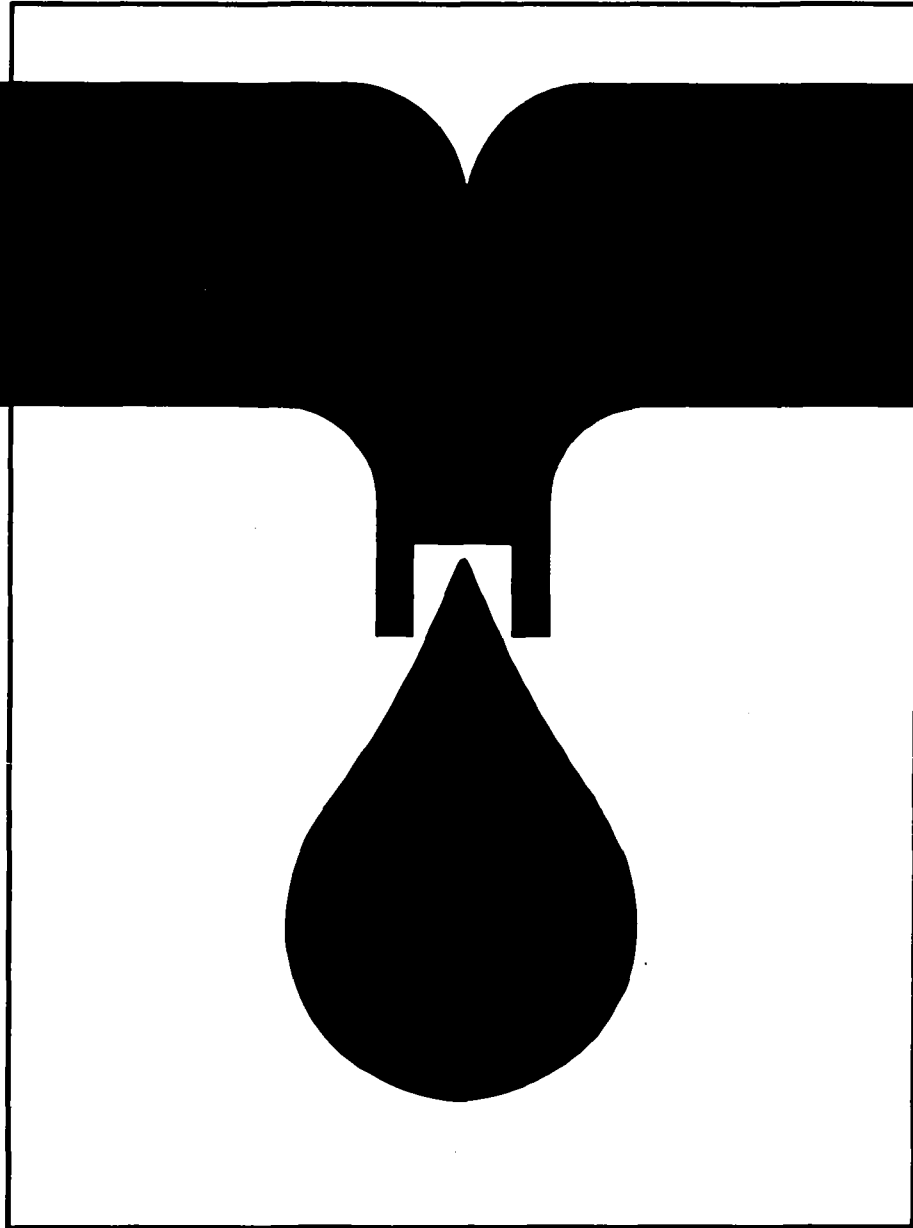




TRAINING MODULES FOR WATERWORKS PERSONNEL



Basic Knowledge

0.3

Basic concepts of water chemistry

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Foreword

Even the greatest optimists are no longer sure that the goals of the UN "International Drinking Water Supply and Sanitation Decade", set in 1977 in Mar del Plata, can be achieved by 1990. High population growth in the Third World combined with stagnating financial and personnel resources have led to modifications to the strategies in cooperation with developing countries. A reorientation process has commenced which can be characterized by the following catchwords:

- use of appropriate, simple and - if possible - low-cost technologies,
- lowering of excessively high water-supply and disposal standards,
- priority to optimal operation and maintenance, rather than new investments,
- emphasis on institution-building and human resources development.

Our training modules are an effort to translate the last two strategies into practice. Experience has shown that a standardized training system for waterworks personnel in developing countries does not meet our partners' varying individual needs. But to prepare specific documents for each new project or compile them anew from existing materials on hand cannot be justified from the economic viewpoint. We have therefore opted for a flexible system of training modules which can be combined to suit the situation and needs of the target group in each case, and thus put existing personnel in a position to optimally maintain and operate the plant.

The modules will primarily be used as guidelines and basic training aids by GTZ staff and GTZ consultants in institution-building and operation and maintenance projects. In the medium term, however, they could be used by local instructors, trainers, plant managers and operating personnel in their daily work, as check lists and working instructions.

45 modules are presently available, each covering subject-specific knowledge and skills required in individual areas of waterworks operations, preventive maintenance and repair. Different combinations of modules will be required for classroom work, exercises, and practical application, to suit in each case the type of project, size of plant and the previous qualifications and practical experience of potential users.

Practical day-to-day use will of course generate hints on how to supplement or modify the texts. In other words: this edition is by no means a finalized version. We hope to receive your critical comments on the modules so that they can be optimized over the course of time.

Our grateful thanks are due to

Prof. Dr.-Ing. H.P. Haug
and
Ing.-Grad. H. Hack

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It is my sincere wish that these training modules will be put to successful use and will thus support world-wide efforts in improving water supply and raising living standards.

Dr. Ing. Klaus Erbel
Head of Division
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Eschborn, May 1987

Basic concepts of water chemistry

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Teaching aids: GTZ publications:

- 1) Methodensammlung zur Wasseruntersuchung; W.Fresenius + W.Schneider, GTZ 1976/77
- 2) Technologie des Trinkwassers; W.Fresenius + W.Schneider, GTZ 1979/80
- 3) Technologie des Abwassers; W.Fresenius, W.Schneider, B.Böhnke and K.Pöppinghaus; GTZ 1982/83
- 4) Traditional Water Purification in Tropical Developing Countries; Samia Al Azharia Jahn, GTZ 1981

0 Introduction

Water is present on the earth in large quantities. For some organisms it is a life-giving environment; for others - man, non-aquatic animals and plants - it is essential for the maintenance of life.

No living creature can exist without water. Without water there can thus be no life on earth.

Life has been very successful in adapting itself to differences in natural water resources. There are, for instance, organisms which can live in hot water, almost up to boiling point (100°) and others needing cold water. Many creatures need the high salt concentration of sea-water, which for others again is directly harmful - e.g. for human beings, many animals and a wide variety of plants.

Whilst it is possible to produce water (H₂O) through a synthesis of the two gases hydrogen and oxygen (detonating gas), according to the equation $H_2 + 1/2 O_2 \rightleftharpoons H_2O$, this is of theoretical interest only and has no practical significance.

The amounts of water distributed over the earth's surface are huge. The problem lies in making water available where it is needed, or in treating a water resource so that it meets the requirements of human beings, animals, plants and industry. Thus a human being requires a supply of about 2 to 3 litres of good-quality water a day for drinking, but the industrialized countries, for example, use more than 200 litres per person and day on top of this for cleaning and technical purposes.

The total amount of water on the earth is distributed roughly as follows:

Oceans and seas (salt water):	1400 million km ³
Lithosphere (bonded water):	76 million km ³
Ice:	47 million km ³
Fresh water in lakes and rivers:	0,5 million km ³
Ground water (varies very widely):	from 1.5 million km ³ up to many times this figure



Atmosphere: 0.01 to 0.02 million km³

The total quantity of water on the earth is estimated at roughly 1,600 million km³.

Of this total resource, about 3% is fresh water, although only about one-tenth of this is usable. Fresh water is water which contains, as an optimum concentration, less than 1 g/l of dissolved salts or minerals; concentrations of up to 5 g/l can still be tolerated if necessary and do not have harmful effects on humans, animals or plants. What remains is water with a more or less high salt content: the concentration in oceans and seas is roughly 35 g/l. This salt water is suitable only for specially adapted organisms.

Water covers 70.8% of the surface of the earth. In a continuous and never-ending cycle - see also Module 1.1 - water evaporates into the atmosphere, falls again in the form of rain, fog, dew, snow or hail to the earth's surface, collects in rivers and lakes or underground and eventually returns to the sea. At various points in this cycle, use is made of the water by plants, animals, human beings and industry. Water also serves as a producer of energy and a means of communication and transport.

It is generally accepted that life began in the oceans, and an infinite variety of plants and animals still live today in the salt waters of the seas. Nearly all creatures living on land need fresh and not salt water, however, whereby the upper limit as given above, i.e. 5 g of dissolved salts and mineral substances per litre can be exceeded only in special cases and the water still used.

Although the total amount of fresh water available on the earth is in fact adequate for all needs, there remains the very considerable problem of transport and distribution already mentioned above.

The chemical compound water (H²) possesses a variety of special properties, e.g. with regard to a number of physical parameters, and including in particular its solvent power.....

for gases, mineral substances, salts, organic compounds etc..
These special characteristics are of particular importance for life
on earth, and are discussed in detail below.

1 Physical properties of water

Water exhibits a number of physical properties which clearly
distinguish it from other substances. Some of these are described
below.

1.1 Physical states of water

Water exists in nature in three different states: the solid (ice),
liquid (water) and gaseous (steam) states. For each of these states
there are a large number of intermediate or metastable phases which
will not be further dealt with here. Transformation from the solid
state of the liquid and directly to the gaseous state is just as
possible as the formation of the solid state (ice) directly from steam
or the condensation of liquid water out of steam.

1.2 Freezing point, boiling point, vapour pressure, compressibility, surface tension

Water which contains only a low concentration of dissolved substances
freezes at 0°C; at standard pressure of 1 bar it boils at 100°C.
The freezing point and boiling point of water serve as fixed points
in the measurement of temperature.

The boiling point of water can be depressed through a reduction
of pressure. In mountainous areas where the atmospheric pressure is
less, water therefore boils at temperatures below 100°C. This fact
is exploited e.g. in the desalination of water by vacuum distillation.

It can be observed that dissolved salts in the water cause the
boiling point to rise and depress the freezing point.

The vapour pressure of water - i.e. its tendency to convert from
the liquid to the gaseous state - is already noticeable at
normal ambient temperature e.g. 20 or 30°C - and is

demonstrated by the fact that water left in an open vessel for a relatively long period eventually dries up through evaporation even at temperatures far lower than 100°, with the dissolved salts remaining in the vessel.

Similarly, water vapour in the air can be condensed, e.g. by cooling, and converted into water in its liquid state. This can be observed in nature e.g. when rain or dew falls.

When water is evaporated or distilled, pure water is converted into the gaseous state (water vapour) and the dissolved mineral substances and salts remain behind. This effect is exploited to desalinate water through distillation. Similarly, pure water freezes out of a saline aqueous solution, leaving behind a saline mother liquor. This is why e.g. icebergs in the polar seas consist of fresh and not salt water, which after thawing can be used as such.

Water is virtually non-compressible, even at highest pressures.

When heated, water expands - but also when it freezes to form ice. This can lead to high pressures and cause pipes, tanks etc. to burst. In nature, the expansion of water on freezing e.g. in crevices enlarges the cracks and is thus one factor in the erosion of the earth's surface.

The expansion of water on conversion from the liquid to the solid state (formation of ice) is paralleled by the behaviour of iron and bismuth under comparable conditions.

The surface tension of water is greater than that of all other liquids, with the exception of the water-like substance hydrogen peroxide.

The surface tension of water is of vital importance for many aquatic creatures. Surface tension is decreased by a number of organic compounds, e.g. the decomposition products of leaves, but also by the addition of surface-active substances; soap solutions or detergents. Alteration of

the surface tension of the water through such secondary influences may have serious, possibly highly destructive effects on aquatic life.

1.3 Anomalous expansion of water

The anomalous expansion of water plays an important part in the preservation of aquatic life, especially during very cold weather.

Water has a maximum density at + 4°C, i.e. 1 g/l or 1 kg/l. Warmer, but also colder water is lighter than water with a temperature of 4°C.

This means that layers having different temperatures form in a body of water. As the temperature of the water falls to 4°C (i.e. the point at which it has its maximum density and therefore greatest specific gravity), it sinks until all the body of water has reached its maximum density at 4°C. If further cooling occurs, any water below 4°C will stay at the top owing to its lower density. In due course, ice will form, which, being lighter than water, floats on the surface. In this way the lower layers of water remain at 4°C even if outer temperatures are much lower, because they can lose heat only by conduction. In deeper water there will always be water underneath the ice in which fish and other creatures can live in the cold weather. This physical property of water is decisive for the survival of aquatic life and is one of the miracles of nature.

Dissolved salts in the water depress its freezing point and delay the formation of ice. Ice has a lower specific density than water and therefore floats on the body of water, which has its maximum density at 4°C.

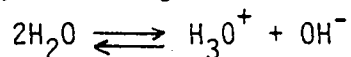
2 Physical chemistry of water

Water has a molecular weight of 18, composed of the atomic weight of oxygen with 16 and that of hydrogen with 1 each

(i.e. $H_2O = 18$). This can be affected by various hydrogen isotopes, i.e., apart from hydrogen itself, by deuterium (heavy hydrogen with an atomic weight of 2) and tritium (super-heavy hydrogen with an atomic weight of 3) but also by the various oxygen isotopes. These peculiarities of water play little part in the physical chemistry and molecular weight of natural water, however.

2.1 Dissociation of water

The dissociation of water is the splitting of its molecules into ions. Ionic compounds consist of oppositely charged atoms or groups of atoms; when an electric current is passed through the compound, the ions are attracted to the oppositely charged electrodes, according to the formula



This phenomenon is of importance for the reaction of water with other substances.

As a general rule, $H_2O \rightleftharpoons H^+ + OH^-$

Thus (form from the water itself) hydrogen ions (H^+) or hydronium ions (H_3O^+) and hydroxyl ions (OH^-). H^+ and H_3O^+ ions cause an acid reaction, OH^- ions an alkaline reaction.

Pure water contains equal numbers of H_3O^+/H^+ and OH^- ions and thus reacts neutrally.

2.2 pH

The pH indicates the acidity of a water and is one of the factors allowing the general character and the aggressivity of a water to be evaluated - e.g. its potential effects on pipes, building materials or animal life.

If there is an excess of hydrogen ions (H^+) or hydronium ions (H_3O^+), there is an acid reaction in the water, and with an excess of hydroxyl ions (OH^-) the water shows an alkaline reaction.

Neutrality is at pH 7. Thus all pH values below 7 indicate acidity and similarly all pH values in excess of 7 indicate alkalinity.

The acidity of a water increases with diminishing pH and conversely the alkaline (basic) reaction increases with increasing pH.

pH values below 1 or in the area of 2 or 3 indicate extreme acidity and are due to the presence in the water of strong acids in solution, such as hydrochloric acid, sulphuric acid, nitric acid, etc.

Although carbonic acid causes only a slightly acid reaction, this may frequently lead to corrosion of metals or other construction materials.

pH values in excess of 10 or 12 indicate extreme alkalinity and are caused by the presence of bases in solution, such as caustic soda or lime milk.

Extremely acid or extremely alkaline (basic) pH values are seldom found in natural water. Sea water, for instance, has a pH on the alkaline side of about pH 8 (slightly more than 8.2), whilst most natural waters are beneath this level. As a general rule, natural water will have a pH somewhere between 5.5 and 8.5.

Some waters which contain iron or sulphates may have a higher acidity, and there are also some waters, e.g. the salt lakes in East Africa, which give an alkaline reaction even higher than that of sea water, in the order of pH 9 to 12.

Extreme pH values in water are also often due, however, to human or industrial activity. For this reason, where such a pH has been determined - e.g. an acidity under pH 5 or alkalinity above pH 10 - a secondary influence should always be looked for.

Thus the pH is a measure of the acid or base (alkali) content of a water, i.e. of an excess of hydrogen ions (H^+ or H_3O^+ ions) or hydroxyl ions (OH^-). The pH can

be defined as the negative decadic logarithm of the hydrogen ion activity.

The pH of a water can be measured by a number of different methods, e.g. by using indicators which have a different colour for different levels of acidity or alkalinity, such as litmus, which shows red for acid and blue for alkaline. Besides this method of measuring pH values with colour indicators, the results of which may be quite strongly affected by a too low or too high concentration of salt in the water, another method has come into increasing use in recent years. This is the so-called "electrometric" measurement of the pH using a glass electrode and an appropriate measuring instrument. Such measurements can be carried out easily, giving accurate results, if the appropriate electrodes and measuring instruments are available.

By using indicators or electrometric measurement of the pH, it is possible to follow the process of neutralization of the water. Thus a water which shows an acid reaction is neutralized by adding a base, i.e. the pH is altered from an excess of acid to neutrality at pH 7.

In the same way, an alkaline water can be neutralized by the addition of acid until it has a pH of 7.

2.3 Conductivity, buffer capacity

The conductivity of a water is due to the dissociation of dissolved salts in a water into negatively and positively charged ions (the word ion comes from the Greek language and means, approximately, "a wanderer", indicating here the movement of ions in an electric field to the negative or positive electrodes). In this way, cations (positively charged ions which are attracted to the negative electrode) are distinguished from anions, negatively charged ions which are attracted to the positive electrode.

The dissociation of water itself has already been discussed under 2.1. It was stated that pure water already partly

dissociates into hydrogen ions (H^+) or hydronium ions (H_3O^+) and hydroxyl ions (OH^-):

Now if, for instance, inorganic salts such as $NaCl$ or $CaSO_4$ are dissolved in water, these salts also dissociate into positive particles (cations) and negative particles (anions). This dissociation depends on the type and the charge of the ions in the dissolved salts. A distinction must be made between cations and anions.

Thus cations are the positively charged ions which are formed on dissociation of the water and which, if an electric current is passed through the water, are attracted to the negative electrode.

Examples:

Hydrogen ions from acids (H^+), sodium ions from sodium salts (Na^+), calcium ions from calcium salts (Ca^{2+}).

Anions, on the other hand, are negatively charged under the same conditions and are attracted to the positive electrode, such as hydroxyl ions (OH^-), e.g. from bases or lyes, or chloride ions (Cl^-), e.g. from common salt, or sulphate ions (SO_4^{2-}), e.g. from gypsum, etc.

Dissociation of the salts dissolved in the water is greater in the case of salts of the "strong" acids and bases, such as e.g. hydrochloric acid, sulphuric acid, caustic soda lye, calcium hydroxide or sodium chloride, sodium sulphate, calcium sulphate or calcium chloride.

The presence of higher concentrations of these acids, lyes or salts in solution in the water is already detectable from the sour, alkaline, salty, bitter or "hard" taste of the water.

In the case of "weak" acids or their salts, such as, for instance, acetic acid or the salts of carbonic acid or ammonium hydroxide, there is less dissociation, and these salts of the weak acids also act as "buffers", i.e. on the addition of a strong acid or a strong base they prevent

a change of pH of the water to extreme acidity or alkalinity. This "buffer" property is important for biological processes because, if salts of carbon dioxide or acetic acid or ammonium are present in solution in the water, an acid or alkaline reaction takes place on addition of acids or bases only after a certain minimum concentration is exceeded.

In other words, if a water contains dissolved hydrogen carbonates or carbonates or dissolved salts of acetic acid or other weak acids, the change of a strongly acid or strongly alkaline reaction through outside influence is held back, i.e. buffered.

The dissociation of the water itself and the dissociation of the salts dissolved in it have a close connection with the ability of the water to conduct electricity. This is caused by the ions present in the water and is highly dependent on its temperature.

In general, the conductivity of a water is measured electrometrically at a certain temperature, e.g. at 20°C or, following ISO guidelines, at 25°C. The measured conductivity is given in S/cm or in fractions of this, such as mS/cm or μ S/cm at a certain temperature.

The measured value of conductivity as μ S/cm at 20°C allows an approximate forecast of the total amount of salt-like substances present in solution in the water to be made. Thus, if at 20°C a measured value of e.g. 1,000 μ S/cm is obtained, this is approximately equivalent to a concentration of dissolved minerals of 1000 mg/l. This relationship can, of course, only be used as a rule of thumb, since it depends not only on temperature, but also on the ion charges of the salts in solution, etc. It is, therefore, an approximation formula, but certainly adequate for making a rough estimate in the field of the probable concentration of salts.

The values measured to determine the conductivity of the water can be converted to the required reference temperatures with the aid of tables.

For human consumption, a water with a conductivity of about 1000 $\mu\text{S}/\text{cm}$ at 20°C or less is more favourable than water with higher conductivity. Considerable problems are caused by the salt concentrations in water with a conductivity greater than 5,000 $\mu\text{S}/\text{cm}$ - i.e. more than 5 mS/cm at 20°C - if such water is to be used for human or animal consumption.

2.4 Water temperature

The temperature of a water is of significance in many of its different uses by human beings, animals or plants, but also for the behaviour of the water when in contact with materials such as pipes, building materials etc..

Generally speaking, the aggressivity of a water increases with its temperature. At higher temperatures, for instance, gases in solution in the water such as oxygen, carbon dioxide or hydrogen sulphide are released and may then cause e.g. corrosion in the pipe system or other structures. Higher water temperatures also increase the solubility of minerals, salts, metals and other building materials in water.

Waters which have temperature permanently higher than the surrounding environment are called thermal waters and may quite well, in addition to the aggressive properties mentioned above, also have a beneficial effect on living creatures - which is demonstrated by the frequent use of hot springs by both human beings and animals.

Water rising to the surface of the earth from a great depth underground may have a temperature as high as boiling point (100°C).

For normal human and animal use, water should have a lower temperature, however, somewhere between 5 and 35°C. A temperature between 10 and 20°C is considered the optimum for human consumption.

The water temperature is also of importance in connection with animal husbandry and irrigation; whereby here too a temperature between 5 and 35°C is considered most favourable.

Of particular importance, however, is the temperature of the water for micro-organisms. At temperatures below 10°C, the reproduction rate of micro-organisms slows down considerably, and a water can be preserved if it is kept at a constant temperature below 4°C. At these temperatures, normal micro-organisms have only a very slight tendency to reproduce. In particular, pathogenic, i.e. disease-causing micro-organisms are able to reproduce only extremely slowly at such low temperatures.

In contrast, at temperatures between 20 and 30°C many micro-organisms reproduce extremely quickly, reaching the highest level of their growth and reproductive capacity here - e.g. certain bacteria form a new generation every 30 minutes at these temperatures.

Since the temperature of a water can be measured very easily in °C using a mercury or liquid thermometer, an evaluation of the water from this point of view and an estimate of its possible harmful effects on people and animals are easily made.

All natural springs with a temperature below 10°C and those with a temperature above 40°C can be expected not to contain pathogenic micro-organisms in any significant concentration.

Measurement of the temperature of a spring or other water resource should therefore always be included in any analysis used in an evaluation of the quality of the water.

2.5 Redox potential

This parameter of a water, determined by indicators or, better, by electrometric measurement, indicates the oxidation or reduction degree or the ratio of one to the other.

A redox potential of 0 or below 0 indicates reductive behaviour or a reductive influence on the water. This means that oxygen is not dissolved in the water and that any oxygen brought into the water is quickly consumed by chemical or micro-biological redox systems. Such a negative redox

potential will therefore be shown by a natural water which is affected by negative redox systems, such as e.g. hydrogen sulphide, divalent iron, etc. but also by a water which has been affected by organic compounds which have led to a high consumption of oxygen, whereby these contaminants may be of natural origin or may result from domestic or industrial effluent.

The less a water is affected in this context, i.e. the more oxygen there is active in the water, the more the redox potential will move into the positive. If an electrometric measurement establishes, however, that the redox potential is greater than e.g. + 300 mV, then the possible influence of an oxidation agent such as chlorine or a compound of chlorine, ozone etc. should be looked for. If a water which is to be used for human or animal consumption shows a redox potential greater than + 500 or + 600 mV due to the addition of chlorine or a chlorine compound, bromine or a compound of bromine, ozone etc., it can be assumed that this water is free of bacteria or has a low bacterial concentration. Thus measurement of the redox potential offers a relatively simple method of determining e.g. the effect of an oxidative treatment process carried out on water for drinking and bathing purposes.

3 Chemistry of water

The study of the chemistry of water is concerned less with the chemistry of the water itself than with the chemical behaviour of the solid, liquid or gaseous substances present in solution in the water

3.1 Solvent power of water

Simple observation shows us that water is an unusually powerful solvent for salts and mineral substances - men and animals have always known this. The property is so marked that the extreme concentrations of salts and minerals in a water may make it virtually unusable by men, animals or plants.

The solubility of gases in water is also quite considerable. For instance, at about 15°C, up to approx. 2,000 mg of carbon dioxide may be present in 1 l. of water. The greater part of this is in the form of physically dissolved CO₂, but hydrated CO₂ (H₂CO₃, i.e. carbonic acid) and carbonic acid ions HCO₃⁻ and CO₃²⁻ are also present. Carbonic acid also causes an acid reaction and is thus responsible for the aggressivity of many waters.

The capacity of a water to dissolve oxygen is one of the most important factors for aquatic organisms inhabiting it. Depending on temperature and pressure, the solubility of oxygen in water varies from about 15 mg/l down to the limit of detection at about 0.1 mg/l. Below a level of about 2 to 3 mg of oxygen per l, no fish can live in a water. Just as the amount of dissolved oxygen in the water is decisive for life in it, the carbon dioxide (CO₂) concentration has a direct effect on the water's solvent power - e.g. for mineral substances. Calcium carbonate (limestone) is only slightly soluble. However, its solubility is greatly increased by the presence of dissolved CO₂ in the water; this reacts with the calcium carbonate to form calcium hydrogen carbonate (cf. p.17).

By no means negligible is also, however, the capacity of water to dissolve organic compounds, such as fuels, oils and fats, alcohols, sugars and many other organic substances. As a rule it can be assumed that a relatively high concentration of organic substances in a water - e.g. more than a few mg/l - indicates contamination by men, animals or industry.

Salts dissolved in water from genuine solutions, i.e. the salt cannot be recovered from the water by simple filtration. Many other mineral substances such as compounds of calcium, magnesium, iron, manganese and aluminium also form genuine solutions under certain pH conditions at a certain concentration of carbon dioxide in the water. Colloidal solutions

may also already form here, however. These represent a degree of dispersion of the dissolved substances, which can then be separated using extremely fine filters. The very strong capacity of water to dissolve salts, mineral substances, gases and also organic compounds must therefore be taken into account and a distinction drawn between genuine solutions and those in which the solute is present in the colloidal state (disperse phase) and thus removable by appropriate filtration.

As a rule, the salts of the alkalis, i.e. of sodium and potassium, are much more readily soluble than the salts of the alkaline earth metals such as magnesium, calcium, strontium or even barium.

The solubility of salts also depends on the anion; thus the chlorides, bromides, iodides and nitrates of sodium, potassium, magnesium and calcium compounds are as a rule easily soluble. The fluorides of sodium and potassium are already slightly less soluble in water, whereas the fluorides of the alkaline earth metals, i.e. calcium fluoride, are relatively insoluble.

As regards the sulphates, a difference in solubility also exists between the alkaline sulphates (Na_2SO_4 and also ammonium sulphate, which are highly soluble), and the alkaline earth sulphates such as magnesium sulphate MgSO_4 and calcium sulphate CaSO_4 , which are considerably less soluble. Magnesium and calcium sulphates in water, if the concentration exceeds a few 100 mg/l, lead to the water having a laxative effect, whilst the highly soluble sodium and potassium sulphates merely tend to make the water taste bitter.

The carbonic acid compounds of the alkaline earth metals (magnesium, calcium, strontium, barium) can only remain in solution in water if a certain excess of dissolved carbon dioxide is also present (lime/carbon dioxide balance).

If this carbon dioxide content is not sufficient, dissolved calcium compounds are precipitated from the water and form stubborn encrustations on tank floors, filters and pipes.

Of particular importance for the solubility of the alkaline earth compounds (e.g. salts of magnesium, calcium, strontium and barium) is the so-called lime/carbon dioxide balance.

It must be assumed that a certain amount of free carbon dioxide must be present in the water for the alkaline earth salts to remain in solution, e.g. as hydrogen carbonates.

If this equilibrium is disturbed, e.g. by an increase of temperature, to the extent that gaseous carbon dioxide can escape, the deposits mentioned above, e.g. of calcium carbonate, can form. This lime/carbon dioxide balance is therefore of intrinsic importance in water chemistry as a whole.

In the absence of oxygen, iron is present in water in the form of dissolved iron(II) ion (Fe^{2+}). On the addition of oxygen this dissolved iron oxidizes very easily to form the trivalent form of iron which is relatively or even completely insoluble in water, e.g. iron(III) hydroxide.

Manganese behaves in a similar way, whereby it is transformed into the form which is insoluble in water, but only after the addition of atmospheric oxygen and at a pH clearly showing alkalinity, e.g. higher than 8.

The outstanding capacity of water to dissolve salts or minerals, gases and also organic compounds is not only of fundamental importance for the use of water by living creatures, but also in technology. The importance of the various groups of substances in biological and technical terms is discussed below.

3.1.1 Inorganic substances in water

Most easily soluble in water are the simple salts, such as sodium chloride (NaCl , common salt) or sodium sulphate (Na_2SO_4), sodium nitrate (NaNO_3) or the sodium salts of

carbonic acid, sodium hydrogen carbonate (NaHCO_3) and sodium carbonate (NaCO_3 , soda).

Equally soluble in water, but generally speaking of less importance in water chemistry, are the analogous salts of lithium, potassium, ammonium, or of the trace elements rubidium and caesium.

Even some of the otherwise relatively insoluble salts of the alkaline earth metals, such as magnesium, calcium, strontium and barium, are also readily soluble in water, such as the chlorides or nitrates of these elements. Much less soluble is, for instance, already calcium sulphate (gypsum); and limestone (CaCO_3 , calcium carbonate) can only be transformed into water-soluble calcium hydrogen carbonate (CaHCO_3) by the presence of carbon dioxide. The solubilities of some inorganic salts in water with a temperature of 20°C are given as examples below.

Salt or salt-like compounds	Approx. solubility in g/l of water
-----------------------------	------------------------------------

Inorganic compounds:

a) Chlorides:

Sodium chloride (NaCl , common salt)	359
Potassium chloride (KCl)	315
Magnesium chloride ($\text{MgCl}_2 \times 6\text{H}_2\text{O}$)	543
Calcium chloride ($\text{CaCl}_2 \times 6 \text{H}_2\text{O}$)	745
Ferric chloride ($\text{FeCl}_3 \times 6\text{H}_2\text{O}$)	919
Manganese chloride ($\text{MnCl}_2 \times 4\text{H}_2\text{O}$)	735

b) Nitrates:

Ammonium nitrate (NH_4NO_3 , ammonium saltpetre)	1,877
Sodium nitrate (NaNO_3 , chile saltpetre)	880
Potassium nitrate (KNO_3 , potassium saltpetre)	315

c) Sulphates:

Sodium sulphate ($\text{Na}_2\text{SO}_4 \times 10\text{H}_2\text{O}$)	191
Calcium sulphate ($\text{CaSO}_4 \times 2 \text{H}_2\text{O}$, gypsum)	2.0
Ferrous sulphate ($\text{FeSO}_4 \times 7\text{H}_2\text{O}$)	266

d) Carbonates:

Sodium carbonate (Na_2CO_3 , soda)	216
Magnesium carbonate (magnesite, MgCO_3)	0.11
Calcium carbonate (CaCO_3 , limestone)	0.014

e) Minerals:

Silica (SiO_2)	0.12
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It can be seen that the ammonium, sodium and potassium salts are generally speaking very soluble, often resulting in high concentrations of these salts in water. In this context it should be pointed out that water already tastes salty if only about 1 g of NaCl per litre is dissolved in it, and that sea water, which is not suitable for human consumption, contains on average approx. 35 g/l.

The table also shows that compounds of magnesium and calcium, especially the carbonates, are rather sparingly soluble in water. Their solubility is increased, however by the presence of dissolved carbon dioxide (CO_2), so that it may well happen that a water contains several 100 mg/l, or more than 1,000 mg/l of dissolved calcium compounds. Water with a higher concentration of calcium is known as "hard" water. Water in which sodium compounds are dissolved, on the other hand, will be regarded as salty.

Besides the salts and similar minerals listed above, other substances can be dissolved in water, e.g. out of silicates or ores. Generally speaking, the silicates or ores in the earth do not dissolve at all readily. However, besides silica, other substances can be dissolved out of these minerals: iron, manganese, aluminium, titanium, copper, zinc, but also the toxic elements arsenic, lead, cadmium and mercury.

The concentration of these minerals or heavy metals in an exploitable water resource should be well below 0.1 mg/l. Anions can also be dissolved into the water: e.g. fluorides or phosphates (cf. heading 4).

As rule of thumb, in judging the chemical composition of a water, especially where water is scarce, it can be assumed that potentially harmful concentrations of inorganic compounds and minerals dissolved in the water nearly always become noticeable through a change in the water's taste. Thus water containing too much salt will have a salty, bitter or alkaline taste, water containing too much copper, zinc, iron, manganese or aluminium will have a metallic, astringent taste. As a general rule, the human or animal organism will not accept water of this quality as drinking water. Other substances in water, however, such as nitrates or fluorides, have little effect on its taste.

Thus it can be assumed that if a water does not seem abnormal in any way - i.e. due to conditions observed at its source, or because of turbidity, colour, smell or taste - it can, as a general rule, be used in emergencies and after boiling as drinking water.

3.1.2 Gases dissolved in water

Carbon dioxide (CO_2), oxygen (O_2), nitrogen (N_2) and hydrogen sulphide (H_2S), also occasionally methane (marsh gas, CH_4) are the gases which are frequently - or, in the case of hydrogen sulphide and methane, occasionally - found in water. Carbon dioxide is readily soluble in water, as was already pointed out under heading 3.1.1. The dissolved carbon dioxide in the water is responsible for its capacity to dissolve minerals in the ground. This capacity increases as a function of the amount of carbon dioxide in the water. Carbon dioxide also plays a major part in determining the aggressivity of a water towards building materials and water pipes, however. A water should exhibit "lime/carbon dioxide equilibrium" (cf. 3.1.1 and 4).

This means that the amount of carbon dioxide should be in optimum ratio to the dissolved minerals, both to preclude precipitations and also to limit the aggressivity of the water. The solubility of carbon dioxide (CO_2) in water at a temperature of 10°C is roughly 2,300 mg/l and at 20°C about 1,700 mg/l.

Oxygen and nitrogen are generally brought into the water by air, although nitrogen may be found in deep water without the presence of oxygen. The solubility of the nitrogen from the air in water is about 17 mg/l at 10°C and about 14 mg/l at 20°C , whilst the solubility of atmospheric oxygen is roughly 11 mg/l at 10°C and roughly 9 mg/l at 20°C .

The solubility of gases in water depends on pressure and temperature, whereby the specific partial pressure of the gas in contact with the water is of special importance.

Hydrogen sulphide dissolved in water may be in the form of a physically dissolved gas, but also of an ion such as hydrogen sulphide (HS^-) or sulphide (S^{2-}). The presence of hydrogen sulphide, even in very small concentrations (e.g. already from 0.05 mg/l) is detectable by its extremely unpleasant smell ("rotten eggs"). This makes the water virtually undrinkable, so that it very seldom happens that anyone is poisoned by drinking water containing hydrogen sulphide. Hydrogen sulphide results from the decomposition of organic matter, but is also a reduction product from sulphate ions, formed in water by micro-organisms, e.g. desulfovibrions, under anaerobic conditions (i.e. without oxygen).

Methane may also be found dissolved in water, i.e. where processes of decay take place, e.g. in an effluent (waste water) or a river containing large amounts of decaying matter, but also very often in stagnant waters where at the deeper levels other processes of decay take place besides the formation of hydrogen sulphide, producing the inflammable gas methane. As a general rule, however, the presence of methane

in a water is also easy to detect from the accompanying phenomena of the decaying process, although the only simple method of determining methane itself is by its inflammability.

The other gases dissolved in water are generally found only in traces, such as the inert gas argon, which is present in the air (approx. 1%), or the trace gases hydrogen (in reduction processes) or gaseous hydrocarbons (e.g. in deep waters in areas where there is natural gas or oil, but also in contaminated surface waters).

3.1.3 Organic compounds

As was already pointed out in section 3.1, water has a pronounced capacity to dissolve certain organic compounds such as alcohols or sugars, but also a certain ability to dissolve typical organic pollutants such as human and animal excreta, industrial pollutants such as fuels, lubricants, chlorinated and non-chlorinated organic solvents, polychlorinated compounds, pesticides such as insecticides, fungicides, herbicides etc., also polycyclic aromatic hydrocarbons and similar compounds.

Some organic compounds dissolve readily in water; most, however, are relatively insoluble. Yet even the slightest traces of organic compounds in a water can make it unfit for human or animal consumption or unable to support plant life. Some organic pollutants can be detected by their smell, e.g. fuels and lubricants (petrol, oil), organic solvents, chlorinated compounds, phenols etc. Others, and also a number of toxic pesticides, or the carcinogenic polycyclic aromatic hydrocarbons, are hardly detectable by the human sense organs. In such cases, other methods of testing the water must be used. Possibilities are, for instance, a determination of the oxidizability of a water, e.g. with a solution of potassium permanganate or potassium dichromate; or a determination of the total of dissolved

organic carbon, or, as a simple method, a measurement of the ultraviolet absorption of a water. Since a number of organic compounds can be driven out of water by boiling, it is always a wise precaution to boil water for a relatively long period, e.g. for more than 5 minutes, if there is any suspicion of pollution. Without a certain amount of analytical equipment, however, organic compounds dissolved in water are very difficult to detect, especially in the case of toxic substances, very small amounts of which can already do considerable harm to humans, animals and plants.

4 Effects of dissolved substances in water

Water analyses may be more or less comprehensive and can be differentiated according to their aims or to the various techniques employed. One possible method of categorization is given below:

a) 1 Simple analysis:

Temperature of the water, pH, conductivity, oxygen content, carbon dioxide content, hardness (sum of the magnesium and calcium compounds, calculated as calcium carbonate).

Nitrogen compounds: ammonium, nitrite, nitrate.

Heavy metals: iron and manganese.

Chloride, sulphate, hydrogen phosphate, hydrogen carbonate.

a) 2 Extended analysis:

In addition to a) 1: redox potential, sodium, potassium, fluoride, oxidizability as non-specific indicator for the presence of dissolved organic substances through potassium permanganate or potassium dichromate consumption or through UV-absorption of the water.

a) 3 Comprehensive analysis:

In addition to a)1 and a)2: solid residue after evaporation, analysis of residue for presence of heavy metals, e.g. by means of qualitative spectral or X-ray fluorescence analysis; or direct testing for heavy metals, especially toxic heavy

metals such as copper, zinc, cadmium, arsenic, lead and mercury. Possibly testing for aluminium and titanium, also, in the case of the anions, for bromide and iodide. Determination of silica content and analysis of the influence of carbon dioxide as hydrogen carbonate ion, carbonate ion, free dissolved carbon dioxide, lime/carbon dioxide balance, pH before and after calcium carbonate saturation etc.; organic substances wherever determination of the total parameters indicated by the oxidizability gives excessively high figures, e.g. more than a few mg/l; attempts to identify the individual substances.

Where there is reason for suspecting their presence, testing for polycyclic aromatic hydrocarbons, chlorinated or halogenated hydrocarbons, pesticides, phenols etc. as possible pollutants.

a) 4 analyses to determine the aggressivity of water towards building materials, metals etc.:

As a rule, these cover measurement of: pH, acid or base consumption up to pH 4.2 or 8.2 respectively, redox potential, conductivity, oxygen content, free carbon dioxide, hydrogen carbonate or carbonate, chloride, sulphate.

b) Microbiological analysis

b) 1 Plain microbiological analysis:

Determination of the total colony count on suitable culture media at 22°C and 37°C from 1 ml each; testing for the presence of coliform bacteria.

b) 2 Extended microbiological analysis:

Determination of the general colony counts at 22°C and 37°C also of the coliform bacteria, *Escherichia coli*, faecal streptococci and *Pseudomonas aeruginosa* from 250 ml each and of the sulphite-reducing sporegenous anaerobes from 50 ml of water.

4.1 Technical importance of the dissolved substances in water

The pH, i.e. the acidity or alkalinity of a water, is an extremely important physico-chemical parameter, giving an immediate indication of the probable aggressivity of the water and possibly also of the necessity of carrying out de-acidification before its technical use.

The redox potential, which is simple to measure, can already give an idea of the concentration of reducing substances in the water, or of the presence of oxidizing agents etc.

The conductivity of the water is a measure of the dissolved salts, a factor of considerable importance for an industrial use of the water. A major part is played here by the so-called alkali salts such as sodium and potassium compounds, which often contribute considerably to the aggressivity of a water e.g. towards metals, but also by magnesium and calcium ions, which together with the lime/carbon dioxide balance may be the cause of encrustations in water systems. The figures established here must be considered in the context of the carbon dioxide concentration. Iron and manganese compounds which may be present in the water in solution or suspension can also make treatment of the water - e.g. filtration - before its technical use necessary.

High chloride or sulphate concentrations, e.g. values above 250 mg/l, may indicate increased aggressivity or corrosiveness of the water.

For an industrial use, the concentration of dissolved organic substances, e.g. indicated by the oxidizability with potassium permanganate or potassium dichromate, is just as important as the presence of micro-organisms. If there is adequate nutritive substance available in the water, micro-organisms in both anaerobic (oxygen-free) and aerobic (with oxygen present) conditions can cause considerable technical problems due to blockages, slime formation or unwanted products of the metabolic process, e.g. hydrogen sulphide.

4.2. The importance of dissolved substances in water for human beings, animals and plants

Water used by men and animals for drinking should be cool, clear and colourless, without smell or taste, and should not contain harmful substances.

Micro-organisms which are potentially harmful to men or animals should not be present in the water in dangerous concentrations, whereby the level at which the concentration becomes dangerous varies according to the type of micro-organism.

The salt content and the concentration of dissolved minerals should not be high enough to make the water unpalatable. This means a maximum concentration of dissolved salts and minerals of about 5 g/l.

Substances which are directly harmful to humans and animals may only be present in a water up to certain levels of concentration: for instance, toxic heavy metals only up to 1 mg/l, fluoride up to a few mg/l. Organic substances, which may cause an unpleasant smell or taste, and can indicate microbiological contamination, should be found, on determining the carbon content, to be below a few mg/l. The microbiological quality of a water used for drinking should be investigated with especial care, whereby the adaption of users to the types of micro-organisms and their concentration in a potable water should be taken into account.

As a general rule, less stringent criteria need be laid down for water which is drunk by animals. Animals usually instinctively avoid water which could be harmful.

The situation is different as regards water used for irrigation. Here, a certain maximum concentration, e.g. of at most a few g of dissolved salts per litre, should not be exceeded, to prevent excessive salt concentrations in the soil and consequent damage to the plants. There are certain general rules by which the risk of excessive salt

concentration, and thus the potential harm to plant life, can be recognized.

Also potentially harmful to plants are boron compounds, if these are present in the water in concentration of more than 1 mg/l, calculated as boron.

Dissolved nitrogen compounds such as ammonium, nitrite and nitrate ions, and equally phosphate or hydrogen phosphate ions, are needed and absorbed by plants as food; whilst other substances which enter the soil via fertilizers or sludge from sewage farms may be harmful, e.g. certain heavy metals. Harmful concentrations of these substances in the soil are, however, very seldom attributable to contaminated water.

In the Federal Republic of Germany, for instance, a special regulation on the use of sewage sludge in agriculture which came into force on April 1st 1982 laid down the following limits (referring to dry substance):

Lead	1200 mg/kg
Cadmium	20 mg/kg
Chromium	1200 mg/kg
Copper	1200 mg/kg
Nickel	200 mg/kg
Mercury	25 mg/kg
Zinc	3000 mg/kg

Water should not, of course, contain other substances harmful to plant life - e.g. herbicides or chlorinated organic compounds, etc. - in any significant concentration. This seldom occurs, however, even in industrial areas. Even normal effluent or the water seeping from refuse tips can still, as a rule, be used without harmful effects for irrigation.

In conclusion, it can be said that it is the microbiological properties of a water which are of paramount importance, especially if the water is intended for human or animal consumption. General bacteriological analyses should be

carried out to determine the microbiological properties of the water. The results of these analyses can then indicate whether the water seems fit for human or animal consumption, or if it would be safer to boil it before use.

Generally speaking, the microbiological composition has no particular significance in connection with use of the water for irrigation.

5 Quality of drinking water

Water which is to be used for drinking must be palatable; it should reach the consumer in a cool, clear and colourless condition and exhibit no harmful chemical or precarious biological properties.

These requirements are laid down in the drinking water regulations of most countries, but also in the relevant guidelines of the World Health Organization and the European Community.

Conditions in some countries may, however, make it necessary to use water which does not reach these standards, there being no other alternative if life is to be sustained.

For this reason, the existing guidelines and regulations on the standard of drinking water laid down in countries with the means to treat their drinking water supplies accordingly must be adapted, with due thought and understanding of the situation, to conditions in countries with water shortage, where there is currently no alternative to accepting lower standards.

5.1 Optimum water quality

The optimum quality of potable water for human beings and animals can be found in the relevant WHO guidelines and especially in the most recent version of the EC directives on drinking water. It will not always be possible in all countries, however, to guarantee such an optimum quality

of the water supply, so that in emergency situations or times of scarcity a poorer quality will have to be accepted. Anybody who has lived or worked outside the industrialized countries - which are in a position to provide drinking water of optimum quality - can confirm this from personal experience. In times of water shortage, the final decision on where to draw the line between acceptable and unacceptable water must rest with the individual.

Drinking water of optimum quality can be defined as clear and colourless, with a temperature between 10 and 20°C, without chemical, inorganic or organic pollutants and of a microbiological composition which makes it fit for human consumption without preliminary boiling.

5.2 Average drinking water quality

Lower or higher water temperatures, occasional turbidity or foreign taste can be tolerated. The microbiological quality of the water should always, however, be such that there is no risk of the water transmitting infectious diseases. This means the absence of pathogenic micro-organisms in the water - whereby these are generally themselves scarcely detectable.

The aim should therefore be, as an average microbiological standard, that coliform bacteria and *Escherichia coli* are not detectable in 100 ml.

5.3 Drinking water in emergency situations

As long as people and animals are still prepared to accept the smell and taste of a water, it can be assumed to be drinkable as far as its chemical composition, i.e. its content of dissolved substances, is concerned. If the water is turbid, it should be filtered through some suitable medium, e.g. a cloth or a filtration bed of sand or vegetable matter. The risk of infection from micro-organisms in the water can generally be adequately precluded in emergency situations by boiling the water. If this is not possible, as little

water should be consumed as possible, since the risk of infection from micro-organisms in the water also depends on their concentration.

In emergency situations, it is the human organism and the will to survive which will finally decide whether to use or to reject whatever water is available.



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- 0.3 Basic concepts of water chemistry
- 0.4 Basic principles of water transport
- 1.1 The function and technical composition of a watersupply system
- 1.2 Organisation and administration of waterworks

Special Knowledge

- 2.1 Engineering, building and auxiliary materials
- 2.2 Hygienic standards of drinking water
- 2.3a Maintenance and repair of diesel engines and petrol engines
- 2.3b Maintenance and repair of electric motors
- 2.3c Maintenance and repair of simple driven systems
- 2.3d Design, functioning, operation, maintenance and repair of power transmission mechanisms
- 2.3e Maintenance and repair of pumps
- 2.3f Maintenance and repair of blowers and compressors
- 2.3g Design, functioning, operation, maintenance and repair of pipe fittings
- 2.3h Design, functioning, operation, maintenance and repair of hoisting gear
- 2.3i Maintenance and repair of electrical motor controls and protective equipment
- 2.4 Process control and instrumentation
- 2.5 Principal components of water-treatment systems (definition and description)
- 2.6 Pipe laying procedures and testing of water mains
- 2.7 General operation of water main systems
- 2.8 Construction of water supply units
- 2.9 Maintenance of water supply units Principles and general procedures
- 2.10 Industrial safety and accident prevention
- 2.11 Simple surveying and technical drawing

Special Skills

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- 3.2 Performance of simple water analysis
- 3.3a Design and working principles of diesel engines and petrol engines
- 3.3b Design and working principles of electric motors
- 3.3c —
- 3.3d Design and working principle of power transmission mechanisms
- 3.3e Installation, operation, maintenance and repair of pumps
- 3.3f Handling, maintenance and repair of blowers and compressors
- 3.3g Handling, maintenance and repair of pipe fittings
- 3.3h Handling, maintenance and repair of hoisting gear
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- 3.4 Servicing and maintaining process controls and instrumentation
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