

## 海水中溶存無機炭素の真空抽出法

### Vacuum extraction method of dissolved inorganic carbon in seawater at Shizuoka University

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#### Abstract

This paper shows a method for dissolved inorganic carbon (DIC) extraction from seawater using a vacuum system for radiocarbon content analysis using an accelerator mass spectrometry. In this method, phosphoric acid is added to the seawater sample, and DIC is extracted with ultrasonic bath. After this operation, the extracted gases are purified to CO<sub>2</sub> gas using n-pentane slush (-130°C) and liquid nitrogen trap (-196°C). The yield of CO<sub>2</sub> gas extracted from seawater is more than 99%.

**Keywords:** DIC, vacuum extraction, carbon isotope

#### Introduction

Dissolved inorganic carbon (DIC) is a useful tracer for the carbon cycle and seawater movement. In the past, measurement of <sup>14</sup>C density was carried out using β-ray liquid scintillation counting. Now, accelerator mass spectrometry (AMS) methods enable to measure <sup>14</sup>C content at shorter time and for small amounts. With the rapid spread of AMS measurement, it is necessary to make many graphite samples for AMS measurements in variety of the carbon form in nature.

When we measure the dissolved inorganic carbon (DIC) in seawater, it needs DIC extraction and graphitization procedure. DIC extraction method has mainly three type, 1) bubbling extraction method, 2) chemical precipitation method, and 3) vacuum extraction method. The bubbling extraction method is carried out under the carrier gas such as nitrogen or helium gas. This method has a possibility contamination of CO<sub>2</sub> gas come from carrier gas. The chemical precipitation method produces strontium carbonate from mixture of seawater and strontium chloride. This method has problems such as low yield of DIC and a waste disposal of strontium compound. The vacuum extraction method is carried out to extract CO<sub>2</sub> gas under the using vacuum system. This method need long time to finish all procedure.

In this paper, we introduce a method for DIC extraction from seawater using a vacuum system and ultrasonic bath. This vacuum extraction method is an improved version of Tsuchiya and Wada (2002).

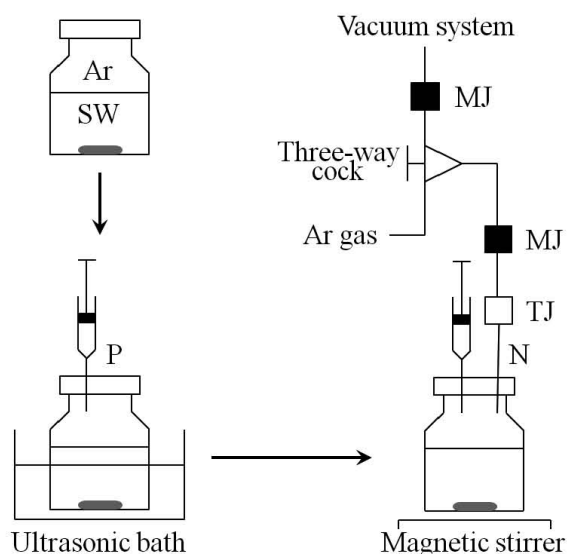
### Vacuum extraction method of DIC

#### 1. Advance preparation and seawater sampling

We used 250-mL glass bottles (DURAN®). Before the seawater sampling, two small holes were drilled on the polypropylene cap. Then, glass bottles were filled with argon gas to prevent contamination by atmospheric CO<sub>2</sub>, and stirring magnet bar was set into glass bottle. We used ethylene-propylene rubber for packing to seal between glass and cap. The bottles were filled with around 150-mL of seawater.

#### 2. Connection of glass bottle with vacuum system

The glass bottle and vacuum system were connected to the connector which is composed of three-way glass cock, Teflon® tube, and joints made from metal and Teflon® (Figure 1). Sample bottle side of the three-way glass cock was jointed with injection needle using epoxy resin (Figure 1). Vacuum system side of three-way glass cock was jointed with vacuum system using metal joint. Another side is connected to pure Ar gas canister.



**Figure 1. Reaction step and connection way.**

P: Phosphoric acid, N: Injection needle, MJ: Cajon® Ultra-Torr coupling, TJ: Teflon® joint

Vacuum system at Shizuoka University was shown in Figure 2. This vacuum system can be used for vacuum extraction and graphitization procedure. It needs wide space in case of expansion of air in the glass bottle. So, this vacuum system provides 1-L gas reservoir (Figure 2). Additionally, it installs two Horibe-traps (T3 and T4 in Figure 2).

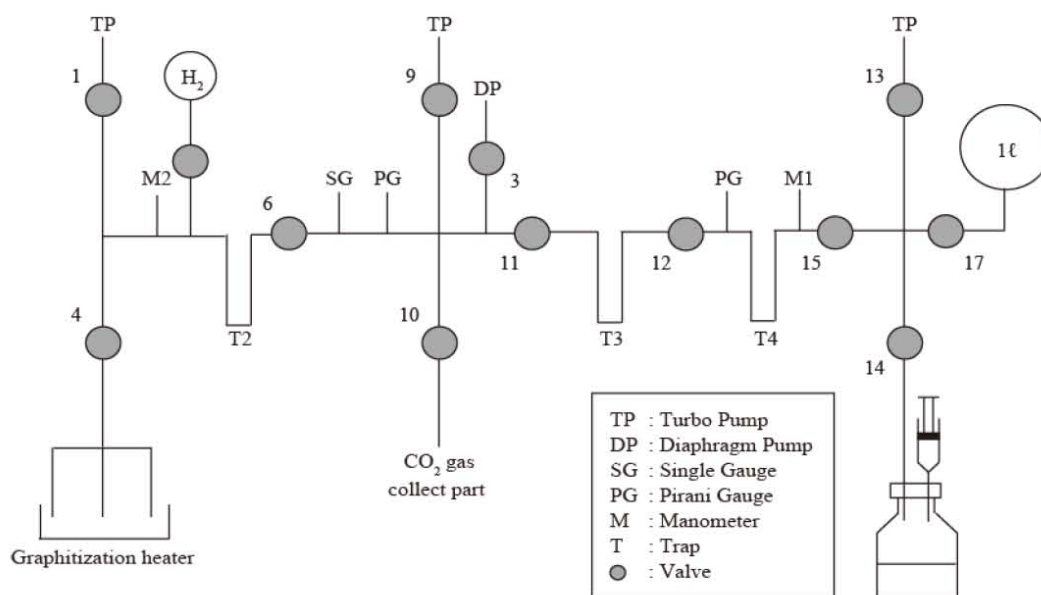


Figure 2. Outline of the vacuum system.

### 3. Vacuum extraction procedure

We looked into some vacuum extraction procedure. Process 1: Extracted DIC after injecting 5-mL of 85% ortho-phosphoric acid and mixed using stirring magnet bar for 5 minutes. Process 2: Extracted DIC two times after injecting 5-mL of 85% ortho-phosphoric acid and mixed using stirring magnet bar for 5 minutes. Process 3: Extracted DIC three times after injecting 5-mL of 85% ortho-phosphoric acid and mixed using ultrasonic bath for 15 minutes. Process 4: Extracted DIC after injecting 5-mL of 85% ortho-phosphoric acid and mixed using stirring magnet bar and ultrasonic bath for 5 and 15 minutes, respectively. Results and yield of each times of extraction procedure were shown in Figure 3 and Figure 4.

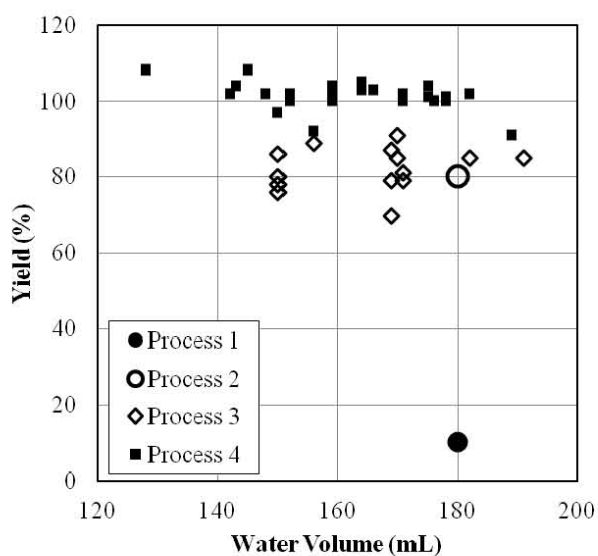


Figure 3. Yield of extracted CO<sub>2</sub> gas.

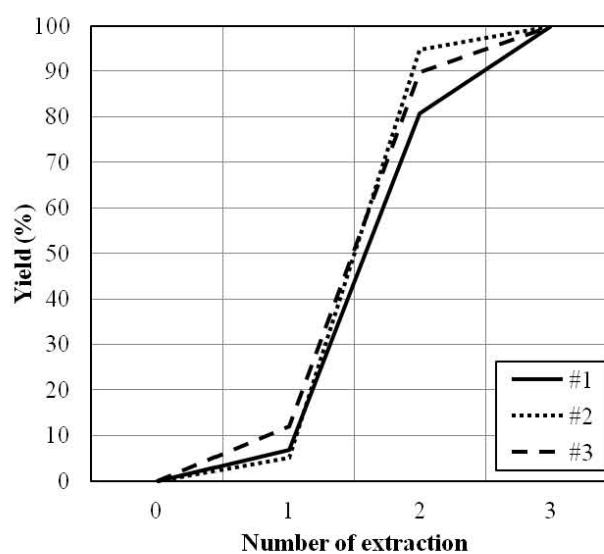


Figure 4. Yield of extracted times.

Around 75-85% of DIC were collected by three times of the extraction procedure using ultrasonic bath, while around 10% and 80% of DIC were collected once and twice during the extraction procedure using stirring magnet bar, respectively (Process 1, 2, and 3 in Figure 3). Additionally, almost all DIC were collected by three times of extraction procedure using stirring magnet bar and ultrasonic bath (Process 4 in Figure 3).

In summary, seawater sample in glass bottle was acidified with 5-mL of 85% ortho-phosphoric acid using syringe attached to an injection needle. Seawater sample and acid are mixed using ultrasonic bath for 15 minutes. Then, glass bottle is connected to vacuum system, and the evolved  $\text{CO}_2$  gas was collected using a liquid nitrogen trap ( $-196^\circ\text{C}$ ). In this case, stirring magnet bar was rotated continuously during the extraction. After that, all of the extracted gas was passed through a chilled n-pentane slush (about  $-130^\circ\text{C}$ ) to completely remove any water vapor. Finally, purified  $\text{CO}_2$  samples were stored in 6-mm $\phi$  glass tubes (Pyrex<sup>®</sup>).

#### 4. Assessment of reproducibility

In order to assess the reproducibility of this vacuum extraction procedure, three seawater samples were collected at the same time in same place. These seawater samples were extracted DIC by vacuum extraction procedure. Extracted  $\text{CO}_2$  gas was reduced to graphite on iron powder using pure hydrogen gas at  $635^\circ\text{C}$  for 4 hours, following the method of graphitization following the procedure for Tsuboi *et al.* (2011). Then, measurements of AMS- $^{14}\text{C}$  were carried out. Moreover, carbon stable isotope measurements also carried out using few amount of extracted  $\text{CO}_2$  gas. Result of AMS- $^{14}\text{C}$  and carbon stable isotope measurements is shown in Figure 5. The values of  $\delta^{14}\text{C}$  and  $\delta^{13}\text{C}$  from three seawater samples were agree within the margin of  $1\sigma$  error.

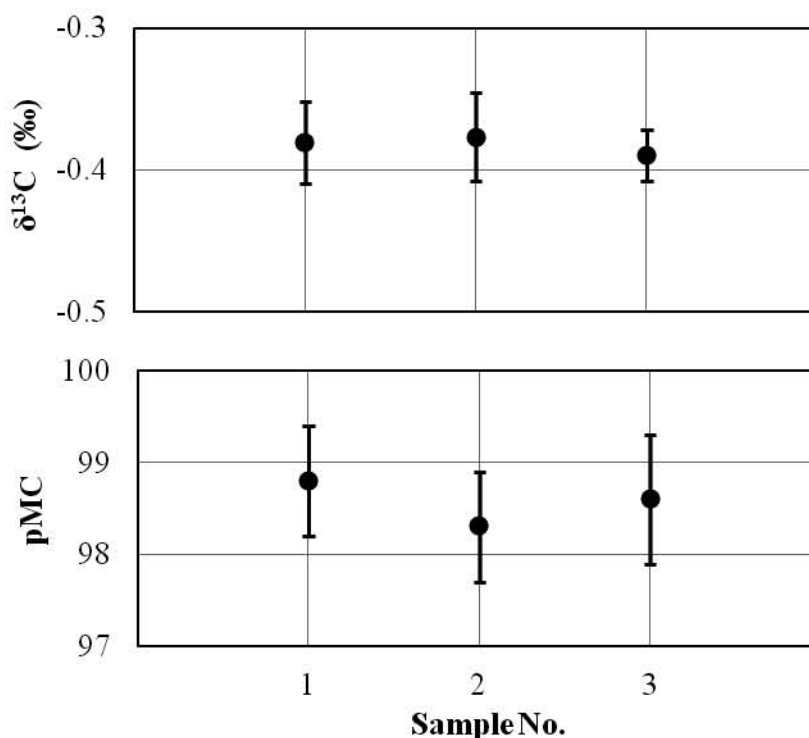


Figure 5. Reproducibility of extraction in seawater samples collected at same time in same place.

### Acknowledgments

We thank Dr. Hiroshi Takahashi (The National Institute of Advanced Industrial Science and Technology), Prof. Hiroyuki Kitagawa (Nagoya University), and Mr. Keisuke Kunita (Shizuoka University) for helpful discussions of seawater preparation. We appreciate Dr. Hiroyuki Matsuzaki (The University of Tokyo) for AMS- $^{14}\text{C}$  measurements.

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