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ARTICLE

A simplified coulometric method for multi-sample measurements of total dissolved inorganic carbon concentration in marine waters

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Natchanon Amornthammarong,^{*ab} Peter B. Ortner,^{*a} James Hendee,^b and Ryan Woosley^c

A new system requiring greatly reduced operator intervention has been developed for the determination of dissolved inorganic carbon concentration in marine waters. Based on a coulometric method, the system has an accuracy and precision comparable to more complex and expensive methods currently employed. A syringe pump equipped with a 12-port distribution valve is used to precisely dispense an acid solution and sample into a gas stripper. The system can autonomously measure eight discrete samples in duplicate or triplicate with no operator input. The best precision (%RSD) obtained was 0.022% (n=14) or less than $\pm 1.0 \mu\text{mol kg}^{-1}$. The system is calibrated against a certified reference material (CRM). Average offset from the CRM was $1.2 \mu\text{mol kg}^{-1}$. Sample throughput was 4 samples/hr. Carryover effects are negligible but field sample analyses suggest that prefiltering may be necessary in highly turbid waters.

Introduction

Dissolved inorganic carbon (DIC) is defined as the sum of the concentrations of dissolved CO_2 , carbonic acid, bicarbonate, and carbonate. DIC concentration, [DIC], is reported as micromoles carbon per kilogram of seawater ($\mu\text{mol kg}^{-1}$).¹ Seawater [DIC] typically range from 1800 to 2300 $\mu\text{mol kg}^{-1}$, but can reach 4300 $\mu\text{mol kg}^{-1}$ in extreme marine environments (e.g. the Black Sea). For investigating the oceanic component of the global carbon cycle the consensus analytical goal is 0.05% for accuracy and precision, or $\pm 1.0 \mu\text{mol kg}^{-1}$ for seawater²⁻⁵.

There are five major methodologies used in [DIC] measurement. (1) Coulometry.⁶ A known amount of seawater is acidified with phosphoric acid, then the released CO_2 is stripped by an inert CO_2 -free carrier gas. The amount of released CO_2 is then measured coulometrically. (2) Non-dispersive infrared absorption (NDIR).^{7,8} After acidifying and stripping, the released CO_2 is passed through a NDIR detector to determine $f\text{CO}_2$. (3) Spectrophotometry.⁹⁻¹¹ A fixed volume of seawater is acidified, then the released CO_2 is allowed to equilibrate with an internal solution containing a pH indicator and alkalinity standard. At equilibration, the pH of the internal solution becomes constant. $f\text{CO}_2$ and [DIC] can then be calculated from pH and the known total alkalinity. (4) Mass spectrometry.^{12,13} A membrane inlet mass spectrometer is used

for measurement of dissolved CO_2 gas after acidifying seawater to $\text{pH} < 3$. (5) Isotope dilution.¹⁴ A seawater sample and a ^{13}C -labeled sodium bicarbonate solution are mixed; then the mixed solution is acidified and sent through a gas permeable membrane contactor, and the released CO_2 first extracted using a CO_2 -free gas stream, and then passed into a cavity ring-down spectrometer to determine its isotope ratio. Furthermore, several systems based on flow injection analysis have been developed in the past years for automated measurements of [DIC].¹⁵⁻²¹

The "Standard Operating Procedure" described by Dickson et al.⁶ is based upon coulometry. A commercial system based upon this approach, the Single Operator Multi-parameter Metabolic Analyzer (SOMMA),²²⁻²⁴ has become the accepted method of automated DIC measurement within the oceanographic community. Unfortunately, the manufacturer of the SOMMA system is no longer in business. However, there is another system called VINDTA 3D (Marianda, Germany),²⁵ which is similar to SOMMA and commercially available. Moreover, while the SOMMA system can achieve accuracy $< 1 \mu\text{mol kg}^{-1}$, or $< 0.06\%$ in most ocean environments, it requires complex protocols and a well-trained operator. Accurate measurements depend upon highly precise dispensing of a known volume of seawater into the stripper where the seawater is acidified.

The instrument reported here shares the same coulometric principle as the SOMMA system and has a similar precision and accuracy. The new system is however much simpler and able to autonomously measure eight discrete samples with absolutely no attention. Instead of the multiple solenoid valves and thermostat-regulated pipette used in SOMMA, a syringe pump equipped with a zero-dead volume syringe and a 12-port distribution valve are used to precisely dispense a dense acid brine solution and seawater samples into the stripper. This solution-dispensing method is adapted from a commercially available DIC analyzer (LI-7000, Apollo Scitech)²⁶, but the dispensed volume is increased 25-fold thereby decreasing the uncertainty in the dispensed volume. Waste remaining in the stripper is automatically withdrawn by a peristaltic pump after each analysis. The system is called the Multi-sample Automated Natural-water Analyzer dubbed MANA by Dr. Rik Wanninkhof, NOAA.

Methods

System Description

A schematic diagram and summary of the system operations are given in Figure 1 and Table 1 respectively. The 12-way syringe pump (55023, Norgren Kloehn) equipped with 25 mL capacity zero dead volume syringe (with 48,000 step resolution), seven sample bottles, and a CRM bottle are all installed in a modified thermostat-regulated cooler (P-85 Krusader, Koolatron), maintained by thermostat at 22.0 °C (the lowest controllable temperature achievable in the laboratory).

Table 1. Summary of the system operation.

Step	Description	Time(min)
1	Rinse the system and rid of all bubbles	0.5
2	Dispense acid and sample solutions into the syringe	4
3	Acidify and titrate the sample/acid solution from step 2	8
4	Drain waste inside the stripper	2.5

First, the system must be rinsed and rid of all bubbles. The syringe pump draws air into the syringe in 2,000 steps at a speed of 200 steps per second (sps) through port L of the 12-port distribution valve, acid solution (R1, port A) and a sample solution into the syringe (2,000 steps (10-sec) and 4,000 steps respectively (20 Sec)) and then pushes all this material out to waste (port K) at speed of 300 sps. Because of the design of the zero dead volume syringe, the system can easily rid all bubbles by one cycle of these steps.

Second, to dispense acid and sample solutions, the syringe pump draws 2 mL (3840 steps) of acid solution (R1) and 23 mL (44160 steps) of sample into the syringe at a speed no greater than 200 sps. Speeds of 60, 100, 200, 250, 300, and 500 sps were tested. At 200 sps the solutions still remain separated in discrete layers as the syringe is filled (Figure 2). The system provides its best precision therefore at speeds no greater than

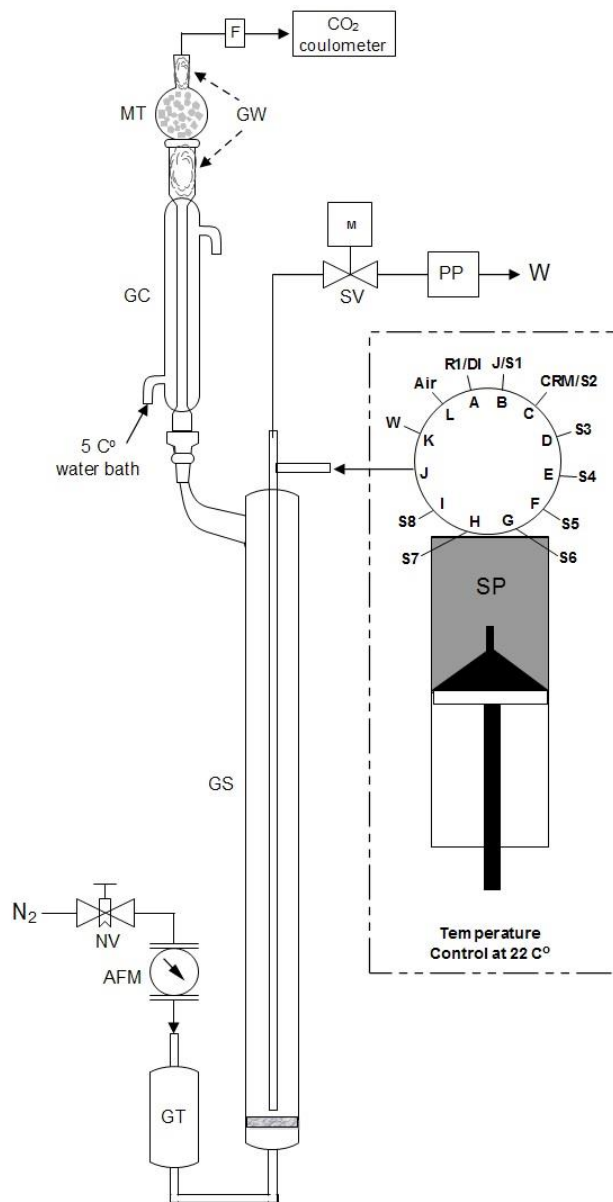


Figure 1. A schematic diagram of the multi-sample automated natural-water analyzer (MANA). Acronyms: NV, needle valve; AFM, air-flow meter; GT, glass trap; GS, glass stripper; GC, glass condenser; MT, moisture trap; GW, glass wool; F, PTFE 0.2 μm filter; SV, pinching valve; PP, peristaltic pump; SP, 12-way syringe pump equipped with 25 mL zero dead volume syringe; W, waste; R1/DI, acid solution or deionised water; J, junk or low nutrient seawater solution; CRM, certified reference materials; S1-S8, samples.

200 sps. The temperature of the solution in the syringe is measured by a platinum resistance temperature detector (OMEGA Engineering, Inc.), which offers an accuracy of ± 0.03 °C at 0 °C, attached to its exterior. Pictures of the syringe are taken by a high definition webcam camera (C310, Logitech) to confirm there are no bubbles inside the syringe before delivering the solution to the stripper for analysis.

Third, for acidification and titration, the sample/acid solution from step 2 is injected into the stripper where Ultra-

Pure™ N₂ gas (UHP, Praxair) is introduced to transport any CO₂ gas derived from the sample to the coulometer (CM5011, UIC Inc.). This CO₂ is dried by the condenser (GC) and moisture trap (MT), passed through a PTFE 0.2 μm filter (F, Gelman, Acrodisc) and then titrated coulometrically. In the titration cell, CO₂ reacts quantitatively with ethanolamine to form hydroxyethyl carbamic acid which is titrated with OH⁻ ions electrogenerated by the reduction of H₂O at a platinum cathode. The titration endpoint is detected photometrically with thymolphthalein as indicator. The cell solution turns blue at pH 10.5 and is colourless at pH 9.3 after the addition of CO₂ in aqueous solution.²² As the cell solution is titrated, pH increases and the blue colour returns, thus causing the titration current to decrease as the endpoint is approached. CO₂ is thus measured by the quantity of electrons required to reach the endpoint, as calculated from the measured current and duration required to reach the end point.



Figure 2. Syringe performance at 200 steps per second. The bottom layer is the dense acid brine solution, R1. The upper layer is seawater dyed for demonstration purposes. Photographs were obtained at 1, 2.5 and 4 minutes.

After titration, the remaining waste inside the stripper is pumped through a pinch valve (SV, 075P2NC12-01B, BIO-CHEM VALVE) using a peristaltic pump (PP, SP201.007, 35 rpm, 12Vdc, APT Instruments). Figure 3(a) shows all the components of the system and 3(b) shows the inside of the thermostatically regulated cooler in which the syringe pump and eight sample bottles are housed.

Reagent Requirements

The dense Acid brine solution (R1) was prepared by dissolving 100 g of NaCl (152575, MP Biomedicals) in 800 mL deionized water, adding 117 mL of 85% H₃PO₄ (7664-38-2, Sigma-Aldrich) to the solution, then making it 1 L with deionized water. All chemicals used were reagent grade. Carbon cathode solution (CM300-001) and carbon anode solution (CM300-002) were purchased from UIC Inc., IL, USA. Potassium Iodide (P1340) was purchased from Spectrum Chemical. Certified Reference Materials (CRM) solutions were

purchased from A. Dickson (Scripps Institution of Oceanography of the University of California San Diego).

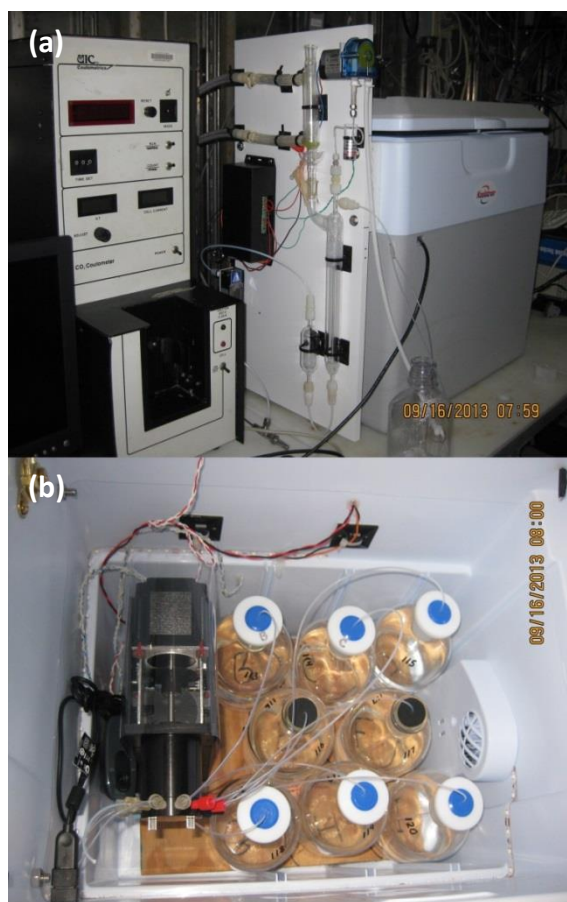


Figure 3. (a) The Multi-sample Automated Natural sample Analyzer (MANA). (b) The interior of the temperature regulated chamber housing the syringe and sample bottles.

System Preparation

Assembly of Mg(ClO₄)₂ moisture trap. A moisture trap (MT) is prepared by inserting phosphoric acid-treated glass wool (2-0383, Supelco) into one arm of the MT, adding magnesium perchlorate, Mg(ClO₄)₂ (Desiccant, 5039-04, Mallinckrodt chemicals), then blocking the bottom of the MT with glass wool. If there are wool hairs protruding from the bottom or arm, they are trimmed with scissors. Grease (type L, APIEZON products, M&I Materials LTD) is then lightly applied to the ground joint of the MT before seating it to the glass condenser (GC) and securing it with rubber bands.

Assembly of the coulometric cell. A magnetic bar is put into the cell and 100 mL of carbon cathode solution is then added. A small amount of Potassium Iodide crystal (KI, P1340, Spectrum) is then put in the bottom of the cell sidearm (the purpose of KI is to keep the electrolytic solution saturated so the amount is not critical). The carbon anode solution is then added to the cell sidearm to about 1 cm below the level of the cathode solution. A cathode cap (the one with platinum wire and gas inlet tube) is then seated on the cell and an anode cap

with a silver electrode put on the cell sidearm. The anode cap should not be airtight because the anode solution will be forced through the frit which separates the cathode and anode solutions. After the cell is put on the coulometer, the position of the cell is adjusted to avoid bubbles in the light path by checking the Percent Transmission, which should remain stable.

Sample Analysis Preparation. Before initiating sample measurements we recommend measuring filtered highly oligotrophic natural seawater samples (LNSW) three times, a blank solution (the dense acid brine solution) at least once, and CRM three times.

System Shutdown

At the end of the day we recommend measuring CRM three more times. Upon completion of all daily operations, the acid solution bottle (R1) is replaced by a deionized water (DI) bottle, and two pumps of 25 mL each of deionized water suffices to clean the stripper. Waste remaining is then drained by the peristaltic pump (PP). The coulometric cell, cathode and anode caps, magnetic bar and moisture trap must then be manually rinsed with distilled water, then acetone-rinsed and all components baked at 60 °C overnight prior to the next operating cycle.

System Performance

Sample Blanks. Blank values are determined by injecting 2 mL of the acid solution and recording the signal for 20 minutes. Figure 4 shows the signals of five blank injections. Within the first two minutes after injections the signals rapidly increase from 0 to about 200 counts (reagent blank), then the signals increases 23.7 counts/min (carrier blank). Therefore, the carrier blank level of the system was set in the range of 24 – 30 counts/min. During subsequent operation, after the system injects 2 mL of acid solution and waits 100 seconds to let all reagent blank out, the system records the signal for 10 minutes and calculates carrier blank counts/min. If the carrier blank signal rose above 30 counts/min the system automatically re-injected the acid solution again until the carrier blank signal returned to the expected value.

Sample Carryover. 100% LNSW samples were placed at ports B, C, F and G and diluted LNSW (90%) bottles at ports D, E and H. The system injected the solutions in duplicate from port B to H to test for carryover. Results are shown in Figure 5. Carryover effects calculated both high-to-low and low-to-high were -0.018% and +0.020% respectively. These are negligible since they are less than the precision of the instrument.

System Response. The system response was linear [$y = (2347.9 \pm 64.5)x$, y =system response(count), x =percent of LNSW] over a range of 50-100% LNSW diluted by deionized water, with a correlation coefficient (R^2) of 0.9992. Reproducibility was tested by injecting LNSW 14 times in

succession. The mean value measured was 2012.5 $\mu\text{mol kg}^{-1}$ with a precision of 0.022%. The accuracy of the system was tested by injecting CRMs, and then calculated [DIC] by using the calibrated volume of the syringe, which was calibrated every time the syringe was changed. The average offset of calculated [DIC] from CRM reported by the Scripps Institution of Oceanography of the University of California was 1.2 $\mu\text{mol kg}^{-1}$ ($n=9$). System software first calculates apparent dissolve inorganic carbon concentration in $\mu\text{mol kg}^{-1}$, then the calculated [DIC] is corrected both to the average CRM value measured before and after daily analysis (a systematic offset error correction) and for field samples to the “added” HgCl_2 volume (volume offset correction). Note: field samples are typically poisoned with HgCl_2 .

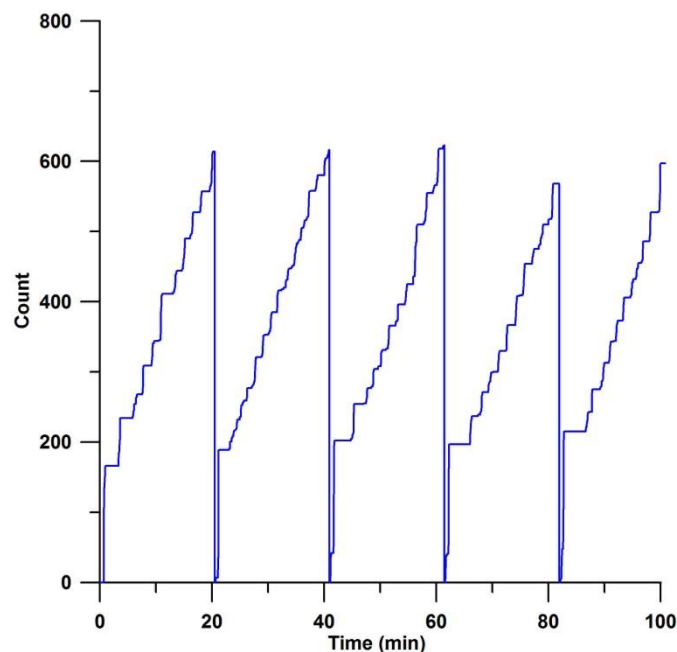


Figure 4. Replicate sample blanks (injections of 2ml of the dense acid brine solution).

Ambient atmospheric exchange with the CRM. To study the extent to which gas exchange into the headspace of the bottle affects the DIC in the 500 mL CRM bottle once it was connected to the system, the system repeatedly measured the CRM solution (Batch 108) until a significant change in output was noted. Results are shown in Figure 6. For each measurement, the system drew 25 mL (2 mL for rinsing and 23 mL for analysis) from the CRM bottle. The signal of the first injection was a little bit low because it is the first injection of that day (system conditioning is recommended). The precision from the first injection to the 15th injection ($n=15$) was 0.029%. After the 15th injection, the signal significantly changed, presumably because of gas exchange. We conclude that one CRM bottle (540 mL) can be repeatedly used for about 220 minutes) without significant gas exchange. Similarly, replicate measurement from field samples should be possible for about the same duration.

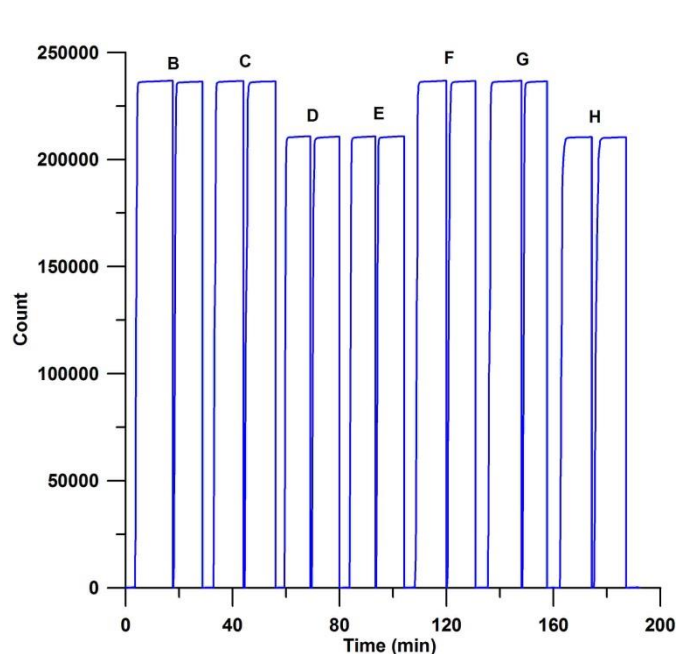


Figure 5. Carryover test results. Signals measured after injecting 100% LNSW (port B, C, F and G) and 90% LNSW (port D, E and H).

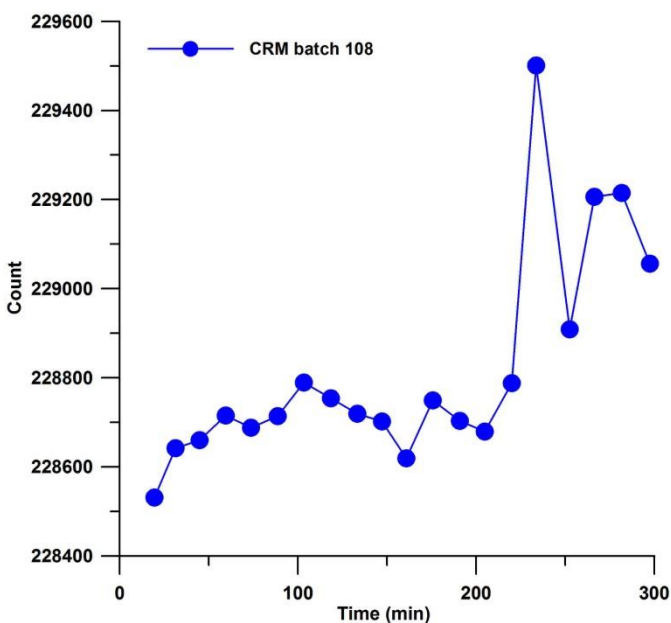


Figure 6. The effect of gas exchange on repeat measurements of a Certified Reference Material.

Intercomparison Experiments

To compare the system with SOMMA, discrete samples ($n=16$) were collected from the flow through system on the *R/V Henry B. Bigelow* from April 4 to May 9, 2013. The result (Figure 7) shows that the two methods agreed closely [$y = (1.0002 \pm 0.012)x$, $y=[\text{DIC}]$ of MANA, $x=[\text{DIC}]$ of SOMMA] with $R^2 = 0.998$. The average and standard deviation of signal difference of the systems are $0.4 \mu\text{mol kg}^{-1}$ and $2.3 \mu\text{mol kg}^{-1}$, respectively.

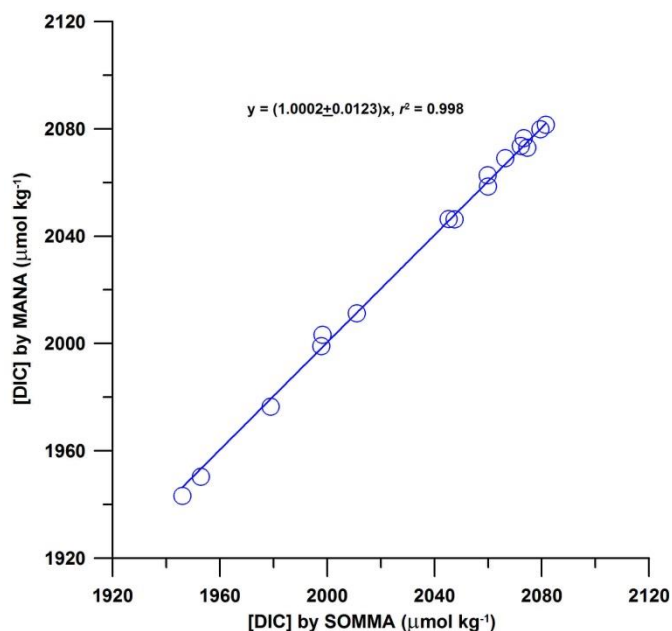


Figure 7. Intercomparison data with the standard method (SOMMA). Seawater samples ($n=16$) were from the *R/V Henry B. Bigelow* collected from April 11 to May 9, 2013.

On November 20, 2013, discrete samples (11 bottles) were collected throughout the Delaware Bay and Delaware River from the flow through seawater sampling system on the *R/V Hugh Sharp*. Samples were collected in 500 mL glass flasks, then fixed with ca. 0.1 mL HgCl_2 . Duplicate sub-samples were then measured both by our system and a new double isotope dilution technique.²⁷ The two methods agreed very well [$y = (1.0008 \pm 0.0145)x$, $y=[\text{DIC}]$ of MANA, $x=[\text{DIC}]$ of isotope dilution] with $R^2 = 0.999$. The samples were measured in duplicate. Salinity and temperature were measured by using a YSI CastAway CTD. Results are shown in Table 2. The average signal difference of duplicate measurements is $1.2 \mu\text{mol kg}^{-1}$.

Table 2. Results of [DIC] measurement of samples collected from Delaware Bay and Delaware River, DE.

Date, UTC (2013)	Time	Latitude	Longitude	Salinity	Temp, °C	Avg. DIC $\mu\text{mol kg}^{-1}$	Diff. $\mu\text{mol kg}^{-1}$
20-Nov	6:10	38.8212	-75.1037	29.81	11.0	1975.3	0.00
20-Nov	6:12	38.8212	-75.1037	30.02	11.1	1970.4	4.10
20-Nov	7:43	38.8206	-75.1065	29.48	10.5	1974.5	0.20
20-Nov	7:46	38.8206	-75.1065	29.48	10.5	1976.5	0.20
20-Nov	10:03	38.8212	-75.1086	29.48	10.4	1966.3	3.40
20-Nov	10:06	38.8212	-75.1086	29.48	10.4	1974.8	0.50
20-Nov	12:02	38.7839	-74.9358	31.5	12.1	1972.7	-
20-Nov	12:04	38.7839	-74.9358	31.5	12.1	1980.5	-
20-Nov	17:45	39.1142	-75.2085	28.38	10.5	1933.4	0.60
20-Nov	17:47	39.1142	-75.2085	28.38	10.5	1943.5	1.40
20-Nov	20:51	39.2593	-75.3421	19.74	9.7	1704.6	0.30

Field Samples

The system was also tested on field samples collected from 13 locations at Flower Garden Banks, TX. Results are shown in Table 3. The samples were taken by holding 500 mL bottles under water until completely full and then fixed with 0.2 mL of HgCl_2 . Salinity and temperature were measured using a handheld meter. Results are shown in Table 3. The average signal difference of duplicate measurements is $0.45 \mu\text{mol kg}^{-1}$ with only one duplicate difference exceeding $1.0 \mu\text{mol kg}^{-1}$.

Table 3. Results of [DIC] measurement of samples collected from Flower Garden Banks, TX.

Date, UTC (2013)	Time	Latitude	Longitude	Salinity	Temp, °C	Avg.DIC $\mu\text{mol kg}^{-1}$	Diff. $\mu\text{mol kg}^{-1}$
3-Sep	7:25	27.90527	-93.60274	37.5	29.9	2047.8	0.36
3-Sep	17:30	27.90936	-93.59819	37.0	31.6	2048.5	0.86
4-Sep	7:47	27.90393	-93.59917	37.4	30.0	2051.7	0.23
4-Sep	8:29	27.90575	-93.59664	37.3	30.2	2048.6	0.81
4-Sep	10:42	27.90935	-93.60022	37.3	30.1	2046.3	0.16
5-Sep	7:30	27.87299	-93.82299	37.5	29.8	2051.5	0.13
5-Sep	9:30	27.87346	-93.81995	37.6	30.0	2048.1	0.11
5-Sep	14:20	27.87393	-93.81741	37.6	30.0	2043.5	0.27
5-Sep	15:30	27.87619	-93.8159	37.4	30.0	2058.6	0.44
5-Sep	17:15	27.87575	-93.81438	37.8	29.9	2048.5	1.18
6-Sep	7:45	27.87259	-93.81435	37.9	29.6	2045.5	0.38
6-Sep	9:30	27.87441	-93.81183	37.6	30.0	2044.8	0.06
6-Sep	10:54	27.8744	-93.81437	37.8	29.9	2043.4	0.91

Table 4. Results of [DIC] measurement of samples collected from Shark River, Everglades, FL.

Date, EST (2013)	Time	Latitude	Longitude	Salinity	Temp, °C	Avg.DIC $\mu\text{mol kg}^{-1}$	Diff. $\mu\text{mol kg}^{-1}$
21-Nov	14:50	25.3646	-81.0779	24.21	25.9	3505.4	8.20
21-Nov	-	25.3630	-81.0906	26.17	26.0	3334.8	26.40
21-Nov	15:40	25.3555	-81.1089	28.49	26.2	2963.2	2.10
21-Nov	16:02	25.3713	-81.0574	22.08	25.8	3749.5	1.90
21-Nov	16:14	25.3743	-81.0450	20.7	25.7	3793.5	0.60
21-Nov	16:24	25.3759	-81.0356	18.78	25.6	3851.4	23.20
21-Nov	16:34	25.3794	-81.0292	17	25.6	3910.3	-
21-Nov	16:42	25.3828	-81.0216	14.92	25.6	3984.1	15.00
21-Nov	16:50	25.3867	-81.0154	11.61	25.6	3987.3	10.60
21-Nov	16:58	25.3927	-81.0103	9.38	25.7	3989.7	8.90
25-Nov	13:02	25.3669	-81.0778	14.43	24.6	4557.6	3.10
25-Nov	13:26	25.3700	-81.0611	3.95	24.8	3903.8	-
25-Nov	13:42	25.3738	-81.0432	5.68	24.8	4007.9	29.70
25-Nov	13:53	25.3791	-81.0296	2.31	24.6	3632.0	14.50
25-Nov	14:18	25.4124	-80.5777	1.2	24.5	3335.7	0.20
25-Nov	15:10	25.4218	-80.9435	0.31	24.0	3462.0	6.10

A set of very turbid samples from Shark River, Everglades, FL was collected using a 5L GO Niskin bottle from a National Park

Service boat from November 21 to 25, 2013. Results are shown in Table 4. Salinity and temperature were measured by using a Y.S.I. CastAway CTD. The samples were then measured in duplicate without filtering. Results are shown in Table 4. The range of values obtained was much larger than in the other areas sampled even for closely adjacent samples. Moreover, the average signal difference of duplicate measurements for these samples is $10.8 \mu\text{mol kg}^{-1}$, which may be caused by particles trapped inside the stripper. The particles also cause high blank level (50-100 counts/min).

Conclusions

We have developed an instrument based on a coulometric method to determine dissolved inorganic carbon in marine waters. The accuracy (average offset from the CRM was $+1.2 \mu\text{mol kg}^{-1}$) and precision (0.022% or less than $\pm 1.0 \mu\text{mol kg}^{-1}$) of the prototype system is similar to that of the accepted commercially available coulometric system,^{1,24} but is simpler, more robust and safer. It can, moreover, autonomously measure eight discrete samples in duplicate without any operator attention needed. See Table 5 for a summary comparison of MANA and the commercially available SOMMA system. Results obtained suggest that prefiltering may be necessary in highly turbid waters to maintain precision. Recently, a straightforward filtration technique²⁸ for total dissolved inorganic carbon has been proposed. The technique has no detectable influence on the sample composition even when using analytical techniques for the analysis of total alkalinity, total dissolved inorganic carbon, and pH.

Table 5. Comparison of SOMMA and MANA.

Features	SOMMA	MANA
Solution-delivery mechanics	Multiple solenoid valves and a glass pipette, which make the system complex and delicate.	A syringe pump equipped with a distribution valve. The system is simpler, more rugged and easier to operate.
Calibration system	Gas loop and CRM. The gas loop calibration system also causes the complexity of the system.	CRM only same as VINDTA 3D. ²⁵ This causes the systems much simpler and need only one gas (carrier gas).
Waste removal from stripper	Uses gas pressure which can cause leakage of acid waste. Moreover a small amount of waste can be left inside stripper.	Uses a peristaltic pump, that can completely draw down waste with little chance of any leakage
Sample injection	Operator needs to change the sample bottles to make repeated measurements	Autonomously measures up to eight samples.
Sample volume	Hard to change	Easy to change. This can be useful for very high [DIC] sample measurement.
Cost	Relatively high and no longer commercially available	Significant lower component costs and not commercially available

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Notes and references

^a Cooperative Institute for Marine and Atmospheric Studies (CIMAS), Rosenstiel School of Marine and Atmospheric Science, University of Miami, 4600 Rickenbacker Causeway, Miami, Florida, 33149, USA. E-mail: natchanon.amornthamarong@noaa.gov; Fax: +1-305-361-4447; Tel: +1-305-361-4537

^b Ocean Chemistry and Ecosystems Division, Atlantic Oceanographic and Meteorological Laboratory, National Oceanic & Atmospheric Administration (NOAA), 4301 Rickenbacker Causeway, Miami, Florida, 33149, USA.

^c Rosenstiel School of Marine and Atmospheric Science, University of Miami, 4600 Rickenbacker Causeway, Miami, Florida, 33149, USA.

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A new system with high precision based on a coulometric method requiring greatly reduced operator intervention has been developed for the determination of [DIC] in marine waters.