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Analytical Chemistry

12.1 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 the concentration of the analyte of interest is being measured accurately.
- 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.

12.2 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 can be 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.
- Concentrations of dissolved gases, such as O_2, can be measured using amperometric cells, such as the Clark sensor.
- Amperometric cells measure the current resulting from an electrolysis reaction at a constant applied voltage.

12.3 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.
- 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.

12.4 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.
- The absorbances of several species in solution are additive so that mixtures of compounds can be analysed.

12.5 Atomic spectroscopy

- 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 from 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.

Learning outcomes

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 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.