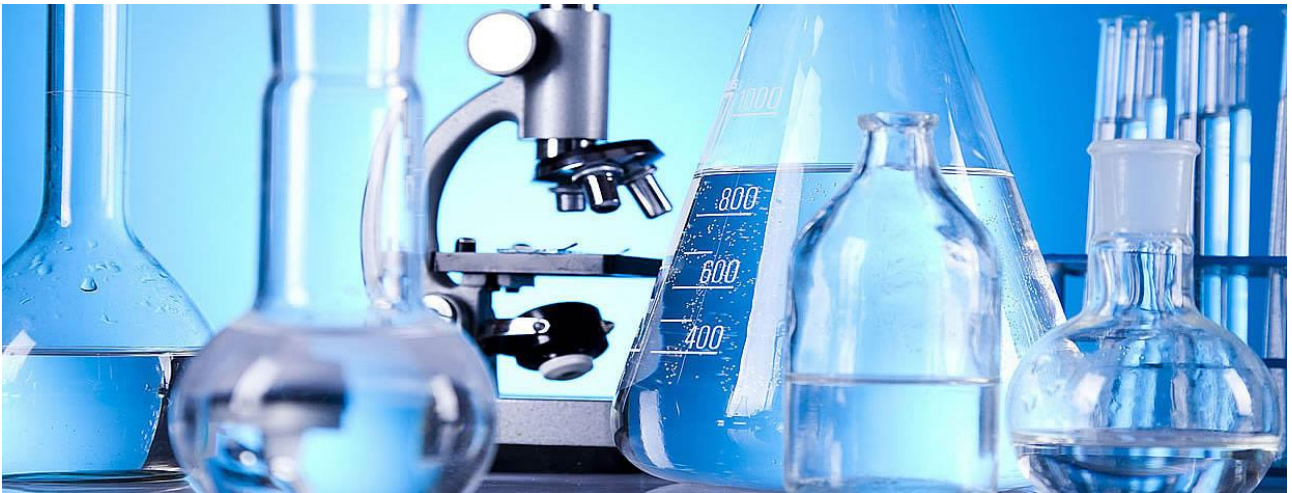


WASTEWATER TREATMENT PLANT

MAIN LABORATORY ANALYSIS



Written by:

Mirko D'Antoni



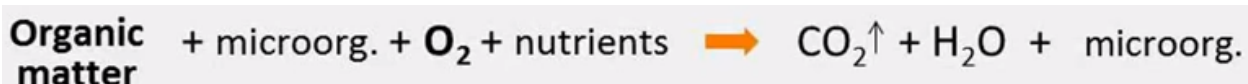
SUMMARY

1	BOD.....	2
2	COD.....	9
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1 BOD

Biochemical oxygen demand (B.O.D.) is an empiric laboratory assay which measures the amount of organic matter contained in a water sample. This assay is the most widely used method for the assessment of water quality.



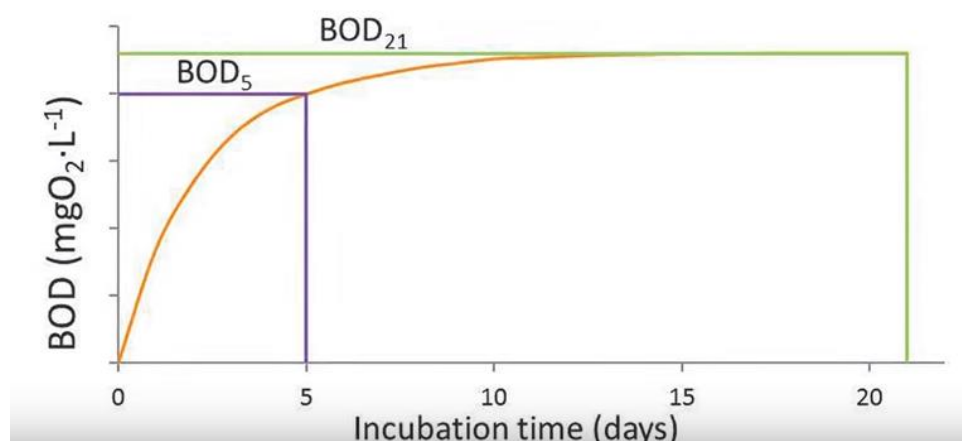
$$[\text{BOD}] = \text{mg O}_2/\text{L}$$

The equation above, describes the biochemical process behind the BOD assay. BOD is, in fact, a measure of the amount of oxygen consumed by heterotrophic bacteria for the oxidation of organic matter. Hence, BOD is expressed in $\text{mg O}_2/\text{L}$ and higher the mount of organic matter in water the higher the BOD value.

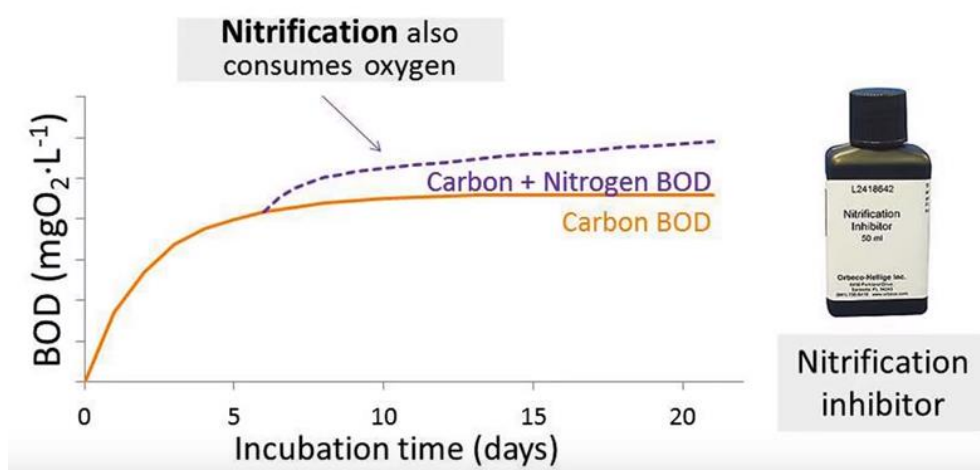
Although there exist various methods for BOD measurement, the principle is the same for all of them: a volume of water sample is put in a recipient where the changes in the oxygen content are measured before and after incubation at 10°C for a certain time.



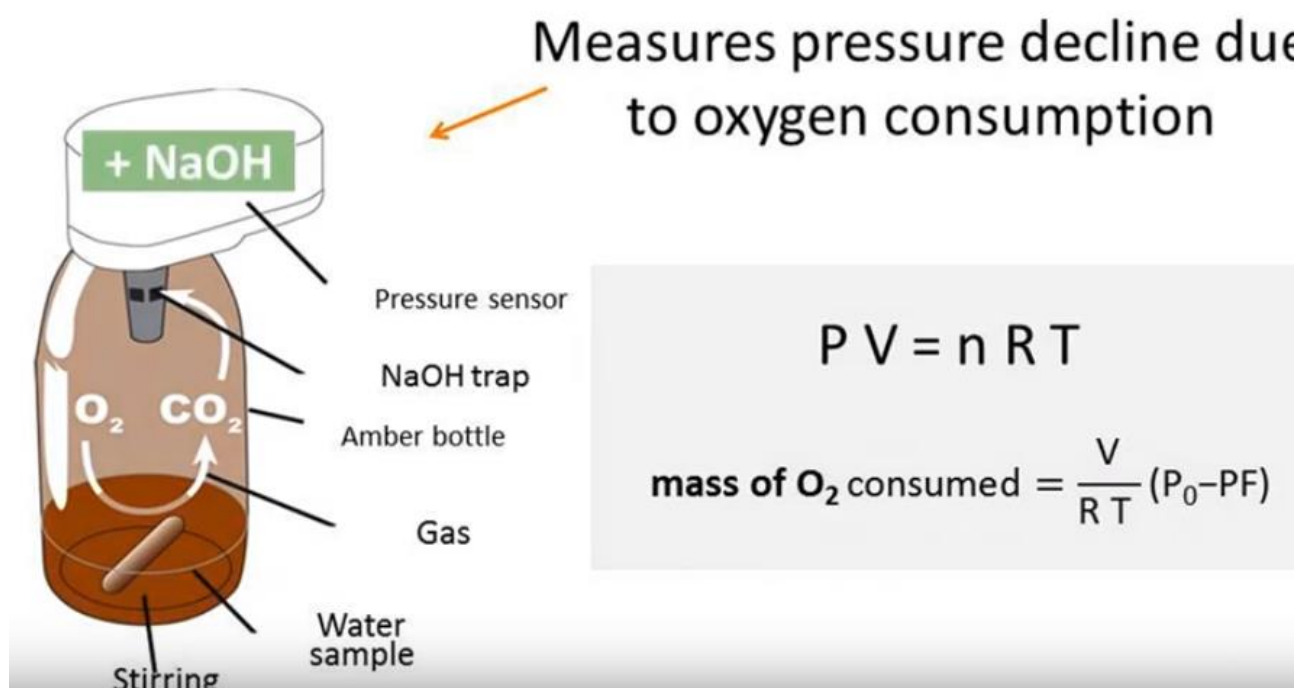
BOD value increase over the time as organic matter is progressively biodegraded. However, after five days the majority of the organic matter contained in the sample has already been degraded. For this reason, BOD₅, which is measured after 5 days of incubation is the most widely used method. On the other hand, if the aim is to measure the total content of biodegradable organic matter, BOD₂₁ is measured after 21 days of incubation.



The oxidation of other compounds present in the water sample can also contribute to the consumption of oxygen. In particular, nitrification could interfere in the measurement of BOD, leading to an overestimation of its value. To prevent this, the use of an inhibitor is required (N-Allylthiourea 98%).



The measurement of BOD₅ in the lab, consists of placing the sample in a recipient sealed with a manometer and in constant agitation in dark conditions. The manometer measures the decline of pressure inside the recipient caused by oxygen consumption. With the measured decline of pressure, the mass of oxygen that has been consumed is calculated using the ideal gas law. Sodium hydroxide (NaOH) is added to absorb the carbon dioxide produced in the process, which might interfere in the pressure measurement.



How to proceed:

- 1) Introduce a magnet inside the bottles, so that when they are placed on the magnetized tray, they remain constantly agitated.
- 2) Determine the volume of the sample which will be introduced in the recipient. For that purpose, we previously need to make an estimation of the expected BOD range if the sample.

	Sample volume (mL)	Factor	Estimated range (mgO ₂ /L)
	22.7	100	0-4000
FOR INLET	43.5	50	0-2000
	97	20	0-800
	164	10	0-400
FOR OUTLET	250	5	0-200
	365	2	0-80
	432	1	0-40

Use range 0-800 for inlet and range 0-200 for outlet. With that information, we go to the table above which establishes the specific volume of sample to be put in the recipient for each BOD range.

For example, we expect that the BOD of our outlet sample is below 200 mg O₂/L. In that case we can see that the volume to incorporate to the recipient is 250 mL.

- 3) To measure the exact volume, it is necessary to use a graduated cylinder as volume measuring tool.
- 4) Once the volume is measured we must introduce it into the recipient using a funnel.
- 5) At this point we will add nitrification inhibitor (few drops or 1 little spoon) into the recipient.

Panta Rei
water solutions

- 6) Now, it is time to put the NaOH into the plastic enclosure located within the manometric cap.



- 7) Next, we can proceed to firmly close the bottles to guarantee an airtight environment.
- 8) After that we make sure that the manometric caps is reset to start measuring from afresh.



9) Once that done, we introduce all recipients containing our samples in the magnetized tray, which is already located inside the incubator at 20°C in dark conditions.



10) After 5 days in the incubator, it is time to take the measurements of the manometric caps.



If the value is out of range, no values will be displayed.

11) Once the value of the manometric caps have been noted down, one more step is needed to get the final BOD₅ value. To that end, we will use the following equation:

$$BOD_5 \left(\frac{mg O_2}{L} \right) = Value * Factor$$

Where the term “factor” in the formula, corresponds the number reported in the Standard table for our specific sample (see point 2).

12) In this case we used a sample volume of 250 mL since we estimated our BOD value would not exceed 200 mg O₂/L.

13) The factor to be used, for this example, is 5 (See point 2). The BOD value obtained, for this example, is 25 (See point 10).

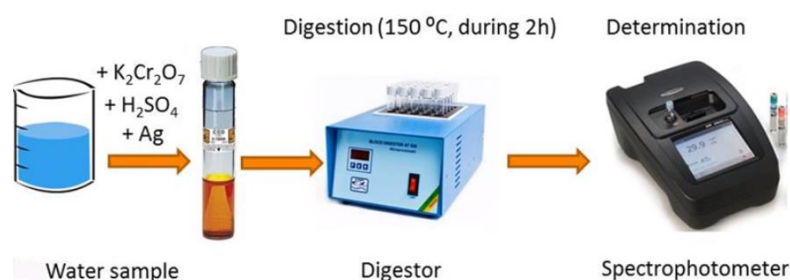
14) The final value of BOD₅, for this example, is BOD₅ = 25 * 5 = 125 mg O₂/L.

An advice is to perform a Blank analysis as well using clean water (the volume of water must be the same used for the sample). Once you get the final BOD₅ value (point 14) for both sample and blank, use this formula to get the real BOD₅ value:

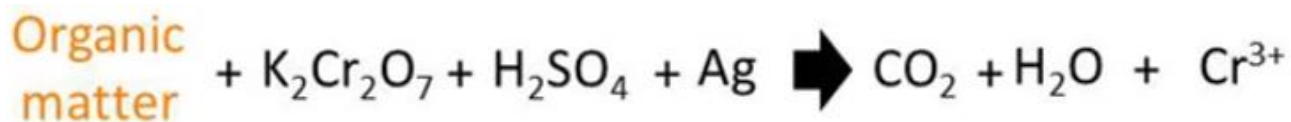
$$BOD_5 \text{ real} = BOD_5 \text{ sample} - BOD_5 \text{ blank}$$

2 COD

The chemical oxygen demand (C.O.D.) is an empiric laboratory assay which indirectly measures the amount of total organic matter (biodegradable and non-biodegradable) contained in a water sample. In particular, COD measures the amount of oxygen consumed for the oxidation of total organic matter. Thus, it is measured in $\text{mg O}_2 \text{ equivalent /L}$. COD is strictly linked to BOD, however, whereas BOD is a measure of the amount of oxygen that bacteria will consume while decomposing organic matter under aerobic conditions, COD does not differentiate between biologically available and inert organic matter, and it is a measure of the total quantity of oxygen required to oxidize all organic material into carbon dioxide and water. In this way, the COD values of a water can be typically related to its BOD values in a more or less constant ratio. COD values are always greater than BOD values, but COD measurements can be made in a few hours while BOD measurements take at least 5 days. Since the COD test can be performed rapidly, it is often used as a rough approximation of the water's BOD, even though the COD tests measures some additional organic matter which is normally not oxidized by biological action. The basis of the COD test is that nearly all organic compounds can be fully oxidized to carbon dioxide with a strong oxidizing agent under acidic conditions at high temperature. After a digestion step, the concentration of organic substances in the sample is calculated from a spectrophotometric determination of the remaining oxidant. The spectrophotometric method consists of adding a strong oxidant ($\text{K}_2\text{Cr}_2\text{O}_7$) to the water sample under acidic conditions (H_2SO_4) and using silver (Ag) as a catalyst.



The sample is then digested for 2h at 148°C, and its determination is done by using a spectrophotometer.



During the digestion, the sample's organic carbon material is oxidized with the ($Cr_2O_7^{2-}$) found in potassium dichromate. The dichromate readily gives up O_2 to bond with carbon atoms to create CO_2 . The oxygen transaction from $Cr_2O_7^{2-}$ to CO_2 reduces the $Cr_2O_7^{2-}$ ion to Cr^{3+} . The amount of Cr^{3+} is determined after oxidation is complete. In essence a COD test determines the amount of carbon based materials by measuring the amount of oxygen the sample will react with.

COD procedure using PF-12 spectrophotometer (see the manual) and NANOCOLER COD Test (see program code to insert in PF-12 on COD kit).



For inlet water use NANOCOLOR COD 1500, while for effluent water use NANOCOLOR COD 160.

REF 985 026

Test 0-26 08.14

NANOCOLOR® COD 160

Chemical Oxygen Demand

en

Method:

Photometric determination of decrease in chromate concentration after oxidation with potassium dichromate / sulfuric acid / silver sulfate

Range:	15–160 mg/L COD	15–160 mg/L COD
Factor:	0.220	0.212
Wavelength (HW = 5–12 nm):	436 nm	445 nm
Reaction time:	2 h	
Reaction temperature:	148 °C	
Short time COD:	30 min at 160 °C*	

Contents of reagent set:

20 test tubes COD 160

Hazard warning:

Test tubes contain sulfuric acid 80–98 % and mercury(II) sulfate 0.74–1.50 %.

H314 Causes severe skin burns and eye damage.

P260, P280, P301+330+331, P303+361+353, P304+340, P305+351+338, P501 Do not breathe vapors. Wear protective gloves / eye protection. IF SWALLOWED: rinse mouth. Do NOT induce vomiting. IF ON SKIN (or hair): Take off immediately all contaminated clothing. Rinse skin with water / shower. IF INHALED: Remove person to fresh air and keep comfortable for breathing. IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing. Dispose of contents / container to regulated waste treatment. For further information ask for a safety data sheet. When shaking COD test tubes use safety bottle (REF 916 37).

Interferences:

For chloride contents above 1500 mg/L the test sample must be diluted or use Chloride complexing agent (REF 918 911). For determination of the concentration of chlorides we recommend a preliminary test with QUANTOFIX® Chloride (REF 913 21). Turbidity in the COD test tube after reaction in the heating block will result in COD readings which are too low. Wait until turbidities caused by precipitation of mercury sulfate have deposited.

Procedure:

Requisite accessories: NANOCOLOR® heating block, piston pipette with tips

Note: For samples with high chloride concentrations it is important to shake the test tube **before** the water sample is added in order to suspend the deposit.

according to DIN ISO 15705 at 148 °C

Open test tube, hold it **diagonally** and **slowly** add

2.0 mL test sample to contents **without** mixing so that two separate layers are formed; screw cap securely on to test tube, hold tube by the cap, place tube into the safety bottle and shake (**Caution, test tube becomes hot / Contents become turbid until heated**), then place tube into the heating block.

After 2 h remove test tube from heating block, after about 10 min (**test tube is still warm**) shake once and allow to cool to room temperature.

Clean outside of test tube and measure.

Short time COD at 160 °C

Open test tube, hold it **diagonally** and **slowly** add

2.0 mL test sample to contents **without** mixing so that two separate layers are formed; screw cap securely on to test tube, hold tube by the cap, place tube into the safety bottle and shake (**Caution, test tube becomes hot / Contents become turbid until heated**), then place tube into the heating block.

After 30 min remove test tube from heating block, after about 10 min (**test tube is still warm**) shake once and allow to cool to room temperature.

Clean outside of test tube and measure.

* In contrast to the conditions described in the ISO 15705, the short time COD is characterized by a higher digestion temperature and reduced reaction time. Therefore we recommend to compare the results of the short time COD from time to time with measurements made under the conditions of ISO 15705 ($150 \pm 5 \text{ °C} / 2 \text{ h} \pm 10 \text{ min}$).

Measurement:

For NANOCOLOR® photometers and PF-12 see manual, test 0-26.

Photometers of other manufacturers:

For other photometers check whether measurement of round glass tubes is possible. Verify factor for each type of instrument by measuring standard solutions.

Analytical quality control:

NANOCOLOR COD 160 (REF 925 26) or Multistandard Sewage outflow 1 (REF 925 011)

Storage:

Store the test kit in a cool and dry place. Avoid exposing the test kit to sunlight.

References:

German standard methods for the examination of water, waste water and sludge (DIN 38 409 - H41-1 and DIN ISO 15 705 - H45)

British standard: Field and on-site test methods for the analysis of waters (BS 1427)

MACHEREY-NAGEL GmbH & Co. KG · Neumann-Neander-Str. 6-8 · 52355 Düren · Germany

REF 985 029

Test 0-29 09.14

NANOCOLOR® COD 1500

Chemical Oxygen Demand

en

Method:

Photometric determination of chromium(III) concentration after oxidation with potassium dichromate / sulfuric acid / silver sulfate

Range:	100–1500 mg/L COD
Factor:	1740
Wavelength (HW = 5–12 nm):	620 nm
Reaction time:	2 h
Reaction temperature:	148 °C
Short time COD:	30 min at 160 °C*

Contents of reagent set:

20 test tubes COD 1500

1 test tube with blank value "NULL"

Hazard warning:

Test tubes contain sulfuric acid 80–98 %, potassium dichromate 0.28–0.56 % and mercury(II) sulfate 0.74–1.50 %. Blank value "NULL" contains sulfuric acid 51–80 %.

H314, H340, H350, EUH203 Causes severe skin burns and eye damage. May cause genetic defects. May cause cancer. Contains chromium(VI). May produce an allergic reaction.

P201, P202, P260, P280, P301+330+331, P303+361+353, P304+340, P305+351+338, P308+313, P405, P501 Obtain special instructions before use. Do not handle until all safety precautions have been read and understood. Do not breathe vapors. Wear protective gloves / eye protection. IF SWALLOWED: Rinse mouth. Do NOT induce vomiting. IF ON SKIN (or hair): Take off immediately all contaminated clothing. Rinse skin with water / shower. IF INHALED: Remove person to fresh air and keep comfortable for breathing. IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing. IF exposed or concerned: Get medical advice / attention. Store locked up. Dispose of contents / container to regulated waste treatment. For further information ask for a safety data sheet. When shaking COD test tubes use safety bottle (REF 916 37).

Interferences:

For chloride contents above 1500 mg/L the test sample must be diluted or use Chloride complexing agent (REF 918 911). For determination of the concentration of chlorides we recommend a preliminary test with QUANTOFIX® Chloride (REF 913 21). Turbidity in the COD test tube after reaction in the heating block will result in COD readings which are too high. Wait until turbidities caused by precipitation of mercury sulfate have deposited.

The method cannot be applied for the analysis of sea water.

Procedure:

Requisite accessories: NANOCOLOR® heating block, piston pipette with tips

Note: For samples with high chloride concentrations it is important to shake the test tube **before** the water sample is added in order to suspend the deposit.

according to DIN ISO 15705 at 148 °C

Open test tube, hold it **diagonally** and **slowly** add

2.0 mL test sample to contents **without** mixing so that two separate layers are formed; screw cap securely on to test tube, hold tube by the cap, place tube into the safety bottle and shake (**Caution, test tube becomes hot / Contents become turbid until heated**), then place tube into the heating block.

After 2 h remove test tube from heating block, after about 10 min (**test tube is still warm**) shake once and allow to cool to room temperature.

Clean outside of test tube and measure.

Short time COD at 160 °C

Open test tube, hold it **diagonally** and **slowly** add

2.0 mL test sample to contents **without** mixing so that two separate layers are formed; screw cap securely on to test tube, hold tube by the cap, place tube into the safety bottle and shake (**Caution, test tube becomes hot / Contents become turbid until heated**), then place tube into the heating block.

After 30 min remove test tube from heating block, after about 10 min (**test tube is still warm**) shake once and allow to cool to room temperature.

Clean outside of test tube and measure.

* In contrast to the conditions described in the ISO 15705, the short time COD is characterized by a higher digestion temperature and reduced reaction time. Therefore we recommend to compare the results of the short time COD from time to time with measurements made under the conditions of ISO 15705 ($150 \pm 5 \text{ °C} / 2 \text{ h} \pm 10 \text{ min}$).

Measurement:

For NANOCOLOR® photometers and PF-12 see manual, test 0-29.

Photometers of other manufacturers:

For other photometers check whether measurement of round glass tubes is possible. Verify factor for each type of instrument by measuring standard solutions.

Analytical quality control:

NANOCOLOR COD 1500 (REF 925 29) or Multistandard Sewage inflow (REF 925 012)

Storage:

Store the test kit in a cool and dry place. Avoid exposing the test kit to sunlight.

References:

German standard methods for the examination of water, waste water and sludge (DIN 38 409 - H41-1 and DIN ISO 15 705 - H45)

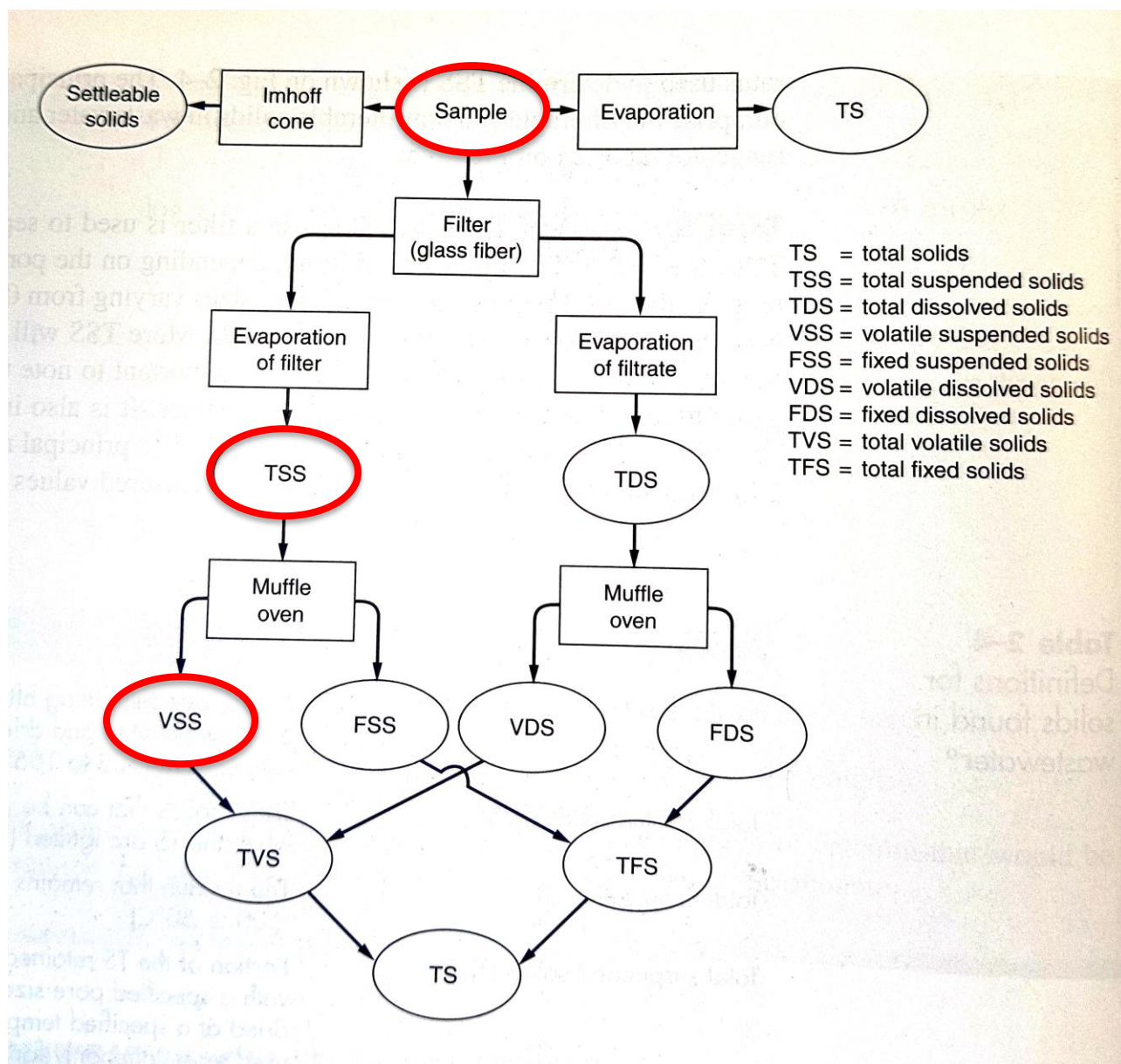
British standard: Field and on-site test methods for the analysis of waters (BS 1427)

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3 SOLIDS

The most important physical characteristic of wastewater is its total solids content, which is composed of floating matter, settleable matter, colloidal matter, and matter in solution. Total solids (TS) are obtained by evaporating a sample of wastewater to dryness and measuring the mass of the residue, while a filtration step is used to separate the total suspended solids (TSS) from the total dissolved solids (TDS).

Test	Description
Total solids (TS)	The residue remaining after a sample has been evaporated and dried at a specific temperature (105°C).
Total volatile solids (TVS)	Those solids that can be volatilized and burned off when the TS are ignited (550°C)
Total fixed solids (TFS)	The residue that remains after TS are ignited (550°C)
Total suspended solids (TSS)	Portion of TS retained on a filter with a specific pore size, measured after being dried at 105°C.
Volatile suspended solids (VSS)	Those solids that can be volatilized and burned off when the TSS are ignited (550°C).
Fixed suspended solids (FSS)	The residue that remains after TSS are ignited (550°C)
Total dissolved solids (TDS) (TS - TSS)	Those solids that pass through the filter, and are then evaporated and dried at specified temperature. It should be noted that what is measured as TDS is comprised of colloidal and dissolved solids.
Total volatile dissolved solids (VDS)	Those solids that can be volatilized and burned off when TDS are ignited (550°C).
Fixed dissolved solids (FDS)	The residue that remains after TDS are ignited (550°C).
Settleable solids	Suspended solids, expressed as ml/L, that will settle out of suspension within a specific period of time.



For our purpose we will perform only TSS and VSS in inlet and outlet of the plant. When we take the sample from the oxidation tank we will analyze MLSS and MLVSS (the procedure is the same).

What we need for determination of TSS:



Whatman filter



Analytical balance



Oven



Glass



Funnel



Pipette

Procedure:

- 1) Put the filter in the oven (105°C) for 10 minutes in order to remove humidity;
- 2) After 10 minutes, take out the filter and let it cool for 15 minutes at room temperature;
- 3) Weight the filter and note down the value in grams (M_0);
- 4) Place the funnel on the top of the glass;
- 5) Place the filter, after folding it, inside the glass;
- 6) Use the pipette and take 5 mL of sample (V_0) - (note down the volume used);
- 7) Pour the sample through the filter and wait the filtration time;
- 8) Once the sample is filtered, take the filter and put it in the oven for 1 day at 105°C;
- 9) After 1 day, take out the filter and let it cool for 30 minutes at room temperature;
- 10) Weight the filter and note down the value in grams (M_1);
- 11) Use the following formula to calculate the TSS:

$$TSS = \left(\frac{(M_1 - M_0) * 1000000}{V_0} \right) \left[\frac{mg}{L} \right]$$

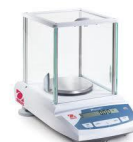
What we need for determination of VSS:



Crucible



Muffle



Analytical balance

Procedure:

- 1) Put the dried filter (M_1) into the crucible;
- 2) Weight the crucible + dried filter and note down the value in grams (M_2);
- 3) Put crucible + dried filter into the Muffle at 550°C for 2h;
- 4) After 2h, take out the crucible and let it cool for 30 minutes at room temperature;
- 5) Weight the crucible + ash and note down the value in grams (M_3);
- 6) Use the following formula to calculate the TSS:

$$VSS = \left(\frac{(M_2 - M_3) * 1000000}{V_0} \right) \left[\frac{mg}{L} \right]$$

Practical example:

Before starting is better prepare a simple table as follow

Samples	TSS or MLSS (105°C for 1 day)				VSS or MLVSS (550°C for 2h)		
Date XX/XX/XXXX	Blank filter (M_0) (g)	Sample vol. (V_0) (ml)	Dried filter (M_1) (g)	Concentration (mg/L)	Crucible + dried filter (M_2) (g)	Crucible + ash (M_3) (g)	Concentration (mg/L)
Inlet	0,2634	15	0,2672	253	10,2321	10,2292	193
Outlet	0,2648	15	0,2652	26	10,2232	10,2229	20
Oxidation tank	0,2639	25	0,3667	4112	10,2254	10,1482	3088
Return sludge	0,2641	25	0,4466	7300	10,2122	10,0750	5475