

5.16 Dissolved oxygen of sampled water

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(2) Objectives

Determination of dissolved oxygen in seawater by Winkler titration.

(3) 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:

APB-620 manufactured by Kyoto Electronic Co. Ltd. / 10 cm³ of titration vessel.

Detector:

Automatic photometric titrator (DOT-01X) manufactured by Kimoto Electronic Co. Ltd.

Software:

DOT Terminal version 1.2.0

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:

Lot EPJ3885, 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 cm³). 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 cm³ 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 cm³ 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 2 sets of the titration apparatus. Dissolved oxygen concentration ($\mu\text{mol kg}^{-1}$) was calculated by sample temperature during seawater sampling, CTD salinity, 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 °C. 1.7835 g potassium iodate weighed out accurately was dissolved in deionized water and diluted to final volume of 5 dm³ in a calibrated volumetric flask (0.001667 mol dm⁻³). 10 cm³ of the standard potassium iodate solution was added to a flask using a volume-calibrated dispenser. Then 90 cm³ of deionized water, 1 cm³ of sulfuric acid solution, and 0.5 cm³ 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 cm³) and II (0.5 cm³) was assumed to be 3.8×10^{-8} mol (Murray *et al.*, 1968). The blank due to other than oxygen was determined as follows. 1 and 2 cm³ of the standard potassium iodate solution were added to two flasks respectively using a calibrated dispenser. Then 100 cm³ of deionized water, 1 cm³ of sulfuric acid solution, and 0.5 cm³ 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 cm³ of KIO₃) titrated volume of the sodium thiosulfate and the second (2 cm³ of KIO₃) one. The results of 3 times blank determinations were averaged.

(4) Preliminary Results

Table 5.16-1 shows results of the standardization and the blank determination during this cruise.

Table 5.16-1: Results of the standardization and the blank determinations.

Data	KIO ₃ ID	Na ₂ S ₂ O ₃	DOT-01X(No.7)		DOT-01X(No.8)	
			E.P.	Blank	E.P.	Blank
2011/09/27	CSK	20110602-22	3.947	-0.005	3.953	0.000
2011/09/27	20110523-03-01	20110602-22	3.951	-0.005	3.956	0.000
2011/10/02	20110523-03-02	20110602-22	3.956	-0.004	3.959	0.004
2011/10/06	20110523-03-03	20110602-22	3.956	-0.003	3.960	0.003
2011/10/06	20110523-03-03	20110602-24	3.951	-0.003	3.957	0.002
2011/10/10	20110523-03-04	20110602-24	3.953	-0.002	3.958	0.004
2011/10/14	20110523-03-05	20110602-24	3.955	-0.002	3.960	0.003
2011/10/18	20110523-03-06	20110602-24	3.957	0.001	3.961	0.006
2011/10/18	20110523-03-06	20110602-25	3.953	-0.003	3.958	0.004
2011/10/22	20110523-03-07	20110602-25	3.953	-0.002	3.958	0.004
2011/10/25	20110523-03-08	20110602-25	3.953	-0.002	3.958	0.004

Table 5.16-1 (cont'd)

Data	KIO ₃ ID	Na ₂ S ₂ O ₃	DOT-01X(No.5)		DOT-01X(No.6)	
			E.P.	Blank	E.P.	Blank
2011/10/30	20110523-03-09	20110602-26	3.947	-0.003	3.953	0.001
2011/11/03	20110523-03-10	20110602-26	3.949	-0.001	3.953	0.002
2011/11/07	20110523-04-01	20110602-26	3.951	-0.002	3.955	0.004
2011/11/07	CSK	20110602-26	3.947	-0.002	3.950	0.004

Data	KIO ₃ ID	Na ₂ S ₂ O ₃	DOT-01X(No.5)		DOT-01X(No.8)	
			E.P.	Blank	E.P.	Blank
2011/11/11	20110523-04-02	20110602-26	3.952	-0.001	3.955	0.002
2011/11/15	20110523-04-03	20110602-26	3.955	-0.001	3.954	0.001
2011/11/18	20110523-04-09	20110602-26	3.959	0.002	3.959	0.002
2011/11/18	20110523-04-09	20110602-27	3.951	-0.002	3.955	0.001
2011/11/23	20110523-04-04	20110602-27	3.951	-0.003	3.955	0.002
2011/11/28	20110523-04-05	20110602-27	3.951	-0.003	3.955	0.000

f. Repeatability of sample measurement

Replicate samples were taken at every CTD casts. Total amount of the replicate sample pairs of good measurement was 413. The standard deviation of the replicate measurement was 0.15 $\mu\text{mol kg}^{-1}$ that was calculated by a procedure in Guide to best practices for ocean CO₂ measurements Chapter4 SOP23 Ver.3.0 (2007).

(5) Data archive

All raw datasets will be submitted to JAMSTEC Data Management Office (DMO).

(6) 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)
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 Japan Meteorological Agency, Oceanographic research guidelines (Part 1). (1999)
 KIMOTO electric CO. LTD., Automatic photometric titrator DOT-01X Instruction manual