# Introduction to Atomic Spectrometry

By

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## Analytical Chemistry Techniques: Overview

This is part four 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
# Atomic Spectrometry

Only inductively coupled plasma (ICP) and X-ray fluorescence are suitable techniques for qualitative and quantitative analysis of a range of elements simultaneously. The other methods described are used only for quantitative determination of individual elements.

Applications include:
1. Determination of trace elements in foods, plants and tobacco
2. Elemental profiles of biological samples to monitor health.
3. Trace elements in artificial fibres
4. Determination of the mode of poisoning in food stuffs and drugs
5. Hair analysis for heavy metal poisons
6. Determinations of ammunition manufacturers through the measurement of trace elements in bullets and cartridges
7. Discrimination of objects made of steel, aluminium, glass and precious metals.

**Table 1: Atomic spectrometric techniques and principal applications**

| **Technique** | **Property measured** | **Applications** |
|---|---|---|
| Atomic absorption spectrometry | Atomic absorption of the light from the lamp after atomisation by flame or electrothermal means | Determination of trace metals and some non-metals at ppm levels. |
| Atomic fluorescence spectrometry | Atomic fluorescence emission after flame excitation | Determination of mercury and arsenic at trace levels |
| Flame emission spectrometry | Atomic emission after flame excitation | Determination of alkali and alkali earth metals |
| Inductively Coupled Plasma – Atomic Emission Spectrometry [ICP-AES] | Atomic emission after excitation in a plasma | Determination of metals and some non-metals at trace levels in environmental and industrial samples. |
| Inductively Coupled Plasma – Mass Spectrometry [ICP-MS] | Mass spectrometry of isotopes following plasma ionisation | Multi-element analysis at ultra-trace levels (ppt) in biological and environmental samples. |
| X-ray Fluorescence Spectrometry | Atomic fluorescence after excitation by X-Ray radiation | Determination of major and minor elemental components of geological and metallurgical samples |
| $\gamma$-Spectrometry | $\gamma$-ray emission after nuclear excitation | Monitoring of radioactive elements in environmental samples |

# Chapter 2
# Flame Atomic Emission

This is an instrumental extension of simple flame tests carried out to measure the Group 1 (Li, Na, K) using a low temperature flame.

## *2.1 Instrumentation*

A flame emission photometer is a very simple device (Figure 1). It consists of a nebuliser and burner arrangement for transferring the liquid sample from a container into the natural gas-air flame, optics designed to gather as much light as possible, optical filters to isolate the emitted light and a photo-detector to measure this radiation. The spectral region of interest is selected by interposing appropriate filters between the flame and the photo-detector. Split beam instruments allow simultaneous determination of Na and K. Response linearity is limited to concentrations between 1 and 100 mg L-1.

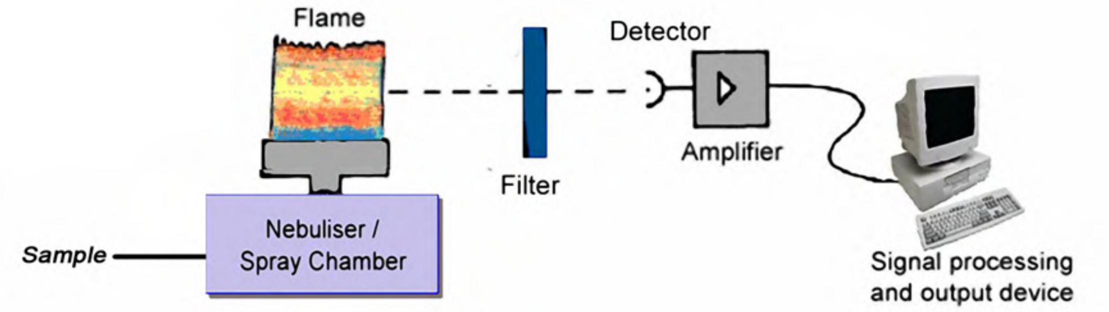


**Figure 1: Diagram of a Flame Photometer**

**Jenway PFP7 Flame Photometer**

When a solution of a metallic salt is sprayed into a flame, the solvent evaporates and fine salt particles are formed and are vaporised. Many of the molecular species are broken down and free atoms are released. Some of these atoms undergo chemical reactions or remain as ground state atoms. Particularly in the case of the alkali metals, a significant portion of free atoms have outer shell electrons thermally excited from the ground state to a higher energy level. When these excited state electrons fall back to lower energies, light is emitted. The energies associated with these transitions correspond to wavelengths in the visible region of the spectrum and so colour the flame, as in the case of sodium and potassium.

The principal stages in the process are summarised below:

$M^+ + A^-$ (Solution)
1) Nebulisation $\downarrow$
$M^+ + A^-$ (Aerosol)
2) Desolvation $\downarrow$
MA (Solid)
3) Liquefaction $\downarrow$
MA (Liquid)
4) Vaporisation $\downarrow$
MA (Gas)
5) Atomisation $\downarrow$
$M\bullet + A\bullet$ (Gas)
6) Excitation $\downarrow$
$M^*$ (Gas)
7) Emission $\downarrow$
$M\bullet$ (Gas)

# Chapter 3
# Atomic Absorption Spectroscopy

The absorption of light by atoms in the ground state is measured when the sample is irradiated by an appropriate source. Solid samples and some liquids require pre-treatment to destroy organic matter followed by dissolution of the inorganic matter in acid solution. This is then aspirated into a flame or injected into a graphite furnace.

The digestion process is carried out in strong acids (nitric, sulphuric or perchloric acids) and over the last decade microwave digestion has predominated. The greatest advantage of AAS is its specificity.

## *3.1 Flame AAS (FAAS)*

- The sample is drawn into the nebuliser by compressed air that propels the solution into a spray chamber where it forms an aerosol, mixes with fuel and then into the burner.

- The hollow cathode lamp provides narrow line width radiation:
  - A potential of 100V across the lamp electrodes ionises the argon or neon fill gas which then strikes the cathode made of the metal being analysed.
  - This releases atoms of the element and after excitation with the fill gas ions, a narrow line emission spectrum of the analyte is produced and shows up in the flame.

- Flame AAS requires at least 5 ml of solution and viscous solutions must be diluted. About 90% of the sample is rejected as large droplets are filtered out before reaching the flame.

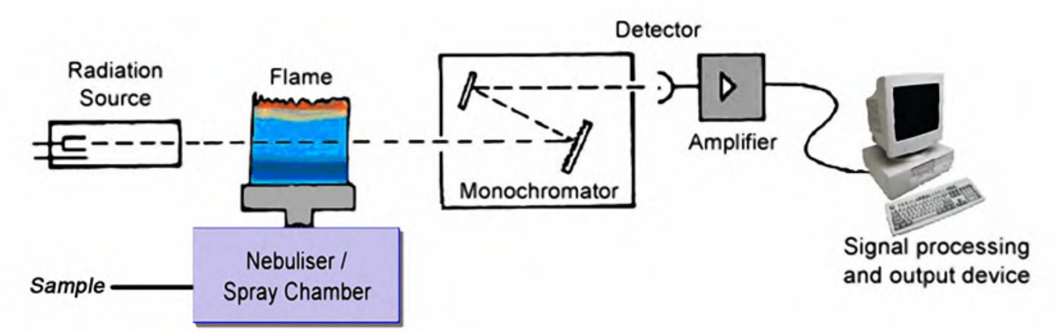


**Figure 2: Diagram of a Flame AAS**

## *3.2 Graphite Furnace AAS (GFAAS) or Electrothermal AAS (ETAAS)*

This technique uses 1-100 μl of solutions which are injected directly in a small graphite tube in the path of the beam from a hollow cathode lamp. In addition, some solids can be analysed. Atoms have longer residence time in the radiation beam and are concentrated into a smaller volume compared to Flame AAS. Therefore, Graphite Furnace AAS is 100-1000 times more sensitive than Flame AAS.

## *3.3 Hydride Generation AAS*

This is used for the determination of As, Bi, Sb, Se and Sn to a very high sensitivity. An alkaline solution of sodium tetrahydroborate reacts with the acid sample solution generating the analyte hydride. The volatile hydride is then swept into the atomiser where it is heated to break down the hydride, and light from the hollow cathode lamp passes though to induce atomic absorption.

## *3.4 Cold Vapour Generation for Mercury*

This technique is a very sensitive method for the atomic absorption analysis of mercury. Organic mercury in the sample is oxidised to Mercury (II) then reduced to Mercury (0) by Tin (II) chloride. The volatile elemental mercury is then carried to a quartz tube (no heating is required) in the path of the light beam from the hollow cathode lamp.

# Chapter 4
# ICP-AES / ICP-OES

Inductively Coupled Plasma – Atomic Emission Spectroscopy [ICP-AES] also known as Inductively Coupled Plasma - Optical Emission Spectroscopy [ICP-OES] is used routinely for the for analysis of:

- products of vegetable or animal origin (milk, meat),
- Water analysis
- air (ashes emitted from incinerators)
- Soils in which elements are present over a wide range of concentrations.
- composition of steel fragments.
- The trace elemental composition of household aluminium can also be used to identify the brand name and production details.
- Waste Acceptance Criteria testing for admission to landfill
- Contaminated land surveys.

This method also has applications in the area of forensic science and clinical medicine (tissue analysis or biological fluids) if the required level are not too small.

## 4.1 Instrumentation

Atomic emission spectroscopy is one of the most useful techniques for determining metal and non-metals. Detection limits are as low as $10^{-6}$ g $L^{-1}$ (ppb) for most elements.

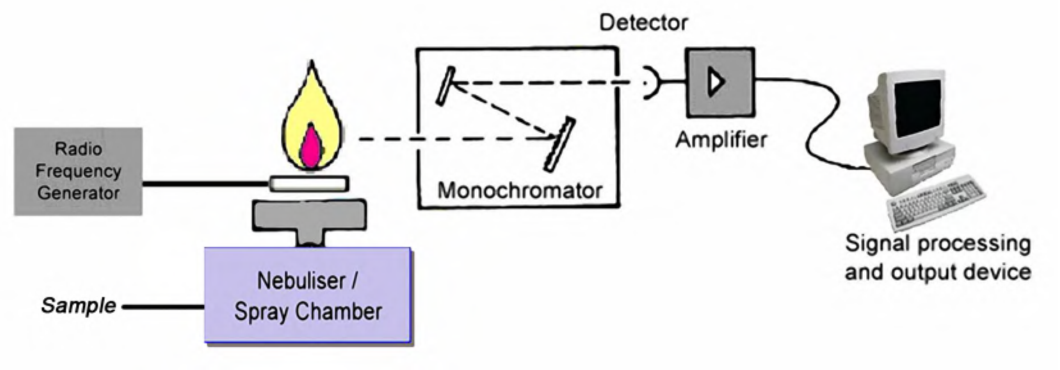


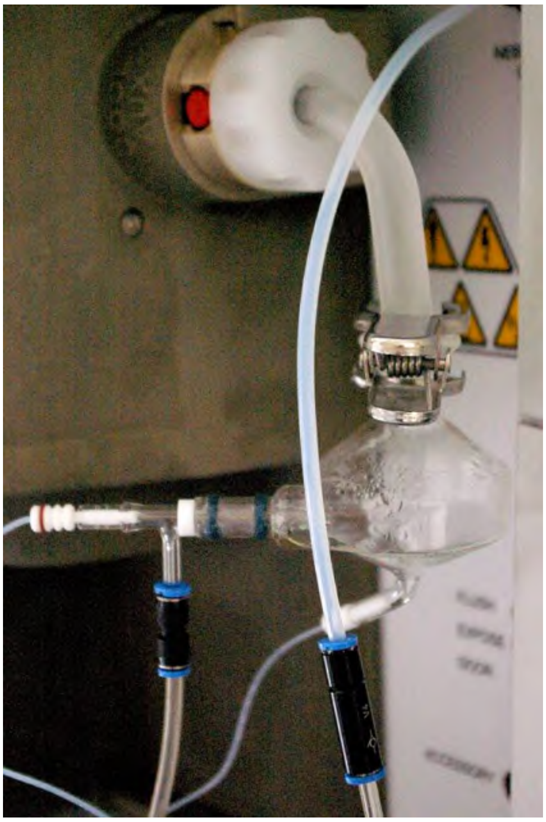
**Figure 3: ICP-AES [ICP-OES]**

Elements in a sample are excited during their residence in the plasma and the light emitted by atoms / ions in their excited state is then collected, separated and detected to produce an emission spectrum. Multi-element analysis can be performed simultaneously or sequentially from very high to trace concentrations. The plasma is a very hot (7,000-10,000K) partially ionised gas. By using an inductively coupled plasma instead of a flame source there is much more energy available and more atoms are therefore excited.

The plasma is formed by passing the inert gas argon through a water-cooled induction coil under a high-frequency field (about 27 MHz) to produce an ion source. Electrons from the Tesla coil undergo acceleration by the induced electric field and so gain the energy required to excite and ionise the gas atoms by collision. Sample particles entering the plasma undergo desolvation, dissociation, atomisation, ionisation and excitation. The excitation results in the emission of light at specific frequencies for the elements in the sample and is proportional to their concentration.

**Thermo ICP-OES is a typical example of the modern bench-top instruments**

**Inside the Thermo ICP-OES**



**Nebuliser and spray chamber of the Thermo ICP-OES**

**Peristaltic pump for sample introduction on the Thermo ICP-OES**

**Chiller for ICP-OES**

**Spectro Ciros ICP-AES designed in the late 1980s is a much larger instrument than those designed today.**

# Chapter 5
# ICP Mass Spectrometry (ICP-MS)

A small stream from the point close to the centre of the ICP torch provides a rich source of free atoms and ions. A small sample of these is passed through narrow orifices in the sampler and skimmer cones into the high vacuum of the mass spectrometer. The mass spectrometer can measure multi-elements/isotopes or be used in the more sensitive single ion monitoring (SIM) mode.

ICP-MS may be applied to the determination of elements across the whole periodic table from lithium to the actinides. Limits of detection (LOD) generally are better than graphite furnace AAS or ICP-OES. The disadvantages of ICP-MS are high purchase and running costs combined with the production of polyatomic ions (e.g. $Ar_2O^+$, $ArN^+$, $ArCl^+$, $ArO^+$ etc.) which can obscure some elemental peaks.

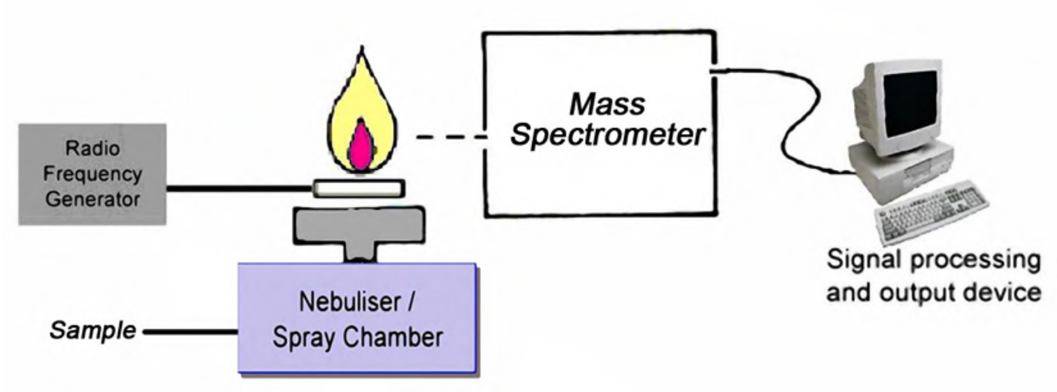


**Figure 4: ICP-MS**

**Table 2: Comparison of ICP-MS to ICP-AES [Meyers (2000)]**

| | ICP-AES | ICP-MS |
|---|---|---|
| *Detection limits* | ppb | ppt |
| *Precision* | 0.3-2% | 1-3% |
| Spectra interference | common | few |
| Chemical interference | few | moderate |
| Isotopes | none | yes |
| Dissolved solids | up to 30% | 0.1-0.4% |
| Sample usage | medium | low |
| Isotope analysis | no | yes |
| Running costs | high | high |
| Capital costs | high | very high |

## *5.1 Types of Mass Spectrometer used in ICP-MS*

As for molecular mass spectrometry, there are several types of mass spectrometer used in ICP-MS: More than 80% of commercial ICP-MS instruments use the Quadrupole Mass Filter:

### *Quadrupole Mass Filter*

Four parallel metal rods have RF and DC voltages applied across opposite pairs of rods. For a given ratio of voltages, only ions of a certain m/z (mass to charge ratio) will reach the detector, so the mass spectrum is scanned by continuously varying the applied voltage, allowing rapid sequential detection across a range of m/z values. Typical scan time is ~20 ms with a resolution of ~300 mass units and detection limits in the ppt range ($10^{-12}$ g $ml^{-1}$).

**Varian ICP-MS at Prague University**

### *Double Focussing Sector Field Mass Spectrometry*

This incorporates magnetic and electrostatic analysers in sequence to separate ions of different m/z with very high resolution (400 - 10,000) and supreme sensitivity (ppq ($10^{-15}$ g $ml^{-1}$) detection limits), but is bigger, heavier and more expensive than the quadrupole system. Scan speeds are also slower, but “multi-collector” instruments are available for simultaneous detection of ions allowing isotope ratio measurements to be made with very high precision.

### *Time-of-Flight Mass Spectrometer*

In this system, ions are accelerated along a flight tube towards the detector by application of an accelerating voltage. Ions are separated according to the time they take to reach the detector,

$$m/z = \frac{2\,U\,t^2}{d^2}$$

Where $U$ = accelerating voltage,
$t$ = time
$d$ = flight path distance.

This type of spectrometer has a resolution of 300-2000, giving a fast, multi-isotope response (3000 spectra per second) and sampling all ions simultaneously, providing good precision for isotope ratios. However, detection limits are poorer (by a factor of 10) than for a quadrupole.

# Chapter 6
# X Ray Fluorescence

This technique, based on the fluorescence of atoms in the X-ray domain, provides qualitative and quantitative elemental composition of a sample. An X-ray beam or bombardment of electrons causes excitation of the inner electrons of atoms. X-rays are emitted when the outer electrons fill the vacancy in the inner shells. X-ray fluorescence (XRF) analysis is non-destructive and can be used on samples without the need for prior treatment through sample preparation using disks or fusion into glass beads is normally carried out to permit superior quantitative results.

XRF to used in
- photographic industry
- semi-conductor manufacturing (for impurity control in silicon chips),
- the petroleum industry,
- geological analysis,
- paper mills,
- gas analysis (e.g. nitrogen).
- Applications include the forensic analysis of metals, gunshot residues, paint, glass and soil, hair, fibres and polymers.
- Toxicology and environmental applications (dust, fumes from combustion, dangerous materials in waste such as Pb, As, Cr, Cd etc).

**Automated XRF at a cement works**

### *6.1 SEM-X-Ray Microanalysis*

X-ray microanalysis allows the mapping of all the elements present in a heterogeneous sample as observed with a scanning electron microscope (SEM), providing that the sample is capable of conducting. Non-conducting samples are coated with a conducting material such as carbon or gold for analysis.

By knowing the growth rate of hair (hair grows on average 1-2 cm per month) data from such analysis of hair samples has been used to determine when a person was exposed to heavy metals.

Another common forensic application of this technique is in the identification of particles of gunshot residue where lead, barium and antimony are identified in spherical particles of residue left on the hands or clothing of a person who had recently fired (or handled) a firearm.

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