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### Background

HELCOM guidelines for hydrography and hydrochemistry are currently being revised. Lead Country Sweden submits draft guidelines for determination of pH in seawater in the HELCOM area as a contribution to the ongoing revision of HELCOM monitoring guidelines. Measurements of pH are currently described in Annex B-14 in the *Manual for marine monitoring in the COMBINE programme*.

The draft for revised guidelines includes updates on procedure, and introduces determinations based on spectrophotometric measurements. This new principle for analysis suggests the use of a pH scale new to large-scale monitoring in the Baltic area.

The draft has been reviewed by representatives from Co-Lead Country Poland, Denmark, Estonia, Finland and Germany. The last round of review delivered detailed and informative feedback from German experts in the field of pH determination (their comments are added to the guideline draft as an attachment). Unfortunately not enough time was given to compose a new draft based on this feedback. The comments from the experts are submitted to give an indication of what the final version of guidelines should include.

### Action requested

The Meeting is invited to

- comment and amend as needed the draft guidelines for determination of pH.

## Determination of pH in seawater

### 1 Background

#### 1.1 Introduction

Since ocean acidification is a growing concern, monitoring of pH is necessary for studies of acidification and its effects on the carbonate buffer system. As many important biological processes are likely to be affected by rapid changes in pH, it is important to include accurate determination of pH among monitoring parameters.

pH is operationally defined, and a number of pH scales are used in environmental monitoring. The NBS (National Bureau of Standards) scale is suitable for waters of low ionic strength, and used for freshwater monitoring. The total hydrogen ion scale is often used for pH determinations in oceanic waters. The salinity gradient from the Bothnian Bay to Skagerrak, or from surface to deep water in the Baltic Proper, makes it difficult to select a pH scale that would be suitable for the entire Baltic area.

pH is also used in marine environmental monitoring as a co-factor in measurements of primary production.

#### 1.2 Purpose and aims

The aim of monitoring is to identify spatial variations and temporal trends in pH.

### 2 Monitoring methods

#### 2.1 Monitoring features

#### 2.2 Time and area

Monitoring covers the entire Baltic area, and is performed throughout the whole year.

#### 2.3 Monitoring procedure

##### 2.3.1 Monitoring strategy

Two different principles are available, based on potentiometric and spectrophotometric detection. Potentiometric detection has the advantages of being fast and simple, and requires no advanced or expensive equipment. Buffers used for calibration should ideally have an ionic strength matching that of the samples, which is challenging when an area with a large salinity gradient is monitored. A number of pH meters, electrodes and buffers are commercially available.

Spectrophotometric detection is more accurate, has a higher precision, but requires expensive equipment. It is widely used in measurements under oceanic conditions, but less in estuarine waters. Commercial applications for the spectrophotometric methods have not yet been developed; users must assemble instruments and software for data processing.

##### 2.3.1.1 Potentiometric determination

pH is measured using a glass/combined electrode. The NBS pH scale should be used (although not ideal, the NBS scale has to this day been considered to be the best option for the wide range of salinity in the monitored area). Temperature is measured and recorded both during pH measurement and at sampling depth.

### *2.3.1.2 Spectrophotometric determination*

pH is determined by spectrophotometric measurement using an indicator dye (m-cresol purple). The total hydrogen ion scale is used. The indicator used must be well characterized; dissociation and extinction coefficients have to be determined for the range of temperature and salinity in the monitored area.

### **2.3.2 Sampling method and equipment**

Subsamples for pH should be drawn from sampler bottles as early as possible (after samples for oxygen and hydrogen sulfide, but before samples for nutrients and salinity) to avoid gas exchange between water and air.

Samples should be collected in gas-tight bottles. Bottles should be rinsed thoroughly with sample water before filling. Bottles are filled with a laminar flow of sample water, allowing 2-3 bottle volumes to overflow before capping. Bottles should be completely filled, leaving no headspace. Avoid trapping bubbles of air when capping bottles.

Samples should preferably be analyzed as soon as possible directly after sampling.

### **2.3.3 Sample handling and analysis**

#### *2.3.3.1 Potentiometric measurement*

The procedure with a glass electrode in the pH range of from 2 to 12 and in the temperature range of 0 °C to 50 °C is described in ISO 10523.

Temperature must be monitored and controlled during calibration of instrument and analysis, preferably by use of a tempered water bath. Make sure temperature of calibrants and samples is constant ( $\pm 1^\circ\text{C}$ ) during the process. To maintain constant temperature, select a bath temperature slightly above ambient temperature (for normal room temperature, set bath temperature to 25°C – in a cooler environment 20°C may have to be used).

pH meter should be calibrated daily when in use. Follow manufacturer's instructions for a 2-point calibration (pH 7 and pH 9 are recommended). Use NBS buffers for calibration. Observe expiry dates of buffers.

Rinse electrode and temperature probe with deionized water and wipe between calibrants/samples.

Allow electrode to equilibrate in sample water for 15 minutes before first measurement. Make sure equilibrium is reached for each sample before recording a reading.

Open-cell measurements allow gas exchange between sample and air during the time of measurements. Closed-cell measurements eliminate the interferences.

Follow manufacturer's instructions for handling and storage of electrodes. Electrodes may require cleaning and conditioning when exposed to samples from intense plankton blooms. Anoxic water containing high concentration of hydrogen sulfide may shorten the life of electrodes.

#### *2.3.3.2 Spectrophotometric measurement*

A method for spectrophotometric pH measurements is described by Hammer et al (2014).

## **2.4 Data analysis**

A correction for *in situ* pH (Gieskes 1969) is sometimes applied, but the correction is not determined for Baltic Sea conditions. A better option is to report measured pH, temperature from pH measurement and *in situ* temperature.

### 3 Data reporting and storage

pH values from potentiometric detection should be reported with two decimals. pH values from spectrophotometric detection should be reported with three decimals. Temperature from measurement and sampling depth should also be reported.

Information on which pH scale is used must be included in metadata.

Data is reported annually to the HELCOM COMBINE database, hosted by ICES.

### 4 Quality control

#### 4.1 Quality control of methods

Laboratories carrying out analyses of nutrients should have established a quality management system according to EN ISO/IEC 17025.

Collect and analyze samples for estimation of measurement uncertainty (repeated measurements from a sample, multiple subsamples from different samplers closed at same depth).

An internal reference material (IRM) should be analyzed daily.

##### 4.1.1 Potentiometric measurement

Use a calibrated temperature probe with the pH electrode.

Make sure emf value of electrode for each buffer is within range recommended by manufacturer.

##### 4.1.2 Spectrophotometric method

Use a calibrated temperature probe to monitor temperature during measurements.

#### 4.2 Quality control of data and reporting

Measurement uncertainty should be estimated using ISO 11352:2012. Estimation should be based on within-laboratory reproducibility, IRM, and, if available, data from proficiency testings and CRM.

### 5 Contacts and references

#### 5.1 Contact persons

Kristin Andreasson, SMHI

Johan Håkansson, SMHI

## 5.2 References

Gieskes J M 1969

Effects of temperature on the pH of seawater

*Limnology and Oceanography* Vol 14 Issue 5, p 679-685

Hammer K, Schneider B, Kuliński K and Schulz-Bull D E 2014

Precision and accuracy of spectrophotometric pH measurements at environmental conditions in the Baltic Sea

*Estuarine, Coastal and Shelf Science* 146 p 24-32

Wedborg M, Turner D R, Andersson L G and Dyrssen D 1999

Determination of pH

Chapter 7, p 109-128 in

Grasshoff K, Kremling K and Erhardt M (ed)

*Methods of Seawater Analysis* 3<sup>rd</sup> ed

Wiley-VCH

ISBN 3-527-29589-5

ISO 10523\*: Water quality – Determination of pH

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

Carter B R, Radich J A, Doyle H L and Dickson A G 2013

An automated system for spectrophotometric seawater pH measurements

*Limnology and Oceanography: Methods* 11, p 16-27

1.

Dickson A G, Sabine C L, Christian J R (ed) 2007

Guide to best practices for ocean CO<sub>2</sub> measurements

PICES Special Publication 3

IOCCP Report No 8

## 6. Attachment

Comments on the „Draft Guidelines for Determination of pH”

### Preface

The Leibniz Institute for Baltic Sea Research (IOW), through Prof. G. Rehder, is coordinating the BONUS Innovation Project BONUS PINBAL that deals with the refinement of a spectrophotometric pH measurement device for monitoring in the Baltic Sea. According to the proposal, “The final product of the project will be a prototype of a spectrophotometric flow-through pH measurement system suitable for monitoring and research purposes, with well-defined precision and accuracy. Progress and possibilities of the system will be disseminated by contact with the agencies responsible for the Baltic Sea monitoring in the involved countries, as well as by using the relevant HELCOM work group meetings ... (and) ... supporting the need for better instrumentation and methods needed to meet the demands for monitoring for the next

decades, defined by the HELCOM Baltic Sea Action Plan and the EU Marine Strategy Framework Directive.” In the light of these commitments and based on the current state of the art concerning pH measurements as documented in standard text books such as Grasshoff et al., “Methods of Seawater Analysis” and in the “Guide to Best Practices for Ocean CO<sub>2</sub> Measurements” by Dickson et al., we feel that after consideration with the BONUS PINBAL group and at the end of the project (April 2017), we could provide essential recommendations for the next guidelines. Therefore, we ask to allow us - as consortium funded by BONUS – to communicate our findings and suggestions during one of the forthcoming meetings of the group responsible for the new guidelines for determination of pH, State & Conservation, 2MA-7. Other than for the document on the determination of alkalinity, where we (as IOW) provided input to the document via the German members of the group responsible for the guidelines, we found that the current version of the guidelines on pH needs modifications which cannot be incorporated into the current draft, and also felt that we would have to iterate our recommendations with the project partners in Sweden (UGot), Poland (IO PAN) and Germany (CONTROS Maritime Systems).

## pH scale

There exists largest consensus within the marine scientific community that the total hydrogen concentration scale is the most appropriate for the definition of pH in saline waters:

$$\text{pH}_t = -\log([\text{H}^+] + [\text{HSO}_4^-])$$

This scale differs conceptually from the traditional NBS scale by considering seawater as the solvent when defining standard conditions for an acid solution. It implies that buffer solutions with a defined pH must be prepared in artificial seawater with a salinity that corresponds to that of the samples to be analyzed. The major advantage of the total pH scale is that it has a clear physico-chemical meaning, whereas the interpretation of pH on the NBS scale when determined for seawater, is dubious because it represents neither the hydrogen ion activity nor the hydrogen ion concentration, “it is just a number” (A. Dickson).

In addition to the total scale, the free hydrogen ion concentration scale:

$$\text{pH}_f = -\log[\text{H}^+]$$

and the seawater scale:

$$\text{pH}_{\text{sws}} = -\log([\text{H}^+] + [\text{HSO}_4^-] + [\text{HF}])$$

have been suggested. The mutual conversion between the three concentration scales is clearly defined if the dissociation constants for HSO<sub>4</sub><sup>-</sup> and HF are known and as long as the concentrations of sulphate and fluoride follow the hypothesis of the constancy of the seawater composition. An unambiguous conversion between the pH on the NBS scale and the pH on any of the concentration scales is not possible. Furthermore, great effort was made during the last decades to establish reliable dissociation constants for carbonic acid, which together with measurements can be used for the full characterization of the marine CO<sub>2</sub> system. As far as documented in the oceanographic literature, these investigations referred exclusively to one of the mentioned pH concentration scales, mainly to the total scale. Hence, to use these constants together with pH measurements for the calculation of any other variable of the marine CO<sub>2</sub> system, requires pH measurements on a corresponding scale.

## Method

The choice of an appropriate method for the determination of the pH is in principle independent on the choice of the pH scale. However, in case of measurements in waters with a wide salinity range, the use of the total pH scale implies that the spectrophotometric pH determination is the most convenient method. This is due to the fact that potentiometric measurements on the total scale require laborious calibration according to the salinity level that may change rapidly along horizontal and vertical salinity gradients in the Baltic Sea. This problem is circumvented by the spectrophotometric method if the dissociation constant and the extinction coefficients of the indicator dye have once been determined as a function of salinity and temperature on the total pH scale. Such functions were established Mosley et al., (2004) and are currently refined within the BONUS Project PINBAL (J. Müller, IOW) in cooperation with the National Metrology Institute of Germany (PTB). Furthermore, spectrophotometric pH measurements are more precise and are as easy to operate as potentiometric measurements if the latter are performed in a scientifically adequate

way (using a closed temperature controlled measurement cell). An example for the application of a spectrophotometric pH measurement device in the Baltic Sea is given in Hammer et al., *Estuarine, coastal and shelf science*, 146, 24 – 32 (2014). New guidelines for the determination of pH for the HELCOM monitoring have to take into account the recent physicochemical and technological advancements of the last decades in order to meet the goals for CO<sub>2</sub>-system parameterization according to the MSFD.

Warnemünde, Sept. 29th, 2016

Dr. Bernd Schneider  
Prof. Gregor Rehder (PI of the PINBAL project)  
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