

Winkler titration accessories for the use with SiS DOA

This text is based on papers from [WOCE](#), J. H. Carpenter and Grasshoff and on experience from SiS. Please see the [reference section](#) for these and other references. Behind the chemical formula of the reagents you will find the required concentration and the cat. no. from [Merck, Darmstadt, Germany](#).

1. Reagents

1.1. Sodium hydroxide - sodium iodide

NaOH 320 g/l, 8 molar Merck No. 106498 (500, 1000, 5000 g)

NaI 600 g/l, 4 molar Merck No. 106523 (100, 250, 1000 g)

1.1.1 Preparation of NaOH solution

Pour approximately 40 % of the water into a beaker. Dissolve the NaOH reagent slowly while stirring. If necessary, add some more water. CAUTION: The chemical reaction produces heat.

1.1.2 Preparation of NaI solution

Pour approximately 35 % of the water into a beaker. Dissolve the NaI reagent slowly while stirring. If necessary, add some more water. The reaction may be speeded up by heating the solution. The final solution must be clear and yellow coloured.

1.1.3 Mixing the solutions

Fill up both solutions to the final concentration and mix them together.

1.2. Manganous chloride solution

$\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ 600 g/l, 3 molar Merck No. 105927 (100, 1000 g)

Pour approximately 80 % of the water volume into a beaker and dissolve the manganous chloride while stirring. Fill up with water to the final concentration.

1.3. Sulfuric acid

H_2SO_4 280 ml/l (28%), 5 molar

The sulfuric acid may be more concentrated (up to 50 %), if the volumes added to the samples will be smaller.

1.4. Sodium thiosulfate solution

$\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ 35g/l, 0.14 molar Merck No. 106516 (100, 500, 1000 g)

The final titer concentration should be optimized for the used equipment (bottle volumes, burette volume) and expected oxygen concentrations. Please see also the SiS paper about choosing optimal titer concentrations: [Selection of the standard and the titer...](#)

1.5. Standard solution

KIO_3 0.3567 g/l, 0.00167 molar

Alternatively commercial prepared solution:

Titrisol 3.567 g KIO_3 for 1 l solution, Potassium iodate solution 1/60 mol/l, 0.1 N solution Merck No. 109917

This concentrated solution has an accuracy of 0.2%. For higher accuracies the standard has to be prepared manually.

2. Sample flasks

Due to the optical endpoint determination of the DOA system, the sample bottles must be clear with vertical sides. Typical flask volumes are in the range from 50 to 250 ml. A good choice are reagent bottles with wide mouth, cone ground and glass stopper. This kind of bottles is available from the Schott company with 50, 100 and 250 ml volumes made from DURAN (borosilicate) or soda-lime glass. Bottles with small mouth may be also used, but may require removing of water before titration to free volume for reagents, stirring bar and titer.

3. Stirring bars

The stirring bars should be optimized for the used bottles, but not too small. For 50 ml bottles we recommend cylindrical 20 x 6 mm bars.

4. Reagent dispensers

Due to the replacement of sample water by the reagents, the used dispensers should have a high precision. A high precision dispenser is also required for the standard solution.

4.1 Dispenser volumes (according to reagent volumes)

The volumes of the NaOH-Nal and MnCl_2 reagents depend on the used bottle volume and the highest expected oxygen concentration. For small bottles (50 ml) volumes of 0.5 ml each are enough. Greater bottles may require volumes of 1.0 ml each. At least there must be enough reagent to react with all free oxygen molecules.

The volume of the sulfuric acid is more critical. The pH value of the final solution must be optimized. Carpenter specifies pH values from 2.0 to 2.7. This seems to be too high for our point of view. According to Grasshoff and others we recommend pH values about 1.0. At SiS we are using volumes of 0.5 ml for the reagents and 1.0 ml for the 50 % sulfuric acid with 50 ml bottles.

The volume of the standard solution depends on various parameters. For best results the volume should be dimensioned to dispense nearly one burette volume of titer at standardization. Please see also the SiS paper [Selection of the standard and the titer...](#)

References

Bigg, P. H., 1967. Density of water in S.I. units over the range 0-40°C. British Journal of Applied Physics, 18, 521-537.

Carpenter, J. H., 1965. The Chesapeake Bay Institute technique for the Winkler dissolved oxygen method. Limnology and Oceanography, 10, 141-143.

Culberson, C. H., 1991. Dissolved oxygen. WOCE Operations Manual, Part 3.1.1 : WHP Operations and Methods, WHP Office Report WHPO 91-1, WOCE Report No. 68/91.

Deutsches Institut für Normung, 1992. Wasserbeschaffenheit; Bestimmung des gelösten Sauerstoffs;

Iodometrisches Verfahren (ISO 5813 : 1983). Deutsche Fassung EN 25 813 : 1992.

Dickson, 1996. Determination of dissolved oxygen in sea water by Winkler titration. WHP

European Committee for Standardization, 1992. Water quality; Determination of dissolved oxygen; Iodometric method (ISO 5813 : 1983). ES 25 813.

Grasshoff, K., 1976. Methods of seawater analysis. Verlag Chemie. Chapter 4; Determination of oxygen.

International Standardization Organization, 1983. Water quality - Determination of dissolved oxygen - Iodometric method. ISO 5813 : 1983.

Millero F. J. and A. Poisson, 1981. International one-atmosphere equation of state of seawater. Deep Sea Res., 28, 625-629.

Murray, C. N., J. P. Riley, and T. R. S. Wilson, 1968. The solubility of oxygen in Winkler reagents used for the determination of dissolved oxygen. Deep Sea Res., 15, 237-238.

Weiss, R. F., 1981. Oxygen solubility in seawater. UNESCO Technical Papers in Marine Science. No. 36:22.

Winkler, L. W., 1888. Die Bestimmung des im Wasser gelösten Sauerstoffes. Ber. dtsh. chem. Ges., 21, 2843-2855.

Links

whpo.ucsd.edu	WOCE Hydrographic Program Office
whpo.ucsd.edu/manuals.htm	WOCE Hydrographic Program Office. Manuals and documentation
www.merck.de/english/index.htm	Merck KGaA, Darmstadt
www.schott.com	Schott
www.schott.com/duran/download	Schott catalogues

SiS Sensoren Instrumente Systeme GmbH
Mühlenkoppel 12
24147 Klausdorf
Germany
Tel.: +49-431-79972-0
Fax: +49-431-79972-11
Email: info@sis-germany.com
WWW: <http://www.sis-germany.com>

HTML version of this document: <http://www.sis-germany.com/doachem.htm>