Achieving High Time-Resolution with a New Flow-through Type Analyzer for Total Inorganic Carbon in Seawater

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A fully automated, continuous-flow-through type analyzer was developed to observe rapid changes in the concentration of total inorganic carbon (C_T) in coastal zones. Seawater and an H_3PO_4 solution were fed into the analyzer's mixing coil by two high-precision valveless piston pumps. The CO_2 was stripped from the seawater and moved into a carrier gas, using a newly developed continuous-flow-through CO_2 extractor. A mass flow controller was used to assure a precise flow rate of the carrier gas. The CO_2 concentration was then determined with a nondispersive infrared gas analyzer. This analyzer achieved a time-resolution of as good as 1 min. In field experiments on a shallow reef flat of Shiraho (Ishigaki Island, Southwest Japan), the analyzer detected short-term, yet extreme, variations in C_T which manual sampling missed. Analytical values obtained by the analyzer on the boat were compared with those determined by potentiometric titration with a closed cell in a laboratory: $C_T(\text{flow-through}) = 0.980 \cdot C_T(\text{titration}) + 38.8$ with $r^2 = 0.995$ ($n = 34$; September 1998).

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Introduction

Extensive effort has been put into elucidating the role of the ocean in the global carbon cycle, especially its ability to absorb the increased amounts of anthropogenic carbon dioxide being released into the atmosphere. Most of the research and many surveys have been focused on the open sea,¹ however, the role of coastal zones in the carbon cycle is also of current interest.^{2,3}

However, it has been difficult to continuously measure the partial pressure of CO_2 (pCO_2) and the carbonate system in coastal zones where shallow waters impede access by large research ships. Compared with the open sea, these zones, which include coral reefs, have a high primary production per unit and have more complex oceanographic conditions. Therefore, more rapid temporal changes take place in the CO_2 system in these coastal zones. For example, the value of pCO_2 changed by as much as 50 ppm within 10 min accompanied with high biological production and tidal currents on a coral reef flat.⁴ These changes in pCO_2 suggest correspondingly rapid changes in C_T and total alkalinity (A_T).

Upon entering the state of solution, CO_2 reaches equilibrium with the two ionic species, HCO_3^- and CO_3^{2-} . The four measurable CO_2 related parameters are: pH, A_T , C_T , and pCO_2 . For the analysis of C_T in seawater, the CO_2 extracted from a seawater sample by acidification is determined by gas chromatography^{5,6} or coulometric titration,⁷ or with an infrared

analyzer.^{8,9} In the direct potentiometric titration of seawater,¹⁰⁻¹⁵ both C_T and A_T can be simultaneously determined by a single titration. The coulometric titration by the SOMMA (single operator multimetabolic analyzer) is acknowledged as the most accurate and precise method.^{16,17} The flowing system previously developed automatically acidifies and strips the CO_2 out of a seawater sample, and determines the concentration by integrating the infrared absorbance.¹⁸ However, an analysis time for one sample, of more than several minutes, is most likely required for the CO_2 extraction and other processes which are conducted between batches.

In this paper, a flow-through type analyzer for C_T in seawater is described along with results that demonstrate continuous, high time-resolution measurement of C_T on a coral reef flat. The continuous flow-through CO_2 extractor¹⁹ developed in this research project permitted the most effective extraction of CO_2 from an acidified sample to date. The CO_2 concentration was measured with a nondispersive infrared gas analyzer (NDIR). A high-precision valveless piston pump was used for seawater sampling and a mass flow controller (MFC) was used to assure a precise flow rate of carrier gas. Errors caused by drifting were periodically compensated for with two C_T standard solutions of different concentrations.

Experimental

Instrumentation

The main components used in the construction of the fully automated, continuous-flow-through C_T analyzer were: two

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Fig. 1 Schematic diagram of the fully automated, continuous-flow-through type C_T analyzer. P1, underwater pump; P3 and P4, valveless piston pumps; P2, P5, P6 and P7, peristaltic tube pumps; V1 and V2, valves; MFC, mass flow controller.

valveless piston pumps (P3, P4; quantitative pumps, with a 0.1% precision; pulse motor driven; RH-00CKC-LF, Fluid Metering Inc., USA), a mixing coil (PTFE tube; i.d. = 1 mm, L = 500 mm), the flow-through CO_2 extraction unit, an NDIR (LI-6252, LI-COR, USA), and a microcomputer to control the entire system. The schematic diagram is shown in Fig. 1.

Seawater was fed by an underwater pump (P1; 3-TM, Tsurumi Manufacturing Co., Ltd., Japan) to the analyzer which was mounted on a small research motorboat (the "Crest"). The underwater pump, made of Ti and plastic, was hung from the boat into the sea. Whenever the pump is activated, a portion of seawater is fed into an approx. 1.5 cm^3 glass debubbler, at which point the main sampling line branches into two paths. Bubbles are removed from the seawater sample by a pump (P2; peristaltic pump, flow rate: approx. $20\text{ cm}^3\text{ min}^{-1}$; pump head: P-07017-20, Masterflex, USA). The amount of seawater required for analysis goes toward a second pump (P5; peristaltic pump, flow rate: approx. $5\text{ cm}^3\text{ min}^{-1}$; pump head: P-07014-20, Masterflex, USA) through a filter (47 mm ϕ ; GF/F, Whatman, UK). The head of the seawater overflow drain was positioned 30 cm higher than P3 in order to keep the pressure at the inlet of P3 constant. P3 was set at a flow rate of $2\text{ cm}^3\text{ min}^{-1}$. The seawater from P3 mixes with a $0.5\text{ mol dm}^{-3}\text{ H}_3\text{PO}_4$ solution, which is supplied by P4 at a flow rate of $0.3\text{ cm}^3\text{ min}^{-1}$. The mixed solution then moves to a gas stripper (continuous-flow-through CO_2 extractor)¹⁹ with CO_2 -free dried air as the carrier gas, at a flow rate of $200\text{ cm}^3\text{ min}^{-1}$, controlled precisely by the MFC (FC-260E, AERA Japan Ltd., Japan). Thus, CO_2 is stripped out of the seawater sample. The precision of P3 and the MFC directly affect quantification, so the temperature was kept at 25 or 28°C in the field depending on the seasonal temperatures and 20°C in the laboratory, 2 to 3°C lower than their surroundings. This was done to control the drift of flow rates due to temperature variation, with an aim of a 0.1% flow rate drift per hour. As shown in Fig. 2, the gas stripper consists of a spiral Teflon® tube wound around a pipe of 48 mm outside

diameter. Care was taken to keep the stream moving down the tube. The optimal conditions for the stripper were a PFA tube with 1.6 mm inside diameter and 2 m length. The gas separated from the liquid is passed through a dehumidifier (Peltier element cooler; DH-10, Komatsu Electronics Inc., Japan) and then a Perma Pure Dryer® (Gas sample Nafion® dryer, 1.8 m; PD-750, Perma Pure Inc., USA) to assure the drying of the carrier gas containing CO_2 . The gas is next passed through a Cu column as a halogen gas trap, and then the CO_2 concentration is measured at 1 s intervals by the NDIR. P6 and P7 in Fig. 1 indicate drain pumps (Pump head: P-07016-20, Masterflex, USA) that remove water from the separator and dehumidifier.

The system was controlled by an industrial computer (IPC-Bx/M400 (PC), Contec Co., Ltd., Japan) with data acquisition and control software written in Borland C++ Builder (Borland Software Corp., USA). The NDIR was controlled *via* serial communication, and the valves and the pumps were controlled with a digital relay board (IBX-2724C, Interface Corp., Japan).

Reagents

Sodium carbonate for volumetric analysis (99.97% purity) was purchased from Asahi Glass Co., Ltd., Japan. By diluting $5\text{ mol dm}^{-3}\text{ HCl}$ (for volumetric analysis, Wako Pure Chemical Industries Ltd., Japan), we obtained a solution of $0.2\text{ mol kg}^{-1}\text{ HCl}$ for use as a titrant for potentiometric titration. The concentration of the HCl solution was determined by titrating with a standardized $AgNO_3$ solution on a balance, using a micropump. The purity of $AgNO_3$ was 99.9%. Unless otherwise specified, all materials were analytical-reagent grade. All solutions were prepared with deionized water from a Milli-Q system.

C_T standard solutions

Two types of standard solution, (Solution 1) $NaHCO_3$ and (Solution 2) a mixture of Na_2CO_3 and HCl, each containing $0.7\text{ mol kg}^{-1}\text{ NaCl}$, were used in order to compensate for the drift

Fig. 2 Detail of the flow-through type CO_2 gas stripper, which consists of a spiral tube wound around a pipe.

and variation in sensitivity. Prior to the preparation of the solutions, deionized water was degassed by heating or keeping under reduced pressure. The C_T concentrations were determined by coulometry and/or potentiometric titration, using a precision A_T and C_T analyzer (EN-501A, Kimoto Electric Co., Ltd., Japan), which is described below.

Approximate 1900 cm^3 of each of the standard solutions was placed into a 2000 cm^3 reinforced oblong bag with an interior made of polyethylene and an exterior made of nylon-6 (Nihon Kimu Co., Ltd., Japan). The bag was equipped with two ports, one of which was used solely to remove air bubbles. The headspace was thus reduced to a negligible volume compared with the solution volume. The solutions were supplied into the lines of the C_T analyzer through a Tygon® tube with 1.6 mm inside diameter.

Calibration

To avoid errors caused by the pumps (especially P3), the MFC, the gas stripper and the NDIR, two standard solutions of different concentrations, (e.g. 1745 and $2368 \mu\text{mol kg}^{-1} C_T$) were periodically supplied through valves V1 and V2 (see Fig. 1) to calibrate the analyzer. It was expected that the C_T values for samples would fall between the two standard values. Typically, the standard solutions were supplied for 6 min each, every 2 h between measurement intervals.

In the experiments to estimate the efficiency of CO_2 stripping from samples, the NDIR was calibrated with a standard gas (480 ppm CO_2 balanced with air; Takachiho Chemical Industrial Co., Ltd., Japan). The flow rate of the MFC was also calibrated with a digital bubbler meter (SF-1100, STEC Inc., Japan).

Other instruments

In contrast to the flow-through type analyzer, the fully automated precision A_T and C_T analyzer consists of eight main components: a sample pipette (approx. 100 cm^3), a closed cell for titration, an automatic piston burette, a pH meter (high input

impedance digital voltmeter, readable to 0.1 mV) a cell for CO_2 generation from acidified seawater, a coulometer (CM5012, UIC Inc., USA), the NDIR (Ir1520, Servomex, UK), and a microcomputer. In principle, the closed cell is based on that in the DOE Handbook,¹ thus, A_T and C_T can be simultaneously determined by a single titration. It takes 20 and 45 min, from sampling to cleaning the cells, for potentiometric titration and coulometry respectively. Therefore, the former method was mainly used in order to finish analyzing many samples during the limited survey term. This analyzer was calibrated with Na_2CO_3 standard solutions.¹⁶ Under optimum conditions, the precision (σ_{n-1}) for C_T analyses by both coulometry and potentiometric titration was within $2 \mu\text{mol kg}^{-1}$ ($n = 10$) for 1800 – 2000 $\mu\text{mol kg}^{-1} C_T$ solutions. The accuracy of the methods was estimated to be approx. $2 \mu\text{mol kg}^{-1}$ in this research.

Salinity was measured with a Portasal salinometer (8410A, Guildline Instruments Ltd., USA).

Manual water samplings

For laboratory analysis of C_T with the aforementioned precision analyzer, each sample was put into a 1 L Duran bottle, leaving a headspace of less than 1% of the bottle volume, and poisoned by the addition of 1 mL of a saturated HgCl_2 solution in order to prevent bacterial activity. In addition, the samples were stored in the dark until analysis. In the survey done in September 1998, the samples had no HgCl_2 added and, pending analysis within 24 h after collection, were stored, in the dark, at $4 - 10^\circ\text{C}$. A 250 mL sample was collected to measure the salinity. The samples for the measurements of C_T and salinity were collected at approx. 1 – 2 h intervals for 2 – 3 d during each survey.

Results and Discussion

Laboratory studies

CO_2 gas stripper. The liquid containing CO_2 , at an initial concentration of $C_T(0)$, is first introduced into the CO_2 gas stripper (Fig. 2) of the flow-through type C_T analyzer, by a carrier gas at a given flow rate. When the liquid has passed through a stripping tube of length L and reaches its outlet, the partial pressure of CO_2 in the carrier gas is given as $p\text{CO}_2^g(L)$ and the concentration of CO_2 remaining in the liquid is given as $C_T(L)$. Let us suppose $p\text{CO}_2$ in the gas and C_T in the liquid is at an arbitrary distance x from the inlet. If the differential of $p\text{CO}_2^g(x)$ is proportional to $C_T(x)$ and the differential of x at a constant flow rate, we can express it as

$$d(p\text{CO}_2^g(x)) = a_1 \cdot C_T(x) dx \quad (1)$$

where a_1 is constant. Since the initial number of moles of CO_2 passing the inlet in a unit of time is equal to the sum of the number of moles of CO_2 in the gas and in the liquid at any distance of x from the inlet, we obtain:

$$C_T(x) = C_T(0) - b \cdot p\text{CO}_2^g(x) \quad (2)$$

where $b = V/pvRT$, p is the density (kg dm^{-3}) of the seawater sample, v is the flow rate ($\text{cm}^3 \text{ min}^{-1}$) of the sample, V is the flow rate ($\text{cm}^3 \text{ min}^{-1}$) of the carrier gas, R is the gas constant ($0.08205 \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}$), and T is the temperature on the Kelvin scale. Using Eqs. (1) and (2), we obtain the following relationships:

Fig. 3 Effect of stripping tube length (L) on NDIR signal intensity (I). C_T ($\mu\text{mol kg}^{-1}$): (a) 2480, (b) 2250, (c) 2030. Plots of I against L were obtained experimentally. The three curves were drawn by using $p\text{CO}_2^g(L)$ values calculated by substituting the values $k = 0.0362 \text{ cm}^{-1}$ and $d = 39.7 \text{ cm}$ into Eq. (3b).

$$\ln\left(\frac{p\text{CO}_2^g(\infty) - p\text{CO}_2^g(L)}{p\text{CO}_2^g(\infty)}\right) = -kx \quad (3a)$$

$$p\text{CO}_2^g(x) = a(pvRT/V)C_T(0) \quad (4)$$

where $a = 1 - \exp(-kx)$, k is constant and C_T approaches 0 as $x \rightarrow \infty$.

Figure 3 shows the effect of stripping tube length, L , on the NDIR signal intensity, indicating that a approaches unity at $L \geq 150 \text{ cm}$; thus, $p\text{CO}_2$ at $x \rightarrow \infty$ can be experimentally obtained. As given in Fig. 4, Eq. (3a) was plotted by use of the values of $p\text{CO}_2^g(x)$ on the ppm scale from Fig. 3 and the relation of $x = L$. A linear regression for experimental plots of $\ln[(p\text{CO}_2^g(\infty) - p\text{CO}_2^g(L))/p\text{CO}_2^g(\infty)]$ ($= y$) vs. L yielded the following relationship: $y = -0.0362L - 1.476$ with $r^2 = 0.997$. This indicates that the above model was experimentally valid when the stripping tube lengths were not longer than 150 cm, at the least. This experimental equation gave an intercept of -1.476 , which suggests that CO_2 was stripped into gas, to some extent, as soon as the liquid containing CO_2 was introduced into the stripper by the carrier gas. When $x = L + d$, Eq. (3a) becomes

$$\ln\left(\frac{p\text{CO}_2^g(\infty) - p\text{CO}_2^g(x)}{p\text{CO}_2^g(\infty)}\right) = -k(L + d) \quad (3b)$$

where L (cm) is the length of the stripper; the following values were obtained: $k = 0.0362 \text{ cm}^{-1}$ and $d = 39.7 \text{ cm}$. In Fig. 3, we drew three curves by using the $p\text{CO}_2^g(x)$ values that were calculated by substituting these k and d values into Eq. (3b). The curves passed through the experimental plots, demonstrating that the theoretical values were valid. The plots were not corrected for the efficiency of CO_2 stripped from samples, $s = (C_T(0) - C_T(L))/C_T(0)$. Figure 4 indicates that the value of a in Eq. (4) approaches unity at $L \geq 150 \text{ cm}$ and $p\text{CO}_2$ at $x \rightarrow \infty$ can be experimentally determined. A stripper of 200 cm in length was used for the analyzer mounted on the "Crest" boat. In this case, $a = 1 - \exp(-k(L + d)) = 0.999$, so we conclude that CO_2 was stripped almost completely into gas.

By using the standard solution with $C_T = 1700 \mu\text{mol kg}^{-1}$ and Eq. (4), we calculated that $98.1 \pm 3.0\%$ of the CO_2 was stripped.

Fig. 4 Plots of $\ln[(p\text{CO}_2^g(\infty) - p\text{CO}_2^g(L))/p\text{CO}_2^g(\infty)]$ against stripping tube length (L). Equation (3a) is plotted by use of $p\text{CO}_2^g(\infty)$ values obtained from Fig. 3 and the relation of $x = L$. In the linear regression, data at $L = 200 \text{ cm}$ were not included. C_T ($\mu\text{mol kg}^{-1}$) and $p\text{CO}_2^g(\infty)$ (ppm): (Δ) 2480 and 533.5, ($\square$) 2250 and 487.5, ($\diamond$) 2030 and 442.5, respectively.

On the other hand, the above s value estimated from the CO_2 concentration in liquid waste collected from the stripper outlet, $C_T(L)$, was $99.4 \pm 0.5\%$. In these experiments, P3, P4, the NDIR and the MFC were all calibrated. The liquid waste was collected and analyzed, taking care not to expose it to air. The $C_T(L)/C_T(0)$ ratio was less than 0.006, in which $C_T(L)$ was calculated from the fugacity of CO_2 in equilibrium with seawater,¹⁶ so the CO_2 distribution in equilibrium between gas and liquid was not considered.

Flow rates of seawater sample and carrier gas, and calibration curve. According to Eq. (4), $p\text{CO}_2$ is proportional to v/V . It was also experimentally supported: $p\text{CO}_2$ was measured for variable v at $V = 400 \text{ cm}^3$ and variable V at $v = 2 \text{ cm}^3$ with the approx. $2000 \mu\text{mol kg}^{-1}$ C_T solution. A linear regression between NDIR signal intensity (I) and v/V gave an equation of $I = 4.223 \cdot 10^4(v/V) + 5.30$; its intercept was much smaller than the measured I values. The NDIR signal intensity was found to be proportional to C_T , with a correlation of $r^2 = 0.999$.

Response stability and time resolution. In order to clarify the response stability of the analyzer, three standard solutions of different concentrations were analyzed repeatedly, one after another, at 5 min intervals, for 8 h. The averages of variation for C_T analytical values were -0.43 , -0.33 and $-0.12\% \text{ h}^{-1}$ for approx. 1300, 1700 and $2100 \mu\text{mol kg}^{-1}$ C_T solutions, respectively, where the variations from data for 1 h were averaged for 8 h. The NDIR signal intensities decreased gradually over time.

The drift of analytical values for an approx. $1700 \mu\text{mol kg}^{-1}$, C_T solution was compensated for by using analytical values for approx. 1300 and $2100 \mu\text{mol kg}^{-1}$ C_T solutions at 2 h intervals. After the compensation, the average variation and the standard deviation (σ_n) for the approx. $1700 \mu\text{mol kg}^{-1}$ C_T solution were $-0.07\% \text{ h}^{-1}$ and $2.1 \mu\text{mol kg}^{-1}$ ($n = 24$), respectively. These findings suggest that the correction performed using data from the two standard C_T solutions obtained at 1–2 h intervals makes it possible to determine C_T with an error of 0.24% as $2\sigma_n$.

The response to CO_2 (Fig. 5) was obtained by enlarging the time scale for a portion of the original raw data. The elapsed

Fig. 5 Response to CO_2 of the C_T analyzer. This figure was obtained by enlarging the time scale for a portion of the original raw data. In the raw data, the NDIR signal intensities (I) were measured at 1 s intervals. C_T standard solutions analyzed (from the left): approx. 1700, 1300 and 2100 $\mu\text{mol kg}^{-1}$.

Fig. 6 Raw data obtained without compensation or correction, as measured on a reef flat of Shiraho, Ishigaki Island, Southwest Japan, over approx. 3.5 days from March 17 – 21, 1999. Japan time is universal time plus 9 h. Two standard solutions (1698 and 2049 $\mu\text{mol kg}^{-1}$ C_T) were introduced into the C_T analyzer every 2 h, between measurement intervals.

response time at $T(90\%)$ was 28 ± 1 s. $T(90\%)$ is the point past which a 90% steady NDIR signal was reached. The median of these data points over a 1 min interval was used; therefore a time resolution of 1 min was obtained.

Field studies

The continuous C_T analyzer was tested together with a continuous A_T analyzer,²⁰ mounted on the “Crest” boat anchored on a shallow reef flat of Shiraho,²¹ Ishigaki Island, Southwest Japan. The reef crest, when exposed during low tides, separates reef water from the outer ocean, causing it to stagnate. During these stagnant periods, reef water provides ideal, naturally-closed conditions in which changes in the reef water carbonate

Table 1 Drift for analytical values of C_T standard solutions

Date	$C_T/\mu\text{mol kg}^{-1}$	Drift/ $\% \text{ h}^{-1}$
Sept. 21 – 23, 1998	1745	0.51
	2368	0.54
Dec. 3 – 5, 1998	1564	0.18
	2278	0.23
Mar. 18 – 19, 1999	1698	$-0.03,^a 0.08^b$
	2049	$-0.04,^a 0.06^b$
Mar. 20 – 21, 1999	1698	0.05
	2049	0.05

a. 0:00 – 18:25, Mar. 18.

b. 20:25, Mar. 18 – 23:59, Mar. 19.

system are directly related to community metabolism. The analyzers were stored in a plastic box on the boat and were powered by a diesel engine generator. All of the system was designed to be self-regulating except for filter replacement and the supplying of solution at 2 d intervals. The analyzer was run for three to six days on three occasions: September 1998, December 1998 and March 1999. Averaged data from the NDIR were recorded at 1 s intervals on a data logger and also at 1 min intervals on a telemeter from the boat by cellular phone.

Response stability. In the field observation, two standard solutions (1698 and 2049 $\mu\text{mol kg}^{-1}$ C_T respectively, in the March observation) were introduced into the C_T analyzer every 2 h, between measurement intervals, to verify stability. Figure 6 illustrates the raw data obtained without compensation or correction, as measured over 3.5 days. Table 1 shows the results of drift for analytical values of C_T standard solutions obtained during the three seasonal observations: September 1998, December 1998 and March 1999. The drift improved with each seasonal survey, because of improvements in the analyzer and operation skill, etc.

Comparing analytical values for the above C_T solutions at 4 h intervals allowed us to compensate for the drift of the intervening analytical values. After the compensation, the standard deviations (σ_n) for the analytical values were obtained as 2.1 and 1.7 $\mu\text{mol kg}^{-1}$ ($n = 40$), respectively, for the 1698 and 2049 $\mu\text{mol kg}^{-1}$ C_T solutions. The response stability was good, in spite of the imperfect conditions: *i.e.* running the analyzer on a small research boat with the electricity supplied by a diesel engine generator.

Comparison of analysis by the C_T analyzer with manual sampling and laboratory analysis. We compared analytical values monitored with seawater from the Shiraho Coral Reef by the flow-through type C_T analyzer with those determined by potentiometric titration with a closed cell in the laboratory (Fig. 7). Samples for the titration were carefully collected by manual water sampling. A rapid change in C_T can be seen: as much as 200 $\mu\text{mol kg}^{-1}$ within approx. 20 min. At the experimental points indicated by black circles, there was a change of approx. 100 $\mu\text{mol kg}^{-1}$ of C_T in just a few minutes. This suggests that inconsistency in sampling time, between automated and manual samplings, probably caused a large error. So, such experimental points are excluded in the following discussion of a correlation between analytical values obtained by the two methods.

In Table 2, analytical values obtained by the C_T analyzer, $C_T(\text{flow-through})$, are compared with those determined by potentiometric titration, $C_T(\text{titration})$. The correlations between $C_T(\text{flow-through})$ and $C_T(\text{titration})$ were best from September 21 – 23, 1998 and worst from March 18 – 19, 1999. Thus, the relationship between $C_T(\text{flow-through})$ and $C_T(\text{titration})$ did not

Fig. 7 Variation in C_T (·) measured by the C_T analyzer on a reef flat of Shiraho, over approx. 3.5 days from March 17 – 21, 1999. Analytical values determined by potentiometric titration in the laboratory are also marked by white (○) and black (●) circles. At the experimental points indicated by black circles, there was a change of approx. $100 \mu\text{mol kg}^{-1}$ of C_T in just a few minutes.

follow the tendency of the drift to improve (see Table 1). From March 18 – 19, waves caused by the prevailing SSW wind rocked the “Crest” boat from side to side; the lowest correlation coefficient can be accounted for by this rocking of the boat. During this period, short-term changes in C_T , probably due to wind effects on the system, were recorded in the continuous data. It is also probable that the wind effect lowered the correlation between analytical values of the seawaters sampled automatically and manually. Consequently, we conclude that automated and continuous measurements by the analyzer can allow data collection with high temporal resolution; such automatic sampling avoids errors from manual sampling on small research boats.

The use of the flow-through type C_T analyzer in the field led to the development of another version which permitted rapid and more precise analysis for laboratory use.²² The new version will be described in other paper.

Conclusion

We have achieved the goal of developing an automated, continuous-flow-through type C_T analyzer that can take measurements with a much higher time-resolution, as good as 1 min, than was previously possible. Thus, it is expected that the newly developed C_T analyzer will be useful for characterizing rapid temporal changes in the CO_2 system in coastal zones. The analyzer can be used for moored buoy based measurements.

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Table 2 Linear regression between analytical values obtained by the continuous C_T analyzer, $C_T(\text{flow-through})$, and those determined by potentiometric titration, $C_T(\text{titration})$, in seawater from the Shiraho Coral Reef, with the equation $C_T(\text{flow-through}) = a \cdot C_T(\text{titration}) + b$

Date	$C_T/\mu\text{mol kg}^{-1}$ range	a	$b/\mu\text{mol kg}^{-1}$	r^2	n
Sept. 21 – 23, 1998	1665 – 2091	0.980	38.8	0.995	34
Dec. 3 – 5, 1998	1723 – 2006	1.032	–58.7	0.971	18
Mar. 18 – 19, 1999	1814 – 2000	0.924	152.9	0.894	16
Mar. 20 – 21, 1999	1847 – 2025	1.020	–39.3	0.987	18

r^2 and n denote the square of the correlation coefficient and the number of data points, respectively.

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