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Continuous-Flow Analysis of Dissolved Inorganic Carbon Content in Seawater

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A rapid, continuous-flow determination of total inorganic carbon (TIC) in seawater samples is presented. The method runs on an autoanalyzer Traacs 800 spectrophotometric system and is calibrated versus certified reference materials readily available. A typical analysis speed of 45 samples/h can be reached with an accuracy of $2-3$ μM and a precision of $\sim$2.5 μM. The analysis requires only a small amount of sample and is thus ideally suited for pore water samples and samples taken from cultures where sample volume is at a premium. The speed of the analysis makes mapping of oceanic surface water characteristics possible. Potential interference of sulfide in anoxic (e.g., pore water) samples can be masked by the addition of a hydrogen peroxide step. Although the latter is a strong oxidative reagent, no significant effect on TIC concentration due to oxidation of (labile) organic matter could be found.

The strong increase in atmospheric concentrations of carbon dioxide[1] has generated considerable interest in the global carbon cycle.[2−4] Techniques for determining the components of the carbonate system have been refined, new techniques have been developed, or both. Among the four measurable parameters (total inorganic carbon (TIC), pH, pCO$_2$, and total alkalinity (TA)) of the carbonate system, the TIC has a typical range of $1900-2450$ μM. TIC is routinely measured with high precision on semiautomated equipment by coulometry,[5,6] which is the generally accepted method for oceanographic research. Calibration is performed by standard procedures[7,8] and certified reference materials as supplied by Dickson.[8] Other methods are determination via IR detection following Sugimura and Suzuki[9] and Wiebinga[10] and by conductivity.[11] The former determines both total organic carbon (TOC) by catalytic oxidation and total inorganic carbon by injection onto a low-temperature column, which does not oxidize any organic matter present. The latter does the same, albeit TIC is determined via acidification of the sample. After diffusion across a silicone membrane in a dialyzer, the increase in conductivity is determined which is proportional to the amount of TIC.[11]

Biogeochemical processes and especially their rates modify the characteristics of the water column.[12] The introduction of underway measurements of carbonate system parameters in combination with temperature/salinity/fluorescence provided insight into the hitherto unexpected high variability and inherent deduced rates found in the surface ocean.[13,14] These data also laid the foundation for a now quite extensive database used for modeling purposes as well as "ground truth" data for satellite observations (GOOS, Global Ocean Observing System; TOGA-COARE, Tropical Ocean Global Atmosphere-Coupled Ocean-Atmosphere Response Experiment). Though temperature and salinity gradients in the surface waters are resolved on a routine basis, resolving the spatial scale of chemical tracers in surface waters is typically limited either by the sample acquisition process (e.g., a station) or by the rate at which samples can be processed on board ship. Recent advancements have been made in shorter analysis times, but for TIC via coulometry, this has been only modest as the electrochemical titration cannot be faster without losing its accuracy.

Hall and Aller[15] described another method based on flow injection analysis for determining TIC and NH$_4$$^+$ in both marine waters and freshwaters. Standards for the TIC analysis were prepared using NaHCO$_3$ in distilled water. For a range of $0-2$ mM (latter the upper limit in seawater) a RSD of 1.4% was found, which equals $\sim$28 μM. A major advantage of their method was the speed at which samples could be analyzed. A drawback, from an oceanographic point of view, is that the precision was less than required to resolve the fine details in the oceanic water column as needed (± 2 μM[16]) for carbon budgets.

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(1) Keeling, C. D.; Whorf, T. P. *ORNL/CDIAC* **1994**, *65*, 16−26.
(2) Sarmiento, J. L. *Nature* **1993**, *365*, 697−698.
(3) Tans, P. P.; Fung, I. Y.; Takahashi, T. *Science* **1990**, *247*, 1431−1438.
(4) Sarmiento, J. L.; Orr, J. C.; Siegenthaler, U. L. *J. Geophys. Res.* **1992**, *C97*, 3621−3645.
(5) Johnson, K. M.; Williams, P. J. leB; Brändstrom, L.; Sieburth, J. M. *Mar. Chem.* **1987**, *21*, 117−133.
(6) Johnson, K. M.; Wills, K. D.; Butler, D. B.; Johnson, W. K.; Wong, C. S. *Mar. Chem.* **1993**, *44*, 167−187.
(7) Goyet, C.; Hacker, S. D. *Mar. Chem.* **1992**, *38*, 37−51.
(8) DOE. Dickson, A. G., Goyet, C., Eds. *ORNL/CDIAC* **1994**, *74*.

(9) Sugimura, Y.; Suzuki, Y. *Mar. Chem.* **1988**, *24*, 105−131.
(10) Wiebinga, C. J. W. Ph.D. Thesis, University of Groningen, 1999.
(11) Godec, R.; O'Neill, K, Hutte, R. *Ultrapure Water* **1984**, 17−22.
(12) Bakker, D. C. E.; de Baar, H. J. W.; Bathmann, U. *Deep-Sea Res.* **1997**, *44* (1/2), 91−127.
(13) Takahashi, T.; Olafsson, J.; Goddard, J. G.; Chipman, D. W.; Sutherland, S. C. *Global Biogechem. Cycles* **1993**, *7*, 843−878.
(14) Hoppema, J. M. J.; Fahrbach, E.; Schröder, M.; Wisotzki, A.; de Baar H. J. W. *Mar Chem.* **1995**, *51*, 177−192.
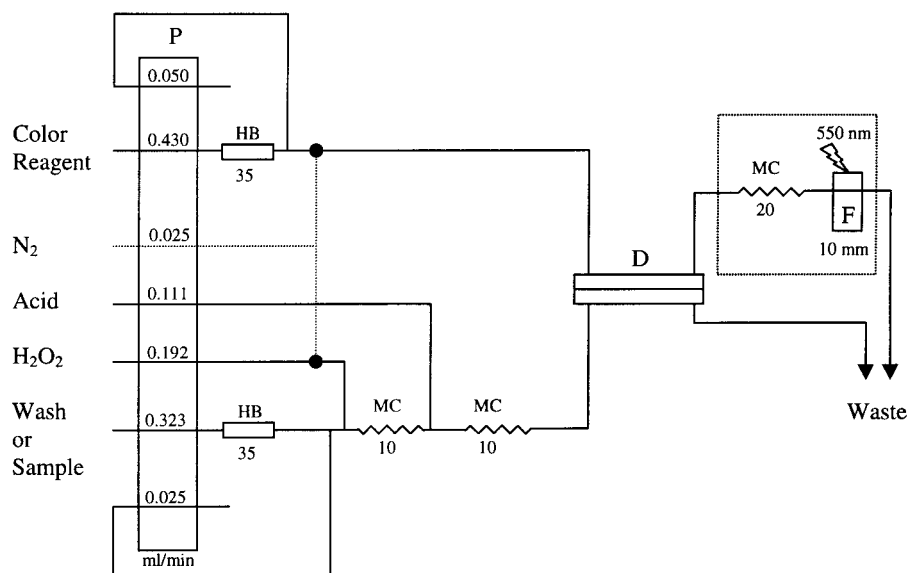(15) Hall, P. O. J.; Aller, R. C. *Limnol. Oceanogr.* **1992**, *37* (5), 1113−1119.

Figure 1. Schematic diagram of the continuous-flow TIC analysis: P, peristaltic pump; HB 35, heating bath at 35 °C; MC 10, mixing coil 10 turns (i.d. 1 mm); MC 20, mixing coil 20 turns (i.d. 1 mm); D, dialyzer; F, flow-through cuvette of 10 mm pathway (extinction of the indicator is measured at 550 nm). In the thermostated flow cell room (dashed line), MC 20 is for bringing the secondary stream up to temperature.

Here we present an updated method for determining TIC in natural seawaters. Notably for the common ranges in seawater (1.9−2.5 mM), resolution is improved vastly over the previous existing technique.[15] The method is fast, accurate, (~2−3 μM) and requires only small amounts of sample. Scaling of the method for the expected range of concentrations in the sample is easily performed. Pore water samples can also be run with high accuracy in which a hydrogen peroxide addition step prevents potential interference from sulfide.

The coulometric method requires large amounts of sample, at least 50−100 mL per measurement, the latter due to preflushing and depending on the size of the pipet. A typical analysis time is between 3 and 8 samples/h (single measurement), which depends on the setup used. With coulometry, an accuracy of 1.5−2.5 μM and a precision of 1.5−2 μM can be obtained. The method requires an even larger volume when the sample is taken, typically between 250 and 500 mL (with replicates). This in sharp contrast with the method presented here, which only requires 533 μL and has an analysis time of 45 samples/h, an accuracy of 2−3 μM, and a precision of ~2.5 μM with a few milliliters sufficing for replicates.

METHODS

Principle. The analysis is run on a Technicon Traacs 800 autoanalyzer and is schematically depicted in Figure 1. A continuous segmented carrier stream is acidified to a pH <1, which forces all carbonate components into the CO_2 gas phase. The carrier stream is led over a semipermeable silicone membrane in the 6-in. dialyzer where the alkaline detector stream absorbs the gas and discolors the indicator (phenolphthalein). Extinction is determined in the flow cell at a wavelength of 550 nm, with the change being a measure of the amount of TIC in the sample. Latter concentration is quantified via a series of standards.

Reagents. The carrier stream is sulfuric acid (1.5 N) with 0.1% solution of Triton/isopropyl alcohol (IPA) (50%/50%). The detector

(16) Houghton, J. T.; Meira Filho, L. G.; Callander, B. A.; Harris, N.; Kattenberg, A.; Maskell, K. *Climate Change 1995: The science of climate change*; Cambridge University Press: New York, 1996.

stream is alkaline and is made with 0.155 mL of NaOH (1 N), and 0.500 mL of phenolphthalein indicator (1 g/100 mL of ethanol) with a 0.1% solution of Triton/IPA in 350 mL of demineralized water. The peroxide reagent is 8 mL of H_2O_2 solution (30%) in 500 mL of demineralized water with 0.1% of Triton/IPA added.

Sample Procedure. Sample processing starts with the autosampler being in the wash position; i.e., the carrier stream contains an acidified solution. Upon moving toward a sample cup, segmentation by an air bubble takes place, which prevents mixing of the sample and baseline solutes. The H_2O_2 is preheated to 35 °C with a heat exchanger (Traacs part no. BLNB70201) and afterward segmented with N_2. The segmentation is removed via a debubbler from the sample stream just before the segmented H_2O_2 stream is added; thus, a negligible sample dispersion is achieved. Sample and H_2O_2 are well mixed within a 10-turn coil (Traacs part no. 165G00502), after which acidification with H_2SO_4 takes place. A second 10-turn coil provides the required mixing of sample and acid. The color reagent stream first passes a preheating step (Traacs part no. BLNB70201), and any possible bubbles due to heating are removed via a debubbler. Immediately afterward, the color stream is segmented again with N_2. The CO_2 gas exchange takes place in the 6-in. dialyzer (Traacs part no. 178253807/8) across the semipermeable silicone membrane (Traacs part no. 178372401). As is evident from the flow scheme (Figure 1), both streams do not have the same rate to avoid pressure effects in the dialyzer which influence the analysis. After gas dialysis has taken place, the color stream is led through a 20-turn coil (Traacs part no. 165G00503) to stabilize the discoloring of the indicator, after which the extinction is measured in the flow cell (10 mm; Traacs part no. 165B03001) at 550 nm (Traacs part no. 165B00622).

Standards Preparation. Standard solutions are prepared fresh daily. Samples are taken into glass vials that are closed with a screw cap with rubber inlay, after poisoning with 10 μL of a saturated solution (8 g/100 mL) of $HgCl_2$. Samples were allowed to reach room temperature, opened, and then immediately covered

with Parafilm to prevent outgassing. The calibrants, gain standards, and the wash (baseline) water were also covered with Parafilm. The wash or baseline solution is in principle a solvent with an ionic strength approximately the same as the samples, albeit having none of the solute of interest, in this case CO_2 (either in ionic or dissolved form). Having the same ionic strength prevents a matrix effect between samples and baseline values, which would cause enhanced or reduced exchange across the gas membrane, not being attributable to differences in concentration.

The original method as described by Hall and Aller[15] used calibrants ranging from the highest expected concentration in the samples to zero. In their experiments, they used concentrations ranging from 0 to 2, 0 to 5, 0 to 10, and up to 0 to 20 mM and obtained respective relative standard deviations of 1.4, 1.1, 0.4, and 1.0%. This translates to an error of $\sim\pm28$ μM (note the unit micromolar) for the first range. Unfortunately, this error would prevent the method from being directly applicable to oceanography where, to constrain the output of existing global circulation models, these require carbonate data to be accurate to $\sim\pm2$ μM.[16]

Additionally, with the typical natural range in TIC in the ocean ($\sim$1900−2450 μM), a baseline value of 0 μM does not use the sensitivity of the method to its full potential. The obvious improvement is to increase the baseline to a value slightly below the lowest value expected in the samples. Calibrants are then made up by standard additions to this stable baseline solution. In this way, an optimal range is obtained for measuring samples. The baseline solution can be either buffered (borate buffer) demineralized water (fortified to the ionic strength of seawater by addition of NaCl) with a known carbonate standard addition or a natural batch seawater with known (low) TIC concentration, both of them in equilibrium with the atmosphere. Several laboratory experiments were performed to test the method (discussed below) and field data in comparison with coulometric data are presented.

Safety Precautions. All chemicals should be handled with care. When the samples contain the highly toxic $HgCl_2$, one should dispose of the waste. One way is to precipitate the sample and the waste with sulfide, which forms HgS ($K_s = 10^{-52}$ mol^2 dm^{-3}). The precipitate can then be disposed of properly. Without $HgCl_2$, the products are essentially nontoxic and self-neutralizing upon mixing.

RESULTS AND DISCUSSION

One experiment was performed to investigate the linearity of the chemistry of the method. As extinction measurements are bound to the law of Lambert−Beer, a proper scaling of the method is required to obtain the measurements in the linear part of the equation. Certified Reference Materials[11] (CRMs) were used for absolute baseline drift correction, and a batch of low-nutrient seawater several years old was used for sample. A typical run starts with baseline measurements, followed by calibration and gain measurements. Samples are measured and to quantify possible drift another set of baseline and gain samples are determined.

A typical range for natural seawaters (1900−2500 μM) was used for the linearity experiment for the calibration line ($N = 3$; pooled standard deviation ±1.45 μM) based on given concentrations and those computed from absorbance readings. An excellent regression coefficient of 0.9996 was found, showing clearly that
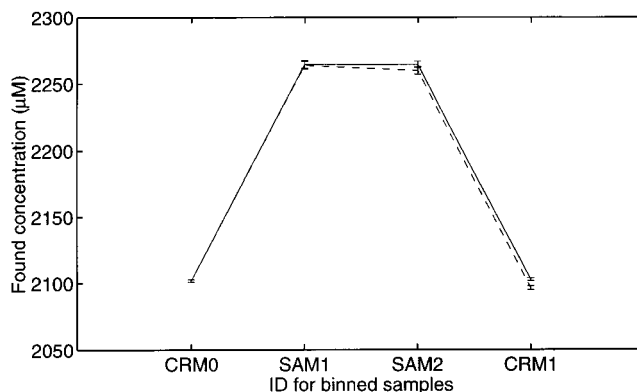

Figure 2. Validity of baseline correction on samples (based on CRM measurements at the beginning and the end of the run). Dashed lines are the uncorrected samples, and solid lines are the baseline-corrected samples. SAM$_{[1-2]}$ are water from the same batch of seawater, CRM$_{[1-2]}$ are both Certified Reference Materials from the same batch.

within this range the calibration is almost perfectly linear. A negligible small offset of -0.5 μM and a coefficient 1.0001 were obtained. One should keep in mind that with larger ranges in the calibration the possibility exists that the highest concentration completely discolors the detector stream. This is circumvented either by decreasing the volume input (if possible) or otherwise by increasing the concentration of the buffer. This is simply obtained by adding a small amount of NaOH. In the latter lies the danger of adding too much, thus resulting in too much extinction (e.g., Lambert−Beer law nonlinear). A proper scaling of the method ensures the highest obtainable accuracy and sensitivity. The addition of NaOH works fine for the high-accuracy range of the experiment (1900−2500 μM) but for a larger range (e.g., 0−2000 μM) one would have to use a carbonate buffer, which is a weaker base. Otherwise, the pH traject of indicator phenolphthalein would be masked by the much stronger base NaOH.

The baseline correction procedure is depicted in Figure 2. A CRM is measured at the start and at the end of the analytical run (for long runs, intermediate determinations of CRMs are required). If there is no drift in the baseline, the two CRM values would match up precisely; however, in these types of analysis, that is hardly the case. Under normal conditions, a linear drift assumption is quite valid and data between the two CRMs can be corrected for the observed drift. The experiment had two batches of samples, both of them from the same batch of seawater. Noncorrected data show clearly a negative drift in the values obtained, as is seen in Figure 2. Upon linear correction, the two batches have the same mean value (see Table 1).

In principle, the determination of the baseline value at the beginning and at the end of the run suffices for obtaining correct values (with a possible additional minor correction due to gain change) and the drift should ideally be as small as possible. For long runs, the assumption of a linear change in baseline might not hold true. The latter can easily be quantified by introducing a stable standard within the calibrant range. A regular determination of this standard within the run ensures a clear picture of the baseline drift and can be used for final correction of the data. It should be realized that there is no difference in calibrating between the coulometric method and the method presented here.

Table 1. Statistics for Experiment 1 in Which the Validity of Baseline Correction Was Tested[a]

	uncorrected		corrected		
ID	mean	std	mean	std	N
CRM0	2101.98	1.01	2101.75	0.96	4
SAM1	2263.95	2.77	2264.63	2.97	8
SAM2	2260.02	2.66	2264.54	2.47	24
CRM1	2096.46	1.44	2102.67	1.15	3

[a] original data were gain corrected and for base line drift by using a Certified Reference Material (DOE[8]). Values are in μM.

Table 2. Statistics for Experiment 2 in Which the Effect of H_2O_2 on TIC Concentration Was Tested[a]

ID[b]	mean	std	N
CRM0	2130.25	1.77	2
S-HO	1962.48	4.89	22
CRM1	2131.85	2.04	4
S+HO	1965.93	3.93	25
CRM2	2133.35	2.09	4
S-HO	1965.56	3.61	18
CRM3	2132.55	0.62	4

[a] Original data were gain corrected and for base line drift by using a Certified Reference Material (DOE[8]). Values are in μM. [b] CRM[0-3], Certified Reference Material (DOE[8]), S-HO (batch S with no H_2O_2 in extraction line), and S + HO (batch S with H_2O_2 in extraction line).

Both methods refer back to the now generally accepted Dickson Certified Reference Material[11] for obtaining calibrated data.

The method is ideal for the analysis of pore water samples due to the small sample requirement. Samples should be filtered since the presence of solid carbonates (e.g., $CaCO_3$) in the sediment would certainly influence the result. The acidification step by H_2SO_4 would quantitatively convert the solid carbonate to CO_2 gas. Samples are loaded into syringes (usually 5−10 mL) and filtered (0.4-μm pore size; Acrodisc LC3A) before being injected into the vial. When the filtering is properly done, i.e., prerinsing the filter and emptying the gastight syringe directly into sample vial without air bubbles, no detrimental effect will be introduced. Due to poisoning with $HgCl_2$ any possible effect of organic matter breakdown due to microbial activity is prevented. The samples in the glass vial with rubber inlay can be easily be kept for several weeks this way.[11,15]

On the other hand, the presence of sulfide in the sample could potentially interfere with the analysis. Upon acidification, the sulfide (also being a gas) crosses the membrane and discolors the indicator as well as does CO_2 gas. This potential sulfide interference can be masked by the addition of H_2O_2 to the sample, before the acid addition step. However, H_2O_2 is a strong oxidative, which can break down organic matter present in the sample, thus increasing the TIC value. The second experiment was set up to investigate this possible interference of H_2O_2.

A batch of seawater (S) was taken during the bloom season in the North Sea, which has then typical high concentrations of labile organic matter.[17] Samples were taken in small glass vials (see above) and poisoned by adding $Hg^{II}Cl_2$. By not poisoning the batch but taking each sample separately, the standard deviation introduced due to sample handling and treatment could be characterized. As the run was long, CRMs were measured at several intervals to characterize the baseline drift. The first group of samples of S was run without the introduction of H_2O_2 into the analysis line. Upon introducing as well as stopping the addition of H_2O_2, a stabilization period was allowed. Data were baseline corrected using the CRMs and gain standards. Table 2 shows the pooled results of each group of samples. The group of samples without H_2O_2 addition has a mean value of 1962.5 μM ($\pm$4.9 μM). In comparison with the group of samples with H_2O_2 addition (mean value 1965.9 μM; $\pm$3.9 μM), there is no statistical difference between the two groups. To verify that the slight system drift did not mask any possible oxidation effects, another group of S was

(17) Ittekkot, V.; Brockmann, U.; Michaelis, W.; Degens, E. T., *Mar. Ecol. Prog. Ser.* **1981**, *4*, 299−305.

Figure 3. Effect of H_2O_2 on the TIC (in μM) concentration. Samples were taken from a $Hg^{II}Cl_2$-poisoned batch of seawater. The latter was taken at the end of a bloom in coastal seawater in the North Sea (characterized by large amount of labile organic matter). CRM[0-3], Certified Reference Material (DOE[8]), S−HO (batch S with no H_2O_2 in extraction line), S + HO (batch S with H_2O_2 in extraction line). See text for detailed explanation.
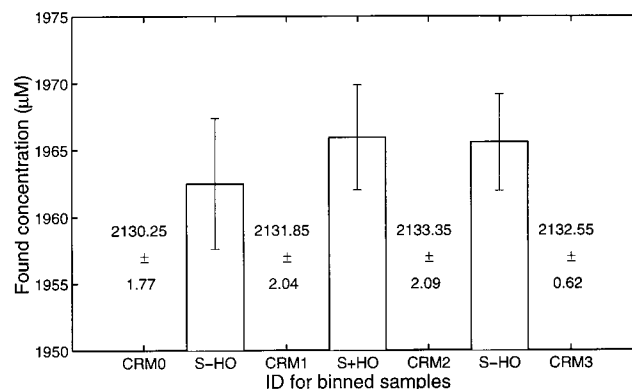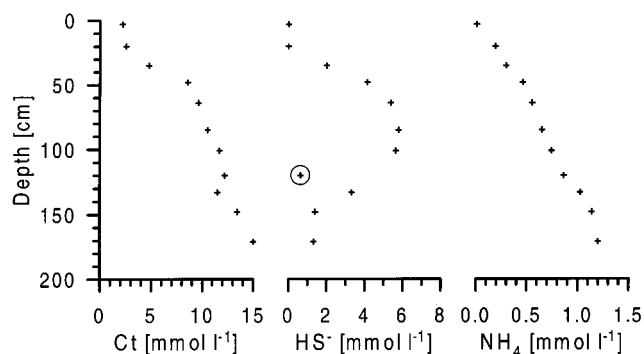

Figure 4. Depth profiles of pore water TIC, sulfide, and ammonia of gravity core MNLGC15. The consistent pattern of TIC distribution reveals an upward flux to the uppermost 50 cm where carbonate is consumed by the precipitation of carbonate minerals. Sulfide builds up due to intensive sulfate reduction. The sulfide value at 120-cm depth appears to be faulty, most likely due to oxygen contamination.

measured after the H_2O_2 was taken offline again. After stabilization, the third group of S comes to a mean value of 1965.6 μM ($\pm$3.6 μM). Again, no statistical difference could be observed between the two groups of samples. Actually, after a slight correction for baseline drift had been implemented, no difference could be observed between all three groups of samples (Figure 3). We conclude that in this system setup the addition of H_2O_2 has no significant effect on TIC concentration, even on a batch of seawater
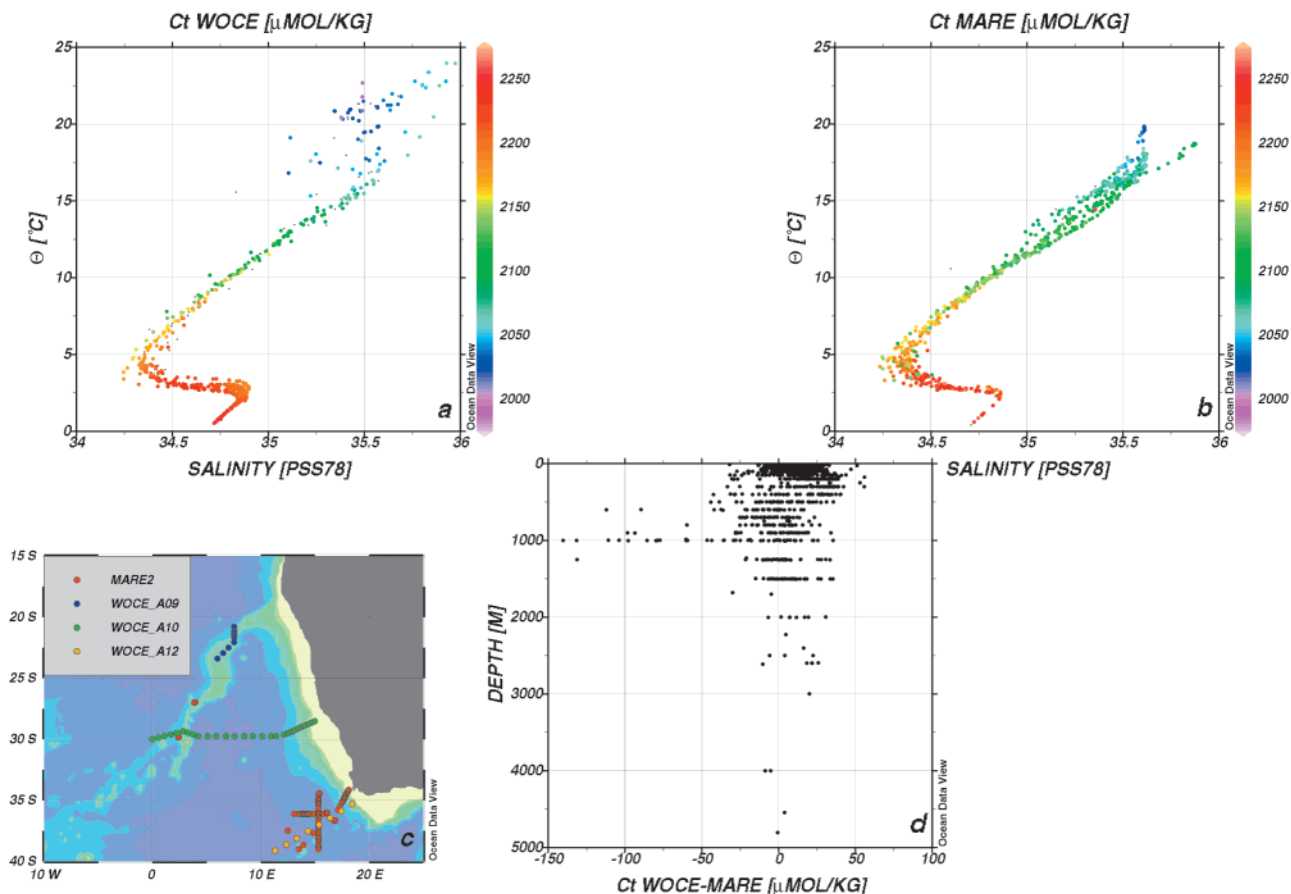
Figure 5. $\Theta-S$ plots of TIC (in μmol/kg) via coulometry (a) and with autoanalyzer method (b) (produced with ODV[23]). The map (c) shows the cruise tracks of the MARE2 cruise and those of the WOCE hydrographic program. The difference plot (d) of TIC vs depth (in m) is by taking data at the same isopycnals.

with easily oxidizable organic matter. The standard deviation caused by sample handling is mostly caused by the addition of a very small volume of $Hg^{II}Cl_2$; the latter was done by pipetting. A constant-dosage pipet would reduce sample handling time and thus improve upon the reproducibility. This was indeed observed in the field data of the MARE2 cruise (see below), where such a procedure was applied.

Pore water of mud volcano sediments from the Florence Rise (eastern Mediterranean Sea) was analyzed to unravel the origin and consequences of deep derived fluid flow.[18] Discrete sediment depth intervals of core MNLGC15 (34°38′.288 E, 31°27′.670 N, 2495 w.d.) were sampled by cutoff syringes (PE, 60 mL of volume) and transferred into centrifuge cups to extract pore water by centrifugation. TIC was measured, including preoxidation of sulfide by H_2O_2 in dilutions. Sulfide was measured spectrophotometrically[19] by continuous-flow analysis. The resulting TIC profile (Figure 4) shows a consistent pattern despite the highly variable sulfide concentrations (note that the scale is in mmol/L), verifying the applicability of the proposed method to sulfide- and TIC-rich seawater. TIC-rich pore water ascends toward the sediment surface and the carbonate reacts in the uppermost 50 cm with downward diffusing calcium and magnesium (data not shown), thus resulting in a consumption of TIC. Sulfide builds up to

concentrations of 6 mmol L^{-1} at the depth where sulfate becomes depleted (data not shown) due to intensive sulfate reduction. The presence of high NH_4^+ concentrations implies anoxic conditions in all samples.

The method has been implemented during the MARE2 cruise on R. V. *Pelagia* near the South African continent.[20] Data were compared with existing data of World Ocean Circulation Experiment (WOCE) cruises (A09, A10, A12) performed in 1990, 1991, and 1993 measured by the coulometric method.[9] Obvious outliers in the data set were deleted and are shown in Figure 5. The $\Theta-S$ plot of the WOCE TIC data (Figure 5a) shows remarkable similarity to the MARE2 data (Figure 5b). The same water mass characteristics are observed by using TIC as a semiconservative tracer.[21] Figure 5c shows the different WOCE sections where the WOCE_A12 crosses the MARE2 study area. The difference plot was based on data from the same isopycnal surfaces (Figure 5d) and shows a natural variation in surface layers due to seasonal influence. Especially at a depth of ~1000 m the variation is quite high. The deep waters show a negligible offset between coulometric data and spectrophotometric data taking into account the large study area. The MARE2 and WOCE_A12 sections are quite close in space, even though this is the upper branch of the thermohaline circulation where a critical link is formed by the

(18) MEDINAUT/MEDINETH shipboard scientific parties. *EOS* **2000**, *81*, 625, 631−632.
(19) Cline, J. D. *Limnol Oceanogr.* **1969**, *14*, 454−458.
(20) Veth, C. *Cruise report. Mixing of Agulhas Rings Experiment*; 2000.
(21) Stoll, M. H. C.; van Aken, H. M.; de Baar, H. J. W.; Kraak, M. *Mar. Chem.* **1996**, *55*, 217−232.

heat and salt exchanges between the Indian and Atlantic oceans around South Africa.[22,23] It is beyond the scope of this paper to fully describe the physics causing the intermittent shedding of large Agulhas Rings at the Agulhas retroflection[24,25] which were the object of the MARE2 cruise.[20] But the latter are undoubtedly the cause of the differences observed at larger depths.

CONCLUSIONS

The method presented here offers distinct advantages over the current techniques for measuring TIC in seawater samples, the latter having a typical range of 1900−2300 μM in the ocean. Its small sample analysis requirements ($\sim$0.5 mL vs 50−100 mL for coulometry) make it ideal for pore water analysis with the H_2O_2 addition step and small culture work for whose range the method is easily scaled. Even though the method here has a negligibly lesser accuracy/precision (2−3 μM/$\sim$2.5 μM) when compared to the coulometric method (1.5−2.5 μM/1.5−2 μM), the speed

of the analysis (45 vs 3−8 samples/h) offers great potential for mapping of CO_2 characteristics in surface water. In comparison with the flow injection analysis method of Hall and Aller,[15] the resolution and accuracy have improved vastly. This is reached by proper scaling of the method for the expected range of concentrations in the sample. In this method, run on a Technicon Traacs 800 autoanalyzer, a slightly lower analysis speed is used (45 vs $\sim$60 samples/h[15]) to obtain the accuracy presented here.

(22) Schmitz, W. J. *Rev. Geophys.* **1995**, *33* (2), 151−173.
(23) Gordon, A. L.; Weiss, R. F.; Smethie, W. M., Jr.; Warner, M. J. *J. Geophys. Res.* **1992**, *97* (C5), 7223−7240.
(24) Goni, G. J.; Garzoli, S. L.; Roubicek, A. J.; Olson, D. B.; Brown, O. T. *J. Mar. Res.* **1997**, *55* (5), 861−883.
(25) Van Ballegooyen, R. C.; Gründlingh, M. L.; Lutjeharms, J. R. E. *J. Geophys. Res.* **1994**, *99* (C7), 14053−14070.
(26) Schlitzer, R. http://www.awi-brermerhaven.de/GEO/ODV, 2000.