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| Computational Methods in Water and Environmental Engineering – WAT 1030E |



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| **WATER ANALYSIS** |
| SUMMARY OF STANDARDS  Autumn 2020 |
| 1. pH 2. Electrical conductivity 3. Turbidity 4. Colour 5. NPOC 6. CODMn 7. Total iron 8. Hardness 9. Chloride 10. Nitrate 11. Total nitrogen 12. Orthophosphate 13. Total phosphorus 14. Bacteria |

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# **Determination of pH value**

Determination of pH is one of the most important and frequently used tests in water chemistry. pH is a term to express the intensity of the acid or alkaline condition of a solution. It is a way to express the hydrogen-ion concentration, or more precisely, the hydrogen-ion activity.

***Reagents:***

1. Commercial pH buffers pH 4, pH 7 and/or pH 9 are used to calibrate the pH-meter depending on the expected (or target) pH of the sample.

***Procedure:***

Take the pH buffer into the beaker and calibrate the pH-meter according to the manufacturer’s instruction. The pH-meter used in these exercises has also temperature probe, so warming up either buffer solutions or samples is not needed. The pH-meter is calibrated beforehand, so it is ready for the use.

Rinse the probes well with reverse osmosis water (RO-water), immerse them in the beaker where the well-shaken sample is, and measure its’ pH. The reading is directly pH of the sample. After measuring, rinse probes well with RO-water and put back into storage solution.

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| --- | --- | --- |
| Sample | pH | Temperature, °C |
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|  |  |  |

The results are reported to one decimal place.

***Literature:***

SFS-EN ISO 10523, dated 2012. Water quality. Determination of pH

# **Determination of electrical conductivity**

Ability to carry electrical current is called the conductivity of a solution. It varies with both the number and type of ions the solution contains. Most of the dissolved inorganic substances in water supplies are in the ionized form, and so contribute to the specific conductance.

Conductivity is reported in unit of milli siemens per meter (mS/m).

***Procedure:***

It is possible to use same sample than in pH-measurement.

First, measure temperature of the sample and adjust the reading to the conductivity meter. Temperature value from pH-measurement can be also used. Rinse the conductivity probe with RO-water, immerse into the sample, and measure the conductivity. Rinse the probe well with RO-water after measuring.

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| --- | --- | --- | --- |
| Sample | Temperature, °C | Reading from the screen | Measuring range |
|  |  |  |  |
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***Literature:***

SFS-EN 27888, dated 1994. Water quality. Determination of electrical conductivity

# **Determination of turbidity**

The term turbidity means reduction of transparency of a liquid, caused by the presence of undissolved matter. The turbidity may be caused by wide variety of suspended materials, which range in size from colloidal to coarse dispersions, depending upon the degree of turbulence.

Turbidity is reported in terms of Formazine Nephelometric Units (FNU).

***Procedure:***

Before measuring, check that in the equipment’s display:

* Range Mode is AUTO
* SIGNAL AVG and SAMPLE have green light.

Handle the turbidity tubes only from spiral part on top of the tube.

Mix sample well, but in a way that that you cause as little air bubbles as possible. Pour the sample into the cell. Wipe off the drops with soft paper and finger marks with the piece of cloth. Close the tube. Put the cell in the turbidity meter and read the turbidity value from the instrument scale. After measuring, rinse the tubes first with warm tap water and after that with RO-water.

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| --- | --- |
| Sample | Turbidity reading, FNU |
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***Calculation:***

Report the results as follows:

* If the turbidity is less than 0.99 FNU, to nearest 0.01 FNU
* If the turbidity is between 1.0 FNU and 9.9 FNU, to the nearest 0.1 FNU
* If the turbidity is between 10 FNU and 40 FNU, to the nearest 1 FNU

***Literature:***

SFS-EN ISO 7027, dated 2000. Water quality. Determination of turbidity

# **Determination of colour**

Natural waters are mostly coloured yellowish brown by particular components of iron, clay particles, and by humic matter. Algae and other impurities can also cause colour to water. True colour of water means the colour due to only dissolved substances, determined after filtration of the water sample through a membrane filter of pore size 0.45 µm (SFS-EN ISO 7887, dated 2011, page 2).

***Reagents:***

1. Colour calibration solution, 100 mg/l Pt

***Procedure:***

Filter the sample through 0.45 µm membrane filter. Measure sample’s absorbance using spectrophotometer at wavelength 410 nm and 4 cm optical glass (OG) cell. Measure also the absorbance of calibration solution. Rinse cell carefully after every measurement.

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| Sample | Absorbance |
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***Calculation:***

Specific absorption for the calibration solution, α (mm-1(mg/l Pt)-1):

α = A410 / (100 \* d)

where,

A410 = absorbance of the colour calibration solution

factor 100 = the concentration of the calibration solution in mg/l Pt

d = the optical path length, in millimetres, of the optical cell

True colour of sample: mg/l Pt = A**410S**/αd

Where, A**410S**=absorbance of the sample

Report the value to the nearest mg/l Pt.

***Literature:***

SFS-EN ISO 7887, dated 2012. Water quality. Examination and determination of colour

# **Determination of total organic carbon (NPOC)**

In addition to organic carbon the water sample may contain carbon dioxide or ions of carbonic acid. Prior to the TOC determination, it is essential that this inorganic carbon is removed by purging the acidified sample with a gas which is free from CO2 and organic compounds. Alternatively, both total carbon (TC) and total inorganic carbon (TIC) may be determined and the organic carbon content (TOC) may be calculated by subtracting the total inorganic carbon from the TC.

NPOC is the most commonly used method for TOC measurement. NPOC (Non-Purgeable Organic carbon) is the quantity of carbon, which is not volatile, when the sample is aerated. First, the sample pH is lowered to 2-3 by hydrochloric acid (HCl) and then the inorganic carbon (IC) as a carbon dioxide is aerated. Total carbon (TC) left is total organic carbon (TOC), but it is called as NPOC.

Shimadzu TOC-V-analyser uses NPOC method.

Results are provided in tables and they are reported in a unit of milligram per litre, using two expressive numbers.

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| --- | --- |
| sample | NPOC, mg/l |
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|  |  |

***Literature:***

SFS-EN 1484 dated 1997, Water analysis. Guidelines for the determination of total organic carbon (TOC) and dissolved organic carbon (DOC) + Shimadzu TOC-5000A – manufactures instruction

# **Determination of chemical oxygen demand (CODMn-value or KMnO4-number)**

The chemical oxygen demand test is widely used as a means of measuring organic matter in the waters. This method (oxidation with permanganate) is used mainly in Finland. Permanganate value indicates the amount of potassium permanganate in unit of milligram per litre, which 1 l of water consumes in the conditions mentioned in the standard 3036.

(Oxidation with potassium permanganate, Summary of Finnish standard SFS 3036 (dated 1981)).

***Reagents:***

1. Sulphuric acid, 4.0 mol/l
2. Potassium permanganate solution, 0.1 mol/l
3. Potassium iodide solution, 0.1 mol/l
4. Starch – indicator
5. Sodium thiosulfate solution (Na2S2O3), 0.01 mol/l

***Procedure:***

Make two identical tubes for each sample. Shake the sample well and pipette 10 ml sample or its’ dilution to both of two tubes. Make two blank sample tubes by pipetting 10 ml RO-water into the tubes and handle them equally with the other samples. Add 0.5 ml 4 M sulphuric acid and 2.0 ml potassium permanganate solution. Put the tubes in the boiling water bath for 20 minutes. Let the tubes cool down.

Just before titrating, add 1 ml potassium iodide and few drops of starch to the tube. Mix content of the tube with magnetic stirrer and titrate with 0.01 M sodium thiosulfate until blue colour disappears.

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| --- | --- | --- | --- |
| Sample | Tube number | Amount of sample, ml | Volume of consumed Na2S2O3, ml |
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Concentration of used sodium thiosulfate solution: \_\_\_\_\_\_\_\_\_\_ mol/l.

***Calculation:***

CODMn = (V2 - V1) \* c1 \* 800 \* f

Where,

CODMn = chemical oxygen demand, mg/l

V1 = the volume of sodium thiosulfate consumed in the sample, ml

V2 = the volume of sodium thiosulfate consumed in the blank sample, ml

c1 = concentration of sodium thiosulfate solution, mol/l

factor 800 = half of the molecular weight of oxygen changed to milligrams and divided by the volume of the sample (16 / 2 \* 1000 / 10)

f = dilution factor

***Literature:***

SFS 3036, dated 1981. Veden kemiallisen happen kulutuksen (CODMn-arvon tai KMnO4-luvun) määritys (only in Finnish)

# **Determination of total iron**

Major part of iron in natural waters, which are normally rich in oxygen, is combined with humic matter in complex form, colloid deposit, or suspended solids. Measuring the amount of total iron, ferrous iron is oxidized to ferric state (Fe2+). Oxidation takes place in an autoclave under high pressure at temperature 120 °C.

***Reagents:***

1. Potassium peroxide sulfate, powder
2. 4 M sulfuric acid
3. Hydroxylammoniumcloride-solution
4. TPTZ-solution
5. Sodium acetate solution

***Procedure:***

Weight 0.25 g ± 0.05 g potassium peroxide sulfate into each oxidation bottle. Pipette 25 ml sample or its dilution and add 250 µl 4 M sulfuric acid. Close the bottles tightly. Put samples in the autoclave for 30 minutes. Let them cool down.

|  |  |  |  |
| --- | --- | --- | --- |
| Sample | Bottle number | Amount of sample, ml | Absorbance |
|  |  |  |  |
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Add 2 ml hydroxylammoniumcloride-solution, 2 ml TPTZ –solution, and 2 ml sodium acetate solution. Mix well after adding each solution.

Measure the absorbance of each sample using the spectrophotometer at the wavelength of 593 nm, after 5 min and before 2 hours. Use 1 cm optical glass (OG) cell. Subtract the absorbance of blank sample from the absorbance of the sample. Use the calibration curve (i.e. regression line) to get the concentration of the total iron. Finally, notice the dilution factor, if samples have been diluted.

***Literature:***

SFS 3028, dated 1976. Veden raudan määritys. Fotometrinen menetelmä (only in Finnish)

# **Determination of hardness – sum of calcium and magnesium**

The sum of the magnesium and calcium concentrates is called hardness. EDTA solution forms a chelated soluble complex when added to a solution of certain metal cations. If a small amount of a dye, such as Eriochrome Black T, is added to an aqueous solution containing calcium and magnesium ions at a pH of 10, the colour of the solution becomes wine red. When EDTA-solution is added as a titrant, the calcium and magnesium will be complexed. When all of the magnesium and calcium has become complexed, the solution turns from wine red to blue, indicating the endpoint of titration.

***Reagents:***

1. Eriochrome Black T, indicator powder
2. Buffer solution pH 10.0
3. EDTA solution, 0.01 mol/l

***Procedure:***

Measure 50 ml well-shaken sample or its’ dilution with measuring glass into the 250 ml Erlenmeyer. Add 4 ml of buffer solution and small amount indicator powder. Mix well. Titrate immediately with EDTA solution using also magnetic stirrer. Colour of the solution turns from wine red to blue.

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| --- | --- | --- |
| Sample | Amount of sample, ml | Amount of used EDTA, mL |
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|  |  |  |

Concentration of used EDTA solution: \_\_\_\_\_\_\_\_\_\_ mol/l.

***Calculation:***

X = a \* c \* (1000 / V), where

* X = the sum of the magnesium and calcium concentrates (Mg2+ + Ca2+), mmol/l (hardness)
* a = the volume of EDTA solution consumed, ml
* c = concentration of EDTA solution, mol/l
* V= amount of sample, ml

The results are reported in accuracy of 0.02 mmol/l.

In Finland, the German degree of hardness, °dH, is used. This can get multiplying the result mmol/l by reading 5.61.

***Literature:***

SFS 3003, dated 1987. Veden kalsiumin ja magnesiumin summan määritys. Titrimetrinen menetelmä (only in Finnish)

**Determination of chloride**

In a neutral or slightly alkaline solution, potassium chromate can indicate the endpoint of the silver nitrate titration of chloride. Silver chloride is precipitated quantitatively before red silver chromate is formed.

***Reagents:***

1. Potassium chromate indicator
2. Silver nitrate solution, approx. 0.028 mol/l

***Procedure:***

Measure 100 ml sample or its’ dilution with measuring glass into the 250 ml Erlenmeyer. Add 1 ml of potassium chromate indicator. Mix well. Titrate immediately with silver nitrate solution using magnetic stirrer. Colour of the endpoint is pinkish yellow. Concentration of used silver nitrate solution: \_\_\_\_\_\_\_\_\_\_ mol/l.

|  |  |  |
| --- | --- | --- |
| Sample | Amount of sample, ml | Amount of used silver nitrate, ml |
|  |  |  |
|  |  |  |

***Calculation:***

X = a \* c \* 35,45 \* (1000 / V), where

* X = amount of chloride, mg/l
* a = amount of used silver nitrate, ml
* c = concentration of silver nitrate solution, mol/l
* V = amount of sample, ml
* 35.45 = molecular weight of chloride
* factor 1000 = factor to get mg/g

***Literature:***

SFS 3002, dated 1982. Veden kloridipitoisuuden määritys (only in Finnish)

Standard Methods for the examination of water and wastewater, 21st edition 2005, pages 4-70 ̶ 4-71

# **Determination of nitrate**

This method is suitable for samples with low organic matter contents, i.e. uncontaminated natural waters and potable water supplies.

***Reagents:***

1. 1 M HCl

***Procedure:***

Filter each sample trough 0.45 µm membrane filter. Fill 25 ml volumetric flask with filtered sample up to mark. Add 0.5 ml 1 M hydrochloride acid and mix. Use wavelength of 220 nm to obtain NO3- -reading, and 275 nm to determine interference due to dissolved organic matter. Use 1 cm UV cell.

|  |  |  |  |
| --- | --- | --- | --- |
| Sample | Amount of sample, ml | Abs220nm | Abs275nm |
|  |  |  |  |
|  |  |  |  |

***Calculation:***

absNO3 = abs220nm – 2 \* abs275 (NOTE: 2 \* abs275 < 10% abs220).

Use standard curve to obtain sample concentrations in mg/l N.

***Literature:***

Standard Methods for the examination of water and wastewater, 21st edition 2005, pages 4-120 - 4-121, 4500-NO3- B. Ultraviolet Spectrophotometric Screening Method

# **Determination of total nitrogen with TOC-TN equipment**

In waters and wastewaters, the forms of nitrogen in greatest interest are nitrate, nitrite, ammonia and organic nitrogen.

Principles of measuring total nitrogen (TN):

When a sample is introduced into the combustion tube (furnace temperature 720 °C), the TN in the sample decomposes to become nitrogen monoxide at this time. Nitrogen gas does not become monoxide at this time. The carrier gas, which contains the nitrogen monoxide, is cooled and dehumidified by the dehumidifier (electronic dehumidifier). Then it enters a chemiluminescence gas analyzer, where the nitrogen monoxide is detected. The detection signal from chemiluminescence gas analyzer generates a peak and the TN concentration in the sample can then be measured.

(Total Organic Carbon Analyzer TOC-L CSH/CSNTM User’s Manual, page 286)

***Procedure:***

Mix the sample and pour it in the sample tube. Add also a small magnet into the tube (for mixing purpose). Place tubes in the sampler.

***Results:***

Results are provided in tables and they are reported in a unit of milligram per litre, using two expressive numbers.

|  |  |
| --- | --- |
| Sample | mg/l N |
|  |  |
|  |  |

***Literature:***

SFS-EN ISO 11905-1 and Standard Methods for the Examination of Water & Wastewater (21st edition 2005), page 4-120 + Total Organic Carbon Analyzer TOC-L CSH/CSNTM User’s Manual

**Determination of orthophosphate and total phosphorus**

Phosphorus is a macronutrient, which is necessary to all living cells. It is limiting nutrient for algal growth in most lakes. Phosphorus determinations are important in assessing the potential biological productivity of surface water. In many areas, there have been established limits for the amounts of phosphorus that may be discharged to receiving bodies of water, particularly lakes and reservoirs. Because of the importance of phosphorus as nutrient in biological methods of wastewater treatment, its’ determination is essential with many industrial wastewaters and in the operation of wastewater treatment plants. In wastewaters, phosphorus is present in several forms. That is why total phosphorus is typically determined for wastewaters.

## **Orthophosphate (PO43-)**

***Reagents:***

1. Ascorbic acid
2. Acid molybdate solution

***Procedure:***

Filter the sample using 0.45 µm filter. Measure 40 ml of the sample into a 50 ml volumetric flask. Add 1 ml of ascorbic acid, mix, and after 30 seconds add 2 ml of acid molybdate solution. Fill up to the mark with RO-water and mix well.

Measure the absorbance of solution using the spectrophotometer at wavelength of 700 nm using 1 cm OG cell after a period between 10 and 30 minutes. After measurements, wash the cell with detergent and water (Do not use a brush!), and finally rinse the cell with RO-water.

|  |  |  |  |
| --- | --- | --- | --- |
| Sample | Bottle number | Amount of sample, ml | Absorbance |
|  |  |  |  |
|  |  |  |  |

***Calculation:***

Subtract the absorbance of blank sample from the absorbance of the samples. Use the calibration curve (i.e. regression line) to get the concentration of the orthophosphate mg/L P. Finally notice the dilution factor, if samples have been diluted.

## **Total phosphorus**

First inorganic phosphorus compounds are oxidized to orthophosphate with persulfate in acid conditions. Oxidation takes place in an autoclave under the pressure at temperature 120 °C. Orthophosphate forms with antimony and molybdate antimony phosphomolybdate complex, which ascorbic acid reduces to blue coloured complex compound.

***Reagents:***

1. Potassium peroxydisulfate solution
2. Ascorbic acid
3. Acid molybdate solution

***Procedure:***

Pipette not more than 40 ml of sample into a 50 ml oxidation flask. Add 4 ml potassium peroxydisulfate solution and mineralize in an autoclave under the pressure and temperature of 120 °C for 30 minutes. Use RO-water as a blank sample and handle it like every other sample.

Let samples cool down. Check pH with the pH-paper. It should be between 3 and 10. If pH is not in that range, adjust it with 2 M sulfuric acid solution or with 2 M sodium hydroxide solution.

Transfer the sample into the 50 ml volumetric flask. Add to each 50 ml volumetric flask 1 ml of ascorbic acid, mix, and after 30 seconds add 2 ml of acid molybdate solution. Fill up to the mark with RO-water and mix well.

Measure the absorbance of each solution using the spectrophotometer at wavelength of 700 nm after a period between 10 and 30 minutes. After measurements, wash the cell with detergent and water (Do not use a brush!), and finally rinse the cell with RO-water.

|  |  |  |  |
| --- | --- | --- | --- |
| Sample | Bottle number | Dilution | Absorbance |
|  |  |  |  |
|  |  |  |  |

***Calculation:***

Subtract the absorbance of blank sample from the absorbance of the samples. Use the calibration curve (i.e. regression line) to get the concentration of the total phosphorus. Finally notice the dilution factor, if samples have been diluted.

Report the concentrations of phosphorus as follows, but not more than three significant figures:

* result mg/L < 0.1 mg/L ± 0.001 mg/l
* result mg/L < 10 mg/L ± 0.01 mg/l
* result mg/L > 10 mg/L ± 0.1 mg/l

***Literature:***

ISO 6878, dated 2004. Water quality. Determination of phosphorus. Ammonium molybdate spectrometric method

# **Determination of bacteria**

**Heterotrophic bacteria:**

R2A-agar, 20 °C

*Growing temperature and time:* 20 °C, 7 days

*Procedure:*

Melt sterile solid agar medium (R2A- agar) in boiling water. Maintain melted medium in an oven between 44 and 46 °C, preferably no more than 3 hours. Use a sterile pipette tips for transferring samples. Select the dilution so that the total number of colonies on a plate will be between 30 and 100. When discharging sample portions, hold pipette at an angle of about 45° with tip not touching bottom of petri dish. Lift cover of petri dish just high enough to insert pipette. Pipette sample so that it stays on the petri dish by drops. Pour liquefied medium into each dish by gently lifting cover just high enough to pour. Mix melted medium thoroughly with test portions in petri dish, taking care not to splash mixture over the edge, by rotating the dish first in one direction and then in the opposite direction. Let plates solidify on a level surface. After medium solidifies, invert plates and place in incubator. Incubate for 48 hours at 22 °C.

*Results:*

Express the results as the number of colony-forming units per millilitre (CFU/ml) of the sample.

**Faecal coliform bacteria:**

E. Coli Total Coliforms Chromogenic Medium

*Growing temperature and time:* 35°C, 24 hours

*Procedure:*

Fecal coliforms bacteria are cultivated using membrane filtration method. The filtration apparatus consists of a vacuum filter connected to a glass container, which is connected to a pump. The filter paper (Cellulose nitrate filter paper, 0.45 µm) is placed on the filter and the filtration cup is fixed over it. The sample to be filtered is poured into the cup and the pump is switched on. After the sample completely passes through the membrane, the filter paper is removed from the filter and placed in a petri dish with the required medium. The petri dishes are then placed in an oven at 35˚C for the required time period. After the incubation period is complete, the petri dishes are removed from the oven and placed on a colonometer to count the colonies formed on the membrane.

*Results:*

Express the results as the number of colony-forming units per millilitre (CFU/mL) of the sample.

**Literature:**

SFS-EN ISO 6222, dated 1999. Water quality enumeration of culturable micro-organisms. Colony count by inoculation in a nutrient agar culture medium.

SFS-EN ISO 8199, dated 2008. Water quality. General guidance on the enumeration of micro-organisms by culture.