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 1

Technical note on the determination of salinity and temperature of seawater

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

ANNEX B-8 APPENDIX 1: TECHNICAL NOTE ON THE DETERMINATION OF SALINITY AND TEMPERATURE OF SEAWATER

PART I: TECHNICAL NOTE ON THE DETERMINATION OF SALINITY OF SEAWATER (LABORATORY SALINOMETER)

1 INTRODUCTION

Many investigations have been performed to present salinity and chlorinity of sea water and the connection between salinity and chlorinity since 1884. Those investigations are thoroughly reviewed by Müller (1999). These guidelines describe the determination of the salinity (S) of seawater samples which is based on measuring conductivity with a laboratory salinometer.

Salinity values have been reported as p.s.u. (practical salinity units), parts per thousand, ppt or U. Numeric values of them (e.g., ppt, psu, per mille) are equal. However, salinity values according to the current definition of the Practical Salinity Scale of 1978 (PSS78) are dimensionless with no units.

2 METHODS

A laboratory salinometer measures the conductivity of sea water relative to a reference standard sea water. The principle of the operation of a salinometer is described in more detail by Müller (1999). General specifications and maintenance of a salinometer are presented in the manual of each manufacturer.

3 SAMPLING

See the Part III: Technical Notes on the Determination of Temperature and Salinity using a CTD Probe.

4 ANALYTICAL PROCEDURE

4.1 CALIBRATION AND STABILITY OF CALIBRATION

Calibration of a salinometer with internationally accepted IAPSO (International Association for the Physical Sciences of the Ocean) Standard Seawater:

S= 35 ‘Normal Standard Seawater’ (suitable for oceans)

S=10 ‘Low Standard Seawater’ (suitable for Baltic Sea conditions)

The conductivity of a laboratory salinometer is calibrated by using standard sea water under controlled temperature conditions. Calibration of the salinometer is always performed after changing temperature or temperature-dependent values, after malfunction of the salinometer or when the range of the measured conductivity is dramatically changed (while changing from brackish water to oceanic sea water or vice versa). The calibration intervals depend strongly on the equipment used, and can vary from daily calibration to calibrations twice a year. Consult the manufacturer’s recommendations. In any case, the stability of the calibration has to be checked using a control seawater sample in every sample batch (see Section 5.1, below).

The stability of temperature during measurement is controlled and documented during conductivity/salinity measurements. Make sure that the temperature reading of the thermometer used is traceable to the respective national reference laboratory for temperature. The thermometer(s) have to be checked against a reference thermometer at least twice a year.

4.2 SALINITY MEASUREMENT WITH SALINOMETER

Follow the instructions of the salinometer's manufacturer during the procedures of measurement.

Check the stability of the temperature of the thermostatted water bath before measurement. Do not start the measurements until the temperature has stabilized.

Avoid air bubbles in the cell during the measurement. If the sample measurement is performed one or more weeks after sampling, mix the bottle and let it rest for at least one hour before the measurement. In case of any deposits, these either have to be removed or settled down before the measurement.

Check that the parallel results of the seawater sample are within accepted limits (0.05; Annex C-2 of the COMBINE Manual).

4.3 DOCUMENTATION

For every sample run, document in a logbook/sheet (in addition to the measured values):

- date, and identity of the analyst;
- identity of the equipment used;
- temperature of the measurement environment and the samples;
- thermometer identity (if separate from the instrument);
- batch number and result of standard seawater and control samples;
- instrument constants (if applicable to the equipment).

5 QUALITY ASSURANCE

5.1 CALIBRATION AND TRACEABILITY

Regular calibrations and checks of the salinometer are described under Section 4.1, above.

Solutions for calibration and control

Calibration of the salinometer is performed with internationally accepted IAPSO Standard Seawater. A control seawater sample (Laboratory Reference Material) should be included in every sample series and the results plotted in control charts.

It is possible to prepare a control seawater solution from sea water which is filtered, aged, bottled in several bottles with tight caps and stored in a cool room for a maximum of one year. The salinity of this control sea water should be measured daily during at least ten days and the average value for the salinity calculated. Salinity values of control sea water that is measured before the sample series may vary within certain accepted limits. If the salinity values are outside the accepted limits, the salinometer should be calibrated with IAPSO Standard Seawater. Standard Seawater is an alternative as a control sample (e.g., calibrating at 35 and use a control of 10).

Calculation

The calculation procedures used should be checked at least once a year by calculating the salinity of IAPSO Standard Seawater using three different temperature values.

6 REPORTING

Calculate the final results according to the formula recommended by the Joint Panel on Oceanographic Tables and Standards for *in situ*measurements with conductivity instruments (UNESCO, 1981), unless this calculation is carried out automatically in the salinometer. The effect of temperature on the conductivity is discussed by Müller (1999). Data should be reported according to the ICES data format (2 decimals).

7 REFERENCES

Müller, T.J. 1999. *In* Methods of Seawater Analysis. Ed. by Grasshoff *et al*. Wiley-VCH, Germany.

UNESCO. 1981. Background papers and supporting data on the Practical Salinity Scale 1978. UNESCO Technical Papers in Marine Science, 37.

PART II: TECHNICAL NOTES ON THE DETERMINATION OF TEMPERATURE WITH REVERSING THERMOMETERS

1 INTRODUCTION

Measurement of temperature using reversing thermometers is carried out for two purposes: (1) to obtain the correct temperature associated with each sample when samples are collected using separate bottles on a wire (in contrast to rosette samplers), and (2) to verify the temperature reading of a CTD probe.

2 METHODS

Reversing thermometers of two main types are available, mercury (Hg) thermometers and digital, electronic, thermometers. The performance of the two types is similar, even though digital thermometers are generally easier to handle and calibrate. It is important to remember that the mercury thermometers should only be handled by skilled and experienced staff. For the monitoring Z

3 MEASUREMENT PROCEDURE

3.1 TEMPERATURE MEASUREMENT

The correct handling of the thermometers should be described in the manufacturer's manual. Some important points have to be stressed concerning Hg thermometers:

The thermometers must be given enough time to equilibrate with the surrounding water before they are locked. Usually this means waiting 5–10 minutes at the correct depths before reversing the thermometers. Digital thermometers normally equilibrate much faster.

When reading the temperature, it is of utmost importance to ensure that the eye is level with the top of the Hg column in order to avoid refraction errors.

3.2 DOCUMENTATION

For every temperature reading, document:

- the name of the person reading the thermometer;
- the identity of the thermometer;
- for Hg-thermometers, the reading of the supporting thermometer.

4 QUALITY ASSURANCE

All reversing thermometers, regardless of type, have to be calibrated against a reference thermometer at least every second year. The reference thermometer in turn has to be calibrated with traceability to the international temperature scale. Mercury reference thermometers are calibrated every 5 years, digital reference thermometers every second year.

The calibration has to be carried out in a thermostatted water bath, capable of being thermostatted to all temperatures within the measured range. Calibration in air does not produce results of the required quality. The calibration of thermometers used in the COMBINE programme has to cover temperatures from approximately –2 °C to 25 °C. Note that special procedures for correcting mercury reference thermometers have to be applied (Theisen, 1947).

The laboratory or the data bank must uphold routines for correcting:

a) the calibrations for deviations from the true temperature of the reference thermometer;

b) the measured temperatures for the calibration results, using an individual calibration curve for each reversing thermometer.

For digital thermometers, the laboratory must uphold routines for changing batteries at regular intervals, or when needed.

5 REPORTING

5.1 DATA PROCESSING

The temperature readings of mercury reversing thermometers have to be corrected for the temperature of the mercury column when reading the temperature. This temperature is given by the supporting thermometer. Correction also has to be made for the calibration. The correction is carried out according to (Anderson, 1974; Theisen, 1947):

$$T_{corr} = \frac{(T_{obs} + I + V_0) \times (T_{obs} + I - t)}{(1/\beta) - (T_{obs} + I + V_0 + (T_{obs} + I - t)/2)}$$

where

Tcorr = the corrected, final, temperature,

Tobs = the observed temperature from the main thermometer,

I = correction according to the calibration,

V0 = a constant, specific for each mercury thermometer (the volume of the mercury),

1/b = a constant, depending on the quality of the glass (approximately = 6000)

t = the temperature of the supporting thermometer (i.e., the temperature of the mercury column when reading the Tobs).

5.2 DATA ACCURACY

The main causes for inaccuracy are usually the calibration and temperature correction procedures. Applying the suggested procedures carefully, an accuracy of at least 0.02 °C is possible. The temperature should be reported according to the ICES data format (two decimals).

6 REFERENCES

Anderson, L. 1974. Correction of reversing thermometers and related depth calculations in Baltic water. Meddelande 166 from Havsfiskelaboratoriet i Lysekil, Hydrografiska avdelningen i Göteborg (SMHI Oceanographical Laboratory, Göteborg, Sweden).

Theisen, E. 1947. Correction of temperatures and a handy way of making correction charts for reversing thermometers. Fiskeridirektoratets Skrifter: Report on Norwegian Fishery and Marine Investigations, Vol. VIII, No. 9.

PART III: TECHNICAL NOTES ON THE DETERMINATION OF TEMPERATURE AND SALINITY USING A CTD PROBE

1 INTRODUCTION

Temperature and salinity are among the most important parameters in physical oceanography. At present, *in situ* measurements of temperature and salinity are possible using automatic temperature and salinity systems (CTD systems), the configuration of which are formed by **C**onductivity, **T**emperature, and pressure (**D**epth) sensors. In order to assure the functioning of a CTD system, it is useful to make comparisons during every cruise by taking water samples with a sampler that is connected to the CTD system for further analysis with a salinometer, and by verifying temperature values with reversing thermometers attached to water samplers of the CTD system. Pressure values obtained from the sensor of the CTD system can be compared with a digital pressure sensor.

2 METHODS

General specifications and maintenance of conductivity, temperature, and pressure sensors that are used in CTD systems are presented in the manual of each manufacturer. For CTD profiling, all parameters are usually measured several times per second.

3 SAMPLING EQUIPMENT

A CTD probe equipped with sensors for temperature, conductivity, and pressure.

Reversing thermometers, the temperature of which is traceable to the national reference laboratory.

A Rosette multisampler for taking water samples.

4 ANALYTICAL PROCEDURE

There are many protocols available for CTD measurements (WOCE, 1991; UNESCO, 1988, 1994). Based on a combination of the previous protocols and field measurement experience from the COMBINE Programme, the following protocol is proposed.

4.1 SENSOR QUALITY CONTROL

It is useful to control the function of the CTD conductivity sensors by analysing water samples, that have been taken from homogeneous water masses during a CTD cast, with a laboratory salinometer that is calibrated under controlled conditions with internationally accepted standard sea water (see Part I of this Technical Note).

Temperature values measured by a CTD system can be controlled by using a pair of reversing thermometers during a CTD cast and comparing those values with each other (see Part II of this Technical Note).

The functioning of the pressure sensor is checked by verifying the measured value with a value from a separate reference probe.

These three procedures should be carried out on every cruise, and the results documented properly so that any drift in the sensor can be traced.

4.2 CTD CAST

1. Stabilization

The CTD and Rosette package are lowered a few metres below the sea surface for at least two minutes before starting the measurements.

2. Starting of CTD cast

The CTD is brought back to near the sea surface. The measurement is started. If the sea state is rough, it is recommended to start the down-cast from a few metres below the sea surface to prevent the bubbles of the breaking waves from entering the conductivity cell.

3. The speed of lowering

It is recommended to keep the lowering speed as constant as possible and between 40 cm s–1 and 120 cm s–1.

4. Documentation

The CTD depth, sonic depth, and all the other information required by the CTD logbook are documented.

5. Water samples

The Rosette bottles should preferably be fired at the selected depths during the up-cast in order to obtain an undisturbed CTD profile during the down-cast and undisturbed water samples on the way up.

Make sure that the Rosette sampling bottles are not leaking. Water for salinity determination should be sub-sampled into clearly identified glass or plastic bottles with screw caps. Plastic under-stoppers are recommended. Water sampling bottles—as well as caps and under-stoppers—are rinsed with the sample water at least two times before bottling. Fill the sample bottle with the sample water by taking into account the thermal expansion of water, e.g., do not fill the glass bottles completely. Store the water samples at room temperature before measurement of salinity with a salinometer (see Part I of this Technical Note).

Flush the CTD and Rosette sampler with fresh water after sampling.

4.3 DOCUMENTATION

Make sure that sufficient, confident, and traceable documentation of the samples and measurements is available for further data handling. One example of data documentation is presented in UNESCO (1988).

5 QUALITY ASSURANCE

5.1 CALIBRATION AND TRACEABILITY SENSORS

The general specifications of the CTD sensors, for example, range, response time, resolution, initial accuracy, settling time, stability, and drift, are presented in the manual of the manufacturer.

Calibration of the CTD sensor via the system provider or in another competent calibration laboratory is necessary every second year or on special request to assure traceability of conductivity, pressure, and temperature. The COMBINE requirements for temperature and salinity accuracy are given in Annex C-2 of the COMBINE Manual.

5.2 MAINTENANCE

Exchangeable, pre-calibrated, spare temperature, conductivity, and pressure sensor modules are recommended to be available on board in case of a breakdown. Note that cleaning of the sensors could be carried out with fresh water and a soft brush, e.g., a tooth brush, or a similar gentle technique. By no means should the sensor be cleaned with hydrochloric acid.

6 REPORTING

6.1 DATA PROCESSING

The modern salinity measurement is based on the high accurate measurement of temperature, conductivity, and pressure. Salinity is calculated according to the Practical Salinity Scale 1978 (PSS-78). Guidelines for CTD data handling are presented by UNESCO (1988, 1991).

6.2 REQUIREMENTS FOR DATA QUALITY

COMBINE Programme requirements for the accuracy of salinity, temperature, and pressure data are presented in the table below.

	Accuracy
Salinity	0.05 (BMP)
	0.1 (CMP)
Temperature	0.05 °C (BMP)
	0.05 °C (CMP)
Pressure	not specified in the manual

7 REFERENCES

UNESCO. 1988. The acquisition, calibration, and analysis of CTD data. A report of SCOR Working Group 51. Technical Papers in Marine Science, 54.

UNESCO. 1991. Processing of oceanographic station data. JPOTS editorial panel.

UNESCO. 1994. Protocols for Joint Global Flux Study (JGOFS) Core Measurements. Manual and Guides, 29.
WOCE. 1991. WOCE Operational Manual, Vol. 3.

WOCE Report 68/91, July 1991.