

## Evaluation of Dissolved Inorganic Carbon in Seawater

Yuki Tamura

### User Benefits

- ◆ It is possible to measure inorganic carbon (IC) with good accuracy, unaffected by salts, even in samples with a high inorganic salt concentration, such as seawater.
- ◆ The IC concentration can be measured in a short time of about 15 minutes per sample, and the dissolved inorganic carbon concentration can be evaluated with high accuracy.
- ◆ The ASI-L autosampler enables automatic measurement of multiple samples.

### Introduction

Global warming due to increased CO<sub>2</sub> in the atmosphere has become a world problem. One method which is expected to provide an effective countermeasure is capture and storage of carbon by marine ecosystems, that is, "blue carbon." Since it has been estimated that the world's oceans can absorb far more CO<sub>2</sub> than forests and other terrestrial carbon sinks, and thus can make a large contribution to mitigating global warming, attention has focused on sequestration of carbon in oceans.

The dissolved inorganic carbon concentration (sum of CO<sub>2</sub>, HCO<sub>3</sub><sup>-</sup>, and CO<sub>3</sub><sup>2-</sup>) is often used in evaluations of the amount of CO<sub>2</sub> absorption by oceans. At present, a measurement method using coulometric titration is the most general method for CO<sub>2</sub> detection, but it is also possible to evaluate the dissolved inorganic carbon concentration by using Shimadzu TOC-L combustion catalytic oxidation-type total organic carbon analyzer. The TOC-L can quantify inorganic carbon (IC), and the dissolved inorganic carbon concentration can then be found by converting the measured IC by molecular weight.

As advantages of the TOC-L, in addition to enabling automatic measurement of multiple samples when used in combination with the Shimadzu ASI-L autosampler, measurement is also possible in a short time of about 15 minutes per sample. Furthermore, the IC concentration can be measured with good accuracy, unaffected by salts, even in samples with high inorganic salt concentrations, such as seawater.

This article introduces an example in which the dissolved inorganic carbon concentration of seawater was evaluated by using the Shimadzu TOC-L combustion catalytic oxidation-type total organic carbon analyzer.

### Analysis Method

Measurement samples ① to ⑤ were prepared by spiking seawater sampled from Tokyo Bay with sodium carbonate as an IC additive so as to obtain 1, 5, 10, or 20 mgC/L (carbon concentration in mg/L) (Table 1). The IC measurements of these samples were carried out under the conditions shown in Table 2. If the "conversion function" provided as a standard feature in the software is used, the IC measurement value can be automatically converted to the dissolved inorganic carbon concentration and output.

Table 1 Measurement Samples

Sample	Added IC concentration (mgC/L) Sodium carbonate
Sample ①	0
Sample ②	1
Sample ③	5
Sample ④	10
Sample ⑤	20

Table 2 Measurement Conditions

Analyzer	: TOC-L <sub>CPH</sub> total organic carbon analyzer
Option used	: ASI-L autosampler
Measurement item	: IC
IC measurement method	: Detection of CO <sub>2</sub> by phosphoric acid acidification
Calibration curve	: 2-point calibration curve by 0 to 50 mg/L sodium carbonate / sodium hydrogen carbonate aqueous solution
Injection	: 50 μL
Sample	: Seawater sampled from Tokyo Bay
IC additive	: Sodium carbonate (special grade)

### Measurement Results

Table 3 shows the results of the IC measurements of the samples, and Fig. 1 shows the correlation diagram of the measured IC concentration and the added IC concentration. The dissolved inorganic carbon concentration was converted from the IC concentration by using the following equation. Fig. 2 shows the measurement data.

$$\text{(Dissolved inorganic carbon concentration)} = \text{(IC concentration)} \times 3.67^*$$

\* Value obtained by dividing molecular weight of CO<sub>2</sub> by atomic weight of C.

A recovery rate of approximately 100% was obtained for all samples. In addition, the correlation coefficient of the measured concentration and the added concentration was 1.0000, showing a satisfactory correlation.

From these results, it can be understood that the IC concentration has been measured with good accuracy, unaffected by coexisting substances such as salts, even when measuring seawater samples, which have a salt content of approximately 3.5%.

Table 3 Measurement Results

Sample	IC measurement value (mgC/L)	Recovery rate (%)	Dissolved inorganic carbon concentration (mg/L)
Sample ① (seawater only)	24.5	-	89.9
Sample ② (seawater + 1 mgC/L)	25.5	101.0	93.6
Sample ③ (seawater + 5 mgC/L)	29.7	102.4	108.6
Sample ④ (seawater + 10 mgC/L)	34.8	102.6	127.5
Sample ⑤ (seawater + 20 mgC/L)	45.3	103.8	166.0

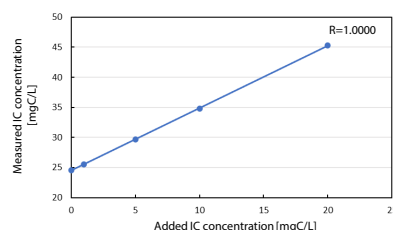
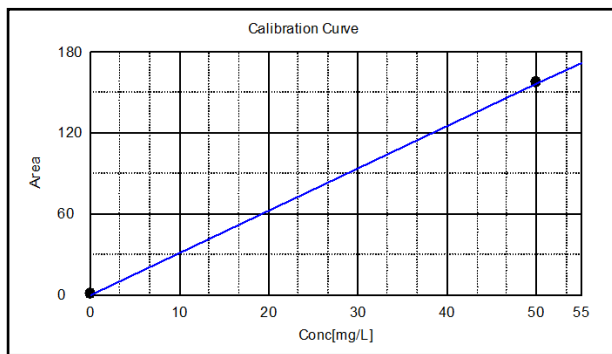
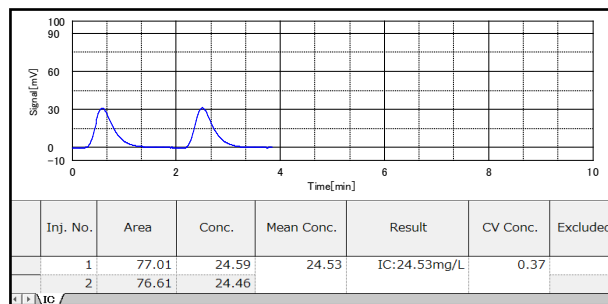


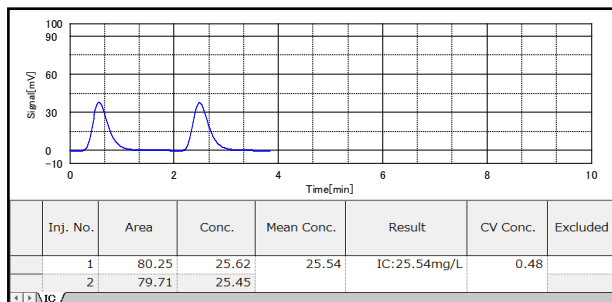
Fig. 1 Correlation of Measured IC Concentration and Added IC Concentration



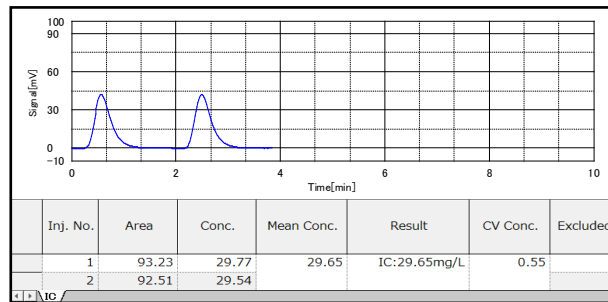
IC calibration curve



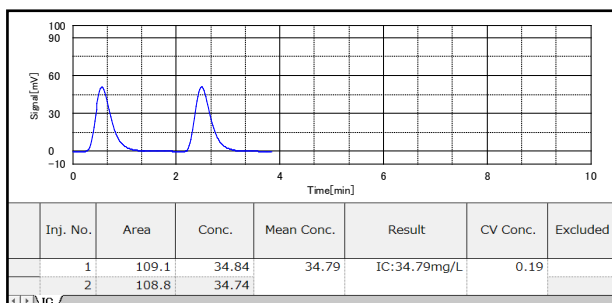
Sample ① (seawater only)



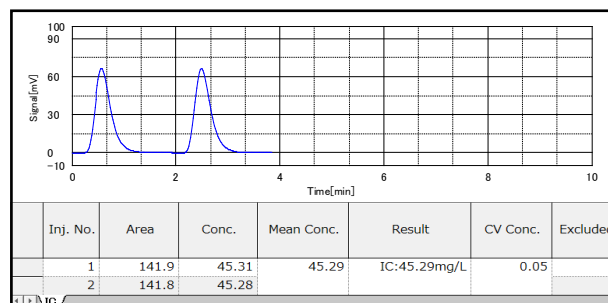
Sample ② (seawater + 1 mgC/L)



Sample ③ (seawater + 5 mgC/L)



Sample ④ (seawater + 10 mgC/L)



Sample ⑤ (seawater + 20 mgC/L)

Fig. 2 Measurement Data

### Conclusion

The Shimadzu TOC-L total organic carbon analyzer (Fig. 3) not only makes it possible to measure IC unaffected by inorganic salts contained in samples, but can also accurately evaluate the dissolved inorganic carbon in samples in a short time. Thus, the TOC analyzer is expected to be a useful tool for research on carbon capture and storage and the carbon cycle.



Fig. 3 (Right) Shimadzu TOC-L Combustion Catalytic Oxidation-Type Total Organic Carbon Analyzer and (Left) ASI-L Autosampler