

# Introduction

## 1.1 THE ENVIRONMENT

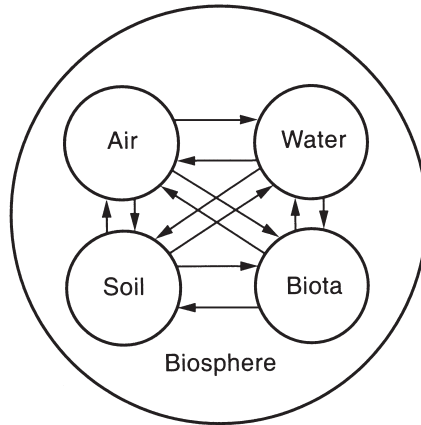
The *environment* is the sum total of human surroundings consisting of the atmosphere, the hydrosphere, the lithosphere, and the biota. Human beings are totally dependent on the environment for life itself. The atmosphere provides us with the air we breathe, the hydrosphere provides the water we drink, and the soil of the lithosphere provides us with the vegetables that we eat. In addition, the environment provides us with the raw materials to fulfill our other needs: the construction of housing, the production of the numerous consumer goods, *etc.* In view of these important functions, it is imperative that we maintain the environment in as pristine a state as is possible. Fouling of the environment by the products of our industrial society (*i.e.* pollution) can have many harmful consequences, damage to human health being of greatest concern.

In addition to the outdoor environment, increasing concern is being expressed about the exposure of individuals to harmful pollutants within the *indoor environment*, both at home and at work. Levels of harmful pollutants can often be higher indoors than outdoors, and this is especially true of the workplace where workers can be exposed to fairly high levels of toxic substances. *Occupational health*, *occupational medicine*, and *industrial hygiene* are subjects that deal with exposure at the workplace.

Pollution is mainly, although not exclusively, chemical in nature. The job of the environmental analyst is therefore of great importance to society. Ultimately, it is the environmental analyst who keeps us informed about the quality of our environment and alerts us to any major pollution incidents, which may warrant our concern and response.

### 1.1.1 Biogeochemical Cycles

The different components of the *biosphere* and their interactions are illustrated in Figure 1.1. The biosphere is that part of the environment where life



**Figure 1.1** *Interactions between component parts of the biosphere*

exists. It consists of the hydrosphere (oceans, rivers, and lakes), the lower part of the atmosphere, the upper layer of the lithosphere (soil), and all life forms. The concept of the biosphere was first introduced by the Russian scientist Vladimir Vernadsky (1863–1945) as the “sphere of living organisms distribution”. Vernadsky was among the first to recognise the important role played by living organisms in various interactions within the biosphere, and he established the first-ever biogeochemical laboratory specifically dedicated to the study of these interactions. He expounded his theories in an aptly entitled book, “Biosphere”, published in 1926.

The various *spheres* act as reservoirs of environmental constituents and they are closely linked through various physical, chemical, and biological processes; there is constant exchange of material between them. Chemical substances can move through the biosphere from one reservoir to another, and this transport of constituents is described in terms of a *biogeochemical cycle*. Biogeochemical cycles of many elements are closely linked to the hydrological cycle. The hydrological cycle acts as a vehicle for moving water-soluble nutrients and pollutants through the environment. If all the components of the cycle are identified and the amounts and rates of material transfer quantified, the term *budget* is used. Both beneficial nutrients and harmful pollutants are transported through biogeochemical cycles with far-reaching consequences. The more commonly discussed biogeochemical cycles are those of important *macronutrients* such as carbon, sulfur, nitrogen, and phosphorus, but, in principle, a biogeochemical cycle could be drawn up for any substance. The cycle is usually illustrated as a series of compartments (reservoirs) and pathways between them. Each reservoir can be viewed in terms of a box model shown in Figure 1.2.



**Figure 1.2** *The box model*

If the input into a reservoir equals the output, the system is said to be in a steady state. The *residence time*,  $\tau$ , is defined as

$$\tau = \frac{\text{Amount of substance in the reservoir (mass)}}{\text{Flux (mass/time)}}$$

Flux is the rate of transfer through the reservoir (*i.e.* the rate of input or output). If the input exceeds the output, there will be an increase in the amount of substance in the reservoir. There are many examples of the build-up of pollution in environmental systems since pollutants are often added at rates greater than the rates of natural processes that act to remove them from the system. On the other hand, if the output is greater than the input, the amount of substance in a reservoir will decrease. An example of this is the depletion of natural resources.

It is debatable whether, in the absence of human activities, natural systems would tend towards some sort of steady state or equilibrium. Natural systems are dynamic, and both natural and human-induced disturbances lead to change, albeit over different time scales. Natural changes to biogeochemical cycles generally take place over geologic time scales, and for millennia these cycles have maintained the delicate balance of nature conducive to life. However, since the industrial revolution, and especially over the last 40 years, human activities have caused significant perturbations in these cycles. The effects of these disruptions are already becoming apparent, and are likely to become even more severe in the coming millennium. Serious environmental problems that have been caused by disruptions of biogeochemical cycles include: global warming, acid rain, depletion of the ozone layer, bioaccumulation of toxic wastes, and decline in freshwater resources. Modelling of biogeochemical cycles is becoming increasingly important in understanding, and predicting, human impacts on the environment, and the possibility of using biogeochemical cycles to solve environmental problems, the so-called *biogeochemical engineering*, has recently been recognised. Some of the major human impacts on biogeochemical cycles are given in Table 1.1.

The extent of human impacts on biogeochemical cycles can be illustrated by comparing the contribution of anthropogenic emissions to the atmosphere with natural emissions (Table 1.2). For some toxic substances, the contribution of industrial emissions is even more striking; the ratio of anthropogenic

**Table 1.1** *Human impacts on biogeochemical cycles*

<i>Cycle</i>	<i>Human interference</i>	<i>Environmental consequence</i>
Carbon	Fossil fuel combustion, clearing of forests	Global warming
Sulfur	Fossil fuel combustion	Acid rain
Nitrogen	Fossil fuel combustion, fertilizers	Acid rain, eutrophication
Phosphorus	Detergents and fertilizers	Eutrophication

**Table 1.2** *Relative contributions of anthropogenic and natural sources (approximate)*

<i>Pollutant</i>	<i>Emissions to the atmosphere (% of total)</i>	
	<i>Natural</i>	<i>Anthropogenic</i>
Sulfur dioxide	50	50
Oxides of nitrogen	50	50
Carbon dioxide	95	5
Hydrocarbons	84	16

to natural emissions to the environment is 3:1 for arsenic, 5:1 for cadmium, 10:1 for mercury, and 28:1 for lead.

### 1.1.2 Environmental Pollution

*Pollution* is commonly defined as the addition of a substance by human activity to the environment, which can cause injury to human health or damage to natural ecosystems. This definition excludes “natural pollution”, although natural processes can also release harmful substances into the environment. There are different categories of pollution: chemical, physical, radioactive, biological, and aesthetic. This book is concerned primarily with chemical pollutants and their determination in environmental matrices.

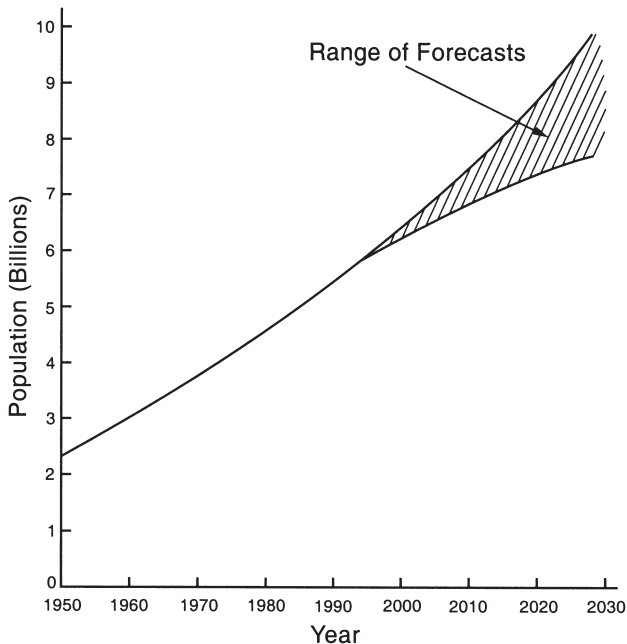
Most substances that are considered as pollutants are actually natural constituents of the environment, albeit at concentrations which are generally harmless. It is the increase in the concentration of these natural constituents, usually by industrial activity, to levels at which they may have harmful effects that is of concern. There are, however, a few pollutants that are entirely synthetic and would not be present in the environment if it were not for human activity (*e.g.* chlorofluorocarbons).

Sources of pollution can be:

- Domestic
- Industrial
- Agricultural
- Transportation
- Warfare

Pollution can be classified according to its geographical scale as *local*, *regional*, or *global*. Local pollution may affect only a single field, small stream, or a city (*e.g.* photochemical smog). Regional pollution may affect a part of a country, a whole country, or even an entire continent. Global warming due to the greenhouse effect of  $\text{CO}_2$  is an example of a pollution problem on a global scale. However, the distinction between these different categories is not always clear-cut. For example, many contemporary megacities extend over enormous areas and many urban conurbations may consist of several cities (Metro Manila, Los Angeles area, north-eastern seaboard of the US, *etc.*). In such areas, photochemical smog is a regional problem. Acid rain was, until lately, considered a regional problem as it affects almost all of Europe and North America. However, acid rain has recently been identified at locations throughout the world, from tropical rainforests in Asia, Africa, and South America to the polar ice caps in the Arctic. Therefore, acid rain may now be viewed as a global problem.

The number of pollution sources is constantly rising throughout the world as a consequence of growing industrial development. The driving force behind the increase in pollution is the rapidly growing population of the world (Figure 1.3). The world's population has more than doubled over the last 40 years, and over the next 30 years it is expected to increase by another



**Figure 1.3** *The world's population growth*

2–4 billion. The consequent demand for energy and resources required to feed, clothe, and house the increasing population will be accompanied by a parallel increase in waste production. Not only is the population rising, but the standard of living is also rising, placing additional stress on the environment. In future, we may expect environmental problems to become more widespread and more severe unless measures are taken to control pollution.

The growing population and the consumer society are also leading to the increasing depletion of non-renewable natural resources. Resource conservation is increasingly important if we are to leave enough for future generations to satisfy their needs.

Problems of environmental pollution have been widely recognised only in the latter half of the 20th century, but they have been known since antiquity. In fact, air pollution has been around since the first humans who started using fire for heating, lighting, and cooking. The air quality in inhabited prehistoric caves must, almost certainly, have been poor, and early humans must have been exposed to elevated levels of combustion products. In antiquity, and in the Middle Ages, the air of towns was polluted by the products of burning wood and coal, and the smelting of ores of iron and other metals. Also, in the absence of a sewage system, human and other wastes were dumped onto the streets contributing to the rise of many epidemics. Furthermore, human beings have been throwing their wastes into surface waters since time immemorial. However, most of these early problems were local and had limited impacts, and natural processes within the environment were capable of rapidly diluting and eliminating the pollution.

It was the Industrial Revolution that greatly accelerated the release of pollutants into the environment. The Industrial Revolution originated in the north of England in the late 18th/early 19th century and quickly spread to other regions of Europe and North America. Rapid industrialisation is still going on throughout the world, especially in the developing countries of Asia, Africa, and South America. The variety of pollutants and the extent of pollution are now greater than ever in history, and this trend looks set to continue through this century. Natural processes can no longer cleanse the environment of the enormous quantities of pollutants that are generated daily, and the pollution is steadily accumulating in the air, the oceans, and the soil. While natural ecosystems may accommodate a certain amount of pollution, this capacity is now being overloaded. When pollution levels reach a critical limit, harmful consequences follow. The legacy of present industrial development may have a dramatic impact on future generations.

Technological progress has been a two-edged weapon. Technology has given us enormous power over nature, to use for better or for worse. Medical and technological advances have eradicated many diseases, improved health

care, provided protection against many natural disasters, increased the standard of living, eliminated many dangerous jobs, improved safety at work, *etc.* On the other hand, we now have the ability not only to destroy isolated ecosystems but all life on the earth, including human life, and not just by means of weapons of mass destruction, but also by our polluting influence on the environment. The “globalisation” of what were previously minor, local environmental problems (*e.g.* acid rain), as well as the emergence of new global threats (*e.g.* destruction of stratospheric ozone, global warming) seems to indicate that we are well on our way to accomplishing this. It would be a sad indictment on the human race if it were to undo, in a small fraction of the geological time scale, what took nature millions of years to achieve: life in its many forms. Clearly, the real-world experiment, which we are conducting, needs to be carefully controlled if we are to slow down, or reverse, this trend. Major environmental problems of the 21st century will include:

- Global warming and climate change
- Stratospheric ozone depletion
- Acid rain
- Urban pollution
- Haze from forest fires
- Declining water resources
- Eutrophication
- Desertification
- Solid and toxic waste disposal
- Radioactive waste disposal
- Depletion of resources

However, it is not all gloom and doom; there have been many environmental success stories over the years. Unfortunately, these successes have so far been mainly limited to the developed nations. For example, air quality of most cities in Western Europe and North America has significantly improved as compared to half a century ago. Concentrations of SO<sub>2</sub> and smoke have decreased steadily since the 1950s and catastrophic smog episodes are no longer a menace to urban populations. More recently, the introduction of catalytic converters has reduced the emissions of automotive air pollutants and improved urban air quality even further. “Car-free” zones have been introduced in some cities and improvements in public transport have been implemented. DDT, organotin compounds, phosphate-containing detergents, and many other harmful chemicals have been banned in most developed nations. Water quality has improved in some countries compared to what it was during the Industrial Revolution. Many countries have phased out the use of lead

in petrol. Strict controls have been imposed on the transport and disposal of toxic wastes. Increasing emphasis is being placed on the so-called “clean technologies”. Re-cycling, re-use, life-cycle analysis, sustainable development, energy conservation, “eco-safe”, environmental impact assessment (EIA), and other such concepts and methods are being increasingly implemented. Considerable research has gone into developing alternative, non-polluting energy sources (solar, wind, *etc.*). The greater general awareness of environmental problems has resulted in the public raising environmental issues and demanding greater environmental accountability from industries and governments. Unfortunately, similar improvements are not evident in developing countries where development has been accompanied by increasing environmental devastation. Over the past 20 years, the relatively unspoiled environment of these countries has regressed to a state on par with that of the developed countries during the Industrial Revolution. However, there is cause for optimism. As these countries increasingly adopt pollution control technologies, much as they have adopted other technologies pioneered by the developed nations, the quality of the environment could yet improve.

### 1.1.3 Effects of Pollution

Effects of pollution are multifarious; however, those of greatest concern are the impacts on human health. Other concerns include impacts on natural ecosystems, effects on weather and climate, and economic and sociopolitical impacts of pollution and its abatement.

Many of the substances considered as pollutants may act as beneficial nutrients in small doses, and the effect of dose or concentration on health is described by means of a *dose–response curve*. For many elements (*e.g.* F, Se, Cu, Cr, Mn), there is a window of dose (or concentration) that is beneficial to health, while levels above this window may be toxic leading to illness or even death. On the other hand, for many essential nutrients, concentrations below the beneficial window may lead to deficiency and consequent illness. Similar dose–response curves exist for plant nutrients (see Figure 6.2). For many substances there is a threshold level below which harmful effects are not apparent. However, for many environmental toxins, especially carcinogens such as benzene, there is no threshold and any concentration can be harmful. Additional problems in evaluating the toxic effects of pollutants include additive effects of several pollutants and synergism. Synergism results in the combined effects of several pollutants producing an effect greater than the sum of the effects of the individual pollutants.

Health effects of pollutants can be classified as acute or chronic. *Acute effects* result from short-term exposure, usually to high concentrations of pollutants and are common following industrial exposure or accidental

releases of toxic chemicals. *Chronic effects* result from long-term exposure, usually to lower, ambient levels of pollution.

#### 1.1.4 Environmental Standards

Whether a specific concentration of a particular chemical substance is harmful or not depends on many factors and is the subject of extensive research among various branches of science. The maximum level of a substance that can be allowed in the environment without any foreseeable harmful effects is called a *standard*, and the establishment of such standards is a complex and difficult process. Many standards change quite frequently as new research sheds more light on the effects of pollution or as better control technologies become available. The tendency is for standard values to decrease (*i.e.* become more stringent) with time. Most countries specify standards for many air pollutants, water pollutants, *etc.* These standards are legally enforceable and offenders may be prosecuted for infringement. There are two types of standards:

- *Quality standards.* These refer to the concentration of a pollutant in the environment. For example, air quality standards specify the concentrations of pollutants in the general atmosphere that are not to be exceeded. Such standards are used to maintain the quality of our environment in a generally unpolluted, if not pristine, state. These standards are more difficult to enforce.
- *Emission standards.* These refer to the maximum levels of a pollutant that may be emitted from a particular pollution source. For example, wastewaters from a particular industry must have concentrations of specific pollutants below the levels required by the emission standard.

Furthermore, there are also *guidelines*. These are not legally binding but they are recommended levels of pollutants, which, if exceeded may result in some harmful effect. Well-known guidelines are the World Health Organisation (WHO) recommendations for drinking water quality and WHO air quality guidelines (see Appendix C). The number of environmental standards, guidelines, and regulations is increasing at an extraordinary rate in order to keep up with the number of synthetic chemicals being produced by industry and the growing and varied threats to human health and the environment.

The job of the environmental analyst is to test for compliance with the various standards. If it is established that permissible levels are being exceeded, technological measures may be required in order to reduce the emissions of pollutants. For example, such measures may include the installation of a water-treatment plant to control the discharge of wastewaters, or the operation of a flue gas desulfurisation plant to reduce atmospheric emissions from a power station. The selection and design of the most appropriate pollution control

technology are made by environmental engineers. Environmental analysts may be required to assess the efficiency of the control technology, and once installed, to confirm that the problem has been eliminated and that legislative standards are being adhered to. International and national guidelines and standards for air, water, soil, sludge, crops, and foods are listed in Appendix C.

## 1.2 ENVIRONMENTAL ANALYSIS

### 1.2.1 Aims of Analysis

The purpose of environmental analysis is two-fold:

- To determine the background and natural concentrations of chemical constituents in the environment (*background monitoring*).
- To determine the concentration of harmful pollutants in the environment (*pollution monitoring*).

Background monitoring is useful in studies of general environmental processes and for establishing concentrations against which any pollution effects could be assessed. It is, however, a fact that pollution has now affected even the most remote areas of the globe, and true background levels of many substances are becoming increasingly difficult to determine.

The objectives of pollution monitoring are:

- To identify potential threats to human health and natural ecosystems.
- To determine compliance with national and international standards.
- To inform the public about the quality of the environment and raise public awareness about environmental issues.
- To develop and validate computer models, which simulate environmental processes and are extensively used as environmental management tools.
- To provide input data for Geographical Information Systems (GISs) used in conjunction with expert systems as an aid to environmental management.
- To provide inputs to policy-making decisions (land-use planning, traffic, *etc.*).
- To assess the efficacy of pollution control measures.
- To investigate trends in pollution and identify future problems.

Environmental analysis is often used in EIA studies. These studies are carried out before any major industrial development is given a go-ahead by the authorities, and their aim is to assess any potential impacts of the development on environmental quality. As part of EIA, it is often necessary to establish the baseline concentrations of various substances at the proposed site so that potential impacts may be assessed. Environmental analysis is also integral to

the field of *environmental forensics*, which forms an important part of environmental law. Environmental forensics involve fingerprinting pollutant releases to determine the source and cause of contamination.

### 1.2.2 Types of Analysis

The chemical substance being determined in a sample is called an *analyte* (*i.e.* atom, ion, molecule). Samples are “analysed” whereas analytes are “determined”. We can broadly define two categories of chemical analysis:

- *Qualitative analysis* – concerned with the *identification* (*i.e.* determining the nature) of a chemical substance.
- *Quantitative analysis* – concerned with the *quantification* (*i.e.* determining the amount) of a chemical substance.

The former answers the question: “Which substance is present?” while the latter answers the question: “How much is present?” Results of quantitative analysis are generally expressed in terms of *concentration*. Concentration is the quantity of analyte (in grams or moles) per unit amount of sample (grams or litres). Obviously, quantitative analysis involves identification as well as quantification since a numerical value must be ascribed to a particular substance. For example, qualitative analysis may simply tell us whether mercury is present in a sample of waste effluent, whereas quantitative analysis will tell us exactly how much mercury is present in the effluent. Often, the so-called “spot tests” based on distinctive colour-forming reactions, or complex schemes of analysis, can be used for purposes of identification. There is, however, a hidden quantitative aspect in qualitative analysis. If a result of a qualitative analysis is negative (*i.e.* the substance in question was not identified) this does not mean that the substance is absent; it merely implies that the substance is present at a level below that at which the spot test, or analysis scheme, responds. For example, mercury is present in seawater at a level of  $3 \times 10^{-5}$  ppm (parts per million). It is unlikely that a routine spot test would be able to identify this. The development of evermore-sensitive instruments capable of quantifying even the minutest traces of substances has exposed the shortcomings of many of the cruder and insensitive schemes of qualitative analysis. Nevertheless, qualitative spot tests still remain useful in many situations where substance levels are high, and they are particularly useful where routine analyses are required, such as in industry.

Chemical analysis may also be categorised with respect to the type of substance being analysed. *Inorganic analysis* is concerned with the determination of atoms and inorganic compounds, whereas *organic analysis* involves the determination of organic compounds.

Quantitative analysis may be classified according to the following categories:

- *Complete analysis* – each and every constituent of the sample is determined.
- *Ultimate analysis* – each and every element in the sample is determined without regard to the compounds present.
- *Partial analysis* – the amount of one or several, but not all, constituents in a sample is determined.

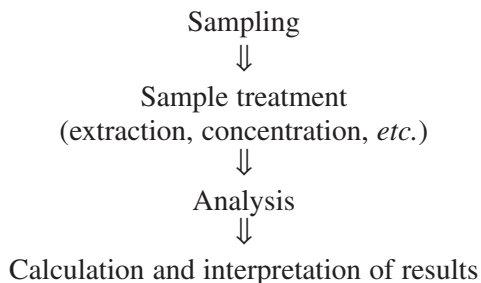
Another way of categorising types of analyses is according to the level of the substance in the sample. *Macroanalysis* involves the determination of major constituents present at high concentration (%), whereas *microanalysis*, or *trace analysis*, involves the determination of constituents present in very small quantities (0.1 ppb–100 ppm). *Ultra-trace analysis* involves the determination of constituents present at levels lower than in trace analysis (<0.1 ppb).

Furthermore, there are other categories still. *Destructive analysis* involves the use of a method, or technique, which destroys the substance in question during analysis (e.g. dissolution of solid sample into acid). *Non-destructive analysis*, as the name implies, does not destroy the sample during analysis (e.g. X-ray fluorescence) and the sample may be re-used for other analyses. *Speciation* involves the determination of all the different forms of a class of compounds in a sample. For example, the speciation of lead in the environment would involve the analysis of all the different inorganic and organic compounds of lead.

### 1.2.3 Stages of Analysis

Both industry and government operate laboratories dedicated to environmental analysis. Furthermore, environmental analysis is performed by commercial analytical laboratories serving smaller industries that find it more cost-effective to sub-contract out analytical work rather than to invest in their own laboratories, and by universities and institutes that carry out research into environmental chemistry and pollution. Hence, there is a wide range of employment options available for trained environmental chemists.

An environmental analyst should be proficient at carrying out all the different stages of an analysis given below:



## 1.3 SAMPLING AND STORAGE

### 1.3.1 Sampling

A *sample* is that portion of the physical environment, which is withdrawn for chemical analysis. A sample can be aqueous (*e.g.* river water), gaseous (*e.g.* air), or solid (*e.g.* soil). The chemical substance being analysed in the sample, whether an atom, ion, or molecule, is referred to as the *analyte* (*e.g.* Pb in dust). *Sampling* is the process by which a sample is obtained, and this can be done in one of the two ways:

- *Batch sampling* involves taking a sample from the environment and performing an analysis either on site or later on in the laboratory. For example, batch sampling of a wastewater effluent for pH analysis would imply that a volume (*e.g.* 100 mL) of the effluent is collected and then analysed for pH. These samples are collected at a specific time and place and are also called *grab* samples.
- *Continuous sampling* involves continuously monitoring the environmental parameter of interest. In the above example, continuous analysis of the effluent pH would involve placing a pH electrode directly into the effluent stream and recording the pH on a chart recorder or a data logger. In this way a continuous record of the effluent pH is obtained. This kind of sampling could detect important changes in the effluent that would be missed by batch sampling.

Batch sampling is the easiest and most common method of obtaining a sample and it is widely used in environmental surveys. Continuous sampling is generally combined with an instrumental method of analysis, and the term given to this combination is *continuous monitoring*. This method of analysis is being adopted more extensively in many applications (*e.g.* effluent monitoring, air monitoring). Usually, the method is combined with some kind of alarm system to alert the operator when standards are being exceeded. For example, if the level of pollutant in an effluent stream is found to exceed the emission standard, an alarm may be activated and the plant personnel could switch off the process and attempt to resolve the problem. In many cities, continuous monitoring of air quality is carried out by the municipal authorities. This allows for alerts to be broadcast to the public via the media when air quality standards are observed to have been breached. The public is then asked to stay indoors, refrain from outdoor exercise, and so on, until the air quality improves. Such a fast response would not be possible in the case of batch sampling, which involves laboratory analysis at some later time.

Another type of sample is a *composite* sample, prepared by mixing several batch samples, usually collected at the same place but at different times. These are used to evaluate the average concentration in a medium in which

the concentration may vary with time. For example, batch samples of wastewater are collected every 2 h over a 24-h period and pooled into one container. The concentration in the mixture is supposed to reflect a 24-h average. Composite samples can also be prepared by mixing samples collected at different places at the same time. For example, in soil surveys, samples collected from different locations in a field are pooled together to give an area average.

Although sampling appears to be a relatively straightforward matter, it is generally one of the most problematic stages of an environmental analysis. The main difficulty lies in obtaining a *representative* sample. The sample represents only a small portion of the system under investigation and it is important that the sample is representative of the whole system as much as possible. In environmental analysis this is not always possible to achieve. Usually, it is easier to obtain representative samples from homogeneous than from heterogeneous systems. An environmental analyst faces unique problems of obtaining representative samples from water, air, effluent gases, dust, and soil. Some of the questions that need to be addresses are:

- When and where should the sample be taken?
- How many samples should be taken?
- How much sample is required?

Some quite sophisticated statistical sampling procedures have been developed that can help the analyst answer some of these questions, nevertheless most sampling is carried out without reference to these statistical considerations. The analyst will usually decide on the best location, time, and number of samples to be taken (the so-called *random sampling*). Considerations of site accessibility, time, and expense are often more influential factors than purely scientific considerations. Anyway, several samples are collected at each site in order to obtain some indication of variability in analyte concentration at the site, and in case some of the samples are lost, spoilt, or incorrectly analysed. Obtaining as representative a sample as possible is paramount since the analyst cannot obtain the same sample again. The environment is a dynamic system, which is constantly changing, and returning to the same site at a later date may give completely different results.

### 1.3.2 Storage

Once the sample has been collected, it is transported to the laboratory for analysis. Sometimes it is possible to carry out the analysis at the site using portable test kits, or inside on-site laboratories (see Section 1.5.4), but most often the sample has to be transported some distance. It is desirable to perform the analysis as soon as possible after sample collection. On many occasions this is not possible and the sample has to be stored until the analysis can be performed. During transportation and storage, it is important to preserve the

integrity of the sample. Once the sample has been collected inside the sampling vessel the following processes may threaten the integrity of the sample:

- Chemical reactions
- Biological reactions
- Interaction with sampling bottle material

The analyte under investigation may be destroyed or created by chemical or biological reactions, it may be adsorbed onto the walls of the sampling bottle, or interfering substances may be leached from the walls of the bottle. The analyst has to be aware of the chemical properties of the analyte he/she is investigating so as to ensure storage conditions that will minimise all these possible effects. He/she may have to adopt different sampling and storage procedures for different analytes even if he/she is dealing with the same sample; for example, in water analysis organic and inorganic analytes require different types of sampling bottle materials. Contamination of the sample during sampling, transport, and storage is a real possibility and all measures must be taken to avoid this. Many of the analytes are present at trace and ultra-trace levels in environmental samples, and it is quite easy to contaminate the sample. Even placing the sample in a well-sealed plastic bottle may in some circumstances not be satisfactory; contaminant gases have been known to permeate through the walls of plastic vessels! However, if the analyst is aware of all the potential problems, he/she can generally take preventive measures. Many analytes are exceedingly reactive and require addition of a preserving agent on site. For example, when analysing for dissolved oxygen in a water sample, it is necessary to “fix” the oxygen at the time of sampling, otherwise its concentration will be reduced by oxidation reactions and aerobic biological processes in the sample. Samples taken for metal ion analysis are acidified to prevent adsorption onto the walls of the bottles prior to storage.

Once collected, the samples are usually stored in a refrigerator at 4°C until analysis can be performed. The length of time for which samples can be stored varies depending on the analyte. Recommendations for bottle material, preservative, and maximum storage times for some analytes are given in Table 1.3. It should be remembered that the table gives “maximum storage times” and the samples should be analysed at the earliest convenient time.

Many sample bottle materials are available: borosilicate glass, Pyrex glass, polypropylene, polyethylene, Teflon, *etc.* Teflon (PTFE) is the most unreactive material but also the most expensive and its use is therefore precluded in surveys requiring large numbers of samples. The general recommendation is that Pyrex glass bottles be used for organic analysis and plastic bottles (polyethylene or polypropylene) for inorganic analysis. Soda-glass bottles are unsuitable since they may leach sodium, calcium, and silicate. All bottles should be cleaned before sampling according to the methods described in

**Table 1.3** Recommended storage conditions for some analytes in water samples. All samples should be stored in a refrigerator at 4°C

Analyte	Bottle material <sup>a</sup>	Preservative	Maximum storage time
Alkalinity	P	None	2 weeks
Ammonia	P	HNO <sub>3</sub> to pH <2	4 weeks
BOD	P, G	None	2 days
Calcium	P	None	4 weeks
COD	P, G	H <sub>2</sub> SO <sub>4</sub> to pH <2	4 weeks
Chloride	P	None	4 weeks
Conductivity	P	None	1 week
Dissolved oxygen	G	MnSO <sub>4</sub>	Analyse as soon as possible
Fluoride	P	None	4 weeks
Hardness	P	None	4 weeks
Magnesium	P	None	4 weeks
Nitrate	P	H <sub>2</sub> SO <sub>4</sub> to pH <2	4 weeks
Nitrite	P	None	Analyse as soon as possible
Pesticides	G	pH 5–9	1 week to extraction, 6 weeks after extraction
pH	P	None	Analyse as soon as possible
Phenols	G	NaOH to pH 12	1 week to extraction, 6 weeks after extraction
Phosphate	P	None	2 days
Potassium	P	None	4 weeks
Sodium	P	None	4 weeks
Sulfate	P	None	4 weeks
Suspended solids	P, G	None	1 week
Total solids	P, G	None	1 week
Trace metals (e.g. Pb, Fe)	P	HNO <sub>3</sub> to pH <2	6 months
Volatile solids	P, G	None	1 week

<sup>a</sup>P= polyethylene; G= pyrex glass.

Appendix B. The bottles should be thoroughly rinsed with laboratory water to remove any traces of cleaning agent and filled with laboratory water when not in use.

## 1.4 SAMPLE TREATMENT

Although some samples may be analysed directly, most often the sample has to be prepared for analysis. A variety of sample-treatment methods are used depending on the type of sample, the analyte to be determined, and the kind of analytical method to be used. The purposes of sample treatment are three-fold:

- To convert the sample and analyte into a form suitable for the analysis by the chosen method.
- To eliminate the interfering substances.
- To concentrate the sample.

Typical sample-treatment methods include:

- *Dissolution/digestion*. A solid sample has to be dissolved in a solution before it can be analysed by most analytical methods. Various methods for decomposing and dissolving solid samples are available: acid digestion on a hot plate, refluxing, ultrasonic digestion, and microwave digestion.
- *Filtration*. Aqueous samples are usually filtered. For example, when determining soluble components it is customary to filter out the suspended particles from solution as these may interfere in the analysis.
- *Solvent extraction*. Organic analytes are usually extracted into an organic solvent. This can also serve to concentrate the sample.

Various other treatments can also be applied: drying, sieving, ignition, boiling, precipitation, complexation, reduction, oxidation, *etc.* Solid samples are usually dried in an oven to remove any water before carrying out any other treatment.

An important consideration when treating the sample is to avoid contamination. Impurities present in many of the reagents can contaminate the sample or cause interferences.

## 1.5 ANALYTICAL METHODS

### 1.5.1 Selection of Method

The analyst can use either a classical method (titrimetry, gravimetry) or one of the many instrumental methods. The selection of the appropriate method is based on the following criteria:

- Expected concentration of analyte in the sample
- Number of samples to be analysed
- Time that can be devoted to the analysis
- Cost of the analysis

Analytical methods employed in environmental analysis are summarised in Table 1.4. More details about the methods used in this book are given in Appendix B. Methods may be classified as specific, selective, or universal. *Specific* methods respond to only one analyte and are therefore not prone to interference from other substances. *Selective* methods respond to certain classes of analytes and may be prone to some interference. *Universal* methods respond to all classes of analytes.

### 1.5.2 Classical Analysis

*Titrimetry* (also called volumetric analysis) is simple, inexpensive, rapid, and accurate. It requires the most rudimentary of laboratory glassware (burettes,

**Table 1.4** Analytical methods, their principles, and typical applications to environmental analysis

<i>Method</i>	<i>Principle</i>	<i>Subclasses</i>	<i>Typical application</i>
Titrimetry	Addition of a standard solution to sample until reaction is complete as shown by colour change in added indicator	Neutralisation Precipitation Complexation Reduction/oxidation	Alkalinity, acidity Chloride Water hardness Dissolved oxygen Sulfate, chloride
Gravimetry	Precipitation of analyte out of solution and weighing the product		
Spectroscopy	Interaction of electromagnetic radiation with sample	UV/visible Infrared (IR) Atomic absorption (AAS) or emission (AES)	Iron in water, SO <sub>2</sub> in air, O <sub>3</sub> in air Oxidants in air Trace metals ( <i>e.g.</i> Pb, Cu, Cd, Zn)
Chromatography	Separation of components in a mixture as they move down a column	Gas chromatography (GC) Ion chromatography	Pesticides, hydrocarbons in air Ions in solution ( <i>e.g.</i> Cl <sup>-</sup> , SO <sub>4</sub> <sup>2-</sup> , NO <sub>3</sub> <sup>-</sup> )
Electrochemical	Measurement of electrical properties	Ion selective electrodes Voltammetry	pH, fluoride Trace metals ( <i>e.g.</i> Pb, Cd, Cu)

pipettes, and volumetric flasks) available in all laboratories. Titrations are generally useful for determining analyte concentrations at levels  $>1 \text{ mg L}^{-1}$  and are of limited use for trace component analysis.

*Gravimetry* is inexpensive and accurate but tedious and slow. It, too, requires the minimum of laboratory equipment and can be carried out in all laboratories.

### 1.5.3 Instrumental Analysis

Instrumental methods in environmental analysis generally involve *spectroscopy* and *chromatography*. Spectroscopic methods used in the analysis of environmental samples include UV/visible, atomic absorption or emission, and infrared (IR). Most laboratories would be equipped with a colorimeter (for visible spectrophotometry) and a flame photometer (for atomic emission spectrophotometer (AES)), but some may also have an atomic absorption spectrophotometer (AAS) and more advanced UV/visible instruments. Other advanced spectroscopic techniques which may not be generally available in all laboratories are: inductively coupled plasma (ICP) spectroscopy, nuclear magnetic resonance (NMR) spectroscopy, and Fourier-transform infrared (FTIR) spectroscopy. Chromatographic methods available in many laboratories include gas chromatography (GC) and high-pressure liquid chromatography (HPLC) including ion chromatography (IC). These are all very useful for analysing environmental samples.

A variety of electrochemical techniques can be used for environmental analysis. The most common are ion selective electrodes (ISE), an example of which is the widely used pH electrode found in all laboratories. Other techniques such as coulometry, polarography, and voltammetry, although useful for some environmental analyses, may not be found in many laboratories.

More advanced techniques that may be used for environmental analysis but may not be available in many laboratories are: gas chromatography/mass spectrometry (GC/MS), X-ray methods, ICP spectroscopy, and a variety of radiochemical techniques.

Experiments in this book require only an AAS, an IC, and a colorimeter or UV/visible spectrophotometer.

### 1.5.4 Test Kits and Portable Laboratories

In many instances, it is necessary to analyse pollution on the spot in the field rather than taking the sample back to the laboratory. This may be necessary for the following reasons:

- To avoid any changes in the sample composition due to chemical or biological reactions during transport to the laboratory.

- To obtain results immediately as, for example, during an emergency following a spillage of hazardous chemicals, when a delay in analysis could have grave consequences.

Many test kits and portable systems are commercially available for the on-site analysis of pollutants. These can vary in sophistication from simple colorimetric methods involving visual comparisons to portable laboratories and instruments.

Kits suitable for rapid and easy determination of various compounds have been developed, and these generally involve adding premeasured reagents supplied in powder or pill form to the sample and matching the developed colour with colour discs, which can be rotated to obtain a colour match with the reacted sample. There are several variations of this methodology available for water testing. Indicator tubes based on visual colorimetry have been developed for determining on-site air pollution (see Section 3.2.6). Test kits are also available for testing acid rains by means of visual colour comparisons after addition of a reagent. Visual methods are suitable for quick spot checks, and although they provide quantitative information, they are not of much use in serious environmental research.

Many different portable instruments are commercially available for the determination of numerous water and air pollutants. Instruments can range from those capable of measuring only one parameter to multisubstance analysers. Portable, battery-operated laboratories consisting of colorimeters and spectrophotometers for comprehensive on-site analysis of a suite of pollutants can also be purchased on the market. More advanced techniques such as GC/MS and XRF are also available as portable instruments.

## 1.6 STANDARDISATION AND CALIBRATION

### 1.6.1 Standardisation

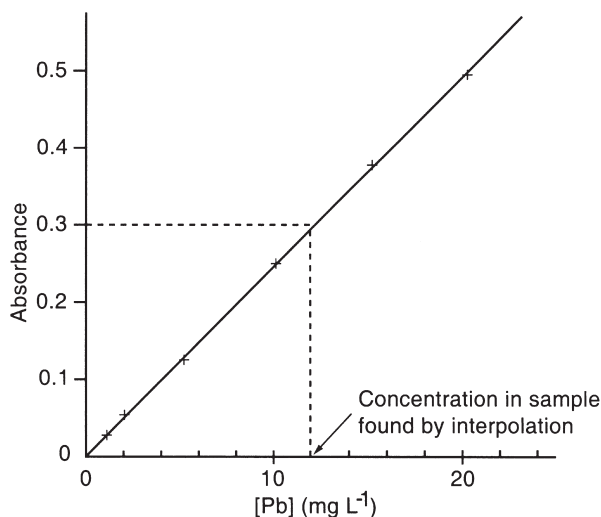
In titrimetric analysis, a standard solution is added to the sample and the concentration of analyte is determined from the volume and the standard solution used up. The exact concentration of the standard solution is not known at the onset but it can be found by titrating the standard solution with another solution called a *primary standard*. The primary standard is prepared from reagents of high purity and stability. For example, in the determination of water hardness, the standard EDTA solution used as a titrant is first titrated against an accurately prepared solution of  $\text{CaCO}_3$ . *Standardisation* is the name given to this process of accurately determining the concentration of a standard solution.

### 1.6.2 Calibration

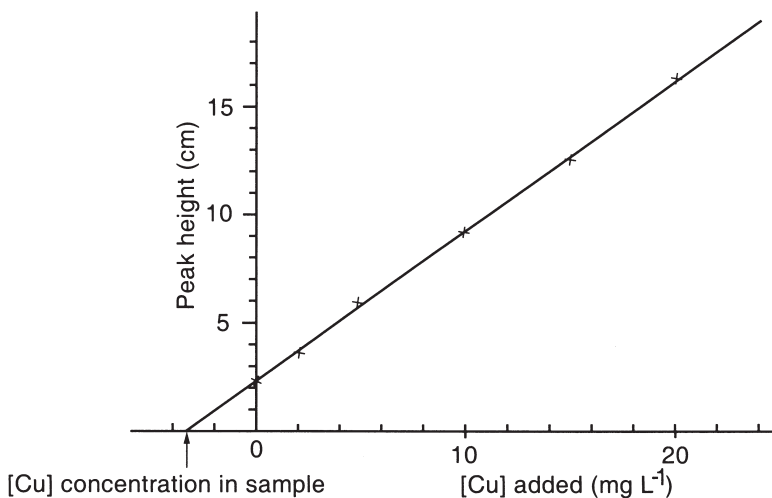
Quantifying the results of an instrumental analysis generally involves the construction of a *calibration graph*. The direct response of the instrument, or the peak height obtained on a chart recorder, is plotted as a function of the analyte concentration for a series of standard solutions containing differing concentrations of the analyte substance. A typical calibration curve for lead (Pb) in AAS analysis is shown in Figure 1.4. The sample is then analysed in the same way and the concentration in the sample is then determined by interpolation. Most calibration curves are straight lines, however, with some graphs curvature can be noted.

### 1.6.3 Standard Addition

An alternative way to quantify the analyte concentration is by means of the *standard additions method*. In this case, a series of solutions containing both the sample and varying concentrations of the substance to be determined are prepared by adding aliquots of a standard solution to the sample. The solutions are analysed and the response of the instrument is plotted against the concentration due to the added standard. The negative intercept on the  $x$ -axis gives the concentration in the sample as shown in Figure 1.5. This method is used to eliminate matrix effects; *i.e.* interferences by other components that may be present in the sample.



**Figure 1.4** Linear calibration graph for lead analysis by AAS. A sample producing an absorbance of 0.3 would have a Pb concentration of 12 mg L<sup>-1</sup>



**Figure 1.5** Standard addition calibration graph. Concentration in sample is determined by extrapolation to the abscissa. In this case the concentration of copper in the sample is  $3.3 \text{ mg L}^{-1}$

Graphs obtained from the calibration method and the standard additions method can be treated using the method of least squares to obtain the best-fit line through the data points (see Section 1.7.8).

#### 1.6.4 Blanks

The water for preparing various reagents and standard solutions should be of the highest purity. Doubly distilled, deionised, or various waters obtained from laboratory purification systems (e.g. Milli-Q) can be used. With many types of analyses, it is also necessary to analyse blanks. Blanks consist of pure laboratory water, while *reagent blanks* contain pure laboratory water and the various reagents used in the analysis. Sometimes *sample blanks* are also analysed. This is common practice when coloured or turbid samples are analysed by colorimetry. In this case, samples are analysed without the addition of the colour-forming reagent. Blanks should be analysed frequently as they can reveal sources of contamination.

### 1.7 ANALYTICAL DATA

#### 1.7.1 Concentration Units

Since analytical measurements are based on physical quantities, every analytical chemist should be familiar with the system of units. The International System (SI) of Units is widely recognised and used, although some non-SI

units are still in use. Different units are related by a *conversion factor*. The most important unit, as far as the chemist is concerned, is the *mole*. The mole is defined as the amount of matter, which contains the same number of elementary units as are present in 0.012 kg of pure  $^{12}\text{C}$ .

Analytical chemists usually express the results of an analysis in concentration units, and the strengths of analytical reagents are also quoted in concentration units. Typical concentration units are defined in Table 1.5.

Normality is generally not used in modern chemistry textbooks; however, many catalogues of reagent manufacturers still employ this unit. Normality depends on the type of reaction. For acids, *equivalent* refers to a mass that has 1 g of  $\text{H}^+$ . For HCl and  $\text{HNO}_3$ , normality = molarity. For a diprotic acid, such as  $\text{H}_2\text{SO}_4$ , normality =  $2 \times$  molarity (*i.e.*  $0.5 \text{ M H}_2\text{SO}_4 = 1 \text{ N H}_2\text{SO}_4$ ). Normality and equivalents are extensively used in environmental analysis, and they are quite useful in titration calculations. Concentrations of analytes are often expressed as *milliequivalents* (meq) or *microequivalents* ( $\mu\text{eq}$ ) per litre in environmental chemistry. Concentrations in  $\text{mg L}^{-1}$  can be converted into  $\text{meq L}^{-1}$  by dividing the ionic charge by the ionic mass (*e.g.*  $1 \text{ mg L}^{-1}$  of  $\text{PO}_4^{3-} = 3/94.97 = 0.03159 \text{ meq L}^{-1}$ ).

For most aqueous solutions that have a density of around  $1 \text{ g mL}^{-1}$ , 1 ppm can be assumed as being equal to  $10^{-6} \text{ g mL}^{-1}$ . Concentrations in solid samples usually refer to dry weight of the sample.

**Table 1.5** Concentration units

Unit	Definition
<i>(a) Solution (water)</i>	
Molarity (M)	Moles per litre of solution
Molality (m)	Moles per kilogram of solvent
Normality (N)	Equivalents per litre of solution
Mole fraction ( $x$ )	Moles of solute per (moles of solute + moles of solvent)
wt%	(Grams of solute per grams of solution) $\times 100\%$
ppm by wt	$10^{-6}$ g solute per g solution (for aqueous solutions this is = $\text{mg L}^{-1}$ or $\mu\text{g mL}^{-1}$ )
ppb by wt	$10^{-9}$ g solute per g solution (for aqueous solutions this is = $\mu\text{g L}^{-1}$ or $\text{ng mL}^{-1}$ )
<i>(b) Gas (air)</i>	
$\mu\text{g m}^{-3}$	$10^{-6} \text{ g m}^{-3}$
ppmv	Parts per million ( $10^6$ ) by volume
ppbv	Parts per billion ( $10^9$ ) by volume
atm	Partial pressure in atmospheres ( <i>e.g.</i> $1 \text{ ppm} = 10^{-6} \text{ atm}$ at sea-level)
%	Percentage by volume
<i>(c) Solid (dust, soil, sediment, plant and animal tissue)</i>	
$\mu\text{g g}^{-1}$	$10^{-6} \text{ g g}^{-1}$
ppm	$\mu\text{g g}^{-1}$ or $\text{mg kg}^{-1}$
ppb	$\text{ng g}^{-1}$ or $\mu\text{g kg}^{-1}$

### 1.7.2 Significant Figures

When numerical data are quoted, it is customary to report all the digits known with certainty plus one uncertain digit. Thus, if a burette reading of 15.38 mL is reported, this implies that numbers 1, 5, and 3 are known with certainty and that there is some doubt about number 8. This burette reading was reported to four significant figures. A burette reading of 5.64 mL would imply three significant figures. In case the numerical values are obtained, say as a result of a calculation using a calculator, with more figures than are significant then the data should be rounded off in accordance with the above rule. Further rules of significant figures are given below (*N.B.* somewhat different rules may be found in other books due to a lack of unanimity on the subject):

- Zero is not a significant figure when it is the first figure in a number (*e.g.* 0.00034 has only two significant figures). A zero in any other position is significant (*e.g.* 102 has three significant figures). In order to avoid confusion, it is preferable to use scientific notation when expressing results (*e.g.*  $6.20 \times 10^4$  has three significant figures).
- When rounding off numbers, add one to the last figure retained if the following figure is greater than 5 (*e.g.* 0.53257 becomes 0.5326 when rounded off to four significant figures).
- Round 5 to the nearest even number (*e.g.* 0.255 becomes 0.26 when rounded off to two significant figures). If the digit just before 5 is even, it is left unchanged (*e.g.* 0.345 becomes 0.34 when rounded off to two significant figures); if it is odd, its value is increased by one (*e.g.* 0.335 becomes 0.34 when rounded off to two significant figures).
- If two or more figures are present to the right of the figure to be retained, they are considered as a group (*e.g.* 6.8[501] should be rounded off to 6.9; 7.4[499] should be rounded off to 7.4).
- In addition and subtraction, the result should be reported to the same number of decimal places as there are in the number with the smallest number of decimal places (*e.g.*  $143.53 + 3.078 + 0.7462 = 147.35$ ).
- In multiplication and division, the result should have an uncertainty of the same order as the number with the greatest uncertainty (*e.g.*  $x = (99 \times 587)/(1067 \times 2.875) = 18.4$ ; the result is reported to three significant figures because the greatest uncertainty is in the number 96, the uncertainty in which is about 1%).
- In the logarithm of a number, we retain the same number of digits to the right of the decimal point as there are significant figures in the original number (*e.g.*  $\log_{10} 8.91 \times 10^{-6} = -5.050$ ).
- In the antilogarithm of a number, we retain as many significant figures as there are digits to the right of the decimal point in the original number (*e.g.*  $10^{3.72} = 5.2 \times 10^3$ ).

Integers or pure numbers (*e.g.* ionic charge) are known with absolute certainty even though the significant figures are not specified (*e.g.*  $32.86/2 = 16.43$ ; the answer is rounded off to four significant figures and not to one significant figure).

### 1.7.3 Accuracy and Precision

*Accuracy* is the degree of agreement of the measured value with the true value (*i.e.* it is the closeness of the measured to the true value). The true value is frequently unknown and it is therefore impossible to determine the accuracy of a method using samples. It is, however, possible to determine the accuracy of a method or technique using *standard reference materials*. Standard reference materials are samples in which the concentration of an analyte has been determined by an external (usually government) laboratory. These materials can then be analysed and the concentration compared to that determined by the external laboratory thus providing an estimate of the accuracy. A whole range of standard reference materials are available (coal, river water, oil, biological materials, *etc.*) (see Section 1.7.10). Accuracy is inversely related to the *bias*; the greater the bias in a method the lower is the accuracy.

*Precision* is the degree of agreement between different measurements carried out in the same way. This can be determined by repeatedly analysing the same sample (*replicate* analysis). Precision is related to the *scatter* in the data; the lower the scatter the greater is the precision.

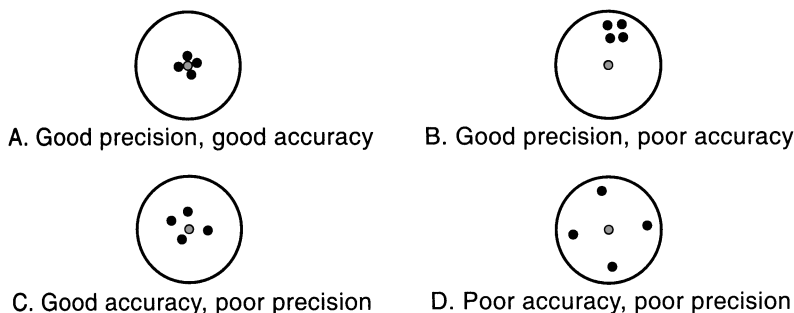
*Repeatability* and *reproducibility* are closely related to precision. *Repeatability* is determined by analysing replicate samples on the same day under the same conditions and this measures within-run precision. *Reproducibility* is determined by analysing replicate samples on different days when conditions may vary (re-optimising and re-calibrating instruments, preparing fresh reagents, *etc.*) and it gives between-run precision.

Preferably, we would like analytical methods to be both precise and accurate, but in practice this is not possible. There will always be some inaccuracy and imprecision in the method as a result of errors and the aim of the analytical chemist is to minimise the sources of these errors. Figure 1.6 illustrates the concepts of accuracy and precision.

### 1.7.4 Errors

*Error* is the difference between the measured and the true value, and as such it is a measure of the accuracy of the method. There are three types of errors:

- *Gross errors (blunders)*. These are errors due to human negligence (misreading instrument, mislabelling sample, errors in calculations, spillage, contamination, *etc.*).



**Figure 1.6** Illustration of precision and accuracy. ○, true (target) value; ●, measured value

- *Systematic (determinate) errors.* These errors are always of the same magnitude and they produce a bias in the method. They relate to the inaccuracy of the method and they have specific and identifiable causes (*e.g.* reagent blank, a meter with a zero error, observer bias, interference). Once these errors are identified, they can be eliminated (*e.g.* removal of interfering substance) or a correction can be applied. Systematic errors may result in a method exhibiting good precision but poor accuracy.
- *Random (indeterminate) errors.* These errors occur by chance, and they vary in sign and magnitude. Random errors are inherent in all measurements, even under the best conditions using the best instruments. Random errors are generally small and have an equal probability of being positive and negative. If a large number of repeated measurements is made, it is found that the data exhibit a *normal (Gaussian) distribution* around the mean (see Figure 1.7). These errors cannot be eliminated; however, they can be determined by replicate measurements and reported as an uncertainty in the result.

The absolute error,  $E_{\text{absolute}}$  is defined as

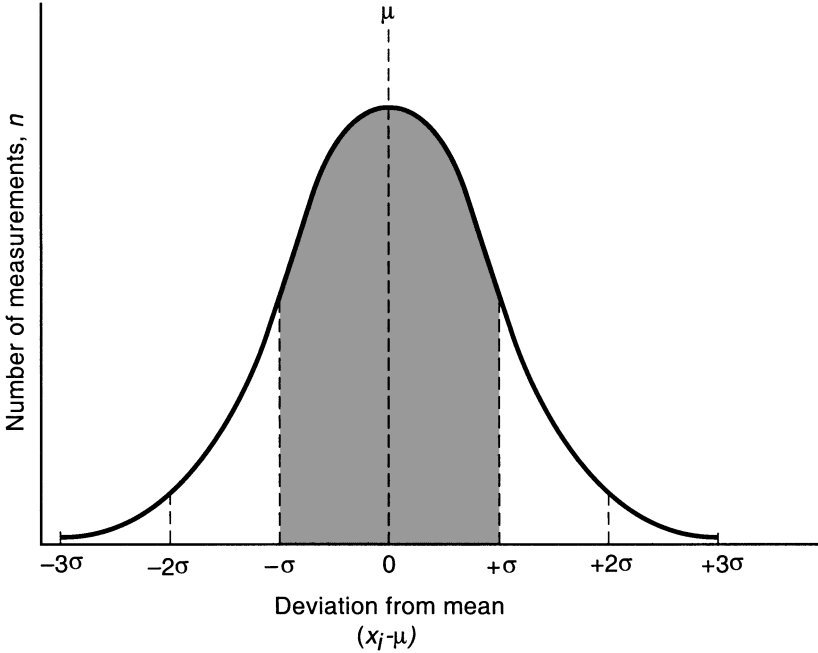
$$E_{\text{absolute}} = \text{measured value} - \text{true value}$$

The relative error,  $E_{\text{relative}}$  is defined as

$$E_{\text{relative}} = (E_{\text{absolute}} / \text{true value}) \times 100\%$$

### 1.7.5 Reporting of Results

If possible, several replicate measurements should be made on the sample in order to test for the variability in the method and obtain some indication of the precision of the measurement. If a sufficiently large number of measurements are carried out, the results are expected to exhibit a Gaussian, or the so-called *normal*, distribution as shown in Figure 1.7.



**Figure 1.7** A Gaussian or normal distribution curve. When the number of measurements ( $n$ ) is infinitely large the population mean,  $\mu$ , and population standard deviation,  $\sigma$ , are used. For real measurements, where  $n$  is finite, the sample mean,  $\bar{x}$ , and the sample standard deviation,  $s$ , are used instead

The *mean*,  $\bar{x}$ , is defined as

$$\bar{x} = \frac{\sum x_i}{n}$$

where  $\sum x_i$  is the sum of the individual measurements and  $n$  the number of measurements. The *standard deviation*,  $s$ , is defined as

$$s = \left[ \frac{\sum (x_i - \bar{x})^2}{n-1} \right]^{1/2}$$

For a normal distribution, 68% of all data lie within one standard deviation of the mean,  $\bar{x} \pm s$ ; 95% of the data lie within two standard deviations,  $\bar{x} \pm 2s$ ; and 99.7% of the data lie within three standard deviations,  $\bar{x} \pm 3s$ . The *variance* is defined as the square of the standard deviation, *i.e.*  $s^2$ . The *coefficient of variation*, CV, is given by

$$CV = \left( \frac{s}{\bar{x}} \right) \times 100\%$$

The mean and standard deviation of the replicate measurements should be calculated and the result should be reported as the mean  $\pm$  the 95% confidence interval. Many authors choose to report the result as the mean  $\pm 2s$  (*i.e.* two standard deviations); however, a better method is to calculate the 95% confidence interval using the *Student t test* (see Example 1.1).

### Example 1.1

Consider the following six measurements of Ca concentration in water sample in  $\text{mg L}^{-1}$ :

16.3, 15.7, 16.8, 15.9, 16.0, and 15.5

The mean is  $16.03 \text{ mg L}^{-1}$  and the standard deviation is  $0.46 \text{ mg L}^{-1}$ . As there are six data points ( $n$ ), we find the Student  $t$  factor by looking up the appropriate statistical table (see Appendix E) under five degrees of freedom ( $n-1$ ). For  $n-1 = 5$ , the Student  $t$  factor at the 95% confidence limit has a value of 2.571. We then use the following equation to calculate the 95% confidence interval for the above measurements:

$$t \times s/n^{1/2} = 2.571 \times 0.46/6^{1/2} = 0.48$$

The result of the analysis is then reported as  $16.03 \pm 0.48 \text{ mg L}^{-1}$ . Note that the result (mean and confidence interval) is reported to one more significant figure than the raw data.

## 1.7.6 Rejection of Data

When several replicate determinations have been made, one result may appear to be much higher or much lower in value than the rest. It may be that the suspect value does not belong with the other values due to inadvertent contamination of the sample or some error in the analysis. In this case, the analyst has to decide whether to retain or reject the suspect value. This is achieved by applying the so-called “ $Q$  test” to the data.  $Q$  is calculated from

$$Q = \frac{|\text{Questionable value} - \text{Nearest value}|}{\text{Highest value} - \text{Lowest value}}$$

The determined value is then compared with a value given in a table for the appropriate number of measurements. This tabulated value is called “ $Q$ -critical”. Values of  $Q$ -critical for different numbers of measurements are given in Appendix E. If the calculated value is higher than the value of  $Q$ -critical, the questionable value is rejected. If, on the other hand, the calculated value of  $Q$  is lower than the value of  $Q$ -critical the suspect value is retained (see Example 1.2).

When a number of measurements have been made, any suspect data should first be considered and the mean, standard deviation, and confidence limit should be based only on the retained values. The analyst should also reject the result of any analysis in which a known error (*e.g.* gross error) has occurred.

### *Example 1.2*

Consider the following six measurements of dissolved oxygen in a water sample in  $\text{mg L}^{-1}$ :

5.6, 5.3, 5.8, 5.6, 5.7, and 7.1

The result of  $7.1 \text{ mg L}^{-1}$  appears suspect and the  $Q$ -test is applied as follows:

$$Q = \frac{|7.1 - 5.8|}{7.1 - 5.3} = 0.722$$

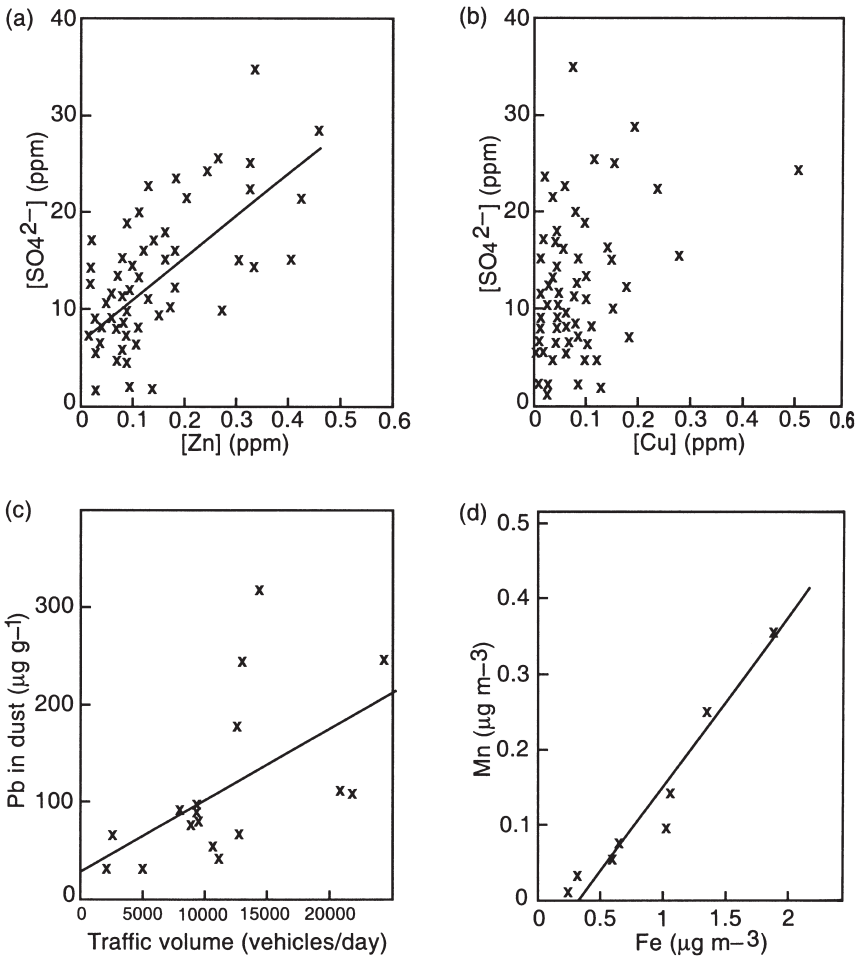
Critical  $Q$  for six data points has a value of 0.621 (Appendix E). Since calculated  $Q$  is greater than critical  $Q$  the result is rejected. Had the suspect result been 6.1 instead of 7.1, the result would have been retained as in the case calculated  $Q = 0.375$ , which is less than critical  $Q$ .

## 1.7.7 Correlation Coefficient

Quite often in environmental analysis we may want to investigate whether there is a significant relationship between two variables ( $x$  and  $y$ ). For example, we may want to compare the results of two different methods over a range of analyte concentrations in order to assess their suitability for a particular analysis, or we may compare the concentrations of two different analytes measured in samples at various sites in order to identify potential pollution sources or investigate some environmental process. Normally, we would plot  $x$  against  $y$  and visually ascertain whether a relationship exists. However, it is not uncommon to find considerable scatter when plotting the results of environmental analysis in this way due to the complex nature of the samples and the environmental processes that influence the concentrations of substances in different samples. Such graphs are called *scatterplots*. We therefore have to rely on statistics to tell us whether a significant relationship exists between different variables.

The *correlation coefficient*,  $r$ , can be used to test whether there is a significant linear relationship between two variables ( $x$  and  $y$ ). Values of  $r$  can vary between  $-1$  and  $1$ . Values of  $1$  or  $-1$  indicate a perfect relationship between the two variables (*i.e.* all the data points would lie exactly on a

straight line if plotted on a graph). Positive values of  $r$  indicate a positive relationship between  $x$  and  $y$ ; *i.e.* as  $x$  increases so does  $y$ . Negative values indicate an inverse relationship between  $x$  and  $y$ . The closer the estimated value of  $r$  is to 1 or  $-1$ , the more significant (*i.e.* stronger) is the relationship between the two variables; the closer  $r$  is to 0, the less significant is the relationship. Also, for low numbers of data pairs ( $n$ ), higher values of  $r$  are needed to show statistical significance, and conversely, for higher numbers of data pairs, lower values of  $r$  may indicate a significant relationship. Some scatterplots and correlation coefficients obtained in environmental studies are illustrated in Figure 1.8. Regression lines are drawn only for those plots



**Figure 1.8** Typical scatterplots of environmental data. (a) Sulfate versus zinc in rainwater ( $r = 0.649$ ); (b) sulfate versus copper in rainwater ( $r = 0.348$ ); (c) lead in road dust versus traffic flow ( $r = 0.570$ ); (d) manganese versus iron in air ( $r = 0.967$ )

where the value of the correlation coefficient indicates a significant relationship.

Pearson's correlation coefficient can be calculated manually from the following equation:

$$r = \frac{n\sum x_i y_i - \sum x_i \sum y_i}{\left( \left[ n\sum x_i^2 - \left( \sum x_i \right)^2 \right] \times \left[ n\sum y_i^2 - \left( \sum y_i \right)^2 \right] \right)^{1/2}}$$

but the process is tedious. Most scientific calculators are programmed to calculate the correlation coefficient. A correlation table (see Appendix E) is used to evaluate the level of significance of a linear relationship between  $x$  and  $y$ . The table gives critical value of  $r$  for different numbers of data pairs ( $n$ ). Critical values of  $r$  are usually taken at  $P = 0.05$ . If the calculated value of  $r$  is greater than that of the critical value given in the table, then in all likelihood there is a significant linear relationship between  $x$  and  $y$ ; *i.e.* there is less than 5% probability (1 in 20) that this could be due to random data points. If  $r$  is lower than the critical value, then there is no significant linear relationship between  $x$  and  $y$ . It should be remembered that although the correlation coefficient is a valid indicator of association between two variables, it does not imply causation.

If a large number of parameters have been determined at one sampling site, possible interrelationships may be illustrated by a correlation matrix. Such a matrix is shown in Table 1.6 for various chemical parameters in rainwater sampled at a single site. The significance of each correlation coefficient must be tested (see Example 1.3). It is apparent that there are many significant correlations between rainfall constituents. These may not necessarily indicate a

**Table 1.6** Correlation matrix<sup>a</sup> for rainwater samples giving values of Pearson's correlation coefficient,  $r$ , for pairs of variables

	<i>mm</i>	<i>cond.</i>	$H^+$	$Cl^-$	$NO_3^-$	$SO_4^{2-}$	$Na^+$	$K^+$	$Mg^{2+}$	$Ca^{2+}$
$Ca^{2+}$	<u>-0.585</u>	<u>0.671</u>	-0.067	0.329	<u>0.597</u>	<u>0.648</u>	<u>0.435</u>	<u>0.703</u>	<u>0.860</u>	1
$Mg^{2+}$	<u>-0.477</u>	<u>0.734</u>	-0.006	<u>0.506</u>	<u>0.362</u>	<u>0.555</u>	<u>0.698</u>	<u>0.732</u>	1	
$K^+$	<u>-0.508</u>	<u>0.696</u>	0.030	<u>0.359</u>	<u>0.413</u>	<u>0.486</u>	<u>0.458</u>	1		
$Na^+$	<u>-0.349</u>	<u>0.530</u>	-0.022	<u>0.692</u>	0.075	<u>0.406</u>	1			
$SO_4^{2-}$	<u>-0.337</u>	<u>0.619</u>	<u>0.369</u>	<u>0.582</u>	<u>0.831</u>	1				
$NO_3^-$	<u>-0.342</u>	<u>0.584</u>	<u>0.399</u>	<u>0.347</u>	1					
$Cl^-$	-0.275	<u>0.504</u>	<u>0.344</u>	1						
$H^+$	0.129	0.247	1							
<i>cond.</i>	<u>-0.478</u>	1								
<i>Mm</i>	1									

<sup>a</sup> Significant correlations ( $P < 0.05$ ) are underlined; *mm*, rainfall amount, *cond.*, conductivity. Taken from Ref. 1.

common source, as high correlations between two parameters may arise out of a co-dependence on a third, such as the rainfall intensity in this example. On the other hand, many of the substances in Table 1.6 have common sources; *e.g.* Na, Cl, Mg, Ca, K, and  $\text{SO}_4^{2-}$  are all present in sea-salt aerosols, while Mg, Ca, and  $\text{SO}_4^{2-}$  (as  $\text{CaSO}_4$ ) are also found in mineral dusts.

### 1.7.8 Linear Regression

Once a significant relationship between two variables  $x$  and  $y$  has been confirmed, either visually or by means of the correlation coefficient, it is often necessary to draw a best-fit line through the data points, or derive an equation relating the two variables. This is typically required when preparing a calibration graph in which some measured parameter,  $y$  (*e.g.* absorbance), is plotted against concentration of standard,  $x$ .

The equation for a straight line is

$$y = a + bx$$

In order to be able to draw the best-fit line, we need to know the slope of the line,  $b$ , and the intercept on the  $y$ -axis,  $a$ . These can be calculated from the following equations:

$$b = \frac{n\sum x_i y_i - \sum x_i \sum y_i}{n\sum x_i^2 - (\sum x_i)^2}$$

and

$$a = \bar{y} - b\bar{x}$$

where  $\bar{x}$  and  $\bar{y}$  are the mean values of  $x_i$  and  $y_i$ . Most scientific calculators contain programmes for linear regression as do computers supplied with modern instruments. With most modern instruments, the calibration graph and the final result can be calculated automatically by the online computer.

#### *Example 1.3*

Concentrations of Pb and Mn in atmospheric particulate matter were determined in 10 air samples. The following results were obtained in  $\mu\text{g m}^{-3}$ :

No.	1	2	3	4	5	6	7	8	9	10
Pb	1.82	0.96	0.37	0.61	0.68	0.38	0.24	0.77	1.52	0.58
Mn	0.36	0.14	0.05	0.08	0.25	0.03	0.01	0.09	0.29	0.07

- (a) Is there a statistically significant linear relationship between Mn and Pb concentrations?

- (b) If there is a significant relationship derive an equation relating Mn to Pb for these samples.
- (a) The correlation coefficient,  $r$ , was calculated using the linear regression programme on a scientific calculator and found to be 0.908. The critical value of  $r$  ( $P = 0.05$ ) for 10 data pairs (*i.e.* eight degrees of freedom) is given as 0.632 in statistical tables (Appendix E). Since calculated  $r >$  critical  $r$ , it can be concluded that there is a significant linear relationship between Pb and Mn in air.
- (b) Using the same programme on the scientific calculator, it was possible to determine the linear regression taking Mn as  $y$  and Pb as  $x$ . The slope,  $b$ , was calculated to be 0.214, and the intercept,  $a$ , was found to be  $-0.033$ . The equation is

$$\text{Mn} = -0.033 + 0.214 \text{ Pb}$$

*Note:* The above problem can also be solved using MS Excel or SPSS and the graph of Mn against Pb plotted together with the best-fit line.

### 1.7.9 Detection Limits

The detection limit (d.l.) is the smallest value that can be distinguished from a blank and there are various ways to calculate this. One method is to use the following expression:

$$\text{d.l.} = 3 \times \frac{\text{standard deviation of the baseline noise}}{\text{sensitivity}}$$

The sensitivity is the instrument response (*e.g.* peak height on a chart recorder output) per unit amount or concentration of substance. If a result of a sample analysis is found to be below this value, it is reported as being  $<$  d.l. and no numerical value is specified. Different analytical methods have different detection limits and the analyst should be aware of these when selecting the appropriate method for a specific analysis.

The practice of not giving numerical values to measurements that are  $<$  d.l. has been repeatedly criticised. Problems arise with this kind of data when statistical analysis of results is carried out, and various assumptions have to be made. For example, values  $<$  d.l. can be replaced with zeros, the value of d.l., or some fraction of the d.l. value, but none of these are satisfactory. It has been suggested that results of all measurements should be reported, whether above or below the d.l., in order to facilitate subsequent statistical analysis.

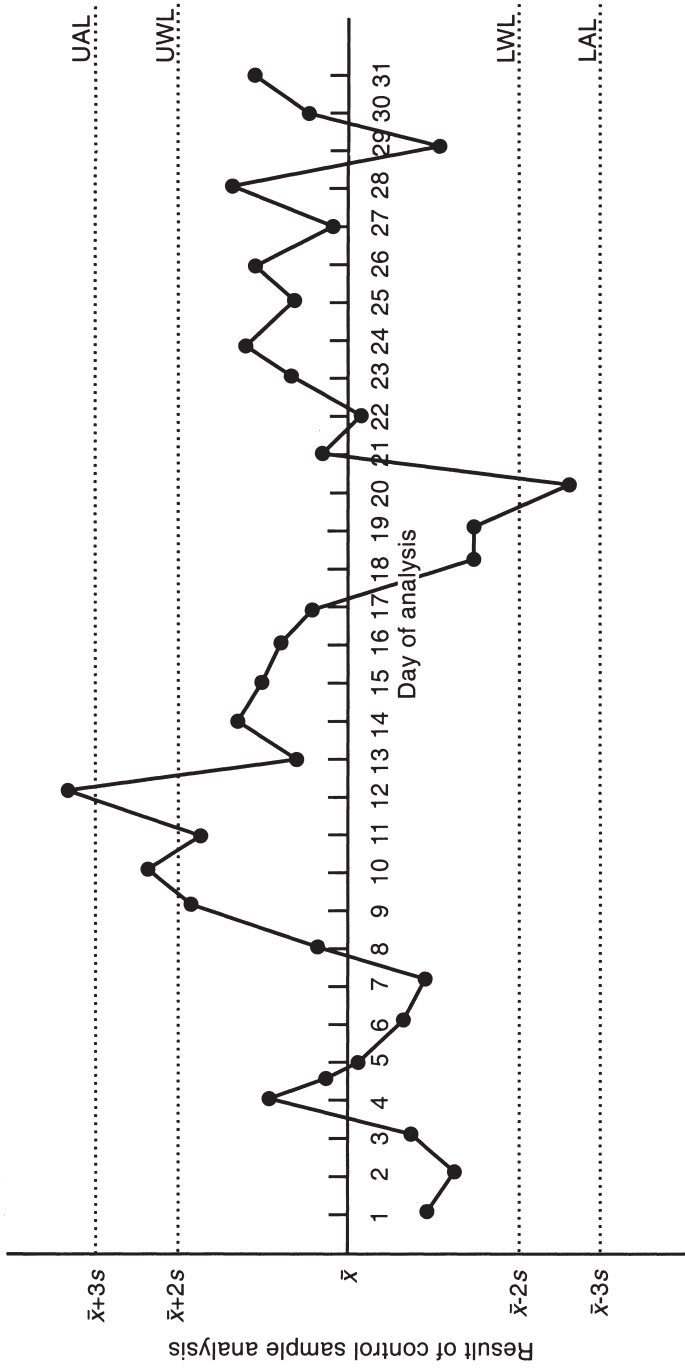
### 1.7.10 Reference Materials

While precision of a method can be tested by means of replicate analysis, the accuracy of the method cannot be determined since the “true” value is unknown. One way to assess the accuracy of a method is by analysing *reference materials*. Reference materials are actual samples (e.g. river water, sediment, soil), which have been carefully analysed by a government laboratory. Concentrations of various analytes in the samples are reported and the material is said to have been *certified* when accompanied by a certificate. These are called *certified reference materials* (CRM) and they can be purchased from government laboratories (e.g. Laboratory of the Government Chemist (LGC) in the UK, Community Bureau of Reference (BCR) of the European Community, National Bureau of Standards (NBS) in the USA). The reference material can then be analysed and the determined concentration compared with that quoted on the certificate accompanying the material to get some indication of the analytical error.

### 1.7.11 Quality Control

There are two types of quality control: *intralaboratory* quality control, which is carried out in one laboratory and *interlaboratory* quality control involving several laboratories. Nowadays, many laboratories participate in government-run quality control schemes in order to earn *accreditation*. The central government laboratory routinely monitors the performance of participating laboratories and those laboratories that show a poor performance may lose their accredited status. If a laboratory loses its accredited status, it may not be allowed to carry out analyses on government contract, its results would not be considered valid in a court of law in case of a dispute over infringement of environmental standards, *etc.* For a commercial laboratory to lose accredited status, it may be a significant blow since customers may lose confidence in it and take their samples elsewhere.

One way of monitoring the quality of laboratory analyses is by means of a control chart. A typical quality control chart is illustrated in Figure 1.9. A *control sample* is routinely analysed with each batch of samples and a day-to-day record of the result of the standard analysis is kept in the form of a time series chart. At the onset of the quality control scheme, the control sample is repeatedly analysed (e.g. 20 times) and the mean and standard deviation are determined. Lines are drawn on the chart corresponding to the concentration of the control sample (mean) and corresponding  $\bar{x} \pm 2s$  and  $\bar{x} \pm 3s$ , where  $s$  is the standard deviation of replicate measurements of the control sample. The  $\bar{x} \pm 2s$  lines are called the *warning limits* and the  $\bar{x} \pm 3s$  lines are called the *action limits*. The performance of the laboratory is satisfactory if the measured values



**Figure 1.9** Example of a control chart where  $\bar{x}$  is the mean of replicate analyses of the control sample and  $s$  is the standard deviation. Concentrations of analyte determined in control sample are plotted for each day when an analysis is carried out. UWL, upper warning limit; UAL, upper action limit; LWL, lower warning limit; LAL, lower action limit

of the standard material fall within  $\bar{x} \pm 2s$ . If the measurement falls outside the  $\bar{x} \pm 3s$  limits, then there is something seriously wrong; the analytical procedure has to be reviewed, and all analytical results obtained on that day have to be rejected. Once the source of the problem has been identified and corrected, the samples have to be re-analysed before the results can be released. If the result on a particular day falls outside the warning limits but below the action limits, there may be a hint of a problem, and the analyst has to pay close attention to the analytical method to ensure that future analyses do not exceed the action limits. Control samples can be either natural environmental samples or samples spiked with a standard of the analyte. Accredited laboratories that participate in interlaboratory quality control schemes can usually obtain control samples from the central government laboratory.

## 1.8 COMMON PROBLEMS OF ENVIRONMENTAL ANALYSIS

The need for data of the highest quality in environmental analysis cannot be overstated as the results of an environmental analysis may have far-reaching implications beyond the immediate laboratory. Data generated by the environmental analyst may be used by government agencies to investigate compliance with environmental emission and quality standards, to assess the status and trends of the environment, and to make policy decisions that could affect not only the environment but society at large. Furthermore, the results of an environmental analysis may be presented in a court of law when there is a dispute between a polluting industry and an aggrieved party. Therefore, the environmental analyst should perform his work conscientiously and diligently. Unfortunately, the fact remains that a lot of environmental data, even that published in reputable academic journals, is of dubious quality. This, however, is not in most cases entirely due to the negligence of the analyst, but is due to the very nature of environmental analysis, which can be quite complex and problematic, to say the least. Unlike many other types of chemical analyses, such as those performed routinely in industrial laboratories, environmental analysis has additional, specific problems, of which the analyst should be aware. Some of these were mentioned earlier, and others will be dealt with throughout the course of this book, but due to their importance they are summarised below:

- *Low concentration of analyte*, often close to, at or below the detection limit of many analytical methods.
- *Complex matrix*, with numerous other compounds (known and unknown) present in the sample and this could lead to several other problems on this list.
- *Interferences* are more likely than in other types of analysis due to the large number of compounds present.

- *Contamination* is more likely due to the low concentrations of analyte and special precautions have to be taken to avoid this during various stages of analysis.
- *Sample variety* is greater than in other types of routine analyses and samples from different sources may require modified or different procedures (e.g. water samples may range from highly polluted wastewaters, to very clean rainwater, to seawater with a very high electrolyte content, etc.).
- *No suitable method* may be available for the analyte, as the analyte may be a new pollutant not previously considered, and the analyst may have to develop a satisfactory method.
- *Speciation* may present a particular problem since a substance (e.g. heavy metal) may be present in different forms, and toxicity of the substance may depend on its form.
- *Reaction of analyte*, which could either increase or decrease its concentration (e.g. biological reactions, chemical reactions, adsorption).

Over the years scientists have become aware of the above problems, and a historical review of environmental literature reveals a steady drop in reported concentrations of many trace substances at re-visited sites not always due to a decrease in pollution, but quite often to improvements in analytical methodology, elimination of interferences, etc. For example, much of the early data on the pH of acid rainwater has been questioned, and is probably unreliable.

## 1.9 ETHICS

Environmental analysts should be aware of ethical issues in relation to research (including reporting of data), publications, and the environment. In the past, ethics were not taught as a subject on science courses, and students basically emulated their professors with regards to the way research was conducted, reported, and published, sometimes picking up practices, which by today's standards may be deemed as unacceptable or unethical. In view of the seriousness attached to ethics in science these days, and the dire consequences for those pursuing unethical practices, it is our opinion that students should be briefed on ethical issue at the earliest stage. Furthermore, as basic environmental research is also the subject of this book, it is necessary to introduce students to the ethics of conducting research studies and publishing their results, and raise their awareness about the issues concerned.

Scientists try to discover the truth about nature and natural processes, and consequently need to be objective in the way they conduct their studies and report their results. Therefore, scientists must report truthfully the results of their studies regardless of their personal motives, interests, or desires. Altering or faking scientific data has no place in science, and such practices

are roundly condemned. A scientist is not concerned whichever way the results may fall, but only with reporting the results truthfully to the scientific community, to his managers, and to the public. Unfortunately, some scientists violate ethical principles for personal gain, and there are increasing cases of scientific fraud and plagiarism being reported.

The scientific method allows observations to be made without opinion, prejudice, or bias, however, scientists live in the real world, and increasingly, subjectivity, vested interests, political persuasions, and social and economic pressures influence scientific research, or at least which type of research will be undertaken. This is especially true when it comes to the funding of scientific research by grant awarding bodies in government and industry, and the publication of research findings, either through the policy of editorial boards of journals or the decisions of grant funding bodies. Regrettably, it is not uncommon for grant funding bodies, especially those in industry, to censor the publication of research results that run contrary to their perceived interests, thus depriving the scientific community and the public of some aspect of uncovered scientific truth. This in itself could be considered a violation of scientific ethics, although according to some, it would be a violation of professional ethics for a scientist to publish results without authorisation by those who funded the research. One can see that research scientists are often faced with a dilemma in situations such as these, and no more so than in the environmental sciences. Vested interests and political, social, and economic considerations play a far greater role in environmental sciences than in most other areas of science and technology, and faced with these, some environmental scientists may experience conflict between their personal interests and their social and environmental conscience.

Furthermore, many scientists nowadays experience pressures to publish extensively in order to maintain their position at work and in the scientific community, and this may also lead some to stray from accepted and ethical practices as well as resulting in low-quality publications. What is considered acceptable and ethical may also change with time, and we can expect the scientific community to become more stringent and rigorous in the future with regard to these issues. A set of tentative guidelines is therefore given below:

- Analysts do not fabricate, alter, or delete data.
- If an analyst discovers major errors in his/her report or publication, he/she takes steps to correct those errors by publishing correction notes, erratum and informing his managers of the errors.
- Scientists do not practice plagiarism; *i.e.* they do not present the work of others as their own.
- Authorship of reports, papers, and other publications should reflect the individual contributions of the participants regardless of their status.

- The student should normally be listed as the principal author if the publication is based substantially on the student's work, unless otherwise agreed upon between the authors and accepted by the student.
- Minor contributions are made in acknowledgments.
- Those who have not contributed to the work or the writing of the paper should not be listed as authors.

Further guidelines can also be recommended for more senior scientists, but the above should be sufficient to guide the student through his/her research and early career. The question of environmental ethics is much broader and beyond the scope of this book, but dilemmas that may arise include whether the student or graduate considers a potential research project of value to the environment and society, whether he/she will accept to work on a project funded by organizations which may be perceived as having a vested interest in harming the environment, which particular career he/she may choose to pursue, *etc.*

### 1.10 A WORD OF ADVICE

Before you embark on the experimental programme, you should read Appendix A, which deals with safety in and out of the laboratory. Always pay particular attention to safety issues when doing practical work. Be especially cautious when handling acids or when boiling or digesting solutions. Concentrated acids are used in many of the experiments and these are extremely dangerous. Use rubber gloves and protective glasses when handling concentrated acids. Reagents and specialised equipment required are listed for each experiment. General laboratory glassware such as balances, beakers, flasks, pipettes, and burettes are not listed. It is assumed that such equipment would be available in every laboratory. The volumes required are given in the experimental procedures. Also, wherever the term "water" is used in the experimental sections, it refers to laboratory grade water: distilled, deionised, doubly distilled, Milli-Q, NANOpure, *etc.* You should use water of the highest quality available.

It should be noted that modifications could readily be made to many of the experimental procedures given in the book. In some cases, the required instruments may not be available but the laboratory may be equipped with some other suitable instrument. For example, an inexpensive flame photometer may be used for the determination of some alkali and alkali earth metals instead of the more expensive AAS. Where an alternative method or technique is available, this is pointed out in the text. Other modifications may be necessary due to the nature of the sample. Environmental samples are not uniform and vary considerably from location to location. For example, the concentration of some substances in rainwater may be rather different at a

remote, rural location than in a polluted city with many pollution sources. In some cases, calibration standards may have to be prepared over a different range than quoted in the experimental procedures, or samples may have to be diluted, or concentrated, as the case may be, to fit them within the range of the calibration curve. These are relatively simple modifications and should present no problem.

Some of the questions and problems may require additional reading in order to be solved. The references given under “Further Reading” at the end of each section should be sufficient for this. Suggestions for various projects are given at the end of some of the experiments. These could be carried out individually as a final year undergraduate research project, or by groups as part of science projects in schools. With a little imagination, it is easy to come up with other projects based on these experiments.

## EXERCISES AND INFORMATION

### Questions and Problems

1. What is a biogeochemical cycle? Give examples of some important cycles and explain how human activities may have affected them.
2. If the mass of a substance in a reservoir is  $60 \times 10^6$  kg and the flux through the reservoir is  $5 \times 10^6$  kg per annum, calculate the residence time assuming a steady state.
3. Differentiate between the following pairs of concepts:
  - (a) random error and systematic error,
  - (b) continuous analysis and batch analysis,
  - (c) qualitative analysis and quantitative analysis,
  - (d) sample and analyte,
  - (e) precision and accuracy, and
  - (f) local pollution and global pollution.
4. Define the following:
  - (a) standard deviation,
  - (b) normal distribution,
  - (c) method of standard addition,
  - (d) calibration, and
  - (e) certified reference material.
5. The chloride ion concentration in a certified reference material (river water) was determined by precipitation titration with  $\text{AgNO}_3$ . Five replicate measurements were made and the following  $\text{Cl}^-$  concentrations were determined (in  $\text{mg L}^{-1}$ ): 15.5, 14.8, 15.9, 15.2, and 15.3.

The reference material was accompanied with a certificate that quoted a  $\text{Cl}^-$  concentration of  $15.1 \text{ mg L}^{-1}$ . Calculate:

- the mean,
  - the standard deviation,
  - the variance,
  - the coefficient of variation,
  - the absolute error, and
  - the relative error.
6. Lead (Pb) in motorway runoff water was determined by flame AAS. A stock solution labelled "S1" contained  $1000 \text{ mg L}^{-1}$  Pb. Fifty  $\mu\text{L}$  of this solution were diluted to 50 mL to give a standard solution labelled "S2". Successive portions (1, 2, 3, 4 and 5 mL) of solution S2 were placed in a series of 50 mL volumetric flasks and diluted to the mark with distilled water. These solutions were then analysed using AAS and the following absorbance values were recorded:

Volume of standard S2 added (mL)	1	2	3	4	5
Absorbance (A)	0.15	0.29	0.45	0.56	0.69

The sample of motorway runoff water gave a response of 0.38 absorbance units.

- Plot a calibration graph with the  $x$ -axis in units of  $\text{mg Pb L}^{-1}$ .
  - Read off the concentration of Pb in the motorway runoff sample.
  - Convert the concentration to units of  $\text{mol L}^{-1}$ .
  - Derive an equation relating A to Pb concentration.
7. A water sample was analysed for iron (Fe) by means of flame AAS by the method of standard additions. Fifty mL aliquots of the sample were placed in 100 mL volumetric flasks and varying quantities of a standard  $100 \text{ mg L}^{-1}$  solution were added. The flasks were made up to the mark with distilled water and analysed. The output from the spectrophotometer was recorded on a chart recorder and the following results were obtained:

Volume of standard added (mL)	0	5	10	15	20
Response (mm)	16	45	77	101	125

- Prepare a calibration plot for the standard addition.
  - Determine the concentration of Fe in the sample.
8. Five aliquots of a water sample were analysed for cadmium (Cd) and the following concentrations (in  $\text{mg L}^{-1}$ ) determined: 38, 36, 41, 40, and 39.
- Calculate the mean, standard deviation, and the 95% confidence interval.

- (b) Express the mean concentration in units of  $\text{mol L}^{-1}$ .
- (c) Analysis of an additional aliquot from the same sample yielded a concentration of 25 ppm. Should this result be accepted or rejected?
9. The concentrations of Fe and Zn were determined in atmospheric particulate matter in eight samples and the following concentrations determined (in  $\mu\text{g m}^{-3}$ ):
- |     |      |      |      |      |      |      |      |      |
|-----|------|------|------|------|------|------|------|------|
| No. | 1    | 2    | 3    | 4    | 5    | 6    | 7    | 8    |
| Fe  | 1.82 | 1.02 | 0.57 | 0.62 | 1.29 | 0.30 | 0.23 | 0.99 |
| Zn  | 0.27 | 0.02 | 0.13 | 0.02 | 0.71 | 0.13 | 0.15 | 0.14 |

Draw a scatterplot and calculate the correlation coefficient. Is there a significant linear relationship between Fe and Zn in these samples? If there is, plot the regression line.

10. The concentration of nitric oxide (NO) was measured in a flue gas from a coal-fired power station. Repeated measurements were made using the same sampling technique and same instrumentation. The following six measurements were recorded (in ppmv): 501, 495, 503, 497, 488, and 531. Should the sixth measurement of 531 ppmv be retained or rejected?

### Suggestions for Projects

1. Select one biogeochemical cycle (*e.g.* nitrogen) and carry out a thorough literature search. Try to read up as much as possible on the topic and write a long essay (*ca.* 4000 words). Discuss how the cycle may have been affected by anthropogenic activities and what could be the potential consequences of this perturbation. Suggest measures that could be taken to redress the balance.
2. Select an environmental problem of your choice (*e.g.* acid rain) and carry out a thorough literature search using books, journals, Internet, *etc.* Try to read as much as possible on the topic and write a long essay (*ca.* 4000 words).
3. Initiate a quality control programme in your laboratory based on the use of quality control charts (Figure 1.9). You will need a large volume of a specific sample or an artificially prepared solution containing the analyte that you are interested in. For example, you may be conducting a survey of chloride in riverwater (but you can do the same for any analyte and any sample). At the start of the monitoring programme take a large volume of one riverwater sample, say, several litres, or prepare an artificial sample by adding NaCl to a similarly large volume of laboratory water to give a concentration in the range of that

expected in real samples. This solution will be your control sample. Analyse a large number of replicates of this control sample (*e.g.* 20) and establish the warning and action limits for your quality control chart. Store this solution in a refrigerator. Each time that an analysis of riverwater samples is carried out in your laboratory, also analyse one aliquot of the stored control sample. Plot the results on the chart and monitor the quality of work in your laboratory. If the analysis is performed by different individuals on different days, the quality control chart can be used to assess the performance of different analysts.

## REFERENCE

1. M. Radojevic and L.H. Lim, A rain acidity study in Brunei Darussalam, *Water, Air, and Soil Pollution*, 1995, **85**, 2369–2374.

## FURTHER READING

*Analytical Chemistry Textbooks.* The following introductory texts provide good coverage of basic analytical techniques (both classical and instrumental) and laboratory practices. Students unfamiliar with the theory and practice of analytical chemistry should read one of these textbooks.

G.D. Christian, *Analytical Chemistry*, 6th edn, Wiley, New York, 2003.

D.A. Scoog, D.M. West, F.J. Holler and S.R. Crouch, *Analytical Chemistry: An Introduction*, 7th edn, Harcourt, Orlando, 2000.

*Environmental Chemistry Textbooks.* The following books provide a good introduction to environmental chemistry and the problems of pollution:

P. O'Neill, *Environmental Chemistry*, 3rd edn, CRC Press, Boca Raton, FL, 1998.

B.J. Alloway and D.C. Ayers, *Chemical Principles of Environmental Pollution*, 2nd edn, CRC Press, Boca Raton, FL, 1997.

J.E. Andrews, P. Brimblecombe, T.D. Jickells, P.S. Liss and B.J. Reid, *An Introduction to Environmental Chemistry*, 2nd edn, Blackwell Science, Oxford, 2003.

R.M. Harrison and S.J. de Mora, *Introductory Chemistry for the Environmental Sciences*, Cambridge University Press, Cambridge, 1996.

R.M. Harrison, (ed) *Understanding our Environment: An Introduction to Environmental Chemistry and Pollution*, 2nd edn, Royal Society of Chemistry, Cambridge, 1999.

R.M. Harrison, (ed) *Pollution: Causes, Effects, and Control*, 4th edn, Royal Society of Chemistry, Cambridge, 2001.

V.N. Bashkin, *Modern Biogeochemistry*, Kluwer Academic Publishers, Dordrecht, 2002.

V.N. Bashkin, *Environmental Chemistry: Asian Lessons*, Kluwer Academic Publishers, Dordrecht, 2003.

The following books are excellent introductory texts to the subject of environmental analytical chemistry and they provide supplementary material to the experiments in the present book.

C.N. Sawyer, P.L. McCarty and G.F. Parkin, *Chemistry for Environmental Engineering*, 5th edn, McGraw-Hill, New York, 2003.

R.N. Reeve, *Environmental Analysis, Analytical Chemistry by Open Learning*, Wiley, Chichester, UK, 1994.

D.N. Boehnke and R.D. Delumyea, *Laboratory Experiments in Environmental Chemistry*, Prentice-Hall, Englewood Cliffs, NJ, 2000.

F.M. Dunnivant, *Environmental Laboratory Exercises for Instrumental Analysis and Environmental Chemistry*, Wiley, New York, 2000.

M.G. Ondrus, *Environmental Chemistry: Experiments and Demonstrations*, 2nd edn, Wuerz Publishing Ltd, Winnipeg, 1996.

S.E. Allen (ed), *Chemical Analysis of Ecological Materials*, 2nd edn, Blackwell, Oxford, 1989.

*Environmental Analysis Journals.* *The International Journal of Environmental Analytical Chemistry* is devoted specifically to environmental analytical chemistry. Articles of relevance to environmental analysis and environmental chemistry can be found in a variety of chemical and environmental journals (Appendix F).