Manual for Marine Monitoring in the

COMBINE

Programme of HELCOM

Part B

General guidelines on quality assurance for monitoring in the Baltic Sea

Annex B-8

Technical note on the determination of hydrographic parameters

Appendix 2
Technical note on the determination of dissolved oxygen in seawater

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ANNEX B-8: TECHNICAL NOTE ON THE DETERMINATION OF HYDROGRAPHIC PARAMETERS

ANNEX B-8 APPENDIX 2: TECHNICAL NOTE ON THE DETERMINATION OF DISSOLVED OXYGEN IN SEAWATER

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, and 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.

2. METHODS

The reference method for the determination of DO is the Winkler titration to the iodine endpoint. 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.

3. TECHNICAL ASPECTS OF SAMPLING

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 hydrochemical investigations can be employed 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 hydrocast bottles. 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 hydrocast bottle 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.

4. STORAGE AND PRE-TREATMENT

DO samples may be stored in the dark for 24 hours, and under water for a maximum of 4 weeks after the reagents have been added and the fixation is completed. Bottles should be kept free of change of temperature.

5. ANALYTICAL PROCEDURES

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).

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. If sulphide is positive, discard the oxygen results.

6. ANALYTICAL QUALITY ASSURANCE

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.

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 programme are exceeded by WOCE (World Ocean Circulation Experiment) standards.

Water stored with air contact for several weeks at a stable temperature can be used as a Laboratory Reference Material for control charts.

7. REPORTING OF RESULTS

DO concentrations should be reported in cm3/dm3 (ml/l) O2 at NTP and/or in % of saturation (Weiss, 1970).

The calculation of saturation also requires the *in situ* temperature known to ±0.1 EC 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.

Conversion factors for other units are:

- $cm^3/dm^3 \times 1.429 = mg/dm^3$;
- $mg/dm^3 \times 0.700 = cm^3/dm^3$;
- $cm^3/dm^3 \times 0.0893 = \mu M\ O_2$;
- $\mu M\ O_2 \times 11.20 = cm^3/dm^3$.

8. PRECISION

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

9. REFERENCES

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