11

Analytical Chemistry

11.1 Carrying out an analysis

- A sample for analysis contains the analyte (or analytes) dispersed in a matrix. The sample must be representative of the whole amount of substance being analysed.
- Analytical procedures can be checked by comparing results obtained using reference samples or materials which have known concentrations.
- A calibration curve may be constructed to determine the relation between the measured quantity and the concentration, using reference samples of known concentrations.
- Appropriate blank experiments must be performed to ensure that it is the concentration of the analyte of interest that is being measured.
- A good analytical procedure produces results that are accurate and precise.
  - Accuracy refers to how close a result is to the true value.
  - Precision describes how well a number of measurements agree with each other.
- The spread of results is described by the range, the standard deviation, and the coefficient of variation.
- The detection limit is the minimum concentration of an analyte that can be distinguished from a blank experiment.
- Errors (uncertainties) may be systematic or random.

For practice questions on this topic, see questions 1–5 at the end of this chapter (p.553).

11.2 Electrochemical methods of analysis

- Electrochemical methods of analysis can be potentiometric or amperometric.
- A pH meter measures the potential difference between a glass electrode and a reference silver/silver chloride electrode, usually combined into a single probe that is inserted in the test solution. The measured voltage depends linearly on the pH of the solution.
- Ion selective electrodes respond selectively to a particular ion in solution. They produce an electric potential that is measured with reference to a reference electrode.
- The potential generated by an ion selective electrode depends in a linear fashion on the logarithm of the ionic concentration in solution.
- pH meters and ion selective electrodes are calibrated by using solutions with accurately known concentrations. For pH measurements, buffer solutions are used.
- Amperometric cells measure the current resulting from an electrolysis reaction at a constant applied voltage.

For practice questions on this topic, see questions 6–9 at the end of this chapter (p.553).

11.3 Chromatography

- Chromatography involves the separation of compounds by distributing them between a mobile phase and a stationary phase.
- The distribution of a compound between two phases is measured by the partition coefficient.
- Analytes interact with the stationary phase to different extents and so move at different speeds through it.
- The degree of separation of two compounds is measured by the relative retention.
- Thin layer chromatography (TLC) is used for qualitative analysis. It involves the separation of compounds by passage of a solution over a plate coated with silica or alumina.
- Column chromatography is used to separate and recover the components of a mixture.
- Gas chromatography (GC) is used to analyse samples that are volatile, using high temperatures if necessary. The detector response is proportional to concentration so the peak area is proportional to the amount of component in the mobile phase.
- Gas chromatography–mass spectrometry (GC–MS) is used to rapidly identify and measure the concentrations of compounds in a mixture.
- Various types of stationary phase can be used in high performance liquid chromatography (HPLC) to analyse a wide range of soluble compounds.

For practice questions on this topic, see questions 10–13 at the end of this chapter (p.554).

11.4 Spectroscopic methods of analysis

- Substances appear coloured due to the absorption of some wavelengths of light and transmission of other wavelengths.
- The absorption of radiation is described by the *Beer–Lambert law*: $A = \varepsilon \times c \times l$
- Compounds with high values of ε, the *molar absorption coefficient*, absorb high intensities of light at a given concentration.
- The *absorbance* of a solution is proportional to its concentration, and spectrophotometry can be used to measure the concentration of absorbing species in solution.
- The absorbances of several species in solution are additive so that mixtures of compounds can be analysed provided they have distinguishable absorption spectra.

For practice questions on this topic, see questions 14–19 at the end of this chapter (p.554).

11.5 Atomic spectrometry

- Atomic spectrometry involves atomizing samples at high temperatures.
- Atomic emission spectrometry (AES) measures radiation emitted when thermally excited atoms return to the ground state.
  - A hot flame or, for better results, an inductively coupled plasma, is used to atomize and excite the elements in the sample.
  - Different elements can be analysed by selecting different wavelengths.
  - Concentrations are usually measured by reading from a calibration graph prepared by measuring standard solutions with accurately known concentrations.
- Atomic absorption spectrometry (AAS) measures the absorption of radiation by atoms in their ground state.
  - A flame can be used to vaporize and atomize samples, although better results are obtained with an electrothermal analyser.
  - Samples are irradiated by a hollow cathode lamp that is specific for a particular element.
  - Concentrations can be measured by preparing a calibration graph or by using the standard addition method.

For practice questions on this topic, see questions 20–23 at the end of this chapter (p.555).

Concept review

By the end of this chapter you should be able to do the following.

- Describe the factors to be considered when planning an analysis.
- Define the terms accuracy and precision and discuss the significance of these in analytical measurements.
- Define and calculate the mean, the range, the standard deviation, and the coefficient of variation of a number of measurements.
- Describe the use of pH meters and ion selective electrodes for chemical analysis.
- Account for the general features of chromatography systems.
- Define the retention factor, R_f, and describe how TLC and column chromatography can be used for separation and qualitative analysis.
- Discuss the operation of gas–solid and gas–liquid chromatographs and explain how analytical data can be obtained.
- Describe the use of gas chromatography–mass spectrometry to find the concentrations and identities of components in a mixture.
- Use the Beer–Lambert law to find the concentration of components in solution.
- Describe the principle of operation and basic features of atomic spectrometry.
- Distinguish between atomic emission spectrometry and atomic absorption spectrometry.
- Describe and explain some applications of the analytical methods described.
- Calculate the concentrations of analyte solutions given appropriate calibration data using calibration curves or the standard addition method as appropriate.
- Suggest suitable methods of analysis for a given analyte.

Key equations

Mean of a set of results	$\bar{x} = \frac{\sum_{i=1}^{i=n} x_i}{n}$	(11.1)
Standard deviation of a set of results	$\sigma = \left(\frac{\sum_i (x_i - \bar{x})^2}{n-1} \right)^{1/2}$	(11.2)
Coefficient of variation of a set of results	$CV = \frac{\sigma}{x} \times 100$	(11.3)
Partition coefficient	$K = \frac{\text{concentration of solute in phase 1}}{\text{concentration of solute in phase 2}}$	(11.8)
Relative retention	$\alpha_{AB} = \frac{t_r(A)}{t_r(B)}$	(11.9)