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



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| **WATER ANALYSIS** |
| SUMMARY OF STANDARDS  Autumn 2023 |
| 1. pH 2. Electrical conductivity 3. Turbidity 4. Colour 5. CODMn 6. Hardness 7. Chloride 8. Nitrate 9. Orthophosphate 10. 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 to 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.

***Procedure:***

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. After measuring rinse, the probe well with RO-water. Readings from the conductivity meter are µmho/cm or mmho/cm, mho = Siemens (S).

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

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

***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 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 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 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 into 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 into 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 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 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.

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| Sample | Amount of sample, ml | Amount of used silver nitrate, ml |
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***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.

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

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.

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

***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, 68h

*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 68 hours at 20 °C.

*Results:*

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

**Faecal coliform bacteria:**

m-Endo Agar LES

*Growing temperature and time:* 36°C, 21 ± 3 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 3016, dated 2011. Water quality. Membrane filter technique for the enumeration of total coliform bacteria.

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