Lesson A 1

CHARACTERISTIC, ANALYTIC AND SAMPLING OF WASTEWATER

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Overview and summary of this lesson

Wastewater is the term for discarded or previously used water from a municipality or industry. The wastewater that is produced due to human activities in households is called domestic wastewater i.e. wastewater from the kitchen, bathroom, toilet and

laundry. Such water usually contains dissolved as well as suspended matter and must be treated prior to its discharge into natural water. To examine the quality of wastewater to be discharged into aquatic environment or to be treated and reused, the characteristics of wastewater in question must be defined precisely. Quantitative assessments of the quality of wastewater are made by considering many criteria, including temperature, dissolved oxygen level and concentration of organic as well as inorganic compounds. The most frequently used parameters are: Biochemical Oxygen Demand (BOD), Chemical Oxygen Demand (COD), Total Organic Carbon (TOC), Alkalinity, Chlorides, Nitrogen, Oil and Grease, Dissolved Oxygen, pH, Phosphorus, Gases, Sulphur, Solids, Temperature, Metals as well as Micro-organisms. In this lesson, these parameters are defined and methods for analysing them are discussed briefly. In addition sampling and determination techniques are discussed.

1. Domestic wastewater sources and its characteristic

Wastewater is the water which is disposed from homes, offices and industry. It comes from toilets, sinks, showers, washing machines and industrial processes and was historically called sewage.

*Fehler! Keine Indexeinträge gefunden.**ure 1: Sources of domestic wastewater (Samwel 2005)***

Wastewater produced due to human activities in households is called domestic wastewater i.e. wastewater from the kitchen, shower, wash basin, toilet and laundry (see figure 1)**.** It is defined as follows:

- **yellow water:** human urine
- **brown water:** human faeces with flushed water (can include paper if used)
- **black water:** human faeces (brown water) mixed with urine (yellow water), in general: wastewater from toilets. It contains human waste and can be a public health risk if not treated properly.
  (Sometimes, water used in kitchen is also classified as black water)
- **grey water:** water used in the kitchen, bathroom including sinks, baths, showers and laundry, etc. or any water that has been used at home, except water from toilets

The strength and composition of the domestic wastewater changes on hourly, daily and seasonal basis, with the average strength dependent on per capita water usage, habits, diet, living standard and life style. The main reason is variation in water usage in households. Households in developed countries use more water than those in developing countries.

Wastewater components can be divided into different main groups as shown in Table 1. They can adversely affect the aquatic life if discharge them into environmental.

Table :1 Components present in domestic wastewater (Henze and Ledin; 2001)

Component	**Of special interest**	**Environmental effect**
Microorganisms	Pathogenic bacteria, virus and worms eggs	Risk when bathing and eating shellfish
Biodegradable organic materials	Oxygen depletion in rivers and lakes	Fish death, odours
Other organic materials	Detergents, pesticides, fat, oil and grease, colouring, solvents, phenols, cyanide	Toxic effect, aesthetic inconveniences, bioaccumulation in the food chain
Nutrients	Nitrogen, phosphorus, ammonium	Eutrophication, oxygen depletion, toxic effect
Metals	Hg, Pb, Cd, Cr, Cu, Ni	Toxic effect, bioaccumulation
Other inorganic materials	Acids, for example hydrogen sulphide, bases	Corrosion, toxic effect
Thermal effects	Hot water	Changing living conditions for flora and fauna
Odour (and taste)	Hydrogen sulphide	Aesthetic inconveniences, toxic effect
Radioactivity		Toxic effect, accumulation

Physically, domestic wastewater is usually characterised by a grey colour, musty odour and has a solids content of about 0.1%. The solid material is a mixture of faeces, food particles, toilet paper, grease, oil, soap, salts, metals, detergents, sand and grit. The solids can be suspended (about 30%) as well as dissolved (about 70%). Dissolved solids can be precipitated by chemical and biological processes. From a physical point

of view, the suspended solids can lead to the development of sludge deposits and anaerobic conditions when discharged into the receiving environment.

Chemically, wastewater is composed of organic (70%) and inorganic (30%) compounds as well as various gases. Organic compounds consist primarily of carbohydrates (25 %), proteins (65 %) and fats (10 %), which reflects the diet of the people. Inorganic components may consist of heavy metals, nitrogen, phosphorus, pH, sulphur, chlorides, alkalinity, toxic compounds, etc. However, since wastewater contains a higher portion of dissolved solids than suspended, about 85 to 90% of the total inorganic component is dissolved and about 55 to 60% of the total organic component is dissolved. Gases commonly dissolved in wastewater are hydrogen sulphide, methane, ammonia, oxygen, carbon dioxide and nitrogen. The first three gases result from the decomposition of organic matter present in the wastewater.

Biologically, wastewater contains various microorganisms but the ones that are of concern are those classified as protista, plants, and animals. The category of protista includes bacteria, fungi, protozoa, and algae. Plants include ferns, mosses, seed plants and liverworts. Invertebrates and vertebrates are included in the animal category. In terms of wastewater treatment, the most important category are the protista, especially the bacteria, algae, and protozoa. Also, wastewater contains many pathogenic organisms which generally originate from humans who are infected with disease or who are carriers of a particular disease. Typically, the concentration of faecal coliforms found in raw wastewater is about several hundred thousand to tens of million per 100 ml of sample.

For samples of microscopically views on micro-organisms see the “Microbiological Garden”: **http://www.icbm.de/pmbio/mikrobiologischer-garten/eng/index.php3**

Or see the slide and video microscope under: **http://www.norweco.com/html/lab/Microscope.htm#**

The composition of typical domestic wastewater is shown in Table 2. Concentrated wastewater represents cases with low water consumption whereas dilute wastewater represents high water consumption.

Table 2. Different parameters in domestic wastewater (Henze and Ledin, 2001)

Analysis parameters		**Wastewater type**			
	Unit	**Concentrated**	**Moderate**	**Diluted**	**Very diluted**
5-days Biochemical Oxygen Demand (BOD_5)	mg O_2/l	350	250	150	100
Chemical Oxygen Demand (COD)	mg O_2/l	740	530	320	210
Total Organic Carbon (TOC)	g C/m^3	250	180	110	70
Suspended Solid (SS)	g SS/ m^3	450	300	190	120
Volatile Suspended Solid (VSS)	g VSS/ m^3	320	210	140	80
Alkalinity	eqv/ m^3 *	37	37	37	37
Conductivity	mS/m **	120	100	80	70
Total Nitrogen	g N/ m^3	80	50	30	20
Total Phosphorous	g P/ m^3	23	16	10	6
Fats, oil and grease	g/ m^3	100	70	40	30

* 1 eqv/ m^3 = 1 m eqv/l = 50 mg $CaCO_3$/l - ** mS/m = 10 μS/cm = 1 m mho/m

2. Definition and measurement of wastewater parameters

2.1 Physical parameters

2.1.1 Solids

Other than gases, all contaminants of water contribute to the solids content. Solids typically include inorganic matter such as silt, sand, gravel, and clay, and organic matter such as plant fibres and microorganisms from natural and man made sources. Classified by their size and state, chemical characteristics, and size distribution, solids can be dispersed in water in both suspended and dissolved forms. In regards to size, solids in wastewater can be classified as suspended, settleable, colloidal, or dissolved. They are also characterised as being volatile or non-volatile.

Photo 1: Separated solids *(source: Stadtentwässerung Göttingen)*

There are different analytical procedures (see figure 3) for analysing solids in wastewater such as settling, filtration, and evaporation; because of their different particle sizes (see figure 2).

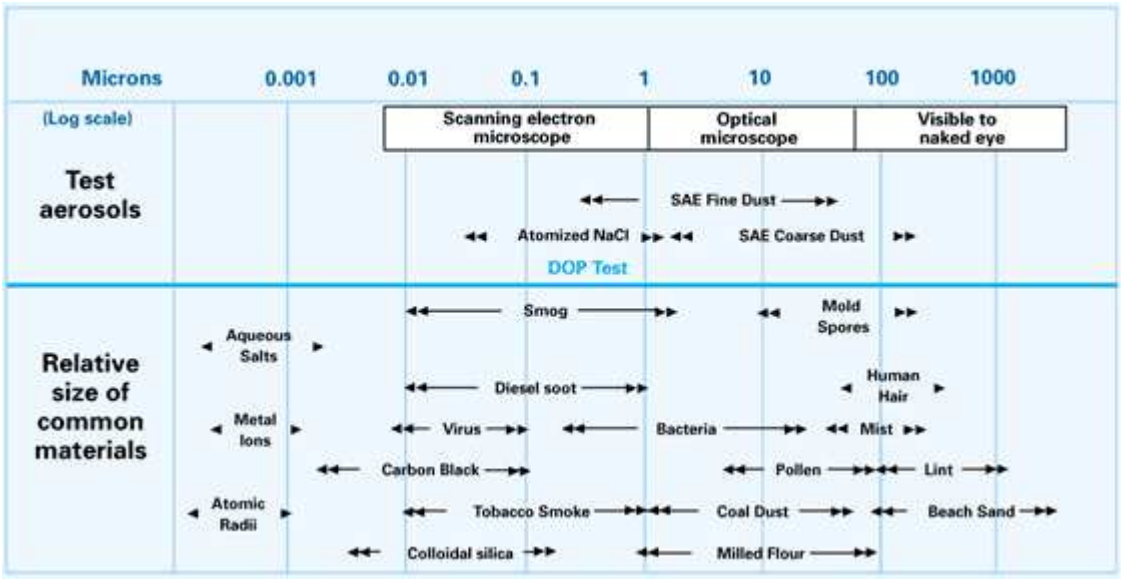


Figure 2: Particle sizes and their scanning method (Dunn, 2003)

Total solids (TS) in wastewater is the amount of all solids, which are determined by drying a known volume of the sample in a preweighed crucible dish at 105 ℃. After cooling in an exsiccator, the crucible dish is again weighed. TS is determined by using the following formula:

$$TS = (M_1 – M_2)/V$$

with
M_1 : mass of crucible dish after drying at 105 ℃ (mg)
M_2 : mass of initial crucible dish (mg)
V : Volume of sample (L))

Volatile solids (VS) are the amount of solid that volatilises when heated at 550 ℃. This is a useful estimation for organic matter present in wastewater and is determined by burning the total solid at 550℃ for about 2 hours in a muffle furnace. After cooling in an exsiccator to room temperature, it is weighed. VS is determined by using the following formula:

$$VS = (M_1 – M_3)/V$$

with
M_1 : mass of crucible dish after drying at 105 ℃ (mg)
M_3 : Mass of crucible dish after ignition at 550 ℃ (mg))
V : Volume of sample (L))

It can be divided in a suspended and a filterable fraction.

Fixed solids (FS) are the amount of solid that does not volatilise at 550 ℃. This measure is used to gauge the amount of mineral matter in wastewater. It is the difference between TS and VS. It can be divided in a suspended and a filterable fraction.

Suspended solids (SS) are the solids retaining in a filter and is usually determined by filtration using glass fibre filters. In all analytical procedures for determination of suspended solids, weighed filters are used for sample filtration, the filters are dried at about 105℃ after filtration, cooled in an exsiccat or to room temperature and the weight of the loaded filter is determined. SS is determined by using the following formula:

$$SS= (M_4–M_5)/V$$

with
M_4 : mass of filter after drying at 105 ℃ (mg)
M_5 : mass of initial filter (mg)
V : Volume of sample (L))

Volatile suspended solids (VSS) are, as indicated in figure 3, one portion of SS which are defined as that part of SS which can be removed by heating the solids at 550℃ in a muffle furnace. The suspended solids is burned at 550℃ for 2 hours in a muffle furnace and weighed after cooling in an exsiccator to room temperature. VSS is determined by using the following formula:

$$VSS=(M_4–M_6)/V$$

M_4 : mass of filter after drying at 105 ℃ (mg)
M_6 : mass of filter after ignition at 550 ℃ (mg)
V : Volume of sample (L))

Fixed suspended solids (FSS) are the solid that are unburnable at 550 ℃ and is determined by subtracting VSS from SS.

Dissolve solids (DS) or **filterable solids** can be determined by subtracting SS from TS. The solids passing through the filter consist of colloidal and dissolved solids.

Settable solids are those solids that will settle to the bottom of an Imhoff cone (a cone-shaped container) in one hour and determined by allowing a wastewater sample to stand for one hour in an Imhoff cone which enables to read the volume of the settled solids. It is expressed as mL/L and is important, because it is related to the efficiency of sedimentation tanks.

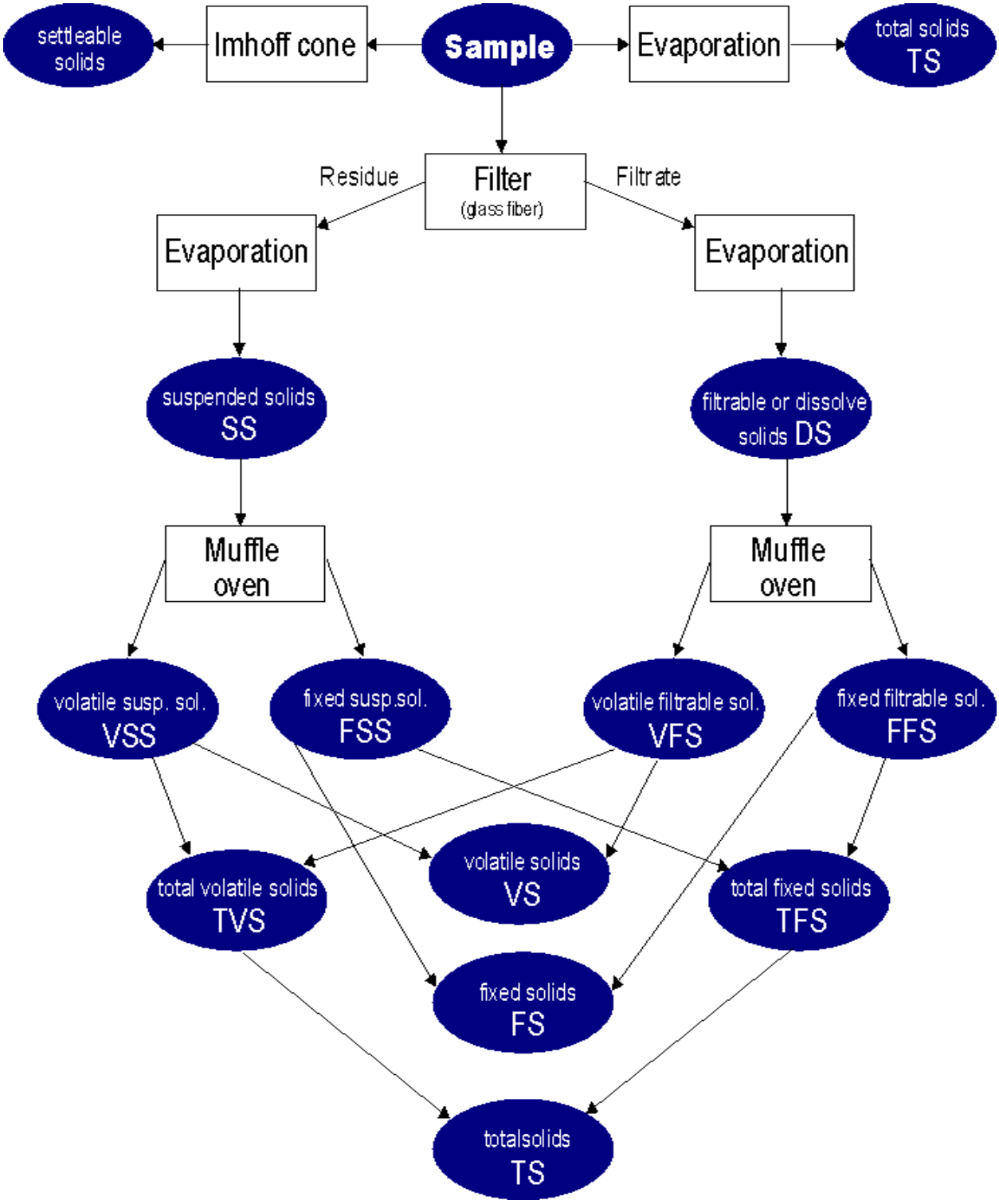


Figure 3: Interrelationships of solids found in water and wastewater

2.1.2 Turbidity

Clarity of water is usually measured by its turbidity. Turbidity is a measure of the extent to which light is either absorbed or scattered by suspended material in water, but it is not a direct quantitative measurement of suspended solids. Both the size and surface characteristics of the suspended material influence absorption and scattering.

Turbidity measurement is an important factor related to the quality of drinking water. It should be measured in treated wastewater effluent if it is reused. If ultraviolet radiation (UV) is used for disinfection of treated wastewater, turbidity measurement will be important because for UV to be effective in disinfecting wastewater effluent, UV light must be able to penetrate the stream flow.

Turbidity is measured by comparing the intensity of light scattered by the sample with the intensity of light scattered by a standard solution. The results are reported in NTU.

2.1.3 Colour

By colour the quality of water can be judged. Pure water is colourless. In wastewater treatment, colour is not necessarily a problem, but instead is a indicator of the condition of the wastewater. Condition refers to the age of the wastewater, which is determined qualitatively by its colour and odour. Fresh wastewater is a light brownish-grey colour.The colour of wastewater changes sequentially from grey to dark grey and ultimately to black as the travel time in collection system increases (flow becomes increasingly more septic) and more anaerobic conditions develop.

2.1.4 Temperature

Temperature is very important parameter because of its effect on chemical reactions on reaction rates, aquatic life, and the solubility of essential gases such as oxygen in water.The temperature of domestic wastewater is higher than that of the water supply, because of the addition of warm water from households. Depending on the geographical location, the mean annual temperature of wastewater varies from about 10 to 21.1 º C. The temperature of a wastewater sample can be measured with the help of ordinary mercury or digital thermometer.

2.1.5 Odour

In wastewater, odours are of major concern, especially to those who reside in close proximity to a wastewater treatment plant. These odours are generated by gases produced by decomposition of organic matter or by substances added to the wastewater. Odour from fresh wastewater is less objectionable than the odour from wastewater that has undergone anaerobic decomposition. The most characteristic odour of stale or septic wastewater is that of hydrogen sulphide (H_2S), which is produced by anaerobic microorganisms that reduce sulphate to sulphide.

The malodorous compounds responsible for producing objectionable odours in water can be detected by diluting a sample with odour free water until the least detectable odour level is achieved. This is recorded as TON (Threshold Odour Number). The concentration of malodorous gases such as hydrogen sulphide, ammonia, mercaptans etc. emitted into the air from wastewater can be measured by any commercially available gas monitor.

2.2 Chemical Parameters

2.2.1 Alkalinity

Alkalinity is the capacity of water to neutralise acids. It results from the presence of hydroxides, carbonates, and bicarbonates of elements such as calcium, magnesium, sodium, potassium, or ammonia. Wastewater is normally alkaline, receiving its alkalinity from the water supply, the groundwater, and the materials added during domestic use. It is determined by titrating against a standard acid and the results are expressed in terms of calcium carbonate $CaCO_3$, mg/l as $CaCO_3$. For most practical purposes alkalinity can be defined in terms of molar quantities.

$$\text{Alk, eq/m}^3 = \text{meq/l} = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^+]$$

The corresponding expression in terms of equivalents is

$$\text{Alk, eq/m}^3 = \text{meq/l} = (HCO_3^-) + 2(CO_3^-) + (OH^-) - (H^+)$$

In practice, alkalinity is expressed in terms of calcium carbonate. To convert from meq/l to mg/l as $CaCO_3$, it is helpful to remember that

$$\text{Milliequivalent mass of } CaCO_3 = (100 \text{ mg/mmole}) / 2 \text{ meq/mmole} = 50 \text{ mg/meq}$$

Alkalinity plays an important role in the treatment of wastewater, as it indicates the buffer capacity of water. This affects the growth and activity of microbes present in activated sludge, which are responsible for the treatment of wastewater. It is also an essential parameter to be estimated to design and implement the corrosion and odour-control processes.

2.2.2 pH

The negative log of the hydrogen ion concentration is called pH ($pH= - \log_{10} [H^+]$). The hydrogen-ion concentration is an important quality parameter of both natural water and wastewater. The pH of wastewater needs to remain between 6 and 9 to protect organisms. Acids and other substances that alter pH can inactivate treatment processes.

The pH of aqueous systems can be conveniently measured with a pH meter (see figure 4). Various pH papers and indicator solutions that change colour at define pH values are also used. The pH is determined by comparing the colour of the paper or solution to a series of colour of standard.

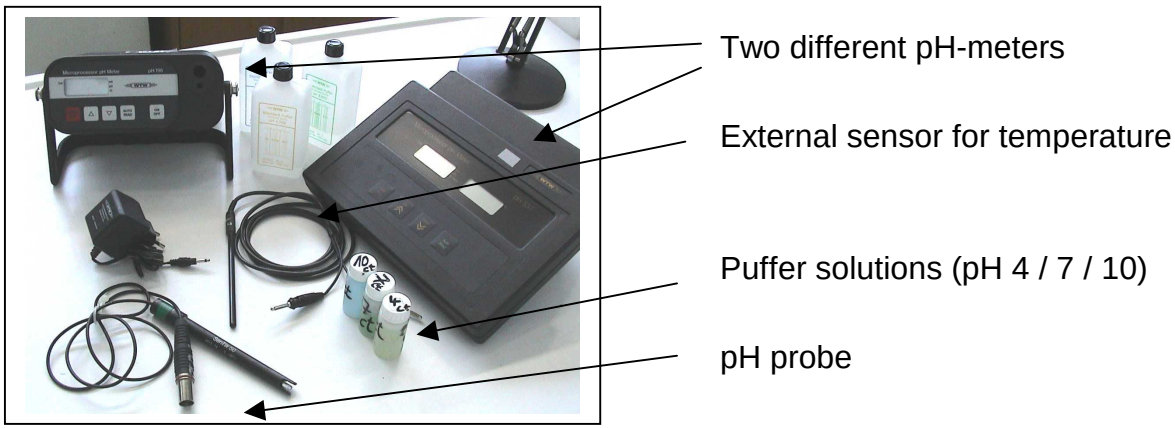


Figure 4: pH meter

Possible errors by measurement of pH can be followings:

- pH-sensor and meter are not connected properly,
- pH-glass electrode is polluted or damaged,
- Diaphragm of the reference electrode is black (Sulphide contamination),
- Reference electrolyte solution is used up,
- pH electrode is placed in distilled water and not in the same concentration and electrolyte solution,
- Wrong temperature for calibration and/or measurement,

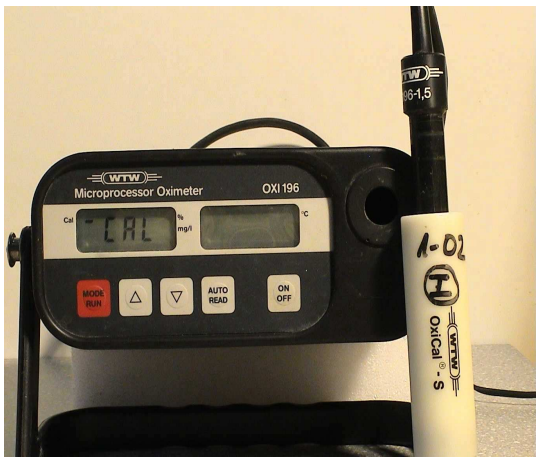
- Wrong or old puffer for calibration,
- probe or cable is broken.

2.2.3 Dissolved Oxygen (DO)

Dissolved oxygen is the amount of molecular oxygen dissolved in water. It is required for the respiration of aerobic microorganisms. However, oxygen is only slightly soluble in water.The actual quantity of oxygen (other gases too) that can be present in solution is governed by;

- the solubility of gas
- the partial pressure of the gas in the atmosphere
- the temperature
- the concentration of the impurities in the water (e.g., salinity, suspended solids, etc.)

The amount of DO decreases with increasing water temperature. So a cool or cold water can contain much more DO than the warm water. As a result, aquatic life in streams and lakes is placed under more oxygen stress during summer months than during the other seasons. DO can be measured using chemicals or oximeter (Figure 5).



Cleaning solution for regeneration, Cathode cleaner, electrolyte solution, new membrane

Figure 5: Oximeter with an electrode in the calibration vessel

To measure oxygen in liquids a minimum flow at the membrane is necessary. In the aeration tank the minimum flow is given in the current of the wastewater, in the laboratory you could attach a flow accessory on the probe and onsite you can move the probe in the water.

Possible errors by measurement of Oximeter can be followings:

- Membrane is contaminated or damaged,
- Electrolyte solution is used up,
- Insufficient flow,
- Sensor and meter are not connect properly,
- Temperature probe must be dry at the calibration,
- Sponge of the OXICAL-vessel must be moist (not dry or wet),
- probe or cable is broken.

2.2.4 Biochemical Oxygen Demand (BOD)

Biochemical Oxygen Demand is a sum parameter and the amount of oxygen required to oxidise organic matter present in the water biochemically. So BOD is an indirect measure of the concentration of organic contamination in water. BOD analysis does not oxidise all of the organic matter present in the waste; only the organics that are biochemically degradable during n days time period at 20℃ are oxidised. The day period is given as index in BOD_n. The standard for usual measurements is a 5-day period.

BOD_5 is the most widely used parameter of organic pollution applied to wastewater and is used:

- to determine the approximate quantity of oxygen that will be required to biologically stabilise the organic matter present,
- to determine the size of wastewater treatment facilities,
- to measure the efficiency of some treatment processes;
- to determine compliance with wastewater discharge permits.

For the measurement of BOD, different volumes of wastewater are mixed in special BOD bottles with a liquid called "dilution water". This may be final effluent of a wastewater treatment plant which still contains some microorganisms or primary clarifier effluent diluted with tap water; it has to be supplemented with nitrogen, e.g. urea, and phosphate, aerated for a period of 3 to 10 days prior to use for BOD analysis, which had been saturated with oxygen prior to BOD analysis by bubbling in air. Moreover, a nitrification inhibitor (e.g. allylthiourea) is added, because only the oxygen consumption due to biochemical oxdation of organic wastewater constituents - and not of ammonia - is desired to be determined. Also blanks are prepared (bottles containing only dilution water and nitrification inhibitor).

The BOD bottles are completely filled and sealed with a glass stopper in such a way that no more air bubbles are contained in the bottles. With every mixture a duplicate of bottles is prepared. In one bottle of each pair, the concentration of dissolved oxygen is determined (e.g. by means of an oxygen probe) immediately after mixing. The other bottle is stored for n days at 20℃ in the dark (to prevent photochemical reactions). At the end of this period, the concentration of dissolved oxygen is measured also in this bottle. The difference of oxygen concentration in the two bottles of a pair is the oxygen consumption (OC) (mg O_2/l). From the oxygen consumption of a particularly diluted wastewater sample and the oxygen consumption of the blanks (OC_{DW}), the BOD_n is calculated as follows:

$$BOD_n = DF \cdot OC - (DF - 1) \cdot OC_{DW}$$

with DF being the dilution factor ($V_{(\text{diluted sample})}/V_{(\text{sample before dilution})}$). BOD values determined for different dilutions should give a straight line when drawn as a function of the term $V_{(\text{sample before dilution})}$. When points corresponding to low dilution factors (i.e. to high $V_{(\text{sample before dilution})}$) in this graph are lying below the extrapolated line, this is a hint, that inhibition of microorganisms occurred in samples with low dilution. These values must not be applied for BOD determination!

2.2.5 Chemical Oxygen Demand (COD)

The equivalent amount of oxygen required to oxidise organic matter present in a water sample by means of a strong chemical oxidising agent is called chemical oxygen demand (COD). COD is also a sum parameter and is used to measure the content of organic matter of wastewater. The COD values include the oxygen demand created by biodegradable as well as non-biodegradable substances. As a result, COD values are greater than BOD. In comparison with BOD_5, COD measurement has an advantage in that it requires a short digestion period of about 3 hours rather than incubation of 5 days period required for BOD_5 measurement. For many types of wastes, it is possible to correlate COD with BOD. Once the correlation has been established, COD measurements can be used to good advantage for treatment-plant control and operation.

In the COD method, not the product (CO_2) formed by oxidation of the organic wastewater constituents is measured, but the consumption of the oxidant (calculated as oxygen O_2). Thus, an exact amount of oxidant has to be used for the oxidation of the organics in a given volume of a wastewater sample, and the excessive oxidant which is not consumed for complete oxidation of organics must be quantified. Complete

oxidation postulates that the only oxidation product formed is CO_2 and not any organic intermediate with high carbon oxidation numbers. Although COD is given as mg of consumed oxygen per litre of wastewater, the oxidant used in the analytical procedure is not oxygen, but potassium dichromate ($K_2Cr_2O_7$) in concentrated sulfuric acid. The substance $K_2Cr_2O_7$ is a powerful oxidant in an acid milieu ($H_2Cr_2O_7$ is formed) at elevated temperature (148℃). Oxidation is the abst raction of electrons from a substance that is oxidized. As one molecule $K_2Cr_2O_7$ can accept 1.5 times more electrons than the molecule O_2, this is considerated by calculation.

The analytical standard procedure prescribes to place 50 ml of the wastewater sample in a 500-ml-refluxing flask, to add 1 g of $HgSO_4$ (caution: toxic!), 5 ml of a mixture of Ag_2SO_4 (which serves as a catalyst for the oxidation of the organics) in concentrated sulfuric acid (caution: corrosive!), to add subsequently 25 ml of a solution of the oxidant $K_2Cr_2O_7$ (caution: powerful carcinogen!) in concentrated sulfuric acid and to heat the mixture under reflux after vigorous mixing for two hours. The $K_2Cr_2O_7$ that has not been consumed for oxidation is then quantified by titration with an aqueous solution of $Fe(NH_4)_2SO_4$ with known concentration. The residual $K_2Cr_2O_7$ oxidizes the Fe^{2+} of the titrant $Fe(NH_4)_2SO_4$ to give Fe^{3+}. When all the residual $K_2Cr_2O_7$ is consumed (reduced by Fe^{2+}), the indicator ferroin, which has to be added to the wastewater/$K_2Cr_2O_7$ mixture prior to titration, turns from blue-green to reddish brown. At this end-point of titration, the volume of the $Fe(NH_4)_2SO_4$ is read from the burette and the residual amount of the oxidant $K_2Cr_2O_7$ after oxidizing the organic constituents in the wastewater sample can be calculated. By this, the consumption of $K_2Cr_2O_7$ during oxidation - and its oxygen equivalent - are calculated, giving the COD.

Besides problems with working safety (use of the carcinogenic $K_2Cr_2O_7$), there are also some analytical problems, because $K_2Cr_2O_7$ does not only oxidize organic, but also some inorganic molecules or ions. Chloride, which is a normal constituent of wastewaters, is oxidized by $K_2Cr_2O_7$ forming Cl_2 gas. In order to prevent oxidation of chloride, it is masked by the addition of $HgSO_4$. Chloride bound to Hg^{2+} is not oxidized by $K_2Cr_2O_7$. However, the addition of mercury sulfate to all samples for COD determinations generates a large amount of toxic waste in laboratories for wastewater analyses (some laboratories purify this liquid waste stream by ion exchange giving the ion exchange regenerates to recycling companies for mercury and also for silver and chromium recovery). If the chloride concentration in the wastewater sample exceeds 1 g/l, the chloride has to be removed prior to COD analysis from the sample by heating it after addition of sulfuric acid and removing the formed hydrochloric acid from the gas phase by absorption to alkaline materials. But there are other substances which can cause troubles with the COD analysis: If the wastewater contains e.g. bromide, iodide, sulfite, Fe^{2+}, Co^{+} or hydrogen peroxide, these reducing agents will also be oxidized by $K_2Cr_2O_7$. This $K_2Cr_2O_7$ consumption, however, is not caused by organics leading to

misinterpretations about the content of organics of the wastewater. Another problem is that not every organic substance is completely oxidized under the conditions of COD analysis. Many nitrogen-containing heterocycles (e.g. pyridine) consume significantly less $K_2Cr_2O_7$ than theoretically assumed.

There are also cuvette tests for COD analyses available from several companies. These cuvette tests offer the advantage, that smaller volumes of reagents (and also of wastewater samples) are used limiting the toxic waste of laboratories

2.2.6 Total Organic Carbon (TOC)

Another means for measuring the organic matter present in water is the TOC test, which is especially applicable to small concentrations of organic matter. Wastewater content of carbon bound in organic molecules is the TOC (total organic carbon). Organic carbon comprises nearly all carbon compounds except a few carbon species which are looked at as inorganic (carbon dioxide, hydrogen carbonate, carbonate, cyanide and some further examples which are not commonly found in wastewaters). For detection of organic carbon in aqueous samples, the whole sample is subdued to oxidation (commonly by incineration of a particular volume of the wastewater sample in the presence of a catalyst at 900℃ using CO_2-free air). The CO_2 formed by incineration of the organic wastewater constituents is quantified in the off-gas of the furnace using an infrared cell (CO_2 absorbs infrared light at a wavenumber of 2349 cm^{-1}, corresponding to a wavelength of 4257 nm) by comparison with measurements using aqueous calibration solutions of a pure organic compound with known concentration. The theoretical TOC of such a calibration solution can be calculated as follows (for the calculation, the formula, the molar mass M and the mass concentration m/V of the standard compound have to be known using the atomic weight of carbon [12 g/mol] and the number of carbons z in the standard compound) using phenol as an example for a standard substance:

Standard compound: phenol
Formula: C_6H_6O
Molar mass of standard compound: (6 x 12 + 6 x 1 + 16) g/mol = 94 g/mol
Carbon mass per mol of standard compound: *z* x 12 g/mol = 6 x 12 g/mol = 72 g/mol
Carbon mass portion of standard compound mass: (72 g/mol)/(94 g/mol) = 0.766
Phenol mass concentration of standard solution: 200 mg/l
Theoretical TOC of standard solution: 0.766 x 200 mg/l = 153.2 mg/l

However, although the analytical method described above will deliver appropriate results if performed with standard solutions in deionized water, it will not work with real

wastewater samples or solutions of organics in tap water, because these matrices also contain inorganic carbon compounds (mainly hydrogen carbonate). The carbon bound in inorganic molecules or ions is designated as total inorganic carbon (TIC). The sum of TOC and TIC gives total carbon (TC). As wastewater usually contains hydrogen carbonate (or dissolved carbon dioxide or carbonate, depending on pH), the TIC has to be removed prior to TOC analysis. This is easily obtained by acidification of the sample and stripping the formed CO_2 with CO_2-free air. However, this method also removes volatile organic compounds and can only be applied if no volatile organics are present in the wastewater sample. In the presence of volatile organics TOC has to be calculated after analysis of TC and TIC by subtraction of both concentrations. TOC analyzers exhibit high technical standards and are thus rather expensive. A German company also offers cuvette tests for TOC analysis which is performed using a photometric method.

2.2.7 Interrelationship between BOD, COD and TOC

Typical values for the ratio of BOD/COD for untreated municipal wastewater are in the range from 0.3 to 0.8 (see in table 3). If the BOD/COD ratio for untreated wastewater is 0.5 or greater, the waste is considered to be easily treatable by biological means. If the ratio is below about 0.3, either the waste may have some toxic components or acclimated microoorganisms may be required in its stabilization. The corresponding BOD/TOC ratio for untreated wastewater varies from 1.2 to 2.0. In using these ratios it important to remember that they will change significantly with the degree of treatment the waste has undergone, as reported in Table 3.

Table 3: Comparison of ratios of various parameters used to characterize wastewater

Type of wastewater	BOD/COD	BOD/TOC
Untreated	0.3 – 0.8	1.2 – 2.0
After primary settling	0.4 – 0.6	0.8 – 1.2
Final effluent	0.1 – 0.3	0.2 – 0.5

2.2.8 Chlorides

Domestic wastewater is a rich source of chlorides, because human excreta, mainly urine, is rich in chloride. It does not present a major pollution threat. But, Chloride ion concentration is an important factor to be considered if treated effluent is used for irrigation. High chloride concentration disturbs the osmotic balance between the plants and the soil, which affects the growth of the plants. The level of chlorides in wastewater

sample is determined by the titration of the sample with mercuric nitrate in the presence of an indicator.

2.2.9 Nitrogen

Nitrogen compounds with environmental relevance frequently analyzed in wastewater are ammonia, nitrite, nitrate, and Kjeldahl nitrogen. Ammonia discharged to surface water can be nitrified in the aqueous environment if nitrifying microorganisms are present. The nitrifying bacteria consume dissolved oxygen for this process, thus depleting the oxygen content of the surface water with the consequence of massive dying of fish. Moreover, if the pH of the surface water is in the alkaline range, NH_3 is formed which is toxic towards fish. The nitrate ion represents a nutrient leading to eutrophication of surface water, and nitrite is toxic and can react with amines (formed e.g. from amino acids of proteins) to yield N-nitosoamines which represent powerful carcinogens. Kjeldahl nitrogen is a sum parameter of compounds containing the nitrogen atom with an oxidation number of -3 (ammonia, amines and many other organic nitrogen compounds). It thus comprises organic nitrogen compounds besides ammonia nitrogen. This is also an important nitrogen parameter, because organic nitrogen compounds can be metabolized to ammonia (this conversion can also take place in surface water). Analytical procedures for the mentioned important nitrogen parameters are given in detail e.g. in the "Standard Methods" (Greenberg et al. 1985). Their principles will be described briefly in this chapter.

As many wastewater analyses (not only for nitrogen compounds) are photometric procedures, a short information about photometry will be given. Photometry uses light as an analytical tool. As particular substances (analytes) absorb photones of different wavelengths to different extents, the wavelength (or colour) of the light applied for photometric analysis affects the specificity of the analytical procedure for a given analyte. The specificity can be increased by converting the analyte by reaction with certain reagents to form coloured products, because (besides the colour) also the reaction with a given reagent is specific for the analyte (other wastewater constituents would not react at all with the reagents used for conversion of a particular analyte). For example, ammonia can be converted to an intensely blue indophenol derivative by the following reactions:

$$NH_4^+ + OH^- \rightarrow NH_3 + H_2O$$

$$NH_3 + OCl^- \rightarrow NH_2Cl + OH^-$$

$$NH_2Cl + \text{Phenol} \rightarrow \text{Indophenol (intensely blue)}$$

The last reaction is catalysed by Mn^{2+} ions. For obtaining the blue product, an aliquot of the wastewater sample is mixed with a small volume of aqueous $MnSO_4$ solution. Then the mixture is stirred and hypochlorous acid reagent and finally an alkaline aqueous phenol solution ("phenate reagent") is added. After 10 min the colour formation is complete for these particular reactions. The coloured product exhibits a maximum absorption at 630 nm (the complementary light causes the blue colour). The solution is transferred to a cuvette which is irradiated with light exhibiting a wavelength of 630 nm (satisfactory results are obtained in the 600 to 660 nm region for this analytical procedure) and an intensity of I_0 in a photometer. In the photometer, the intensity of the light entering (I_0) as well as the light leaving the cuvette (I) is determined (by means of a photodiode or a photomultiplyer) as shown schematically in figure 6. The absorbance, i.e. $\log(I_0/I)$, is linearly related to the indophenol concentration as given by the Beer-Lambert law:

$$\text{absorbance} = \log(I_0/I) = \varepsilon \cdot c \cdot d$$

With the proportionality constant ε (molar absorptivity or molar extinction coefficient), the length d of the way of the light through the cuvette (frequently 1 cm) and the molar concentration c of the coloured substance, resp. the concentration of the analyte in the sample (as one molecule of ammonia will yield one molecule of the coloured substance, the absorbance will also be linearly related to the ammonia concentration in the wastewater or in calibration solutions, resp.).

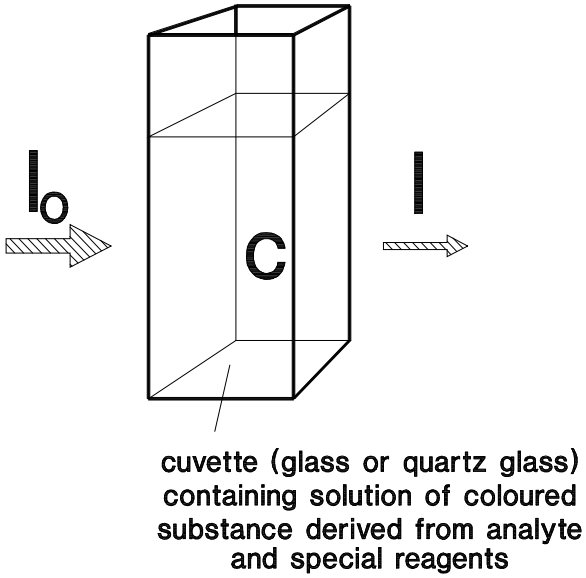


Figure 6: Principle of photometric analysis measuring the decrease of intensity of light that passes a solution of a substance (concentration: c) that absorbs light of the applied wavelength; I: intensity after passing the cuvette; I_0: intensity of the light before passing the cuvette.

The colourless nitrite ion NO_2^- is also transformed to a coloured substance prior to photometric analysis. A standard method used for nitrite analysis suitable for determinations down to 1 µg NO_2^-N/l is the reaction of nitrite at pH 2 (formation of nitrous acid) with sulfanilic acid to give a diazonium salt which reacts with another reagent, (1-naphthyl)-ethylenediamine, in order to form a reddish purple azo dye that can be detected photometrically at 543 nm. For quantification the nitrite concentration in wastewater samples, standard solutions containing known nitrite concentrations are also analyzed in the same way. As for all the other analytical methods mentioned here, the exact procedure can be read in the "Standard Methods" (Greenberg et al. 1985).

As for other analytes, also for nitrate determination several analytical methods can be applied. Greenberg et al. (1985) describe the chromotropic acid method as one of the possible procedures. Two molecules of nitrate react with one molecule of chromotropic acid (4,5-dihydroxy-2,7-naphthalene sulfonic acid) and the absorbance of the product is measured at 410 nm. The method interferes with nitrite. The nitrite ion is destroyed by reaction with urea which is also added to the test assay.

The German standard procedure for nitrate analysis utilizes the reaction of nitrate with 2,6-dimethylphenol under acid conditions to form 4-nitro-2,6-dimethylphenol with an absorbance maximum at 324 nm.

As already mentioned, the Kjeldahl method determines nitrogen in the trinegative state. Thus, it does not account for nitrogen in compounds like azide, azine, azo, hadrazone, nitrate, nitrite, nitrile, nitro, nitroso, oxime, and semi-carbazone (Greenberg et al. 1985). In the Kjeldahl method, the amino nitrogen of many organic nitrogen compounds is transformed to $(NH_4)_2SO_4$ in the presence of H_2SO_4, K_2SO_4, and $HgSO_4$ (this acts as a catalyst for the conversion) by boiling the mixture of wastewater sample and reagent solutions in a flask until fumes are occurring. A mercury ammonium complex generated in this procedure is decomposed by the addition of sodium thiosulfate/sodium hydroxide reagent after digestion of the organic nitrogen compounds. Ammonia and ammonium are also present as $(NH_4)_2SO_4$ after treatment. Finally, the flask used for digestion is connected to a steamed-out distillation apparatus, and the ammonia which has been generated from $(NH_4)_2SO_4$ by addition of hydroxide solution is distilled to a receiving flask containing a boric acid solution. Afterwards the distilled ammonia is determined by acid/base titration. If it is to be analysed by the above-mentioned phenate method for ammonia determination, the receiving flask must contain sulfuric acid. If small sample volumes have to be analysed for Kjeldahl nitrogen, an all-glass micro-Kjeldahl distillation apparatus (figure 7) is used for distillation of formed (and original) ammonia.

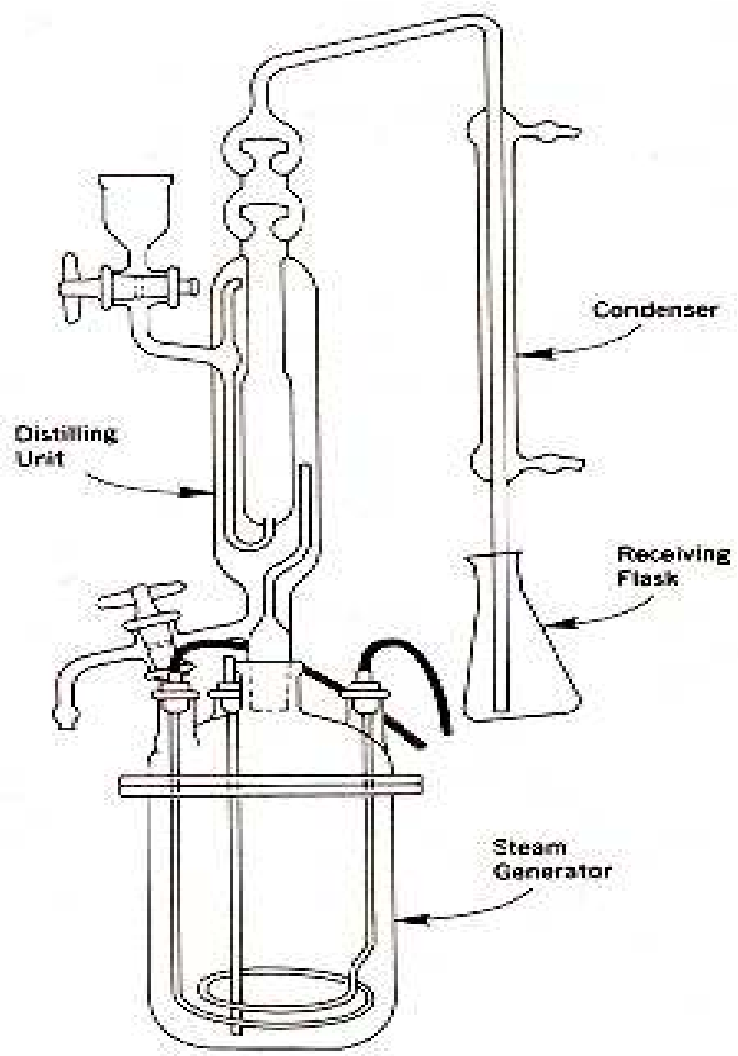


Figure 7: Micro-Kjeldahl distillation apparatus; Greenberg et al. (1985).

2.2.10 Phosphorus

Phosphorus is essential to the growth of algae and other biological organisms. The amount of phosphorus compounds present in wastewater discharge has to be controlled in order to avoid noxious algal blooms occurred in surface water. The usual forms of phosphorus found in aqueous solutions include the orthophosphate, polyphosphate, and organic phosphate. Three groups of phosphorus compounds have to be distinguished in phosphorus analysis of aqueous samples. The ortho-phosphate anion PO_4^{3-}, poly- and metaphosphates (examples see figure 8) which can be hydrolyzed to form ortho-phosphate, and phosphorus compounds which will not yield ortho-phosphate by hydrolysis but by oxidative treatment. The latter group is mainly

represented by organic phosphorus compounds. The sum of all three phosphorus species is designated as total phosphorus.

The ortho-phosphate anion is again determined by photometry after it has been transformed by addition of ammonium molybdate, potassium antimonyl tartrate and ascorbic acid to yield the intensely blue compound "molybdenum blue" (Greenberg et al. 1985) which is quantified by means of a photometer at 880 nm using phosphate calibration solutions of known phosphate concentrations.

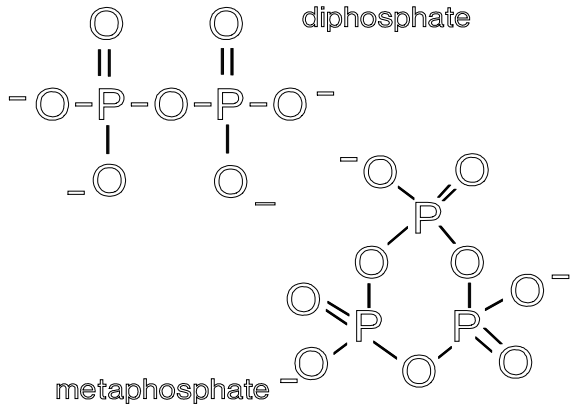


Figure 8: Two examples of acid-hydrolyzable phosphates: diphosphate, $P_2O_7^{4-}$, and metaphosphate, $P_3O_9^{3-}$

The sum of ortho-phosphate and acid-hydrolyzable phosphorus is determined nearly in the same way except a hydrolysis step prior to quantification of original and hydrolysis-generated ortho-phosphate. The hydrolysis is performed by gentle boiling of the wastewater sample after addition of a mixture of concentrated H_2SO_4 and concentrated HNO_3 (Greenberg et al. 1985). After cooling and neutralization with NaOH solution, the ortho-phosphate can be analyzed following the procedure given above.

Determination of total phosphorus requires oxidation as well as hydrolysis prior to ortho-phosphate analysis. This is realized by boiling the wastewater sample after addition of concentrated HNO_3, evaporation on a steam bath, addition of 70 % perchloric acid and concentrated HNO_3, boiling until the mixture clears. After cooling the mixture, NaOH solution is added and the ortho-phosphate is determined as given above (Greenberg et al. 1985).

2.2.11 Oil and Grease

Oils, fats, waxes and fatty acids are the major constituents included in this category in domestic wastewater. The presence of a significant amount of oil and grease in wastewater hinders the transportation of wastes through pipelines. It causes scum in aeration basins of activated sludge plants, which interferes with the biological oxidation of wastes and produces a low quality settling sludge.

These substances are determined by extracting them with an organic solvent 1,1,1-trichloroethane. The two immiscible solvents (organic solvent and water) make separate layers. The solvent containing the oil and grease fraction of the wastewater is separated from the aqueous layer. It is dried and evaporated to determine the extractable residue.

2.2.12 Gases

Gases commonly found in untreated wastewater include nitrogen (N_2), oxygen (O_2), carbon dioxide (CO_2), hydrogen sulfide (H_2S), ammonia (NH_3), and methane (CH_4). The first three are common gases of the atmosphere and will be found in all waters exposed to air. The latter three are derived from the decomposition of the organic matter present in wastewater

2.2.13 Sulphur

The sulphate ion occurs naturally in most water supplies and is present in wastewater as well.
Sulphate is reduced biologically under anaerobic conditions to sulphide, which in turn can combine with hydrogen to form hydrogen sulphide (H_2S).
The following generalised reactions are typical.

$$\text{Organic matter} + SO_4^{2-} \xrightarrow{\text{bacteria}} S^{2-} + H_2O + CO_2$$

$$S^{2-} + 2H^+ \longrightarrow H_2S$$

The H_2S accumulated in sewers can be oxidised to sulphuric acid, which is corrosive to sewer pipes.

2.2.14 Adsorbable organic halides (AOX)

Adsorbable organic halides (AOX) is an organic sum parameter comprising such organics that contain chlorine, bromine or iodine (not fluorine!) atoms and are adsorbable to activated carbon. For AOX determination a particular volume of the wastewater sample is agitated sufficiently long with powdered activated carbon. Subsequently the activated carbon is separated by filtration using a membrane filter which retains the activated carbon (adsorption can also be executed in small activated carbon columns which are treated - after adsorption has been completed - in the same way as the loaded activated carbon removed by filtration). Then the membrane filter is incinerated together with the activated carbon in a stream of pure oxygen at temperatures around 900℃. The halogen atoms origin ally bound in organics adsorbed to the activated carbon form HCl, HBr, or HI, resp., which are contained in the exhaust gas of the incineration furnace and can be absorbed e.g. in acetic acid. Microcoulometric titration, an electrochemical quantification method, analyses chloride, bromide, or iodide, resp., of these acids. Bromide and iodide are calculated as chloride equivalents (one mol bromide or iodide is looked at as one mol chloride and is calculated as chloride mass), and the final chloride mass determined is related to the volume of the wastewater sample which had been subdued to activated carbon adsorption. The result is mg AOX (chloride)/l wastewater. For details of the method, see Greenberg et al. (1985).

In the AOX analysis procedure, artefacts can easily be produced: First, also inorganic chloride adsorbs to a certain amount to activated carbon. This adsorbed inorganic chloride will also be detected e.g. by microcoulometric analysis of the incineration off-gass and may result in the so-called "chloride error". Secondly, in wastewaters with high TOC mainly represented by non-halogenated organic compounds a competition of halogenated and non-halogenated organic compounds for adsorption sites on the activated carbon occurs leading to a very low extent of halogenated organic molecules being adsorbed. This can be prevented by dilution of the wastewater sample. However, by dilution also the AOX is diluted which is disadvantageous if the AOX content of the sample is decreased to be below the detection limit of the method. AOX analyses must be performed in laboratory rooms where no halogenated organic solvents are used at all, because these volatiles would also adsorb on the activated carbon during the AOX procedure. In recent years, AOX analyses in the Institute of Wastewater Management of Hamburg University of Technology had been performed in a laboratory where a thermostatized chamber was located. When there was a leakage in the cooling system of the chamber, some fluorochlorohydrocarbons were volatilized in the laboratory leading to severe analytical errors in AOX determinations.

Other parts of organics contained in wastewaters (usually comprised in TOC or COD) are the organic sum parameters hydrocarbons, phenols, anionic surfactants, neutral surfactants, cationic surfactants etc. Methods for analyzing these organic sum parameters are also given in the "Standard Methods" (Greenberg et al. 1985).

2.3 Selected other parameters

The world of chemical analyses - even that of environmental or more restricted that of wastewater analyses - is hardly to survey. For many analytes, there exist several analytical methods, and additionally wastewaters contain innumerable different kinds of constituents. The routineously measured wastewater parameters are mainly given above. But these are really the minority of possible parameters.

For the determination of metals, there exist special methods as flame emission photometry (e.g. important for the fertilizer component potassium). In this procedure the aqueous sample is transferred into a flame where the metals are electronically excited resulting in an emission of light of a particular wavelength. This emission can be detected and used for quantification of the concerning metal ion.

A similar method is also useful for the determination of some toxic heavy metals (atomic emission spectrometry/inductively coupled plasma, AES/ICP). The aqueous solution is pumped into a small plasma generated by high frequency fields where the metals are electronically excited leading to emission of light of that wavelength which is characteristic for the particular metal of concern. With this method, several metals can be determined simultaneously.

On the other hand, aqueous solutions of metal salts can also absorb distinct wavelengthes of light, when they are heated to very high temperatures (flame or graphite furnace) and converted from ions to atoms by this. The light absorbed by the atoms can be used for quantification of particular metal ions in aqueous solutions like wastewaters. The method is called atomic absorption spectrometry (AAS). Solids have to be digested prior to AAS analysis if their metal content is to be analyzed. Details for such methods can be read in the "Standard Methods" (Greenberg et al. 1985).

Sometimes, there is interest in the concentrations of particular organic compounds contained in wastewaters. For such analyses, gas chromatography is a useful tool, but very complex in execution. For many gas chromatographic methods, wastewater samples have to limits for particular trace organics. and the final concentrate is then analyzed. A very small volume of the concentrate (in the range of one µl) is transferred to the so-called injector of the gas chromatograph by a syringe. The injector is heated to

temperatures in the range of 200°C and flushed by the inert carrier gas (very often helium is used). At these high temperatures the total solution evaporates at once and the analytes as well as the extractant are transported by the carrier gas to a separation device, the so-called column. The column is usually a capillary made of fused silica (a material that has substituted glass which had been used earlier for manufacturing capillaries for gas chromatography) of some 10 m length. The inner wall of the capillary is lined by thin films of particular polymers which control the separation characteristics of the column. Different analytes (as well as the extractant) show different interactions with the polymer film material and thus exhibit different velocities passing the column. The temperature of the column also affects separation of analytes and varies - depending on the separation problem - between room temperature and around 300°C. It can also be changed during the chromatographic run ("temperature program"). At the end of the column the carrier gas (and the analytes as well as the extractants arriving at different times) are detected by devices like flame ionisation or electron capture detectors giving signals which are related to the concentrations of the analytes in the extract**.** Very useful are mass spectrometers for detection**,** because the detected mass fragments of the analytes can serve as "fingerprints" resulting in identification of particular organic compounds after comparison to computerized mass spectra of known organics.

However, not every organic compound can be analyzed by gas chromatography. If the boiling point of an organic is very high (> 400°C) the analyte is not sufficiently volatile to enter the column of the gas chromatograph and it will stay in the injector being subdued to thermal decay. That is why injectors have to be cleaned from time to time. It has been shown that only a minority of organic wastewater constituents are susceptible to gas chromatography. Gulyas (1997) could only identify 1 to 2 % of the TOC of biologically treated municipal wastewater as particular organic compounds by gas chromatography/mass spectrometry. Even in an untreated oil reclaiming wastewater only 2 % of TOC corresponded to particular organics identified in a dichloromethane extract of this wastewater (Gulyas and Reich, 2000).

Microbiological parameters of wastewaters are extremely important for judging their pathogenic potential. On the other hand, there exist also microorganisms which are useful for wastewater purification. The principal microorganisms of concern in water and wastewater include bacteria, fungi, algae, protozoa, worms, rotifers, crustaceans and viruses (Tchobanoglous and Schroeder 1987). Methods for the detection of pathogenic microorganisms are available. However, indicator organisms for faecal contamination are rather used than tests for pathogens, because procedures for the isolation of certain pathogenic bacteria are tedious and complicated and are not recommended for routine use (Greenberg et al., 1985). Therefore, indicator organisms are determined with the coliform group being a principal indicator of faecal bacteria. The coliform group density

in waters is looked at as a criterion of the degree of pollution and thus of sanitary quality. For microbiological analyses, culture media are used allowing the microorganisms contained in waters to grow under certain conditions resulting in an amount of cultured bacteria which can be detected by inspection and quantified by counting the grown bacteria colonies. It has to be noted that different bacterial species have different nutrient and environment requirements. This selectivity is very useful when it is desired to enumerate one or a very few species of bacteria to the exclusion of others. Therefore, nutrient medium and environmental conditions have to be carfully selected. For the coliform group of bacteria used as an indicator for faecal contamination of waters and probable presence of pathogens there exist particular media which can be prepared and sterilized in the microbiological laboratory. For more convenient microbiological analyses, several of these media are also commercially available. Prerequisites for microbiolgical laboratories can be found in the "Standard Methods" (Greenberg et al., 1985).

For the determination of bacteria in waters with low bacterial content, in general three techniques are available: the membrane-filter technique, the solid medium technique (plate count method) and the liquid medium technique (Tchobanoglous and Schroeder, 1987). For details of execution of bacterial counts, see Greenberg et al. (1985). Applying the membrane-filter technique, a known volume of water is filtered over a membrane filter with 0.45 µm pore width. Then the filter is removed from the filtration unit and transferred to a small petri dish containing a sterile absorbent pad saturated with a suitable culture medium. The filter membrane is placed face up on the culture medium. After incubation in the inverted position, the bacterial colonies are counted and the counts are related to the volume which had been filtered (Tchobanoglous and Schroeder, 1987).

For waters with higher numbers of bacteria (e.g. the effluent of a wastewater tretament plant or river water receiving the effluent or even raw sewage) the other two methods are suitable which include dilution steps of the water containing the bacteria (see figure 9).

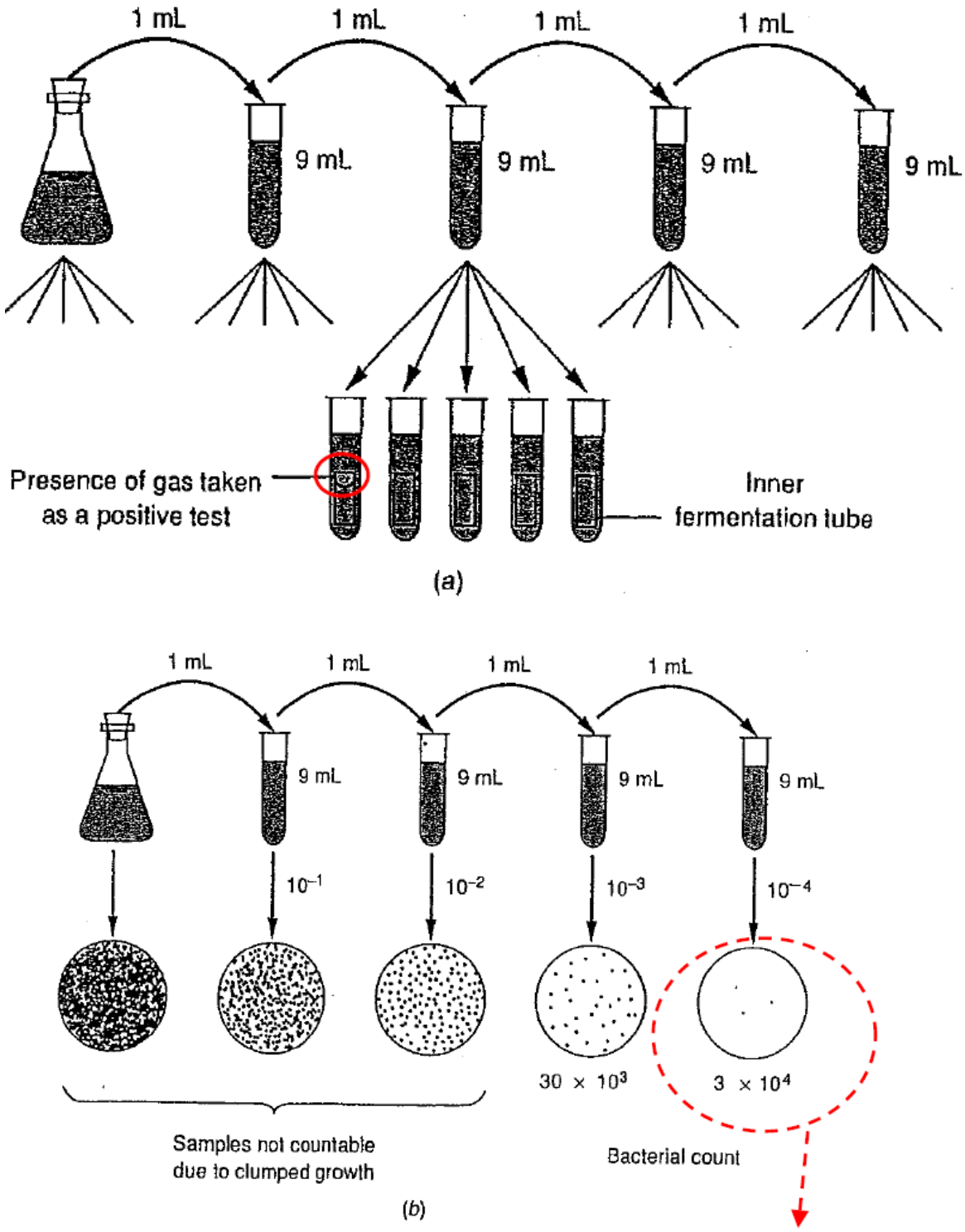


Figure 9: Illustration of methods to obtain bacterial counts: (b) use of a solid medium; (a) use of a liquid medium (Tchobanoglous and Schroeder 1987)

In the plate count method (see figure 9b) the first operation is preparation of 10-fold dilutions of the sample. Of each dilution as well as of the original sample 1 ml is pipetted into separate sterile petri dishes. Subsequently 12 to 20 ml of liquified culture medium is poured into each petri dish. After mixing medium and sample the mixture is allowed to solidify and subsequently the petri dishes are inverted and incubated at 35℃ for 48 hours. The next operation is counting of the developped bacterial colonies. For quantification, only dishes with colony numbers between 30 and 300 are utilized. At higher numbers of colonies clumped growth of bacteria will occur resulting in too low numbers of counted colonies.

Coliforms are capable of fermenting lactose with the production of an abundance of gas. This effect is utilized in counts of coliforms given in figure 9a. Again, 10-fold dilutions of the sample are prepared. Of each dilution 1 ml is transferred to the test tubes in multiplicate. The test tubes contain the fermentation medium and an inverted gas collection tube. After a 24 hour period of incubation at 44.5℃, gas observed in the inner fermentation tube indicates the presence of coliforms in the diluted sample. For example, if a 10-fold serial dilution is made and growth, as measured by gas production, is observed in the 10^{-n} but not in the $10^{-(n+1)}$ dilution, then it can be concluded that the sample contains at least 10^{n} cells per ml but less than 10^{n+1} cells per ml.

Another group of parameters useful for judging the quality of effluents of wastewater treatment plants is toxicity. Toxicity determination comprises a huge variety of tests because the test organisms can be varied (even using parts of living organisms like cell cultures) and the endpoint of toxic action can also be varied (using different metabolic events in the organism, occurrence of different diseases, damages or finally death of the investigated organism). For characterizing toxicity of waters, several tests using organisms living in water (e.g. algae, ciliated protozoa, daphnia, corals, annelids, crustaceans, aquatic insects, mollusks, fish) have been standardized (Greenberg et al. 1985). Tragically, also toxicity tests with humans are run (which of course are unintentional) in epidemiological studies which try to find associations e.g. between constituents of drinking water (chemical hazardous substances as well as pathogenic microorganisms) and excessive mortalities in terms of particular diseases in collectives consuming the drinking water of concern. However, these epidemiological studies are no routineously applied "toxicity tests" because they require huge efforts and usually exhibit high statistical uncertainties.

3 Sampling and preparation techniques of wastewater samples

Representative sampling of wastewater streams is decisive for correct modelling of wastewater treatment processes. While in laboratories usually high efforts are made to execute chemical analyses of wastewater samples with high accuracy, wastewater sampling is sometimes carried out by people who are not trained in sampling. Thus, experts assume that errors in wastewater analyses caused by mistakes during sampling are several orders of magnitude higher than by analytical errors in the chemical laboratory (Sommer, 1995).

Different kinds of sampling are possible: grab (or catch) samples and composite samples (a mixture of grab samples collected at the same sampling point at different times) can be taken. Both kinds of sampling can either be carried out manually or automatically. Automatic samplers are being used increasingly. They are effective and reliable and can significantly increase the frequency of sampling. Especially for composite samples taken during long periods (days, weeks), automatic samplers are convenient and help to save manpower. An example is outlined in figure 10. With this type a variable number of constant volumes of single samples can be combined to composite samples. At desired times, which can be programmed by means of a control unit, the vacuum pump A is switched on automatically until the sample reaches the level indicator sensor C in the dosing vessel D. Then the level indicator gives a signal to switch off the vacuum pump. The sample flows back through the tube B until the level in the vessel D is reached which is given by the length the tube B is inserted into vessel D (adjustable). Then the valve E is opened automatically and the sample is flowing into the desired bottle H (also programmed via control unit of the automatic sampler). In many parts of the world, composite samples representing a 24-h period are considered standard. In Germany, for many control parameters composite samples consisting of five grab samples collected within a two hours period are according to regulations.

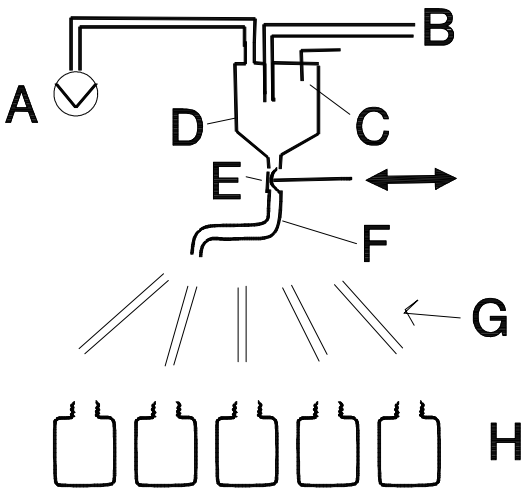


Figure 10: Scheme of an automatic sampler taking samples by means of vacuum; A: vacuum pump; B: pipe for sample transport from wastewater stream; C: level indicating sensor; D: dosing vessel; E: valve; F: cock which is moved by steps by a small motor in order to select sample containers H for different composite samples; G: channels for distribution of samples to sample bottles H; Gulyas (1999).

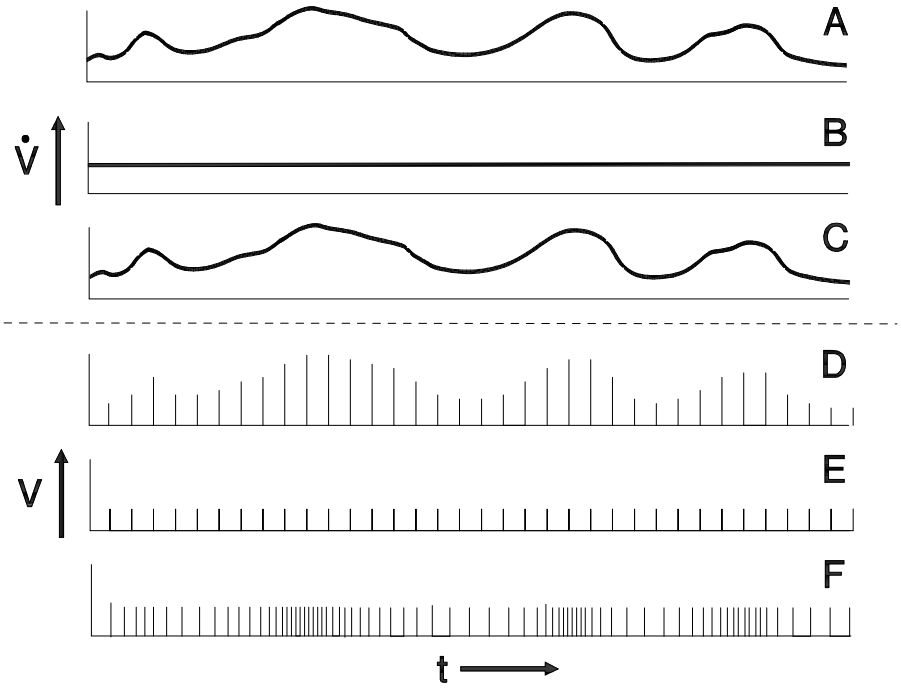


Figure 11: Different types of sampling using automatic samplers; A: volume flow of the wastewater stream which has to be characterized; B and C: continuous sampling modes; D, E, F: discontinuous sampling modes; for details see text; Gulyas (1999).

Figure 11 shows the volume flow of a wastewater stream (A) and different types of composite samples (B to F). For continuous sampling, pumps are used either with a continuous flow (time-continuous sampling, A) or with a flow which is adapted to the flow of the wastewater stream (flow-continuous sampling, B). In the schemes D to F (discontinuous sampling) at particular intervals grab samples are taken (being combined to form composite samples) in different ways: In scheme D the frequency of taking grab samples is constant, but the volume of each grab sample is adapted to the volume flow of the wastewater stream (flow-proportional sampling); in sampling mode E frequency as well as volume of grab samples are constant (time-proportional sampling); in scheme F the volume of each single sample is constant, but the frequency is controled by the flow of the wastewater (high sampling frequency during high wastewater flows, low sampling frequency during low wastewater flows, volume-proportional sampling). For sampling modes C, D, and F a flow meter is needed to determine the wastewater flow. The flow meter must be able to transfer its signals to the automatic sampler in order to control flow (mode C), volume (mode D), or frequency (mode F) of grab samples. The automatic sampler drawn schematically in figure 10 can only be applied for sampling modes E and F, because the volume of each grab sample cannot be varied during the sampling period and because it is a device for discontinuous sampling. It has to be noted, that automatic samplers have to be cleaned before and after sampling campaigns. Careful maintenance is a prerequisite for appropriate function.

Table 3 shows different conditions of wastewater flow and concentrations of wastewater constituents and the suitable sampling mode to yield representative samples.

***Table 3: Selection of appropriate sampling mode (from several possibilities given in figure 9) yielding representative samples with different conditions concerning wastewater flow and concentration of wastewater constituents*.**

Concentration	**Flow of wastewater**	
	constant	**varying**
constant	grab sample	grab sample
varying	composite sample following mode B or E	composite sample following mode C, D, or F

Besides sampling times, also the location of sampling is very important in order to obtain representative samples. It is recommended to sample below the surface of the wastewater in order to avoid contamination of the sample with materials with a lower density than water which are eventually enriched at the surface but not representative for the bulk wastewater stream. It should also be avoided to take samples directly at the walls or at the floor of e.g. wastewater channels or tanks, because in this case solid

substances fixed at the walls (growing biofilms) will be added to the sample although they are not representative for the wastewater stream.

If suspended wastewater constituents are to be analysed care has to be taken, because particle size is easily affected by sampling measures. By transferring mechanical energy to samples (e.g. by shaking or by pumping) two effects can occur with the particles: flocculation or destruction of flocs leading to a greater particle number but lower particle diameters. This can lead to artefacts when particle properties are measured which correspond to particle size: e.g. determination of settleable solids or particle size distribution. For the determination of these parameters, samples taken manually and with care are favorable. Moreover, these parameters should be measured immediately after sampling, before flocculation or floc destruction has occurred.

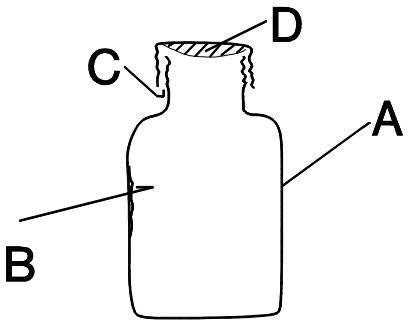


Figure 12: Analytical errors caused by unsuitable sample containers; A: unsuitable container materials; B: impurities; C: leaky seals; D: unsuitable gaskets; Gulyas (1999).

There are also particular requirements concerning the containers for collection and storage of samples (see figure 12.): First of all, sample bottles have to be clean (to prevent sample contamination) and dry (in order to prevent sample dilution). Cleaning should be performed in the laboratory prior to sampling following standard cleaning procedures. Besides contamination, impurities (B in figure 12.) can also cause adsorption of analytes (i.e. the substances which are to be analyzed in the sample) leading to analytical results below the true concentrations of the analytes in the wastewater. The material (A in figure 12.) of the sample container may also affect the results of analyses: analytes can be adsorbed by unsuitable container materials, sometimes they can pervaporate through the material (e.g. halogenated organic solvents in wastewaters can permeate the walls of polyethylene bottles resulting in too low results or they can contaminate the sample if they diffuse from the air in the laboratory into the bottle), and some constituents of container walls (e.g. plasticizers in PVC bottles) may migrate into the sample leading to sample contamination (resulting in too high results for organic sum parameters like total organic carbon). When sample

containers are not tightly sealed (C in figure 12) either volatile analytes can leave the bottle. On the other hand, a laboratory environment bearing relatively high concentrations of volatiles may cause contamination of the sample. Long term storage of the samples with leaky seals may result in water evaporation from the sample bottle leading to increased concentrations of all non-volatile analytes. Unsuitable gaskets of seals (D in figure 12) may also cause problems either with contamination of the sample (e.g. organic materials) or with adsorption of analytes. Another aspect is the transparency of the container material: Wastewater constituents which are susceptible to photoreactions require bottles which prevent the sample from light (using brown glass of Teflon bottles). Generally, samples should not be allowed to stand in the light, but always stored in the dark.

As most wastewaters are not at all sterile, it can be assumed that biochemical processes (which are desired in biological treatment stages) will not stop when the wastewater sample is transferred to a bottle. Examples for such processes are nitrification (oxidation of ammonia to nitrite or nitrate if still oxygen is dissolved in the sample resulting in too low ammonia and too high nitrite, or nitrate concentrations determined), denitrification (reduction of nitrate or nitrite to nitrogen gas resulting in too low nitrate or nitrite concentrations determined) or oxidation of organic wastewater constituents (resulting in errors of organic sum parameters analyzed in the sample). To prevent biochemical reactions, the microorganisms in the wastewater sample have to be killed or at least their metabolic activity has to be inhibited. This can be obtained by preserving the samples. Preservation can be realized by the addition of substances which are inhibiting or toxic towards microorganisms (acids, bases, mercury salts, azide) or by reducing the temperature (storage of samples in refrigerators or freezers), thus decelerating biochemical reactions.

For different analysts there might be different optimum preservation procedures. For additional details for preservation of samples see appendix in page 40. This means that sometimes a sample has to be divided and the sample parts must be preserved in different ways each adapted to the parameters that are aimed to be analyzed. In the past, there have been attempts to find optimum preservation methods for several wastewater routine parameters. The "Working Party on Stabilization of Samples from the Hydrochemistry Team of the German Chemists Association" (1981) analyzed primary clarifier effluent of a municipal wastewater treatment plant for different parameters after different storing periods and applying different preservation methods (see table 4) and compared the analyses to those executed with the same samples directly after sampling. By this, they could determine the periods of stability for several parameters under different preservation conditions (storing at room temperature without any addition of preservatives and with addition of acid or base or mercury chloride and storing in a freezer).

In the "Standard Methods" also effective preservation methods are given for several parameters (Greenberg et al. 1985). It has to be mentioned that freezing is not a good preservation method for samples to be analyzed for suspended solids. It can be observed, that even in filtered samples after freezing and thawing solids are generated. These solids are a consequence of flocculation of colloidals (dissolved macromolecules like humic substances). During the freezing process more or less pure ice is formed at the walls of the sample bottle leading to increasing concentrations of dissolved wastewater constituents in the remaining solution. The more ice freezes the more concentrated the residual solution will become. Macromolecules come so close to each other that some of them "stick" together and will no longer be dissolved because of the huge size of the agglomerates. When the whole sample is frozen, these solids are also frozen in the ice, but after thawing they are not re-dissolved, but stay solids. Another fact that has to be remembered when applying freezing as preservation is to avoid glass bottles because they can be destroyed during freezing the aqueous sample and can no longer protect the sample against contamination or evaporation of water molecules.

Table 4: Recommendations of the "Working Party on Stabilization of Samples from the Hydrochemistry Team of the German Chemists Association" (1981) for preservation of primary clarifier effluent for analyzing different parameters

Parameter	**Preservation Method**	**Period of stability of parameter [d]**
Oxidation with $KmnO_4$	no preservation -18 to -22℃ acidified (pH 2) alkaline (pH 12) $HgCl_2$	0 32 16 8 8
COD	no preservation -18 to -22℃ acidified alkaline	0 32 0 0
TOC	no preservation -18 to -22℃ acidified alkaline	0 32 2 8
BOD	no preservation -18 to -22℃ acidified alkaline	0 32 4 8
ammonia	no preservation -18 to -22℃ acidified alkaline $HgCl_2$	0 0 16 32 32

nitrate	no preservation -18 to -22℃ acidified alkaline $HgCl_2$	0 8 1 4 0
sulfate	no preservation $HgCl_V$	0 32
anionic surfactants	no preservation acidified $HgCl_2$	0 0 32

Efficiency of particular preservation methods strongly depends on concentration of microorganisms in the samples. Therefore, preservation recommendations given in the literature may not always be suitable and applied preservation methods should be verified with samples routineously collected. When using chemical preservatives like acids etc. one should take care, that certain analytes can no longer be determined in a sample preserved in such a way. It is impossible to measure e.g. nitrate or total nitrogen in a sample that had been preserved by addition of nitric acid. Chloride cannot be determined if hydrochloric acid had been used as a preservative.

A couple of parameters are recalcitrant against preservation and have to be measured immediately after sampling. Such parameters are given in table 5.

Table 5: Parameters which cannot be stabilized by sample preservation and have to be measured immediately after sampling at the sampling location or directly in the wastewater

Parameter	**Measures to be taken**
turbidity	immediate inspection and documentation; analytical quantification should be carried out on the same day
settleable solids	immediate analysis using Imhoff cone
suspended solids	filtration and gravimetric analysis must be performed as soon as possible
colour	immediate inspection and documentation
odor	immediate check and documentation
concentration of dissolved oxygen	analysis with oxygen probe
pH	analysis with pH probe
conductivity	analysis with conductivity probe
nitrite	transport samples as fast as possible to laboratory for analysis; reflectometric analysis at sampling location
temperature	directe determination in the wastewater

Each step of handling the samples has to be documented in the sampling protocol which should also contain the sample designation (which has to be marked also on the sample container), date and day time of sampling, sampling location, name of person collecting the samples, purpose of sampling, mode of sampling (grab or composite sample etc.), results of measurements performed at the sampling site, sample preparation measures (e.g. sedimentation of sample), preservation procedure(s), sample storing conditions until delivery to laboratory, comments upon reference samples simultaneously collected, comments about subsequent changes occurring in the sample, comments about deviations from routineously performed sampling (e.g. application of another automatic sampler, more frequent transfers of samples to other bottles than usually done), observations at sampling site (weather, wastewater irregularities as foam, bulking sludge, odor etc.), comments about irregularities observed on the sampling site (e.g. construction operations within a treatment plant etc.). Sampling documentation forms can serve as check lists.

For further analyses in the laboratory, samples must be transported as soon as possible to the laboratory. For keeping the samples unchanged during the transport, the sample containers should be tightly sealed, kept cool (e.g. using a cooling bag - which should be exclusively used for sampling but not for food transport for safety reasons) and dark. In vehicles used for sample transport, samples must be protected against being tilt over. If samples are shipped by mail or express services, by railway, ship or aeroplane, special safety measurements have to be taken. The bottles must be sealed absolutely tight and protected against shock in order to avoid leakages of the sample bottles.

It is clear that sampling of wastewater (and also of other media) has to be carefully prepared (providing sampling equipment like suitable sample bottles in sufficient number etc.). There must be a good communication between sampling staff and the analytical laboratory concerning number of samples, parameters which must be analyzed, time of delivery of samples to the laboratory, because the laboratory has to organize the enforcement of the analyses as well as to provide storing space in refrigerators or freezers. The samples as well as the sampling protocols have to be received by the laboratory staff in a responsible manner because of registration and eventual transfer of some samples to other laboratories for special analyses.

Working safety has to be obeyed not only in laboratories, but also during sampling (e.g. marking samples with symbols for hazardous materials if harmful preservatives like concentrated acids or bases or even toxic materials like $HgCl_2$ are added to samples).

Another step which is often performed prior to sample analyses is sample homogenization. This is necessary when samples which contain solids are divided. Measures have to be taken that the divided samples are identical with the original

sample. This is not possible if a sample contains e.g. settleable solids and is not sufficiently agitated during sample division. Then the solids will settle, the sample is no longer homogeneous and the sample is divided into one part being poor in solids and the other one being more concentrated in solids than the original sample. This can be avoided by transferring an aliquot from the stirred sample. Sometimes high speed stirring devices have to be used in order to keep the sample in a homogeneous state during sample division, see also the presentation (slides of lesson A1).

4 Statistics

For design of wastewater treatment plants, a couple of chemical parameters of the collected wastewaters have to be analyzed following the above-mentioned procedures. For example, for designing the nitrification process, the wastewater content of ammonia is relevant. As concentrations of wastewater constituents are not constant, it is necessary to know how the relevant parameter varies with time (day-time, weekly time-course, seasonal deviations). Of course, also the volume flow of the wastewater is important, to calculate the mass flows of the relevant parameters. But which of the measured concentrations (or mass flows) should be taken into consideration? Is it good to select the highest value determined e.g. within a year? Or the mean? Using the maximum parameters determined will lead to "oversize" wastewater treatment processes which will cause high investment as well as high operational costs. A reasonable amount of the operational costs are caused by energy consumption. Thus, oversized treatment processes are not ecologically beneficial.

On the other hand, one of the most serious deficiencies results when the design of a treatment plant is based on average flow rates and average concentration of design-relevant wastewater constituents, with little or no recognition of peak conditions (Tchobanoglous and Burton 1991). Therefore, in Germany commonly that concentration of a parameter is used for design that is not exceeded by 85 % of all values determined within a campaign of measurements (85 percentile). However, this requires sufficient data being analyzed to yield a statistical safety of 95 % (Bever et al. 1993). Statistical analysis of flow data is given by Tchobanoglous and Burton (1991).

A method that can be used for deriving design parameters from a large amount of determined concentrations of one parameter is the method of Groche (1977).

lfd Nr. i	3i−1	x_i	Σ%	lfd Nr. i	3i−1	x_i	Σ%
1	2	4,5	1,8	26	77	15	74,8
2	5	5,5	4,8	27	80	15,5	77,7
3	8	6	7,8	28	83	16	80,6
4	11	6,5	10,7	29	86	17	83,5
5	14	8	13,6	30	89	18,5	86,4
6	17	8	16,5	31	92	24	89,3
7	20	8	19,4	32	95	25	92,2
8	23	8,5	22,3	33	98	25,5	95,1
9	26	9	25,2	34	101	41	98,1
10	29	9	28,2	35	104		
11	32	9	31,1	36	107		
12	35	9,5	34,0	37	110		
13	38	10	36,9	38	113		
14	41	10	39,8	39	116		
15	44	10,5	42,7	40	119		
16	47	11	45,6	41	122		
17	50	11	48,5	42	125		
18	53	11,5	51,6	43	128		
19	56	12	54,4	44	131		
20	59	12	57,3	45	134		
21	62	13	60,2	46	137		
22	65	13,5	63,1	47	140		
23	68	14	66,0	48	143		
24	71	14,5	68,9	49	146		
25	74	14,5	71,8	50	149		

Figure 13: An example for recording wastewater parameters x_i (BOD_5) analysed in a wastewater stream during a certain period) in a table in ascending order and deriving the part of all values that are equal to or less than the indicated value x_i following the method described by Groche (1977)

In this method, a table is created containing all analysed data of a design parameter x_i (BOD_5 in the depicted example) in ascending order (see figure 13, 3rd column). In the first column of the table in figure 13 the rank serial number i is written starting with number 1. From the rank serial number i, a term (3·i - 1) is calculated and written into the 2nd column. This term divided by a term (3·n + 1) with n being the number of all analytical data obtained within the campaign gives the part of all values, that are equal to or less than the indicated value x_i:

$$\sum\% = \frac{(3 \cdot i - 1) \cdot 100}{(3 \cdot n + 1)}$$

These values Σ% are noted in the 4th column. Finally, the data Σ% can be drawn as a function of x_i using log-probability paper (see figure 14). The dashed lines drawn in figure 14 give a statistical certainty of 95 % and are dependent on the total number of analyses performed (n). For an infinite number of analyses, this is given for the 85 percentile value (corresponding to an x_i of 17.7 mg BOD_5/l in the given example). However, as only 34 data were available in this particular example, a statistical certainty

of 95 % is not obtained with the 85 percentile. The helping line for this statistical certainty is intersected by the drawn line at an x_i of 21.5 mg BOD_5/l giving the tolerance limit for the determined 85 percentile BOD_5 in this example. The helping lines are drawn using the right-hand ordinate, the so-called probits. The probits are depending on the number n of all analytical data of the parameter of concern measured in the campaign. Table 6 gives the probits as a function of the number of all data (n).

Table 6: Probits corresponding to the number of n of all available data of one parameter taken into consideration for design of treatmant processes; Bever et al. (1993)

n	7	10	15	20	30	40	50	100	∞
probits	7.29	6.97	6.72	6.60	6.47	6.41	6.36	6.26	6.04

Another aspect of statistics in chemical analyses is the complex of accuracy, reproducibilty, and detection limits of analytical procedures. Scattering of results of multiple analyses performed with one sample reflects sources of errors caused by the experimentator's actions (taking aliquot volumes from samples e.g. by pipetting, dosing reagents, contaminations of technical devices and reagents needed for the analyses etc.) as well as by inconstancies of technical devices used during the analytical procedure (e.g. instabilities of lamps - especially when aged - or photomultipliers in photometers). These errors are of increased relevance the smaller the concentration of analytes is. For analytical experts, Funk et al. (1995) is recommended as further reading material.

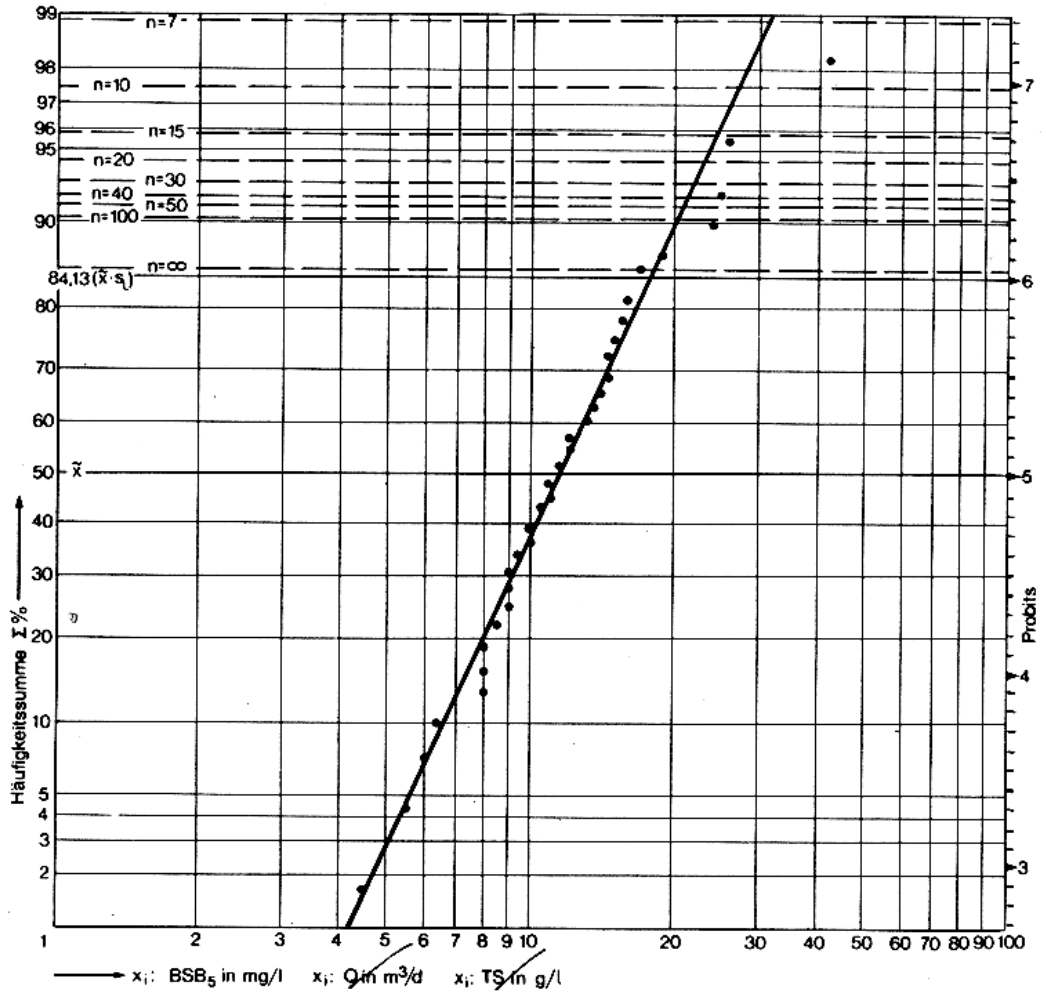


Figure 14: Example for applying the method described by Groche (1977) for deriving the 85 percentile of 34 BOD_5 analyses of a wastewater (*see figure 13*)

5. Working safety

An important issue in analytical laboratories is working safety, because many hazardous materials are used during analytical procedures. Safety aspects for laboratories are described by Hawkins (1988) while Spellman (1997) gives useful advices especially for the environmental laboratory. Moreover, in the "Standard Methods" a chapter about safety in laboratories is contained (Greenberg et al. 1985). Not only work in laboratories is health-threatening, but also sampling of wastewater (Gulyas 1999). First of all, pathogens imply an important risk during sampling. Therefore, measures have to be taken to keep minimum hygienic standards for sampling staff (water-tight gloves, protection clothes only worn in the wastewater-near environment but not in homes or during meals etc., disinfectants). Small wounds occurring during sampling have to be disinfected at once. Drinking and eating must be avoided during sampling. Moreover, sewers are risky because of the development of toxic gases like H_2S. Therefore, it is dangerous to enter sewers alone and without securing (fixing the person entering the sewer by a rope which is hold tight by a second person outside the sewer giving the possibility to remove the sampling person from the sewer in case of swooning or falling). Another important risk in sewers is the possible generation of methane gas in anaerobic zones. For detecting this gas, carrying along of methane sensors is recommended in sewers. Electrical devices used during sampling (e.g. pumps) must be secure from explosion. When corroding sample preservatives (concentrated acids or alkaline solutions) are used for sample stabilization, goggles must be available on the sampling site. Because of all these reasons, the sampling staff have be instructed concerning safety once a year. Vaccination of the sampling staff against wastewater-born diseases is advisable.

6. Controlling of process of a wastewater treatment plant

Figure 15 shows the activated sludge process for wastewater treatment. In the figure, some monitoring units, and sampling points of the process are given.
Some parameters for controlling the process of the activated sludge system are pH, dissolved oxygen concentration (DO) and acid capacity with electrodes. The pH value and acid capacity are often used for dosage of liquids to stabilise the activated sludge process. The concentration of dissolved oxygen is used to control the activity of the aeration system. If the aeration system produce more oxygen than the process needs, the operation costs increase.

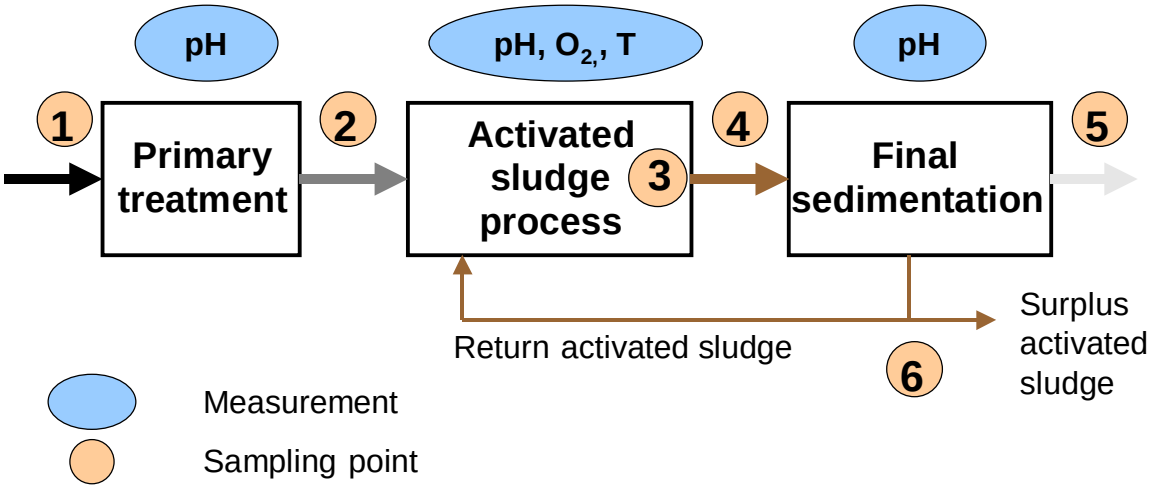


Figure 15: Flow chart of the activated sludge process

To get informations of the efficiency of the wastewater purification, taking samples at every stages of the process (influent, effluent, aeration tank, etc.) should be necessary. Parameters e.g. like ammonium, nitrate, nitrite, biochemical oxygen demand (BOD_t), chemical oxygen demand (COD), suspended solids (SS), the mixed liquor suspended solids (MLSS) and the sludge volume index (SVI) should be analysed regularly. (For further information: *http://www.atv-dvwk.de/download/betriebspers-klaeranl.pdf)*

Control measurement, monitoring and your own work

Support and control of the technical units as well as care and attention of human work are prerequiresite for the good working process. By creating a monitoring list of the maintenance of measurements could be helpful to organise the support and control e.g. of pH, oxygen and automatically working sampling units. A journal for sampling and the results of analyses will complete the monitoring.

Taking samples with human error and technical failure

The sampling points 1, 2, 4, 5 and 6 as shown in figure 15 can be piped with a bypass (by closing closed the valve) to take grab samples or can be connected with an automatically working sample taking system to take composite samples. At sampling points 3 a grab sample will be taken directly out of the aeration tank to determine the concentration of the mixed liquor suspended solids (MLSS) and the sludge volume index (SVI).

In the following you will find some hints for taking samples:

- Use a clean glass or plastic bottle for samples
- Label a bottle (e.g. point and kind of sampling, date and time, name of sample collector, parameters of analyses)
- Do not touch the inner of the bottle with your fingers (contamination)
- Through the first flush out of a pipe away and than take your sample
- Stir the sample before you fill it into the flask
- Fill the bottle up to the top. Oxygen in the flask let continue a biological process and the concentration of ammonium will decrease and the concentration of nitrate will increase
- Take care that the volume of the samples will be big enough for analyses
- Carry the sample as soon as possible to the laboratory or analyse it onsite (biological degradation still takes place!)
- Cool the sample, do not leave it in the sun
- Sample should be stirred, homogenised or filtrated before you start the analyse (depends on the kind of parameter for analyses)
- Check and clean automatically working sampling units frequently
- Control the cooling system (wrong temperature will change the ingredients
- Take care that the whole volume of the connected samples will not be bigger than the volume of the flask

7. References

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http://www.ns.ec.gc.ca/epb/issues/wstewtr.html
http://www.atv-dvwk.de/download/betriebspers-klaeranl.pdf
http://www.italocorotondo.it/tequila/module2/analysis/method_analysis.htm

Strongly recommended

http://www.chemeng.queensu.ca/courses/CHEE370/lectures/

Appendix

Determination	Container	Sample size mL	Preservation	Storage recommended/ Regulatory (1)
Acidity	P, G(B)	100	Refrigerate	24 h / 14 d
Alkalinity	P, G	200	Refrigerate	24 h / 14 d
BOD	P, G	1000	Refrigerate	6 h / 48 h
Boron	P	100	None required	28 d / 6 months
Bromide	P, G	-	None required	28 d / 28 d
Carbon, organic, total	G	100	Analyze immediately or refrigerate and add HCl to pH<2	7 d / 28 d
Carbon dioxide	P, G	100	Analyze immediately	Stat/ N.S.
COD	P, G	100	Analyze as soon as possible or add H_2SO_4 to pH<2, refrigerate	7 d / 28 d
Chlorine, residual	P, G	500	Analyze immediately	0.5 h / Stat
Chlorine dioxide	P, G	500	Analyze immediately	0.5 h / N.S.
Chlorophyll	P, G	500	30 d in dark	30 d / N.S.
Color	P, G	500	Refrigerate	48 h / 48 h
Conductivity	P, G	500	Refrigerate	28 d / 28 d
Cyanide				
Total	P, G	500	Add NaOH to pH>12, refrigerate in dark	24 h / 14 d (24 h If sulfide present
Amenable to chlorination	P, G	500	Add 100 mg $Na_2S_2O_3$/ L	Stat / 14 d (24 h If sulfide present
Fluoride	P	300	None required	28 d / 28 d
Hardness	P, G	100	Add HNO_3 to pH<2	6 months / 6months
Iodine	P, G	500	Analyze immediately	0.5 h / N.S.
Metals, general	P(A), G(A)	-	For dissolved metals filter immediately, add HNO_3 to pH<2	6 months / 6months
Chromium VI	P(A), G(A)	300	Refrigerate	24 h / 24 h
Copper by colorimetry				
Mercury	P(A), G(A)	500	Add HNO_3 to pH<2, 4ºC, refrigerate	28 d / 28 d

Nitrogen				
Ammonia	P, G	500	Analyze as soon as possible or add H_2SO_4 to pH<2, refrigerate	7 d / 28 d
Nitrate	P, G	100	Analyze as soon as possible or refrigerate	48 h / 48 h (28 d for chlorinated samples)
Nitrate + nitrite	P, G	200	Add H_2SO_4 to pH<2, refrigerate	None / 28 d
Nitrite	P, G	100	Analyze as soon as possible or refrigerate	None / 48 h
Organic Kjeldahl	P, G	300	Refrigerate, add H_2SO_4 to pH<2	7 d / 28 d
Oil	G	500	Analyze as soon as possible, refrigerate	6h / N.S.
Oil and grease	G, wide-mouth calibrated	1000	Add H_2SO_4 to pH<2, refrigerate	28 d / 28 d
Organic compounds				
Pesticides	G (S), TFE-lined cap	-	Refrigerate; 1000 mg ascorbic acid/ L if residual chlorine present	7 d / 7 d until , 40 d after extraction
Phenols	P, G	500	Refrigerate, add H_2SO_4 to pH<2	7 d / 28 d
Purgeables by purge and trap	G, TFE-lined cap	50	Refrigerate, add HCl to pH<2, 1000 mg ascorbic acid/ L if residual chlorine present	7 d / 14 d
Oxygen, dissolved:	G, BOD bottle	300		
Electrode			Analyze immediately	0.5 h / Stat.
Winkler			Titration may be delayed after acidification	8 h / 8 h
Ozone	G	1000	Analyze immediately	0.5 h / N.S.
pH	P, G	-	Analyze immediately	2 h / Stat.
Phosphate	G(A)	100	For dissolved phosphate filter immediately; refrigerate	48 h / N.S.
Salinity	G, wax seal	240	Analyze immediately or use wax seal	6 months / N.S.
Silica	P	-	Refrigerate, do not freeze	28 d / 28 d
Sludge digester gas	G, gas bottle	-	-	N.S.

Solids	P, G	-	Refrigerate	7 d / 2-7 d see cited reference
Sulfate	P, G	-	Refrigerate	28 d / 28 d
Sulfide	P, G	100	Refrigerate, add 4 drops 2N zinc acetate/100 mL, add NaOH to pH>9	28 d / 7 d
Taste	G	500	Analyze as soon as possible, refrigerate	24 h / N.S.
Temperature	P, G	-	Analyze immediately	Stat. / Stat.
Turbidity	P, G	-	Analyze same day; store in dark up to 24 h, refrigerate	24 h / 48 h

Refrigerate= storage at 4 ºC, in the dark.; P= plastic (polyethylene or equivalent); G= glass; G(A) or P(A): rinsed with 1+1 HNO_3; G(B)= glass, borosilicate; G(S)= glass rinsed with organic solvents; N.S.= not stated in cited reference; stat= no storage allowed; analyzed immediately.

(1)Environmental Protection Agency, Rules and Regulations. *Federal Register 49, No.209, October 26, 1984.* See this citation for possible regarding container and preservation requirements.