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**Agenda item 5: Parallel CORMON Sessions for Pollution, including Marine Litter and Biodiversity**

**Monitoring Guidelines/Protocols for Determination of Hydrographic Physical Parameters**

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## Annexes

Annex I: References

## **Note by the Secretariat**

In line with the Programme of Work 2020-2021 adopted by COP21 the MED POL Programme has prepared the Monitoring Guidelines related to IMAP Common Indicators 13, 14, 17 and 20 for consideration of the Integrated Meeting of the Ecosystem Approach Correspondence Groups on Monitoring (December 2020), whilst the Monitoring Guidelines for Common Indicator 18, along with the Monitoring Guidelines related to data quality assurance and reporting are under finalization for consideration of the Meeting on CorMon on Pollution Monitoring planned to be held in April 2021.

These Monitoring Guidelines present coherent manuals to guide technical personnel of IMAP competent laboratories of the Contracting Parties for the implementation of the standardized and harmonized monitoring practices related to a specific IMAP Common Indicator (i.e. sampling, sample preservation and transportation, sample preparation and analysis, along with quality assurance and reporting of monitoring data). For the first time, these guidelines present a summary of the best available known practices employed in marine monitoring by bringing integrated comprehensive analytical practices that can be applied in order to ensure the representativeness and accuracy of the analytical results needed for generation of quality assured monitoring data.

The Monitoring Guidelines/Protocols build upon the knowledge and practices obtained over 40 years of MED POL monitoring implementation and recent publications, highlighting the current practices of the Contracting Parties' marine laboratories, as well as other Regional Seas Conventions and the EU. A thorough analysis of presently available practices of UNEP/MAP, UNEP and IAEA, as well the HELCOM, OSPAR and European Commission Joint Research Centre was undertaken in order to assist an innovative approach for preparation of the IMAP Monitoring Guidelines/Protocols.

In order to support national efforts, this Monitoring Guidelines for Determination of Hydrographic Physical Parameters provides the two following Technical Notes: a) Technical Note for the measurement of temperature and salinity which includes the three following Protocols: Protocol for determination of temperature and salinity using CTD; Protocols for the determination of temperature using reversing thermometers; Protocol for sample preparation and analysis of salinity using bench salinometer; and b) Technical Note for the measurement of the seawater transparency through the determination of the Secchi depth which includes the Protocol for measuring Secchi depth, for consideration of Integrated Meeting of the Ecosystem Approach Correspondence Groups on Monitoring (CORMON) Biodiversity and Fisheries, Pollution and Marine Litter, and Coast and Hydrography.

The Monitoring Guidelines/Protocols for IMAP Common Indicators 13 and 14, including the one related to Determination of Hydrographic Physical Parameters, establish a sound ground for further regular update of monitoring practice for a purpose of successful IMAP implementation.

## List of Abbreviations / Acronyms

<b>AHC</b>	Active Heave Compensation system
<b>BODC</b>	British Oceanographic Data Centre
<b>CI</b>	Common Indicator
<b>COP</b>	Conference of the Parties
<b>CORMON</b>	Correspondence Group on Monitoring
<b>EcAp</b>	Ecosystem Approach
<b>EO</b>	Ecological Objective
<b>EOS-80</b>	Equation Of State of seawater of 1980
<b>EU</b>	European Union
<b>GES</b>	Good Environmental Status
<b>HELCOM</b>	Baltic Marine Environment Protection Commission - Helsinki Commission
<b>IAPSO</b>	International Association for the Physical Sciences of the Oceans
<b>IMAP</b>	Integrated Monitoring and Assessment Programme of the Mediterranean Sea and Coast and Related Assessment Criteria
<b>INFO/RAC</b>	Information and Communication Centre of the Barcelona Convention
<b>IPTS-68</b>	International Practical Temperature Scale of 1968
<b>IRM</b>	Internal Reference Material
<b>ISO</b>	International Standard Organization
<b>ITS-90</b>	International Temperature Scale of 1990
<b>IUPAC</b>	International Union of Pure and Applied Chemistry
<b>JPOTS</b>	Joint Panel on Oceanographic Tables and Standards
<b>MAP</b>	Mediterranean Action Plan
<b>MEDPOL</b>	Programme for the Assessment and Control of Marine Pollution in the Mediterranean Sea
<b>MSFD</b>	Marine Strategy Framework Directive
<b>OSPAR</b>	Convention for the Protection of the Marine Environment for the North-East Atlantic
<b>PSS-78</b>	Practical Salinity Scale of 1978
<b>SI</b>	International System of Units (SI, abbreviated from the French Système international (d'unités))
<b>SCOR</b>	Scientific Committee on Oceanic Research
<b>UNESCO</b>	United Nation Educational Scientific and Cultural Organization
<b>WOCE</b>	World Ocean Circulation Experiment

## 1. Introduction

1. In this Guideline for Determination of Hydrographic Physical Parameters the supporting parameters temperature, salinity and transparency are presented. Temperature and salinity are essential in the basic calculation of other parameters as are dissolved oxygen and pH. On the other hand, they also serve as proxy for the definition of the water typology important tool in the water classification scheme on which the assessment of GES is based on as presented in details in the IMAP Guidance Factsheets (UNEP/MAP, 2019)<sup>1</sup>.

2. The IMAP Protocols elaborated within this Monitoring Guidelines for Determination of Hydrographic Physical Parameters provide detail guidance on the necessary equipment, chemical reagents, analytical procedures along with appropriate methodologies for measurement of the core hydrography physical supporting parameters, calculations, data transformation if necessary and identify weak points, including important specific notes and elaborated possible problems. However, they are not intended to be analytical training manuals, but guidelines for Mediterranean laboratories, which should be tested and accordingly modified, if need be, in order to validate their final results.

3. This Monitoring Guidelines builds upon the UNEP/MAP Integrated Monitoring and Assessment Programme (IMAP) respectively IMAP Guidance Fact Sheets for IMAP Common Indicators 13 and 14 (UNEP/MAP, 2019); standardized protocols (UNEP/MAP, 2019a)<sup>2</sup> and Data Quality Assurance schemes (UNEP/MAP, 2019b)<sup>3</sup> in order to allow the comparability of the data and build of regional assessment schemes. They also take into account previous Sampling and Analysis Techniques for the Eutrophication Monitoring Strategy of MED POL (UNEP/MAP/MED POL, 2005)<sup>4</sup>, however providing detail procedures that are of relevance for IMAP implementation. With the details of the protocols for hydrographic chemical parameters, the needs of the measurements both in off-shore areas and in narrow coastal areas are addressed.

4. In the Subchapters “Symbol, units and precision” at the end of each Protocol, for all parameters described in it, the symbol and unit suggested by the International System of Units (SI) are presented. The expected accuracy, precision and where possible the Limit of Detection (LOD) are also presented. The Method identifiers are also presented as it is provided in the Library P01 of the British Oceanographic Data Centre (BODC) Parameter Usage Vocabulary respectively included in Data Dictionaries and Data Standards for eutrophication built in IMAP Pilot Info System.

5. The below flow diagram informs on the category of this Monitoring Guideline related to determination of hydrographic physical parameters within the structure of all Monitoring Guidelines prepared for IMAP Common Indicators 13, 14, 17, 18 and 20.

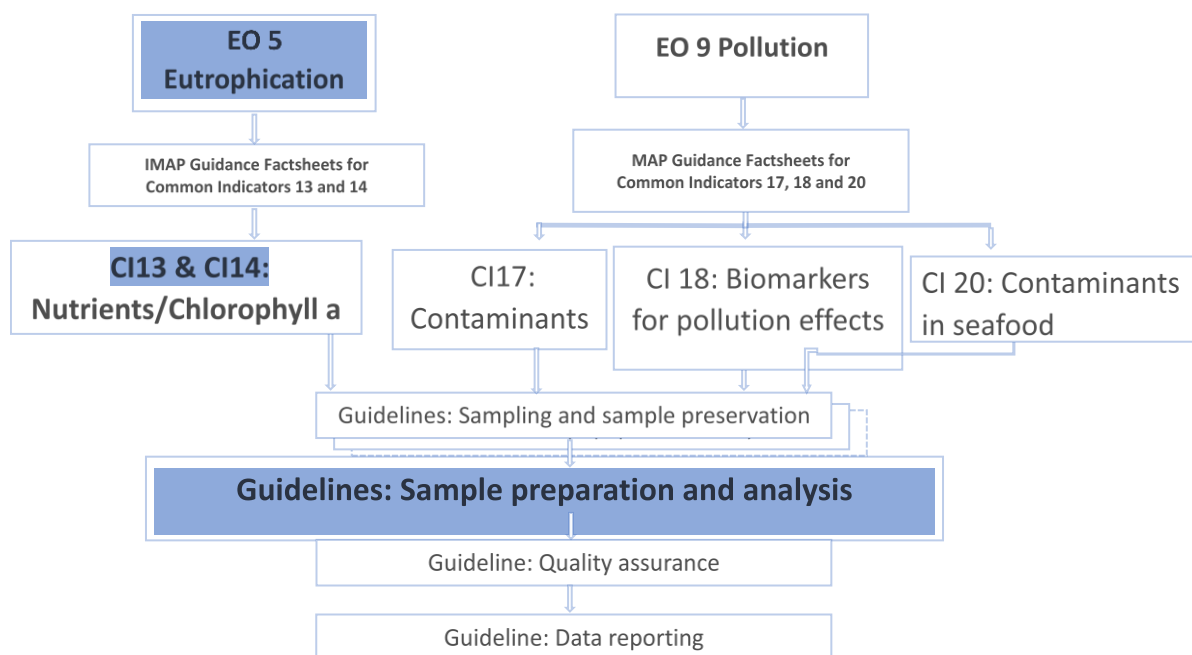
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<sup>1</sup> (UNEP/MAP, 2019), UNEP/MED WG.467/5. IMAP Guidance Factsheets: Update for Common Indicators 13, 14, 17, 18, 20 and 21: New proposal for candidate indicators 26 and 27

<sup>2</sup> (UNEP/MAP, 2019a), UNEP/MED WG.463/6. Monitoring Protocols for IMAP Common Indicators related to Pollution.

<sup>3</sup> (UNEP/MAP, 2019b), UNEP/MED WG.467/10. Schemes for Quality Assurance and Control of Data related to Pollution

<sup>4</sup> (UNEP/MAP/MED POL), 2005. Sampling and Analysis Techniques for the Eutrophication Monitoring Strategy of MED POL. MAP Technical Reports Series No. 163. UNEP/MAP, Athens, 46 pp.



**Flow Diagram: Monitoring Guidelines for IMAP Ecological Objectives 5 and 9**

## 2. Technical note for determination of temperature and salinity of seawater

6. **Temperature** is the property that regulates the transfer of thermal energy or heat between two bodies: the heat flow is directed from the warmer body to the colder one until thermal equilibrium is reached. Temperature measuring instruments are based on this basic principle. The temperature, together with salinity, is useful for identifying the mass of water sampled and for calculating, using an equation of state, the density and other derived quantities. This parameter also has effects on biological systems and in general on the chemical-physical balances in the marine environment, including the solubility of gases (e.g. oxygen solubility) and pH.

7. Prior to January 1, 1990, the temperature was expressed in the International Practical Temperature Scale of 1968 (IPTS-68). The 1990 International Temperature Scale (ITS-90) was subsequently adopted, which currently represents the best approximation of the thermodynamic temperature (T). In oceanography the convention is to measure the temperature on the Celsius (t) scale, whose unit is °C and with  $t = T - 273.15$ . The conversion between the old scale ( $t_{68}$ ) and the new one ( $t_{90}$ ) is given by the formula (Saunders, 1990)<sup>5</sup>:

$$t_{68} = 1.00024 t_{90}$$

8. **Salinity** is a measure of the content of dissolved materials in sea water. Together with the temperature it is a parameter of fundamental importance for identifying the mass of water sampled and for calculating the density (using an equation of state) and other derived quantities. It affects other parameters such as dissolved oxygen and has effects on many biological and chemical processes and systems in the marine environment.

9. Absolute salinity (SA) is defined as the ratio between the total mass of materials dissolved in sea water and the total mass of water. SA is very difficult if not impossible to measure directly,

<sup>5</sup> Saunders, P., 1990. The International Temperature Scale of 1990, ITS-90. Woce Newsletter, 10, IOS, Wormley, UK.

because it would be necessary to fully know the composition of sea water. Therefore, in practice, an approximate definition is given, the measurement of which is more easily achievable.

10. The first practical definition of salinity is that given in 1899 by the International Commission for the study of the oceans led by Prof. Martin Knudsen which established that salinity is the residual mass of salt (measured in grams) per kilogram of sea water, when all the carbonates have been transformed into oxides, the bromides and iodides replaced by chlorides and all the organic substance has been oxidized (Forch et al., 1902)<sup>6</sup>. Since the various components contribute to salinity according to a practically constant ratio and the main component, chloride, is easy to accurately measure by a simple chemical analysis (titration), for a long time the salinity of seawater has been determined indirectly by measuring the mass of chlorides dissolved in the water and using empirical relationships (Forch et al., 1902; Wooster et al., 1969)<sup>7</sup>.

11. The definition of salinity was revised when a technique was developed to be able to determine it from water conductivity measurements. In 1978, the JPOTS (UNESCO, 1981)<sup>8</sup> introduced the Practical Salinity Scale (PSS-78), which defines the practical salinity as a function of the ratio  $K_{15}$  between the electrical conductivity of a sample of sea water at temperature  $t_{68} = 15\text{ }^{\circ}\text{C}$  (defined in the IPTS-68 temperature scale) and at the pressure of a standard atmosphere (101325 Pa in the SI, corresponding to 1013.15 millibar), and that of a solution of potassium chloride (KCl), in which the molar fraction of KCl is 0.0324356, under the same conditions of temperature and pressure. A  $K_{15} = 1$  corresponds to a practical salinity of 35.

12. At  $15\text{ }^{\circ}\text{C}$ , the standard solution of KCl has an electrical conductivity which is equivalent to that of a North Atlantic seawater sample with chlorinity of 19.3740 at the same temperature. This fact guarantees:

- a certain continuity between the salinity measurements in the Practical Scale and the previous ones, which were largely based precisely on the measurement of chlorinity;
- the use of sea water with  $K_{15} \gg 1$  as a secondary standard for the routine calibration of instruments for measuring salinity.

13. Practical salinity is a dimensionless quantity, whose order of magnitude coincides with that of Knudsen's definition. Although it is an adopted practice, it is technically wrong to use the abbreviation "psu" (practical salinity units), and this practice should be absolutely avoided. This quantity enters into all the algorithms that are currently in use for calculating the thermodynamic properties of sea water (UNESCO, 1983)<sup>9</sup> and is also the one that is stored in databases.

14. Under this Technical Note, the Monitoring Guidelines for Determination of Hydrographic Physical Parameters elaborates the three following Protocols:

- Protocol for determination of temperature and salinity using CTD;
- Protocols for the determination of temperature using reversing thermometers;
- Protocol for sample preparation and analysis of salinity using bench salinometer.

## 2.1. Protocol for determination of temperature and salinity using CTD

15. The multiparameter probe, the only device with which the simultaneous and *in situ* measurement of temperature, salinity, pressure and any other bio-chemical parameters of interest are

<sup>6</sup> Forch C., Knudsen M., Sorensen S.P.L., 1902. Berichte über die Konstantenbestimmungen zur Aufstellung der hydrographischen Tabellen. Kgl. Danske Vidensk Selsk. Skrifter, 6 Raekke Naturvidensk, Mathem. Afd., 12: 1-151.

<sup>7</sup> Wooster W.S., Lee A.J., Dietrich G., 1969. Redefinition of salinity. Deep-Sea Res., 16: 321-322.

<sup>8</sup> UNESCO, 1981. The practical salinity scale 1978 and the international equation of seawater 1980. UNESCO Technical Papers in Marine Science, 36: 1-25.

<sup>9</sup> UNESCO, 1983. Algorithms for computation of fundamental properties of seawater. UNESCO Technical Papers in Marine Science, 44: 1-53.

allowed. Multiparameter probes for oceanographic measurements have been in use since the middle of the last century. The central unit that incorporates and manages the sensors that measure the quantities of interest is their main part. The probes for the measurement of physical parameters at sea are commonly called CTD, an acronym that summarizes the three basic physical parameters measured (C = Conductivity, T = Temperature, D = Depth, i.e. conductivity, temperature and depth). In reality, CTD probes do not measure depth directly, but provide an indirect measure of it by detecting pressure. CTD probes have a dual use, as profilers, when they are dropped along the water column from the surface to the bottom or to a desired intermediate depth, or as fixed-point sampling instruments (as happens when they are installed on a buoy or on an instrumented anchor). In the first case, the measurement of a vertical profile of the parameters and in the second one a time series at a precise point in space are collected. The vertical resolution of the profile and the temporal resolution are related on the sampling frequency of the instrument.

16. To check the correct functioning of a CTD system during an oceanographic campaign, it is useful to make comparisons by collecting water samples with a sampler connected to the system, to be analysed with a salinometer and by carrying out temperature measurements using reversing thermometers mounted on the sampler. The pressure values measured by the sensor of the CTD system can be compared with those provided by an independent pressure sensor.

a. Equipment

17. *CTD*: preferably be equipped with dual sensors for salinity and temperature, to prevent loss of data and provide a first instance of quality control. For stratified waters CTDs should preferably have a sampling rate of 12 Hz or higher. A CTD equipped with a rosette for water samplers is preferred to individual sampling flasks clamped to a wire. It is recommended that the CTD is mounted vertically within the frame of the rosette frame to avoid fouling of sensors by debris or bubbles and promote free flow of water.

18. *Reversing thermometers*, mounted on the rosette frame or on samplers from which reference data for temperature is obtained.

19. *Sampling bottles* attached to the CTD-rosette or attached on a line from which reference samples for bench salinometers are obtained.

b. Procedure

20. Many protocols for CTD measurements (WOCE 1991<sup>10</sup>, UNESCO 1994<sup>11</sup>, UNESCO, 1988<sup>12</sup>) are available. Starting from what is suggested by these protocols and taking into account the field experience the following protocol is preferable:

21. The manufacturer's recommendations on preparations of the CTD and rosette sampler must be followed. If the CTD has not been used for a long time, e.g. the first cast of the cruise, problems with bottles leaking may occur since the O-rings for the bottle's caps are dehydrated. If this is known to happen, it can be prevented by rinsing and filling all bottles with freshwater for at least 1 hour before sampling.

22. When the CTD is on deck the system is started and the CTD pressure and temperature in the logbook noted.

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<sup>10</sup> WOCE, 1991. WOCE Operational Manual WHPO 91-1, WOCE Report No68/. (<http://whpo.ucsd.edu/manuals.html>).

<sup>11</sup> UNESCO, 1994. Protocols for Joint Global Flux Study (JGOFS) Core Measurements. Manual and Guide, 29: 1-181.

<sup>12</sup> UNESCO, 1988. The acquisition, calibration and analysis of CTD data. A report of SCOR Working Group 51. UNESCO Technical Papers in Marine Science, 54: 1-59.



23. The CTD must be lowered below the sea surface for at least 1 minute before starting the measurements. This gives time for all sensors to acclimatize and air bubbles have time to be flushed out by the pump.
24. The CTD is bring back to the surface and the measurement of the profile started. If the sea state is rough it is recommended to start the downcast from a few meters below the sea surface to prevent bubbles from breaking waves entering the sensors.
25. Care must be taken to keep the lowering speed as constant as possible, and around  $0.5 \text{ m s}^{-1}$ . If an Active Heave Compensation (AHC) system is available, a slower speed ( $0.3 \text{ m s}^{-1}$ ) can be used.
26. The CTD as close to the bottom as possible is lowered, though without risking bottom contact. The bottom depth and all the other information required by the CTD log or monitoring protocol are noted.
27. The rosette bottles should preferably be fired at selected standard 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. If the winch is maneuvered manually between each sampling depth, attention must be paid to approach the set depth as gentle as possible to reduce the disturbance of the water profile. This is especially important in stratified waters.
28. At each sampling depth the sampling bottles should have time to acclimatize and the effect of dragging water from deeper depth should be avoided. Wait at least 1 minute before the sampling bottles to be fired. If the CTD values still are not stable wait another 3 minutes before firing. If the bottles are equipped with reference sensors do not forget to wait the appropriate time for the sensors to measure after firing the bottle.
29. However, if the CTD and rosette is equipped and prepared for free-flow sampling bottles, it can be configured to fire water samples on predefined standard depths during the down-cast. Note that samples near the surface should be collected during up-cast to avoid trapping air bubbles mixed into the water by breaking waves and turbulence when the CTD is lowered.
30. When the CTD is back on deck, the pressure and temperature in the CTD log are noted. The pressure value must be approximately the same as that read before the cast; differences are due to thermal and mechanical hysteresis of the pressure sensor. Deck pressure as offsets to correct pressure is not used. Deck pressure should only be used as consistency check against laboratory measured historical drift.
31. If there is any leakage or malfunction to the CTD, water sampler or water bottles it must be reported. Questionable sensor readouts should also be noted. All events happened during the cast also must be noted. Manufacturer's instructions for cleaning the CTD after each cast must be followed.
32. Between casts and after the cruise; the CTD and rosette in a way to prevent contamination must be stored. All sensors should be treated and stored according to the manufacture's recommendations.
33. Reference data for temperature is obtained from reversing thermometers, mounted on the rosette frame.
34. CTD-rosette or line; It is recommended that reference samples are collected in triplicates. For general requirements for sampling, preservation, handling, transport and storage of water samples, chapter 1.2.1. Protocol for the sample preservation of seawater for the determination of salinity must be consulted.

*c. Symbol, units and precision*

35. For the parameters described in this protocol, the symbols and units suggested by the International System of Units (SI), as well as the expected accuracy, along with the Method identifiers as provided in the Library P01 of BODC Parameter Usage Vocabulary are provided as follows:

***Depth:***

**Symbol:** *z*                      **Unit:** m

**Precision:**                      Pressure sensor:  $\pm 0,01$  m

**Method identifier:** SDN:P01::**DEPHPR01**      Depth (spatial coordinate) relative to water surface in the water body by profiling pressure sensor and conversion to seawater depth using UNESCO algorithm

***Temperature:***

**Symbol:** *t*                      **Unit:** °C (degree Centigrade)

**Precision:**                      Temperature sensor:  $\pm 0,01$  °C      **Accuracy:**  $\pm 0,0001$  °C

**Method identifier:** SDN:P01::**TEMPCC01**      Temperature of the water body by CTD and verification against independent measurements

***Salinity:***

**Symbol:** *S*                      **Unit:** -

**Precision:**                      Conductivity sensor:  $\pm 0,01$

**Method identifier:** SDN:P01::**PSALCC01**      Practical salinity of the water body by CTD and computation using UNESCO 1983 algorithm and calibration against independent measurements

**2.2.      Protocols for the determination of temperature using reversing thermometers**

**2.2.1.    Digital electronic reversing thermometers**

36. The digital reversing electronic thermometer, can perform the same functions as the mercury one, but with higher precision. Having the same dimensions of the mercury one it enters the housings provided for this type of thermometer. In this thermometer the temperature is measured by a platinum thermometer similar to the sensors used on the CTD probes. The advantages are that it does not use mercury, it covers a larger range of measurement, reading is easier because it is provided in digital form reducing the risk of loss of data, it is robust and easy to use.

*a. Procedure*

37. The thermometers are placed in the special thermometer holders with which the sampling bottles are equipped. In thermometer holders without a locking mechanism, the thermometers must be locked using para or neoprene rubber cylinders, usually supplied with thermometer holders, which cushion any mechanical shocks.

38. With the thermometer holder armed, a small magnet (supplied with the thermometer or common) is slid three times along the major axis of the thermometer, until on the display shows

written "Samp"; in this way the thermometer is set in reversing mode. For information, the "Cont" mode is used to display the instantaneous temperature measured in real time by the thermometer, while the "Hold" mode displays the temperature data recorded after reversing the thermometer, while it was in "Samp" mode.

39. The bottles with the thermometers must be kept at the programmed depths for the time necessary to reach the balance with the surrounding medium. The time required for digital thermometers is about 30 seconds. Then the command to close is send the bottle and to reverse the thermometer and wait at least ten seconds after the closing confirmation signal before changing deep or to retrieve the bottle.

40. Once the bottles are brought back to the surface, sliding the long magnet once along the major axis of the thermometer, the temperature value will appear on the display for a few seconds recorded by the thermometer during the reversal.

41. The data are written in a form, reporting the serial number for each thermometer.

### **2.2.2. Mercury reversing thermometers**

42. Mercury reversing thermometers consist of a main and a secondary thermometer, coupled in a glass container that protects them from mechanical changes induced by the water pressure. The main thermometer has a relatively large mercury tank that communicates, by means of a serpentine strangled in one point (called "break-off point") with a thin capillary ending with a small widening which constitutes a secondary tank. When the thermometer is in a straight position, at the desired depth, the mercury contained in the main tank changes volume according to the external temperature and occupies part of the thin capillary. When the thermometer overturn, due to the considerable surface tension, the mercury contained in the capillary breaks in the coil at the height of the choke and separates from the rest. The amount of mercury that separated, collected in the secondary tank and in part of the capillary, indicates the water temperature at the time of reversing. The auxiliary thermometer, mounted next to the reversing thermometer, is used to measure the ambient temperature, once the thermometer is brought back to the surface. **NOTE:** The use of mercury containing thermometers is not recommended and will be prohibited soon in compliance with the Minamata Convention.

#### *a. Procedure*

43. The thermometers are placed in the special thermometer holders with which the sampling bottles are equipped. In thermometer holders without a locking mechanism, the thermometers must be locked using para or neoprene rubber cylinders, usually supplied with thermometer holders, which cushion any mechanical shock.

44. The bottles with the thermometers are kept at the programmed depths for the time necessary to reach balance with the surrounding medium. The time required for mercury thermometers is 5-10 minutes. The reversing of the thermometer is then triggered.

45. The bottles are then returned to the surface and placed on a special support, making sure that are not directly affected by the sun, possibly covering them with a wet towel to avoid large fluctuations in temperature.

46. Once the balance between the temperature of the thermometers and the ambient temperature has been reached, using the appropriate eyepiece, the water temperature is read on the main thermometer (t'') with accuracy to one hundredth of a degree or higher in relation to the characteristics of the scale.

47. Similarly, on the auxiliary thermometer, the air temperature ( $t'_a$ ) is read with tenth degree precision. The eye must be in level with the upper part of the mercury column, to avoid errors due to refraction.

48. The data are written in a form, reporting the serial number for each thermometer.

*b. Calculations*

49. The reading provided by the thermometer, for the error caused by the capillary imperfections must be corrected proceeding as indicated in the calibration certificate that accompanies the thermometer. In the certificate, for temperature ranges of 5 °C, the correction to be made to the value read on the thermometer to obtain the real temperature value, or the value of the actual temperature at a given temperature value read, is reported. The temperature value read on the thermometer will probably not exactly match those indicated on the certificate, therefore first must be calculated the correction to be made to this value by applying a simple linear relationship between read values and real values. From the manufacturer's tables the values  $t''_{inf}$  and  $t''_{sup}$  within which the reading ( $t''$ ) is included and the corresponding correct values  $t'_{inf}$  and  $t'_{sup}$ , are read and the correct temperatures for the main thermometer  $t'$  and for the auxiliary thermometer  $t'_a$  calculated from the following equations:

$$t' = t'_{inf} + (t'' - t''_{inf}) (t'_{sup} - t'_{inf}) / (t''_{sup} - t''_{inf})$$

$$t'_a = t'_{a,inf} + (t''_a - t''_{a,inf}) (t'_{a,sup} - t'_{a,inf}) / (t''_{a,sup} - t''_{a,inf})$$

$t'$  and  $t'_a$  are inserted in the following equation:

$$c = (V_0 + t') / (t' - t'_a) / [K - \frac{1}{2} (t' - t'_a) - (V_0 + t')]$$

where:

$c$  = correction to be made,

$K$  = inverse of the thermal expansion coefficient of the glass with which the thermometer is built.

$V_0$  = volume of mercury at 0 °C.

The values of  $K$  and  $V_0$  are obtained from the calibration certificate.

The water temperature *in situ* is calculated from the formula:

$$t_w = t' + c$$

*a. Important notes related to both types of reversing thermometers*

50. All reversing thermometers, regardless of type, must be calibrated with a reference thermometer at least once a year. The reference thermometers must in turn be properly calibrated. Calibration must take place in thermostated baths.

51. Mercury thermometers must be treated gently, avoiding sharp strokes as they can cause microfractures in the capillary compromising its functioning; digital electronic thermometers are less delicate, but like all electronic instruments, they must be treated with care.

52. For mercury thermometers, if mercury does not return to the tank, avoid the common practice of gently tap the thermometer, because this causes small damages to the capillary. The reunification must be produced by forcing the expansion of mercury with a heat source.

53. The main malfunction that mercury thermometers may face concerns the possibility that during the reversal the mercury contained in the capillary will break at a height other than the "break-off point". This can happen due to the presence of bubbles formed by residual gas remained inside the thermometer during construction. This gas should remain confined at the upper end of the thermometer, in the secondary tank, but it can happen that a bubble penetrates the column of mercury, causing it to break in the wrong place. To avoid the problem, the thermometers must be stored and transported in a vertical position (with the main tank down) and handled gently.

*b. Symbol, units and precision:*

54. For the parameter described in this protocol, the symbol and unit suggested by the International System of Units (SI), as well as the expected accuracy, along with the Method identifiers as provided in the Library P01 of BODC Parameter Usage Vocabulary are provided as follows:

**Symbol:** *t*                      **Unit:** °C (degree Centigrade)

**Precision:**                      Mercury reversing thermometer: ± 0,01 °C

   Digital electronic thermometer: **Accuracy:** ±0,0001 °C

**Method identifier:** SDN:P01::**TEMPRTNX**      Temperature of the water body by reversing thermometer

   SDN:P01::**TEMPR601**      Temperature (IPTS-68) of the water body by reversing thermometer

   SDN:P01::**TEMPR901**      Temperature (ITS-90) of the water body by reversing thermometer

### **2.3.            Protocols for sample preparation and analysis of salinity using bench salinometer**

*a. Equipment*

55. The equipment for for sample preparation and analysis of salinity include: i) a laboratory salinometer; ii) IAPSO standard water bottles.

*b. General analytical procedure:*

*b.1 Preparation*

56. The salinometer must be turned on well in advance (at least two hours before the analysis), to stabilize the operation of its electrical parts and, when present, the temperature of the thermostatic bath.

57. Two bottles of standard water and the samples must be bring in the vicinity of the salinometer with which the measurement is carried out and allow a certain period of time to pass until they reach the same temperature.

*b.2 Standardization*

58. The measuring cell must be rinsed at least ten times with sea water with a salinity of about 35. There are bottles of water with these characteristics on the market, alternatively the standard water residues used in previous operations can be used.

59. The standard water bottles must be shaken carefully and gently to homogenize their contents, avoiding the formation of bubbles.

60. The standard water bottle must be opened and inserted into the salinometer sampling device.
61. The measuring cell must be rinsed at least four or five times with standard water.
62. The measuring cell is then filled with standard water and the salinometer standardized according to the procedure indicated by the manufacturer.
63. At least two or three measurements of the same standard water must be carried out, unloading and filling the cell each time and checking that the salinity value read after standardization coincides with the salinity value indicated on the standard bottle. If the value does not match, the standardization procedure with a new bottle of standard water must be repeated.

*b.3 Measurement*

64. With repeated overturning of the bottle the sample is homogenize avoiding too vigorous shaking not to allow the formation of air bubbles.
65. The measuring cell must be rinsed with the sample at least four or five times.
66. The measuring cell is filled with the sample and the outputs read.
67. The measuring cell is unloaded and filled again with the sample for new reading.
68. The operation referred to in the previous point is repeated until the difference between two consecutive readings is not less than the level of precision declared by the manufacturer of the instrument.

*c. Calculations:*

69. Having determined the conductivity ratio,  $R_t$ , between the sample and the standard water at temperature  $t_{68}$  (expressed on the IPTS-68 scale), the practical salinity is calculated according to the following equation, valid in the interval for  $S$  [2,42] (UNESCO, 1983):

$$S = a_0 + a_1R_t^{1/2} + a_2R_t + a_3R_t^{3/2} + a_4R_t^2 + a_5R_t^{5/2} + \Delta S$$

where

$$\Delta S = (b_0 + b_1R_t^{1/2} + b_2R_t + b_3R_t^{3/2} + b_4R_t^2 + b_5R_t^{5/2}) \cdot (t_{68} - 15) / [1 + k(t_{68} - 15)]$$

$t_{68}$  is expressed in °C. The temperature in the ITS-90 scale is converted in  $t_{68}$  with the equation,

$$t_{68} = 1.00024 \cdot t_{90}.$$

The values of constants are listed below:

$a_0 =$	0,0080	$b_0 =$	0,0005	$k =$	0,0162
$a_1 =$	-0,1692	$b_1 =$	-0,0056		
$a_2 =$	25,3851	$b_2 =$	-0,0066		
$a_3 =$	14,0941	$b_3 =$	-0,0375		
$a_4 =$	-7,0261	$b_4 =$	0,0636		
$a_5 =$	2,7081	$b_5 =$	-0,0144		

*d. Important notes*

70. Depending on the salinometer in use for the measurement, the procedure indicated may require some modification. It is recommended to check it, following the instructions in the instrument's instruction manual.

71. The formation of air bubbles in the sample during the pouring or mixing of the sample itself must be avoided. If this happens, the problem can be solved emptying and refilling the cell.

72. In the presence of deposits and / or air bubbles on the internal components of the measuring cell during use, washing attempts by pumping soapy water or weakly acid solutions into the cell must be avoided, because in addition to the possibility of being ineffective in solving the problem, can have a negative effect on factory calibration and instrument standardization. In the case, the cell must be repeatedly rinsed with deionized water. If the problem persists, the cell can be removed carefully, disassembled and cleaned as indicated in the instrument's instruction manual.

73. It is recommended to repeat the standardization procedure at least once a day with which the stability of the measuring apparatus electronics is maintained. If variations in the standardization values is observed, it is advisable to check the quality of the standard water bottle in use by repeating the operation with a new bottle. If the variations persist, it may be that the salinometer needs maintenance and needs to be sent to the service company.

74. The exposure to the air of standard water must be minimized.

75. For each sample, the time taken to obtain a valid measurement must be limited to the minimum time necessary as the minimum number of readings, avoiding that the volume used falls below the minimum necessary for the analysis.

76. The use of standard water bottles from the same batch for the same campaign is recommended, otherwise it is necessary to take into account the differences between batches as described by Mantyla (1987)<sup>13</sup> to correct the final salinities. In addition, if the bottles are older than two or three years, it is recommended to compare them with fresher standards to highlight any changes in conductivity due to aging.

*e. Symbol, units and precision*

77. For the parameter described in this protocol, the symbol and unit suggested by the International System of Units (SI), as well as the expected accuracy, along with a Method identifier as provided in the Library P01 of BODC Parameter Usage Vocabulary are provided as follows:

***Salinity:***

**Symbol:** *S*                      **Unit:** -

**Precision:**                      Conductivity sensor:  $\pm 0,01$

**Method identifier:** SDN: P01::PSALBSTX      Practical salinity of the water body by bench salinometer and computation using UNESCO 1983 algorithm

**3.                      Technical note for measuring Secchi depth**

78. Water transparency serves as an index for the trophic state of a water body. It reflects eutrophication through changes in the phytoplankton abundance; increase in the ambient nutrient status in the water leads to higher phytoplankton biomass that diminishes the propagation of light in

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<sup>13</sup> Mantyla, A.W., 1987. Standard seawater comparison. J. Phys. Oceanogr., 17: 543-548.

the water. Water transparency is approached by Secchi depth (Cialdi and Secchi 1865<sup>14</sup>, Whipple 1899<sup>15</sup>). Secchi depth is influenced by dissolved and/or colloidal inorganic and organic substances as well as total suspended solids and resident seston. It is thus affected by substances unrelated to eutrophication as well.

79. Secchi depth relates to primary production by being a proxy for the thickness of the euphotic zone wherein the large bulk of the gross production takes place. In principle, the euphotic depth is twice Secchi depth, but this relation varies largely in practice (French et al., 1982)<sup>16</sup>.

80. Under this Technical Note, the Monitoring Guidelines for Determination of Hydrographic Physical Parameters elaborate the IMAP Protocol for measuring Secchi depth.

### 3.1. Protocol for measuring Secchi depth

81. The methodology is based on the ISO 7027-2:2019<sup>17</sup> standard.

#### a. Equipment:

82. *Testing disk* (Secchi disk). A white disk with a diameter of 30 cm. The disk should weigh at least 1.7 kg to descend quickly and not be affected by horizontal water movements. Should the disk be lighter, an additional weight can be fastened to the down-facing side of the disk. As the observed Secchi depth tends to increase with the diameter of the disk (Aas et al., 2014)<sup>18</sup>, the disks of other sizes are not advised to be used.

83. *Measuring tape/rope* of non-elastic material. Depth<sup>19</sup> recognition:

- colour-coded marks at 10 cm intervals. The upper side of the disk equals 0 cm. Half and full meters should be marked to be easily distinguishable.
- depth indicator of a winch.

84. *Weight* for waters with currents, fixed in the middle of the down-facing side of the disk.

85. *Optional devices* for suppression of reflections, e.g., polarized glasses for the observer.

#### b. Measuring:

86. The observer should try to ensure that the measuring rope stays in an as upright position as possible. Deviations from the upright position stem from water currents and waves as well as ship's movement and thruster operation.

87. The Secchi depth is measured on the shaded side of the ship to avoid direct sunlight reflections from the water surface. However, the observer must consider the source of error in the shaded side that

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<sup>14</sup> Cialdi, M. and Secchi, P. A., 1865., Sur la transparence de la mer. Comptes Rendu de l'Academie des Sciences 61: 100–104.

<sup>15</sup> Whipple, George C., 1899., The microscopy of drinking-water. New York: John Wiley & Sons. pp. 73-75.

<sup>16</sup> French RH, Cooper JJ, Vigg S., 1982., Secchi disc relationships. Water Resources Bulletin 18: 121-123.

<sup>17</sup> ISO 7027-2:2019 Water quality — Determination of turbidity — Part 2: Semi-quantitative methods for the assessment of transparency of waters.

<sup>18</sup> Aas, E., Høkedal, J., Sørensen, K., 2014., Secchi depth in the Oslofjord–Skagerrak area: theory, experiments and relationships to other quantities. Ocean Science 10: 177–199.

<sup>19</sup> Secchi depth measurement is dependent on the observer's eyesight, and any aids for vision tend to increase Secchi depth, which should be considered, e.g., in the context of long-term data series.



occurs whenever the Secchi depth stretches beyond the shade of the ship. In this case, the disk is suddenly lighted by the sun and a higher reading will be attained.

88. Enough time must be allowed (preferably 2 min) when looking at the disc near its extinction point for the eyes to completely adapt to the prevailing luminance level. The disc must be lowered further until it is no longer visible. The achieved depth is to be read and written down. After that, the disc is lowered by another 0.5 m. Then, during a slow elevation, the disc becomes visible as a greenish-bluish spot. The achieved depth is to be read and written down. It is recommended to repeat the test two times as a minimum. The Secchi depth is the arithmetic average of all readings.

89. The precision of a Secchi measurement depends on the turbidity of the water. In the waters of high turbidity, the precision can approach 0.1 m under calm seas. In clearer waters, the precision ranges from 0.2 to 0.5 m, depending on actual conditions (e.g., waving or sun glitter).

*c. Important notes*

90. Secchi depth determination is sensitive to weather conditions:

- *Waving*: Optimally, Secchi depth should be measured when the sea is relatively calm. Waving introduces a source of error in the Secchi measurement by worsening the overall visibility, and waves > 0.5 m in height obscure the identification of the actual surface. The length reading of the rope at the surface should be judged to be an average of the extreme values due to waving. The determination of Secchi depth is not meaningful in high seas.
- *Sunlight*: Secchi depth should be determined to avoid direct sunlight reflections from the water surface. Sun glitter decreases the Secchi depth estimation irrespective of optical properties of water; on the average by 12% (Aas et al., 2014).

91. The length markings of the rope should be checked and made clearer annually. The rope should be changed whenever it stretches > 5%.

*d. Symbol, units and precision*

92. For the parameter described in this protocol, the symbol and unit suggested by the International System of Units (SI), as well as the expected accuracy, along with a Method identifier as provided in the Library P01 of BODC Parameter Usage Vocabulary are provided as follows:

**Symbol:**  $z_{SD}$     **Unit:** m

**Precision:**    0.2-0.5 m

**Method identifier:**    SDN:P01::SECCSDNX    Visibility in the water body by Secchi disk

**Annex I**  
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