



## Baltic Marine Environment Protection Commission

Working Group on the State of the Environment and Nature  
Conservation

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<b>Submitted by</b>	Sweden

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### Background

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

Determination of hydrogen sulphide is currently described in Annex B-8 in the *Manual for monitoring in the COMBINE programme in HELCOM*. The draft for revised guidelines includes 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 hydrogen sulphide.

# Determination of hydrogen sulphide (H<sub>2</sub>S) in Seawater

## Background

### Introduction

Hydrogen sulphide is a poisonous gas that readily dissolves in water. The sulphide is formed in stagnant waters, where the oxygen has been consumed by bacteria oxidizing organic matter to carbon dioxide, water, and inorganic ions. Sulphate-reducing bacteria then use the oxygen bound in sulphate ions as an electron acceptor while reducing the sulphate ions to sulphide. No higher life forms can exist in water containing hydrogen sulphide, and these areas are thus turned into oceanic deserts. Hydrogen sulphide in a water sample is easily detected by its characteristic smell, even at concentrations lower than those measurable with the method below.

### Purpose and aims

The purpose of the monitoring is to map the spatial distribution of dissolved oxygen 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.

## Monitoring methods

### Monitoring features

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

### Time and area

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

### Monitoring procedure

#### Monitoring strategy

The reference method for sampling and determination of hydrogen sulphide in the Baltic area is the spectrophotometric method described in Fonselius et al. (1999). This book should be consulted for exact reagent compositions and procedures. For concentrations up to approximately 250 µM, the method by Fonselius et al. (1999) is recommended. Samples containing higher concentrations may be diluted after precipitation with a zinc acetate solution containing 2 g l<sup>-1</sup> of gelatin (Grasshoff and Chan, 1971). This solution can be homogenized and diluted. However, higher levels of sulphide are better quantified using the method by Cline (1969).

Minimum analytical requirements are: simply note, by smelling at the water sample, if hydrogen sulphide is present or not.

### Sampling method and equipment

Sampling is carried out using the same technique as for oxygen. Samples are taken from ordinary water samplers immediately after the oxygen samples, using the same sampling technique (cf. Determination of Dissolved Oxygen in Sea Water). If no oxygen is present, the sulphide samples should be taken first. Sulphide reacts with many metals, and the samplers should thus preferably be all-plastic. 50–100 ml oxygen bottles are recommended.

The two reagents are added simultaneously using piston pipettes or dispensers. The tips of the pipetting devices should be close to the bottom of the bottle. No air bubbles should be trapped in the bottle. Note that the amount of reagents added has to be adjusted according to the size of the bottles used. As concentrations rather than amounts are measured, no exact knowledge of the bottle volume is required.

### Sample handling and analysis

The absorbance is measured in a spectrophotometer or a filter photometer at 670 nm. Measurements should be performed no sooner than 1 hour and no later than 48 hours after the reagent addition. The bottles should be kept in dark and any change in temperature should be avoided.

Samples that cannot be analysed within 48 hours may be preserved with zinc acetate, which precipitates the sulphide as zinc sulphide. The preserved samples can be stored for a few months, if light and temperature changes are avoided. Prior to analysis, the reagents are added in the same way as for unpreserved samples. When the bottle is turned, the precipitate dissolves easily, and the colour develops normally.

(However, according to Fonselius et al. 1999, there seems to be debate on how long the samples can be stored after addition of reagents and it will depend on the concentration. Hydrogen sulphide samples of moderate concentrations (<300  $\mu\text{M}$ ) may be stored for several days after adding the reagents. )

### Data analysis

The concentration of hydrogen sulphide is usually expressed as  $\mu\text{mol l}^{-1}$  ( $\mu\text{M}$ ), or in some cases as  $\text{ml l}^{-1}$   $\text{H}_2\text{S}$ .

### Data reporting and storage

*Format for data reporting, where the data is reported e.g. specific database*

## Quality control

### Quality control of methods

No certified reference materials (CRMs) are available for control charts. The difference between double samples in a control chart with zero as the reference line provides information on both precision and the validity of the subsampling. Ideally, the result (Sample 1 – Sample 2) should be evenly distributed around zero. Any deviations from this suggest subsampling problems. The parameter is very rarely included in interlaboratory comparison exercises, mainly due to problems in withdrawing multiple samples with the same sulphide concentration from one sample container. The relatively poor precision of the method, often 5-10 %, could probably be attributed to the combined effects of all steps in the sampling and sample pretreatment procedure.

The following steps need to be taken to assure the quality of the measurements:

- The performance of the photometer with regard to absorbance and wavelength correctness must be checked and documented using a certified set of filters, or by an equivalent method.
- The reagents must be calibrated using the procedure described in Fonselius *et al.* (1999). For measuring volumes in this procedure, only calibrated or class A glassware should be used. It is essential that the working solutions are freshly prepared, and that the sulphide content of the stock solution is measured, not calculated from the weighing of Na<sub>2</sub>S (as Na<sub>2</sub>S of sufficient purity is not available).
- New reagents should be prepared at one-year intervals. The old reagents always must be checked against the newly prepared reagents in order to prove their stability.
- Very high concentrations of sulphide in certain unusually stagnant areas will cause problems. In some cases, the absorption of the sample will lie outside the working range of the spectrophotometer. Dilution of the sample is possible, but will undoubtedly introduce more uncertainty into the measurement.

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 data from intercalibrations.

### Quality control of data and reporting

Using the method recommended in Fonselius *et al.* (1999), the analytical precision will be approximately  $\pm 1 \mu\text{mol l}^{-1}$ .

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

## Contacts and references

### Contact persons

Kristin Andreasson, SMHI

### References

Cline, J.D. 1969. Spectrophotometric determination of hydrogen sulfide in natural waters *Limnology and Oceanography*, 14: 454–458.

Fonselius, S., Dyrssen, D., and Yhlen, B. 1999. Determination of hydrogen sulphide. *In* Methods of seawater analysis, 3rd edition. Ed. by K. Grasshoff *et al.* Wiley-VCH, Germany.

Grasshoff, K., and Chan, K.M. 1971. An automatic method for the determination of hydrogen sulphide in natural waters. *Analytica Chimica Acta*, 53: 442–445.

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

### Additional literature

Lysiak-Pastuszek E and Krysell M (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.