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The accuracy and limitations of a new meter used to measure aqueous carbon dioxide

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ARTICLE INFO

ABSTRACT

The OxyGuard CO_2 Analyzer is a novel meter that can directly measure aqueous CO_2 gas pressure using a water-resistant gas-permeable membrane and infra-red absorption cell. The pCO_2 is converted to a concentration via a solubility factor determined from the calibration procedure and a thermistor. We undertook to independently validate the precision and utility of this meter. Water flow over the probe membrane was a key determinant of the reaction time. At water velocities of $\geq 30\,cm\,s^{-1}$ the time to 99% span was 6–7 min, while at $0\,cm\,s^{-1}$ it was 55–60 min. Temperature and $CO_{2(aq)}$ concentration did not appreciably affect reaction time. The meter had a precision of $\pm 0.5\,mg\,L^{-1}$ $CO_{2(aq)}$, and high linearity (correlation 0.99–1.01) above $1\,mg\,L^{-1}$ in both freshwater and seawater. The standard meter will not be useful for measuring low concentrations such as atmospheric CO_2 levels, but will be useful in situations where accurate pH and carbonate alkalinity determinations are difficult to obtain, such as saline waters and waters of high organic loadings.

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1. Introduction

The measurement of CO_2 partial pressure (pCO_2) or concentration in water is carried out in a wide range of disciplines and industries. Oceanographers measure dissolved CO_2 in order to better understand the carbon cycle (Lueker et al., 2000), hydraulic and aquaculture engineers need to measure CO_2 in order to treat water high in dissolved CO_2 (La Motta, 1995; Summerfelt et al., 2000; Fattah et al., 2008), and biologists are interested in measuring CO_2 when assessing the effects of hypercapnia on aquatic organisms (Ishimatsu and Kita, 1999). The two predominant methods of measuring dissolved CO_2 ($CO_{2(aq)}$) are the pH/alkalinity method (and variations thereof) and the gas stream infra-red detection method. The pH/alkalinity method relies on the dissociation of CO_2 in water to form carbonates and H^+. The alkalinity is used as a proxy of the concentration of carbonates, and the concentration of $CO_{2(aq)}$ can be determined from the pH and carbonate alkalinity using dissociation constants (Millero, 1995; Lueker et al., 2000). This method is probably the most widely used in the water quality and water treatment field, and forms the basis of the often cited American Public Health Association 4500-CO_2 standard methods for the measurement of free CO_2 (A.P.H.A., 2005). The gas stream infra-red detection method involves the infra-red measurement of CO_2 in a

carrier gas stream equilibrated with the water sample. There are a number of methods that can be used to achieve equilibration between the sample and carrier gas stream, and equilibrator volumes vary from 2 to 60 L (Wanninkhof, 2004). Watten et al. (2004) used a head space equilibrator coupled with infra-red detection to continuously measure dissolved $CO_{2(aq)}$ in a stream of water taken from a recirculating aquaculture system. The $CO_{2(aq)}$ measurement precision of the gas stream equilibrator technique is better than that of the pH/alkalinity method, and is important in the measurement of CO_2 gas flux in the oceans (Wanninkhof and Thoning, 1993; Frankignoulle and Borges, 2001).

This study evaluates a recently developed meter that measures dissolved CO_2 in a different manner to the aforementioned methods. The portable CO_2 meter utilizes a gas permeable membrane and an infra-red absorption cell to directly measure the pCO_2 in liquids, and is manufactured by OxyGuard International A/S (Birkerød, Denmark). To our knowledge this is the only type of meter commercially available that uses this measurement principle to quantify $CO_{2(aq)}$. The units displayed on the screen of the meter are $mg\,L^{-1}$ $CO_{2(aq)}$, which is derived from pCO_2 using a solubility factor. A thermistor built into the probe allows the meter to account for the effect of temperature on solubility. The effect of salinity on solubility is accounted for during the calibration procedure, as users are required to carry out the calibration at the salinity in which samples will be measured. The meter was primarily designed for water quality assessment in biological and engineering applications, where the use of the $mg\,L^{-1}$ $CO_{2(aq)}$ units are commonplace. The informa-

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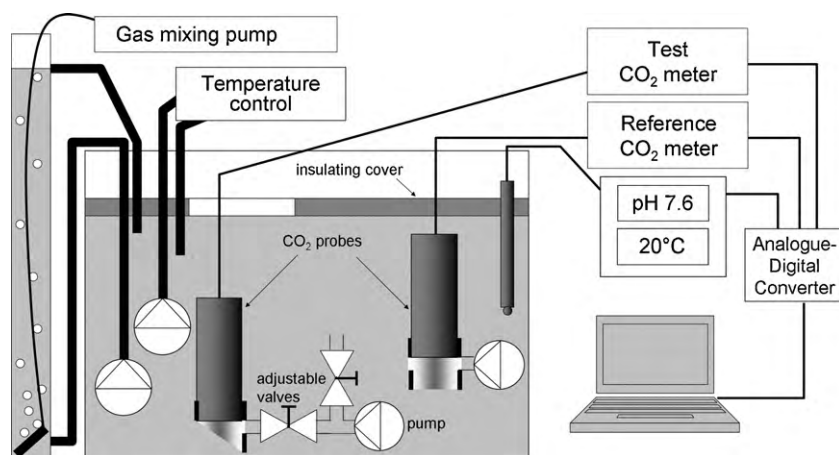E-mail address: dmo@aqua.dtu.dk (D. Moran).

Fig. 1. Experimental apparatus used to test the CO_2 meter. See Section 2 for detailed description of set up.

tion supplied by the manufacturer states that the standard meter has a $CO_{2(aq)}$ measurement range of 0–50 mg CO_2 L^{-1}, and a practical accuracy of ± 1 mg L^{-1}. The response time for the standard meter is purportedly better than 10 min at 20 °C. This device, which is already in commercial production, has the potential to overcome some of the short-comings of the aforementioned techniques in particular applications, and is being used in a number of laboratories and industrial settings. However, we are aware of widespread uncertainty as to the accuracy of this device in our fields of expertise, therefore, we thought it pertinent to undertake independent validation testing in order to determine the utility and limitations of this meter. Tests were undertaken to evaluate the response time of the probe under different water flow rates, temperatures, concentrations, calibration spans and to measure precision.

2. Materials and methods

2.1. Experimental set up

All experiments were carried out at the Helsingør Marine Laboratory between June and December 2008. The OxyGuard CO_2 Analyzer was evaluated in a set up that allowed the water temperature, $CO_{2(aq)}$ and water velocity over the probe membrane to be adjusted (Fig. 1). A plastic aquarium tank ($440 \times 270 \times 270$ mm) was partially filled using a mixture of water from the municipal water supply and distilled water. Temperature in the tank was controlled within ± 0.1 °C using a pump (10 W Eheim Universal 1048, 600 L h^{-1}, Eheim GmbH, Deizisau, Germany) to pass water through a heat exchanger placed inside a thermostatically controlled laboratory water bath. Temperature and pH in the tank were measured using a combination pH–temperature meter (pH electrode SenTix 41, WTW 340i meter, Wissenschaftlich-Technische Werkstätten GmbH, Weilheim, Germany). The pCO_2 was controlled by pumping (10 W Eheim Universal 1046, 300 L h^{-1}) water through an equilibrator column (700 mm high $\times$ 80 $\varnothing$mm) that was constantly bubbled with the preset gas mixture. A Wösthoff Digamix 5 gas mixing pump (H Wösthoff Messtechnik GmbH, Bochum, Germany) was set to 95%:5% N_2:CO_2 output and connected in series to a Wösthoff Digamix 6 gas mixing pump (0, 1, 2, 3, ..., 100% output), allowing for a range of gas mixtures from 0 to 100% CO_2 in 0.05% increments. The output from the gas mixing pump series was tested using a LI-COR infra-red CO_2 gas analyzer (model LI820, LI-COR Environmental, Nebraska, USA), and found to deviate less than 1% of the programmed gas mix. The gas partial pressure was converted into a concentration using the solubility constants described by Weiss (1974). The $CO_{2(aq)}$ concentration in the test apparatus was checked

via the pH/alkalinity method (Stumm and Morgan, 1996). Alkalinity was measured following the method of Almgren et al. (1983), and pH was measured using a double-junction combination glass electrode (model TPS WP-91, TPS Pty. Ltd., Brisbane Australia) with an accuracy of 0.01 pH units.

A polystyrene cover reduced the surface area for degassing to occur, although there was a space available to pass the test CO_2 probe through. One OxyGuard CO_2 Analyzer probe was placed permanently inside the tank to act as a reference probe. The end of the probe was fitted with a 40 $\varnothing$mm PVC plumbing union into which the outlet of a small aquarium pump (5 W Eheim Compact 1000, 5 L min^{-1}) was located, so that a constant stream of water passed over the probe membrane. Holes were cut out of the PVC union opposite the pump outlet so that the water could flow unidirectionally past the probe membrane. A second OxyGuard CO_2 Analyzer probe could be inserted into a PVC holder which was supplied with a water flow of adjustable velocity. To initiate a test run the test probe was inserted into the holder so that the membrane was at the same level as the water flow outlet, which took 3–5 s from the time the probe entered the water. Water flow to the test probe was supplied by a 5 W Eheim Compact 1000 pump (5 L min^{-1}). The water velocity over the probe membrane could be changed by adjusting the supply and bypass valves. The water velocity was measured to an accuracy of ± 1 cm s^{-1} by placing a Höntzsch HFA water velocity meter (Höntzsch GmbH, Waiblingen, Germany) into the probe holder.

The 0–1 V output from the OxyGuard CO_2 Analyzers and the output from the temperature/pH meter were connected to an analogue-digital converter (PMD 1208LS 12 bits, Measurement Computing Corp., Massachusetts, USA), which was in turn connected to a computer. The pH probe output passed through an isolation amplifier (model 2704, PR Electronics, Rønde, Denmark) prior to the analogue-digital converter. The software program Labtech Notebook and Realtime VisionPro (Laboratory Technology Corp., Massachusetts, USA) was used to acquire, display and log the data from the instruments. The output from the CO_2 meters was configured so that the range corresponded to 0–50 mg L^{-1}. The data sampling rate was set to 10 Hz with a 10 point moving average, and the data was recorded and displayed with a frequency of 1 Hz.

The calibration procedure used to calibrate the meter was based on the most recent recommended procedures supplied by the manufacturer, with our own minor modifications. The procedure was as follows:

(1) Approximately 100 mL of demineralized water (reverse osmosis plus distillation) was placed into the stirring mixer along

with 1 mL of the supplied carbonate solution. This raised the pH of the water above 10, thereby converting any CO_2 into carbonates. The probe was placed into the stirring mixer and the zero adjusted after 5 min. The zero screw was positioned to the minimum rotation point that allowed the meter to display '000'.

(2) The stirring mixer was emptied and thoroughly rinsed with demineralized water, along with the probe, to remove any carbonate residuals. 199 mL of demineralized water was added to the stirring mixer along with the citric acid powder using the supplied measuring device. The citric acid solution lowered the pH of the water to below 3.5, liberating any inorganic carbon in the water into free CO_2. The probe was then placed into the mixer and left for 10 min to measure background $CO_{2(aq)}$. The concentration displayed on the meter screen was noted (termed 'C_i', which in the present study was typically 1 mg L^{-1}).

(3) The probe was removed from the stirring mixer and 1 mL of carbonate solution added using an adjustable micropipette. The plastic syringe supplied with the calibration kit was found to under-administer by between 17 and 20 μl. This is equivalent to approximately 2% of the expected span concentration, or 1 mg L^{-1} in a 50 mg L^{-1} span calibration. Once the carbonate solution had been added and mixed for 10 s (thereby converting carbonates to free CO_2 due to the acidity of the solution), the probe was placed back in the stirring mixer and left for 12–15 min. The new screen value (termed 'C_t') was noted and a correction value (U) calculated: $U = (50 \cdot C_i)/(C_t - C_i)$. The U value was summed with the target span concentration and a new span slope value (K) calculated to account for the background inorganic carbon: $K = U + 50$. The slope screw was adjusted as follows: (i) adjust slope screw to the target value (e.g. 50); (ii) slowly turn screw to 1 unit lower (e.g. 49) and note the screw position where the screen value changes; (iii) note screw position where screen value changes to 1 unit higher (e.g. 51); (iv) adjust the slope screw to the middle point between the two noted positions. When a calibration was carried out to a span concentration of 25 mg L^{-1}, only 0.5 mL of carbonate solution was added, and the span concentration adjusted appropriately.

2.2. Effect of water velocity on reaction time

The effect of water velocity on the reaction time of the probe was assessed by analyzing the digital computer log of the test probe output at different water velocities. The water velocities tested were 0, 9, 20, 30 and 39 cm s^{-1}. The temperature and $CO_{2(aq)}$ concentration were held constant (20 °C and 17 mg L^{-1}). The water velocity inside the probe holder was pre-set and measured before inserting the probe. To initiate a measurement run the probe was taken from the air and quickly placed into the probe holder in the test tank. The probe was then left to measure the $CO_{2(aq)}$ concentration for 30–90 min depending on the rate at which the measurement values were changing. Once the reading was deemed to have stabilized the probe was removed and the water velocity re-measured. This process was repeated so that three replicated measurements of the reaction time were made at each water velocity.

The digital computer file for each measurement run was opened in the software program TableCurve (v4.0, Jandel Scientific Software, California, USA), and a sigmoid curve of best fit added of the form $[CO_{2(aq)}] = a + b/(1 + \exp(-(\text{time} - c)/d))$. This function gave a high regression coefficient ($r^2 > 0.999$), and allowed for a smooth curve to be fitted to data. The specific sigmoid function for each measurement run was then used to iteratively calculate the rate of measurement change per second, until the rate of change was at 1×10^{-5}% s^{-1}. At this time the meter was deemed to have reached 100% of the span, and once this time point had been determined the time to 99%, 95% and 80% span was also calculated. A mean time (±1 SD) was then derived from the three replicates for each span

and velocity. Significant differences in reaction time between water velocities were tested using analysis of variance (ANOVA) and Tukey post hoc tests in Statistica (v8.0 StatSoft, Oklahoma, USA). The reaction times at 0 cm s^{-1} water velocity were not included in the significance tests because they were clearly different and skewed the variance distribution.

2.3. Use of calibration stirrer to make measurements

The utility of the stirring mixer (provided as part of the calibration kit) in making bench top measurements was investigated. This device is a custom designed magnetic stirring mixer that provides a shear force close to the probe membrane, and due to its low surface area effectively acts as closed system once the probe is inserted. The calibration stirrer was filled with 200 mL of water that had been kept at 20 °C and equilibrated with 1% CO_2 for 3 h. The 1% CO_2 continued to be bubbled into the stirring mixer for a further 10 min to account for any CO_2 was degassed during the transfer (water pH and alkalinity measurements confirmed that the water was at the correct pCO_2). The diffuser providing 1% CO_2 was then removed, the probe inserted into the calibration stirrer and the $CO_{2(aq)}$ concentration recorded for 25 min using the computer logging system. This process was repeated two more times ($n = 3$). A second trial was carried out to test how much of an effect the process of pouring a water sample into the calibration stirrer causes CO_2 to be lost due to degassing. A water sample was equilibrated with 1% CO_2 for 3 h at room temperature (24 °C), and then approximately 200 mL was poured into the calibration stirrer. The CO_2 probe was then inserted into the calibration stirrer and the concentration displayed on the meter screen recorded after 10 min. This process was repeated two more times ($n = 3$). A third trial was carried out to check that the probe thermistor properly compensated for the water temperature increase caused by the infra-red source when the probe was submerged in the calibration stirrer. Refrigerator-chilled water was added to the calibration stirrer and a known amount of inorganic carbon (Na$_2$CO$_3$) added to the water sample. The water was acidified to convert the carbonates to CO_2, and the probe inserted into the stirring mixer. A temperature probe was also inserted into the stirring mixer to measure the temperature increase caused by the infra-red source inside the CO_2 probe. This process was repeated two more times ($n = 3$).

2.4. Effect of temperature on reaction time

The effect of temperature on reaction time was tested at three different water velocities and a single pCO_2 (water equilibrated with 1% CO_2). The trial was carried out at 10, 20 and 30 °C, and at each temperature a probe membrane water velocity of 0, 20 and 39 cm s^{-1} was tested. The reaction time to 99%, 95% and 80% of the span were also calculated according to the methods above. Significant differences between reaction times at each temperature were investigated using ANOVA and Tukey post hoc tests.

2.5. Effect of CO_2 concentration on reaction time

The effect of $CO_{2(aq)}$ concentration on the reaction time of the meter was tested at 20 °C and 20 cm s^{-1} water velocity over the probe membrane. The $CO_{2(aq)}$ concentrations tested were 9, 17 and 34 mg L^{-1} (water equilibrated at 0.5%, 1% and 2% CO_2, respectively). Three replicate measurements were made at each concentration. The reaction time to 99%, 95% and 80% of the span were also calculated according to the methods above. Significant differences between reaction times at each concentration and span level were investigated using ANOVA and Tukey post hoc tests.

2.6. Precision and linearity of measurement

Three trials were undertaken to test the precision and linearity of measurement. All tests were performed in a 2 L glass conical flask set atop a magnetic stirring plate. Approximately 1.75 L of water was added to the flask and the pH probe placed in the water. A small pump drew water from the flask and circulated it through a heat exchanger placed inside a water bath to maintain the temperature at $20 \pm 0.1\,^{\circ}C$. The water was equilibrated with the target CO_2 gas mix until the water pH was constant (this took approximately 1 h). To make a CO_2 measurement, the probe was inserted into the flask so that the membrane was 1 cm above the magnetic stirring bar. The water continued to be gassed with CO_2 during the measurement period and the opening of the flask was covered with Parafilm so that there was a positive pressure of CO_2 exiting the vessel.

2.6.1. Inter-calibration variation

The inter-calibration variation was quantified by calibrating the meter to $25\,mg\,L^{-1}$ $CO_{2(aq)}$ span, and then measuring the $CO_{2(aq)}$ concentration in the testing apparatus set to $25\,mg\,L^{-1}$ $CO_{2(aq)}$. This was repeated five times. The concentration at 100% span was determined according to the methods above. The coefficient of variation ($CV = SD/mean \times 100$) and the percentage difference between the minimum and maximum $CO_{2(aq)}$ concentration were used as a measure of the inter-calibration variation.

2.6.2. Linearity of measurement

The linearity of measurement was carried out by calibrating the meter at 25 and $50\,mg\,L^{-1}$ $CO_{2(aq)}$ span, and measuring the $CO_{2(aq)}$ concentration in the testing apparatus over a range of concentrations from 0 to $50\,mg\,L^{-1}$ $CO_{2(aq)}$. The $CO_{2(aq)}$ concentration on the meter display was recorded after 20 min of measurement. The linearity was also tested using seawater (31 ppt salinity) taken from the Kattegatt area (north of the Danish island of Sjælland). The OxyGuard meter was recalibrated to $50\,mg\,L^{-1}$ $CO_{2(aq)}$ span following the manufacturer's recommended protocol of performing the calibration at the salinity of the sample water. The measurements were plotted against the test concentrations, and a linear regression fitted to the data to describe the linearity of measurement.

2.6.3. Inter-measurement variation

The inter-measurement variation (i.e. precision) was tested by calibrating the meter at $25\,mg\,L^{-1}$ $CO_{2(aq)}$ span using the manufacturer supplied equipment, and then repeatedly measuring the concentration in the testing apparatus (set to $25\,mg\,L^{-1}$ $CO_{2(aq)}$) five times. The meter was then calibrated at $50\,mg\,L^{-1}$ $CO_{2(aq)}$ span and five measurements carried out of water with $25\,mg\,CO_2\,L^{-1}$. The concentration at 100% equilibrium was determined according to the methods above. The CV and the percentage difference between the minimum and maximum $CO_{2(aq)}$ concentration at each calibration span were used as a measure of the inter-measurement variation.

3. Results and discussion

The reaction time of the OxyGuard CO_2 Analyzer was highly affected by the water velocity, or more accurately, the shear force over the probe membrane. At a water velocity of $0\,cm\,s^{-1}$ the response time to 99% span was 60 min, however, response time decreased rapidly with increasing water velocity (Fig. 2). There was no statistically significant difference in the response time between 30 and $39\,cm\,s^{-1}$ (Fig. 2), velocities at which it took 6–7 min to change 99% of the span. The time to 95% span was less than 10 min at water velocities of $9\,cm\,s^{-1}$ and above. The slow reaction time at low water flow rates is one of the key limitations of the OxyGuard CO_2 Analyzer. However, depending on the specific application, the
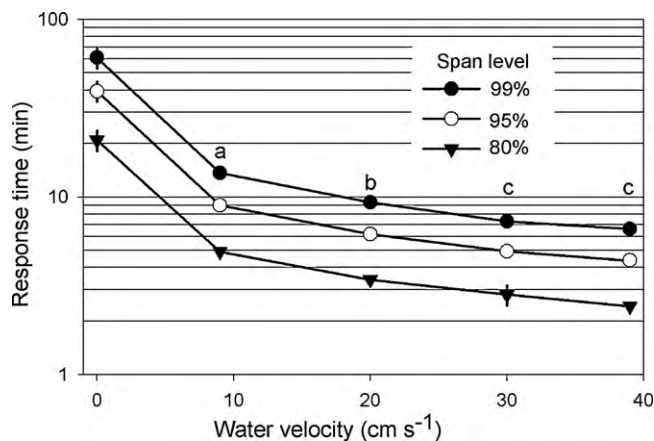

Fig. 2. Response time of the OxyGuard CO_2 Analyzer at different water velocities across the probe membrane. The response times were derived by measuring the time taken for the probe to adjust to 80%, 95% and 99% of the span difference between air and water maintained at $20\,^{\circ}C$ and a CO_2 concentration of $17\,mg\,L^{-1}$ ($pCO_2 = 7.5\,mm\,Hg$). Each data point represents the mean $\pm$ SD of 3 replicates. The letters in the diagram indicate statistically significant differences (Tukey post hoc test, $p < 0.05$) between mean values for each span level. The data for $0\,cm\,s^{-1}$ were not included in the significance testing as they were obviously different and skewed the variance distribution.

slow reaction time may not be of practical importance at relatively low $CO_{2(aq)}$ concentrations and moderate water flow rates. This is because the smallest unit of measurement displayed by the meter is $1\,mg\,CO_2\,L^{-1}$, and as the 95% span response times were reasonable (<10 min) at flow rates above $9\,cm\,s^{-1}$, the slow reaction time will be negligible if the span concentration is relatively small (e.g. $<15\,mg\,L^{-1}$).

The dependence of the reaction time of the probe on water flow over the membrane probably explains why a number of researchers and laboratories have been reporting that the meter significantly under-reads the $CO_{2(aq)}$ concentration (D. Moran, pers. obs.). If stationary probes were installed for some form of process engineering application, then one would have to ensure the probe was placed in a location with adequate water velocity, or install a pump discharging across the membrane. The reaction times at high water velocities ($>30\,cm\,s^{-1}$) are probably reasonable for engineering processes where the required measurement–response cycle is ca. 10 min.

If sample water velocities are low and a pump cannot be fitted to the probe head, then it is feasible to use the stirring mixer provided with the calibration kit to make bench-top measurements. The time taken (mm:ss) for the calibration stirrer to reach 99%, 95%, and 80% of the span level was 7.29 ± 0.38, 5.06 ± 0.20 and 3.02 ± 0.06 (mean $\pm$ SD), respectively. These were equivalent to the response times recorded at water velocities of $30\,cm\,s^{-1}$ and above. The act of pouring water into the calibration stirrer resulted in the degassing of CO_2, such that the concentration was $1\,mg\,L^{-1}$ below the sample concentration in all three replicates (pre-transfer $CO_{2(aq)}$ concentration was calculated to be $15\,mg\,L^{-1}$). The loss of CO_2 during water sampling and transfer to the stirring mixer will have to be taken into account when interpreting results using this measurement method. The temperature increase caused by the infra-red light source inside the probe was considerable, however, the probe thermistor and solubility-temperature compensation circuit adequately compensated for the increase in pCO_2, so that the original $CO_{2(aq)}$ concentration was correctly measured using the calibration stirrer (Fig. 3). There was a slow downward drift in concentration due to degassing when the water sample was left for longer than approximately 40 min (data not shown), although this is a much longer time than was needed to get a reliable reading. The maintenance of sample measurement accuracy despite a change in
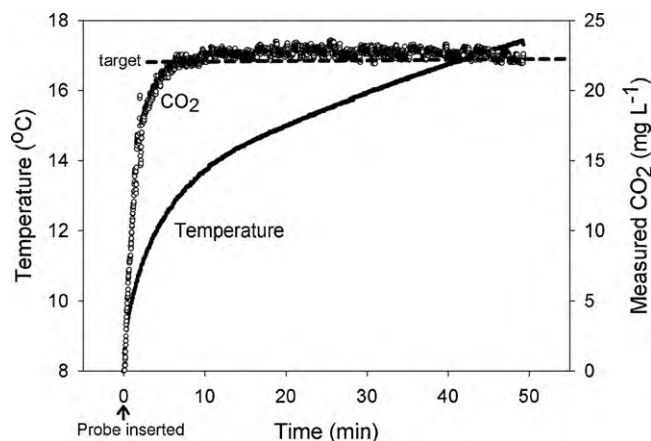
Fig. 3. Temperature increase of water inside in the stirring mixer used in the calibration procedure for the Oxyguard CO_2 Analyzer. The CO_2 concentration of the water sample was measured correctly as the stirring mixer is effectively a closed system and the Analyzer has a temperature compensation circuit, meaning the increase in pCO_2 due to temperature-induced desolubilization is compensated for.
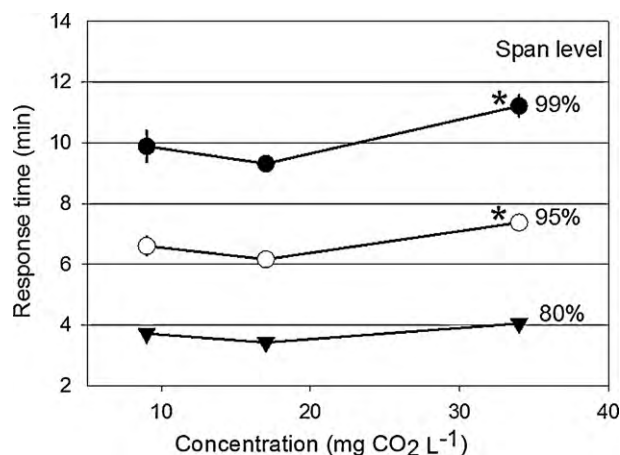

Fig. 4. Effect of $CO_{2(aq)}$ concentration on the response time of the OxyGuard CO_2 Analyzer at $20\,°C$ and $20\,cm\,s^{-1}$ water velocity. Each data point represents the mean $\pm$ SD of 3 replicates. Data points with '*' are significantly different (Tukey post hoc test, $p < 0.05$) to other data points within a span level that do not share the symbol.

temperature, solubility and pCO_2 relies on the fact that the stirring mixer is effectively a closed system, and no de-solubilized free CO_2 is degassed. Bench-top measurements using an open system (e.g. an open beaker atop a magnetic stirring platform) would be problematic, as de-solubilized free CO_2 would be lost from the sample.

At water velocities of $39\,cm\,s^{-1}$, the response time to 80%, 95% and 99% span was significantly (ANOVA, $p < 0.05$) slower at $10\,°C$ compared to 20 and $30\,°C$, although the effective time difference was negligible (<1.5 min, Table 1). There was no significant difference (ANOVA, $p > 0.05$) in response time between the different water temperatures at $0\,cm\,s^{-1}$ water velocity (Table 1). The response time of the OxyGuard CO_2 Analyzer to 99% and 95% span was significantly different (ANOVA, $p < 0.05$) at $34\,mg\,L^{-1}$ compared to the other concentrations tested, however, the magnitude of the difference in response time was small (<2 min, Fig. 4). The conclusions from the temperature and $CO_{2(aq)}$ concentration tests are that these variables had no practical effect on the performance of the meter for the ranges tested.

The inter-calibration accuracy test showed that the calibration procedure was highly repeatable. The CV of measurement at $25\,mg\,L^{-1}$ following five re-calibrations was 1.61%, and the maximum difference between any two measurements was 3.7% (equivalent to $0.9\,mg\,L^{-1}$ at a measurement level of $25\,mg\,L^{-1}$). The OxyGuard CO_2 Analyzer showed a high, but not perfect, correlation between measured and actual concentration (Fig. 5). In some instances, the meter display showed the Analyzer under-measuring the concentration by $1\,mg\,L^{-1}$ $CO_{2(aq)}$. Observations of the readings from the analogue output when the meter was apparently under-reading showed that the concentration was in fact within $0.5\,mg\,L^{-1}$ of the expected concentration. For reasons we are unaware of, the OxyGuard CO_2 Analyzer did not always average and round the probe signal output to the nearest whole $mg\,L^{-1}$
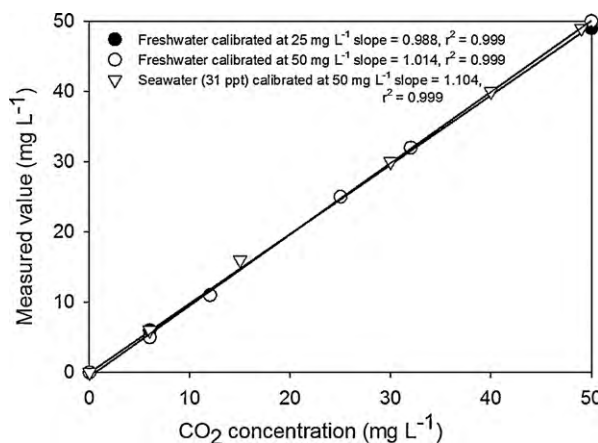

Fig. 5. Relationship between known CO_2 concentration and concentration measured by the OxyGuard CO_2 Analyzer. The Analyzer was calibrated before each individual measurement to a span concentration of 25 and $50\,mg\,CO_2\,L^{-1}$.

value for display on the meter screen. If researchers were using the analogue output and computer software to read and record the concentration, then the precision of the meter could be increased to within $\pm 0.5\,mg\,L^{-1}$ $CO_{2(aq)}$ with appropriate averaging settings to account for signal noise. The signal noise was too great to measure below a precision of $\pm 0.5\,mg\,L^{-1}$ $CO_{2(aq)}$ with the standard meter. However, we have been informed by the manufacturer that other meters can be made for higher and lower measurement ranges, and utilize the same measurement principle but with different primary probes (E. Höffner, pers. comm.).

The results of the inter-measurement variation test indicated that the OxyGuard CO_2 Analyzer has a measurement precision of 0.37–0.48%. When the meter was calibrated to a span $CO_{2(aq)}$

Table 1
Response time (mm:ss) of the OxyGuard CO_2 Analyzer at different water temperatures, span levels and water velocities.

Span	99%			95%			80%		
Veloc.	$39\,cm\,s^{-1}$	$20\,cm\,s^{-1}$	$0\,cm\,s^{-1}$	$39\,cm\,s^{-1}$	$20\,cm\,s^{-1}$	$0\,cm\,s^{-1}$	$39\,cm\,s^{-1}$	$20\,cm\,s^{-1}$	$0\,cm\,s^{-1}$
$10\,°C$	8.08 ± 0.05	10.19 ± 0.40	55.30 ± 3.10	5.21 ± 0.03	6.45 ± 0.26	35.00 ± 2.02	2.55 ± 0.02	3.40 ± 0.15	19.07 ± 1.02
$20\,°C$	6.37 ± 0.16	9.19 ± 0.13	60.49 ± 7.53	4.16 ± 0.09	6.10 ± 0.10	39.25 ± 5.07	2.26 ± 0.05	3.25 ± 0.06	20.53 ± 2.43
$30\,°C$	6.19 ± 0.23	9.25 ± 0.17	59.35 ± 1.22	4.16 ± 0.14	6.26 ± 0.20	38.49 ± 1.03	2.27 ± 0.07	3.33 ± 0.06	20.45 ± 0.45

Each data point represents the mean $\pm$ SD of 3 replicates. Significance testing was carried out for each column, so means that do not share the same superscript are significantly different to other means within each velocity and span level. Span represents the difference in pCO_2 between air and water equilibrated with 1% CO_2.

concentration of $25\,mg\,L^{-1}$, the CV between measurements was 0.48%, with the maximum difference between any two measurements 1.2%. At a span calibration concentration of $50\,mg\,L^{-1}$, the CV was 0.37%, with the maximum difference 0.93% (equivalent to $0.2\,mg\,L^{-1}$ at a measurement level of $25\,mg\,L^{-1}$). The pH/alkalinity methods used to calculate $CO_{2(aq)}$ can have a comparable level of precision if very careful measurements are made. Almgren et al. (1983) reported that alkalinity can be measured with a precision of 1–0.1% depending on the method employed. However, not all sources of acid neutralizing capacity are necessarily from carbonates alone, and the origin of the water sample can greatly affect the measurement of alkalinity. For example, oceanographers must take into account the contribution of boron (Stumm and Morgan, 1996), phosphate and silica (Almgren et al., 1983), and for those working with waters of high organic loadings (e.g. waste water or recirculated aquaculture systems), there are numerous substances that can affect the alkalinity, including tannic and fulvic acids, amino acids, fatty acids, sulfides, phosphates and ammonia (Almgren et al., 1983; Končalová et al., 1989; Hemond, 1990; Ritchie and Perdue, 2003). If waters contain significant concentrations of non-carbonate alkalinity agents, and their concentrations are not determined, then methods to derive $CO_{2(aq)}$ based on alkalinity have a greatly reduced precision. As a result of these limitations, the commonly cited APHA 4500-CO_2 method for $CO_{2(aq)}$ is not recommended for seawater, wastewater, or waters of moderate-high organic loading (A.P.H.A., 2005).

Accurate pH measurement is another limitation of pH/alkalinity methods used to derive $CO_{2(aq)}$. Electrodes are commonly used in field testing of water pH, however, a number of designs are known to be prone to the problem of electrolyte depletion in the liquid junction from immersion in test solutions of high ionic concentration (Illingworth, 1981), such as saline porewater or seawater (Covington and Whitfield, 1988; Marcus, 1989). In addition, alkali ion error, caused by the pH electrode responding to alkali ions in addition to H^+ ions, can result in an overestimation of H^+ ion concentration (Gray, 2004). Illingworth (1981) was concerned with inaccurate measurement of pH for the purpose of measuring $CO_{2(aq)}$, so carried out a survey of 30 pH probes in a number of laboratories. The mean pH error was 0.2 pH units (Illingworth, 1981). According to the A.P.H.A., the accuracy of pH probes under normal operating conditions is reported to be ±0.1 pH units or greater (A.P.H.A., 2005). In waters of reasonably high alkalinity, such as seawater (>2 meq kg^{-1}), a pH error of 0.1 units translates into a pCO_2 difference of 20% or more. Illingworth (1981) also reported that measurement artefacts can arise relatively quickly, even within a matter of weeks.

Gas stream infra-red detection techniques and the OxyGuard CO_2 Analyzer directly measure pCO_2, therefore, they avoid the problems of accurate alkalinity and pH measurement. Gas stream infra-red detection can measure pCO_2 to within 1 μatm (Murphy et al., 1998; Pierrot et al., 2009), which is two orders of magnitude better than the OxyGuard CO_2 Analyzer can achieve. However, the respective pCO_2 analyzers are designed for different purposes and measurement ranges, therefore, the measurement precision needs to be considered in the context of the application. Gas stream infra-red detectors are typically employed to measure small changes in dissolved atmospheric CO_2 (i.e. 350–400 μatm CO_2), and are relatively large, fixed, ship-board devices requiring samples to be pumped through equilibrator vessels (Wanninkhof, 2004). In contrast, the OxyGuard CO_2 Analyzer is primarily designed for water quality assessment, such as monitoring boiler feed water, wastewater and aquaculture water. From our experience, the probe is robust and easy to use in fieldwork involving wastewater and aquaculture water, and circumvents the problem of controlling and monitoring CO_2 via pH probes permanently placed in laboratory seawater systems. The measurement precision of the OxyGuard CO_2 Ana-

lyzer over the 0–$50\,mg\,L^{-1}$ $CO_{2(aq)}$ range is adequate for most of the aforementioned applications, and the relatively low cost (ca. US$2500) and portability of the OxyGuard CO_2 Analyzer compares favorably with gas stream infra-red detectors. The OxyGuard CO_2 Analyzer is a useful substitute for pH/alkalinity measurement techniques where it is difficult to ascertain accurate measurements of these variables.

4. Conclusions

- The OxyGuard CO_2 Analyzer requires a significant sample shear force over the probe membrane (i.e. >30 $cm\,s^{-1}$) in order to have reasonable response times.
- The measurement precision of the standard OxyGuard CO_2 Analyzer is not adequate for low concentrations, such as water in equilibration with atmospheric CO_2 concentrations.
- If temperature and salinity are known, the instrument can be used to measure pCO_2 via the use of appropriate CO_2 solubility constants.
- Providing $CO_{2(aq)}$ is >1 $mg\,L^{-1}$, the standard meter will be of considerable use in waters where it is difficult to obtain accurate pH and carbonate alkalinity measurements (e.g. waste water, waters of high organic loading and microbial activity, and saltwater).
- Compared to pH/alkalinity and gas stream infra-red detection methods, the OxyGuard CO_2 Analyzer gives a rapid measurement of $CO_{2(aq)}$, and depending on the specific water conditions and $CO_{2(aq)}$ concentration, the measurement precision lies somewhere between the two methods.

Acknowledgements

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