### 3.3.3 Dissolved oxygen

(1) Personnel

Ryosuke MAKABE (NIPR): Principal investigator

Shinichiro YOKOGAWA (MWJ): Operation leader

(2) Objection

To monitor long-term variability of dissolved oxygen along 110$^{o}$ E transect.

To evaluate the Antarctic Deep Water in the sea ice area.

(3) Pramerter

Dissolved oxygen measured by Winkler titration method

(4) Instruments and Methods

Following procedure is based on an analytical method, entitled by "Determination of dissolved oxygen in sea water by Winkler titration", in the WHP Operations and Methods (Dickson, 1996).

a. Instruments

Burette for sodium thiosulfate and potassium iodate;

808 Titrando manufactured by Metrohm / 10 cm$^{3}$ of titration vessel

789 MPT Titrino manufactured by Metrohm / 10 cm$^{3}$ of titration vessel

b. Reagents

Pickling Reagent I: Manganese chloride solution (3 mol dm$^{-3}$)

Pickling Reagent II: Sodium hydroxide (8 mol dm$^{-3}$) / sodium iodide solution (4 mol dm$^{-3}$)

Sulfuric acid solution (5 mol dm$^{-3}$)

Sodium thiosulfate (0.025 mol dm$^{-3}$)

Potassium iodide (0.001667 mol dm$^{-3}$)

CSK standard of potassium iodide:KPG6393 Wako Pure Chemical Industries Ltd., 0.0100N

c. Sampling

Seawater samples were collected with Niskin bottle attached to the CTD-system and surface bucket sampler. Seawater for oxygen measurement was transferred from sampler to a volume calibrated flask (ca. 100 cm$^{3}$). Three times volume of the flask of seawater was overflowed. Temperature was measured by digital thermometer during the overflowing. Then two reagent solutions (Reagent I and II) of 0.5 cm$^{3}$ each were added immediately into the sample flask and the stopper was inserted carefully into the flask. The sample flask was then shaken vigorously to mix the contents and to disperse the precipitate finely throughout. After the precipitate has settled at least halfway down the flask, the flask was shaken again vigorously to disperse the precipitate. The sample flasks containing pickled samples were stored in a laboratory until they were titrated.

d. Sample measurement

At least two hours after the re-shaking, the pickled samples were measured on board. 1 cm$^{3}$ sulfuric acid solution and a magnetic stirrer bar were added into the sample flask and stirring

began. Samples were titrated by sodium thiosulfate solution whose morality was determined by potassium iodate solution. Temperature of sodium thiosulfate during titration was recorded by a digital thermometer. During this cruise, we measured dissolved oxygen concentration using 1sets of the titration apparatus. Dissolved oxygen concentration (μmol $L^{-1}$) was calculated by sample temperature during seawater sampling, flask volume, and titrated volume of sodium thiosulfate solution without the blank.

e. Standardization and determination of the blank

Concentration of sodium thiosulfate titrant was determined by potassium iodate solution. Pure potassium iodate was dried in an oven at 130 $^{o}$C. 1.7835 g potassium iodate weighed out accurately was dissolved in deionized water and diluted to final volume of 5 $dm^3$ in a calibrated volumetric flask (0.001667 mol $dm^{-3}$). 10 $cm^3$ of the standard potassium iodate solution was added to a flask using a volume-calibrated dispenser. Then 90 $cm^3$ of deionized water, 1 $cm^3$ of sulfuric acid solution, and 0.5 $cm^3$ of pickling reagent solution II and I were added into the flask in order. Amount of titrated volume of sodium thiosulfate (usually 5 times measurements average) gave the morality of sodium thiosulfate titrant.

The oxygen in the pickling reagents I (0.5 $cm^3$) and II (0.5 $cm^3$) was assumed to be 3.8 x $10^{-8}$ mol (Murray *et al.*, 1968). The blank due to other than oxygen was determined as follows. 1 and 2 $cm^3$ of the standard potassium iodate solution were added to two flasks respectively using a calibrated dispenser. Then 100 $cm^3$ of deionized water, 1 $cm^3$ of sulfuric acid solution, and 0.5 $cm^3$ of pickling reagent solution II and I each were added into the flask in order. The blank was determined by difference between the first (1 $cm^3$ of $KIO_3$) titrated volume of the sodium thiosulfate and the second (2 $cm^3$ of $KIO_3$) one. The results of 3 times blank determinations were averaged.

Table 3.3.3 shows results of the standardization and the blank determination during this cruise.

| Date | $KIO_3$ ID | $Na_2S_2O_3$ | 808 Titrando | | Stations |
|---|---|---|---|---|---|
| | | | E.P. | Blank | |
| 2016/01/14 | K1504G01 | T1505P-1&2 | 3.967 | 0.000 | - |
| 2016/01/16 | CSK_KPG6393 | T1505P-1&2 | 3.968 | - | - |
| 2016/01/16 | K1504G02 | T1505P-1&2 | 3.965 | 0.006 | KC1,KC2, KC3,KC4 |
| 2016/01/23 | K1504G03 | T1505P-1&2 | 3.966 | -0.001 | KC5, KC6 |
| 2016/01/31 | K1504G04 | T1505P-1&2 | 3.969 | 0.003 | |

f. Repeatability of sample measurement

Replicate samples were taken at every CTD casts. Total amount of the replicate sample pairs of good measurement was 15. The standard deviation of the replicate measurement was 0.15 μmol $L^{-1}$ that was calculated by a procedure in Guide to best practices for ocean $CO_2$ measurements Chapter4 SOP23 Ver.3.0 (2007).

(4) Data archive

All raw data were attached in appendix of this cruise report. Quality checked data are archived in National Institute of Polar Research (NIPR), and published as JARE data reports within one year.

(5) References

Dickson, A.G., Determination of dissolved oxygen in sea water by Winkler titration. (1996)

Dickson, A.G., Sabine, C.L. and Christian, J.R. (Eds.), Guide to best practices for ocean CO2 measurements. (2007)

Culberson, C.H., WHP Operations and Methods July-1991 “Dissolved Oxygen”, (1991)

Japan Meteorological Agency, Oceanographic research guidelines（Part 1）. (1999)