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The Framework of Water Analysis

1.1 INTRODUCTION

Water represents one of the basic elements supporting life and the natural environment, a primary component for industry, a consumer item for humans and animals, and a vector for domestic and industrial pollution. Various European Directives already provide a framework for the control of aquatic substances, the quality of bathing, surface and drinking waters, and effluent control. Such regulatory measures are closely related to 'classical' analytical measurements (involving sample collection and laboratory analysis). Other approaches are, however, followed to comply with these regulations on a permanent basis, which are based on the use of automated measuring techniques (e.g. sensors) to obtain suitable warning alarm systems and facilitate the management of water resources and decision-making process (Colin and Quevauviller, 1998), often using telemetry to allow remote control of water management systems.

The analysis of water media reveals the presence of gases, suspended or dissolved mineral and organic matter and micro-organisms. Many water components occur naturally, originating from, e.g. rocks, soils and air, or from human and animal sources. To these components, anthropogenic substances will be added by human forces, these merely being due to urban, industrial and agricultural activities. Treatment techniques of urban or industrial waste-water will also lead to the formation and subsequent release of contaminants in processed waters (e.g. bromate due to ozonation, various other disinfection by-products, etc.). The quality and amount of the various (natural and/or anthropogenic) constituents actually form the basis for the definition of the quality of water, upon which the adequacy for various uses will be decided (e.g. human and domestic animal consumption, domestic or industrial use, irrigation, etc.). In this view, the quality of analytical data is of paramount importance since it will form the basis of decisions regarding the management of water environments.

The range of water matrices, parameters and measuring techniques is extremely broad. This present chapter aims to give a (not exhaustive) view of the purpose of water analysis in various sectors (research, routine laboratories, etc.), the different types of waters, and the parameters currently being monitored.

1.2 PURPOSE OF ANALYSIS

1.2.1 Support of regulations

EC regulations

The European Community actively participates in the preparation of international conventions on the environment, including the monitoring of water quality, and in the implementation of those conventions. European Union (EU) Member States are free to adopt national legislation in the absence of Community legislation, but where the Community has acted, Community legislation is supreme and binding on both past and future Member State actions. The European Community can adopt (i) non-binding recommendations and resolutions, (ii) regulations that are binding and directly applicable in all Member States, (iii) decisions that are directly binding on the persons to whom they are addressed, including Member States, and (iv) directives which must be implemented by the laws or regulations of the Member States. A series of principles and priorities regarding environmental protection have been set out within the first five-year environmental action programme (1973–1977) adopted by the European Community. These principles are summarized below and have remained valid in subsequent action programmes:

1. Prevention is better than cure.

2. Environmental impacts should be taken into account at the earliest possible stage in decision-making.

3. Exploitation of nature which causes significant damage to the ecological balance must be avoided.

4. Scientific knowledge should be improved to enable actions to be taken.

5. The cost of preventing and repairing environmental damage should be borne by the polluter.

6. Activities in one Member State should not cause deterioration of the environment in another.

7. Environmental policy in the Member States must take into account the interests of the developing countries.

8. The EC and Member States of the European Union should promote international and world-wide environmental protection through international organizations.

9. Environmental protection is everyone's responsibility, and therefore education is necessary.

10. Environmental protection measures should be made at the most 'appropriate level', taking into account the type of pollution, the action needed, and the geographical zone to be protected. This is known as the 'subsidiarity principle'.

11. National environmental programmes should be co-ordinated on the basis of a common long-term concept and national policies should be harmonized within the Community, not in isolation.

A historical perspective of EC regulations related to waters is given below (this list is not exhaustive):

1975 Directive on the quality of bathing water, 8 March 1975 (EC Official Journal of 9 June).
Directive on the quality of surface water for human consumption, 16 June 1975, modified by the Directive 79/869/EEC of 9 October 1979.

1976 Council Directive 76/464/EEC on the pollution caused by dangerous substances discharged in aquatic media of the Community.

1979 Directive on measurement methods and frequency of sampling and analysis of surface water for human consumption, 9 October 1979.
Council Directive 79/923/EEC on shellfish waters.

1980 Council Directive 80/778/EEC relating to the quality of water intended for human consumption.

1982 Council Directive 82/176/EEC on mercury discharge.

1983 Council Directive 83/513 on cadmium (threshold values and quality objectives for wastes).

1984 Council Directive 84/491/EEC on lindane (HCH) (threshold values and quality objectives for wastes).

1985 Council decision 85/613/EEC on mercury and cadmium discharge.

1986 Council Directive 86/280/EEC on threshold values and quality objectives for the discharge of certain dangerous substances.

1988 Council Directive 88/347/EEC on threshold values and quality objectives for the discharge of certain dangerous substances, list I of the Directive 76/464/EEC; modification of Annex II of Directive 86/280.

1991 Council Directive 91/271/EEC on the treatment of residual urban waters.
Council Directive 91/676/EEC on the pollution of waters by nitrates from agricultural sources.
Council Directive 91/692/EEC on the standardization of reports requested by Directives related to the environment.

Other examples of EC regulations involving water quality monitoring are given below.

The Council Decision 75/437/EEC on Marine Pollution from Land-based Sources approves on behalf of the Community the 'Paris Convention' which aims at preventing pollution of the north-east Atlantic and Arctic Oceans, the North and Baltic Seas and part of the Mediterranean Sea from land-based sources. Three categories of polluting substances are listed in the Annexes, namely a first group of substances (Annex A, Part I) which should be eliminated, includes persistent chemical groups such as, e.g. organohalogen compounds, mercury, cadmium and persistent hydrocarbon compounds, while a second group of substances (Annex A, Part II) of which the pollution should be limited, includes less persistent organic compounds and certain heavy metals. The chemical forms of elements appear in this Part II and concern, in particular, organic compounds of phosphorus, silicon, and tin, plus substances which may form such compounds in the marine environment, excluding those which are biologically harmless, or which are rapidly converted in the sea into substances which are biologically harmless, and the following elements and their compounds–arsenic, chromium, copper, lead, nickel and zinc.

The Council Decision 77/585/EEC on the Mediterranean Sea concludes on behalf of the Community the 'Barcelona Convention' for the protection of the Mediterranean Sea against pollution, and the Protocol for the prevention of pollution of this area by dumping from ships and aircraft. The dumping of wastes or matter listed in Annex I is prohibited–this includes organohalogen and organosilicon compounds, organophosphorus compounds, organotin compounds, mercury and cadmium and their compounds, persistent synthetic materials, crude oil and hydrocarbons. This Decision has been supplemented by a series of three other Decisions, namely 81/420/EEC, 83/101/EEC and 84/132/EEC, in which additional substances, 'the dumping of which requiring special care', are found in Annex II, namely arsenic, lead, copper, zinc, beryllium, chromium, nickel, vanadium, selenium, antimony and their compounds.

The Council Decision 77/586/EEC on the Rhine River concludes on behalf of the Community the 'Berne Convention' for the protection of the Rhine against chemical pollution, implying that discharges of a range of toxic substances should be gradually eliminated (Annex I)–these include organohalogen, organophosphorus and organotin compounds, carcinogens, mercury and cadmium compounds, plus persistent mineral oils and hydrocarbons. Annex II of this Decision lists other dangerous substances for which pollution should be reduced, namely a range of 20 metalloids and metal compounds, biocides and their derivatives not appearing in Annex I.

The Council Directive 80/68/EEC on groundwater pollution caused by certain dangerous substances also aims at preventing or limiting the direct or indirect introduction to the groundwater of families or groups of dangerous substances. List I substances includes organohalogen, organophosphorus and organotin compounds, carcinogenic, mutagenic or teratogenic substances, mercury and cadmium compounds, mineral oils and hydrocarbons, and cyanides. List II substances (for which general investigation and authorization procedures are requested prior to direct discharges, disposal or tipping) include 20 metalloids and metal compounds, biocides and their derivatives not appearing in List I.

Other regulations

This present book does not aim to give an exhaustive list of regulations related to water, which would require several volumes. Let us simply stress that many organizations are concerned with the quality of water and issue international or national regulations, e.g. the World Health Organization (WHO, 1993) and the US Environmental Protection Agency (Pontius, 1997), which, similarly to EC Directives, establish Maximum Concentration Levels on physical, chemical, organoleptic and microbial parameters, or recommend Guidelines values. The UK has introduced some very stringent *Cryptosporidium* regulations (UK Statutory Instrument 1999, No. 1524) where a comprehensive chain of evidence is required from the initial taking of the specified 24-hour sample through an approved filter to eventually reporting the final result. All 'at-risk' water treatment works final waters have to have daily 24-hour samples taken and analyzed in this way (365 samples per annum).

1.2.2 Wide-scale monitoring programmes

Member States of the European Union have monitoring networks in place to assess inland water quality (Lack and Nixon, 2000), essentially to determine the state and trends in the physico-chemical and biological quality of rivers, lakes and groundwaters according to their national or international/European requirements. Information provided by countries to the European Environment Agency (EEA) is primarily for assessing implementation of and compliance with directives rather than for assessing the status of and temporal changes in water resources. Network activities exist to evaluate and ensure the reliability and comparability of data, thus enabling the further development or modification of European environmental policy, e.g. the European monitoring and observation network for inland waters–EUROWATERNET–which is based almost entirely on existing national monitoring networks (Lack and Nixon, 2000).

Other wide-scale monitoring programmes focus on coastal and open seawaters (Wells and Cofino, 1995), e.g. the North Sea Monitoring Programme which is performed under the auspices of the Oslo and Paris Commission (OSPARCOM), the Baltic Monitoring Programme of the Helsinki Commission (HELCOM) and the Barcelona Convention in the Mediterranean. European marine monitoring programmes are a multinational undertaking, and those countries which contribute to these programmes formulate a joint policy and agree on those measures necessary for the protection of the marine environment.

Chemical and biological data produced in the framework of monitoring programmes form the core of the decision-making process with respect to the water quality status. These data, along with associated information, e.g. on sample location and conditions of sampling, must have a high and well-defined level of reliability if the interpretation and subsequent regulations are to have a sound basis (Wells and Cofino, 1995). Hence, the quality of these data has a direct influence on the formulation of environmental policy. It also has a significant economic impact. Any chemical analysis undertaken to provide specific environmental information has a finite cost, e.g. detection of a trend, say a 10% decline over 10 years, may not be possible in economic terms unless the quality of the data is very high. The cost of this information is directly related to the accuracy of the measurements. Knowledge of any bias is essential. An imprecise measurement will require a significantly greater number and frequency of samples to detect a given change with a specified confidence limit. For many measurements, the savings can be very substantial. Data that do not conform to the standard required will ultimately mean that all of the resources invested are wasted (Wells and Cofino, 1995). There is also a diplomatic benefit in that improved quality will result in greater trust in the data generated in different countries.

1.2.3 Research

In a similar way to the above section on regulations, a further objective of this book is not to establish a comprehensive list of research needs in the sector of water analysis. At this present stage, let us only briefly mention some of the most obvious research needs that are generally tackled by the relevant laboratories.

Research needs are mainly focused on the determination of harmful substances which present environmental risks. Activities are mostly turned toward the better understanding of contaminant interactions between water media and living media (human and biota). The research activities are hence of a multidisciplinary nature, involving disciplines such as, e.g. ecotoxicology, geochemistry, microbiology, biology, analytical chemistry, etc. Besides the development of ecotoxicity tests, efforts are made to ensure a sound quality framework for measurements carried out with existing techniques and to develop more powerful multi-substance methods. Research in this area concerns the development of, e.g. sophisticated reference materials and new analytical techniques.

A wide array of research activities is also related to water quality management (Benoliel, 1998). Indeed, daily drinking water distribution system management involves identifying changes in water quality at the customer's tap–this may be associated either with the raw water, the treatment plant or the distribution network. In fact, water passing through the distribution system is subject to a number of processes that may affect its chemical and microbial composition (e.g. degradation and leaching reactions, precipitation, corrosion, disinfection by-product formation, formation and effect of biofilms, etc.). These research areas are more focused on consumer safety and needs. They cover, e.g. the development of rapid screening techniques to detect chemical and microbial contamination (sensor-type methods), on-line analyzers, rapid ecotoxicity tests, etc.

1.3 TYPES OF WATERS CURRENTLY ANALYZED

Various types of waters are analyzed for the purpose of environment monitoring and for controlling the quality of water for human consumption and use. As indicated above, numerous regulations have been implemented within the last 25 years. The main types of waters currently analyzed in the framework of monitoring programmes or for research purposes are as follows:

- Surface waters originating from, e.g. lakes, estuaries or seas, the purpose of which is merely for environmental monitoring and research
- Groundwaters for environmental monitoring and control of water for human consumption
- Drinking waters for quality assurance

- Waste-waters, before and after treatment, to control the efficiency of treatment and the possibilities of reuse, e.g. for irrigation
- Rain-waters for the monitoring of atmospheric contamination, e.g. acid rains

1.4 CHEMICAL PARAMETERS

The environmental parameters present for all types of water are numerous and cannot be summarized in just a few pages. The information given in this section aims to recall the main parameters that are frequently analyzed in the framework of monitoring programmes or for the purpose of research activities. Most of the information given here is adapted from Rodier *et al.* (1998).

1.4.1 Physico-chemical parameters

The main physico-chemical parameters that are analyzed for water are the pH (hydrogen ion concentration of a water medium), the redox potential, the conductivity, the hardness (calculated from the calcium and magnesium concentrations), the colour and turbidity, the alkalinity or acidity, etc. Other parameters are defined operationally, e.g. the biological oxygen demand (BOD) or the chemical oxygen demand (COD). The dissolved oxygen is also frequently analyzed, along with the temperature and salinity of the medium being employed (as these have an effect on oxygen solubility).

The amount of suspended and colloidal matter (turbidity) is an important parameter. The mineral and organic composition is very variable according to the characteristics of the water source (sandy, clayey, high-organic-particle loading, presence of plankton, etc.), and in relation to the nature of the ground, seasonal factors, rainfalls, wastes, etc. Suspended matter (in particular clays and organic particles) have a large adsorption surface and constitute an ideal support for ions, various molecules and micro-organisms. In this view, the analysis of suspensions provides useful information on the mobility of hydrophobic pollutants in aquatic environments.

1.4.2 Inorganic parameters

In practice, laboratories responsible for environment monitoring determine the target elements included in various regulations. Tables 1.1 (trace elements) and 1.2 (major elements) give an overview of the elements frequently determined by routine and research laboratories, as well as giving some background information on their origin and use. Most of these elements are regulated by WHO (establishing threshold values in relation to their toxicity) and EC Council Directives.

Other types of elements are less frequently determined by routine laboratories but are nevertheless considered in the framework of research programmes, e.g.

Table 1.1 Trace elements frequently encountered in water analysis

Element	Symbol	Comments
Antimony	Sb	Metalloid (principal ore, stibnite (Sb_2S_3)) used in association with lead and tin to increase their hardness, and in the form of salts as catalysts for rubber vulcanization. Moderate toxicity
Arsenic	As	Largely present in the biosphere, principally in the form of As_2S_2 our As_2S_3. The main derivatives are As_2O_3 and As_2O_5, and mineral salts. This element is used in metallurgy (alloys), electronics (semiconductors), the tanning industry (as sulphides), paint formulations, glass coloration, etc.[a]
Barium	Ba	Element found in nature in the form of sulphates (barite, hepatite, spath, etc.) or carbonates (witherite). Widely used in industry, e.g. photography, ceramics, glass, paints, rubbers, etc.
Boron	B	Metalloid extracted from borax and rosorite ores. It does not exist in its elementary state in nature, but in the form of boric acid (used as an antiseptic), borates (used in the glass and ceramic industries, and in the formulation of cosmetics, paints and phytosanitary products), and boron hydrides (used for rocket propulsion and as accelerating agents for polymerization in the perfume and pharmaceutical industries). It is frequently found in urban and industrial waste-waters
Bromine	Br	Present in the lithosphere at a level of 0.001%. In water, this element is in the form of the bromide (natural state or linked to pollution, e.g. chloride or sodium hydroxide preparations), organobromine derivatives and bromates (issued from waste-water ozonation processes), with these last forms being carcinogenic
Cadmium	Cd	This element is used in the polymer and nuclear industries and in galvanoplasty. It may be solubilized from varnished pottery, metal cans or galvanized tools. It is also present in fertilizers, and sewage sludges from water treatment plants. This metal is associated with a toxic syndrome known as 'Itai Itai' (bone decalcification) which first appeared in Japan
Chromium	Cr	Metal used in industry (generally as dichromates), e.g. for electrolytic chromium plating, and in leather and skin tanning. Chromium salts are widely used as colouring agents. Some chromium compounds are sometimes added to industrial cooling waters as anticorrosion agents. Owing to its low natural concentration, the occurrence of this element in environmental waters is mainly of anthropogenic origin[a]
Cobalt	Co	Element present in low concentration in nature. Used in the metallurgy of special steels. Cobalt salts are also employed as coloured pigments (paints, ceramics, etc.) and as catalysts. This element may be found in the divalent or trivalent state in the environment
Copper	Cu	Element present in nature in the form of native copper ores, oxides or sulphides. Constituent of alloys such as, e.g. brass

(*continued overleaf*)

Table 1.1 *(continued)*

Element	Symbol	Comments
		(copper and zinc) and bronze (copper and tin), being largely employed owing to its thermal and electrical conductivity properties. Copper salts (sulphates, acetates and organic derivatives) are used as fungicides in agriculture, for skin tanning, paint formulations and ceramics, etc. In addition to industrial or agricultural pollution, this metal mainly originates from corrosion of water pipes
Cyanide[b]	CN	Cyanides generally originate from industrial waste-waters (issued from gold and silver extraction processes, cleaning waters of blast furnaces, synthesis processes in the chemical and petrochemical industries, etc.). Their toxicities vary in relation to the associated cation and the possibility of release of cyanhydric acid (the less stable alkaline cyanides are the most toxic; complex cyanides such as ferrocyanides or thiocyanates are less dangerous)
Fluorine	F	This halogen is the most electronegative element and hence the most powerful oxidizing agent found in chemistry. Owing to its great reactivity, it is not present in the free state in nature, but in the gaseous state as F_2, and as fluorides, including organic and mineral derivatives. The main minerals containing fluorine are fluorine (CaF_2), cryolite or sodium alumino-fluoride (AlF_3) and apatite ($CA_5(PO_4)_3F$). The latter is an essential constituent of phosphates used as fertilizers. Fluorine and its derivatives are widely used in industry (aluminium production, glass and ceramic industries, catalysts, insecticides, etc.)
Iodine	I	Iodine is present in trace quantities in the environment. This element is an indicator of seawater infiltration. It is used in the chemical industry, photography and radiography, and also in the pharmaceutical industry owing to its therapeutic properties
Lead	Pb	As lead ores, this element is widely found in the earth's crust. It may be present in the form of carbonates and phosphates, but mainly as sulphides. This metal is frequently used in industrial applications, and pollution sources are hence numerous, e.g. the use of tetraethyllead in gasoline as an anti-knock agent, ore fusion, fossil fuel combustion, water distribution networks, etc.[a]
Mercury	Hg	This element is not widespread in the earth's crust, being mainly present as sulphidic minerals (HgS). It is naturally released through evaporation, erosion, and volcanic eruptions. Furthermore, the geological contamination of numerous ores explains its occurrence in some industrial wastes (mining extraction, refineries, cement factories, steel industries, phosphate treatment, fossil fuel and coal combustion, paper paste industry, etc.). This element is used in the fabrication of electric apparatus (lamps and batteries), control instruments (thermometers and barometers), marine paints and some

Table 1.1 (*continued*)

Element	Symbol	Comments
		fungicides. Mercury in the metallic state is practically insoluble in water. Mercury salts are generally weakly toxic, although mercury chloride has a high toxicity. The most toxic compounds are the organomercury derivatives[a]
Molybdenum	Mo	An element present in nature in the form of molybdenum sulphide and lead molybdate. It may originate from soil leaching, fossil fuel combustion, industrial wastes, and mining activities. This element is used in the production of special steels and electric resistors, as well as in the chemical (reagents and catalysts), glass and ceramic industries
Nickel	Ni	The principal ores are magnesium and nickel silicates, and pyrites (iron, nickel and copper sulphides). Nickel forms a constituent of numerous alloys, is used for the protection of metallic articles (resistance to corrosion) and in pre-treatment before chromium plating. In association with cadmium, this element is also used in the fabrication of batteries
Plutonium	Pu	An industrially produced metal. Among the 15 known isotopes, the most important ones are plutonium 238, 239 and 240 (all α-emitting) and plutonium 241 (β-emitting). This artificial radioelement exists at natural trace levels (plutonium 239) in uranium ores
Selenium	Se	An element which is widespread in nature. It is found at trace levels in pyrites and in the sulphide ores of copper, lead, gold, nickel and silver. This element is used as a colouring agent, in glass making, metallurgy, textile treatment, photoelectric cell and semiconductor production, the rubber and chemical industries (catalysts), phytosanitary products (fungicides and insecticides), the pharmaceutical industry, etc.[a]
Thallium	Tl	An element present in the form of impurities in pyrites and blendes. It is used in insecticide products, the fabrication of photoelectric cells, optical glasses, lamps, etc.
Thorium	Th	A metal which is not wide spread in the environment (occurs mainly in the forms of phosphates, silicates and rare-earth elements). Twelve radioactive isotopes are known (223 to 235). Thorium measurements, associated with stable ^{208}Pb, enable mineral dating. This element is used in industry for the production of special alloys (plane reactors), electronic components, etc.
Tin	Sn	The natural distribution of this element in nature is heterogeneous. The principal ore is cassiterite (tin oxide). This element is used in industrial alloys, the chemical industry (catalysts and coloured pigments), for welding, etc. Tin salts are also employed in the glass industry. In most cases, the tin is in the form of Sm(IV)[a]
Tritium	^{3}H	Radioactive isotope of hydrogen encountered in the cooling waters of nuclear reactors and during thermonuclear explosions.

(*continued overleaf*)

Table 1.1 (*continued*)

Element	Symbol	Comments
		This isotope is frequently used to control the (nuclear) reactions taking place in nuclear plants
Uranium	U	Metal extracted from pitchblende and uranite, consisting of a mixture of three isotopes, i.e. uranium 234, 235 and 238. The development of nuclear energy has led to the occurrence of uranium residues at various phases of preparation or utilization of this metal (extraction, waste-waters, treatment, purification, etc.)
Vanadium	V	An element used in the chemical industry as a catalyst, in metallurgy as paint formulating, as a colouring agent in ceramics, etc. Some insecticides and herbicides contain vanadium salts. Its toxicity increases with valency, with the pentavalent state being the most toxic
Zinc	Zn	An element present in rocks in the forms of sulphides, with the most widespread being zinc blende. It forms a constituent of numerous alloys, and it is used in the galvanization of metallic articles, the production of paint pigments, varnish, phytosanitary products, etc. In the form of the orthophosphate, it is used as a corrosion inhibitor in lead pipes. This metal is often found in association with cadmium and lead

[a]See also Table 1.3.
[b]Although, of course, not a 'pure' element, cyanide is included here on account of its significance as a trace component in water analysis.

lanthanides (also named rare-earth elements) which form a group of fifteen elements with atomic numbers ranging from 57 (lanthanum) to 71 (lutetium). In addition, many of the noble metals, which include platinum and palladium, are also starting to attract the attention of researchers, owing to the increasing use of car exhaust catalysts that employ noble metals to reduce emissions.

1.4.3 Chemical forms of elements ('speciation')

Table 1.3 gives some examples of chemical forms of those elements which are increasingly becoming more regularly determined by chemical laboratories, either in the framework of regulations (e.g. organotin compounds and methylmercury species) or in research activities related to environmental quality, ecotoxicology, and/or studies of the biogeochemical element cycle.

Definitions

The term 'speciation' is used for various types of analyzes, including the determination of the well-defined 'species' (e.g. elements with different oxidation

Table 1.2 Major elements frequently encountered in water analysis

Element	Symbol	Comments
Aluminium	Al	Extracted in the metallic state from bauxite. Widespread on earth (e.g. in aluminosilicate forms). It is present in the form of the Al^{3+} ion in acid waters, precipitating in the form of the hydroxide $Al(OH)_3$ with increasing pH. Toxic element
Calcium	Ca	An element wide spread in nature, in particular in calcareous rocks in the form of carbonates ($CaCO_3$). In water, it exists mainly in the form of hydrogencarbonates and, in lesser amounts, as sulphates, chlorides, etc. Calcium oxide is used in construction works, the paper industry, water treatment, etc
Chlorine	Cl	Owing to its oxidizing power, chlorine (gaseous chlorine, chloride dioxide or hypochlorite) is the most widely used reagent for water decontamination. Its form varies according to the pH of the system. The salts most often used are potassium and sodium chlorates (fabrication of detonating mixtures, synthetic dyes, herbicides, etc.). Sodium chlorite is used for disinfecting. Chloride concentrations in waters are very variable according to soil leaching, pollution (road treatment during winter), seawater infiltration in groundwaters, etc.
Magnesium	Mg	Magnesium is one of the most widespread elements in nature (ca. 2.1% of the earth's crust). Most of the magnesium salts are water-soluble. This element is present in the forms of carbonates and hydrogencarbonates. Similarly to calcium, it constitutes a significant element of water hardness
Nitrogen	N	Nitrogen (N_2) is a major constituent of the atmosphere (78%) and plays an essential role in the biosphere. The different mineral (ammonium, nitrites and nitrates) and organic (amino acids and proteins) forms are subject to continuous reversible exchanges. Ammonium nitrogen (or ammonia) in its ionized form (NH_4^+) or as non-ionized NH_3 indicates a degradation process of organic matter (often upstream of industrial pollution sources or waste-waters). Ammonia is rapidly transformed into nitrites and nitrates through oxidation processes
Kjeldahl nitrogen	(N)	The determination of Kjeldahl nitrogen is related to a specific analytical method. This parameter does not represent the total nitrogen amount but only the reduced organic and ammonium forms. Nitrogen of industrial origin, added to domestic urban sewage, originates from chemical industries (paper, textile, steel, etc.) and agro-food industries. Kjeldahl nitrogen is an indicator of environmental pollution and its monitoring enables the following of contamination trends

Table 1.3 Examples of chemical forms of elements frequently determined in water analysis

Compound	Symbol[a]	Comments
Lead	TML TEL	As indicated in Table 1.1, ethylated or methylated lead compounds of anthropogenic origin are widely found in the environment and determined in dusts or rain-water (in the control of atmospheric pollution). Naturally formed methylated lead compounds are also determined in studies of the geochemical cycle of this element
Methylmercury	MeHg	Among the organomercury derivatives, methylmercury is considered to the most toxic, owing to increasing risks of bioaccumulation. This compound is either naturally formed (methylation of mercury through microbiological actions) or originates from industrial pollution (e.g. polyvinyl waste)
Selenium	Se(IV) Se(VI)	Insoluble selenium as a metalloid can become soluble in waters through its transformation into selenites and selenates, with the latter form being considered as toxic
Tin	MBT DBT TBT MPhT DPhT TPhT (and others)	Organotin derivatives are used for the stabilization of polymers, wood and textile protection, pesticides, fungicides, herbicides, etc., in particular, as butyltins (e.g. tributyltin) and phenyltins (e.g. triphenyltin). These compounds may be found in waters along with their degradation products (di- and monobutyl- or phenyltin compounds). Methylated tin compounds are also determined in studies of the geochemical cycle of this element. Organotin toxicity is more acute for the trisubstituted forms
Arsenic	As(III) As(V)	Although displaying high toxicity in the trivalent state, arsenic is mostly found in the pentavalent state. It is also present in some waters (at low concentrations) in methylated forms
Chromium	Cr(III) Cr(VI)	Chromium may be found in either the trivalent or hexavalent states, with the latter being the most toxic form

[a]TML, tetramethyllead; TEL, tetramethyllead; MBT, monobutyltin; DBT, dibutyltin; TBT, tributyltin; MPhT, monophenyltin; DPhT, diphenyltin; TPhT, triphenyltin.

states or for specified organometallic compounds), plus forms of elements which are operationally defined (i.e. linked to a given extraction procedure); this latter category mainly concerns solid matrices (soils and sediments) and is not relevant to this present book (further information can be obtained from Quevauviller, 1998).

The following definitions have been discussed and accepted by three International Union for Pure and Applied Chemistry (IUPAC) Commissions, for which a report has been recently published (Templeton *et al.*, 2001):

Chemical species – *specific form of a chemical element defined as to molecular, complex, electronic or nuclear structure.*
Speciation analysis – *measurement of the quantities of one or more individual chemical species in a sample.*
Speciation of an element – *distribution of defined chemical species of an element in a system.*

1.4.4 Organic parameters

Besides contamination of anthropogenic origin, the organic matter likely to be found in various waters consists of decomposition products of animal or vegetable origin resulting from microbial activities (degradation of cellulose and organic debris). These complex materials are generally formed of humic/fulvic substances, with variable molecular masses, of acid and hydrophobic character. In lesser quantity, non-humic substances are sometimes encountered, e.g. proteins, polysaccharides, etc. The amount of organic matter is often determined by the difference between the dry and ashed residues (at 550°C), as well as by the determination of elements such as total organic carbon and total or Kjeldahl nitrogen. The total organic carbon measurement permits monitoring of the treatment processes of waste-waters. A variety of organic compounds of anthropogenic origin are described in Table 1.4.

1.5 MICROBIOLOGICAL PARAMETERS

Microbiology testing of water is particularly important because it offers the most sensitive method for the detection of faecal and therefore potentially dangerous pollution. Biological examination is used to detect the presence of algae and animal life, where these may gain access to water supplies through deficiencies in water treatment or because of faults in the distribution network. While the proper operation of water treatment works is of the utmost importance, frequent bacteriological tests are necessary in order to ensure adequate assessment of the bacterial purity and safety of drinking water. Chemical and biological tests, other than those required for treatment control purposes, can be made less frequently.

Monitoring for the presence of specific pathogenic bacteria, viruses and other agents in water is impracticable and is indeed not considered necessary for routine control purposes. Any pathogenic micro-organisms present in water are usually greatly outnumbered by, and in general also tend to die out more rapidly than, the normal commensal bacterial flora of the human or animal intestine. Although it may be possible to isolate microbial pathogens from contaminated water, especially when it is heavily polluted, large amounts (e.g. several litres) of the water may need to be examined using conventional techniques, selective media are required for isolation, and the subsequent identification of

Table 1.4 Examples of organic compounds found in various water samples

Compound	Comments
Chlorobenzene	Chrorinated benzene derivatives are widely used in industry. Mono- and orthodichlorobenzene compounds are employed as diluting agents in paints and varnishes, degreasing agents in the textile industry, in metallurgy, fabrication of dielectric products, colouring agents, inks and the pharmaceutical industry. They are also used, as well as trichloro-, tetrachloro- and hexachlorobenzene compounds, in organic synthesis and in fungicides and insecticides
Chlorophenols	Mono-, di-, tri- and tetrachlorophenols are used as fungicides, bactericides and in chemical synthesis. Pentachlorophenol (PCP) is the most widely employed in industry, being mainly used as a wood-protection agent. Organic microcontaminants (polychlorinated dibenzo-*p*-dioxins and dibenzofurans) are found in technical-grade PCP
Dioxin	Dioxin or tetrachlorodibenzo-*p*-dioxin (TCDD-2,3,7,8) belongs to the class of halogenated derivatives of oxygenated polycyclic hydrocarbons. This substance is a (heat-induced) degradation product of pyralene (a mixture of polychlorinated biphenyls and trichlorobenzene). It is characterized by a high liposolubility, a slow biodegradation and a high stability to heat (hence present as an important persistence in the environment)
Ethylenediamine-tetracetic acid	This is a chelating agent with strong complexing properties, in particular for cations (e.g. Ca, Cu, Pb, Fe, Cr, etc.). It is used in vapour generators to avoid precipitation of calcium, magnesium, etc., in the chemical and paper industries, in tanneries, and in the nuclear industry for surface treatments (decontamination)
Glycols	Ethylene glycol is a viscous liquid used in the chemical industry, in hydraulic fluids and as an antifreeze agent. Owing to its solubility in water, it can be responsible for high toxicity risks
Hydrazine	A powerful reducing agent used in the chemical industry (colouring agents, insecticides, pharmaceutical products, polymers, etc.), agents to prevent corrosion, etc. Above 100°C, excess hydrazine is decomposed into ammonia
Hydrocarbons	The huge consumption of petroleum derivatives leads to the transport and storage of enormous quantities of hydrocarbons, with the associated risks of leakage and losses. Some polycyclic hydrocarbons could have a natural origin (e.g. forest fires, phytoplankton, etc.). Several families can be distinguished, i.e. *benzene hydrocarbons* (benzene, toluene, xylene and ethylbenzene), *aliphatic chlorinated hydrocarbons* (or chlorinated solvents), such as dichloromethane, dichloropropane, tetrachloromethane,

Table 1.4 (*continued*)

Compound	Comments
	dichloroethane, and di-, tri- and tetrachloroethylene, and *polycyclic aromatic hydrocarbons* (PAHs) with several benzene groups (e.g. benzo-*a*-pyrene)
Mercaptans (or thiols)	These compounds are sulphurated homologues of alcohols. Among them can be distinguished the aliphatic and aromatic mercaptans. They can be formed by putrefaction of sulphurated aromatic substances and the decomposition of sulphurated organic substances during refinery operations involving petroleum products
Pesticides	These are phytosanitary products used to fight harmful organisms (insecticides, fungicides, herbicides, etc). Besides mineral substances such as sulphur, copper sulphate, lead and calcium arsenate, various organic compounds have been and are still being used. Organochlorinated compounds include compounds such as DDT, lindane (HCH), aldrin, dieldrin, endrin, chlordane, heptachlor, toxaphen, etc. The other organic compounds mostly include organophosphorus compounds (parathion, malathion, phosdrin, etc.), sulphonates (e.g. fenizon), carbamates (carbaryl, aldicarbe, carbofuran, dithiocarbamates, etc.), and various groups of compounds used as herbicides (alachlor, bentazon, metolachlor, molinate, permethrine, paraquat, propanil, triazines (atrazine and simazine), trifularine, etc.)
Phenols	Under the term ‘phenols’ are designated various types of hydroxybenzene compounds which are determined with a method using phenol as a standard. The decomposition of vegetable products such as lignin, as well as industrial cellulose-containing waste-waters, may lead to the emission of phenolic products. These substances may also appear via the degradation of phytosanitary products (pesticides, fungicides, herbicides, etc.). Phenolic products may also be present in domestic waste-waters, being released as human secretions
Phthalates	These products, of low volatility, are largely used in paints, inks, lacquers, etc. In nature, the oxidation of humic substances by microbial action may also lead to the formation of phthalates
Polychlorinated biphenyls	Polychlorinated biphenyls (PCBs) and their impurities, e.g. polychlorinated terphenyls (PCTs), are complex mixtures of different isomers obtained by chlorination of biphenyl and terphenyl. They are used in numerous applications, e.g. paints, varnishes, plastics, synthetic resins, inks, greasing agents, oils, electrical isolating agents, liquids for hydraulic machines, etc. Their non-inflammable character makes them the products of choice for the fabrication of condensers,

(*continued overleaf*)

Table 1.4 (*continued*)

Compound	Comments
	transformers, etc. They are easily dissolved in oil and fat, but have low solubility in water. Moreover, they are extremely resistant to biological degradation, oxidation, and to the action of acids and bases. PCBs are characterized by the number of chlorine atoms present, with the most dangerous being those containing more than three chlorine atoms. Their occurrence in the environment is related to industrial wastes, leaks in transformer circuits, volatilization after incineration, etc. Owing to their low degradability, such compounds are widespread in the environment and have a high bioaccumulating power
Styrene	An alkylbenzene containing a benzene group on which is fixed a lateral non-saturated chain resulting from the fixation of a very active vinyl radical. This compound is slowly polylmerized at ambient temperatures. It is used in plastics, synthetic rubbers, and copolymers. The use of the polymer in food packaging has been criticized, although its harmful character has not yet been demonstrated with any certainty
Vinyl chloride	Vinyl chloride monomer is obtained industrially via ethylene chlorination. Autoclave polymerization enables the production of poly(vinyl chloride) (PVC). Toxicity risks are related to the possible residual monomer in the polymer, which thus requires strict control of various PVC components, e.g. pipes
Volatile organochlorinated compounds	The compounds most often identified in the environment belong to the trihalomethane group, i.e. chloroform ($CHCl_3$), bromodichloromethane ($CHBrCl_2$), chlorodibromomethane ($CHBr_2Cl$), chlorobromomethane CH_2ClBr) and bromoform ($CHBr_3$). In addition, the following compounds have been found after accidental pollution (industrial, domestic or agricultural): carbon tetrachloride (CCl_4), trichloroethylene ($CHCl{=}CCl_2$) and dichloroethane ($CH_2Cl{-}CH_2Cl$). Haloforms appear during water chlorination (fixation of chlorine atoms on polyphenols, humic or fulvic acids, etc.). Some of these compounds may be produced by algae biomass after chlorination

the organisms involves biochemical, serological and other tests on pure cultures. Reliance is therefore placed on relatively simple and more rapid (indicator) bacteriological tests for the detection of certain commensal intestinal indicator bacteria (in particular, *Escherichia coli* and other coliform organisms). These are easier to isolate and characterize and because they are always present in the faeces of man and warm-blooded animals (and hence in sewage), in large numbers. The presence of faecal indicator organisms in a sample of drinking water thus denotes that intestinal pathogens could be present, and that the supply is therefore potentially dangerous to health. It is far more important to microbiologically examine a water supply frequently by a simple test than occasionally by a more complicated test or serious of tests. However, there is no absolute correlation between the numbers of *E.coli* or other coliform organisms and the actual presence or numbers of enteric pathogens, nor between the risk of illness occurring and the numbers of *E.coli* present in a given sample. The finding of *E.coli* in a properly treated water sample indicates the presence of material of faecal origin and thus a potentially dangerous situation, the nature and extent of which is best determined by 'on-site' and laboratory investigations. Conversely, the absence of faecal organisms is an indication that, in all probability, intestinal pathogens are also absent in the relevant sample (HMSO 1994).

Of the pathogens and facultative pathogenic types of bacteria which can occur in contaminated water, the bacteria of the Enterobacteriaceae family are of particular importance. The species *Salmonella*, *Shigella* and *Escherichia*, the so-called coliform bacteria, and *Proteus*, *Yersinia* and *Erwinia* all belong to this family. *Salmonella* and *Shigella* are classed as extremely pathogenic, whereas most of the others are considered as facultatively pathogenic. When testing the microbiological quality of water, analyses mainly focus on *E.coli* and coliforms, with lesser emphasis being placed on Clostridium perfringens and Enterococci, employing total viable counts at 22 and 37°C In addition, the eggs/cysts/oocysts of various parasites can be present in water (Rump, 1999; HMSO, 1994).

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