

Article

Underway Measurement of Dissolved Inorganic Carbon (DIC) in Estuarine Waters

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Abstract: Dissolved inorganic carbon (DIC) is an important parameter of the marine carbonate system. Underway analyses of DIC are required to describe spatial and temporal changes of DIC in marine systems. In this study, we developed a microvolume flow detection method for the underway determination of DIC in marine waters, using gas-diffusion flow analysis in conjunction with electrical conductivity (EC) measurement. Only an acid carrier reagent (0.2 mol.L^{-1}) and an ultrapure water acceptor are required for the DIC monitoring system. In this system, a sampling loop ($100 \mu\text{L}$) is used to quantify the injection sample volume, allowing micro-sample volume detection. The water sample reacts with the acid reagent to convert carbonate and bicarbonate species into CO_2 . The water sample is then carried into a gas-diffusion assembly, where the CO_2 diffuses from the sampling stream into the acceptor stream. CO_2 in the acceptor is detected subsequently by an electrical conductivity. The limit of DIC detection using ultrapure water is 0.16 mM . A good repeatability is obtained, with a relative standard deviation (RSD) of 0.56% (1 mM , $n = 21$). The time interval for detecting one sample is 5 min . During the observation period, measurements can be switched between standard solutions and water samples automatically. Accuracy and precision of the instrument is sufficient for the underway observation of marine DIC in estuarine waters.

Keywords: dissolved inorganic carbon (DIC); underway measurement; conductivity detector

1. Introduction

Dissolved inorganic carbon (DIC), which is typically comprised of CO_3^{2-} , HCO_3^- and CO_2 (aq) [1], is a major constituent of sea water and an important indicator of ocean acidification [2–6]. DIC concentrations range from less than $20 \mu\text{M}$ in poorly acidic buffered waters to more than $5000 \mu\text{M}$ in highly alkaline hard waters. However, DIC ranges from about 100 to $10,000 \mu\text{M}$ in most freshwater, and averages about $2400 \mu\text{M}$ in the ocean.

The carbonate systems can be described by four main parameters, such as DIC, pH, total alkalinity (TA), and pCO_2 . Measuring two of this parameters allows the calculation of the other two based on the thermodynamic equations of the carbonate system [7,8]. The determination of pH using glass electrodes is often affected by the variable ionic strength of seawater. Hence, colorimetric methods have been developed for the measurement of both pH and TA, to improve accuracy and precision [9–11]. Compared with the other three carbonate system parameters, DIC can be detected with the greatest accuracy and precision [3].

Coulometric and nondispersive infrared (NDIR) gas analysis methods are commonly used to measure DIC in seawater [12,13]. High accuracy and precision for DIC measurement with NDIR, as well

as coulometric detection, has been reported in previous studies [7,14]. Though NDIR gas analysis has been used for rapid measurements of DIC [15], neither of these approaches is practicable for the underway measurement of the large number of samples that are required to adequately describe spatial and temporal changes in dissolved carbonate species in marine systems [16]. High time-resolution and accurate observation techniques are required to understand the changes in ocean acidification and carbonate species. Rapid flow injection analysis for total DIC was first developed by Hall and Aller (1992) [17]. For the natural waters, the flow injection analysis method had a linear calibration range for DIC of 0.1–20 mM, with repeatability of 1% RSD. Recently, a gas-diffusion flow analysis system has been developed for the online determination of DIC [16,18–20]. Various techniques have been used to detect carbonate species or CO₂, such as photometric detection, C⁴D detection, a bulk acoustic wave detection, and a tungsten oxide sensing etc. [16,21,22]. The gas-diffusion approach has been widely used to measure carbonate species in aqueous solutions. Though the gas-diffusion analysis in combination with different detectors can be used for the rapid and sensitive determination of DIC, large sample volume flow rates are often needed to meet the accuracy and detection limit. In this case, large amounts of indicator solution and acid solution are consumed. For example, gas-diffusion flow injection with photometric detection typically consumes 60–120 mL.h⁻¹ of buffered indicator solution. This level of consumption is impractical for long-term detection of DIC. However, sample volumes can be significantly reduced, by using an electrical conductivity detector, as sample volumes of only 100 µL are required. Conductivity detection is highly accurate and precise, and does not require an additional indicator solution. Hence, the measurement of electrical conductivity is considered to be a suitable method for the determination of DIC.

In this study, we developed an online DIC determination method and instrument that provides fast, repeatable, and sensitive measurement of DIC in seawater. This monitoring system uses the gas-diffusion flow injection technique, in combination with an electric conductivity detector. We use a microvolume flow detection method to minimize the consumption of acceptor solution and acid reagent solution. No additional indicator solutions are needed during the detection process, reducing the reagent cost and waste disposal. The advantage of our instrument is to determine DIC in seawater rapidly and continuously. The gas-diffusion system in combination with electric conductivity detection can be used to provide continuous, underway DIC measurements with high spatial and temporal resolution along the cruise tracks and in estuarine areas within a short time. Hence, the DIC instrument is beneficial for underway and field DIC measurements.

2. Measurement System

2.1. DIC Analysis System

The online DIC observation system (Figure 1a) is consisting of two injectors (Liyuan Analysis Instrument Co. Ltd., Beijing, China), a six-port valve and a triple-injection valve (Liyuan Analysis Instrument Co. Ltd., Beijing, China), a plunger pump (Liyuan Analysis Instrument Co. Ltd., Beijing, China), a gas-diffusion assembly, a CO₂ removal cell (anion suppressor), and an electrical conductivity (EC) detector (Liyuan Analysis Instrument Co. Ltd., Beijing, China).

The scheme of the gas-diffusion assembly (Figure 1b) consists of an outer tube (1/8 inch id, 20 mm length, Teflon) through which the acidified water sample stream flows. The inner tube is used as membrane (1/16 inch od, AF2400 membrane), through which the acceptor stream flows. In this study, two inner tubes were used in the gas-diffusion assembly to enhance the diffusion surface area and accelerate the diffusion of CO₂ into the acceptor stream. T-piece connectors allow the donor stream to flow across the outside of the membrane, and allow the acceptor stream to flow across the inside of the membrane, seen in Figure 1b. In this study, the flow velocities of the donor and acceptor streams are about 0.6 m.s⁻¹ and 2.5 m.s⁻¹, respectively.

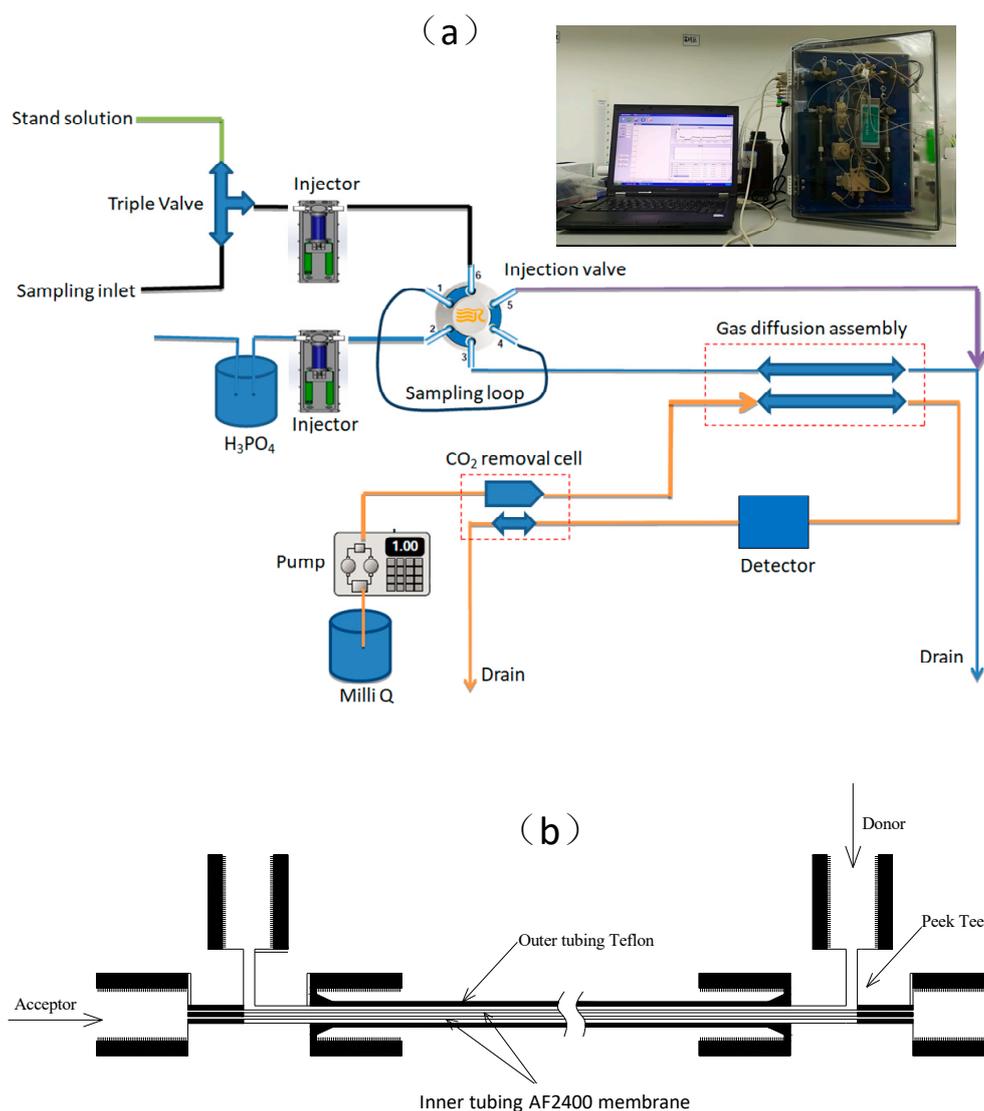


Figure 1. The schematic image of the DIC instrument, (a) DIC measurement system and image of DIC instrument, (b) Scheme of gas-diffusion assembly.

For DIC measurement, the acid reagent (H_3PO_4 , 0.2 mol.L^{-1} , flow rate $0.2\text{--}2.0 \text{ mL.min}^{-1}$) is first injected into the six-port valve, using a syringe pump. The acid reagent passes continuously through the sampling loop ($100 \mu\text{L}$), then flows into the gas-diffusion assembly during the detection and standby periods. When sample injection starts, the six-port valve is switched to the sample injection position. At the same time, the sample (1 mL) is pumped into the six-port valve and passes through the sampling loop. When the sampling injection ends, the six-port valve position is switched back to the original position. Then, the acid reagent passes through the sampling loop again and is mixed with the water sample. The water sample is acidified and the carbonate and bicarbonate are converted into CO_2 .

In the diffusion assembly, the acceptor stream and the sampling stream flow in opposite directions to improve the efficiency of CO_2 acceptance. The acidified sample is carried by the acid reagent to the gas-diffusion assembly, where CO_2 diffuses through the membrane and is absorbed by the acceptor. Finally, the acceptor solution is detected by electrical conductivity. In this study, ultrapure water was used as an acceptor stream with a flow rate of 0.5 to 2 mL.min^{-1} . Generally, the air CO_2 dissolved into the acceptor may change the acceptor background conductance and impact the baseline drift. To minimize the potential effect of CO_2 in the atmosphere on the acceptor stream, a CO_2 removal cell (anion suppressor) is used in the measuring system. The carbonate species contained in the ultrapure

water are removed before entering the electrical conductivity detector. In fact, the CO₂ trap is beneficial to minimize the system drift. Furthermore, we also used a single point correction method to check the system drift. A triple valve was used to automatically switch the water samples and standard solutions injection. The standard seawater was determined automatically after water samples were measuring for a certain time. Hence, we can check the DIC instrument performance easily.

2.2. Performance of the DIC System with Standard Solutions

To detect DIC in standard solutions, the triple valve was switched to the standard sample injection position, then the standard samples were pumped into the six-port valve by the sample injector. The injector and the sampling loop were flushed two to three times with the standard solutions before measurement. The standard solutions were detected from low to high DIC concentrations. Previous studies have reported that the measurement sensitivity can be improved, when NaOH was used as an acceptor stream [23]. However, the background conductivity would also increase significantly when NaOH was used as an acceptor stream. It is the case that NaOH acceptor stream may improve the CO₂ gas-diffusion, as CO₂ is more easily absorbed by acceptor streams with high pH, the linear calibration range was limited (0.2–2 mM) using a NaOH acceptor [24]. Typically, DIC concentrations average about 2.4 mM in the ocean [2,3], which is beyond the linear range of 0.2–2 mM. Hence, in this study, we used ultrapure water as the acceptor stream for EC detection, which has a constant background conductivity of 0.37 μs/m.

Different standard solutions (0.2, 0.5, 1.0, 2.0, 3.0, 4.0, 5.0, 7.0, 9.0, 10.0 mM) of NaHCO₃ were selected for DIC calibration. Every standard solution sample was measured for five times to obtain mean values. The ultrapure water acceptor calibration data can be fitted to a quadratic function for the range from 0.1 to 10 mM ($y = ((4.70 \times 10^{-5} \pm 4.56 \times 10^{-7}) * x^2 + (0.015 \pm 1.52 \times 10^{-4}) * x, R^2 = 0.999$, Figure 2). Please note that good linear correlation was present for the DIC concentration below 5 mM using water acceptor ($R^2 = 0.996$, Figure S1). The linear range for NaOH acceptor was ~4 mM, with R^2 of 0.998 (Figure S1). For low DIC concentration determination, both water and NaOH acceptors were applicable. In this study, water acceptor was used, because water can be better used than NaOH solution in the field. The detection limit of the DIC instrument with ultrapure water was 0.16 mM, based on the regression method, seen in Figure S2, which was a substantial improvement over the photometric detection method (limit of detection, 0.42 mM) [16].

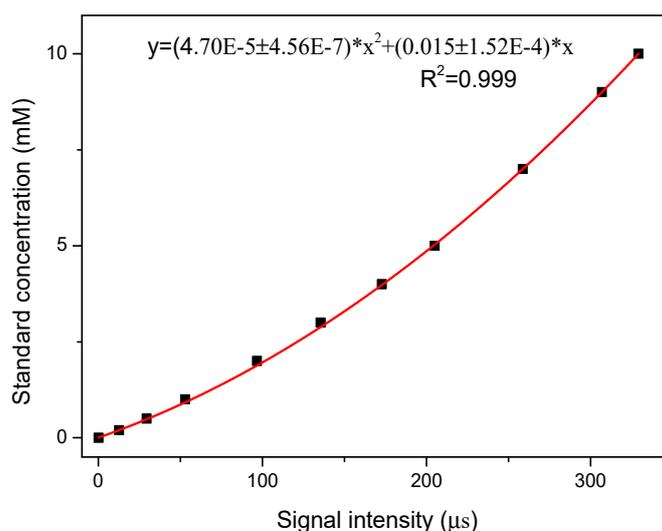


Figure 2. Correlation between signal intensity and standard solution concentration.

The 1 mM standard solution was measured continuously to determine the repeatability (RSD%) performance of the instrument. The RSD for EC detection with an ultrapure water acceptor stream was about 0.56% (1 mM, n = 21; Figure S1). The detection time for one sample was estimated to be 5 min (Figure S2), i.e., the system is capable of processing 12 samples per hour, which is sufficient for the underway observation of marine DIC, and which will provide DIC concentration data with high spatial and temporal resolution.

2.3. Comparisons with other DIC Determination Systems

Simultaneous analyses of seawater samples from Xiamen coastal regions were performed with both C⁴D and EC detectors. H₃PO₄ solution with 0.2 mol/L and ultrapure water were used as carrier and acceptor streams, respectively, for both C⁴D and EC detection. The DIC concentrations detected using EC ranged from 1.91 to 1.96 mM, with an average of 1.94 ± 0.013 mM (n = 52, RSD 0.60%, Figure 3). The EC detection results were well consistent those determined using C⁴D, with an average of 1.93 ± 0.014 mM (n = 24, RSD 0.72%, Figure 3). The accuracy of the DIC instrument was also tested using standard sea water, seen in Figure S5. The standard sea water samples were measured three times to obtain the mean values of DIC concentration. The accuracy in standard seawater with 0.5 mM of DIC is about 0.002 mM, while the accuracy in standard seawater with 5 mM of DIC is about 0.008 mM. Measured DIC concentrations correlated well with the standard seawater DIC concentration. It indicated that the DIC detection with EC was accurate and precise.

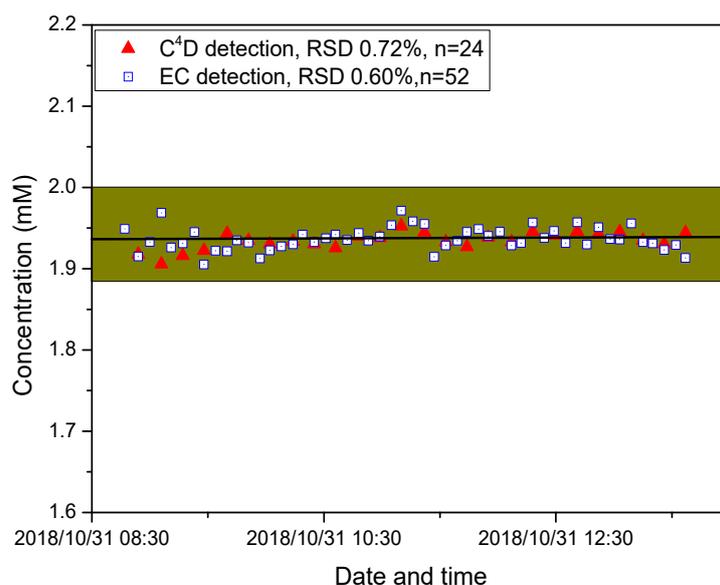


Figure 3. Comparison of DIC determination results with EC detection method and C4D detection method.

Four seawater samples with different DIC concentrations were analyzed using the titration detection method and the underway DIC measurement system. The measurement of DIC using titration detection has been described in detail by Johnsonn (1985) [12] and Ji (2002) [25]. Each sample was determined for five times by both instruments. The results obtained using the underway DIC system were well correlated with those obtained using the titration method (Figure 4). The relationship between the two sets of measurements can be described using the following linear regression ($R^2 = 0.998$; slope = 1.001).

$$DIC_{ED} = (1.001 \pm 0.004)DIC_{TR}, R^2 = 0.998 \tag{1}$$

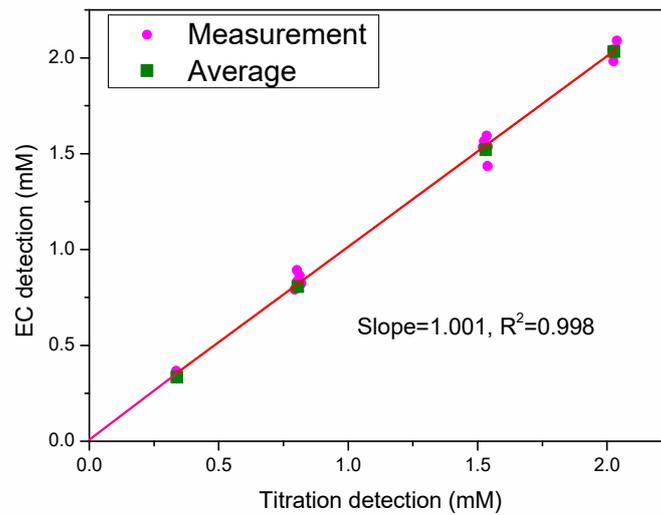


Figure 4. The relationship of DIC determination between titration detection and this study.

2.4. Shipboard Measurements

Onboard DIC measurements were carried out by R/V “Discovery” in Terengganu river estuary, Malaysia (Figure 5). The Terengganu River basin is situated on the east coast of Peninsular Malaysia. The Terengganu River is approximately 65 km in length and flows from Hulu Terengganu to the mouth of the river at Kuala Terengganu and discharges into the southern part of the South China Sea. The Terengganu Estuary (5.34° N, 103.13° E) is a sheltered estuary where the constructed breakwater at the river mouth shelters the estuary from direct influence of the open sea. Additionally, a hydroelectric dam located at the upper stretches of catchment area is regulated by the freshwater runoff capacity in the estuary. The tidal regime in this area is dominated by diurnal tide; with the mean tidal range being approximately 1.60 m, while the tidal range during the spring and neap tide are 2.40 m and 0.80 m, respectively [26]. The residence time of Terengganu estuary is relatively short (5–10 h), due to high volume of freshwater discharged upstream.

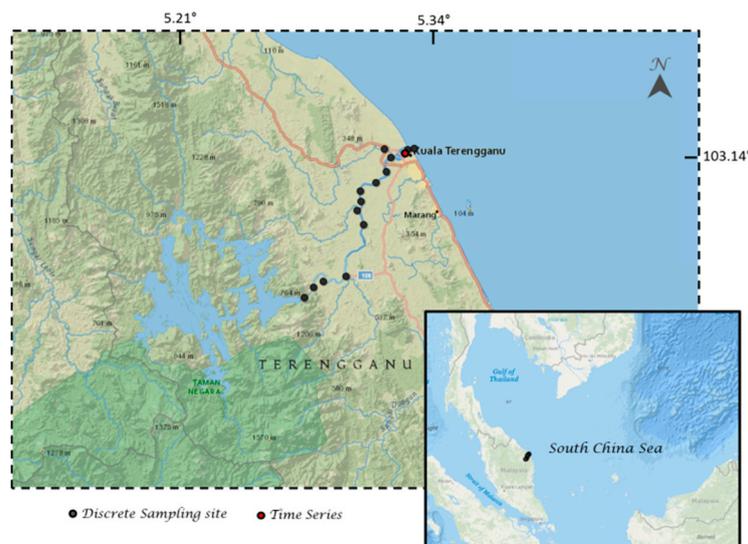


Figure 5. Map showing the observation region on the Terengganu river estuary, Malaysia.

In this study, DIC analyses were performed over 24 h while the ship was anchored in the Terengganu Estuary (at 5.34° N, 103.13° E). Temporal variability in carbon and nitrogen, as well as the magnitudes of the carbon and nitrogen biogeochemical fluxes, were measured during the diurnal

tidal cycle. Water samples were pumped from the sea using a peristaltic pump deployed on the R/V “Discovery”. In addition, the seawater samples were collected using Niskin bottles. A sonde was used to measure temperature, salinity and pH, as well as chlorophyll-a.

3. Results and Discussion

Application of On Board Sea Water DIC Observation

The DIC instrument was installed on R/V “Discovery” (University Malaysia Terengganu, Figure S6). DIC, pH and salinity were measured simultaneously during a diurnal tidal cycle from 4th to 5th August 2019. Surface sea water DIC and salinity, as well as the tidal levels, are illustrated in Figure 6. The large data gap in the field test was caused by the peristaltic pump deployed on the R/V “Discovery”, but was not caused by the DIC monitoring instrument. In this study, samples were pumped from the seawater using a peristaltic pump. However, the peristaltic pump broke down during the low tide. Hence we could not get the water samples during that period. Variations in DIC concentration were consistent with the variations in salinity and tidal levels in the estuary. DIC concentration profile well reflected the whole tidal cycle, indicating that the temporal resolution of the underway DIC observation instrument was sufficient for estuarine seawater analysis. High DIC levels, as well as salinity value were present in high tide. DIC concentrations and salinity values decreased from 1.98 mM to 0.51 mM and from 30.2 to 4.6, respectively, as the tidal level decreased from 2.1 m to 0.8 m. A similar relationship between DIC and salinity was also observed during a cruise on the Yarra River estuary, SE Australia, on 19 May 2011 [16]. They observed variations in salinity indicated that the Terengganu Estuary is dominated by seawater at high tide and by freshwater at low tide.

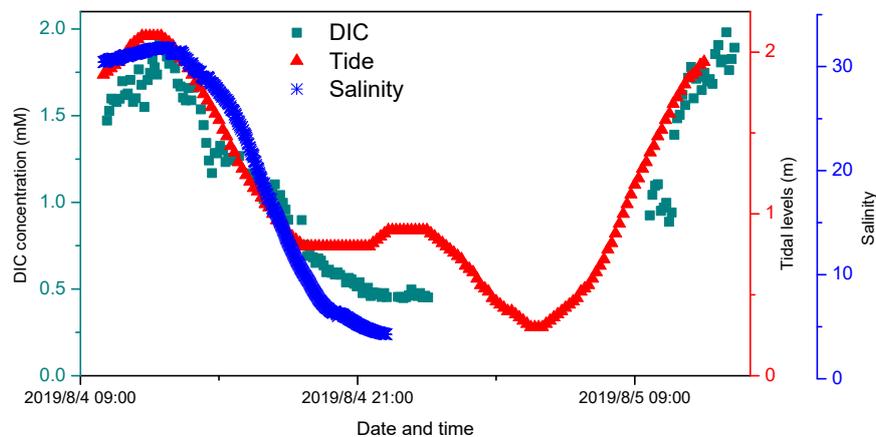


Figure 6. Time series of DIC, salinity and tidal height determined during the observation in Kuala Terengganu on 4–5 August 2019.

Surface sea water samples were also collected and analyzed at two hours intervals, simultaneously. These measurements were compared with the underway DIC analyses. During the measurement period, standard seawater samples (2.02 mM) were also measured automatically every two hours by the DIC instrument (Figure 7), for the purposes of quality checking and data calibration. The analyses of the seawater standards during the observation period indicated that the instrument was performing well. Our results showed that the surface water DIC concentrations were consistent with those made underway (Figure 7). Thus, the tidal cycle had a significant effect on seawater DIC concentrations in the Terengganu Estuary.

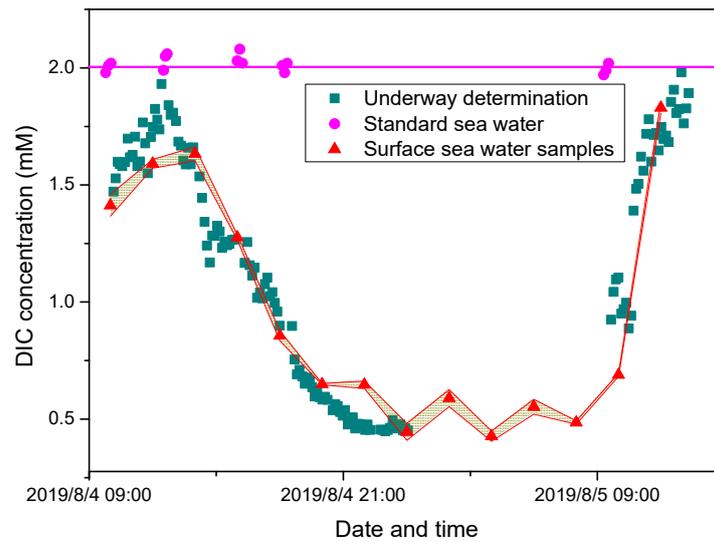


Figure 7. Relationship between surface sea water samples DIC detection and underway DIC observation results.

Strong positive linear correlation between DIC concentration and salinity was present ($R^2 = 0.95$, Figure 8), indicating that DIC concentrations in the estuarine area were determined by the rate of mixing between seawater and freshwater.

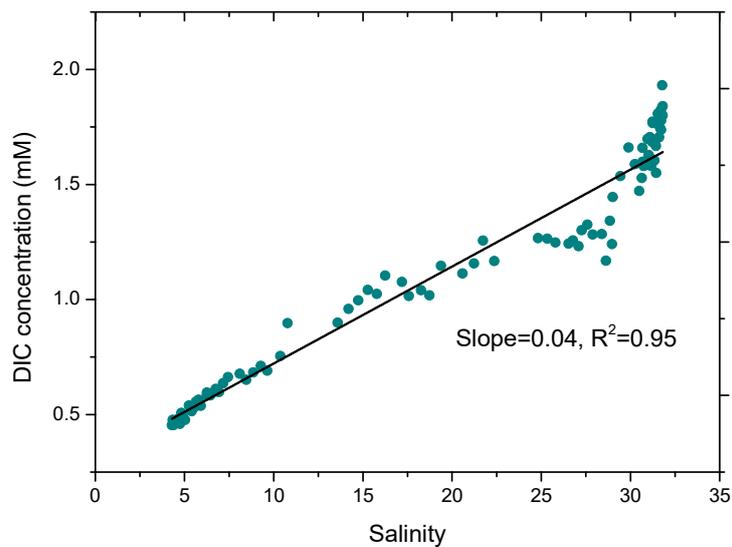


Figure 8. Correlation between DIC and salinity.

To further clarify the impact of tidal level on seawater DIC, water samples were collected at various depths (0.5, 3.0, and 5.0 m) over two-hour intervals. Each water sample was determined three times, and the mean of the three measurements was retained. The variations in DIC concentration at different depths were associated with tidal level. DIC concentrations were greatest at a depth of 5.0 m, followed by those at a depth of 3.0 m and those at a depth of 0.5 m (Figure 9). This indicated the relative impact of seawater increased with water depth. Please note that the discrepancy in DIC concentrations between the surface water and bottom water was small at high tide, but DIC concentration in the bottom water was much greater than that in the surface water at low tide. This indicated that in the estuary, seawater stratification was obvious at low tide, but freshwater and seawater were well mixed at high tide.

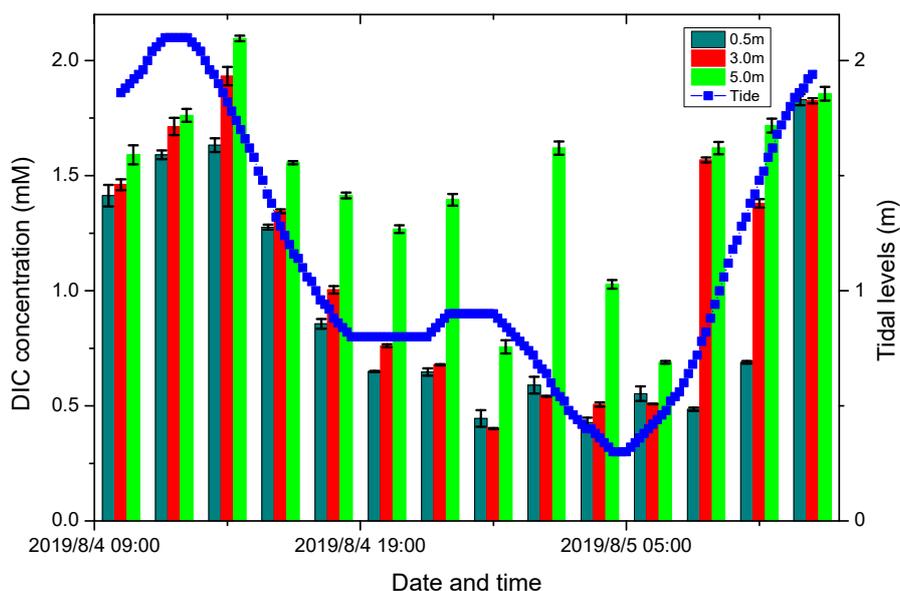


Figure 9. Observations of DIC samples at different water depth.

4. Conclusions

An underway DIC measurement instrument was developed using gas-diffusion flow in combination with electrical conductivity (EC) detector, which was suitable for the measurement of DIC in estuarine waters with high spatial and temporal resolution. A microvolume flow technique with 100 μL was achieved for DIC determination. A high efficiency AF2400 membrane gas-diffusion device was constructed. Only an acid carrier stream and an ultrapure water acceptor stream were required for the DIC detection. The limits of detection for the DIC instrument with ultrapure water was 0.16 mM. Repeatability was also high, with an RSD of 0.56% (1 mM, $n = 21$). The detection time for one sample was estimated to be 5 min, equivalent to approximately 12 samples per hour. The instrument switches automatically between the standard solution and seawater samples during underway use. High accuracy and precision of the DIC observation instrument provides high spatial and temporal resolution DIC measurements.

The underway DIC instrument was used to measure seawater DIC in the Terengganu river estuary, Malaysia. This method was used to obtain DIC data with high temporal resolution, and to clarify the impact of the diurnal tidal cycle on seawater DIC. Changes in DIC concentrations were well correlated with variations in salinity and tidal level in the estuary. The DIC concentration profile obtained in this study accurately reflected the entire tidal cycle, indicating that the temporal resolution of the underway DIC analysis instrument was sufficient for DIC detection in estuarine waters.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2077-1312/8/10/765/s1>, Figure S1: Correlation between DIC concentration and Signal intensity, Figure S2: The signal spectrum of the DIC instrument of different DIC concentration, Figure S3: Time series of repeatability detection with standard samples, Figure S4: Spectrograms of the repeatability detection with 1mM standard sample, Figure S5: Measurement results of standard seawater using the DIC instrument, Figure S6: Application of the underway DIC detection in estuarine waters.

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Conflicts of Interest: The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.

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