



Revised JAMP Eutrophication Monitoring Guideline: Oxygen¹

(Agreement 2013-05)

1. Introduction

Dissolved oxygen concentration is used as an indicator of ecosystem health. Under Descriptor 5 of the Marine Strategy Framework Directive, oxygen deficiency in bottom waters is an indication of adverse effect of human-induced eutrophication. It is also used within the Water Framework Directive and an OSPAR ecological quality objective (EcoQO) has been established within an ecological quality framework for an ecosystem-based approach to the management of the North Sea (OSPAR, 2009).

Biological activity and hydrodynamic processes are the main causes of change in the oxygen concentration in seawater. Nutrient enrichment/eutrophication may give rise to increased rates of oxygen consumption, decreased oxygen concentrations and saturation percentages, mainly in deeper layers of stratified waters.

These guidelines are intended to support the monitoring requirements of the OSPAR Eutrophication Monitoring Programme (OSPAR, 2005) and will also support monitoring in accordance with the above Directives. The reader should refer to detailed guidance on sampling and measurement of dissolved oxygen in marine waters provided in Aminot (1997).

2. Purposes

The measurement of oxygen concentrations in water is carried out, *inter alia*, to:

- establish the spatial distribution and frequency of low oxygen concentrations;
- establish temporal trends in oxygen concentration over periods of several years;
- fulfil requirements of the Eutrophication Monitoring Programme and contribute to EU Member States' monitoring under the Marine Strategy Framework Directive.

3. Quantitative objectives

The quantitative objectives of the monitoring programme must take into account the characteristics (e.g. diurnal and seasonal variability in dissolved oxygen) of the marine areas concerned and the purpose of the programme.

It is intended that the region-specific temporal trend monitoring programme should have the power (e.g. 90%) to detect a change in concentration (e.g. 10%) over a selected period (e.g. 6 years, consistent with the MSFD). If necessary, to clarify the situation and to help define achievable objectives, contracting parties should undertake statistical analyses of their existing data sets. This would help to determine the representativeness of the monitoring stations and thus the selection of suitable sampling stations and sampling strategies to meet achievable quantitative objectives.

A spatial distribution monitoring programme should enable contracting parties to determine the representativeness of their monitoring stations with regard to spatial variability in oxygen concentrations. This would include a definition of the extent of the monitoring area.

¹ Replaces Agreement 1997-03

4. Sampling strategy

Oxygen deficits tend to occur in the deeper layers of stratified water, including semi-enclosed basins and in some specific environments such as light-limited deep channels and dredged estuaries. Low oxygen concentrations can be found at times of increased oxygen consumption following maximum primary production and are concomitant with certain meteorological and hydrographic conditions (including temperature and wind speed). Oxygen concentrations may vary considerably within and between years as a result of many influences and trends may therefore be difficult to establish. However, establishing trends in some semi-enclosed basins may be easier, using the frequency of occurrence or spatial extent of the oxygen deficiency events.

For the interpretation of oxygen measurements it is essential to have corresponding measurements of temperature and salinity to enable the calculation of oxygen saturation as some species will respond to concentrations while others are more susceptible to saturation levels. It is also essential to have background information on hydrographic characteristics of the water column, such as stratification at the sampling site. For some areas, additional information including nutrients, organic matter, chlorophyll, pigments, and turbidity may also be helpful.

5. Sampling and in situ measurement

This chapter deals with sampling and using of dissolved oxygen sensors for measurements.

Oxygen is normally determined using electrochemical or optical sensors. A standard procedure for the determination of oxygen in water with electrochemical sensors is given in EN ISO 5814. Dissolved oxygen sensors can be deployed from vessels and may be used attached to a CTD system, as part of an autonomous system on moored platforms or installed on ships for continuous measurements. For onboard continuous sampling, it is essential that the sample is not exposed to oxygen and that a pumping system is leak free. A sufficient volume of water must be pumped over the sensor for its proper operation and flow rates should be high to keep the residence time within the pumping system to a minimum. The sensor and the pumping system should be checked and calibrated against discrete samples using the standard Winkler chemical analysis method according to EN 25813.

A number of seawater samplers are suitable for the collection of discrete samples for sensors or chemical Winkler oxygen determination. It is essential, however, that the water sampler used completely isolates the sample from its surroundings so that no leakage or exchange occurs. There are particular difficulties in collecting seawater samples very close to the seabed. Immediately after taking the water sample, a sub-sample for chemical analysis must be transferred into a calibrated Winkler bottle. This is a crucial step and one that could introduce significant errors. Great care must be taken to ensure there is no contact between the sub-sample and the atmosphere.

The advantage of sensor measurements is that they can provide continuous high resolution spatial and temporal data and capture short-term oxygen deficiency or supersaturation events. Sensors are also available for use in analysing discrete samples. Dissolved oxygen sensors designed for continuous *in situ* measurements may not be suitable for analysis of discrete samples. Examples of suitable equipment are described in Moore *et al.* (2009).

As all sensors have limitations in their performance it is not possible to give general recommendations for one type of sensor over the others. These limitations may include the sensitivity, the precision of measurement, response time, the stability of measured results, instability due to varying environmental conditions, poisoning in anoxic waters, etc. Therefore it is necessary to consider and test different sensors and select the one most suitable for measurements in the area to be observed.

Oxygen sensors need to be calibrated, handled, and maintained according to the manufacturer's instructions, and should be subject to proper validation. This includes regular checks of calibration and correct functioning of the sensor (stability, reproducibility, precision of results). The Winkler method should be used as reference method for this purpose and calibration should be carried out over a range appropriate for the samples being measured. The validation process should include a description of the operation of the sensor in order to obtain the specified and desired precision of the sensor. This requires regular calibration against the standard Winkler chemical analytical method as reference. Intervals of calibration, control of measurements, and maintenance depend on the type of sensor and the environmental conditions in which the sensor is used and is one element in the validation process. End-point calibration can be achieved using seawater purged with nitrogen to remove oxygen and seawater purged with oxygen for the 100% saturation, taking appropriate account of the temperature and salinity of the seawater being used. Additional calibration points can be obtained by partial de-oxygenation of water, or purging with different mixtures of oxygen and nitrogen. However, in practice it is often convenient to

perform regular check calibrations at sea using actual seawater samples. This has the advantage of providing close to real-time confirmation of the continuing accuracy of sensors.

6. Storage and pre-treatment of samples

For general requirements for sampling, preservation, handling, transport and storage of water samples see EN ISO 5667-3.

Oxygen in discrete (and calibration) samples for Winkler analysis must be fixed immediately after collection to eliminate the removal or production of oxygen in the sample. After fixation, samples should be stored in a dark place at a constant temperature - if possible the same as the *in situ* temperature - for at least one hour. The fixed sample should be titrated within 24 hours of collection. In some cases, longer storage of the fixed sample is unavoidable, but storage conditions and handling procedures must be validated and clearly documented. Zhang *et al.* (2002) noted that storage under seawater is advisable in such circumstances.

7. Analytical procedures

Reference procedures for the determination of oxygen in discrete water samples (e.g. as sensor calibration samples) are based on the Winkler method according to EN 25813. Modifications of this method, which have been verified in intercalibration exercises, are described elsewhere (e.g. Carpenter, 1965a; Grasshoff *et al.*, 1999; Strickland and Parsons, 1968). Modifications mainly concern composition of the reagents, titration devices (manual titration, automatic systems), and the method used for detecting the end point of the titration (e.g. visible colour change of indicator dyes, conductivity measurement, photometric detection). As verified by intercalibration exercises, reliable results can be obtained with many methods, providing proper procedures are followed.

8. Analytical quality assurance

Laboratories carrying out analyses of oxygen have to establish a quality management system according to EN ISO/IEC 17025. An accreditation by a recognized accreditation authority is recommended. The quality assurance programme should ensure that the data are fit for the purpose for which they have been collected, i.e. that they satisfy detection limits and levels of accuracy compatible with the objectives of the monitoring programme.

At present no certified reference material is available for oxygen in water. The calibration of sensors is dependent on the Winkler method and therefore it is recommended to use internal laboratory procedures according to Grasshoff *et al.* (1999) for quality assurance of the chemical analysis. In order to demonstrate reliable results, each laboratory must establish, validate, and document a quality assurance system suitable for the sample collection, storage, and analysis by both sensor and Winkler methods. Specific technical information on quality assurance is to be found in Carpenter (1965b), Vijverberg and Cofino (1987), Aminot (1997), and in the Nordtest report (2006). The effectiveness of the quality assurance system should be verified by participation in appropriate interlaboratory comparisons on an ongoing basis.

9. Reporting requirements

Oxygen must be reported in ml l^{-1} together with *in situ* salinity, temperature, and sample depth data. Data reporting to the ICES database should be in accordance with the requirements of the latest ICES reporting formats, together with QA information on methods used, detection limits, reference values, and any other comments or information relevant to an assessment of the data.

10. References

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EN ISO 5667-3*: Water quality - Sampling - Part 3: Preservation and handling of water samples

EN ISO 5814*: Water quality - Determination of dissolved oxygen - Electrochemical probe method

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

EN 25813*: Water quality – Determination of dissolved oxygen – Iodometric method

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