

Using Chemistry: water analysis

Water, the substance that dominates the environment and is a vital component of living processes is not pure H_2O . The water that society depends on may contain other species that make it unsuitable for human consumption. Moreover, water treatment processes add impurities that make water more suitable for human use. The chemical analysis and treatment of water performs a vital process for the well-being of society.



A solution is a homogenous mixture at a molecular, ionic or atomic level. If H_2O is the solvent, then this is described as an aqueous solution.

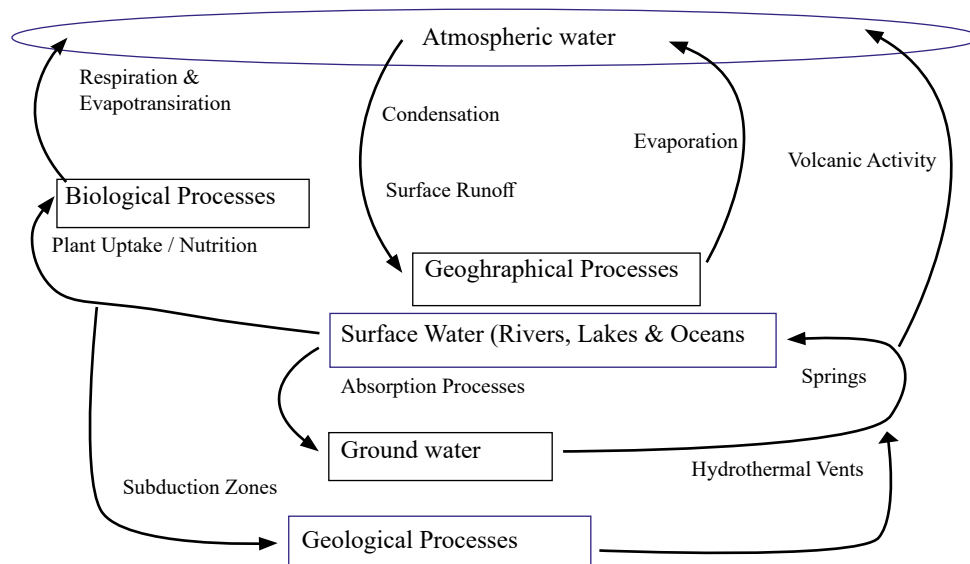
Freshwater can be considered as a homogenous, aqueous solution, as it will contain dissolved chemical substances such as shown in Table 1.

Table 1.

Species (Type)	Examples
Dissolved Gases	O_2 and CO_2
Ions	Na^+ , Ca^{2+} , HCO_3^-

To fully understand how these different chemical species get into the water supply, a simple overview of the natural water cycle is provided in Fig 1.

Fig. 1



Examining each process, H_2O can be considered as contributing to an aqueous solution. Gases may dissolve in different processes in the water cycle. Minerals, that is ions, will dissolve during water runoff and erosion processes. Other minerals will be introduced during human activity.

Water analysis

Water is an essential resource for living systems. It is a key requirement in industrial processes, agricultural production and for domestic use. When analysing water quality the following factors are measured:

(a) Turbidity

Turbidity is a measure of the level of cloudiness in water. This is caused by large numbers of particles suspended in water, although some individual particles may be so small that they appear invisible to the

naked eye. Such particles will settle very slowly or not at all if the water sample is regularly agitated. Larger particles will be heavy enough to settle to the bottom of the container. In natural sources, turbidity can be caused by the growth of phytoplankton or by natural sediment. Rivers will often contain materials originating from human activities, such as agriculture, construction and mining. These can contribute to high levels of turbidity.

Measurement of turbidity relies on the amount of light scattered by the solid particles suspended in the water sample. The scattered light can be captured by a photodiode, which produces a signal calibrated to the concentration of suspended particles in the sample. Alternatively, a Secchi disk (a black and white disk) is lowered into the water until it can no longer be seen and the depth (the Secchi depth) is recorded as a measure of the transparency of the water sample.

High turbidity levels in drinking water can lead to instances of gastrointestinal diseases where contaminants, such as viruses or bacteria, are attached to the suspended solids. These solids can act as shields, protecting viruses and bacteria, from water treatments such as disinfection with chlorine and sterilisation of water using ultraviolet radiation.

Turbidity is usually treated by settling or filtration processes. Chemical reagents are often added to improve the effectiveness of these processes. Natural, disposed sources of water may be treated with a flocculent. The resulting flocs settle to the bottom where they remain or are removed by filtration processes. Commonly used chemical agents include aluminium sulphate (alum) and calcium sulphate (gypsum).

(b) Alkalinity and pH

The pH of a solution is a measure of the hydrogen ion (H^+) concentration in that solution. Natural water samples will tend to have pH values between pH 5.0 and pH 8.5. Water samples with a pH outside this range are likely to be heavily contaminated. Obtaining the pH of a sample is therefore an important test in the analysis of water. This can be completed in the field or in the laboratory using midrange pH paper between pH 5 and pH 9; pH meters or colour-based indicators.

The alkalinity of a water solution is the quantitative capacity of that solution to buffer and resist changes in its pH. Rain water will typically be within a range of pH 5.5 to pH 6.0 depending on the degree of acid rain in the area. Ground waters and surface waters may have an increased pH due to the solubility of hydrogencarbonate ions (HCO_3^-) carbonate ions (CO_3^{2-}) or hydroxide ions (OH^-) leached from rocks such as limestone and dolomite.

Water required for human use and consumption should not have a $pH < 6.5$. Acidic water will leach metal ions such as iron, copper, lead and zinc, leading to elevated levels of toxic metals. It will also damage piping and will have a sour or metallic taste. Water with a $pH > 8.5$ indicates hard water due to high concentrations of hydrogencarbonate ions. Hard water does not pose a health risk, but leads to the formation of lime-scale in piping and on water-heating units.

The analysis of the pH of water is a key indicator of pollution. Rain water with a $pH < 5.0$ is classed as acid rain, formed from dissolved sulphur and nitrogen oxides. If the surrounding soils are not buffering then the resulting acid ground waters can lead to the leaching of toxic heavy metals into rivers. At $pH > 9.0$, harmless ammonium ions form toxic ammonia, which is harmful to aquatic lifeforms. Agricultural runoffs lead to increased concentrations of ammonium ions, which, in turn, could lead to increased levels of ammonia.

(c) Total Dissolved Solids (TDS)

Natural waters may contain trace elements and minerals such as nitrates, phosphates, halides (chloride and fluoride ions), alkali metals (sodium and potassium ions) and calcium and magnesium ions. Collectively, these are referred to as Total Dissolved Solids (TDS). The concentration of TDS can be determined by gravimetric analysis where the water is evaporated and the residue masses measured. Alternatively, conductivity meters can be used to measure conductivity of the water sample due to the dissolved ions present. The amounts of nitrogen, sulphur and phosphorus is obtained by measuring ions containing these elements.

Primary sources for TDS are agricultural and residential runoff and the leaching of soil contaminants due to associated pollution discharge from industrial or sewage treatment plants.

High sodium ion (Na^+) concentration is linked to high salinity, possibly linked to seawater intrusion into fresh water or runoff from wintery climates related to de-icing salts.

Nitrates are produced by the biological breakdown of organic nitrogen compounds through the oxidation of ammonia. High levels of nitrates are a general indicator of poor water quality.

More harmful examples of TDS originate from pesticides arising from surface runoff.

Water for human consumption is closely monitored for its levels of TDS and for values below 500 mg dm^{-3} there are no issues relating to the colour, taste or odour of water. Fresh water is defined as having a TDS below 1000 mg dm^{-3} . The analytical applications of TDS have other commercial benefits with producers of freshwater oysters, trout, and other high value seafood mimicking the TDS of the species' natural environment to maximise productivity. Ion-exchange chromatography is widely used in the analysis of TDS in aqueous samples, including drinking water.

(d) Ion exchange chromatography

Ion exchange chromatography works by retaining the analytic species within a column by ionic interactions, that is, by the stationary phase surface containing ionic groups that interact with analytic ions with an opposing charge. The type of charge contained in the column defines whether a cation exchange or anion exchange is completed. Fig. 2 consists of a sequence of diagrams illustrating the how cation exchange chromatography retains positively charged cations because the stationary phase has a negatively charged group.

Fig. 2(a)

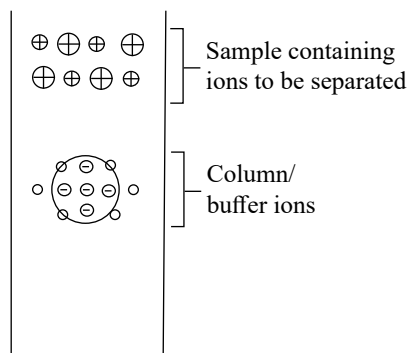


Fig. 2(b)

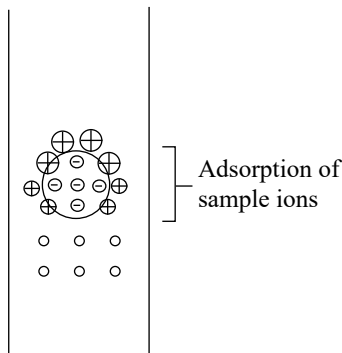
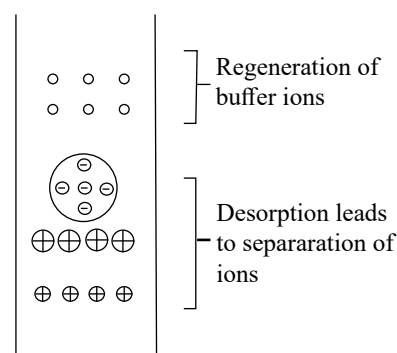


Fig. 2(c)



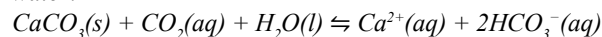
The sample is introduced and a buffered aqueous solution, known as the mobile phase, carries it through a column containing a resin or gel matrix. This stationary phase consists of cellulose beads covalently bonded to a charged chemical species. The target analytic ions are retained through adsorption onto this stationary phase, but can be eluted by increasing the concentration of a similarly charged species that displaces the analytic ions from the stationary phase.

(e) Water hardness

Hard water contains a high mineral content, including positively charged metal ions, typically with a charge of 2+. This occurs when water percolates through chalk and limestone deposits increasing the concentrations of calcium and magnesium ions in the water. In contrast, rainwater and distilled water are described as soft water as they contain few ions.



The following equilibrium reaction describes the dissolving and formation of calcium hydrogen carbonate and hence hard water:



Water hardness is determined using dedicated instruments measuring the total hardness due to the combined concentrations of calcium and magnesium ions, the two most prevalent divalent cations. Other multivalent ions, for example; iron and aluminium, can be present at elevated levels in some locations.

Hard drinking water is not harmful and the higher levels of calcium ions may be considered as being beneficial. Unfortunately, there are issues with hard water due to the build-up of lime-scale on heating elements leading to costly replacements of boilers and cooling towers. Hard water will result in a lack of suds when soap is agitated with water. Water softening processes are often applied to reduce hard water's adverse effects. This involves the removal of calcium and magnesium ions by water softeners. These processes do not reduce the overall TDS level of the water as they typically involve replacing magnesium and calcium ions with sodium or potassium ions.

(f) Microorganisms

Bacteriological water analysis requires estimating the total numbers of bacteria in the sample and identifying the type of bacteria present. It is from this analysis that the assessment of the quality of the water is made to decide whether it is fit for human consumption and human recreational use or is simply unsafe.

There are very stringent levels applied to drinking water. The screening process focuses on primary indicators rather than actual pathogens.

The reasoning is that levels of primary indicators such as *Escherichia coli* and *Pseudomonas aeruginosa* are produced at much higher levels than a more pathogenic bacterium and is therefore easier to detect. If the level of primary indicators exceeds trigger targets then specific analysis for pathogens can be completed using specific culture methods or molecular biology. When the levels of the primary indicators are low then it is reasonable to assume that the level of pathogens will be very low or absent. The presence of high levels of primary indicators are often evidence that raw sewage has contaminated the water supply. Judgements on the suitability of water are based upon the bacteria population found in a given water sample and the probability it leads to an infective rate. This analysis is completed using biochemical or cultural methods.

(g) Dissolved oxygen content (DOC)

Small quantities of dissolved oxygen in rivers, lakes and the oceans are required to maintain aquatic life. If the amount of dissolved oxygen drops significantly then that body of water can no longer sustain life and living organisms will die due to hypoxia.

Typically, there is 11 mg of oxygen dissolved per dm³ of water, but the actual amount dissolved depends on several factors including water temperature, depth of the water, salinity and whether there are any photosynthetic organisms in the water. Analysing oxygen depletion involves measuring the amount of oxygen dissolved as a percentage of the amount of oxygen that should dissolve under prevailing conditions. For an aquatic environment to maintain and promote a successful ecosystem, levels should exceed 80%. Hypoxic conditions occur when dissolved oxygen levels are below 30%. Most fish, for example, are unable to survive with such oxygen depletion.

There are several causes for oxygen depletion. For example water pollution, including eutrophication, where plant nutrients enter water systems from the land. Another cause of oxygen depletion occurs where freshwater flows into the sea. Freshwater is less dense than saltwater, which restricts vertical mixing, restricting the supply of oxygen from the air to the bottom layers.

(h) Water Analysis

The chemical analysis of water provides a vital function ensuring that the quality of water meets necessary standards. The quantitative analysis, including pH, concentrations of key cations and anions, trace elements and other important foreign agents, enables scientists to determine the possible uses a water source may have. It may also initiate studies into how a body of water interacts with the local environment or provide the groundwork for studies of water quality, pollution, hydrothermal vents and hydrology.

Questions

1. Provide definitions for the following key terms relating to the analysis of water and water quality:
 - (a) Evaporation
 - (b) Condensation
 - (c) Water vapour
 - (d) Homogenous solution
 - (e) Hypoxia
 - (f) Eutrophication
 - (g) Hydrothermal vents
 - (h) Hydrology

Answers

1.
 - (a) The process by which molecules undergo the spontaneous transition from the liquid phase to the gas phase.
 - (b) A change in the state of matter from the gas phase to the liquid phase.
 - (c) A dispersion, in air, of molecules of water as produced by evaporation at ambient temperatures rather than by boiling.
 - (d) A mixture which has uniform composition and properties throughout. For example, table salt dissolved in a glass of water.
Contrast this with a heterogeneous mixture composed of visibly different phases, e.g. sand mixed with water.
 - (e) Decrease below normal levels of oxygen in inspired gases, arterial blood, or tissue, without reaching anoxia.
 - (f) The undesirable overgrowth of vegetation caused by high concentrations of plant nutrients in bodies of water.
 - (g) Located near volcanically active areas, geothermally heated waters are forced up through the surface, e.g. hot springs, geysers.
 - (h) The scientific study of the movement, distribution, and quality of water.