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Chemical analysis

1.1 Introduction

'Chemical analysis' may be reasonably stated as the application of a process or series of processes in order to identify and/or quantify a substance, the components of a solution or mixture, or the determination of the structures of chemical compounds.

This means that the scope of analytical chemistry is very broad and embraces a wide range of manual, chemical and instrumental techniques and procedures. Most people apply some form of chemical analysis almost every day, such as when smelling food to see if it has deteriorated or tasting substances to determine if they are sweet or sour. These constitute simple analytical processes, as compared with some of the more complex processes described in this volume that can be achieved with modern instruments. It is not always necessary to apply advanced instrumental procedures to carry out accurate analyses and there may be many times when a simple, rapid analysis may actually be more desirable than a more complicated and time-consuming process. The objective and purpose of the analysis has to be sensibly assessed before selecting an appropriate procedure.

When a completely unknown sample is presented to an analyst, the first requirement is usually to ascertain what substances are present in it. This fundamental problem may sometimes be encountered in the modified form of deciding what impurities are present in a given sample, or perhaps of confirming that certain specified impurities are absent. The solution lies within the province of **qualitative analysis** and is outside the scope of this book.

Having ascertained the nature of the constituents of a given sample, the analyst is then frequently called upon to determine how much of each component, or of specified components, is present. Such determinations lie within the realm of **quantitative analysis.** A variety of techniques are available for carrying out quantitative analysis. The techniques may broadly be classified into (i) classical or wet chemical methods of analysis and (ii) instrumental methods of analysis. The classical methods include the macro analytical methods of *gravimetry, titrimetry* and *volumetry* and are based on quantitative performance of suitable chemical reactions and measuring the amount of reagent needed to complete the reaction, or ascertaining the amount of reaction product obtained (vide Chapters 10 and 11). Instrumental methods are based on measurement of some physical property such as weight, voltage, current flow, absorption and emission spectra, etc. The methods may be sub-classified into *thermal analysis* (Chapter 12); *electroanalytical methods* (Chapter 13); *spectral methods* including atomic absorption spectrometry (Chapter 15), atomic emission spectroscopy (Chapter 16), molecular electronic spectroscopy (Chapter 17), vibrational spectroscopy (Chapter 18), and nuclear magnetic resonance spectroscopy (Chapter 14); *separation methods*

(Chapter 6) including thin layer chromatography (Chapter 7), liquid chromatography (Chapter 8) and gas chromatography (Chapter 9) and *mass spectrometry* (Chapter 19).

1.2 Applications

With increasing demands for pure water, better food control and cleaner atmospheres, the analytical chemist has a greater and greater role to play within modern society. From the study of raw materials, such as crude oil and minerals to the finest quality scents and perfumes, the analytical chemist is called upon to play a part in determining composition, purity and quality. Manufacturing industries rely upon both qualitative and quantitative chemical analysis to ensure their raw materials meet certain specifications, and to check the quality of the final product. Raw materials are examined to ensure there are no unusual substances present which might upset the manufacturing process or appear as a harmful impurity in the final product. Furthermore, since the value of the raw material may be governed by the amount of the required ingredient it contains, a quantitative analysis is performed to establish the proportion of the essential component: this procedure is often called **assaying**. The final manufactured product is subject to **quality control** to ensure its essential components are present within a predetermined range of composition, whereas impurities do not exceed certain specified limits. The semiconductor industry is an example of an industry whose very existence depends on very accurate determination of substances present in extremely minute quantities.

The development of new products (which may be mixtures rather than pure materials, e.g. a polymer composition, or a metallic alloy) also requires the services of the analytical chemist. It will be necessary to ascertain the composition of the mixture which shows the optimum characteristics for the purpose for which the material has been developed.

Many industrial processes give rise to pollutants which can present a health problem. Quantitative analysis of air, water, and sometimes soil samples, must be carried out to determine the level of pollution, and to establish safe limits for pollutants.

In hospitals, chemical analysis is widely used to assist in the diagnosis of illness and in monitoring the condition of patients. In farming, the nature and level of fertiliser application is based on information obtained by analysing the soil to determine its content of the essential plant nutrients nitrogen, phosphorus and potassium, and the trace elements required for healthy plant growth.

Geological surveys require the services of analytical chemists to determine the composition of the numerous rock and soil samples collected in the field. One example is the qualitative and quantitative examination of moon rock brought back to Earth in 1969 by the first American astronauts to land on the moon.

Much government legislation can only be enforced by the work of analytical chemists, e.g. national and international agreements on water pollution and atmospheric pollution, food safety measures, regulations on substances hazardous to health, and laws governing the misuse of drugs.

When copper(II) sulphate is dissolved in distilled water, the copper is present in solution almost entirely as the hydrated copper ion $[Cu(H_2O)_6]^{2+}$. But if a natural water (spring water or river water) is substituted for the distilled water, then some of the copper ions will interact with various substances present in the natural water. These substances may include acids derived from vegetation (such as humic acids and fulvic acid), colloidal materials such as clay particles, carbonate ions (CO_3^{2-}) and hydrogencarbonate ions (HCO_3^-) derived from atmospheric carbon dioxide, and various other cations and anions leached from the rocks with which the water has been in contact. The copper ions which become adsorbed on colloidal particles, or those which form an organic complex, perhaps with fulvic acid, will no

Table 1.1 *Stages in a chemical analysis*

Stages	Examples of procedure
1. Sampling	Depends on the size and physical nature of the sample
2. Preparation of analytical sample	Reduction of particle size, mixing for homogeneity, drying, determination of sample weight or volume
3. Dissolution of sample	Heating, ignition, fusion, use of solvent(s), dilution
4. Removal of interferences	Filtration, solvent extraction, ion exchange, chromatographic separation
5. Sample measurement and control of instrumental factors	Standardisation, calibration, optimisation, measurement of response; absorbance, emission signal, potential, current
6. Result(s)	Calculation of analytical result(s) and for the sample, statistical evaluation of data
7. Presentation of data	Printout, data plotting, storage (archiving)

longer show the usual behaviour of hydrated copper(II) ions, so their biological and geological effects will be modified. To investigate these problems in natural waters, the analyst must devise procedures that determine the various copper-containing species in the solution and how the copper is distributed among them. These procedures are called '**speciation**'.

1.3 Stages of analysis

A complete chemical analysis, even for a single substance, involves a series of steps and procedures. Each one of them has to be carefully considered and assessed in order to minimise errors and to maintain accuracy and reproducibility. The steps are listed in Table 1.1 along with some of the procedures that may be employed. To obtain reliable results it is essential to choose a sample that is representative of the entire material.

The analyst must therefore be acquainted with the standard sampling procedures for different types of material as sample preparation can be the most difficult step in the overall analytical process. This is especially true when dealing with solid samples which may require a number of stages before measurements can be made on the analyte. If all operational stages in Table 1.1 take place without any human involvement, the analysis is considered fully automatic. Many autoanalysers used in clinical laboratories are totally automatic from the sampling stage right through to the presentation of data. Examples of automatic control are given throughout this text.

1.4 Selecting the method

Several approaches can often be used to analyse a particular sample. To choose the most appropriate, analysts must be familiar with the practical details of the various techniques and the theoretical principles on which they are based. They must also understand the conditions under which each method is reliable, consider possible interferences which may

arise, and find ways to circumvent any problems. Analysts will also be concerned with accuracy and precision, time and costing. The most accurate method for a certain determination may prove to be lengthy or it may require expensive reagents, and in the interests of economy it may be necessary to choose a method which, although somewhat less exact, yields results of sufficient accuracy in a reasonable time.

Important factors which must be taken into account when selecting an appropriate method of analysis include (a) the nature of the information which is sought, (b) the size of sample available and the proportion of the constituent to be determined, and (c) the purpose for which the analytical data is required.

The information sought may require very detailed data, or perhaps more general results. Chemical analyses may be classified into four types according to the data they generate:

Proximate analysis determines the amount of each element in a sample but not the compounds that are present.
Partial analysis determines selected constituents in the sample.
Trace constituent analysis is a type of partial analysis that determines specified components present in very minute quantity.
Complete analysis determines the proportion of each component in the sample.

On the basis of sample size, analytical methods are often classified as follows:

Macro for quantities of 0.1 g or more
Meso (semimicro) for quantities ranging from 10^{-2} g to 10^{-1} g
Micro for quantities in the range 10^{-3} g to 10^{-2} g
Submicro for samples in the range 10^{-4} g to 10^{-3} g
Ultramicro for quantities below 10^{-4} g
Trace for 10^{2} to 10^{4} $\mu g\, g^{-1}$ (100–10 000 parts per million)*
Microtrace for 10^{-1} to 10^{2} $pg\, g^{-1}$ (10^{-7} to 10^{-4} ppm)
Nanotrace for 10^{-1} to 10^{2} $fg\, g^{-1}$ (10^{-10} to 10^{-7} ppm)

The term 'semimicro' given as an alternative name for 'meso' is not very apt, referring as it does to samples larger than micro.

A major constituent accounts for 1% to 100% of the sample under investigation; a minor constituent is present in the range 0.01% to 1%; a trace constituent is present at a concentration of less than 0.01%.

When the sample weight is small (0.1–1.0 mg), the determination of a trace component at the 0.01% level may be called subtrace analysis. If the trace component is at the microtrace level, the analysis is called submicrotrace. With a still smaller sample (not larger than 0.1 mg) the determination of a component at the trace level is called ultratrace analysis, and with a component at the microtrace level, the analysis is called ultramicrotrace.

1.5 Searching the literature

The analytical chemist will often have to design a completely novel analysis and will have to seek information from previously published data. This may involve consulting multi-volume reference works such as Kolthoff and Elving, *Treatise on analytical chemistry*; Wilson and Wilson, *Comprehensive analytical chemistry*; Fresenius and Jander, *Handbuch*

* Concentrations are commonly quoted in parts per million (ppm), but this should be avoided as ppm is a dimensionless quantity.

der analytischen Chemie; a compendium of methods such as Meites, *Handbook of analytical chemistry*; or specialised monographs dealing with particular techniques or types of material. Details of recognised procedures for the analysis of many materials are published by various official bodies, such as the American Society for Testing and Materials (ASTM), the British Standards Institution and the European Commission. However, an initial search through the abstracting journals (e.g. *Analytical Abstracts*, *Chemical Abstracts*) will often provide additional information on recent developments and specific analytical procedures. Other general assessments of methods and results are available in review publications (e.g. *Annual Reports of the Chemical Society*), whereas current research is always available in journals specifically devoted to analytical chemistry (*The Analyst* and *Analytical Chemistry*).

1.6 Quantitative analysis by classical methods

The quantitative execution of chemical reactions is the basis of the traditional or 'classical' methods of chemical analysis: gravimetry, titrimetry and volumetry. In **gravimetric analysis** the substance being determined is converted into an insoluble precipitate which is collected and weighed. In **titrimetric analysis** (sometimes called volumetric analysis) the substance to be determined is allowed to react with an appropriate reagent added as a standard solution, and the volume of solution needed for complete reaction is determined. The common titrimetric reactions are neutralisation (acid–base) reactions, complex-forming reactions, precipitation reactions and oxidation–reduction reactions. **Volumetry** measures the volume of gas evolved or absorbed in a chemical reaction.

1.7 Quantitative analysis by instrumental methods

Instrumental methods are usually much faster than purely chemical methods and are applicable at concentrations far too small to be determined by classical methods. They find wide applications in industry.

Electrical methods of analysis (apart from electrogravimetry) involve the measurement of current, voltage or resistance in relation to the concentration of a certain species in solution. Electrical techniques include **voltammetry** (measurement of current at a microelectrode at a specified voltage); **coulometry** (measurement of current and time needed to complete an electrochemical reaction or to generate sufficient material to react completely with a specified reagent); and **potentiometry** (measurement of the potential of an electrode in equilibrium with an ion to be determined). In **electrogravimetry** electrolysis is carried out and the material deposited on one of the electrodes is weighed.

Thermal methods of analysis are based on weight measurements or energy changes as a function of temperature. **Thermogravimetry (TG)** records the change in weight; **differential thermal analysis (DTA)** records the difference in temperature between a test substance and an inert reference material; **differential scanning calorimetry (DSC)** records the energy needed to establish a zero temperature difference between a test substance and a reference material.

Spectroscopic methods of analysis depend on measuring the amount of radiant energy of a particular wavelength absorbed by the sample, or measuring the amount of radiant energy of a particular wavelength emitted by the sample. Absorption methods are usually classified according to the wavelength involved as **visible, ultraviolet** or **infrared spectrophotometry**; visible spectrophotometry is sometimes called colorimetry. In addition to these techniques there is the increasing use of **nuclear magnetic resonance spectroscopy** in the quantitative analysis of organic compounds.

Atomic absorption spectroscopy involves atomising the specimen, often by spraying a solution of the sample into a flame, and then studying the absorption of radiation from an electric lamp producing the spectrum of the element to be determined. **Turbidimetric and nephelometric methods** measure the amount of light stopped or scattered by a suspension. They are not absorption methods in the strictest sense, but they deserve to be mentioned here.

Emission methods subject the sample to heat or electrical treatment so that atoms are raised to excited states causing them to emit energy; the intensity of this energy is then measured. Here are some of the common excitation techniques:

Emission spectroscopy subjects the sample to an inductively coupled plasma then examines the emitted light (which may extend into the ultraviolet region).

Flame photometry uses a solution of the sample injected into a flame.

Fluorimetry takes a suitable substance in solution (commonly a metal–fluorescent reagent complex) and excites it using visible or ultraviolet radiation.

Chromatographic and **electrophoretic** methods are essentially separative processes for mixtures of substances, but they are also adapted to identify components of mixtures. The nature of modern detector systems means that chromatography and electrophoresis can be used for reliable quantitative determinations.

In **mass spectrometry** the material under examination is vaporised using a high vacuum and the vapour is bombarded by a high-energy electron beam. Many of the vapour molecules undergo fragmentation and produce ions of varying size. These ions can be distinguished by accelerating them in an electric field, and then deflecting them in a magnetic field where they follow paths dictated by their mass/charge ratio (m/ze) to detection and recording equipment; each kind of ion gives a peak in the **mass spectrum**. Non-volatile inorganic materials can be examined by vaporising them using a high-voltage electric spark.

Mass spectrometry can be used for gas analysis, for the analysis of petroleum products and in examining semiconductors for impurities. It is particularly useful for establishing the structure of organic compounds.

1.8 Special techniques

X-ray methods

X-rays are produced when high-speed electrons collide with a solid target (which can be the material under investigation). These X-rays are often known as **primary X-rays**. They arise because the electron beam may displace an electron from the inner electron shell of an atom in the target; the lost electron is then replaced by an electron from an outer shell, and energy is emitted as X-rays. It is possible to identify certain emission peaks which are characteristic of elements contained in the target. The wavelengths of the peaks can be related to the atomic number of the elements producing them, so they provide a means of identifying elements present in the target sample. Furthermore, under controlled conditions, the intensity of the peaks can be used to determine the amounts of the various elements present. This is the basis of **electron probe microanalysis**, in which a small target area of the sample is pinpointed for examination. This has important applications in metallurgical research, in the examination of geological samples, and in determining whether biological materials contain metallic elements.

When a beam of short-wavelength primary X-rays strikes a solid target, a similar mechanism as described above will cause the target material to emit X-rays at wavelengths