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Water quality — Sampling —

Part 26: Guidance on sampling for the parameters of the oceanic carbon dioxide system

Qualité de l'eau – Echantillonnage —

Partie 26: Lignes directrices pour l'échantillonnage d'eau de mer en vue de l'analyse des formes du carbone

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This document was prepared by Technical Committee ISO/TC 147, *Water quality*, Subcommittee SC 6, *Sampling (general methods)*.

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Introduction

The ocean is currently absorbing about one quarter of the carbon dioxide that humans are emitting. When carbon dioxide combines with seawater, chemical reactions occur that reduce the seawater pH, hence the term ocean acidification. Acidification can affect many marine organisms, but especially those that build their shells and skeletons from calcium carbonate. Over the past few years, several high-profile reports have highlighted the urgent need to better understand the effects of changes in carbonate chemistry on marine organisms and ecosystems. Research in this field was limited to a few groups around the world until recently but the number of scientists involved in ocean acidification research has been rapidly rising over the past few years. The reliable characterization and manipulation of the carbonate system involves good analytical skills and measuring facilities and continuous monitoring of seawater chemistry in the field and during experimentation. The predictive power of field surveys and the robustness of results from experiments critically depend on proper sampling and experimental protocols.

The oceanic carbonate system can be described by measuring at least two parameters of the following four parameters, total dissolved inorganic carbon (C_T), total alkalinity (A_T), fugacity of carbon dioxide (f_{CO2}) and pH in seawater. This document describes how to collect and preserve discrete seawater samples, from a Niskin bottle or other water samplers, for the analysis of four measurable inorganic carbon parameters including: $C_{T,}$ $A_{T,}$ f_{CO2} and pH, according to highest standard levels accepted by global ocean carbon community.

NOTE This document is based on Reference [5].

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Water quality — Sampling —

Part 26:
Guidance on sampling for the parameters of the oceanic carbon dioxide system

1 Scope

This document specifies how to collect discrete seawater samples, from a Niskin or other water sampler, that are suitable for the analysis of the four measurable inorganic carbon parameters: total dissolved inorganic carbon, total alkalinity, pH and CO_2 fugacity.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 5667-14, *Water quality — Sampling — Part 14: Guidance on quality assurance and quality control of environmental water sampling and handling*

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3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

ISO and IEC maintain terminology databases for use in standardization at the following addresses:

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at https://www.electropedia.org/

3.1
total alkalinity
A_T
<sea water> number of moles of hydrogen ion equivalent to the excess of proton acceptors (bases formed from weak acids with a dissociation constant K ≤ $10^{-4,5}$ at 25 °C and zero ionic strength) over proton donors (acids with K > $10^{-4,5}$) in 1 kg of sample

Note 1 to entry: The formula to determine A_T is:

$$A_T = \left[HCO_3^-\right] + 2\left[CO_3^{2-}\right] + \left[B(OH)_4^-\right] + \left[OH^-\right] + \left[HPO_4^{2-}\right] + 2\left[PO_4^{3-}\right] + \left[SiO(OH)_3^-\right] + [NH_3] + \left[HS^-\right] + \ldots - \left[H^+\right]_F - \left[HSO_4^-\right] - [HF] - [H_3PO_4] - \ldots$$

Note 2 to entry: The brackets represent total concentrations of these constituents in solution, $[H^+]_F$ is the free concentration of hydrogen ion and the ellipses stand for additional minor acid or base species that are either unidentified or present in such small amounts that they can be safely neglected. In open ocean water, the concentrations of NH_3 and HS^- are typically so low that they can be neglected; they may, however, be significant in anoxic environments.

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3.2
total dissolved inorganic carbon
C_T
dissolved inorganic carbon content of sea water is defined as

$$C_T = \left[CO_2^*\right] + \left[HCO_3^-\right] + \left[CO_3^{2-}\right]$$

where the brackets represent total concentrations of these constituents in solution (in µmol kg^{-1}) and $[CO_2^*]$ represents the total concentration of all unionized carbon dioxide, whether present as H_2CO_3 or as CO_2

3.3
fugacity
f
chemical potential of an individual component of a vapor phase

Note 1 to entry: The fugacity of carbon dioxide, f_{CO2}, is not the same as its partial pressure the product of mole fraction and total pressure, $x_{CO2}.p$ but rather takes account of the non-ideal nature of the gas phase. The fugacity of gas such as CO_2 can be determined from knowledge of its formula of state:

$$f_{CO2} = x_{CO2}.p.\exp\left[\frac{1}{RT}\int_0^p (V_{CO2} - RT\,p')dp'\right]$$

where

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x_{CO2} is the mole fraction of CO_2;

p is the total pressure;

p' is the partial pressure of CO_2;

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V_{CO2} is the volume of CO_2;

R is the molar gas constant which is 8.31446261815324 J K^{-1} mol^{-1};

T is the temperature in kelvin.

It should be noted that to apply the results of four measurable inorganic carbon parameters to calculate carbonate chemistry of seawater, the in-situ temperature, pressure, salinity as well as phosphate and silicate concentration of the seawater may need to be measured.

3.4
total hydrogen ion concentration
total hydrogen ion concentration of sea water is defined as:

$$\left[H^+\right] = \left[H^+\right]_F (1 + S_T / K_S)$$

$$\approx \left[H^+\right]_F + \left[HSO_4^-\right]$$

where

$[H^+]_F$ is the free concentration of hydrogen ion in sea water;

S_T is the total sulfate concentration ($[HSO_4^-]+[SO_4^{2-}]$);

K_S is the acid dissociation constant for HSO_4^-

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3.5
pH
negative of the base 10 logarithm of the hydrogen ion concentration:

$$\mathrm{pH} = -\log_{10}\left[\mathrm{H}^{+}\right]$$

where $\left[\mathrm{H}^{+}\right]$ is the hydrogen ion concentration, expressed in expressed in mol kg-soln $^{-1}$

4 Principle

For the analysis of A_T, C_T, pH and f_{CO2} in seawater, samples are collected in clean glass containers in a manner designed to minimize gas exchange with the atmosphere.

NOTE CO_2 exchange affects the various carbon parameters to differing degrees ranging from the very sensitive CO_2 fugacity, f_{CO2}, to alkalinity which is not affected by gas exchange.

If the sample is treated with a mercuric chloride solution to prevent biological activity, this occurs prior to the container being closed to prevent exchange of carbon dioxide or water vapour with the atmosphere.

5 Apparatus

5.1 General

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The sample containers are somewhat different depending on which parameter is being collected, but the basic concept is similar for the four possible inorganic carbon samples. In general, a flexible plastic drawing tube, a clean glass sample container with stoppers, a container and dispenser for the mercuric chloride solution (if it is being used) and a sampling log to record when and where each of the samples were collected.

5.2 Drawing tube

Tygon® tubing[1)] is normally used to transfer the sample from the Niskin water sampler to the sample container (5.3); however, if dissolved organic carbon samples are being collected from the same Niskins, then it may be necessary to use silicone tubing to prevent contamination from the Tygon®. The drawing tube can be pre-treated by soaking in clean seawater for at least one day. This minimizes the amount of bubble formation in the tube when drawing a sample.

5.3 Sample container

5.3.1 General

Sample containers depends on the parameter being measured, volume of sample required for analysis, length of anticipated storage and collection method. Important considerations in bottle choice include volume, leaching of bottle material, gas permeability, opening size, neck size, and sealing[1]. Ideally, sample containers should be prepared by cleaning in a 1 M HCl bath for approximately 24 h, followed by rinsing for approximately 24 h in Milli-Q water (18,2 MΩ cm^{-1} resistivity). However, care shall be taken to remove all residual acid during rinsing. Then, containars should be wrapped in aluminium foil and placed in a 450 °C muffle furnace for 4 h to remove organic carbon.

1) Tygon® tubing is an example of a suitable product available commercially. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of this product.

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5.3.2 Samples for f_{CO2} measurement

Typically, the f_{CO2} samples are analysed directly from a sample container. Borosilicate glass should be used along with a cap that is impermeable to gas exchange (e.g. 500 cm^3 volumetric flasks that have been pre-calibrated for a documented volume and sealed with screw caps that have internal plastic conical liners). f_{CO2} samples should be collected with a headspace approximately 1 % of the bottle volume. This is done to prevent possible breakage due to the expansion of the sample if its temperature increases. Required sample volume depends on instrument and analysis. Systems for measuring discrete f_{CO2} samples are not common and are often custom made in research laboratories. More commonly, f_{CO2} measurements are taken using a flow-through system which present a separate set of protocols to be followed to ensure that a representative environmental sample is measured[1].

5.3.3 Samples for C_T and A_T measurement

For C_T and A_T, high quality borosilicate glass bottles, such as Schott Duran[2] (l.c.e. 32 × $10^{-7}K^{-1}$), are recommended for both temporary and longer-term storage. The bottles should be sealed by using greased ground glass stoppers held in place with some form of positive closure, or in some alternate gas-tight fashion (e.g. some groups use screw-cap bottles with apparent success, but this method has not been thoroughly tested and should not be used if samples are stored for long extended periods). Storing samples in soda lime glass is not recommended because it can cause significant increases in alkalinity concentrations as seawater can leach sodium and other compounds from the glass over time (see Reference [7]). Alkalinity samples are less sensitive to gas exchange than C_T samples so it is less critical but still advisable to collect them in gas impermeable containers.

5.3.4 Samples for pH measurement

Samples for pH are typically analysed directly from the sample containers. For spectrophotometric pH measurements[2], the samples are collected directly into 10 cm path-length optical cells and sealed with polytetrafluoroethylene (Polytetrafluoroethylene (PTFE)®[3]) caps ensuring that there is no headspace. In the case of applying wet chemical flow spectrophotometric systems for determination of pH (e.g. CONTROS HydroFIA®[4]), custom Schott Duran borosilicate glass bottles that is impermeable to gas exchange can be used for collection of samples[3]. Samples collected for analysis using the potentiometric method shall be collected with minimal headspace and the volume should be sufficient to allow the electrode to be immersed. Due to gas exchange driven pH changes and ion consumption by the electrode, a larger volume of sample collected potentially gives more stable and precise readings[1]. The headspace should be entirely avoided when filling the sample container.

5.4 Mercury dispenser

Any appropriately sized Eppendorf pipette can be used to add the mercuric chloride solution; it can be more convenient to use a repipetter that can be mounted near the sample collection area. All equipments should be properly labelled for safety.

6 Reagent: Mercuric chloride solution, $HgCl_2$

Samples are collected for f_{CO2}, C_T and A_T, and in some cases, should be preserved with a mercuric chloride solution to stop biological activity from altering the carbon distributions in the sample container before analysis. A typical solution is saturated mercuric chloride in deionized water. However, saturated solutions have been known to clog the pipette in very cold weather, so some laboratory examiners use

2) Schott Duran borosilicate glass bottle is an example of a suitable product available commercially. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of this product.

3) Polytetrafluoroethylene (PTFE)® is an example of a suitable product available commercially. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of this product.

4) CONTROS HydroFIA® is an example of a suitable product available commercially. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of this product.

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