Coalition Clean Baltic
For protection of the Baltic Sea environment

River monitoring

Manual for public environmental monitoring

APPENDIX 5. Determination of general and integral parameters of water

§ 1. Temperature

Temperature fluctuations affect plants and aquatic animals differently. Some animals feel well in warmer water, while others can survive only in cooler water. Development of phyto- and zooplankton also depends on the water temperature.

In addition, water temperature influences various chemical parameters of water. It affects the dissolved oxygen and other gases, levels of which go down as the temperature goes up.

If the goal is to detect thermal pollution, water temperature should be measured in several locations of the water reservoir about several hundred meters away from one another at the point where thermal pollution is expected and at the control point (temperature background). It is necessary to take into account that the selected locations should have similar physical and hydrological conditions, namely, the river flow rate, depth, wind conditions, sun exposure, etc. In a river, the control point should be upstream from the potential source of thermal pollution. It makes no sense to measure temperature in the areas of natural water warm-up, e.g., at sandbanks, vegetation beds of aquatic plants, etc., because water temperature in such areas is usually noticeably higher than the general temperature background.

Water temperature measurement method

Equipment:

Calibrated thermometer, water sampler (for deep water measurement)

Measurement:

Water temperature should be measured in the water reservoir by a calibrated thermometer with 0.1–0.5°C scale division value (in some cases, 1°C scale division value is reasonable). Fix the thermometer in the water sampler, place it at the selected depth, and hold it there for no less than 5-10 minutes. Then pull the water sampler up and read the temperature with the thermometer still in the water.

For deep measurements, it is necessary to use tipping water samplers that are filled with water at the indicated depth. Temperature of surface water is measured with the thermometer at the depth of 15-20 cm. The surface temperature might differ markedly (by 3–5°C and more) from the temperature at the depths of several meters. Pay special attention to rivers, canals, and waste channels running into the water reservoir. In the presence of water reservoir feeders (waste channels, creeks, and rivers), measure the temperature in the mixing zones at the places where they flow into the water reservoir. If the difference between the temperature measurements is several degrees, one can speak of thermal pollution of the water reservoir.

You can reduce the observation error to minimum if the following rules are conformed:

- Use only calibrated thermometers for measurements (to calibrate the thermometer or verify its accuracy, place it into thawing ice (0°C) and in boiling water (100°C);
- Measure temperature at different points with the same thermometer and take the arithmetic mean of several measurements as the ultimate result.

Conclusions:

Temperature of water in surface water sources depends on the temperature of the air and its humidity, the flow rate and water flow pattern, and a number of other factors. It may vary significantly with seasons (from 0.1 and up to 20°C and higher).

To reach a reliable conclusion if the water temperature you measured is the normal rate or not, it is important to compare your measurements with the monitoring data of many years for this parameter if such data are available. An insignificant temperature increase may indicate a long-term human impact on the river, particularly, by cutting down trees that shade the water flow. Erosion of soils caused among other reasons by deforestation of the river banks due to inexpert economic activities, construction development, etc. may also be the cause of water heating. Erosion of soils impacts water muddiness which in its turn leads to the rise of temperature.

Short-term water temperature rise may be caused by a volley industrial effluent. Thermal power plants may be the major source of river pollution. Thermal pollution of a river in summer may be caused by rain waters from streets, pavements, and parks[1].

§ 2. Power of hydrogen

Under normal conditions, pH in most rivers varies from 6.5 to 8.5. Values of pH beyond this range are adverse for hydrobionts (aquatic organisms). The pH value depends upon many factors including aquatic plant functioning. In the daytime, plants appropriate oxygen dioxide from water and diminish its acidity, which raises the pH , and in the night the process goes backwards.

The pH value can be measured using pH-metry and visual colorimetric measurements. pH-metry presumes measuring pH index using pH meters and permanent (laboratory) instruments, while visual colorimetric measurement is held using portable testing kits based on the reaction of a universal or combined indicator with hydrogen ions accompanied by change of color of the solution. Accuracy of measuring with a pH-meter can be quite high (up to 0.1 pH units and less), while with a visual colorimetric testing kit it is about 0.5 pH units.

In certain cases, pH indicator paper may be used for a quick (alarm) analysis of unknown solutions; its accuracy in pH measurement is no greater than ±1, which is not sufficient for natural drinking water measurements. However, indicator paper can be helpful for a rough estimate (initial level, classes from 5 to 8).

Below we describe the ***visual colorimetric method*** for pH measurement as the easiest and handiest one.

Equipment and chemical reagents:

Dropper pipette (0.50ml); colorimetric test tubes with “5 ml” mark

Solution of universal indicator

Control scale of sample solution colors for pH measurement (pH: 4.5; 5.0; 5.5; 6.0; 6.5; 7.0; 7.5; 8.0; 8.5) from the testing kit or prepared individually.

See below how to prepare solutions.

Measurements:

1. Rinse the test tube with the tested water several times. Fill the test tube with analyte water up to the mark (5 ml).

2. Using the dropper pipette, add 3-4 drops (about 0.10 ml) of the universal indicator solution and shake the test tube.

3. Compare the color of the solution with the control scale immediately after; choose the sample of the scale that is the closest by color. Observe the color from above through the open end of the test tube on white background in a sufficient light.

Accuracy check of the pH indicator measurement can be made by testing specially prepared control buffer solutions which have pH values close to the ones of the control scale samples. It is recommended to use a pH-meter to verify the pH values of buffer solutions. For descriptions of buffer compositions for preparation of control solutions, see Appendix 1 of the *Manual for Measuring Water Quality Indicators Using Field Methods* by A.G. Muraviev (Christmas+, St. Petersburg. 2009).

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[1] Mitchel M. K., Stapp W. B. *Water Quality Indicator*. *Field Manual for Water Quality Monitoring* (GREEN, USA): translation from English - SPb.: “Prozrachnye Vody Nevy”, 1995. – 36 p.

Universal indicator solution

Solution A. Place 0.10 g of bromothymol blue indicator into a porcelain jar and dissolve it with contusing in 8.0 ml of sodium hydrate solution with 0.02 mol/l concentration. Add 50 ml of rectified ethyl alcohol, transfer the mixture into a measuring cup of 250 ml capacity and make up the volume with distilled water.

Solution B. Place 0.025 g of methyl red indicator into a porcelain jar and dissolve it with contusing in 4.6 ml of sodium hydrate solution with 0.02 mol/l concentration. Add 50ml of rectified ethyl alcohol and transfer the mixture into a measuring cup of 250ml capacity and make up the volume with distilled water.

Mix solutions A and B in 1:1 proportion. The universal indicator solution is storage-stable.

Conclusions:

If in the result of your measurements you found out that if the pH indicator does not correspond to the norm, it is necessary to identify the reason for the deviation. It is important to understand that the pH value for natural water to a certain extent depends on the hydrogeology of the water catch basin. Humic acids and particularly fulvic acids that are present in abundance in the soils of forest zones and have high migrating capacities (i.e., running down the river flow) can be a natural cause for lower pH values. Among various anthropogenic impacts on pH fluctuations, acidic rains are the most typical causes of pH increase in rivers.

§ 3. Dissolved oxygen. BOD

Biological oxygen demand (BOD) is an important characteristic of natural water. BOD is the measure of the amount of oxygen used by aerobic bacteria during decomposition. BOD tells about the water's self-purification capacity and is an indirect indicator of the amount of organic material in the water.

The Winkler Method

Equipment and chemical reagents:

Barometer of any type; rubber squeeze bulb or medical syringe; conical flask of 250–300 ml capacity; calibrated oxygen stopper bottle (100–200 ml); stirrer (glass ball, stick, etc.) of known volume; 1 ml and 10 ml measuring pipettes; thermometer with the scale division value no bigger than 0.5°C; tray.

Permanganate solution; sulphur acid solution (1:2); sodium thiosulphate solution (0.02 mol/l eq.); starch solution (0.5%); alkaline potassium iodide solution.

If the laboratory has oxygen meters (devices that measure the proportion of oxygen in water), they can well be used for testing in field conditions. .

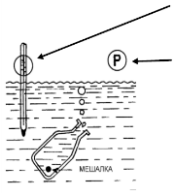
See below how to prepare solutions.

Sampling:

Sampling for DO has a number of features. Normally, for DO sampling you can use a batometer with a 20-25 cm rubber tube attached to its cock. Enameled or glass containers are used for taking samples from surface layers. If the sample is taken for general analysis of various components, the DO sample should be the first one to take for further processing. Rinse clean calibrated flasks from the kit two or three times with water from the sample or (if special preparation of a sample for analysis, e.g., subsidence, is needed) glass bottles.

Flasks are filled with water from the batometer using a siphon pipe through a rubber tube submerged to the bottom of the flask. After the oxygen flask is filled completely, its filling should go on until about 100 ml of water has poured out of it, i.e., until all water which has contacted the air in the flask and one more flask volume is displaced. Pull the tube out of the flask without interrupting the water flow from the batometer. Similarly, fill the flask from the bottle with analyzed water or the bottle from the batometer (in the latter case, submerge the rubber tube of the siphon half way of the bottle water column). Fix the oxygen right after the filling as described below.

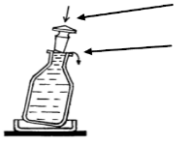
Sampling for measuring DO concentration in a water reservoir on the spot is performed as follows.



- Measure and register the temperature value

- Measure and register the value of atmospheric pressure

- Fill a flask with a mixer brim-full with sample water



- Stopper the bottle. (You need to know the exact values of the temperature and atmospheric pressure for calculating the degree of the sample saturation with oxygen)

Notes: 1. No air bubbles should stay in the flask.

2. Analyze the sample as quickly as possible.

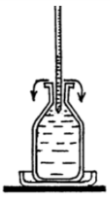
Procedure:

A. Fixation of oxygen in the tube

1. Using different calibrated pipettes, add 1 ml of manganese sulfate solution to the flask, then 1 ml of alkali-iodide solution and 1-2 drops of sulfamic acid solution; stopper the flask with care. If the water does not contain nitrites or their content is below 0.05 mg/l, adding sulfamic acid solution is not necessary. However, normally one does not know the nitrite concentration, and we recommend adding sulfamic acid solution at each testing.

2. Mix the content of the flask using the mixer inside it and holding the flask in your hand. Allow the residuum to settle for no less than ten minutes. Note: The flask with the “fixed” sample can be stored for no more than 24 hours in a dark place.

B. Titration

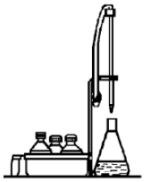


3. Using a pipette, add 2 ml of sulfur acid solution to the flask inserting the pipette down to the residuum (do not stir it up!) and gradually lifting it up by emptying the pipette.

4. Stopper the flask and mix the content to dissolve the residuum.

5. Move all the content of the flask to the 250 ml conical flask.

Note. You can measure the DO concentration in water by titrating a part of the sample. To do this, move 50.0 ml of the sample with dissolved residuum into the 100 ml flask using a cylinder. Proceed as described below for processing the entire sample.



6. Collect 10 ml of thiosulphate solution into a burette (pipette) fixed in a holder from the kit and titrate the sample till light-yellow color. Then add 1 ml of starch solution (solution in the flask will become blue) with a pipette and keep titrating till the solution turns clear.

7. Measure the full volume of thiosulphate solution used for titration (both before and after adding the starch solution). In the case of obstructing impurities in the analyte water (suspended and colored substances, reducing agents, iron in concentrations above 1 mg/l), special sample treatment is required (see detailed description in the “Diluted oxygen” certificate). Then fill the oxygen flask with the sample, fix it, and titrate as described above.

Calculation of the analysis results

In the case of titration of the entire volume of the solution in the oxygen flask, calculate the mass DO concentration in the analyte water sample (DOC) in mg/l by the formula:

$$C_{PK} = \frac{8 \times C_T \times V_T \times 1000}{V - V_1}$$

where: 8 is the equivalent mass of atomic oxygen;

C_T is the concentration of standard titrated thiosulphate solution, mol/l eqv.;

V_T is the total volume of titrated thiosulphate solution spent on titration (both before and after adding the starch solution), ml;

V is the internal volume of calibrated oxygen stoppered flask (identified beforehand for each flask individually), ml;

V1 is the sum volume of manganese chloride and alkali-iodide solutions added to the flask while fixing DO and of the mixer, ml (calculated as V1=1+1+0.5=2.5ml);

1000 is the ratio of measurement unit conversion from g/l to mg/l.

Note. It is assumed that losses of dissolved oxygen in fixed form in course of pouring off extra liquid from the flask and other operations is much less that measurement results (losses are negligibly small).

In the case of titration of a part of the sample (50.0ml) in the oxygen flask, the mass DO concentration in the analyte sample (DOC in mg/l) is calculated by the formula:

$$C_{PK} = \frac{8 \times C_T \times V_T \times 1000}{50 \times (V - V_1)}$$

Example of calculation of the dissolved oxygen concentration in water

With the total volume of thiosulphate solution used for titration amounting to 4.7ml, concentration of thiosulphate solution of 0.02 mmol/l eqv., and oxygen flask volume of 102.5ml, the content of dissolved oxygen is calculated as follows:

$$C_{PK} = \frac{4{,}7 \times 0{,}02 \times 8 \times 1000}{102{,}5 - 2{,}5} = 7{,}52 \text{ мг/л.}$$

For determining the oxygen percent saturation, find the concentration of oxygen- saturated solution (C_H, mg/l) from Table 1 based on the water temperature value registered at the time of sampling.

Then calculate the oxygen percent saturation (R) taking into account the factual value of the atmospheric pressure by the formula:

$$R = \frac{C_{PK} \times 100 \times 760}{C_H \times P}$$

where: 100 is the ratio of measurement unit conversion mg/l to %;

760 is standard atmospheric pressure, millimeter of mercury;

C_H is the concentration of oxygen saturated solution for the sampling conditions identified by Tab. 1.

P is the factual value of the oxygen-saturated solution at the moment of sampling.

Note. If there is no data on atmospheric pressure at the time of sampling, it is allowed to assume it equal to standard atmospheric pressure (i.e., 760 millimeter of mercury).

Table 1

Temperature dependence of oxygen equilibrium concentration in water (760 mm Hg atmospheric pressure)

Temperature	Equilibrium DO concentration (mg/l) dependence on temperature (C_H)

Температура	Равновесная концентрация растворенного кислорода (в мг/л) при изменении температуры на десятые доли °С ($C_в$)									
°С	0	0,1	0,2	0,3	0,4	0,5	0,6	0,7	0,8	0,9
0	14,65	14,61	14,57	14,53	14,49	14,45	14,41	14,37	14,33	14,29
1	14,25	14,21	14,17	14,13	14,09	14,05	14,02	13,98	13.94	13,90
2	13,86	13,82	13,79	13,75	13,71	13,68	13,64	13,60	13,56	13,53
3	13,49	13,46	13,42	13,38	13,35	13,31	13,28	13,24	13,20	13,17
4	13,13	13,10	13,06	13,03	13,00	12,96	12,93	12,89	12,86	12,82
5	12,79	12,76	12,72	12,69	12,66	12,52	12,59	12,56	12,53	12,49
6	12,46	12,43	12,40	12,36	12,33	12,30	12,27	12,24	12,21	12,18
7	12,14	12,11	12,08	12,05	12,02	11,99	11,96	11,93	11,90	11,87
8	11,84	11,81	11,78	11,75	11,72	11,70	11,67	11,64	11,61	11,58
9	11,55	11,52	11,49	11,47	11,44	11,41	11,38	11,35	11,33	11,30
10	11,27	11,24	11,22	11,19	11,16	11,14	11,11	11,08	11,06	11,03
11	11,00	10,98	10,95	10,93	10,90	10,87	10,85	11,82	10,80	10,77
12	10,75	10,72	10,70	10,67	10,65	10,62	10,60	10,57	10,55	10,52
13	10,50	10,48	10,45	10,43	10,40	10,38	10,36	10,33	10,31	10,28
14	10,26	10,24	10,22	10,19	10,17	10,15	10,12	10,10	10,08	10,06
15	10,03	10,01	9,99	9,97	9,95	9,92	9,90	9,88	9,86	9,84
16	9,82	9,79	9,77	9,75	9,73	9,71	9,69	9,67	9,65	9,63
17	9,61	9,58	9,56	9,54	9,52	9,50	9,48	9,46	9,44	9,42
18	9,40	9,38	9,36	9,34	9,32	9,30	9,29	9,27	9,25	9,23
19	9,21	9,19	9,17	9,15	9,13	9,12	9,10	9,08	9,06	9,04
20	9,02	9,00	8,98	8,97	8,95	8,93	8,91	9,90	8,88	8,86
21	8,84	8,82	8,81	8,79	8,77	8,75	8,74	8,72	8,70	8,68
22	8,67	8,65	8,63	8,62	8,60	8,58	8,56	8,55	8,53	8,52
23	8,50	8,48	8,46	8,45	8,43	8,42	8,40	8,38	8,37	8,35
24	8,33	8,32	8,30	8,29	8,27	8,25	8,24	8,22	8,21	8,19
25	8,18	8,16	8,14	8,13	8,11	8,11	8,08	8,07	8,05	8,04
26	8,02	8,01	7,99	7,98	7,96	7,95	7,93	7,92	7,90	7,89
27	7,87	7,86	7,84	7,83	7,81	7,80	7,78	7,77	7,75	7,74
28	7,72	7,71	7,69	7,68	7,66	7,65	7,64	7,62	7,61	7,59
29	7,58	7,56	7,55	7,54	7,52	7,51	7,49	7,48	7,47	7,45
30	7,44	7,42	7,41	7,40	7,38	7,37	7,35	7,34	7,32	7,31

Example of oxygen percent saturation

For the values of C_{PK}=7,52mg/l, C_H=9,82mg/l, P=735 mm Hg and 16°C water temperature at the moment of sampling, the oxygen percent saturation amounts to:

$$R = \frac{7{,}52 \times 100 \times 760}{9{,}82 \times 735} = 79{,}2\ \%$$

Measurement accuracy control

Measurement accuracy control for measuring DO concentration in water should be performed with a verified (standard) oxymeter.

Concentration of dissolved oxygen in the course of water testing for BOD analysis can be determined by different methods. The most widespread method for DO determination in BOD analysis is the method of iodometric titration, the Winkler Method (see detailed description above).

In its field version, the proposed method of BOD determination presumes measurement of BOD5 for natural surface waters that are relatively unpolluted and usually sufficiently saturated with oxygen; for this reason, aeration of samples, addition of dissolving water and introduction of nitrification inhibitors is

not necessary. The method used is applicable for arbitrage analysis of surface and sewage waters with content of organic substances corresponding to oxygen utilization for their combustion under 6 mg/l. However, with high content of organic substances in water, this method cannot bring accurate results in the proposed simplified version (the entire DO is spent prior to the end of the 5-day incubation), and for this reason it is necessary to dilute the sample with uncontaminated aerated water.

An alternative method for BOD determination is the **method with electrode (potentiometric) measurement of DO concentration by an oximeter.** You should take consideration of all above-mentioned peculiarities of BOD as of a water quality indicator as well as biochemical processes in the sample.

Equipment and chemical reagents:

Equipment, chemical reagents, and appliances for determination of dissolved oxygen by the Winkler Method (see above); calibrated oxygen flasks for incubating the sample; Petri dishes; thermostat incubator providing for permanent temperature (20±1)°C.

Testing:

1. Sample water to oxygen flasks (at least 3) as described in the DO determination method.

Note. To receive a representative sample, sampling should be made as far as possible from the banks, bottom, aquatic plants, etc., which can discharge organic substances and/or micro organisms into water.

2. Fix oxygen right away in the first flask and determine DO.

3. Put the other incubation flasks (two or more) into the incubator in the darkness through a water-seal from the Petri dish as it is shown on the picture (this will prevent the contact of the flask water with the air).

Note. It is better to incubate several samples because in case of error results it will be impossible to repeat the test.

4. After 5 days of incubation in the flasks, determine concentration of the residual DO as the arithmetic mean of all incubation flasks.

5. Calculate the value of BOD5 in mg/l by the formula:

BOD5 = C1 – C2,

where: C1 is DO concentration in the initial sample, mg/l;

C2 is the DO median concentration by the end of the incubation period, mg/l.

Solution preparation:

Permanganate solution:

The solution should be prepared in an appropriate container of four-hydrate manganese sulfate (480 g/l concentration) or four-hydrate manganese chloride (425g/l concentration) in distilled water.

Sulfuric acid solution (1:2):

Add 10 ml of concentrated sulfuric acid to 20 ml of distilled water gradually. (Remember of safety precautions!)

Sodium thiosulphate solution (0.02 mol/l eqv.):

The solution is prepared of one ampoule of fixanal (standard titer) of sodium thiosulphate (0.1 mol/l eqv.).

To prepare 0.02 mol/l eqv. of thiosulphate solution, measure 20.0 ml of the solution with 0.1 mol/l eqv. concentration using a cylinder and place that into a 100 ml measuring flask; then make the solution volume up to the mark with distilled water.

To increase stability of thiosulphate solutions, add 10 ml of amyl alcohol or isobutyl alcohol (or 1–2 ml of xylol or chloroform) per 1 l of solution.

Solutions should not be used earlier than 10 days after their preparation.

In the process of using the solution, you should periodically (e.g., before the start of field works) determine the exact concentration of standard thiosulphate solution by the method of titration with potassium bichromate solution.

Starch solution (0.5%):

Mix 0.5 g of soluble starch with 10 ml of water till the mixture becomes homogeneous and then gradually pour it stirring into 90 ml of boiling water and boil it for 2-3 minutes. After cooling, preserve the solution with 2–3 drops of chloroform. The solution will stay stable after preservation for up to one month if kept in a cool dark place. It is recommended to use the solution prepared before the start of field works.

Alkali potassium iodide solution:

Make the solution mixing solutions (a) and (b) of the following compositions:

a) Solution of 150 g of potassium iodide in 100 ml distilled water;

Make this solution using potassium iodide specifically cleaned of traces of free iodine;

b) Solution of 500 g sodium hydrate in 500 ml boiled and cooled distilled water. Mark up the total volume of mixed solution with distilled water to 1000 ml in an appropriate container. (Remember of safety precautions!)

Conclusions:

Depending on the type of the water reservoir, BOD_5 (5-day BOD) of surface water fluctuates from 0.5 to 5.0 mg/l; it is subject to seasonal and daily variations. BOD above-limit value can be a consequence of anthropogenic organic pollution of environmental waters. If sources of pollution can be identified by discharge points, such sources are called local. These include pulp and paper mills and wood processing factories (lignines), meat processing plants (albuminous compounds), and agricultural enterprises.

Non-local pollutions originate from many sources which are hard to identify. They include:

- Rain and melt water flows bringing pollution from unauthorized sewages into systems of rainfall run-offs; cats and dogs' faeces from streets and pavements;
- Agricultural waters containing biogenic elements from fields;
- Cattle yards run-offs containing faeces.