Ocean Sci., 5, 547–558, 2009
www.ocean-sci.net/5/547/2009/

Ocean Science

Sensors and instruments for oceanic dissolved carbon measurements

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Received: 30 January 2009 – Published in Ocean Sci. Discuss.: 27 February 2009
Revised: 19 August 2009 – Accepted: 23 August 2009 – Published: 10 November 2009

Abstract. Highly accurate and precise measurements of marine carbon components are required in the study of the marine carbon cycle, particularly when investigating the causes for its variability from seasonal to interannual timescales. This is especially true in the investigation of the consequences of anthropogenic influences.

The analysis of any marine carbon component requires elaborate instrumentation, most of which is currently used onboard ships, either in manual or automated mode. Technological developments result in more and more instruments that have sufficient long-term reliability so that they can be deployed on commercial ships, surface moorings, and buoys, whilst the great technological and operational challenges mean that only few sensors have been developed that can be used for sub-surface in situ measurements on floats, robots, or gliders. There is a special need for autonomous instruments and sensors that are able to measure a combination of different components, in order to increase the spatial and temporal coverage of marine carbon data.

This paper describes analytical techniques used for the measurement of the marine dissolved carbon components, both inorganic and organic: the fugacity of CO_2, total dissolved inorganic carbon, pH, alkalinity, and dissolved organic carbon. By pointing out advantages, disadvantages, and/or challenges of the techniques employed in the analysis of each component, we aim to aid non-carbon marine scientists, sensor developers and technologists, in the decision of which challenges to address in further development.

1 Introduction

This paper is the outcome of the OceanSensors08 workshop, which was held at the Leibniz-Institut für Ostseeforschung, Warnemünde, Germany, from 31 March to 4 April 2008. The workshop was, and the resulting papers are, intended for "marine scientists, sensor developers and technologists with an interest in determining and shaping the future of ocean sensing" (http://www.io-warnemuende.de/conferences/oceans08/; accessed 26 August 2009). The workshop itself covered four broad areas: climate, ecosystems, hazards, and cross-cutting issues and emerging technologies. This paper covers instruments and sensors employed in measuring the components of the marine dissolved carbon cycle, none of which can be measured directly. The sections below describe the analytical principles, which are mainly used in instruments (defined here as analytical systems installed onboard ships, buoys, and moorings), and sensors (defined here as analytical systems which can be installed in situ on sub-surface floats or robots).

The oceanic carbon cycle is complex, being influenced by chemical, physical, as well as biological processes. Figure 1 shows a simplified schematic of the main processes involved[1].

Atmospheric CO_2 is taken up by the oceans by transfer through the sea surface: the air-sea flux of CO_2. Through the "physical carbon pump", this dissolved sea surface carbon can be transported in inorganic form out of the sun-lit surface layers by vertical mixing to intermediate or deep layers in the oceans, a process also depicted as intermediate and deep

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[1] Components such as methane, carbon monoxide, and carbon isotopes are not included in this paper. Neither do we cover principles to measure marine particulate carbon.

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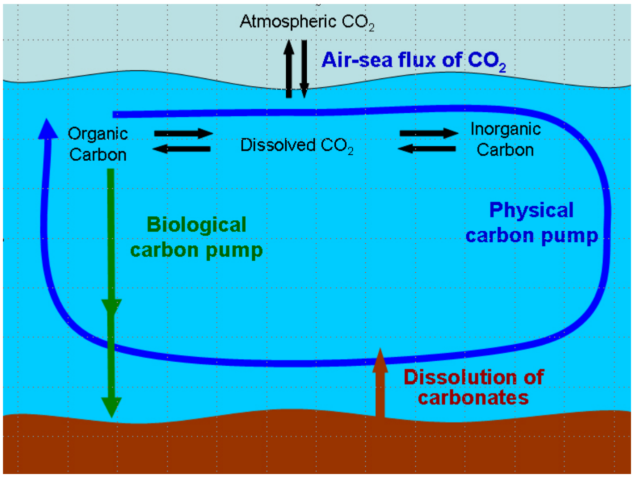

Fig. 1. Schematic of the oceanic carbon cycle, including air-sea flux, biological pump, physical pump and dissolution of carbonates.

Table 1. Scientific areas of interest when studying the oceanic dissolved carbon cycle, and the parameters most commonly measured during such studies. Parameters listed are the fugacity of CO$_2$ (fCO$_2$), total dissolved inorganic carbon (DIC), total alkalinity (TA), pH, and dissolved organic carbon (DOC). "X" depicts the main parameter(s) to be measured.

Scientific areas of interest	Parameters commonly measured				
	fCO$_2$	DIC	TA	pH	DOC
Air-sea flux of CO$_2$	X				
Ocean acidification		X	X	X	
Carbon storage and transport in the oceans		X	X		
Carbon "export", i.e. the removal of carbon from the surface waters to depth					X

water formation. Upwelling, also part of the physical carbon pump, can bring such carbon-rich deep water back into contact with the sea surface, reducing the uptake of atmospheric CO$_2$ or even re-emitting CO$_2$ to the atmosphere. The dissolved sea surface CO$_2$ can also be converted to organic carbon by biological activity. As part of the "biological pump", this organic carbon is either re-cycled into the sea surface, or it sinks, to be mostly recycled at depth and, to a minor extent, to leave the ocean carbon cycle for >1000 years through burial in sediments. Many marine primary biological producers and consumers form tissue of calcium carbonate, i.e. particulate inorganic carbon, which can also undergo vertical export through the water column as well as burial in sediments.

Thus, oceanic carbon occurs in both inorganic and organic form, and as such as both dissolved and particulate carbon. The sections below, describing the technological principles employed to measure oceanic dissolved carbon, are therefore divided into dissolved inorganic carbon (Sect. 2) and dissolved organic carbon (Sect. 3). Note that particulate carbon is not covered in this paper. A specific scientific interest determines which parameters have to be measured. Table 1 summarizes scientific areas of interest when studying the oceanic dissolved carbon cycle, and the parameters most commonly measured in such studies.

Measurements of all of the oceanic dissolved carbon components are being done

- from surface waters to the greatest depths accessible;
- in discrete mode (using discrete seawater samples) as well as in continuous mode (in situ or in pumped surface waters);
- in natural waters as well as samples from experiments (such as mesocosm studies);
- in (land-based) laboratories as well as field platforms, defined here as research ships or commercial vessels, and autonomous moorings, drifting buoys, floats, and other robotic platforms.

Challenges in developing instruments and sensors for oceanic carbon measurements, as common in the development of any instrument or sensor, include:

- accuracy/precision[2];
- routines for quality assessment (QA)/quality control of measurements (QC);
- long term drift
- size/weight;
- power requirements and power consumption;
- costs for installation and maintenance;
- sensitivity to biofouling/sedimentation;
- frequency of measurements;
- ruggedness;
- ease of use/maintenance;
- modularity;
- response time.

The first two challenges are naturally the same for all measurements, whilst others, e.g. size, weight, power requirements and power consumptions, are more dependent on the

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[2] A glossary of terms and abbreviations used in this paper is given in Table 3.

platform to be used. Hence the order of these challenges is parameter as well as platform dependent.

In order to achieve the required accuracy and precision of measurements, easy access is often essential for calibration and maintenance. Therefore, a significant number of scientific marine carbon studies use instruments operated either manually or automatically onboard ships. The technologies are included in this paper. We also extend to sensors that can be used in situ, i.e. submerged below surface waters. Development, quality control, and calibration also requires suitable instruments in land laboratories; with or without modifications, most of these instruments can also be used onboard ships.

A report of the methodologies employed in oceanic carbon research in the late 1980s was published in 1992 (UNESCO, 1992). Since then, a huge number of instruments and sensors has been developed. Describing all in detail is far beyond the scope of this paper. Hence the emphasis here is on the technological principles employed, attempting to outline advantages and disadvantages, together with challenges for future developments. An internet-based catalogue of instruments and sensors currently used by the oceanographic carbon community is available through the International Ocean Carbon Coordination Project, UNESCO-IOC, Paris, France (IOCCP; http://ioc3.unesco.org/ioccp/Index.html; "Sensors"). This gives information and links for individual instruments and sensors. Most of the chemical methods are described in (Grasshoff et al., 1983). A handbook outlining the chemistry, thermodynamical and physical data, and standard operating procedures (SOPs) for the ship-board study of dissolved inorganic and organic carbon has recently been published (Dickson et al., 2007). Details of the marine carbonate chemistry are given in (Zeebe and Wolf-Gladrow, 2001).

2 Oceanic carbon in dissolved inorganic form

CO_2 is taken up from the atmosphere by air-sea flux through the sea surface:

$$\mathrm{CO_2\ (gaseous)} \leftrightarrow \mathrm{CO_2\ (aqueous)} \tag{1}$$

Three equilibria then describe the aqueous reactions of inorganic carbon chemistry in seawater:

$$\mathrm{CO_2+H_2O} \leftrightarrow \mathrm{H_2CO_3} \tag{2}^*$$

* Strictly speaking CO_2 as shown there refers to a hypothetical species (often referred to as CO_2*(aq)) which is defined as the sum of the concentrations of CO_2(aq) and H_2CO_3(aq).

$$\mathrm{H_2CO_3} \leftrightarrow \mathrm{H^+ + HCO_3^-} \tag{3}$$

$$\mathrm{HCO_3^-} \leftrightarrow \mathrm{H^+ + CO_3^{2-}} \tag{4}$$

None of the concentrations of the components involved in the dissolved inorganic carbon chemistry can be measured directly in seawater. The inorganic dissolved carbon system is described by temperature, salinity, pressure, and the following four measurable parameters:

1. fugacity of CO_2 ($f\mathrm{CO_2}$),
2. dissolved inorganic carbon (DIC, i.e. the sum of the concentrations of dissolved CO_2, bicarbonate and carbonate; also depicted as C_T or $\Sigma\mathrm{CO_2}$),
3. pH, and
4. total alkalinity (TA; also depicted as TAlk or A_T)

If at least two of these four parameters are measured in a sample, the other two can be calculated using equilibrium constants, temperature, pressure, and salinity (Lewis and Wallace, 1998; Dickson et al., 2007). The particular research question which has to be answered determines which of the four parameters are measured, in order to obtain the highest accuracy.

In the following 4 sections, the analytical principles for the dissolved inorganic carbon parameters are described separately. However, a great need in the marine community are instruments or sensors that are able to measure a combination of these parameters to the required accuracy and precision, in addition to at least seawater temperature and salinity.

2.1 The fugacity of CO_2 ($f\mathrm{CO_2}$)

The partial pressure of CO_2 ($p\mathrm{CO_2}$) is equivalent to the mole fraction of CO_2 ($x\mathrm{CO_2}$) in air that is in equilibrium with seawater, multiplied with the total pressure (p) of equilibration:

$$p\mathrm{CO_2} = x\mathrm{CO_2} * p \tag{5}$$

The fugacity of CO_2 in seawater ($f\mathrm{CO_2}$) is defined as the partial pressure of CO_2 in air that is in equilibrium with seawater, taking into account that CO_2 is not an ideal gas, i.e. considering molecular interactions of CO_2 (e.g. with H_2O and other CO_2 molecules). The non-ideal character of CO_2 at atmospheric pressure is rather small in the concentration range of interest here, so the $p\mathrm{CO_2}$ is frequently used. For very precise calculation the non-ideal behaviour has to be taken into account, however, and $f\mathrm{CO_2}$ should be used. In this present work, we use the term $f\mathrm{CO_2}$ throughout.

The calculation of fCO2 is given in Dickson et al. (2007), SOP number 24, and is reported in units of pressure. For historical reasons this is usually microatmospheres [μatm] rather than Pascal [Pa]. Surface seawater $f\mathrm{CO_2}$ typically ranges from 250 to 550 μatm, yet can reach 2000 μatm at depth (at 20°C). In order to reliably detect anthropogenic influences on the air-sea exchange of CO_2, sea surface $f\mathrm{CO_2}$ should be determined to an accuracy of 1 μatm.

Seawater $f\mathrm{CO_2}$ cannot be measured directly in the water phase. Hence, the first step of measurement is to equilibrate seawater with a medium, in which CO_2 can be measured. Seawater $f\mathrm{CO_2}$ is therefore determined by

Table 2. Different techniques employed to determine oceanic fCO_2, with the different techniques of equilibration used, together with detection of CO_2 through to the platforms on which they are used.

Mode of equilibration	discrete	continuous	continuous	continuous
Equilibration of CO_2 in seawater with CO_2 in	air	air	air	a pH-sensitive indicator solution
Equilibration achieved	in a sample flask	in an equilibrator	through a membrane	through a membrane
Detection of CO_2 by	GC, IR	GC, IR	Spectrophotometry	Spectrophotometry
Platforms used:	commercial ships, research ships	commercial ships, research ships	Moorings, gliders, buoys	Moorings, gliders, buoys

1. the measurement of the mole fraction of CO_2 (xCO_2) in air that has been equilibrated with seawater, or
2. the measurement of the pH of an indicator dye solution, after the solution has been equilibrated with seawater (the pH is determined by the equilibrated CO_2 it contains).

Table 2 outlines the different techniques of equilibration used, together with analyses of CO_2 through to the platforms on which they are used.

The exact technique of equilibration chosen depends on the scientific question under investigation, the platform used for measurements, and the geographical location. Equilibration between seawater and air is mainly used for continuous surface measurements, on board either research or commercial vessels, and for analysing discrete samples, taken during mesocosm experiments or at depth onboard research ships. In geographical locations where continuous shipboard measurements are rare or impossible, e.g. in the Southern Ocean or at depth using floats, equilibration is typically done through membrane-based approaches.

2.1.1 Determination of fCO_2 by measurement of xCO_2 in air

CO_2 is firstly equilibrated between seawater and air (described in (b) below), followed by the measurement of xCO_2 in the air. xCO_2 in air can be measured by gas chromatography (GC) or by non-dispersive infrared spectrometry (NDIR).

(a) Analytical principle for xCO_2 in air:

(a-1) The analytical technique of xCO_2 in equilibrated air by GC is based on the catalytic conversion of the CO_2 to CH_4, followed by flame ionization detection (FID) of the CH_4 (Weiss, 1981; Weiss et al., 1992; Robertson et al., 1993; Dickson et al., 2007). Underway analytical systems with GCs for the measurement of xCO_2 were developed in the 1970s and extensively used until the 1990s, when the analysis by NDIR absorption spectrometry began to be used more widely.

The advantages of using a gas chromatograph include the need for only small air samples, the non-interference of moisture in the air sample, and the linear response of the FID over a large range of xCO_2 concentrations. The latter is particularly advantageous for discrete measurements due to the large concentration range encountered throughout the water column.

(a-2) The analytical technique of xCO_2 in equilibrated air by NDIR absorption spectrometry is based on the absorption of infrared radiation by CO_2 molecules.

Advantages are that NDIR analysers can easily be included in automated instruments, making them suitable for systems on buoys and moorings. With care (e.g. temperature control) and automatic zero-ing of the CO_2 channel in the analyser, long term drift can be kept to a minimum. Disadvantages are that moisture absorbs infra-red radiation and that the equilibrated air is at 100% humidity at the temperature of equilibration; this requires that either the air to be analysed dried prior to the measurement, or xH_2O has to be measured parallel to the xCO_2, followed by mathematical moisture correction. Additionally, NDIR analyser can be affected by vibration, e.g. on ships, causing increased instability of the readings. For highly accurate measurements, temperature control of the optical cell in the NDIR is also required (Pierrot et al., 2009; Murphy et al., 1998).

(b) Equilibration of CO_2 between air and seawater can be achieved either by direct contact between air and seawater (discrete or continuous), or by permeation of CO_2 through a membrane (continuous).

(b-1) Equilibration in discrete seawater samples is achieved either by pumping, using a closed loop, a known volume of air through a known volume of seawater in a flask, or by introducing a known small volume of air into a sealed sample bottle filled with seawater. Once equilibrium of CO_2 between the two phases is achieved, xCO_2 in the equilibrated air can then be measured by either GC or NDIR, described above. The air used for equilibration needs to contain a known initial amount of CO_2, ideally close to the fCO_2 of the seawater sample, in order to minimise the perturbation in the sample's CO_2 concentration. During the equilibration process, a constant known temperature and pressure within the closed circuit needs to be maintained.

These measurements are carried out during mesocosm experiments, or onboard research vessels to predominately determine $f\mathrm{CO}_2$ in samples collected at depth. A standard operating procedure for these measurements, applying gas chromatography for analysis, is described by Dickson et al. (2007), SOP number 04.

A disadvantage of such instrumentation is that it is elaborate, since it requires the control and measurement of temperature of the seawater sample to ±0.05°C, pressure measurement to ±0.5 mbar, several standard (and head space) gases, and CO_2-free carrier gas (for GC analysis). It also requires a major correction to in situ temperature, since the measurements are usually performed at a standard temperature (e.g. 20°C). Yet with care, precision of below 0.25% of $f\mathrm{CO}_2$ can be achieved. Typically, discrete $f\mathrm{CO}_2$ measurements are combined with measurements of at least one other CO_2 system parameter (e.g. DIC or TA).

(b-2) Continuous mode equilibration is achieved by pumping a fixed volume of air around a circuit that contains an "equilibrator", where the CO_2 equilibrates between a continuous flow of seawater and a counter-flow of air. The flow of seawater needs to be sufficiently large that it can be considered infinite. The volume of air, in contrast, should be minimised, ensuring that the CO_2 in the air adjusts to the equilibrium value with the seawater, without changing the CO_2 in the seawater noticeably. Once equilibrium of CO_2 between the two phases is achieved, the mole fraction of CO_2 ($x\mathrm{CO}_2$) in the equilibrated air can then be measured by either GC or NDIR, described above. Throughout, temperature and pressure within the equilibrator need to be measured to within ±0.01°C and ±0.5 mbar, respectively, to achieve $f\mathrm{CO}_2$ to within 2 μatm (http://ioc3.unesco.org/ioccp/Docs/TsukubaWSdocs/NOAApCO2workshop_report.doc, and ideally to within ±0.01°C and ±0.2 mbar, respectively. Additionally, in situ seawater temperature needs to be measured, so that the effect of the temperature change from seawater inlet to equilibrator can be corrected for (ideally $<\pm 0.5$°C change). A good recommendation is to measure in situ salinity as well.

A number of different types of equilibrators have been developed, all of which attempt to optimise the surface area between seawater and air. They include the shower-head type (Robertson et al., 1993; Weiss et al., 1992; Feely et al., 1998), the percolator type (Cooper et al., 1998; Schuster and Watson, 2007), the bubble type, the laminar flow type, and a combination of these types in one equilibrator (Lüger et al., 2004; Nojiri et al., 1999; Körtzinger et al., 1996). Measurements using an equilibrator are predominately carried out onboard ships, both on research and on commercial vessels, yet can be adapted to be installed on moorings.

The advantage of equilibrator based systems is that with care, highly accurate and precise data can be obtained. Disadvantages of equilibrators are their size, possible biofouling progressively blocking the seawater inlet to the equilibrator. Additionally, equilibrators need to be vented to maintain ambient pressure inside them, which can lead to contamination of the air inside the equilibrator. Also onboard ships, the position of the seawater inlet needs to be chosen carefully, in order to minimise artefacts caused by the ship's movement and hull-structure. A very detailed standard operating procedure of one such ship-board system for the underway, continuous determination of $f\mathrm{CO}_2$ in surface seawater is given by Dickson et al. (2007), SOP number 05.

(b-3) Continuous mode equilibration through a membrane is achieved by separating the gas phase from the seawater by e.g. a silicon or teflon membrane, and analysing the $x\mathrm{CO}_2$ in air by NDIR. In these systems, the hydrostatic pressure of the ambient seawater requires to be resisted by special measures (i.e. rigid membrane support in planar or tubular form).

The advantage of these instruments include that they can be installed on sub-surface platforms such as floats, and their potentially small size. Disadvantages include biofouling of the membrane and drift over time.

2.1.2 Determination of $f\mathrm{CO}_2$ by the pH of an indicator dye solution

This analytical technique of CO_2 in seawater is based on the pH change of a pH-sensitive colour indicator dye solution, in which the CO_2 is equilibrated across a membrane with seawater. The pH of the equilibrated indicator dye then depends on the CO_2 content.

In such instruments (e.g. Lefevre et al., 1993; deGrandpre et al., 2000), the equilibrated dye is transferred to an optical cell, where the absorbance is measured spectrophotometrically at wavelengths of the absorbance maxima of the indicator dye's acid and base forms, and at a non-absorbing wavelength (baseline). The indicator dye solution is prepared by diluting a concentrated solution of the pH indicator with synthetic seawater. The colour indicator solution has to have an ionic strength close to that of seawater (by salinity and bicarbonate content), to minimise the osmotic pressure across the membrane. The alkalinity of the dye solution is adjusted in order to optimise the pH change across the expected $f\mathrm{CO}_2$ range. A mercuric chloride solution is usually added to the colour indicator solution, to prevent biofouling of the membrane.

The $f\mathrm{CO}_2$ values can be calculated from the spectrophotometric absorbance and temperature data, together with the dissociation constant of the dye, dissociation constants of carbonic acid in seawater, the solubility coefficient, and the alkalinity and concentration of the dye. This technique has been developed primarily for buoys and moorings, in order to obtain oceanic measurements at remote locations, such as the Southern Ocean. Alternatively, the absorbance of the specific dye solution can be calibrated in the laboratory across the expected ranges in $f\mathrm{CO}_2$ and temperature, so that measurements in the field can be directly related to $f\mathrm{CO_2}$, albeit at lower accuracy.

A challenge for any instrument deployed on buoys or moorings is to minimise long-term drift. Since the dye solutions fade over time, an longer-term stability can be achieved by adding the measurement of the absorbance at the wavelength of the isosbestic point of the indicator dye's acid and base forms. Additionally, a pH based technique requires sufficiently high sensitivity to resolve $f\mathrm{CO_2}$ changes in seawater.

2.1.3 $f\mathrm{CO_2}$ instrument/sensor intercomparisons

A number of intercomparison experiments of $f\mathrm{CO_2}$ instruments have been carried out. In 1994, a laboratory intercomparison was carried out at Scripps Institution of Oceanography. In 1996, a ship-board intercomparison was carried out onboard *FS Meteor* during a cross-Atlantic cruise (Körtzinger et al., 1998). This identified that the temperature in the equilibrator was not always measured to the accuracy required for high-quality $f\mathrm{CO_2}$ data. In 2003, a pool-side intercomparison experiment was carried out in Japan (http://ioc3.unesco.org/ioccp/Docs/TsukubaWSdocs/WG1SummaryRpt.pdf). This identified that the performance of equilibrators can introduce differences in measured $f\mathrm{CO_2}$. For 2009, two intercomparisons are planned: one again as a pool-side intercomparison in Japan, continuing the 2003 experiment, and an open-ocean one by the Alliance for Coastal Technologies (http://www.act-us.info/tech_evaluations.php).

2.2 Dissolved inorganic carbon (DIC)

DIC in seawater is defined as the sum of the concentrations of dissolved $\mathrm{CO_2}$, carbonic acid, bicarbonate, and carbonate:

$$\mathrm{DIC} = [\mathrm{CO_2(aq)}] + [\mathrm{H_2CO_3}] + [\mathrm{HCO_3^-}] + [\mathrm{CO_3^{2-}}] \qquad (6)$$

It is reported as micromoles carbon per kilogram of seawater [μmol kg^{-1}]. Seawater DIC concentrations typically range from 1800 to 2300 μmol kg^{-1}, yet can reach 4300 μmol kg^{-1} in extreme environments (e.g. the Black Sea). For anthropogenic investigations, it needs to be determined to an accuracy of 1 μmol kg^{-1}. Certified calibration standards for DIC measurements are available since 1991 from Scripps Institution of Oceanography (http://andrew.ucsd.edu/co2qc/index.html), enabling a globally consistent standardization of quality control of measurements.

DIC is measured by

1. coulometry, after acidifying a known amount of seawater with phosphoric acid, stripping the released $\mathrm{CO_2}$ by an inert, $\mathrm{CO_2}$-free carrier gas, and measuring the amount of $\mathrm{CO_2}$ in this gas by coulometry, or
2. NDIR, after acidifying a known amount of seawater with phosphoric acid, stripping the released $\mathrm{CO_2}$ by an inert, $\mathrm{CO_2}$-free carrier gas, and measuring the amount of $\mathrm{CO_2}$ in this gas by absorption spectrometry, or
3. potentiometry, during which a seawater sample of known mass is titrated with a strong acid in a closed cell.

2.2.1 Determination of DIC by coulometry

The $\mathrm{CO_2}$ released from a seawater sample by acidification is passed into a solution containing a pH-sensitive colour indicator, where $\mathrm{CO_2}$ reacts to form a strong acid, which can then be titrated coulometrically by electrochemical generation of a strong base. Due to the necessity to carefully control the performance of a coulometer, coulometer-based systems can only be used for discrete samples on board research vessels. Such a system using coulometers is described by Dickson et al. (2007), SOP02.

Disadvantages are that such measurements are elaborate. They require careful dispensation of a precisely known volume of seawater into the chamber where the sample is acidified, high-quality measurement of temperatures, careful monitoring of coulometer background levels, and regular calibration. Additionally, hazardous chemicals are used in the analysis; since these chemicals need to be replaced at least at daily intervals, coulometers are affected by down-times of hours for the chemical conditioning of the coulometer solution. For improved quality of measurements, the coulometer cell should be temperature controlled.

The advantage is that with care, the highest precision and accuracy can be achieved.

2.2.2 Determination of DIC by non-dispersive infrared absorption

The $\mathrm{CO_2}$ released from a seawater sample by the acidification is passed through a NDIR (e.g. Friederich et al., 2002), such as described in Sect. 2.1.1 for the determination of $f\mathrm{CO_2}$. To achieve the required accuracy and precision, the analyser needs to be carefully temperature controlled in such systems.

2.2.3 Determination of DIC by potentiometry

A seawater sample of known mass is titrated with a strong acid (e.g. 0.1 M HCl) in a closed cell. The addition of the acid changes the electromotive force (e.m.f.) of the seawater, which can be followed by a pH sensitive electrode (combination electrode or electrode pair). During titration, the titration cell needs to be kept at constant temperature. Since $\mathrm{CO_2}$ gas is produced near the location of acid addition in the seawater solution, this gas must be kept from escaping the system so that it re-dissolves; hence a closed titration cell is used.

This technique can be used if a combined analysis of DIC and total alkalinity is required (Dickson et al., 2007, SOP number 03a). However, a higher accuracy of DIC measurements can be achieved if DIC measurement by coulometry is done, as described in Sect. 2.2.1 above.

2.3 pH

pH is a measure of the acidity or basicity of a solution. It is defined as the negative of base 10 logarithm of the hydrogen ion concentration of a solution. pH has been expressed on a number of different scales, i.e. the total scale, the National Bureau of Standards (NBS) scale, the seawater scale, and the free scale.

On the *total scale*, it is defined as:

$$\mathrm{pH} = [\mathrm{H}^+]_{\mathrm{free}} + [1 + S_T/K_S] \approx [\mathrm{H}^+]_{\mathrm{free}} + [\mathrm{HSO}_4^-] \quad \text{(for pH} > 4) \tag{7}$$

where S_T is the total sulfate concentration, and K_S is the acid dissociation constant for HSO_4^-.

A full discussion on the other scales in beyond this paper, and we refer the interested reader to e.g. (Dickson, 1984, 1993) for a detailed discussion of the various pH scales that have been used in seawater.

Oceanic pH ranges from 7.8 to 8.3, but can reach more extreme values in e.g. anoxic basins such as the Black Sea or in hydrothermal fluids (e.g. Charlou et al., 2000). For oceanic carbon research purposes, it should be determined to an accuracy of ±0.002 pH units.

Certified calibration standards for pH systems are not yet available, yet a limited number of prototype reference material is available (http://andrew.ucsd.edu/co2qc/index.html).

pH of seawater can be measured by

1. potentiometry or
2. spectrophotometry.

2.3.1 Determination of pH by potentiometry

In the field of electroanalytical chemistry, potentiometry is the measurement of the electrical potential difference that develops between the ion activity in two different solutions separated by an interface. The potential is the result of the free energy change that would occur if the chemical phenomena were to proceed until equilibrium. If the activity of ions on one side of the interface is held constant, the electrical potential is related to the activity of ions on the other side.

A combined pH glass electrode, for example, has a thin membrane of hydrogen-sensitive glass, formed into a bulb and melted to a glass shaft. The inside is filled with a liquid of known, constant composition, which creates a potential difference across the glass membrane against the liquid of interest on its outside. The difference in electrical potential is measured by an electrode inside the glass bulb, and a reference electrode outside. The reference electrode can be separated from the glass electrode, or as in the combined pH glass electrode, the reference electrode is placed inside a mantle surrounding the glass electrode, but its liquid connected to the outside through a glass frit. The measured potential represents the sum of several individual potentials along the entire setup. Since only the potential across the glass membrane is of interest, all others (e.g., junction potential, asymmetry potential) as well as their change with time need to be accounted for by frequent calibration.

The response of any pair of glass electrode/reference electrode is calibrated using buffers prepared in the laboratory. Besides having a known pH, buffer solutions are required to be very stable over time. A large number of different buffers have been developed for pH in seawater measurements, and need to be chosen according to the measurements to be made.

A combined glass electrode and reference electrode can be used, yet often better measurements are achieved with separate glass electrode and reference electrode. The glass electrode/reference electrode pair measures the e.m.f. in a standard buffer to obtain background value, and then in a seawater sample, whilst both liquids are at the same temperature. The e.m.f. of the electrode pair can be measured with a voltmeter of high input impedance. The seawater pH can then be calculated using the e.m.f. of the buffer and seawater sample, temperature, and salinity. The standard operating procedure of such a measurements is given by Dickson et al. (2007), SOP06a.

Challenges of such instrumentation are careful temperature control of solutions used, electrode drift, extremely careful preparation of the buffer solutions, problems with reference electrodes, and the need for frequent calibrations. SCOR Working Group 75 reported that by 1988, the precision of pH measurements was ±0.02 pH units, yet with care precisions of 0.002 pH units can be achieved (Byrne and Breland, 1989).

2.3.2 Determination of pH by spectrophotometry

Spectrophotometry has been used increasingly especially since the late 1980s. First the multi-wavelength absorbance is measured in a seawater sample, then again after a pH-sensitive indicator dye is added to the seawater sample. It is based on the principle that the corresponding acid and base forms of a pH indicator dye have different colours, hence different absorption bands. The total hydrogen concentration is then calculated from the absorbances measured, temperature, salinity, and the dissociation constant of the indicator dye used.

A number of different indicator dyes are used for pH determination, and research is continuing for optimal combinations of e.g. indicator dye and multi-wavelength chosen. The standard operating principle for ship-board measurements of discrete samples using *m*-cresol purple as indicator is given by Dickson et al. (2007), yet developments are being made to develop an automated system for the deployment on ships, buoys and moorings (DelValls, 1999; Bellerby et al., 2002).

Challenges of these systems are careful temperature control of solutions and spectrophotometer cell, preparing indicator solution with ionic strength close to that of seawater, homogenous mixing of sample and dye solution.

Potential accuracy is ±0.002 pH, sensitivity and long-term reproducibility can be better than ±0.001 pH (e.g. Friis et al., 2004).

2.4 Total Alkalinity (TA)

The total alkalinity of seawater is defined as the "number of moles of hydrogen ion equivalent to the excess of proton acceptors (bases formed from weak acids with a dissociation constant $K \leq 10^{-4.5}$ at 25°C and zero ionic strength) over proton donors (acids with $K > 10^{-4.5}$) in 1 kilogram of sample" (Dickson, 1981). Total alkalinity encloses contributions from the alkalinity of all relevant ions in the sample. For seawater with conservative composition, the contribution from total borate can be derived from salinity; other concentrations, such as phosphate and silicate, which normally constitute very small contributions to the total alkalinity, are often available from parallel nutrient measurements. Concentrations of ammonia and sulfide are typically so low in the open ocean that their contributions to total alkalinity can (in most cases) be neglected. In coastal waters and anoxic waters, the situation can be different; these contributions, though minor, need to be estimated or measured separately.

A recent definition of alkalinity (Wolf-Gladrow et al., 2007), which is entirely consistent with the one of (Dickson, 1981), takes a different approach that helps to infer the effects of biogeochemical processes on alkalinity.

TA is reported as micromoles per kilogram of seawater [μmol kg^{-1}] or as microequivalent per kilogram [μEqu kg^{-1}]. Please note that in some literature, alkalinity is reported as [μmol l^{-1}] or [μEq l^{-1}], which is not independent of seawater density, i.e. temperature and salinity.

Oceanic values are usually between 2000 and 2500 μmol kg^{-1}, yet can reach 4600 μmol kg^{-1} (e.g. Black Sea). Total alkalinity needs to be measured to within ±1 μmol kg^{-1} in ocean carbon studies to detect anthropogenic influences. For calculations in the sea water CO_2 system, the carbonate alkalinity is important. This is therefore calculated by subtracting all other alkalinity contributions from the measured total (or titration) alkalinity.

In principle, alkalinity is determined by adding acid to a seawater sample and analyzing the change in the e.m.f. of a pH electrode caused hereby. The number of steps can range from one to a full titration (20 or more acid increments added). As for pH, the pH change caused by the acid addition can be measured by

1. potentiometric titration or
2. spectrophotometrically.

The most common method today, however, is potentiometric titration in a closed or open cell.

Determination of TA by potentiometric titration

Potentiometric titration in a *closed cell* follows the same procedure as outlined for the determination of DIC by potentiometry (Sect. 2.3.3) and is needed only if a DIC value is to be derived from the titration. It should be noted that this determination of DIC is of lower accuracy than the coulometric technique described in Sect. 2.2.1.

So, if other methods are used for DIC measurements, the alkalinity titration cell can be *open*, since CO_2 exchange only affects the DIC value, but not alkalinity. The seawater sample is titrated with hydrochloric acid, which has an ionic strength similar to that of seawater. Titration is monitored by reading the e.m.f. of a glass electrode/reference electrode pair. The detection of the titration end point from the titration results is difficult and requires mathematical procedures. This can be the linearization of the titration curve by a GRAN plot, or the comparison of the experimental titration curve to a theoretical calculated titration curve and mathematical minimization of the difference by adjusting the parameters of the theoretical curve fit.

Although, in principle, alkalinity could be determined from the pH change by a single acid addition, precision greatly increases if more titration points can be used for the calculation. Temperature needs to be kept constant during titration and good mixing is required. However, the stabilization of the potential in the solution is a rather slow process (faster at higher temperature), so a full titration does take some time (typically 10–20 min).

Spectrophotometric titrations of alkalinity have been described, but are not (yet) widely used. The need for one or (better) more titration step(s) in all methods proposed so far, makes it difficult to develop a sensor based on this analytical approach.

3 Dissolved oceanic carbon

Dissolved organic carbon (DOC) is defined as the fraction of organic carbon that passes through a filter (typically of 0.2–0.45 μm pore size) and survives acidification and sparging (Dickson et al., 2007). The determination of DOC concentrations has been the topic of considerable attention and activity (e.g., see discussions in Pilson, 1998; Hansell and Carlson, 2001).

There are two noteworthy facts about DOC and its measurement:

(a) The introduction in 1988 of a high temperature catalytic oxidation technique to analyse for DOC (e.g. Sugimura and Suzuki, 1988) initiated an international effort to resolve the long-standing lack of coordination and consensus in DOC analysis (e.g. UNESCO, 1992). Subsequent intercalibration exercises have led to the resolution of many analytical issues (Hedges et al., 1993; Sharp, 1993) and have shown that experienced DOC analysts and the use of suitable reference materials can produce comparable results regardless of the method used (Dafner and Wangersky, 2002a; Hansell and Carlson, 2001; Sharp et al., 2002).

(b) Characterization of the measured DOC has advanced significantly in recent decades (Lee and Henrichs, 1993; Aluwihare et al., 1997; Dafner and Wangersky, 2002b), with specific carbohydrates and aminoacids being readily identifiable as components of DOC (Hansell and Carlson, 2001). However, a significant proportion of DOC is often characterized as a whole class of compounds, e.g., humic acids and fulvic acids, or not characterized at all (Hansell and Carlson, 2001). Moreover, information about the labile or refractory nature of DOC and its role in ocean biogeochemistry is often deduced by its age using radiocarbon dating (e.g. Bauer et al., 1992; Druffel et al., 1992) or by its size (e.g. Dafner and Wangersky, 2002b). Therefore, reported DOC values should always be used by keeping the analytical methodologies and operational definitions which accompany them in perspective.

DOC is the second largest pool of carbon in the ocean after DIC (Pilson, 1998; Houghton, 2007), with oceanic DOC concentrations varying from just under 39 μmol kg^{-1} in the deep open ocean to over 195 μmol kg^{-1} at river-ocean margins (Sharp et al., 2002). The sheer size of the DOC pool, as well as the current interest in monitoring the fate of anthropogenic carbon emissions, yield a necessity for measuring DOC systematically, reliably and in high spatial and temporal frequency.

3.1 Colored dissolved organic matter (CDOM)

There is currently no sensor that can measure DOC. The greatest advance in this direction has been the development of sensors for CDOM, which is defined as the component of total dissolved organic matter (DOM) that absorbs light over a broad range of visible and UV wavelengths (Coble, 2007). Two optical properties of CDOM, absorbance and fluorescence, have been used to quantify CDOM. The absorption spectrum of CDOM in a sample can be used to calculate a spectral slope, which is empirically related to an absorption coefficient. Alternatively, the fluorescence of the fraction of CDOM that does fluoresce can be measured by excitation in the ultraviolet and measurement in the visible spectrum.

Both absorption coefficient and fluorescence of DOM have been correlated with each other and DOC concentrations (Bowers et al., 2004; Belzile et al., 2006; Coble, 2007; Röttlers and Doerffer, 2007), even though this is a case-specific endeavor, given that a direct correlation is not always the case (Hansell, 2002). However, the ability to measure CDOM remotely via satellite or aircraft, coupled with commonly positive correlations between the two parameters in coastal areas, where DOC concentrations and dynamics are some of the most intense in oceanic settings, has elevated CDOM to the status of a DOC proxy (see discussion in Coble, 2007).

There are numerous commercially available CDOM sensors (see Sect. 3.1 in Moore et al., 2008), and some have been successfully used on moored buoys to collect high-frequency CDOM fluorescence data (Belzile et al., 2006). A suite of suitable fluorometers has recently been evaluated by the Alliance of Coastal Technologies (http://www.act-us.info/evaluation_reports.php).

3.2 Measurements of hydrocarbons

Hydrocarbons are multi-carbon and multi-hydrogen saturated, unsaturated, and aromatic compounds, and include Polycyclic Aromatic Hydrocarbons (PAHs), which are products of the diagenetic alteration of organic material and usually the object of sensor development for petroleum detection (e.g., Zielinski et al. 2009).

Multispectral sensors employ the effect of hydrocarbon presence on the properties of absorption, fluorescence, and reflection to detect their presence and quantify their concentration (Zielinski et al., 2009). Of particular interest is the generation of excitation-emission matrices (EEM), by both sample excitation and spectrophotometric emission measurements of a single sample at multiple wavelengths (Moore et al., 2004). Another notable application of these sensors is the use of differences in fluorescence lifetime (defined as the average duration of time an organic molecule remains excited before relaxing and radiating a photon) to distinguish between different organic compounds or groups of compounds (Moore et al., 2008).

Special mention should be made of the demonstrated use of Surface-Enhanced Raman Scattering (SERS) in a sensor (“SERS optode”) to measure PAHs (Schmidt et al., 2004). Raman Scattering is the technique by which a shift in the frequency of scattered laser light is related to the excitation of vibrational modes which are compound-specific. In SERS, molecules of the compounds under study are attached onto the surfaces of metallic nanostructures contained in suitable substrates to enhance the Raman signals. The reported limits of detection for this sensor ranged from 10^{-1} to 10^{2} nmol kg^{-1} (Schmidt et al., 2004).

4 Summary

Highly accurate and precise measurements of dissolved marine carbon are top priority to elucidate the causes for the variability of the marine carbon cycle on a global scale and to understand the anthropogenic impacts on the carbon cycle. The technological and operational challenges, however, to achieve such accurate and precise measurements, are numerous. In recent years, a great number of instruments and sensors have been developed, together with standards for e.g. DIC and TA (allowing globally consistent calibration) and standard operating procedures for dissolved inorganic carbon components. Yet there remains a great need for further developments to achieve the urgently needed increased spatial and temporal coverage of data; required improvements include e.g. smaller size, less power consumption, and longer-term stability. Additionally, instruments and sensors that are able to measure a combination of the marine carbon components are needed. In geographical regions where the access is difficult, such as the Southern Ocean, lower quality measurements might still be acceptable in order to obtain any data at all; yet in general, a range of instruments and sensors is needed for deployment on more ships, buoys, moorings, floats, robots, and gliders.

Appendix A

Glossary of terms used in this paper.

Abbreviation	Term	Description
	Accuracy	The closeness of a measured quantity to the its true value.
AT, ALK	Alkalinity	See TA
	Biological pump	The "export" of biologically bounded carbon from surface waters to depth.
CDOM	Coloured Dissolved Organic Carbon	The optically measurable fraction of the dissolved inorganic carbon.
DIC	Dissolved Inorganic Carbon	The sum of the concentrations of dissolved CO_2, bicarbonate and carbonate; also depicted as C_T or ΣCO_2, or TCO_2.
DOC	Dissolved Organic Carbon	Organic carbon remaining in a sample after filtering the sample, typically using a $<0.45\,\mu$m filter.
DOM	Dissolved Organic Matter	
$f CO_2$	Fugacity of CO_2	pCO_2 in air that is in equilibrium with seawater, taking into account the non-ideal behaviour of CO_2 in seawater at atmospheric pressure.
FID	Flame Ionisation Detector	Used to convert CO_2 to CH_4 for gas chromatographic detection of CO_2 in air.
GC	Gas Chromatography	Detection technique used to measure xCO_2 in air.
	Instrument	An analytical system installed onboard ships, buoys, and moorings; it cannot be used in situ in subsurface deployments.
NDIR	Non-Dispersive Infrared Absorption	Detection technique used to measure xCO_2 in air.
NPOC	Non-Purgeable Organic Carbon	Commonly referred to as TOC; organic carbon remaining in a sample after purging the sample with gas.
PAH	Polycyclic Armoatic Hydrocarbons	Multi-carbon and -hydrogen saturated, unsaturated, and aromatic compounds.
pCO_2	partial pressure of CO_2	The partial pressure of CO_2 in air that is in equilibrium with seawater. pCO_2 does not take into account the non-ideal behaviour of CO_2 in seawaterat atmospheric pressure.
	Platform	Where an instrument/sensor is installed, e.g. a ship, a buoy, a mooring, etc.
POC	Purgeable (volatile) Organic Carbon	Organic carbon that has been sparged or removed from a sample.
	Precision	A measure of the agreement between repeated measurements of the same sample; also referred to as reproducibility or repeatability.
QA	Quality Assessment	
QC	Quality Control	
	Sensor	An analytical system that can be installed in situ on subsurface floats, gliders, and robots.
SOP	Standard Operating Procedure	See Dickson et al. (2007).
TA	Total Alkalinity	The number of moles of H^+ equivalent to the excess of proton acceptors in 1 kg of sample. Also depicted as TAlk, or A_T.
TC	Total Carbon	All the carbon in the sample, including both inorganic and organic carbon, and both dissolved and particulate.
TOC	Total Organic Carbon	Material derived from decaying vegetation, bacterial growth, and metabolic activities of living organisms or chemicals; excluding total inorganic carbon.
VOS	Voluntary Observing Ships	In most cases commercial ships on which automated instrumentation is installed. Also called Ships Of Opportunity (SOOP).
xCO_2	Mole fraction of CO_2	The number of moles of CO_2 as part of the total number of moles within a parcel of air.

Acknowledgements. The authors acknowledge the large number of past and present marine carbon scientists and technologists, in their effort in improving existing sensors/instruments as well as developing new ones. The lead author is supported by the European Integrated Project CARBOOCEAN, grant number EVK2-CT-2000-00088.

Edited by: G. Griffiths

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