A high accuracy method for determining nitrogen, argon and oxygen in seawater

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Abstract

An improved gas chromatographic system was constructed to analyze oceanic dissolved N₂, Ar and O₂ with a higher accuracy and shorter analytical time. To obtain a higher accuracy of N₂, Ar and O₂ measurements, the following was added to the system: (I) an air trapping system; (II) a N₂–CO₂ trapping system after the operation of the air trapping system; (III) an active carbon column system for separating N₂ and CO₂ completely and (IV) the introduction of automatic valves controlling most of the system. Compared to previous studies, the precision of the measurements of N₂, Ar and O₂ concentrations was higher at 0.04%, 0.05% and 0.02%, respectively, and our analytical time was shorter at 600 s. Using the improved analytical technique, concentrations of N₂ (\(C_{\text{N₂}}\), 561.69–611.81 μmol/kg) and Ar (\(C_{\text{Ar}}\), 15.126–16.238 μmol/kg), saturation states of N₂ (\(\Delta N₂\), −5.1–0.9%) and Ar (\(\Delta Ar\), −7.0 to −1.1%) from 0 m to 3000 m depth in the western North Pacific were observed during March 2005. Based on these data, we propose a new concept for estimating the amount of bubble injection (\(B\)). The total error in calculating \(B\) was estimated to be about 20%. We estimated \(B\) from 12 to 43 μmol/kg in this region using the observational values of N₂ and Ar. As each water mass had a significantly different value of \(B\) even with an error of 20%, it is possible to use it as an index of sea surface state for when each water mass is produced in the sea surface mixed layer. Moreover, based on our values of \(B\), we estimated preformed dissolved oxygen (DO) (\(C_{\text{preDO}}\), 309–332 μmol/kg) and the saturation state of \(C_{\text{preDO}}\) (\(\Delta \text{preDO}\), −7.0 to −1.2%) in this region. Thus, the difference between \(C_{\text{preDO}}\) and DO content in the ocean interior may be a more useful index for biogenic organic decomposition in the ocean field compared to Apparent Oxygen Utilization (AOU). Until now, the estimation of oceanic uptake of anthropogenic CO₂ has used AOU as a major parameter. Therefore, it may be necessary to re-evaluate the oceanic uptake of anthropogenic CO₂ based on our new concept of \(B\).

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1. Introduction

IPCC climate change 2001 (Houghton et al., 2001) reported that artificial fossil fuel CO₂ is expected to cause an increase in atmospheric temperature of 1.4–5.8 °C by the end of this century. A recent model calculation predicts that a decrease in water formation rate will occur as a response to global warming in the future (e.g., Sarmiento et al., 1998).

In the North Pacific, there have been several recent studies using repeated measurements to observe the variability of ocean ventilation (e.g., Watanabe et al.,...
2001; Ono et al., 2001; Emerson et al., 2004). Based on the revisit of two sections along 47°N and 165°E, Watanabe et al. (2001) demonstrated that both pCFC ages and apparent oxygen utilization (AOU) increased from 1985 to 2000, suggesting that the formation of subsurface waters had slowed down in this region, possibly as part of a long-term climate trend in the northwestern North Pacific (Ono et al., 2001). Emerson et al. (2004) indicated that the general trend of AOU along these repeated cross sections in the North Pacific has increased from the mid 1980s to the mid 1990s. They suggested that the formation of the subsurface water had slowed down over the northern North Pacific. Ocean thermohaline circulation plays an important role in the earth eco-system. If the circulation slows down, it might lead to a change in meridional heat flux and climate change may bring forward a positive feedback on global warming. Moreover, Watanabe et al. (2003) reported that O2, PO4, and T showed clear bidecadal oscillations of about 18 years superimposed on the linear trends of O2 decrease and PO4 increase in both Japan Sea Deep Water and North Pacific Intermediate Water. These oscillations and trends synchronized with the North Pacific Index (index of atmospheric barometric condition on the northern North Pacific), reported by Minobe (2000). The water mass formation in the North Pacific has decreased with decadal oscillations, and it is possible to correlate this oceanic decadal change with the change of atmospheric condition due to global warming. Thus, changes in air–sea interactions are one of the most important factors being affected by climate change.

However, detailed information about the process and/or change in air–sea interactions has not yet been obtained, hence we focused on this process utilizing non-reactive gases. In calm oceanic conditions, concentrations of non-reactive gases (e.g. N2, Ar, He and Ne) generally depend on each gas solubility and diffusion properties of gases affect their behavior of bubble injection in the ocean interior and to reveal the process and/or change of air–sea interaction. Craig and Weiss (1971) quantitatively estimated the amount of bubble injection (B) using He and Ne as non-reactive gases. However, their analytical procedure is complicated to observe these gases because they are minor component gases with low concentrations. It is difficult to clarify the behavior of bubble injection in the ocean interior and to reveal the process and/or change of air–sea interaction.

After their study, theoretical considerations and modeling studies demonstrated that differences in solubility and diffusion properties of gases affect their transfer to the ocean by bubbles that do not fully dissolve (e.g., Keeling, 1993). Moreover, there are two processes of bubble effect, air bubble injection (B) and gases exchange across the bubble–seawater interface (Vex). Hamme and Emerson (2002) found B/Vex ratio of 0.3 in the North Pacific deep water using a quasi-steady-state model based on concentrations of N2, Ar and Ne. However, their estimation was based on a complicated technique and did not show the amount of bubble injection.

The bubble injection is an index of the sea surface state and air–sea heat flux as a part of the process of air–sea interactions in the subsurface water formation region. For example, when strong storms frequently occur in the region producing subsurface water, the heat flux between air and sea becomes high with the increase of bubble injection and strong water ventilations. Thus, N2 and Ar are the major atmospheric components that allow us to obtain information about the changes of the sea surface state and heat flux.

In addition, estimating the extent of marine biological activity indirectly, we usually use a concept of AOU based on the difference between saturated and observed contents of oxygen. AOU has also been used for estimating the ocean uptake of atmospheric anthropogenic CO2 in general back calculation methods (e.g., Ono et al., 2000). However, the concept of AOU carries a large uncertainty due to the assumption that the oxygen content is saturated with the atmosphere in the surface mixed layer (e.g., Millero, 2005). Here, measuring N2, Ar and O2 simultaneously in the ocean, and estimating the ratio of them, it is also possible to
estimate more accurately the oxygen utilization to clarify the actual extent of biological activity.

Until now, some studies have already been carried out to establish simultaneous analytical methods of N$_2$, Ar and O$_2$ in the ocean. Gamo and Horibe (1980) developed an analytical system of N$_2$, Ar and O$_2$ using an ultrasonic detector and molecular sieve 5A with an analytical time of 16 min, and obtained the precisions for N$_2$, Ar and O$_2$ of 0.5%, 0.3% and 0.2%, respectively. Furthermore, Nakayama et al. (2002) improved the method of Gamo and Horibe (1980) using dual-TCD and a wide bore capillary column filled with molecular sieve 5A with an analytical time of 10 min, and had precisions of N$_2$ and Ar to be 0.36% and 0.28%, respectively. Emerson et al. (1991) also measured N$_2$, Ar and O$_2$ using a combination of air–water equilibrium sample bottle and mass spectrometer. Their method had high precisions of O$_2$/N$_2$ of 0.05% and O$_2$/Ar of 0.05% using mass spectrometry, while the precisions of N$_2$ and Ar concentrations were about 0.3% due to the sum of errors of O$_2$/N$_2$ and O$_2$/Ar, and the results of O$_2$ content showed a precision of 0.3% based on the Winkler method (Carpenter, 1965). In general, their method is complicated and needs longer analytical time, thus making it more difficult in measuring many samples.

However, the above methods had not shown the temporal changes of N$_2$ and Ar concentrations in the ocean interior due to the lack of necessary precision describing them. In improving the methods of Gamo and Horibe (1980) and Nakayama et al. (2002), we tried to develop a simultaneous analytical method for N$_2$, Ar and O$_2$ with a higher precision and short analytical time to clarify the temporal changes of these gases.

2. Method

2.1. New concepts for high precise analytical method of N$_2$, Ar and O$_2$

Based on the analytical methods of Gamo and Horibe (1980) and Nakayama et al. (2002), we propose some new concepts for measuring N$_2$, Ar and O$_2$ simultaneously to achieve a higher precision and short analytical time: (I) The previous methods showed broad peaks due to the lack of a purge-trap column, and consequently led to a lower precision of N$_2$, Ar and O$_2$ estimating the changes of N$_2$ and Ar ratios in the ocean interior. Thus, we added a purge-trap column (Air Trap) system to concentrate N$_2$, Ar and O$_2$ with CO$_2$ (5 cm of 60/80 mesh MS-5A packed in a 1/8 in. o.d. ss tubing put into a –198 °C liquid nitrogen bath). (II) The method of Nakayama et al. (2002) split amounts of stripped gas samples to detect N$_2$, Ar and O$_2$ by using a dual-TCD-GC system. However, their system led to contamination of the Ar–O$_2$ separation column by N$_2$ samples, thus to lower precisions of Ar and O$_2$. Using the dual-TCD-GC system without splitting, we added a N$_2$–CO$_2$ Trap column system (5 cm of 60/80 mesh MS-5A packed in a 1/8 in. o.d. ss tubing put into a –78 °C cooling bath) after the operation of the Air Trap system. Consequently, all amounts of stripped gases were analyzed by the dual-TCD-GC system. (III) The method of Nakayama et al. (2002) also led to the contamination of CO$_2$ in the observed N$_2$ peak due to the insufficient removal of CO$_2$ from the stripped gas in the streamline. We added a CO$_2$ backflushing system (pre-column made by active carbon of 60/80 mesh in a coil of 1/8 in. o.d. ss tubing (30 cm) and main column made by active carbon of 60/80 mesh in a coil of 1/8 in. o.d. ss tubing (3 m) put into 100 °C GC oven) for separating N$_2$ and CO$_2$ completely. (IV) Finally, we introduced automatic valves to most of the valves controlling the system to improve analytical precision.

Newly adding the above four concepts to the previous analytical methods, more precise measurements of N$_2$, Ar and O$_2$ were obtained (compared to previous studies with precisions of N$_2$, Ar and O$_2$ of 0.04%, 0.05% and 0.02%, respectively). In the following sections, we will provide details in the improvements used.

2.2. Extraction system

A schematic diagram of the extraction and analytical systems is shown in Fig. 1. In these systems, we used He gas as a carrier gas. Pressures from gas cylinder A containing He of 99.99995% is first reduced to be approximately 0.6 Mpa by using a high purity two-stage pressure regulator. In the downstream of the regulator of He gas cylinder A, the gas enters the extraction part through V-1 (a), and streams from the extraction system to TCD-GC. He gas in regulator B plays a role in pushing out water from the sample bottle to a constant volume tube via V4 (t). Flow rates in the extraction part and TCD-GC system were adjusted by flow controllers (EFC-300; HORIBA STEC Co. Ltd.). Flow rates of the flow controllers-A, B and C were about 30, 10 and 10 mi/min, respectively. To remove impurities (N$_2$, O$_2$ and other gases) in the carrier gas, the carrier gas was passed through a Gas Purifier Model HP2 (Valco Instruments Co. Inc.).

2.3. Valves and components

All valves and conduits were composed of stainless steel. Valves with electric actuators in Fig. 1 were
manufactured by Valco Instruments. Valves with the symbol “(t)” were triggered to start the integrator EZchrom Elite, and those with “(a)” were automatically controlled by a program of the integrator EZchrom Elite. The solid lines from V-1(t) to V-9(a) show the flow pathways used for stripping dissolved gases from a seawater sample and collecting the air in the Air Trap (held at −196 °C by liquid nitrogen bath). During this stripping process, the GC gas stream flows via V9(a) directly into the GC column and through the TCD-GC2. After the process of the Air Trap, these gases are purged (dotted line) by heating the trap (about 100 °C, electric heater into boiling water bath), and enter the N₂–CO₂ Trap (about −78 °C, electric cooler into Fluorinert FC-72 bath). Ar and O₂ pass through the N₂–CO₂ Trap and run into Ar and O₂ separation column. After this process, V8(t) position is changed to dotted line and gases are purged (dotted line) by heating the trap (about 100 °C, electric heater into boiling water bath), after 30 s, V8(t) position is changed to solid line, the trapped N₂ and CO₂ gases run into backflushing system (surrounded by dashed line) of CO₂ that set on V-10(a) via V-9(a) (dotted line), and only N₂ runs into TCD-GC2. Our improved points from this study are shown by (I), (II), (III) and (IV).

2.4. Extraction of dissolved N₂, Ar and O₂

This section includes our new concepts (I) and (II) as mentioned in Section 2.1: (I) the addition of the Air Trap system to concentrate N₂, Ar and O₂ with CO₂, and (II) the addition of the N₂–CO₂ Trap system without splitting the sample. For processing the water sample, a butyl rubber cap on a vial vessel (see Section 2.7) was connected via a hypodermic needle to a water inlet tube on V-4(t). Approximately 10 ml of the water sample was flushed through this valve to vent 1. The position of V-4 (a) was changed to allow the water sample to enter the

Fig. 1. Schematic diagram for the N₂, Ar and O₂ analytical system. FC, NV and V indicate flow controller, needle valve and valve, respectively. a in parentheses of V indicates automatic valves. t in parentheses of V indicates trigger of the integrator (EZchrom Elite) and control the program of automatic valves. The solid lines from V-1(t) to V-9(a) show the flow pathways used for stripping dissolved gases from a seawater sample and collecting the air in the Air Trap (held at −196 °C by liquid nitrogen bath). During this stripping process, the GC gas stream flows via V9(a) directly into the GC column and through the TCD-GC2. After the process of the Air Trap, these gases are purged (dotted line) by heating the trap (about 100 °C, electric heater into boiling water bath), and enter the N₂–CO₂ Trap (about −78 °C, electric cooler into Fluorinert FC-72 bath). Ar and O₂ pass through the N₂–CO₂ Trap and run into Ar and O₂ separation column. After this process, V8(t) position is changed to dotted line and gases are purged (dotted line) by heating the trap (about 100 °C, electric heater into boiling water bath), after 30 s, V8(t) position is changed to solid line, the trapped N₂ and CO₂ gases run into backflushing system (surrounded by dashed line) of CO₂ that set on V-10(a) via V-9(a) (dotted line), and only N₂ runs into TCD-GC2. Our improved points from this study are shown by (I), (II), (III) and (IV).
constant volume tube. The constant volume tube was overflowed by approximately 30 ml of water. For measurements for volume of the constant volume tube, we infused ultra pure water into the tube following an analytical procedure and measured the weight of the drain water using a Sartorius Genius precise electronic balance (significant digit of the balance was 6 figures, \( n=5 \), precision was 0.1%). Finally, we obtained 3.258 cm³ as the sample volume.

In order to extract \( \text{N}_2 \), \( \text{Ar} \) and \( \text{O}_2 \) from the water sample, the carrier gas with the water sample was directed into the stripping chamber through V-5(\( a \)). The gas stream then passes through the desiccant column and into the Air Trap (5 cm of 60/80 mesh MS-5A packed in a 1/8 in. o.d. ss), where the \( \text{N}_2 \), \( \text{Ar} \), \( \text{O}_2 \) and \( \text{CO}_2 \) were collected by the Air Trap for 90 s. Prior to the initiation of the above process, the Air Trap was pre-cooled to \(-196 \)°C by immersion in a stainless steel bath of Liquid nitrogen (our new concept (I)).

The gases in the Air Trap were purged by heating the trap (100 °C boiling water bath), and entered the \( \text{N}_2–\text{CO}_2 \) Trap (5 cm of 60/80 mesh MS-5A packed in a 1/8 in. o.d. ss tubing put into the \(-78 \) °C cooling bath used by Fluorinart FC-72 (3M Co. Ltd.) and electric cooler). \( \text{Ar} \) and \( \text{O}_2 \) passed through this trap while \( \text{N}_2 \) and \( \text{CO}_2 \) were preserved (our new concept (II)).

In the sequence time of our analysis, the stripping time of \( \text{N}_2 \), \( \text{Ar} \), \( \text{O}_2 \) and \( \text{CO}_2 \) from the seawater sample was 90 s in the stripping chamber, at a flow rate of about 30 ml/min for pressures inside the stripping chamber. After 120 s from the sample injection, we heated the Air Trap (trapping time for \( \text{N}_2 \), \( \text{Ar} \), \( \text{O}_2 \) and \( \text{CO}_2 \) was 120 s) and the sample gases ran into the \( \text{N}_2–\text{CO}_2 \) Trap (trapping time for \( \text{N}_2 \) and \( \text{CO}_2 \) was 180 s).

Checking the efficiency of the stripping process of the water sample by changing the stripping time of 60–120 s with the change of water sample temperature, we confirmed that dissolved \( \text{N}_2 \), \( \text{Ar} \) and \( \text{O}_2 \) in the water sample were completely removed via the carrier gas. An estimate of the stripping blank derived from this procedure could be obtained by passing the carrier gas through the gas-free water (remained sample water in the bubbler). Such stripping blanks were normally below the precisions of the analytical system.

2.5. Standard gas and air samples

Two types of gas samples can be flushed through the sample loops via valve V-1(\( t \)): the standard inlet connected to a cylinder of compressed calibrated standard gas, and the air inlet used to inject the air sample collected with syringes. The pressure of the standard cylinder was reduced to approximately 2 atm by a two-stage regulator with a stainless steel diaphragm. The regulator had a small internal volume, and did not measurably alter the \( \text{N}_2 \), \( \text{Ar} \) and \( \text{O}_2 \) contents of the standard flowing through it. Such system blanks were run frequently during the processing of water and air samples analysis, and were normally below the detection limit of the analytical system.

During flushing, the standard gas or air sample streams pass from V-1(\( t \)), V-2(\( t \)) and V-3(\( t \)) through the three sample loops in series, and through an isolation coil (2 m, a 1/16 in. o.d. ss) to the atmosphere. After flushing for 1 min, the flow was halted by V-1(\( t \)), V-2(\( t \)) and V-3(\( t \)), and the gas in the loops was allowed to equilibrate to room temperature and atmospheric pressure for 30 s after the injection of the standard gas or air sample. The isolation coil restricts the diffusion of \( \text{N}_2 \), \( \text{Ar} \) and \( \text{O}_2 \) from lab air into the sample loop during this period. At the time of injection, we measured the atmospheric pressure and the temperature of the sample loop with accuracy of 0.1 atm and 0.1 °C. Passing V-4(\( t \)) to V-8(\( t \)), the gas sample then follows the same pathway through the system to a cold trap as do gases extracted from the stripping chamber during a water sample analysis. By using a combination of multiple gas loops, standard gas or air sample in any optional volume can be selected and collected together in the Air Trap.

2.6. Chromatography

This section includes the new concepts (III) and (IV) in Section 2.1: (III) the addition of a backflushing system to separate \( \text{N}_2 \) and \( \text{CO}_2 \) completely and (IV) the introduction of automatic valves to most of the valves controlling the system to improve the analytical precision. Valves of this system had been controlled automatically by the chromatographic system of EZChrom Elite (GL-Science Co. Ltd.) (New concept (IV)). As an initial setting, the Air trap and the \( \text{N}_2–\text{CO}_2 \) trap were cooled by baths of liquid nitrogen (-196 °C) and Fluorinart FC-72 (-78 °C). 120 s after the sample injection (standard gas or air was used by V1(\( t \)) to V3(\( t \)), water sample was used by V4(\( t \)), the Air Trap was rapidly heated to 100 °C in a boiling water bath to separate sample gases. Only \( \text{Ar} \) and \( \text{O}_2 \) flowed over the \( \text{N}_2–\text{CO}_2 \) Trap and these ran into TCD-GC1 via the \( \text{Ar}–\text{O}_2 \) separation column (MS-5A wide bore capillary column, Agilent Technologies 19095P-MS0E HP-MOLSIV) held at \(-78 \) °C in the Fluorinert liquid FC-72 (3M Co. Ltd.) bath by using a refrigeration system. After 60 s, the \( \text{N}_2–\text{CO}_2 \) Trap was isolated from the main gas stream by switching V-8(\( t \)), and it was rapidly heated
to 100 °C in a bath of boiling water. The main gas stream flowed into the CO2 backflushing system by switching V-9(a). After 30 s of heating, the main gas stream was directed into the N2–CO2 Trap by switching V-8(t), and N2 and CO2 ran into TCD-GC2 via the CO2 backflushing system (pre-column made by the active carbon of 60/80 mesh in a coil of 1/8 in. o.d. ss tubing (30 cm), main column made by the active carbon of 60/80 mesh in a coil of 1/8 in. o.d. ss tubing (3 m), these columns were kept at 100 °C in the oven of the HP GC-6890 (Hewlett Packard Co. Ltd.) (New concept (III)).

Both temperatures of TCD-GC1 and TCD-GC2 were held at 155 °C. The frequency analog signals from the TCD-GCs were converted to digital signals by the A/D converter (GL Science Co. Ltd.). The signals were then sent to the EZChrom Elite for plotting and integrating the peak area. The times required for a chromatographic run of TCD-GC1 (600 s) and TCD-GC2 (420 s) were determined by the retention time to separate Ar and O2 and to hold N2 adequately. During each analysis, information on sample identification, temperature and pressure were entered manually via a keyboard into the EZChrom Elite. At the completion of each run, the original program in the EZChrom Elite was used to identify the N2, Ar and O2 peaks, based on the retention time. The sample data and chromatographic peak data were saved as an EZChrom Elite original data file.

Examples of chromatograms for a seawater sample are shown in Fig. 2. The Ar and O2 peaks were eluted at 300 and 480 s in TCD-GC1 after injection (Fig. 2a). The N2 peak was eluted at 240 s in TCD-GC2 after injection (Fig. 2b). These peaks were completely separated from each other. The concentrations reported for N2, Ar, and O2 in Fig. 2 were 598.58 μmol/kg, 15.965 μmol/kg and 307.41 μmol/kg, respectively.

2.7. Water sampling

We collected seawater samples for measuring dissolved N2, Ar and O2 using CTD-RMS (Rosette Multi Sampler) with 10-L Niskin bottles. The concentrations of dissolved gases could change rapidly because seawater could get in contact with headspace air in the Niskin bottle. Water samples for N2, Ar and O2 analysis were especially weak for air contaminations during this sampling process after recovering CTD-RMS, therefore, the samples were collected as soon as possible. Seawater for N2, Ar and O2 was transferred to a 60 ml glass vial vessel from the Niskin bottle. After opening the vent of the Niskin bottle, the vessel was washed by two times and overflowed by three times the vial content. For final filling, we added saturated HgCl2 solution of 50 μl to prevent biological activity, and covered the vial vessel with a butyl rubber cap and aluminum seal, taking attention that no air bubble contamination occurred. Typically, about 200 ml of seawater was required for the flushing and filling process. We preserved these vial vessels in the dark and in a cool bath of seawater.

2.8. Standards and calibration curves

The standard gases of N2, Ar and O2 were made by Taiyo Nippon Sanso Co. Ltd. by using a precise gravimetric method, of which concentration was close to the modern air composition. Calibration curves of N2, Ar and O2 were made by 5 different mole fraction points by gas loops S, M and L (Fig. 1) and the above standard gas. Each calibration curve had a high linear correlation between chromatographic peak area and mole fraction ($R^2>0.9999$).

3. Results and discussion

3.1. Comparison of N2, Ar and O2 between previous studies and our method

We improved the analytical method for N2, Ar and O2 with a higher precision and short analytical time due to an installation of the purge and trap in the system. The detection limits for N2, Ar and O2 calculated by three
times the area of baseline noise were 0.002, 0.002 and 0.020 μmol/kg, respectively. For measurements of precision, we prepared seawater equilibrated with laboratory air in a 45 L tank. We collected the equilibrated seawater to a vial vessel, and used the same sampling method as that for field water (see Section 2.7.). We analyzed six samples to obtain our analytical precisions of N₂, Ar and O₂, those being 0.04%, 0.05% and 0.02%, respectively, which were higher than in the previous studies. We compared the analytical performance for precision and analytical time between the previous studies (Gamo and Horibe, 1980; Emerson et al., 1991; Nakayama et al., 2002) and our study in Table 1. We also achieved the analytical time of 600 s, which was shorter compared to those in previous studies, suggesting that our system is suitable for measuring many samples with high precision.

### 3.2. Observational results

On the research vessel R/V Hokko-Maru of the Hokkaido National Fisheries Institute (March in 2005), we carried out sampling of natural seawater from 24 layers from 0 m to 3000 m at two observational points (Sta. A4: 42°15′N–145°08′E; Sta. A7: 41°30′N–145°30′E) using 10-L Niskin bottles mounted on a CTD.

We show the observed Temperature (T), Salinity (S) and T–S diagram in Fig. 3. In general, if the water temperature at 100 m depth is below 5 °C, the surface

![Fig. 3. Vertical distribution of salinity (S), temperature (T) and T–S diagram in March, 2005 at Sta. A4 and Sta. A7. (a) S (b) T (c) T–S diagram. The solid circles and open squares are the results at Sta. A4 and A7, respectively.](image_url)
water belongs to the Oyashio domain due to the winter mixed layer reaching $\sim 100$ m (Kawai, 1972). In this study, the surface water was occupied by the Oyashio with water temperatures below 5 °C (Fig. 3b). Intermediate water in the North Pacific generally occurs at about 100–1000 m depth, and is called the North Pacific Intermediate Water (NPIW) and generally has a minimum in salinity of 26.8 $\sigma_T$ (e.g., Talley, 1988). Its origin was derived from the dense shelf water from the Sea of Okhotsk (Yasuda, 1997). In this study, we found NPIW at 100–300 m depth. Below NPIW, at 300 m to 1000 m, we also found the warm water having high salinity and high temperature compared to the average vertical distribution of $T$ and $S$ in the North Pacific, which was derived from the water flow from the subtropical region (Nagata et al., 1992). We also defined the water mass below 1000 m as the North Pacific Deep Water (NPDW).

We showed the observed concentrations of $N_2$ and Ar ($C_{N_2}$ and $C_{Ar}$) (Fig. 4) and their saturation states $\Delta$ ($\Delta N_2$ and $\Delta Ar$) (Fig. 5) based on the solubility of these gases (Hamme and Emerson, 2004). Both the distributions of $C_{N_2}$ and $C_{Ar}$ are spatially similar to each other. We found that both maxima of $C_{N_2}$ and $C_{Ar}$ were almost at 100 m and 2250 m. The positions of the maxima seemed to be consistent with the surface water and the NPDW. The origins of water masses with the maxima were derived from the high latitudinal area due to higher content of $N_2$ and Ar caused by the colder and more severe sea surface state.

Moreover, we found that $\Delta N_2$ was almost under saturation ($-5.0$–$-0.8\%$) and all of $\Delta Ar$ was under saturation ($-7.0$ to $-1.1\%$) (Fig. 5). The vertical distribution of $\Delta N_2$ and $\Delta Ar$ were almost similar to each other, however, $\Delta Ar$ was always lower than $\Delta N_2$. The positions of maxima of $\Delta N_2$ and $\Delta Ar$ were the
same as those of $C_{N_2}$ and $C_{Ar}$. By considering the above information on $C_{N_2}$, $C_{Ar}$, $\Delta N_2$ and $\Delta Ar$, we also suggested that NPDW consists of two different water masses with the difficulty of distinction between the two by using salinity and temperature.

3.3. Concept for estimating the amount of bubble injection

We attempted to devise the equation in estimating the amount of bubble injection ($B$) using $N_2$ and $Ar$. Generally, gas exchange is generated at the air–sea surface interface. The gas exchange can be expressed as follows (e.g., Wanninkhof, 1992).

\[
F = k \Delta C = k(C_s - C) \quad (1)
\]

and

\[
k_{N_2}/k_{Ar} = (S_{C_{N_2}}/S_{C_{Ar}})^{-n} \quad (2)
\]

where $F$, $k$, $\Delta C$, $S_c$ and $n$ are gas flux from air to sea ($\mu$mol/m$^2$/day), transfer velocity (m/day), difference in concentration between equilibrated value ($C_s$) and observed one ($C$), the Schmidt number of each gas and value of the Schmidt number of exponent ($n = 0.5$; e.g., Nightingale et al., 2000), respectively.

Most of the subsurface water mass is formed in winter in the high latitudinal region. In winter at high latitudes, sea surface water is strongly cooled by cold air and the sea surface is strongly perturbed by the strong severe sea surface state, which tends to lead to the undersaturation of non-reactive gases. In the surface, waves collapse and many air bubbles are generated. The process of sending the bubbles to the ocean interior has been confirmed (Farmer et al., 1993). There are two processes of bubble effect, bubble injection and gases exchange across the bubble–seawater interface (e.g., Hamme and Emerson, 2002). If there is a direct injection to the sea surface in the wintertime, it is possible that $\Delta N_2$ is always higher than $\Delta Ar$ because the increase in content of each gas is inversely proportional to their solubility.

In order to obtain the information on sea surface state, we focused on the amount of bubble injection ($B$) because it gave a significant signal to each concentration of dissolved gases. To estimate $B$, we assumed that Eq. (1) with Eq. (2) represented gas exchange on the sea surface and gas exchange across the bubble–seawater interface. Nightingale et al. (2000) indicated that the value of $n$ in Eq. (2) was influenced by bubble effect under the condition of strong wind. Because SF$_6$ and $^3$He were artificially used in their experiment, their results were almost not contaminated by the background level of these tracers. Thus, it is possible that their estimation of the bubble effect had gas exchange on sea surface and gas exchange across the bubble–seawater interface without bubble injection.

To estimate $B$ from the observed data of $C_{N_2}$ and $C_{Ar}$ with Eqs. (1) and (2), we can express $B$ through our new concept as follows:

\[
C_{N_2}(\text{obs}) = A C_{N_2}(\text{sat}) + 0.7980 B \quad (3)
\]

\[
C_{Ar}(\text{obs}) = E_{Ar} A C_{Ar}(\text{sat}) + 0.0090 B \quad (4)
\]

where $C_{(\text{obs})}$ and $C_{(\text{sat})}$ are the observed ($C_{N_2(\text{obs})}$ and $C_{Ar(\text{obs})}$, $\mu$mol/kg) and saturated concentrations of each gas ($C_{N_2(\text{sat})}$ and $C_{Ar(\text{sat})}$, $\mu$mol/kg), respectively. $A$ is the imaginary saturation state of $N_2$ gas without $B$. $E_{Ar}$ defined the ratio of imaginary saturation state of $Ar$ to $N_2$, it was corrected different between $S_{C_{N_2}}$ and $S_{C_{Ar}}$, used by a one-box model (see next paragraph). $B$ is the amount of bubble injection ($\mu$mol/kg) in seawater. We also used the constant coefficients of 0.7980 and 0.0090 as the atmospheric mixing ratio of $N_2$ and $Ar$, respectively.

To obtain $E_{Ar}$ derived from the difference of $k$ between $N_2$ and $Ar$, we used a one-box model with Eqs. (1) and (2) ($n = 0.5$; e.g., Nightingale et al., 2000). Based on the observed winter mixed layer depth (Fig. 3b), we also used 100 m as the thickness of the box ($H$). Similarly, based on the hydrographic observation in this field (Fig. 3b), we used salinity ($S$) of 33.5 and temperature ($T$) of 4 °C in the box. We assumed 80% as the primary value of $R_{N_2}$ and $R_{Ar}$, because the saturation ratios of $N_2$ and $Ar$ were about 80% when the average surface water temperature changed from 12 °C to 4 °C from autumn to winter based on A-line data home page including Sta. A4 and A7 (FRA, 2005). We used constant wind speed in this model and calculated $E_{Ar}$ during 90 days due to the wintertime sea surface state lasting generally about 90 days in this area.

Because $E_{Ar}$ depends on $S$, $T$ and $H$, we need to estimate the sensitivity of $E_{Ar}$. With the ranges of $S$ of 33.5–35.0, $T$ of 0–5 °C and $H$ of 100–200 m found in the high latitudinal region of the North Pacific, we estimated $E_{Ar}$ in the wintertime (Fig. 6). We found the same temporal change of $E_{Ar}$, even if $S$ and $T$ changed in the case of the same $H$ (Fig. 6 (a) and (c)). For other values of $H$, we found a different change of $E_{Ar}$; the temporal change of $E_{Ar}$ ($H=100$ m) was faster than that of $E_{Ar}$ ($H=200$ m) (Fig. 6 (a) and (b)).

We estimated $E_{Ar}$ for $S=33.5$, $T=0$ and $H=100$ m because these conditions are close to the values in the observational sea area. We obtained 0.9940–0.9999
from 0 to 90 days (Fig. 6(a)). The uncertainty of $E_{Ar}$, 0.9940–0.9999 may cause significant errors in $A$ and $B$. Thus, we tried to estimate the sensitivity of $A$ and $B$ using the above estimation of $E_{Ar}$ and the actual $C_{N2(obs)}$ and $C_{Ar(obs)}$ in the western North Pacific (sampling water depth 50 m, Sta. A4, March 2005). We obtained $R'_{N2}$ as 0.978–0.989, and $B$ as 29–42 μmol/kg. This showed that average $B_{N2}$ was 36±7 μmol/kg, which had an error of about 20% if we used average $E_{Ar}$ of 0.9970.

The change of Schmidt number exponent $n$ Eq. (2) might affect the uncertainty of $E_{Ar}$. We checked the uncertainty with changes of $n$. For higher wind speeds, the value of $n$ reaches close to 0.2 (ex. Jean-Baptiste and Poisson, 2000). We obtained value for $E_{Ar}$ ($n=0.2$) of 0.9987 and $B$ of 32 μmol/kg (sampling water depth 50 m, Sta. A4, March, 2005). We here ignored the change of $n$ because it was significantly smaller compared to values of $E_{Ar}$.

3.4. Distribution of $B$ in the western North Pacific

Based on our concept with Eqs. (3) and (4), we tried to clarify the vertical distribution of $B$ in the actual ocean field. By applying $C_{N2(obs)}$ and $C_{Ar(obs)}$ in Sta. A4 and Sta. A7 into these equations, we obtained the vertical distributions of $B$ in the western North Pacific (Fig. 7).

We show the range of values for $B$ for each water mass at Sta. A4 and A7 in Table 2. In the surface layer from 0 m to 100 m, the range of values for $B$ was from 24
to 43 μmol/kg at Sta. A4 and from 12 to 22 μmol/kg at Sta. A7. The average value of $B$ was 35 ± 2 μmol/kg at Sta. A4 and 17 ± 2 μmol/kg at Sta. A7. In NPIW from 100 m to 300 m, the range of values for $B$ was from 27 to 43 μmol/kg at Sta. A4 and from 12 to 22 μmol/kg at Sta. A7. The average value of $B$ was 35 ± 3 μmol/kg at Sta. A4 and 17 ± 2 μmol/kg at Sta. A7. In the warm water layer from 300 m to 1000 m, the range of values for $B$ was from 20 to 35 μmol/kg at Sta. A4 and from 15 to 35 μmol/kg at Sta. A7. The average value of $B$ was 24 ± 3 μmol/kg at Sta. A4 and 26 ± 3 μmol/kg at Sta. A7. In NPDW from 1000 m to 3000 m, the range of values for $B$ was from 21 to 27 μmol/kg at Sta. A4 and 15 to 35 μmol/kg at Sta. A7. The average value of $B$ was 24 ± 1 μmol/kg at Sta. A4 and 25 ± 3 μmol/kg at Sta. A7.

The surface water at Sta. A4 had higher values of $B$ with lower $T$ and $S$, compared to the other water masses. The effect of strong severe sea surface state in the high latitudes may cause the higher value of $B$ at Sta. A4 because this water mass was Oyashio water derived from higher latitudinal regions northward, and because the surface water at Sta. A7 has lower values of $B$ with higher $T$ and $S$, which is a mixture between Oyashio and Kuroshio waters derived from the lower latitudinal region with relatively calm sea surface state.

For NPIW between 100 and 300 m, $B$ at Sta. A4 and A7 were the same average value as the surface water. In general, the origin of NPIW was derived from the dense shelf water from the Sea of Okhotsk (Yasuda, 1997). The Sea of Okhotsk region is located at a higher latitude than Sta. A4, and $B$ should be expected to be higher than the surface water. However, we observed an unexpected value of $B$ in NPIW. When forming the dense shelf water in the wintertime, sea surface water of the Sea of Okhotsk is covered by ice due to the strong cooling from the air mass of Siberia. Therefore, the air–sea gas exchange may be weakened by the sea ice coverage, and consequently we could observe the lower value of $B$ in NPIW.

The warm water between 300 and 1000 m had a middle value of $B$ between the surface water and NPDW. This water mass is produced in the south area (Nagata et al., 1992) and might be influenced by the relatively calm sea surface state than at high latitudes or the mixture of water mass having bubble injection with ambient water mass having no bubble injection.

NPDW between 1000 and 3000 m had a large fluctuation of $B$. We found that its maxima and minima were upper and lower parts in NPDW at Sta. A7, respectively. NPDW is generally produced by a mixture of North Atlantic deep water and Antarctic circumpolar deep water (e.g. Orsi et al., 2002). Therefore, it is difficult to discuss $B$ in detail in this water. Craig and Weiss (1971) found that Atlantic deep water had $B$ of about 22 to 45 μmol/kg using saturation anomalies of He and Ne, based on the amounts of saturation of each gas with the changes of water temperature, atmospheric pressure and air injection. In our study, $B$ in NPDW was estimated to be 12–35 μmol/kg, which almost agreed with results of Craig and Weiss (1971) within uncertainty (Table 2). In this study, as each water mass had a different value of $B$, it is possible that we can use $B$ as an index of the sea surface state.

### 3.5. Estimation of the preformed DO

Applying our new concept of $B$ to dissolved oxygen (DO), we can obtain new information on the actual oxygen utilization in the ocean field. Generally, in the wintertime when the sea surface is at high latitudes, the generation of oxygen derived from photosynthesis is minimal, and the oxygen concentration will be

<table>
<thead>
<tr>
<th>$B$ (μmol/kg)</th>
<th>$C_{\text{PreDO}}$ (μmol/kg)</th>
<th>$\Delta\text{preDO}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Range</td>
<td>Average (SE)</td>
<td>Range</td>
</tr>
<tr>
<td>Surface water</td>
<td>Sta. 4 ($n=8$)</td>
<td>24–43</td>
</tr>
<tr>
<td>(0–100 m)</td>
<td>Sta. 7 ($n=7$)</td>
<td>12–22</td>
</tr>
<tr>
<td>NPIW</td>
<td>Sta. 4 ($n=5$)</td>
<td>27–43</td>
</tr>
<tr>
<td>(100–300 m)</td>
<td>Sta. 7 ($n=5$)</td>
<td>12–22</td>
</tr>
<tr>
<td>Warm water</td>
<td>Sta. 4 ($n=5$)</td>
<td>20–35</td>
</tr>
<tr>
<td>(300–1000 m)</td>
<td>Sta. 7 ($n=7$)</td>
<td>15–35</td>
</tr>
<tr>
<td>NPDW</td>
<td>Sta. 4 ($n=7$)</td>
<td>21–27</td>
</tr>
<tr>
<td>(1000–3000 m)</td>
<td>Sta. 7 ($n=9$)</td>
<td>15–35</td>
</tr>
</tbody>
</table>

Atlantic deep water 22–45*  –  –  –  –  –  –  –  Kester (1975)

* This value was obtained from Ne, Ar and He (Kester, 1975).
controlled by the air–sea gas exchange. Therefore, it is possible to estimate the preformed DO $(C_{\text{preDO}})$ by using $B$ required for N$_2$ and Ar (see details in Section 3.3).

We estimate $C_{\text{preDO}}$ using the following equation;

$$C_{\text{preDO}} = E_{O_2} A C_{O_2(\text{sat})} + 0.2095 B$$  \(5\)

where $E_{O_2}$ defines the ratio of imaginary saturation state of O$_2$ to N$_2$ correcting the difference between $S_{C_N2}$ and $S_{C_O2}$, similar the case with $E_{Ar}$ (we estimated $E_{O2}$ for $S=33.5$, $T=0$ and $H=100$ m, see details in Section 3.3). We also used the constant coefficient of 0.2095 as the atmospheric mixing ratio of O$_2$. We calculated the saturated content of DO $(C_{O_2(\text{sat})})$ by using the equation of Garcfa and Gordon (1992) with in situ $T$ and $S$.

We showed the vertical distributions of $C_{\text{preDO}}$ and saturation state of $C_{\text{preDO}}$ $(C_{\text{preDO}}/C_{O_2(\text{sat})} - 1$, $\Delta_{\text{preDO}}$) based on the observational values of $A$ and $B$ derived from N$_2$ and Ar with Eq. (5) (Fig. 8). We found $C_{\text{preDO}}$ had values from 309 to 332 $\mu$mol/kg, and $\Delta_{\text{preDO}}$ from $-7.0$ to $-8.0$% (Table 2). All values of $C_{\text{preDO}}$ were undersaturated, hence this indicates that AOU was overestimated. Thus, it is possible that $C_{O_2(\text{sat})}$ cannot show the actual oxygen content in the surface layer derived from the gas exchange, compared to $C_{\text{preDO}}$. The difference between $C_{\text{preDO}}$ and content of DO in the ocean interior may be useful as an index of biogenic organic reductions in the ocean field instead of AOU.

Moreover, until now, AOU has been used to estimate the ocean uptake of anthropogenic CO$_2$ in the general back calculation methods (e.g., Ono et al., 2000). If AOU of these methods interchanges with the difference between $C_{\text{preDO}}$ to $C_{O2}$, anthropogenic CO$_2$ can be increased. Due to the actual decrease of $C_{O2}$ from preformed oxygen being caused by organic decomposition, it is necessary to re-estimate the oceanic uptake of anthropogenic CO$_2$ by using our new concept of N$_2$ and Ar.

4. Conclusion

In this study, we proposed a new concept on the estimation of the amount of bubble injection $(B)$ with a high accuracy and short analytical time for N$_2$, Ar and O$_2$ compared to previous studies (Gamo and Horibe, 1980; Nakayama et al., 2002), we have improved the following four points: (I) To improve the precision of these gases, we added a purge-trap column (Air Trap) system (5 cm of 60/80 mesh MS-5A packed in a 1/8 in. o.d. ss tubing put into a $-198 \degree$C liquid nitrogen bath) to concentrate N$_2$, Ar, and O$_2$ with CO$_2$. (II) To remove the contamination of samples N$_2$ from Ar–O$_2$ separation column, we added an N$_2$–CO$_2$ Trap system (5 cm of 60/80 mesh MS-5A packed in a 1/8 in. o.d. ss tubing put into a $-198 \degree$C liquid nitrogen bath) after operation of the Air Trap system. Consequently, all amounts of stripping gases were analyzed by dual-TCD-GC system. (III) To improve the accuracy of N$_2$, Ar and O$_2$, we added a CO$_2$ backflushing system (pre-column made by 60/80 mesh the active carbon in a coil of 1/8 in. o.d. ss tubing (30 cm) and main column made by 60/80 mesh the active carbon in a coil of 1/8 in. o.d. ss tubing (3 m) put into 100 $\degree$C GC oven) for separating N$_2$ and CO$_2$ completely. (IV) Finally, we introduced automatic valves to most of valves controlling the system to improve the analytical precision of N$_2$, Ar and O$_2$. Consequently, the precisions of these...
measurements were 0.04%, 0.05% and 0.02%, which were higher than those in the previous studies. Moreover, we achieved the analytical time of 600 s, which was shorter compared to the previous studies, suggesting that our system is suitable for measuring many samples with high precision.

Using our improved analytical technique, we observed N2 concentration (C_{N2}, 561.69–611.81 μmol/kg), Ar concentration (C_{Ar}, 15.126–16.238 μmol/kg), saturation state of N2 (∆N2, −5.1–0.9%) and saturation state of Ar (∆Ar, −7.0 to −1.1%) at Sta. 4 and Sta. 7 of the A-line in March 2005. We also estimated B (12–43 μmol/kg) in this region using their observational values with Eqs. (3) and (4). As each water mass had a different value of B in the vertical distribution, it is possible that we can use B as an index of the sea surface state for water masses formed on the sea surface.

Moreover, we estimated the preformed dissolved oxygen (DO) (C_{preDO}, 309–332 μmol/kg) and supersaturation of C_{preDO} (∆preDO, −7.0 to −1.2%), using B with Eq. (5). Assuming that C_{O2(sat)} cannot show the actual oxygen content in the surface layer derived from the gas exchange, compared to C_{preDO}. Thus, the difference between C_{preDO} and DO in the ocean interior may be a useful index of biogenic organic reductions in the ocean field instead of Apparent Oxygen Utilization (AOU). Until now, AOU has been used to estimate the ocean uptake of atmospheric anthropogenic CO2 in the general back calculation methods (e.g., Ono et al., 2000). Due to the actual decrease of DO from preformed oxygen being caused by organic decomposition, it may be necessary to re-evaluate the oceanic uptake of anthropogenic CO2 based on our new concept of B.

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