

Introduction to Analytical Chemistry

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Analytical Chemistry Techniques: Overview

This is part one of four separate techniques guides that provide introductions to different aspects of analytical chemistry:

Part 1: Introduction to Analytical Chemistry:

A basic introduction to analytical science in general, and analytical chemistry in particular, including an overview of the analytical process, quality assurance, and guidance on solution preparation including volumetric and concentration calculations. It also includes a bibliography of useful texts for the analytical chemist.

Part 2: Introduction to Molecular Spectroscopy:

An introduction to the different types of molecular spectroscopic analysis, including UV-Vis, fluorescence, IR, MS and NMR, describing the basic principles of each technique and practical considerations including sample preparation. It is illustrated with simple diagrams, photographs of equipment and information to aid interpretation of spectra.

Part 3: Introduction to Chromatography:

An introduction to chromatographic analysis, describing the different types of chromatography, including TLC, GC, HPLC and ion chromatography, their application areas and basic principles of operation. It is illustrated with simple diagrams, photographs of equipment and chromatograms illustrating practical aspects of the technique.

Part 4. Introduction to Atomic Spectrometry:

An introduction to the different types of atomic spectrometric analysis, including ICP-AES, ICP-MS, XRF and AAS, describing the basic principles of each technique, their application areas and modes of operation, including practical comparison of the techniques. It is illustrated with simple diagrams and photographs of equipment.

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Chapter 1

Analytical Science

Analytical science engages a number of scientific disciplines including chemistry, biochemistry, physics, mathematics, and engineering. It is a science of measurement and ultimately of metrology when all the variables are understood and controlled. Analytical chemistry comprises of:

- **Qualitative analysis** identifies the elements, species and compounds in a sample
- **Quantitative analysis** determines absolute or relative amounts of elements, species and compounds in a sample.
- **Structural analysis** determines the spatial arrangements of atoms or identifies the functional groups.

The analytical scientist must comprehend their client's needs as well as quality assurance (QA), quality control (QC), statistics, accreditation and validation. One of the most important skills is choosing the correct method of analysis. The solving of unfamiliar problems requires both analytical and critical thinking. Analytical science is a technical, creative and hands-on subject. It is an interface between disciplines as diverse as human imagination. The communication and translation of data is an essential part of analytical science (see Figure 1) so that other disciplines can act upon the results.

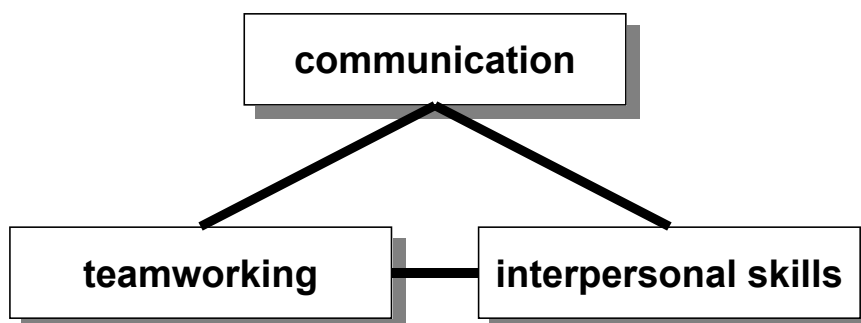


Figure 1: Team working to solve problems

1.1 Terminology

The **sample** is a material that we wish to analyse and also has a statistical meaning. The **analyte** is the substance or element in the sample whose presence or concentration we wish to determine. The matrix is other components of the sample other than the analyte.

1.2 The Analytical Process

Every scientist requires an understanding of analytical science so that the data produced fit the purpose. Analytical science can be considered as the science of problem solving. As can be seen in Figure 2, analytical science is a process rather than an end in itself:

- The technical approach to solving the problem requires the analyst to consider the analytical information, required level of accuracy, the cost, timing, availability of instruments and facilities before selecting the method.
- Knowledge and practical skills start with sampling. Without a representative sample, the results from the time consuming analysis are of little use. This is followed by the sample treatment to produce the analyte into suitable form for detection/measurement

by the selected analytical technique. This may involve dissolution, separation of the analyte from the sample matrix or converting the analyte to another form.

- Interpretative skills are essential to determine the significance of the analytical results and their relevance in solving the original problem.

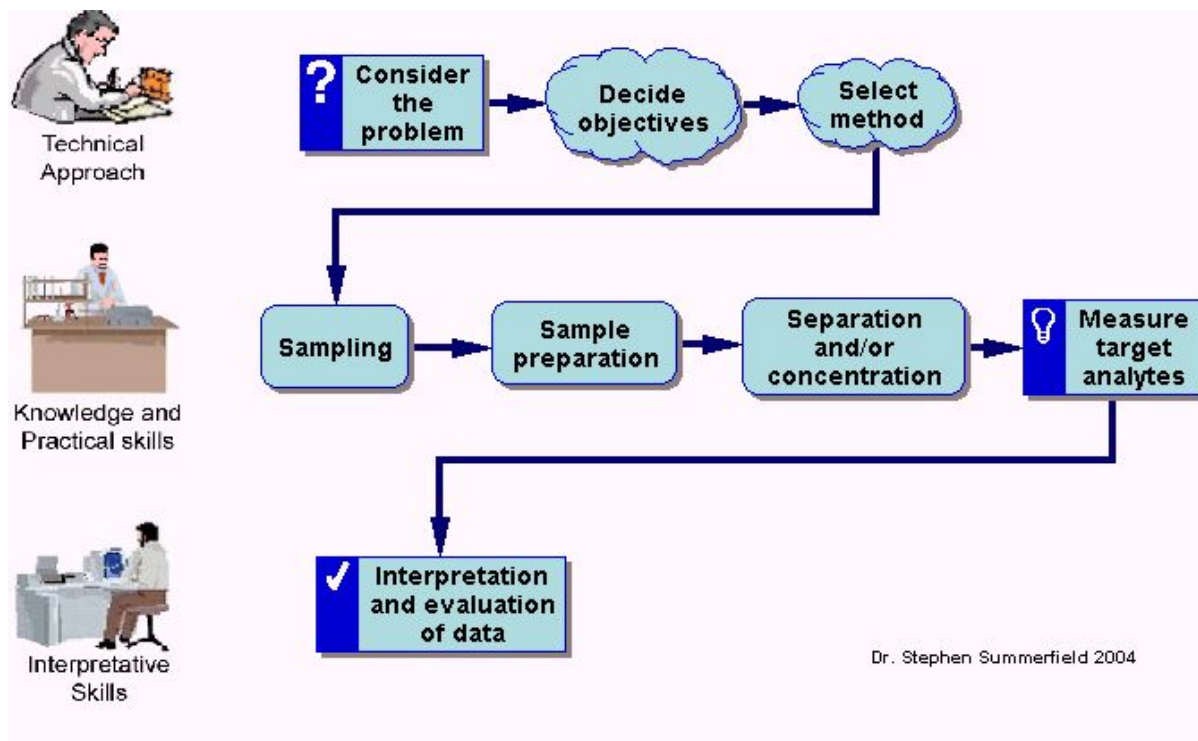


Figure 2: The Analytical Process

An example of methodology used to identify and quantify drugs is shown in Figure 3.

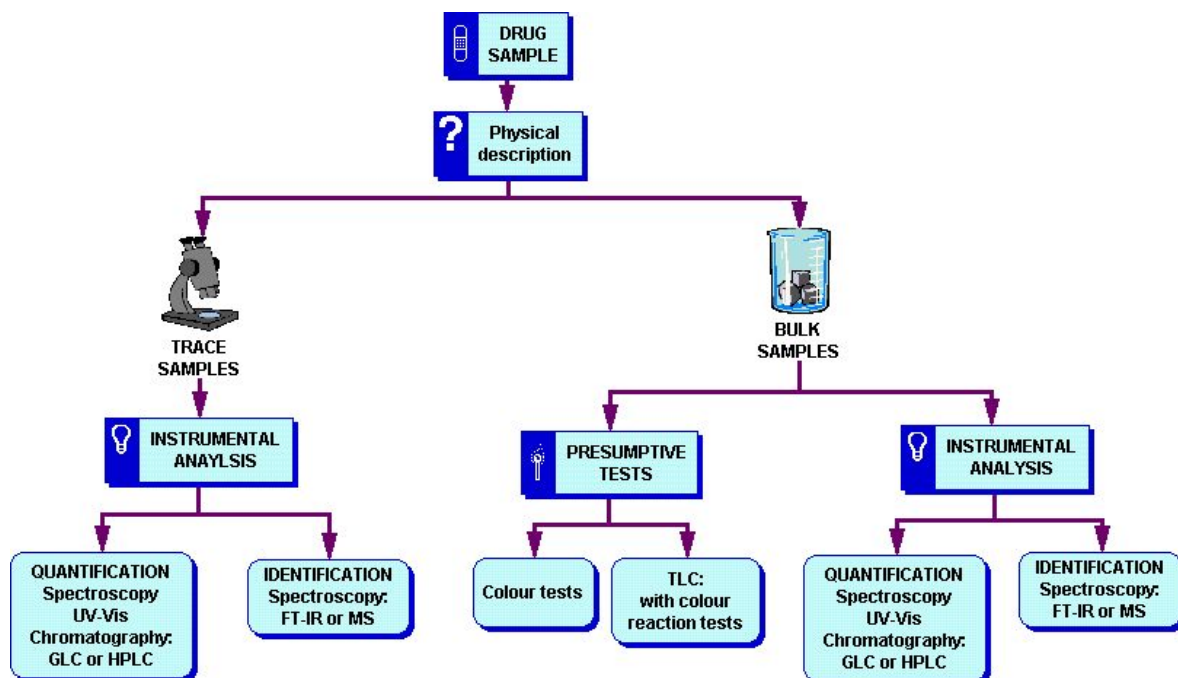


Figure 3: A Schematic for the identification and quantification of drugs [After Moffat (1986)]

Chapter 2

Valid Analytical Measurements

The VAM (Valid Analytical Measurement) programme was set up in 1988 by the Department of Trade and Industry [DTI] with the aim to improve the quality of analytical measurements. The VAM Project was replaced by the National Measurement System (NMS). More information information can be found on www.nmschembio.org.uk.

2.1 Six VAM Principles

The six VAM principles provide a framework to enable organisations to deliver reliable results first time, every time. Laboratories that adopt VAM provide customers and users of data with increased confidence that results of analytical measurements are valid and fit for purpose. More information can be found at www.nmschembio.org.uk/

1. Analytical measurements should be made to satisfy an agreed requirement.
2. Analytical measurements should be made using methods and equipment, which have been tested to ensure they are fit for purpose.
3. Staff making analytical measurements should be both qualified and competent to undertake the task.
4. There should be a regular independent assessment of the technical performance of a laboratory.
5. Analytical measurements made in one location should be consistent with those elsewhere.
6. Organisations making analytical measurements should have well defined quality control and quality assurance procedures.

2.2 Validation

Validation is essential to ensure that the results are reproducible and accurate, [Burgess (2000)] and that the performance characteristics of the method are adequate for the intended use of the analytical results. Typical steps in the validation process include:

1. A validated method of measurement should be used to assess the efficiency and precision of any extraction method used to isolate the analyte from the sample matrix.
2. The recovery of the analyte from the sample matrix can be assessed by adding a known amount of analyte to a substrate and leaving overnight to allow analyte-matrix interactions to occur before extraction. This 'spiked' sample is then analysed to determine the amount of analyte that can be recovered. The experiment should be replicated a number of times at each of a number of analyte concentrations.
3. Comparison of the results obtained with those obtained using an alternative method of extraction can also be used to validate the extraction step.
4. Replicate analysis of samples during method validation allows the variability of results obtained to be assessed. Such studies give information about the precision of the analytical method.
5. Performing tests on the reagents used during the analysis serves to check whether there is any contamination or possible interfering compounds in the reagents.

6. Tests on blank sample matrix materials (i.e. the sample matrix with none of the analyte present) are performed to check for the presence of possible interfering compounds in the sample matrix.
7. Using certified reference materials containing a known certified concentration of the analytes of interest is the ultimate test of a method and of the analyst. A number of organisations produce and supply reference materials.
 - LGC Promochem www.lgcpromochem.com
 - NIST (National Institute of Standards and Technology, www.nist.gov)
 - IRMM (Institute for Reference Materials and Measurements www.irmm.jrc.be)
8. Collaborative studies and proficiency testing schemes between laboratories are useful to make certain that the results are comparable and hence considered reliable.
 - European database of proficiency testing schemes can be found at www.eptis.bam.de

2.3 Quality Standards

Quality standards set out a working framework for laboratories to enable them to produce reliable results. Accreditation or certification to a particular standard can be defined as the formal recognition that a laboratory is compliant with certain specified international standards. There are a number of different quality standards available to laboratories:

1. **ISO 17025**, '*General requirements for competence of testing and calibration laboratories*' is the current international standard for the accreditation of testing and calibration laboratories.
 - In the UK, laboratories are accredited to this standard by UKAS (the United Kingdom Accreditation Service, www.ukas.com).
 - Further information on ISO 17025 can be found at www.questanalytical.com.
2. **ISO 9001**, 'Quality Management Systems – Requirements' is a general quality assurance standard, www.iso.org
 - In the UK, laboratories are certified to ISO 9001 by organisations such as BSI.
3. **GLP**, '*The Good Laboratory Practice Regulations*', is the system adopted as a legal requirement for the accreditation of laboratories engaged in regulatory studies (e.g. laboratories testing pharmaceuticals or pesticides).
 - The standard is maintained by the OECD (Organisation for Economic Co-operation and Development, www.oecd.org)
 - Administered in the UK by the Medicines and Healthcare Regulatory Authority.
4. **GMP**, '*The Good Manufacturing Practice Regulations*', are mandatory if the company produces pharmaceuticals or medical devices.
5. **GCP**, '*The Good Clinical Practice Regulations*' regulate clinical trials.

GLP, GMP and GCP are legally binding. ISO 17025 is only mandatory for certain types of testing. ISO 9001 is only advisory. Therefore, it is a commercial decision as to whether a laboratory seeks certification or accreditation for the latter two. In other words, a laboratory that is not accredited may lose business to competitors who are.

Chapter 3

Traditional Analytical Techniques

3.1 Inorganic Spot Tests

Physical tests give good indications as to what the substance is. Colour and pH are often good indications. Solid samples should be dissolved in water or suitable acid before the addition of reagents. Colour change or precipitation is indicative of the ions present. This is useful in determining the instrumental analysis to follow.

3.2 Titrimetry

It is still widely used for precise routine and non-routine determination of acidic and basic impurities in finished products, control of reaction conditions, mineral and metallurgical analysis. Titrimetry relies upon fast solution reactions between the analyte and a reagent with the end point detected by visual indicators, precipitation indicators or electrochemical means. Requires the storage of large volumes of solutions and scrupulously clean glassware but is cheap in time, and apparatus with good precision of 0.1 to 1%.

3.3 Gravimetry

Extensive numbers of inorganic ions are determined with excellent relative precision (0.1-1%) and accuracy. It is widely used in routine assays of metallurgical and mineralogical samples. A solution reaction with the analyte creates a sparingly soluble product that is filtered and dried or ignited and then accurately weighed. Requires careful and time-consuming procedures with scrupulously clean apparatus and very accurate weighing.

Chapter 4

Volumetric Calculations

- 1 Remember to use consistent units. E.g. grams (g) or kilograms (kg) for mass and cm^3 or dm^3 for volume
- 2 It is also useful to convert to standard form and indices i.e. using 1×10^3 rather than 1000. Adding indices is a quick way to multiply and subtracting is a quick way to divide.
- 3 Always write in the units and cancel them down to get the final expected units. This is a good check that you have the correct equation.
- 4 The equation should be written down with full substitution of known quantities then simplified by cancelling down before using a calculator so reducing errors.
- 5 Quote to the number of significant figures that is appropriate. Calculators churn out lots of numbers but many of them will be meaningless. When deciding how many significant figures to quote a result to the analyst must consider the various stages of the method, e.g. the accuracy of the analytical balance or the readability of a burette.

Number of Moles	=	$\frac{\text{mass (g)}}{\text{molar mass (g/mol)}}$	
Concentration (g dm^{-3})	=	$\frac{\text{mass (g)}}{\text{volume (dm}^3\text{)}}$	
Specific Gravity	=	$\frac{\text{mass (kg)}}{\text{volume (dm}^3\text{)}}$	= Normally at 20 °C.
	=	$\frac{\text{mass (g)}}{\text{volume (cm}^3\text{)}}$	Normally at 20 °C.

For Example

What is the molarity of sulphuric acid if 25 cm³ of 0.1 molar NaOH neutralises 20 cm³ of sulphuric acid?

**METHOD 1**

1000 cm³ of 0.1 Molar NaOH contains 0.1 moles of NaOH

$$\begin{aligned} \text{Therefore 25 cm}^3 \text{ of 0.1 Molar NaOH contains} &= 0.1 \text{ moles} \times \frac{25}{1000} \\ &= 2.5 \times 10^{-3} \text{ moles} \end{aligned}$$

From the above equation, 2 moles of NaOH neutralises 1 mole of sulphuric acid.

So 2.5 x 10⁻³ moles of NaOH react with 1.25 x 10⁻³ moles of sulphuric acid.

$$\begin{aligned} \text{Molar concentration of sulphuric acid} &= \frac{2.5 \times 10^{-3}}{2} \times \frac{1000}{20} \\ &= \underline{6.25 \times 10^{-2} \text{ mol dm}^{-3}} \end{aligned}$$

METHOD 2 (this is using the equation but does not show reasoning)

$$n_2 V_1 M_1 = n_1 V_2 M_2$$

Rearrange equation to solve for M₁

$$M_1 = \frac{n_1 V_2 M_2}{n_2}$$

n ₁	=	number of moles of sulphuric acid in equation	=	1
V ₁	=	volume of sulphuric acid (cm ³)	=	20 cm ³
M ₁	=	molarity of sulphuric acid (mol dm ⁻³)	=	unknown
n ₂	=	number of moles of sodium hydroxide in equation	=	2
V ₂	=	titre of sodium hydroxide (volume in cm ³)	=	25 cm ³
M ₂	=	molarity of sodium hydroxide (mol dm ⁻³)	=	0.1 mol dm ⁻³

$$\begin{aligned} M_1 &= \frac{1 \times 25 \text{ cm}^3 \times 0.1 \text{ mol dm}^{-3}}{2 \times 20 \text{ cm}^3} \\ &= \underline{6.25 \times 10^{-2} \text{ mol dm}^{-3}} \end{aligned}$$

Chapter 5

Concentration Units

Analytical scientists tend to focus particularly on the quantitative aspects of analysis. Most liquid samples are made up on a mass per volume basis, but they can be made more accurately on a weight for weight basis i.e. gravimetrically.

Table 1: Units of concentration

% w/v	=	percentage weight per volume (normally used in chemistry)
% w/w	=	percentage weight for weight (used in industry especially in the analysis of solids)
% v/v	=	percentage volume for volume (used when dealing with gases and volatile liquids)

	By parts	Weight per volume	Weight for weight	Volume for volume
1000 ppm	1000 parts per million	1 g per litre	1 g per kg	1 ml per litre
1 ppm	part per million	1 mg per litre	1 mg per kg	1 μ l per litre
1 ppb	part per billion	1 μ g per litre	1 μ g per kg	-
1 ppt	part per trillion	1 ng per litre	1 ng per kg	-

Table 2: Parts per million conversion

parts per million (ppm)	parts per billion (ppb)	grams per litre (g/l)	weight per volume (w/v)
0.001 ppm	1 ppb	10^{-6} g/l	-
0.01 ppm	10 ppb	10^{-5} g/l	
0.1 ppb	100 ppb	10^{-4} g/l	
1ppm	1000 or 10^3 ppb	0.001 g/l	-
10 ppm	10000 or 10^4 ppb	0.01 g/l	0.001% w/v
100 or 10^2 ppm	100000 or 10^5 ppb	0.1 g/l	0.01% w/v
1000 or 10^3 ppm	10^6 ppb	1 g/l	0.1% w/v
10000 or 10^4 ppm	10^7 ppb	10 g/l	1.0% w/v
100000 or 10^5 ppm	10^8 ppb	100 g/l	10.0% w/v

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