CHAPTER 1
INTRODUCTION

1.1 CHEMICAL ANALYSIS

'The resolution of a chemical compound into its proximate or ultimate parts; the determination of its elements or of the foreign substances it may contain': thus reads a dictionary definition.

This definition outlines in very broad terms the scope of analytical chemistry. 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 of such problems lies within the province of **qualitative analysis** and is outside the scope of the present volume.

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**, and to supply the required information a variety of techniques is available.

1.2 APPLICATIONS OF CHEMICAL ANALYSIS

In a modern industrialised society the analytical chemist has a very important role to play. Thus most manufacturing industries rely upon both qualitative and quantitative chemical analysis to ensure that the raw materials used meet certain specifications, and also to check the quality of the final product. The examination of raw materials is carried out to ensure that there are no unusual substances present which might be deleterious to the manufacturing process or appear as a harmful impurity in the final product. Further, since the value of the raw material may be governed by the amount of the required ingredient which it contains, a quantitative analysis is performed to establish the proportion of the essential component: this procedure is often referred to as **assaying**. The final manufactured product is subject to **quality control** to ensure that its essential components are present within a pre-determined range of composition, whilst impurities do not exceed certain specified limits. The semiconductor industry is an example of an industry whose very existence is dependent upon very accurate determination of substances present in extremely minute quantities.

The development of new products (which may be mixtures rather than pure materials, as for example 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 is being developed.

Many industrial processes give rise to pollutants which can present a health problem. Quantitative analysis of air, water, and in some cases soil samples, must be carried out to determine the level of pollution, and also 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 upon information obtained by analysis of the soil to determine its content of the essential plant nutrients, nitrogen, phosphorus and potassium, and of the trace elements which are necessary 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. A particular instance of such an exercise is the qualitative and quantitative examination of the samples of 'moon rock' brought back to Earth in 1969 by the first American astronauts to land on the moon.

Much legislation enacted by governments relating to such matters as pollution of the atmosphere and of rivers, the monitoring of foodstuffs, the control of substances hazardous to health, the misuse of drugs, and many others are dependent upon the work of analytical chemists for implementation.

When copper(II) sulphate is dissolved in distilled water, the copper is present in solution almost entirely as the hydrated copper ion $[Cu(H_2O)_6]^{2+}$. If, however, 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 with (for example) fulvic acid, will no longer show the usual behaviour of hydrated copper(II) ions and thus their biological and geological effects are modified. For the investigation of such problems in natural waters, it is therefore necessary for the analyst to devise procedures whereby the various copper-containing species in the solution can be identified, and the distribution of the copper among them determined. Such procedures are referred to as 'speciation'.

1.3 SAMPLING

The results obtained for the proportion of a certain constituent in a given sample may form the basis of assessing the value of a large consignment of the commodity from which the sample was drawn. In such cases it is absolutely essential to be certain that the sample used for analysis is truly representative of the whole. When dealing with a homogeneous liquid, sampling presents few problems, but if the material under consideration is a solid mixture, then it is necessary to combine a number of portions to ensure that a representative sample is finally selected for analysis. The analyst must therefore be acquainted

with the normal standard sampling procedures employed for different types of materials.

1.4 TYPES OF ANALYSIS

With an appropriate sample available, attention must be given to the question of the most suitable technique or techniques to be employed for the required determinations. One of the major decisions to be made by an analyst is the choice of the most effective procedure for a given analysis, and in order to arrive at the correct decision, not only must he be familiar with the practical details of the various techniques and of the theoretical principles upon which they are based, he must also be conversant with the conditions under which each method is reliable, aware of possible interferences which may arise, and capable of devising means of circumventing such problems. He will also be concerned with questions regarding the accuracy and the precision to be expected from given methods and, in addition, he must not overlook such factors as time and costing. The most accurate method for a certain determination may prove to be lengthy or to involve the use of 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 are required.

The nature of the information sought may involve requirement for very detailed data, or alternatively, results of a general character may suffice. With respect to the information which is furnished, different types of chemical analysis may be classified as follows:

1. *proximate analysis*, in which the amount of each element in a sample is determined with no concern as to the actual compounds present;
2. *partial analysis*, which deals with the determination of selected constituents in the sample;
3. *trace constituent analysis*, a specialised instance of partial analysis in which we are concerned with the determination of specified components present in very minute quantity;
4. *complete analysis*, when the proportion of each component of the sample is determined.

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

1. *macro*, the analysis of quantities of 0.1 g or more;
2. *meso* (*semimicro*), dealing with quantities ranging from 10^{-2} g to 10^{-1} g;
3. *micro*, for quantities in the range 10^{-3} g to 10^{-2} g;
4. *submicro*, for samples in the range 10^{-4} g to 10^{-3} g;
5. *ultramicro*, for quantities below 10^{-4} g.

The term 'semimicro' given as an alternative name for classification (2) is not very apt, referring as it does to samples larger than micro.

A **major constituent** is one accounting for 1–100 per cent of the sample under investigation; a **minor constituent** is one present in the range 0.01–1 per cent; a **trace constituent** is one present at a concentration of less than 0.01 per cent.

With the development of increasingly sophisticated analytical techniques it has become possible to determine substances present in quantities much lower than the 0.01 per cent upper level set for trace constituents. It is therefore necessary to make further subdivisions: **trace** corresponds to 10^2–10^4 μg per gram, or 10^2–10^4 parts per million (ppm), **microtrace** to 10^2–10^{-1} pg per gram, (10^{-4}–10^{-7} ppm), **nanotrace** to 10^2–10^{-1} fm per gram (10^{-7}–10^{-10} ppm).

When the sample weight is small (0.1–1.0 mg), the determination of a trace component at the 0.01 per cent level may be referred to as **subtrace analysis**. If the trace component is at the microtrace level, the analysis is termed **submicrotrace**. With a still smaller sample (not larger than 0.1 mg) the determination of a component at the trace level is referred to as **ultratrace analysis**, whilst with a component at the microtrace level, the analysis is referred to as **ultra-microtrace**.

The purpose for which the analytical data are required may perhaps be related to process control and quality control. In such circumstances the objective is checking that raw materials and finished products conform to specification, and it may also be concerned with monitoring various stages in a manufacturing process. For this kind of determination methods must be employed which are quick and which can be readily adapted for routine work: in this area instrumental methods have an important role to play, and in certain cases may lend themselves to automation. On the other hand, the problem may be one which requires detailed consideration and which may be regarded as being more in the nature of a research topic.

1.5 USE OF LITERATURE

Faced with a research-style problem, the analyst will frequently be dealing with a situation which is outside his normal experience and it will be necessary to seek guidance from published data. This will involve consultation of multi-volume reference works such as Kolthoff and Elving, *Treatise on Analytical Chemistry*; Wilson and Wilson, *Comprehensive Analytical Chemistry*; Fresenius and Jander, *Handbuch der analytischen Chemie*; of a compendium of methods such as Meites, *Handbook of Analytical Chemistry*; or of 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, as for example the American Society for Testing Materials (ASTM), the British Standards Institution and the Commission of European Communities. It may be necessary to seek more up-to-date information than that available in the books which have been consulted and this will necessitate making use of review publications (e.g. *Annual Reports of the Chemical Society*; reviews in *The Analyst* and *Analytical Chemistry*), and of abstracts (e.g. *Analytical Abstracts*; *Chemical Abstracts*), and referring to journals devoted to analytical chemistry and to specific techniques: see Section 1.7.*

Such a literature survey may lead to the compilation of a list of possible procedures and the ultimate selection must then be made in the light of the criteria previously enunciated, and with special consideration being given to questions of possible interferences and to the equipment available.

* Selected Bibliographies and References are given at the end of each part of the book; for Part A, see Sections 3.38 and 3.39.

1.6 COMMON TECHNIQUES

The main techniques employed in quantitative analysis are based upon (*a*) the quantitative performance of suitable chemical reactions and either measuring the amount of reagent needed to complete the reaction, or ascertaining the amount of reaction product obtained; (*b*) appropriate electrical measurements (e.g. potentiometry); (*c*) the measurement of certain optical properties (e.g. absorption spectra). In some cases, a combination of optical or electrical measurements and quantitative chemical reaction (e.g. amperometric titration) may be used.

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, or in the special case of **electrogravimetry** electrolysis is carried out and the material deposited on one of the electrodes is weighed.

In **titrimetric analysis** (often termed volumetric analysis in certain books), 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 types of reaction which are used in titrimetry are (*a*) neutralisation (acid–base) reactions; (*b*) complex-forming reactions; (*c*) precipitation reactions; (*d*) oxidation–reduction reactions.

Volumetry is concerned with measuring the volume of gas evolved or absorbed in a chemical reaction.

Electrical methods of analysis (apart from electrogravimetry referred to above) involve the measurement of current, voltage or resistance in relation to the concentration of a certain species in solution. Techniques which can be included under this general heading are (i) **voltammetry** (measurement of current at a micro-electrode at a specified voltage); (ii) **coulometry** (measurement of current and time needed to complete an electrochemical reaction or to generate sufficient material to react completely with a specified reagent); (iii) **potentiometry** (measurement of the potential of an electrode in equilibrium with an ion to be determined); (iv) **conductimetry** (measurement of the electrical conductivity of a solution).

Optical methods of analysis are dependent either upon (i) measurement of the amount of radiant energy of a particular wavelength absorbed by the sample, or (ii) the emission of radiant energy and measurement of the amount of energy of a particular wavelength emitted. Absorption methods are usually classified according to the wavelength involved as (*a*) **visible spectrophotometry** (colorimetry), (*b*) **ultraviolet spectrophotometry**, and (*c*) **infrared spectrophotometry**.

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.

Although not strictly absorption methods in the sense in which the term is usually employed, **turbidimetric and nephelometric methods** which involve measuring the amount of light stopped or scattered by a suspension should also be mentioned at this point.

Emission methods involve subjecting the sample to heat or electrical treatment

so that atoms are raised to excited states causing them to emit energy: it is the intensity of this emitted energy which is measured. The common excitation techniques are:

(*a*) *emission spectroscopy*, where the sample is subjected to an electric arc or spark plasma and the light emitted (which may extend into the ultraviolet region) is examined;
(*b*) *flame photometry*, in which a solution of the sample is injected into a flame;
(*c*) *fluorimetry*, in which a suitable substance in solution (commonly a metal–fluorescent reagent complex) is excited by irradiation with visible or ultraviolet radiation.

Chromatography is a separation process employed for the separation of mixtures of substances. It is widely used for the identification of the components of mixtures, but as explained in Chapters 8 and 9, it is often possible to use the procedure to make quantitative determinations, particularly when using Gas Chromatography (GC) and High Performance Liquid Chromatography (HPLC).

1.7 INSTRUMENTAL METHODS

The methods dependent upon measurement of an electrical property, and those based upon determination of the extent to which radiation is absorbed or upon assessment of the intensity of emitted radiation, all require the use of a suitable instrument, e.g. polarograph, spectrophotometer, etc., and in consequence such methods are referred to as 'instrumental methods'. Instrumental methods are usually much faster than purely chemical procedures, they are normally applicable at concentrations far too small to be amenable to determination by classical methods, and they find wide application in industry. In most cases a microcomputer can be interfaced to the instrument so that absorption curves, polarograms, titration curves, etc., can be plotted automatically, and in fact, by the incorporation of appropriate servo-mechanisms, the whole analytical process may, in suitable cases, be completely automated.

Despite the advantages possessed by instrumental methods in many directions, their widespread adoption has not rendered the purely chemical or 'classical' methods obsolete; the situation is influenced by three main factors.

1. The apparatus required for classical procedures is cheap and readily available in all laboratories, but many instruments are expensive and their use will only be justified if numerous samples have to be analysed, or when dealing with the determination of substances present in minute quantities (trace, subtrace or ultratrace analysis).
2. With instrumental methods it is necessary to carry out a calibration operation using a sample of material of known composition as reference substance.
3. Whilst an instrumental method is ideally suited to the performance of a large number of routine determinations, for an occasional, non-routine, analysis it is often simpler to use a classical method than to go to the trouble of preparing requisite standards and carrying out the calibration of an instrument.

Clearly, instrumental and classical methods must be regarded as supplementing each other.

1.8 OTHER TECHNIQUES

In addition to the main general methods of analysis outlined above there are also certain specialised techniques which are applied in special circumstances. Among these are X-ray methods, methods based upon the measurement of radioactivity, mass spectrometry, the so-called kinetic methods, and thermal methods.

X-ray methods. When high-speed electrons collide with a solid target (which can be the material under investigation), X-rays are produced. These are often referred to as **primary X-rays**, and arise because the electron beam may displace an electron from the inner electron shells of an atom in the target, and the electron lost is then replaced by one from an outer shell; in this process energy is emitted as X-rays. In the resultant X-ray emission 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, and thus provide a means of identifying elements present in the target sample. Further, 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 primary X-rays of short wavelength strikes a solid target, by a similar mechanism to that described above, the target material will emit X-rays at wavelengths characteristic of the atoms involved: the resultant emission is termed **secondary or fluorescence radiation**. The sample area can be large, and quantitative results obtained by examining the peak heights of the fluorescence radiation can be taken as indicative of sample composition. **X-ray fluorescence analysis** is a rapid process which finds application in metallurgical laboratories, in the processing of metallic ores, and in the cement industry.

Crystalline material will diffract a beam of X-rays, and X-ray powder diffractometry can be used to identify components of mixtures. These X-ray procedures are examples of **non-destructive methods of analysis**.

Radioactivity. Methods based on the measurement of radioactivity belong to the realm of radiochemistry and may involve measurement of the intensity of the radiation from a naturally radioactive material; measurement of induced radioactivity arising from exposure of the sample under investigation to a neutron source (**activation analysis**); or the application of what is known as the **isotope dilution technique**.

Typical applications of such methods are the determination of trace elements in (*a*) the investigation of pollution problems; (*b*) the examination of geological specimens; (*c*) quality control in the manufacture of semiconductors.

Mass spectrometry. In this technique, the material under examination is vaporised under 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/e) 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 by subjecting them to 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 also a very useful tool for establishing the structure of organic compounds.

Kinetic methods. These methods of quantitative analysis are based upon the fact that the speed of a given chemical reaction may frequently be increased by the addition of a small amount of a catalyst, and within limits, the rate of the catalysed reaction will be governed by the amount of catalyst present. If a calibration curve is prepared showing variation of reaction rate with amount of catalyst used, then measurement of reaction rate will make it possible to determine how much catalyst has been added in a certain instance. This provides a sensitive method for determining sub-microgram amounts of appropriate substances.

The method can also be adapted to determine the amount of a substance in solution by adding a catalyst which will destroy it completely, and measuring the concomitant change in for example, the absorbance of the solution for visible or ultraviolet radiation. Such procedures are applied in clinical chemistry.

Optical methods. Those of particular application to *organic compounds* are:

1. Use of a **refractometer** to make measurements of the refractive index of liquids. This will often provide a means of identifying a pure compound, and can also be used (in conjunction with a calibration curve) to analyse a mixture of two liquids.
2. Measurement of the **optical rotation** of optically active compounds. Polarimetric measurements can likewise be used as a method of identifying pure substances, and can also be employed for quantitative purposes.

Thermal methods. Changes in weight, or changes in energy, recorded as a function of temperature (or of time) can provide valuable analytical data. For example, the conditions can be established under which a precipitate produced in a gravimetric determination can be safely dried. Common techniques include the recording as a function of temperature or time of (*a*) change in weight (**Thermogravimetry, TG**); (*b*) the difference in temperature between a test substance and an inert reference material (**Differential Thermal Analysis, DTA**); (*c*) the energy necessary to establish a zero temperature difference between a test substance and a reference material (**Differential Scanning Calorimetry, DSC**).

1.9 FACTORS AFFECTING THE CHOICE OF ANALYTICAL METHODS

An indication has been given in the preceding sections of a number of techniques available to the analytical chemist. The techniques have differing degrees of sophistication, of sensitivity, of selectivity, of cost and also of time requirements, and an important task for the analyst is the selection of the best procedure for

a given determination. This will require careful consideration of the following criteria.

(*a*) The type of analysis required: elemental or molecular, routine or occasional.
(*b*) Problems arising from the nature of the material to be investigated, e.g. radioactive substances, corrosive substances, substances affected by water.
(*c*) Possible interference from components of the material other than those of interest.
(*d*) The concentration range which needs to be investigated.
(*e*) The accuracy required.
(*f*) The facilities available; this will refer particularly to the kinds of instrumentation which are at hand.
(*g*) The time required to complete the analysis; this will be particularly relevant when the analytical results are required quickly for the control of a manufacturing process. This may mean that accuracy has to be a secondary rather than a prime consideration, or it may require the use of expensive instrumentation.
(*h*) The number of analyses of similar type which have to be performed; in other words, does one have to deal with a limited number of determinations or with a situation requiring frequent repetitive analyses?
(*i*) Does the nature of the specimen, the kind of information sought, or the magnitude of the sample available indicate the use of non-destructive methods of analysis as opposed to the more commonly applied destructive methods involving dissolution of the sample (possibly in acid) prior to the application of normal analytical techniques?

Some information relevant to the choice of appropriate methods is given in condensed form in Table 1.1, which is divided into three sections: the 'classical' techniques; a selection of instrumental methods; some 'non-destructive' methods.

Table 1.1 Conspectus of some common quantitative analytical methods

Method	Speed	Relative cost	Concentration range (p*C*)*	Accuracy
Gravimetry	S	L	1–2	H
Titrimetry	M	L	1–4	H
Coulometry	S–M	L–M	1–4	H
Voltammetry	M	M	3–10	M
Potentiometry	M–F	L–M	1–7	M
Spectrophotometry	M–F	L–M	3–6	M
Atomic spectrometry	F	M–H	3–9	M
Emission (plasma) spectrometry	F	H	5–9	M
Chromatography (GLC; HPLC)	F	M–H	3–9	M
Neutron activation	S	H	†(*a*)	M
X-ray fluorescence	F	H	†(*b*)	H

* $pC = \log_{10}\frac{1}{\text{Concn}}$, where Concentration is expressed in moles per litre.

† Concentration range has little significance: detection values are (*a*) 10^{-5}–10^{-12} g; (*b*) 10^{-3}–10^{-6} g.
Abbreviations: F, Fast; H, High; L, Low; M, Moderate; S, Slow.

1.10 INTERFERENCES

Whatever the method finally chosen for the required determination, it should ideally be a **specific method**; that is to say, it should be capable of measuring the amount of desired substance accurately, no matter what other substances may be present. In practice few analytical procedures attain this ideal, but many methods are **selective**; in other words, they can be used to determine any of a small group of ions in the presence of certain specified ions. In many instances the desired selectivity is achieved by carrying out the procedure under carefully controlled conditions, particularly with reference to the pH of the solution.

Frequently, however, there are substances present that prevent direct measurement of the amount of a given ion; these are referred to as **interferences**, and the selection of methods for separating the interferences from the substance to be determined are as important as the choice of the method of determination. Typical separation procedures include the following:

(*a*) *Selective precipitation.* The addition of appropriate reagents may convert interfering ions into precipitates which can be filtered off, careful pH control is often necessary in order to achieve a clean separation, and it must be borne in mind that precipitates tend to adsorb substances from solution and care must be taken to ensure that as little as possible of the substance to be determined is lost in this way.

(*b*) *Masking.* A complexing agent is added, and if the resultant complexes are sufficiently stable they will fail to react with reagents added in a subsequent operation: this may be a titrimetric procedure or a gravimetric precipitation method.

(*c*) *Selective oxidation* (*reduction*). The sample is treated with a selective oxidising or reducing agent which will react with some of the ions present: the resultant change in oxidation state will often facilitate separation. For example, to precipitate iron as hydroxide, the solution is always oxidised so that iron(III) hydroxide is precipitated: this precipitates at a lower pH than does iron(II) hydroxide and the latter could be contaminated with the hydroxides of many bivalent metals.

(*d*) *Solvent extraction.* When metal ions are converted into chelate compounds by treatment with suitable organic reagents, the resulting complexes are soluble in organic solvents and can thus be extracted from the aqueous solution. Many ion-association complexes containing bulky ions which are largely organic in character (e.g. the tetraphenylarsonium ion $(C_6H_5)_4As^+$) are soluble in organic solvents and can thus be utilised to extract appropriate metals ions from aqueous solution. Such treatment may be used to isolate the ion which is to be determined, or alternatively, to remove interfering substances.

(*e*) *Ion exchange.* Ion exchange materials are insoluble substances containing ions which are capable of replacement by ions from a solution containing electrolytes. The phosphate ion is an interference encountered in many analyses involving the determination of metals; in other than acidic solutions the phosphates of most metals are precipitated. If, however, the solution is passed through a column of an anion exchange resin in the chloride form, then phosphate ions are replaced by chloride ions. Equally, the determination of phosphates is difficult in the presence of a variety of metallic ions, but

if the solution is passed through a column of a cation exchange resin in the protonated form, then the interfering cations are replaced by hydrogen ions.

(*f*) *Chromatography.* The term chromatography is applied to separation techniques in which the components of solutions travel down a column at different rates, the column being packed with a suitable finely divided solid termed the stationary phase, for which such diverse materials as cellulose powder, silica gel and alumina are employed. Having introduced the test solution to the top of the column, an appropriate solvent (the mobile phase) is allowed to flow slowly through the column. In **adsorption chromatography** the solutes are adsorbed on the column material and are then eluted by the mobile phase: the less easily adsorbed components are eluted first and the more readily adsorbed components are eluted more slowly, thus effecting separation. In **partition chromatography** the solutes are partitioned between the mobile phase and a film of liquid (commonly water) firmly absorbed on the surface of the stationary phase. A typical example is the separation of cobalt from nickel in solution in concentrated hydrochloric acid: the stationary phase is cellulose powder, the mobile phase, acetone containing hydrochloric acid; the cobalt is eluted whilst the nickel remains on the column. If compounds of adequate volatility are selected, then '**gas chromatography** may be carried out in which the mobile phase is a current of gas, e.g. nitrogen. For liquids it is frequently possible to dispense with a column and to use the adsorbent spread as a thin layer on a glass plate (**thin layer chromatography**) and in some cases a roll or a sheet of filter paper without any added adsorbent may be used (**paper chromatography**): these techniques are especially useful for handling small amounts of material. Of particular interest in this field are the developments associated with **high performance liquid chromatography (HPLC)** and with **ion chromatography.**

1.11 DATA ACQUISITION AND TREATMENT

Once the best method of dealing with interferences has been decided upon and the most appropriate method of determination chosen, the analysis should be carried out in duplicate and preferably in triplicate. For simple classical determinations the experimental results must be recorded in the analyst's notebook. However, many modern instruments employed in instrumental methods of analysis are interfaced with computers and the analytical results may be displayed on a visual display unit, whilst a printer will provide a printout of the pertinent data which can be used as a permanent record.

A simple calculation will then convert the experimental data into the information which is sought: this will usually be the percentage of the relevant component in the analytical sample. When using computer-interfaced instruments the printout will give the required percentage value. The results thus obtained will be subject to a degree of uncertainty as is true for every physical measurement, and it is necessary to establish the magnitude of this uncertainty in order that meaningful results of the analysis can be presented.

It is, therefore, necessary to establish the **precision** of the results, by which we mean the extent to which they are reproducible. This is commonly expressed in terms of the numerical difference between a given experimental value and the mean value of all the experimental results. The **spread** or **range** in a set of results is the numerical difference between the highest and lowest results: this

figure is also an indication of the precision of the measurements. However, the most important measures of precision are the standard deviation and the variance: these are discussed in Chapter 4.

The difference between the most probable analytical result and the true value for the sample is termed the **systematic error** in the analysis: it indicates the **accuracy** of the analysis.

1.12 SUMMARY

Summarising, the following steps are necessary when confronted with an unfamiliar quantitative determination.

1. Sampling.
2. Literature survey and selection of possible methods of determination.
3. Consideration of interferences and procedures for their removal.

Pooling the information gathered under headings (2) and (3), a final selection will be made of the method of determination and of the procedure for eliminating interferences.

4. Dissolution of sample.
5. Removal or suppression of interferences.
6. Performance of the determination.
7. Statistical analysis of the results.

For References and Bibliography see Sections 3.38 and 3.39.