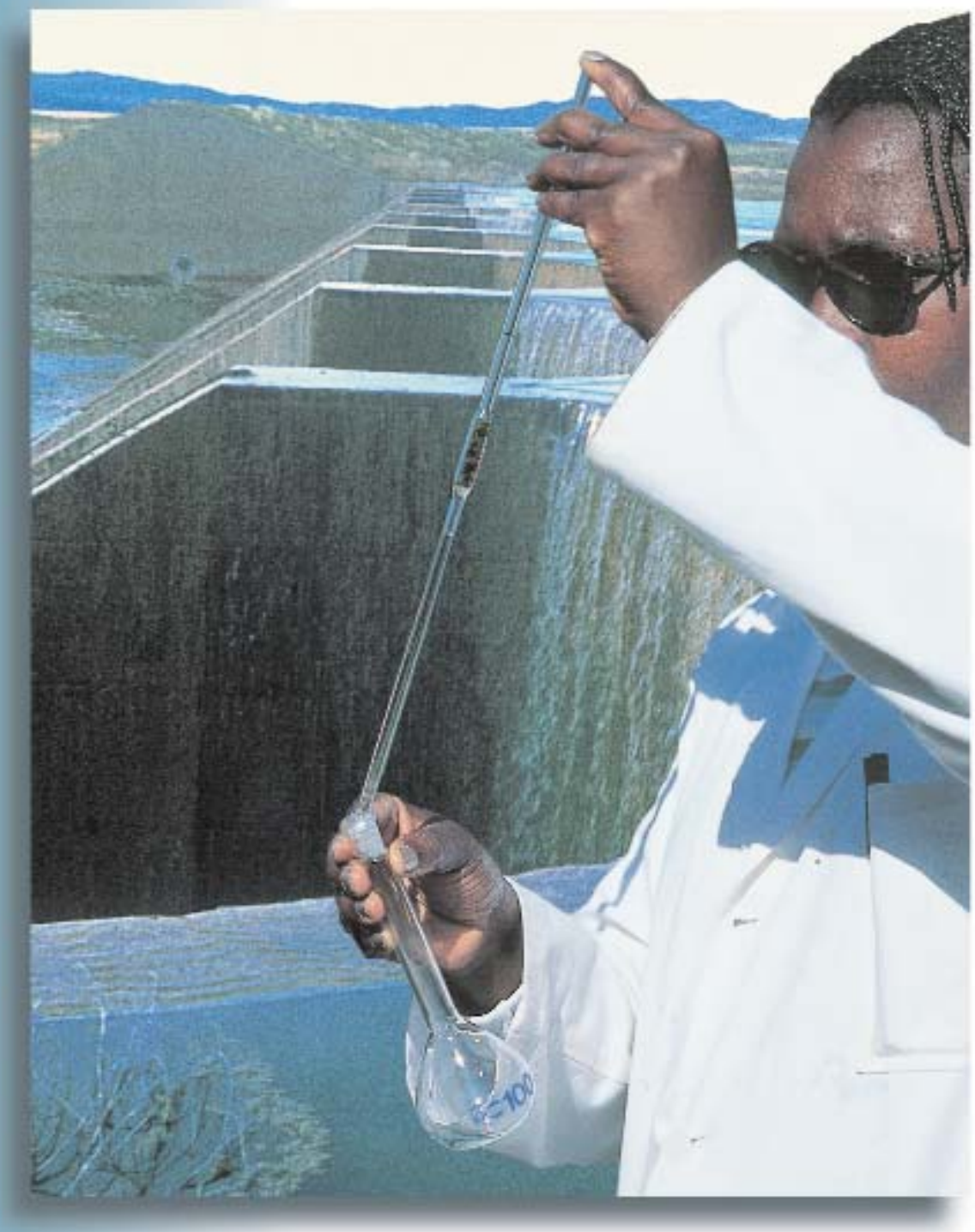
Quality of Domestic Water Supplies

Volume 3: Analysis Guide



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Water Research Commission

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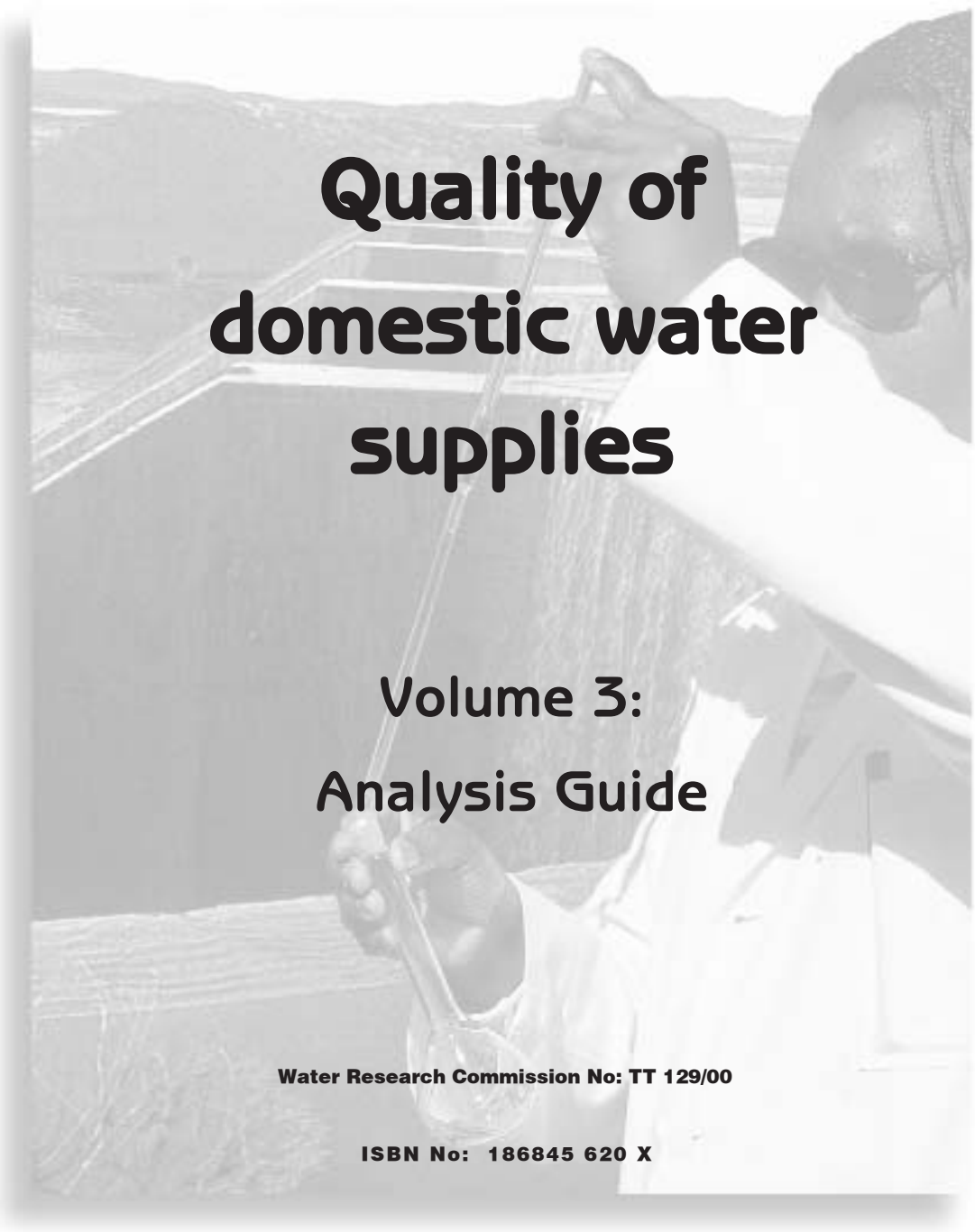

Quality of domestic water supplies

Volume 3: Analysis Guide

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OTHER REPORTS IN THIS SERIES

This Analysis Guide forms part of a series which is intended to provide water supply agencies, water resource managers, workers in the field, as well as communities throughout South Africa, with the information they need to sample, analyse, assess and interpret the quality of domestic water supplies.

The following documents form the series:

Quality of domestic water supplies -
Volume 1 Assessment Guide

Quality of domestic water supplies -
Volume 2 Sampling Guide

Quality of domestic water supplies -
Volume 3 Analysis Guide

Quality of domestic water supplies -
Volume 4 Treatment Guide

Quality of domestic water supplies -
Volume 5 Management Guide

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FOREWORD

An essential component of managing water resources and the environment is that of monitoring and analysis of samples taken from the environment. Without the chemical and microbiological analysis of water samples, it would not be possible to determine the status and safety of drinking water supplies, which are so essential a requirement for the well-being of communities, and the sustenance of life.

Water resources are subject to ever-increasing pollution pressures, paralleling an overgrowing demand for water for drinking purposes and other uses. The determination of the chemical and microbiological quality of the water supplies is essential to establish the need and adequacy of treatment, and to safeguard human health.

The Department of Health and the Department of Water Affairs and Forestry, in partnership with the Water Research Commission, embarked earlier on a venture to produce a series of user-friendly guidelines. Encouraged by the demand of the first two guidelines in the series, *viz.,* the assessment and sampling guides, the pressure was on to continue the series of capacity-building guidelines, and the third guideline in the series has now been produced, i.e. the Analysis Guide.

This guide is specifically aimed at explaining the concepts related to the laboratory analytical techniques. These techniques are often viewed as mysterious alchemy and a closed book by non-technical experts and managers alike. By attempting to explain some of the more basic concepts of analytical science, and conditions necessary to perform a valid analysis, it is hoped that this guide will serve as an educational tool to inspire more of our young people to study the science of measurement and analysis. This will help to ensure the supply of a skilled work-force so necessary for reaching the goal of safe drinking water for all.

As in the case of the first two guides specific attention was placed on the user-friendliness of the document. In addition to water resource managers and water chemists the needs of the high-school, technicon and university educators for appropriate text-book material, have also been taken into account to empower the upcoming generation, which constitute the hope and the guarantee of our sustained well-being.

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STRUCTURE OF THE GUIDE

This guide consists of three parts and each part consists of a number of sections. The pages of each section are marked in the top right hand corner with the icon corresponding to that section.

Part 1 provides general information on water quality analysis, substances of concern in water for domestic use, their general characteristics and units in which analysis results are reported and general methods of analysis.

Part 2 describes the analysis process and gives information on general methods of analysis, the planning for and execution of analyses and reporting of results.

Part 3 deals with quality assurance considerations that include concepts of accuracy and uncertainty of analysis results.

Part 1

General information on water quality analysis

- Familiarise yourself with the concept of water quality analysis
- Familiarise yourself with the substances of concern in water for domestic use

Part 2

Analysis Process

- Familiarise yourself with the general methods of analysis for domestic water
- Plan for the analysis
- Performing the analysis
- Reporting of results

Part 3

Quality assurance considerations

- Familiarise yourself with the concepts of measurement and associated uncertainty
- Analytical quality assurance

NOTE: Aspects of a more technical nature are given in a series of "**note boxes**". These note boxes provide detail on certain basic concepts and also illustrate some concepts in the form of examples and case studies.

The different units in which the chemical quality of domestic water is processed are discussed in **boxes marked SET 1 to SET 5** on pages 14 to 17.

TABLE OF CONTENTS

PURPOSE OF THE GUIDE

What is the purpose of the Analysis Guide?

The purpose of this guide is to provide general information on water quality analysis specifically on the aspects listed below:

- General overview of analytical methods for the analysis of water for domestic use
- The suitability and limitations of different methods of analysis
- Characteristics of substances of concern in domestic water and units in which they are expressed
- The concept of uncertainty associated with water quality analysis
- Quality assurance in water quality analysis.

NOTE

It is not the purpose of this guide to go into the technical details of the different methods of analysis or to go into the details of statistical analysis of results. These details are provided in handbooks such as those listed as reference books.

It is also important to note that this Guide is the third in a series of guides on the quality of domestic water supplies. It should therefore be used in conjunction with the other guides: *Volume 1 - Assessment Guide* and *Volume 2 – Sampling Guide*.

Who should use the Analysis Guide?

The level of presentation in this guide is aimed specifically at people with limited training in analytical methods or with limited experience in this field. The main objective is to empower people in smaller laboratories and in rural areas to be effective in water quality analysis and assessment. These people are:

- Laboratory analysts responsible for water analysis
- Environmental health officers who have to assess water quality for domestic use
- Field workers who do inspections, take samples and do on-site analyses
- Treatment plant operators who have to do analyses to assess plant performance
- Water supply agencies
- Educators and students.

PART 1A

General information on water quality analysis

PART 1

GENERAL INFORMATION ON WATER QUALITY ANALYSIS

SECTION 1A

Familiarise yourself with the concept of water quality analysis

YOU ARE HERE

SECTION 1B

Familiarise yourself with the substances of concern in water for domestic use

PART 2

PLANNING, PREPARING FOR AND PERFORMING THE ANALYSIS

SECTION 2A

Familiarise yourself with the general methods of analysis for domestic water

SECTION 2 B

Plan for the analyses

SECTION 2C

Performing the analyses

SECTION 2D

Reporting of results

PART 3

QUALITY ASSURANCE CONSIDERATIONS

SECTION 3A

Familiarise yourself with the concepts of accuracy and uncertainty of analysis results

SECTION 3B

Analytical quality assurance

SECTION 3C

The implications of the quality of test results

Section 1A: Familiarise yourself with the concept of water quality analysis

In order to evaluate the concepts of water quality analysis and water quality assessment for domestic use it is important to have a clear understanding of the following aspects:

- Water quality and fitness for domestic use
- Analytical methods: Which methods are available and what their limitations are
- Expression of analytical results: Different units for different constituents
- Uncertainty of testing: What the causes are and how uncertainty can be quantified.

What is water quality?

The term "water quality" is used to describe the microbiological, physical and chemical properties of water that determine its fitness for a specific use. These properties are determined by substances which are either dissolved or suspended in the water.

Dissolved substances

Water is a unique substance. One of its unique characteristics is its excellent dissolving capability. As water moves through its cycle of rainfall, runoff, infiltration, impounding, use and evaporation, (hydrological cycle) it comes into contact with a vast range of substances which may be dissolved by the water to a greater or lesser extent (see *Volume 1: Assessment Guide*). The type and amount of these dissolved substances (together with suspended and colloidal substances) determine the properties (quality) of the water.

Substances that can be dissolved by water include gasses such as oxygen (O_2) and carbon dioxide (CO_2), inorganic compounds such as sodium chloride (NaCl) and calcium sulphate ($CaSO_4$), and organic substances such as humic acids and carbohydrates.

In order to evaluate the quality of water one has to determine the concentration of dissolved substances that are relevant to the particular use of the water, (together with the physical and microbiological properties of the water).

Suspended substances

In addition to the substances that are dissolved in water, some substances may not dissolve in water but remain in suspension as very small suspended or colloidal particles. These particles also affect the quality of the water and their presence and concentration in water must also be determined. An example of this category of substances is micro-organisms. They are so small that they cannot be seen individually with the naked eye but they may have important effects on water quality.

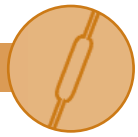
What is fitness for use?

Fitness for use describes the required water quality for a specific use.

Water use

Different water uses require different qualities of water. For example, water of a relatively poor quality may be fit for use as irrigation water but will not be fit for use as domestic water. On the other hand, water which is fit for domestic use may not be fit for industrial use such as boiler feed water where water of high purity is required.

NOTE: Water quality is only meaningful when evaluated in relation to the use of the water.



In order to evaluate fitness for use, water use is divided into four main categories:

- Domestic use (e.g. for drinking, food preparation, clothes washing, bathing, gardening)
- Recreational use (e.g. swimming, fishing, boating)
- Industrial use (e.g. power generation, process water, food processing)
- Agricultural use (e.g. water for animals, irrigation).

What is domestic use of water?

Domestic use of water includes all the different uses in and around the home:

- *For survival (sustenance) – drinking and food preparation*
- *For personal hygiene – bathing, washing and sewage removal*
- *For gardening – watering of a vegetable patch or lawn.*

Sustenance. Water consumed by the domestic user (for drinking and in food preparation) only represents a small portion of the water used for domestic purposes. However, it is the most important aspect when considering the quality of water for domestic use as it directly affects the health of the consumer.

Water to be consumed must also be **aesthetically** pleasing, i.e. the appearance, taste and odour of the water must be pleasing.

Water for personal hygiene must be safe and pleasing, but it need not be of such high quality as for water to be consumed.

Water for gardening purposes can be of a lower quality than for other domestic uses. However, water used for irrigation of crops which are eaten uncooked such as lettuce must not be contaminated since diseases could be transmitted in this way.

Why is it necessary to do a water quality analysis?

*Water may contain dissolved substances or micro-organisms which may not **necessarily** affect the appearance or taste of the water but which may have serious health or other effects, making the water unfit for domestic use. The fitness for domestic use of a particular water can therefore only be assessed if an analysis of the water is available which includes the substances of concern for domestic use (see page 8-10).*

Appearance and taste of water may be misleading. When water looks clean and tastes good many people will accept it as a good quality drinking water. This may be dangerous because the water may contain excessive amounts of harmful substances such as mercury or micro-organisms which may have both short-term and long-term health effects on consumers. These substances are not apparent by looking at, or tasting the water. They can only be quantified by a proper analysis of the water.

What does water quality analysis entail?

Although the actual analytical procedure forms a very important part of water quality analysis, it is only one action in a series of actions in water quality analysis, namely: (see road map page 5)

- *Identification of the need for water quality information*
- *Taking of sample(s) to be analysed*
- *On-site analysis of samples*
- *Preservation (if necessary), transport and storage of samples*

- *Analysis of sample*
- *Calculation of results*
- *Reporting of results*
- *Assessment of water quality*
- *Information transfer/reporting.*

The need for water quality information may arise from a number of different sources, such as:

- Environmental health officers who have to assess the quality of domestic water at the point of use or in the distribution system
- Water suppliers who have to assess the quality of surface or groundwater sources to be used as a supply for domestic water
- Treatment plant operators who have to monitor the performance of treatment processes and the quality of water produced.

Each one of these will have specific needs for the types of analyses to be performed (also see *Volume 1: Assessment Guide*, Table 3, page 16), the frequency of analysis, the accuracy required, etc. It is important, therefore, that these requirements be communicated very clearly to the sampler as well as the analyst so that they are fully aware of all requirements.

Taking of sample. It is important that the sample must be representative of the water on which the information is required, that the correct type and volume of sample is taken, that the correct procedure is followed for the type of sample and that the correct type of container is used. These requirements are discussed in detail in the Sampling Guide: *(Quality of Domestic Water Supplies, Volume 2)*.

On-site analysis. In some cases samples are analysed on-site for certain substances, using field instruments or test kits. There are test kits available which makes field analysis of a number of substances possible. However, care must be taken when deciding on analyses to be done on-site because results are not always reliable (see Note Box 1, page 6).

The substances and properties which are normally determined on-site include pH, temperature, residual chlorine and electrical conductivity. The reason for on-site determination for these parameters is that they are easy to measure and some of them may change as soon as the sample is taken.

Preservation, transport and storage of water samples are important elements of the process of water quality analysis. The most important requirement is that the sample must be delivered as soon as possible to the laboratory for analysis, especially for microbiological analysis. This should preferably be within six hours. Where this is not possible, the samples must be cooled during transport and storage and be delivered to the laboratory within 24 hours for analysis. If this is not possible, instructions must be obtained from the laboratory for preservation of the samples. It is important in all cases that the time and date be noted when the sample was taken, and that the sample be unambiguously identified with a unique name and/or number.

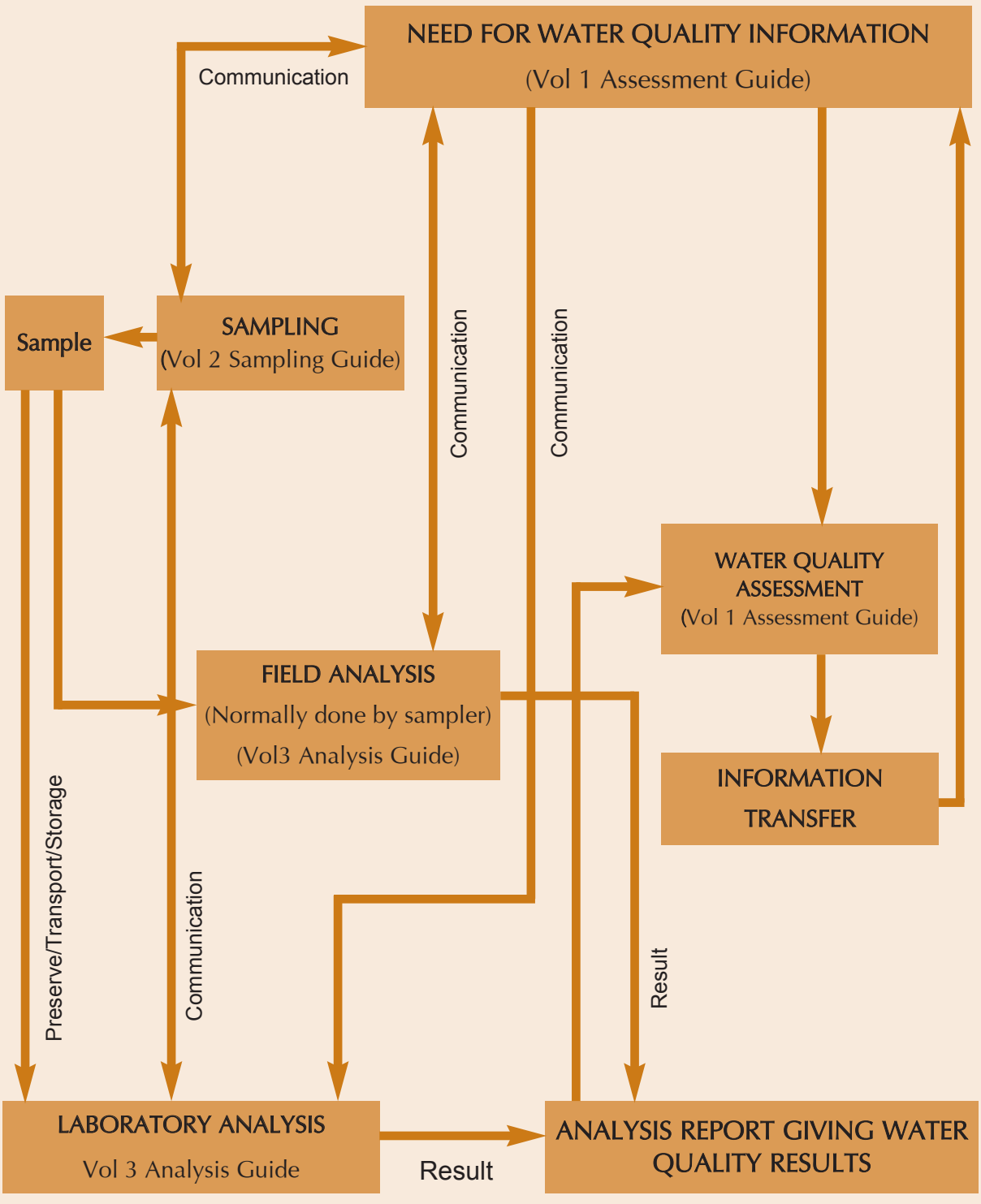
Samples for microbiological analysis containing residual chlorine must be dechlorinated, kept cool and delivered to the laboratory within six hours for analysis. Dechlorination is usually achieved by the addition of sodium thiosulphate.

Appropriate preservation of samples for chemical analysis depends on the substance being measured as well as the type of analytical method being used by the laboratory.

Analysis. The analytical method used for the analysis will depend on a number of factors, such as whether it is a once-off analysis or whether it can be done as part of daily routine. In general the most reliable available method must be used for the analysis in accordance with prescribed procedures.

Calculation and reporting of analytical results must be done to provide the results in the correct units and format as requested by the person who initiated the process. Any specific information that may be relevant must be noted in the report, such as time between sampling and analysis, any sign of contamination, sediments, etc.

Road map for the process of sampling, analysis and reporting



Note Box 1: Use and place of test kits in water quality analysis

What are test kits?

Test kits are simplified analytical methods designed to be portable, so that the kits can be taken out into the field, where on-site analytical results can be obtained, facilitating immediate on-site decision-making.

How reliable are test kits?

The reliability of test kits varies tremendously, depending on the type of test kit, the type of substance being analysed, and the success or not that has been achieved in the miniaturisation process that was used in designing the particular test kit method under consideration. Some test kit methods can give fairly reliable results, while others may give a crude indication only of the presence or absence of the particular substance in question. In general test kits tend to be less accurate than full laboratory methods, i.e. the test kits methods tend to be more subject to deviations from the true concentration value than the full laboratory methods.

What is the place and purpose of test kits?

Test kits serve a number of useful purposes and may be used to good effect in conjunction with full laboratory methods to strengthen the analytical capabilities of the laboratory. Test kits are useful for the following purposes:

- To provide results for substances that cannot be preserved or are not easily preserved and which must, preferably, be measured on-site, in the field. Examples are the measurement of pH, or free residual chlorine in treated drinking waters.
- To provide a rapid, rough and ready answer of the concentration level of a substance as a screening tool. Test kits can serve a very useful purpose here to optimise sampling site selection so as to reduce the number of samples that need to be sent for proper laboratory analysis.
- As awareness building tools. The lay-person often finds the result report produced by a laboratory difficult to understand. Test kits, particularly those showing a colour reaction as the method of detection, help make the concept of good vs. poor water quality, more meaningful to the lay-person.

PART 1B

General information on water quality analysis

PART 1

GENERAL INFORMATION ON WATER QUALITY ANALYSIS

SECTION 1A

Familiarise yourself with the concept of water quality analysis

SECTION 1B

Familiarise yourself with the substances of concern in water for domestic use

YOU ARE HERE

PART 2

PLANNING, PREPARING FOR AND PERFORMING THE ANALYSIS

SECTION 2A

Familiarise yourself with the general methods of analysis for domestic water

SECTION 2 B

Plan for the analyses

SECTION 2C

Performing the analyses

SECTION 2D

Reporting of results

PART 3

QUALITY ASSURANCE CONSIDERATIONS

SECTION 3A

Familiarise yourself with the concepts of accuracy and uncertainty of analysis results

SECTION 3B

Analytical quality assurance

SECTION 3C

The implications of the quality of test results

Section 1B: Familiarise yourself with the substances of concern in water for domestic use

What are the substances of concern in domestic water?

A very large number of substances can be found in water. However, only a few of these commonly occur at concentrations which cause them to be of concern to domestic water users. The substances of main concern can be categorised in the groups indicated in Tables 1A to 1D.

Group A substances listed in Table 1A gives an indication of **general water quality**. These substances are indicators of potential problems and should be frequently determined at different points in the water supply system, irrespective of the source of water. (Residual chlorine has to be determined only if the water is treated with chlorine-based disinfectants. (see Note Box 7).

Table 1A: Substances which are general indicators of water quality

GROUP A	
Electrical conductivity (total dissolved salts)	Conductivity is an indicator of total dissolved salts (TDS), and also establishes if the water is drinkable and capable of slaking thirst.
Faecal coliforms	This is an indicator of the possible presence of disease-causing organisms. It establishes if water is polluted with faecal matter.
pH value	This has a marked effect on the taste of the water and also indicates possible corrosion problems resulting from dissolution of metals such as copper, zinc and cadmium that can be toxic.
Turbidity	This affects the appearance, and thus the aesthetic acceptability, of the water. Turbidity is commonly high in surface waters.
Free available chlorine (Residual chlorine)	This is a measure of the effectiveness of the disinfection of the water. Residual chlorine is the chlorine concentration remaining at least 30 minutes after disinfection. There should be residual chlorine in the water, but if concentrations are too high it may impart an unpleasant taste and smell to the water.
Group A substances are indicators of potential problems and should be frequently tested at all points in the water supply system, irrespective of the source of the water. (Free available (or residual) chlorine has to be measured only if the water has been treated with chlorine-based disinfectants).	

Group B substances listed in Table 1B include substances which are normally present in most waters at concentrations which may affect the health of consumers. These substances should be determined in all waters supplied for domestic use. They would normally be determined at relatively low frequencies because the concentration levels of these substances can be expected to remain relatively stable unless pollution occurs.

Table 1B: Substances which are commonly present at concentrations which may lead to health problems.

GROUP B	
Nitrate & nitrite	These are common in groundwater (borehole) samples, particularly in areas of intensive agricultural activity, or where pit latrines are used. Severe toxic effects are possible in infants.
Fluoride	This is often elevated in groundwater in hot, arid areas. Can cause damage to the skeleton and the staining of teeth.
Sulphate	This is particularly common in mining areas. Causes diarrhoea, particularly in users not accustomed to drinking water with high sulphate concentrations.
Chloride	This is often elevated in hot, arid areas, and on the western and southern Cape coasts (particularly in groundwater). May cause nausea and vomiting at very high concentrations.
Arsenic	This may be present in groundwater, particularly in mining areas. Can lead to arsenic poisoning.
Total coliforms	This provides an additional indicator of disease-causing organisms, and the effectiveness of disinfection.
The presence/concentration of Group B substances should be determined before the water is supplied. The frequency of testing depends on the source and the treatment applied. Note that substances of concern due to pollution sources in the area, may have to be added to Group B.	

Group C substances listed in Table 1C include substances which do not occur frequently at concentrations of concern to health. These substances are typically present in soft corrosive waters which cause them to be leached from pipes and appliances.

Table 1C: Substances which occur less frequently at concentration of concern to health

GROUP C	
Cadmium	This usually occurs along with zinc in acidic waters where it may have been dissolved from appliances.
Copper	This affects the colour of the water and can cause upset stomachs. Normally occurs only when copper piping is used to carry water with a low pH value.
Group C substances should be tested for at point of use only in areas of the country where soft water of a low pH value is used.	

Group D substances listed in Table 1 D include substances which may commonly be present in water at concentrations which may affect aesthetics, e.g. staining of clothes or may have economic effects such as corrosion.

Table 1D: Substances which may commonly be present at concentrations of aesthetic or economic concern in domestic water sources

GROUP D	
Manganese	This is a common reason for brown or black discolouration of fixtures and for stains in laundry. Can be common in bottom waters of dams, or in mining areas.
Zinc	This affects the taste of water. Usual cause is acidic water dissolving zinc from galvanised pipes or from appliances.
Iron	This affects the taste of the water and may also cause a reddish brown discolouration. Can be common in bottom waters of dams, or in mining areas. Can cause growth of slimes of iron-reducing bacteria that ultimately appear as black flecks in the water.
Potassium	This affects the taste of the water and is bitter at elevated concentrations.
Sodium	This affects the taste of the water. Often elevated in hot, arid areas and on the western and southern Cape coasts (particularly in groundwater).
Calcium	This can cause scaling and can reduce the lathering of soap.
Magnesium	This affects the taste of the water. It is bitter at high concentrations. Common in some areas and it adds to the effect of calcium.
Hardness, total	This is a combination of calcium and magnesium. It is associated with scaling and inhibition of soap lathering.
The presence of Group D substances should be determined at least when assessing the water for the first time. Thereafter they can be included when there is reason to believe that their concentrations may have changed.	

What are the general properties of the substances in domestic water and how do they affect water quality?

The general properties of substances of concern in domestic water vary over a wide spectrum and can be categorised as:

- *Chemical*
- *Physical or*
- *Microbiological in nature.*

The properties of each substance determine how water quality is affected by that substance.

What are the chemical properties of domestic water?

The chemical properties of water are determined by the following groups of dissolved substances:

- **Metallic substances** such as arsenic, cadmium, calcium, copper, iron, magnesium, manganese, potassium, sodium and zinc
- **Inorganic non-metallic substances** such as chloride, fluoride, nitrate, sulphate
- **Aggregate organic substances** measured as total organic carbon (TOC), chemical oxygen demand (COD) and trihalomethanes (THM)
- **Aggregate inorganic substances**, such as those measured by total dissolved solids (TDS), hard ness and chemical stability.

These substances occur in dissolved form in water and have a wide range of effects on the chemical properties of the water. For example, some of these substances can cause the water to be toxic (arsenic), some can cause the water to be scale-forming (calcium carbonate), while other chemical compounds may affect the taste of the water (sodium chloride). These substances can be either *inorganic or organic* in nature.

Inorganic chemical compounds can be present in surface and ground water. These compounds such as sodium chloride (NaCl) and calcium sulphate ($CaSO_4$), dissolve in water in the form of the respective ions, i.e. Na^+, Ca^{2+}, Cl^- and SO_4^{2-} .

(See **Note Box 2** for a discussion on elements, atoms, ions, molecules, compounds).

The **ions with positive electrical charges are called cations** and **ions with negative charges are called anions**.

When doing an analysis, for ionic substances, the concentration of the ions is determined and reported rather than the concentration of the compounds.

Organic compounds have carbon as a main element in their composition. They behave differently when they go into solution. They mostly do not dissolve as ions but go into solution as **molecules** of the compound.

A large number of organic compounds (often called organics) can be present in water. This includes natural organic compounds such as algae- and bacterial by-products; carbohydrates and proteins; synthetic organic compounds such as pesticides and herbicides; and products formed during water treatment such as chloroform and other chlorinated products. These organic compounds are usually present in very low concentrations, but they may be harmful even at low concentrations.

It is not always possible to determine each individual organic compound in water and it would also be very costly because of the large variety of compounds that may be present at very low concentrations.

An indication of the general organic quality of the water can be obtained by means of the determination of aggregate substances such as total organic carbon (TOC) and chemical oxygen demand (COD).

What are the physical properties of domestic water?

The physical properties of water include properties such as turbidity, temperature, electrical conductivity, pH as well as colour, taste and odour. The physical properties of water largely determine its aesthetic properties, i.e. appearance, taste and general drinkability of the water.

What are the microbiological properties of water?

The microbiological properties of water are determined by the type and numbers of

Note Box 2: Elements, atoms, ions, molecules

All physical objects are composed of the following elementary particles:

- Electrons
- Protons
- Neutrons.

These elementary particles occur in various combinations to form atoms. The atom is the smallest unit of matter that has unique chemical characteristics. Protons and neutrons occur in the nucleus of the atom, while electrons orbit the nucleus.

ELEMENTS

There are 92 naturally occurring kinds of atoms, each called an **element**. An element is defined by its **atomic number** (the number of protons in the nucleus). The **atomic mass** of an element is equal to the sum of neutrons and protons in the nucleus. The atomic mass is an important entity because it is used to calculate the **molar or formula mass** of compounds and molarity and normality of solutions.

Elements occur in "families" or groups with similar properties but with different atomic masses. Each family appear in a vertical column of the Periodic Table (see back page). For example, calcium, strontium and barium are all found together as metal carbonates, while chlorine, bromine and iodine are all reactive volatile elements, readily forming halide salts such as NaCl, NaBr, NaI. The Periodic Table of Elements consists of all the elements (natural and man-made) arranged according to their atomic numbers and in their "families".

IONS

All atoms are electrically neutral because the number of electrons with negative charge equals the number of protons with positive charge. However, an atom may gain or loose one or more electrons, in which case it acquires a net electrical charge and becomes an ion. If the overall charge is positive the ion is called a cation (e.g. Na^{+}, Ca^{2+} , Al^{3+}), if the overall charge is negative it is called an anion (e.g. Cl^{-}, O^{2-}).

Ions may also be formed by a combination of atoms with an overall charge, called polyatomic ions (e.g. NH_4^{+}, OH^{-} , SO_4^{2-}).

MOLECULES

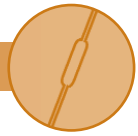
Molecules are formed through a linking of atoms by means of different kinds of bonding. The water molecule H_2O is formed through covalent bonding of 2 hydrogen atoms with 1 oxygen atom.

SALTS

Molecules of salts such as table salt, NaCl, or $CaSO_4$ do not exist individually. They join together to form a crystal, large enough to be visible. The crystals are formed through ionic bonding between the positively charged sodium and negatively charged chloride ions.

When NaCl crystals are added to water, each sodium ion and each chloride ion is surrounded by a shell of water molecules. These "hydration shells" keep the ions separated or dissociated and allows the salt to dissolve readily in water.

Other substances such as sugar also dissolve readily in water although they contain no ionic bonds. The reason is that these substances are made up of polar molecules containing chemical groups with a net electric charge, or polarity. Compounds that do not contain polar groups and do not ionise have very low solubilities in water.



micro-organisms *present in the water. A variety of micro-organisms can be present even in very good quality domestic waters. Most of these micro-organisms are harmless but if the water is polluted* ***pathogens*** *may be present.*

NOTE: Pathogens are disease-causing micro-organisms such as those causing cholera, gastro–enteritis, hepatitis, etc. (Pathogen from the Greek words *pathos*, meaning suffering and *gen*, meaning to give rise to).

It is difficult to determine the presence of all the different pathogenic organisms and therefore the presence of certain **indicator organisms** are used to give an indication of the possible presence of pathogens.

Indicator organisms are specific types of micro-organisms which are present in very large numbers in the intestines of people and warm-blooded animals. They are easy to detect. The presence of these organisms in water serves as an indication of pollution of the water by human wastes. Such water is therefore unsafe to drink and must be disinfected before use. Indicator organisms generaly do not multiply in drinking water or once a sample has been taken.

There are different types of indicator organisms. The most common indicator organisms used for domestic water quality assessment are **total coliforms, and faecal coliforms**.

How is the chemical, physical and microbiological quality of water determined and expressed?

The chemical, physical and microbiological quality of water is determined by analysing the water for the different substances of concern. The quality is expressed as the concentration, or the quantity of a substance, or the number of organisms per volume of water. The physical properties are expressed in different units.

It is very important that the analytical result be reported as a specific value together with the units in which it has been determined. There are different units in which an analysis can be reported and if the units are not stated the result can be interpreted using the wrong units. This will give rise to incorrect quality assessments and wrong decisions about the fitness for use of a particular water.

SI units are to be used where possible. However, non-SI units are often used in the literature and it is therefore important that everyone involved in water quality analysis and assessment be aware of the different units.

What are the units in which the chemical quality of domestic water is expressed?

The quantity of dissolved chemical constituents in water is normally expressed in concentration units, i.e. mass per volume, mostly in milligram per litre (mg/ℓ). There are, however, also other concentration units which are used for certain chemical constituents as is shown in the following sections.

The concentration of substances in water may be expressed using different sets of units. These different sets are used for different purposes, e.g. concentration in milligramme per litre (mg/ℓ) is normally used in water quality assessment, while molar concentrations (mol/ℓ) are used when doing calculations of the mass of substances that react in chemical reactions. Different sets of units are also used for expressing hardness or chemical stability of water.

The different sets of units are discussed in more detail below in the boxes marked **Set 1 to Set 5**.

- Concentration in physical mass per volume (Set 1)
- Concentration in molar mass units per volume (Set 2)
- Concentration in mass per volume on a defined basis (Set 3)
- Units of expression for chemical stability of water (Set 4)
- Units of expression for water hardness (Set 5).

SET 1: PHYSICAL MASS PER VOLUME

Concentration units of (physical) mass per volume

1. Milligram per litre, mg/ℓ – most commonly used concentration unit for most substances in water.
2. Parts per million, ppm - for dilute solutions ppm is practically identical to mg/ℓ, but it is not acceptable in the SI system and should preferably not be used.
3. Microgram per litre, µg/ℓ - used for very low concentrations. 1000 µg/ℓ = 1 mg/ℓ.
4. Parts per billion, ppb – for dilute solutions ppb is practically identical to µg/ℓ, but is not acceptable in the SI system and should preferably not be used.
5. Gram per litre, g/ℓ – used for high concentrations. 1000 mg/ℓ = 1 g/ℓ.
6. Percentage, % - used for high concentrations, e.g. for the concentration of process chemicals chemicals. Percentage is similar to parts per hundred, or pph or g/100g.

SET 2: MOLAR MASS UNITS PER VOLUME

Concentration units in molar mass units per volume

For certain purposes it is essential to express the concentration of a substance in chemical mass units, rather than physical mass units. For example, for calculations involving titrations, solubility- and reaction equilibria the units discussed below must be used.

Molarity

1. Number of moles of solute (dissolved substance) per litre of solution, mol/ℓ. One mole of a substance is defined as an amount consisting of 6,023 x 10^{23} particles of the substance (atoms, ions, molecules or formula units). The mass of one mole of a substance can conveniently be calculated as the molecular or formula mass expressed in grams (see **Note Box 3**). Concentration in mol/ℓ is known as the molar concentration or molarity of the solution.
2. Millimoles per litre, mmol/ℓ where one millimole is 1/1000 of one mole or the mass of one millimole calculated as the molecular or formula mass expressed in milligrams.

Normality

3. Equivalents of solute per litre of solution, eq/ℓ where one equivalent is equal to one mole multiplied by a factor to represent the reacting power of the substance (see **Note Box 3**). This is known as the **normality** of the solution. A 1Normal solution is equal to 1 equivalent of solute per litre of solution.
4. Milli-equivalents of solute per litre of solution, meq/ℓ where one milli-equivalent is equal to 1/1000 of one equivalent.

NOTE: Normality does not form part of the SI system of units (see p18)

SET 3: MASS PER VOLUME ON DEFINED BASIS

Concentration units in mass per volume expressed on a defined basis

1. Milligram per litre expressed on the basis of the particular compound or ion or an element in the compound. The concentration of nitrate (NO_3^-) , for example, may be expressed either as mg/ℓ NO_3^- (nitrate) or as mg/ℓ NO_3^-N (nitrogen). Similarly, the concentration of phosphate may be expressed as mg/ℓ PO_4^{3-} or mg/ℓ P.

   The conversion between the different nitrogen units from mg/ℓ NO_3^- to mg/ℓNO_3^--N or from mg/ℓ N to mg/ℓ NO_3^- is done by multiplying the measured concentration by the ratio of the molar masses of N/ NO_3^- or NO_3^-/N respectively. The conversion is as follows:

   mg/ℓ NO_3^-x Molar mass of N / Molar mass of NO_3^- = mg/ℓ NO_3^-x 14,01/62,01 =mg/ℓ N

   where 14,01 is the molar mass of nitrogen and 62,01 is the molar mass of NO_3^-.

   To convert from mg/ℓ NO_3^-N to mg/ℓ NO_3^-

   mg/ℓ NO_3^- N x 62,01/14,01 = mg/ℓ NO_3^-

2. Milligram per litre expressed as mg/ℓ of another compound. In the case of hardness, alkalinity and the concentration of chemicals used for softening of water, concentrations are conventionally expressed as mg/ℓ calcium carbonate, mg $CaCO_3$/ℓ. This means that the concentration given is not that of the element, ion or compound itself but it is converted to equivalent amounts of $CaCO_3$ units.

   The calculation to convert mg/ℓ calcium as Ca^{2+} to mg/ℓ as $CaCO_3$ is done by multiplying mg/ℓ Ca^{2+} by the ratio of the molar mass of $CaCO_3$ to the molar mass of Ca^{2+}:

   mg/ℓ Ca^{2+} x 100,09/40,08 = mg/ℓ $CaCO_3$,

   where 100,09 is the molar mass of $CaCO_3$ and 40,08 is the molar mass of Ca^{2+}.

   It should be noted that conversions of other substances (e.g. Na^+) to mg/ℓ as $CaCO_3$ is more complex than for Ca^{2+} since the conversion is done by multiplying the measured concentration by the ratio of the equivalent mass of $CaCO_3$ to the equivalent mass of the paticular substance.

See **Note Box 4** for an example of these calculations and a table of conversions.

SET 4: CHEMICAL STABILITY UNITS

Units of expression of chemical stability of water

Chemical stability of water has to do with corrosion and scale-forming properties of water. Chemically-stable water is defined as water that would neither form calcium carbonate scale nor dissolve precipitated calcium carbonate, i.e. is saturated with respect to $CaCO_3$. Water that is undersaturated with respect to $CaCO_3$ tends to dissolve precipitated $CaCO_3$ leaving the metal surface unprotected and subject to corrosion.

There are different methods to determine chemical stability. The most-generally used indices are the *Langelier saturation index (LSI) and the Ryznar stability index (RI).*

Langelier saturation index

$LSI = pH - pH_s$, where pH_s is known as the saturation pH of $CaCO_3$ for the water at the specific temperature, and pH is the actual measured pH of the water.

If $LSI > 0$, the water is supersaturated with respect to $CaCO_3$ and would tend to precipitate $CaCO_3$, i.e. it is scale-forming.

If $LSI < 0$, the water is undersaturated with respect to $CaCO_3$ and will tend to dissolve $CaCO_3$, i.e. it is corrosive.

Ryznar index

$RI = 2\ pH_s - pH$

The following values may be used to interpret RI values:

RI = 4-6 water has scaling tendency
RI = 6-7 water is not corrosive and not scaling
RI = 7-9 water is corrosive.

The calculation of pH_s is rather complex and the reader is referred to the reference books where tables are available to facilitate calculation.

Calcium carbonate precipitation potential (CCPP) of the water. A quantitative, and therefore more satisfactory way of determining the chemical stability of water is to calculate the calcium carbonate precipitation potential of the water. A positive CCPP of about 4 mg/ℓ for domestic water has been shown to give adequate protection against corrosion without excessive $CaCO_3$ precipitation.

The determination of CCPP has been made very simple by using the ***Stasoft*** computer program which is available from the Water Research Commission. The same information required to calculate the LSI is also required to calculate the CCPP.

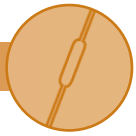
The information required to calculate pH_s as well as that required as input for the Stasoft program, include pH, total alkalinity, temperature, Ca^{2+} concentration as well as the ionic strength or total dissolved solids (TDS).

The *pH* is normally determined electrometrically using a pH meter.

Total alkalinity of water is a measure of its acid-neutralising capacity. It is principally a function of the carbonate, bicarbonate and hydroxide content of the water and is determined by titrating the water to a specific end point. Total alkalinity is determined by titrating with a strong acid to a pH end point of 4,5.

The *calcium concentration* can be determined using wet chemistry or more conveniently by means of atomic absorption.

The *ionic strength* is a function of the total dissolved ionic solids (salts) in the water and can be determined gravimetrically or more conveniently, by means of the electric conductivity.



A check on the accuracy of the analysis can be done by means of a cation/anion balance. This is done by comparing the total cation concentration in meq/ℓ to the total anion concentration in meq/ℓ (or the concentrations expressed as mg/ℓ $CaCO_3$). In the example in Note Box 5 the totals differ by less than 1% and the analysis is therefore accepted as accurate enough. (see p 18)

SET 5: WATER HARDNESS UNITS

Units of expression of water hardness

The hardness of water is determined by the concentration of divalent cations in the water, mostly calcium and magnesium. Hardness affects the lather-forming ability of water with soap. The different forms of hardness are:

- carbonate or temporary hardness, which is caused by calcium and magnesium associated with bicarbonate in the water,
- non-carbonate or permanent hardness, which is caused by calcium and magnesium associated with ions other than bicarbonate such as chloride and sulphate,
- calcium hardness, caused by all the calcium ions in solution,
- magnesium hardness, caused by all the magnesium ions in solution, and
- total hardness, which is the sum of calcium and magnesium hardness.

The following table gives an indication of classification of waters in terms of hardness:

Hardness classification	Total hardness as mg/ℓ $CaCO_3$
Soft	Less than 50
Reasonably soft	50 to 100
Slightly hard	100 to 150
Reasonably hard	150 to 250
Hard	250 to 350
Very hard	More than 350

All the different forms of hardness are expressed in mg/ℓ $CaCO_3$. There are a number of other hardness units which are also used, e.g. those specified by manufacturers of washing machines for water used in washing machines. The following table gives the conversion between the different sets of hardness units.

Conversion of hardness units

	mg/ℓ $CaCO_3$	°G	°E	°F
mg/ℓ $CaCO_3$ 1	0,056	0,0702	0,100	
German degree (°G)	17,8	1	1,25	1,78
English degree (°E)	14,3	0,798	1	1,43
French degree (°F)	10,0	0,560	0,702	1

Note Box 3: Moles and molarity

The gram mole or mole is derived from the concept of the "chemical amount" of a substance. It is convenient to group atoms or molecules in so-called counting units which contain the same number of atoms or molecules.

This counting unit is called a **mole** (after the Latin *moles* meaning "heap" or "pile"). One mole of a compound e.g. water contains $6{,}023 \times 10^{23}$ molecules and is a quantity with a mass in gram equal to the molecular or formula mass of water, i.e. 18,02 g/mol.

It is significant that one mole contains the same number of molecules, atoms or ions whatever the compound or element involved. This number of molecules is called Avogadro's number and is approximately $6{,}023 \times 10^{23}$

By definition one mole of a substance contains an Avogadro's number of atoms, molecules, or ions.

Therefore $6{,}023 \times 10^{23}$ atoms of oxygen = 15,9994 g O (usually rounded off to 16); and

$6{,}023 \times 10^{23}$ molecules of oxygen = 31,998 g O_2 (usually rounded off to 32).

Similarly, 6×10^{23} molecules of water = 18,02 g H_2O (usually rounded off to 18).

The **molar mass** of a substance (MM) is the mass in grams of one mole of particles (atoms, molecules or ions) of that substance (element, compound or ion).

A one **molar solution** consists of one mole of a substance dissolved in water to make a solution of one litre and is indicated as 1 M. A 0,5 M solution will contain 0,5 moles of substance per litre.

A one **molal solution**, on the other hand, consists of one mole of substance dissolved in one kg of water (note: 1 mole + 1 kg water, compared to 1 mole made up to 1 litre).

NOTE: Normality and equivalents per litre (eq/ℓ) do not form part of the SI system of units. These concepts are, however, included in this Guide since they are useful to illustrate the concept of the cation/anion balance in water analysis. Furthermore, concentration units of eq/ℓ are generally used in certain sectors of the water industry, notably ion exchange.

Note Box 4: Normality and equivalent mass

The **Normality** (concentration expressed in equivalents per litre) is a measure of the reacting power of a solution.

One equivalent of one substance always reacts with one equivalent of another substance.

The equivalent mass of a compound is that mass of the compound which contains one mole of available hydrogen or its chemical equivalent. The equivalent mass of a compound can be determined as follows:

Equivalent mass = Molar mass / z,

where z is a factor which depends on the chemical context (chemical reaction involved). For acids the value of z is equal to the number of moles of H^+ displaceable from one mole of acid, e.g. for HCl, z = 1, while for H_2SO_4 , z = 2.

For bases, the value of z is equal to the number of moles of H^+ with which the base will react. For NaOH, z = 1 and for $Ca(OH)_2$, z = 2.

For oxidation/reduction reactions, the value of z equals the change in oxidation number of the particular compound involved in the reaction.

For other compounds such as salts which are not involved in oxidation/reduction reactions, the value of z equals the valence (bonding ability) of the compound.

Calculation

What is the equivalent mass of NaOH?

The molar mass of NaOH equals 22,990 + 15,9994 + 1,00797 = 39,998 g/mol (usually rounded off to 40).

The equivalent mass of NaOH equals 39,998 / 1 = 39,998 g/eq. (z = 1)

What is the normality of a solution containing 10,0 g of NaOH per litre?

Normality = Number of equivalents of NaOH per litre

10,0 / 39,998 = 0,250 equivalents per litre (0,250 eq/ℓ)

Normality = 0,250 N.

Note Box 5: Cation/anion balance

A water analysis giving the major inorganic constituents (cations and anions) and their concentrations in mg/ℓ is shown in the first two columns of the table below.

Column 3 shows the molar, or formula mass of each ion which are given in the Periodic Table of Elements and in chemistry handbooks, g/mol or mg/mmol.

Column 4 shows the molarity (in mmol/ℓ) calculated by dividing mg/ℓ of the ion by its molar mass. For example, for Ca^{2+} : 107 / 40,078 = 2,68 mmol/ℓ.

Column 5 shows the equivalent mass calculated by dividing the molar mass by the valence of the ion (z). For example, for Ca^{2+} : 40,078 / 2 = 20,039 g/eq..

Column 6 shows the normality in meq/ℓ calculated by dividing mg/ℓ of ion by the equivalent mass. For Ca^{2+} : 107 / 20,039 = 5,35 meq/ℓ.

Column 7 shows the concentration expressed in mg/ℓ $CaCO_3$ calculated by multiplying mg/ℓ of the ion by the ratio of the equivalent mass of $CaCO_3$ (50,044 mg/meq) to equivalent mass of ion.

For Ca^{2+}: 107 x 50,004 / 20,039 = 267 mg/ℓ as $CaCO_3$.

Cations	**Concentration of ion, mg/ℓ**	**Molar mass, mg/mmol**	**Molarity, mmol /ℓ**	**Equivalent mass, mg/meq**	**Normality, meq/ℓ**	**Concentration mg$CaCO_3$/ℓ**
Ca^{2+}	107	40,078	2,67	20,039	5,34	267
Mg^{2+}	20	24,305	0,82	12,152	1,64	82
Na^{+}	50	22,990	2,17	22,990	2,17	109
K^{+}	15	39,098	0,38	39,098	0,38	19
Total cations					**9,53**	**477**
Anions	**Concentration of ion, mg/ℓ**	**Molar mass, g/ℓ mg/mmol**	**Molarity mmole /ℓ**	**Equivalent mass, mg/meq**	**Normality, meq/ℓ**	**Concentration mg$CaCO_3$/ℓ**
Total Alkalinity as HCO_3^-	260	61,017	4,26	61,017	4,26	213
SO_4^{2-}	117	96,064	1,22	48,032	2,44	122
Cl	90	35,453	2,54	35,453	2,54	127
NO_3^-	20	62,005	0,32	62,005	0,32	16
Total anions					**9,56**	**478**
% Difference= 100 (Total cations-total anions)/ Total anions					-0,31%	-0.21%

What are the units in which the physical quality of domestic water is expressed?

*The physical and aesthetic properties of water are normally **not** expressed in concentration units. Each property is expressed in specific units as indicated below.*

- **Electrical conductivity (EC)** of water is measured in units of milliSiemens per metre, mS/m. Other non-SI units which are still used include µS/cm which is numerically equal to mmho/cm. Conversion to mS/m is as follows:

  mS/m = µS/cm x 0,1.

  Electrical conductivity is a measure of the ability of the water to conduct an electric current. Since the electric current is conducted through the movement of ions in solution, EC also gives an indication of the concentration of the ions or total dissolved salts (TDS) in the water. For domestic water the EC value may be used to estimate the TDS concentration in mg/ℓ by multi plying the EC in mS/m by a factor of 6,5 (this factor of 6,5 may vary to some extent for different waters).

  mg/ℓ TDS = EC x 6,5.

- **The pH of water** is measured in pH units. The pH value is a measure of the molar concentration of hydrogen ions, $[H^+]$ in the water expressed as a logarithmic value. The pH gives an indication of how acidic or basic the water is.

  Definition: $pH = -\log [H^+]$, where $[H^+]$ is the concentration of hydrogen ions in mol/ℓ.

  The reason that $[H^+]$ is expressed in this manner is because the concentration values are extremely small. For example, the $[H^+]$ at a pH of 7 is equal to 10^{-7} moles/ℓ. (See Note Box 6)

- **Turbidity** is expressed in nephelometric turbidity units, NTU. It is determined by comparing the intensity of light scattered by the water sample to the intensity of light scattered by a standard reference in the turbidity meter. Older instruments may still measure in Formazin turbidity units (FTU) or in Jackson turbidity units (JTU). These units are numerically equal to NTU.

- **Colour** of water is expressed in Hazen units where one Hazen unit **represents** the colour when 1 mg/ℓ platinum (as chloroplatinate) is dissolved in 1 litre water. **True colour** is caused by dissolved substances in the water while **apparent colour** includes colour caused by colloidal substances in the water. True colour is determined after filtration and apparent colour on the unfiltered sample

- **Taste** and odour of water are expressed as threshold taste number (TTN) and as threshold odour number (TON) respectively. The threshold numbers are determined by diluting the sample with taste-free or odour-free water until the least perceptible taste or odour is detected.

  TON = (mℓ sample + mℓ odour free water)/mℓ sample.

  TTN = (mℓ sample + mℓ taste free water)/mℓ sample.

What are the units in which the microbiological quality of water is expressed?

*The microbiological quality of water is reported as **counts** or **numbers** of colony-forming units (cfu) of specific organisms **per volume** of water, e.g. 10 cfu/100mℓ.*

Unlike chemical substances which are dissolved and evenly distributed in water, micro-oganisms occur as particles and are therefore not uniformly distributed in water. They may cluster together with the result that there could be sections of a reservoir or water body with higher numbers of micro-organisms than in other sections. This means that one could find relatively large variations in the numbers of micro-organisms determined in different samples of water from the same source, or even the same sample.

It is, therefore, necessary to take more than one sample for analysis from a water source and to do determinations (usually) in triplicate on each sample. By analysing the results statistically a good indication of the microbiological quality of the water may be obtained.

Note box 6: The pH of a solution

In pure water small amounts of water molecules dissociate to form H^+ and OH^- ions.

$$H_2O \qquad H^+ + OH^-$$

The product of the molar concentrations of these ions is a fixed value at (a specified temperature) and is called the ion-product constant of water, K_w

$$[H^+][OH^-] = K_w = 1{,}000 \times 10^{-14} \text{ (at } 25^0\text{C)}$$

When acids or bases are added to water the concentration of H^+ and OH^- ions change and a new equilibrium is established, but the value of K_w must remain constant. This means that if $[H^+]$ increases, $[OH^-]$ will decrease to maintain the value of K_w.

Because the $[H^+]$ and $[OH^-]$ can vary over the very wide range of 10^{-1} to 10^{-14} mol/ℓ it is convenient to use a logarithmic scale to express the concentration. For this purpose the pH function was introduced as:

$$pH = - \log [H^+], \text{ where } [H^+] \text{ is the concentration of hydrogen ions in mol/}\ell.$$

This means that an H^+ concentration of 10^{-7} mol/ℓ is expressed as a pH of 7. At this pH the concentration of $[OH^-]$ must therefore also be 10^{-7} mol/ℓ in order to maintain the value of K_w. This value is therefore referred to as the neutral pH because the concentration of both ions is equal.

Similarly an $[H^+]$ of 10^{-3} mol/ℓ is expressed as a pH of 3 and the $[OH^-]$ must then be 10^{-11} mol/ℓ. All pH values below 7 are **acidic** and those above 7 are **alkaline**.

Because the pH scale is logarithmic, it means that a change of one pH unit is equal to a 10 times increase in concentration of the one type of ion and a 10 times decrease in concentration of the other type.

Note Box 7: Residual chlorine and breakpoint chlorination

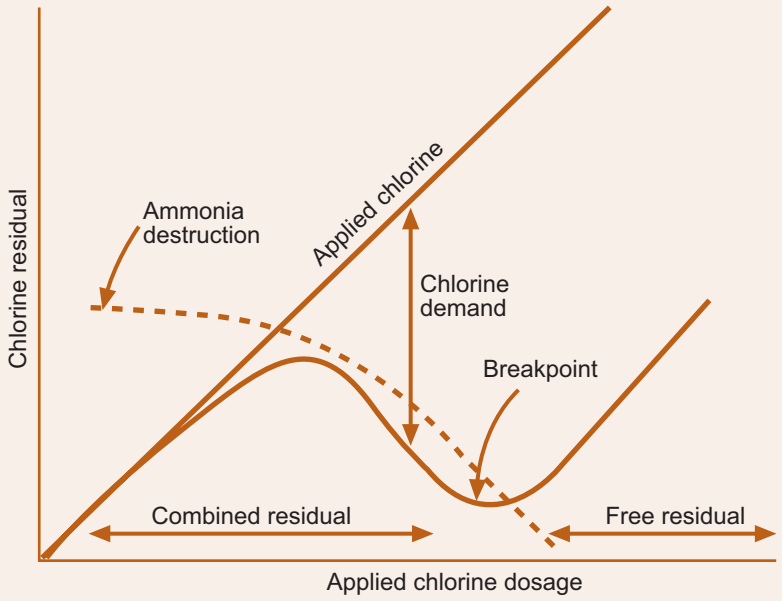
Chlorine may be applied to water in the form of chlorine gas, Cl_2 or in granular form, $Ca(OCl)_2$ or in solution form as bleach, NaOCl.

When these compounds are added to water they all yield the same chlorine species in solution, i.e. hypochlorous acid, HOCl and hypochlorite ion, OCl^- . These chlorine species are termed **free available chlorine**.

However, when ammonia, NH_3 is present in the water, the chlorine reacts with the NH_3 to form chloramines (monochloramine, dichloramine, trichloramine). These species are termed **combined available chlorine**. It is important to distinguish between these two catogories of chlorine types because free available chlorine is a much more powerful disinfectant than combined available chlorine.

An important concept in disinfection by means of chlorine is that of **breakpoint chlorination**.

Breakpoint chlorination refers to the reaction between chlorine and ammonia in water. When chlorine is added to water it will first react with ammonia (and other substances such as iron and manganese and certain organics) to form chloramines. When more and more chlorine is added it breaks down (oxidise) the chloramines and the point where all chloramines have been oxidised is termed the **breakpoint**. The following figure illustrates the concept of breakpoint chlorination:



Typical breakpoint chlorination curve

PART 2A

Planning, preparing for and performing the analysis

PART 1

GENERAL INFORMATION ON WATER QUALITY ANALYSIS

SECTION 1A

Familiarise yourself with the concept of water quality analysis

SECTION 1B

Familiarise yourself with the substances of concern in water for domestic use

PART 2

PLANNING, PREPARING FOR AND PERFORMING THE ANALYSIS

SECTION 2A

Familiarise yourself with the general methods of analysis for domestic water

YOU ARE HERE

SECTION 2 B

Plan for the analyses

SECTION 2C

Performing the analyses

SECTION 2D

Reporting of results

PART 3

QUALITY ASSURANCE CONSIDERATIONS

SECTION 3A

Familiarise yourself with the concepts of accuracy and uncertainty of analysis results

SECTION 3B

Analytical quality assurance

SECTION 3C

The implications of the quality of test results

Section 2A: Familiarise yourself with the general methods of analysis for domestic water

What are the general methods used for water quality analysis?

Methods for water quality analysis can be divided into three general categories:

- *Manual laboratory analytical methods (or so-called "wet" chemical methods of analysis)*
- *Instrumental and automated chemical and physical methods of analysis*
- *Microbiological methods of analysis.*

Chemical/physical methods of analysis

What are the manual laboratory methods of analysis?

The manual laboratory methods include:

- *Gravimetric methods (analysis by mass)*
- *Volumetric methods (analysis by volume)*
- *Colorimetric methods (analysis by colour).*

What are gravimetric methods of analysis?

Gravimetric methods of analysis means analysis by mass and include all determinations where the final results are obtained by means of precipitation and weighing of a solid, or where solids are filtered from the water (such as the determination of total suspended solids, TSS), or where water is evaporated to determine a residue (such as TDS).

In general, gravimetric methods are time-consuming and are avoided if alternative methods are available.

An accurate analytical balance is the key to good gravimetric analyses. These are delicate instruments and must be properly cared for in order for them to remain accurate. They should be kept on a stable and level base, be calibrated and kept clean and dry in a protected area to ensure accurate weighing.

The constituent to be determined is usually filtered from the water (precipitates or suspended solids) or the water is evaporated and the residue weighed. In the case of filtration an appropriate pre-weighed filter paper with the right pore size must be used and the solids must be transferred quantitatively to the filter.

Following filtration the filter paper with filtered material must be dried at a specified temperature e.g.105±2^{0}C until constant mass, then cooled to room temperature before weighing and calculating of the final mass.

What are volumetric methods of analysis?

Volumetric methods of analysis means analysis by volume and includes all those determinations where the volume of a standard solution is determined to reach the end point of a reaction, also known as titrimetry.

The equipment required for volumetric analysis include:

- a standard solution for the titration
- an indicator to show when the end-point of the reaction is reached
- volumetric glassware, i.e. pipettes and burettes.

A standard solution is defined as a solution whose strength (concentration) is known. Primary standards are usually salts of high purity which can be very accurately weighed and made up into a known volume solution. These are used to standardise secondary standards which are used in volumetric analyses.

It is convenient to use solutions which are equivalent in strength to one another for volumetric analysis because identical volumes of equivalent solutions will react. For this reason the concentration of laboratory solutions is often expressed in normality units, e.g. 1 N or as a fraction such as 0,5 N. However, the correct concentration units in the SI system are molar units, i.e. moles or millimoles per litre (See Note Boxes 4 and 5)

An **indicator** is a means of indicating that the end-point of a reaction is reached. There are two main types of end-point indicators, i.e. colour indicators and potentiometric indicators.

Two types of **colour indicators** may be distinguisehed: **Acid/base indicators** are organic compounds which undergo a definite colour change in well-defined pH ranges and which are therefore useful to indicate the end-point of neutralisation. It is obvious that the analyst should have good colour sense when using colour indicators otherwise the determination can be completely wrong.

Phenolphthalein is perhaps the best-known acid/base indicator. It changes from colourless to pink in the pH region of 8,2 – 8,4 and is used to indicate the end-point when caustic alkalinity (strong base) is determined. It is also used to measure carbonate ion (carbonate alkalinity) by indicating when all carbonate has been converted to bicarbonate.

Redox indicators are organic compounds which undergo a definite colour change in well-defined regions of redox potentials of test solutions. These indicators show different colours when they are in their reduced or oxidised structural forms. Where the colour change corresponds to the redox end-point, they can be used for redox titrations. Potentiometric titrations for redox reactions are also considered superior to the use of redox colour indicators.

A **potentiometric indicator** (pH meter) is superior to colour indicators in acid-base titration because the pH of the equivalence point of solutions vary depending on ionisation constants and concentration. Such titrations are referred to as potentiometric titrations.

Calculations. The data obtained during a titration must be translated into mass terms to be practically useful. If concentration is expressed in normality units of concentrations each mℓ of a 1,0 Normal solution contains 1 milli-equivalent (meq) of solute (see Note Box 4).

Therefore:

mℓ titrant x N = milli-equivalents of active material in titrant.

= milli-equivalents of active material (analyte) in sample solution.

The advantage of using equivalent solutions is that the milli-equivalents of active material in the titrant used is equal to the milli-equivalents of active material in the sample being titrated. These calculations are somewhat more complicated where concentrations are expressed as mol/ℓ (molarity).

What are colorimetric methods of analysis?

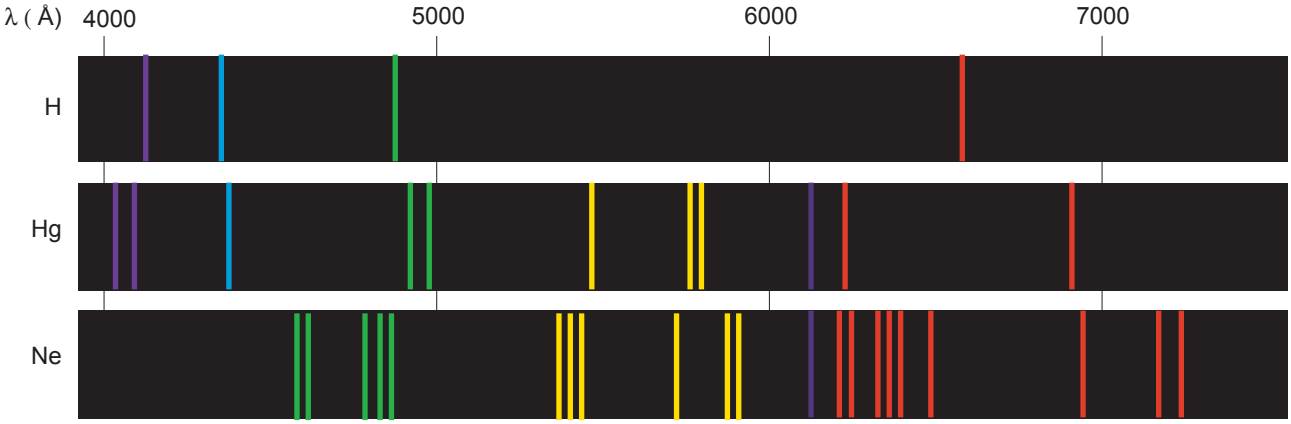
Colorimetric methods of analysis are methods where the colour of a solution to which a reagent has been added is directly proportional to the concentration of the solute of interest. The concentration can then be determined by comparing the colour intensity of the solution with the colour intensity of a reference standard.

Colorimetric methods are convenient, fast and economical for determining the concentration of a variety of compounds of interest in water for domestic use. These measurements may be made with different types of equipment ranging from colour-comparison tubes, photo-electric colorimeters to spectrophotometers.

Colour-comparison tubes, also known as Nessler tubes, have been used for many years for making colorimetric measurements (with the human eye as detector). However, their use in the laboratory has largely been replaced by photo-electric and spectrophotometric methods because these methods are more convenient and accurate. Colour-comparison tubes are still used as part of test kits for field use.

Colorimetric analysis can also be done using instruments such as photoelectric colorimeters. Use is made of a photo-electric cell as sensing device and these methods are therefore more sensitive and accurate than visual colour comparisons. These methods require a separate colour filter for each different chemical determination and this can add to the cost if many different substances have to be determined.

The modern spectrophotometer is an extremely valuable instrument for colorimetric analyses. It has a wide range of adaptability and is particularly useful where a wide range of determinations have to be made. Its versatility allows the best wavelength to be used for each determination. The spectrophotometer is discussed in greater detail below in the section on instrumental methods.



What are instrumental methods of analysis?

Instrumental methods involve the use of an instrument such as a pH meter or a spectrophotometer for the basic measuring function. There are a variety of sensitive instruments available for determination of a wide range of constituents in water for domestic use. These include instruments using:

- *optical methods,*
- *electrical methods and*
- *chromatographic methods of analysis.*

This category also includes other advanced methods such as mass spectroscopy, X-ray analysis, and nuclear magnetic resonance spectroscopy (NMR).

Instrumental methods tend to be more popular than manual methods (because manual methods involve a lot of manual laboratory work) but not all laboratories can afford the more sophisticated

and expensive instruments. Instrumental methods are also more sensitive than manual methods (i.e. can determine concentration at lower levels) These methods are better suited for routine analyses, especially when large numbers of samples have to be analysed.

Special training on a particular instrument is normally required to enable the analyst to operate the instrument effectively. However, many instruments such as pH meters and electrical conductivity meters are very simple to operate and can be regarded as "standard" laboratory instruments.

Most inorganic constituents can be determined using either an instrument or a manual method of analysis. For example, metals may be determined using atomic absorption spectrometry (AAS), while anions may be determined by means of ion chromatography. Both categories can also be determined using manual methods.

What are optical methods of instrumental analysis?

Optical methods of analysis measure interactions between radiant energy (such as visible light or ultraviolet radiation) and substances dissolved in water (solutes).

The basis of these methods of analysis is that when a beam of radiant energy such as white light is passed through a solution, the emergent beam will be lower in intensity than the entering beam. If the solution does not contain suspended material which scatter the entering beam, the reduction in intensity is due primarily to absorption of the light by the solution. If the degree of **absorption** is directly proportional to the solute concentration, then absorption measurement can be used as a method of analysis.

The intensity of the emerging beam and therefore the degree of absorption is usually measured using a spectrophotometer. Spectrophotometers may vary from simple and relatively inexpensive colorimeters to very sophisticated and expensive instruments that automatically scan the ability of a solution to absorb radiation over a wide range of wavelengths and automatically record the results of such measurements.

i) **High-temperature absorption methods.** Atomic absorption spectrometry (AAS) is a very useful method of analysis for a wide variety of elements at very low concentrations in water (trace elements). Elements such as iron, copper, nickel, zinc, calcium etc. can be deter mined fairly accurately to a fraction of a mg/ℓ.

   Each element has a characteristic wavelength that its atoms will absorb in a flame. A light source with wavelength readily absorbed by the element to be determined is directed through a flame into which the sample has been aspirated. The decrease in intensity of the light beam is a measure of the concentration of the element. A disadvantage of AAS is that a different light source must be used for each element. Because of the cost, the use of AAS is only viable where large numbers of samples have to be analysed.

ii) **High-temperature emission methods** of analysis rely on the fact that many elements, when subjected to suitable excitation (by means of heating or exposure to other high energy sources) will emit radiation of characteristic wavelength. The intensity of the emitted radiation at a particular wavelength can be correlated with the quantity of the element present.

   Emission methods include older methods such as flame photometry (for detection of metals such as sodium, potassium and calcium) to emission spectrometry methods such as inductively coupled plasma (ICP) methods. ICP is now used as a standard for determination of many metals in water. However, because of high instrument and operating costs and the need for skilled operators, its use is limited to larger laboratories where many samples have to be analysed on a routine basis.

iii) **Dispersion and scattering methods** of analysis are mainly used for the determination of turbidity in water. Turbidity is measured either by its effect on the transmission of light

(turbidimetry) or by its effect on the scattering of light (nephelometry).

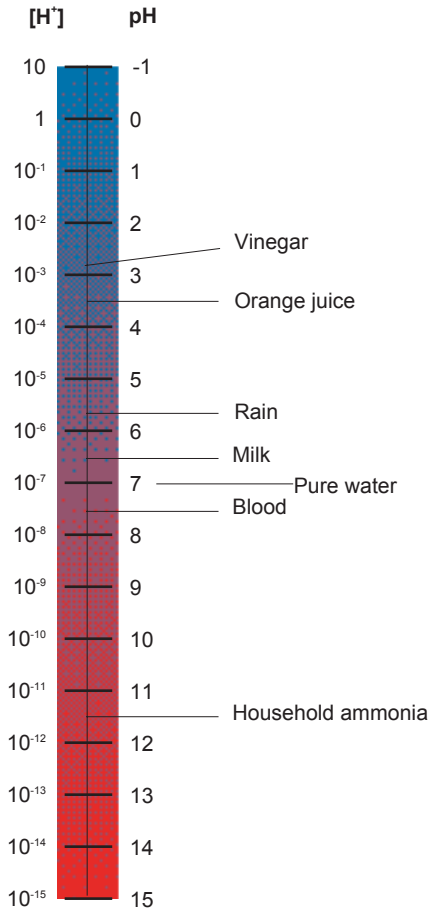
What are electrical methods of instrumental analysis?

The most widely-used electrical methods of analysis for water include pH and electrical conductivity measurements as well as the use of ion-selective electrodes.

The pH meter uses a glass electrode and a reference electrode which are immersed in the test solution and the electrical potential difference or voltage across these electrodes is a measure of the hydrogen ions concentration in solution and therefore of the pH of the solution. pH is defined as the negative logarithm of the hydrogen ion concentration expressed in moles per litre (see Note Box 6).

Electrical conductivity measurement is another widely-used electrical method of analysis. The conductivity of a solution is a measure of its ability to carry an electrical current. This ability varies with the number and type of ions in solution. Conductivity therefore gives an indication of the concentration of ions and therefore of the dissociated dissolved salts concentration in solution.

Ion-selective electrodes are selectively sensitive to a variety of ions such as potassium, sodium, fluoride, nitrate, ammonium and others. These ions can be determined by direct potentiometric measurement making this a very convenient method of determination of different ions.



It must be kept in mind that electrodes measure the activity of ions in solution and not concentration. Activity can be regarded as the "active or effective concentration" of an ion and is a function of the ionic strength of a solution. *Thus to use an electrode to determine concentration it has to be standardised in a solution of similar ionic strength.* Furthermore, electrodes measure specific ionic species and not complexes of that species. This means that the concentration of an element can be under-estimated if complex ions are present.

What are chromatographic instrumental methods of analysis?

Chromatographic analysis entails the separation of the components of a solution based on their relative affinity for partitioning between two phases. For example, different compounds may travel at different velocities in a mobile medium through a column packed with a certain medium (as a function of their affinity for the two mediums) and this allows separation of the different compounds.

Two different phases are commonly used in chromatography.

- **The stationary phase** may be either a solid or a liquid and
- **The moving phase** may be either a gas or a liquid.

When the moving phase is a gas and the stationary phase a liquid, the method is called **gas chromatography** and when the moving phase is a liquid and the stationary phase a solid,it is called **liquid chromatography**.

High performance liquid chromatography (HPLC) is especially useful for separating *non-volatile species and those that are not thermally stable* such as pesticides and proteins, thus extending the range of separations possible with chromatography. Some instruments use ion exchange resins as the stationary phase and the procedure is then called ion chromatography.

Gas chromatography (GC) entails the vapourisation of a liquid sample into a mobile gas phase followed by the separation of the different components so that they can be individually identified and quantified. The vapourised components are continuously swept through the packed column by a mobile phase (carrier gas). The components travel through the column at different rates so that they emerge from the column at different times. Their presence in the emerging gas is detected by chemical or physical means and the response recorded.

Each peak represents a specific chemical compound. The time taken for each compound to emerge from the column is a characteristic of that compound and is used to identify the compound. The area under the peak is proportional to the concentration of the compound in the sample.

Mass spectroscopy is often used in conjunction with gas chromatography (GC/MS) to give positive identification and quantification for a large number of individual organic compounds present in water. Basically a mass spectrophotometer is an instrument that sorts out charged gas molecules or ions according to the mass of the species.

It is important to note that the use of these methods requires well-trained and experienced analysts and that a great deal of skill is required to use chromatographic methods effectively.

Microbiological methods of analysis

What are microbiological methods of analysis?

There are different microbiological methods of analysis available including methods such as the membrane filter technique and the multiple tube fermentation technique which give quantitative information on specific groups of organisms. There are also qualitative methods available which give qualitative information on the presence or absence of organisms as well as advanced methods such as molecular methods of analysis.

What is the membrane filtration technique of microbiological analysis?

The membrane filter (MF) technique comprises filtering a specified volume (usually 100 mℓ) of the water to be tested through a presterilised membrane filter, placing of the membrane filter on a culture medium and incubating the filter plus medium for a specified period and time and then counting the number of viable colonies.

This technique is highly reproducible, can be used to test relatively large volumes of samples, and yields numerical results more rapidly than the multiple-tube technique. The MF technique has limitations particularly when testing water with high levels of turbidity, algae and non-coliform bacteria. In such cases it is advisable to conduct parallel multiple-tube tests to demonstrate the applicability of the MF test.

Coliform bacteria in the sample grow into colonies which can easily be counted using a suitable magnification device. The typical coliform colony has a specific colour and sheen, depending on the culture media. Sheen colonies can be verified as faecal coliforms by gas production after incubation in a suitable broth for 48 hours.

Coliform density is reported as coliforms/100 mℓ.

What is the multiple tube fermentation technique for total and faecal coliforms?

The multiple tube fermentation technique involves the fermentation of a specific substrate by organisms in the water sample which allows detection and identification of specific groups of organisms.

The coliform organisms comprise a large group of organisms that live in the intestines of warm-blooded animals as well as in other environments such as in soil. These organisms have the ability to ferment lactose with formation of gas and acid within 48 hours at 35°C. This ability to form gas and acid from lactose forms the basis of the multiple tube fermentation technique for total coliforms.

Faecal coliforms are much more specific indicators of pollution by human wastes as they can only grow in the intestines of warm-blooded animals. They have the ability to produce gas from a more specialised growth medium (EC medium) at an elevated temperature of 44,5°C. This ability forms the basis of the multiple tube fermentation test for faecal coliforms which is used to distinguish faecal coliforms from non-faecal coliforms.

Results of the examination of the multiple-tube technique is reported in terms of the most probable number (MPN) of organisms present. This number, based on certain probability formulas from statistical analysis, is an estimate of the mean density of coliforms in the sample. Bacterial density can be estimated from tables or from formulas.

What other methods are available to test the microbiological quality of water?

Other tests include:

- *Screening tests (available from different suppliers) which give an indication of the microbiological quality of water within a short period.*
- *Microscopic evaluation which gives information on larger organisms such as protozoa and algae. Special training and skills are required for effective interpretation.*
- *Free residual chlorine testing which gives an indication of disinfection of the water.*

All microbiological tests (with the exception of screening tests) yield an answer on the microbiological quality of water 24 or 48 hours after testing. This means that the water has been distributed and drunk by the time results become available. In contrast, the residual chlorine test give an immediate result which shows whether the water was disinfected and should therefore be of acceptable quality. This test only applies to situations where water is treated, e.g. in a treatment plant or disinfected at home by addition of chlorine compounds such as bleach.

Field test methods

For which analyses can field tests and test kits be used?

There are different field test methods and test kits available for a range of constituents. These methods are useful for determinations such as pH, electrical conductivity and residual chlorine. Test kits can also be used for screening samples and to get an indication of water quality.

Test kits typically include test strips and relatively inexpensive equipment to do certain basic analyses in the field or laboratory. The accuracy of the methods included in these kits vary over a wide spectrum from good to acceptable to poor. It is advisable to always calibrate the instruments before using them. The limitations of test kit methods must be recognised: they are useful to get an indication of water quality but it is not always advisable to use them as normal laboratory methods. Test kit analyses are expensive in terms of cost per analysis even though the test kit as such may not be expensive.

Test kits or field test methods are very useful to determine properties or substances such as pH, electrical conductivity and residual chlorine in the field (See Note Box 1, 6).

PART 2B

Planning for the analysis

PART 1

GENERAL INFORMATION ON WATER QUALITY ANALYSIS

SECTION 1A

Familiarise yourself with the concept of water quality analysis

SECTION 1B

Familiarise yourself with the substances of concern in water for domestic use

PART 2

PLANNING, PREPARING AND PERFORMING ANALYSES

SECTION 2A

Familiarise yourself with the general methods of analysis for domestic water

SECTION 2 B

Plan for the analyses

YOU ARE HERE

SECTION 2C

Performing the analyses

SECTION 2D

Reporting of results

PART 3

QUALITY ASSURANCE CONSIDERATIONS

SECTION 3A

Familiarise yourself with the concepts of accuracy and uncertainty of analysis results

SECTION 3B

Analytical quality assurance

Section 2B: Planning for the analysis

What does planning for an analysis involve?

Proper planning of the following aspects is essential to ensure a successful analysis:

- *Which substances and characteristics to analyse for*
- *The number and frequency of samples to analyse*
- *The form in which results must be reported and accuracy required*
- *The analytical methods to be used*
- *The required reporting format.*

Planning in large laboratories. In laboratories which are geared to do large numbers of analyses for different customers (in-house or external) on a daily basis a different level of planning is required compared to the smaller laboratory. Planning on a macro level is important for these laboratories to ensure sufficient resources to meet budgeted outputs. They normally have established analytical set-ups to do the typical analyses required for the assessment of water for domestic use and to monitor the performance of treatment plants.

Planning in smaller laboratories. The smaller laboratory, on the other hand, is normally not equipped to handle on a routine basis all the requests that it might receive for different analyses. Such laboratories, therefore, require more detailed planning on specific analytical aspects to ensure a good level of service to its customers.

Effective planning is only possible if it is done jointly between the analyst, the sampler and the person requesting the analysis. It sometimes happens that a sampler is simply instructed to take a sample at a particular site without proper briefing on the purpose of the sample. The analyst in turn is then confronted with a sample which has to be analysed also without proper briefing on the purpose. Very often the results from such an exercise are useless, for example because certain precautions may not have been taken since both sampler and analyst were not aware of what was expected.

The person requesting that a sample be taken and an analysis be done must consult with the analyst as to whether the laboratory is equipped to do the particular analysis to the required accuracy within the period that the result is required or whether it must be sent to another laboratory. Both sampler and analyst must be informed of the purpose of the analysis and any special requirements or precautions that have to be taken.

The person requesting sampling and analysis must communicate clearly requirements on the following aspects:

- The purpose for which the analysis is required
- The location, number and type of samples required
- The accuracy and precision of analysis required
- The required reporting format.

The sampler must communicate in the sampling report any relevant factors observed during sampling which could affect the analysis. This could include (refer to the *Sampling Guide, Volume 2):*

- Unusual physical appearance of the water body such as prolific algal growth
- Unusually high rate of inflow caused by heavy rains
- Unusual high or low water levels of the water body
- Possible sources of contamination such as animals in and around the water body, inflow of contaminated streams, etc.
- Any unusual factors or problems encountered such as possible contamination during sampling or possible problems with preservation or transport, etc.

On what basis are the substances to be determined selected?

The substances are selected on the basis that the use of the water dictates the substances that are to be determined.

Water use. Tables 1A to 1D, p 8-10, list all the different groups of substances that are relevant to the domestic use of water. When planning for an analysis the selection of substances from these groups must be carefully considered and all relevant factors should be taken into consideration.

For example, if the purpose is to assess the quality of domestic water at the point of use, the list of substances and the criteria will be different to that if the purpose is to evaluate water from a stream or a borehole as a possible raw water source for domestic use; or if the purpose is to investigate possible pollution of a reservoir or distribution system, or if the purpose is to monitor the performance of a treatment plant.

What are the main purposes for which water for domestic use are to be analysed?

The main purposes for which water for domestic use are analysed are:

- *domestic water at the point of use*
- *domestic water in a distribution system*
- *a water source that is used for domestic water*
- *domestic water during and after treatment.*

a) Point of use

The main objective when testing the quality of domestic water **at the point of use** is to determine the fitness of the water for human consumption, i.e. whether it is safe to consume. This means the water should be microbiologically safe, and also safe with respect to the presence of potentially harmful substances.

Testing the water for microbiological safety involves testing for the presence of total and/or faecal coliforms together with free chlorine and turbidity. These parameters give a very good indication of the microbiological quality of the water. If the free chlorine is >0,2 mg/ℓ and turbidity is <1 NTU it could be accepted that disinfection is effective and there should therefore be no faecal coliforms present (the reason that turbidity must be <1 NTU is that organisms might be shielded against the action of chlorine by colloidal material in the water). Total coliforms give additional information on bacteriological quality.

Domestic water at the point of use must also meet non-health related requirements, i.e. requirements related to aesthetics (mainly turbidity, colour, odour, taste). It should further also meet requirements associated with economics, i.e. it should not be corrosive or excessively scale-forming in order to avoid damage to pipes and fixtures such as geysers.

Testing water for potentially harmful substances is a difficult task since there can be many different harmful substances in water. These include substances which occur naturally in water, for example fluoride, substances introduced into the water through pollution such as nitrates and pesticides, as well as substances resulting from the treatment of the water such as trihalomethanes (THM).

Testing for organic compounds in water such as pesticides and THMs requires specialised equipment such as a gas chromatograph and mass spectrophotometer which is normally not available to smaller laboratories. Such analyses should therefore be referred to larger laboratories with the required equipment.

The substances to be included in an analysis programme to determine fitness for use at the point of use should be selected on the basis of the raw water source and quality, specifically the rate of change in quality, the treatment processes and reliability of operation of these processes as well as case-specific factors.

The frequency of analysis must also be specified in the programme. The important substances as far as health aspects are concerned should be analysed on a regular basis. Those related to aesthetics and economics can be done at lower frequencies.

b) Distribution system

The main objective when testing **domestic water in a distribution system** is to ensure that the water is fit for domestic use, specifically with respect to its microbiological quality. It is normally accepted that water leaving a treatment plant complies with all requirements for domestic water. This means that the water should contain sufficient residual chlorine to prevent bacterial regrowth in the distribution system and to afford disinfection should the water for some reason be contaminated in the distribution system.

The most important constituents in a monitoring programme for a distribution system should therefore be total and/or faecal coliforms and residual chlorine. It is important to recognise that when breakpoint chlorination is practiced (see Note Box 7) residual chlorine will be in the free available chlorine form. However, when chloramination is used the residual chlorine will be in the combined available chlorine form.

c) Raw water source

The main objective when analysing **water to be used as a raw water source** is to determine what treatment would be necessary to produce water that is fit for domestic use. The analysis programme for this purpose would normally include a comprehensive list of all substances which are relevant to domestic use. Such a comprehensive analysis programme would normally not be done by smaller laboratories but would be submitted for analysis to a large laboratory.

The full analysis programme could be repeated on a low frequency of once or twice per year, but certain key quality indicators should be determined on a regular basis especially if the quality is subject to changes.

d) Treatment plant

The main purpose when analysing **water from treatment processes** or a treatment plant is to monitor the performance of the processes or plant. The substances to be determined depend on the processes employed and the substances to be removed from the raw water. The substances to be determined in the final water from the plant are similar to those for domestic water at the point of use.

The frequency of analysis in this case is determined by the requirements to ensure efficient plant operation. For example, turbidity would be determined on a very regular basis (every few hours) to monitor the operation of sand filters, while other substances such as sulphate would be determined at much lower frequencies.

PART 2C

Performing the analysis

PART 1

GENERAL INFORMATION ON WATER QUALITY ANALYSIS

SECTION 1A

Familiarise yourself with the concept of water quality analysis

SECTION 1B

Familiarise yourself with the substances of concern in water for domestic use

PART 2

PLANNING, PREPARING FOR AND PERFORMING THE ANALYSIS

SECTION 2A

Familiarise yourself with the general methods of analysis for domestic water

SECTION 2 B

Plan for the analyses

SECTION 2C

Performing the analyses

YOU ARE HERE

SECTION 2D

Reporting of results

PART 3

QUALITY ASSURANCE CONSIDERATIONS

SECTION 3A

Familiarise yourself with the concepts of accuracy and uncertainty of analysis results

SECTION 3B

Analytical quality assurance

SECTION 3C

The implications of the quality of test results

Section 2C: Performing the analysis

What are the important aspects to observe when performing analyses?

The main points to observe during an analysis relate to safety, adherence to prescribed analytical procedures, use of prescribed quality chemicals and use of calibrated equipment and instruments according to the manufacturer's specifications.

What safety precautions have to be taken?

Standard safety precautions such as wearing of protective glasses, clothing, gloves, and shoes should be observed when working with hazardous substances such as acids, alkalis and other harmful substances. In addition, the analyst should ascertain any special hazards and risks associated with specific chemicals and observe the prescribed safety precautions. Furthermore, procedures for safe disposal of wastes generated during analysis such as waste toxic chemicals must be observed.

Safety equipment. It is the responsibility of the laboratory management to provide safety equipment such as fire extinguishers, eye-wash solutions, safety showers and protective gear but it is the responsibility of each individual to use the equipment as prescribed and to request equipment if it is not available. It is the responsibility of management to provide safety training to laboratory staff but it is the responsibility of each individual to request training if he/she feels a need for specific safety training.

What is the correct quality of chemicals, glassware, and equipment ?

Laboratory handbooks give the relevant information on quality requirements for different analyses and the level of accuracy required.

Normally "analytical reagent grade" chemicals and calibrated volumetric glassware should be used. Reagent grade water is usually prepared in the laboratory by means of distillation, reverse osmosis and/or ion-exchange.

PART 2D

Performing the analysis

PART 1

GENERAL INFORMATION ON WATER QUALITY ANALYSIS

SECTION 1A

Familiarise yourself with the concept of water quality analysis

SECTION 1B

Familiarise yourself with the substances of concern in water for domestic use

PART 2

PLANNING, PREPARING FOR AND PERFORMING THE ANALYSIS

SECTION 2A

Familiarise yourself with the general methods of analysis for domestic water

SECTION 2 B

Plan for the analyses

SECTION 2C

Performing the analyses

SECTION 2D

Reporting of results

YOU ARE HERE

PART 3

QUALITY ASSURANCE CONSIDERATIONS

SECTION 3A

Familiarise yourself with the concepts of accuracy and uncertainty of analysis results

SECTION 3B

Analytical quality assurance

SECTION 3C

The implications of the quality of test results

Section 2D: Reporting of results

How is an analysis report prepared?

An analysis report is a "contract document" which provides requested information on the quality of a water sample to a client. The information must be in the format requested by the client and must be accurate within the confidence level agreed with the client.

The analysis report normally consists of a table of values for each substance and property determined with the units in which the results are reported together with an indication of the confidence limits of the result

The report should also contain comments on any aspect which the analyst wishes to bring to the attention of the client, for example if the sample appears to have been contaminated or if it contained sediment, etc.

Finally, the report should be certified by the analyst and the laboratory manager as having been performed according to a quality assurance programme and within the confidence limits specified (see Part 3).

PART 3A

Quality assurance considerations

PART 1

GENERAL INFORMATION ON WATER QUALITY ANALYSIS

SECTION 1A

Familiarise yourself with the concept of water quality analysis

SECTION 1B

Familiarise yourself with the substances of concern in water for domestic use

PART 2

PLANNING, PREPARING FOR AND PERFORMING THE ANALYSIS

SECTION 2A

Familiarise yourself with the general methods of analysis for domestic water

SECTION 2 B

Plan for the analyses

SECTION 2C

Performing the analyses

SECTION 2D

Reporting of results

PART 3

QUALITY ASSURANCE CONSIDERATIONS

SECTION 3A

Familiarise yourself with the concepts of accuracy and uncertainty of analysis results

YOU ARE HERE

SECTION 3B

Analytical quality assurance

SECTION 3C

The implications of the quality of test results

Section 3 A: Familiarise yourself with the concept of measurement and associated uncertainty

How can one tell if a test result is exactly right?

It is not possible to tell if a test result is exactly right. The reason is that the result of a measurement (test) is only a best-estimate or approximation of the true value of the determinand being measured (e.g. the concentration of a dissolved substance in water).

Why is a test result only a best-estimate?

When an analysis is repeated many times on the same sample of water, it will only very rarely happen that the analyst gets exactly the same result for each analysis. This is due to the inherent variability associated with all analytical techniques (Note Box 8). It is therefore, not possible to tell which of the different results is exactly right.

The final measurement result is, therefore, not an exact truth, but a best-estimate of the true value of the test with an associated measurement uncertainty (Note Box 8).

Note. The full statistical analysis of test results is a complex subject and falls outside the scope of this manual. This section, therefore presents only a simplified discussion of the most important aspects.

Note Box 8: The concept of uncertainty

The following example illustrates the concept of uncertainty. It is a simple example and has nothing to do with water analysis (in order that we don't get distracted by the merits of the analytical methods).

The assignment is to determine the number of salt grains in a 500 g pack of table salt.

Two possible approaches can be followed, i.e. *the full counting technique* in which it is attempted to count each grain of salt; or the *partial counting and extrapolation technique* in which the grains, in a small sample are counted and this result is extrapolated for the full pack.

The full counting technique would require extreme dedication and patience to physically count each and every grain – it will take about 16 months to complete the counting!! (0,5 hours to count 0,1 g gives 500 g/0,1 g x 0,5 hours = 2 500 hours).

If one uses the partial counting and extrapolation technique, a 0,1g sample could be taken and the grains counted. The result is then extrapolated by multiplying the result by 5 000 (the ratio of the mass of the full pack to the mass of the sample).

In both cases it would be highly unlikely that one would end up with a result which matched the true number of grains in the pack because of the following possible sources of error:

Full counting technique

- fatigue, loss of concentration, variable visual ability of the person counting;
- the number of crushed or damaged grains;
- inconsistent record keeping;
- spillages, etc.

Note Box 8: Continued

Partial counting & extrapolation technique

- the accuracy of the balance used to weigh the 0,1g of salt;
- the compounded error resulting from the multiplication factor of 5 000;
- the representivity of the 0,1 gram sample taken from the pack;
- the homogeneity of the grain sizes and mass, etc.

Both measurement techniques would therefore produce different results. In fact, if one were to repeat the counting many times, one would get different results each time. This is due to the inherent sources of errors (Note Box 8) associated with each technique and which contribute to the overall measurement uncertainty.

Both mesurement methods have inherent errors which will contribute different degrees of uncertainty to the final results of each measurement. Each of these errors is controllable to some extent. Some can be eliminated but many can be reduced to specified levels.

The final result from each mesurement is the number of grains counted (in the full counting technique) or calculated (in the partial counting technique). Neither of these results is an exact truth, but at the same time neither of the results would be wrong. Each result is an estimate of the exact truth with an associated uncertainty. The uncertainty can be quantified for each technique as is explained in Note Box 9.

Note Box 9: Sources of errors / variability

There are two types of errors which commonly contribute to measurement uncertainty. These are random errors and systematic errors.

Random errors result from many different non-measurable contributing sources of error, e.g:

- non-detectable variance in individual measurements used in the overall measurement, e.g. volume, mass, titration values, end-point distinction, etc;
- fluctuations in light intensity, temperature, humidity, power supply, electromagnetic effects; instrumental background noise and drift;
- human variance;
- standard reference variances; and
- non-detectable deterioration in resources - human (alertness/fatigue), equipment (calibration/ standardisation) and chemicals (quality).

The estimation of random error components can be done by repeating the measurement to obtain a replicate set of results. If the measurement is repeated often enough the results will display a pattern similar to that shown in Figure 1.

The normal (or Gaussian) distribution represents the expected distribution of results when a large number of repeated measurements are made.

Note Box 9: Continued

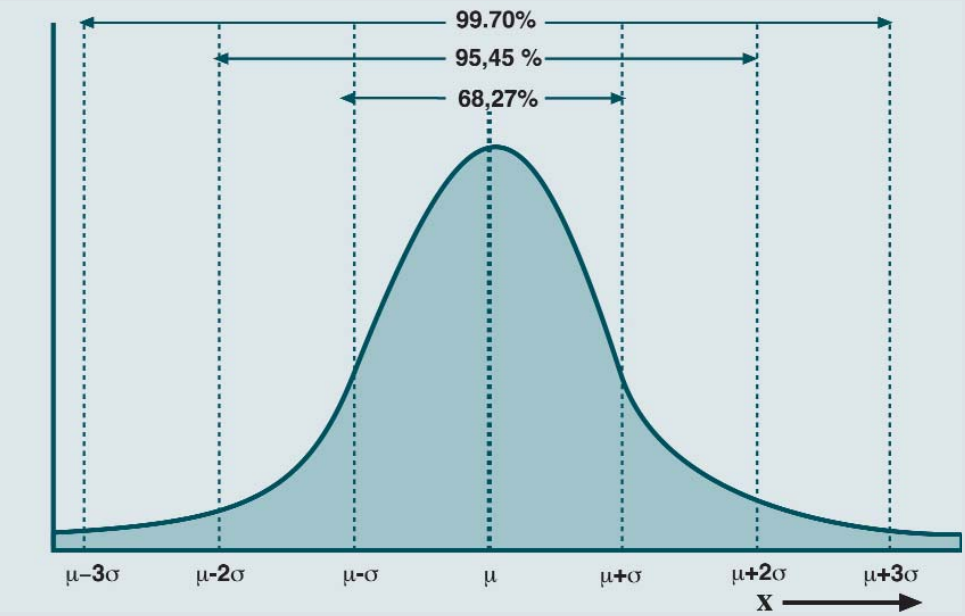


Fig 1 - Normal distribution curve

This distribution is due entirely to the inherent *random errors* present in the measurement technique.

The distribution is characterised by the **mean** (the average of all the values in the full set of results) and **standard deviation** (a measure of the spread of results around the mean).

The mean can be expressed as $\bar{x}$ (sample average) for small sets of data (less than 30) or as **μ** (population average) for large sets of data.

The standard deviation can be expressed as ***s*** for small sets of data (or as σ for large sets of data).

The important characteristic of the distribution of the results (see Figure 1) is that:

- 68,3 % will lie between the mean and ±1 standard deviations;
- 95,5% will lie between the mean and ±2 standard deviations; and
- 99,7% will lie between the mean and ±3 standard deviations.

To obtain a confidence area or interval of 95% associated with the mean (i.e., 5% uncertainty) one would need the mean ±1,96 standard deviations.

Systematic errors result from a variety of distinct, measurable sources which can be determined, reduced and in some cases eliminated. Systematic errors usually produce a bias (shift) of the result from the true value. The sources of such error can be associated with the measurement technique (e.g. the technique only results in 83% recovery of an analyte due to incomplete

Note Box 9: Continued

extraction/digestion/fusion, etc.), and/or the resources used to implement the measurement technique (e.g. poor training of the analysts, poor calibration of equipment, etc.).

A measurement result with systematic error will also have the random error component. If the measurement is repeated often enough the results will display a pattern similar to that shown in Figure 2.

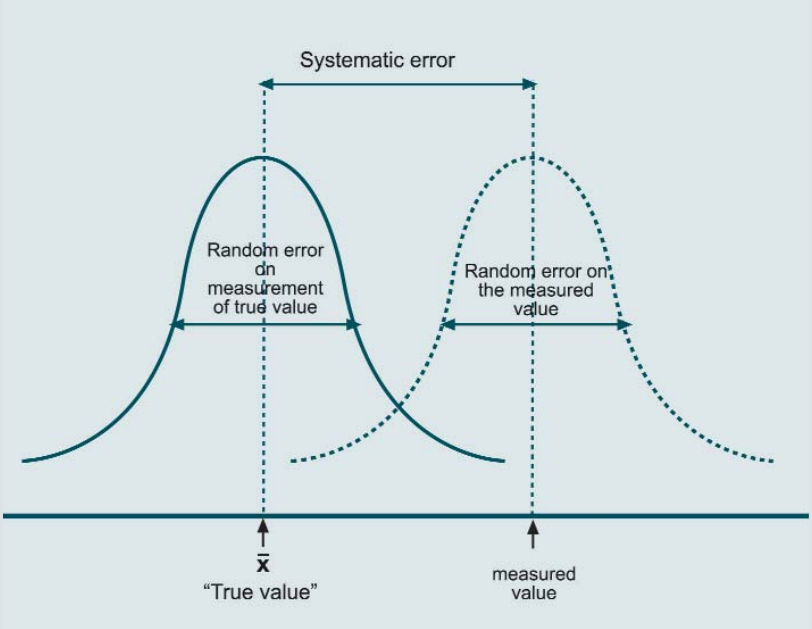


Figure 2 - Comparison of Systematic and Random Errors.

Note Box 10: Determination of the mean, standard deviation and 95% confidence Interval of results from a measurement

A water sample was submitted to the laboratory with the request to determine the concentration of nitrate (as N) in the sample and to express the result with a 95% confidence interval. The analysis was performed and a set of results obtained.

Before we do the calculations, it is necessary to refer to Figure 1 in Note Box 9. The first aspect to note is the basis of the normal distribution curve.

The normal distribution represents results from a large number of repeated measurements which can be approximated as the total population of values. This distribution is characterised by the Mean and the standard deviation of the population.

For a large set of data or **population** the **mean** is expressed as **μ**, while for a small set of data, or **sample** (less than 30) the **mean** is expressed as $\bar{\mathbf{x}}$.

Similarly the **standard deviation** for a **population** is expressed as **σ**, while for a **sample** the **standard deviation** is expressed as **s**.

The distinction between **population** and **sample** when evaluating a measurement is important because it is normally assumed that an estimation of the mean and standard deviation of a population

Note Box 10: Continued

is available, while no such estimation is available for a sample (small number of mesurements).

The second aspect to note from Figure 1 is the fact that 95,4% of all the values fall between -2 and +2 standard deviations. For a 95% confidence interval, therefore, we have to include all values between -1,96 and +1,96 standard deviations.

How do we determine the confidence interval if we have only one result available?

If we only have one *result* from the analysis of the water sample available, and we have no information on the population mean and standard deviation, it is not possible to quantify uncertainty. If, for example an inexperienced analyst produces a result of, say 45,3 mg/ℓ it is not possible to determine the level of uncertainty and the result has to be accepted at face value.

However, if we have only one result from an experienced analyst who has done many determinations over a long period of time using the same calibrated equipment an estimate of the population standard deviation, σ, will be available. If the measurement is 39,5 and σ is say 0,3 mg/ℓ we can proceed as follows to determine the 95% confidence interval (CI 95):

CI = 39,5 mg/ℓ ± (z x σ) mg/ℓ,

where z = 1,96 which is the statistical factor for 95%confidence interval, and σ =population standard deviation.

CI 95 = 39,5 mg/ℓ ± 1,96 x 0,3

= 39,5 mg/ℓ ± 0,59 mg/ℓ N

This expression of uncertainty indicates that there is a 95% probability of the true result lying between 38,91 and 40.09 mg/ℓ N.

How do we determine the confidence interval if we have a small number of results available?

(1) If we have an estimate of σ (population standard deviation) the range at the 95% confidence interval can be reduced by replicating the measurement, e.g. by doing four mesurements. The experienced analyst has done 3 more measurements on the same sample and we now have the following results:

39,5; 40,6; 40,2; 39,7 mg/ℓ N

The mean of these four values is 40,0 mg/ℓ N

{(39,5 + 40,6 + 40,2 + 39,7)/4}

The 95 confidence interval is then = 40,0 mg/ℓ ± (1,96 x 0,3)$\sqrt{n}$

Where n = number of replicates.

CI 95 = 40,0 mg/ℓ ± (1,96 x 0,3)/$\sqrt{4}$

= 40,0 mg/ℓ ± 0,29 mg/ℓ N

This means we have reduced the CI 95 by 50% by making four measurements instead of only one.

(ii) In the situation where we have four test results without an estimate of the population standard deviation, the CI 95 can be determined as follows:

The inexperienced analyst has returned after training on the analytical method and has produced the following four results on the sample:

Note Box 10: Continued

39,5; 41,2; 40,6 and 38,7 mg/ℓ N

The *mean* of the four test results, $\bar{x}$ =40,0 mg/ℓ N

(39,5 + 41,2 + 40,6 + 38,7)/4

The **standard deviation s** is calculated from:

$s = \sqrt{\Sigma} (x_i - \bar{x})^2 /(n-1)$

where x_i = the individual results, and

n = the number of results

The standard deviation of the four results s = 1.12 mg/ℓ N

In order to determine the 95% confidence interval in this case we have to use statistical tables, called Student t tables to determine the CI 95. These tables give a factor for the desired level of confidence and for the number of replicates tested.

CI 95 = 40,0 mg/ℓ ± (txs)$\sqrt{}$n mg/ℓ

where t = 2,35, the Student t factor for 4 tests, i.e. 3 degrees of freedom (n-1), n=number of results.

CI 95 = 40,0 mg/ℓ ± (2,35 x 1,12)$\sqrt{}$4

= 40,0 mg/ℓ ± 1,32 mg/ℓ N

The confidence interval is wider in this case due to a wider spread of the results resulting in a higher standard deviation, the lack of information of σ and the small sample size. The larger the sample size, the larger n becomes thereby reducing the confidence interval. Eventually when the sample size becomes very large, s approaches σ and the z factor can be used instead of the student t factor.

NOTE: There are a number of different versions of student t tables. All are correct but are based on different probability premises.

Are there different ways of reporting uncertainty of results?

There are mainly two methods used for reporting uncertainty.

One method is where the results are reported without an uncertainty figure with the numbers rounded, using the significant figure convention, to a figure which infers the degree of uncertainty (Note Box 10)

For example, a result reported as 39,5 mg/ℓ infers that the last digit, 5 is uncertain while a result reported as 39 mg/ℓ infers that the last digit, 9 is uncertain.

The second method of reporting the results includes an associated measurement uncertainty. This is usually reported at a 95% confidence interval in which the true value has a 95% probability of being within the defined range defined by the uncertainty.

Note Box 11: Significant figure convention

The significant figure convention is based on the rule that all digits in a result should be reliable or certain, except for the last digit which may be doubt.

For example, given the following four measurements: 9,76 mg/ℓ; 9,74 mg/ℓ; 9,79 mg/l; and 9,81 mg/ℓ, the mean is 9,775 mg/ℓ and the standard deviation is 0,031. It is obvious that the digit in the second decimal place is doubtful and all numbers in succeeding decimal places are therefore meaningless. Consequently, we need to round off the mean value.

The convention is that one rounds off to the nearest significant figure which would be 9,77 if the next digit was less than 5 or 9,78 if the last digit was greater than 5. However since the last digit is 5, do we round to 9,77 or 9,78? The rule of thumb is that if the value is midway between the upper and lower rounded values, it should be rounded to the nearest **even** number. Thus, our rounded value is 9,78 mg/ℓ.

The following examples explain the number of significant figures in various results:

0,00123	has 3 significant figures
1	has 1 significant figure
1,4	has 2 significant figures
1,46	has 3 significant figures
16	has 2 significant figures
16,7	has 3 significant figures
16,78	has 4 significant figures
179	has 3 significant figures
179,8	has 4 significant figures
179,89	has 5 significant figures
100 000	has 5 significant figures

In the process of calculating, how do we know how many significant figures we should keep? There are a few rules:

- For **addition and subtraction**, the number in the calculations which has the lowest number of decimal places determines the number of significant figures in the final result. For example: 5,6 + 6,089 + 1,3256, rounded off to

  5,6 + 6,1 + 1,3 = 13

- For **multiplication and division**, the individual components of the calculation are not rounded prior to the calculation. In general it is good practice to carry one extra digit beyond the last significant figure, saving the rounding to the final result. This avoids compounding rounding in a calculation which can result in rounding errors.

The final answer is rounded to the same number of significant figures as the smallest number of significant figures in the values being multiplied or divided. For example:

$$\frac{14,1 \times 0,1777}{8,7} = 0,28799$$, rounded to two significant figures gives 0,29

PART 3B

Quality assurance considerations

PART 1

GENERAL INFORMATION ON WATER QUALITY ANALYSIS

SECTION 1A

Familiarise yourself with the concept of water quality analysis

SECTION 1B

Familiarise yourself with the substances of concern in water for domestic use

PART 2

ANALYSIS PROJECTS

SECTION 2A

Familiarise yourself with the general methods of analysis for domestic water

SECTION 2 B

Plan for the analyses

SECTION 2C

Performing the analyses

SECTION 2D

Reporting of results

PART 3

QUALITY ASSURANCE CONSIDERATIONS

SECTION 3A

Familiarise yourself with the concepts of accuracy and uncertainty of analysis results

SECTION 3B

Analytical quality assurance

YOU ARE HERE

SECTION 3C

The implications of the quality of test results

How are the concepts of measurement and the associated uncertainty, applied to control analytical testing of water samples?

A quality assurance system is the orderly application of a set of operating principles, practices and actions necessary to remove or reduce errors that may occur in analytical operations as caused by personnel, equipment, supplies and analytical methodology.

Good laboratory practice requires the implementation of an effective quality assurance system in a laboratory in order to control, monitor, correct and improve operating conditions which contribute to the test result.

Laboratories will differ in their approach to quality management, depending on their commitment to quality, but in general a quality assurance programme could include the following:

- Staff organisation and responsibilities - assigning responsibility for detailed functions and activities throughout the laboratory
- Documenting all policies, procedures and methods for laboratory activities
- Developing and implementing an effective training programme for analysts which also provides for testing and verifying competency
- Controlling and monitoring, where appropriate, test and environmental conditions
- Implementing an effective maintenance programme for equipment
- Implementing a calibration programme for equipment which is traceable to national standards (**Note Box 12**)
- Validating test methods so that the capability of each method is known in terms of accuracy, precision, working range, detection levels, interferences, etc. (**Note Box 13**)
- Maintaining all records of tests on file
- Ensuring that results are reported clearly in a recognized and understandable unit of expression
- Implementing an effective control system which ensures that
  a) all quality aspects are audited regularly so that any potential problems can be identified and corrected
  b) internal quality control checks schemes are developed (**Note Box 14**)
  c) external proficiency testing schemes (bench marking) are joined (**Note Box 15**).

As indicated, the extent of quality assurance implementation is dependent on how serious the laboratory manager is about the reliability of the test result. Remember, once a test result is produced, it is but a number without any supportive evidence of closeness or accuracy to the true result. It cannot be inspected, measured or examined to say that it is a result of good quality. The quality has to be built into the result during the process of producing it and it is because of this fact that quality in the laboratory is so vitally important.

In recognition of its importance, a formal means of third party assessment for competence of laboratory practise has emerged worldwide. This form of **Competency Accreditation** has become the real benchmark of effective quality management in testing and calibrating laboratories. In South Africa, the SA National Accreditation System (SANAS) is the accreditation authority responsible for laboratory accreditation. A laboratory seeking accreditation will need to implement a quality management system that complies to:

- ISO 17025 (previously ISO/IEC Guide 25) General requirements for the competence of calibration and testing laboratories; and
- SANAS requirements.

The laboratory is accredited for competency in specified methods, i.e. the laboratory does not gain overall accreditation. It is accredited for the competent performance of specified tests as indicated in its scope/schedule of accreditation.

Note Box 12: Calibration

Equipment calibration using standards that are traceable to national and/or international standards is a vital part of the overall quality assurance programme of a laboratory.

The activity of calibration involves identifying the specific error associated with an instrument and making provision for such error in the measurement result or correcting the instrument so that the error is negated before the measurement. If the reference calibrating item or instrument is itself biased then all instruments that are calibrated with this item/instrument will be biased in their measurements. For this reason it is extremely important to maintain traceability to national standards.

There are eight base international standards to which traceability is sought. These are:

1. the *metre* for length;
2. the *kilogram* for mass;
3. the *second* for time;
4. the *ampere* for electric current;
5. the *kelvin* for temperature;
6. the *mole* for amount of substance;
7. the *candela* for luminous intensity; and
8. the *radian* for angular magnitude.

A typical programme of calibration within a well managed laboratory would involve:

- calibration of all mass balances by a **SANAS** accredited calibration laboratory (the SANAS accredited calibration laboratory will use mass pieces that have been calibrated against national standards by the National Metrology Laboratory (**NML**);
- calibration of reference standard temperature devices by the **NML**;
- calibration or verification of all incubators, water baths, ovens, furnaces, fridges, etc. using the reference standard device;
- calibration/verification of critical volumetric glassware (i.e. those used for preparation of primary standard solutions (volumetric flasks) and those used in critical parts of the test method (pipettes and burettes)
- calibration of spectrophotometers using standard spectrum filters or standard solutions; and
- instituting an equipment standardisation/calibration programme using well controlled high quality standards.

Note Box 13: Method validation

A test method is a technique which if applied or utilised under controlled conditions will produce a result with known uncertainty.

Once a laboratory has ensured that its analysts are trained and competent, and when all variables are controlled, it will need to determine the capability of the method, i.e.

- what accuracy or, conversely, what uncertainty can be expected from the method over its practical working range;
- what types of interferences can be expected and to what extent do they interfere with the result; and
- what detection levels can be achieved in different sample types.

This process is commonly called validation. A typical way of approaching validation is to prepare a validation trial where various studies are performed using reference materials, samples, spiked samples and samples with varying matrices to determine by replicate testing the precision (standard deviation), bias, interferences and detection levels.

Note Box 14: Internal quality control

Various techniques are used by laboratories in order to monitor the ongoing performance of a test so that the laboratory has a defined measure of assurance that the test is being applied under controlled conditions and that the method is producing reliable results.

The most common form of control is by use of *Control Charts* (See Figure 3) . The laboratory would typically use a standard material or sample, spiked or unspiked, and analyse this sample at a frequency of no less than 5% of throughput, i.e. once in every batch of 20 samples. The frequency can go as high as 15-20% depending on the complexity of the analysis.

The objective of the use of these control samples/standards is to ensure that the result produced by the method is within the acceptable tolerances, which are prescribed by the expected result (known or mean), together with the expected standard deviation associated with that result (refer Note Box 9 and 12).

Note Box 14 continued

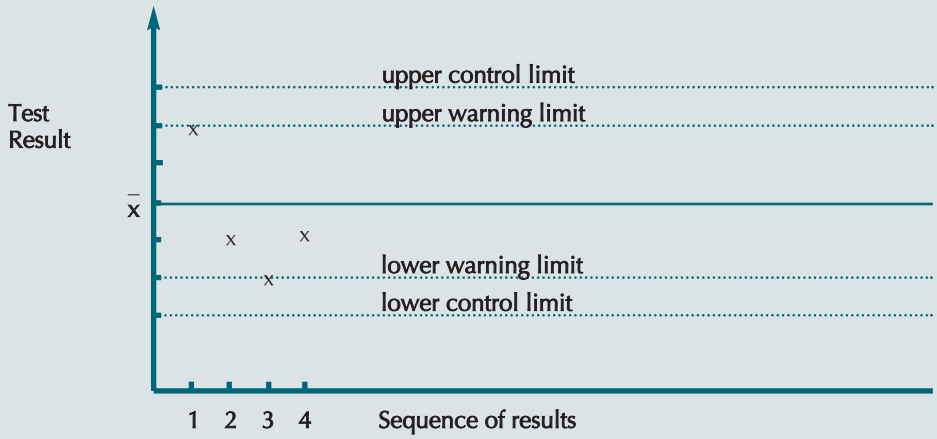


Figure 3 - Example of control chart with breach indicators

A typical range of control parameters would be:

- ± 2 x *s* as warning limits - if **two successive control results** breach this limit the method is considered out of control and needs to be investigated and corrected;
- ± 3 x *s* as control limits - if **one control result** breaches this limit, the method is considered out of control and needs to be investigated and corrected; and
- either side of the mean/known value - if **seven successive control results** are on the same side of the mid-line, the method is considered out of control and needs to be investigated and corrected.

Other, more sophisticated control charts may also be used, e.g., the x-R control charts, which controls both the accuracy (through the mean, $\bar{x}$) and precision (through the range, R)

Note Box 15: External proficiency testing (Benchmarking)

A Proficiency Testing Scheme is a programme whereby participating laboratories can benchmark their performance in testing a given set of samples against other participating laboratories.

Usually, the co-ordinator of a scheme will send out identical subsamples of a set of real and synthetic samples to all participating laboratories at the same time. The laboratories analyse these samples for the prescribed set of determinands and then return the results to the co-ordinator.

The co-ordinator of the scheme statistically analyses the results in such a way that laboratories can determine how close they were to the reference values (mean or standard/spiked values) and the extent of variance the laboratory has from the reference values.

Usually, the laboratories are coded so that each participant only knows its own code for benchmarking purposes.

PART 3C

Quality assurance considerations

PART 1

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SECTION 1B

Familiarise yourself with the substances of concern in water for domestic use

PART 2

ANALYSIS PROJECTS

SECTION 2A

Familiarise yourself with the general methods of analysis for domestic water

SECTION 2 B

Plan for the analyses

SECTION 2C

Performing the analyses

SECTION 2D

Reporting of results

PART 3

QUALITY ASSURANCE CONSIDERATIONS

SECTION 3A

Familiarise yourself with the concepts of accuracy and uncertainty of analysis results

SECTION 3B

Analytical quality assurance

SECTION 3C

The implications of the quality of test results

YOU ARE HERE

What are the implications of receiving test results from an uncontrolled test?

Results from uncontrolled tests can have serious implications:

- Since a result is a number without any tangible indication of its quality, the user of the results has no idea as to how accurate, or inaccurate, that result may be.
- Decisions made on the basis of inaccurate results may well have health or financial implication beyond the cost of paying for useless information. Such decisions could be focused around:

  a) compliance, or non-compliance, to specification limits;

  b) levy allocation or local authority discharge costs;

  c) process control of municipal and industrial treatment plants; and

  d) design of process and plant.

The implications of appropriate decision-making based on inappropriate data can be huge resulting in financial loss and increased health risk.

What are the implications of receiving test results from a controlled test?

Here the implications appear obvious, but some aspects may need detailed discussion:

- There is an assurance that the result is fit for purpose. It is reliable and if required it can be supplied with an associated indication of uncertainty. (Although many laboratories will supply the result as a rounded value, an accredited laboratory is obliged to supply uncertainty values for accredited tests upon request). Assurance is therefore added to the decision-making process resulting in a sound data base for planning.
- The uncertainty of the result can be used to assist in determining compliance or non-compliance to specification limits.

Why do we need uncertainty estimates to determine compliance or non-compliance to specification limits?

A test result with an uncerainty estimate allows one to calculate the range within which the result may fall taking into account the level of uncertainty.

This means that even though the given result may fall outside the specification, the probability exists that the true result may comply with the specification – given the range associated with the uncertainty. (see case study).

CASE STUDY

Let's consider the following two case scenarios:

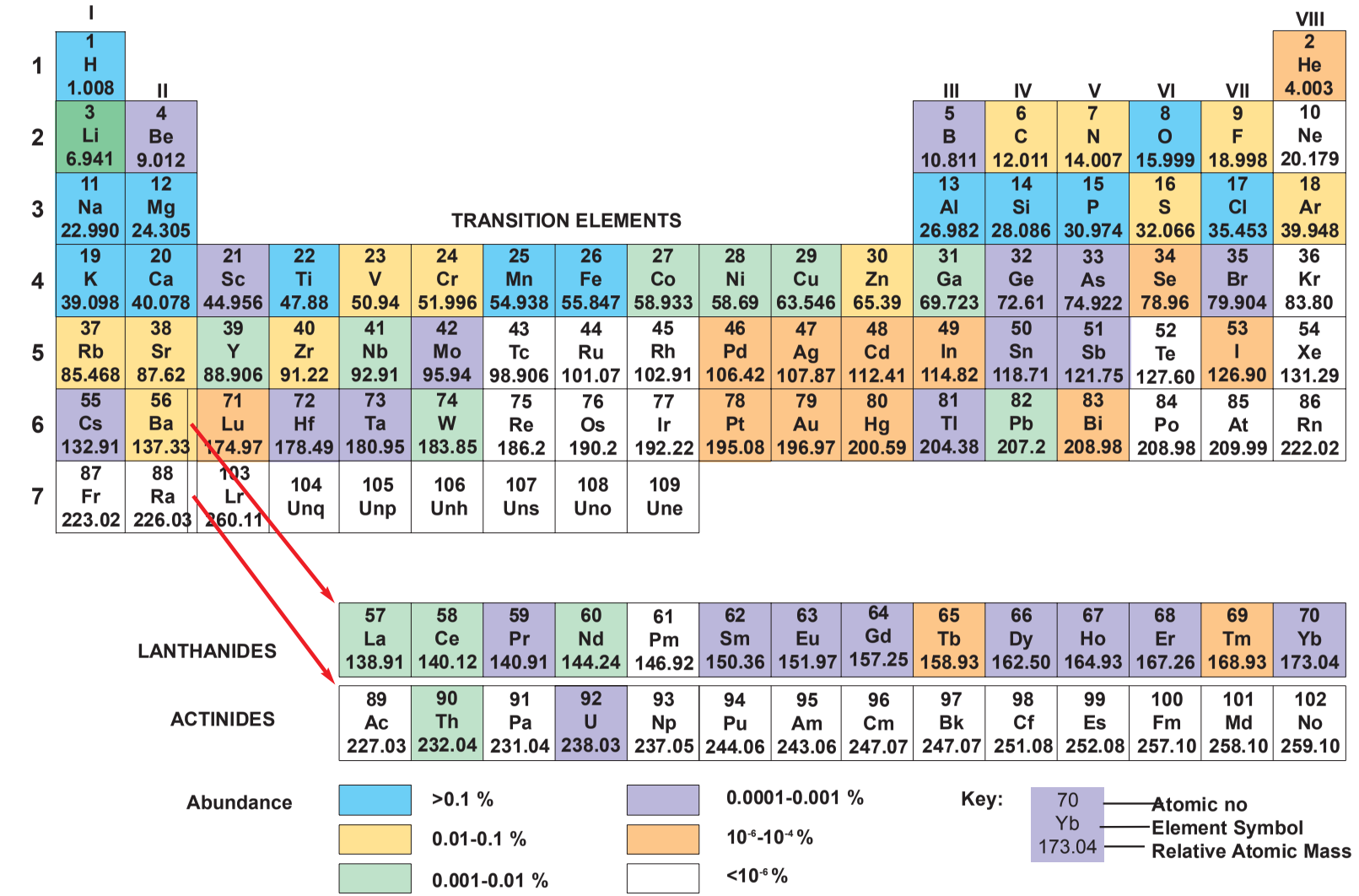
1) A test result is supplied for chemical oxygen demand (COD) for an effluent discharge which indicates that the COD is 81 mg/ℓ The prescribed limit for discharge is set at, for example, 75 mg/ℓ. Has the effluent COD level exceeded the prescribed limit?

Assume the result has been supplied by a laboratory that is accredited for COD. We have requested an indication of uncertainty which the laboratory has supplied in the form of a confidence interval at 95% as being ± 8 mg/ℓ. This means that there is a 95% probability that the true COD result is within 81 mg/lℓ± 8 mg/ℓ or between 73 mg/ℓ and 89 mg/ℓ. The result does not conclusively prove non-compliance since there is still a probability that the true result could lie between 73 mg/ℓ and 75 mg/ℓ. We cannot say with certainty, therefore, that the result indicates that the effluent has exceeded the limit of 75 mg/ℓ.

2) A test result is supplied for an effluent discharge which indicates that the COD is 87 mg/ℓ. The prescribed limit for discharge is set at, for example, 75 mg/ℓ. Has the effluent COD level exceeded the prescribed limit?

As in Scenario A, the 95% confidence interval is ± 8 mg/ℓ at this concentration level. This means that there is a 95% probability that the true COD result is within 87 mg/ℓ ± 8 mg/ℓ or between 79 mg/ℓ and 95 mg/ℓ. The result, in this case conclusively proves non-compliance to the 75 mg/ℓ limit based on a 95% probability level, i.e., we are 95% confident that the 75 mg/ℓ limit was exceeded.

PERIODIC TABLE



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