UNIVERSITY OF
MINING AND GEOLOGY
"ST. IVAN RILSKI"

MARINELA PANAYOTOVA

WATER CHEMISTRY

(LECTURE NOTES)

SOFIA, 2024

UNIVERSITY OF MINING AND GEOLOGY
"SAINT IVAN RILSKI"

MARINELA PANAYOTOVA

WATER CHEMISTRY

(LECTURE NOTES)

SOFIA, 2024

These lecture notes present basic knowledge on water structure, integral water variables, water incredients (macro-, meso- and microcomponents, dissolved gases), as well as water pollutants and their sources.

Sampling and samples handling, on site measurements and analytical methods (in brief) applicable in water chemistry analysis are revealed.

The material presented aimes at ensuring broader background for students and staff working in the fields of environment protection, water monitoring, water-treatment and use.

Author: Prof. Marinela Ivanova Panayotova, PhD

Water chemistry

University of Mining and Geology "Saint Ivan Rilski"

First Edition

Reviwer: Prof. Dr. Vladimir Hristov

ISBN: 978-954-353-479-1

Publishing House „Saint Ivan Rilski“ at UMG "Saint Ivan Rilski" Sofia, 2024

LECURE NOTES ON WATER CHEMISTRY

Compiled by Prof. M. Panayotova, Dept. of Chemistry, University of Mining and Geology (UMG), Sofia, Bulgaria

To be used only for educational purposes for the related curricula subjects at UMG.

Table of contents

1. Water - structure and properties

"Water is the material cause of all things" (Thales, 624–546 bc). Water is a unique substance that present everywhere and that is a major component of all living forms. Its nature and properties have engaged the attention of scientists and philosophers since antiquity. Water continues to intrigue scientists today. This is because water ehxibits many anomalous physical and chemical properties. Some of water's properties are very essential for life, others have great effects on the size, shape and work of living organisms, and the physical constraints within which living organisms must operate. This was acknowledged by Lawrence Henderson in 1913 in his book "The Fitness of the Environment: An Inquiry into the Biological Significance of the Properties of Matter". Since that time more has been learned about the structure and properties of water at the molecular level, mainly by using spectroscopic studies. The recent computer simulation has also played a vital role, having achieved such a level in the water study in which it can be used to interpret experiments and simulate properties that can not be directly studies by experiments. Many of water's physical properties can now be clarified, at least semiquantitatively, in molecular and structural terms.

1.1. Basic physical properties

Chosen physical properties of water are given in Table 1.1. A comparison is also shown with the organic solvents - methanol and dimethyl ether, where one and two of the hydrogen atoms are replaced by a methyl group, correspondingly. Water is a good solvent, although with volume of only 0.03 nm^3 per molecule in the liquid state at room temperature and pressure. However, it is highly cohesive due to the strong intermolecular interactions (hydrogen bonds known as H-bonds) between the oxygen and hydrogen atoms. This causes its high boiling point, high surface tension and the large amount of heat needed to vaporize it. Replacement of one or both of the hydrogens weakens these intermolecular interactions, decreasing the magnitude of these water parameters. The strong cohesive interactions in water also result in:
(a) A high viscosity, since interactions between neighbouring molecules must constantly be broken to allow a liquid to flow;
(b) A high specific heat capacity – the quantity of heat (J) absorbed per unit mass (kg) of the material when its temperature increases with one degree, units are J/(kg$_x$K) or J/(kg $_x$°C).
Partially, the water's high specific heat and heat of vaporization, compared to other liquids, results from its small size. More intermolecular interactions are contained in a given volume of water than in liquids with similar molecular mass. When the specific heat and heat of vaporization are expressed on a molar basis, methanol and water are comparable. However, the surface tension of water is still anomolously large after accounting for differences in size. Water possesses one of the highest dielectric constants of any nonmetallic liquid. It also has the unique property of expanding when it is cooled from 4 °C to its freezing point, and again when it freezes. This preserves life under the ice. The high dielectric constant and this unique expansion of water reflect the speciffic structural features of liquid water at the molecular level.

1.2. Biological relevance of water's physical properties

Water, due to its high boiling temperature, exists predominantly in its liquid form in the range of environments where life grows, although the other two phases, ice and vapour, play an important environmental role. The high heat of vaporization of water and specific heat practically determine the efficiency of processes involving heat transfer, temperature regulation, cooling, etc. in living organisms. Viscosity is the major parameter of water that controls how fast ions and molecules are transported and how rapidly they diffuse in aqueous solution. This determines a physical upper limit to the rates of many molecular level conditions, within which organisms must live and develop. These include the rates of association of substrates with enzymes, binding rates, rates of macromolecular assembly and ion channel conductance as well as the rate of diffusion biological

processes. The high surface tension of water causes two types of effects: a) below a length scale of about 1 mm surface tension forces dominate over viscous and gravitational forces, and the air–water interface behaves as an effectively impenetrable barrier. This is a major factor in the environment and life style of small insects, bacteria and other microorganisms; b) at the molecular scale (0.1–100 nm) the surface tension, together with the high dielectric constant of water, plays a key role in water's solvent properties.

Table 1.1. Selected physical properties of water

Property	Water	Methanol	Dimethyl ether
Formula	H_2O	CH_3OH	$(CH_3)_2O$
Molecular weight (g / mol)	18	32	46
Density (kg / L)	0.998	0.7914	0.713
Boiling point (K)	373	338	248
Molecular volume (nm^3)	0.0299	0.0420	0.107
Volume of fusion (nm^3)	0.0027	Negative	Negative
Liquid density maximum (K)	277	None	None
Specific heat J / (K x g) J / (K x mol)	4.18 75.2	2.53 81.0	2.37 109.0
Specific heat J / (K x g) J / (K x mol)	4.18 75.2	2.53 81.0	2.37 109.0
Heat of vaporization (kJ / g) (kJ / mol)	2.3 41.4	1.16 37.1	0.40 18.4
Surface tension (mN / m)	72.8	22.6	16.4
Viscosity (μPa x s)	1002	550	233
Dielectric constant	78.6	33.6	5.0
Dipole moment (Cm x 10^{30})[a]	6.01	5.68	4.34

Values at 293 K unless indicated; [a] In the gas phase

1.3. Molecular structure and polarity

The geometry of the water molecule is shown in Figure 1.1a. It consists of two O–H bonds of length 0.096 nm positioned at an angle of 104.58. The oxygen atom is in sp^3 hybridization state. However, due to the presence of two electron pairs, belonging only to the oxygen atom, the ideal tetrahedral angle of 109.5° is deformed. Other properties of water molecule are its size, polarity and shape. Atoms that are not bonded repel each other if they are brought close enough and their electron orbitals overlap. At bigger distances two atoms attract each other weakly due to an induced dipole-induced dipole (London dispersion) force. The combination of attractive and repulsive interactions is termed the van der Waals interaction. The point at which the repulsive and attractive forces balance is used to define the diameter of an atom, which for hydrogen and oxygen are 0.16 nm and 0.32 nm, respectively. This leads to the approximately spherical shape of water molecule. Water molecule is electrically neutral, but because the electronegativity of oxygen is much greater than that of hydrogen the electron distribution is concentrated more around the oxygen, i.e. water is electrically polarized, having a permanent dipole moment of 6×10^{-30} C x m in the gas phase. The water dipole moment is larger in liquid and ice (c.a. 8×10^{-30} C x m) because neighbouring water dipoles mutually polarize each other. The polarity of a molecule is represented by assigning a partial charge to each atom, in order to reproduce the molecule's net charge, dipole moment, and possibly higher-order electrical moments (Figure 1.1.b). The magnitude of an atom's partial charge is a measure of its polarity. For water the charge is about +0.5 on each hydrogen, and a charge of negative sign and twice this magnitude on the oxygen. For comparison, in an apolar molecule such as methane, the hydrogen partial charge is ≅0.1, and methane's dipole

moment is zero. Due to the fact that water molecule is a very polar, it posessess the ability to participate in strong electrostatic interactions with other water molecules (Figure 1.1c) to form hydrogen bonds, as well as other molecules (Figure 1.1d), and ions (Figure 1.1e). Many of liquid water's properties, such as its high heat of vaporization and high dielectric constant, its surface tension and cohesiveness can be explained with this simple molecular model. Other properties, such as the temperature dependence of the density, need a more sophisticated model that includes water's polarizability, flexibility, and quantum mechanical effects.

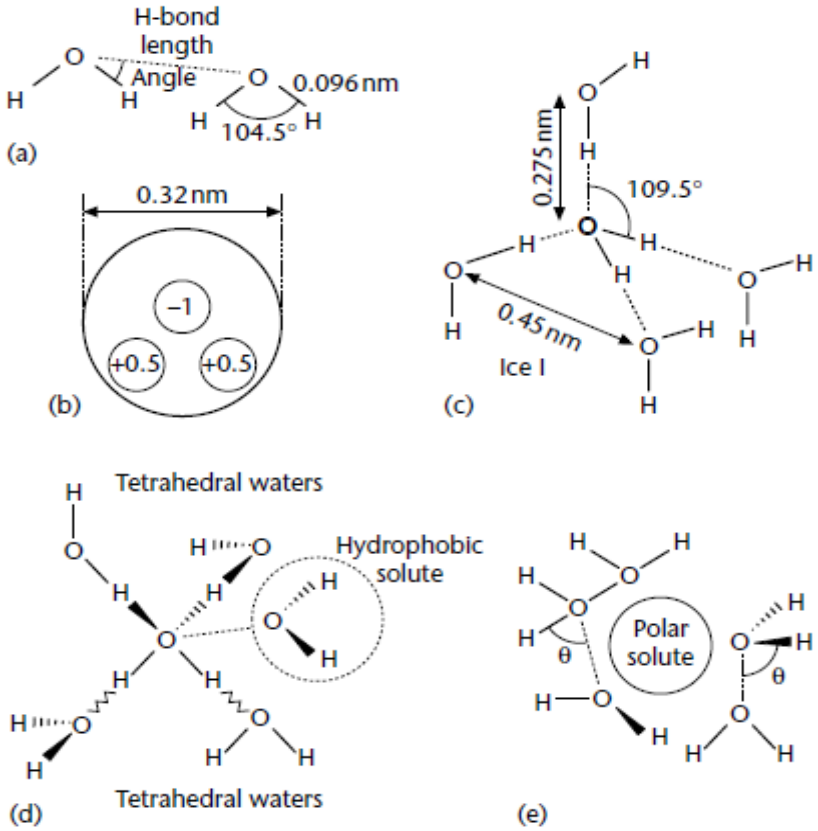

Figure 1.1. Structure of water: (a) Definition of key lengths and angles, (b) Model of water, (c) Structure of ice I, (d) Schematic of H-bonding structure in liquid water, and in presence of an apolar solute, (e) Schematic of H-bonding structure around a positively charged ion of polar atom

Solutes perturb the water structure, primarily in the solute's first hydration shell (the layer of water in contact with the solvent), with a lesser effect on more distant water molecules. Apolar solutes and groups increase the ordering of water by decreasing the less ordered population of H-bonds. These solutes interact with water primarily through the van der Waals potential. Ions and polar solutes and groups can form strong electrostatic interactions with water consequently distorting the water–water H-bond. Water dipoles tend to align towards or away from the atoms with large atomic partial charges (Figure 1.1e).

1.4. Dielectric Constant

The dielectric constant is a measure of how easily a material is polarized by an electric field relative to vacuum. It is defined by the magnitude of the dielectric polarization (dipole moment per unit volume) induced by a unit field. Water posesses nearly 80 times the dielectric constant of vacuum. It is an order of magnitude more polarizable than most organic solvents with similar molecular mass. The dielectric constant of a polar liquid such as water depends on four major factors: the density of dipoles, the permanent dipole moment of the molecule, how easily the dipoles can reorient in response to a field action, and how collaborative this reorientation is. Water

has a high dipole moment and it is small molecule. This ensures a large number of dipoles per unit volume, and in the liquid state they are easily and rapidly (within 10 ps) reoriented. Additionally, because water is H-bonded, the polarization response is collaborative: water molecules cannot reorient independently of their neighbours. They reorient in groups of about three. In addition, a small contribution to the dielectric constant of water comes from its polarizability and flexibility. All these factors explain the very high dielectric constant of water. The dielectric constant increases with decreasing the temperature because temperature decrease reduces the randomizing thermal fluctuations that oppose dipole alignment by an electrostatic field. The static dielectric constant of water increased further through the freezing point. The high dielectric constant of ice (Table 1.2) shows the importance of the cooperative effect of dipole reorientation.

Table 1.2. Selected physical properties of liquid water and ice

	Liquid (293 K)	Ice I (269 K)
Coordination number	4.7	4
Dipole moment ($Cm \times 10^{30}$)	8.0–8.7	8.7–9.4
Polarizability (nm)	0.144	0.144
Static dielectric constant	78.6	93
Ionization constant (mol / L)	1.82×10^{-16}	3.8×10^{-22}
Dissociation rate (s^{-1})	2.5×10^{-5}	3×10^{-9}
Dielectric relaxation time	9.5 ps	10 μs
Molecular reorientation time	10 ps	10 μs
Molecular translation time	20 ps	10 μs
H_3O^+ lifetime	1 ps	0.1 ps
H–bond lifetime	1 ps	–
Diffusion constant (m^2 / s)		
H_2O	2×10^{-9}	3.9×10^{-15}
H^+	9×10^{-9}	2×10^{-8}
Coordination water exchange time		
Around water	1 ps	–
Around a typical ion	1–10 ns	–

1.5. Ionization

The electron density around the hydrogen atom is very low due to the fact that the O–H bond of water is strongly polarized. This results in the fact that the O–H bond is rather weak compared with most covalent bonds. Thermal fluctuations in the liquid are sufficient to further polarize the O–H bond to the extend where the hydrogen nucleus can dissociate as a proton, or H^+ ion. Water solvates the resulting OH^- and H^+ ions, especially H^+ ion to form H_3O^+. As a consequence, dissociated water enhibits a relatively long lifetime (about 100 μs) in pure water before recombination. The spontaneous ionization of water is characterized by a dissociation constant, derived using eqn (1.1).

$$K_w = [H^+] \times [OH^-] / [H_2O]^2 \qquad (1.1)$$

where [ ] denotes activity. For pure water $[H_2O] = 1$.
The K_w value depends on the temperature and at 25 °C it is $1.0 \times 10^{-14,}$ which gives $[H^+] = [OH^-] = 1.0 \times 10^{-7}$ mol/L. In order to avoid use of so small figures the concept of pH is intrfduced as

$$pH = - \log_{10}([H^+]) = 7 \qquad (1.2)$$

The hydrogen ion is highly mobile in liquid water. It diffuses about five times more rapidly than water itself (Table 1.2). In ice, the mobility of a proton is even higher, thus demonstrating that proton transport occurs not so much by movement of a single proton, but by a hopping mechanism

between H-bonded water moleculs. According to it, a water molecule accepts a proton on one side, and releases a proton on the other side. Due to the fact that the lifetime of an individual H_3O^+ ion is ≅1 ps, about five orders of magnitude shorter than the lifetime of dissociated water, many hopping events occur before recombination. This lifetime is also shorter than the translation time of the water molecule, indicating that direct diffusion of the H_3O^+ cannot account for the high proton mobility. The ionization constant of water is orders of magnitude higher than that of most organic solvents. Water's ability to ionize easily and to solvate OH^- and H^+ ions, allows it to take part in OH^- and H^+ exchange with many polar solutes. Water can accept (solvate) H^+ from an acid or donate its H^+ to a base. Acid–base and proton exchange reactions are widespead in biology, occurring in protein binding, protein folding, enzyme catalysis, ion channel reactions, ion pumping, bioenergetic pathways, synthesis of ATP, etc. Transmission of energy or communication of a biological signal via protons is also extremely rapid due to the facile ionization of water and the high proton mobility.

1.6. Water as solvent

The logarithm of the solubility of a solute is proportional to the thermodynamic work, or hydration free energy (ΔG^{hyd}) necessary to transfer it into water from a reference solvent. High water solubility corresponds to a negative (favourable) ΔG^{hyd}, low solubility to a positive ΔG^{hyd} (work must be performed to dissolve the solute). ΔG^{hyd} is directly related to the properties of the solute, the water, and the strength of interactions between water and solvent. In this process the high surface tension and dielectric constant of water are decisive. The surface tension is the work necessary to create a unit area of water–vacuum interface (unit of energy per unit area is equivalent to unit of force per length). Work is necessary since interactions must be overcome to bring water from the interior to the surface. Hydrating a solute can be separated into two stages:

- Creation of a solute-shaped cavity in water, which requires work to be done against the surface tension of water;
- Placing the solute in the cavity, which involves interactions of the solute with water molecules and restructuring of the water.

The first step invariably opposes dissolution of any solutes. If the interactions between the solute and water are weak, as they are for apolar solutes and groups, the cavity term dominates and the solubility will be low. The cavity term pushes aggregation of apolar molecules to reduce the surface area in contact with solvent. This is known as the hydrophobic effect. In contrary, when an ionic or polar solute is dissolved in water the electric field from the solute's partial atomic charges induces a large polarization (reorientation) of the water dipoles provoking an attractive electrostatic field (the reaction field) back at the solute. This brings about a high solubility – a consequence of water's high dielectric constant. That is why water can dissolve a wide range of ionic and polar solutes.

Many biological macromolecules, such as proteins, nucleic acids and lipids, contain both hydrophilic and hydrophobic groups. Water's differential ability to solvate the different groups produces a driving force for them to adopt structures or self-assemble in ways where the hydrophilic groups are exposed to water and the hydrophobic groups are sequestered from water. This is a major factor in the folding, assembly and maintainence of precise, complex three-dimensional structures of proteins, membranes, nucleic acids and protein–nucleic acid assemblies.

The above lecture is based mainly on the following publications: Stumm and Morgan, 1996; Sharp, 2001.

2. Analytical methods applicable in water chemistry analysis - in general

Different analytical methods are used to determine the concentration of natural and anthropogenically introduced water ingredients.

In ***volumetric titration***, chemicals are analysed by titration with a standardized titrant. The titration end-point is identified by the development of colour resulting from the reaction with an indicator, by

the change of electrical potential or by the change of pH value, or by the change of conductivity of the sample.

Colorimetric methods are based on measuring the intensity of colour of a coloured target chemical or reaction product. The optical absorbance is measured using light of a suitable wavelength. The concentration is determined by means of a calibration curve obtained using known concentrations of the determinant. The Beer-Lambert law describes the relationship between concentration and absorbance.

The ultraviolet (UV) method is similar to this method except that UV light is used. Some organic compounds absorb UV light (wavelength 190–380 nm) in proportion to their concentration. ***UV absorption*** is useful for qualitative estimation of organic substances because a strong correlation may exist between UV absorption and organic carbon content.

For ionic materials, the ion concentration can be measured using an ***ion selective electrode***. The measured potential is proportional to the logarithm of the ion concentration.

Atomic absorption spectrometry (AAS) is commonly used in many analytical laboratories for determination of trace elements in water samples and in acid digests of sediment or biological tissues. Most often it is used for the determination of metals. It is based on the phenomenon that the atom in the ground state absorbs the light of wavelengths that are characteristic to each element when light is passed through the atoms in the vapour state. Because this absorption of light depends on the concentration of atoms in the vapour, the concentration of the target element in the water sample is determined from the measured absorbance. The Beer-Lambert law describes the relationship between concentration and absorbance.

In *flame atomic absorption spectrometry (FAAS)*, a sample is aspirated into a flame and atomized. A light beam from a hollow cathode lamp made of the same element as the target metal is radiated through the flame, and the amount of absorbed light is measured by the detector. This method is much more sensitive than other methods and free from spectral or radiation interference by co-existing elements. Pretreatment is either unnecessary or straightforward. However, it is not suitable for simultaneous analysis of many elements, because the light source is different for each target element.

Many metals can be determined by direct aspiration of sample into an air-acetylene flame. So called “chemical” interference occurs when the flame is not hot enough to dissociate the molecules or when the dissociated atoms are oxidised to a compound that will not dissociate further at the flame temperature. Such interferences can sometimes be overcome by adding specific elements or compounds to the sample solution. Dissociation of the molecules of silicon, aluminium, barium, beryllium and vanadium requires a hotter flame, and nitrous oxide-acetylene mixture is used. Molecular absorption and light scattering caused by solid particles in the flame can cause high absorption values and consequently positive errors. Background correction techniques can be used to obtain correct values.

The used apparatus, namely the atomic absorption spectrophotometer consists of a light source emitting the line spectrum of an element, a device for vaporising the sample, a means of isolating an absorption line and a photoelectric detector with its associated electronic amplifying and measuring equipment.

Electrothermal atomic absorption spectrometry (EAAS) is based on the same principle as FAAS, but an electrically heated atomizer or graphite furnace replaces the standard burner head for determination of metals. In comparison with FAAS, EAAS gives higher sensitivities and lower detection limits, and a smaller sample volume is required. EAAS suffers from more interference through light scattering by co-existing elements and requires a longer analysis time than FAAS.

The principle of ***inductively coupled plasma atomic emission spectrometry (ICP-AES)*** for determination of dissolved metals and non-metals is as follows: An ICP source consists of a flowing stream of argon gas ionized by an applied radio frequency. A sample aerosol is generated in a nebulizer and spray chamber and then carried into the plasma through an injector tube. A sample is heated and excited in the high-temperature plasma. The high temperature of the plasma causes the atoms to become excited. On returning to the ground state, the excited atoms produce

ionic emission spectra. A monochromator is used to separate specific wavelengths corresponding to different elements, and a detector measures the intensity of radiation of each wavelength. A significant reduction in chemical interference is achieved. In the case of water with low pollution, simultaneous or sequential analysis is possible without special pretreatment to achieve low detection limits for many elements. This, coupled with the extended dynamic range from three digits to five digits, means that multielement determination of metals can be achieved. ICP-AES has similar sensitivity to FAAS or EAAS.

In *inductively coupled plasma mass spectrometry* (ICP-MS), elements are atomized and excited as in ICP-AES, then passed to a mass spectrometer. Once inside the mass spectrometer, the ions are accelerated by high voltage and passed through a series of ion optics, an electrostatic analyser and, finally, a magnet. By varying the strength of the magnet, ions are separated according to mass/charge ratio and passed through a slit into the detector, which records only a very small atomic mass range at a given time. By varying the magnet and electrostatic analyser settings, the entire mass range can be scanned within a relatively short period of time. In the case of water with low pollution, simultaneous or sequential analysis is possible without special pretreatment to achieve low detection limits for many elements. This, coupled with the extended dynamic range from three digits to five digits, means that multielement determination of metals can be achieved. The sensitivity is higher compared to ICP-AES.

Flame photometry makes possible the determination of trace amounts of lithium, potassium, sodium and strontium, although other methods of analysis for lithium and strontium are preferred.

In this method the sample, after dilution, if necessary, is sprayed into a butane-air or propane-air flame. The alkali metals absorb energy from the flame and become raised to an excited energy state in their atomic form. As these individual atoms “cool” they fall back into their original unexcited (or ground) state and re-emit their absorbed energy by radiation of specific wavelengths, some of which are within the visible region of the electromagnetic spectrum. This discrete emission is isolated by an optical filter and, for low concentrations, is proportional to the number of atoms returning to the ground state. This, in turn, is proportional to the number of atoms excited and, hence, to the concentration of the element in the solution. The minimum detection level for both potassium and sodium is approximately 100 µg/L. The upper limit is approximately 10.0 mg/L, but this may be extended by diluting the samples. The apparatus is a flame photometer, either direct reading or internal standard type, or an atomic absorption spectrophotometer in the flame emission mode.

Chromatography is a separation method based on the different affinity of the component under determination towards two phases, the stationary and mobile phases. A sample is injected into a column, either packed or coated with the stationary phase, and separated by the mobile phase based on the difference in interaction (distribution or adsorption) between compounds and the stationary phase. Compounds with a low affinity for the stationary phase move more quickly through the column and elute earlier. The compounds that elute from the end of the column are determined by a suitable detector.

In *ion chromatography*, an ion exchanger is used as the stationary phase, and the eluant for determination of anions is typically a dilute solution of sodium hydrogen carbonate and sodium carbonate. Colorimetric, electrometric or titrimetric detectors can be used for determining individual ions. In suppressed ion chromatography, anions are converted to their highly conductive acid forms; in the carbonate–bicarbonate eluant, anions are converted to weakly conductive carbonic acid. The separated acid forms are measured by conductivity and identified on the basis of retention time as compared with their standards.

High-performance liquid chromatography (HPLC) is an analytical technique using a liquid mobile phase and a column containing a liquid stationary phase. Detection of the separated compounds is achieved through the use of absorbance detectors for organic compounds and through conductivity or electrochemical detectors for metallic and inorganic compounds.

Gas chromatography (GC) permits the identification and quantification of trace organic compounds. In GC, gas is used as the mobile phase, and the stationary phase is a liquid that is

coated either on an inert granular solid or on the walls of a capillary column. The carrier gas is nitrogen, argon-methane, helium or hydrogen. For packed columns, the stationary phase is a liquid that has been coated on an inert granular solid (the column packing) that is held in a length of borosilicate glass tubing. The column is installed in an oven with the inlet attached to a heated injector block and the outlet attached to a detector. Precise and constant temperature control of the injector block, oven and detector is maintained.
Stationary phase material and concentration, column length and diameter, oven temperature, carrier gas flow and detector type are the controlled variables.
When the sample is injected into the column, the organic compounds are vaporized and moved through the column by the carrier gas at different rates depending on differences in their partition coefficients between the mobile and stationary phases. The gas exiting the column is passed to a suitable detector. A variety of detectors can be used, including flame ionization (FID), electron capture (ECD) and nitrogen–phosphorus. As separation ability is good in this method, mixtures of substances with similar structure are systematically separated, identified and determined quantitatively in a single operation.
Some interferences occur because of sample, solvent or carrier gas contamination or because large amounts of a compound were injected into the GC and some of it lingered in the detector. Methylene chloride, chloroform and other halocarbon and hydrocarbon solvents are frequent contaminants. These solvents should not be used anywhere in the vicinity of the equipment. Another contaminant is sulphur; interference may be eliminated by adding a small amount of copper filings or mercury to samples to precipitate sulphur as metallic sulphide.
There may also be sources of interference within the equipment itself. Septum bleed occurs when silicon compounds used in the construction of the septum on the injection port “bleed” from the heated septum. This can be prevented by septum sweep - passing clean carrier gas over the septum to flush out bleed compounds. Column bleed can occur when column temperatures are high and water or oxygen is introduced into the system. Solvent injection can damage the stationary phase and some organic compounds can degrade the column coating. Injection of certain surface-active agents can completely destroy GC columns. Ghost peaks can occur because a sample that has been passed through the system contained either a large quantity of a given compound or a compound that adsorbed to the column coating. Measurements on subsequent sample(s) will show a peak resulting from the residue of the previous sample. This can be avoided by selecting a column coating that precludes such interactions or by flushing out the system with a solvent blank between samples.
As it has been already mentioned various types of detectors are available for use with GC systems. The *electrolytic conductivity detector* contains reference and analytical electrodes, a gas-liquid contactor and a gas-liquid separator. The conductivity solvent enters the cell and flows by the reference electrode. It combines with the gaseous reaction products in the gas-liquid contactor. This mixture is separated into gas and liquid phases in the gas-liquid separator with the liquid phase flowing past the analytical electrode. The electrometer monitors the difference in conductivity between the reference electrode and the analytical electrode. Only organic compounds containing halogen, nitrogen, sulphur or nitrosamine can be detected in this way.
The *electron capture detector* (ECD) is operated by passing the effluent from the gas chromatographic column over a radioactive beta-particle emitter, usually nickel-63 or tritium, adsorbed on platinum or titanium foil. An electron from the emitter ionises the carrier gas and produces a burst of electrons. About 100 secondary electrons are produced for each initial beta-particle. After further collisions the energy of these electrons is reduced to the thermal level and they can be captured by electrophilic sample molecules. The electron population is collected by applying a voltage pulse to the cell electrodes, and the pulse interval is automatically adjusted to maintain a constant current. The change in the pulse rate when a sample enters the detector is related to the concentration of contaminant in the sample. The detector is highly sensitive to molecules containing halogens, peroxides, quinones and nitro- groups but is insensitive to functional groups such as amines, alcohols and hydrocarbons.

The *flame ionisation detector* (FID) consists of a small hydrogen/air diffusion flame burning at the end of a jet. When organic compounds enter the flame from the column, electrically charged intermediates are formed. These are collected by applying a voltage across the flame; the resulting current is measured after amplification by an electrometer. The FID is sensitive to nearly all organic carbon-containing compounds but does not respond to carrier gas impurities such as water and carbon dioxide. It has a wide linear response range, is relatively insensitive to small changes in flow rate, and is reliable, rugged and easy to use. It is, however, a destructive detector that changes irreversibly the physical and chemical characteristics of the sample. Nevertheless, the FID is probably the most widely used detector for gas chromatography.
The *photoionisation detector* (PID) detects organic and some inorganic species in the effluent of a gas chromatograph, with detection limits in the picogram range. The detector is equipped with an ultraviolet light source that emits photons that pass through an optically transparent window into an ionisation chamber where they are absorbed by the eluted species. Compounds with ionisation potential less than the UV source are ionised. A positively charged high-voltage electrode accelerates the resulting ions to a collecting electrode. An electrometer measures the resulting current, which is proportional to the concentration of the eluted species. The PID has high sensitivity, low noise and excellent linearity, is non-destructive and can be used in series with a second detector for a more selective detection.
The *mass spectrophotometer* (MS) has the ability to detect a wide variety of compounds, coupled with the capacity to deduce compound structures from fragmentation patterns. It detects compounds by ionising molecules into charged species with a 7-eV beam. The next component is a mass analyser, which uses a magnetic field to separate the positively charged particles according to their mass. Several types of separating techniques exist; the most common are quadrupoles and ion traps. The ions are accelerated towards a quadrupole mass filter through a series of lenses and the differently sized charged fragments are separated according to mass-to-charge ratio. A computer control permits fragments of only one mass-to-charge ratio to pass at any one time and be detected by an electron multiplier. Most chemicals have a unique fragmentation pattern (mass spectrum), and the computer searches an internal library of known mass spectra to identify an unknown compound exhibiting a particular spectrum.
The *purge-and-trap packed column GC-MS* method or *purge-and-trap packed column GC* method is applicable to the determination of various purgeable organic compounds that are transferred from the aqueous to the vapour phase by bubbling purge gas through a water sample at ambient temperature. The vapour is trapped with a cooled trap. The trap is heated and backflushed with the same purge gas to desorb the compounds onto a GC column. The principles of GC or GC-MS are as referred to above.
The principle of ***enzyme-linked immunosorbent assay (ELISA)*** is as follows. The protein (antibody) against the chemical of interest (antigen) is coated onto the solid material. The target chemical in the water sample binds to the antibody, and a second antibody with an enzyme attached is also added that will attach to the chemical of interest. After washing to remove any of the free reagents, a chromogen is added that will give a colour reaction due to cleavage by the enzyme that is proportional to the quantity of the chemical of interest. The ELISA method can be used to determine microcystin and synthetic surfactants.
The analytical achievability for chemicals for which guideline values have been established are presented in Table 2.1.

Total, organic and inorganic carbon determination

The following definitions apply to this procedure:
• *Total carbon (TC) is* all of the carbon present as dissolved matter and/or in suspension in the water.
• *Total inorganic carbon (TIC)* is all of the carbon present as inorganic matter, dissolved and/or in suspension in the water.

Table 2.1. Analytical achievability for inorganic chemicals for which guideline values have been established, by source category

	Field methods		Laboratory methods				
	Col	Absor	IC	FAAS	EAAS	ICP	ICP-MS
Naturally occurring chemicals							
Arsenic	+++	#		++(H)	+	++(H)	+++
Barium				++	+++	+++	+++
Boron		++				+++	+++
Chromium		#			++	++	+++
Fluoride	#	+	+++				
Manganese	#			++	+++	++[b]	+++
Selenium		#		++(H)	++	++(H)	+++
Uranium							+++
Chemicals from industrial sources and human dwellings							
Cadmium		#			++	++	+++
Mercury				+++			
Chemicals from agricultural activities							
Nitrate/nitrite	+++	+++	+++				
Chemicals used in water treatment or materials in contact with drinking-water							
Antimony				+++(H)		++(H)	+++
Copper	#	+++		+++	+++	+++	+++
Lead		#			+	+	+++
Nickel		+		+	++	++	+++

+ The detection limit is between the guideline value and 1/10th of its value.
++ The detection limit is between 1/10th and 1/50th of the guideline value.
+++ The detection limit is less than 1/100th of the guideline value.
# The analytical method is available for detection of the guideline value concentration, but it is difficult to detect the concentration of 1/10 of the guideline value.
(H) This method is applicable to the determination by conversion to their hydrides by hydride generator

• *Total organic carbon (TOC)* is all of the carbon present as organic matter, dissolved and/or in suspension in the water.

Measurement of TOC is a much more rapid means of determining the organic content of water and wastewater than is the measurement of biochemical oxygen demand (BOD). In addition, two of the carbon measuring methods also provide more rapid measurement than the chemical oxygen demand (COD) test. Because of the presence of non-biodegradable organic compounds, BOD is not directly related to total organic carbon, and COD analyses may include reduced inorganic compounds. However, if the relative concentrations of organic compounds in the samples do not change greatly, empirical relationships can be established between TOC and BOD or COD to permit speedy and convenient estimations of the latter.

Measurement of TOC can be used to monitor processes for the treatment or removal of organic contaminants without undue dependence on the oxidation states, and is valid at low concentrations.

The concentration of organic carbon present in surface water is generally less than 10 mg/L, except where a high concentration of municipal or industrial waste is present. Higher levels of organic carbon may be encountered in highly coloured water, and water collected from swamps

may have organic carbon concentrations exceeding 100 mg/L. For municipal wastewater treatment plants, influent TOC concentrations may reach several hundred milligrams per litre, but effluent concentrations from a secondary treatment facility are typically less than 50 mg of organic carbon per litre.

Samples have to be collected and stored in bottles made of glass, preferably brown. Plastic containers are acceptable after tests have demonstrated the absence of extractable carbonaceous substances. Samples that cannot be examined promptly should be protected from decomposition or oxidation by preservation at 0-4 °C, minimal exposure to light and atmosphere, or acidification with sulphuric acid to a pH not greater than 2. Storage time should be kept to a minimum under any conditions. It should not exceed seven days and, depending on the type of sample, even shorter storage may be needed.

The *principle of all methods for the determination of total carbon* in water is oxidation of the carbon to carbon dioxide (CO_2). Oxidation may be carried out by combustion, chemical reaction by the wet method using appropriate oxidising agents, UV irradiation or any other appropriate procedure. The CO_2 formed may be determined directly, or indirectly following reduction to another component (methane, for example). Various analytical methods have been suggested, some of which are: IR spectrometry, volumetric determination, thermal conductivity, conductimetric measurement, coulometric measurement, use of specific CO_2 electrode, flame ionisation following methanisation.

Different techniques and types of equipment exist for the analysis of *organic carbon*. The French Standardisation Association (Association Française de Normalisation (AFNOR), Paris) proposed a selection of an appropriate analytical procedure in relation to the type of water to be analysed.

A water sample may contain variable amounts of:

• dissolved and particulate organic carbon,

• organic carbon originating from more or less volatile substances, and

• dissolved mineral carbon (carbonates, carbon dioxide) and particulate carbon (active charcoal).

The different matrices of the specimens that result from the presence of these forms of carbon in variable proportions must be taken into consideration before the analysis, because they largely determine what apparatus and procedure to select.

Selection of procedure in relation to the matrix of the sample

A. Presence of dissolved carbonates and carbon dioxide

When the carbon derived from dissolved carbonates and CO_2 is considerably in excess of the TOC, estimation by the separate measurement of total carbon and mineral carbon to arrive at the arithmetic difference may be somewhat inaccurate because of the errors connected with each measurement. Carbonates and CO_2 may be eliminated by acidification at pH 1 with H_3PO_4 followed by degassing in a stream of gas which is free of CO_2 and organic components. Thereafter, TOC is determined in the degassed sample. In this case it is important to check the efficiency of the degassing apparatus of each user (gas flow, duration of degassing and geometry of the degasser).

B. Presence of particulate mineral carbon and suspended matter

It has to be borne in mind that it is impossible to ensure total oxidation of particles by low temperature wet methods. In addition, the difficulties inherent in the sampling of heterogeneous media still persist. Suitable techniques have to be chosen.

C. Presence of volatile substances

It has to be remebered that the pretreatment by degassing modifies the initial composition of the sample by almost completely eliminating the volatile components. The presence of surfactants may interfere with degassing.

D. Presence of dissolved mineral matter

Depending on the method used, the dissolved mineral load may interfere with the operation of the apparatus (for example, the sooting of UV lamps in the photochemical technique; clogging of the catalytic mass of the furnaces in high-temperature and low-temperature oxidation procedures; precipitation of calcium salts; release of chlorine resulting from the oxidation of chlorides).

Note: Depending on the method, the carbon present in some inorganic compounds (cyanides, cyanates, thiocyanates, carbon disulphide, etc.) will be regarded as organic carbon if not taken into account.

E. Effect of the nature of the inorganic matter

The oxidation of organic matter is related to its structure, that is why the degree to which complete oxidation is achieved will depend on the method used.

Surface waters and water intended for human consumption or domestic use

The characteristics of surface waters and water intended for human consumption or domestic use are: low TOC concentrations (of the order of 0.1 to 10 mg/L), with the proportion of the carbon derived from volatile organic compounds generally being slight as compared with TOC, a content of dissolved salts that does not appreciably affect the operation of the apparatus, a concentration of mineral carbon (carbonates and bicarbonates) that is generally greatly in excess of the TOC, and small amounts of suspended matter.

For TOC concentrations greater than 2 mg/L, any of the various analytical procedures is acceptable. Precise measurement of TOC is more difficult for concentrations below 2 mg/L. Laboratory experience has shown that, of the apparatus currently available, photochemical systems are preferable for analysis of waters of the type under consideration. The contribution of carbon derived from volatile organic compounds (carbon usually less than 1000 µg/L) may be regarded as insignificant compared with measurement errors.

In methods that depend on the difference between TC and TIC, the measurement errors for TC and TIC are at least 5 per cent for waters containing about 50 mg TC per litre or about 200 mg of carbonates per litre. Consequently, the calculated value of TOC (TC - TIC) will not agree with the measured value of TOC.

Seawater or water with a high content of dissolved salts

The characteristics of these waters are: a high chloride content, a low TOC concentration, and a high TIC concentration.

The main difficulty arises from the presence of chlorides which interfere with the operation of the apparatus, either by the destruction of catalyst masses and corrosion of high-temperature furnaces, or by considerable modification of oxidation kinetics in photochemical oxidation techniques that necessitate the use of a special oxidising medium. In general, the addition of a soluble mercury salt is recommended to complex the chlorides and thus prevent their oxidation.

Wastewater and surface water with a high TOC content

The characteristics of these waters are: a high content of organic matter, a large amount of suspended matter, and more frequent presence of volatile compounds.

The main difficulty arises from suspended matter because of the heterogeneity of the medium (which makes representative sampling a difficult operation when the volume of the analytical sample is small) and mechanical incompatibility of solid particles with some parts of the apparatus (valves, etc.).

Recognising the diverse origins of organic matter, some substances, especially in suspension, may prove difficult to oxidise by chemical oxidation techniques (incomplete oxidation is often revealed by protracted peaks). It is sometimes possible to overcome this problem by modifying the oxidising medium and increasing the length of the reaction time. No clear choice of technique is possible. However, techniques employing a high temperature furnace system are usually best.

More precisely methods used for determining the different water parameters are presented in Table 2.2.

The above lecture is based mainly on the following publications: Chapman, 1996; WHO, 2022.

Table 2.2. Analytical methods for determination of major chemical variables

Variable	Gravimetric	Titrimetric	Visual	Photometric	Electrochem. probe	Flame photometry	UV-VIS and IR	Fluorimetry	AES	AAS GC	Flow injection	Stripping VA	ICP-AES	IC	LC	GC/MS
Residue	L															
Suspended matter			F	FL												
Conductivity					FL											
pH			F		FL											
Acidity, alkalinity		L														
Eh					F											
Diss. O_2		L			F											
CO_2		L			F											
Hardness		L														
Chloro-phyll a				L			L	FL								
Nutrients			F	L	FL						L			L		
Organic matter (TOC, COD, BOD)		L			FL		L									
Major cations			F		FL	L				L				L		
Major anions		L	F	L	FL									L		
Sulphide		L		L												
Silica				L												
Fluoride				L	FL											
Boron				L												
Cyanide				L							L			L		
Trace elements			F	L					L	L	L	L	L			
Mineral oil	L						L	L								
Phenols				L						L					L	L
Pesticides										L					L	L
Surfa-ctants			F	L								L				
Other organic micropollutants								L		L					L	L

F Field methods; L Laboratory methods; TOC Total organic carbon; COD Chemical oxygen demand; BOD Biochemical oxygen demand; UV-VIS Ultraviolet and visual spectrophotometry; AES Atomic emission spectrophotometry; AAS Atomic absorption spectrophotometry; GC Gas chromatography; VA Voltammetry; ICP-AES Inductively coupled plasma atomic emission spectrometry; IC Ion chromatography; LC Liquid chromatography; GC/MS Gas chromatography/mass spectrometry

3. Sampling and samples handling, on site measurements

Correct sampling is an extremely important task. Poor quality sampling can compromise any analysis performed.

Sample containers

Containers for the transportation of samples have to ensure that large enough samples are obtained for the planned analyses. Plastic containers (from highly polimerised polyethylene) or glass containers are commonly used. It is essential to have enough containers to hold the difffrent samples collected during a sampling expedition. Sample containers should be used only for water

samples and never for the storage of chemicals or other liquids. Plastic has the obvious advantage that it is less likely to break than glass. Sample containers must be scrupulously clean so that they do not contaminate the samples placed in them. Table 3.1 provides general information on appropriate types of sample containers and the recommended procedures for cleaning them when water samples are to be used for chemical analysis.

Table 3.1. Sample containers and their recommended washing procedures for selected water quality variables

Variable(s) to be analysed	Recommended container[1]	Washing procedure
Organochlorinated pesticides and PCBs Organophosphorus	1,000 mL glass (amber) with teflon-lined cap	Rinse three times with tap water, once with chromic acid[2], three times with organic-free water, twice with washing acetone, once with special grade[3] acetone, twice with pesticide grade hexane and dry (uncapped) in a hot air oven at 360 °C
Pentachlorophenol Phenolics Phenoxy acid herbicides	1,000 mL glass (amber) with teflon-lined cap	Rinse three times with tap water, once with chromic acid[2], three times with organic-free water, twice with washing acetone, once with special grade[3] acetone, twice with pesticide grade hexane and dry (uncapped) in a hot air oven at 360 °C for at least 1 h
Aluminium, Antimony, Barium, Beryllium, Cadmium, Chromium[4], Cobalt, Copper, Iron, Lead, Lithium, Manganese, Molybdenum, Nickel, Selenium, Strontium, Vanadium, Zinc	500-1,000 mL polyethylene (depending upon number of metals to be determined)	Rinse three times with tap water, once with chromic acid[2], three times with tap water, once with 1:1 nitric acid and then three times with ultrapure distilled water[5] in that order
Silver	250 mL polyethylene (amber)	Rinse three times with tap water, once with chromic acid[2], three times with tap water, once with 1:1 nitric acid and then three times with ultrapure distilled water[5] in that order
Mercury	100 mL glass (Sovirel)	Rinse three times with tap water, once with chromic acid[2], three times with tap water, once with 1:1 nitric acid and then three times with ultrapure distilled water[5] in that order
Acidity, Alkalinity, Arsenic, Calcium, Magnesium, Chloride, Colour, Fluoride, Hardness, Non-filterable residue, pH, Sodium, Potassium, Specific conductance, Sulphate, Turbidity	1,000 mL polyethylene	Rinse three times with tap water, once with chromic acid[2], three times with tap water, once with 1:1 nitric acid and then three times with distilled water in that order
Carbon, total organic Nitrogen: ammonia Nitrogen: nitrate, nitrite Nitrogen: total	250 mL polyethylene	Rinse three times with tap water, once with chromic acid[2], three times with tap water, and three times with distilled water, in that order
Phosphorus, total	50 mL glass (Sovirel)	Rinse three times with tap water, once with chromic acid[2], three times with tap water, and three times with distilled water, in that order

[1] Teflon containers can also be used to replace either the recommended polyethylene or glass containers
[2] Chromic acid - 35 mL saturated $Na_2Cr_2O_7$ per litre reagent grade conc. H_2SO_4
[3] Special grade acetone - pesticide grade when GC analysis to be performed, UV grade for LC analysis
[4] Chromic acid should not be used when the sample will be analysed for chromium
[5] Ultrapure distilled water is obtained by passing distilled water through an all-glass distillation unit and then through a filter containing an activated carbon cartridge and a mixed bed deionisation cartridge
[6] Details for sampling with the aim to determin the total, organic and inorganic carbon are described in lecture 2

To prepare sample bottles, they should be washed with a non-ionic detergent and rinsed at least three times (five is better) with distilled or deionised water. For samples for microbiologal analysis the glass sample bottles have to be autoclaved. New bottles require the same preparation. If distilled or deionised water is not available, clean chlorine-free water may be used.
For microbiological analysis bottles with a minimum capacity of 300 mL should be used. They should have screw caps of a type that will maintain an effective seal. Sometimes the bottles' caps are covered with Kraft paper before autoclaving to protect them from contamination during handling.
Some water quality variables are unstable and, unless an analysis can be carried out immediately after the sample is obtained, it is necessary to stabilize the sample by adding a chemical preservative. It is often convenient to add chemical preservatives to containers in the laboratory rather than in the field. When this is done, it is essential that the containers be clearly labeled with the name, concentration and quantity of the preservative chemical, the volume of the sample to be collected and the variables for which the sample is to be analyzed. If preservatives are not added to containers in the laboratory, the chemicals, pipettes and directions for adding preservatives must be included in the kit of supplies and equipment taken on the sampling expedition.

Sampling surface waters

Two different types of sample can be taken from rivers, lakes and similar surface waters. The simplest, a "*grab" sample*, is taken at a selected location, depth and time. Normally, the quantity of water taken is sufficient for all the physical and chemical analyses that will be done on the sample. Sometimes, if the sampler is small and many analyses are to be done, two grab samples will be taken at the station and will be mixed in the same transport container. Grab samples are also known as "spot" or "snap" samples.
Composite or integrated samples, i.e. samples made up of several different parts, are often needed to fulfil some specific monitoring objectives. Composite samples may be of the following types:
• *Depth-integrated:* most commonly made up of two or more equal parts collected at predetermined depth intervals between the surface and the bottom. A piece of flexible plastic piping of several metres in length, and which is weighted at the bottom, provides a simple mechanism for collecting and integrating a water sample from the surface to the required depth in a lake / river.
The upper end is closed before hauling up the lower (open) end by means of an attached rope. Integrated samples can also be obtained using a water pump (submersible pumps are available which allow sampling at depth) which is operated at a steady pumping rate while the water inlet is drawn upwards between the desired depths at a uniform speed.
• *Area-integrated:* made by combining a series of samples taken at various sampling points spatially distributed in the water body (but usually all at one depth or at predetermined depth intervals).
• *Time-integrated:* made by mixing equal volumes of water collected at a sampling station at regular time intervals.
• *Discharge-integrated:* It is first necessary to collect samples and to measure the rate of discharge at regular intervals over the period of interest. A common arrangement is to sample every 2 hours over a 24-hour period. The composite sample is then made by mixing portions of the individual sample that are proportional to the rate of discharge at the time the sample was taken.

Sampling groundwater

Groundwater samples are normally obtained from existing drilled wells, dug (shallow) wells or springs. Occasionally, during the course of a hydro-geological survey, test wells may be drilled and these can be used for monitoring purposes. The usual situation, however, is that a producing well or spring will be a groundwater quality monitoring station.

If the groundwater source is a flowing spring or a well equipped with a pump, the sample can be obtained at the point of discharge. The water should flow for several minutes before sampling until it has reached constant conductivity or temperature in order to avoid any water resident in the system's piping being taken as a sample (the piping material may have contaminated the water). The water should be allowed to flow into the bottle for sufficient time to displace the contents of the bottle at least three times. Samples for dissolved oxygen analysis should be taken by inserting one end of a plastic tube into the discharge pipe and the other end into a sample bottle. Care should be taken to ensure that no air bubbles are introduced to the sample while the bottle is being filled, since this could alter the dissolved oxygen concentration.

Special care must be taken when sampling from springs that do not have an overflow and from shallow wells without pumps. The sampling container must not be allowed to touch the bottom of the well or spring catchment since this would cause settled particles to become resuspended and to contaminate the sample. Sometimes, a spring catchment is higher than the surrounding ground and this permits water to be siphoned into the sample bottle. If this is done, water should be allowed to run through the hose for 2 - 3 minutes to rinse it thoroughly before the sample is collected. Siphoned samples are suitable for dissolved oxygen determination provided that the sample bottle is allowed to overflow a volume of at least three times its capacity.

The depth within an aquifer from which a sample of water is collected from a well is determined by the location of the well screen and cannot be varied by the collector, because water enters a well at the level of the screen. Similarly, water enters a spring through fissures in the rock. Consequently, a groundwater sample can only be obtained as a grab sample. The greatest danger of getting a non-representative sample occurs when insufficient water has been pumped before the sample is collected and that the sample obtained is representative of the well rather than of the aquifer.

Water samplers

Several different types of samplers are available, many of them designed for specific purposes. The three types described here are those that are most useful for a general water sampling programme.

Dissolved oxygen sampler

A dissolved oxygen sampler is a metal tube, usually about 10 cm in diameter and 30 cm in length, sealed at one end and with a removable cap (usually threaded) at the other. A bracket is located inside the tube in such a way that a 300-mL BOD bottle can be placed in the bracket with the top of the bottle 2 - 3 cm below the top of the sampler. The sampler cap has a tube extending from its underside down into the BOD bottle when the cap is in place. The upper end of this tube is open and flush with the outside face of the sampler top. A second tube in the sampler cap is flush with the inside face and extends upwards for about 8 - 10 cm. This second tube is sometimes incorporated into the frame to which the lowering rope is fastened. Figure 3.1 shows a typical dissolved oxygen sampler. When the sampler is used, a BOD bottle is placed in the bracket, the sampler cap is fitted in place, and a lowering rope is fastened to the sampler which is then lowered vertically to the depth from which the sample is to be taken. Air in the sampler flows out through the highest tube and, consequently, water enters the BOD bottle through the lower tube. The volume of the sampler is about five times the volume of the bottle, therefore the incoming water flushes out the bottle at least four times and the water that finally remains in the bottle will have had no contact with the air that was originally in the sampler. Provided that the sampler is lowered quickly to the desired sampling depth, the sample obtained should be representative, in terms of its dissolved oxygen content. If a sample needs to be taken from great depth, inflow to the sampler can be prevented with a cork or similar device that can be removed when the desired depth is reached. When the sampler is returned to the surface, the cap is removed and a ground-glass stopper is placed in the (ground-glass) neck of the BOD bottle before it is taken out of the sampler.

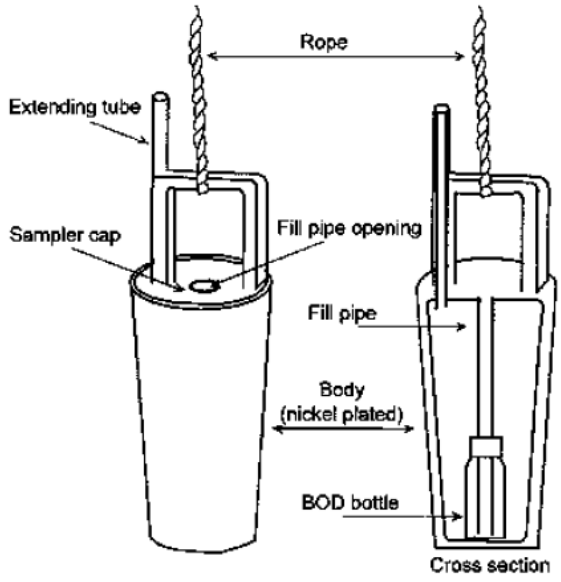

Figure 3.1 Dissolved oxygen sampler

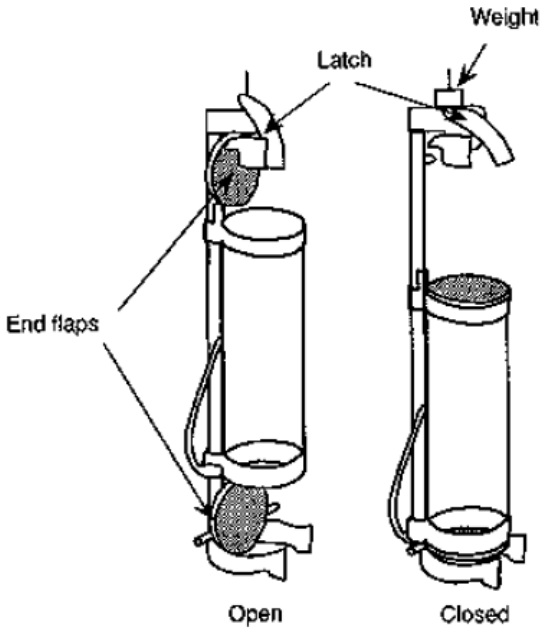

Figure 3.2 Depth sampler

Depth sampler

The depth sampler, which is sometimes called a grab sampler, is designed in such a way that it can retrieve a sample from any predetermined depth. A typical depth sampler is shown in Figure 3.2. It consists of a tube, approximately 10 cm in diameter and 30 cm in length, fastened to a frame along which it can slide. The frame has projections at each end so that the tube can not slide off. The ends of the tube are covered by spring-loaded flaps, which can be held in the fully open position by latches. The latches can be released by applying a small amount of pressure to a lever. To accomplish this, a weight (called a “messenger”) is dropped down the lowering rope, the latch is tripped and the ends of the tube close. When the sampler is in use, the end flaps are latched into the open position. As the sampler is lowered to the required depth with the lowering rope, water passes through the open ends so that, at any depth, the water in the sampler is the water from that depth. When the desired depth is reached, the messenger weight is dropped down the rope, the latch is tripped and the end flaps close. The sampler is brought to the surface and its contents are transferred to a sample bottle. A sample obtained in this way can be used for all chemical analyses except dissolved oxygen. A simpler and less expensive model of depth sampler, suitable for moderate depths (< 30 m) is illustrated in Figure 3.3.

Multi-purpose sampler

A multi-purpose sampler is most frequently used for taking samples in flowing streams or rivers. It consists of a weighted platform equipped with clamps or similar means of holding a sample bottle, a rudder to maintain its position in the flowing water, and rings at the top and bottom to which lowering ropes can be attached as shown in Figure 3.4.
One end of the rope may be attached to the top ring and a friction release device, connected between the rope and the bottom ring, holds the bottle in an inverted position during lowering. An alternative arrangement is to use two ropes, one fastened to the lower ring and one to the upper. Both arrangements permit the collection of samples from a deep location by allowing the sampler to be lowered in an inverted position and then restored to the upright position when the required depth is reached. The multi-purpose sampler is very easy to use for sampling near the surface.

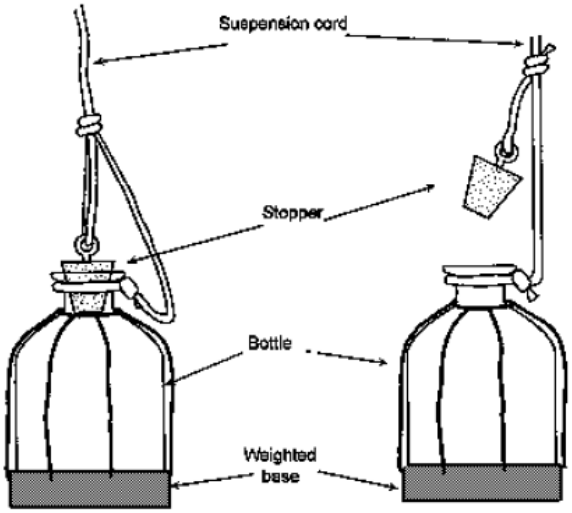

Figure 3.3 Depth sampler suitable for moderate depths

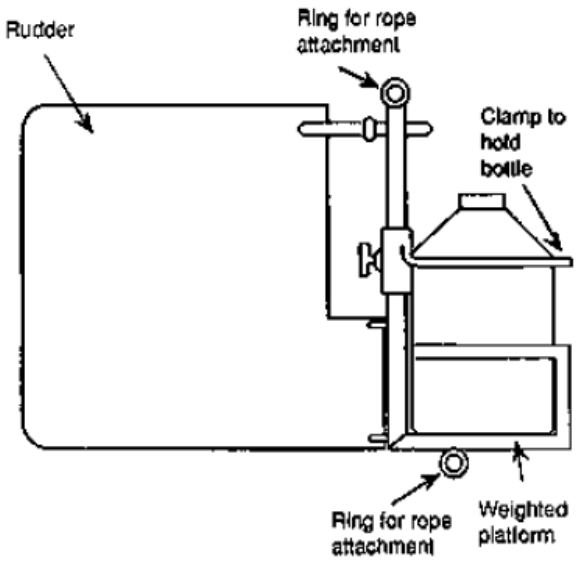

Figure 3.4 Multi-purpose sampler

It is simply immersed in the water and allowed to fill up. For samples from greater depths, it must be lowered in the inverted position and then, when the desired depth is reached, righted either by a sharp tug on the rope (for the one-rope configuration) or by transferring restraint to the rope connected to the upper ring. Although some water may enter the sampler during its descent, this type of sampler has the advantage that the sample does not need to be transferred to another container for shipment because it can remain in the container in which it was collected. Samples taken with the multi-purpose sampler cannot be used for dissolved oxygen determination.

When samples are taken for chemical and physical analysis from rivers and lakes, it is often sufficient merely to immerse an open-mouthed vessel, such as a bucket, below the water surface. The contents can then be poured into an appropriate set of sample bottles. Alternatively, the sample bottle can be immersed in the water and allowed to fill up. Care should be taken to avoid the entry of water from the surface since this will often contain very fine floating material that cannot be easily seen. If the water is flowing, the open mouth of the bottle should point upstream.

Manual sampling gudelines and procedures

Guidelines

Samples for physical and chemical analyses

The minimum sample size varies widely depending on the range of variables to be considered and the analytical methods to be employed, but it is commonly between 1 and 5 litres. The volumes required for individual analyses are summarised in Table 3.2.

The following general guidelines can be applied to the collection of water samples (to be analysed for physical or chemical variables) from rivers and streams, lakes or reservoirs and groundwater:

• Before collecting any sample, make sure that you are at the right place. This can be determined by the description of the station, from the position of landmarks and, in lakes, by checking the depth. If samples must be taken from a boat, a sampling station may be marked by placing a buoy at the desired location; otherwise, it is necessary to identify the sampling station by the intersection of lines between landmarks on the shore.

• Do not include large, non-homogeneous pieces of detritus, such as leaves, in the sample. Avoid touching and disturbing the bottom of a water body when taking a depth sample, because this will cause particles to become suspended. The upper size limit of particulate matter should be 0.063 mm. To remove larger material, pass the water sample through a sieve and collect it in a bottle for transport.

• Sampling depth is measured from the water surface to the middle of the sampler.
• Samples taken to describe the vertical profile should be taken in a sequence that starts at the surface and finishes at the bottom. When taking the sample at the maximum depth it is important to ensure that the bottom of the sampler is at least 1 m above the bottom of the water body.
• Do not lower a depth sampler too rapidly. Let it remain at the required depth for about 15 seconds before releasing the messenger (or whatever other device closes the sampler).

Table 3.2 Sample volumes usually required for individual physico-chemical analyses of some water parameters

Analysis	Sample volume (mL)	Analysis	Sample volume (mL)
Alkalinity	100	Kjeldahl nitrogen	400
Aluminium	25	Nitrate nitrogen	200
BOD	1000	Nitrite nitrogen	50
Boron	100	Phosphorus	100
Calcium	50	Potassium	100
Chloride	100	Selenium	1000
Fluoride	50	Silica	50
Iron	50	Sodium	100
Magnesium	75	Sulphate	200
Manganese	90	TOC	200
Ammonia nitrogen	400	TSS	1000

BOD Biochemical oxygen demand; TOC Total organic carbon; TSS Total suspended solids

The lowering rope should be vertical at the time of sampling. In flowing water, however, this will not be possible and the additional lowering necessary to reach the required depth should be calculated.
• A bottle that is to be used for transport or storage of the sample should be rinsed three times with portions of the sample before being filled. This does not apply, however, if the storage / transport bottle already contains a preservative chemical.
• The temperature of the sample should be measured and recorded immediately after the sample is taken.
• The sample to be used for dissolved oxygen determination should be prepared immediately after the temperature is measured. If an electronic technique is being used, a portion of the sample is carefully poured into a beaker for measurement. If the Winkler method is being used, the chemical reagents are added to the bottle in accordance with the corresponding directions.
• Separate portions of the sample should be set aside for pH and conductivity determinations. The same portion must not be used for both determinations because of the possibility of potassium chloride diffusing from the pH probe.
• At any time that the sample bottles are not closed, their tops must be kept in a clean place.
• All supporting information should be recorded in the field notebook before leaving the sampling station. Such conditions as the ambient air temperature, the weather, the presence of dead fish floating in the water or of oil slicks, growth of algae, or any unusual sights or smells should be noted, no matter how trivial they may seem at the time. These notes and observations will be of great help when interpreting analytical results.
• Samples should be transferred to sample bottles immediately after collection if they are to be transported. If analysis is to be carried out in the field, it should be started as soon as possible.

Samples for bacteriological analysis

Most of the guidelines for sampling for physical and chemical analyses apply equally to the collection of samples for bacteriological analyses. Additional considerations are:

• Samples for bacteriological analyses should be taken in a sterile sampling cup and should be obtained before samples for other analyses.

• Care must be exercised to prevent contamination of the inside of the sampling cup and sampling containers by touching with the fingers or any non-sterile tools or other objects.

• Bottles in which samples for bacteriological analyses are to be collected (or transported) should be reserved exclusively for that purpose.

Procedures

Sampling from a tap or pump outlet

The following steps have to be followed:

1. Clean the tap. Remove any attachments that may cause splashing from the tap and that are a frequent source of contamination able to influence the perceived quality of the water supply. Use a clean cloth to wipe the outlet and to remove any dirt.
2. Open the tap. Turn on the tap to maximum flow and let the water run for 1-2 minutes. Turn off the tap.

Note: Some people omit the next two steps and take the samples at this stage, in which case the tap should not be adjusted or turned off, but left to run at maximum flow.

3. Sterilize the tap for 1 minute with a flame (from a gas burner, cigarette lighter or an alcohol-soaked cotton wool swab).
4. Open the tap before sampling. Carefully turn on the tap and allow water to flow at medium rate for 1 - 2 minutes. Do not adjust the flow after it has been set.
5. Fill the bottle. Carefully remove the cap and protective cover from the bottle, taking care to prevent entry of dust that may contaminate the sample. Hold the bottle immediately under the water jet to fill it. Replace the bottle cap.

Sampling water from a water-course or reservoir

Open the sterilised bottle as described in step 5 above.

Fill the bottle (see Figure 3.5). Hold the bottle near its bottom and submerge it to a depth of about 20 cm, with the mouth facing slightly downwards. If there is a current, the bottle mouth should face towards the current. Turn the bottle upright to fill it. Replace the bottle cap.

Sampling from dug wells and similar sources

1. Prepare the bottle: With a length of string, attach a weight to the sterilised sample bottle (Figure 3.6).
2. Attach the bottle to the string: Take a 20 m length of string, rolled around a stick, and tie it to the bottle string. Open the bottle as described above.
3. Lower the bottle: Lower the weighted bottle into the well, unwinding the string slowly. Do not allow the bottle to touch the sides of the well (see Figure 3.6).
4. Fill the bottle: Immerse the bottle completely in the water and continue to lower it to some distance below the surface (see Figure 3.6). Do not allow the bottle to touch the bottom of the well or disturb any sediment.
5. Raise the bottle: Once the bottle is judged to be full, bring it up by rewinding the string around the stick. Cap the bottle.

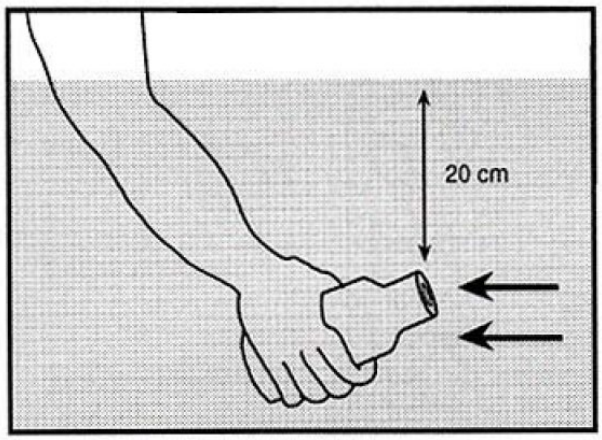

Figure 3.5 Collecting a sample from surface water

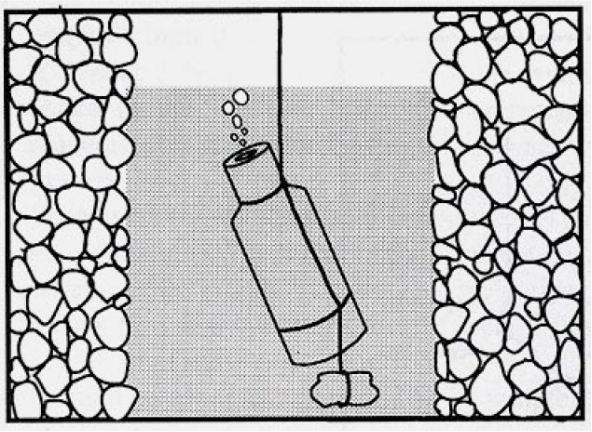

Figure 3.6 Lowering a weighted bottle into a well

Recording field observations

All relevant details have to be recorded in a field notebook at the time. Full books should not be discarded but stored for future reference because they represent data in original form and are sometimes invaluable for reference purposes.

Details recorded should include: those noted on the sample bottle, what type of samples were collected, and what measurements were made in situ, how they were made, and the results obtained (including blanks, standards, etc., and the units employed).

All supporting information (any unusual local features at the site and time of sampling) should also be noted. If there has been any variation from the agreed sampling station, this should be noted, with reasons. Any need for a permanent change in sampling station should be brought to the attention of the programme co-ordinator and the inventory should be changed if necessary.

Preservation, transportation and storage of samples

The sample collection process should be co-ordinated with the laboratory that further will make analyses. Each sample bottle must be provided with an identification label on which the following information is written:

• Name of the study.
• Sample station identification and / or number.
• Sampling depth.
• Date and time of sampling.
• Name of the individual who collected the sample.
• Brief details of weather and any unusual conditions prevailing at the time of sampling.
• Record of any stabilising preservative added.
• Results of any measurements completed in the field.

This information, as discussed earlier, will also be recorded in the field notebook.

The samples have to be preserved. Suggested preservative treatments and maximum permissible storage times are given in Table 3.3.

Sample bottles should be placed in a coller bag or box (wooden or plastic) for transport to the laboratory. They insulate samples from sunlight, prevent the breakage of sample bottles, and should allow a temperature of 4 °C to be attained and maintained during transport. Figure 3.7 shows a suitable transport bag / box. Rapid cooling of samples for BOD and / or microbiological analyses requires that the transport box should contain cold water in addition to ice or an “ice pack”. The use of a solid coolant alone is inadequate because heat transfer and sample cooling are too slow. Bottles containing samples for bacteriological analysis should ideally be placed in clear plastic bags to protect them from external contamination.

Table 3.3. Suggested preservative treatments and maximum permissible storage times

Variable	Recommended container[1]	Preservative	Max. permissible storage time
Alkalinity	Polyethylene	Cool 4 °C	24 h
Aluminium	Polyethylene	2 mL conc. HNO_3 /L sample	6 months
Arsenic	Polyethylene	Cool 4 °C	6 months
BOD	Polyethylene	Cool 4 °C	4h
Boron	Polyethylene	Cool 4 °C	6 months
Cadmium	Polyethylene	2 mL conc. HNO_3 /L sample	6 months
Calcium	Polyethylene	Cool 4 °C	7 days
Carbamate pesticides	Glass	H_2SO_4 to pH < 4, 10 g Na_2SO_4 /L	Extract immediately
Carbon - inorganic/organic	Polyethylene	Cool 4 °C	24 h
Carbon particulate	Plastic Petri dish	Filter using GF/C filter; Cool, 4 °C	6 months
Chloride	Polyethylene	Cool 4 °C	7 days
Chlorinated hydrocarbon	Glass	Cool 4 °C	Extract immediately
Chlorophyll	Plastic Petri dish	Filter on GF/C filter; freeze -20 °C	7 days
Chromium	Polyethylene	2 mL conc. HNO_3 /L sample	6 months
COD	Polyethylene	Cool 4 °C	24 h
Copper	Polyethylene	2 mL conc. HNO_3 /L sample	6 months
Dissolved oxygen (Winkler)	Glass	Fix on site	6h
Fluoride	Polyethylene	Cool 4 °C	7 days
Iron	Polyethylene	2 mL conc. HNO_3 /L sample	6 months
Lead	Polyethylene	2 mL conc. HNO_3 /L sample	6 months
Magnesium	Polyethylene	Cool 4 °C	7 days
Manganese	Polyethylene	2 mL conc. HNO_3 /L sample	6 months
Mercury	Glass or teflon	1 mL conc. H_2SO_4 + 1 ml 5% $K_2Cr_2O_7$ per L	1 month
Nickel	Polyethylene	2 mL conc. HNO_3 /L sample	6 months
Nitrogen - Ammonia	Polyethylene	2 mL conc. HNO_3 /L sample, Cool 4 °C	24 h
Nitrogen - Kjeldahl	Polyethylene	Cool 4 °C	24 h
Nitrate + Nitrite	Polyethylene	Cool 4 °C	24 h
Organic nitrogen	Polyethylene	Cool 4 °C	24 h
Organic particulates	Plastic Petri dish	Filter using GF/C filter, Cool 4 °C	6 months
Organophosphorus pesticides	Glass	Cool, 4 °C, 10% HCl to pH 4.4	Extraction on site
Pentachlorophenol	Glass	H_2SO_4 to pH < 4, 0.5 g $CuSO_4$ / L sample; Cool 4 °C	24 h
pH	Polyethylene	None	6h
Phenolics	Glass	H_3PO_4 to pH<4, 1.0 g $CuSO_4$ /L sample; 4 °C	24 h
Phenoxy acid herbicides	Glass	Cool 4 °C	Extract immediately
Phosphorus - Dissolved	Glass	Filter on site using 0.45 µm filter	24 h
Phosphorus - Inorganic	Glass	Cool 4 °C	24 h
Phosphorus - Total	Glass	Cool 4 °C	1 month
Potassium	Polyethylene	Cool, 4 °C	7 days
Residue	Polyethylene	Cool, 4 °C	7 days
Selenium	Polyethylene	1,5 mL conc. HNO_3 /L sample	6 months
Silica	Polyethylene	Cool, 4 °C	7 days
Sodium	Polyethylene	Cool, 4 °C	7 days
Electrical conductivity	Polyethylene	Cool, 4 °C	24 h
Sulphate	Polyethylene	Cool, 4 °C	7 days
Zinc	Polyethylene	2 mL conc. HNO_3 /L sample	6 months

[1] Teflon containers can also be used to replace either the polyethylene or glass containers shown in the table.

If the delay between sample collection and bacteriological analysis will be less than 2 hours, samples should simply be kept in a cool, dark place. When more than 2 hours will elapse, samples should be chilled rapidly to about 4 °C by placing them in a cold water / ice mixture in an insulated container, where they should remain during shipment. If the time between collection and analysis exceeds 6 hours, the report of the analysis should include information on the conditions and duration of sample transport.
In practice, it is difficult to ensure the transport of samples under conditions that do not affect their bacteriological quality and equipment designed for conducting analyses in the field is, therefore, becoming increasingly popular. It is also possible to filter samples in the field and to place the filters on a holding medium for later treatment in the laboratory.

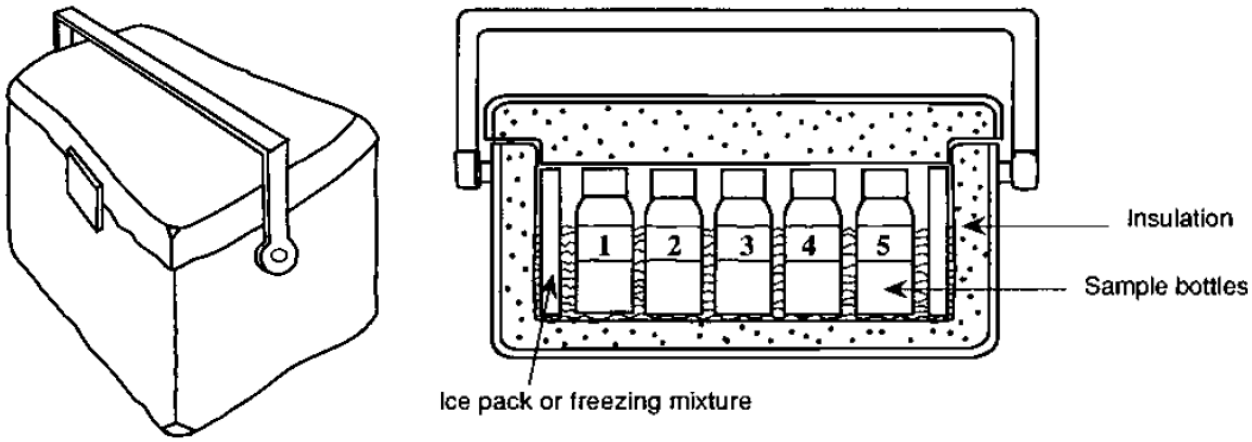

Figure 3.7 Sample transport box

On arrival at the laboratory, samples for bacteriological analysis should be placed in a refrigerator and analysis should be started within 2 hours. Any samples reaching the laboratory more than 24 hours after they were collected, or arriving unchilled more than 2 hours after they were collected, should be discarded. Such samples are unlikely to reflect the bacteriological condition of the water at the time of sampling.
Samples for chemical analysis should arrive at the analytical laboratory and be analysed within 24 hours of collection, since some variables can be changed during storage (although others, such as fluoride, chloride and sulphate, are stable for 2 - 3 weeks).

Needed physical measurements on site

Velocity

The velocity (sometimes referred to as the flow rate) of a water body can significantly affect its ability to transport and self-clean from pollutants. Thus, velocity measurement is very important. It enables the prediction of movement of pollutants within water bodies, including groundwaters. Knowledge of water velocity enables the prediction of the time of arrival downstream, of a contaminant accidentally discharged upstream.
Water velocity can vary from season to season, day to day and even within a day, depending on the nature of the catchment area and hydrometeorological influences. It is important, therefore, to record the time when measurements are taken. Every attempt should be made to measure velocity at the same sites where water samples are collected. Velocity is determined (in m/s) with current meters or tracers, such as dyes. Measurements are usually averaged over a period of 1-2 minutes.

Discharge

The discharge is the volume flowing for a given period of time. For rivers, it is usually expressed as m^3/s or m^3/a. The amount of suspended and dissolved matter in a water body depends on the discharge and is a product of the concentration and the discharge.

Natural substances arising from erosion (suspended matter) increase in concentration exponentially with increased discharge. Substances introduced artificially into a water body, such as trace elements and organic matter, tend to occur at decreasing concentrations with increasing river discharge. If a pollutant is introduced into a river at a constant rate, the concentration in the receiving water can be estimated from the quantity input divided by the river discharge. Sedimentation and resuspension can, however, affect this simple relationship.
Discharge can be estimated from the product of the velocity and the cross-sectional area of the river. It should be measured at the time of sampling and preferably at the same position as water samples are taken. As cross-sectional area varies with different discharges, a series of measurements are needed in relation to the different discharges. Measurements of depth across a transect of the water body can be used to obtain an approximate cross-sectional area. Specific methods for calculating discharge are available.

Water level

It is important to measure the water level in order to determine the hydrological regime of lakes, reservoirs and groundwaters and the interaction between groundwaters and surface waters. Measurement of water level is necessary for mass flow calculations in lakes and groundwaters and must be measured at the time and place of water sampling.
Water can flow to or from an aquifer which is in continuity with a river, depending on the relative water levels in the river and aquifer. Low water levels in the river can induce groundwater flow to the river, and high water levels can reverse the flow and produce losses from the river to the aquifer. Similarly, when groundwater levels are low (or deep) surface water infiltrates downwards to the water table. Depending on the relative water levels in the aquifer and river, areas which gain or lose water may occur in the same river. Also, a particular area may be gaining water at one time of year and losing at another, as river levels change with the seasons. Due to the fact that the river water and groundwater may be of very different qualities, significant variations in water quality may be experienced in wells close to rivers, and in the river itself. Measurement of groundwater levels is particularly important in relation to saline intrusion.

Suspended matter dynamics

Suspended particulate matter consists of material eroded from river banks or lake shores resuspended from the bed of the water body or originating from the surface of the catchment area. Measurement of suspended matter transport is very important where it is responsible for pollutant transport and in these cases its measurements should be undertaken frequently. Usually sediment concentration and load increase exponentially with discharge. Particles may also settle, or be resuspended, under different discharge conditions.
Suspended matter concentrations should be measured along with the other hydrological variables. A single sample point may be adequate in rivers of uniform cross-section. In the other cases multiple point or multiple depth, integrated sampling is necessary. Such samples should be taken at the same points where other water quality samples are taken and the water velocity is measured. In addition to analysing suspended matter, grain size should be determined. Anytime when it is possible, samples from bottom sediments should also be examined.

Selecting operational monitoring parameters

Operational monitoring assesses the performance of water control measures at appropriate time intervals. The intervals may vary widely - from online control of residual chlorine to quarterly verification of the integrity of the plinth surrounding a well.
A range of parameters can be used in operational monitoring:
• For source waters: turbidity, ultraviolet absorbency, algal growth, flow and retention time, colour, conductivity, local meteorological events and integrity of protective (e.g. fences) or abstraction (e.g. well seals) infrastructures.
• For treated water: disinfectant concentration and contact time, ultraviolet intensity, pH, light absorbency, membrane integrity, turbidity and colour.

• In piped distribution systems:
- *Chlorine residual monitoring* - it provides a rapid indication of problems that will direct measurement of microbial parameters. A sudden disappearance of an otherwise stable residual concentration can indicate ingress of contamination. Difficulties in maintaining or a gradual disappearance of residual concentration in a distribution system may indicate that the water or pipework has a high oxidant demand due to growth of bacteria.
- *Oxidation–reduction potential* (or redox potential) - it can also be used in the operational monitoring of disinfection efficacy. It is possible to define a minimum level of oxidation–reduction potential necessary to ensure effective disinfection. This value has to be determined on a case-by-case basis; universal values cannot be recommended.
- *Heterotrophic bacteria* present in a supply - they can be a useful indicator of changes, such as increased microbial growth potential, increased biofilm activity, extended retention times or stagnation and a breakdown of integrity of the system. The numbers of heterotrophic bacteria present in a supply may reflect the presence of large contact surfaces within the treatment system, such as in-line filters, and may not be a direct indicator of the condition within the distribution system.
- *Pressure measurement and turbidity* - also useful operational monitoring parameters for piped distribution systems integrity.
Some pictures of real samplic are given as isslustration in Fig 3.8

Fig 3.8. Water sampling

The above lecture is based mainly on the following publications: Bartram and Ballance, 1996; WHO, 2022; United Nations Environment Programme, 2023.

4. Integral water variables

Temperature

Water bodies experience temperature variations due to the normal climatic fluctuations. These variations occur seasonally and over periods of 24 hours. Lakes and reservoirs may also exhibit vertical stratification of temperature within the water column. The temperature of surface waters is influenced by latitude, altitude, season, time of day, cloud cover, air circulation and the flow and depth of the water body. In turn, temperature influences physical, chemical and biological processes in water bodies and, consequently, the concentration of many variables. The rate of chemical reactions generally increases with the increase in water temperature, together with the evaporation and volatilisation of substances from the water. Increased temperature also decreases the solubility of gases in water, such as O_2, CO_2, N_2, CH_4, etc. The metabolic rate of aquatic organisms is also connected to temperature, and in warm waters, respiration rates increase leading to increased oxygen consumption and increased decomposition of organic matter. Growth rates also increase (especially for bacteria and phytoplankton which double their populations in very short time periods) leading to increased water turbidity, macrophyte growth and algal blooms, when nutrient conditions are suitable.

Surface waters are usually within the temperature range 0 °C to 30 °C, although “hot springs” may reach 40 °C or more. These temperatures fluctuate seasonally with maxima in the summer or dry seasons and minima occurring during winter or wet periods, particularly in shallow waters. Abnormally high temperatures in surface water can arise from thermal discharges, usually from power plants, metal foundries and sewage treatment plants.
Ground-water usually maintains a reasonably constant temperature which, for surficial aquifers, is normally close to the mean annual air temperature. The deep aquifers possess higher temperatures due to the earth’s thermal gradient.
Temperature should be measured *in situ,* using a thermometer or thermistor. Some hand-hold devices designed to measure oxygen or conductivity can also measure temperature. As temperature has an influence on so many other aquatic variables and processes, it is important always to include it in a sampling regime, and to take and record it at the time of collecting water samples. For a detailed understanding of biological and chemical processes in water bodies it is often necessary to take a series of temperature measurements throughout the depth of the water, particularly during periods of temperature stratification in lakes and reservoirs. This can be done with a recording thermistor linked to a pressure transducer, directly reading temperature with depth, or by reversing thermometers built into a string of sampling bottles, or by direct, rapid measurements of water samples taken at discrete depths.

Colour

The colour and the turbidity of water determine the depth to which light is transmitted. This, in turn, controls the amount of primary productivity that is possible by controlling the rate of photosynthesis of the algae present. The visible colour of water is the result of the different wavelengths not absorbed by the water itself or the result of dissolved and particulate substances present. It is possible to measure both true and apparent colour in water. Natural minerals such as ferric hydroxide and organic substances such as humic acids give true colour to water. True colour can only be measured in a sample after filtration or centrifugation. Apparent colour is caused by coloured particulates and the refraction and reflection of light on suspended particulates. Polluted water may, therefore, have quite a strong apparent colour. Different species of phyto- and zooplankton can also give water an apparent colour. A dark or blue-green colour can be caused by blue-green algae, a yellow-brown colour by diatoms or dinoflagellates and red and purple - by the presence of zooplankton such as *Daphnia* sp. or copepods.

Odour

Water odour is usually the result of labile, volatile organic compounds and may be produced by phytoplankton and aquatic plants or decaying organic matter. Industrial and human wastes can also create odours, either directly or as a result of stimulating biological activity. Organic compounds, inorganic chemicals, oil and gas can all impart odour to water although an odour does not automatically indicate the presence of harmful substances.
Usually, the presence of an odour suggests higher than normal biological activity and is a simple test for the suitability of drinking water, since the human sense of smell is far more sensitive to low concentrations of substances than human taste. Warm temperatures increase the rate and production of odour-causing metabolic and decay products. Different levels of pH may also affect the rate of chemical reactions leading to the production of odour. Although odour does not provide information about specific chemicals in water, it may be considered as an indicator of water quality problems, particularly if it changes with time. Odour is recommended as a parameter in all levels of assessment because it is virtually cost-free and a good indicator of water quality problems. In basic / initial assessments, a qualitative assessment of whether or not the water is objectionable is sufficient. Odour should be tested on all water samples taken.
Experienced analysts can use odour to identify possible types of pollution (to be confirmed by quantitative analysis). Odour can be measured in terms of the greatest dilution of a sample, or the number of times a sample has to be halved with odour-free water, that yields the least definitely

perceptible odour. The former method is known as the Threshold Odour Number (TON) and the latter method as the Odour Intensity Index (OII). Both methods suffer from the subjective variability of different human judges.

Taste

Taste can originate from natural inorganic and organic chemical contaminants and biological sources or processes (e.g. aquatic microorganisms), from contamination by synthetic chemicals, from corrosion or as a result of problems with water treatment (e.g. chlorination).
There are four basic tastes of water with: salty (due to the presence of chlorides), bitter (due to the presence of magnesium ions), acidic (due to the elevated concentration of dissolved carbon dioxide) and sweet (due to the presence of dissolved organic compounds). Water with a given taste may also have a corresponding aftertaste, for example metallic, fishy.
It is inadvisable to taste water of unknown chemical and / or microbial quality. Therefore, its inclusion in basic / initial assessments as a core parameter is not recommended.
Water should be free of tastes and odours that would be objectionable to the majority of consumers. They can lead to customer dissatisfaction and complaints and may also require an additional treatment process for their removal from raw waters.
There are no WHO health-based guideline values for odour and taste but the water should not be objectionable to consumers.

Solids (total, suspended, dissolved)

The general term ‘‘solids’’ refers to matter that is suspended (insoluble solids) or dissolved (soluble solids) in water. Solids can affect water quality in several ways. Drinking water with high dissolved solids may not taste good and may have a laxative effect. Boiler water with high dissolved solids requires pretreatment to prevent scale formation. Water high in suspended solids may harm aquatic life by causing abrasion damage, clogging fish gills, harming spawning beds, and reducing photosynthesis by blocking sunlight penetration, among other consequences. On the other hand, hard water (caused mainly by dissolved calcium and magnesium compounds) reduces the toxicity of metals to aquatic life.
Total solids (sometimes called residue) are the solids remaining after evaporating the water from an unfiltered sample. It includes two subclasses of solids that are separated by filtering (generally with a filter having a nominal 0.45 mm or smaller pore size):
1. Total suspended solids (TSS, sometimes called filterable solids) in water are organic and mineral particulate matter that do not pass through a 0.45 mm filter. They are determined after drying the material retained by the filter to a constant weight at 105 °C. They may include silt, clay, metal oxides, sulfides, algae, bacteria, and fungi. TSS is generally removed by flocculation and filtering. TSS contributes to water turbidity, which limits light penetration for photosynthes and visibility in recreational waters.
2. Total dissolved solids (TDS; some times called non-filterable solids) are substances that will pass through a 0.45 mm filter. If the water passed through the filter is evaporated, the TDS will remain behind as a solid residue. TDS may include dissolved minerals and salts, humic acids, tannin, and pyrogens. TDS is removed by precipitation, ion exchange, and RO. In natural waters, the major contributors to TDS are carbonate, bicarbonate, chloride, sulfate, phosphate, and nitrate salts. Taste problems in water often arise from the presence of high TDS levels with certain metals present, particularly iron, copper, manganese, and zinc. Waters having TDS over 500 - 600 ppm can taste poor.
The difference between suspended and dissolved solids is a matter of definition based on the filtering procedure. Solids are always measured as the dry weight, and careful attention must be paid to the drying procedure to avoid errors caused by retained moisture or loss of material by volatilization or oxidation.
Samples for determining TDS and TSS should preferably be kept in hard-glass bottles until analysis can be performed, although polythene bottles can be used if the suspended material does

not stick to the walls of the bottle. To help prevent precipitation occurring in the sample bottles they should be completely filled and then analysed as soon as possible after collection. Long-term preservation of a sample is not practical. Transportation and short-term storage of a sample will not normally affect the results of the test.

Some general rules:

1. TSS is detrimental to fish health by decreasing growth, disease resistance, and egg development.
2. Suspended solids should be restricted so they do not reduce the maximum depth of photosynthetic activity by more than 10% from the seasonally established norm.
3. Water with TDS < 1200 mg/L generally has an acceptable taste. Higher TDS can adversely influence the taste of drinking water and may have a laxative effect.
4. In water to be treated for domestic potable supply, TDS < 650 mg/L is a preferred goal.
5. For (everyday) drinking water, recommended TDS is < 500 mg/L; the upper limit differes depending on the regulator body (i.e USA, EU, etc.) but it is usually 1000 mg/L.

Turbidity and transparency

The type and concentration of suspended matter controls the turbidity and transparency of the water. Turbidity results from the scattering and absorption of incifent light by the particles, and the transparency is the limit of visibility in the water. Both can vary seasonally according to biological activity in the water column and surface run-off carrying soil particles. Heavy rainfall can also result in hourly variations in turbidity. At a given river station turbidity can often be related to TSS, especially where there are large fluctuations in suspended matter. Therefore, following an appropriate calibration, turbidity is sometimes used as a continuous, indirect measurement for TSS.

Transparency is a water quality characteristic of lakes and reservoirs and can be measured quickly and easily using simple equipment. This characteristic varies with the combined effects of colour and turbidity. Some variation may also occur with light intensity and with the apparatus used.

Transparency can be measured easily in the field and is, therefore, included in many regular sampling programmes, particularly in lakes and reservoirs, to indicate the level of biological activity. It is determined by lowering a circular disc, called a Secchi disc (see also Fig. 5.1), on a calibrated rope into the water until it just disappears. The depth at which it disappears, and just reappears, is recorded as the depth of transparency.

Turbidity should be measured in the field but, if necessary, samples can be stored in the dark for not more than 24 hours. Settling during storage, and changes in pH leading to precipitation, can affect the results during storage. The most reliable method of determination uses nephelometry (light scattering by suspended particles) by means of a turbidity meter which gives values in Nephelometric Turbidity Units (NTU). Normal values range from 1 to 1000 NTU and levels can be increased by the presence of organic matter pollution, other effluents, or run-off with a high suspended matter content.

A visual method of determination is also available in Jackson Turbidity Units (JTU), which compares the length of the light path through the sample against a standard suspension mixture.

At low concentrations, TSS (in mg/L for soil erosion or μg chlorophyll/L for algae) is roughly equal to turbidity in NTU - Table 4.1.

TDS and salinity both indicate dissolved salts. Table 4.2. offers a qualitative comparison between the terms.

The results of a determination of total dissolved solids (TDS) can be used to check the accuracy of analyses when relatively complete analyses have been made on a water sample. This is accomplished by comparing the value of calculated TDS with the measured value.

The TDS concentration should be equal to the sum of the concentrations of all the ions present plus silica. Ion concentrations in mg/L of constituents required to calculate the TDS are as follows:

Calculated TDS = 0.6 (alkalinity) + Na^+ + K^+ + Ca^{2+} + Mg^{2+} + Cl^- + SO_4^{2-} + SiO_3^{2-} + (NO_3^--N) + F^-

Table 4.1. Total suspended solids concentration estimated from turbidity measurement

Turbidity (NTU)	2	5	10	20	50
Corresponding TSS due to soil sediment (mg/L)	2,2	6,3	12	24	64
Corresponding TSS due to algae (μg chlorophyll/L)	2,2	4,7	10	36	54

Table 4.2. Comparison of TDS and salinity

TDS, mg/L	1000 - 3000	3000 - 10000	10000 - 35000	< 35000
Degree of salinity	Slightly saline	Moderately saline	Very saline	Briny

The measured TDS concentration should always be equal to or somewhat larger than the calculated value, because a significant contributor may not be included in the calculation. If the measured value is less than the calculated value, all values are suspect. If the measured value is considerably higher than the calculated value, the low ion sum is suspect and selected constituents should be reanalysed.

- An analysis is acceptable if the ratio of measured - to - calculated TDS is in the range

$$1.0 < \frac{\text{measured TDS}}{\text{calculated TDS}} < 1.2$$

- If $TDS_{meas} < TDS_{calc}$, the sample should be reanalyzed.
- If $TDS_{meas} > 1.2 \times TDS_{calc}$, the sample should be reanalyzed, perhaps with a more complete set of ions.

Conductivity

Conductivity, or specific conductance, is a measure of the ability of water to conduct an electric current. It is sensitive to variations in dissolved solids, mostly mineral salts. The degree to which these dissociate into ions, the amount of electrical charge on each ion, ion mobility and the temperature of the solution all have an influence on conductivity. Conductivity is expressed as micro-Siemens per centimetre (μS/cm) and, for a given water body, is related to the concentrations of total dissolved solids and major ions (see as an example Figure 4.1). Total dissolved solids (in mg/L) may be obtained by multiplying the conductance by a factor which is commonly between 0.55 and 0.75. This factor must be determined for each water body, but remains approximately constant provided the ionic proportions of the water body remain stable. The multiplication factor is close to 0.67 for waters in which sodium and chloride dominate, and higher for waters containing high concentrations of sulphate.

The conductivity of most freshwaters ranges from 10 to 1000 μS/cm but may exceed 1000 μS/cm, especially in polluted waters, or those receiving large quantities of land run-off. In addition to being a rough indicator of mineral content when other methods cannot easily be used, conductivity can be measured to establish a pollution zone, e.g. around an effluent discharge, or the extent of influence of run-off waters. It is usually measured *in situ* with a conductivity meter, and may be continuously measured and recorded. Conductivity meter has to be calibrated (most often with solution of KCl with a suitable concentration). The dependence of the conductivity on the temperature has to be considered. Such continuous measurements are particularly useful in rivers for the management of temporal variations in TDS and major ions.

Specific conductivity is directly related to TDS and serves as a check on TDS measurements.

<u>Some general rules:</u>

1. Conductivity units are μmhos/cm or μSiemens/cm (μS/cm): 1 μmho/cm = 1 μSiemens/cm
2. TDS in mg/L can be estimated from a measurement of specific conductivity.

a. For seawater (NaCl-based):

TDS (mg/L) ≅ (0.5) x (Sp. Cond. in µS/cm)
b. For surface and ground waters (carbonate or sulfate-based):
TDS (mg/L) ≅ (0.55 to 0.7) x (Sp. Cond. in µS/cm)
3. If the ratio "$TDS_{measured}$ / Sp. Cond." is demonstrated to be consistent, the simpler specific conductivity measurement may sometimes be substituted for TDS analysis.

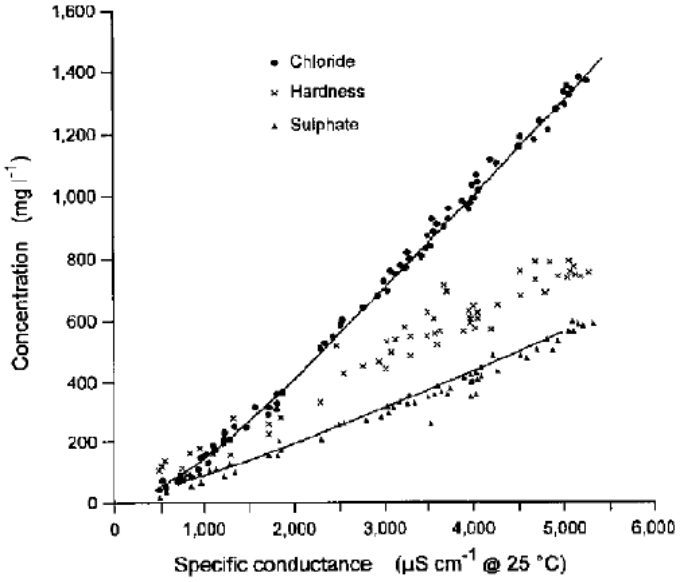

Figure 4.1 Regression plot to show the relationship of specific conductance to chloride, hardness and sulphate in the Gila River, USA

pH, acidity and alkalinity

The pH is an important variable in water quality assessment as it influences many biological and chemical processes within a water body and all processes associated with water supply and treatment. When measuring the effects of an effluent discharge, it can be used to help determine the extent of the effluent plume in the water body.
The pH is a measure of the acid balance of a solution and *is defined as the negative of the logarithm to the base 10 of the hydrogen ion concentration (more correctly - activity).*

$$pH = - \log_{10} [H^+] \text{ and similarly } pOH = - \log_{10} [OH^-]$$

In dilute solution, the hydrogen ion activity is approximately equal to the concentration of hydrogen ion. Pure water is very slightly ionized and at equilibrium the ionic product is:

$$[H^+] \times [OH^-] = K_w = 1.0 \times 10^{-14} \text{ at } 25°C$$

Or

$$[H^+] = [OH^-] = 1.005 \times 10^{-7}$$

Or

$$pH + pOH = pK_w = 14$$

The pH scale runs from 0 to 14 (i.e. very acidic to very alkaline), with pH 7 representing a neutral condition. At a given temperature, pH (or the hydrogen ion activity) indicates the intensity of the acidic or basic character of a solution and is controlled by the dissolved chemical compounds and biochemical processes in the solution. In unpolluted waters, pH is principally controlled by the balance between the carbon dioxide, carbonate and bicarbonate ions (see Figure 4.2) as well as other natural compounds such as humic and fulvic acids. The natural acid-base balance of a water body can be affected by industrial effluents and atmospheric deposition of acid-forming substances. Changes in pH can indicate the presence of certain effluents, particularly when

continuously measured and recorded, together with the conductivity of a water body. Daily variations in pH can be caused by the photosynthesis and respiration cycles of algae in eutrophic waters.

The pH of most natural waters is between 6.0 and 8.5, although lower values can occur in dilute waters with high in organic content, and higher values in eutrophic waters, groundwater brines and salt lakes.

Ideally, *pH* should be determined *in situ,* or immediately after the sample is taken, as many natural factors can influence it. Accurate measurement of pH is usually undertaken electrometrically with a glass electrode and suitable reference electrode (or more often by using a combined electrode), many of which are suitable for field use and for continuous measurement and recording. The device with the connected electrode(s) has to be calibrated before the use with buffering solutions. The dependence of the pH on the temperature has to be considered. A rough indication of pH can be obtained colorimetrically with indicator dyes. As pH is temperature dependent, the water temperature must also be measured in order to determine accurately the pH. If field measurement is not possible, samples must be transported to the laboratory in completely full, tightly stoppered bottles with no preservatives added.

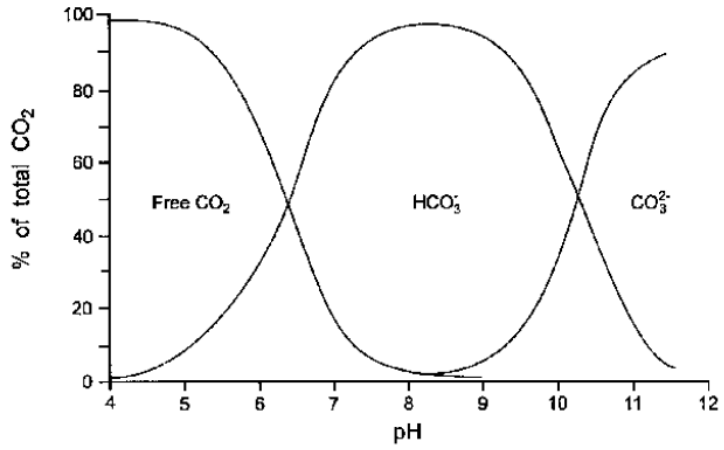

Figure 4.2. The relative proportions of different forms of inorganic carbon in relation to the pH of water under normal conditions

Acidity and alkalinity are the base- and acid-neutralising capacities of water correspondingly and are usually expressed as mmol/L. Both parameters are related to the buffering capacity of water (the ability to resist changes in pH when an acid or base is added). Water with high alkalinity can neutralize a large quantity of acid without large changes in pH. Water with high acidity can neutralize a large quantity of base without large changes in pH. When the water has no buffering capacity alkalinity and acidity are interrelated with pH. However, as most natural waters contain weak acids and bases, acidity and alkalinity are usually determined, as well as pH.

The acidity of water is controlled by the presence of strong mineral acids, weak acids such as carbonic, humic and fulvic, and hydrolising salts of metals (e.g. iron, aluminium). It is determined by titration with a strong base, up to pH 4 (free acidity, accounts for the presence of strong mineral acids, acids, such H_2SO_4, HCl and HNO_3) or to pH 8.3 (total acidity).

The alkalinity of water is controlled by the sum of the titratable bases. It is mostly taken as an indication of the concentration of carbonate, bicarbonate and hydroxide, but may include contributions from borate, phosphates, silicates and other basic compounds. Waters of low alkalinity (< 24 mmol/L as $CaCO_3$) have a low buffering capacity and can, therefore, be susceptible to alterations in pH, for example from atmospheric acidic deposition. Alkalinity is determined by titration. The amount of strong acid needed to lower the pH of a sample to 8.3 gives the free alkalinity (the amount of carbonate ion (CO_3^{2-}) present, and to pH 4.4 gives the total alkalinity.

Because alkalinity is a property caused by several constituents, a convention is used for reporting it quantitatively. The alkalinity is expressed as the ppm or mg/L of calcium carbonate ($CaCO_3$) that would produce the same alkalinity (would neutralize the same amount of acid) as measured in the the actual water sample. This is done by calculating how much $CaCO_3$ would be neutralized by the same amount of acid as was used in titrating the water sample when measuring either phenolphthalein or methyl orange alkalinity. Whether it is present or not, $CaCO_3$ is used as a proxy for all the base species that are actually present in the water. The alkalinity value is written as, for example, alkalinity =1200 mg/L as $CaCO_3$.
Water with high alkalinity generally has a high concentration of dissolved inorganic carbon - DIC (in the forms of HCO_3^- and CO_3^{2-}), which can be converted to biomass by photosynthesis. A minimum alkalinity of 20 mg/L as $CaCO_3$ is recommended for environmental waters and levels between 25 and 400 mg/L are generally beneficial for aquatic life. A range between 100 and 250 mg/L is considered normal for surface waters.
It is not unusual for alkalinity to range from 0 to 750 mg/L as $CaCO_3$. For surface waters, alkalinity levels less than 30 mg/L are considered low, and levels greater than 250 mg/L are considered high. Average values for rivers are around 100–150 mg/L. Alkalinity in environmental waters is beneficial because it minimizes pH changes. The chemical species that cause alkalinity, such as carbonate, bicarbonate, hydroxyl, and phosphate ions, can form chemical complexes with many toxic heavy metal ions, often reducing their toxicity.

Redox potential

Similarly to pH, the negative logarithm of the electron activity (p_e) is accepted as the master variable for describing the equilibrium position for all redox couples in a given system:

$$p_e = - \log [e^-]$$

It can be shown that p_e is related to oxidation - reduction potential (Eh) by

$$Eh = p_e \times (2.303 \times R \times T) / F$$

where: R - gas constant = 8.314 J/(K x mol), T - temperature, ^oK; F - Faraday constant = 96.485×10^3 C/mol
At 25°C (298°K) this simplifies to

$$Eh = p_e \times 0.05916 \quad \text{and} \quad p_e = Eh / 0.05916$$

The redox potential can be considered as a quantitative measure of electron availability and is indicative of the intensity of oxidation or reduction in both chemical and biological systems. When based on a hydrogen scale against platinum indicator electrode, the redox potential is denoted as Eh. It is derived from the Nernst equation for the oxidation / reduction pair.
The redox potential characterises the oxidation-reduction state of natural waters. Ions of the same element but different oxidation states form the redox-system which is characterised by a certain value. Organic compounds can also form redox-systems. The co-existence of a number of such systems leads to an equilibrium which determines the redox-state of the water and is, in turn, characterised by the Eh value. Oxygen, iron and sulphur, as well as some organic systems are the most influential in determining Eh. For example, Eh values increase and may reach +700 mV when dissolved oxygen concentrations increase. The presence of hydrogen sulphide is usually associated with a sharp decrease in Eh (down to -100 mV or less) and is evidence of reducing conditions. Generally, the Eh may vary in natural waters from -500 mV to +700 mV. Surface waters and groundwaters containing dissolved oxygen are usually characterised by a range of Eh values between +100 mV and +500 mV. The Eh of mineral waters connected with oil deposits is significantly lower than zero and may even reach the limit value of -500 mV.
A solution with a higher (more positive) reduction potential than the added to water new species will have a tendency to gain electrons from the new species (i.e. to be reduced by oxidizing the

new species) and a solution with a lower (more negative) reduction potential will have a tendency to lose electrons to the new species (i.e. to be oxidized by reducing the new species).
The stability of water and the range of natural redox and pH environments is presented in Fig. 4.3.
Redox potential is determined potentiometrically (with an Eh meter and a combined Eh electrode) and may be measured *in situ* in the field. The device with connected electrode has to be calibrated / checked with Eh calibration solutions. The dependence of the Eh on the temperature has to be considered. Considerable difficulty has been experienced by many workers in obtaining reliable Eh measurements. Therefore, the results and interpretation of any Eh measurements should be treated with caution. As Eh depends on the gas content of the water it can be very variable when the water is in contact with air.

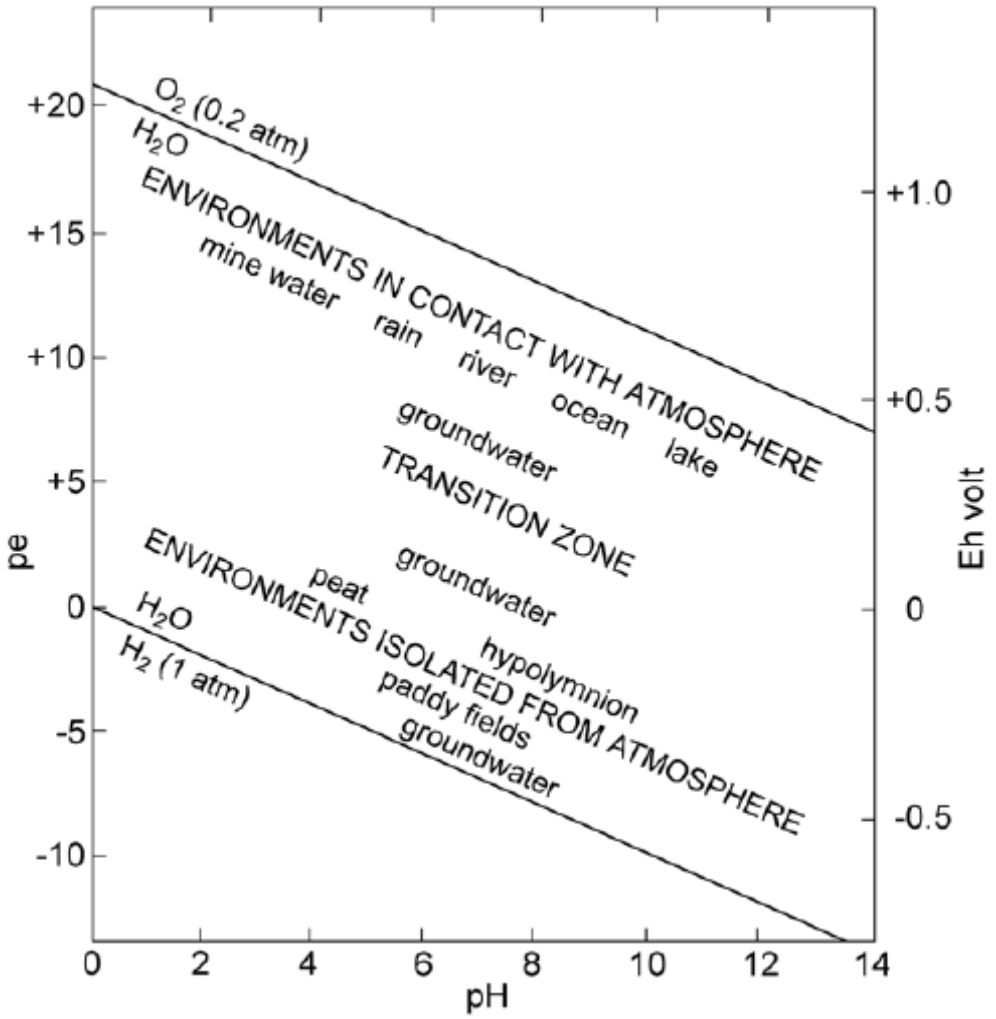

Figure. 4.3. The stability of water and the range of natural redox and pH

Therefore, determination of Eh should be made immediately after sampling. Whenever *in situ* determination is not possible, and for groundwater it is recommended that Eh is measured “in-line” in the flowing discharge of a pump.

Chlorophyll

The green pigment chlorophyll (which exists in three forms: chlorophyll *a, b* and *c*) is present in most photosynthetic organisms and provides an indirect measure of algal biomass and an indication of the trophic status of a water body. It is usually included in assessment programmes for lakes and reservoirs and is important for the management of water abstracted for drinking water supply, since excessive algal growth makes water unpalatable or more difficult to treat.

In waters with little input of sediment from the catchment, or with little re-suspension, chlorophyll can give an approximate indication of the quantity of material suspended in the water column. The growth of planktonic algae in a water body is related to the presence of nutrients (principally nitrates and phosphates), temperature and light. Therefore, concentrations of chlorophyll fluctuate seasonally and even daily, or with water depth, depending on environmental conditions. Water bodies with low levels of nutrients (e.g. oligotrophic lakes) have low levels of chlorophyll (< 2.5 µg/L) whereas waters with high nutrient contents (especially those classed as eutrophic) have high levels of chlorophyll (5-140 µg/L), although levels in excess of 300 µg/L also occur.
Chlorophyll fluoresces red when excited by blue light and this property can be used to measure chlorophyll levels and indicate algal biomass. Direct, and continuous, measurement of chlorophyll fluorescence can be made with a fluorimeter which can be used *in situ* by pumping water through it or, for some specially designed instrument, by lowering it into the water. Samples taken for chlorophyll analysis in the laboratory should be collected in polythene bottles and 0.1 to 0.2 mL of magnesium carbonate suspension should be added immediately as a preservative. Samples should also be filtered immediately although they can be stored in a cool dark place for up to 8 hours. However, once filtered through a glass fibre (GF/C grade) filter, the filter can be stored frozen for a short period prior to analysis. The chlorophyll pigments are solvent-extracted and measured spectrophotometrically. The most common determination is for chlorophyll *a,* although some methods allow for the combined measurements of chlorophylls *a, b* and *c*. The presence of chlorophyll degradation products, such as phaeophytin, can interfere with the estimate of chlorophyll concentrations in the solvent extract. This can be overcome by reading the optical density before and after acidification of the extract.

The above lecture is based mainly on the following publications: Stumm and Morgan, 1996; Chapman, 1996; Weiner, 2007; Gautam, 2011; Michael Roberts, 2023.

5. Field testing

Analyses for many important physical, chemical and microbiological variables can be carried out in the field using apparatus made specifically for field use. A significant advantage of field analysis is that tests are carried out on fresh uncontaminated samples whose characteristics have not been changed as a result of storage in a container. This is of special importance for samples that are to undergo microbiological analysis but cannot be transported to a laboratory within the time limits. Some variables must be measured in the field, either *in situ* or very soon after the sample has been collected. Field analysis is necessary for temperature, transparency, pH, Eh and alkalinity / acidity.
Dissolved gases may be determined in the field or the sample may be treated (fixed) in the field and the remainder of the analysis completed in a laboratory. If samples are to be chemically preserved before being transported to the laboratory, conductivity (if required) must be measured before preservative chemicals are added.

Temperature

Temperature must be measured *in situ* because a water sample will gradually reach the same temperature as the surrounding air. If it is not possible to measure the temperature *in situ*, a sample must be taken from the correct location and depth of the sampling station and its temperature measured immediately it is brought to the surface.
Temperature is measured with a glass thermometer, with 0.1 °C graduations, or an electronic thermometer of the type that is usually an integral part of a dissolved oxygen meter or a conductivity meter.
Procedure
The procedure to follow depends on the type of thermometer being used and on whether direct access to the point at which the temperature is to be measured is impossible (as, for example,

when the water to be tested is in a deep well or when a water sample can be taken only from a bridge). The procedure:
1. When a glass thermometer is used and the testing point can be reached, the thermometer has to be immersed in the water until the liquid column in the thermometer stops moving (approximately 1 minute, or longer if necessary). For a pumping well, the thermometer (or the probe) is immersed in a container with water flowing through until the temperature stabilises. The reading is recorded to the nearest 0.1 °C.
2. When either a glass thermometer or an electronic thermometer is used and the measurement point is inaccessible, at least 1 litre of the water sample has to be obtained. The thermometer (or the probe) is rinsed with a portion of the sample and this portion is discarded. Then the thermometer (or the probe) is immersed in the sample and hold there for approximately 1 minute (longer if the temperature reading has not become constant). The reading is recorded to the nearest 0.1 °C.
3. When an electronic thermometer having a probe with long leads is used, the probe is lowered to the required depth. It has to be hold at that depth until the reading on the meter is constant. The reading is recorded to the nearest 0.1 °C and the depth to the nearest 10 cm. The probe is lowered (or raised) to the next measurement point for the next reading.

Colour

Colour can be measured by the comparison of water samples with a series of dilutions of potassium chloroplatinate and crystalline cobaltous chloride. The units are called platinum-cobalt units based on 1 mg/L Pt. Natural waters can range from < 5 in very clear waters to 300 units in dark peaty waters.
The total absorbance colour (TAC) method measures integrated absorbance of the filtered sample (at pH 7.6) between 400 and 700 nm and the true colour (TUC) is determined by measuring the absorbance at 465 nm. One TAC unit is equivalent to the colour of 2 mg/L Pt. The TAC units range from 1 to 250. As the compounds determining the colour of the water are not very stable, measurements should be made within two hours of collection.

Transparency

The apparatus used for transparency measurement is called a Secchi disc - named after Secchi, who first used it in 1865 to measure the transparency of the Mediterranean Sea. The disc is made of rigid plastic or metal, but the details of its design are variable. It may be 20 to 30 cm in diameter (although the result is not affected by the disc diameter), or even larger in diameter and is usually painted white. Alternatively, it may be painted with black and white quadrants. The disc is suspended on a light rope or chain so that it remains horizontal when it is lowered into the water. The rope is graduated at intervals of 0.1 and 1 metre from the level of the disc itself and usually does not need to be more than 30 m in length. A weight fastened below the disc helps to keep the suspension rope vertical while a measurement is being made. Figure 5.1 shows a typical Secchi disc.
The same size and pattern of disc should be used at any given sampling station so that a series of measurements made over a number of years will be as free as possible from distortions arising from differences in apparatus. A boat has to be used to reach the measurement site. The observation should not be made early in the morning or late in the afternoon.
Procedure
1. The Secchi disc is lowered, where possible, through a shaded area of water surface (glare on the water surface can distort the observation).
2. As the disc is lowered, the depth is noted at which it just disappears from view.
3. The disc is lowered a little further, then raisen and the depth is noted at which it reappears.
The average of the two depth readings is reported as the Secchi disc transparency. The report must also state the diameter of the disc and the pattern, if any, on the upper surface of the disc.

Figure 5.1 The Secchi disc

pH

Determination of the pH of water should, if possible, be made *in situ*. If this is not possible, for example with well water or when access to a lake or river is very difficult, the measurement should be made immediately after the sample has been obtained.

There are three different methods of pH measurement: pH indicator paper, liquid colorimetric indicators and electronic meters. The use of pH indicator paper is simple and inexpensive, but the method is not very accurate and requires a subjective assessment of colour by the user.

Liquid colorimetric indicators change colour in accordance with the pH of the water with which they are mixed. The colour that develops can then be compared with a printed card, with coloured glass standards, or with a set of prepared liquid standards. Colorimetric methods are reasonably simple and accurate to about 0.2 pH units. Their main disadvantage is that standards for comparison or a comparator instrument must be transported to the sampling station. Moreover, physical or chemical characteristics of the water may interfere with the colour developed by the indicator and lead to an incorrect measurement.

The third method, electrometric pH measurement, is accurate and free from interferences. Pocketsized, battery-powered, portable meters that give readings with an accuracy of ± 0.05 pH units are suitable for field use. Larger, more sophisticated models of portable meter can attain an accuracy of ± 0.01 pH units. Care must be taken when handling such equipment. The electrodes used for measurement generally need cleaning and replacing periodically (e.g. yearly). Old or poor-quality electrodes often show a slow drift in the readings.

Useful information

1. The pH of natural unpolluted river water is generally between 6.5 and 8.5.
2. The pH of natural unpolluted groundwater is generally between 6.0 and 8.5.
3. Clean rainwater has a pH of about 5.7 because of dissolved CO_2. After reaching the surface of the earth, rainwater usually acquires alkalinity from carbonate minerals while moving over and through the earth, which may raise the pH and buffer the water against considerable pH changes.
4. The pH of drinking water supplies should be between 5.0 and 9.0.
5. Fish acclimate to ambient pH conditions. For aquatic life, pH should be between 6.5 and 9.0 and should not vary more than 0.5 units beyond the normal seasonal maximum or minimum.

Oxidation-reduction potential (ORP)

ORP measurement systems are a practical implementation of electrochemical cells, which use metal electrodes in a solution to generate an electric current or voltage.

ORP instruments must be **verified** or **calibrated**, depending on the device used. Standard laboratory practice in making ORP measurements is to **verify** the accuracy of the instrument prior to use, and this practice should be followed when true quantitative results are required. In a **verification,** the instrument is checked against a standard solution in a pass / no-pass test, and no corrections are applied to subsequent measurements. The instrument is set to absolute mV reading mode or the internal calibration offset is zeroed out. The instrument probe should then be placed in the standard solution and the reading verified to fall within +/-10 mV of the predicted reading for the standard. Instruments with single-purpose electrodes are most suitable for this approach. If the instrument fails the verification, standard solution quality should be considered and instrument maintenance performed per the manufacturer's procedures.

In most applications, the ORP information is used semi-quantitatively and for these applications, the instruments may be **calibrated** to the standard solutions. In an instrument **calibration**, the instrument probe is placed in the standard solution and the difference between the standard measurement and the known ORP value of the standard is used by the instrument to make adjustments to the subsequent measurements. The manufacturer's recommended procedure has to be followed. One minute after the calibration, the instrument should display a stable reading within +/-10 mV of the predicted reading. An instrument failing this test should be recalibrated to determine if the problem is inadequate equilibration time. In the event of continued, the instrument failure, aging or contamination of the standard solution should be considered. Subsequently the electrode should be serviced according to the manufacturer's procedures.

Common service procedures include cleaning the platinum electrode with mild abrasives or acids and refilling or replacing the reference electrode.

During the field use, each instrument has to be calibrated or verified prior to, and verified after, each day's use or deployment. Verification solutions should be managed per the manufacturer's directions regarding storage and handling. After instrument verification or calibration, the solution cannot be returned to the stock solution container, although a separate container of working solution can be maintained.

ORP measurements should be conducted in a fashion that prevents the addition or loss of any potential oxidants or reductants. Results could be compromised by exposing the sample to air or allowing H_2S to off-gas from anoxic samples. ORP measurements should be conducted in situ or by using a flow-through cell evacuated of air. Good results are commonly obtained with the use of an overtopping cell where the environmental media is pumped into the bottom of a narrow cup containing the instrument sensors. The sensors are continually flushed with fresh media as the cup is allowed to overflow. Caution should be exercised at very low flow rates where the media in the cup could potentially re-oxygenate.

ORP probes must be operated and maintained in accordance with the manufacturer's instructions. Reference electrodes in multi-parameter probes may require regular filling or replacement. Single parameter ORP electrodes may require regular filling and operation in an upright position to assure that proper salt bridge flow is maintained. Platinum electrode surfaces are easily contaminated and polishing or cleaning of the electrodes should be performed as recommended by the manufacturer.

Measurements in field logbooks should be recorded to the nearest mV. The type of reference electrode in use and its filling solution should be recorded in at least one logbook as part of the field project records.

ORP is a temperature sensitive measurement, but sometimes ORP instruments are not temperature compensated. Consequently, the media temperature should always be recorded simultaneously with the ORP measurement.

In the absence of a specified reference scale, ORP data has **no** meaning. Therefore, the reference scale used should always be specified in reporting or discussing the ORP data. ORP measurements converted to a hydrogen scale can be reported as "Eh". Data reported as the direct field measurement without correction might be described as "ORP referenced to Ag/AgCl electrode" or "$E_{Ag/AgCl}$".

Conductivity (or specific conductance)

The ability of water to conduct an electric current is known as conductivity or specific conductance and depends on the concentration of ions in solution. Conductivity is measured in Siemens per metre (1 S/m = 10 mS/cm = 0.01 mho/cm; 1 μmho/cm = 1 μSiemen/cm). The measurement should be made *in situ*, or in the field immediately after a water sample has been obtained, because conductivity changes with storage time. Conductivity is also temperature-dependent; thus, if the meter used for measuring conductivity is not equipped with automatic temperature correction, the temperature of the sample should be measured and recorded.

The apparatuses used (conductivity meters) consists of a conductivity cell containing two rigidly attached electrodes, which are connected by cables to the body of the meter. The meter contains a source of electric current (a battery in the case of portable models), a Wheatstone bridge (a device for measuring electrical resistance) and a small indicator (usually a galvanometer). Some meters are arranged to provide a reading in units of conductance (mhos, mS), while others are graduated in units of resistance (ohms). The conductivity cell forms one arm of the Wheatstone bridge. The design of the electrodes, i.e. shape, size and relative position, determines the value of the cell constant, K_c, which is usually in the range 0.1 to 2.0. A cell with a constant of 2.0 is suitable for measuring conductivities from 20 to 1000 mS/m.

Dissolved oxygen

The dissolved oxygen concentration depends on the physical, chemical and biochemical activities in the water body, and its measurement provides a good indication of water quality. Changes in dissolved oxygen concentrations can be an early indication of changing conditions in the water body.

Two main methods are available for the determination of dissolved oxygen: the Winkler method and the electrometric method using membrane electrodes. Use of the Winkler method requires the addition of three chemical reagents to the sample very soon after it is obtained. The dissolved oxygen concentration (in mg/L) is then determined by titration with sodium thiosulphate solution (after the sample acidification), which may be done in the field or up to 6 hours later in a laboratory.

The electrometric method is suitable for the field determination of dissolved oxygen and is simple to perform. It requires an electrically powered meter (oxymeter) and an appropriate electrode. The result it gives requires the application of correction factors to compensate for salinity and temperature; some meters have built in temperature compensation. The usual procedure:

1. Calibration procedure described in the manufacturer's operating instructions has to be followed exactly. Generally, electrodes are calibrated by reading against air or against a sample of known dissolved oxygen content. This "known" sample could be one for which dissolved oxygen concentration has been determined by the Winkler method or one that has been saturated with oxygen by bubbling air through it. The zero end of a calibration curve can be determined by reading against a sample containing no dissolved oxygen, prepared by adding excess sodium sulphite, Na_2SO_3, and a trace of cobalt chloride, $CoCl_2$, to the sample.
2. The electrode is rinsed in a portion of the sample which is to be analysed for dissolved oxygen.
3. Then the electrode is immersed in the water, ensuring a continuous flow of water past the membrane to obtain a steady response on the meter.
4. The meter reading and the temperature ae recorded as well as the maker and model of the meter.

Thermotolerant (faecal) coliforms

Samples for microbiological testing are very prone to changes during transport and storage and there is therefore considerable advantage in field testing for variables such as thermotolerant (faecal) coliforms.

Almost all kits for field testing for thermotolerant coliforms are based on the membrane filtration method. The instructions of the kit producer have to be observed.

Disinfection of equipment is essential for many microbiological analytical procedures, but some of the devices used for this purpose in a laboratory are unsuitable for transporting to the field. Some of the methods for disinfecting equipment in the field are:

• *Dry heat:* The flame from a gas cigarette-lighter, for example, can be used to disinfect forceps for manipulation of membrane filters. It must be a butane or propane gas lighter, not one that uses gasoline or similar liquid fuel, which would blacken the forceps.

• *Formaldehyde:* This gas is a powerful bactericide. It may be generated by the combustion of methanol (but no other alcohol) in a closed space where oxygen becomes depleted. In the field, this is a convenient way to disinfect the filtration apparatus between uses. A minimum contact time of 10 minutes is recommended.

• *Disinfecting reusables:* The two main items of reusable equipment, Petri dishes (glass or aluminium) and bottles, may be disinfected by immersion in boiling water for a few minutes, by dry heat sterilisation in an oven or by heating in a pressure cooker for at least 20 minutes.

• *Disposal of contaminated material:* Autoclaving (or pressure cooking) of contaminated material is impractical in the field. Contaminated materials such as membrane filters and pads may be burned.

Acidity and alkalinity

Acidity is determined by measuring how much standard base must be added to raise the water pH value to a specified value. Acidity is the net effect of the presence of several constituents, including dissolved CO_2, dissolved multivalent metal ions, strong mineral acids such as sulfuric, nitric, and hydrochloric acids, and weak organic acids such as acetic acid. Dissolved CO_2 is the main source of acidity in unpolluted waters. Acidity from sources other than dissolved CO_2 is not commonly encountered in unpolluted natural waters and is often an indicator of pollution.

Titrating an acidic water sample with base to pH 8.3 measures phenolphthalein acidity or total acidity. Total acidity measures the neutralizing effects of essentially all the acid species present, both strong and weak. Titrating with base to pH 4.4 measures methyl orange acidity. Methyl orange acidity primarily measures acidity due to the presence of strong mineral acids, such as sulfuric, hydrochloric, and nitric acids.

In natural waters that are not highly polluted, *alkalinity* is more commonly found than acidity. The alkalinity of water is its capacity to neutralise acid. Alkalinity is often a good indicator of the total DIC (dissolved inorganic carbon - bicarbonate and carbonate anions) present. All unpolluted natural waters can be expected to have some degree of alkalinity. Since all natural waters contain dissolved CO_2, they all will have some alkalinity contributed by carbonate species - unless acidic pollutants have consumed the alkalinity.

Alkalinity is the net effect of the presence of several constituents, but the most important are the bicarbonate, carbonate, and hydroxyl anions. Alkalinity is often taken as an indicator for the concentration of these constituents. There are other, usually minor, contributors to alkalinity, such as ammonia, phosphates, borates, silicates, and other basic substances.

Alkalinity is determined by measuring how much standard acid must be added to a given amount of water to lower the pH to a specified value. Water having a pH above 8.3 contains carbonates and possibly hydroxides in addition to bicarbonates. Titrating with acid a water sample having pH greater than 8.3 down to the end-point of pH 8.3 measures phenolphthalein alkalinity, *P*. Phenolphthalein alkalinity (free alkalinity) primarily measures the amount of carbonate ion (CO_3^{2-}) present. This fraction is contributed by the hydroxide, if present, and half of the carbonate (the pH range of 8.3 is approximately that of a dilute bicarbonate solution). The stoichiometric relationships between hydroxide, carbonate and bicarbonate are valid only in the absence of significant concentrations of other weak anions. This applies especially to the alkalinity (and acidity) of polluted waters and wastewaters.

Titrating with acid to the endpoint of pH 4.4 (pail orange color) measures methyl orange alkalinity or total alkalinity, *T*. Total alkalinity measures the neutralizing effects of essentially all the bases present. It is reported in mg/L as $CaCO_3$. The alkalinity of some waters is due only to the

bicarbonates of calcium and magnesium. The pH of such water does not exceed 8.3 and its total alkalinity is practically identical with its bicarbonate alkalinity.
Due to the fact that the alkalinity is caused by several constituents, a convention is used for reporting it quantitatively as a concentration. The usual convention is to express alkalinity as the ppm or mg/L of calcium carbonate ($CaCO_3$) that would produce the same alkalinity as measured in the sample. It is calcualted how much $CaCO_3$ would be neutralized by the same amount of acid as the amount used in titrating the water sample when measuring either phenolphthalein or methyl orange alkalinity.
Low alkalinities (below approximately 10 mg/L) are best determined by electrometric titration.
Wherever possible, the titration should be carried out on filtered water at the point of sampling. If this is not possible, the sampling bottle must be completely filled, cooled and the alkalinity determined within 24 hours. Colour, turbidity and suspended matter may interfere with the visual titration by masking the colour change of an indicator. Turbidity and suspended matter can be eliminated by filtration. The colour of the sample can be reduced by activated carbon and filtration. Free chlorine may affect the indicator colour response and should be removed by the addition of a small amount (usually one drop) of 0.1 mol/L sodium thiosulphate solution. The presence of finely divided calcium carbonate suspensions in some natural waters may cause a fading end-point and should be removed by filtration. Silicate, phosphate, borate, sulphide and other anions of weak inorganic and organic acids (e.g. humic acids) will be included in the total alkalinity estimate. They do not interfere with the titration but can influence the validity of stoichiometric relationships.
The usual procedure:
1. 100 mL of the sample are mixed with two or three drops of phenolphthalein indicator in a conical flask over a white surface. If no colour is produced, the phenolphthalein alkalinity is zero. If the sample turns pink or red, the alkalinity is determined by titrating with standard acid until the pink colour just disappears.
2. 100 mL of the sample are mixed with a few drops of methyl orange indicator. If the sample is orange without the addition of acid, the total alkalinity is zero. If the sample turns yellow, titration with standard acid is carried out until the first perceptible colour change towards orange is observed.
Calculation:
Phenolphthalein alkalinity as $CaCO_3$

$$P = (A \times M \times 100000) / V \quad mg/L$$

Total alkalinity as $CaCO_3$

$$T = (A \times B \times 100000) / V \quad mg/L$$

where *A* = volume of standard acid solution (mL) to reach the phenolphthalein end-point of pH 8.3; *B* = volume of standard acid solution (mL) to reach the end-point of methyl orange; *M* = concentration of acid (mol/L); *V* = volume of sample (mL).
Using 100 mL of sample and 0.01 mol/L standard acid solution, the numerical value of alkalinity as mg/L $CaCO_3$ is 10 times the number of millilitres of titrant consumed.

The above lecture is based mainly on the following publications: Bartram and Ballance, 1996; Weiner, 2007.

6. Dissolved gases

Oxygen

Sufficient dissolved oxygen (DO) is important for high-quality water (Table 6.1). DO is crucial for the survival of fish and most other aquatic life forms. It oxidizes many sources of objectionable tastes and odors. Oxygen becomes dissolved in surface waters by diffusion from the atmosphere and from aquatic–plant photosynthesis. On average, most oxygen dissolves into water from the atmosphere; only a little net DO is produced by aquatic–plant photosynthesis. Although water

plants produce oxygen during the day, they consume oxygen at night as an energy source. When they die and decay, dead plant matter serves as an energy source for microbes, which consume additional oxygen. The net change in DO is small during the life cycle of aquatic plants. Oxygen is essential to all forms of aquatic life, including those organisms responsible for the self-purification processes in natural waters.

The oxygen content of natural waters varies with temperature, salinity, turbulence, the photosynthetic activity of algae and plants, and atmospheric pressure. The solubility of oxygen decreases as temperature and salinity increase. Saturation concentration of O_2 in water at sea level is 14.7 mg/L (ppm) at 0 ^oC; 8.3 mg/L (ppm) at 25 ^oC; 7.0 mg/L (ppm) at 35 ^oC. Concentrations in unpolluted waters are usually close to, but less than, 10 mg/L. Variations in DO can occur seasonally, or even over 24-hour periods, in relation to temperature and biological activity (i.e. photosynthesis and respiration).

Dissolved oxygen is consumed by the degradation (oxidation) of organic matter in water. Because the concentration of DO is never very large, oxygen-depleting processes can rapidly reduce it to near zero in the absence of efficient aeration mechanisms. Concentrations below 5 mg/L may adversely affect the functioning and survival of biological communities and below 2 mg/L may lead to the death of most aquatic life. Fish need at least 5–6 ppm DO to grow and thrive. They stop feeding if the level drops to around 3–4 ppm and die if DO falls to 1 ppm. Many fish kills are not caused by the direct toxicity of contaminants but instead by a deficiency of oxygen caused by the biodegradation of organic contaminants.

Typical aquatic life standards for DO are:

. 7.0 ppm for cold water spawning periods

. 6.0 ppm for cold water biota

. 5.0 ppm for warm water biota

Table 6.1. Dissolved oxygen and water quality

Dissolved O_2, mg/L	above 8.0	6.5 - 8.0	4.5 - 6.5	4.0 - 4.5	below 4.0
Qater quality	Good	Slightly polluted	Moderately polluted	Heavily polluted	Severely polluted

Dissolved oxygen can also be expressed in terms of percentage saturation (eq. 6.1) , and levels less than 80 per cent saturation in drinking water can usually be linked with detected by consumers poor odour and taste.

$$O_2 \text{ saturation, } \% = [O_{2,\,meas.}] \times 100 / [O_{2,.equil.}] \qquad (6.1)$$

where$O_{2,.meas.}$ is the experimentally determinedconcentration, $O_{2,.equil.}$ is the equilibrium concentration of dissolved O_2 at the temperature of the measurement.

Wastewater discharges high in organic matter and nutrients can lead to decreases in DO concentrations as a result of the increased microbial activity (respiration) occurring during the degradation of the organic matter. In severe cases of reduced oxygen concentrations (whether natural or man-made), anaerobic conditions can occur (i.e. 0 mg/L of oxygen), particularly close to the sediment-water interface as a result of decaying, sedimenting material.

Determination of DO concentrations is a fundamental part of a water quality assessment since oxygen is involved in, or influences, nearly all chemical and biological processes within water bodies. The measurement of DO can be used to indicate the degree of pollution by organic matter, the destruction of organic substances and the level of self-purification of the water. Its determination is also used in the measurement of biochemical oxygen demand (BOD).

Dissolved oxygen is of much more limited use as an indicator of pollution in groundwater, and is not useful for evaluating the use of groundwater for normal purposes. In addition, the determination of DO in groundwater requires special equipment and it has not, therefore, been widely carried out. Nevertheless, measurement of DO is critical to the scientific understanding of the potential for

chemical and biochemical processes in groundwater. Water that enters groundwater systems as recharge can be expected to contain oxygen at concentrations similar to those of surface water in contact with the atmosphere. Organic matter or oxidisable minerals present in some aquifers rapidly deplete the dissolved oxygen. Therefore, in aquifers where organic materials are less plentiful, groundwater containing measurable concentrations of DO (2-5 mg/L) can be found.
There are two principal methods for determination of dissolved oxygen. The older, titration method (often called the *Winkler method*) involves the chemical fixation of the oxygen in a water sample collected in an air-tight bottle. Fixation is carried out in the field and the analysis, by titration, can be carried out in the laboratory. The method is time-consuming but can give a high degree of precision and accuracy. It is suitable for most kinds of water and enables samples to be taken and stored.
The alternative O_2 determining method is the use of membrane electrode, or oxygen probe. The method is quick and can be used *in situ* or for continuous monitoring, although a high degree of accuracy may be difficult to achieve.
Electrochemical DO electrodes are composed of anode and cathode, which are submerged in electrolyte solution and enclosed in a cap fitted with hydrophobic, gas permeable membrane. They are also integrated with temperature sensors to measure the temperature of standards and samples and allow the DO meter to compensate the temperature effect on the measured DO values. The measurement is based on the catalyzed oxygen reduction reaction:

$$O_2 + 4\ e^- + 4\ H^+ \rightarrow 2\ H_2O$$

The electrode is isolated from the water by a thin membrane that is permeable to molecular oxygen and allows it to reach the cathode, where the above reduction reaction takes place.
Electrochemical DO electrodes available in the market have replaceable electrolyte and either loose membranes or membrane cap assemblies (caps pre-fitted with membranes). The usual maintenance involves periodic changing of the membrane or membrane cap assembly, refilling the electrolyte, and cleaning the anode and cathode.
One or two calibration points can be performed on the DO meter / electrode system before measuring samples. For most applications, air calibration is sufficient. Calibration should be checked daily and after relevant changes of ambient conditions (i.e. temperature or pressure). If DO is a critical parameter or sample has low DO value, it is recommended to perform a second calibration point or a check using a zero DO solution.
The atmospheric pressure (also called air pressure) has to be introduced in the DO meter before calibrating in either saturation ratio (%) mode, also known as percent saturation mode, or DO (mg/L) mode. If measurement will be carried out at sea level, there is no need to adjust the default setting 101.3 kPa (equal to 1 atm = 760 mmHg). The atmospheric pressure decreases as altitude increases. The meter manual has to be followed for the atmospheric pressure setting and calibration procedures in saturation ratio (%) mode and DO (mg/L) mode.
The air calibration is performed in clean air. There should be no water droplets on the membrane or temperature sensor, since evaporation of moisture on the membrane and temperature sensor of DO electrode may influence the readings during calibration. The electrode manual shows what data have to be displayed, either as saturation ratio (%) or as DO (mg/L).
Zero calibration is performed in an oxygen-free solution. A zero DO solution can be prepared by dissolving 1 g or more of sodium sulfite (Na_2SO_3), an oxygen scavenger, with 1 L of distilled or deionized (DI) water in a container. This solution should be freshly prepared and the volume should be enough to cover the membrane and temperature sensor. If available, 1 mg of cobalt salt (e.g., $CoCl_2 \cdot 6H_2O$) can be added in the solution to act as catalyst and indicator. Immediately after preparation, the container hs to be closed with a cap or film to prevent it from absorbing oxygen. The solution can be used after an adequate reaction time (usually at least 30 min). At calibration the meter has to display the readings given by the producer (very often 0% saturation ratio or less than 0.2 mg/L DO). After calibration the electrode has to be rinsed to avoid contaminating samples. After calibrationg by one or two calibration points, the meter will display a slope (%). The slope

should be within the range 50 - 100%. If the slope is less than 50% or more than 100%, the DO tip (membrane and solution or clean electrode and calibrate again) has to be replaces
When measuring samples, the following has to be noted:
- Measurements are carried out directly in the water body on site. If not possible, the discrete sample is measured immediately after sampling.
- The factors that affect DO in samples are temperature, atmospheric pressure, and salinity. DO meters detect the temperature from DO electrodes so it has to be ensured that the temperature sensor is submerged in the sample. The atmospheric pressure and the salinity values of samples have to be entered into the meter, if necessary.
- Stir the sample by using stirrer or moving the electrode to prevent loss of signal due to consumption of oxygen by the DO electrode.
- Formation of any air bubbles in the samples have to be avoided.
- Between measurements, the DO electrode has to be rinsed with clean water and blot dry with soft tissue.
- The care about electrode includes cleaning and storage. The recommendations of the electrode producer have to be followed.

Carbon dioxide

Carbon dioxide is present in the atmosphere and in soil pore space as a gas, and in surface waters and groundwaters as a dissolved gas. Carbon dioxide (CO_2) is highly soluble in water and atmospheric CO_2 is absorbed at the air-water interface. In addition, CO_2 is produced within water bodies by the respiration of aquatic biota, during aerobic and anaerobic heterotrophic decomposition of suspended and sedimented organic matter. Carbon dioxide dissolved in natural water is part of an equilibrium involving bicarbonate and carbonate ions. The concentrations of these forms are related with the pH value, as indicated in Figure 4.2. The reactive inorganic forms of environmental carbon are CO_2, bicarbonate (HCO_3^-), and carbonate (CO_3^{2-}). Organic carbon, such as cellulose and starch, is made by plants from CO_2 and water during photosynthesis. The carbon cycle is based on the mobility of CO_2, which is distributed readily through the environment compartments as a gas in the atmosphere and dissolved in rainwater, surface water, and groundwater. Most of the earth's carbon, however, is relatively immobile, being contained in ocean sediments and on continents as minerals. The atmosphere, with about 360 ppmv (parts per million by volume) of mobile CO_2, is the second smallest of the earth's global carbon reservoirs, after life forms which are the smallest. On land, solid forms of carbon are mobilized as particulates, mainly by weathering of carbonate minerals, biodegradation and burning of organic carbon, and burning of fossil fuels.
Carbon dioxide plays a fundamental role in determining the pH of natural waters. Although CO_2 itself is not acidic, it reacts in water (reversibly) to make an acidic solution by forming carbonic acid (H_2CO_3). Carbonic acid can subsequently dissociate in two steps to release hydrogen ions:

$$CO_2 + H_2O \leftrightarrow H_2CO_3$$

$$H_2CO_3 \leftrightarrow H^+ + HCO_3^-$$

$$HCO_3^- \leftrightarrow H^+ + CO_3^{2-}$$

The equilibria among only the carbon species (omitting the H^+ species) are

$$CO_2(gas, atm) \leftrightarrow CO_2(aq) \leftrightarrow H_2CO_3(aq) \leftrightarrow HCO_3^-(aq) \leftrightarrow CO_3^{2-}(aq)$$

These dissolved carbon species are sometimes referred to as dissolved inorganic carbon (DIC).
As pH increases, all above equilibria shift to the right. As pH decreases, all equilibria shift to the left.
At equilibrium with the atmosphere, free CO_2 is that part which presents in water as hydrated gas or as H_2CO_3, and bound forms are bicarbonate (HCO_3^-), and carbonate (CO_3^{2-}).

Summary (total) CO_2 is the sum of all inorganic forms of carbon dioxide, i.e. CO_2, HCO_3^- and CO_3^{2-}. Both CO_2 and HCO_3^- can be incorporated into organic carbon by autotrophic organisms.
At high concentrations of free carbonic acid (pH 4.5 or lower), water becomes corrosive to metals and concrete as a result of the formation of soluble bicarbonates. The ability to affect the calcium carbonate component of concrete has led to the term aggressive carbonic acid or aggressive CO_2, which is actually the CO_2 that present in water in concentration higher that the equilibrium.
Determination of free CO_2 is usually by titration methods (most often with NaOH solution till pH 8.3 for water with 4.4 < pH < 8.3).
As it was already mentioned, the pure water exposed to air is not acid-base neutral (with a pH near 7.0) because dissolved CO_2 makes it acidic, with a pH around 5.7.
The pH dependence of different forms of CO_2 are presented in Fig. 4.2 and Table 6.2.

Table 6.2 pH dependence of carbonate fractions

pH	Fractions as CO_2	Fraction as HCO_3^-	Fraction as CO_3^{2-}
<< 6.35	Essentially 1.00	Essentially 0	Essentially 0
6.35	0.50	0.50	Essentially 0
0.5 x (6.35 + 10.33) = 8.34	0.01	0.98	0.01
10.33	Essentially 0	0.50	0.50
>> 10.33	Essentially 0	Essentially 0	Essentially 1.00

In summary:
- Above pH 10.3, carbonate ion (CO_3^{2-}) is the dominant species.
- Below pH 6.3, dissolved CO_2 is the dominant species.
- Between pH 6.3 and 10.3, a range common to most environmental waters, bicarbonate ion (HCO_3^-) is the dominant species.

Hydrogen sulfide (H_2S)

There are two important sources of H_2S in the environment: the anaerobic decomposition of organic matter containing sulfur, and the reduction of mineral sulfates and sulfites to sulfide. Both mechanisms require reducing, or anaerobic, conditions, and are strongly accelerated by the presence of sulfur-reducing bacteria. H_2S is not formed in the presence of an abundant supply of oxygen.
Water conditions promoting the formation of H_2S are sulfate > 60 mg/L (or presence of sulfur-containing organic matter such as protein), oxidation-reduction potential (Eh) < 200 mV, and pH < 6 – 7. These conditions frequently occur in standing or slowly moving water, such as in detention ponds, wetlands, sewers, etc. where organic litter can accumulate and where the water or soil contains sulfate. Since surface waters seldom contain more than 8 – 9 mg/L of dissolved oxygen (more often less), decay of organic matter can quickly reduce dissolved oxygen to anaerobic levels (< 1 mg/L). Such waters often develop a bottom layer of black sediments containing iron and other metal sulfides along with organic matter in various stages of decay. In still water, oxygen diffusion into this sediment layer is slow and anaerobic conditions can be maintained with minimal water cover, less than 20-30 cm in depth. If all water is removed and the soil allowed to dry, diffusion of oxygen into the sediment quickly oxidizes the sulfides to sulfate and H_2S disappears. Blackening of soils, wastewater, sludge, and sediments in locations with standing water, in addition to the odor of rotten eggs, is an indication that sulfide is present. The black material results from a reaction of H_2S with dissolved iron and other metals to form precipitated FeS, along with other metal sulfides.
Sulfide is often present naturally in groundwater as the dissolved anion S^{2-}, especially in natural hot springs. There, it arises from soluble sulfide minerals and anaerobic bio-reduction of dissolved sulfates. Sulfide reacts with water to form H_2S - a colorless, highly toxic gas that smells like rotten eggs.

$$S^{2-} + 2H_2O \leftrightarrow OH^- + HS^- + H_2O \leftrightarrow H_2S(g) + 2OH^-$$

The human nose is very sensitive to the odor of low levels of H_2S. The odor threshold for H_2S dissolved in water is 0.03–0.3 mg/L. A typical concentration of H_2S in unpolluted surface water is < 0.25 mg/L. In aerated water, H_2S is bio-oxidized to sulfates and elemental sulfur.

In water under reducing conditions, depending on pH, H_2S has two stages of dissociation - to hydrogen sulfide (HS^-) ion and sulfide ion (S^{2-}):

$$H_2S \leftrightarrow H^+ + HS^- \leftrightarrow 2H^+ + S^{2-}$$

S^{2-} and HS^- are soluble, nonvolatile anions with no odor. Analytically, the three sulfur species S^{2-}, HS^-, and H_2S are collectively called sulfide - Fig. 6.1.

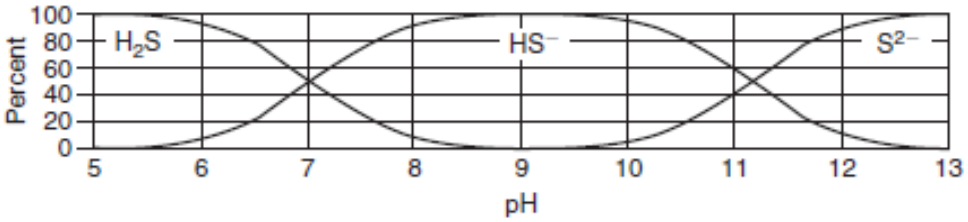

Fig. 6.1 Hydrogen sulfide forms in dependence on pH

- At pH 5, about 99% of dissolved sulfide is in the form of H_2S, the unionized form.
- At pH 7, dissolved sulfide is 50% HS^- and 50% H_2S.
- At pH 9, about 99% is in the form of HS^-.
- S^{2-} becomes prevailing species only above pH 11.5.

General observations:

- H_2S is the most toxic and volatile form; HS^- and S^{2-} are nonvolatile and much less toxic. H_2S > 2.0 mg/L constitutes a long-term hazard to fish.
- Raising the pH shifts the equilibrium to the convertion of the malodorous gas H_2S into nonodorous and nonvolatile HS^- and S^{2-}.
- Lowering the pH shifts the equilibrium to creation of more malodorous H_2S gas from the nonvolatile forms, HS^- and S^{2-}.
- Lowering the temperature leads to formation of more H_2S at any pH - Fig. 6.2.
- Well water, groundwater, or stagnant surface water that smells of H_2S (rotten eggs), is usually a sign of pres ence of sulfate-reducing bacteria.

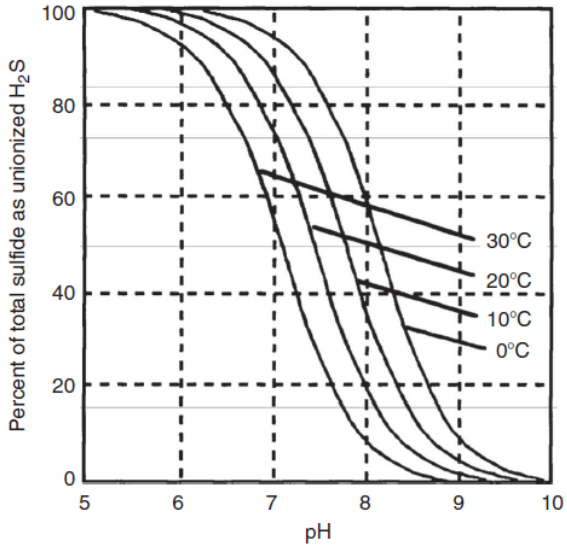

Fig. 6.2. Fraction of hydrogen sulfide in unionized form (H_2S) as a function of temperature and pH.

Hydrogen sulfide is traditionally determined using an acid displacement procedure; the hydrogen sulfide is displaced by acidification, followed by analysis by gas chromatography using a flame photometric detector. The procedure is used for water, sewage, and effluents containing 0–2.0 mg/L of sulfide.

The methylene blue colorimetric method is another standard analytical procedure for hydrogen sulfide determination, at concentrations ranging between 0.1 and 20 mg/L.

The determination of the concentration of sulfide ions (in the range from 0.04 to 4000 mg/L of sulfide) in water can be carried out by direct measurement using an Ag/S ion-selective electrode according to ASTM D4658.

The standard is withdrawn as Jan 05, 2024 but the method is still useful for fast evalluation of the pollutant amount. For the measurement, a volume of 50 mL of the water solution is pipetted into a sample beaker. Immediately prior to the measurement, a 50 mL volume of SAOB (Sulfide anti-oxidant buffer, containing NaOH 2.0 mol/L, ascorbic acid 0.2 mol/L, EDTA 0.2 mol/L) is added and the solution is stirred vigorously 15 seconds. Following a 3-minute waiting period, the electrodes are placed into the sample solution and the sulfide concentration is measured without stirring.
If not directly measuerd on the spot, prior to analysis, samples must be preserved, as sulfide is a highly volatile. For 100 mL water 200 µL $Zn(C_2H_3O_2)_2$ with concentration 2.0 mol/L (equivalent to 128 mg/L S^{2-}) and 50 µL NaOH with concentration 6.0 mol/L are added. In laboratory conditions a colour compound is formed by the suitable reagent's addition to the perserved sample (following the specific procedure described in the corresponsing methods that transform all forms to S^{2-}) and spectrophotometry is applied.

The above lecture is based mainly on the following publications: Stumm and Morgan, 1996; Weiner, 2007; Gautam, 2011; American Public Health Association, American Water Works Association, and Water Environmentp 2023.

7. Water macro-components

Macro-components are components whose natural concentrations in pure water are higher than 5 mg/L. The major anions are bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) anions (see also the pages for CO_2 forms), chlorides (Cl^-) and sulfates (SO_4^{2-}). The major cations are calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^+), and potassium (K^+). Major ions are naturally very variable in surface and groundwaters due to local geological, climatic and geographical conditions.

Calcium

Calcium is present in all waters as Ca^{2+} ions and is readily dissolved from rocks rich in calcium minerals, particularly in carbonates and sulphates, especially limestone and gypsum. The cation is abundant in surface and groundwaters. The salts of calcium, together with those of magnesium, are the main ions responsible for the hardness of water. Industrial, as well as water and wastewater treatment processes also contribute calcium to surface waters. Acidic rainwater can increase the leaching of calcium from soils.
Calcium compounds are stable in water when carbon dioxide is present, but calcium concentrations can fall when calcium carbonate precipitates due to increased water temperature, photosynthetic activity or loss of carbon dioxide. Calcium is an essential element for all organisms and is incorporated into the shells of many aquatic invertebrates, as well as the bones of vertebrates. Calcium concentrations in natural fresh waters can vary from < 15 mg/L till 30-100 mg/L and more (for waters associated with carbonate-rich rocks). Salt waters have concentrations of several hundred milligrams per litre or more.
The amount of calcium ions dissolved in water and migrating with it can be reduced mainly as a result of precipitation of calcium carbonate or calcium sulfate, accumulation as calcium carbonate in the shells of organisms, adsorption on rocks and soils, with which water comes into contact. Its remobilization is observed as a result of complex formation processes and/or dilution of water, e.g. during heavy rainfall.
Samples for calcium analysis should be collected in plastic or borosilicate glass bottles without a preservative. They should be analysed immediately, or as soon as possible, after collection and filtration. They have to be kept cool. If any calcium carbonate precipitate forms after filtration and during storage, it must be re-dissolved with hydrochloric or nitric acid and then neutralised before analysis. Acidification of unfiltered waters prior to analysis should be avoided since it causes a dissolution of carbonates, calcite and dolomite. Calcium can be determined by a titrimetric method using EDTA (ethylenediaminetetracetic acid or its sodium salt) or by atomic absorption spectrophotometry.

Principle of the titration method is the following: When EDTA is added to water containing calcium and magnesium ions, it reacts with the calcium before the magnesium. (Magnesium hydroxide may be precipitated at high Mg concentrations and high pH values). Calcium can be determined in the presence of magnesium by EDTA (with known concentration) titration; the indicator used (murexide) is one that reacts with calcium only. Murexide indicator gives a colour change (from pink to purple) when all of the calcium has been complexed by EDTA at a pH of 12-13.
Some iterferences have to be considered: Orthophosphate precipitates calcium at the pH of the test. Strontium and barium interfere with the calcium determination, and alkalinity in excess of 300 mg/L may cause an indistinct end-point with hard waters. Under the conditions of the test, normal concentrations of the following ions cause no interference with the calcium determination: Cu^{2+}, Fe^{2+}, Fe^{3+}, Mn^{2+}, Zn^{2+}, Al^{3+}, Pb^{2+} and Sn^{4+}. Heavily polluted water containing considerable organic matter should be treated by nitric acid digestion before the analysis.

Magnesium

Magnesium is common in natural waters as Mg^{2+} ions, and along with calcium, is a main contributor to water hardness. Magnesium arises principally from the weathering of rocks containing ferromagnesium minerals and from some carbonate rocks. Magnesium occurs in many organometallic compounds and in organic matter, since it is an essential element for living organisms. Waters associated with granite or siliceous sand may contain less than 5 mg of magnesium per litre. Water in contact with dolomite or magnesium-rich limestone may contain 10-50 mg/L and several hundred milligrams per litre may be present in water that has been in contact with deposits containing sulphates and chlorides of magnesium. Although magnesium is used in many industrial processes, these contribute relatively little to the total magnesium in surface waters.
The amount of magnesium ions dissolved in water and migrating with it can be reduced mainly as a result of precipitation of secondary minerals, uptake by living matterr, manly plants, adsorption on rocks and soils, with which water comes into contact. Its remobilization is observed as a result of complex formation processes.
Samples for magnesium analysis should be collected in plastic or borosilicate glass containers without preservative. Samples can be analysed using the EDTA titrimetric method or by atomic absorption spectrophotometry. The magnesium concentration in a sample can also be estimated by calculating the difference between the total hardness and the calcium concentration. Here this method will be described briefly.
When EDTA is added in a titration to water containing calcium and magnesium ions, it reacts both with the calcium and the magnesium at pH 10.0. A small amount of Eriochrome Black T is added to the solution which is titrated with EDTA or its sodium salt (with known concentration) till the color changes from violet to blue.
The sum of Ca^{2+} and Mg^{2+} is determined, in mol or mmol per liter. Magnesium may be determined by calculating the difference between the sum of Ca^{2+} and Mg^{2+} and the calcium concentration (in mol or mmol per liter) of the sample.
Eventual interferences of some heavy metal ions that present in elevated concentrations in the analyzed water can be minimised by addition of sodium sulphide (Na_2S) that precipitates insoluble sulphides which can be removed. To determine whether addition of the Na_2S is necessary, the analyst should compare the results of two titrations, one with and one without inhibitor.

Sodium

All natural waters contain some sodium (Na^+) ions since sodium salts are highly water soluble and sodium is one of the most abundant elements on earth. It is found in the ionic form (Na^+) in water, and in plant and animal matter (it is an essential element for living organisms). Increased concentrations in surface waters may arise from sewage and industrial effluents and from the use

of salts on roads to control snow and ice. The latter source can also contribute to increased sodium in groundwaters. In coastal areas, sea water intrusion can also result in higher concentrations.
Concentrations of sodium in natural surface waters vary considerably depending on local geological conditions, wastewater discharges and seasonal use of road salt. Values can range from 1 mg/L or less to 105 mg/L or more in natural brines. Sodium concentrations higher than a few milligrams per litre are undesirable in feed water for high-pressure boilers. The WHO guideline limit for sodium in drinking water is 200 mg/L. When compounded with chloride, sodium imparts a salty taste to drinking water and, if the concentration is sufficiently high, consumers may not be willing to drink it. Many surface waters, including those receiving wastewaters, have concentrations well below 50 mg/L. However, ground-water concentrations frequently exceed 50 mg/L. Sodium ions remain the main mobile ions in water with very high mineralisation due to the fact that they do not form low soluble compounds, are not accumulated by living organisms and are not adsorbed significantly on rocks and soils, with which water comes into contact.
Sodium is commonly measured where the water is to be used for drinking or agricultural purposes, particularly irrigation. Elevated sodium in certain soil types can degrade soil structure thereby restricting water movement and affecting plant growth. The sodium adsorption ratio (SAR) is used to evaluate the suitability of water for irrigation. The ratio estimates the degree to which sodium will be adsorbed by the soil. High values of SAR imply that the sodium in the irrigation water may replace the calcium and magnesium ions in the soil, potentially causing damage to the soil structure. The SAR for irrigation waters is defined as follows:

$$SAR = \frac{Na^{+}}{\sqrt{(Ca^{2+} + Mg^{2+})/2}}$$

where the concentrations of sodium, magnesium and calcium are expressed in milliequivalents per litre (meq/L).
Samples for sodium analysis should be stored in polyethylene bottles to avoid potential leaching from glass containers. Samples should be analysed as soon as possible because prolonged storage in polyethylene containers can lead to evaporation losses through the container walls or lid. Filtration may be necessary if the sample contains solid material. Analysis is best performed using flame atomic emission.

Potassium

Potassium (K^{+}) ions are found in low concentrations in natural waters since rocks which contain potassium are relatively resistant to weathering. In addition, potassium is absorbed by plants. However, potassium salts are widely used in industry and in fertilisers for agriculture and enter freshwaters with industrial discharges and run-off from agricultural land. Potassium is usually found in the ionic form and the salts are highly soluble. It is readily incorporated into mineral structures and accumulated by aquatic biota as it is an essential nutritional element. Concentrations in natural waters are usually less than 10 mg/L, whereas concentrations as high as 100 and 25000 mg/L can occur in hot springs / seawater, and brines, respectively.
Samples for potassium analysis should be stored in polyethylene containers to avoid potential contamination as a result of leaching from glass bottles. However, samples should be analysed as soon as possible as prolonged storage in polyethylene containers can lead to evaporation losses through the container walls or lid. Samples containing solids may require filtration prior to storage. Analysis is best carried out using flame atomic emission as for sodium.

Carbonates and bicarbonates

The presence of carbonates (CO_3^{2-}) and bicarbonates (HCO_3^{-}) influences the hardness and alkalinity of water. The dissolved CO_2 arises from the atmosphere and biological respiration. The weathering of rocks contributes carbonate and bicarbonate salts. In areas of noncarbonate rocks, the HCO_3^{-} and CO_3^{2-} originate entirely from the atmosphere and soil CO_2, whereas in areas of

carbonate rocks, the rock itself contributes approximately 50 per cent of the carbonate and bicarbonate present in water.
The relative amounts of carbonates, bicarbonates and carbonic acid in pure water are related to the pH as shown in Figure 4.2. As a result of the weathering process, combined with the pH range of surface waters (~6-8.2), bicarbonate is the dominant anion in most surface waters. Carbonate is uncommon in natural surface waters because they rarely exceed pH 9, whereas groundwaters can be more alkaline and may have concentrations of carbonate up to 10 mg/L. Bicarbonate concentrations in surface waters are usually < 500 mg/L. The amount of bicarbonates dissolved in water and migrating with it may decrease as a result of precipitation of calcium carbonate, at high concentrations of dissolved calcium and carbonate ions, especially with an increase in temperature.
The concentration of carbonates and bicarbonates can be calculated from the free and total alkalinity. However, the calculation is valid only for pure water since it assumes that the alkalinity derives only from carbonates and bicarbonates. In some cases, hydroxyl ions are also present, and even unpolluted or mildly polluted waters contain components which affect the calculation.

Chloride

Chloride ions (Cl^-) are widely distributed in nature, usually in the form of sodium, potassium, and calcium salts (NaCl, KCl, and $CaCl_2$), although many minerals contain small amounts of chloride as an impurity. Chloride in natural waters arises from weathering of chloride minerals, salting of roads for snow and ice control, seawater intrusion in coastal regions, irrigation drainage, ancient groundwater brines, geothermal waters, and industrial wastewater.
Concentrations in unpolluted surface waters and nongeothermal groundwaters are generally low, usually below 100 mg/L. Thus, chloride concentrations in the absence of pollution are normally less than those of sulfate or bicarbonate.
Chloride ion is extremely mobile; all chloride salts are very soluble except for lead chloride ($PbCl_2$), silver chloride (AgCl), and mercury chlorides (Hg_2Cl_2, $HgCl_2$). Chloride is not sorbed to soils and mineral surfaces and generally moves with water with little or no retardation. Chloride ion is almost chemically and biologically inert when compared with the other major environmental ions. Under environmental conditions, chloride ions do not significantly enter into redox reactions. Chloride ions are the major mobile ions in water with very high mineralisation. Consequently, it eventually moves to closed water basins or to the oceans.
Fortunately, it participates in few important biological processes, and have extremely low toxicities for mammalian and aquatic species. Tests on fish showed no effect for concentrations of NaCl between 5000 and 30000 mg/L, depending on the species, exposure time, and water quality. Chloride circulates through the hydrologic cycle mainly by physical processes. Its lack of environmental reactivity led to the common use of chloride as a conservative tracer for groundwater movement.
The main environmental problems associated with chloride are reactivity with concrete, metal corrosion, adverse taste effects in drinking water, and toxicity to irrigated crops (less than 100 mg/L chloride is recommended for most crops).
There are no primary drinking water standards for chloride. The EPA secondary standard for chloride is 250 mg/L, based on adverse effect on taste. A salty taste in water depends on the ions with which the chlorides are associated. With sodium ions the taste is detectable at about 250 mg/L Cl^-, but with calcium or magnesium the taste may be undetectable at 1000 mg/L.
As chloride is frequently associated with sewage, it is often incorporated into assessments as an indication of possible faecal contamination or as a measure of the extent of the dispersion of sewage discharges in water bodies.
Samples for chloride determination need no preservation or special treatment and can be stored at room temperature. Analysis can be done by standard or potentiometric titration methods. Direct potentiometric determinations can be made with chloride sensitive electrodes. One of the most

widely used methods is titration (in a neutral or slightly alkaline solution) with standard silver nitrate solution, using potassium chromate as indicator. Silver chloride is quantitatively precipitated before red silver chromate is formed. In this method bromide, iodide and cyanide are measured as equivalents of chloride. Thiosulphate, sulphite and sulphide interfere and the end-point may be difficult to detect in highly coloured or very turbid samples.
Chloride can be titrated with mercuric nitrate, $Hg(NO_3)_2$, because of the formation of insoluble, slightly dissociated mercuric chloride. In the pH range 2.3 to 2.8, diphenylcarbazone indicates the titration end-point by formation of a purple complex indicator and an end-point enhancer. Increasing the strength of the titrant and modifying the indicator mixtures extend the range of measurable chloride concentrations. Bromide and iodide are titrated with $Hg(NO_3)_2$ in the same manner as chloride. Chromate, ferric and sulphite ions interfere when present in concentrations that exceed 10 mg/L.

Sulphate

Sulphate ions (SO_4^{2-}) in surface waters arise mainly from the leaching of sulphur compounds, either sulphate minerals such as gypsum or sulphide minerals such as pyrite, from sedimentary rocks. It is the stable, oxidised form of sulphur. All sulfate salts are very soluble except for calcium and silver sulfates (that are moderately soluble), and barium, mercury, lead, and strontium sulfates, which are insoluble.
Industrial discharges and atmospheric precipitation can also add significant amounts of sulphate to surface waters. Mine and tailings drainage, smelter emissions, agricultural runoff from fertilized lands, pulp and paper mills, textile mills, tanneries, sulfuric acid production, and metal working industries are all sources of sulfate-polluted water.
Sulphate can be used as an oxygen source by bacteria which convert it to hydrogen sulphide (H_2S, HS^-) under anaerobic conditions. Sulfate water concentrations that are too low have a detrimental effect on both land and aquatic plant growth.
Sulphate concentrations in natural waters are usually between 2 and 80 mg/L, although they may exceed 1000 mg/L near industrial discharges or in arid regions where sulphate minerals, such as gypsum, are present. High concentrations (> 400 mg/L) may make water unpleasant to drink. The lowest taste threshold concentration for sulfate is approximately 250 mg/L as the sodium salt but higher as calcium or magnesium salts (up to 1000 mg/L). Seawater contains about 2700 mg/L of sulfate. Sulfate is a major contributor to salinity in many irrigation waters. Sulfate in irrigation water is a plant nutrient, and irrigation water often carries enough sulfate for maximum production of most crops. However, at very high concentrations sulfate can interfere with uptake of other nutrients.
The sulfate anion is generally considered nontoxic to animal, aquatic, and plant life. Available data suggest that people acclimate rapidly to the presence of sulfates in their drinking water. No upper limit likely to cause detrimental human health effects has been determined for sulfate in drinking water. However, concentrations of 500–750 mg/L may cause a temporary mild laxative effect, although doses of several thousand milligrams per liter generally do not cause any long-term ill effects. WHO therefore suggests that health authorities should be notified when concentrations of sulphate in drinking water exceed 500 mg/L.
The amount of sulfate ions dissolved in the water and migrating with it can decrease as a result of gypsum precipitation or as a result of the vital activity of sulfate-reducing bacteria, converting sulfates into sulfides and the latter form insoluble compounds with a number of metals present in the water.
Samples collected in plastic or glass containers can be stored in the refrigerator for up to seven days, although when intended for analysis soon after collection they may be stored at room temperature. Prolonged storage should be avoided, particularly if the sample contains polluted water. Sulphate can be determined. Other methods are available including a titrimetric method.

The principle of the gravimetric method is the following: Sulphate is precipitated in a hydrochloric acid solution as barium sulphate ($BaSO_4$) by the addition of barium chloride ($BaCl_2$). The precipitation is carried out near the boiling temperature and after a period of digestion the precipitate is filtered, washed with water until free of Cl^-, dried and weighed as $BaSO_4$. The gravimetric determination of SO_4^{2-} is subject to many errors, both positive and negative. Interferences that lead to high results are suspended matter, silica, $BaCl_2$ precipitant, NO_3^-, SO_3^{2-} and water occluded in the precipitant. Interferences leading to low results are alkali metal sulphates, heavy metals (especially chromium and iron) and the solubility of the $BaSO_4$, especially in acid solution.
Sulphate can be deteremined by titration with $Pb(NO_3)_2$ solution with dithizone as indicator (color change from green to violet-red) or by turbidimetry.

Hardness

The property of water to precipitate saponified fatty acids is called water hardness. Water hardness is defined as the sum of the divalent and polyvalent metallic ions in the water. The main contributors to the hardness of the water are calcium and magnesium ions. Additional contributors to the hardness of the water include iron (Fe^{2+}), strontium (Sr^{2+}), zinc (Zn^{2+}), manganese (Mn^{2+}) and other ions. However, their concentrations are usually significantly lower than the concentration of calcium and magnesium ions. In most cases, summing up the calcium and magnesium in the water gives an adequate hardness measure.
The total content of calcium and magnesium ions is known as general hardness, which can be further divided into carbonate hardness (determined by concentrations of calcium and magnesium hydrocarbonates), and non-carbonate hardness (determined by calcium and magnesium salts of strong acids). Hydrocarbonates are transformed during the boiling of water into carbonates, which usually precipitate.

$$Ca(HCO_3)_{2(aq)} \rightarrow CO_{2(g)} + H_2O_{(l)} + CaCO_{3(s)}$$
$$Mg(HCO_3)_{2(aq)} \rightarrow CO_{2(g)} + H_2O_{(l)} + MgCO_{3(s)}$$

Therefore, carbonate hardness is also known as temporary or removable, whereas the hardness remaining in the water after boiling (non-carbonate hardness) is called permanent.
Different countries have different harness units as indicated in Table 7.1.
Hardness may vary over a wide range. Calcium hardness is usually prevalent (up to 70 per cent), although in some cases magnesium hardness can reach 50-60 per cent. Seasonal variations of river water hardness often occur, reaching the highest values during low flow conditions and the lowest values during floods. Groundwater hardness is, however, less variable. Where there are specific requirements for water hardness in relation to water use it is usually with respect to the properties of the cations forming the hardness.

Table 7.1. Conversion factors for various national grades of water hardness

	mmol/L	Germany °DH	UK °clark	France degree F	USA ppm
mmol/L	1	5.61	7.02	10	100
Germany °DH	0.178	1	1.25	1.78	17.8
UK °clark	0.143	0.80	1	1.43	14.3
France degree F	0.1	0.56	0.70	1	10
USA ppm	0.01	0.056	0.07	0.1	1

Samples for hardness determination must be filtered but not preserved. If during storage a calcium carbonate sediment appears, it must be dissolved with a small volume of hydrochloric acid (1:1) after decanting the clear liquid above the sediment. Total hardness is usually determined by EDTA complexometric titration. Depending on the indicator used, either general hardness (using eriochrome black T) or calcium hardness (using murexide) can be determined. Magnesium

hardness is calculated from the difference between the two determinations. Carbonate hardness is determined by acid-base titration. Hardness may also be determined from the sum of the divalent ions analysed individually (e.g. by atomic absorption spectrophotometry).
As a result, from the titration with EDTA, the total hardness is obtained in *mmol/L*. 1 mmol/L is equivalent to 100.09 mg/L $CaCO_3$ or 40.08 mg/L Ca^{2+}.
The USA Geological Survey uses the following classification of water in dependence of its hardness - Table 7.2.

Table 7.2. Water classification in dependence of its hardness

Classification	Soft	Moderately hard	Hard	Very hard
Hardness in mg-$CaCO_3$/L	0–60	61–120	121–180	≥ 181
Hardness in mmol/L	0–0.60	0.61–1.20	1.21–1.80	≥ 1.81

Examples of the concentrations of ions - macrocomponents occurring in pristine waters are presented in Table 7.3. Data are averages from a survey of 250 pristine streams in France and from 75 sites world-wide, corrected for oceanic cyclic salts.
The natural geographic variation of selected dissolved constituents in rivers is given in Table 7.4. for pristine streams and major world rivers (highly polluted rivers in Europe and North America are not included).

Table 7.3. Geographic variability of dissolved major elements in pristine waters

	Electrical conductivity (µS/ cm)	pH	Sum of cations µeq/L	SiO_2	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	Cl^{-}	SO_4^{2-}	HCO_3^{-}
***A.** Pristine streams draining most common rock types* (*corrected for oceanic aerosols*)											
Granite	35	6.6	166	9.0	0.78	0.38	2.0	0.3	0	1.5	7.8
Gneiss	35	6.6	207	7.8	1.2	0.69	1.8	0.4	0	2.7	8.3
Volcanic	50	7.2	435	12.0	3.1	2.0	2.4	0.55	0	0.5	25.9
Sandstone	60	6.8	223	9.0	1.8	0.75	1.2	0.82	0	4.5	7.6
Shale			770	9.0	8.1	2.9	2.4	0.78	0.7	6.9	35.4
Carbonate	400	7.9	3247	6.0	51	7.8	0.8	0.51	0	4.1	195
***B.** Pristine streams draining rare rock types or in a rare geological formation*											
Amazonian dear waters	5.7	5.1	111	1.9	tr	0.13	1.2	1.4	0.7		
Amazonian Black waters	29.1	3.7	212	0.6	tr	0.02			1.2		
Coal shale			40700	7.0	87	121	600	10.2	14.8	1400	652
Salt rock		8.0	312000	1.2	607	68	6300	7.7	9400	1330	183
***C.** Rivers influenced by evapotranspiration*											
Horocallo R., Ethiopia	2230	9.2	21800	79	2.2	1.45	480	2.5	195	65	975
***D.** Rivers influenced by oceanic aerosols*											
Clisson R., France	227	6.2		14.6	6.4	4.8	22.0	2.6	40.0	5.8	32.9

The above lecture is based mainly on the following publications: Stumm and Morgan, 1996; Bartram and Ballance, 1996; Chapman, 1996; Weiner, 2007; Gautam, 2011; American Public Health Association, American Water Works Association, and Water Environment, 2023.

Table 7.4. Natural ranges of dissolved constituents in rivers

	Streams (1-100 km^2)				Rivers (100000 km^2)				Global average	
	Minimum		Maximum		Minimum		Maximum		MCNC	
	μeq/L	mg/L	μeq/L	mg/L	μeq/L	mg/L	μeq/L	mg/L	neq/L	mg/L
SiO_2[5] (µmol/L)	10	0.6	830	50	40	2.4	330	20	180	10.8
Ca^{2+}	3	0.06	10500	210	100	2.0	2500	50	400	8.0
Mg^{2+}	4	0.05	6600	80	70	0.85	1000	12.1	200	2.4
Na^{+}	2.6	0.06	15000	350	55	8	1100	25.3	160	3.7
K^{+}	3	0.1	160	6.3	13	0.5	100	4.0	27	1.0
Cl^{-}	2.5	0.09	15000	530	17	0.6	700	25	110	3.9
SO_4^{2-}	2.9	0.14	15000	720	45	2.2	1200	58	100	4.8
HCO_3^{-}	0	0	5750	350	165	10	2800	170	500	30.5
Sum of cations	45		20000		340		4000		800	
pH	4.7		8.5		6.2		8.2			
TSS		3		15000		10		1700		150
DOC		0.5		40		2.5		8.5		4.2
POC		0.5		75						3.0
POC %	0.5			20						2.0
TOC		1.5		25						
$N\text{-}NH_4^{+}$						0.005		0.04		0.015
$N\text{-}NO_3^{-}$						0.05		0.2		0.10
Norganic						0.05		1.0		0.26
$P\text{-}PO_4^{3-}$						0.002		0.025		0.010

Streams: Distribution based on 75 unpolluted monolithological watersheds from all countries in which the rock type proportion is close to the estimated global proportion, particularly for the most soluble rocks; oceanic cyclic salts have been grossly subtracted.
Rivers: The figures are derived from the discharge-weighted distribution of constituents in 60 major rivers without any correction of oceanic cyclic salts.
Minimum and maximum values correspond to 2% and 98% of the distribution except for nutrients which represent 10% and 90%.
MCNC (most common natural concentrations) corresponding to the median value obtained for the same 60 major rivers as above.
TSS Total suspended solids; DOC Dissolved organic carbon; POC Particulate organic carbon; TOC Total organic carbon; POC % is the percentage of organic carbon in the TSS

8. Water meso-components - natural and polluting concentrations

Water meso-components are those whose natural concentrations in pure water are generally between 1 and 5 mg/L.

Nitrogen compounds

Nitrogen compounds of greatest interest to water quality are those that are biologically available as nutrients to plants or exhibit toxicity to humans or aquatic life. Atmospheric nitrogen (N_2) is the primary source of all nitrogen species, but it is not directly available to plants as a nutrient because the N-N triple bond is too strong to be broken by photosynthesis. Atmospheric nitrogen must be converted to other nitrogen compounds before it can become available as a plant nutrient.
The conversion of atmospheric nitrogen to other chemical forms is called nitrogen fixation and is accomplished by certain bacteria that are present in water, soil, and root nodules of alfalfa, clover, peas, beans, and other legumes. Atmospheric lightning is another significant source of fixed nitrogen because the high temperatures generated in lightning strikes are sufficient to break N_2 and O_2 bonds, making possible the formation of nitrogen oxides. Nitrogen oxides created within

lightning bolts dissolve in rainwater and are absorbed by plant roots, thus entering the nitrogen nutrient subcycles (see Figure 8.1).

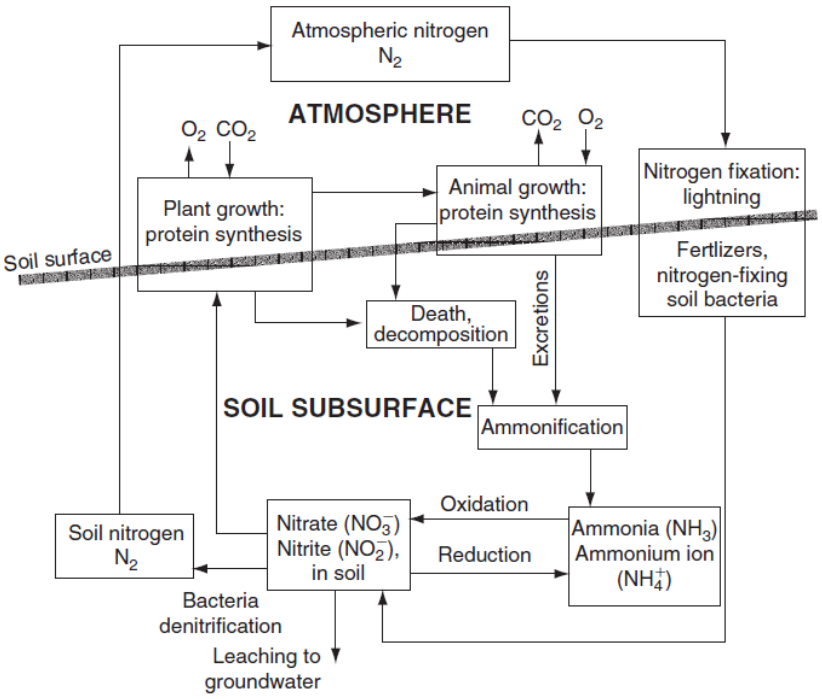

Figure 8.1. Nitrogen cycle

The rate at which atmospheric nitrogen can enter the nitrogen cycle by natural processes is too low to support today's intensive agricultural production. The shortage of fixed nitrogen is made up with fertilizers containing nitrogen fixed by industrial processes.

In the nitrogen cycle plants take up ammonia and nitrogen oxides dissolved in soil pore water and convert them into proteins, DNA, and other nitrogen compounds. Animals get their nitrogen by eating plants or other plant-eating animals.

Once in terrestrial ecosystems, nitrogen is recycled through repeated biological birth, growth, death, and decay steps. There is a continual and relatively small loss of fixed nitrogen when specialized soil bacteria convert fixed nitrogen back into nitrogen gas (denitrification), which is then released to the atmosphere, from which it can eventually reenter the nutrient subcycles again.

When nitrogen is circulating in the nutrient subcycles, it undergoes a series of reversible oxidation - reduction reactions that convert it from nitrogenous organic molecules, such as proteins, to ammonia (NH_3), nitrite (NO_2^-), and nitrate (NO_3^-).

Ammonia

Ammonia is the first product in the oxidative decay of nitrogenous organic compounds. Ammonia is naturally present in most surface- and wastewaters. Under aerobic conditions, ammonia is oxidized to nitrites and nitrates, consuming dissolved oxygen

$$\text{Organic N} \longrightarrow NH_3 \xrightarrow{O_2} NO_2^- \xrightarrow{O_2} NO_3^-$$

In water, ammonia reacts as a base, raising the pH by generating OH^- ions:

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

The equilibrium of depends on pH and temperature (see Fig. 8.2). Unionized ammonia that presents in water is more toxic to fish, compared to NH_4^+ ions.

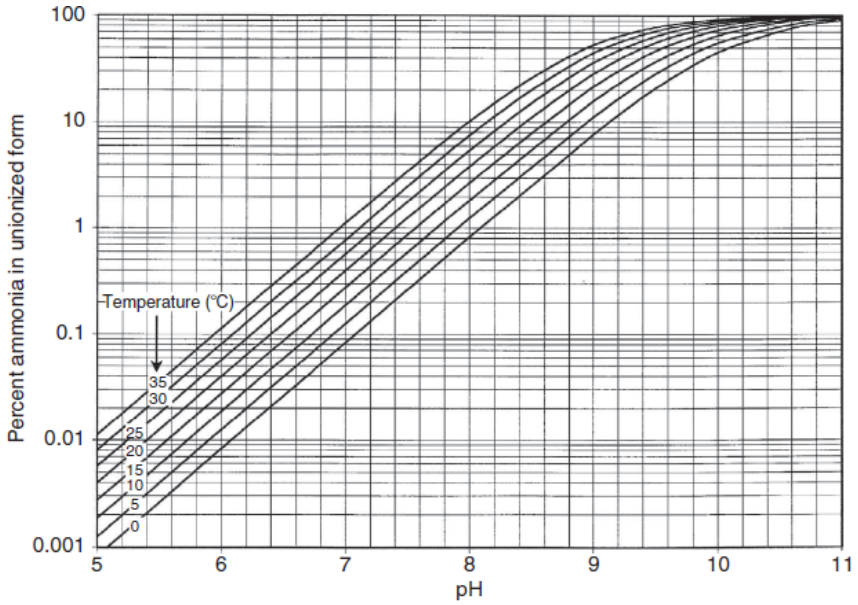

Fig. 8.2. Percent unionized ammonia (NH_3) as a function of pH and temperature

As it can be seen in the figure, ammonia toxicity increases with pH and temperature. At 20 ºC and pH > 9.4, the equilibrium between NH_4^+ and NH_3 favors NH_3 formation, the toxic form. At 20 ºC and pH < 9.4, the equilibrium favors formation of NH_4^+, the (generally) nontoxic form. Temperature increase favours formation of the NH_3 form. NH_3 concentrations > 0.5 mg NH_3–N/L cause significant toxicity to fish.

In a laboratory analysis, total ammonia (NH_3 + NH_4^+) is measured and the distribution between unionized ammonia (NH_3) and ionized ammonia (NH_4^+) is calculated from the knowledge of water pH and temperature at the sampling site. Since the unionized form is far more toxic to aquatic life than the ionized form, field measurements of water pH and temperature at the sampling site are very important.

The two forms of ammonia have different mobilities in the environment. Ionized ammonia is strongly adsorbed on mineral surfaces, where it is effectively immobilized. In contrast, unionized ammonia is only weakly adsorbed and is transported readily by water movement. If suspended sediment carrying sorbed NH_4^+ is carried by a stream into a zone with a higher pH, a portion will be converted to unionized NH_3, which can then desorb and become available to aquatic life forms as a toxic pollutant. Unionized ammonia is also volatile and a fraction of it is transported as a gas.

As discussed above, nitrogen passes through several different chemical forms in the nutrient subcycle. To allow quantities of these different forms to be directly compared with one another, analytical results often report their concentrations in terms of their nitrogen content. For example, 10.0 mg/L of unionized ammonia may be reported as 8.23 mg/L NH_3–N (ammonia nitrogen); 10.0 mg/L of nitrate may be reported as 2.26 mg/L NO_3–N (nitrate nitrogen).

Typical standards for unionized ammonia (NH_3) for aquatic life are: cold water biota = 0.02 mg/L NH_3–N, chronic; warm water biota = 0.06 mg/L NH_3–N, chronic.

Conversion of organic nitrogen to ammonia may occur in samples between collection and analysis. If it is not possible to carry out the determination very soon after sampling, the sample should be refrigerated at 4 °C. Chemical preservation may be achieved by adding either 20-40 mg $HgCl_2$ or 1 mL H_2SO_4 to 1 litre of sample (to pH 2).

Ammonia can be quantitatively recovered from a sample by distillation under alkaline conditions into a solution of boric acid followed by titration with standard acid. The method is particularly suitable for the analysis of polluted surface and ground waters that contain sufficient ammonia to neutralise at least 1 mL of 0.00714 mol/L HCl. Volatile amines, if present, interfere with the acid titration. Generally, however, this method is less subject to interferences than other methods.

Kjeldahl nitrogen is defined as the sum of ammonia nitrogen and those organic nitrogen compounds converted to ammonium sulphate under the conditions of the digestion. The organic

Kjeldahl nitrogen is obtained by subtracting the value of ammonia nitrogen from the Kjeldahl nitrogen value.
The principle of the Kjeldahl method is as it follows:
The sample is heated in the presence of sulphuric acid and a catalyst, alcohol also being added to ensure removal of oxidised nitrogen. After digestion, the solution is diluted. The ammonia is determined by photometry (by indophenol blue spectrophotometry at a wavelength around 630 nm) or, if sufficiently large amounts are present, distilled from the solution and titrated.
Neither this nor any other single method can guarantee that every organic nitrogen compound will be broken down to ammonia. This is unlikely to lead to serious difficulty, but analysts should be watchful for exceptional cases. Nitrate and nitrite are removed in the procedure and so cause no important errors.
Ammonium ions are determined by spectrophotometry at 415 nm, based on their reaction with potassium tetraiodomercurate(II) in alkaline medium (Nessler's reagent - a pale solution). This pale solution becomes deeper yellow in the presence of ammonia.

$$NH_4^+ + 2\ [HgI_4]^{2-} + 4\ OH^- \rightarrow HgO{\cdot}Hg(NH_2)I \downarrow + 7\ I^- + 3\ H_2O$$

Nitrate and nitrite

Nitrate, the most highly oxidized form of nitrogen compounds, is commonly present in surface and ground waters, because it is the end product of the aerobic decomposition of organic nitrogenous matter. Ammonia and other nitrogenous materials in natural waters tend to be oxidized by aerobic bacteria, first to nitrite and then to nitrate. Therefore, all organic compounds containing nitrogen should be considered as potential nitrate sources. Significant sources of nitrate are chemical fertilisers from cultivated land and drainage from livestock feedlots, as well as domestic and some industrial waters. Organic nitrogen compounds enter the environment also from wild animal and fish excretions, and dead animals, human sewage, livestock manure.
The determination of nitrate helps the assessment of the character and degree of oxidation in surface waters, in groundwater penetrating through soil layers, in biological processes and in the advanced treatment of wastewater.
Unpolluted natural waters usually contain only minute amounts of nitrate. Both nitrite and nitrate are important nutrients for plants, but they are toxic to fish and humans at sufficiently high concentrations.
Nitrates and nitrites are very soluble, do not adsorb readily to mineral and soil surfaces, and are very mobile in the environment. Consequently, where soil nitrate levels are high, contamination of groundwater by nitrate leaching is a serious problem. High concentrations (>1–2 mg/L) of nitrate or nitrite in surface or groundwater generally indicate agricultural contamination from fertilizers and manure seepage. Unlike ammonia, nitrites and nitrates do not evaporate and remain in water until they are consumed by plants and microorganisms.
Drinking water standards for nitrate are strict because the nitrates can be reduced to nitrites in human saliva and in the intestinal tracts of infants during the first 6 months of life. Nitrite is readily absorbed into the blood. Nitrite oxidizes iron in blood hemoglobin from ferrous iron (Fe^{2+}) to ferric iron (Fe^{3+}). The resulting compound, called methemoglobin, cannot carry oxygen. The resulting oxygen deficiency is called methemoglobinemia. It is especially dangerous in infants (blue baby syndrome) because of their small total blood volume. It can be fatal for young babies.
Typical states' water quality standards for nitrate (NO_3^-) are:
- Agriculture MCLs: Nitrate, 100 mg/L NO_3–N; Nitrite, 10 mg/L NO_2–N (1 day average).
- Domestic water supply MCLs: Nitrate, 10 mg/L NO_3–N; Nitrite, 0 (sometimes 1.0) mg/L NO_2–N (1 day average).
To prevent any change in the nitrogen balance through biological activity, the nitrate determination should be started as soon as possible after sampling. If storage is necessary, samples should be kept at a temperature just above the freezing point, with or without preservatives, such as 0.8 mL

of concentrated sulphuric acid (d = 1.84 g/cm^3) per litre of sample. If acid preservation is employed, the sample should be neutralised to about pH 7 immediately before the analysis.
The determination of nitrate in water is difficult because of interferences, and much more difficult in wastewaters because of higher concentrations of numerous interfering substances.
There are different methods for nitrate determination, each one with many modifications. This fact points that there is not a method accepted as the best. Generally, the methods can be classified in 3 groups:
The first group is based on the ability of nitrate to react in acidic medium with some aromatic compounds to form colored nitro derivatives. The absorbance of the formed compound is proportional to the concentration of nitrate present, so spectrophotometry is applied. The method is best working at NO_3^- concentrations > 0.5 mg/L. Colloidally dispersed organic compounds, colored compounds and heavy metals have to be preliminary removed, for example by precipitation and / or ion exchange.
The second method is based on the direct spectrophotometry in the UV range (220 nm). Preliminary separation of organic compounds, especially detergents is needed - usually chemical coagulation (with $Al_2(SO_4)_3$) of samples is applied.
The third method is based on potentiometry and applies ion sensitive electrode. Use of special buffering solution is required in order to avoid the interferences.
Nitrite is an unstable, intermediate stage in the nitrogen cycle and is formed in water either by the oxidation of ammonia or by the reduction of nitrate. Thus, biochemical processes can cause a rapid change in the nitrite concentration in a water sample. In oxygenated natural waters, nitrite is rapidly oxidized to nitrate, so normally there is little nitrite present in unpolluted surface waters (a few tenths of a milligram per litre). Higher concentrations may be present in sewage and industrial wastes, in treated sewage effluents and in polluted waters. Measurable nitrite concentrations in groundwater are more common because of low oxygen concentrations in the soil's subsurface.
The determination should be made promptly on fresh samples to prevent bacterial conversion of the nitrite to nitrate or ammonia. In *no* case should acid preservation be used for samples to be analysed for nitrite. Short-term preservation for 1 to 2 days is possible by the addition of 40 mg mercuric ion as $HgCl_2$ per litre of sample, with storage at 4 °C.
The determination is based on the reaction of nitrite, in strongly acid medium, with sulphanilamide. The resulting diazo compound is coupled with *N*-(1-naphthyl)-ethylenediamine dihydrochloride to form an intensely red coloured azo-compound. The absorbance of the dye is proportional to the concentration of nitrite present. The method is applicable in the range of 0.01-1.0 mg/L nitrite nitrogen. Samples containing higher concentrations must be diluted.
There are very few known interferences at concentrations less than 1000 times that of the nitrite. However, the presence of strong oxidants or reductants in the samples will readily affect the nitrite concentrations. High alkalinity (> 600 mg/L as $CaCO_3$) will give low results owing to a shift in pH.

Phosphorus

Phosphorus is a common element in igneous and sedimentary rocks and in sediments but it tends to be a minor element in natural waters because most inorganic phosphorous compounds have low solubility.
The natural background of total dissolved phosphorus has been estimated to be about 0.025 mg P/L; that of dissolved phosphates about 0.01 mg P/L. The solubility of phosphates increases at low pH and decreases at high pH. Particulate phosphorus (sorbed on sediments and insoluble phosphorous compounds) is about 95% of the total phosphorus in most cases. Dissolved concentrations are generally in the range of 0.01–0.1 mg/L and seldom exceed 0.2 mg/L. The environmental behavior of phosphorus is largely governed by the low solubility of most of its inorganic compounds, its strong adsorption to organic components of soil particles and clay minerals and oxides of aluminum and iron, and the fact that it is an essential nutrient for most life forms - animal, plant, and microbial. In carbonate soils, dissolved phosphorus can react with

carbonate to form the mineral precipitate hydroxyapatite (calcium phosphate hydroxide), $Ca_{10}(PO_4)_6(OH)_2$.

Because of its low dissolved concentrations, phosphorus is usually the limiting nutrient in natural waters. The dissolved phosphorous concentration is often low enough to limit algal growth. Because phosphorus is essential to metabolism, it is always present in animal wastes and sewage. Too much phosphorus in wastewater effluent is frequently the main cause of algal blooms and other precursors of eutrophication.

The critical level of inorganic phosphorus for forming algal blooms can be as low as 0.01–0.005 mg/L under summer growing conditions but is more frequently around 0.05 mg/L. To control eutrophication, EPA recommends that total phosphates should not exceed 50 mg/L (as phosphorus) in a stream where it enters a lake or reservoir, or 100 mg/L in streams that do not discharge directly into lakes or reservoirs.

Phosphorous compounds are used for corrosion control in water supply and industrial cooling water systems. Certain organic phosphorous compounds are used in insecticides. Perhaps the major commercial uses of phosphorous compounds are in fertilizers and in the production of synthetic detergents. The widespread use of detergents instead of soap makes a major contribution to the available phosphorus in domestic wastewater. As a consequence of detergent use, the concentration of phosphorus in treated municipal wastewaters has increased from 3 to 4 mg/L in predetergent days, to the present values of 15–20 mg/L.

Phosphorus in the environment is cycled between organic and inorganic forms. Phosphorus has no such global redistribution mechanism like nitrogen; the closest approaches are by bird migration and international shipping of fertilizers.

Organic compounds containing phosphorus are found in all living matter. Phosphorous exists in anionic forms ($H_2PO_4^-$ / HPO_4^{2-}), which are not subject to retention by exchange reactions. Phosphate anions are largely immobilized in the soil by the formation of insoluble compounds, chiefly iron, calcium, and aluminum phosphates, and by adsorption to soil particles.

Orthophosphate (PO_4^{3-}) is the only form readily used as a nutrient by most plants and organisms. The two major steps of the phosphorous cycle, conversion of organic phosphorus to inorganic phosphorus and back to organic phosphorus, are both bacterially mediated. Conversion of insoluble forms of phosphorus, such as calcium phosphate, $Ca(HPO_4)_2$, into soluble forms, principally PO_4^{3-}, is also carried out by microorganisms. Organic phosphorus in the tissues of dead plants and animals and in animal waste products is converted bacterially to PO_4^{3-}. The PO_4^{3-} thus released to the environment is taken up again into plant and animal tissue.

Reducing (anaerobic) conditions, as in water-saturated soil, may increase phosphorous mobility because insoluble ferric iron, to which phosphorus is strongly adsorbed, is reduced to soluble ferrous iron, thereby releasing adsorbed phosphorus. In acid soils, aluminum and iron phosphates precipitate, while in basic soils, calcium phosphates precipitate. The immobilization of phosphorus to water is therefore dependent on soil properties, such as pH, aeration, texture, cation-exchange capacity, the amount of calcium, aluminum, and iron oxides present, and the uptake of phosphorus by plants.

In surface waters, phosphorous concentrations are influenced by the sediments, which serve as a reservoir for adsorbed and precipitated phosphorus. Sediments are an important part of the phosphorous cycle in streams. Bacteria-mediated exchange between dissolved and sediment-adsorbed forms plays a role in making phosphorus available for algae and therefore contributes to eutrophication.

Dissolved phosphate species exhibit the pH-dependent equilibria (see Figure 8.3.):

$$H_3PO_4 \Leftrightarrow H_2PO_4^- + H^+ \Leftrightarrow HPO_4^{2-} + 2H^+ \Leftrightarrow PO_4^{3-} + 3H^+$$

As pH becomes higher, the equilibrium shifts increasingly to the right.

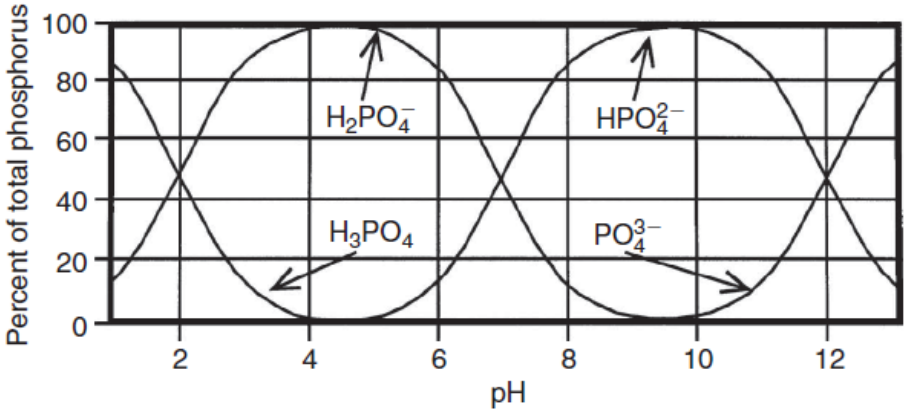

Figure 8.3. pH dependence of phosphate species

Compounds containing phosphorus that are of interest to water quality include orthophosphates (all contain PO_4^{3-}), trisodium phosphate, Na_3PO_4, disodium phosphate, Na_2HPO_4, monosodium phosphate (NaH_2PO_4), diammonium phosphate $(NH_4)_2HPO_4$. Orthophosphates are soluble and (as already mentioned) are considered the only biologically available form. In the environment, hydrolysis slowly converts polyphosphates /sodium hexametaphosphate, $Na_3(PO_4)_6$; sodium tripolyphosphate, $Na_5P_3O_{10}$; tetrasodium pyrophosphate, $Na_4P_2O_7$; organic phosphate (biodegradation or oxidation of organic phosphates releases orthophosphates)/ to orthophosphates.

Water samples have to be cooled and analyzed in 48 hours.

Analytical methods measure orthophosphates. To measure total phosphate, all inorganic forms of phosphate are chemically converted to orthophosphates (hydrated forms). Organically combined phosphorus and all organic phosphates are first converted to orthophosphate. To release phosphorus from combination with organic matter, a digestion or wet oxidation technique is necessary. The least tedious method, wet oxidation with potassium peroxydisulphate, is often recommended.

Orthophosphate reacts with ammonium molybdate to form molybdophosphoric acid. This is transformed by reductants to the intensely coloured complex known as molybdenum blue suitable for using photometric determination. The method based on reduction with ascorbic acid is preferable. Addition of potassium antimonyl tartrate increases the coloration and the reaction velocity at room temperature. For concentrations of phosphate below 20 µg/L, the recommended procedure involves extraction of the molybdenum blue complex from up to 200 mL of water into a relatively small volume of hexanol, so that a considerable increase in sensitivity is obtained. The method is relatively free from interferences. Changes in temperature of ± 10 °C do not affect the result.

Silica

After oxygen, silicon is the most abundant element in the earth's crust. It is a major constituent of igneous and metamorphic rocks, of clay minerals such as kaolin, and of feldspars and quartz. Although crystalline silica is a major constituent of many igneous rocks and sandstones, it has low solubility and is therefore of limited importance as a source of silica in water. It is likely that most of the dissolved silica in water originates from the chemical breakdown of silicates in the processes of metamorphism or weathering.

Silica always present in surface and groundwaters. It exists in water in dissolved, suspended and colloidal states. Dissolved forms are represented mostly by silicic acid, products of its dissociation and association, and organosilicon compounds. Reactive silicon (principally silicic acid H_4SiO_4 but usually recorded as dissolved silica (SiO_2) or sometimes as silicate) mainly arises from chemical weathering of siliceous minerals.

The concentration of silica in most natural waters is in the range 1-30 mg/L. Concentrations in ground and volcanic waters are higher, and thermal waters may reach concentrations up to 1 g/L or more. In the weakly mineralised waters of arctic regions, as well as in marsh and other coloured waters, the reactive silica may account for 50 per cent of the total dissolved solids.
Silica may be discharged into water bodies with wastewaters from industries using siliceous compounds in their processes such as potteries, glass works and abrasive manufacture.
Samples for silica determination should be stored in plastic bottles to prevent leaching of silica from glass. Samples should be passed through a membrane filter of 0.45 µm pore size as soon as possible after sample collection and should be stored at 4 °C without preservatives. Analysis should be performed within 1 week of sample collection.
Forms of silicon and total silica are converted to the reactive form prior to analysis using a colourimetric method. The determination is based on the following principle: Ammonium molybdate at a pH of approximately 1.2 reacts with silica and phosphate to form heteropoly acids. Addition of oxalic acid destroys any molybdophosphoric acid but not the molybdosilicic acid. The yellow molybdosilicic acid is reduced by aminonaphtholsulphonic acid to heteropoly blue. The blue colour of the heteropoly blue is more intense than the yellow colour of the molybdosilicic acid, so that this reaction increases the sensitivity of the method. Silica can be measured at either 815 nm or 650 nm. The sensitivity at 650 nm is approximately half that at 815 nm.
Both the apparatus and the reagents may contribute silica. The use of glassware should be avoided as far as possible and only reagents low in silica should be used. A blank determination should be carried out to correct for silica introduced from these sources.
Tannin, large amounts of iron, colour, turbidity, sulphide and phosphate are potential sources of interference. The treatment with oxalic acid eliminates the interference from phosphate and decreases the interference from tannin. Photometric compensation may be used to cancel interference from colour or turbidity in the sample.
Atomic emission spectrophotometry can also be used.

The above lecture is based mainly on the following publications: Stumm and Morgan, 1996; Chapman, 1996; Bartram and Ballance, 1996; Weiner, 2007; United Nations Environment Programme, 2023.

9. Water micro-components (inorganic) - natural and polluting concentrations

Water micro-components are whose natural concentrations in pure water are less than 1 mg/L.

Metals

General principles

Generally, trace amounts of metals are always present in freshwaters from the weathering of rocks and soils. The ability of a water body to support aquatic life, as well as its suitability for other uses, depends on many trace elements. Some metals, such as Mn, Zn and Cu, when present in trace concentrations are important for the physiological functions of living tissue and regulate many biochemical processes. The same metals, however, discharged into natural waters at increased concentrations in sewage, industrial effluents or from mining operations and other industrial activities can have severe toxicological effects on humans and the aquatic ecosystem. This situation is aggravated by the lack of natural elimination processes for metals. As a result, metals shift from one compartment within the aquatic environment to another, including the biota, often with detrimental effects. Where sufficient accumulation of the metals in biota occurs through food chain transfer, there is also an increasing toxicological risk for humans. As a result of adsorption and accumulation, the concentration of metals in bottom sediments is much higher than in the water above and this sometimes causes secondary pollution problems.
Dissolved trace element contents are very difficult to analyse correctly since samples are easily contaminated and analytical detection limits are sometimes higher than natural levels. The values

given in Table 9.1 are the estimates found in the scientific literature for uncontaminated waters, resulting from utmost care in sampling, water treatment, and analysis.

Table 9.1. World average values of trace elements carried in solution by major unpolluted rivers

	Al	As	B	Cd	Cr	Co	Cu	F	Fe	Mn	Mo	Ni	Pb	Sr	Zn
Dissolved (µg/L)	40	1.0	30	0.001	0.1	0.1	1.4	100	50	10	0.8	0.4	0.04	100	0.2

To discuss their chemical behavior, the elemental metals may be divided into three general classes:

1. Alkali metals: Li, Na, K, Rb, Cs, and Fr (periodic table group 1A).
2. Alkaline metals: Be, Mg, Ca, Sr, Ba, and Ra (periodic table group 2A).
3. Metals not in the alkali or alkaline groups include the transition metals (all the group B periodic table metals), the metals and metalloids* in groups 3A through 6A, and metals whose classifications are not based primarily on periodic table groups, the so-called trace or heavy metals**.

* Metalloids are those elements in periodic table groups 3A through 6A that have electrical and chemical properties intermediate between those of metals and nonmetals. They are B, Si, Ge, As, Sb, Te, and Po. For regulatory purposes, it is sometimes useful to group metals and metalloids together, as when they share the same analytical method (e.g., ICP, ion-coupled plasma spectroscopy).

** The term ‘‘heavy metals’’ is often encountered in texts and reports, usually meaning metals with atomic numbers equal to or greater than Cu (at. no. 29), especially metals exhibiting toxicity. However, the term ‘‘heavy metals’’ has no precise definition and its use is inconsistent. Another designation often used is trace metals, generally used for those metals found in the earth’s crust with average concentrations less than 1%. Nearly all the metals are included in this class, the exceptions (with average crustal concentrations greater than 1%) being Na, K, Ca, Mg, Fe, and Al.

Metals in natural waters can exist in truly dissolved, colloidal and suspended forms. The proportion of these forms varies for different metals and for different water bodies. Consequently, the toxicity and sedimentation potential of metals change, depending on their forms. The toxicity of metals in water depends on the degree of oxidation of a given metal ion together with the forms in which it occurs. For example, the maximum allowable concentration of Cr (VI) in many countries is 0.001 mg/L whereas for Cr (III) it is 0.5 mg/L, since the latter forms low soluble compounds. As a rule, the ionic form of a metal is the most toxic form. However, the toxicity is reduced if the ions are bound into complexes with, for example, natural organic matter such as fulvic and humic acids. Under certain conditions, metallo-organic, low-molecular compounds formed in natural waters exhibit toxicities greater than the uncombined forms. An example is the highly toxic alkylderivatives of mercury (e.g. methylmercury) formed from elemental mercury by aquatic micro-organisms.

The assessment of metal pollution is an important aspect of most water quality assessment programmes. The Global Environment Monitoring System programme (GEMS/WATER) for fresh water includes ten metals: Al, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Zn. Arsenic and Se (which are not metals) are also included (Table 9.2). The United States Environmental Protection Agency (US EPA) considers eight trace elements as high priority: As, Cd, Cu, Cr, Pb, Hg, Ni and Zn. Most other countries include the same metals in their priority lists. However, other highly toxic metals such as Be, Tl, V, Sb, Mo should also be monitored where they are likely to occur.

The absence of iron and manganese in some priority lists results from their frequent classification as major elements. The occurrence of iron in aqueous solution is dependent on environmental conditions, especially oxidation and reduction. Flowing surface water, that is fully aerated, should not contain more than a few micrograms per litre of uncomplexed dissolved iron at equilibrium in the pH range 6.6 to 8.5. In groundwater, however, much higher levels can occur. In anoxic groundwaters with a pH of 6 to 8, ferrous iron (Fe^{2+}) concentrations can be as high as 50 mg/L and concentrations of 1 to 10 mg/L are common.

Table 9.2. Variables included in the GEMS/WATER monitoring programme

Variable	Baseline stations		Global river flux stations
	Streams	Headwater lakes	
Basic monitoring			
Water discharge/level	X		X[2]
Total suspended solids	X		X
Transparency		X	
Temperature	X	X	X
pH	X	X	X
Conductivity	X	X	X
Dissolved oxygen	X	X	X
Calcium	X	X	X
Magnesium	X	X	X
Sodium	X	X	X
Potassium	X	X	X
Chloride	X	X	X
Sulphate	X	X	X
Alkalinity	X	X	X
Nitrate plus nitrite	X	X	X
Ammonia	X	X	X
Total phosphorus, unfiltered	X	X	X
Total phosphorus, dissolved	X	X	X
Reactive silica	X	X	X
Chlorophyll *a*	X	X	X
Expanded monitoring			
Total phosphorus, unfiltered			X
Dissolved organic carbon	X	X	X
Particulate organic carbon			X
Dissolved organic nitrogen	X	X	X
Particulate organic nitrogen			X
Aluminium	X[3]	X[3]	X[4]
Iron	X[3]	X[3]	X[4]
Manganese	X[3]	X[3]	X[4]
Arsenic[5]	X[3]	X[3]	X[4]
Cadmium[5]	X[3]	X[3]	X[4]
Chromium			X[4]
Copper			X[4]
Lead[5]	X[6]	X[6]	X[4]
Mercury[5]	X[6]	X[6]	X[4]
Selenium			X[4]
Zinc[5]	X[3]	X[3]	X[4]
Total hydrocarbons			X[7]
Total polyaromatic hydrocarbons			X[7]
Total chlorinated hydrocarbons			X[7]
Dieldrin			X[7]
Aldrin			X[7]
Sum of DDTs[5]	X	X	X[7]
Atrazine	X	X	X[7]
Sum of PCBs[5]			X[7]
Phenols			X[7]

Explanations to Table 9.2:
[1] The selection of variables for trend monitoring is related to different pollution issues; [2] Continuous monitoring; [3] Dissolved only; [4] Dissolved and particulate; [5] Included as contaminant monitoring at baseline stations; [6] Total; [7] Unfiltered water samples

The iron originates by solution at sites of either reduction of ferric hydroxides or oxidation of ferrous sulphide and the process is strongly influenced by microbiological activity. Reduced groundwater is clear when first brought from a well but becomes cloudy, and then orange in colour, as oxidation immediately occurs with the precipitation of ferric hydroxide. Consequently, obtaining representative samples for iron determination from groundwaters presents special difficulties. Similar problems can be found in anoxic waters for Mn^{2+}, although the concentrations reached are usually ten times less than ferrous iron.

As mentioned above, metals and metal-containing compounds in natural waters may be in dissolved, colloidal, or particulate forms, depending on water quality parameters of pH, redox potential, and the presence of other dissolved species such as sulfide or carbonate which can form compounds with metal ions.

Dissolved forms are:

- Cations: Ca^{2+}, Fe^{2+}, K^{+}, Al^{3+}, Ag^{+}, etc.
- Complexes: $[Zn(OH)_4]^{2-}$, $[Au(CN)_2]^{-}$, $[Ca(P_2O_7)]^{2-}$, PuEDTA, etc.
- Organometallic compound: $Hg(CH_3)_2$, $B(C_2H_5)_3$, $Al(C_2H_5)_3$, carbonate and hydroxy complexes, etc.

Dissolved forms of metals move with surface water and groundwater flows.

Particulate forms are:

- Mineral sediments - these may be colloid size or larger. Metals pose the greatest environmental risks when particulate metals encounter environmental conditions that increase their solubility.
- Precipitated oxides, hydroxides, sulfides, carbonates, silicates, etc. These may be particles of colloid size or larger. Colloids remain suspended in water and are mobilized by water movement. Larger particles may settle out and require stronger flows to move them as sediments. Metals in particulate form can be transported with sediments by wind and in moving water.
- Cations and complexes adsorbed to mineral sediments (clays, oxides, hydroxides, sulfides, carbonates, silicates, etc.) and organic matter. Both dissolved and particulate forms of metals may adsorb to organic soil solids, where they can be immobilized or carried along with the solids. Sorption processes may be reversible to some degree, resulting in a retardation of dissolved metal movement relative to water flow, or irreversible, resulting in immobilization of metal species, except for erosion mechanisms.

The behavior of metals in natural waters may be described in terms of how they become distributed between dissolved and solid species. Metal species undergo continuous changes between dissolved, precipitated, and adsorbed-to-sediment forms. The rates of adsorption, desorption, and precipitation processes depend on pH, redox potential, water chemistry, and the composition of bottom and suspended sediments. Adsorption of dissolved metal species to sediments removes the metal from the water column and stores it in the sediments, where it is less biologically available. Desorption returns the metal to the water column, where it becomes biologically available again and where water flow may carry the metal to a new location where sorption and precipitation can re-ocur. Metals may be desorbed from sediments if the water undergoes increases in salinity, decreases in redox potential, or decreases in pH.

In the water environment, nonradioactive metals are of greatest environmental and health concern when in dissolved forms, where they are more mobile and more biologically available than are particulate forms, although ingestion and inhalation of particulates containing metals also can be a serious health hazard. Radioactive metals are hazardous because of their ionizing emissions as well as their chemical toxicity and may be harmful in both dissolved and particulate forms, even without metal species entering the body.

General behavior of dissolved metals in water

It can be misleading to think in terms of the solubility of elemental metals. For example, to say that ‘‘iron is more soluble under reducing conditions than under oxidizing conditions,’’ does not call attention to the fact that it is not elemental iron that is more soluble; it is the iron compounds that can be formed which may (or may not) be more soluble under reducing conditions.

Reactions of metal cations with water (hydrolysis) are the usual criteria for assessing whether a metal is soluble or insoluble under certain redox and pH conditions. When a metal such as iron is said to be insoluble under oxidizing conditions and soluble under reducing conditios, what actually is meant is that the compounds formed by reaction of the metal cation with water under oxidizing conditions are insoluble; under reducing conditions iron does not hydrolyze in water and can remain as a dissolved cation (with a hydration shell). The same is true for pH conditions; metals tend to be less soluble at high pH because their cations often react with hydroxide ions in high pH water to form low-solubility hydroxides and oxides. At low pH, where hydroxide concentrations are low, they may remain as soluble hydrated cations.

The simplest form of a dissolved metal is an elemental cation, such as Fe^{3+} or Zn^{2+}.

However, elemental cations cannot exist as such in water solutions. Any charged species in solution will interact with other charged or polar species because of electrical forces. Because water molecules are polar, metal cations always attract a multilayered hydration shell of water molecules by electrostatic attraction of the negative end of the water molecules (the oxygen end) to the positive charge of the cation, as described by Equation (9.1):

$$Me^{n+} + x\ H_2O \rightarrow Me(H_2O)_x^{n+} \qquad (9.1)$$

where: Me is a metal cation, n is the number of positive charges on the cation, x is the maximum number of water molecules in the innermost hydration shell (x is 6 for most cations).

Hydrated metal ions can behave as acids by releasing protons (H^+) from their water ligands that then become attached to the surrounding free H_2O molecules, forming acidic hydrated protons. The stronger the bond between the water ligand and the metal cation, the more readily a proton is released to surrounding water molecules and the more acidic is the hydrated metal cation.

$$Me(H_2O)_6^{n+} + H_2O \Leftrightarrow Me(H_2O)_5^{(n-1)+} + H_3O^+ \qquad (9.2)$$

$$Me(H_2O)_5^{(n-1)+} + H_2O \Leftrightarrow Me(H_2O)_4^{(n-2)+} + H_3O^+ \qquad (9.3)$$

For example, with Fe^{3+}, it takes a three proton transfer steps to form neutral ferric hydroxide:

$$Fe(H_2O)_3^{3+} + H_2O \Leftrightarrow Fe(H_2O)_2OH^{2+} + H_3O^+ \qquad (9.4)$$

$$Fe(H_2O)_2OH^{2+} + H_2O \Leftrightarrow Fe(H_2O)_2(OH)_2^{+} + H_3O^+ \qquad (9.5)$$

$$Fe(H_2O)_2(OH)_2^{+} + H_2O \Leftrightarrow Fe(OH)_{3(s)} + H_3O^+ \qquad (9.6)$$

The overall reaction is

$$Fe(H_2O)_3^{3+} + 3\ H_2O \Leftrightarrow Fe(OH)_{3(s)} + 3\ H_3O^+ \qquad (9.7)$$

Influence of pH on the solubility of metals

All the reactions (Equations (9.2) through (9.7)) are reversible, with H_3O^+ on the right side. This means that the equilibria of these reactions shift to the left if the concentration of H_3O^+ is increased (by adding more acid) and to the right if it is decreased (by adding a base). Thus, the formation of metal hydroxides by hydration of metal cations is sensitive to the solution pH. Considering the overall reaction, Equation 9.7, we see that lowering the pH (increasing the concentration of H_3O^+) shifts the equilibrium of Equation 9.7 to the left, tending to dissolve any solid metal hydroxide that has precipitated. Raising the pH (increasing the concent ration of OH^-) consumes H_3O^+ and shifts the equilibrium of Equation 9.7 to the right, precipitating more insoluble metal hydroxide. Thus, one may say that the metal becomes more soluble at lower pH and less soluble at higher pH, even

though what actually occurs is that the hydrated metal forms less soluble hydroxide at higher pH. However, if the pH is raised too high, some of the precipitated metal hydroxides can redissolve (see Figure 9.1). At high pH values, a metal hydroxde may form complexes with OH^- anions to become a negatively charged ion having increased solubility. For example, precipitated $Fe(OH)_3$ can react with OH^- anions as follows:

$$Fe(OH)_{3(s)} + OH^- \Leftrightarrow Fe(OH)_4^- \quad (9.9)$$

$$Fe(OH)_4^- + OH^- \Leftrightarrow Fe(OH)_5^{2-} \quad (9.10)$$

Negatively charged polyhydroxide anions are more soluble because their ionic charge attracts them strongly to polar water molecules. As shown in Figure 9.1, the high value of pH, where solubility begins to increase again, varies from metal to metal. Alkaline water provides a buffer against pH changes. In a lkaline water, the tendency of metals to make water acidic is diminshed.

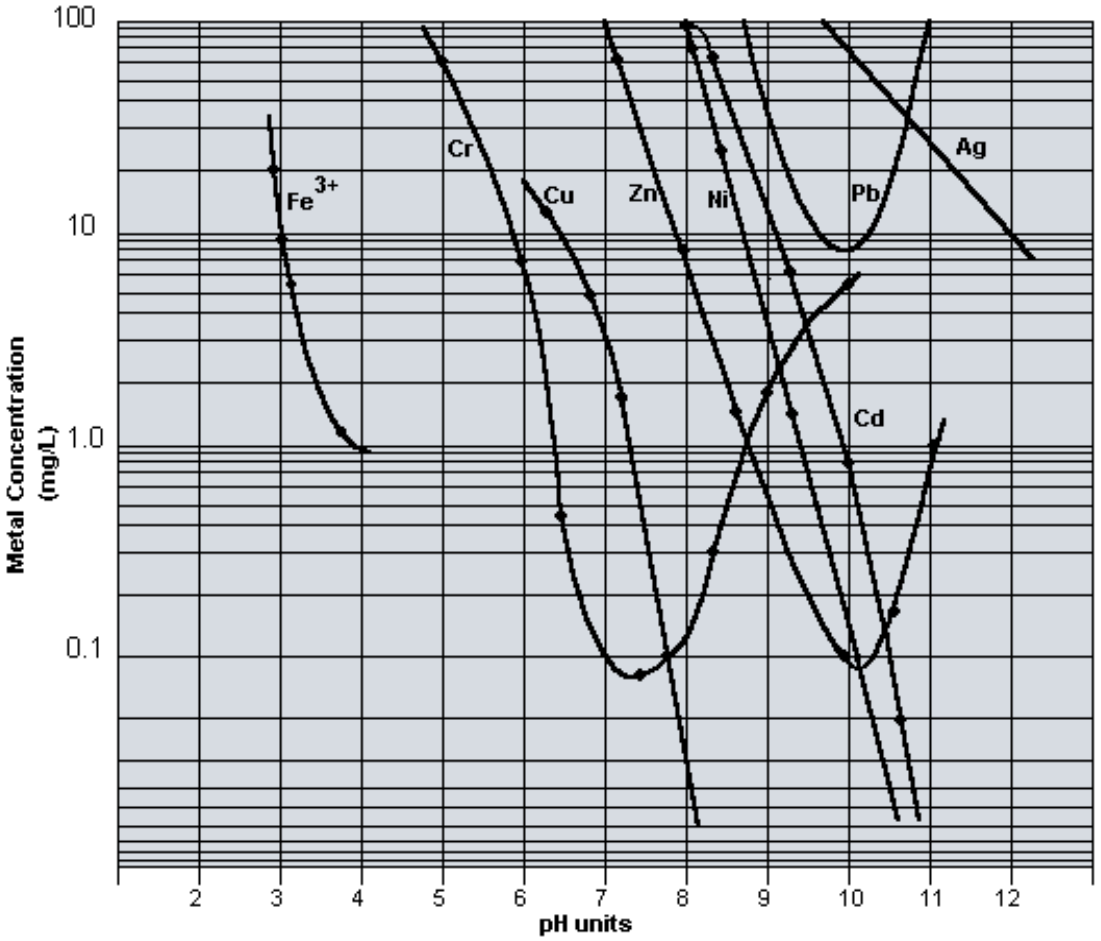

Figure 9.1. Theoretical solubilities of some metals versus pH.

Influence of redox potential on the solubility of metals

The redox potential influences metal solubility because it can influence the electron structure of metal atoms and, thereby, the metal's ability to react with other substances to form compounds of varying solubilities. However, the redox potential may also influence other substances, such as sulfate, in a manner more significant than its effect on metal species. For example, the oxidation state of lead is not particularly sensitive to redox changes within common environmental conditions. However, if sulfate is present, a zero or negative value for the redox potential (anaerobic conditions) will cause the reduction of sulfate to sulfide and dissolved lead speces will precipitate as insoluble lead sulfide. In the absence of sulfate or sulfide, the lead species may remain relatively soluble.

It is useful to classify metals as redox sensitive or insensitive, according to their redox-dependent solubility.

Redox-sensitive metals: Cr, Cu, Hg, Fe, Mn

Redox-sensitive metals are those that can undergo changes in oxidation state (valence shell electron structure) under common environmental conditions, often resulting in changes in solubility because of the formation of new compounds by reaction with water.

Under oxidizing conditions and pH greater than about 5.5, redox-sensitive metals react with water to form low solubility hydroxides and oxides. For example, under oxidizing conditions, concentrations of dissolved iron are limited by precipitation of insoluble $Fe(OH)_3$, of dissolved manganese - by precipitation of insoluble MnO_2, of dissolved chromium - by precipitation of insoluble $Cr(OH)_3$, and of dissolved copper - by precipitation of an insoluble cupric ferrite mineral $CuFe_2O_4$.

Under reducing conditions and pH less than 7, with no sulfide present, iron exists as the soluble cation Fe^{2+}. Above pH 7, $Fe(OH)_2$, is formed that is about 105 times more soluble than $Fe(OH)_3$. The other redox-sensitive metals behave similarly under reducing conditions, being present as either cation or a relatively soluble compound.

Redox-insensitive metals: Al, Ba, Cd, Pb, Ni, Zn

These metals do not change their oxidation state within the redox conditions common in the environment. In their normal oxidation state, these metals do not react strongly with water to form insoluble oxides and hydroxides. Under oxidizing conditions and the absence of anions with which they can react, they tend to remain as dissolved cations. In the presence of reactants other than water, they can form carbonates, phosphates, sulfates, and oxides / hydroxides whose solubilities depend more on pH than on redox potential. Although, reducing conditions have little direct effect on these metals as cations, under reducing conditions, with sufficient sulfide present, they all can form low soluble sulfides.

Redox-sensitive metalloids: As, Se

Arsenic and selenium behave oppositely to the redox-sensitive metals. They are more soluble under oxidizing conditions than under reducing conditions. Under oxidizing conditions, they form the oxygen anions - arsenate (AsO_4^{3-}) and selenite (SeO_3^{2-}). The produced species react with Fe, Mn, and Pb cations to form moderately soluble compounds. Under reducing conditions, selenium forms insoluble elemental selenium and iron selenide ($FeSe_2$). Arsenic forms sulfides of very low solubility.

In conclusion we have to stress that:

1. Only polyvalent cations (e.g., Fe^{3+}, Zn^{2+}, Mn^{2+}, and Cr^{3+}) have large enough charges to attract water molecules strongly enough to act as acids, by causing the release of H^+ from water molecules in the hydration sphere. Monovalent cations, such as Na^+, do not act as acids at all.
2. The interactions of metal cations with water, Equations (9.2) through (9.7), cause the solubility of metal species in water to be dependent on pH and redox potential.

- Low pH (high H_3O^+ concentration and high acidity) increases metal solubility by shifting the equilibria of Equations (9.2) through (9.7) to the left, decreasing the formation of less soluble metal polyhydroxides.
- High pH (low H_3O^+ concentration and low acidity) decreases metal solubility by shifting the equilibria of Equations (9.2) through (9.7) to the right, increasing the formation of less soluble metal polyhydroxides.
- Low redox potentials (reducing conditions, low-to-zero dissolved oxygen levels, where electron donors are more common than electron acceptors) increase the solubility of many metals (by promoting lower oxidation numbers for metal cations (lower positive charge, e.g., Fe^{2+} rather than Fe^{3+}). For cations with lower positive charge, the equilibria of (9.2) through (9.7) are maintaned more strongly to the left, resulting in less formation of low-solubility polyhydroxides.
- High redox potentials (oxidizing conditions, high DO levels, where electron acceptors are more common than electron donors) decrease the solubility of many metals by promoting higher oxidation numbers for metal cations (higher positive charge, e.g., Fe^{3+} rather than Fe^{2+}). For

cations with higher positive charge, the equilibria of Equations (9.2) through (9.7) are maintained more strongly to the right, resulting in greater formation of low-solubility polyhydroxides.
3. The presence of dissolved species such as sulfide or carbonate, which form low-solubility compounds with metal cations, can largely invalidate the above generalizations by competing with hydroxide formation.

Sampling and measurement

The concentration of different metals in waters varies over a wide range (0.1-0.001 µg/L) at background sites and can rise to concentrations which are dangerous for human health in some water bodies influenced by human activities. Dissolved metal concentrations are particularly difficult to measure due to possible contamination during sampling, pre-treatment and storage. As a result, large differences may be observed between analyses performed by highly specialised teams. As dissolved metals occur in very low concentrations, it is recommended that metals are also measured in the particulate matter.
The variety of metal species is the main methodological difficulty in designing metal-based monitoring programmes. When checking compliance with water quality guidelines, as an example, metals should always be determined in the same forms as those for which the guidelines or standards are set. If the quality standards refer to the dissolved forms of metals, only dissolved forms should be monitored. More than 50 per cent of the total metal present (and up to 99.9 per cent) is usually adsorbed onto suspended particles; this is particularly relevant when assessing metal discharge by rivers. Consequently, monitoring and assessment programmes such as GEMS/WATER include the determination of both total (unfiltered) and dissolved (filtered through 0.45 µm filter) concentrations of metals when assessing the flux of contaminants into the oceans.
Samples for metal analysis are usually pre-treated by acidification prior to transportation to the laboratory to suppress hydrolysis, sorption and other processes which affect concentration. However, such preservation techniques destroy the equilibrium of the different forms of the metals, and can be used only for determination of total concentrations. For determination of dissolved metals, it is recommended that the samples are filtered through 0.45 µm pore diameter membrane filters (using ultra-clean equipment in a laminar flow hood). The filtered sample should be acidified for preservation. Removal of the particulate matter by filtration prevents dissolution or desorption of trace metals from the particulate phase to the dissolved phase within the sample. A very high degree of cleanliness in sample handling at all stages of collection and analysis is necessary (such as, use of ultra-pure acids to clean glassware or PTFE (polytetrafluoroethene) utensils, use of a laminar flow hood for sample manipulation and special laboratories with air filtration and purification systems) to avoid contamination and incorrect results.
The low concentrations of metals in natural waters necessitate determination by instrumental methods. Photometric methods, sometimes in combination with extraction, are the oldest and most inexpensive techniques. However, as these have high detection limits, they can only be used for analysis of comparatively polluted waters. Atomic absorption methods are the most widely used. Atomic absorption with flame atomisation is the most simple and available modification of this method, but application for direct determination of metals is possible only if concentrations exceed 50 µg/L. In other cases, it is necessary to use preconcentration. Atomic absorption with electrothermal atomisation allows direct determination of metals at virtually the full range of concentrations typically found in freshwaters. However, this is a more expensive method requiring specially trained personnel. Even with this method special measures may be needed to eliminate matrix effects. Inductively coupled plasma atomic emission spectrometry is able to determine a large number of elements simultaneously, in wide range of quantifiable determinations.
A metal water quality "good practice" may be written for the dissolved, potentially dissolved, total recoverable, or total forms.
- Dissolved: Sample is filtered on site immediately after or, preferably, during collection through a 0.45 mm filter and is then acidified to pH 2 for preservation before analysis. Acidification prevents

precipitation of any dissolved metal before analysis. This procedure omits from the analysis metals adsorbed on suspended sediments. It is essential that the sample be filtered immediately after or during collection. A true measure of dissolved metals in the source water cannot be obtained after transporting an unfiltered sample to a laboratory. An unfiltered sample collected for dissolved metals cannot be acidified for preservation because the lower pH could cause some precipitated metals in the original sample to dissolve. It cannot be transported without acidification because potential gain or loss of dissolved CO_2 or O_2 can result in changes in pH or redox potential that could dissolve or precipitate metals en route, resulting in a measurement not representative of the source water.
- Potentially dissolved: Sample is acidified to pH 2, held for 72–90 h, then filtered through a 0.45 mm filter and analyzed. This procedure is intended to simulate the possibility that metals bound in suspended sediments might be transported into more acidic environmental conditions and partially dissolve. It measures the metals dissolved at the time of sampling, in addition to a portion of the metals initially bound to suspended sediments and released during the holding period at low pH.
- Total recoverable: Sample is acidified to pH 2 and analyzed without filtering. This procedure measures all metals, dissolved and initially bound to suspended sediments. Some ‘‘unrecoverable’’ metals may remain as suspended mineral sediments or strongly sorbed to sediments and not be analyzed.
- Total: Sample is ‘‘digested’’ in an acidic solution until essentially all the metals present are extracted into soluble forms for analysis.

Below is paid attention to the 3 metals that are the most often found in the natural water.

Aluminium
Although aluminium is among the most abundant elements in the earth’s crust, it is present in only trace concentrations in natural waters. Due to the fact that it occurs in many rocks, minerals and clays, aluminium is present in practically all surface waters, but its concentration in waters at nearly neutral pH rarely exceeds a few tenths of a milligram per litre because of the fact that at this pH values low soluble $Al(OH)_3$ is formed. In addition, in treated water or wastewater, it may be present as a residual from the alum coagulation process. The median concentration of aluminium in river water is reported to be 0.24 mg/L with a range of 0.01 to 2.5 mg/L.
Sample handling
Because aluminium may be lost from solution to the walls of sample containers, samples should be acidified with concentrated nitric acid till pH less than 2. If only soluble aluminium is to be determined, a portion of unacidified sample has to be filtered through a 0.45 μm membrane filter, and after discarding the first 50 mL of filtrate, the succeeding filtrate has to be used, after acidification, for transport and determination. Filter paper, absorbent cotton or glass wool have not be used for filtering any solution that is to be tested for aluminium because these materials will remove most of the soluble aluminium.
Spectrophotometry can be used for analysis, based on the fact that dilute aluminium solutions, buffered to a pH of 6.0, at addition of Eriochrome cyanine R dye, produce a red to pink complex with a maximum absorption at 535 nm. Alternatively, ICP can be used.

Iron
Iron is an abundant element in the earth’s crust, but exists generally in minor concentrations in natural water systems. The form and solubility of iron in natural waters are strongly dependent upon the pH and the oxidation-reduction potential of the water. Iron is found in the +2 and +3 oxidation states. In a reducing environment, ferrous (+2) iron is relatively soluble. An increase in the oxidation-reduction potential of the water readily converts ferrous ions to ferric (+3) and allows ferric iron to hydrolyse and precipitate as hydrated ferric oxide. The precipitate is highly insoluble. Consequently, ferric iron is found in solution only at a pH of less than 3. The presence of inorganic or organic complex-forming ions in the natural water system can enhance the solubility of both ferrous and ferric iron.

Surface waters in a normal pH range of 6 to 9 rarely carry more than 1 mg of dissolved iron per litre. However, subsurface water removed from atmospheric oxidative conditions and in contact with iron-bearing minerals may readily contain elevated amounts of ferrous iron. For example, in ground-water systems affected by mining, the quantities of iron routinely measured may be several hundred milligrams per litre.
It is the formation of hydrated ferric oxide that makes iron-laden waters objectionable. This ferric precipitate imparts an orange stain to any settling surfaces, including laundry articles, cooking and eating utensils and plumbing fixtures. Additionally, yellow-orange colloidal suspensions of the ferric precipitate can be formed. This coloration, along with associated tastes and odour, can make the water undesirable for domestic use when levels of iron exceed 0.3 mg/L.
Sample handling
In the sampling and storage process, iron in solution may undergo changes in oxidation form and it can readily precipitate on the sample container walls or as a partially settleable solid suspension. For total iron measurements, precipitation can be controlled by the addition of of concentrated HNO_3 to the sample immediately after collectionq till pH less than 2.
For total iron determinations, precipitated iron is brought into solution by boiling with acid. Ferric iron is reduced to the ferrous state by the addition of hydroxylamine hydrochloride. Ferrous iron is chelated with 1,10-phenanthroline to form an orange-red complex. Colour intensity is proportional to iron concentration and spectrophotomety can be used. Absorbance can be measured spectrophotometrically at 510 nm. For cell lengths of 1 cm, Beer's law is obeyed in iron solutions containing 0.1-5 mg/L. The colour intensity is unaffected by a pH between 3 and 9.
If large amounts of organic materials are present, the sample must first be digested with H_2SO_4 to destroy organic structures and to bring all the iron into solution. Hydrochloric acid is then added until the HCl concentration is between 7 and 8 mol/L and the iron is extracted as $FeCl_3$ into diisopropyl ether. Iron is then re-extracted into water and reduced with hydroxylamine.
Strongly oxidising substances may interfere. Cyanide, nitrite, phosphates, chromium, zinc, cobalt and copper interfere if concentrations exceed 10 times that of iron. Additionally, cobalt or copper present in excess of 5 mg/L and nickel in excess of 2 mg/L result in interferences. Bismuth, cadmium, mercury, molybdate and silver cannot be present because they precipitate phenanthroline. Cyanide and nitrite may be removed by boiling with acid. The same procedure converts polyphosphates into orthophosphates, which cause less interference. Excess hydroxylamine addition will reduce strongly oxidising agents, and excess phenanthroline is required to guarantee complete iron complexation if large concentrations of interfering metal ions are present. The milky solution produced from molybdate interference can be overcome by adjusting the pH to greater than 5.5. For samples that are highly coloured or that contain large amounts of organic material, ashing procedures should precede analysis. The sample may be wet-ashed with sulphuric acid and nitric acid or dry-ashed at temperatures not exceeding 700 °C.
Preparation for the analysis of highly contaminated water and industrial wastewater must include careful consideration of possible interferences. The general procedures for correcting the interferences described above will aid in dealing with specific interferences. The ultimate choice may be to eliminate interferences by extracting the iron with diisopropyl ether from a hydrochloric acid solution and then back-extracting the iron with water.
Concentrations of iron can be determined also by ICP analysys where the effect of the complex matrix has to be considered.

Manganese
Although manganese in groundwater is generally present in the soluble divalent ionic form because of the absence of oxygen, part or all of the manganese in surface waters (or water from other sources) may be in a higher valence state.
There is evidence that manganese occurs in surface waters both in suspension in the quadrivalent state and in the trivalent state in a relatively stable, soluble complex. Although rarely present at concentrations in excess of 1 mg/L, manganese imparts objectionable and tenacious stains to

laundry and plumbing fixtures. The low manganese limits imposed on an acceptable water stem from these, rather than toxicological, considerations. Special means of removal are often necessary, such as chemical precipitation, pH adjustment, aeration and use of special ion exchange materials. Manganese occurs in domestic wastewater, industrial effluents and receiving water bodies.

Sample handling

Manganese can be determined spectrophotometrically. Initially persulphate oxidation of soluble manganese compounds to permanganate is carried out in the presence of silver nitrate. The resulting colour is stable for at least 24 hours if excess persulphate is present and organic matter is absent. Interferences of chloride (in concentration 2 g/L) can be prevented by adding mercuric sulphate, $HgSO_4$, to form slightly dissociated complexes. Bromide and iodide will still interfere and only trace amounts may be present. The persulphate procedure can be used for potable water with trace to small amounts of organic matter. For wastewaters containing organic matter, preliminary digestion with nitric and sulphuric acids is needed. If large amounts of Cl^- are also present, boiling with HNO_3 helps remove them. Coloured solutions from other inorganic ions are compensated for in the final colorimetric step.

Samples that have been exposed to air may give low results because of precipitation of manganese dioxide, MnO_2. In this case 1 drop of 30 per cent hydrogen peroxide, H_2O_2, has to be added to the sample (after adding the $HgSO_4$) to redissolve precipitated manganese.

Alternatively, manganese concentration can be determined also by ICP analysys.

Radionuclides in water

General information

A radionuclide is an atom that possesses a radioactive nucleus. A radioactive nucleus is an atomic nucleus that emits radiation in the form of particles or photons, by that losing mass and energy and changing its internal structure to become a different kind of nucleus, perhaps radioactive, perhaps a different element, perhaps neither. The process of losing energy and mass and new structures forming is named radioactivity or radioactive decay. The photons and nucleons released are collectively called radiation or emissions. All radionuclides have finite lifetimes; however, the ranges are extremely wide - between billions of years to less than nanoseconds. Each time when a particle is emitted, the original radionuclide is transformed into a different species. The emitted particles can possess enough energy to penetrate into solid matter, altering and damaging the molecules with which they collide.

Radionuclides cannot be neutralized by any chemical or physical treatment; they can only be confined and shielded until their activity decreases to a negligible level. Radionuclides are the only pollutants that can act at a distance, harming life forms and the environment without physical contact.

The most common forms of radionuclide emissions are named alpha (α), beta (β), and gamma (γ).

All nuclides with Z > 82 (Pb) are radioactive and most of these undergo a decay.

An α particle is identical to a helium-4 nucleus, ^4_2He, and will become a helium atom when it comes to rest and acquires two electrons from its surroundings. It carries two positive charges and has a mass number of four. α emission is the ejection of an α particle, which is a nuclide unit consisting of two protons and two neutrons, from a nucleus. After emitting an α particle, the nucleus lowers its atomic number by two units and its mass number by four units. For example, the nuclide uranium-238, $^{238}_{92}U$, becomes thorium-234, $^{234}_{90}Th$.

β emission is the ejection of a β particle (an electron) and an antineutrino from a nucleus. β decay changes a neutron into a proton. The term ‘‘beta particle’’ is an historical term used in the early description of radioactivity. A nucleus that has too many neutrons can decrease the N/Z ratio by emitting an electron in β decay.

γ emission usually occurs after a prior emission of an α or β particle leaves the nucleus in an excited energy state. It can then relax to the more stable ground state by emitting a high-energy γ photon. γ radiation is the highest energy form of electromagnetic radiation.

The rate of radioactive decay of a nuclide can only be determined by counting the emitted particles. Radioactive decay follows a first-order rate law, which means that the rate of decay of a given radionuclide at any time is directly proportional to the number of radioactive nuclei remaining at that time.

For radioactive decay, it is usual to express the rate in terms of the half-life. The half life ($t_{1/2}$) is the time required for ½ of the radioactive nuclei initially present at any time to undergo disintegration.

There are just three radioisotopes found naturally on earth with halflives long enough to have persisted since earth's creation. They are uranium-238 ($^{238}_{92}U$, $t_{1/2} = 4.67 \times 10^9$ years), uranium-235 ($^{235}_{92}U$, $t_{1/2} = 7.13 \times 10^8$ years), and thorium -232 ($^{232}_{90}Th$, $t_{1/2} = 1.39 \times 10^{10}$ years). All the other naturally occurring radioisotopes found on earth today are daughter isotopes of these three parent radioisotopes. There are just three naturally occurring radio active decay series. Each series starts with one of the long-lived parent radioisotopes whose half-life exceeds that of any of its daughter products. A series continues forming one radioactive daughter after another by emitting α and β particles until a stable isotope is finally made. The half-life of each daughter is an indication of its stability; a longer half-life means a more stable nuclide. The three decay series, starting with $^{238}_{92}U$, $^{235}_{92}U$, and $^{232}_{90}Th$, terminate in the stable isotopes of lead $^{206}_{82}Pb$, $^{207}_{82}Pb$, and $^{208}_{82}Pb$, respectively.

The mentioned above three types of radiations present great environmental concerns because they are produced by radionuclides that are commonly found in minerals and waste products and have a long enough half-life to allow dangerous quantities to accumulate.

Alpha particles interact strongly with matter and lose their kinetic energy over very short distances of travel. In air, they may travel about 10 cm, whereas in water or tissues the range is about 0.05 cm. α emitting wastes do not require shielding. In their passage through matter, α particles cause intense ionization of the molecules. Since α particles do not penetrate through liquids or solids very far, α emitters (such as Ra, Th, U, and Pu) cause little radiation damage unless they are ingested or inhaled. If transported inside an organism by inhalation or ingestion, α emitters can cause profound damage to tissues around their immediate location. Ra, ^{90}Sr, and ^{133}Ba (all α emitters) substitute for calcium in bone tissue and the intense localized α radiation can destroy the tissue's ability to produce blood cells by causing ionization and bond-breaking in the DNA and RNA molecules of the cells.

Beta particles interact less strongly with matter and have greater penetrating power and less ionizing capacity. Higher energy β particles can penetrate skin and travel up to 9 m in air. Although their damage is less localized, their cumulative effects can be as serious as those of α particles. Because their range in matter is so long, β-emitting wastes require shielding by a minimum of 5 mm of aluminum or 2 mm of lead.

Gamma rays and X-rays are photons (electromagnetic radiation), they are uncharged, and have no mass. They interact with matter relatively weakly by quantum mechanical processes rather than by collisional impact. They have a much greater penetrating power than α or β particles and deposit their energy over much longer path lengths. γ- and X-ray sources require extensive shields to block their emissions. The attenuation of γ radiation by shielding is exponential and, in principle, there always is some probability that a percentage of γ particles penetrate any thickness of shielding. For this reason, γ shielding is usually described in terms of the thickness required to attenuate γ radiation by a certain factor.

The damage produced in matter by any of these particles depends on the activity (number of particles emitted per second) and on their energy.

Naturally occurring radionuclides become widely distributed in low concentrations in soil and water by weathering and erosion of rocks followed by transport dissolved in groundwater or as a gas. Naturally occuring radionuclides with Z > 82 are those in the three radioactive decay series of uranium-238, uranium-235, and thorium -232. The radionuclides most commonly found in groundwater are radon-222, radium-226, uranium-238, and uranium-234 from the uranium-238 decay series, and radium-228 from the thorium-232 decay series. Other radionuclides of these two decay series, and all isotopes of the uranium-235 decay series, are usually not present in

significant amounts in ground water because they are present as highly insoluble compounds or have very short half-lives that preclude the buildup of large concent rations. Unless there have been releases from nearby facilities that make or use enriched uranium, the uranium-235 series is much less important than the others because of the low natural abundanc e of U-235.
Naturally occurring radionuclides with Z < 82, like hydrogen-3, carbon-14, potassium-40, rubidium-87, etc., either have long enough half-lives to have persisted since the Earth's formation or are formed continuously by the action of radioisotope and cosmic radiation on stable atoms in the Earth's atmosphere and geosphere.

Uranium
Uranium (U, atomic number 92) has 18 isotopes with atomic masses ranging from 222 to 242. All are radioactive. Only 234U, 235U, and 235U are found naturally. Pure uranium emits only α particles accompanied by a low level of γ radiation. The mass differences among the uranium isotopes are small and the isotopes do not normally fractionate through natural physical or chemical processes. Uranium exists in U(III), U(IV), U(V), and U(VI) oxidation states, of which the U(IV) - uranous and U(VI) - uranyl states are most commonly found in the environment. Uranium is the only radionuclide for which the chemical toxicity has been found to be greater or equal to its radiotoxicity and for which its drinking water standard is expressed in terms of a reference dose (RfD). The reference dose (is an estimate of a daily ingestion exposure to the population, including sensitive subgroups, that is likely to be without an appreciable risk of deleterious effects during a 70-year lifetime. Dissolved uranium is a kidney toxin and the risk of toxic kidney effects from uranium depends on the mass of uranium ingested. The EPA oral RfD for uranium is 0.6 μg/kg body weight/day. Since α emission is the most common measurement of uranium, an activity-to-mass conversion is useful. EPA has assumed that the mix of uranium isotopes commonly found in public water systems will have a conversion factor of 0.9 pCi/μg, which means that a drinking water MCL of 30 μg/L will typically correspond to 27 pCi/L. EPA considers that 30 μg/L (27 pCi/L) is protective of both chemically caused kidney toxicity and radiation caused cancer.
Uranium occurs naturally in the earth's crust with an average concentration of around 2–3 mg/kg. Because of its chemical reactivity, it is not present as free uranium in the environment. In nature, uranium is generally found as an oxide - mineral pitchblende, which contains triuranium octaoxide (U_3O_8) that is the most stable form. Uranium dioxide (UO_2) is the chemical form most often used for nuclear reactor fuel. Both oxide forms are solids that have a low solubility in water and are relatively stable over a wide range of environmental conditions. At ambient temperatures, UO_2 will gradually convert to U_3O_8. Uranium oxides are extremely stable in the environment and are thus generally considered the preferred chemical form for storage or disposal. Under reducing conditions, uranium is mainly found as the oxide UO_2, an insoluble compound found in minerals. With oxidizing conditions, it forms the oxide UO_3, a moderately soluble compound found in surface waters. Oxidized species [U(VI)], such as the uranyl cation UO_2^{2+} or anionic species formed at high pH, are the most soluble, favoring the wide distribution of uranium in the oxidized portion of the Earth's crust. The reduced species [U(IV)] are only slightly soluble. Uranium is a very mobile element in the environment because of the solubility of its oxidized forms.
Uranium in surface water comes mainly from phosphate deposits and mine tailings, as well as from runoff of phosphate fertilizers (which can contain up to 150 ppm of uranium) from agricultural land. Greater than 99% of uranium transported by runoff from land to fresh water systems is in suspended particles and remains in the sediment. Levels in U.S. streams are usually between 0.1 and 10 mg/L, but can exceed 20 mg/L in irrigation return flows because of phosphates and evaporative concentration. In waters associated with uranium ore deposits, uranium concentrations may be greater than 1000 μgL. Uranium is widely dispersed in groundwater because of its presence in soluble minerals, its long half-life, and its relatively high abundance. The highest concentrations in groundwater are found in granite rock and granitic sediments. Uranyl cation (U^{6+}) forms strong carbonate complexes in most waters above pH 6. Complexation with carbonate anions greatly increases the solubility of uranium minerals, facilitating uranium mobility. Solubility

of uranium is also enhanced by complexation with phosphate, sulfate, and fluoride ions, and with organic compounds, especially humic substances. Because it is readily dissolved and transported by oxidizing groundwaters, it can be transported to areas far from its original location. Uranium is less mobile in reducing groundwater, where U(IV) forms solids of low solubility and the dominant uranous ion (U^{4+}) and its aqueous complexes tend to adsorb very strongly to humic material and mineral surfaces in the aquifer. U(IV) concentrations in reducing groundwater are usually less than 10 μg/L.

Radium

All the isotopes of radium between Ra-223 and Ra-230 have been observed. Only Ra-223, Ra-224, Ra-226, and Ra- 228 occur naturally. Ra-226 and Ra-228 are usually the only radium isotopes of environmental interest because their half-lives (1620 and 6.7 years, respectively) are long enough to allow substantial environmental accumulation.

In addition to their own radiation emissions, these radium isotopes present additional environmental and health concerns due to the fact that they decay into radon. Radon is a gas at room temperature and is thus more mobile in the environment.

. Ra-223, in the uranium-235 decay series, decays to radon-219 by α emission.

. Ra-224, in the thorium-232 decay series, decays to radon-220 by α emission.

. Ra-226, in the uranium-238 decay series, decays to radon-222 by α emission.

. Ra-228, in the thorium-232 decay series, decays to actinium-228 by β emission.

Radium-226 is of greatest concern because it not only is the most abundant, but it also decays into the most abundant radon isotope, radon-222.

Radium belongs to periodic table group 2A, the alkaline earth metals, and its chemical properties are, therefore, most similar to those of barium, strontium, and calcium. In the body, radium behaves like calcium, and becomes incorporated into bone structure, where it poses a serious risk of bone cancer. In public water systems with radium problems, radium is often found precipitated as a carbonate or sulfate along with calcium and magnesium deposits in pipes of the distribution system. Radium exists in only the Ra(II) oxidation state in solution and does not easily complex in water. It forms carbonate and sulfate salts of very low water solubility. Radium salts of chloride, nitrate, and bromide are soluble. Sorption can remove radium from solution by adsorption and coprecipitation by scavengers such as iron hydroxide and barium sulfate.

Radium-226 and radium-228 are frequently found in concentrations that exceed EPA drinking water standards wherever uranium-238 and thorium-232 minerals are abundant. In general, shallow groundwater has less radium than deep aquifers, and treated water has less radium than raw groundwater. The radium content of surface water is usually very low, lower than most groundwater supplies.

The solubility of radium generally is low, but increases with decreasing pH. Dissolved radium occurs mainly as Ra^{2+} ions within the pH range 3–10. Radium tends to be most soluble in reducing waters, high in iron and manganese and low in sulfate. Increased concentrations of total dissolved solids also increase the solubility of radium because fewer sorption sites are available for radium species.

Radium-226, a daughter product of U-238, is the most common radium isotope in natural waters because of the abundance and mobility of its parent uranium-238 in groundwater. It is more abundant than Ra-228, a daughter product of Th-232, because uranium is generally more abundant and is more soluble than thorium.

Although ^{228}Ra is chemically similar to ^{226}Ra, its distribution in groundwater is very different for several reasons. The relatively short half-life of ^{228}Ra limits the potential for transport without the parent being present. Consequently, ^{228}Ra cannot migrate far from its source before it decays to another progeny. Thorium-232, the parent of ^{228}Ra, is extremely insoluble and is not subject to mobilization in most groundwater environments. The very low solubility of thorium (much lower than uranium) limits the distribution of ^{228}Ra in groundwater.

Radon

It is a naturally occurring chemically inert gas, in the same family as helium, neon, and argon. Radon is produced in the natural decay chains of ^{238}U, ^{235}U, and ^{232}Th and is the only naturally occurring gaseous element that is radioactive.

It has no odor, color, or taste and is about 7.4 times denser than air. All radon isotopes are radioactive and decay by α emission. Radon accounts for about 50% of the average radiation exposure of people in the United States.

There are three naturally occurring isotopes of radon:

. ^{219}Rn, half-life = 3.9 s; in decay chain of ^{235}U

. ^{220}Rn, half-life = 54.5 s; in decay chain of ^{232}Th

. ^{222}Rn, half-life = 3.8 days; in decay chain of ^{238}U

Because of its longer half-life, only ^{222}Rn is environmentally important. Wherever ^{238}U is in the soil, ^{222}Rn is formed continuously as a daughter product. Because radon is an inert gas, it moves freely through soil fissures and pore spaces without reacting to become a less mobile radionuclide. Its half-life of 3.8 days is long enough for significant amounts of radon to travel far from their point of origin and dissolve in groundwater, diffuse to the surface atmosphere, and collect in underground voids such as caves, building basements, subways, water wells, sewers, etc. On the other hand, its half-life is short enough that after 40 days (about 10 half-lives) an isolated sample has decayed to a negligible activity.

Radon is sufficiently soluble in water to reach concentrations as high as 300000 pCi/L where uranium minerals in granites and uranium minerals in pegmatites associated with metamorphic rocks are in the area. However, radon concentrations around 10000 pCi/L are more typical. As with most gases, its solubility in water varies inversely with water temperature; the colder the water, the greater is radon's solubility.

Because it is an inert gas and unreactive in the environment, it is the most mobile radioisotope and can travel long distances dissolved in groundwater and through voids and fissures in the vadose zone as a gas. Radon is found nearly everywhere in soil, air, and water; even outdoor air contains low levels of radon (typically about 0.4 pCi/L).

Radon also is drawn into the low-pressure zone within a pumping well's cone of depression. The result is that radon is drawn from remote crevices and fractures into the well. For buildings whose water is supplied by a well, radon dissolved in groundwater can enter through the water distribution system, becoming volatilized into the indoor air space as the water is used. Public water supplies tend to have lower radon levels than wells because the longer residence times allow more complete radioactive decay. Also, where radon is a known problem, public supplies often treat their water by aeration, venting the radon gas to the atmosphere.

Radon is a known human lung carcinogen and is reported to be the second leading cause of lung cancer in the United States. It is the largest source of radiation exposure to the public and is considered a serious health risk.

By far, the primary health risk for radon is exposure through inhalation, not ingestion. Drinking radon-rich water appears to result in only a very minor increase in the risk of stomach cancer. The primary concern of exposure to radon-rich water is its contribution to radon in indoor air as it volatilizes out of the water phase. This occurs during normal household water use, particularly during showers and during the washing of dishes and clothes.

Most radon that is inhaled is also exhaled. However, radon remaining in the lung decays in several steps to form daughter radioactive isotopes of polonium, lead, bismuth, and tellurium, all with short half-lives. These radon decay products are chemically toxic metals that are readily retained in the respiratory system and, over time, will damage sensitive lung and bronchial tissues. Also, the short half-lives of the daughter products allow them to undergo further decay before the action of mucus in the bronchial tubes can clear them out. Thus, the lungs and bronchia are exposed to additional α and β emissions. Generally speaking, health risks associated with radon are due to long-term exposure, from about 5–25 years.

The EPA has proposed an MCL for radon in water of 300 pCi/L, and an alternate MCL of 4000 pCi/L for public water suppliers that have radon mitigation programs for their customer base.

Non-metals

Boron

Boron is a natural component of freshwaters arising from the weathering of rocks, soil leaching, volcanic action and other natural processes. Industries and municipal wastewaters also contribute boron to surface waters. In addition, agricultural run-off may contain boron, particularly in areas where it is used to improve crop yields or as a pesticide. Boric acid, which does not readily dissociate, is the predominant species in freshwaters.

In most natural waters boron is rarely found in concentrations greater than 1 mg/L, but even this low concentration can have deleterious effects on certain agricultural products, including citrus fruits, walnuts and beans. Water having boron concentrations in excess of 2 mg/L can adversely affect many of the more common crops. Groundwater may have greater concentrations of boron, particularly in areas where the water comes in contact with igneous rocks or other boron-containing strata. Higher concentrations of boron (up to 48 mg/L) are found in some mineral waters which are sometimes used for special health-related bathing, but not as drinking water. World Health Organization recommended a maximum boron concentration of 0.3 mg/L in water bodies used for drinking. Recommended concentrations of boron in waters used for irrigation vary from 0.5 mg/L for sensitive crops to 6 mg/L for short-term irrigation or for tolerant crops.

Many types of glass contain boron and their use should therefore be avoided in sampling. Containers for samples intended for boron determination must be made of polyethylene or alkali-resistant, boron-free glass. Analysis is normally by ICP or photometric (curcumin) methods. The latter method is based on the fact that when a sample of water containing boron is acidified and evaporated in the presence of curcumin, a red-coloured product called rosocyanine is formed. The rosocyanine is taken up in ethanol, and the red colour is compared photometrically with standards. The minimum detectable amount of boron is 0.2 µg. The method is not applicable if more than 20 mg of NO_3-N per litre is present. When the total “hardness” of the sample exceeds 100 mg/L as $CaCO_3$, the colour measurement may be affected by the formation of an opalescence in the alcoholic solution of rosocyanine. This interference may be prevented by passage of the sample through a cation exchange column.

Fluoride

Fluoride originates from the weathering of fluoride-containing minerals and enters surface waters with run-off and groundwaters through direct contact. Liquid and gas emissions from certain industrial processes (such as metal- and chemical-based manufacturing) can also contribute fluoride ions (F^-) to water bodies. Fluoride mobility in water depends, to a large extent, on the Ca^{2+} ion content, since fluoride forms low solubility compounds with divalent cations. Other ions that determine water hardness can also decrease F^- solubility.

Fluoride concentrations in natural waters vary from 0.05 to 100 mg/L, although in most situations they are less than 0.1 mg/L in fresh water and 1.3 mg/kg in seawater. Groundwater concentrations are often as high as 10 mg/L. Very high concentrations of fluoride, far exceeding the WHO guideline value of 1.5 mg/L, are encountered in volcanic aquifers. Localised occurrences of high fluoride in groundwater are associated with some sedimentary and metamorphic rocks. Measurement of fluoride content is especially important when a water body is used for drinking water supply. At high concentrations fluoride is toxic to humans and animals and can cause bone diseases. However, a slight increase in natural concentrations can help prevent dental caries although, at higher concentrations (above 1.5-2.0 mg/L), mottling of teeth can occur.

Water samples for fluoride determination do not usually require any preservation and can be analysed up to several days following collection. Storage in polyethylene containers is recommended. Glass and borosilicate glass bottles should be avoided; however, they may be used

provided that low pH is not maintained, and that the containers have been thoroughly cleaned and have not previously been in contact with solutions of high fluoride concentration.
Determination of the fluoride ion can be made potentiometrically (with a fluoride ion selective electrode) or photometrically (for example by using aluminium-resorcin blue complex or lanthanum alizarin complex). In the potentiometric measurements since it is the free fluoride ion activity that yields the electrode response, formation of complex species (Al, Fe) or undissociated hydrofluoric acid must be prevented. The water pH must be between 5 and 8 in photometric determination. The method is based on the reaction of fluoride with the colored complex to produce colorless aluminium fluoride complex and releasing of the free ligand. Interference effects from metals in the water can be eliminated by distillation or ion-exchange chromatography.

Sulphide

Sulphide enters groundwaters as a result of the decomposition of sulphurous minerals and from volcanic gases. Sulphide formation in surface waters is principally through anaerobic, bacterial decay of organic substances in bottom sediments and stratified lakes and reservoirs. Traces of sulphide ion occur in unpolluted bottom sediments from the decay of vegetation, but the presence of high concentrations often indicates the occurrence of sewage or industrial wastes. Under aerobic conditions, the sulphide ion converts rapidly to sulphur and sulphate ions.
Dissolved sulphides exist in water as non-ionised molecules of hydrogen sulphide (H_2S), hydrosulphide (HS^-) and, very rarely, as sulphide (S^{2-}). The equilibrium between these forms is a function of pH (Figure 9.2). Sulphide concentrations need not be considered if the pH is lower than 10. Suspended matter may also contain various metallic sulphides.
When appreciable concentrations of sulphide occur, toxicity and the strong odour of the sulphide ion make the water unsuitable for drinking water supplies and other uses.

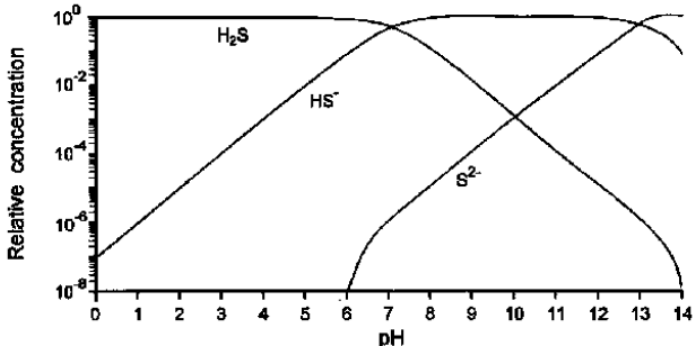

Figure 9.2. Relative concentrations of the different forms of sulphide in relation to the pH of pure freshwaters

Sulphide determination should be done immediately after sampling. If this is not possible, the sample should be fixed with cadmium acetate or zinc acetate, after which it can be stored for up to three days in the dark. During sampling, aeration of the sample must be prevented. Total sulphide, dissolved sulphide and free H_2S are the most significant determinations. Variations of pre-treatment (filtration and pH reduction) are used for their speciation. Photometric methods or, at high concentrations, iodometric titration are generally used for sulphide determination. At S^{2-} concentrations >1 mg/L determination can be carried out with ion-sensitive electrode for sulfides.

Selenium

The chemistry of selenium is similar in many respects to that of sulphur, but selenium is a much less common element. The natural selenium concentrations usually found in water are of the order of a few micrograms per litre, but may reach 50-300 µg/L in seleniferous areas and have been reported to reach 1 mg/L in drainage water from irrigated seleniferous soil.

Selenium appears in the soil as basic ferric selenite, as calcium selenate and as elemental selenium. Although the solubility of elemental selenium is limited, selenium may be present in water in the elemental form as well as the selenate (SeO_4^{2-}), selenite (SeO_3^{2-}) and selenide (Se^{2-}) anions. In addition, many organic compounds of selenium are known.
Selenium is an essential, beneficial element required by animals in trace amounts but toxic when ingested at higher levels. A guideline value of 0.01 mg/L for selenium in drinking water has been recommended by WHO on the basis of long-term health effects. In humans, the symptoms of selenium toxicity are similar to those of arsenic and the toxic effects of longterm exposure are manifested in nails, hair and liver.
Selenium in concentrations of around 1 µg/L has been found to be adsorbed on Pyrex glass. Samples are collected in a polyethylene bottle and acidified by the addition of 1.5 mL of concentrated HNO_3 per litre if the sample is to be stored.
Two methods are mainly applied for selenium analysis - photometric and ICP. The photometric diaminobenzidine method is less sensitive, but with sample preconcentration the limit of detection is generally acceptable.

Cyanide

Cyanides enter freshwaters with wastewaters from industries such as the electroplating industry. Cyanides occur in waters in ionic form or as weakly dissociated hydrocyanic acid. In addition, they may occur as complex compounds with metals. The toxicity of cyanides depends on their speciation; some ionic forms and hydrocyanic acid are highly toxic. The toxicity of complex compounds of cyanide depends on their stability. Weak complexes formed with metals such as zinc, lead and cadmium are extremely toxic. Copper complexes are less toxic, and cobalt and ferrous complexes are only weak toxicants.
Ionic cyanide concentration in water is reduced by carbonic and other acids transforming the ionic form into the volatile hydrocyanic acid. However, the principal mechanism to decrease cyanide levels is oxidation, including biochemical oxidation, followed by hydrolysis:

$$2CN^- + O_2 \rightarrow 2CNO^-; \qquad CNO^- + 2H_2O \rightarrow NH_4^+ + CO_3^{2-}.$$

Strong sunlight and warm seasons favour biochemical oxidation causing a reduction in cyanide concentrations. Cyanides, especially ionic forms, are easily adsorbed by suspended matter and bottom sediments.
Concentrations of cyanides in waters intended for human use, including complex forms (except hexacyanoferrate), are strictly limited (usually to < 0.05 mg/L) because of their high toxicity.
Samples for cyanide determination must be analysed as soon as possible because it is a highly active and unstable variable. If necessary, samples collected in polyethylene bottles can be preserved with sufficient sodium hydroxide to raise the pH to 11 or more and then stored at about 4° C. A photometric method is normally used for the determination of cyanides in natural waters.

The above lecture is based mainly on the following publications: Stumm and Morgan, 1996; Chapman, 1996; Weiner, 2007; Gautam, 2011; WHO, 2022; American Public Health Association, American Water Works Association, and Water Environment, 2023.

10. Water micro-components (organic) - natural and polluting concentrations

General principles

Many thousands of individual organic compounds enter water bodies as a result of human activities. These compounds have significantly different physical, chemical and toxicological properties. Monitoring every individual compound is not feasible. However, it is possible to select priority organic pollutants based on their prevalence, toxicity and other properties. Mineral oil, petroleum products, phenols, pesticides, polychlorinated biphenyls (PCBs) and surfactants are

examples of such classes of compounds. Recently pharmaceuticals are entering in this classification. However, these compounds are not monitored in all circumstances, because their determination requires sophisticated instrumentation and highly trained personnel. In the future much effort will be needed in monitoring these classes of compounds because they are becoming widespread and have adverse effects on humans and the aquatic environment.
When selecting a list of variables for a survey of organic contaminants, the gross parameters - total organic carbon (TOC), chemical oxygen demand (COD) and biochemical oxygen demand (BOD) should be included. In addition, during preliminary surveys and in emergencies, the whole range of individual organic compounds should be identified. This required instrumental methods as gas chromatography (GC), liquid chromatography (LC) and gas chromatography / mass spectrometry (GC/MS), in combination with effective pre-concentration. In intensive surveys, the following classes of organic pollutants should be identified: hydrocarbons (including aromatic and polyaromatic), purgeable halocarbons, chlorinated hydrocarbons, different pesticide groups, PCBs, phenols, phthalate esters, nitrosamines, nitroaromatics, haloethers, benzidine derivatives and dioxins. In most cases, analysis for organic contaminants is performed on unfiltered water samples. However, variations observed in samples from turbid rivers may largely reflect variations in total suspended solids. Consequently, it is recommended that analysis of the less soluble organic contaminants (e.g. organochlorine pesticides) is carried out on the particulate material (collected by filtration or centrifugation) in the samples.

Organic matter - gross parameters

Most freshwaters contain organic matter which can be measured as TOC. For comparative purposes an indication of the amount of organic matter present can be obtained by measuring related properties, principally the BOD or the COD. The COD usually includes all, or most, of the BOD as well as some other chemical demands. In most samples COD > BOD > TOC. However, in some situations this relationship may not be true, such as when the sample contains toxic substances.

Total organic carbon

Organic carbon in freshwaters arises from living material (directly from plant photosynthesis or indirectly from terrestrial organic matter) and also as a constituent of many waste materials and effluents. Consequently, the total organic matter in the water can be a useful indication of the degree of pollution, particularly when concentrations can be compared upstream and downstream of potential sources of pollution, such as sewage or industrial discharges or urban areas. In surface waters, TOC concentrations are generally less than 10 mg/L, and in groundwater less than 2 mg/L, unless the water receives municipal or industrial wastes, or is highly coloured due to natural organic material, as in swamps. In such situations, TOC concentrations may exceed 100 mg/L (TOC concentrations in municipal wastewaters range from 10 to > 100 mg/L, depending on the level of wastewater treatment). Total organic carbon consists of dissolved and particulate material and is, therefore, affected by fluctuations in suspended solids, which can be quite pronounced in rivers. The dissolved and particulate organic carbon (DOC and POC respectively) can be determined separately after filtering the sample through a glass fibre filter (approximately 0.7 µm pore diameter), and this is recommended for river studies. In most surface waters, DOC levels exceed POC levels and are in the range 1- 20 mg/L. During river floods, and throughout the year in many turbid rivers, POC is the most abundant form.
Total organic carbon is determined without filtration of the sample. Samples for TOC determination should be stored in dark glass bottles, with minimum exposure to light and air, at 3-4 °C for no more than seven days prior to analysis. Alternatively, samples can be acidified with sulphuric acid to pH 2 or less.
There are various methods available for determining organic carbon depending on the type of sample to be analysed. Methods are based on the principle of oxidation (e.g. by combustion,

chemical reaction or ultra violet irradiation) of the carbon in the sample to carbon dioxide which is then determined by one of several methods (e.g. volumetric determination, thermal conductivity or specific CO_2 electrode).

Biological oxygen demand (Biochemical oxygen demand)

Biological (biochemical) oxygen demand (BOD) is an approximate measure of the amount of biochemically degradable organic matter present in a water sample. It is defined by the amount of oxygen required for the aerobic micro-organisms present in the sample to oxidise the organic matter to a stable inorganic form.

BOD is an indicator of the potential for a water body to become depleted in oxygen and possibly become anaerobic because of biodegradation. BOD measurements do not take into account re-oxygenation of water by naturally occurring diffusion from the atmosphere or mechanical aeration. Water with a high BOD and an active microbial population can become depleted in oxygen and may not support aquatic life, unless there is a means for rapidly replenishing DO.

As noted above, BOD measurements are usually lower than COD measurements. Unpolluted waters typically have BOD values of 2 mg/L O_2 or less, whereas those receiving wastewaters may have values up to 10 mg/L O_2 or more, particularly near to the point of wastewater discharge. Raw sewage has a BOD of about 600 mg/L O_2, whereas treated sewage effluents have BOD values ranging from 20 to 100 mg/L O_2 depending on the level of treatment applied. Industrial wastes may have BOD values up to 25000 mg/L O_2.

Water samples collected for BOD measurement must not contain any added preservatives and must be stored in glass bottles. Ideally the sample should be tested immediately since any form of storage at room temperature can cause changes in the BOD (increase or decrease depending on the character of the sample) by as much as 40 per cent during the first 8 hours of storage. Storage should be at 5 °C and only when absolutely necessary. In the case of individual samples collected over a long period, it is desirable to keep all the samples at about 5 °C until the composite sample can be made up for the BOD determination.

The BOD determination method is subject to various complicating factors such as the oxygen demand resulting from the respiration of algae in the sample and the possible oxidation of ammonia (if nitrifying bacteria are also present). The presence of toxic substances in a sample may affect microbial activity leading to a reduction in the measured BOD. The conditions in a BOD bottle usually differ from those in a river or lake. That is why standardised laboratory procedures are used to estimate the relative oxygen requirements of wastewaters, effluents and polluted waters. The 5-day incubation period has been accepted as the standard for this test (although other incubation periods are occasionally used). This gives rise to the commonly used term "BOD_5".

Standardised laboratory procedures are used to determine BOD_5 by measuring the amount of oxygen consumed after incubating a specified volume of water sample in the dark at a specified temperature, which is usually 20° C, for five days. Nutrients (nitrogen and phosphorus) are generally added to the solution, following standardized procedure. The oxygen consumption is determined from the difference between the dissolved oxygen concentrations in the sample before and after the incubation period. If the concentration of organic material in the samples is very high, samples may require dilution with distilled water prior to incubation so that the oxygen is not totally depleted. It is necessary that excess dissolved oxygen be present during the whole period of incubation, and desirable that at least 30 per cent of the saturation value remains after 5 days. Since the solubility of atmospheric oxygen at the temperature of incubation is only 9 mg/L, samples that absorb more than about 6 mg/L during incubation for 5 days will not fulfil this condition. This is the case with sewage, nearly all sewage effluents, and many other waste liquids. The additional oxygen is supplied by diluting the sample with clean, well aerated water. The amount of dilution depends upon the nature of the sample. The standards prescribe the needed dilution in dependence on the expected concentrations of organic pollutants.

The pH of the samples has to be between 6.5 and 8.5. In order to avoid results showing lower than the true organic content, higher concentrations of chlorine, and of many compounds being able to release chlorine, have to be removed by treating a portion of the sample with sodium bisulphite. The treated portion is then used for the BOD test.

Chemical oxygen demand

Chemical oxygen demand (COD) refers to the amount of chemically oxidizable materials present in the wastewater. Ii is a measure of the oxygen equivalent of the organic matter in a water sample that is susceptible to oxidation by a strong chemical oxidant, such as dichromate. Actually, it provides a measure of the oxygen equivalent of that portion of the organic matter in a water sample that is susceptible to oxidation under the conditions of the test. COD is sometimes used as a measure of general pollution, a measure of the susceptibility to oxidation of the organic and inorganic materials present in water bodies and in the effluents from sewage and industrial plants. The test for COD is non-specific, in that it does not identify the oxidisable material or differentiate between the organic and inorganic material present. Similarly, it does not indicate the total organic carbon present since some organic compounds are not oxidised by the dichromate method whereas some inorganic compounds are oxidised. The method fails to include some organic compounds, such as acetic acid, that are biologically available to the aquatic organisms but does include some biological compounds, such as cellulose, that are not part of the immediate biochemical demand on the available oxygen of the receiving water.

Nevertheless, COD is a useful, rapidly measured, variable for many industrial wastes. With certain wastes containing toxic substances, COD or a total organic carbon determination may be the only method for determining the organic load.

The concentrations of COD observed in surface waters range from 20 mg/L O_2 or less in unpolluted waters to greater than 200 mg/L O_2 in waters receiving effluents. Industrial wastewaters may have COD values ranging from 100 mg/L O_2 to 60000 mg/L O_2.

Samples for COD analysis should be collected in bottles which do not release organic substances into the water, such as glass-stoppered glass bottles. Ideally samples should be analysed immediately, or if unpolluted, within 24 hours provided they are stored cold. If analysis cannot be carried out immediately, the samples should be preserved with sulphuric acid (2 mL H_2SO_4 (d = 1.84) diluted 1: 2 to each 100 mL of sample). For prolonged storage samples should be deep frozen. If appropriate, samples can be filtered prior to analysis using glass fibre filters. When determinations on unfiltered and filtered samples are carried out, the difference gives the COD of the particulate matter. Samples containing settleable solids should be homogenised sufficiently by means of a blender to permit representative sampling for the COD determination in unfiltered samples. For the analysis of filtrate, the original (not homogenised) sample is used. Filtration through glass-fibre filters is recommended, but hard paper filters may be used if the sample has a high COD. The filters should be pre-rinsed with water.

The standard method for measurement of COD is oxidation of the sample with potassium dichromate in a sulphuric acid solution (although other oxidants can be used which may have different oxidation characteristics) followed by a titration. It is extremely important that the same method is followed each time during a series of measurements so that the results are comparable.

The sample is boiled under reflux with potassium dichromate and silver sulphate catalyst in strong sulphuric acid. Part of the dichromate is reduced by organic matter and the remainder is titrated with ferrous ammonium sulphate.

Straight-chain aliphatic compounds, aromatic hydrocarbons and pyridine are not oxidised to any appreciable extent, although this method gives more complete oxidation compared to the case when permanganate is used as oxidant. The straight-chain compounds are more effectively oxidised when silver sulphate is added as a catalyst. However, silver sulphate reacts with chlorides, bromides or iodides to produce precipitates that are only partially oxidised. Adding a catalyst in the oxidation of aromatic hydrocarbons is useless, but it is essential to the oxidation of

straight-chain alcohols and acids. The problems caused by the presence of chlorides in the sample may be overcome by adding mercuric sulphate before refluxing, in order to bind the chloride ion as a soluble mercuric chloride complex, which significantly reduces its ability to react further. Nitrite nitrogen exerts a COD of 1.14 mg/mg of nitrite nitrogen. To eliminate the interference due to nitrites, 10 mg of sulphamic acid for every 1 mg of nitrite nitrogen in the refluxing flask may be added. If a series of samples containing nitrite is analysed, the sulphamic acid may be added to the standard dichromate solution, since it must be included in the distilled water blank.
Ferrous iron and hydrogen sulphide exert COD of 0.14 mg/mg - Fe^{2+} and 0.47 mg/mg - H_2S respectively. Appropriate corrections can be calculated and subtracted from the result or both interferences can be removed by bubbling air through the sample, if easily volatile organic matter is not present.
The dichromate oxidation procedure can be used to determine COD values of 50 mg/L with the standard dichromate solution (0.0417 mol/L). With the dilute dichromate, values are less accurate, especially below 10 mg/L, but may be used to indicate an order of magnitude.
BOD is a subset of COD. The COD analys oxidizes organic matter that is both chemically and biologically oxidizable. If a reliable correlation between COD and BOD can be established at a particular site, the simpler COD test may be used in place of the more complicated BOD analysis.

Humic and fulvic acids

Organic matter arising from living organisms makes an important contribution to the natural quality of surface waters. The composition of this organic matter is extremely diverse. Natural organic compounds are not usually toxic, but exert major controlling effects on the hydrochemical and biochemical processes in a water body. Some natural organic compounds significantly affect the quality of water for certain uses, especially those which depend on organoleptic properties (taste and smell). During chlorination for drinking water disinfection, humic and fulvic acids act as precursor substances in the formation of trihalomethanes such as chloroform. In addition, substances included in aquatic humus determine the speciation of heavy metals and some other pollutants because of their high complexing ability. As a result, humic substances affect the toxicity and mobility of metal complexes. Therefore, measurement of the concentrations of these substances can be important for determining anthropogenic impacts on water bodies.
Humus is formed by the chemical and biochemical decomposition of vegetative residues and from the synthetic activity of micro-organisms. Humus enters water bodies from the soil and from peat bogs, or it can be formed directly within water bodies as a result of biochemical transformations. It is operationally separated into fulvic and humic acid fractions, each being an aggregate of many organic compounds of different masses.
Fulvic acid has molecular masses mostly in the range 300-5000 whereas the dominant masses in humic acid exceed 5000. The relative content of fulvic acid in the dissolved humic substances present in freshwaters is between 60 and 90 per cent. Humic and fulvic acids are stable (i.e. their BOD is low). However, these substances are chemically oxidisable and influence the results of COD determinations.
Fulvic and humic acid concentrations in river and lake waters are highly dependent on the physico-geographical conditions and are usually in the range of tens and hundreds of micrograms of carbon per litre. However, in waters of marshy and woodland areas, their concentrations can reach milligrams of carbon per litre. In natural conditions fulvic and humic acids can comprise up to 80 per cent of the DOC, which can be used as an approximate estimate of their concentrations.
Samples for fulvic and humic acid determination are not usually filtered or preserved. They can be stored for some months in a refrigerator (3-4° C). Total fulvic and humic acid content can be determined photometrically and their separate determination can be made with spectrophotometric methods.

Phenols

Phenols enter water bodies by the waste discharges of different industries. They are also formed naturally during the metabolism of aquatic organisms, biochemical decay and transformation of organic matter, in the water column and in bottom sediments. Phenols are aromatic compounds with one or few hydroxy groups. They are easily biochemically, photochemically or chemically oxidised. As a result, they have detrimental effects on the quality and ecological condition of water bodies through direct effects on living organisms and the significant alteration of biogeneous elements and dissolved gases, principally oxygen.

The presence of phenols causes a pronounced deterioration in the organoleptic characteristics of water and as a result they are strictly controlled in drinking water and drinking water supplies. Concentrations of phenols in unpolluted waters are usually less than 0.02 mg/L. Toxic effects on fish can be observed at concentrations of 0.01 mg/L and above.

Phenols are usually divided into two groups: steam-distillable phenols (phenol, cresols, xylenes, chlorphenols, etc.) and non-distillable phenols (catechol, hydroquinone, naphthols, etc.). The analytical method used with steam distillation determines only the volatile phenol fractions; these have the worst effects on organoleptic water characteristics. The method does not detect non-volatile phenols which, unfortunately, are often present in greater quantities than the volatile phenols and, furthermore, tend to be highly toxic. Chromatographic determination of individual phenols is more informative.

Samples, particularly if required for the determination of volatile phenols, must not be stored for long periods and, ideally, determination should be carried out within four hours. If this is not possible, samples can be preserved with sodium hydroxide and stored for 3-4 days at 2-4° C.

Pesticides

Pesticides are chemical compounds toxic to some living organisms, from bacteria and fungi up to higher plants and even mammals. Most pesticides are compounds which do not occur naturally in the environment and, consequently, detectable concentrations indicate pollution. There are around 10000 different pesticides currently available. The most widely used are insecticides (for extermination of insects), herbicides (for extermination of weeds and other undesirable plants) and fungicides (for preventing fungal diseases).

The mode of action of a pesticide is determined by its chemical structure. These structures are similar for the related compounds which comprise separate classes of pesticides such as the organochlorine pesticides, organophosphorus pesticides, the carbamate pesticides, the triazine herbicides and chlorphenolic acids.

Pesticides monitoring is difficult, particularly for groundwaters. There is a wide range of pesticides in common agricultural use, and many of them break down into toxic products. Screening of water samples for all compounds is very expensive; therefore, a preliminary survey of local pesticide use needs to be carried out to reduce the number of target compounds in each specific assessment programme.

Internationally there is considerable variation between, and uncertainty over, guidelines on permissible concentrations of pesticides in drinking water. Nevertheless, the guideline values are at the microgram per litre level and for the most toxic compounds, are close to the limits of analytical detection. Analytical procedures normally require a combination of a directly-coupled gas chromatograph (GC) and mass spectrometer (MS) or high-pressure liquid chromatography. A high degree of cleanliness is necessary for sample handling at all stages, such as the use of ultra-clean solvents to clean glass or stainless-steel apparatus.

Organochlorine pesticides

Environmental levels of organochlorine pesticides tend to be higher than other pesticides because of their widespread and prolonged use, combined with their great chemical stability. In the 1950s, DDT was used liberally around the world, but at the beginning of the 1970s most countries limited,

or prohibited its use. However, concentrations of DDT and its metabolites (DDD, DDE) are still high in many environments, especially in arid areas.
Organochlorine pesticides are chlorine derivatives of polynuclear hydrocarbons (e.g. DDT), cycloparaffins (e.g. hexachlorocyclohexane (HCH)), compounds of the diene series (e.g. heptachlor) and aliphatic carbonic acids (e.g. propanide). Most of the compounds are hydrophobic (insoluble in water) but highly soluble in hydrocarbons and fats. They have the ability to accumulate in biological tissues, reaching much higher concentrations in certain aquatic biota than in the surrounding water and sediments. The affinity of pesticides for adsorption onto mineral suspended matter and organic colloids is important for their distribution and mobility in water bodies. Bottom sediments also play a significant role in storage and transformation of organochlorine pesticides.
Where present, concentrations of organochlorine pesticides in water bodies tend to be in the range 10^{-5}-10^{-3} mg/L. These compounds and their metabolites have been found in sites as distant as the Arctic and Antarctic regions as a result of long-range atmospheric transport. They are sometimes found in groundwaters, where leaching from disposal sites for hazardous waste or from agricultural land usually accounts for their presence. As these compounds are hydrophobic, their occurrence in groundwater may be the result of “solubilisation” in fulvic acid materials.
Due to their toxicity, the maximum allowable concentrations of organochlorine pesticides must be strictly adhered to in waters important for fish communities or used for drinking water supplies.

Organophosphorus pesticides
Organophosphorus pesticides are complex esters of phosphoric, thiophosphoric and other phosphorus acids. They are widely applied as insecticides, acaricides and defoliants. Their relatively low chemical and biochemical stability is an advantage because many decompose in the environment within a month. Organophosphorus pesticides, like organochlorine pesticides, are readily adsorbed onto suspended matter. Photolysis, as well as hydrolitic, oxidation and enzyme decay processes are the principal mechanisms of decay, resulting in detoxification. When found, the concentrations of organophosphorus pesticides in surface waters range from 10^{-3}-10^{-2} mg/L.
Unfiltered samples for organochlorine and organophosphorus determination should be collected in glass containers with PTFE caps. Samples can be stored for a short time at low temperature. However, immediate extraction followed by storage at -15° C is preferable. In this case, samples may be stored for up to three weeks.

Surfactants

Synthetic surfactants are compounds belonging to different chemical classes but containing a weak-polar hydrophobic radical (e.g. alkyl or alkylaryl) and one or more polar groups. The latter can be classified into anionic (negatively charged), cationic (positively charged) and nonionic (non-ionising). Anionic surfactants are the most widely produced and used, usually as detergents.
Surfactants enter water bodies with industrial and household wastewaters. Surfactants can exist in surface waters in the dissolved or adsorbed states, as well as in the surface film of water bodies, because they have a pronounced ability to concentrate at the air-water or water-sediment interface. Although surfactants are not highly toxic, they can affect aquatic biota. Detergents can impart taste or odour to water at concentrations of 0.4-3 mg/L and chlorination can increase this effect. Surfactants are responsible for foam formation in surface waters and other pollutants, including pathogens, can become concentrated in the foam. The presence of foam on the water surface makes water aeration difficult, lowering oxygen levels, reducing self-purification processes and adversely affecting aquatic biota. The threshold concentration for foam formation is 0.1-0.5 mg/L depending on the structure of the surfactant.
In terms of biodegradability, surfactants are divided into highly degradable, intermediate and stable, or non-degradable, with corresponding biochemical oxidation rate constants of > 0.30 day^{-1}, 0.30-0.05 day^{-1} and < 0.05 day^{-1} respectively. There is a tendency to substitute non-degradable

surfactants for degradable ones. However, this approach to reducing pollution has the drawback of causing a significant decrease in dissolved oxygen concentrations.
The inherent properties of surfactants require special procedures for sample preservation, principally to avoid foam formation and their adsorption onto the walls of the sample containers. Photometric methods are the most widely used for determination of all three types of surfactants and are well documented.

Polychlorinated biphenyls

Polychlorinated biphenyls (PCBs) are a family of stable man-made organic compounds. PCBs found wide application as coolant and insulation fluids in transformers and capacitors, and as flame retardants, plasticizers, solvent extenders, organic diluents, additives to epoxy paints, heat transfer fluids, in hydraulic fluids, in pesticides, and in printing inks. PCB ’s are also by-products of many industrial processes, such as the manufacturing of chlorinated solvents and chlorinated benzenes. PCBs are very stable species and do not degrade readily in the environment. Most of the released PCBs are believed to remain in mobile environmental reservoirs. They even survive ordinary incineration and can escape as vapors up the smoke stack.
The wide use of PCBs has resulted in their common presence in soil, water, and air. PCBs' dispersion from source regions to global distribution occurs mainly through atmospheric transport and subsequent deposition. Because of their low vapor pressure and water solubility, PCBs typically have very high partition coefficients to abiotic and biotic particles. In aquatic systems, sediments are an important reservoir.
When it was discovered that PCBs did not easily biodegrade, their use was restricted. Nevertheless, although they are no longer manufactured, they still leak from old electrical devices, including power transformers, capacitors, television sets, and fluorescent lights, and can be released from hazardous waste sites and historic and illegal refuse dumps. They also persist in fatty foods, such as certain fish, meat, and dairy products. The toxicity of PCBs is a complicated issue since each congener differs in its toxicity. All PCBs are listed by EPA as known carcinogens and priority pollutants. When they are incinerated, they can produce dioxins, which are rated by EPA among the most toxic substances.
The gas chromatograph / mass spectroscopy (GC/MS) patterns of the different PCB mixtures show considerable overlap and common petroleum products, such as motor oil, also generate peaks in the PCB region. For these reasons, unambiguous identification of particular PCBs requires meticulous laboratory technique.

Crude oil (unrefined petroleum) and petroleum products

Crude oil and petroleum products are major pollutants responsible for ecological damage especially in inland surface waters. At present, more than 800 individual compounds have been identified in crude oils. Among them are low- and highmolecular weight aliphatic, aromatic and naphthenic hydrocarbons (or petroleum products), high-molecular unsaturated heterocyclic compounds (resins and asphaltenes) as well as numerous oxygen, nitrogen and sulphur compounds (Table 10.1).
Oil is distributed in water bodies in different forms: dissolved, film, emulsion and sorbed fractions. Interactions between these fractions are complicated and diverse, and depend on the specific gravities, boiling points, surface tensions, viscosities, solubilities and sorption capabilities of the compounds present. In addition, transformation of oil compounds by biochemical, microbiological, chemical and photochemical processes occurs simultaneously. Due to the high ecological risk associated with oil extraction, transportation, refining and use, mineral oil is considered a priority pollutant and its determination is important for assessments related to these activities.
The permissible concentration of crude oil and petroleum products in water depends on the intended use of the water. The recommended maximum concentrations for drinking water supplies

and fisheries protection are generally between 0.01 and 0.1 mg/L. Concentrations of 0.3 mg/L or more of crude oil can cause toxic effects in freshwater fish.

Table 10.1. The main components of crude mineral oils

Component group	Content (%)
Hydrocarbons:	
paraffinic	10-70
naphthenic (mono- and polycyclic)	25-75
aromatic (mono- and polycyclic)	6-40
naphthenon-aromatic	30-70
Unsaturated heterocyclic compounds:	
resins	1-40
asphaltenes	0-80
asphaltenic acids and their anhydrites	0-7

Since hydrocarbons are the principal component fraction of the unrefined petroleum, the definition “petroleum products” applies only to this fraction to ensure comparability of analytical data. The total concentration of dissolved and emulsified oils is the more usual determination and dissolved, emulsified and other fractions should only be determined separately in special cases.

Petroleum hydrocarbons and their components enter the group of commonly called nonaqueous phase liquids (NAPLs). NAPLs are nonpolar or low-polarity liquids that are minimally soluble in water. Gasoline and diesel fuels, oils, chlorinated solvents, and pesticides are examples. NAPLs are furher subdivided into light nonaqueous phase liquids (LNAPL) and dense nonaqueous phase liquids (DNAPL). LNAPLs are those liquid hydrocarbon compounds or mixtures that are less dense than water, such as gasoline and diesel fuels and their individual components. DNAPLs are liquid hydrocarbon compounds or mixtures denser than water, such as creosote, polychlorinated biphenyls (PCBs), coal tars, and most chlorinated solvents (chloroform, methylene dichloride, tetrachloroethene, etc.).

The distinction between LNAPLs and DNAPLs is important because of their different behavior in the subsurface. When a NAPL spill occurs in the vadose zone, LNAPL will travel downward through soils only to the water table, where they remain ‘‘floating’’ on the water table surface. DNAPLs can sink through the water saturated zone to impermeable soil structures such as bedrock, where they collect in bottom pools.

As already mentioned, petroleum liquids are complex mixtures of many different hydrocarbons, with minor amounts of nitrogen, oxygen, sulfur, and some metals. The behavior of these compounds in a ground water environment depends on the physical and chemical nature of the particular hydrocarbon blend as well as the particular soil environment.

For example, the partition coefficients and migration potential of each individual compound in a mixture depend on the overall composition of the petroleum mixture in which it is found, on the properties of the pure compound, and on the characteristics of the surrounding soil. Furthermore, the composition and properties of petroleum contaminants change with time as the petroleum ages and weathers.

In addition, because many organic pollutants are soluble in NAPLs, analysis of spilled petroleum products will often detect other organic compounds, such as pesticides, that were previously sorbed to the soil but were not originally present in the NAPL spill being investigated.

The first step in refining crude oil into petroleum products is usually fractional distillation, a process that separates the crude oil components according to their boiling points. The resulting products are groups of mixtures, or fractions, each of which has boiling points within a specified range.

Gasoline is among the lightest liquid fractions of petroleum and consists mainly of aliphatic and aromatic hydrocarbons in the carbon number range C4–C12. Aliphatic hydrocarbons consist of:

. Alkanes: Saturated hydrocarbons in which all carbons are connected by single bonds. They may have linear, branched, or cyclic carbon-chain structures, such as pentane, octane, decane, isobutane, and cyclohexane.
. Alkenes: Unsaturated hydrocarbons in which there are one or more double bonds between carbon atoms. They also may have linear, branched, or cyclic carbon-chain structures, such as ethylene (ethene), 1-pentene, and 1,3-cyclohexadiene.
. Alkynes: Unsaturated hydrocarbons in which there are one or more triple bonds between carbon atoms. They also may have linear, branched, or cyclic carbon-chain structures, such as acetylene (ethyne), propyne, and 1-butyne.
. Aromatic hydrocarbons (also called arenes) are hydrocarbons based on the benzene ring as a structural unit. They include monocyclic hydrocarbons such as benzene, toluene, ethylbenzene, and xylene (the BTEX group) and polycyclic hydrocarbons such as naphthalene and anthracene.
As a general rule, gasoline mixtures are volatile, include somewhat soluble components, and are mobile in the groundwater environment.
Gasolines contain a much higher percentage of the BTEX group of aromatic hydrocarbons (benzene, toluene, ethylbenzene, and the ortho- and para-xylene isomers) than do other fuels, such as diesel. They contain lower concentrations of heavier aromatics like naphthalene and anthracene than do diesel and heating fuels. In general, light weight aromatics such as the BTEX group, are the most soluble components of fuel mixtures. Therefore, the presence of BTEX in appropriate concentration ratios is often a useful indicator of gasoline contamination. If MTBE (methyl-tert-butyl ether) or ethanol additives are present, they are the most soluble components by far.
Middle distillates cover a broad range of hydrocarbons in the range of C6 to about C25. They include diesel fuel, kerosene, jet fuels, and lighter fuel oils. Typical middle distillate products are blends of up to 500 different compounds. They tend to be denser, more viscous, less volatile, less water soluble, and less mobile than gasoline. They contain low percentages of the lighter weight aromatic BTEX group, which may not be detectable in older releases of middle distillates due to degradation or transport.
Heavier fuel oils and lubricating oils are composed of heavier molecular compounds than the middle distillates, encompassing the approximate range of C15–C40. They are more viscous, less soluble in water, and less mobile in the subsurface than the middle distillates.
The larger the hydrocarbon compound and the more carbon atoms it contains, the higher are its boiling point and viscosity, and the lower is its volatility.
When a pollutant consisting of a mixture of different compounds, such as diesel fuel or gasoline, is released to the environment, its composition and physical properties change as time passes:
- The most volatile components tend to leave the free product and pass into the atmosphere or into air in the soil pore space.
- The most water-soluble components tend to dissolve into any surface water or groundwater they contact.
- The least volatile and soluble components tend to sorb to soil and sediment surfaces as the pollutant is moved by gravity and water flow forces.
- The remaining free product progressively becomes denser, more viscous, less mobile, and more resistant to further change.
The environmental impact of a contaminant release is determined mainly by mobility and water solubility of the different components of the contaminant.
LNAPL solubility in water is variable and depends on the chemical mixture. Literature data for solubility of pure compounds *can be misleading* because the solubility of a specific compound decreases when it is part of a blend (Table 10.2.).
The aqueous solubility of a particular compound in a multicomponent NAPL can be approximated by multiplying the mole fraction of the compound in the NAPL mixture by the aqueous solubility of the pure compound. Solubility of component *i* in an NAPL mixture is

$$S_i = X_i S_i^0 \quad (10.1)$$

where: S_i is the solubility of component *i* in the mixture; X_i is the mole fraction of component *i* in the mixture; S_i^0 is the solubility of pure component *i.*

Table 10.2. Solubility variability of gasoline components from different fuel mixtures

Concentration dissolved in water (mg/L)

Compound	Regular Leaded	Regular Unleaded	Super Unleaded	Pure Compound
Benzene	30.5	28.1	67.0	1740–1860
Toluene	31.4	31.1	107.0	500–627
Ethylbenzene	4.0	2.4	7.4	131–208
1,2-Dichloroethane	1.3	—	—	8,524
Methyl-tert-butyl ether (MTBE)	43.7	35.1	966.0	48000
t-Butyl alcohol	22.3	15.9	933.0	Miscible
m-Xylene	13.9	10.9	11.5	134–196
o-, p-Xylene	6.1	4.8	5.7	157–213
1,2-Dibromoethane	0.58			4300

In the subsurface soil environment, petroleum compounds can be present in four phases, each of which can create its own contaminant plume. The four phases are:

1. Liquid petroleum free product (LNAPL)
2. Petroleum compounds adsorbed to soil particles
3. Dissolved petroleum components
4. Vaporized petroleum components

Each phase behaves differently and poses different remediation problems. The liquid free product originates directly from the contamination source and initially has the same composition. When free product is present, the dissolved phase in the groundwater is generally less than 1% of the total mass.

General findings:

- The overall water solubility of commercial gasoline without additives is between 50 and 150 mg/L, depending on its exact composition. When free product gasoline is present, the dissolved portion generally accounts for less than 1% of the total contaminant mass present in the subsurface.
- The overall solubility of fresh No. 2 diesel fuel in water is around 0.4–8.0 mg/L, again depending on its composition. When free product diesel fuel is present, the dissolved portion generally accounts for less than 0.1% of the total contaminant mass present in the subsurface.
- Nevertheless, because of their typically high toxicity, dissolved contaminants can greatly exceed concentrations where water is regarded as seriously polluted.

The adsorbed, dissolved, and vapor phases are extracted from the liquid free product as it contacts soil, water, and air in the soil pore spaces. Each phase moves independently in its own distinct contaminant plume.

Generally, the vapor contaminant plume moves most rapidly. The dissolved plume moves more slowly, at groundwater velocity or less, depending on its retardation factor. Depending on whether its viscosity is greater or less than water, the free product plume may move slower or faster than the dissolved plume. The adsorbed plume may be immobilized or, in the saturated zone, part of it may be sorbed to mobile colloids and move at approximately the groundwater velocity.

Dissolved contaminants become a part of the water system and move with the groundwater, but they usually move at a lower velocity because of retardation by sorption processes. Sorption to soil and desorption back into the dissolved phase is a continual process that retards the movement of dissolved contaminants. The amount of retardation for any particular contaminant depends mainly on the organic content of the soil; retardation is greater in soils with more organic matter. Because

their water solubilities are low, dissolved fuel contaminants continue to partition between the dissolved phase and soil particle surfaces, especially in soils with a high organic content.
Typical retardation factors for BTEX in sandy soil range from 2.4 for dissolved benzene (groundwater moves 2.4 times faster than benzene) to 6.2 for the dissolved xylene isomers.
As oil can be biochemically oxidised very easily, it is necessary to extract it from the sample immediately after sampling with carbon tetrachloride or trichlorotrifluoroethane. The extract can then be stored in a cool, dark place for several months. Gravimetric methods of oil determination are the simplest, but are not very sensitive and can give erroneous results due to the loss of volatile components. Ultra violet (UV), infrared (IR) spectrophotometric and luminescent methods are the most popular. Analysis based on column and thin-layer chromatographic separation allows the possibility of the separate determination of volatile and non-volatile polyaromatic hydrocarbons, resins and asphaltenes. Identification and determination of individual oil components is a complicated analytical task which can be undertaken only with the application of capillary gas chromatography, with either mass-spectrometric detection or luminescent spectrometry.
Figure 10.1 relates the carbon number of a petroleum compound to its properties, uses, and the usual instrumental methods used for its analysis.

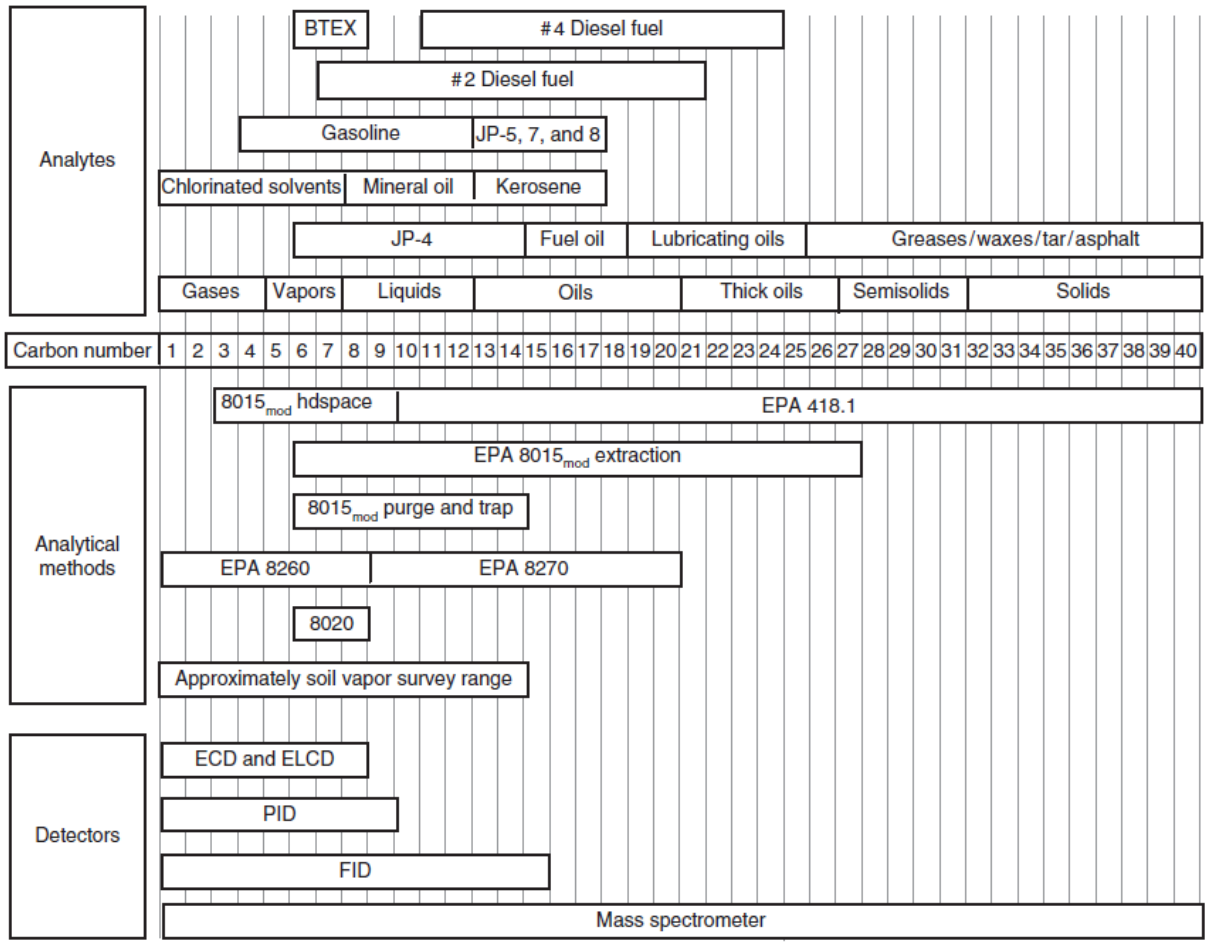

Figure 10.1 Hydrocarbon ranges, corresponding uses, and analytical methods

It is very difficult to locate DNAPL free product with monitoring wells. First, DNAPL remains at the bottom of the monitoring well and may go unnoticed. Second, DNAPL free product may be present in locations seemingly unrelated to the spill location, such as perched on low permeability layers in pools and cracks, or upgradient of the spill at the bottom of the aquifer in pools and fractures in the bedrock. If any of the following conditions exist in ground water, there is a high probability that DNAPL free product is near the sampling location.

Ground water concentrations of DNAPL-related chemicals are > 1% of either their pure-phase solubility (S_{pure}) for a single component DNAPL or the effective solubilities (S_{eff}) for components of a DNAPL mixture. The factor of 1% of the solubility is intended to roughly account for the expected concentration decrease due to dilution, dispersion, and degradation of the DNAPL component while moving from the source zone to a montoring well that is ‘‘near’’ the source. The higher the percentage factor, the closer the well is likely to be to the source zone.
. Soil concentrations of DNAPL-related chemicals are > 10000 mg/kg (1% of soil mass).
. Ground water concentrations of DNAPL-related chemicals increase with depth or appear in anomalous upgradient / cross -gradient locations with respect to ground water flow.
Ground water concentrations of DNAPL-related chemicals calculated from water–soil partitioning relationships are greater than their pure-phase solubility or effective solubility.

Oil and grease

The analysis for oil and grease (O&G) actually measures a group of substances that have similar solubility characteristics in a designated solvent. ‘‘Oil and grease’’ is defined as any substance recovered from an acidified sample by extracting it into a designated solvent, and which is not volatilized during the analysis. The extraction process is called ‘‘liquid–liquid extraction (LLE).’’ After the sample is extracted, the extract may be measured either gravimetrically (drying and weighing) or by infrared spectroscopy.
The solvents used have the ability to dissolve not only O&G but also other organic substances. Some non-O&G materials commonly included in the determination of ‘‘O&G’’ are certain sulfur compounds, chlorophyll, and some organic dyes. There is no known solvent that will dissolve selectively only O&G. Some heavier residuals of petroleum (coal tar, used motor oil, etc.) may contain significant amounts of material that do not extract into the solvent. The method is entirely empirical and duplicate results with a high degree of precision can be obtained only by strict adherence to all details of the analytical procedure.
The ‘‘total oil and grease’’ designation includes oils and fats of biological origin (animal and vegetable fats and oils) as well as mineral oils (petroleum products). Silica gel has the ability to adsorb certain organic compounds known as ‘‘polar compounds.’’ Since petroleum hydrocarbons are mostly nonpolar, and most hydrocarbons of biological origin are polar, silica gel is used to separate these different types of hydrocarbons. If a solution of nonpolar and polar hydrocarbons is mixed with silica gel, the polar hydrocarbons, such as fatty acids, are removed selectively from the solution. The materials not eliminated by silica gel adsorption are designated as ‘‘petroleum hydrocarbons’’ by this test. Normally, total O&G is measured first and then petroleum hydrocarbons are determined after the animal and vegetable fats are removed by silica gel adsorption. The difference between total O&G and petroleum hydrocarbons is designated as biologically derived hydrocarbons.

Microbiological indicators of water quaility

The most common risk to human health associated with water stems from the presence of disease-causing micro-organisms. Freshwaters contain indigenous micro-organisms, including bacteria, fungi, protozoa (single-celled organisms) and algae (micro-organisms with photosynthetic pigments), a few of which are known to produce toxins and transmit, or cause, diseases. Sewage, agricultural and urban run-off, and domestic wastewaters are widely discharged to water bodies, particularly rivers. Pathogens associated with these discharges subsequently become distributed through the water body presenting a risk to downstream water users. The most common water-borne bacterial pathogens associated with these anthropogenic discharges are *Salmonella, Shigella,* enterotoxigenic *Escherichia coli, Campylobacter, Vibrio* and *Yersinia.* Other pathogens occasionally found include *Mycobacterium, Pasteurella, Leptospira* and *Legionella* and the enteroviruses (poliovirus, echo virus and *Coxsackie* virus). Adenoviruses, reoviruses, rotaviruses and the hepatitis virus may also occur in water bodies. All viruses are highly infectious.

Typical municipal raw sewage can contain 10 to 100 million coliform bacteria (bacteria originating from the gut) per 100 mL, and 1 to 50 million *Escherichia coli* or faecal streptococci per 100 mL. Different levels of wastewater treatment may reduce this by a factor of 10 to 100 and concentrations are reduced further after dilution by the receiving waters.

Counts of bacteria of faecal origin in rivers and lakes around the world which suffer little human impact vary from < 1 to 3000 organisms per 100 mL. However, water bodies in areas of high population density can have counts up to 10 million organisms per 100 mL.

Natural groundwaters should contain no faecal bacteria unless contaminated, whereas surface waters, even in remote mountain areas, may contain up to 100 per 100 mL. To avoid human infection, the WHO recommended concentration for drinking water is zero organisms per 100 mL.

Detection of pathogens other than faecal bacteria, particularly viruses, is less common partly due to the lack of appropriate, routinely available methodology. Where faecal coliform bacteria counts are high, viruses may also be detectable, but only in volumes of 20 to 100 litres of water. Enteroviruses occur in raw sewage at very much lower concentrations than bacterial pathogens.

Monitoring for the presence of pathogenic bacteria is an essential component of any water quality assessment where water use, directly or indirectly, leads to human ingestion. Such uses include drinking, personal hygiene, recreation (e.g. swimming, boating), irrigation of food crops and food washing and processing. Monitoring to detect pathogens can be carried out even without accompanying physical and chemical measurements and, therefore, can be very inexpensive.

Sampling localities should be carefully chosen so that the source of the contamination can be identified and removed. Even when drinking water sources have been subjected to treatment and disinfection, it is essential that routine examination of the supply is carried out at weekly, or even daily intervals where the population at risk is large (tens or hundreds of thousands). Where water is used mainly for personal hygiene or recreation, there is still a risk of accidental ingestion of intestinal pathogens as well as a risk of other infections, particularly in the eyes, ears and nose. Less than 1 coliforms per 100 mL presents little risk of intestinal diseases although the risk of virus-borne infections always remains.

Where irrigation with wastewater is carried out by spraying food crops, it is advisable to monitor for faecal bacteria as there is a risk of contamination to those eating the crop.

This risk is less when irrigation is ceased some time before harvest, as many bacteria do not survive for long periods unless in ideal conditions of temperature and nutrients. The use of contaminated water in any stage of food processing presents a serious risk to human health as food provides an ideal growth medium. All water which may come into contact with food must, therefore, be checked for faecal contamination. Where treated water is temporarily stored in a tank it should be examined immediately prior to use.

Faecal contamination can be measured to indicate the presence of organic pollution of human origin. Methods for detection of the presence of faecal material have been developed which are based on the presence of “indicator” organisms, such as the normal intestinal bacterium *Escherichia coli*. Such methods are cheap and simple to perform and some have been developed into field kits. Positive identification of the pathogenic bacteria *Salmonella, Shigella* or *Vibrio* spp. can be quite complex, requiring several different methods. A special survey may be undertaken if a source of an epidemic is suspected, or if a new drinking water supply is being tested. As these organisms usually occur in very low numbers in water samples, it is necessary to concentrate the samples by a filtration technique prior to the analysis. Although methodologies for identification of viruses are constantly being improved and simplified, they require advanced and expensive laboratory facilities. However, suitably collected and prepared samples can easily be transported, making it feasible to have one national or regional laboratory capable of such analyses. Sample collection kits have been developed for use in such situations.

The above lecture is based mainly on the following publications: Bartram and Ballance, 1996; Chapman, 1996; Weiner, 2007; Gautam, 2011; American Public Health Association, American Water Works Association, and Water Environment, 2023.

11. Water pollution - pollutants sources and pathways, parameters related to water quality

Water bodies types

All freshwater bodies are inter-connected, from the atmosphere to the sea, via the hydrological cycle. Thus, water constitutes a continuum, with different stages ranging from rainwater to marine salt waters. The inland freshwaters appear in the form of rivers, lakes or groundwaters. These are closely inter-connected and may influence each other directly, or through intermediate stages, as shown in Table 11.1 and Figure 11.1. Each of the principal types of water body has distinctly different hydrodynamic properties as described below.

Table 11.1. The hydrological cycle: water volumes, residence times and fluxes

	Total cycle volume		Freshwater volume (%)	Freshwater volume* (%)	Residence times
	(10^6 Km^3)	(%)			
Oceans and seas	1370	94			~4,000 years
Lakes and reservoirs	0.13	<0.01	0.14	0.21	~10 years
Swamps and marshes	< 0.01	< 0.01	< 0.01	< 0.01	1-10 years
River channels	< 0.01	< 0.01	< 0.01	< 0.01	~2 weeks
Soil moisture	0.07	< 0.01	0.07	0.11	2 weeks-1 year
Groundwater	60	4	66.5	99.65	2 weeks-50000 years
Icecaps and glaciers	30	2	33.3		10-1000 years
Atmospheric water	0.01	< 0.01	0.01	0.02	~10 days
Biospheric water	< 0.01	< 0.01	< 0.01	< 0.01	~1 week
Fluxes					
Evaporation from oceans	425				
Evaporation from land	71				
Precipitation from oceans	385				
Precipitation from land	111				
Run-off to oceans	37.4				
Glacial ice	2.5				

*without icecaps and glaciers

Rivers are characterised by uni-directional current with a relatively high, average flow velocity ranging from 0.1 to 1 m/s. The river flow is highly variable in time, depending on the climatic situation and the drainage pattern. In general, thorough and continuous vertical mixing is achieved in rivers due to the prevailing currents and turbulence. Lateral mixing may take place only over considerable distances downstream of major confluences.

Lakes are characterised by a low, average current velocity of 0.001 to 0.01 m/s (surface values). Therefore, water or element residence times, ranging from one month to several hundreds of years, are often used to quantify mass movements of material. Currents within lakes are multi-directional. Many lakes have alternating periods of stratification and vertical mixing; the periodicity of which is regulated by climatic conditions and lake depth.

Groundwaters are characterised by a rather steady flow pattern in terms of direction and velocity. The average flow velocities commonly found in aquifers range from 10^{-10} to 10^{-3} m/s and are largely governed by the porosity and permeability of the geological material. As a consequence, mixing is rather poor and, depending on local hydrogeological features, the ground-water dynamics can be highly diverse.

There are several transitional forms of water bodies which demonstrate features of more than one of the three basic types described above and are characterised by a particular combination of

hydrodynamic features. The most important transitional water bodies are illustrated in Figure 11.1 and are described below.

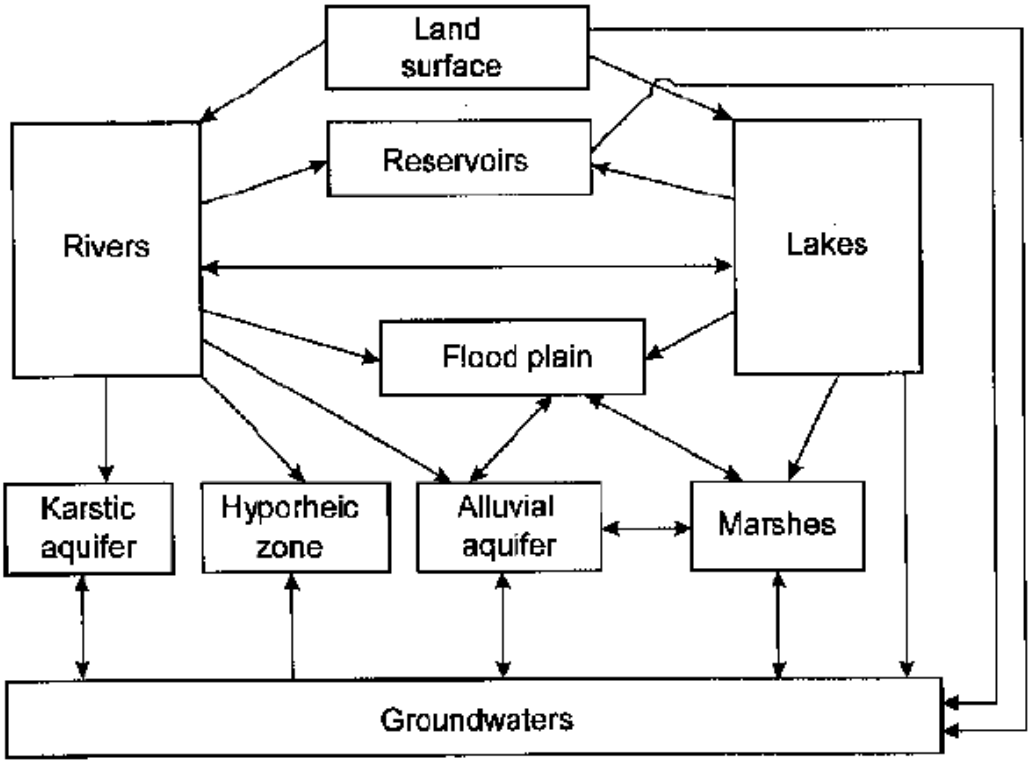

Figure 11. 1. Inter-connections between inland freshwater bodies (intermediate water bodies have mixed characteristics belonging to two or three of the major water bodies)

Reservoirs are characterised by features which are intermediate between rivers and lakes. They can range from large-scale impoundments, such as Lake Nasser, to small dammed rivers with a seasonal pattern of operation and water level fluctuations closely related to the river discharge, to entirely constructed water bodies with pumped in-flows and out-flows. The cascade of dams along the course of the river Dnieper is an example of the interdependence between rivers and reservoirs. The hydrodynamics of reservoirs are greatly influenced by their operational management regime.

Flood plains constitute an intermediate state between rivers and lakes with a distinct seasonal variability pattern. Their hydrodynamics are, however, determined by the river flow regime.

Marshes are characterised by the dual features of lakes and phreatic aquifers. Their hydrodynamics are relatively complex.

Alluvial and karstic aquifers are intermediate between rivers and ground-waters. They differ, generally, in their flow regime which is rather slow for alluvial and very rapid for karstic aquifers. The latter are often referred to as underground rivers.

As a consequence of the range of flow regimes noted above, large variations in water residence times occur in the different types of inland water bodies. The hydrodynamic characteristics of each type of water body are highly dependent on the size of the water body and on the climatic conditions in the drainage basin. The governing factor for rivers is their hydrological regime, i.e. their discharge variability.

Lakes are classified by their water residence time and their thermal regime resulting in varying stratification patterns. Although some reservoirs share many features in common with lakes, others have characteristics which are specific to the origin of the reservoir. One feature common to most reservoirs is the deliberate management of the inputs and/or outputs of water for specific purposes.

Groundwaters greatly depend upon their recharge regime, i.e. infiltration through the unsaturated aquifer zone, which allows for the renewal of the ground-water body.

The knowledge of the hydrodynamic properties of a water body must be acquired before an effective water quality monitoring system can be established. Interpretation of water quality data cannot provide meaningful conclusions unless based on the temporal and spatial variability of the hydrological regime.

Anthropogenic impacts on water quality

With the advent of industrialisation and increasing populations, the range of requirements for water have increased together with greater demands for higher quality water. Over time, water requirements have emerged for different water uses - for drinking and personal hygiene, fisheries, agriculture (irrigation and livestock supply), navigation for transport of goods, industrial production, cooling in fossil fuel and in nuclear power plants, hydropower generation, and recreational activities such as bathing or fishing. Luckily, the largest demands for water quantity, such as for agricultural irrigation and industrial cooling, require the least in terms of water quality (i.e. critical concentrations may only be set for one or two variables). Drinking water supplies and specialised industrial manufacturers exert the most sophisticated demands on water quality but their quantitative needs are relatively moderate. In parallel with these uses, water has been considered, since ancient times, the most suitable medium to clean, disperse, transport and dispose of wastes (domestic and industrial wastes, mine drainage waters, irrigation returns, etc.).

Each water use, including abstraction of water and discharge of wastes, leads to specific, and generally rather predictable, impacts on the quality of the aquatic environment. In addition to these intentional water uses, there are several human activities which have indirect and undesirable effects on the aquatic environment. Examples are uncontrolled land use for urbanisation or deforestation, accidental (or unauthorised) release of chemical substances, discharge of untreated wastes or leaching of noxious liquids from solid waste deposits. Similarly, the uncontrolled and excessive use of fertilisers and pesticides has long-term effects on ground and surface water resources.

Structural interventions in the natural hydrological cycle through canalisation or damming of rivers, diversion of water within or among drainage basins, and the over-pumping of aquifers are usually undertaken with a beneficial objective in mind. Experience has shown, however, that the resulting long-term environmental degradation often outweighs these benefits. The most important anthropogenic impacts on water quality, on a global scale, are summarised in Table 11.2, which also distinguishes between the severity of the impairment of use in different types of water bodies.

Pollution and water quality degradation interfere with vital and legitimate water uses at any scale, i.e. local, regional or international. As shown in Table 11.3, some types of uses are more prone to be affected than others. Water quality criteria, standards and the related legislation are used as the main administrative means to manage water quality in order to achieve user requirements. The most common national requirements are for drinking water of suitable quality, and many countries base their own standards on the World Health Organization (WHO) guidelines for drinking water quality.

Pollutant sources and pathways

In general, pollutants can be released into the environment as gases, dissolved substances or in the particulate form. Ultimately pollutants reach the aquatic environment through a variety of pathways, including the atmosphere and the soil. Figure 11.2 illustrates, in schematic form, the principal pathways of pollutants that influence freshwater quality.

Pollution may result from point sources or diffuse sources (non-point sources). There is no clear-cut distinction between the two, because a diffuse source on a regional or even local scale may result from a large number of individual point sources, such as automobile exhausts.

An important difference between a point and a diffuse source is that a point source may be collected, treated or controlled (diffuse sources consisting of many point sources may also be controlled provided all point sources can be identified).

Table 11.2 Major freshwater quality issues at the global scale[1]

Issue	Water body			
	Rivers	**Lakes**	**Reservoirs**	**Groundwaters**
Pathogens	xxx	x[2]	x[2]	x
Suspended solids	xx	na	x	na
Decomposable organic matter[3]	xxx	x	xx	x
Eutrophication[4]	x	xx	xxx	na
Nitrate as a pollutant	x	0	0	xxx
Salinisation	x	0	x	xxx
Trace elements	xx	xx	xx	xx[5]
Organic micropollutants	xxx	xx	xx	xxx[5]
Acidification	x	xx	xx	0
Modification of hydrological regimes[6]	xx	x		x

xxx Severe or global deterioration found; xx Important deterioration; x Occasional or regional deterioration
0 Rare deterioration; na Not applicable;
[1] This is an estimate for the global scale. At a regional scale these ranks may vary greatly according to the stage of economic development and land-use. Radioactive and thermal wastes are not considered here.
[2] Mostly in small and shallow water bodies
[3] Other than resulting from aquatic primary production
[4] Algae and macrophytes
[5] From landfill, mine tailings
[6] Water diversion, damming, overpumping, etc.

Table 11.3. Limits of water uses due to water quality degradation

Pollutant	Uses						
	Drinking water	Aquatic wild life, fisheries	Recreation	Irrigation	Industrial uses	Power and cooling	Transport
Pathogens	xx	0	xx	x	xx[1]	na	na
Suspended solids	xx	xx	xx	x	x	x[2]	xx[3]
Organic matter	xx	x	xx	+	xx[4]	x[5]	na
Algae	x[5,6]	x[7]	xx	+	xx[4]	x[5]	x[8]
Nitrate	xx	x	na	+	xx[1]	na	na
Salts[9]	xx	xx	na	xx	xx[10]	na	na
Trace elements	xx	xx	x	x	x	na	na
Organic micropollutants	xx	xx	x	x	?	na	na
Acidification	x	xx	x	?	x	x	na

xx Marked impairment causing major treatment or excluding the desired use; x Minor impairment; 0 No impairment; na Not applicable; + Degraded water quality may be beneficial for this specific use; ? Effects not yet fully realised
[1] Food industries; [2] Abrasion; [3] Sediment settling in channels; [4] Electronic industries; [5] Filter dogging; [6] Odour, taste; [7] In fish ponds higher algal biomass can be accepted; [8] Development of water hyacinth (*Eichhomia crassipes*); [9] Also includes boron, fluoride, etc. [10] Ca, Fe, Mn in textile industries, etc.

The major point sources of pollution to freshwaters originate from the collection and discharge of domestic wastewaters, industrial wastes or certain agricultural activities, such as animal husbandry. Most other agricultural activities, such as pesticide spraying or fertiliser application, are considered as diffuse sources. The atmospheric fall-out of pollutants also leads to diffuse pollution of the aquatic environment. The various sources of major pollutant categories are summarised in Table 11.4.

Atmospheric sources

The atmosphere is proving to be one of the most pervasive sources of pollutants to the global environment. Significant concentrations of certain contaminants are even being observed in Arctic and Antarctic snow and ice, with high levels of bioaccumulation magnified through the food chain to mammals and native human populations.

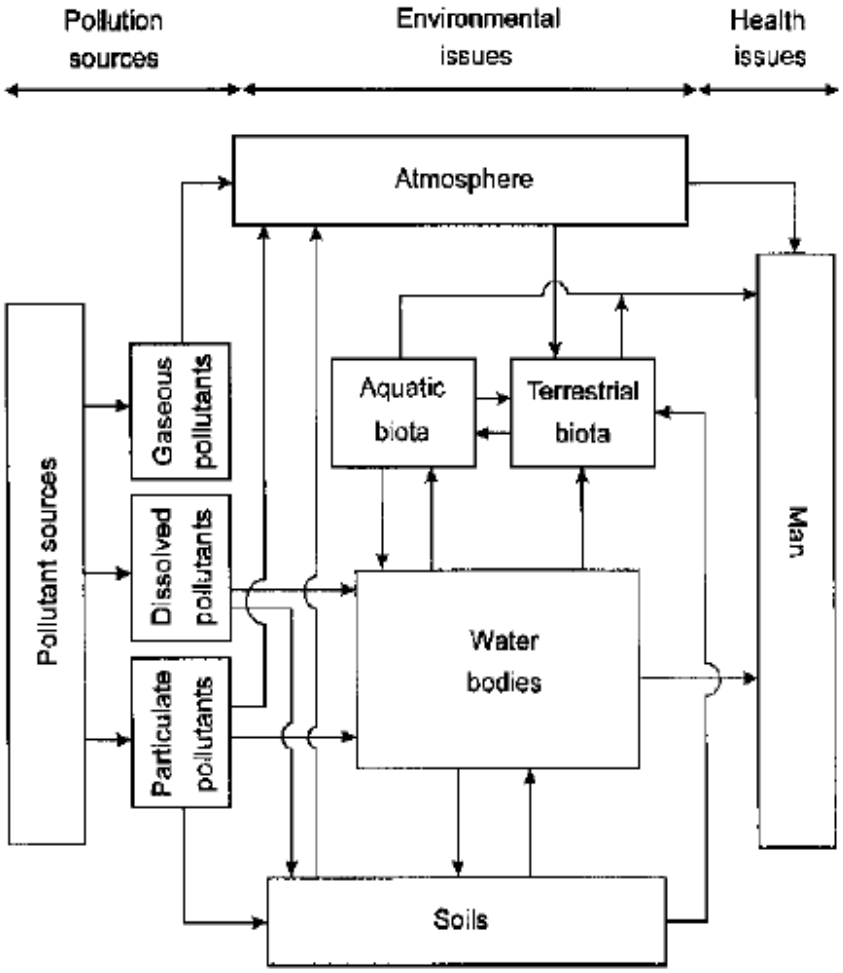

Figure 11.2 Potential pollutant pathways related to the aquatic environment

Table 11.4. Anthropogenic sources of pollutants in the aquatic environment

Source	Bacteria	Nutrients	Trace elements	Pesticides/ herbicides	Industrial organic micro pollutants	Oils and greases
Atmosphere		x	xxxG	xxxG	xxxG	
Point sources						
Sewage	xxx	xxx	xxx	x	xxx	
Industrial effluents		x	xxxG		xxxG	xx
Diffuse sources						
Agriculture	xx	xxx	x	xxxG		
Dredging		x	xxx	xx	xxx	x
Navigation and harbours	x	x	xx		x	xxx
Mixed sources						
Urban run-off and waste disposal	xx	xxx	xxx	xx	xx	xx
Industrial waste disposal sites		x	xxx	x	xxx	x

x Low local significance; xx Moderate local/regional significance; xxx High local/regional significance; G Globally significant

Sources of anthropogenic materials to the atmosphere include:
• combustion of fossil fuels for energy generation,
• combustion of fossil fuels in automobiles, other forms of transport, heating in cold climates and industrial needs (e.g. steel making),
• ore smelting, mainly sulphides,
• wind blown soils from arid and agricultural regions,
• volatilisation from agriculture, from waste disposal and from previously polluted regions.
These sources, together, provide an array of inorganic and organic pollutants to the atmosphere which are then widely dispersed by weather systems and deposited on a global scale.

Point sources
By definition a point source is a pollution input that can be related to a single outlet. Untreated, or inadequately treated, sewage disposal is probably still the major point source of pollution to the world's waters. Other important point sources include mines and industrial effluents. As point sources are localised, spatial profiles of the quality of the aquatic environment may be used to locate them.
Some point sources are characterised by a relatively constant discharge of the polluting substances over time, such as domestic sewers, whereas others are occasional or fluctuating discharges, such as leaks and accidental spillages.
A sewage treatment plant serving a fixed population delivers a continuous load of nutrients to a receiving water body. Therefore, an increase in river discharge causes greater dilution and a characteristic decrease in river concentration. This contrasts with atmospheric deposition and other diffuse sources where increased land run-off often causes increased pollutant concentrations in the receiving water system.

Non-atmospheric diffuse sources
Diffuse sources cannot be ascribed to a single point or a single human activity although, as pointed out above, they may be due to many individual point sources to a water body over a large area. Typical examples are:
• Agricultural run-off, including soil erosion from surface and sub-soil drainage. These processes transfer organic and inorganic soil particles, nutrients, pesticides and herbicides to adjacent water bodies.
• Urban run-off from city streets and surrounding areas (which is not channelled into a main drain or sewer). Likely contaminants include derivatives of fossil fuel combustion, bacteria, metals and industrial organic pollutants, particularly PCBs.
Pesticides and herbicides may also be derived from urban gardening, landscaping, horticulture and their regular use on railways, airfields and roadsides. In the worst circumstances pollutants from a variety of diffuse sources may be diverted into combined storm / sewer systems during storm-induced, high drainage flow conditions, where they then contribute to major point sources.
• Waste disposal sites which include municipal and industrial solid waste disposal facilities; liquid waste disposal (particularly if groundwater is impacted); dredged sediment disposal sites (both confined and open lake). Depending on the relative sizes of the disposal sites and receiving water bodies, these sources of pollution can be considered as either diffuse or point sources, as in the case of groundwater pollution.
• Other diffuse sources including waste from navigation, harbour and marina sediment pollution, and pollution from open lake resource exploitation, in particular oil and gas (e.g. Lakes Erie and Maracaibo).
The time variability of pollutant release into the aquatic environment falls into four main categories. Sources can be considered as permanent or continuous (e.g. domestic wastes from a major city and many industrial wastes), periodic (e.g. seasonal variation associated with the influx of tourist populations, or food processing wastes), occasional (e.g. certain industrial waste releases), or accidental (e.g. tank failure, truck or train accidents, fires, etc.). The effects of these various types

of pollutants on receiving water bodies are rather different. The continuous discharge of municipal sewage, for example, may be quite acceptable to a river during high river discharge periods when dilution is high and biodegradation is sufficient to cope with the pollution load. During low discharges, however, pollution levels and effects may exceed acceptable levels in downstream river stretches. Figure 11.3A shows these two seasonal situations for rivers. The example of the effects of an episodic pollution event on a lake is given in Figure 11.3B which shows the influence of residence time on the elimination of the pollutant from the lake, as measured at its natural outlet. Lake volume and initial dilution are also factors codetermining the prevalence of the pollutant in the lake.

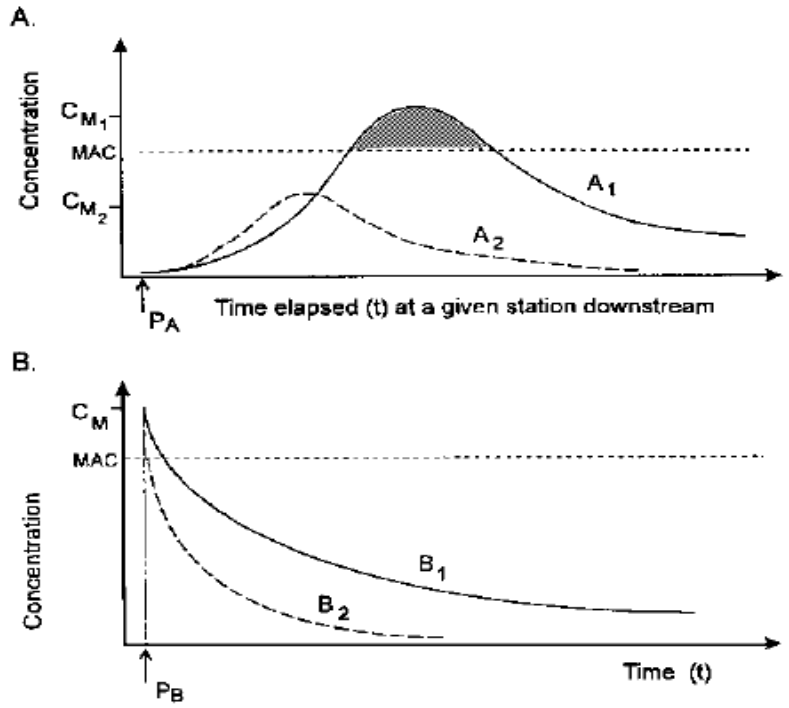

Figure 11.3. The influence of hydrodynamic characteristics on the environmental fate of pollutants (C_M maximum concentration reached, MAC maximum allowable concentration) A. Schematic response observed at a given river station downstream of a chronic point source of pollution (PA) (non-reactive dissolved substances). High (A_2) and low (A_1) river discharge. B. Schematic response observed at lake outlets following a single episode of pollution (PB) (non-reactive dissolved substances) for long (B_1) and short (B_2) residence times in lakes of equal volumes

The temporal variation of the chemical quality of water bodies can be described by studying concentrations (also loads in the case of rivers) or by determining rates such as settling rates, biodegradation rates or transport rates. It is particularly important to define temporal variability. Five major types are generally considered:

• Minute-to-minute to day-to-day variability resulting from water mixing, fluctuations in inputs, etc., mostly linked to meteorological conditions and water body size (e.g. variations during river floods).

• Day variability (24-hour variations) limited to biological cycles, light / dark cycles, etc. (e.g. O_2, nutrients, pH), and to cycles in pollution inputs (e.g. domestic wastes).

• Days-to-months variability mostly in connection with climatic factors (river regime, lake overturn, etc.) and to pollution sources (e.g. industrial wastewaters, run-off from agricultural land).

• The seasonal hydrological and biological cycles (mostly in connection with climatic factors).

• Year-to-year trends, mostly due to human influences.

Groundwater pollution

Groundwater constitutes about two thirds of the freshwater resources of the world and, if the polar ice caps and glaciers are not considered, groundwater accounts for nearly all usable freshwater. Groundwater bodies are distinguished from surface water bodies by two principal features:

a) The relatively slow movement of water through the ground means that residence times in groundwaters are generally orders of magnitude longer than in surface waters. As a consequence, once polluted, a groundwater body could remain so for decades, or even for hundreds of years, because the natural processes of self-cleaning are very slow. b) There is a considerable degree of physico-chemical and chemical interdependence between the water and the material containing this water.
Groundwater quality is the sum of natural and anthropogenic influences. Processes which may influence groundwater composition are presnted in Table 11.5.

Table 11.5 Processes which may affect constituents of groundwater

Constituent	Physical		Geochemical						Biochemical	
	Dispersion	Filtration	Complexation	Ionic strength	Acid-base	Oxidation-reduction	Precipitation-solution	Adsorption-desorption	Decay, respiration	Cell synthesis
Cl^-, Br^-	xx									
NO_3^-	xx					xx			xx	xx
SO_4^{2-}	xx		x	x	x	xx		x	x	
HCO_3^-	xx		x	x	xx		xx		xx	
PO_4^{3-}	xx		xx	xx	xx		xx	xx	xx	xx
Na^+	xx			x				xx		
K^+	xx			x				xx		
NH_4^+	xx		xx	x	xx	xx		xx	xx	xx
Ca^{2+}	xx		x	xx			x	xx		
Mg^{2+}	xx		x	xx			x	xx		
Fe^{2+}	xx		xx	xx	xx	xx	xx	xx		
Mn^{2+}	xx		xx	xx	xx	xx	xx	xx		
Fe^{3+} and Mn^{4+} oxyhydroxides	xx	xx			xx	xx	xx			
Trace elements	xx		xx	xx		xx	xx	xx		
Organic solutes	xx		xx	x	xx	xx	x	x	xx	xx
Microorganisms	xx	xx				xx			xx	xx

xx Major control; x Minor control

The principal activities able to cause groundwater pollution are presented in Table 11.6

Table 11.6 Principal activities potentially causing groundwater pollution

Activity	Principal characteristics of pollution					Stage of development[1]			Impact of water use		
	Distribution	Category	Main types of pollutant	Relative hydraulic surcharge	Soil zone bypassed	I	II	III	Drinking	Agricultural	Industrial
Urhanisation											
Unsewered sanitation	ur	P-D	pno	x	√	xxx	xx	x	xxx		x
Land discharge of sewage	ur	P-D	nsop	x		x	x	x	xx	x	x
Stream discharge of sewage	ur	P-L	nop	xx	√	x	x		xx	x	x
Sewage oxidation lagoons	u	P	opn	xx	√	x	xx	x	xx		x
Sewer leakage	u	P-L	opn	x	√			xx	x		x
Landfill, solid waste disposal	ur	P	osnh		√	x	xx	xx	x		x

Activity	Principal characteristics of pollution					Stage of evelop ment[1]			Impact of water use		
	Distribu tion	Cate gory	Main types of pollutant	Relative hyd raulic surcharge	Soil zone bypassed	I	II	III	Drin king	Agricul tural	Industrial
Highway drainage soak-aways	ur	P-L	so	xx	√	x	xx	xx	xx	x	x
Wellhead contamination	ur	P	pn		√	xxx	x		xxx		
Industrial development											
Process water/ effluent lagoons	u	P	ohs	xx	√	x	xx	xx	xx		x
Tank and pipeline leakage	u	P	oh		√	x	xx	xxx	xx		xx
Accidental spillages	ur	P	oh	xx		x	xx	xxx	xxx		xx
Land discharge of effluent	u	P-L	ohs	x		x	xx	xx	x	x	x
Stream discharge of effluent	u	P-L	ohs	xx	√	x	x	x	x	x	x
Landfill disposal residues and waste	ur	P	ohs		√	x	xx x	xxx	xx		x
Well disposal of effluent	u	P	ohs	xx	√		x	x	xx		x
Aerial fallout	ur	D	a					xx	x	x	x
Agricultural development											
Cultivation with:											
Agrochemicals	r	D	no			x	xx	xxx	xxx	x	x
Irrigation	r	D	sno	x		xx	xx	x	xxx	xxx x	x
Sludge and slurry	r	D	nos			x	x	xx	xx	x	x
Wastewater irrigation	r	D	nosp	x			xx	x	xx	xx	
Livestock rearing/mcropprocessing:											
Unlined effluent lagoons	r	P	pno	x	√	x	x	xx	x	x	
Land discharge of effluent	r	P-D	nsop	x	√	x	x	xx	x	x	
Stream discharge of effluent	r	P-L	onp	x	√	x	x	xx	x	x	
Mining development											
Mine drainage discharge	ru	P-L	sha	xx	√	x	xx	xx	xx	x	x
Process water/ sludge lagoons	ru	P	hsa	xx	√	x	xx	xx	xx	x	x
Solid mine tailings	ru	P	hsa		√	x	xx	xx	xx	x	x
Oilfield brine disposal	r	P	s	x	√		x	x	xx	x	x
Hydraulic disturbance	ru	D	s		na		x	x	xx	x	x
Groundwater resource management											
Saline intrusion	ur	D-L	s		na	x	x	xx	xxx	xxx	xx
Recovering water levels	u	D	so		na			x	x		x

Distribution: u Urban; r Rural; Category: P Point; D Diffuse; L Line; Types of pollutant: p Faecal pathogens; n Nutrients; o Organic micropollutants; h Heavy metals; s Salinity; a Acidification; x to xxxx Increasing importance or impact; na Not applicable ; [1] Stages of development: I Low development; II Newly industrialising; III Highly industrialised

Definitions and parameters related to water quality

In view of the complexity of factors determining water quality, and the large choice of variables used to describe the status of water bodies in quantitative terms, it is difficult to provide a simple definition of water quality. Furthermore, our understanding of water quality has evolved over the past century with the expansion of water use requirements and the ability to measure and interpret water characteristics.
Very often terms quality and pollution are used. Their fedinitions, as given by the WHO, are presented in Table 11.7

Table 11.7 Terms and definition used by the WHO in relateion to water quality

Term	Definition
QUALITY of the aquatic environment	• Set of concentrations, speciations, and physical partitions of inorganic or organic substances. • Composition and state of aquatic biota in the water body. • Description of temporal and spatial variations due to factors internal and external to the water body.
POLLUTION of the aquatic environment	Introduction by man, directly or indirectly, of substances or energy which result in such deleterious effects as: • harm to living resources, • hazards to human health, • hindrance to aquatic activities including fishing, • impairment of water quality with respect to its use in agricultural, industrial and often economic activities • reduction of amenities.
Water quality ASSESSMENT	The overall process of evaluation of the physical, chemical and biological nature of water in relation to natural quality, human effects and intended uses, particularly uses which may affect human health and the health of the aquatic system itself.
Water quality MONITORING	The actual collection of information at set locations and at regular intervals in order to provide the data which may be used to define current conditions, establish trends, etc.

The physical and chemical quality of pristine waters would normally be as occurred in pre-human times, i.e. with no signs of anthropogenic impacts. The natural concentrations could, nevertheless, vary by one or more orders of magnitude between different drainage basins. In practice, pristine waters are very difficult to find as a result of atmospheric transport of contaminants and their subsequent deposition in locations far distant from their origin.
Description of the quality of the aquatic environment can be carried out in a variety of ways. It can be achieved either through quantitative measurements, such as physicochemical determinations (in the water, particulate material, or biological tissues) and biochemical / biological tests (BOD measurement, toxicity tests, etc.), or through semiquantitative and qualitative descriptions such as biotic indices, visual aspects, species inventories, odour, etc. These determinations are carried out in the field and in the laboratory and produce various types of data which lend themselves to different interpretative techniques. The terms monitoring and assessment are frequently confused and used synonymously. The most often used definitions by the WHO are presented in Tablw 11.7.
Water quality assessment includes the use of monitoring to define the condition of the water, to provide the basis for detecting trends and to provide the information enabling the establishment of cause-effect relationships. Important aspects of an assessment are the interpretation and reporting of the results of monitoring and the making of recommendations for future actions. Thus, there is a logical sequence consisting of three components: monitoring, followed by assessment, followed by

management. In addition, there is also a feedback loop because management inevitably requires compliance monitoring to enforce regulations, as well as assessments at periodic intervals to verify the effectiveness of management decisions.
DPSIR conceptual framework is proposed to be used in order to the assess the worldwide water quality situation - Figure 11.4. This framework divides different aspects of a entire system into linked “drivers” (D), “pressures” (P), “states” (S), impacts” (I) and “responses” (R). “Drivers” are the underlying factors influencing changes in water quality. “Pressures” are factors that lead to a direct change in water quality. “State” refers to spatial and temporal aspects of the state of water quality. “Impacts” are the consequences of water pollution. “Response” refers to options that society has to mitigate to the impacts of water pollution.

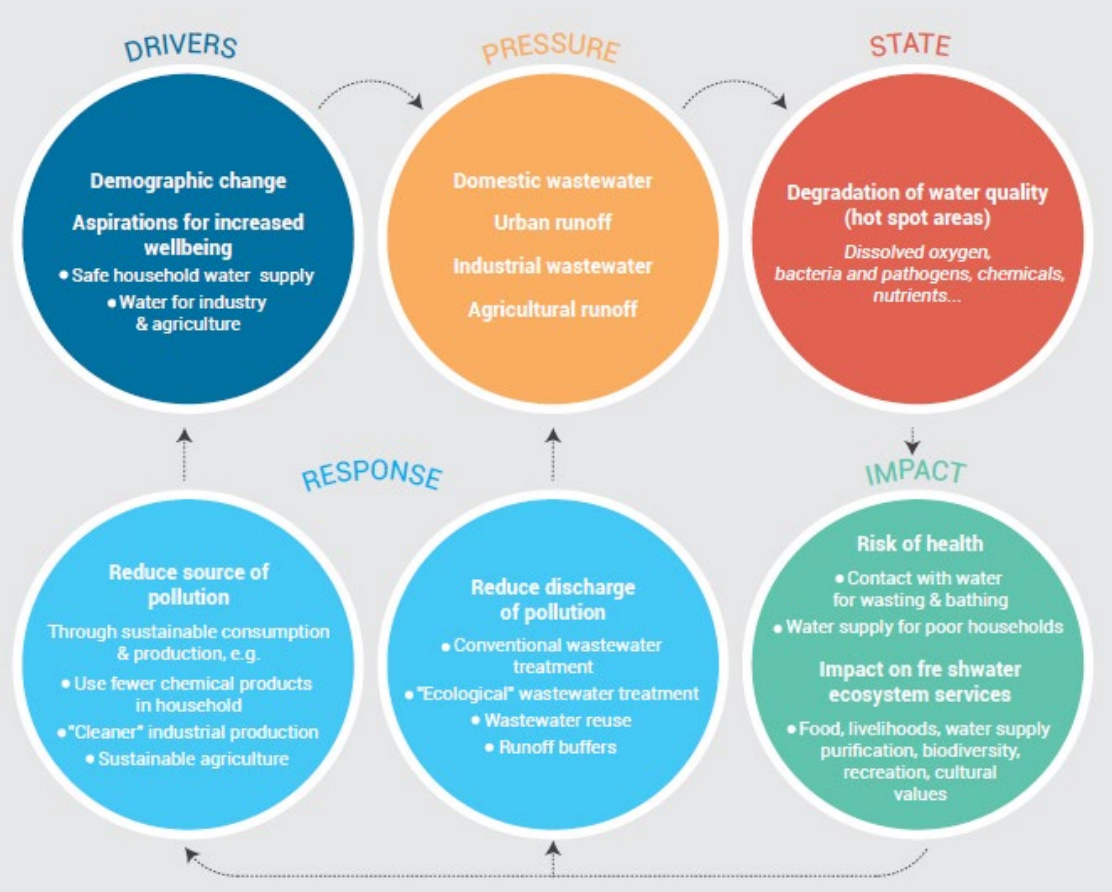

Figure 11.4 . Scheme of the DPSIR conceptual framework

Many uses of water have specific requirements with respect to contaminants or physical and chemical variables. The required quality of the water is defined by guidelines, standards or maximum allowable concentrations. These consist of mandatory (as in the case of standards) or recommended (as in the case of guidelines) concentrations of selected variables which should not be exceeded for the prescribed water use. For some variables, the defined concentrations vary from country to country. Existing standards and guidelines define the minimum set of variables for inclusion in assessment programmes. Table 11.8 presents variables suitable for assessment of water quality in relation to nonindustrial water use and can be used where guidelines are not available.
The requirements of industry for water quality are diverse, depending on the nature of the industry and the individual processes using water within that industry. Table 11.9 shows variables for the assessment of water quality in relation to some major industrial uses or processes
The guidelines proposed have to be considered in relation to the specific industrial needs and water availability.

Table 11.8. Selection of variables for assessment of water quality in relation to nonindustrial water use[1]

	Background monitoring	Aquatic life and fisheries	Drinking water sources	Recreation and health	Agriculture	
					Irrigation	Livestock watering
General variables						
Temperature	xxx	xxx		x		
Colour	xx		xx	xx		
Odour			xx	xx		
Suspended solids	xxx	xxx	xxx	xxx		
Turbidity/transparency	x	xx	xx	xx		
Conductivity	xx	x	x		x	
Total dissolved solids		x	x		xxx	x
pH	xxx	xx	x	x	xx	
Dissolved oxygen	xxx	xxx	x		x	
Hardness		x	xx			
Chlorophyll a	x	xx	xx	xx		
Nutrients						
Ammonia	x	xxx	x			
Nitrate/nitrite	xx	x	xxx			xx
Phosphorus or phosphate	xx					
Organic matter						
TOC	xx		x	x		
COD	xx	xx				
BOD	xxx	xxx	xx			
Major ions						
Sodium	x		x		xxx	
Potassium	x					
Calcium	x				x	x
Magnesium	xx		x			
Chloride	xx		x		xxx	
Sulphate	x		x			x
Other inorganic variables						
Fluoride			xx		x	x
Boron					xx	x
Cyanide		x	x			
Trace elements						
Heavy metals		xx	xxx		x	x
Arsenic & selenium		xx	xx		x	x
Organic contaminants						
Oil and hydrocarbons		x	xx	xx	x	x
Organic solvents		x	xxx[2]			x
Phenols		x	xx			x
Pesticides		x	xx			x
Surfactants		x	x	x		x
Microbiological indicators						
Faecal coliforms			xxx	xxx	xxx	
Total coliforms			xxx	xxx	x	
Pathogens			xxx	xxx	x	xx

TOC Total organic carbon; BOD Biochemical oxygen demand; COD Chemical oxygen demand
x - xxx Low to high likelihood that the concentration of the variable will be affected and the more important it is to include the variable in a monitoring programme. Variables stipulated in local guidelines or standards for a specific water use should be included when monitoring for that specific use. The selection of variables should only include those most appropriate to local conditions and it may be necessary to include other variables not indicated under the above heading
[1] For industrial uses see Table 11.9; [2] Extremely important in groundwater

Water quality assessment often studies the effects of specific human activities on water quality. The selection of variables is governed by knowledge of the pollution sources and the expected impacts on the receiving water body.

Table 11.9. Selection of variables for the assessment of water quality in relation to some key industrial uses

	Heating	Cooling	Power generation	Iron and steel	Pulp and paper	Petrol	Food processing
			General variables				
Temperature	xxx	xxx		xxx	x		
Colour	x				x		xx
Odour							xxx
Suspended solids	xxx	xxx	xx	xx	x	xxx	xx
Turbidity	xx				xx		xx
Conductivity	x	x					
Total dissolved solids	xx	xx	xxx	xx	xxx	x	xxx
pH	x	xxx	xxx	xx	xx	xxx	xxx
Dissolved oxygen	xxx		x	xxx	x		
Hardness	xxx	xx	xxx	xx	xxx	xxx	xxx
			Nutrients				
Ammonia	xxx		x				x
Nitrate/nitrite						x	xx
Phosphorus or phosphate					x		
Organic matter							
COD		x	xx				
Major ions							
Calcium		xxx	xxx		x	xxx	x
Magnesium			x		x	xxx	x
Carbonate components	xx		xxx		xxx	x	x
Chloride	x	x	xx	xx	x	xxx	xxx
Sulphate		x	xx	xx	xx	x	xxx
			Other inorganic variables				
Hydrogen sulphide	xxx	x					xx
Silica	xx	xx	x		x	x	x
Fluoride						x	xx
			Trace elements				
Aluminium		x	x				
Copper		x	x				
Iron	xx	x	x		x	x	xx
Manganese	xx	x	x		x		xx
Zinc			x				
			Organic contaminants				
Oil and hydrocarbons	x	x	x	x			x
Organic solvents							x
Phenols							x
Pesticides							x
Surfactants	x	x	x				x
			Microbiological indicators				
Pathogens							xxx

COD Chemical oxygen demand
x - xxx Low to high likelihood that the concentration of the variable will be affected and the more important it is to include the variable in a monitoring programme. The precise selection of variables depends on the required quality of the water in the individual industrial processes and any standards or guidelines that are applied.

It is also reccomendable to know the quality of the water prior to anthropogenic inputs. This can be obtained, for example, by monitoring upstream in a river or prior to the development of a proposed waste disposal facility. When this cannot be done, background water quality from an adjacent, uncontaminated, water body in the same catchment can be used. Suitable variables for assessing water quality in relation to difffrent sources of pollutants are given in Tables 11.10 and 11.11.

Table 11.10. Selection of variables for the assessment of water quality in relation to nonindustrial pollution sources

Variables	Sewage and Municipal wastewater[1]	Urban run-off	Agricultural activities	Waste disposal to land		Long range atmospheric transport
				Solid municipal	Hazardous chemicals	
General variables						
Temperature	x	x	x			
Colour	x	x	x	x		
Odour	x	x	x			
Residues	x	x	xxx	xxx	xx	
Suspended solids	xxx	xx	xxx	xx	xx	
Conductivity	xx	xx	xx	xxx	xxx	xxx
Alkalinity				xx		xxx
pH	x	x	x	xx	xxx	xxx
Eh	x	x	x			
Dissolved oxygen	xxx	xxx	xxx	xxx	xxx	
Hardness	x	x	x		x	x
Nutrients						
Ammonia	xxx	xx	xxx	xx		
Nitrate/nitrite	xxx	xx	xxx	xx		xxx
Organic nitrogen	xxx	xx	xxx	xx		
Phosphorus or phosphate	xxx	xx	xxx	x		x
Organic matter						
TOC	x	x	x			
COD	xx	xx	x	xxx	xxx	
BOD	xxx	xx	xxx	xxx	xx	
Major ions						
Sodium	xx	xx	xx			
Potassium	x	x	x			
Calcium	x	x	x			
Magnesium	x	x	x			
Carbonate components	x					
Chloride	xxx	xx	xxx	xx	xx	
Sulphate	x	x	x			xxx
Other inorganic variables						
Sulphide	xx	xx	x		x	
Silica	x	x				
Fluoride	x	x				
Boron			x			
Trace elements						
Aluminium						xx
Cadmium		x		xxx	xxx	x
Chromium		x		xxx	xx	x
Copper	x	x	xx[2]	xxx	xx	x
Iron	xx	xx		xxx	xx	x
Lead	xx	xxx		xxx	xx	xx
Mercury	x	xx	xxx[2]	xxx	xxx	
Zinc			xx[2]	xxx	xx	x

Variables	Sewage and Municipal wastewater[1]	Urban run-off	Agricultural activities	Waste disposal to land		Long range atmospheric transport
				Solid municipal	Hazardous chemicals	
Trace elements						
Arsenic		x	xxx[2]	xx	xxx	x
Selenium		x	xxx[2]	x	x	
Organic contaminants						
Fats	x	x				
Oil and hydrocarbons	xx	xxx		xx	x	
Organic solvents	x	x		xxx	xxx	
Methane				xxx[3]		
Phenols	x			xx	xx	
Pesticides		x	xxx[4]	xx	xxx	xxx
Surfactants	xx		x		x	
Microbiological indicators						
Faecal coliforms	xxx	xx	xx	xxx		
Other pathogens	xxx		xx	xxx		

TOC Total organic carbon
COD Chemical oxygen demand
BOD Biochemical oxygen demand
x - xxx Low to high likelihood that the concentration of the variable will be affected and the more important it is to include the variable in a monitoring programme. The final selection of variables to be monitored depends on the products manufactured or processed together with any compounds present in local industrial effluents. Any standards or guidelines for specific variables should also be taken into consideration.
1 Assumes negligible industrial inputs to the wastewater
2 Need only be measured when used locally or occur naturally at high concentrations
3 Important only for groundwater in localised industrial areas
4 Specific compounds should be measured according to their level of use in the region.

Table 11.11. Selection of variables for the assessment of water quality in relation to some common industrial sources of pollution

	Food processing	Mining	Oil extraction/ refining	Chemical/ pharmacy	Pulp and paper	Metallurgy	Machine production	Textiles
General variables								
Temperature	x	x	x	x	x	x	x	x
Colour	x	x	x	x	x	x	x	x
Odour	x	x	x	x	x	x	x	x
Residues	x	x	x	x	x	x	x	
Suspended solids	x	xxx	xxx	x	xxx	xxx	xxx	xxx
Conductivity	xxx	xxx	xxx	x	xxx	xxx	xxx	xxx
pH	xxx	xxx	x	xxx	x	xxx	x	x
Eh	x	x	x	x	x	x	x	x
Dissolved oxygen	xxx	xxx	xxx	xxx	xxx	x	x	xxx
Hardness	x	x	x	x	x	xx	x	x
Nutrients								
Ammonia	xxx	x	xx	xx	x	x	x	x
Nitrate/nitrite	xx	x		xx	x	x		x
Organic nitrogen	xx			x	x			x
Phosphorus compounds	xx			xx			x	x

	Food processing	Mining	Oil extraction/ refining	Chemical/ pharmacy	Pulp and paper	Metallurgy	Machine production	Textiles
Organic matter								
TOC	x	x	x	xx	xxx	x	x	x
COD	x	x	x	xxx	xxx	x	x	x
BOD	xxx	x	xxx	xx	xxx	x	x	xxx
Major ions								
Sodium	x	x	x	x				x
Potassium	x	x	x	x				
Calcium	x	x	x	x	x	xx	x	x
Magnesium	x	x	x	x	x	x		x
Carbonate components	x	x	x	x				
Chloride	xx	xxx	xx	xx	x	x	x	xxx
Sulphate	x	x	xx	xx	xxx	x	x	x
Other inorganic variables								
Sulphide		x	xxx	xxx	xxx	xxx		x
Silica		x	x	x			x	x
Fluoride		x	x	xx		x		x
Boron		x	x	x	x	x	x	x
Cyanide		x		x		x	x	x
Trace elements								
Heavy metals		xxx	xx	xx	x	xxx	xxx	xx
Arsenic		x		x		x		x
Selenium		x		x		x	x	x
Organic contaminants								
Fats	xx							
Oil and hydrocarbons			xxx	xx		xx	xxx	x
Organic solvents				xxx	xxx		x	x
Phenols	x		xx	xxx	xxx	x		x
Pesticides	x			xxx				
Other organics				xxx	xxx	x		
Surfactants								
Microbiological indicators								
Faecal coliforms	xxx							
Other pathogens	xxx							

TOC Total organic carbon
COD Chemical oxygen demand
BOD Biochemical oxygen demand
x - xxx Low to high likelihood that the concentration of the variable will be affected and the more important it is to include the variable in a monitoring programme. The final selection of variables to be monitored depends on the products manufactured or processed together with any compounds present in local industrial effluents. Any standards or guidelines for specific variables should also be taken into consideration.

The above lecture is based mainly on the following publications: Chapman, 1996; Weiner, 2007; UN-Water, 2016.

12. Used references and further reading

- American Public Health Association, American Water Works Association, and Water Environment Federation. Standard Methods for the Examination of Water and Wastewater. Lipps WC, Baxter TE, Braun-Howland E, editors. Washington DC: APHA Press. 24th Edition, 2023 C. P. Gautam, Guide Manual: Water and wastewater analysis, Central Pollution control Board, Ministry of Environment & Forest, India, 2011.
- Deborah Chapman, Ed. Water Quality Assessments - A Guide to Use of Biota, Sediments and Water in Environmental Monitoring - Second Edition, UNESCO/WHO/UNEP, Geneva, 1996.
- Eugene R. Weiner, Applications of environmental aquatic chemistry: a practical guide - 2nd ed. CRC Press, Taylor & Francis Group, Broken Sound Parkway NW, 2007.
- Jamie Bartram, Richard Ballance, Eds., Water Quality Monitoring - A Practical Guide to the Design and Implementation of Freshwater Quality Studies and Monitoring Programmes, UNEP/WHO, Geneva, 1996.
- Kim A Sharp, Water: Structure and Properties, Encyclopedia of life sciences, John Wiley & Sons, 2001.
- Michael Roberts, Field Measurement of Oxidation-Reduction Potential (ORP) ID: LSASDPROC-113-R4, U.S. Environmental Protection Agency Laboratory Services & Applied Science Division Athens, Georgia 2023.
- United Nations Environment Programme, Water Quality Monitoring and Assessment in Rivers, Lakes and Reservoirs. Nairobi, 2023.
- UN-Water, Towards a Worldwide Assessment of Freshwater Quality, A UN-Water Analytical Brief, 2016.
- Werner Stumm, James J. Morgan, Aquatic Chemistry: Chemical Equilibria and Rates in Natural Waters 3rd Edition, Wiley-Interscience, 1996.
- WHO, 2022, Guidelines for drinking-water quality: fourth edition incorporating the first and second addenda. Geneva: World Health Organization, 2022.

Annex I

Guideline values for chemicals that are of health significance in drinking-water (WHO, 2022)

Chemical	Guideline value mg/l	Guideline value µg/l	Remarks
Acrylamide	0.0005[a]	0.5[a]	
Alachlor	0.02[a]	20[a]	
Aldicarb	0.01	10	Applies to aldicarb sulfoxide and aldicarb sulfone
Aldrin and dieldrin	0.000 03	0.03	For combined aldrin plus dieldrin
Antimony	0.02	20	
Arsenic	0.01 (A, T)	10 (A, T)	
Atrazine and its chloro-*s*-triazine metabolites	0.1	100	
Barium	1.3	1300	
Benzene	0.01[a]	10[a]	
Benzo[*a*]pyrene	0.0007[a]	0.7[a]	
Boron	2.4	2 400	
Bromate	0.01[a] (A, T)	10[a] (A, T)	
Bromodichloromethane	0.06[a]	60[a]	
Bromoform	0.1	100	
Cadmium	0.003	3	
Carbofuran	0.007	7	
Carbon tetrachloride	0.004	4	
Chlorate	0.7 (D)	700 (D)	
Chlordane	0.0002	0.2	
Chlorine	5 (C)	5 000 (C)	For free chlorine. For effective disinfection, there should be a residual concentration of free chlorine of ≥0.5 mg/l after at least 30 min contact time at pH <8.0. A chlorine residual should be maintained throughout the distribution system. At the point of delivery, the minimum residual concentration of free chlorine should be 0.2 mg/l.
Chlorite	0.7 (D)	700 (D)	
Chloroform	0.3	300	
Chlorotoluron	0.03	30	
Chlorpyrifos	0.03	30	
Chromium	0.05	50	For total chromium
Copper	2	2 000	Staining of laundry and sanitary ware may occur below guideline value
Cyanazine	0.0006	0.6	

Annex I (continued)

Chemical	Guideline value mg/l	Guideline value µg/l	Remarks
Cylindrospermopsins (cyanobacterial toxin)	0.0007 (P)	0.7 (P)	
	0.003 (P)	3 (P)	For short-term exposure[b] Values are for total cylindrospermopsins (sum of all congeners, free plus-cell bound)
2,4-D[c]	0.03	30	Applies to free acid
2,4-DB[d]	0.09	90	
DDT[e] and metabolites	0.001	1	
Dibromoacetonitrile	0.07	70	
Dibromochloromethane	0.1	100	
1,2-Dibromo-3-chloropropane	0.001[a]	1[a]	
1,2-Dibromoethane	0.0004[a] (P)	0.4[a] (P)	
Dichloroacetate	0.05[a] (D)	50[a] (D)	
Dichloroacetonitrile	0.02 (P)	20 (P)	
1,2-Dichlorobenzene	1 (C)	1 000 (C)	
1,4-Dichlorobenzene	0.3 (C)	300 (C)	
1,2-Dichloroethane	0.03[a]	30[a]	
1,2-Dichloroethene	0.05	50	
Dichloromethane	0.02	20	
1,2-Dichloropropane	0.04 (P)	40 (P)	
1,3-Dichloropropene	0.02[a]	20[a]	
Dichlorprop	0.1	100	
Di(2-ethylhexyl)phthalate	0.008	8	
Dimethoate	0.006	6	
1,4-Dioxane	0.05[a]	50[a]	Derived using tolerable daily intake approach as well as linearized multistage modelling
Edetic acid	0.6	600	Applies to the free acid
Endrin	0.0006	0.6	
Epichlorohydrin	0.0004 (P)	0.4 (P)	
Ethylbenzene	0.3 (C)	300 (C)	
Fenoprop	0.009	9	
Fluoride	1.5	1 500	Volume of water consumed and intake from other sources should be considered when setting national standards
Hexachlorobutadiene	0.0006	0.6	
Hydroxyatrazine	0.2	200	Atrazine metabolite
Isoproturon	0.009	9	

Annex I (continued)

Chemical	Guideline value mg/l	Guideline value µg/l	Remarks
Lead	0.01 (A, T)	10 (A, T)	
Lindane	0.002	2	
Manganese	80 (P)	0.08 (P)	For total manganese. Aesthetic as well as health aspects should be considered when setting national standards
Mecoprop	0.01	10	
Mercury	0.006	6	For inorganic mercury
Methoxychlor	0.02	20	
Metolachlor	0.01	10	
Microcystins (cyanobacterial toxin)	0.001 (P)	1 (P)	
	0.012 (P)	12 (P)	For short-term exposure[b] Values are for total microcystins (sum of all congeners, free plus-cell bound)
Molinate	0.006	6	
Monochloramine	3	3 000	
Monochloroacetate	0.02	20	
Nickel	0.07	70	Based on long-term effects, but protective for short-term effects
Nitrate (as NO_3^-)	50	50 000	Based on short-term effects, but protective for long-term effects
Nitrilotriacetic acid	0.2	200	
Nitrite (as NO_2^-)	3	3 000	Based on short-term effects, but protective for long-term effects
N-Nitrosodimethylamine	0.0001	0.1	
Pendimethalin	0.02	20	
Pentachlorophenol	0.009[a] (P)	9[a] (P)	
Saxitoxins (cyanobacterial toxin)	0.003	3	For acute exposure For total saxitoxins (sum of all congeners, free plus-cell bound)
Selenium	0.04 (P)	40 (P)	
Simazine	0.002	2	
Sodium dichloroisocyanurate	50	50 000	As sodium dichloroisocyanurate
	40	40 000	As cyanuric acid
Styrene	0.02 (C)	20 (C)	
2,4,5-T[f]	0.009	9	
Terbuthylazine	0.007	7	
Tetrachloroethene	0.1	100	
Toluene	0.7 (C)	700 (C)	
Trichloroacetate	0.2	200	
Trichloroethene	0.008	8	

Annex I (continued)

Chemical	Guideline value		Remarks
	mg/l	µg/l	
2,4,6-Trichlorophenol	0.2[a] (C)	200[a] (C)	
Trifluralin	0.02	20	
Trihalomethanes			The sum of the ratio of the concentration of each to its respective guideline value should not exceed 1
Uranium	0.03 (P)	30 (P)	Only chemical, not radiological, aspects of uranium addressed
Vinyl chloride	0.0003[a]	0.3[a]	
Xylenes	0.5 (C)	500 (C)	

Notes:
A, provisional guideline value because calculated guideline value is below the achievable quantification level;
C, concentrations of the substance at or below the health-based guideline value may affect the appearance, taste or odour of the water, leading to consumer complaints;
D, provisional guideline value because effective disinfection may result in the guideline value being exceeded;
P, provisional guideline value because of uncertainties in the health database;
T, provisional guideline value because calculated guideline value is below the level that can be achieved through practical treatment methods, source protection, etc.
a For substances that are considered to be carcinogenic, the guideline value is the concentration in drinking-water associated with an upper-bound excess lifetime cancer risk of 10−5 (one additional case of cancer per 100 000 of the population ingesting drinking-water containing the substance at the guideline value for 70 years). Concentrations associated with upper-bound estimated excess lifetime cancer risks of 10−4 and 10−6 can be calculated by multiplying and dividing, respectively, the guideline value by 10.
b See the specific chemical fact sheet in for considerations for bottle-fed infants.
c 2,4-Dichlorophenoxyacetic acid.
d 2,4-Dichlorophenoxybutyric acid.
e Dichlorodiphenyltrichlorethane.
f 2,4,5-Trichlorophenoxyacetic acid.

Annex II

1. Instrumental determination of basic hydrochemical characteristics of water (pH, ΔpH, Eh, specific electrical conductivity, neutralization capacity)

pH determination

The pH is an important variable in water quality assessment. It can be measured by colorimetric method - by comparison with a standard, colored scale or electrometrically. The colorimetric determination is semi-quantitative and is used for indicative evaluation. The electrometric determination is accurate.

Principle of pH determination using a pH meter

The pH is determined by measurement of the electromotive force (emf) of a cell comprising of an indicator electrode (an electrode responsive to hydrogen ions such as glass electrode) immersed in the test solution and a reference electrode (usually a silver chloride electrode). Contact is achieved by means of a liquid junction, which forms a part of the reference electrode. The emf of this cell is measured with pH meter.
Since the pH is defined operationally on a potentiometric scale, the measuring instrument is calibrated potentiometrically with an indicating (glass) electrode and a reference electrode, connected to the device, using standard buffers having assigned pH value so that

$pH_B = -\log_{10} [H^+]$

where pH_B = assigned pH of standard buffer.
The operational pH scale is used to measure sample pH and it is defined as:

$pH_s = pH_B + F (E_s – E_B) / (2.303 RT)$

where, pH_s = potentiometrically measured sample pH value; F = Faraday constant = 9.649 x 10^4 coutomb/mole; E_s = sample emf, V; E_B = buffer emf, V; R = gas constant 8.314, J / (mol·K); T = absolute temperature, K

Useful tips

There are many models of pH meter. The common features are a sensing electrode (glass electrode) and a reference electrode connected to an electronic circuit that amplifies the voltages produced when the electrodes are immersed in a solution or water sample. The amplified voltage is displayed on a meter graduated in pH units. Sensing and reference electrodes designed for field use are often combined in one element - Figure II.1.1. The electronic circuitry in a portable meter is powered by either disposable or rechargeable batteries, depending on the design of the meter. It is possible to purchase a more complex instrument that is designed for measurement of conductivity and temperature as well as pH. It is not possible to provide detailed operating instructions for all of the many makes and models of pH meter. Operating and maintenance instructions are supplied by the manufacturer. There is, however, a general procedure that should be followed. The sensing (glass) electrode must be soaked in distilled water for several hours before use when it is new or if it has dried out during storage of more than a day. When a glass electrode is not in use for more than a few hours, its tip (the lower 1-2 cm) should be kept immersed in distilled water (if a combined electrode is used distilled water is NOT suitable, the electrode has to be kept in a storage solution, purchased from the electrode supplier). The tips of glass electrodes should be carefully protected against abrasion and breakage. Usually, a rubber cap is used. The reference electrode is also usually supplied with a rubber cap that protects the tip against breakage as well as preventing the crystallisation of dissolved salts on the tip. Some storage solution is placed in the cup and then the electrode is immersed. A hole in the side of the electrode is provided for filling the body of the electrode with saturated (or other known concentration) potassium chloride (KCl) solution. The correct liquid level is approximately 5 mm below the bottom edge of the hole. When the electrode is not in use the hole should be covered with a rubber sleeve that slides over the body of the electrode.

One or more buffer solutions are necessary for standardising the meter with electrodes connected to it. It is usual for the manufacturer to provide containers of buffer solutions with the meter, and the supply may be replenished with purchases from either the manufacturer or a chemicals supplier. The usual procedure:

Calibrating the meter

1. Remove the protective rubber cap and slide the rubber sleeve up to expose the hole in the side of the reference electrode.
2. Rinse both electrodes (or the combined electrode) with distilled water and blot dry with soft absorbent paper.
3. Pour sufficient buffer solution into a beaker to allow the tips of the electrodes (or the combined electrode) to be immersed to a depth of about 2 cm. The electrodes (the combined electrode) should be at least 1 cm away from the sides and the bottom of the beaker.
4. Measure the temperature of the buffer solution with a thermometer and set this on the temperature adjustment dial of the meter (if the meter is so equipped). Some meters have an automatic temperature adjustment feature.
5. Turn on the pH meter.
6. Adjust the pH dial to the known pH of the buffer. If you are using only one buffer solution to calibrate the system it should be with pH 7. Rinse the electrodes with distilled water, wipe with filter paper and repeat the procedure with the second buffer. It is better to calibrate at least with 2 buffer solutions (with pH 7 and the other with a buffer with pH value in the acidic (pH 3 or 4) or alkaline (pH 9 or 10) range. However, pH 7 should be calibrated first.
7. Turn the instrument to stand-by (if it is equipped for this).
8. Raise the electrodes to clear of the buffer solution. Remove the buffer and rinse the electrodes with distilled water.
9. Proceed to determination of pH of the sample. If the sample is not ready, place the electrodes in distilled water.

pH 7 is the zero point for calibration (or first point) and pH 4 or pH 10 is the slope point (i.e. second point) - Figure II.1.2. The theoretical voltage output is 59 mV change of the pH sensor for every pH unit change. The *asymmetry potential* is an indication of the condition of the reference electrode. Theoretically when the electrodes are placed in a buffer 7, the milivolt output from the electrode pair (pH and reference) should be zero.

At a value above pH 10 the gel layer structure of the glass membrane of the measurement electrode is subjected to some changes which lead to a measuring inaccuracy - known as *alkaline error* or sodium ion error. This is caused by the presence of a high concentration of alkaline ions, especially sodium ions (Na^+) in the solution. These ions replace, partly or completely, the hydrogen ions at the outer gel layer of the glass membrane, and by doing so, contribute to the voltage potential at the outer phase boundary. As a result, a lower pH value will be measured than the actual pH value of the measured solution.

At low pH values (< pH 2) the potential difference between measurement and reference electrode does not follow exactly the Nernst equation. This is due to the fact that the gel layer of the pH sensitive glass membrane will absorb acid H^+ ions at very low pH values. This decreases the activity of the H^+ ions in the electrode vicinity and results in a lower potential at the outer membrane phase boundary. The pH measurement shows a higher pH value than the actual pH value of the measured liquid solution. This effect is known as the *acid error*. Manufacturers are trying to supply specialized measuring electrodes with glass membranes having especially low acid and alkaline errors.

Determination of pH of sample

1. The electrode(s) are either immersed in, or have been rinsed with, distilled water. Remove them from the water and blot dry.
2. Rinse the electrode(s) and a small beaker with a portion of the sample.

3. Pour sufficient of the sample into the small beaker to allow the tips of the electrodes to be immersed to a depth of about 2 cm. The electrode(s) should be at least 1 cm away from the sides and the bottom of the beaker.
4. Measure the temperature of the water sample and set the temperature adjustment dial accordingly (if the instrument does not have automatic temperature compensation).
5. Turn on the pH meter.

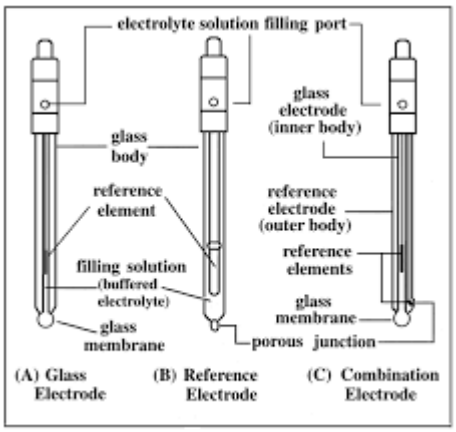

Figure II.1.1. Glass, reference and combined electrodes

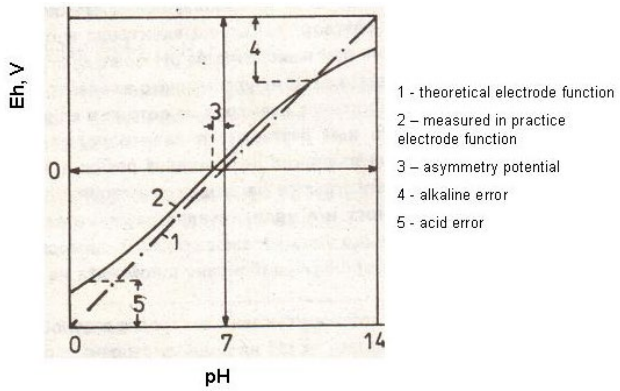

Figure II.1.2. Theoretical and real Nernst response of the glass electrode

6. Read the pH of the water sample on the meter. Make sure that the reading is stable before the pH is recorded. Sometimes it is needed to wait longer - 10-15 min because *pH is an equilibrium value* and the equilibrium has to be reached.
7. Turn the pH meter to stand-by and raise the electrodes out of the sample. Remove the sample and discard it. Rinse the electrodes and the beaker with distilled water, and blot the electrodes with soft tissue.
8. If other samples are to be measured, repeat steps 2 to 7.
9. If no other samples are to be tested, slide the rubber sleeve down to cover the hole in the side of the reference electrode and replace the protective rubber cap on the tip.
10. Switch the meter off (and pack it in its carrying case for transport).
Report the pH and the temperature of the water at the time the measurement was made.

Express Δ pH test
The change in the equilibrium pH value of the water after the addition of calcium carbonate can be used as a measure of the aggressiveness of the water towards limestone (and towards other building materials).

$$\Delta pH = pH_{water} - pH_{CaCO3} \quad (1)$$

where pH_{water} is the measured value of tested water, pH_{CaCO3} is the measured value of the same water when an equilibrium is reached after addition of $CaCO_3$.
If $\Delta pH < -0.05$ the water is aggressive towards $CaCO_3$, if $\Delta pH > +0.05$ the water is oversaturated with respect of $CaCO_3$ (carbonate can be precipitated from the water), if $-0.05 < \Delta pH < +0.05$ the water is in equilibrium with $CaCO_3$.
Procedure
1. Measure the pH value of 100 mL water. Take out the pH electrode.
2. Add 2 g pure $CaCO_3$ powder to the same water. Stir for 2 min to reach the equilibrium.
3. Measure the pH.
4. Take out the pH electrode and carefully wash it with tap water.
5. Calculate ΔpH and make the corresponding conclusion.

Eh determination

The redox potential characterises the oxidation-reduction state of natural waters. When based on a hydrogen scale against platinum indicator electrode, the redox potential is denoted as Eh. The Eh may vary in natural waters from -500 mV (alkaline water, reducing conditions) to +700 mV (acidic water, oxidizing conditions). Surface waters and groundwaters containing dissolved oxygen are usually characterised by a range of Eh values between +100 mV and +500 mV. The Eh of mineral waters connected with oil deposits is significantly lower than zero and may even reach the limit value of -500 mV.

The Eh value of water depends on the presence of oxidizing or reducing agents in the system. The presence of oxidants leads to higher Eh values, while low Eh values of are associated with reductants presence in the system (including sulfate reducing bacteria - SRB).

The dependence between pH and Eh is inversely proportional. At low pH values (acidic medium) the Eh values are high and conversely, low values of Eh are observed at high values of pH (alkaline environment). Eh depends on temperature. Most of nowadays devices have an inbuilt temperature compensation.

Eh is measured with Eh-meter and corresponding electrode(s). The potential difference is measured between an indicator (most often platinum or platinized titanium) electrode and a reference electrode (most often silver chloride). Usually, the two electrodes are combined in one body - Figure II.1.3.

Figure II.1.3. Combined Eh electrode

	Molarity of KCl filling solution			
T(°C)	3M	3.3M*	3.5M	Sat/4M
10	220	217	215	214
15	216	214	212	209
20	213	210	208	204
25	209	207	205	199
30	205	203	201	194
35	202	199	197	189
40	198	195	193	184

* Interpolated value

Table II.1.1. Potential of Ag/AgCl reference electrode, mV

Procedure

Most electrodes are factory calibrated and only checked. The electrode is immersed in a solution prepared by the equipment manufacturer and the reading must fall within a certain range of values specified by the manufacturer.

If the reading is outside this range, the purity and expiration date of the calibration solution, the integrity and cleanliness of the electrode are checked consecutively. The electrode can be cleaned with polishing paste, water, hydrochloric acid (1:4), water, distilled water and re-immersed in the calibration solution. If the calibration solution is within the expiration date and uncontaminated and after cleaning the electrode reading is out of range, the electrode must be replaced with a new one.

If the reading is in the range, the electrode is rinsed several rimes with water to be studied, immersed in water carefully (trying to avoid additional introduction of oxygen) and the reading is recorded.
In order to obtain Eh from the direct measurement, the known potential of the reference electrode is added to the displayed by the device ORP value:

$$Eh_{sample} = ORP_{sample} + E_{ref} \quad (2)$$

E_{ref} - potential of reference electrode
Table II.1.1 presents the potential of a silver/silver chloride reference electrode at various temperatures and with various molarities of KCl filling solutions.
Sometimes rH (hydrogen ion exponent) value of the water is calculated

$$rH = Eh(V) / 0.0295 + 2\ pH = (ORP + E_{ref})\ (mV) / 29.5 + 2\ pH \quad (3)$$

Practice has shown that the properties of water are strongly reducing at rH in the range of 0 - 9, at rH 9 -17 they are weakly reducing, at rH 25 - 34 the water possesses weakly oxidizing properties, while at rH 34 - 42 they are strongly oxidizing. For values of rH between 17 and 25, specific hydro-chemical indicators are important, especially temperature.

Conductivity measurement
Conductivity, or specific conductance, is a measure of the ability of water to conduct an electric current. It is sensitive to variations in dissolved solids, mostly mineral salts. The degree to which these dissociate into ions, the amount of electrical charge on each ion, ion mobility and the temperature of the solution - all have an influence on conductivity. Conductivity is expressed as micro-Siemens per centimetre (μS/cm) and, for a given water body, is related to the concentrations of total dissolved solids and major ions.
The apparatuses used (conductivity meters) consists of a conductivity cell containing two rigidly attached electrodes, which are connected by cables to the body of the meter. The meter contains a source of electric current (a battery in the case of portable models), a Wheatstone bridge (a device for measuring electrical resistance) and a small indicator (usually a galvanometer). The design of the electrodes, i.e. shape, size and relative position, determines the value of the cell constant, K_c, which is usually in the range 0.1 to 2.0 (usually on teh range 0.7 to 1.1). A cell with a constant of 2.0 is suitable for measuring conductivities from 20 to 1000 mS/m.
Procedure
First, the constant of the conductivity meter is determined: The measuring cell (electrode) of the device is rinsed several times with distilled water, followed by several rinses with a KCl solution of defined concentration. The electrical conductivity G of the KCl solution at the corresponding temperature is measured. (At least 3 parallel measurements are made and the results are averaged.) The cell constant is determined by the dependence:

$$k = \chi / G \quad (4),$$

where χ - specific electrical conductivity of the KCl solution with a precisely determined concentration at the corresponding temperature (taken from Table II.1. 2).
Based on the electrical conductivity G of the investigated solution, measured with the conductometer (average of 3 parallel measurements), its specific electrical conductivity χ is calculated according to the dependence:

$$\chi = k \times f \times G \quad (5),$$

where f is a correction factor for recalculating the measured χ at a temperature other than 20 °C. The value of f is found in Table II.1.3.
Care must be taken to ensure that measured and true conductivities are expressed in the same units.
Based on the experience, a dependence between water mineralization M (in mg/L) and specific electrical conductivity χ (in μS/cm) was deduced:

Table II.1.2. Specific electrical conductivity χ (mS/cm) of KCl solutions as a function of temperature

Temperature, °C; Concentration	0,01 M	0,1 M	1,0 M
18	1,225	11,19	98,24
19	1,251	11,43	100,16
20	1,278	11,67	102,09
21	1,305	11,91	104,02
22	1,332	12,15	105,94
23	1,359	12,39	107,89
24	1,386	12,64	109,84
25	1,413	12,88	111,80

Table II.1.3. Temperature factors for correcting the measured specific electrical conductivity

t°C	0	1	2	3	4	5	6	7	8	9
0	1,784	1,778	1,772	1,765	1,758	1,751	1,744	1,737	1,731	1,724
1	1,717	1,711	1,705	1,699	1,692	1,686	1,680	1,673	1,667	1,661
2	1,665	1,649	1,642	1,637	1,631	1,626	1,619	1,614	1,609	1,603
3	1,597	1,591	1,586	1,580	1,574	1,569	1,564	1,558	1,553	1,548
4	1,543	1,537	1,532	1,527	1,522	1,517	1,512	1,507	1,502	1,497
5	1,492	1,487	1,482	1,478	1,473	1,468	1,463	1,459	1,454	1,449
6	1,444	1,440	1,435	1,431	1,427	1,422	1,417	1,413	1,409	1,405
7	1,400	1,396	1,391	1,387	1,382	1,378	1,374	1,370	1,366	1,363
8	1,359	1,355	1,351	1,347	1,343	1,339	1,335	1,331	1,327	1,323
9	1,319	1,315	1,311	1,307	1,303	1,300	1,297	1,293	1,289	1,286
10	1,282	1,278	1,275	1,272	1,268	1,264	1,260	1,257	1,254	1,250
11	1,247	1,244	1,240	1,237	1,233	1,230	1,226	1,223	1,219	1,216
12	1,213	1,210	1,207	1,204	1,201	1,198	1,194	1,191	1,188	1,185
13	1,182	1,179	1,176	1,173	1,169	1,166	1,163	1,160	1,157	1,154
14	1,151	1,148	1,145	1,143	1,140	1,138	1,135	1,132	1,129	1,126
15	1,123	1,120	1,117	1,115	1,112	1,110	1,107	1,104	1,101	1,098
16	1,095	1,093	1,090	1,088	1,086	1,084	1,081	1,078	1,075	1,073
17	1,071	1,068	1,066	1,063	1,060	1,057	1,055	1,052	1,050	1,048
18	1,046	1,044	1,042	1,039	1,037	1,034	1,032	1,030	1,027	1,025
19	1,023	1,021	1,019	1,016	1,013	1,011	1,009	1,006	1,004	1,002
20	1,000	0,998	0,996	0,994	0,992	0,990	0,987	0,985	0,983	0,981
21	0,979	0,977	0,975	0,973	0,971	0,969	0,967	0,965	0,963	0,960
22	0,958	0,956	0,954	0,952	0,950	0,948	0,945	0,943	0,941	0,939
23	0,937	0,936	0,934	0,933	0,931	0,929	0,927	0,925	0,923	0,921
24	0,919	0,918	0,916	0,914	0,912	0,910	0,908	0,906	0,904	0,903
25	0,901	0,900	0,898	0,896	0,894	0,892	0,890	0,888	0,886	0,885

$$M = A \times \chi^B \quad (6)$$

where values of A and B can be taken from Table II.1.4, in dependence of water type and measured conductivity.

Table II.1.4. Coefficients for calculating water mineralization based on conductivity data

Water type	χ measured	A	B
weakly mineralized	χ < 250 µS/cm	0.37	1.17
calcium bicarbonate	χ < 800 µS/cm	1.4	1
calcium sulfate	500 < χ < 3000 µS/cm	1.07	1
sodium chloride	1 < χ < 130 mS/cm, then M is in g/kg	0.31	1.216
sodium chloride	130 < χ < 250 mS/cm, then M is in g/kg	0.0485	1.6

2. Determination of gasses dissolved in water (oxygen, carbon dioxide)

Dissolved carbon dioxide

Carbon dioxide is present in surface waters and groundwaters as a dissolved gas. Carbon dioxide (CO_2) is highly soluble in water and atmospheric CO_2 is absorbed at the air-water interface. Carbon dioxide dissolved in natural water is part of an equilibrium involving bicarbonate and carbonate ions.

At water pH value in the range 4.4 < pH < 8.3, the free CO_2 controls the total water acidity. It is usually determined by titration with NaOH solution till pH 8.3 at indicator phenolphthalein.

Procedure

1. Take 100 mL water sample in a measuring flask and transfer it into a clean conical flask
2. Add 3 drops of phenolphthalein solution
3. Fill the burette (washed!) with 0.02 M solution of NaOH - with exactly known concentration ($C_{titrant}$).
4. Begin the titration, making sure that there are no air bubbles in the burette tip and that there is no funnel on the burette. Shake the sample in the flask and observe the color.
5. When the color changes to pale pink that does not change for 30 seconds, stop the supply of NaOH solution and record the volume used ($V_{titrant}$)
6. Wash the conical flask and burette.
7. Calculate the concentration of dissolved CO_2

$$C_{sample} = C_{titrant} \times V_{titrant} \times 10^3 / V_{sample} \quad (1)$$

where C_{sample} (mmol/dm^3) and V_{sample} (cm^3) are the value to be determined in the analyzed water sample and the sample volume taken for analysis, $C_{titrant}$ (mol/dm^3) and $V_{titrant}$ (cm^3) are the titrant concentration and volume used to reach the equivalent point.

Convert to mg/L.

Dissolved oxygen - by *Winkler method*

Sufficient dissolved oxygen (DO) is important for high-quality water. DO is crucial for the survival of fish and most other aquatic life forms. It oxidizes many sources of objectionable tastes and odors. Dissolved oxygen is consumed by the degradation (oxidation) of organic matter in water. That is why DO can be used to indicate the degree of water pollution by organic matter.

Dissolved oxygen should be measured as quickly and carefully as possible. Ideally, samples should be measured in the field immediately after collection. If thie si not possible, they have to be preserved and cooled.

Procedure

1. The sample is taken directly into a 100-120 cm^3 collection bottle with a ground stopper using DO sampler.
2. Immediately add 1 cm^3 of manganese sulfate to the collection bottle by inserting the calibrated pipette just below the surface of the liquid. (If the reagent is added above the sample surface, you

will introduce oxygen into the sample.) Squeeze the pipette slowly so no bubbles are introduced via the pipette.
3. Add 1 cm^3 of alkali-iodide-azide (KOH + KI + $NaNO_3$) reagent in the same manner. $NaNO_3$ is poison, be careful! (In real practice $NaNO_3$ is used to remove the interfering effect of nitrite ions, in the laboratory exercise $NaNO_3$ is not added).
4. Stopper the bottle with care to be sure no air is introduced. Mix the sample by inverting the bottle several times. Check for air bubbles; discard the sample and start over if any are seen. If oxygen is present, a brownish-orange cloud of precipitate or floc will appear. The precipitate is white if the sample is devoid of oxygen. When this floc has settled to the bottom, mix the sample by turning it upside down several times and let it settle again. At this point, the sample is "fixed" and can be transported, can be stored for up to 8 hours if kept in a cool, dark place.
5. In laboratory - add 2 cm^3 of sulfuric acid (1:4) by inserting the calibrated pipette just below the surface of the liquid. Carefully stopper and invert the bottle with the sample several times to dissolve the floc. Wait 5-10 min for the precipitate to dissolve.
6. The entire content of the collection bottle is transferred to a conical flask, the bottle is rinsed with a little distilled water and this is transferred to a flask, then the solution in the flask is titrated with standard sodium thiosulphate solution ($Na_2S_2O_3$) with known concentration $C_{titrant}$ to a light brown color. 1-2 cm^3 of 0.5% starch solution are added (the solution in the flask turns blue due to the reaction of starch and I_2) and the titration continues until discoloration (sample turns clear as clear water). The volume of titrant used $V_{titrant}$ is counted. It is sometimes helpful to hold the flask up to a white sheet of paper to check for absence of the blue color. The total duration of the titration should not be more than 5 minutes in order not to intoduce oxygen from the air.
The DO concentration is calculated using the equation (2)

$$DO \text{ in mg/L} = V_{titrant} \times C_{titrant} \times (M / 4) \times 1000 / (V_{sample} - 2) \quad (2)$$

where $C_{titrant}$ (in mol/dm^3) and $V_{titrant}$ (in cm^3) are the titrant ($Na_2S_2O_3$) concentration and volume used to reach the equivalent point, V_{sample} (in cm^3) is equal to the volume of the collection bottle (cm^3), M - molecular mass of oxygen (32 g/mol), 4 - a coefficient derived from reactions stoichiometry, 2 - the volume of fixing reagents added, cm^3.

Proceeding reactions:
At the oxygen fixation

$MnSO_4 + 2\ KOH = Mn(OH)_2 + K_2SO_4$

$2Mn(OH)_2 + 0.5\ O_2 + H_2O = 2Mn(OH)_3$

At the sample acidification in the lab

$2Mn(OH)_3 + 3H_2SO_4 = Mn_2(SO_4)_3 + 6H_2O$

$Mn_2(SO_4)_3 + 2KI = I_2 + K_2SO_4 + 2MnSO_4$

KI is present in the sample since it is added during the fixation stage.
At the sample titration

$I_2 + 2\ Na_2S_2O_3 = 2\ NaI + Na_2S_4O_6$

3. Determination of characteristic macrocomponents in surface and underground waters (calcium, magnesium, chlorides, hydrogen carbonates). Estimating the hardness of water samples

Macro-components are components whose natural concentrations in pure water are higher than 5 mg/L. The major anions are bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) anions, chlorides (Cl^-) and sulfates (SO_4^{2-}). The major cations are calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^+), and potassium (K^+). They enter into the water as a result of leaching/ dissolution of minerals from rocks

and soils with which the water comes into contact. Chloride in natural waters arises also from salting of roads for snow and ice control, seawater intrusion in coastal regions. Major ions are naturally very variable in surface and groundwaters due to local geological, climatic and geographical conditions.

Determination of Na^+ and K^+ is best performed using flame atomic emission.

The property of water to precipitate saponified fatty acids is called water hardness. Water hardness is defined as the sum of the divalent and polyvalent metallic ions in the water. The main contributors to the hardness of the water are calcium and magnesium ions. Additional contributors to the hardness of the water include iron (Fe^{2+}), strontium (Sr^{2+}), zinc (Zn^{2+}), manganese (Mn^{2+}) and other ions. However, their concentrations are usually significantly lower than the concentration of Ca^{2+} and Mg^{2+} ions. In most cases, summing up the Ca^{2+} and Mg^{2+} in the water gives an adequate hardness measure.

As written above (Lecture 7), the total content of Ca^{2+} and Mg^{2+} ions is known as general hardness, which can be further divided into carbonate hardness (determined by concentrations of calcium and magnesium hydrocarbonates), and non-carbonate hardness (determined by calcium and magnesium salts of strong acids). Hydrocarbonates are transformed during the boiling of water into carbonates, which usually precipitate. Therefore, carbonate hardness is also known as temporary or removable, whereas the hardness remaining in the water after boiling is called permanent.

Different countries have different harness units as indicated in Table 7.1. Waters can be classified according to their hardness - see Table 7.2.

Determination of Ca^{2+} and Mg^{2+} ions can be performed using ICP.

However, enough correct results are obtained in the much more cheaper titration method. Principle of the titration method is the following: When EDTA (or its sodium salt) is added to water containing calcium and magnesium ions water soluble complexes of these ions with EDTA are formed. The indicator Eriochrome Black T is used that is blue in its deprotonated form. It is violet when it forms complexes with Ca^{2+} and Mg^{2+} or other metal ions at pH 10. When sufficient EDTA is added and the metal ions are bound by EDTA leaving the free indicator molecule, the characteristic blue end-point of titration is reached. This way the sum of Ca^{2+} and Mg^{2+} ions (equal to the water hardness of clean water, in mol or mmol per liter) is determined.

At pH 12-13 magnesium hydroxide is precipitated and only Ca^{2+} ions can be determined in the presence of Mg^{2+} by EDTA (with known concentration) titration; the indicator used (murexide) is one that reacts with calcium only. Murexide indicator gives a colour change (from pink to purple) when all of the calcium has been complexed by EDTA.

The magnesium concentration in a sample can also be estimated by calculating the difference between the total hardness and the calcium concentration (both in mmol/l!). Here this method will be described briefly.

When the pH value of the analyzed water is in the range of $4.4 < pH < 8.3$ the concentration of bicarbonate (HCO_3^-) is equal to the water total alkalinity. The alkalinity of water is controlled by the sum of the titratable bases. It is mostly taken as an indication of the concentration of carbonate, bicarbonate and hydroxide, but in the mentioned pH range practically the carbonate and hydroxide ions do not present in significant concentrations. Alkalinity is determined by titration with HCl solution with known concentration to pH 4.4 at an indicator methyl orange that changes it color from yellow to pale orange.

Titration (in a neutral or slightly alkaline solution) with standard silver nitrate solution, using potassium chromate (K_2CrO_4) as indicator is one of the most widely used methods for Cl^- ions determination. Silver chloride is quantitatively precipitated before red silver chromate is formed (initially the water with added to it K_2CrO_4 is yellow). In this method bromide, iodide and cyanide are measured as equivalents of chloride but in drinking water samples these interfering ions have to be missing.

Calculations

In all cases of titration, the concentration of the ions under determination is calculated using the formula

$$C_{sample} = C_{titrant} \times V_{titrant} \times 10^3 / V_{sample} \quad (1)$$

where C_{sample} and V_{sample} are the value to be determined in the analyzed water sample and the sample volume taken for analysis, $C_{titrant}$ and $V_{titrant}$ are the titrant concentration and volume used to reach the equivalent point.

Sometimes when the distilled water is used to prepare solutions, and it is expected to contain an ion to be determined (for example Cl^-), a modification is used:

$$C_{sample} = C_{titrant} \times (V_{titrant} - V_{d.w.}) \times 10^3 / V_{sample} \quad (1')$$

where $V_{d.w.}$is the volume of the titrant used to titrate the distilled water.

When the $C_{titrant}$ is measured in mol/L, the C_{sample} is obtained in mmol/L. To be converted to mg/L the obtained value has to be multiplied by the atomic mass of the corresponding ion (mass of the hydrogen carbonate) ion. This not applies for the hardness.

Experimental procedure

For determination of total hardness (sum of Ca^{2+} and Mg^{2+} ions)

1. Take 100 mL water sample in a measuring flask and transfer it into a clean conical flask.
2. Add 10 mL ammonia buffer (pH 10) and stir.
3. Add Eriochrome Black T to the solution - the tip of the measuring spoon and stir. The color should be purple.
4. Fill the burette (washed!) with EDTA solution of known concentration ($C_{titrant}$).
5. Begin the titration, making sure that there are no air bubbles in the burette tip and that there is no funnel on the burette. Shake the sample in the flask and observe the color.
6. When the color changes to blue, immediately stop the supply of EDTA solution and record the volume used $V_{titrant}$.
7. Calculate the sum of calcium and magnesium ions, i.e. the hardness of water in mmol/L using eq (1).
8. Make conclusions about the water harness using Table 7.2.
9. Empty the conical flask and wash it.

For determination of Ca^{2+} ions

1. Take 100 mL water sample in a measuring flask and transfer it into a clean conical flask.
2. Add 2 mL 5M solution of NaOH (pH achieved is 12-13) and stir.
3. Add Murexide to the solution - the tip of the measuring spoon and stir. The color should be pink.
4. Fill the burette with EDTA solution of known concentration ($C_{titrant}$) - the same as in the total hardness determination.
5. Begin the titration, making sure that there are no air bubbles in the burette tip and that there is no funnel on the burette. Shake the sample in the flask and observe the color.
6. When the color changes to purple, immediately stop the supply of EDTA solution and record the volume used $V_{titrant}$.
7. Calculate the sum of calcium ions, in mmol/L using eq (1). Converted to mg/L.
8. Empty the conical flask and wash it.

Determination of Mg^{2+} ions

From the obtained concentration for the sum of calcium and magnesium ions **in mmol/L**, subtract the concentration of calcium ions in mmol/L. Converted to mg/L.

Determination of HCO_3^- ions

1. Take 100 mL water sample in a measuring flask and transfer it into a clean conical flask.

2. Add 3-4 drops of indicator methyl orange and stir. The color is yellow.
3. Wash burette 3 times with tap water and with d. H_2O followed with a small amount of 0.1 M solution of HCl.
4. Fill the burette with solution of HCl of known concentration ($C_{titrant}$).
5. Begin the titration, making sure that there are no air bubbles in the burette tip and that there is no funnel on the burette. Shake the sample in the flask and observe the color.
6. When the color changes to pale orange, immediately stop the supply of HCl solution and record the volume used $V_{titrant}$.
7. Calculate the concentration of HCO_3^- ions, in mmol/L using eq (1). Convert to mg/L.
8. Empty the conical flask and wash it.

Determination of Cl^- ions
1. Take 100 mL water sample in a measuring flask and transfer it into a clean conical flask
2. Add 1 mL of K_2CrO_4 solution and stir. The color is yellow.
3. Wash burette 3 times with tap water and 2 times with d. H_2O followed with a small amount of 0.05 M solution of $AgNO_3$.
4. Fill the burette with $AgNO_3$ solution of known concentration ($C_{titrant}$).
5. Begin the titration, making sure that there are no air bubbles in the burette tip and that there is no funnel on the burette. Shake the sample in the flask and observe the color.
6. When the color changes to orange, immediately stop the supply of $AgNO_3$ solution and record the volume used $V_{titrant}$.
7. Repeat consecutively the steps 1,2,5 and 6, with distilled water - the volume read is $V_{d.wt.}$
7. Calculate the concentration of Cl^- ions, in mmol/L using eq (1'). Convert to mg/L.
8. Empty the conical flask and wash it.

4. Application of mathematical-statistical methods in hydrochemistry - on the example of sulfate ions determination by turbiditimery

The essence of the turbidimetric method for determining sulphate ions (SO_4^{2-}) is the preparation in an acidic medium of suspensions of slightly soluble barium or lead sulphates. The intensity of the light passed through them is used as a measure of the concentration of sulphate ions. The main problem lies in obtaining sufficiently stable, reproducibly sized barium sulphate ($BaSO_4$) particles. The turbidimetric method proposed here is suitable for sulphate concentrations from 1 to 100 mg/dm^3 and is characterized by accuracy and reproducibility. The essence of the method - a pre-prepared solution for controlled micro-heterogeneous precipitation is added to the acidified water samples, and the diffuse density is measured after a precisely determined time or after intensive shaking of the test tube before passing the suspension to the cuvette of the spectrophotometer. The amounts of reagents in the solution for micro heterogeneous precipitation are selected so that as a result of the high degree of supersaturation, a large number of crystal seeds of $BaSO_4$ with very small sizes are obtained. These nuclei then grow proportionally to the concentration of sulphate ions and the measured diffuse density of the samples is proportional to this concentration of $BaSO_4$, i.e. to the concentration of sulphate ions.

Protocol

Preparation of the solution for controlled micro-heterogeneous precipitation (15 min after its preparation, the solution is stable for 4-5 hours): For a final volume of 50 cm^3, take successively 5 cm^3 of the calibration solution, 44 cm^3 distilled water, 10 drops of 3M HCl and about 2.25 g of $BaCl_2$, then mix well.

The analytical method works using a calibration curve that is constructed each time sulphates are quantified. For this purpose, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10 cm^3 of the calibration solution (1 cm^3 of this solution contains 50 μg SO_4^{2-}) are placed in 10 test tubes using a burette, all are brought to 10 cm^3 with distilled water and added 2 drops of 3M HCl each. 1 cm^3 of the solution for controlled micro-heterogeneous precipitation is added to each of the test tubes, mixed and the diffuse density of the

obtained micro-heterogeneous systems is measured at a wavelength of 440 nm compared to distilled water. Before pouring the suspension into the cuvette of the spectrophotometer, the test tubes must be shaken vigorously.
The determination of SO_4^{2-} in 10 parallel water samples is done by taking 10 cm^3 of water in 10 test tubes, adding 2 drops of 3M HCl and adding 1 cm^3 of the solution for controlled precipitation to each test tube. After that, the diffusion density is measured at the same wavelength, and before the suspension is poured into the cuvette of the spectrophotometer, the test tubes are shaken intensively.
It is important to observe absolutely identical conditions during the processing and determination of the diffuse density of the standard solutions and the investigated water samples.
Calculations for the exact concentrations of sulphate ions are made with the help of the calibration graph "diffuse density as a function of concentration". It is built based on the data on the measured diffusivity of the solutions with a known concentration. From the measured diffuse density, the unknown concentration is calculated using the calibration graph and the resulting value is multiplied by 1.10 to account for the dilution. Results are rounded up to 0.5 mg/dm^3.
The SO_4^{2-} concentration data obtained for the ten parallel samples are used to calculate the standard deviation, coefficient of variation and confidence interval.
The concepts of accuracy and reproducibility characterize the magnitude of systematic and random errors when performing a given determination. Precision is a measure of how close the obtained result is to the actual one, and reproducibility reflects the probability of obtaining the same result if the determination is carried out again using the same method and under the same conditions.
Absolute and relative error are used to characterize the measurement accuracy. The absolute error is the difference between the found and the true value of a given characteristic, and the relative error is the ratio between the absolute error and the true value. The relative error is usually expressed as a percentage.
The standard deviation σ is used to characterize reproducibility. For a series of n number of measurements, the standard deviation σ is defined by the dependence

$$\sigma = \sqrt{\frac{\sum(x_i - \bar{x})^2}{n}} \qquad (1)$$

where x_i is the value found for a given measurement, and $\bar{x}$ is the arithmetic mean value of all n definitions.
Sometimes in practice, the square of the standard deviation σ^2 is also used, called the variance of the results.
If the standard deviation is calculated as a percentage of the arithmetic mean, the so-called coefficient of variation is obtained

$$K_v = \sigma \times 100 / \bar{x} \qquad (2)$$

In practice, due to the relatively small number of parallel trials and the possibility of making systematic errors, the so-called confidence interval CI is defined, in which the sought value is found with a certain statistical probability. The expression is used:

$$CI_{SO42-} = \bar{x} \pm t \times \sigma / n^{1/2} \qquad (3)$$

The coefficient **t** is known as Student's criterion (factor) and has a different value depending on the statistical probability and the degrees of freedom f, where f = n - 1 (Table II.4.1). As the statistical probability increases, the limits of the confidence interval expand.

Table II.4.1. Student's criterion at different poropabilities and fegrees of freedom

Student-t Distribution

ν	t_{50}	t_{90}	t_{95}	t_{99}
1	1.000	6.314	12.706	63.657
2	0.816	2.920	4.303	9.925
3	0.765	2.353	3.182	5.841
4	0.741	2.132	2.770	4.604
5	0.727	2.015	2.571	4.032
6	0.718	1.943	2.447	3.707
7	0.711	1.895	2.365	3.499
8	0.706	1.860	2.306	3.355
9	0.703	1.833	2.262	3.250
10	0.700	1.812	2.228	3.169
11	0.697	1.796	2.201	3.106
12	0.695	1.782	2.179	3.055
13	0.694	1.771	2.160	3.012
14	0.692	1.761	2.145	2.977
15	0.691	1.753	2.131	2.947
16	0.690	1.746	2.120	2.921
17	0.689	1.740	2.110	2.898
18	0.688	1.734	2.101	2.878
19	0.688	1.729	2.093	2.861
20	0.687	1.725	2.086	2.845
21	0.686	1.721	2.080	2.831
30	0.683	1.697	2.042	2.750
40	0.681	1.684	2.021	2.704
50	0.680	1.679	2.010	2.679
60	0.679	1.671	2.000	2.660
∞	0.674	1.645	1.960	2.576

5. Experimental determination of oil and oil products in contaminated water (spectrophotometric method)

Waste water from oil extraction and oil processing is polluted with oil and oil products (lubricating oils, fractions from oil processing, etc.). The transportation of oil by sea, accidents with tankers or their cleaning is another source of pollution. The concentration of these pollutants can vary from tens of g/dm^3 (in untreated water) to several mg/dm^3 (after water purification). The aliphatic hydrocarbons that are part of the composition of oil and oil products have primarily a narcotic effect, and some of the aromatic ones (benzene, condensed aromatic hydrocarbons) have proven carcinogenic effects for humans. Due to its high lipo-solubility, the oil has a skin absorption effect.

Given the great diversity in the qualitative and quantitative composition of oil and petroleum-contaminated waters, most methods of analysis give the total content of organic substances extracted with an organic solvent in the waste water. Sufficiently sensitive methods for determining petroleum products in water are spectrophotometric methods in the UV and IR ranges of the spectrum.

The spectrophotometric method for determination of oil and oil products is based on the measurement of the optical density of the solution of oil and oil products in tetra chloromethane in the ultraviolet region of the spectrum at a wavelength of λ= 262 nm. The sensitivity of the method is different for different types of oil and for individual oil products. Therefore, it is necessary to draw

up the standard curve for the relevant oil or oil product that has contaminated the water. This method determines the total content of oil or oil products (volatile and non-volatile fractions).

Procedure

The tested water in a volume of 250 to 1000 cm^3 (depending on the expected amount of oil and oil products) is placed in the separatory funnel, saturated with sodium chloride and then 25 cm^3 of tetrachloromethane are added. The mixture is shaken for 5 min, the two layers are separated, the tetrachloromethane solution is filtered through a glass filter and spectrophotometered at λ= 262 nm and the thickness of the cuvette is 10 mm.

In the event that the optical density is greater (over 0.8), the solution is diluted with a measured amount of tetrachloromethane, so that the optical density is in the interval 0.3÷0.8.

Standard curve construction

Weigh 0.10 g of the crude oil or processable product (pre-dried in a desiccator) and dissolve in 25 cm^3 of tetrachloromethane. Part of this solution (with concentration 4 mg/cm^3) is further diluted with tetrachloromethane (CCl_4) so as to obtain a standard working solution with a concentration of 0.1 mg/cm^3 (40 times dilution). From thus prepared solution a standard scale from 0.01 mg/cm^3 to 0.1 mg/cm^3 with an interval of 0.01 mg/cm^3 is prepared by appropriate dilution, and the absorbance at λ= 262 nm is spectrophotometered with a comparative sample of pure tetrachloromethane. From the obtained results, a standard curve is constructed with the abscissa being the oil concentration (mg/cm^3) and the ordinate being the reported absorption.

The calculation of the amount of oil and oil product - x (mg/dm^3) is made using the formula

$$x = 1000 \times a \times V_1 / V$$

where **a** is the amount of oil reported on the standard curve (mg/cm^3), V_1 — the amount of CCl_4 used in the extraction (cm^3) and V — the volume of water taken for analysis (cm^3).

6. Experimental determination of the full dynamic sorption (purification) capacity of various media with respect to heavy metal ions

Cation exchange resins are a suitable means of removing metal ions from polluted waters when the concentration of pollutants is not very high. The resin retains contaminant ions and releases an equivalent amount of ions of the same charge previously retained on it (hydrogen or sodium ions). Most often, resins are used in a dynamic mode, where there is a relative movement of the water subjected to treatment relative to the cationite.

A small amount of metal ions can also be retained by physical adsorption on another medium, e.g. sand.

The aim of the work is to determine the sorption capacity of cationite and sand with respect to copper ions - water pollutants when working in dynamic mode.

Procedure

In 2 vertical glass columns with glass cotton placed on the bottom, and on top of it – 5 g of cationite in first column and 15 g of sand in the second column, H_2O is passed respectively to wet the adsorbents. After the outflow of H_2O, in the columns to the top a solution of Cu^{2+} ions is poured (a high hydrostatic pressure is maintained, i.e. a high level of the liquid during the entire experiment). The valve of the column is opened and samples of the liquid passed through the column are collected in flasks of 25 cm^3, and the speed of passing the liquid is such that one flask is filled in 8-10 min. In each sample, including the initial one, the content of copper is determined by iodometric titration, taking the entire contents of the measuring flask ($V_{Cu^{2+}}$) for titration. Sampling is stopped when the concentration of copper ions in the filtrate equals that in the starting solution (or at least reaches 95 % of it).

Iodometric determination of copper

A titration with 0.05 N $Na_2S_2O_3$ solution is carried out with starch as an indicator. Filtrate ($V_{Cu^{2+}}$ = 25 cm^3) is transferred to a flask for Iodometric determination, 4 cm^3 of 2 N solution of H_2SO_4, 10 cm^3 of 10% solution of KI are added consecutively. The flask is allowed to stand in the dark for 5 min,

after which the solution is titrated with 0.05 N $Na_2S_2O_3$ solution of precisely known concentration ($C_{Na2S2O3}$). When a light brown to yellowish colour of the sample is reached, 3-4 drops of starch solution are added to it and the addition of 0.05 N $Na_2S_2O_3$ solution continues until the blue colour disappears. The concentration of copper ions in the filtrate (C_{Cu}^{2+}) is calculated from the volume of the spent $Na_2S_2O_3$ ($V_{Na2S2O3}$) solution, using the dependence:

$$C_{Cu}^{2+} \times V_{Cu}^{2+} = C_{Na2S2O3} \times V_{Na2S2O3} \quad (1)$$

Processing of experimental results

The dependence C/C_o as a function of the volume of the solution (W) passed through the column is plotted graphically - Figure II.6.1, where C_o - initial concentration of copper ions, C – concentration determined for a given sample. The three characteristic points corresponding to 0.16, 0.50 and 0.84 of the initial concentration of copper ions are determined from the curve and then (graphically) corresponding volumes $W_{0.16}$; $W_{0.50}$ and $W_{0.84}$ are determined. It is checked how symmetric the curve $C/C_o = f(W)$ is around $W_{0.50}$ and therefore the method of characteristic points can be applied to calculate the sorption capacity under dynamic conditions Θ. To carry out the check, the parameter ε is calculated, as

$$\varepsilon = (W_{0.50} - W_{0.16}) / (W_{0.84} - W_{0.50}) \quad (2)$$

If $0.5 < \varepsilon < 1.5$, the method of characteristic points is applicable and then the sorption capacity (Θ, meq/g) is calculated by the formula:

$$\Theta = (W_{0.50} \times C_o \times 10^3) / m \quad (3)$$

where $W_{0.50}$ is in dm^3, C_o is in geq/dm^3, and m is the mass of the filtration medium in g.

A conclusion is made about the influence of the nature of the adsorbent on the sorption process and sorption capacity.

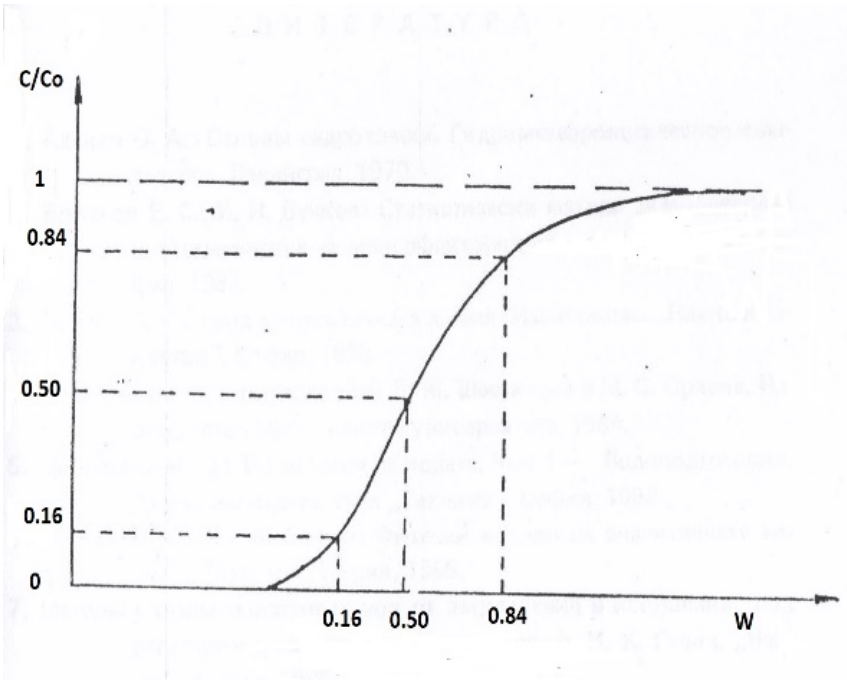

Figure II.6.1. Breakthrough curve with characteristic points

Marinela Panayotova

Water chemistry

First Edition

Reviwers: Prof. Dr. Vladimir Hristov

ISBN: 978-954-353-479-1

Publishing House „Saint Ivan Rilski“ at UMG "Saint Ivan Rilski" Sofia, 2024

UNIVERSITY OF MINING AND GEOLOGY
"ST. IVAN RILSKI"

mgu.bg