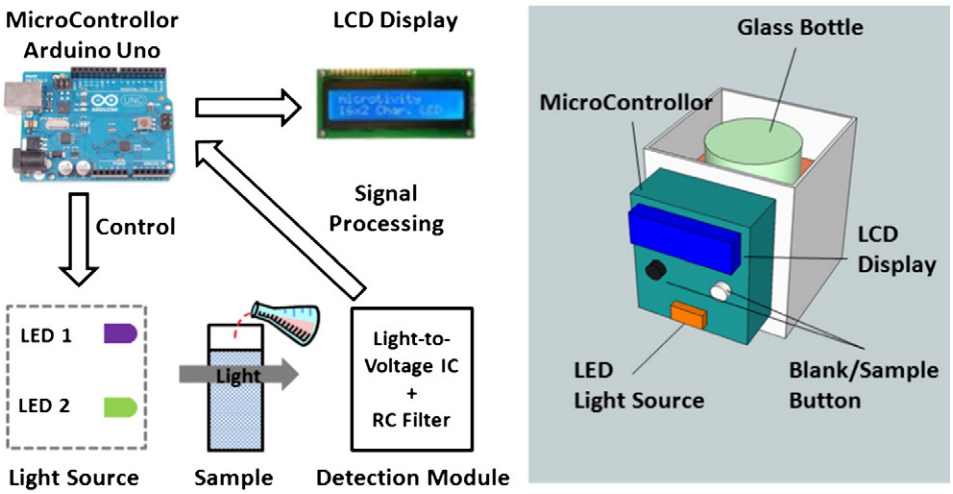

Fig. 1. LED photometer developed for measurements of seawater pH. Dimensions are 90 × 90 × 100 mm.

During each measurement, the two LEDs are activated alternately, and the signals obtained from each LED are sent to the microcontroller via a simple 1 s RC filter. A 16 MHz open-source Arduino Uno microcontroller, which has a 10-bit analog-to-digital (A/D) converter, 32 kb of flash memory, 2 kb RAM, and 1 kb EEPROM, is used for controlling and data processing. The optical absorbance readings are averaged over 1 s and then displayed on a 16 × 2-character liquid crystal display (LCD). The readings are manually recorded.

Sample temperature was measured with a Testoterm® 7010 digital thermometer (Testoterm Inc., Germany), and salinity was measured with a Sper Scientific® 850036 Salinity Pen (SperDirect.com, USA). The accuracies of the temperature and salinity measurements were ±0.1 °C and ±0.1, respectively.

2.4. Seawater pH measurement protocol

Seawater was collected into the 100 mL glass bottle, which was capped, wiped clean, and seated in the photometer for a blank (baseline) measurement of absorbances. The bottle cap was then removed, and mCP indicator (0.03 mL) was injected into the sample with a 1 mL plastic syringe (B-D, USA) to provide a final mCP concentration of 3 μmol kg^{-1}. The sample and indicator were manually mixed with a glass stir rod, the bottle was recapped, and mCP absorbances were measured and recorded. Finally, temperature and salinity were measured and recorded. The entire procedure for a single sample takes ~3 min.

To calculate pH_T, the ratio of final (baseline-corrected) absorbances was calculated. This broadband R_B was converted to the R_N of Eq. (4) according to a previously determined calibration (described below). Finally, sample pH_T was calculated as a function of R_N, S, and T (Eqs. (4)–(7)).

To assess the accuracy of the photometer pH measurements, sample pH values were also measured using an Agilent 8453 benchtop spectrophotometer. As such, the "accuracy" of LED photometer measurements reported in this work refers to the differences between photometer measurements and state-of-the-art pH measurements obtained with a benchtop spectrophotometer. Standard operating procedures were followed (Dickson et al., 2007). In brief, a 10 cm optical cell was filled with seawater sample, and a blank measurement was taken. Then 10 μL of 10 mmol·L^{-1} stock mCP solution was added to the sample, and absorbances were again measured. Sample pH_T was calculated using Eqs. (4)–(7).

2.5. Calibration of the LED photometer

A key point in our photometer pH measurement protocol is that for every R_B value measured with the broadband LED photometer there is a corresponding R_N value (Eq. (4)) that a narrowband spectrophotometer would report for the same sample. The functional relationship between R_N and R_B depends solely on physical factors (e.g., emission and absorbance bandwidths, system geometries) and is independent of the solution chemistry of the measured samples. As such, with an experimentally determined transform function ($R_N = f(R_B)$), photometer R_B values can be converted to R_N values, which (along with samples' T and S) can be used to calculate seawater pH_T (Eqs. (4)–(7)).

To experimentally determine the $f(R_B)$ function, we used the broadband LED photometer and a narrowband benchtop spectrophotometer to measure mCP absorbance ratios (R_B and R_N, respectively) in well-buffered seawater samples over a range of pH_T. Stock tris-buffered synthetic seawater ($S = 35$) was prepared gravimetrically, following the method of Dickson et al. (2007). The synthetic seawater had an initial pH_T of 8.113 (determined using mCP and the narrowband spectrophotometer). A series of solutions with pH_T values ranging from 7.6 to 8.2 was then prepared by adding 1 N HCl or 1 N NaOH to the buffered synthetic seawater. Indicator (mCP) was added, and R_N was measured. Corresponding R_B values were measured using the LED photometer at the same sample temperature.

2.6. Indicator perturbation

An addition of an acid–base pair (e.g., the HL^- and L^{2-} forms of mCP) to natural (unbuffered) seawater creates a small perturbation from the original pH of the sample. For our natural seawater samples, perturbation corrections for R_N were determined and applied according to standard procedures (Clayton and Byrne, 1993; Dickson et al., 2007). No perturbation corrections were applied to R_B. Such perturbations are too small for the photometer to reliably measure, and pH_T errors caused by indicator additions (on the order of ~0.002 at $pH_T = 7.9$) are much smaller than the target accuracy for the photometer measurements (±0.01). For our tris-buffered artificial seawater samples, the solutions were sufficiently buffered that indicator-induced pH perturbations were negligible.

2.7. Laboratory comparisons

Laboratory analyses were conducted using surface seawater collected at two locations in the Gulf of Mexico (29°44′N, 86°20′W and 29°50′N, 86°11′W). Original sample salinities were 36.2 and 36.1, respectively. Sample compositions (S and pH_T) were varied by adding deionized H_2O and 1 N HCl. These additions produced a total of 136 seawater samples of $31.0 \le S \le 36.2$ and $7.6 \le pH_T \le 8.2$. Paired measurements of sample pH_T were then made using the narrowband spectrophotometer and the LED photometer.

To evaluate the performance of the LED photometer at different sample temperatures, the laboratory seawater samples were warmed or

cooled with a Huber Polystat CC3 Water Bath (Huber Kaltemaschinenbau GmbH, Germany) to achieve a temperature range of $15 \le t \le 30$ °C. At each target temperature, pH_T was measured using the narrowband spectrophotometer and the LED photometer.

2.8. Field comparisons

One field test was conducted during an August 2013 *R/V Weatherbird II* cruise to the Gulf of Mexico. The pH_T of seawater samples (collected at 28.75°N, 88.40°W) was measured shipboard ($t = 25$ °C) using the LED photometer and the Agilent 8453 benchtop spectrophotometer.

A second field test was conducted in an aquarium setting. In this case, seawater samples were drawn from a 350-gallon saltwater reef aquarium system. The tank contained artificial seawater with a salinity of approximately 33–34 (made from deionized water and Seachem's Aqua Vitro Salinity sea salt blend). Also present were "live rock" from the Florida Keys, several species of scleractinian corals (*Acropora cervicornis*, *Montastaraea faveolata*, *Montastraea cavernosa*, *Diploria strigosa*, *Diploria clivosa*, and *Colpophyllia natans*), and two types of urchins (*Diadema antillarum* and *Eucidaris tribuloides*). The system was controlled by an Apex AquaController (Neptune Systems, Inc.), which consisted of two 1000-watt 10,000-kelvin ReefLux® metal halide lamps (Coral Vue, Inc.), a water circulation pump, protein skimmer, heater, thermometer, and two pH probes. The probes were standard pH electrodes (Neptune Systems, Inc.) with an internal Ag/AgCl reference. Both probes were calibrated in standard buffer solutions ($pH_{NBS} = 7.01$ and $pH_{NBS} = 10.01$; Milwaukee Instruments, Inc.). Immediately following this calibration, four pH instruments (the LED photometer, the narrowband spectrophotometer, and two electrodes) were used to monitor the pH of the aquarium water over a 16 h period (measurement interval = 30 min).

3. Results

3.1. LED characteristics

The emission bandwidths of the LEDs in the photometer are substantial compared to the absorbance bandwidths of the L^{2-} (basic) and HL^- (acidic) forms of mCP (Fig. 2). LED1 has an emission maximum at $\lambda = 427$ nm (near the HL^- absorbance maximum of $\lambda_1 = 434$ nm) with a full width half maximum (FWHM) of 66 nm. LED2 has an emission maximum at $\lambda = 574$ nm (near the L^{2-} absorbance maximum of $\lambda_2 = 578$ nm) with a FWHM of 13 nm.

Ideally, the peaks of the light sources should provide output at the two absorbance peaks of the indicator. In this case, to minimize the cost of instrument construction, no monochromator was used and the match was approximate. A calibration was necessary to link absorbance ratios measured with the broadband photometer to absorbance ratios determined using a narrowband spectrophotometer.

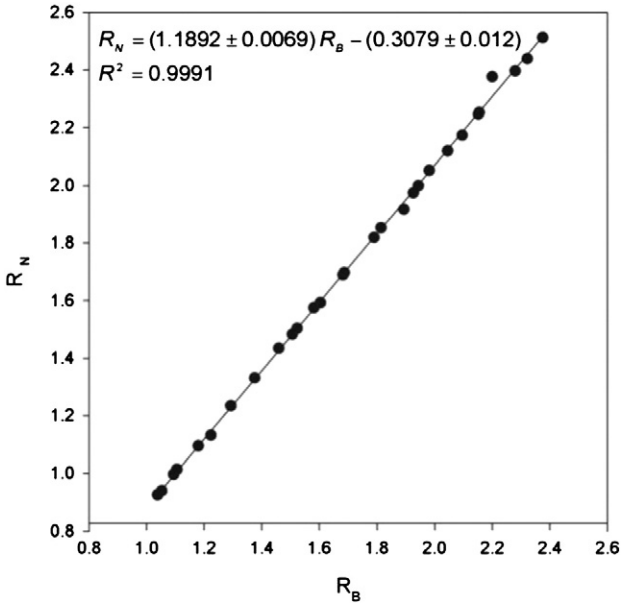

Fig. 3. Calibration of the LED photometer.

3.2. Photometer calibration

Calibration of the LED photometer was required to link the broadband measurements of absorbance ratios (R_B) to the original narrowband measurements (R_N) on which the pH_T and indicator characterizations of Eqs. (4)–(7) are based (Liu et al., 2011). The relationship between R_N and R_B, derived from data obtained in well-buffered solutions, is shown in Fig. 3. To a very good approximation, R_N is a linear function of R_B:

$$R_N = (1.1892 \pm 0.0069) R_B - (0.3079 \pm 0.012). \quad (8)$$

Operationally, this equation is used to convert the photometer measurements of R_B for seawater samples to their corresponding R_N values (i.e., the sample absorbance ratios that would have been reported by a narrowband spectrophotometer). These R_N values are then used in Eq. (4) to calculate the pH_T of the seawater sample.

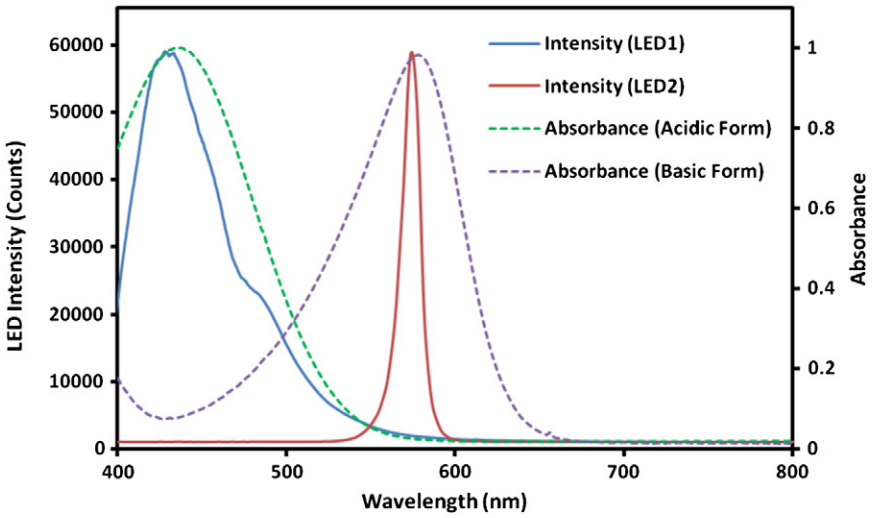

Fig. 2. Intensity spectra of the LED light sources (solid lines) and absorbance spectra of the acidic and basic forms of mCP (dashed lines).

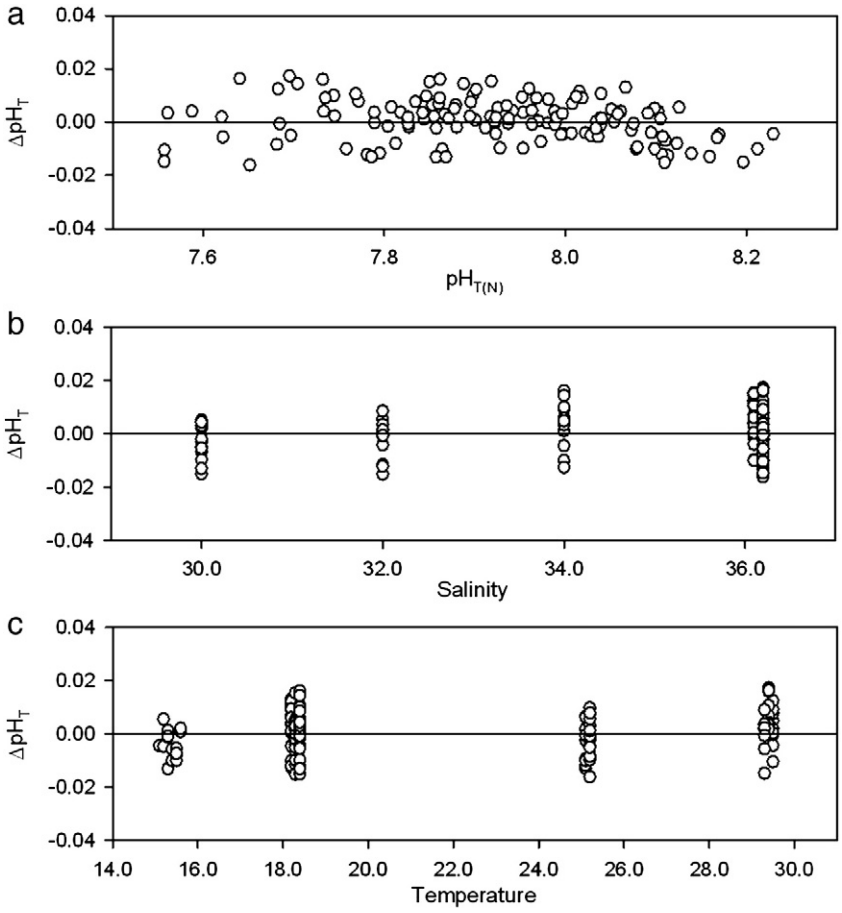

Fig. 4. Differences between pH_T measurements obtained using the broadband (B) LED photometer and the narrowband (N) benchtop spectrophotometer as a function of (a) $pH_{T(N)}$, (b) salinity, and (c) temperature. $\Delta pH_T = pH_{T(B)} - pH_{T(N)}$.

This particular relationship (Eq. (8)) is specific to the photometer system used in our study. The function may vary somewhat for other systems, even those of nominally identical construction, because the electrical and optical characteristics of the components (i.e., LEDs and optical converter) may vary by producer and batch. Only one calibration is needed for the lifetime of a broadband LED photometer. Purified indicator should be used in the initial instrument calibration and all subsequent pH_T measurements.

3.3. Laboratory comparisons

Differences between seawater pH values determined using the broadband LED photometer ($pH_{T(B)}$) and the narrowband benchtop spectrophotometer ($pH_{T(N)}$) are shown in Fig. 4a. These samples covered a typical range of surface seawater conditions: $7.6 \le pH \le 8.2$, $30 \le S \le 36.2$, and $15\ °C \le t \le 30\ °C$. The average difference between the prototype and research-grade measurements was 0.001 ($n = 136$). The standard deviation ($SD = \pm 0.008$) can be considered as an index of photometer measurement accuracy relative to conventional state-of-the art spectrophotometric procedures. The precision of the broadband measurements was ± 0.002 (at $pH_{T(B)} = 7.991$; $n = 6$). Fig. 4b and c shows that no systematic pH deviations were observed for measurements obtained over a sizable range of salinity and temperature.

3.4. Field comparisons

Although the LED photometer was not designed for high-precision open-ocean work, we tested its performance at sea (relative to the performance of a standard seagoing spectrophotometer) in order to evaluate (a) its durability in a demanding shipboard environment and (b) its accuracy over the full range of pH_T values encountered in a surface-to-deep vertical ocean profile. The DIY photometer worked properly during the research cruise without any issues. Fig. 5 shows

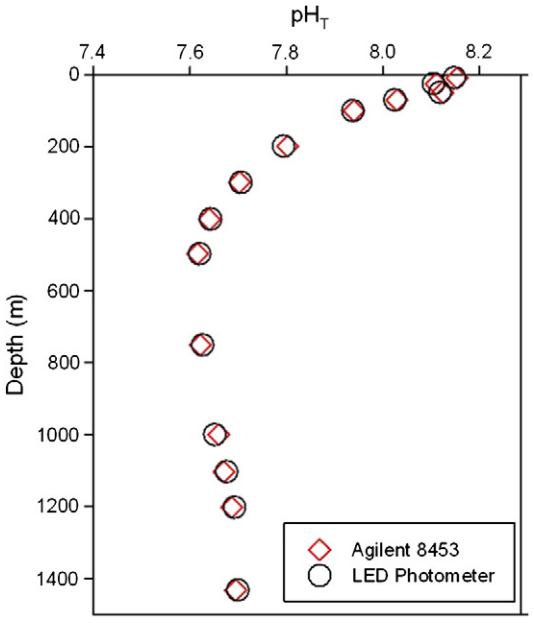

Fig. 5. Profiles of seawater pH measured by the broadband LED photometer (pH_B) and a narrowband spectrophotometer (pH_N) at a station in the northeastern Gulf of Mexico.

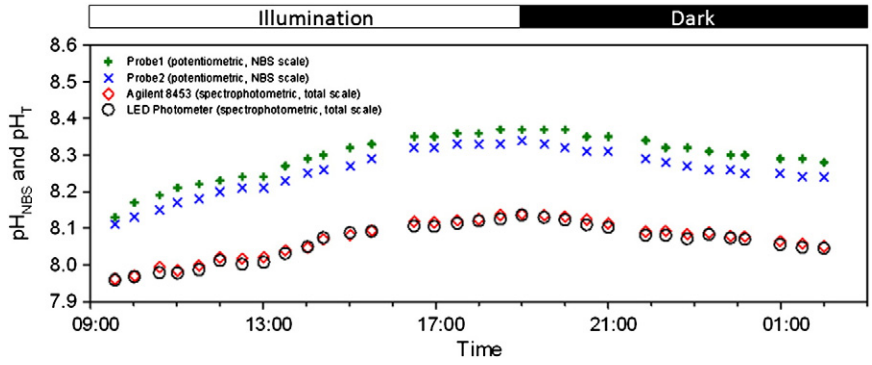

Fig. 6. Temporal evolution of seawater pH in a reef aquarium over a 16 h period, as measured by two potentiometric pH probes, a narrowband spectrophotometer (Agilent 8453), and the broadband LED photometer. The aquarium was illuminated from 9:00 to 19:00.

vertical profiles of seawater $pH_{T(B)}$ and $pH_{T(N)}$ measured at a sample station in the northeastern Gulf of Mexico (sea surface to 1450 m depth). The results are generally in good agreement. Average ΔpH_T for the station profile was −0.001 (SD = 0.006, $n = 14$).

A second field test was conducted in an aquarium setting. Fig. 6 shows temporal changes in the pH of a saltwater reef aquarium as measured by four different instruments: the LED photometer, a research-grade spectrophotometer, and two glass pH electrodes designed for aquarium use.

Over the course of the 16 h monitoring period (Fig. 6), all of the instruments showed a similar temporal pattern of aquarium chemistry, with pH increasing over the course of illumination, then decreasing in the dark. In terms of absolute pH values, however, the four instruments differed. The identical potentiometric probes reported pH_{NBS} values that differed by as much as 0.05 from each other and by as much as 0.2 from the pH_T measured spectrophotometrically. The nearly constant offset of approximately 0.2 units is due to the pH scale established by the standard buffers supplied with the aquarium electrodes. The buffers were of low ionic strength, with pH values reported on a scale different from the total hydrogen ion concentration scale of the spectrophotometric measurements (Dickson and Millero, 1987; Dickson, 1993; Millero, 1995). Values of pH_T obtained using the LED photometer showed good agreement with those obtained using the narrowband spectrophotometer. Average ΔpH_T was −0.008 (SD = 0.006, $n = 32$).

4. Discussion

Based on a single calibration, our DIY photometer provided quality pH measurements over the range of $7.6 \le pH_T \le 8.2$ and a substantial range of salinity ($30 \le S \le 36.2$) and temperature ($15\ °C \le t \le 30\ °C$). Agreement relative to narrowband spectrophotometric pH_T measurements (relative accuracy) was on the order of ±0.008, with a precision of ±0.002. These results demonstrate that LED photometers can be conveniently and routinely used to make seawater pH_T measurements in the field and that these measurements will be closely comparable to measurements obtained using research-grade spectrophotometers in the laboratory.

Table 1 summarizes the characteristics of several types of pH sensors, including the new LED photometer. The photometer's inexpensive hardware, comparatively good accuracy, and one-time calibration make this instrument suitable for applications where cost-effective pH precision and accuracy are desirable but extremely high precision is not required. Such applications might include aquaculture, aquarium management, coastal environmental monitoring, and citizen science and educational programs. Photometer construction is straightforward. All components are readily available off the shelf, and their assembly requires only a moderate level of do-it-yourself technical expertise.

The portable broadband photometer can also be adapted for other chemical analyses through the use of different colorimetric indicators and LED light sources. Because different sulfonephthalein indicators (e.g., cresol red, thymol blue) are well suited for different pH ranges, judicious selection of indicators and LEDs can provide accurate pH measurements over much of the broad range of conditions characteristic of both natural and manipulated fresh and marine waters. Combined with other techniques (e.g., acidimetric titration) and other colorimetric indicators (e.g., bromocresol purple, bromocresol green), LED photometers could also be used to measure concentrations other than hydrogen ions—for example, concentrations of total alkalinity, total dissolved inorganic carbon, and nutrients. In summary, LED photometers show great promise for providing convenient, high-quality, low-cost measurements of seawater pH and other analytes in a variety of marine and freshwater settings.

Acknowledgments

J. Kolesar's work on the printed circuit board, A. Ringelpaugh's help with the aquarium test, the insightful comments of T. Clayton, C. Lembke and R. Russell, and the programming advice of M. Lindemuth, Dr. D. Mann and J. Patten are greatly appreciated. We acknowledge support from the NOAA Ocean Acidification Program and fellowship support to Bo Yang from the C.W. Bill Young Endowed Fellowship.

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.marchem.2014.01.005.

Table 1
Specifications of instruments used for seawater pH measurements.

Instrument	Cost (USD)	Accuracy	Repeated calibration required?
LED photometer (this study)	<50	0.01 (or better)	No
pH electrode for general use	50	0.1	Yes
pH electrode for aquarium use	300	0.01	Yes
pH electrode for scientific use	1500	0.002	Yes
Diode array (narrowband) spectrophotometer	8000	0.0004	No
In situ spectrophotometric pH sensor	20,000	0.001	No

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