



Baltic Marine Environment Protection Commission

Working Group on the State of the Environment and Nature
Conservation

STATE & CONSERVATION
5-2016

Tallinn, Estonia, 7-11 November, 2016

Document title	Determination of dissolved oxygen – draft monitoring guidelines
Code	2MA-6
Category	CMNT
Agenda Item	2MA – Revision of HELCOM monitoring
Submission date	14.10.2016
Submitted by	Sweden

Background

HELCOM guidelines for hydrography and hydrochemistry are currently being revised. Lead Country Sweden submits draft guidelines for determination of dissolved oxygen in the HELCOM area as a contribution to the ongoing revision of HELCOM monitoring guidelines.

Determination of dissolved oxygen is currently described in Annex B-8 in the *Manual for monitoring in the COMBINE programme in HELCOM*. The draft for revised guidelines include updates on procedure. The QA/QC section is expanded and a reference for estimation of measurement uncertainty has been added.

The draft has been reviewed by representatives from Co-Lead Country Poland, Denmark, Estonia, Finland and Germany. The representatives from contributing countries agreed that the draft guidelines need further work before it is ready for endorsement.

Action requested

The Meeting is invited to comment and amend as needed the draft guidelines for determination of dissolved oxygen.

Determination of dissolved oxygen in seawater

1 Background

1.1 Introduction

The dissolved oxygen (DO) content in sea water is controlled by several unrelated processes including exchange with air, metabolism of plants and animals, microbial and chemical decomposition of organic matter, hydrodynamic features such as mixing, advection, convection, and up- or down-welling. The DO content is always the result of multifactorial influences and the reasons for changes may be difficult to assess. In stratified Baltic waters, DO depletion occurs regularly below the halocline.

When only physical processes are involved, the DO concentration in water is governed by the laws of solubility, i.e., it is a function of atmospheric pressure, water temperature, and salinity. The corresponding equilibrium concentration is generally called solubility. It is an essential reference for the interpretation of DO data. Precise solubility data, tables, and mathematical functions have been established (Carpenter, 1966; Murray and Riley, 1969; Weiss, 1970) and adopted by the international community (UNESCO, 1973). However, Weiss (1981) drew attention to an error in the international tables in which the values are low by 0.10 % since they are based on ideal gas molar volume instead of actual dioxygen molar volume. Later, the Joint Panel on Oceanographic Tables and Standards (JPOTS) recommended that the oxygen solubility equation of Benson and Krause (1984), which incorporated improved solubility measurements, be adopted and the tables updated (UNESCO, 1986). However, the UNESCO paper only referred to the equation that gives concentrations in the unit $\mu\text{mol kg}^{-1}$.

1.2 Purpose and aims

The purpose of the monitoring is to map the spatial distribution of DO and hydrogen sulphide, with the aim to be able to assess the status of the seafloor and the waters above. The monitoring should be carried out a few times per year especially during late summer/autumn.

2 Monitoring methods

2.1 Monitoring features

The monitoring of DO is done in combination with hydrogen sulphide measurements to assess the level of oxygen depletion.

2.2 Time and area

The DO/hydrogen sulphide should be monitored a few times per year, particularly in critical areas and season (e.g. the late summer/autumn).

2.3 Monitoring procedure

2.3.1 Monitoring strategy

The standard procedure for the determination of DO in water is the Winkler method in several modifications (e.g., Carpenter, 1965; Hansen, 1999; ICES, 1997). It is based on the reaction of DO with iodide ion to iodine in alkaline solution in the presence of manganese (II) ion. Iodine is back titrated with standardized thiosulphate in acid solution. The endpoint can either be detected visually (see EN 25813: 1993 and ISO 5813: 1983) or in automated methods, by spectrometric or electrochemical means.

Electrochemical probes for DO exploit the reduction of oxygen to produce a current that is expressed in DO equivalents. Sensors on a polarographic or galvanic basis also exist (see EN 25814: 1992 and ISO 5814: 1990). In connection with a CTD probe, continuous profiling is feasible. Hysteresis between down- and up-profiling is possible and depends on the response times of the sensors. Many of these sensors are poisoned by hydrogen sulphide and not suited for use in anoxic waters. The best way to avoid this is not to lower the sond into any anoxic water layers, which will make it rather impractical in many areas of the Baltic Sea. If a sensor has been lowered into hydrogen sulphide containing water, it must be checked immediately.

2.3.2 Sampling methods and equipment

The basic method for the determination of oxygen concentration is the Winkler method (Grasshoff et al., 1983). Oxygen sensors may be used, though it is highly recommended to take water samples in areas with low oxygen concentration (below 2 ml l⁻¹).

It should first of all be noted that the subsampling of oxygen samples is the most critical step of the total analysis. It is of utmost importance that this step is carried out by trained and experienced staff. Samplers suitable for other water sampling can be used for oxygen. A special bottom water sampler could be useful for studying the oxygen conditions in the near-bottom water layer.

DO samples should be the first to be drawn from the water samplers. For subsampling and titration, only glass bottles with conical-shaped tops and with glass ground stoppers meet the requirements of the Winkler method. Subsample bottles must be calibrated and identified with their stoppers since they must not be interchanged. Subsamples are drawn with a flexible plastic tube attached to the water samplers reaching to the bottom of the glass bottle. Fill and overflow each bottle with at least three volumes. Make sure not to draw any air bubbles into the sample. Reagents are added with the dispenser tip submerged at least 1 cm below the neck of the vial. The inserted stopper displaces the excess of water. Carefully avoid contact with reagent and trapping bubbles. The sample is mixed by thoroughly shaking, as this is a very critical step in the fixation of the oxygen. Some laboratories prefer to mix a second time after a few

minutes to maximize the contact between the sample and the reagents.

If oxygen sensors are used (e.g., attached to the CTD), regular checks of the reproducibility of the sensor have to be carried out by titration of water samples by the Winkler method. At least the surface reading has to be calibrated. Oxygen sensors cannot be properly calibrated against moist air (100% saturation).

2.3.3 Sample handling and analysis

Oxygen samples may be stored for up to 24 hours after adding the reagents and after complete fixation. The bottles should be kept in the dark and any change in temperature should be avoided. The bottles can be stored under a waterlock for up to one month.

If sensors for DO are used (at fixed stations or attached to the CTD), regular checks and calibrations have to be made by titration of water samples by the Winkler method.

2.4 Data analysis

The 100% saturation of DO can be calculated for the specific water when salinity and temperature are known. Below, equations are given for the calculation of solubility values of DO, in various units, according to the UNESCO recommendation. These equations are directly taken from the paper of Benson and Krause (1984), where two equations are provided for calculation in either $\mu\text{mol kg}^{-1}$ or in $\mu\text{mol l}^{-1}$. The calculation of saturation requires the *in situ* temperature known to ± 0.1 °C and salinity within 0.2 (PSS 78). To allow conversion between different units, the sample temperature at the addition of the reagents should be reported, if significantly different from the *in situ* sample temperature.

The following symbols are used:

T : temperature in Kelvin (K) = temperature in (t °C) + 273.15,

S : salinity on the Practical Salinity Scale 1978 (PSS78),

Cs : DO solubility concentration (the unit is mentioned using subscripts).

The equations can be expressed as follows:

$$\ln C_{s(\mu\text{mol kg}^{-1})} = A + B/T + C/T^2 + D/T^3 + E/T^4 - S \times (F + G/T + H/T^2),$$

and

$$\ln C_{s(\mu\text{mol l}^{-1})} = I + J/T + K/T^2 + L/T^3 + M/T^4 - S \times (N + P/T + Q/T^2).$$

The constants A to Q are the following:

micromole per kilogram	micromole per litre
A = -135.29996	I = -135.90205
B = +1.572288 × 10⁵	J = +1.575701 × 10 ⁵
C = -6.637149 × 10⁷	K = -6.642308 × 10 ⁷
D = +1.243678 × 10¹⁰	L = +1.243800 × 10 ¹⁰
E = -8.621061 × 10¹¹	M = -8.621949 × 10 ¹¹
F = +0.020573	N = +0.017674
G = -12.142	P = -10.754
H = +2363.1	Q = +2140.7

Application domain: $t = 0-40$ °C; $S = 0-40$.

Cs is obtained as:

$$Cs = \exp(\ln Cs),$$

Solubility in **milligram per litre** is obtained from the value in micromole per litre by multiplying by the molar mass of O₂ and 10⁻³ for unit consistency:

$$Cs_{(\text{mg l}^{-1})} = Cs_{(\text{μmol l}^{-1})} \times 31.9988 \text{ g mol}^{-1} \times 10^{-3}$$

Solubility in **millilitre per litre** is obtained from the value in micromole per litre by multiplying by the molar volume of the gas at standard temperature and pressure (STP; 0 °C, 1 atmosphere). For that conversion, some data previously published refer to the molar volume (STP) of dioxygen (O₂; 0.0223916 ml μmol⁻¹), like those of Weiss (1970), while others refer to that of an ideal gas (0.022414 ml μmol⁻¹), like those of the UNESCO tables and Benson and Krause (1984).

Referring to exact O₂ molar volume:

$$Cs_{(\text{ml l}^{-1})} = Cs_{(\text{μmol l}^{-1})} \times 0.0223916 \text{ ml μmol}^{-1}$$

The saturation is then expressed as the % O₂ measured compared to the O₂ calculated.

The calculations can be checked against the oceanographic calculator at the ICES webpage, where the same equations are used. They are available on the ICES website at <http://ocean.ices.dk/Tools/Calculator.aspx>.

3 Data reporting and storage

DO concentrations should be reported in ml/l O₂ at NTP and/or in % of saturation (Weiss, 1970).

4 Quality control

4.1 Quality control of methods

Minimum analytical requirements are;

limit of detection (LOD) 0.02 ml l⁻¹,

accuracy 0.03 ml l⁻¹,

limit of quantification (LOQ) 0.1 ml l⁻¹.

With the Winkler method, a repeatability of 0.1 % can be achieved in the upper concentration range.

There is no Certified Reference Material for oxygen in water. The reference method is the properly performed Winkler method (Hansen, 1999). The quality assurance relies to a very high degree on good practice applied by experienced staff. Water stored with air contact for several weeks at a stable temperature can be used as a Laboratory Reference Material for control charts.

Essential procedures include:

1. calibration and identification of sample bottles and their respective stoppers
2. calibration of volumetric flasks and dispensers
3. control charts for reagent and titration blanks
4. control charts of precision by replicate samples
5. in case automated titration is used, check the accuracy of the addition of the titrand

Replicate samples can be taken from the same sampler, but ideally from different samplers triggered at the same depth in deep water.

Blanks can be checked by adding double or triple amounts of reagents to identical samples.

Several publications contain descriptions of how the calibration should be performed and quality assurance can be achieved (WOCE, 1994; ICES, 1997). The demands of the COMBINE program are exceeded by WOCE (World Ocean Circulation Experiment) standards.

Laboratories should have established a quality management system according to EN ISO/IEC 17025.

Measurement uncertainty should be estimated using ISO 11352. Estimation should be based on within-laboratory reproducibility, and, when available, data from proficiency testings and intercalibrations.

4.2 Quality control of data and reporting

If hydrogen sulphide is positive, discard the oxygen results.

Data must be flagged if normal QA routines or recommended storage conditions cannot be followed.

5 Contacts and references

5.1 Contact persons

Kristin Andreasson SMHI

5.2 References

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

Hansen, H.-P. 1999. Determination of oxygen. *In* *Methods of seawater analysis*, 3rd edition, pp. 75–89. Ed. by K. Grasshoff *et al.* Wiley-VCH, Germany.

ICES. 1997. Report of the Advisory Committee on the Marine Environment, 1997. ICES Cooperative Research Report, 222: 129–136.

ISO. 1983. Water quality; determination of dissolved oxygen; iodometric method. ISO 5813.

ISO. 1990. Water quality; determination of dissolved oxygen; electrochemical probe method. ISO 5814.

WOCE. 1994. Operational Manual. Volume 3: The Observational Programme.

ISO 11352*: Water quality – Estimation of measurement uncertainty based on validation and quality control data

EN ISO/IEC 17025*: General requirements for the competence of testing and calibration laboratories

* For undated references, the latest edition of the referenced document (including any amendments) applies

5.3 Additional literature

Benson, B.B., and Krause, D., Jr. 1984. The concentration and isotopic fractionation of oxygen dissolved in freshwater and seawater in equilibrium with the atmosphere. *Limnology and Oceanography*, 29: 620–632.

Carpenter, J.H. 1966. New measurements of oxygen solubility in pure and natural water. *Limnology and Oceanography*, 11: 264–277.

Culberson, C.H. 1991. Dissolved oxygen. *WOCE Hydrographic Programme Operations and Methods* (July 1991). 15 pp.

Lysiak-Pastuszak, E. and M. Krysell (Eds.).

Chemical measurements in the Baltic Sea: Guidelines on quality assurance.

ICES Techniques in Marine Environmental Sciences, No. 35. 149pp, ISBN 87-7482-021-4.

Murray, C.N., and Riley, J.P. 1969. The solubility of gases in distilled water and sea water - II. Oxygen. *Deep-Sea Research*, 16: 311–320.

UNESCO. 1973. *International oceanographic tables*, Vol. 2. NIO-UNESCO, Paris.

UNESCO. 1986. *Progress on oceanographic tables and standards 1983–1986: work and recommendations of the UNESCO/SCOR/ICES/IAPSO Joint Panel*. UNESCO Technical Papers in Marine Science, 50. 59 pp.

Weiss, R.F. 1970. The solubility of nitrogen, oxygen and argon in water and seawater. *Deep-Sea Research*, 17: 721–735.

Weiss, R.F. 1981. On the international oceanographic tables, Vol. 2, UNESCO 1973, Oxygen solubility in seawater. UNESCO Technical Papers in Marine Science, 36: 22.