

## Chapter 7. Determination of Total Inorganic Carbon ( $C_T$ ) by the Coulometric Procedure

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### 1.0 Scope and field of application

This procedure describes a method for the determination of total dissolved inorganic carbon ( $C_T$ ) in sea water, expressed as moles of carbon per kilogram of sea water. A highly precise automatic gas extraction coulometric detection system is described. The method is suitable for the assay of oceanic levels of total dissolved inorganic carbon (1800-2400  $\mu\text{mol kg}^{-1}$ ) and also for higher levels such as are found in the Black Sea (3800-4300  $\mu\text{mol kg}^{-1}$ ). For a more definitive and comprehensive treatment of the analysis, the reader is referred to the D.O.E. (1994) handbook (Dickson, A.G., and Goyet, C., eds.), Johnson *et al.* (1993) and the SOMMA manual (Johnson, 1992). The D.O.E. (1994) handbook by Dickson and Goyet provides protocols for other carbon dioxide system parameters (i.e. pH, alkalinity,  $p\text{CO}_2$ ).

### 2.0 Definition

The total dissolved inorganic carbon content of seawater is defined as:

$$C_T = [\text{CO}_2^*] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]$$

where brackets represent total concentrations of these components in solution ( $\mu\text{mol kg}^{-1}$ ) and  $[\text{CO}_2^*]$  represents the concentration of all unionized carbon dioxide, whether present as  $\text{H}_2\text{CO}_3$  or as  $\text{CO}_2$  (UNESCO, 1991).  $C_T$  can also be referred to as total carbon dioxide ( $\text{TCO}_2$ ).

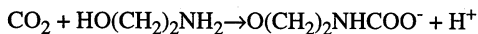
### 3.0 Principle of Analysis

Total dissolved inorganic carbon ( $C_T$ ) is measured by acidifying a seawater sample to convert  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$  to undissociated  $\text{CO}_2$ , and then extracting this  $\text{CO}_2$  as a gas, trapping and titrating the amount evolved (Johnson *et al.*, 1987, 1993). A high degree of precision and accuracy is maintained by using a computer-controlled automated dynamic headspace analyzer that extracts total carbon dioxide ( $C_T$ ) from seawater using a SOMMA (Single-Operator Multiparameter Metabolic Analyzer) designed by K. Johnson of Brookhaven National Laboratory (Johnson, 1992, Johnson *et al.*, 1993), now

commercially available from the University of Rhode Island. This apparatus is coupled to a commercial coulometer that detects the extracted CO<sub>2</sub> (Huffman, 1977, Lindberg and Cedergren, 1978).

The analytical system forces a sample (either seawater, Na<sub>2</sub>CO<sub>3</sub> standard solution or distilled water) into a volume-calibrated pipette using a pressurized headspace gas of air. This known sample volume (~30 ml) is then dispensed into a stripping chamber previously acidified with ~1.5 ml of phosphoric acid (the chamber and phosphoric acid are purged with pure nitrogen or helium carrier gas prior to the addition of each sample). CO<sub>2</sub> gas evolved from the acidified sample is then passed through a thermostated condenser (4°C) and a magnesium perchlorate trap to remove water vapor. Any acidic or reactive gases are removed by passing through activated silica gel trap (ORBO 53<sup>®</sup> tube).

The amount of CO<sub>2</sub> gas extracted from the acidified sample by a continuous flow of pure N<sub>2</sub> through the chamber is determined coulometrically by trapping and titrating the CO<sub>2</sub> with a DMSO based absorbent containing ethanolamine. The resulting hydroxyethylcarbamic acid which is formed with electrochemically generated hydroxide ions is titrated to maintain the absorbing solution at constant pH. Relevant chemical equations occurring in the solution are:



Hydroxide ions are generated by electrolysis of water at the platinum cathode and the total amount of CO<sub>2</sub> extracted from the sample is based on the time integrated current of the OH<sup>-</sup> generated to maintain the absorbing solution at a constant, colorimetrically defined pH.

The determination of seawater total dissolved inorganic carbon is calibrated with known volumes of pure CO<sub>2</sub> (Johnson, 1992, Johnson *et al.*, 1985, 1987, 1993, Wilke *et al.*, 1993).

## 4.0 Apparatus

4.1 *SOMMA (Single-Operator Multi-Parameter Metabolic Analyzer)*, available from University of Rhode Island. Includes:

4.1.1 Eight port gas chromatography valve

4.1.2 Two loops of stainless steel tubing of known volume

4.1.3 Three thermistors accurate to ± 0.05°C

- 4.1.4 SOMMA glassware (e.g. stripping chamber, calibrated water-jacketed pipette, water-cooled condenser, aerosol traps, magnesium perchlorate trap)
  - 4.1.5 Temperature controlled water bath circulators
  - 4.1.6 Temperature controlled sample bottle holder
  - 4.1.7 The newer versions have a Sea-Bird conductivity cell for determining salinity.
- 4.2 A model 5011 CO<sub>2</sub> *coulometer* (UIC Inc., P.O. Box 863, Joliet, IL 60434)
- 4.2.1 Coulometer cell (temperature controlled)
  - 4.2.2 Electrodes: platinum spiral cathode and silver rod anode
  - 4.2.3 Rubber cell top, silicone O-ring
  - 4.2.4 Stir bar
- 4.3 *Computer system*
- 4.3.1 PC (e.g. 286 or higher)
  - 4.3.2 Printer
  - 4.3.3 Software GW Basic program (K. Johnson)
- 4.4 *Sampling equipment*
- 4.4.1 Clean 500 or 1000 ml borosilicate reagent bottles and ground-glass stoppers
  - 4.4.2 Apiezon L grease
  - 4.4.3 Tygon<sup>®</sup> drawing tube
  - 4.4.4 Pipette to dispense mercuric chloride
- 4.5 *Other*: Barometer, e.g. Paroscientific transducer; Circulator; Chiller

## 5.0 Reagents

- 5.1 *Compressed gases*:

- 5.1.1 Carrier gas: Nitrogen (>99.9995%) or Helium (>99.995%)
- 5.1.2 Calibration gas: CO<sub>2</sub> (>99.999%)
- 5.1.3 Headspace gas: Air (350  $\mu$ atm CO<sub>2</sub>)
- 5.2 *Phosphoric acid* (reagent grade): Phosphoric acid, diluted with Milli-Q water by a factor of 10:1 (~8%) is used to acidify seawater samples.
- 5.3 *Magnesium perchlorate* (reagent grade): For the removal of water vapor.
- 5.4 *Activated silica gel*: For the removal of reactive acidic gases. Glass tubes (ORBO-53 traps) with activated silica are custom-made by Supelco Inc., U.S.A.
- 5.5 *Cathode solution*: UIC Coulometrics, Inc. proprietary mixture of water, ethanolamine, tetraethylammonium bromide, and thymolphthalein in solution in dimethyl sulfoxide (DMSO).
- 5.6 *Anode solution*: UIC Coulometrics, Inc. proprietary solution containing saturated potassium iodide in water and DMSO.
- 5.7 *Potassium iodide* (reagent grade): Added to anode solution.
- 5.8 Saturated solution of *Mercuric chloride*:
- 5.9 *Ascarite*: For the removal of CO<sub>2</sub> from the carrier gas.
- 5.10 *Sodium carbonate* (optional): Na<sub>2</sub>CO<sub>3</sub> (99.95% pure: Alkimetric standard, Fisher Scientific Co.): Six solutions are prepared for standard calibration ranging in concentration from distilled water to 500, 1000, 1500, 2000, and 2500  $\mu$ mol C.kg<sup>-1</sup>.

## 6.0 Sampling

- 6.1 Seawater sample for C<sub>T</sub> analysis are collected in the Teflon-coated OTE bottles either on the General Oceanics rosette or individually mounted on stainless steel hydrowire. C<sub>T</sub> seawater is collected after the first and any replicate oxygen samples.
- 6.2 The samples are drawn into 12 individually numbered, clean, one liter borosilicate glass bottles. Water is also drawn into at least two duplicate bottles. In obtaining sea-

water samples, care is taken to minimize turbulence and to prevent the retention of air bubbles in the bottles. A 30-50 cm length of Tygon<sup>®</sup> tubing is connected to the OTE bottle spout. The end of the tube is elevated before the spout is opened to prevent the trapping of bubbles in the tube. With the water flowing, the tube is placed in the bottom of the bottle. The bottle is slowly rotated and the side of the bottle tapped with the stopper to ensure that no air bubbles adhere to the bottle walls. At least two to three volumes of water are allowed to overflow from the bottle. A headspace of >1% of the bottle volume is left to allow for water expansion. 200 µl of saturated mercuric chloride is then added to the sample bottle to prevent further biological activity. The bottle neck is dried with a Kim-Wipe stick and then the bottle is sealed with an Apiezon grease coated ground-glass stopper, ensuring that it remains gas-tight. Rubber bands are placed around the lip of the bottle and stopper in a criss-cross manner as a further precaution.

6.3 The samples are then stored in a cool, dark location until analysis.

## 7.0 Procedures

7.1 *Bottle preparation:* Bottles should be carefully cleaned before use. Used bottles are emptied and any grease on the bottle neck is removed with kim-wipes. Bottles are thoroughly washed with a commercial detergent, then rinsed with a 10% HCl solution. Copious rinsing with Milli-Q/distilled water is followed by an acetone rinse. The bottles are then allowed to air dry for an hour and sealed with ground-glass stoppers.

### 7.2 Maintenance of SOMMA-Coulometer system

7.2.1 The titration cell is cleaned with copious rinses of Milli-Q water and a rinse with acetone. The sidearm of the cell is then filled with acetone which is then left to drain overnight through the frit separating the cathode compartment from the sidearm. The cell is then rinsed with Milli-Q water and left to dry overnight at 55°C.

7.2.2 The rubber top, electrodes, stir bar and perchlorate trap are thoroughly cleaned with Milli-Q water.

7.2.3 The titration cell, rubber stopper, stir bar, electrodes, magnesium perchlorate glass trap, and Teflon carrier gas lines are dried overnight at 55°C.

7.2.4 The ORBO-53 tubes and magnesium perchlorate traps are renewed with each newly prepared coulometer cell.

### 7.3 Determination of the background level

- 7.3.1 Each analysis session, fresh coulometer cell solutions are used.
- 7.3.2 An aliquot of phosphoric acid is introduced into the coulometer cell. CO<sub>2</sub>-free N<sub>2</sub> carrier gas is allowed to run through the SOMMA system and into coulometer cell. Once the background titration rate is stable, a background level is determined by averaging over a 10 minute period.

### 7.4 Calibration

- 7.4.1 The electrical calibration of the coulometer is not perfectly accurate and the current efficiency of the electrode processes occurring in the coulometer cell have been shown to vary from 100% (Johnson *et al.*, 1993, D.O.E., 1994). It is therefore necessary to calibrate the coulometer using known volumes of pure CO<sub>2</sub> or with a suite of Na<sub>2</sub>CO<sub>3</sub> solutions (e.g. Goyet and Hacker, 1992). The amount of C<sub>T</sub> titrated by the coulometer is recorded by microcomputer.
- 7.4.2 Valves that operate the CO<sub>2</sub> calibration and sample extraction systems are controlled by microcomputer (Johnson 1992, Johnson *et al.*, 1993).
- 7.4.3 A stainless-steel loop of known volume is filled with pure CO<sub>2</sub>. The loop is then flushed with carrier gas into the coulometer cell and titrated. A mean calibration factor is calculated from two different loops.
- 7.4.4 Standard concentrations of C<sub>T</sub> ranging from 500 to 2500 μmol.C kg<sup>-1</sup> can also be prepared using distilled water and variable amounts of dried Na<sub>2</sub>CO<sub>3</sub> salt (D.O.E., 1994, Goyet and Hacker, 1992). Sodium carbonate solutions are treated as if they were seawater samples. A blank standard solution (distilled water without any Na<sub>2</sub>CO<sub>3</sub>) is also prepared.

### 7.5 Analysis of a seawater sample

- 7.5.1 Once the background level and calibration factor have been determined satisfactorily, the coulometric system can be used to analyze seawater samples.
- 7.5.2 The stripping chamber is drained of any previous sample. An aliquot of phosphoric acid (~1.5 ml) is dispensed into the stripping chamber. The pipette and the silicone sample lines are flushed with a new sample. The pipette is then filled and allowed to drain into the stripping chamber. CO<sub>2</sub> gas evolved is transferred with carrier nitrogen or helium gas to the coulometer cell and titrated.

7.6 *Post-analysis*: The dispensing and stripping systems are cleaned by rinsing with Milli-Q/distilled water.

## 8.0 Calculation and expression of results

The amount of  $C_T$  titrated by the coulometer for a seawater sample is multiplied by the calibration factor (slope of calculated vs. measured concentration), giving the seawater  $C_T$ , expressed in  $\mu\text{mol kg}^{-1}$  of seawater, computed as follows:

$$C_T = \left( \frac{N - (b \cdot t)}{c} \right) \left( \frac{1}{V \cdot p} \right)$$

Where:

$C_T$	=	total dissolved inorganic carbon ( $\mu\text{mol kg}^{-1}$ )
$N$	=	coulometer reading in counts
$b$	=	background level of the system
$c$	=	coulometer calibration factor
$t$	=	time required to measure pipette
$V$	=	volume of seawater sample
$p$	=	density of seawater

## 9.0 Quality assurance

### 9.1 *Quality control*:

Written instructions outlining the standard operating procedures are maintained and continually reviewed and updated. Standard operating procedures are kept within guidelines proposed by the D.O.E. CO<sub>2</sub> survey science team (D.O.E., 1994).

### 9.2 *Quality assessment*:

9.2.1 The background level is usually within  $0.1 \mu\text{g C min}^{-1}$ .

9.2.2 The recovery of CO<sub>2</sub> compared to theory during gas calibration is maintained at better than 0.2%. The two gas loops must give the same calibration factor within 0.05% before analysis of samples begin.

- 9.2.3 Within-bottle replicate and between-bottle duplicate measurement of over 100 samples give a standard deviation of approximately  $0.3 \mu\text{mol kg}^{-1}$  and  $0.5 \mu\text{mol kg}^{-1}$  respectively, well within guidelines proposed (D.O.E., 1994).
- 9.2.4 Stable seawater certified reference materials (CRM's), supplied by A. Dickson (Scripps Institute of Oceanography), are analyzed regularly to maintain the day to day and year to year accuracy of the measurements. Analyses of these reference materials at BBSR are within the standard deviation of the mean reported by the Scripps Institution of Oceanography ( $0.3 \mu\text{mol kg}^{-1}$ ). Intercomparison exercises are also undertaken with other laboratories.

## 10.0 References

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