Analytical Science

oer Skills for Scientists

A course (in 15 Chapters) developed as an Open Educational Resource, designed for use at 2nd year UK & Wales undergraduate level and as a CPD training resource

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Description	This chapter considers and compares the techniques that come under the heading of 'Atomic Spectroscopy' – flame emission, atomic absorption, plasma emission and atomic fluorescence together with sample preparation procedures. In addition it considers UV/visible and X-ray techniques where applied to the measurement of elemental species.
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Chapter 12 – Spectroscopic techniques for the measurement of elemental species

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Introduction

This chapter covers the analytical techniques of:

- **Atomic absorption spectroscopy (AAS)**

  This will include the use of a flame, graphite furnace, hydride generation and cold vapour techniques
- **Atomic emission spectroscopy (AES)**

  This will include the techniques of flame and an inductively coupled plasma emission
- **Atomic fluorescence spectroscopy (AFS)**
- U**ltraviolet / visible spectroscopy (UV-Visible)**
- **X-ray fluorescence spectroscopy (XRF)**
- **X-ray diffraction (XRD)**

In addition, some guidance on **sample preparation** approaches for the above techniques will be described, together with **applications** of the key techniques will be illustrated.

Sample preparation for AAS, AES and AFS

Much of this material has already been covered in Chapter 3 of this teaching & learning programme

Analysis for **major, minor and trace metals** in **solid samples** is typically done after decomposition of the matrix, using normally, acid(s) and heat, to liberate the metal. Whereas in the case of **liquid samples,** metals are either analysed directly with minimal sample preparation (except perhaps filtering) or after some form of pre-concentration method.

Major, minor and trace metals are analysed in a range of matrices that encompass environmental, biological, pharmaceutical, chemical, forensic and clinical sample types.

Figure 12.1 - a range of different sample types commonly analysed for their elemental content (A) soil, (B) food sample, (C) chemicals, (D) pharmaceuticals.

Solid sample decomposition methods

Decomposition, involves the liberation of the metal from a sample matrix using a reagent (mineral/oxidizing acids or fusion flux) and/or heat. This can be done using a range of approaches:

- Dry ashing,
- Acid digestion (including microwave dissolution)
- Fusion methods.

Dry ashing: The sample is heated in a silica or porcelain crucible in a muffle furnace in the presence of air at 400-800^{o}C (this allows organic matter to be destroyed). After decomposition, the residue is dissolved in acid and transferred to a volumetric flask prior to analysis. The major limitations of this method are:

- Loss of volatile elements e.g. Hg, Pb, Cd, Ca, As, Sb, Cr, Cu, due to volatilisation;
- Resistance of some materials to ashing;
- Difficulty in dissolving ashed materials;
- High risk of contamination.

The next slide shows photographs of a typical furnace and crucibles used in the above procedures.

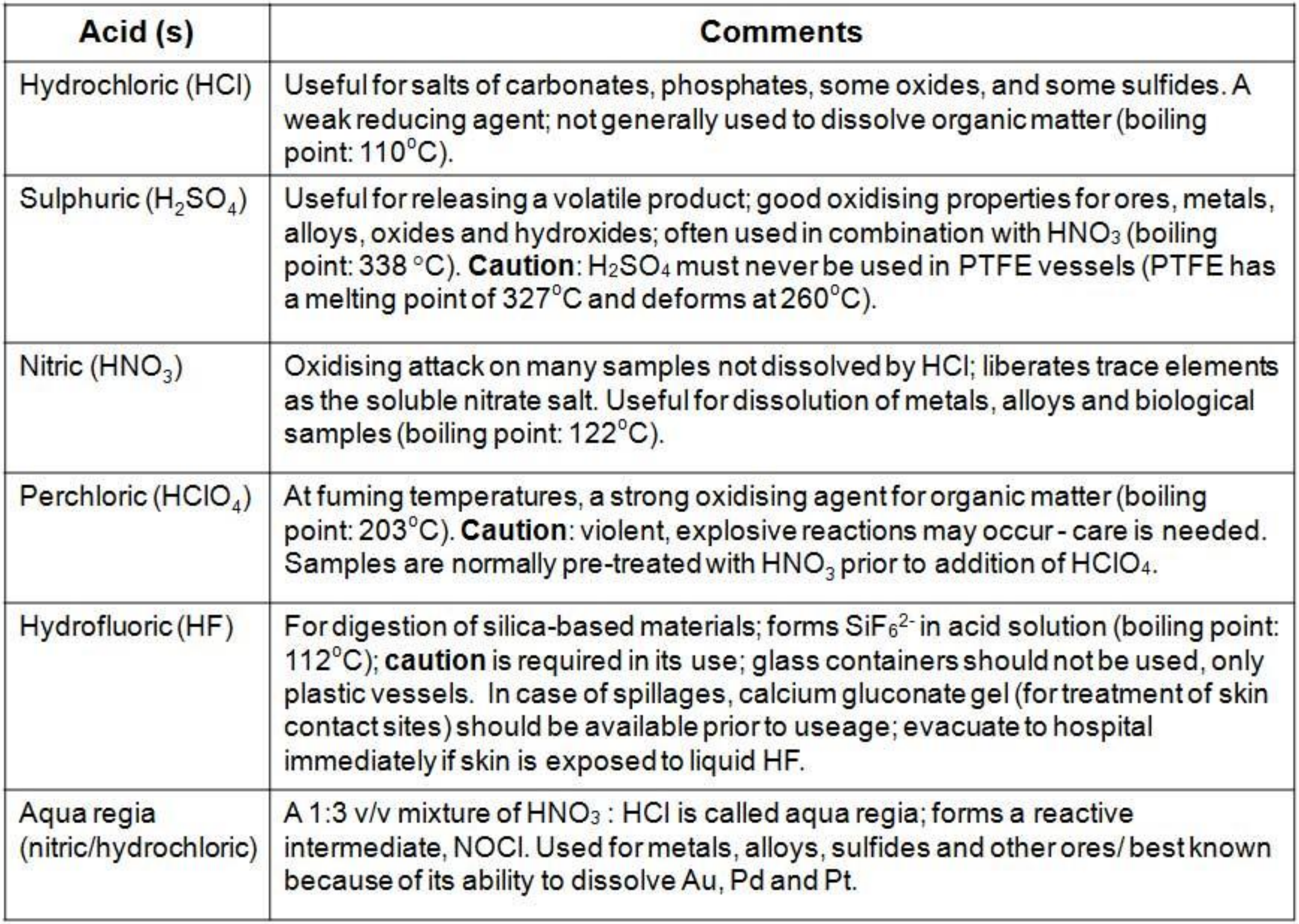
Figure 12.2 - a typical small muffle furnace used for dry ashing (sample containing crucible located inside the furnace)

Figure 12.3 - a crucible containing a sample for dry ashing

Acid digestion

This involves the use of mineral or oxidising acids and an external heat source to decompose the sample matrix. The choice of an individual acid or combination of acids is largely dependent upon the nature of the matrix to be decomposed. The most common acids and acid combination are summarised in Table (12.1). which is shown on the next slide.

Warning: Protective clothing and eyewear (safety glasses) are essential when using concentrated acids. All of the acids should be handled with care, and digestions carried out in a fume cupboard.

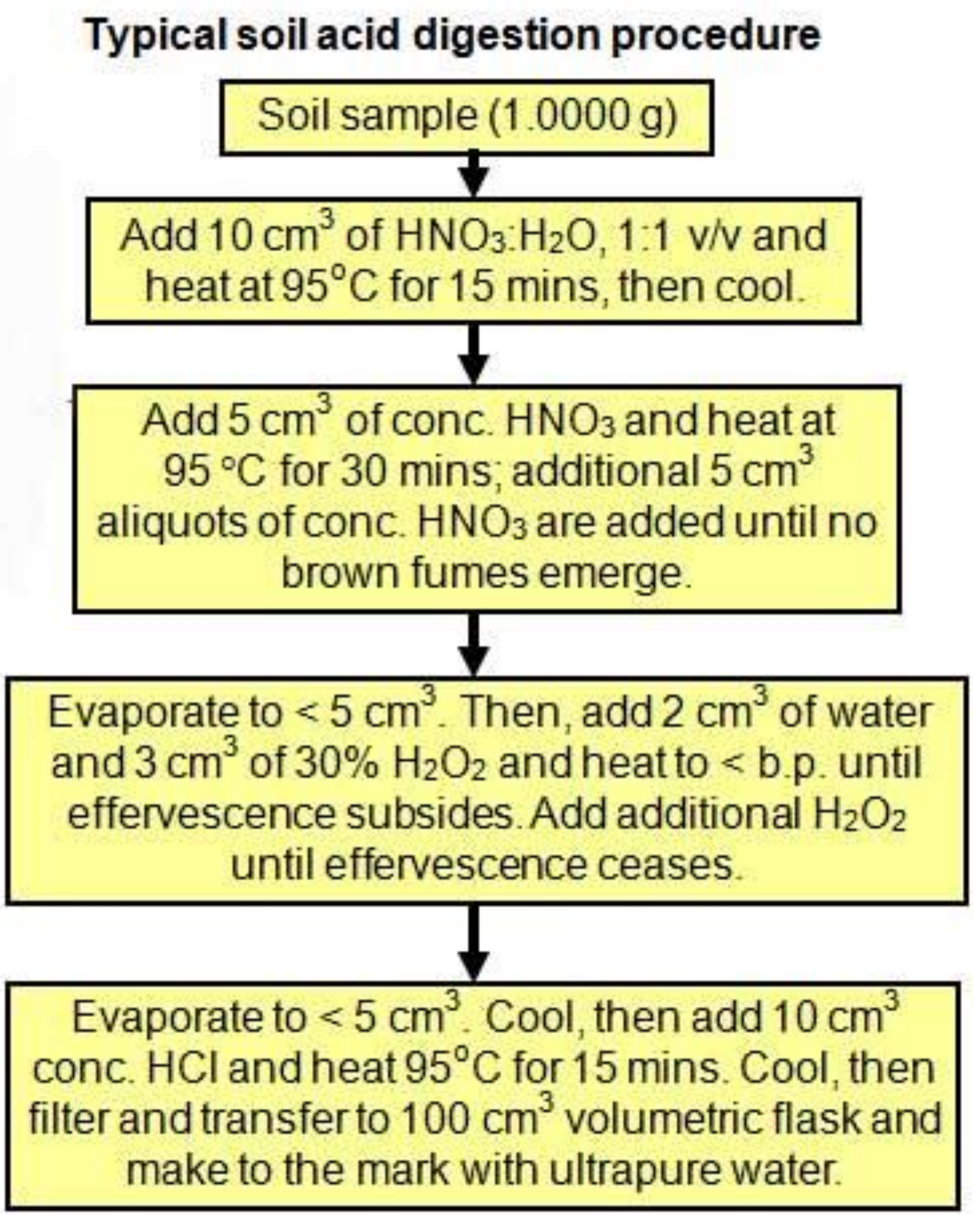


Acid (s)	Comments
Hydrochloric (HCl)	Useful for salts of carbonates, phosphates, some oxides, and some sulfides. A weak reducing agent; not generally used to dissolve organic matter (boiling point: 110°C).
Sulphuric (H_2SO_4)	Useful for releasing a volatile product; good oxidising properties for ores, metals, alloys, oxides and hydroxides; often used in combination with HNO_3 (boiling point: 338 °C). **Caution**: H_2SO_4 must never be used in PTFE vessels (PTFE has a melting point of 327°C and deforms at 260°C).
Nitric (HNO_3)	Oxidising attack on many samples not dissolved by HCl; liberates trace elements as the soluble nitrate salt. Useful for dissolution of metals, alloys and biological samples (boiling point: 122°C).
Perchloric ($HClO_4$)	At fuming temperatures, a strong oxidising agent for organic matter (boiling point: 203°C). **Caution**: violent, explosive reactions may occur - care is needed. Samples are normally pre-treated with HNO_3 prior to addition of $HClO_4$.
Hydrofluoric (HF)	For digestion of silica-based materials; forms SiF_6^{2-} in acid solution (boiling point: 112°C); **caution** is required in its use; glass containers should not be used, only plastic vessels. In case of spillages, calcium gluconate gel (for treatment of skin contact sites) should be available prior to useage; evacuate to hospital immediately if skin is exposed to liquid HF.
Aqua regia (nitric/hydrochloric)	A 1:3 v/v mixture of HNO_3 : HCl is called aqua regia; forms a reactive intermediate, NOCl. Used for metals, alloys, sulfides and other ores/ best known because of its ability to dissolve Au, Pd and Pt.

Table 12.1 - a summary of use of acids in sample digestion

Acid digestion: An accurately weighed sample is placed in a suitable digestion vessel (e.g. boiling tube) followed by an appropriate quantity of acid and heated using a temperature controlled multiple-sample digestor, which can allow a number of samples to be digested simultaneously. A typical digester is shown in figure (12.4)

Figure 12.4 - an acid digester



Typical soil acid digestion procedure

Soil sample (1.0000 g)

Add 10 cm^3 of HNO_3:H_2O, 1:1 v/v and heat at 95°C for 15 mins, then cool.

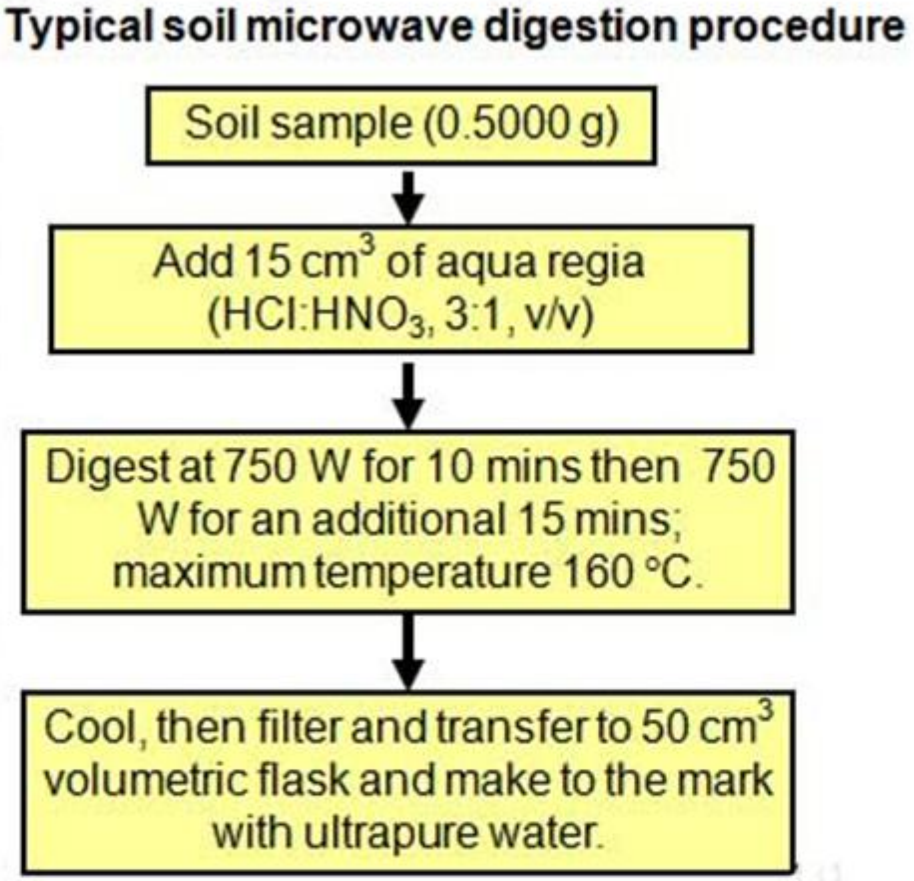
Add 5 cm^3 of conc. HNO_3 and heat at 95 °C for 30 mins; additional 5 cm^3 aliquots of conc. HNO_3 are added until no brown fumes emerge.

Evaporate to < 5 cm^3. Then, add 2 cm^3 of water and 3 cm^3 of 30% H_2O_2 and heat to < b.p. until effervescence subsides. Add additional H_2O_2 until effervescence ceases.

Evaporate to < 5 cm^3. Cool, then add 10 cm^3 conc. HCl and heat 95°C for 15 mins. Cool, then filter and transfer to 100 cm^3 volumetric flask and make to the mark with ultrapure water.

Microwave acid digestion: In this form of acid digestion a microwave oven (operating at 2.45 GHz) is used as the heat source (Figure 12.5). Samples (up to 41) are placed in PTFE vessels and heated under pressure for a specific time. The combined effect of temperature and pressure allows samples to be digested faster with minimal contamination risk. After digestion the sample vessels need to be cooled before opening.

Figure 12.5 – a microwave oven



Typical soil microwave digestion procedure

Soil sample (0.5000 g)

Add 15 cm^3 of aqua regia ($HCl:HNO_3$, 3:1, v/v)

Digest at 750 W for 10 mins then 750 W for an additional 15 mins; maximum temperature 160 °C.

Cool, then filter and transfer to 50 cm^3 volumetric flask and make to the mark with ultrapure water.

Fusion: The use of acid and their combinations does not always destroy some substances e.g. silicates and oxides. In this situation, fusion offers an alternative approach. Fusion involves the addition of a 10-fold excess of reagent to the finely ground sample placed in a platinum crucible. The mixture is then heated in a muffle furnace (300 - 1000°C) until a clear 'melt' (indicating completeness of the decomposition) results [Figure (12.6]. After cooling, the melt is dissolved in a mineral acid.

Typical reagents include:

- Sodium carbonate (12-15 g of flux required per g of sample; heat to 800°C; dissolve with HCl);
- Lithium meta- or tetra-borate (10-20 fold excess of flux required; heat to 900 - 1000°C; dissolve with HF);
- Potassium pyrosulphate (10-20 fold excess of flux required; heat to 900°C; dissolve with H_2SO_4).

Figure 12.6 - a muffle furnace

Practical issues: The use of excess reagent (flux) can lead to a high risk of elemental contamination. Also, the high salt content of the final solution may lead to problems in the subsequent analysis (nebulizer blockages).

Atomic Absorption Spectroscopy (AAS)

The instrumentation for AAS can be described by considering **four** major, but inter-related components.

Radiation source — Atom cell — Wavelength selection — Detection

Radiation source

A special light source to identify and emit light characteristic of a specific element.

The special light source is called a **hollow cathode lamp (hcl).** If analysing for zinc then a Zn hcl is required.

Atom cell

A component of the sample is introduced in to the atom cell.

Atom cells are available in different formats including a:

- **flame**
- **graphite furnace**

Wavelength selection

A device for isolating a specific wavelength characteristic of an element.

This type of wavelength selector or “spectrometer” is called a **monochromator.**

Detection

A device for converting incident light in to an electric current

The detector is called a **photomultiplier tube (PMT).**

Radiation source: hollow cathode lamp (hcl)

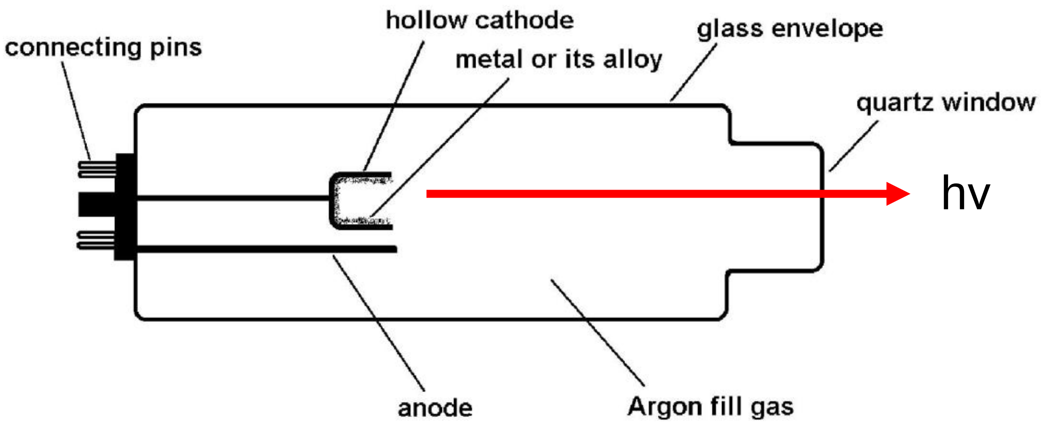


Figure 12.7. - schematic diagram of an hcl

The hcl consists of a cylindrical hollow **cathode**, containing the metal (or its alloy) of interest, and a tungsten **anode**. They are enclosed in a sealed glass vessel with a **quartz window** to allow ultraviolet light (the main part of the electromagnetic spectrum for observing atomic wavelengths) to escape. The lamp is under reduced pressure and filled with an **inert gas**, usually argon (Ar) or neon (Ne). A schematic diagram of an hcl is shown in figure (12.7)

Principal of operation of an hcl:

- Applying a high voltage across the terminals (i.e. **cathode** and **anode**) causes the fill gas atoms e.g. argon, to ionise ($Ar \rightarrow Ar^+ + e^-$).
- The argon ion (Ar^+) is then attracted to the negative terminal (i.e. cathode) causing some of the metal to be “sputtered” and become vaporized.
- The vaporized metal is excited to higher electronic levels by collision with the fill gas ions (Ar^+) resulting in characteristic emission light of the metal (and also the fill gas).

A photograph of a typical hcl is shown on the next slide

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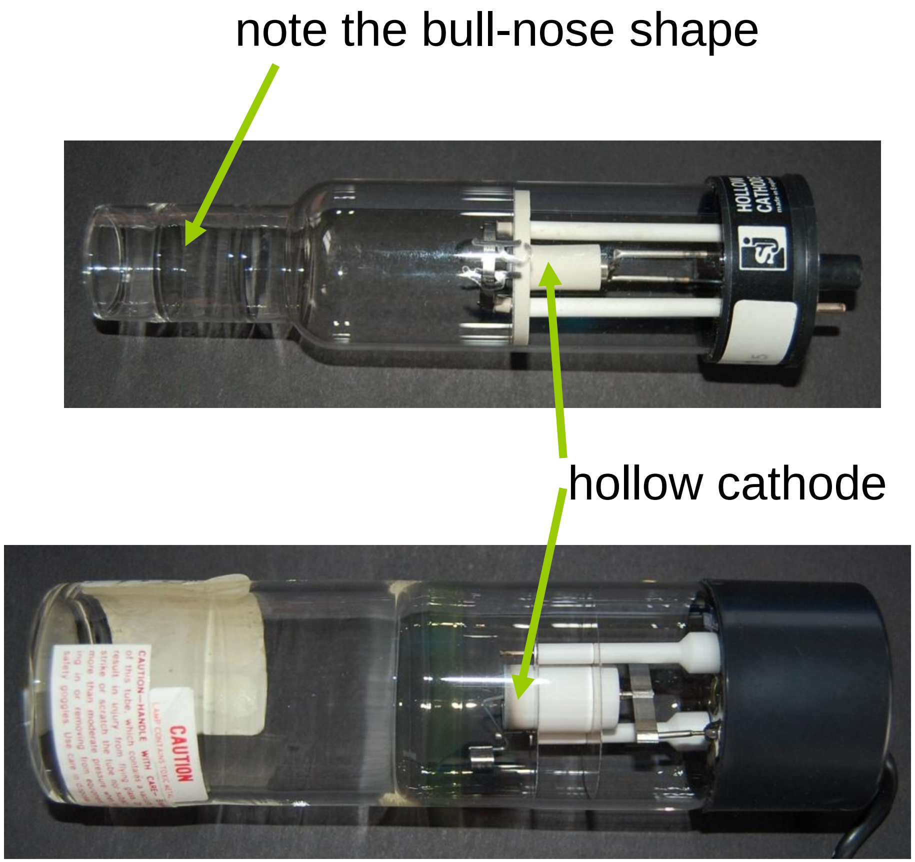


Figure 12.8 - photographs of different hollow cathode lamp designs

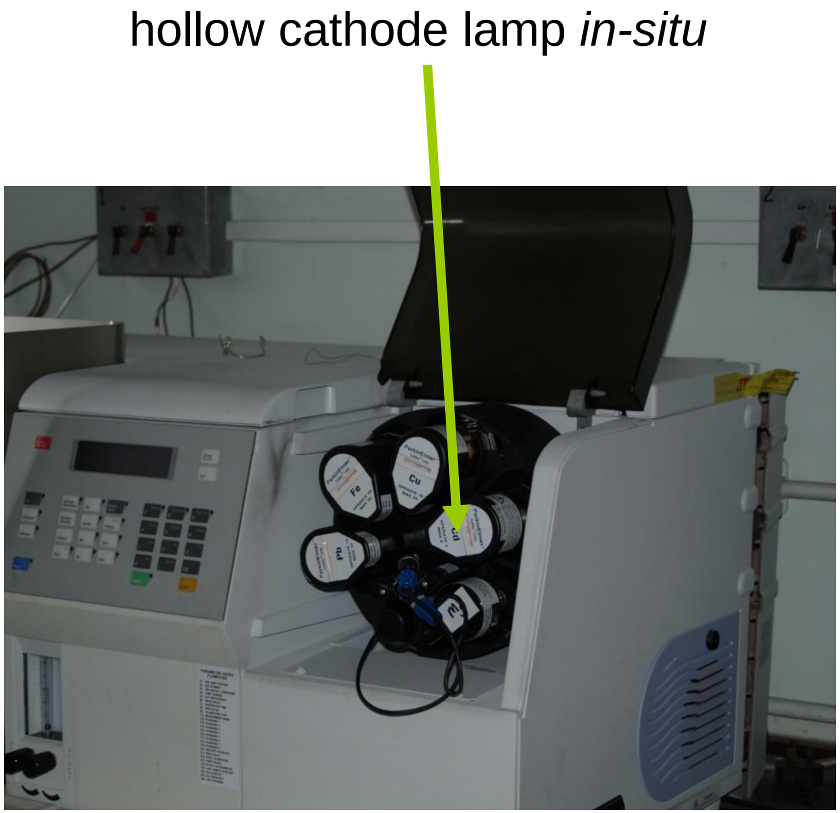


Figure 12.9 - a hollow cathode lamp located within AAS instrument

Atom cell: flame

The most common atom cell in atomic absorption spectroscopy, is the pre-mixed flame (FAAS) as illustrated in Figure (12.10). Within the pre-mixed flame it is possible to identify specific regions: pre-mixed gases **(see sample introduction in to the flame on slide 19)**are heated in the **pre-heating zone** where they reach the ignition temperature. Located round the pre-heating zone is the **primary reaction zone** in which reactions between the gases and sample aerosol components constitute the flame. This zone is characterised by its cone-like shape with the highest gas velocity occurring in the centre. The **inter-conal zone** is the hottest part of the flame and the area in which the light from the hcl passes through. The partly combusted gases interact further with the surrounding air leading to residual flame products in the **secondary reaction or diffusion zone**.

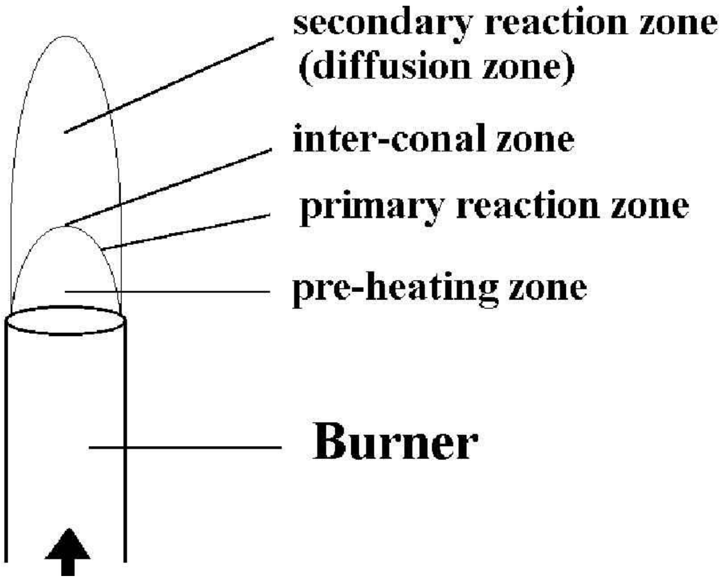


Figure 12.10 - zonal diagram of a pre-mixed flame

Continued on the next slide

A range of pre-mixed flames are used for FAAS. The most common are the **acetylene-air** and the **acetylene-nitrous oxide** with temperatures in the range 2250°C and 2955 °C, respectively. The hotter flame is used for those elements which form heat-stable oxides, the so-called ‘refractory elements’.

The flame is located in a **burner** optically aligned between the hcl and monochromator. The flame resides in a long-slot; 5 cm for the hotter C_2H_2-N_20 flame and 10 cm for the cooler C_2H_2-air flame.

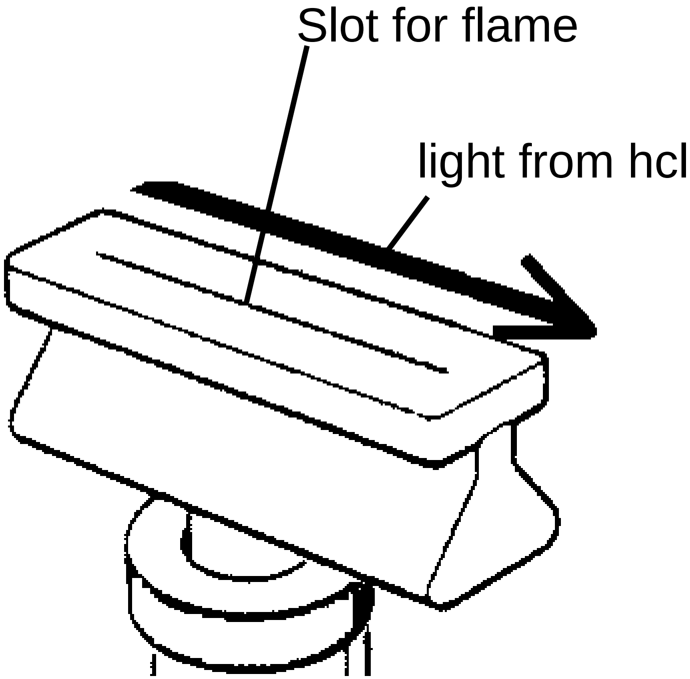


Figure 12.11 - a diagram of burner

Figure 12.12 FAAS instrument

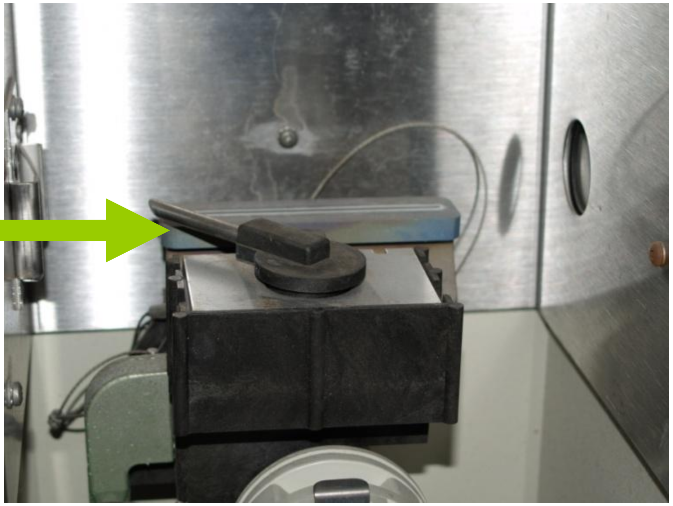
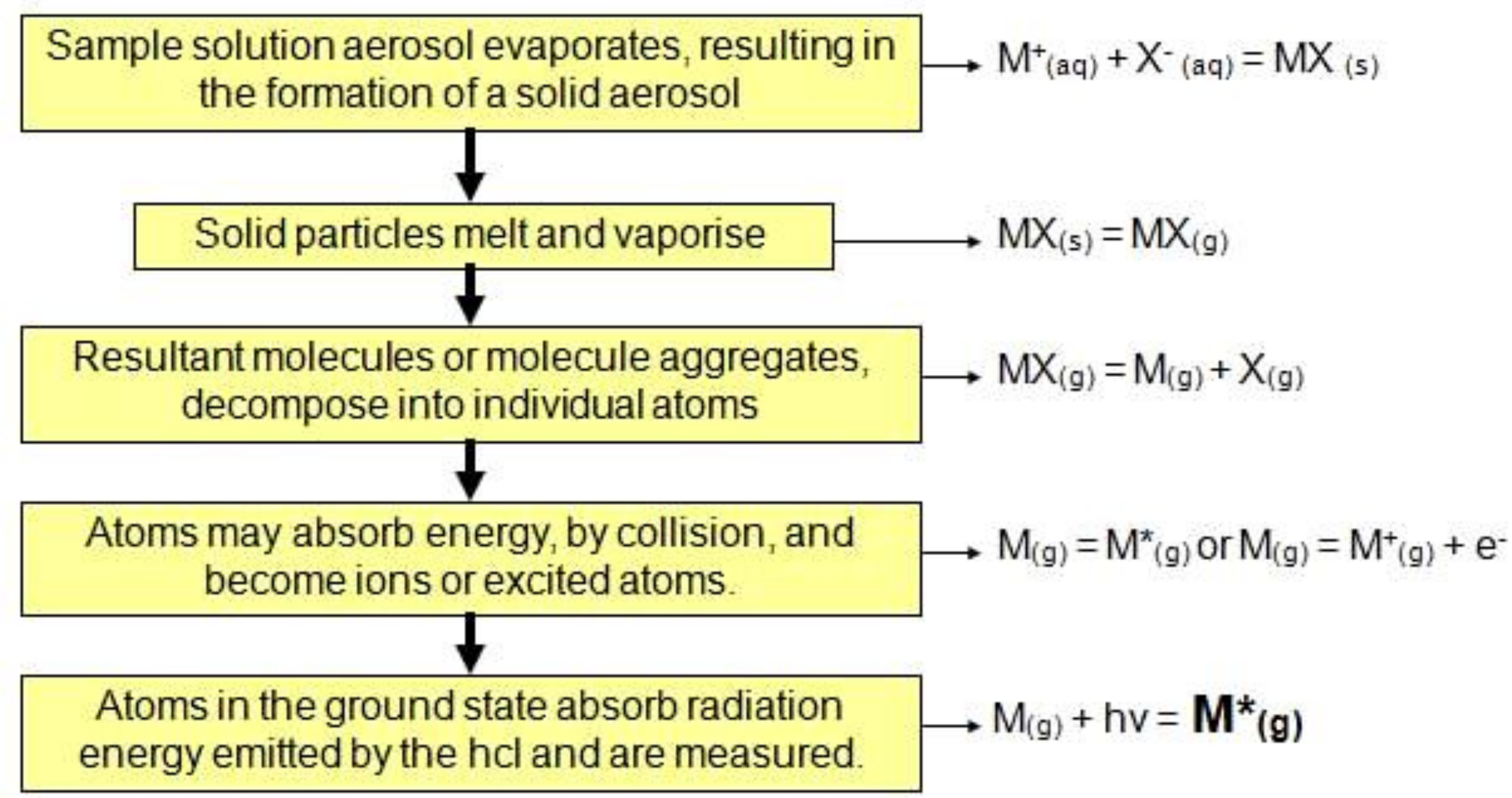


Figure 12.13 - burner assembly

Atom cell: flame processes

A complex series of processes occur in the flame resulting in the formation of atoms. The aqueous sample solution e.g. a metal salt, enters the flame in the form of an aerosol.



Sample solution aerosol evaporates, resulting in the formation of a solid aerosol → $M^{+}_{(aq)} + X^{-}_{(aq)} = MX_{(s)}$

Solid particles melt and vaporise → $MX_{(s)} = MX_{(g)}$

Resultant molecules or molecule aggregates, decompose into individual atoms → $MX_{(g)} = M_{(g)} + X_{(g)}$

Atoms may absorb energy, by collision, and become ions or excited atoms. → $M_{(g)} = M^{*}_{(g)}$ or $M_{(g)} = M^{+}_{(g)} + e^{-}$

Atoms in the ground state absorb radiation energy emitted by the hcl and are measured. → $M_{(g)} + hv = \mathbf{M^{*}_{(g)}}$

Alternative atom cell: graphite furnace (GFAAS)

A graphite furnace atomizer (also known as electrothermal atomizer) can be used to replace the flame burner in AAS. It consists of a graphite tube in to which are placed small quantities (5 – 50 µL) of (normally) aqueous sample and standards. A major issue with this approach is the presence of matrix interferences and it is often necessary, to stabilise the target element during the **ashing** stage by addition of a matrix modifier e.g. excess Ni in the determination of Se. Figure (12.14) shows the essential features of a GFAAS

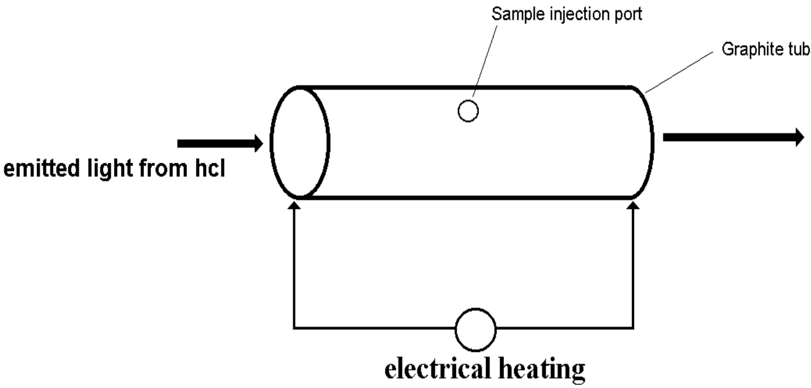


Figure 12.14 - graphite tube

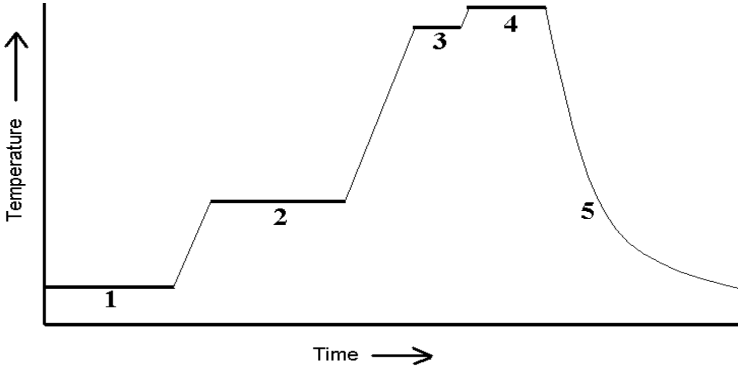


Figure 12.15 - graphite furnace heating cycle

The aqueous sample and standards are heated through a cycle as illustrated in Figure (12.15) to allow: 1 = **drying** (typically 105^{o}C for 40 s to allow removal of water); 2 = **ashing** (typically 1500^{o}C for 20 s to allow removal of the sample matrix, but not the element of interest); 3 = **atomisation** (typically 2200^{o}C for 2 s. This is the time when the signal absorbance is measured); 4 = **cleaning** (typically 2300^{o}C for 3 s to allow removal of any residual sample); and, 5 = **cooling** (typically 40 s to allow the graphite tube to cool in readiness for the next sample).

Sample introduction into the flame

An aqueous sample or standard is introduced in to an **expansion or cloud chamber** via a **pneumatic concentric nebulizer** (Figure 12.16). The nebulizer is able to directly aspirate the aqueous sample in the Pt-Ir capillary, by the **Venturi effect**, using air. This results in the formation of a coarse aerosol. The resultant coarse aerosol enters the expansion chamber. Two processes occur in the expansion chamber: (**1**) the coarse aerosol collides with baffles creating a finer aerosol and condensation. The condensate exits the chamber as waste (water trap), (**2**) the oxidant (air) and fuel (C_2H_2) mix to form the pre-mixed constituents for the flame burner. For a typical sample, 90% of the sample goes to waste (water trap) while only 10% exists the expansion chamber and enters the flame-burner assembly.

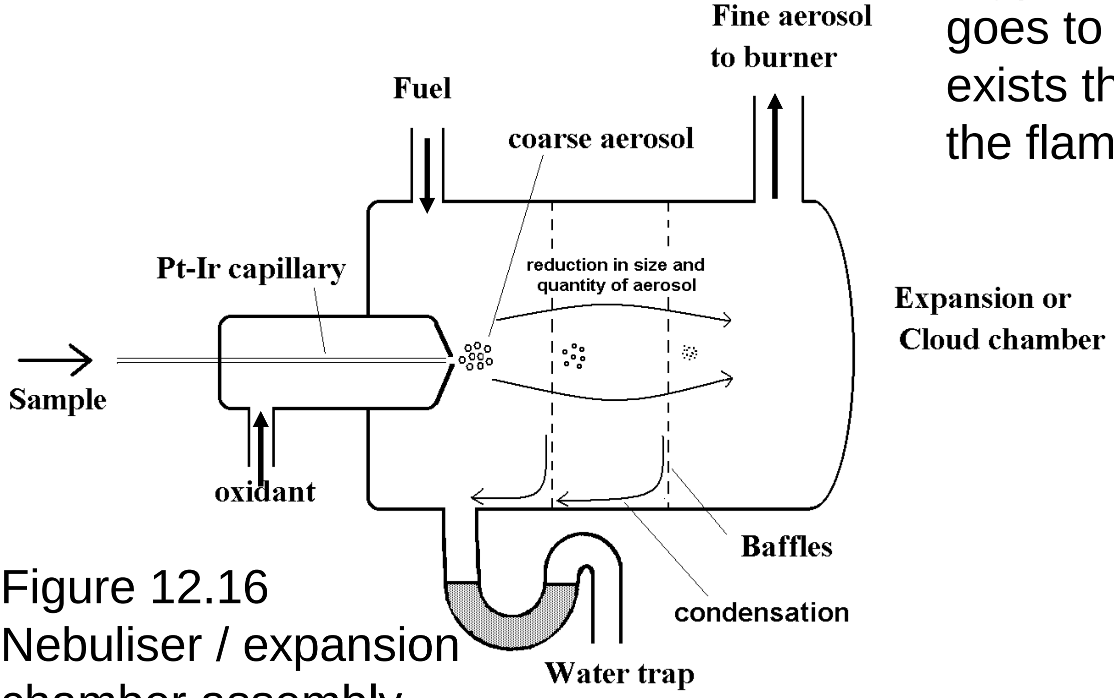


Figure 12.16
Nebuliser / expansion
chamber assembly

Definition of **Venturi effect**

The escape of gas through a narrow constriction in the nebulizer, causes a pressure reduction at that point. This reduced pressure, at the tip of the nebulizer, in turn draws liquid up the capillary tube without the need for a peristaltic pump.

Sample introduction: hydride generation (HGAAS)

The generation of chemical hydrides is limited to a few elements in the Periodic Table e.g. AsH_3, SbH_3, BiH_3, H_2Se, H_2Ge, H_2Te and SnH_4. Under acid conditions and in the presence of a reducing agent e.g. 1% w/v sodium tetraborohydride, the covalent hydrides are formed. The principle of hydride generation can be described in four steps and illustrated in Figure (12.17).

- Chemical generation of the hydrides e.g.

$$3BH_4^- + 3H^+ + 4H_3AsO_3 \rightarrow 3H_3BO_3 + \mathbf{4AsH_3} + 3H_2O$$

- Collection and pre-concentration of the evolved hydrides, if necessary.
- Transport of the hydrides and gaseous by-products with a flow of N_2 in to a narrow-bore silica tube mounted either over an air-C_2H_2 flame or one which is electrically heated (i.e. the atom cell).
- Atomisation of the hydrides in the atom cell and measurement of the absorbance signal.

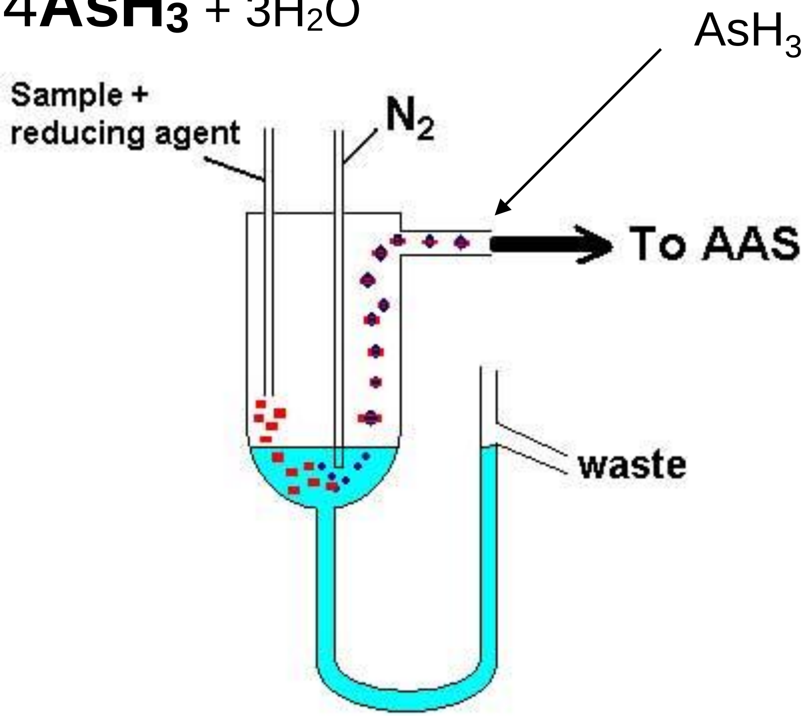


Figure 12.17 - gas-liquid separator

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Sample introduction: cold vapour (CVAAS)

The process of cold vapour generation is limited to **ONE** element in the Periodic Table - mercury, Hg. The mercury present in the sample is chemically reduced, usually using tin (II) chloride (stannous chloride), to elemental mercury:

$$Sn^{2+} + Hg^{2+} \longrightarrow Sn^{4+} + \mathbf{Hg^{o}}$$

The generated mercury vapour, being in the form of elemental mercury, is transported to an atom cell. In this special case, the flame atom cell is replaced in favour of a long silica tube into which the mercury vapour is introduced. No flame is required, as the elemental mercury can absorb directly the radiation emitted by a mercury hcl.

In order to increase the sensitivity of this approach it is sometimes necessary to pre-concentrate the mercury by amalgamation with silver or gold. The mercury is then released by heating and transported to the atom cell.

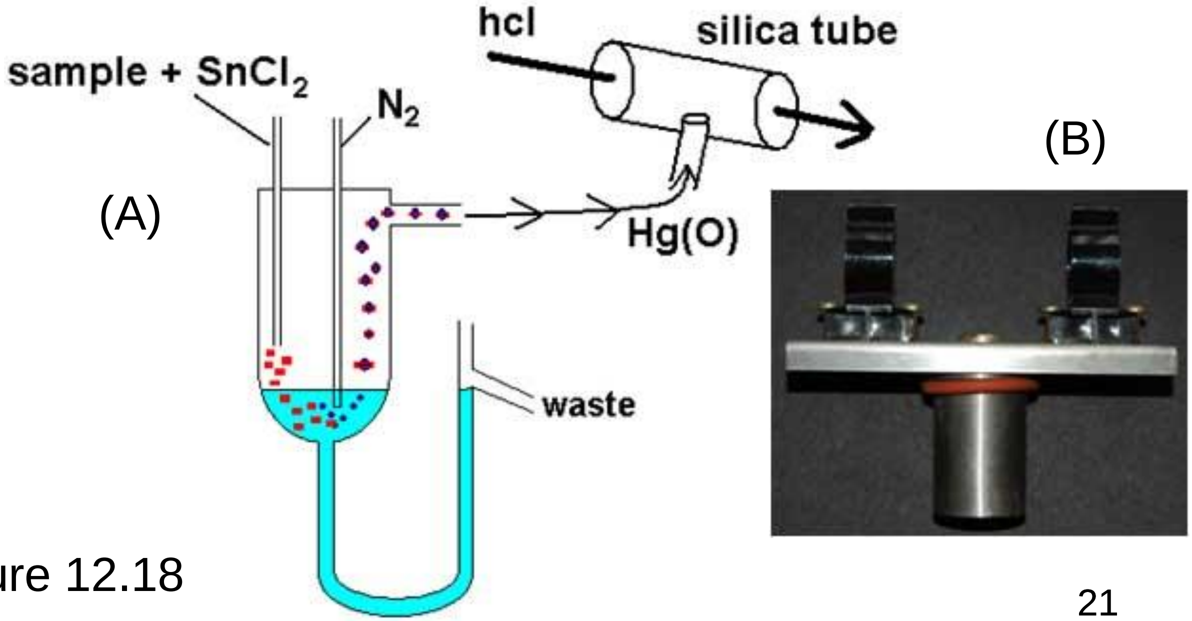


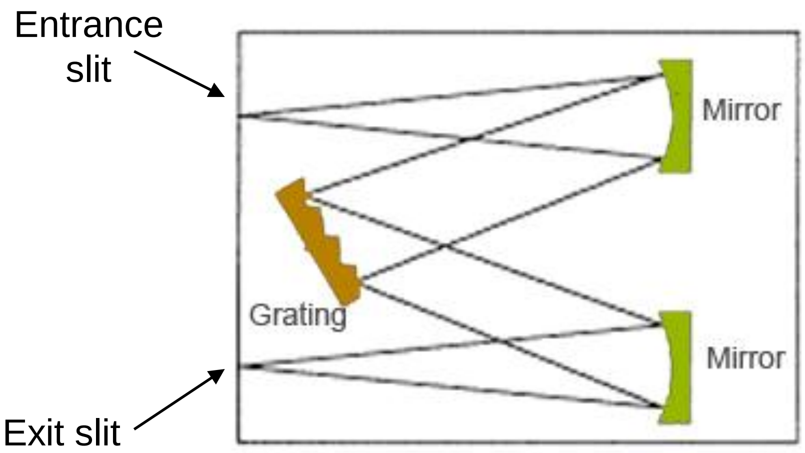
Figure 12.18

(A) diagram of cold vapour AAS, (B) holder for silica tube

Wavelength selection: Monochromator

Isolation of the characteristic light takes place with a monochromator. A typical optical layout for this device is the **Czerny-Turner configuration** as illustrated in figure (12.19), in which incident light enters (entrance slit) the monochromator, strikes a mirror and is then reflected to a diffraction grating where wavelength separation occurs. The radiation finally exits the monochromator, after being reflected from a second mirror.

Figure 12.19 - diagrammatic representation of a Czerny-Turner diffraction grating



A **diffraction grating** allows incident white light to be separated in to its component wavelengths. In this situation it allows the characteristic light from the element under investigation to be selected e.g. 232 nm for Cu analysis. ***More details on diffraction gratings and their operation can be found in the section on AES (see slides 46 - 49).***

Detection: Photomultiplier tube (PMT)

A PMT allows incident light to be converted in to an electric signal. By a process called the ‘photoelectric effect’ a photon of light is converted to an electron. The generated electron is then focused on to a dynode. As one electron hits the first dynode, it generates two electrons. The generated two electrons then hit the next dynode producing 4 electrons and so on. At the end all the generated electrons are collected at an anode and converted to a measurable electric current. The PMT [Figure (12.20)] is located behind the exit slit of the spectrometer.

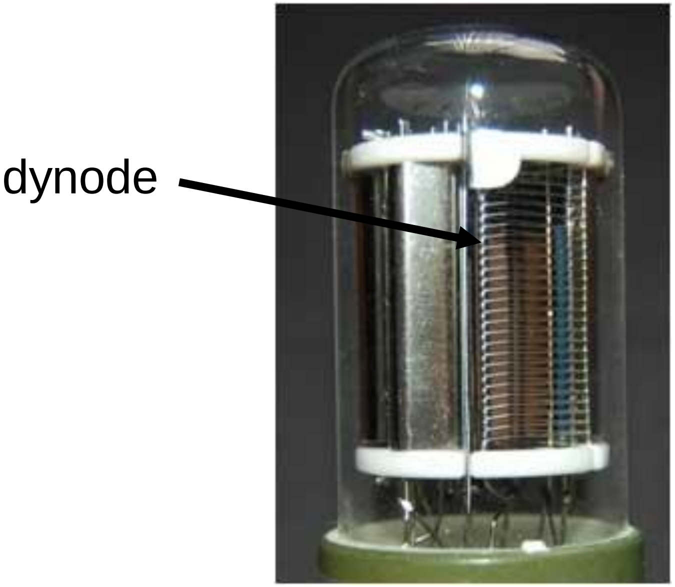


Figure 12.20 - photograph of a side window photomultiplier tube

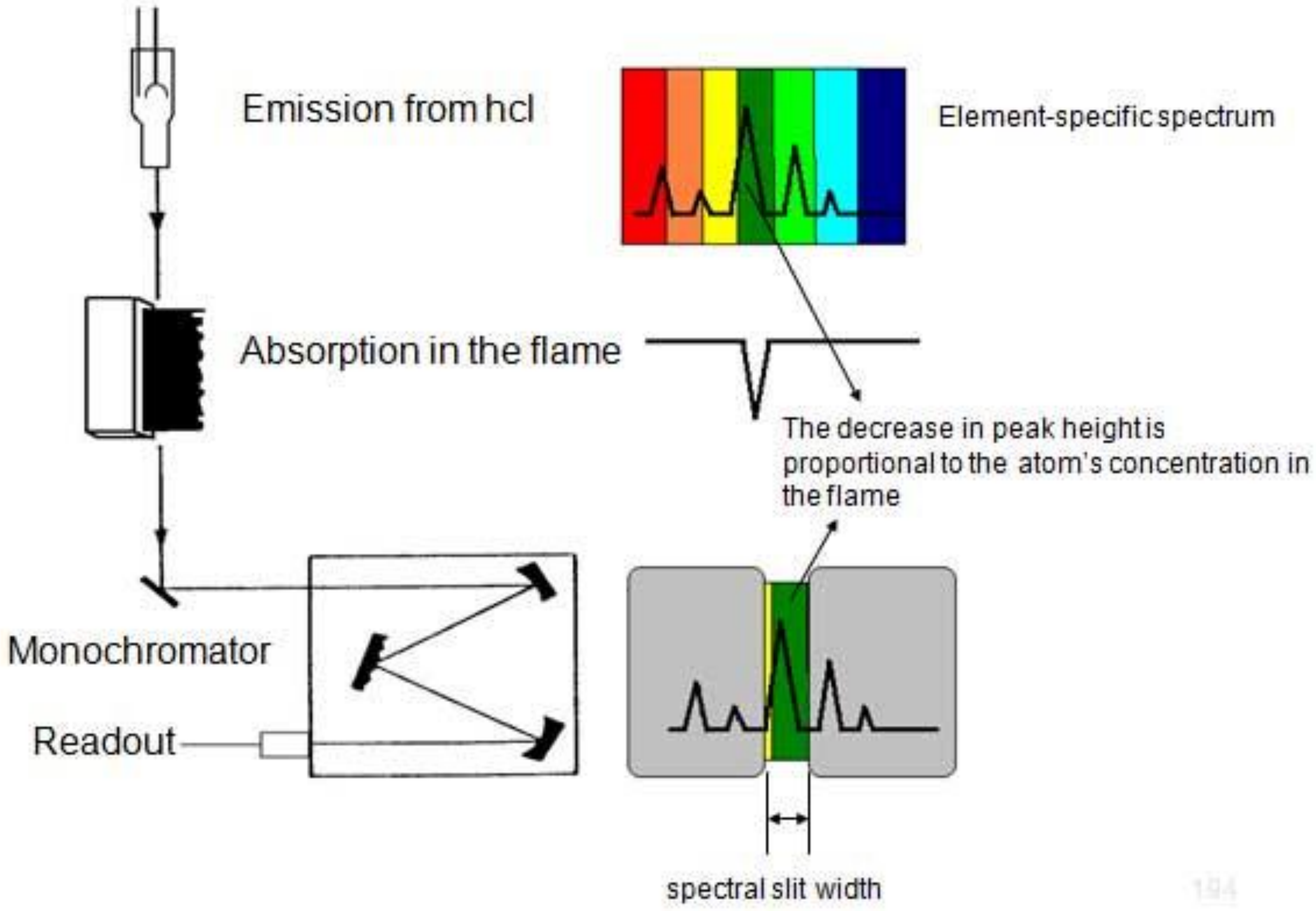


Figure 12.21 - an illustration of the principle of AAS

Single and double-beam AAS instruments

A single beam instrument allows direct alignment between the radiation source (hcl), via the atom cell, to the monochromator and detector (Figure 12.22).

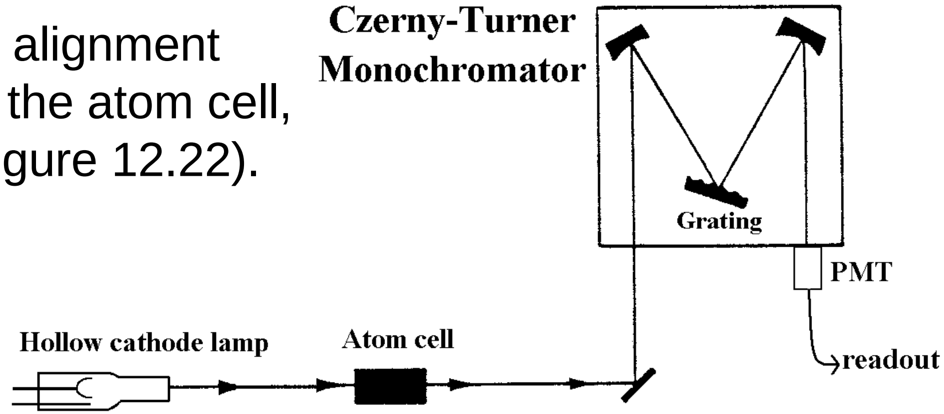


Figure 12.22 - single beam AAS

In a double beam instrument (Figure 12.23), light from the radiation source (hcl) is split in to two beams via a chopper. At this point, one beam passes through the atom cell while the other beam passes behind the atom cell. Both beams are then re-combined and continue to the monochromator and detector.

Double beam instruments are able to compensate for radiation source drift, instrument warm-up and source noise. This leads to data that is more precise (i.e. absorbance values, that are closer to each other).

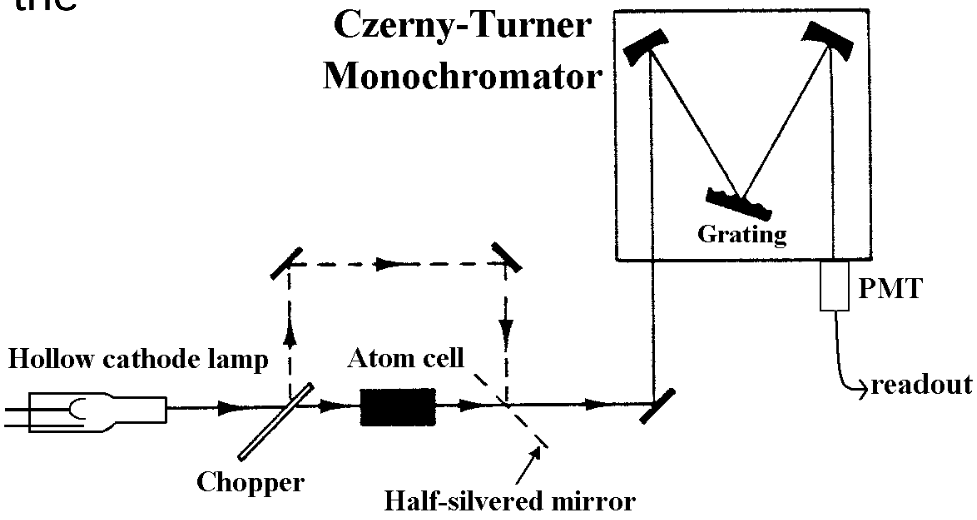


Figure 12.23 - double beam AAS

Interferences in FAAS

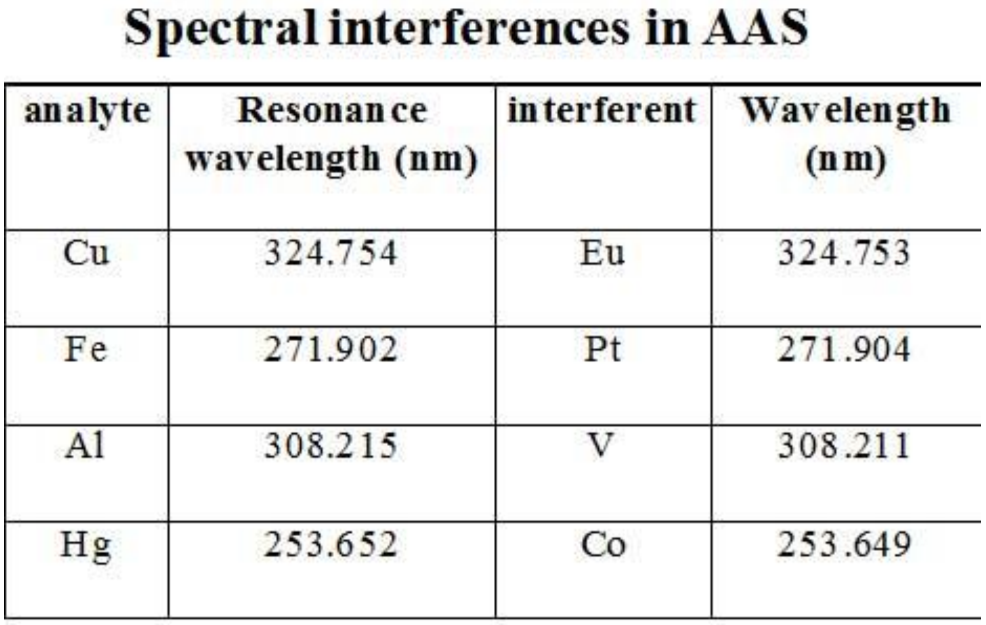
Although AAS is sometimes referred to as an analytical specific technique, this is not strictly the case, as there are occasions when interferences are known to occur. The interferences can be classified of the following types:

- Spectral;
- Chemical;
- Ionisation;
- Physical.

The following 5 slides describes each of these and gives examples of analyses that are likely to suffer interference.

Spectral interferences

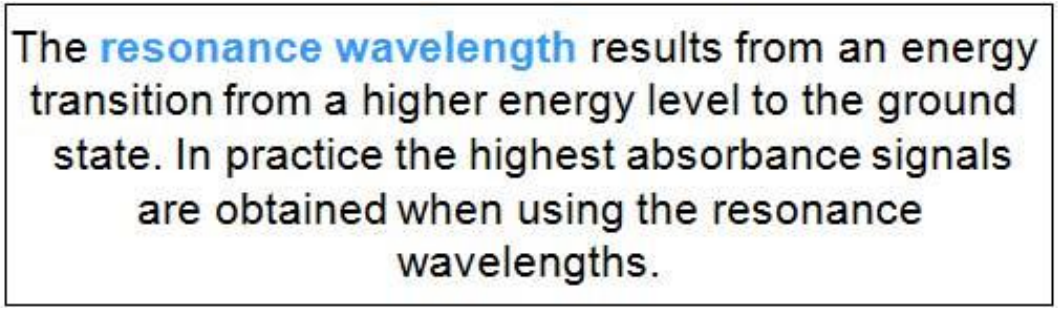
These are well characterised and result from spectral overlap between the wavelength of an element of interest that coincides with the wavelength of an interfering element. For example, if copper was to be determined at 324.7 nm, then from Table (12.2) it is possible to identify that an interfering element, having an absorbing wavelength close to that of copper, is europium. This interference however, is only critical, if the Eu is present in considerable excess compared t the Cu. Spectral interference will result in an absorbance signal that is larger than expected and will correspond to an over-estimation of the concentration of the element of interest in the sample.



Spectral interferences in AAS

analyte	Resonance wavelength (nm)	interferent	Wavelength (nm)
Cu	324.754	Eu	324.753
Fe	271.902	Pt	271.904
Al	308.215	V	308.211
Hg	253.652	Co	253.649

Table 12.2 - examples of spectral interferences



The **resonance wavelength** results from an energy transition from a higher energy level to the ground state. In practice the highest absorbance signals are obtained when using the resonance wavelengths.

Chemical interferences (also known as refractory compound formation)

This results from the formation of **stable complexes in the sample solution, that cannot be dissociated in the flame**. Several remedies to overcome this type of interferences are possible:

- Chemically protect the element of interest, in solution, by the addition of a **chelating** or **releasing agent**. The choice of chelating agent is important as it needs to dissociate in the flame (air-C_2H_2).
- Increase the temperature of the flame, by switching from an air-C_2H_2 flame to a N_20-C_2H_2 flame. This is particularly effective when measuring refractory elements such as Al, Ti, Mo and V.

An example of this type of interference is the determination of **calcium in the presence of phosphate** as illustrated in Figure (12.24). Phosphate reacts with calcium ions in the sample solution to form calcium pyrophosphate ($Ca_2P_2O_7$). This results in a decrease in the absorbance signal, since less Ca is now available in the atomic form.

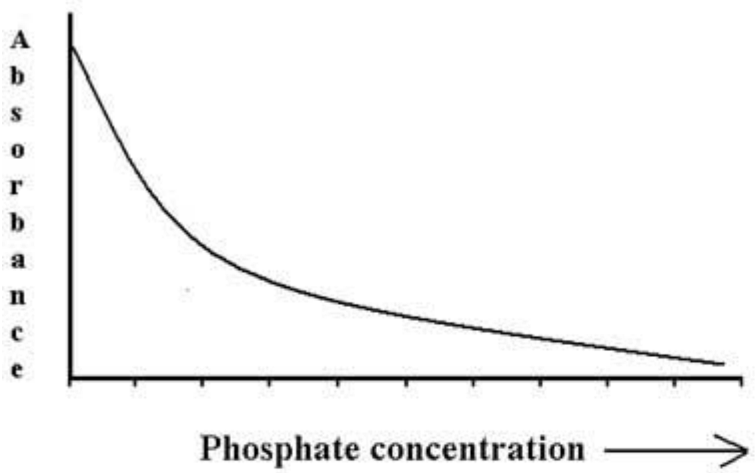


Figure 12.24 - effect of phosphate on The analysis of calcium

Continued on the next slide

The addition of either a **chelating** or **releasing agent** can reduce or eliminate this type of interference.

For instance in the case of the analysis or calcium in the presence of phosphate, the addition of a **chelating agent**, [e.g. ethylenediaminetetraacetic acid (EDTA)], preferential chelation occurs with Ca^{2+} which prevents complexation with phosphate. In the flame, the calcium-EDTA complex is easily dissociated, allowing measurement of Ca atoms.

The alternative approach is to add (ca. 1%) strontium chloride or lanthanum nitrate as a **releasing agent** into the sample solution. In this case the Sr^{2+} or La^{3+} preferentially react with the phosphate, thus preventing its reaction with the Ca^{2+}.

Ionization interferences

This results from the formation of partly ionized species in the hot flame leading to a decrease in the absorption signal. This type of interference is particularly important for elements that have a low **ionization potential** i.e. alkali metals such as Na, and alkaline earth elements such as Ca. This type of interference can be avoided by adding an excess of another element that is more readily ionized (termed an **ionization suppressor or buffer**) than the element being determined.

Ionization potential

This is the ability of an element to ionize: $Na = Na^+ + e^-$. An element in Group 1 of the Periodic Table (an alkali metal) will have a low ionization potential e.g. Na, 5.14 eV, whereas an element in Group IV will have a higher first ionization potential e.g. Pb, 7.42 eV.

For example, in the determination of sodium (Na), it is necessary to add excess caesium (Cs) to the solution. This ensures that the equilibrium between Na and Cs is such, that the preference is for Cs to become ionized (Cs^+) thereby ensuring that the Na present remains as atoms, and hence can be detected. This process is termed the **mass action** effect and is illustrated in Figure (12.25).

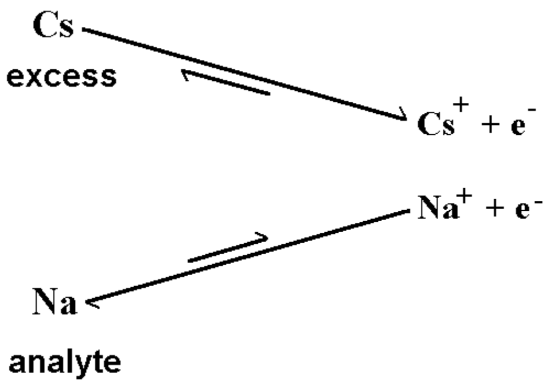


Figure 12.25 - illustration of mass action effect

Physical interferences

This occurs as a result of differences in ***sample uptake*** by the nebulizer / expansion chamber compared to the calibration standards. It can result from:

- A higher dissolved solids content in the sample compared to the calibration standards;

- Sample viscosity being higher or lower in the sample than in the standards;

- Atomization efficiency due to changes in flame temperature.

Physical interferences can largely be overcome in FAAS by the use of matrix-matched standards and frequent calibration.

Background correction techniques

A major problem in FAAS are interferences from the existence of molecular species in the flame. These can occur as a result of aspirating salt solutions in to the flame leading to incomplete desolvation or the inability to dissociate molecules in to atoms (and hence not measured in AAS). Several approaches to correct for this type of interference exist including:

- Deuterium background correction

- Smith-Hieftje background correction

- Zeeman effect background correction.

The Smith-Hieftje background correction is described on the next slide.

The simplicity of Smith-Hieftje background correction, is that it uses a single hollow cathode lamp, operating at higher and lower electric current. In these operating mode the atomic profile for the element profile is subject to self-reversal under a high operating current as illustrated in Figure (12.26).

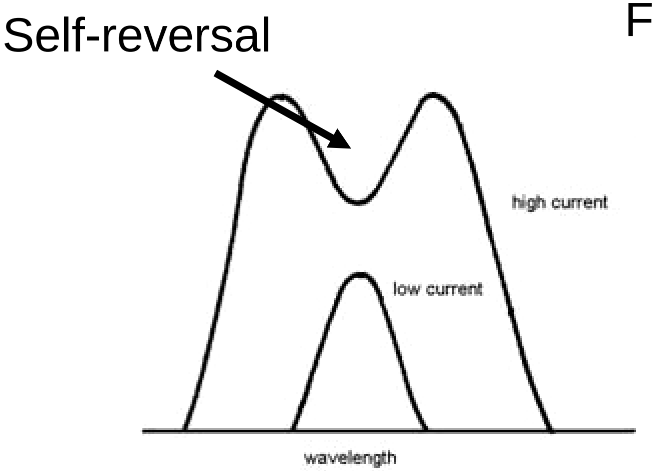


Figure 12.26 - atomic profile of hcl under low and high current.

As a result in low hcl operating mode, Figure (12.27A), the atomic and interfering molecular absorption coincide leading to measurement of an erroneous signal. However, in high hcl operating mode Figure (12.27B), only the broad band molecular absorption is measured (as the atomic profile from the atoms in the flame no longer coincides with the emission profile from the hcl). The difference between these signals is the measurement required.

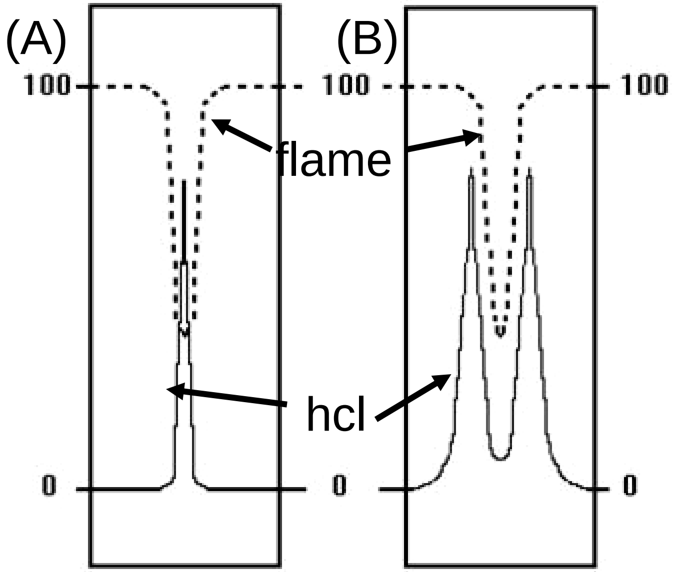


Figure 12.27 - separation of atomic and (interfering) molecular absorption.

Atomic Emission Spectroscopy (AES)

The instrumentation for AES can be described by considering **three** major, but inter-related components.

Atom / Ionization cell

A component of the sample is introduced in to the atom cell.

Atom / ionization cells are available in different formats including a:

- **flame**
- **inductively coupled plasma (ICP)**

Wavelength selection

A device for isolating specific wavelength(s) characteristic of element(s).

This type of wavelength selector or “spectrometer” is called a **monochromator** (for isolation of one wavelength) or **polychromator** (for isolation of several wavelengths simultaneously).

Detection

A device for converting incident light in to an electric current

The detectors available include: **photomultiplier tube (PMT)** or **charged coupled / injection devices (CCD/CID).**

Continued on the next slide

The most common source for AES is the inductively coupled plasma (referred to as ICP-AES), although for certain applications most notably the analysis of elements of Group I and II, a flame is often used.

Flame emission spectroscopy

This technique is also known as flame photometry and is typically used for the analysis of alkali metals i.e. Na, K, Li or the alkali earth metal i.e. Ca, in a range of sample types e.g. agricultural or clinical samples. The simple instrumentation consists of a low temperature flame, typically air-natural gas (2000 K), which results in a relatively simple emission spectrum i.e. only a relatively few emission wavelengths. Emission wavelengths are isolated using glass or interference filters (e.g. to determine K for instance, the K interference filter is required) and measured using a barrier layer photocell with a galvanometer readout or photomultiplier tube and digital readout. Samples are introduced in to the flame using a nebulizer / expansion chamber similar to that found in AAS.

Figure 12.28 - flame photometer instrument.

Inductively coupled plasma (ICP)

Introduction

This can be described as a hot gas, normally argon, in which a proportion of the atoms present are ionized:

$$\mathrm{Ar} \rightarrow \mathrm{Ar}^{+} + e^{-}$$

However, because atoms, positive ions and and electrons co-exist together, the plasma is electrically neutral. The ionized gas that constitutes the plasma is inductively coupled via a water cooled load, or induction coil, to a high frequency generator (27 or 40 MHz) operating at an output power of 0.5-1.5 kW. The plasma is located within the confines of a torch, situated within the load coil, and consisting of three concentric quartz tubes as illustrated in Figure (12.29).

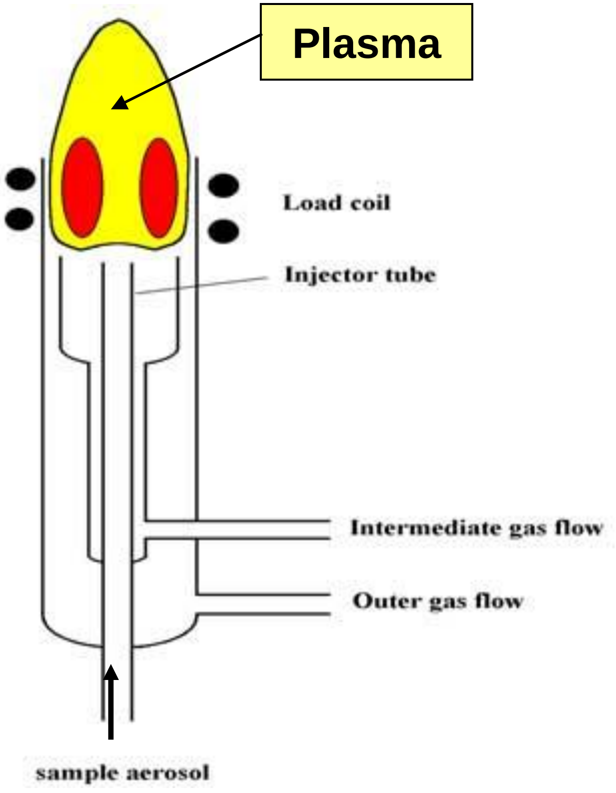


Figure 12.29 - ICP torch

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Argon gas is introduced into the torch as illustrated in Figure (12.30), at three locations:

- a tangentially flowing outer or coolant gas (12 L/min) which prevents the outer quartz tube from melting;
- a tangentially flowing intermediate gas (0.5 L/min) to sustain the plasma;
- a laminarly flowing injector gas (1.0 cm^3/min) by means of which the sample is introduced into the plasma.

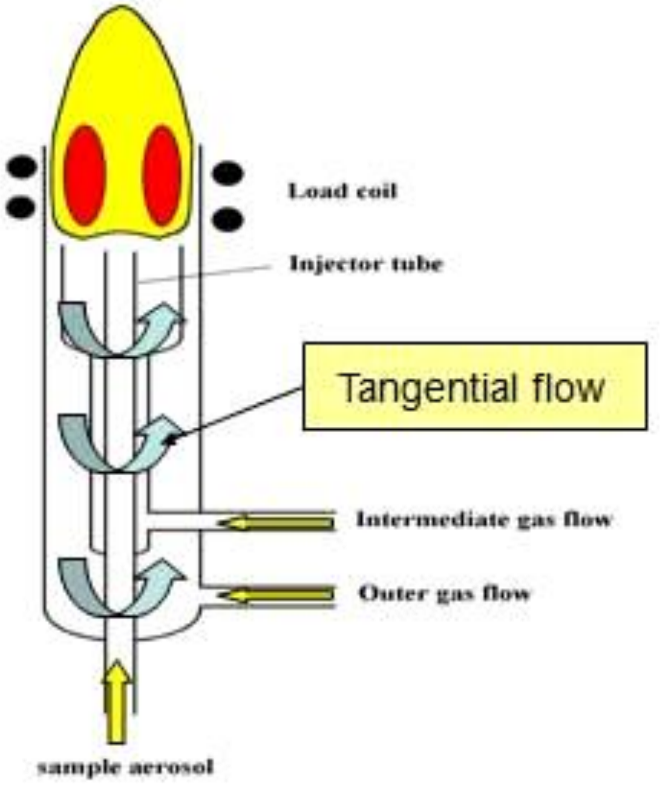
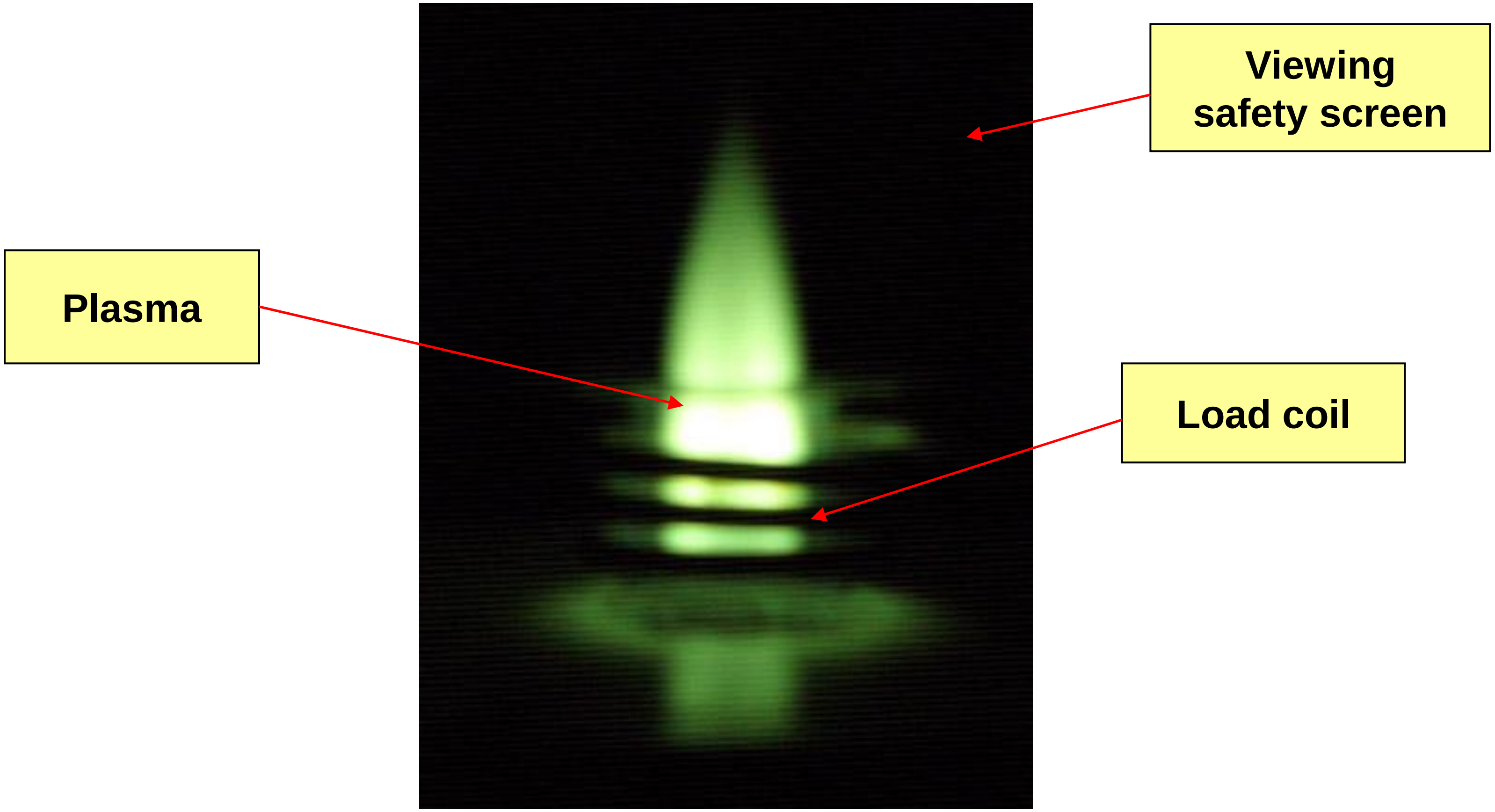


Figure 12.30 - ICP torch showing gas flows

The sample is introduced into the plasma as a fine aerosol formed by a nebulizer / spray chamber combination and a description of this is shown on the next 3 slides.

http://en.wikipedia.org/wiki/File:ICP-small.jpg



Viewing safety screen

Plasma

Load coil

Figure 12.31 - inductively coupled plasma viewed through a safety screen

Formation of the plasma

This occurs by ‘seeding’ the flowing argon gas with free electrons from an external source i.e. a high voltage spark or ***Tesla discharge***. A magnetic field, formed by the high frequency current flowing in the load coil, generates oscillating magnetic fields whose lines of force are axially orientated inside the quartz plasma torch and follow elliptical closed paths outside the load coil [Figure (12.32)]. The induced axial oscillating magnetic field interacts with the free electrons from the Tesla discharge causing them to be accelerated as they flow in closed annular paths, inside the quartz plasma torch. These accelerated electrons meet resistance to their flow causing Joule or Ohmic heating which leads to ionization of the argon gas. As this entire process takes place in a very short time scale (milliseconds) a plasma is formed within the torch almost instantaneously.

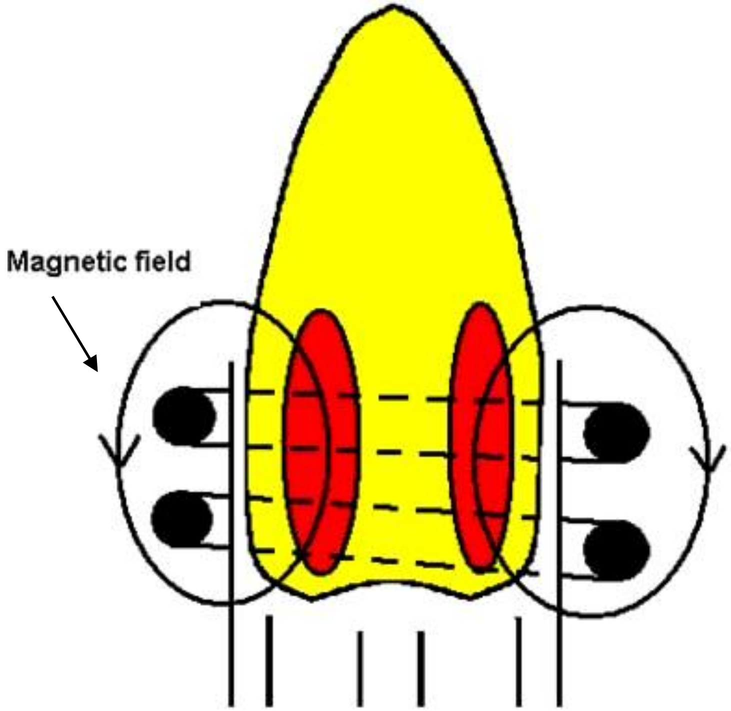


Figure 12.32 - formation of an ICP

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The escaping high velocity argon gas causes air entrainment back towards the plasma torch thereby forming the characteristic bullet shape of the ICP. For efficient atomization and excitation of elements to occur the injected sample aerosol must remain in the high temperature interior of the plasma for as long as possible. This is achieved by introducing the sample aerosol laminarly such that a hole is punched in the tangentially flowing vortex stabilized plasma creating the characteristic doughnut or ***toroidal shape*** of the ICP [Figure (12.33)].

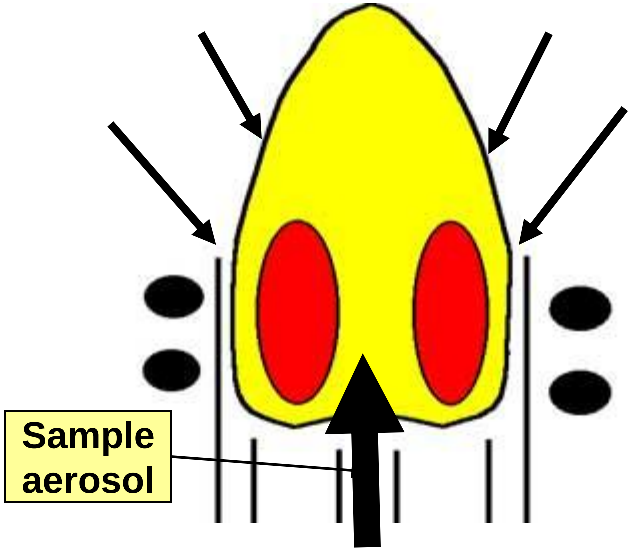


Figure 12.33 - shape of an ICP

Although electrically neutral, the ICP, is not in thermodynamic equilibrium meaning that it is not possible to characterize a single **temperature** within the argon plasma. The temperature of the ICP is often quoted as in the range **6000 – 8000 K**, depending upon which approach was used to determine the temperature. Temperature can be determined as:

- the **electron temperature**, determined by the kinetic energy of the electrons,
- the **gas temperature**, determined by the kinetic energy of the atoms,
- the **excitation temperature**, determined by the population density of the different ionization states, and
- the **ionization temperature**, determined by the population of different ionization states.

Sample introduction in to the ICP: nebulizer

The most common approach for introduction of a sample in to an ICP is via a nebulizer / **spray chamber**.

The most common nebulizer is the **pneumatic concentric glass nebulizer**. The nebulizer operates via the **Venturi effect** and results in the formation of a ‘coarse’ aerosol. Alternative nebulizers include the cross-flow, high solids (V-groove, Babington or Burgener), direct injection and ultrasonic.

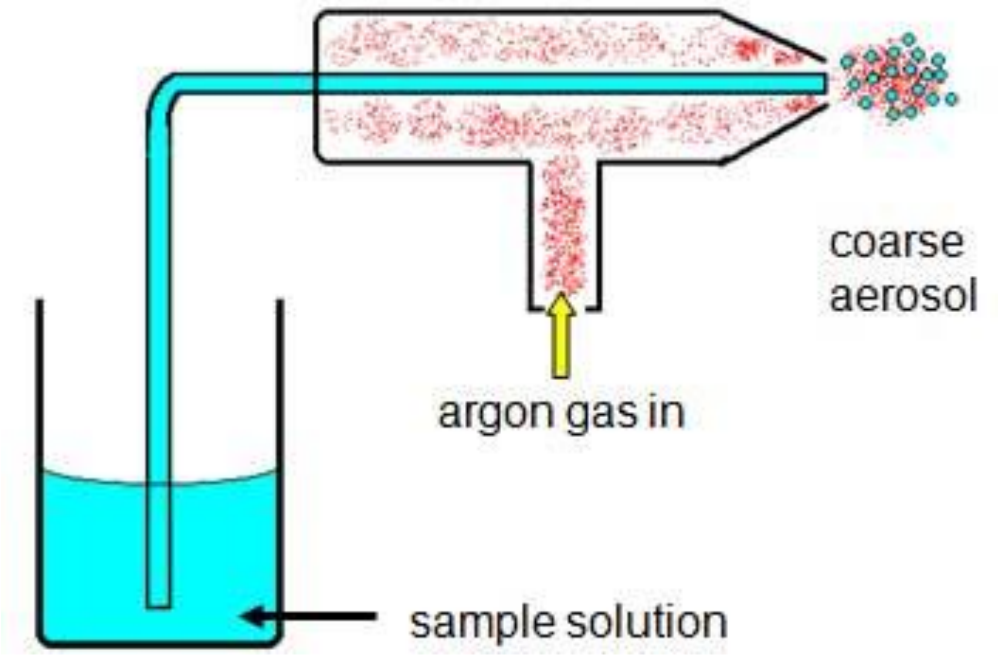


Figure 12.34 - operation of pneumatic concentric nebulizer

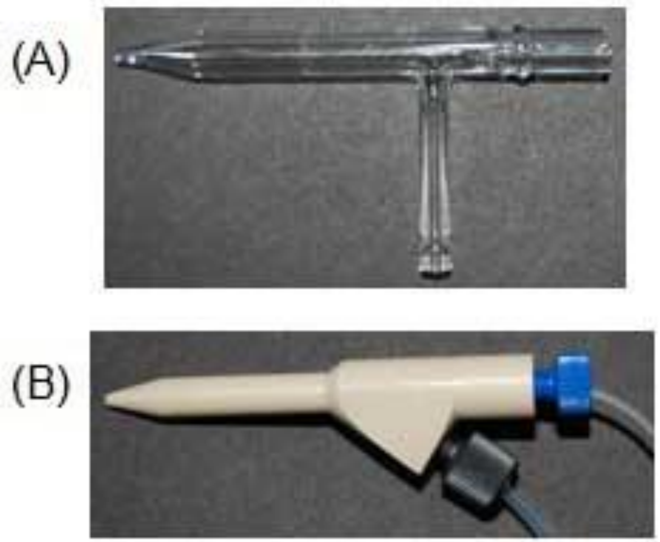


Figure 12.35 - (A) concentric glass nebulizer, and (B) Burgener nebulizer.

Sample introduction in to the ICP

Although a number of spray chambers have been devised, the most common is is the **double-pass** spray chamber as illustrated in Figure (12.36).

The **spray chamber** has several functions including:

- Reducing the amount of sample aerosol reaching the ICP;
- Decreasing the turbulence associated with the nebulization process;
- Reducing the aerosol particle size to approximately 10 µm.

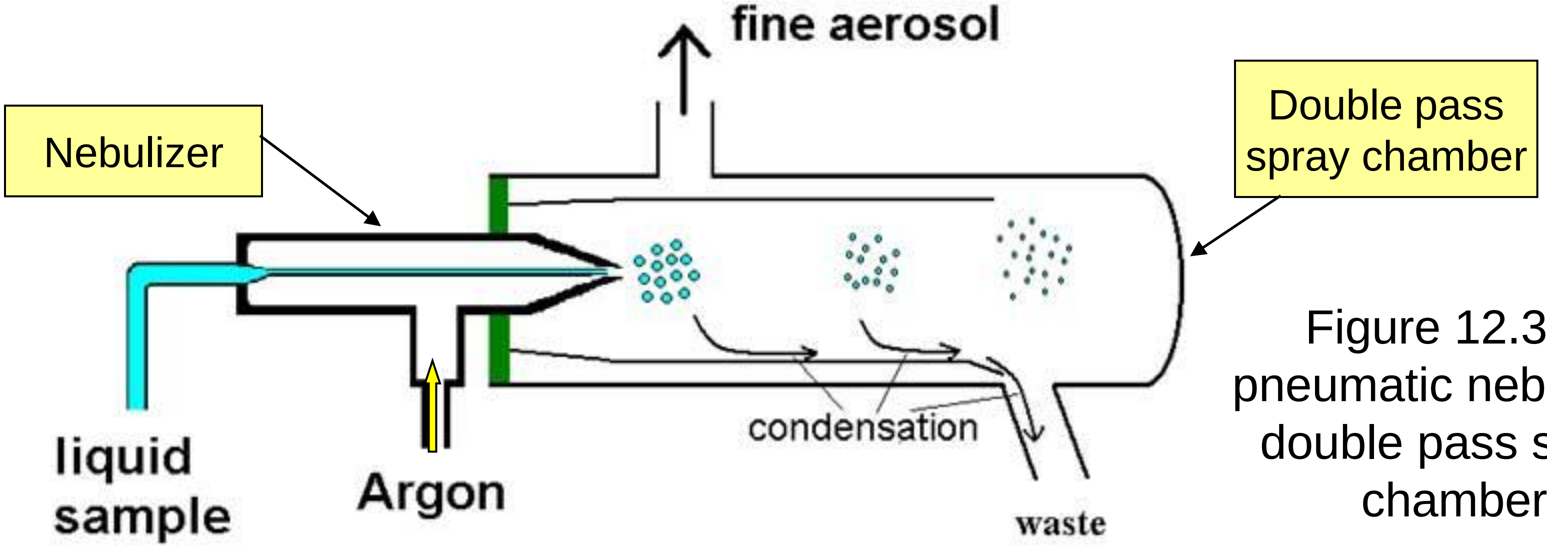


Figure 12.36 - pneumatic nebulizer-double pass spray chamber

All combinations of nebulizer and spray chamber are inefficient with transport efficiencies (amount of liquid sample reaching the ICP) of approximately 2% for a pneumatic concentric nebuliser / double pass spray chamber arrangement.

Sample introduction: Alternatives

Although the nebulizer/spray chamber arrangement is the most common method of introducing samples into the ICP, alternative devices are also available. These include:

- Hydride generation and cold vapour approaches (**see slides 20 - 21 earlier in this chapter*),***
- **Laser ablation;**
- **Electrothermal vaporization**.

Electrothermal vaporization (ETV)

An aqueous sample (up to 100 µL) is introduced onto a graphite surface (electrothermal vaporizer) and heated in a 4 stage process [see slide 18] to allow (a) removal of water, (b) destruction and removal of the sample matrix (ashing) without loss of the element of interest, (c) ***vaporization of the element directly into the ICP***, and (d) additional heating to ensure the graphite surface is clean.

Laser ablation

A solid sample is ablated by a laser and the ultra-fine particles of material released, are transported ***directly to the ICP*** via an argon carrier gas. A commonly used laser is the **Nd:YAG**. which operates both in the near infra-red and UV/visible regions of the electromagnetic spectrum.

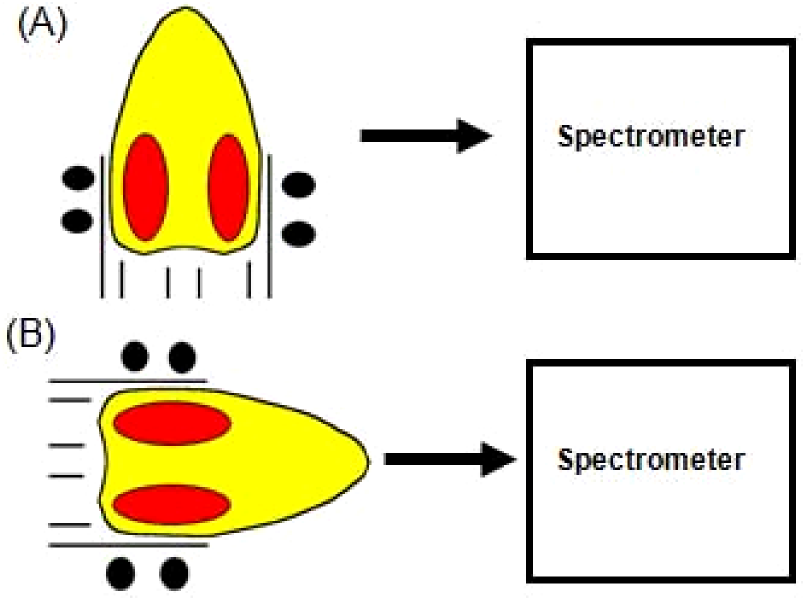
The major advantages of laser ablation include:

- Applicability to any solid sample;
- No sample size requirements;
- No sample preparation;
- No reagents or solution waste;
- Can provide spatial characterisation information.

The major disadvantages of laser ablation include:

- The amount of sample ablated is dependent upon the type of laser and sample properties;
- Matrix-matched standards required for calibration;
- Fractionation occurs for samples with low melting points.

ICP-Spectrometer alignment



In the conventional ICP system the emitted radiation is viewed by the spectrometer laterally, or **side-on**. In this situation, the emitted element radiation is "viewed" through the luminous plasma, which leads to a higher background signal.

Alternatively the ICP can be viewed by the spectrometer axially, or **end-on**, thereby reducing background emission.

Figure 12.37 - (A) Side-on, and (B) end-on ICP spectrometer alignments

Major features of the **emission spectra** are:

- The presence of a large number of emission lines (due to the Ar source gas, atmospheric gases e.g. N_2, and the breakdown components of water e.g. OH).
- Background continuum (due to radiative recombination of electrons and ions ($M^+ + e^- \rightarrow M + h$) and the radiation loss of energy by accelerated electrons.

ICP-AES for sequential multielement analysis

One of the major advantages of ICP over AAS for elemental analysis, is the feasibility of carrying out multi-element analysis, either sequentially or simultaneously. In the sequential mode, the light emitted from the sample is measured at one wavelength at a time, each wavelength being appropriate for a particular element of interest. A typical optical arrangement for a sequential spectrometer (monochromator) is based on the Czerny-Turner configuration as illustrated in Figure (12.38).

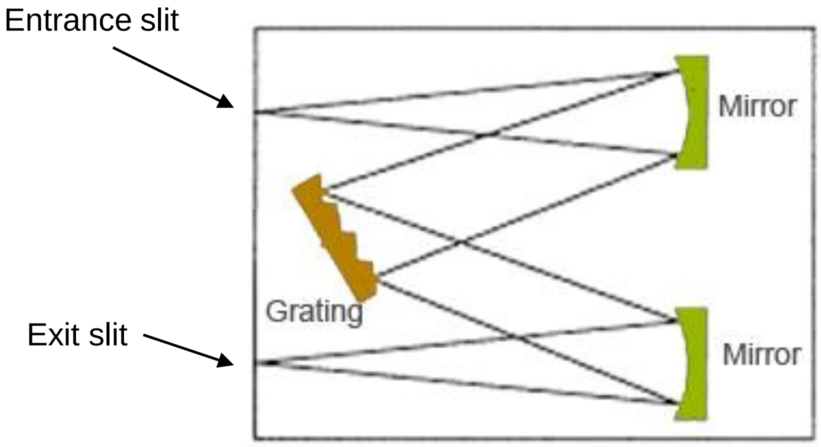


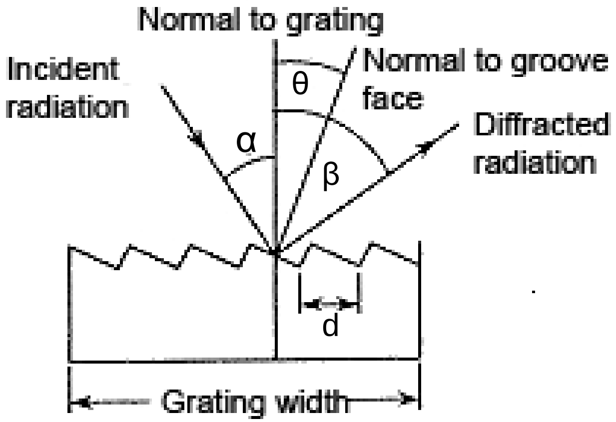
Figure 12.38 - diagram of Czerny-Turner monochromator configuration.

The monochromator as illustrated in figure (12.38) consists of entrance and exit optics, a diffraction grating and a single detector. This type of spectrometer provides flexibility in terms of wavelength coverage e.g. from Al at 167 nm to Cs at 852 nm. Selection of the desired wavelength (and hence specific element) is achieved by computer-controlled rotation of the grating within its spectrometer mounting.

Diffraction Grating

The main component in the spectrometer that allows light to be separated into component wavelengths is the **diffraction grating**, a diagram of which is illustrated in Figure (12.39). A diffraction grating consists of a series of closely spaced lines or grooves etched on to the surface of a mirror (between 1200 to 3200 lines mm^{-1}) in a saw-tooth pattern. As light strikes the grating it is diffracted at an angle which corresponds to the wavelength for a particular element.

Figure 12.39 - illustration of the working of a diffraction grating.



Diffraction grating: d = distance between grooves; θ = angle of a groove (blaze angle); α = angle of incidence; β = angle of reflection

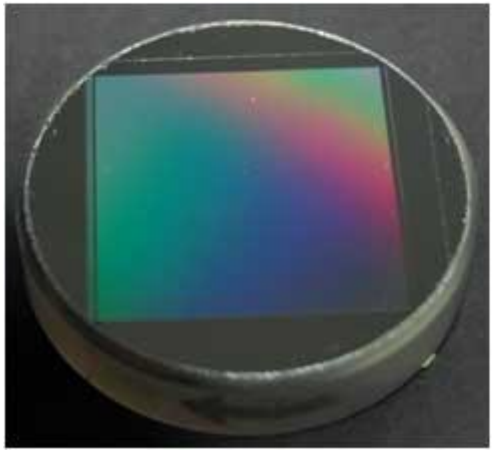
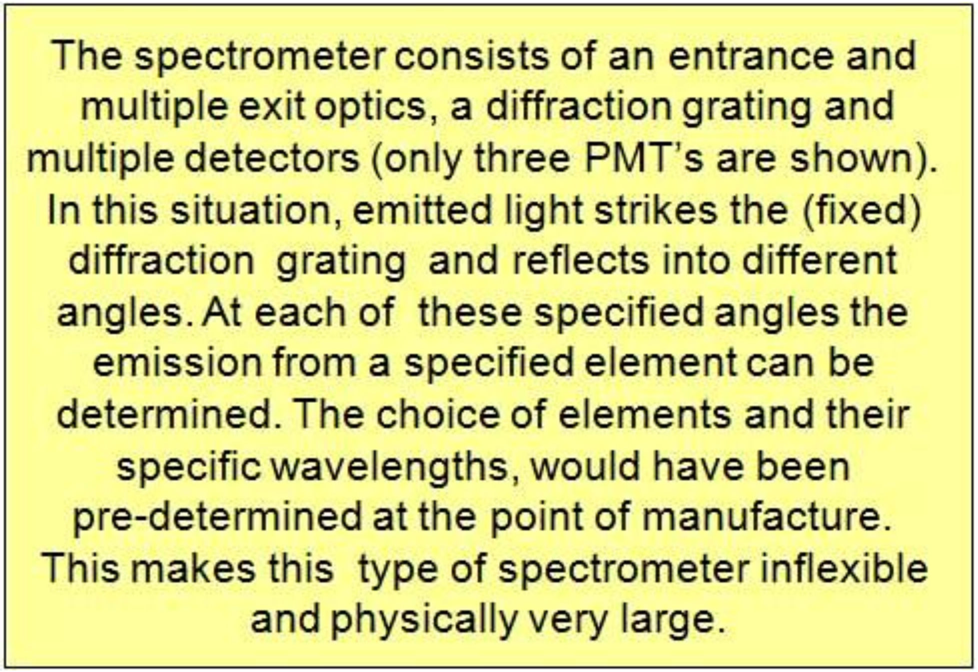


Figure 12.40 - photograph of a diffraction grating

ICP-AES for simultaneous multielement analysis

In **simultaneous multielement analysis,** emitted light is measured at many wavelengths at the same time. A traditional optical arrangement for a simultaneous spectrometer (**polychromator**) is based on the Paschen-Runge configuration as illustrated in Figure (12.41).



The spectrometer consists of an entrance and multiple exit optics, a diffraction grating and multiple detectors (only three PMT's are shown). In this situation, emitted light strikes the (fixed) diffraction grating and reflects into different angles. At each of these specified angles the emission from a specified element can be determined. The choice of elements and their specific wavelengths, would have been pre-determined at the point of manufacture. This makes this type of spectrometer inflexible and physically very large.

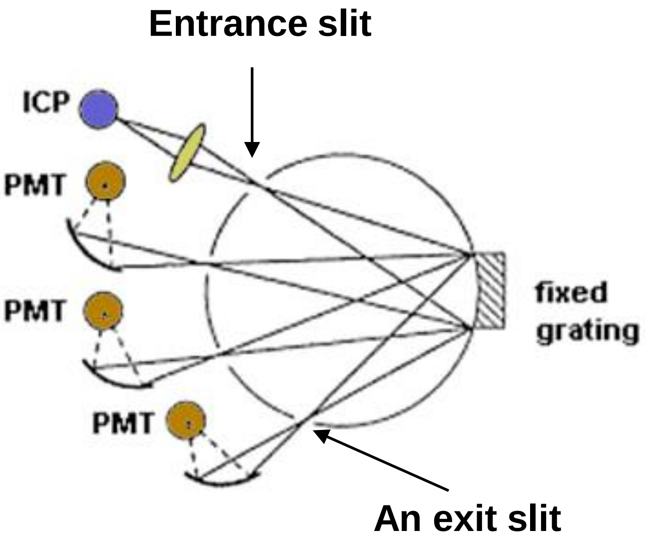
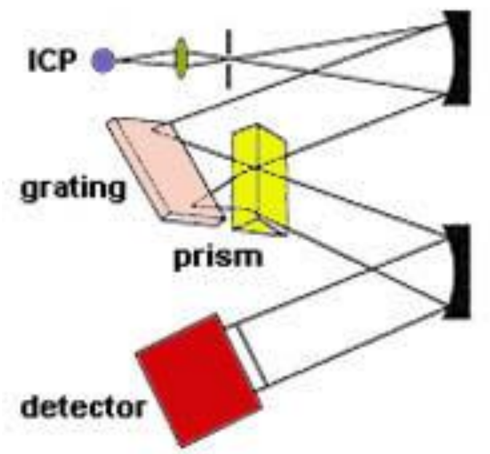


Figure 12.41 - diagram of a polychromator

In this type of spectrometer, it is possible to have up to 75 elements measured simultaneously, however this requires the need for multi-element standards to calibrate the instrument beforehand.

Simultaneous multielement analysis using an Echelle spectrometer

Figure 12.42 - spectral layout of an Echelle spectrometer.



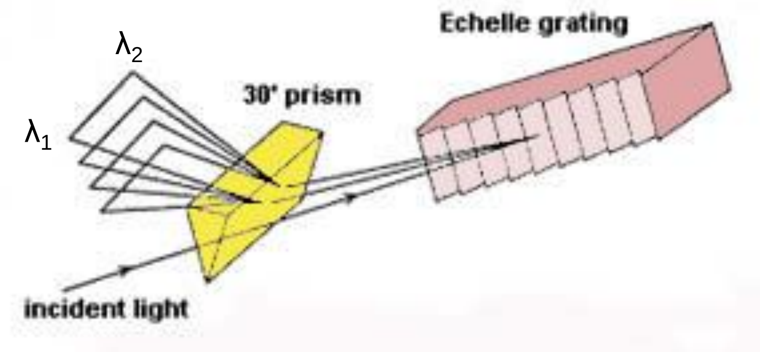


Figure 12.43 - two-dimensional separation using Echelle spectrometer

Light strikes a grating ruled with only 50-100 lines mm^{-1}. However, by placing a prism immediately after the grating, wavelength separation also occurs at **right angles** to that of the diffraction grating, producing a 2-dimensional output. The higher resolving power and resolution of this type of spectrometer allow simultaneous multi-element analysis to be carried out – figure (12.43)

Emission from each element in the sample is detected via a **charged coupled device** (CCD). Major advantages of CCD's include: flexibility in emission (wavelength) selection; potential to use several wavelengths for the same element in order to extend the linear dynamic range or to improve accuracy and to identify potential matrix or spectral interferences; the possibility of performing qualitative analysis; and, the possibility of calibration using internal standardization.

Interferences in ICP-AES

The major interferences in ICP-AES are due to **spectral overlap** and **matrix effects**.

Three common types of **spectral overlap** are shown in Figure (12.44):

- Direct wavelength (1) coincidence from an interfering emission line e.g. 267.716 nm for Pt and Cr. This maybe allowed for, by choosing an alternative wavelength for the analyte element.
- Partial overlap of the emission line of interest (2), with that of an interfering line from another element present in the sample. e.g. Cd resonance line at 214.438 nm with a wing overlap from Al. This can be corrected by using a higher resolution spectrometer or a different wavelength for measurement of the analyte
- Presence of an elevated (or depressed background) continuum (3) e,g. W at 207.911 nm from Al. This may be corrected, by measurement of the background on either side of the wavelength of interest.

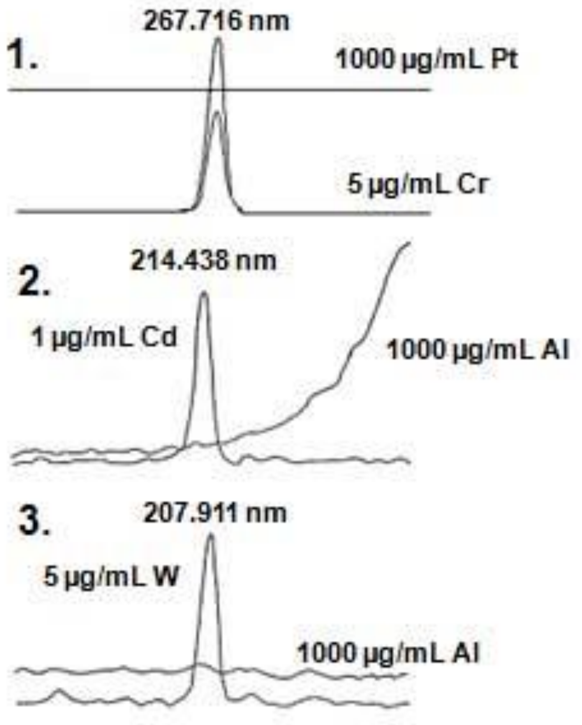


Figure 12.44 - spectral overlap interferences in ICP-AES

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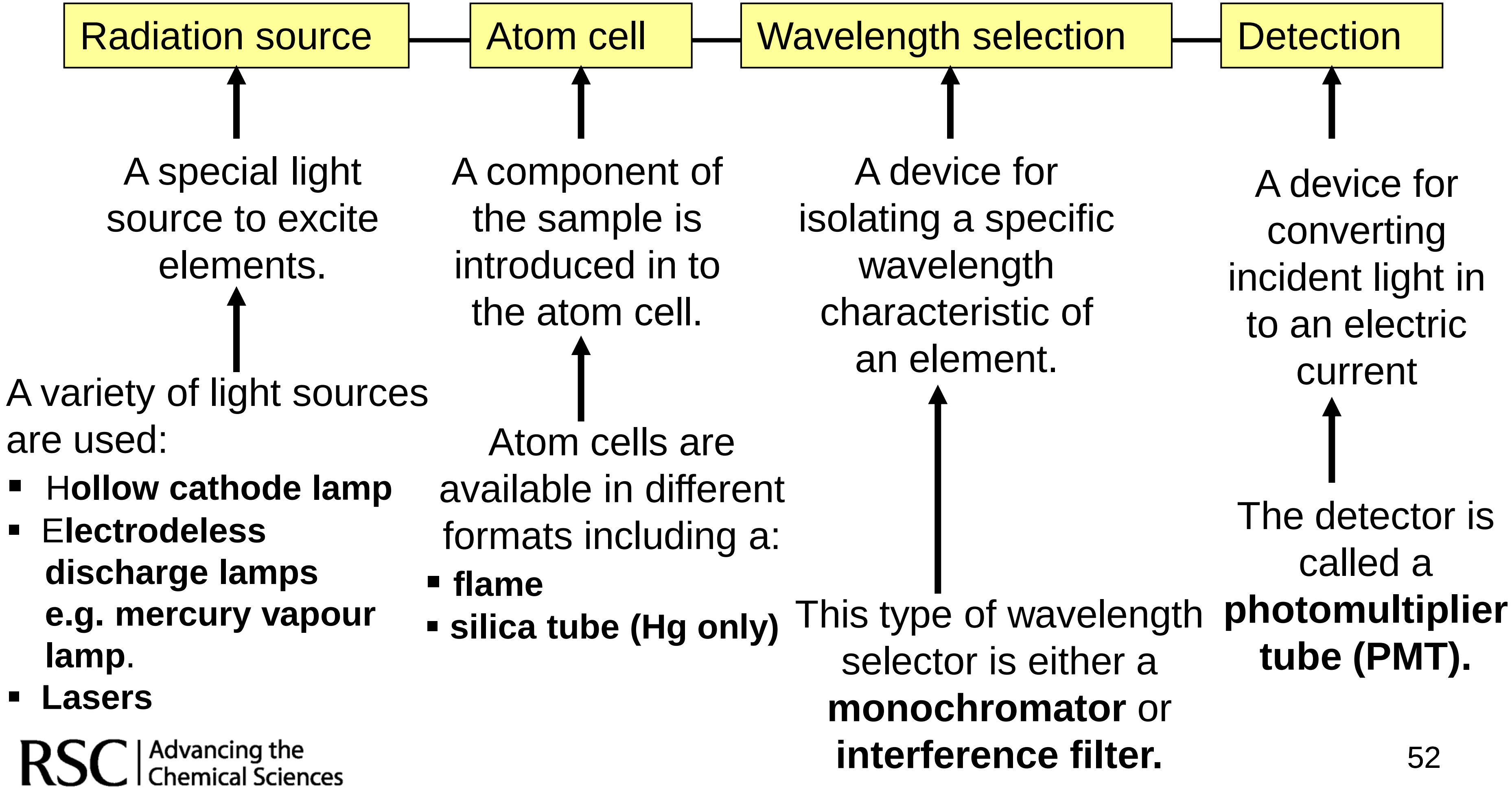
Matrix effects

These are often associated with the sample introduction process i.e. the nebulizer is affected by the presence of dissolved solids in the sample which will affect its uptake rate. Matrix effects that are encountered in the ICP are due to the presence of easily ionizable elements e.g. alkali metals, which can lead to signal suppression or enhancement. These effects are more pronounced in the axially (end-on) viewed ICP, than the laterally (side-on) viewed ICP.

Atomic Fluorescence Spectroscopy (AFS)

The instrumentation for AFS can be described by considering **four** major, but inter-related components.



Radiation source

A special light source to excite elements.

A variety of light sources are used:

- **Hollow cathode lamp**
- **Electrodeless discharge lamps e.g. mercury vapour lamp**.
- **Lasers**

Atom cell

A component of the sample is introduced in to the atom cell.

Atom cells are available in different formats including a:

- **flame**
- **silica tube (Hg only)**

Wavelength selection

A device for isolating a specific wavelength characteristic of an element.

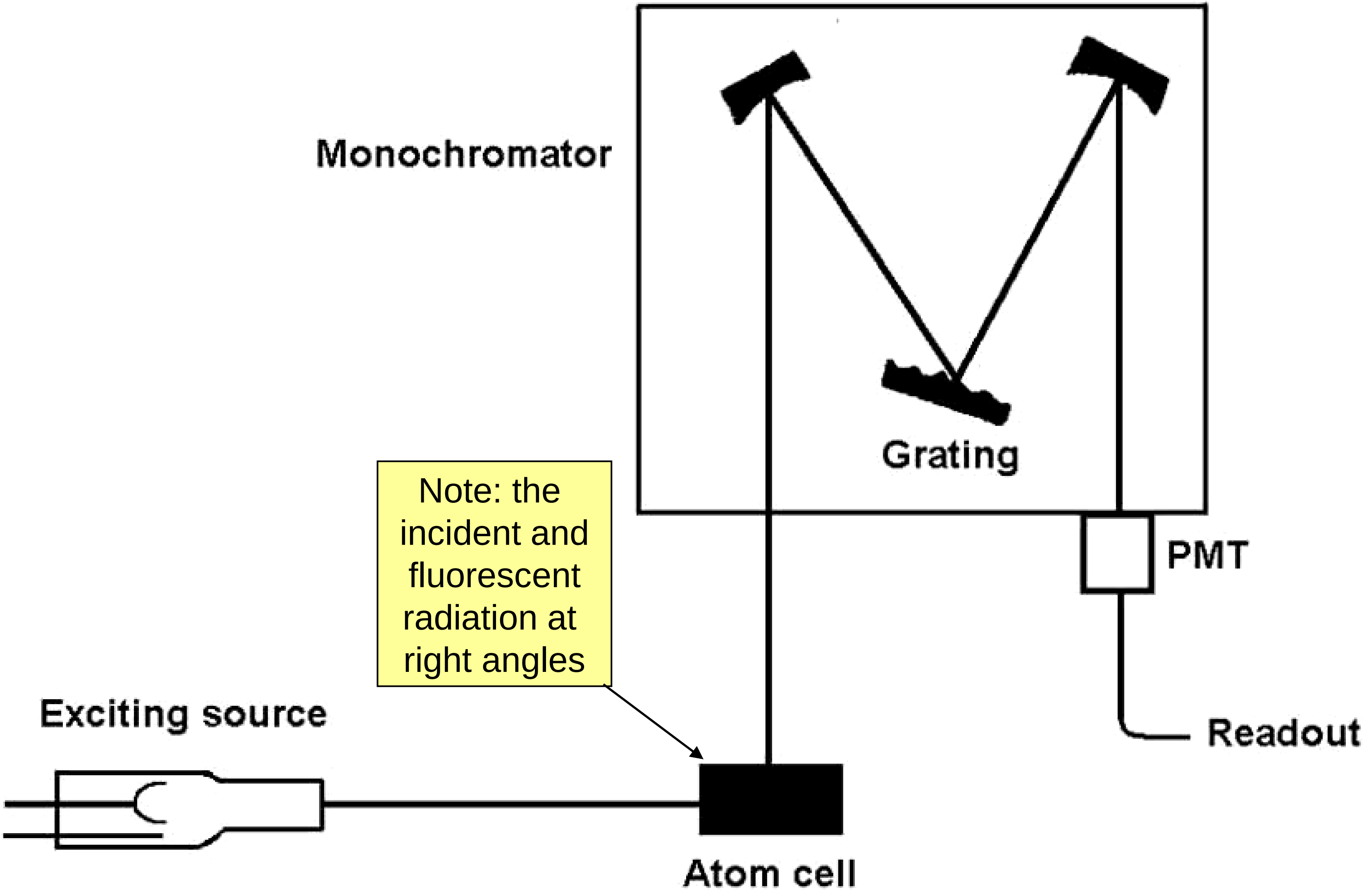
This type of wavelength selector is either a **monochromator** or **interference filter.**

Detection

A device for converting incident light in to an electric current

The detector is called a **photomultiplier tube (PMT).**

Figure 12.45 - optical layout of an AFS instrument



Note: the incident and fluorescent radiation at right angles

In AFS, free element atoms formed in the atom cell e.g. flame (**see slide 15**), absorb radiation from an external source [hollow cathode lamp (**see slides 13/14**), electrodeless discharge lamp e.g. mercury lamp or lasers] are then excited to higher electronic states, and return to the ground state by fluorescence producing characteristic wavelengths of the element under investigation .

In AFS, the exciting source is positioned at right-angles to the atom cell i.e. a flame or silica tube, and the optical axis of the monochromator [**see figure (12.45) on the previous slide**].

Samples are introduced into the flame either using a nebulizer / expansion chamber for lead (**see slide 19**), hydride generation for arsenic, selenium etc. (**see slide 20**) or cold vapour generation for Hg (**see slide 21**).

Atomic fluorescence is measured using a monochromator (**see slide 22**) and detected using a photomultiplier tube (**see slide 23**).

Comparison of AES, AFS and AAS

In comparing the techniques of AFS, FAAS, GFAAS, HGAAS and ICP-AES it is necessary to consider the following important factors:

- Which elements can be analysed?
- Sample throughput;
- Amount of sample per analysis;
- Detection limits;
- Linear and dynamic range of the analytical technique;
- Capital and running costs.

Which elements?

Apart from hydride generation AAS/AFS which are limited to a few elements (**see slide 20**), the other techniques can analyse all of the metallic, and some of the other elements, in the Periodic Table.

Continued on the next slide

Sample throughput

The number of samples to be analysed is not necessarily limited to the analytical technique itself. Often the issue is related to whether an autosampler is being used to deliver the next sample to the instrument. From the analytical instrument perspective, the use of a polychromator or Echelle spectrometer coupled with an ICP allows simultanueous multielement analysis within the same sample. In the case of the other techniques only one element can be detected in a sample at any one time. It is important also to consider the length of time per sample; GFAAS, HGAAS and HGAFS take the longest amount of time – typically 2 mins, whereas FAAS and ICP-AES are relatively fast - typically 15-30 seconds.

How much sample?

All nebulizer based systems (FAAS, ICP-AES) require, normally, a minimum of 5 cm^3 of sample. Hydride generation (applicable to AAS, AFS or ICP-AES), graphite furnace (for AAS) or electrothermal vaporization (for ICP-AES), require a sample size between 5 – 100 µl.

What concentrations levels? (or the detection limits)

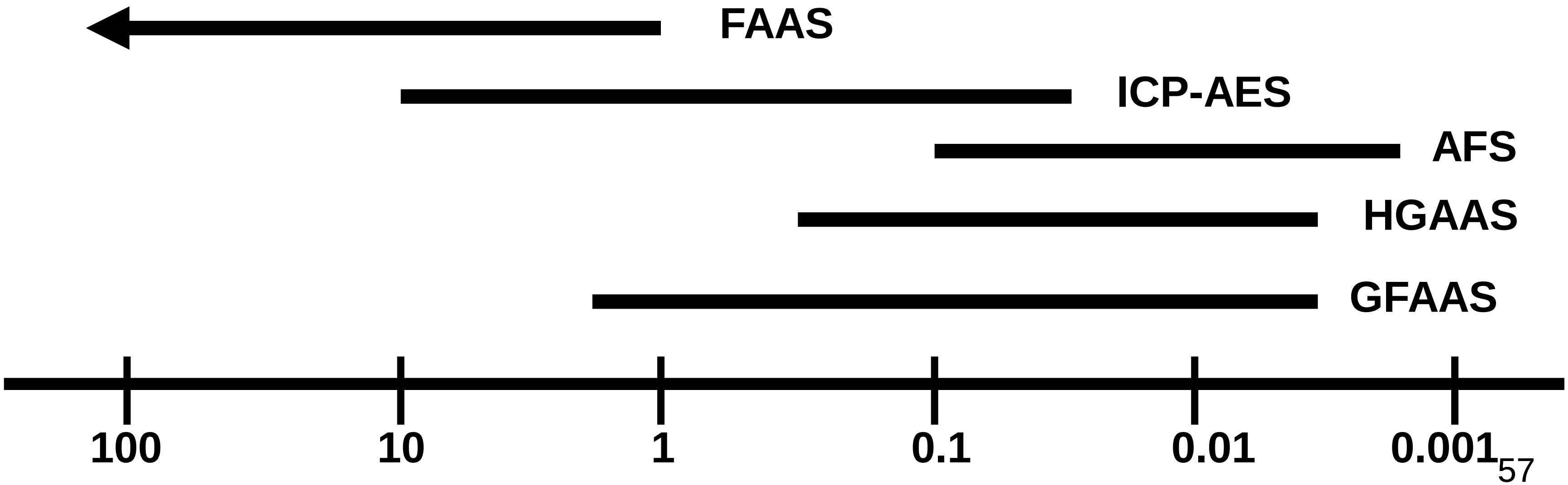
The detection limit is defined as the lowest amount of element in a sample which can be detected but not necessarily quantified as an exact value [**see Chapter 5 of this teaching and learning package**]. The limit of detection (LOD) can be expressed as the concentration, derived from the smallest signal, that can be detected with reasonable certainty for a given procedure. The value of the smallest signal can be given by the equation:

$$x_L = x_{bl} + k.s_{bl}$$

Smallest signal that can be detected

Mean of the blank measurements

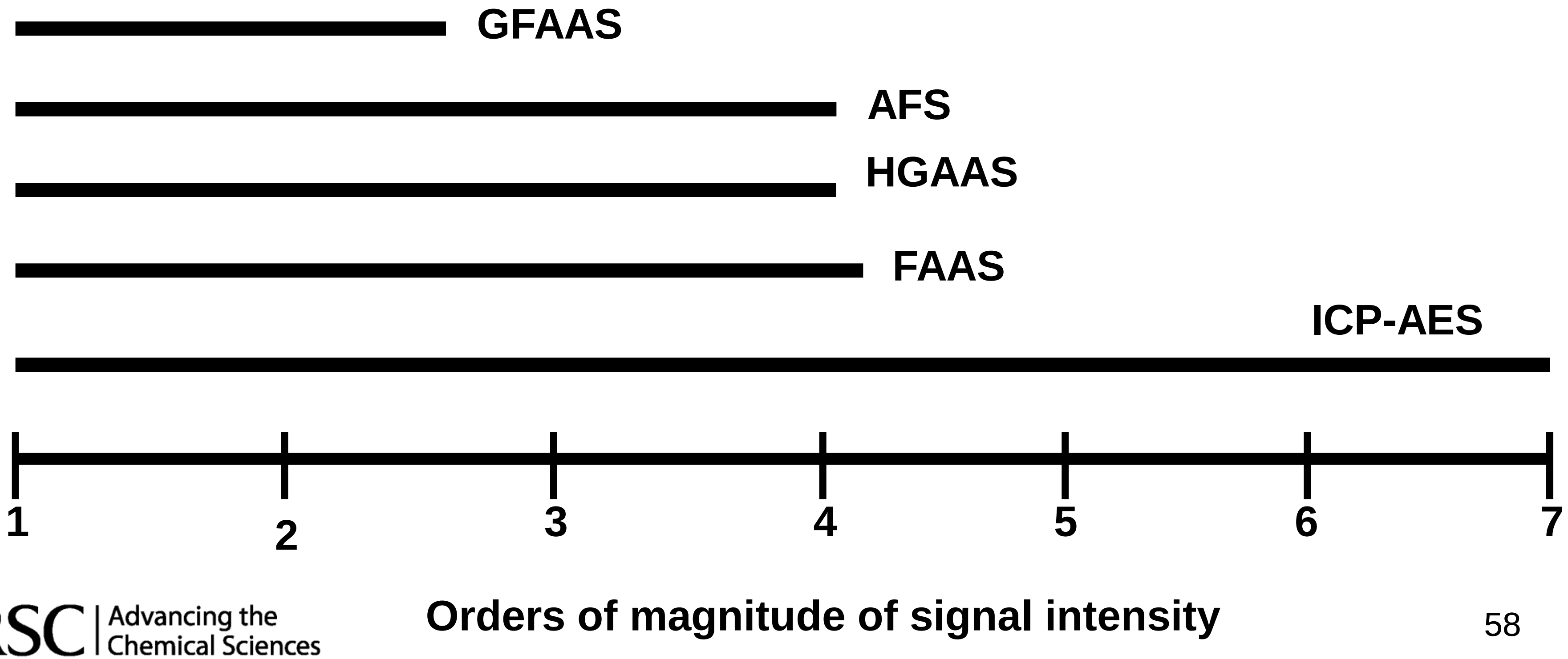
Standard deviation of the blank values X constant (k) –usually 3



Detection limit ranges (ppb or µg/L or pg/mL)

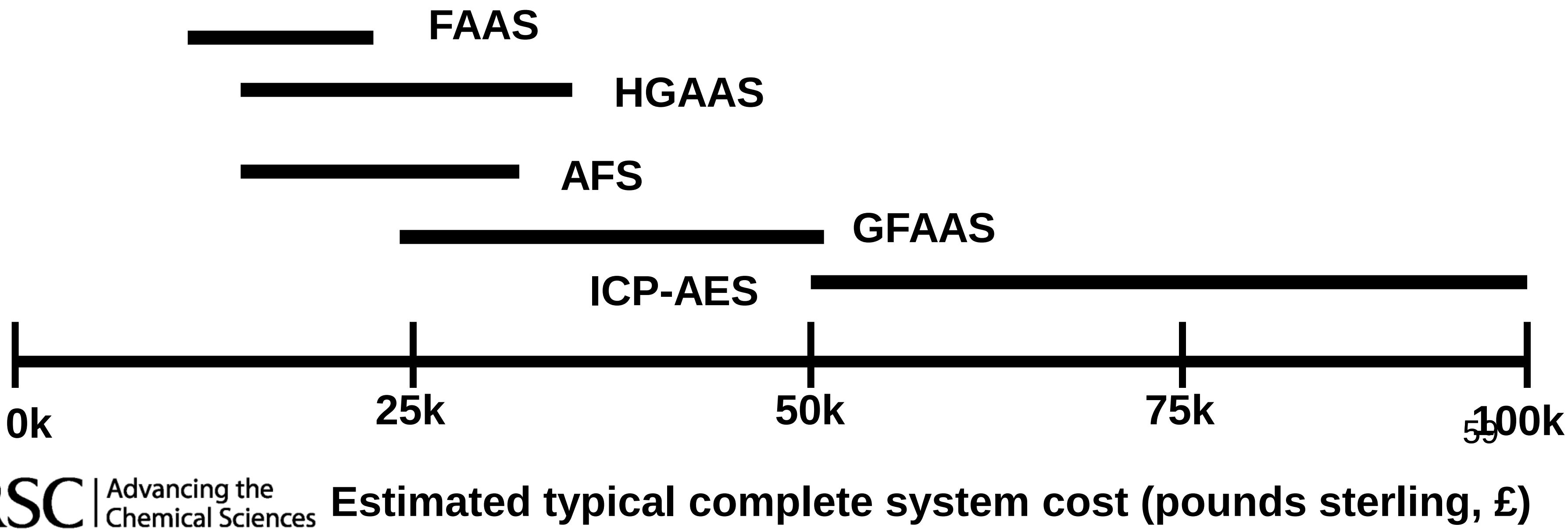
Linear and dynamic ranges

The analytical working range is the concentration range over which the analytical working calibration plot remains preferably linear or at least reproducible. [**refer to Chapter 4 of this teaching and learning package**]. The extent of the linear range has the considerable advantage of allowing samples with different element concentrations to be determined without further dilution or pre-concentration (thereby saving analysis time). The analytical working range is expressed in terms of the order of magnitude of signal intensity, one order representing a factor of 10.



Capital and running costs

The capital equipment purchase of any of the analytical techniques is relatively high, with ICP technology being the highest. Both AAS, AFS and AES techniques can utilise specific sample introduction features. However, ICP-AES is capable of multielement analyses, with high sensitivity and the ability to measure more than one element in a sample. In terms of running costs the cost of argon and the amount consumed by the ICP add significantly to its operating costs whereas in AAS and AFS techniques the main costs are associated with the use of flame gases e.g. acetylene and the acquisition of appropriate hollow cathode lamps. All techniques also require the use of high grade reagents and standard solutions, volumetric glassware and ultrapure water in order to achieve their potential.



Applications

Atomic spectroscopic techniques (AAS, AFS and AES) can be applied to a range of applications including:

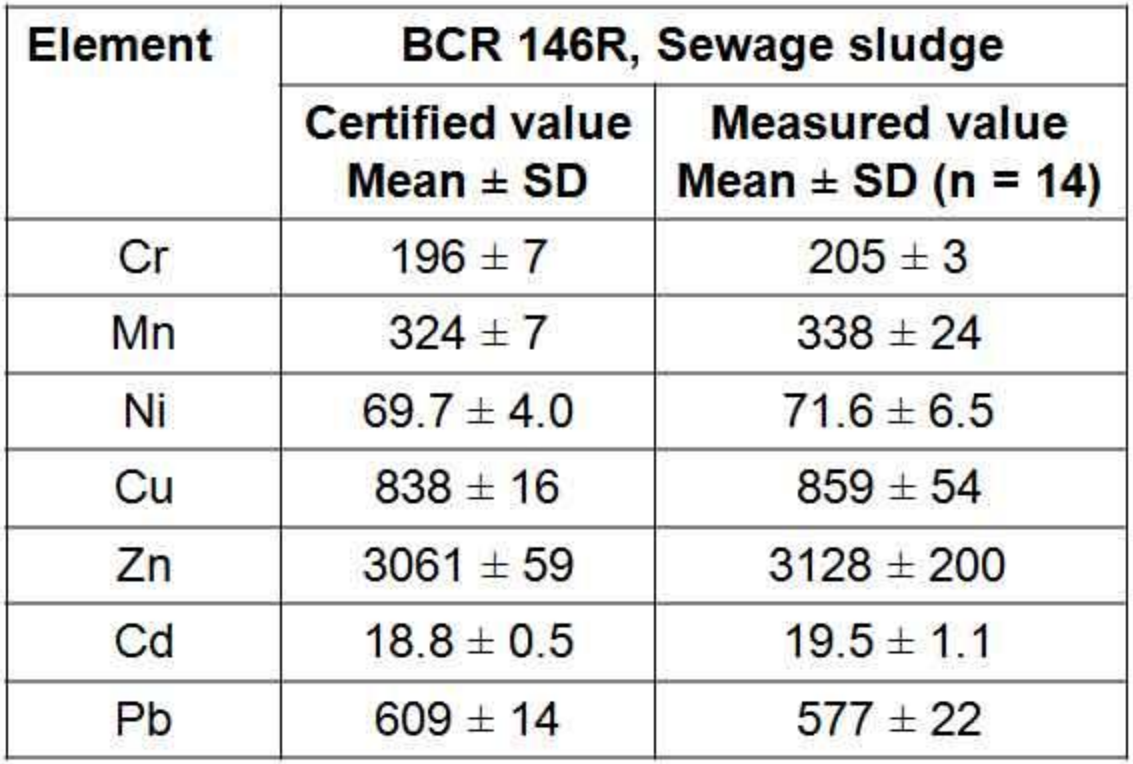
- Environmental (e.g. heavy metals in air, water, soil)
- Pharmaceutical (e.g. drugs analysis)
- Industrial (e.g. metal catalysts; chemical impurities)
- Material science (e.g. metal impurities in silicon chips)
- Forensic (e.g. forgery and counterfeiting)
- Clinical and biological matrices (e.g. determination of essential elements; toxicity
- Studies in blood / urine)
- Food studies (e.g. essential elements in foodstuffs).

Selected **case studies** to exemplify the role of atomic spectroscopic techniques are now described:

- Total metal analysis using ICP-AES (although AAS could also be used) in soil samples: use of acid digestion and microwave digestion.
- Sequential metal analysis, using ethylenediaminetetraacetic acid (EDTA) or acetic acid (CH_3COOH), to assess the availability of specific trace elements. Measurement using ICP-AES (although AAS could also be used).
- Mercury in water using cold vapour AFS (although cold vapour AAS and AES could also be used).

Case study 12.1: Total metal analysis in soil samples using acid digestion.

Seven elements were determined in a **certified reference material** (CRM) using acid digestion followed by ICP analysis. The CRM selected was BCR146R – a sewage sludge. The sewage sludge was acid digested using a combination of concentrated HNO_3, 30% H_2O_2 and HCl (method shown on slide 9) and analysed 14 times, over several weeks (n = 14).



Element	BCR 146R, Sewage sludge	
	Certified value Mean ± SD	Measured value Mean ± SD (n = 14)
Cr	196 ± 7	205 ± 3
Mn	324 ± 7	338 ± 24
Ni	69.7 ± 4.0	71.6 ± 6.5
Cu	838 ± 16	859 ± 54
Zn	3061 ± 59	3128 ± 200
Cd	18.8 ± 0.5	19.5 ± 1.1
Pb	609 ± 14	577 ± 22

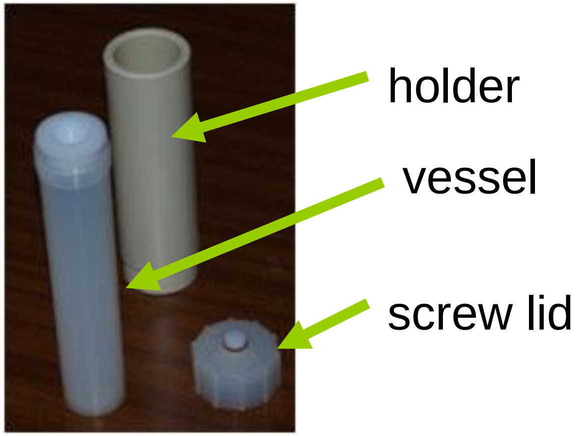
Figure 12.46 - glass digestion vessel.

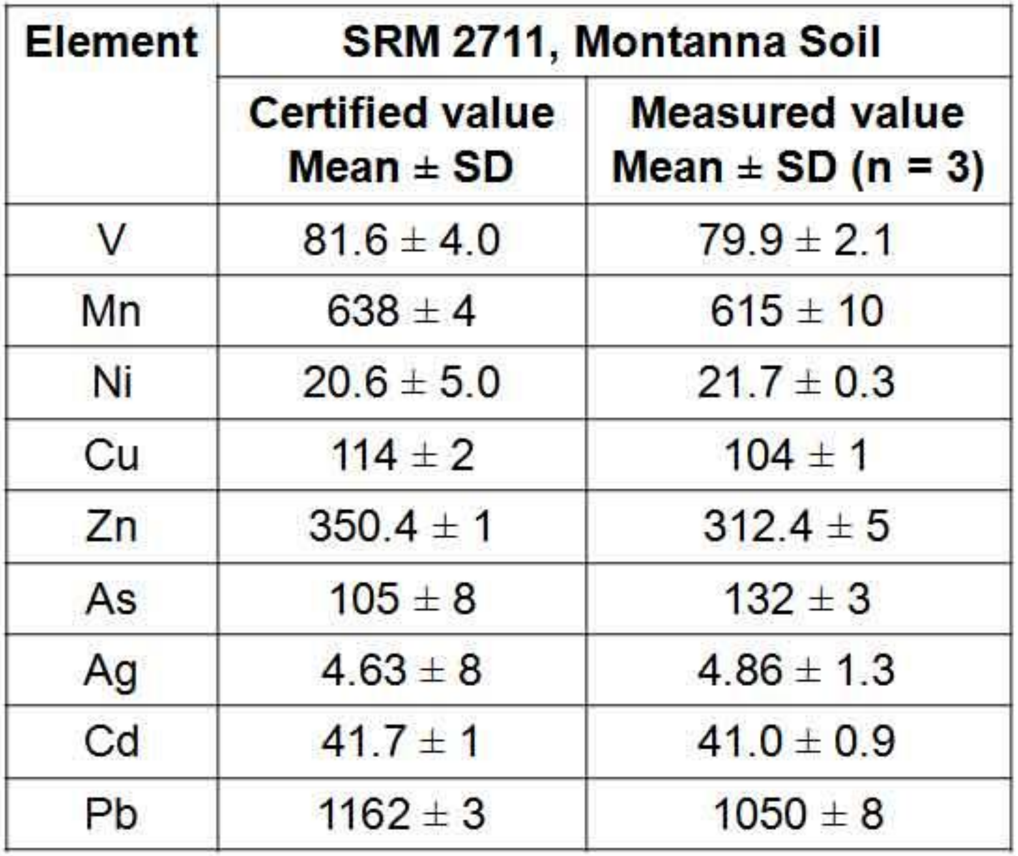
The results indicate good agreement between the certified values and the measured values. By using the same approach (acid digestion / ICP analysis) the seven elements could be measured in samples of sewage sludge.

Case study 12.2: Total metal analysis in soil samples using microwave digestion.

Seven elements were determined in a **certified reference material** (CRM) using microwave acid digestion followed by ICP analysis. The CRM selected was NIST SRM 2711 – a Montana soil. The soil sample was acid digested using 15 cm^3 aqua regia at a maximum temperature of 160 ^{0}C and a microwave oven power of 750 W for 10 mins followed by an additional 750 W for 15 mins and analysed by ICP.

Figure 12.47. Microwave digestion vessel



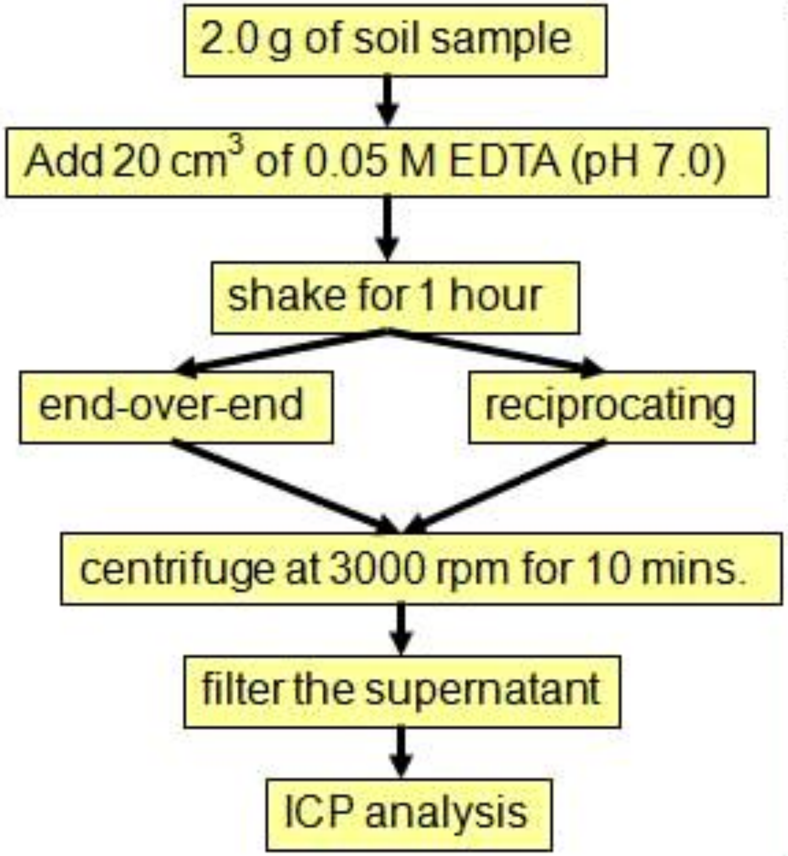


Element	SRM 2711, Montanna Soil	
	Certified value Mean ± SD	Measured value Mean ± SD (n = 3)
V	81.6 ± 4.0	79.9 ± 2.1
Mn	638 ± 4	615 ± 10
Ni	20.6 ± 5.0	21.7 ± 0.3
Cu	114 ± 2	104 ± 1
Zn	350.4 ± 1	312.4 ± 5
As	105 ± 8	132 ± 3
Ag	4.63 ± 8	4.86 ± 1.3
Cd	41.7 ± 1	41.0 ± 0.9
Pb	1162 ± 3	1050 ± 8

The results indicate good agreement between the certified values and the measured values. By using the same approach (microwave acid digestion / ICP analysis) the seven elements could be measured in soil samples

Case study 12.3: sequential metal analysis using ethylenediaminetetraacetic acid (EDTA) to assess the availability of specific trace elements.

Selective chemical extraction of a **certified reference material** (BCR 700 – an organic rich soil) was carried out in order to estimate the proportion of the total metal content that is available for plant uptake. EDTA is used to assess the organically and carbonate bound metal fractions.



2.0 g of soil sample

Add 20 cm^3 of 0.05 M EDTA (pH 7.0)

shake for 1 hour

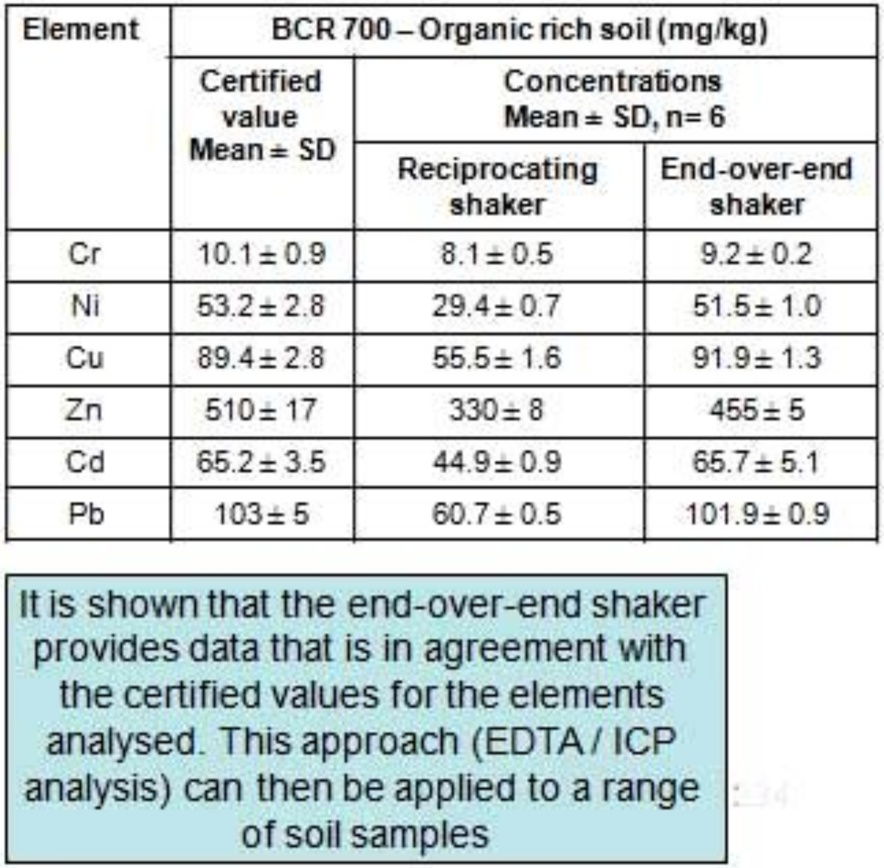
end-over-end

reciprocating

centrifuge at 3000 rpm for 10 mins.

filter the supernatant

ICP analysis

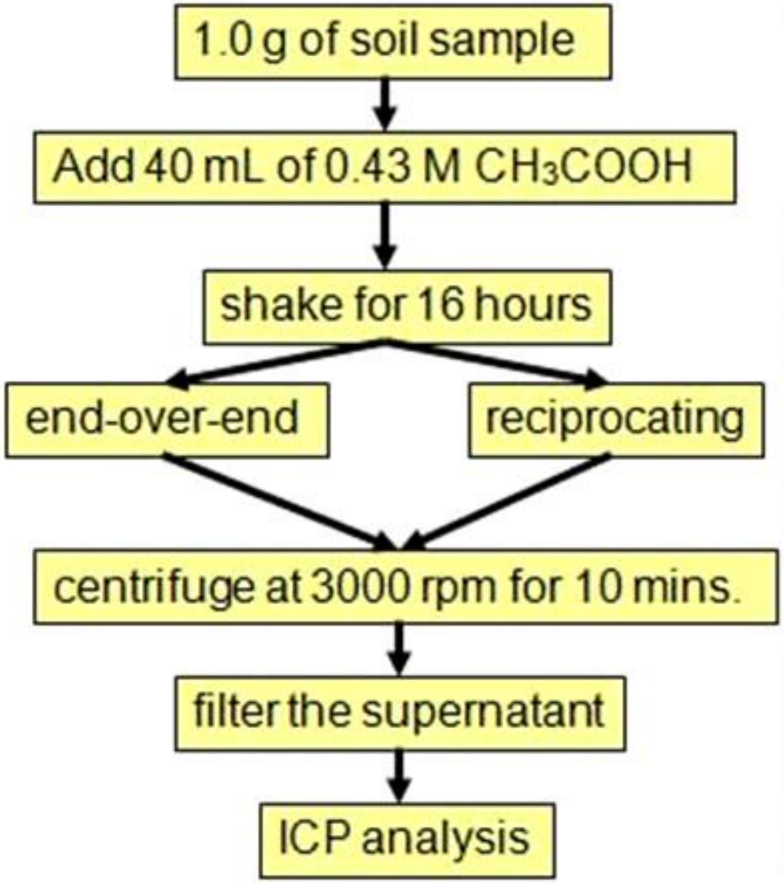


Element	BCR 700 – Organic rich soil (mg/kg)		
	Certified value Mean ± SD	Concentrations Mean ± SD, n= 6	
		Reciprocating shaker	End-over-end shaker
Cr	10.1 ± 0.9	8.1 ± 0.5	9.2 ± 0.2
Ni	53.2 ± 2.8	29.4 ± 0.7	51.5 ± 1.0
Cu	89.4 ± 2.8	55.5 ± 1.6	91.9 ± 1.3
Zn	510 ± 17	330 ± 8	455 ± 5
Cd	65.2 ± 3.5	44.9 ± 0.9	65.7 ± 5.1
Pb	103 ± 5	60.7 ± 0.5	101.9 ± 0.9

It is shown that the end-over-end shaker provides data that is in agreement with the certified values for the elements analysed. This approach (EDTA / ICP analysis) can then be applied to a range of soil samples

Case study 12.4: sequential metal analysis using acetic acid (CH_3COOH) to assess the availability of specific trace elements.

Selective chemical extraction of a **certified reference material** (BCR 700 – an organic rich soil) was carried out in order to estimate the proportion of the total metal content that is available for plant uptake. Acetic acid is used to assess the exchangeable and carbonate bound metal fractions.



1.0 g of soil sample

Add 40 mL of 0.43 M CH_3COOH

shake for 16 hours

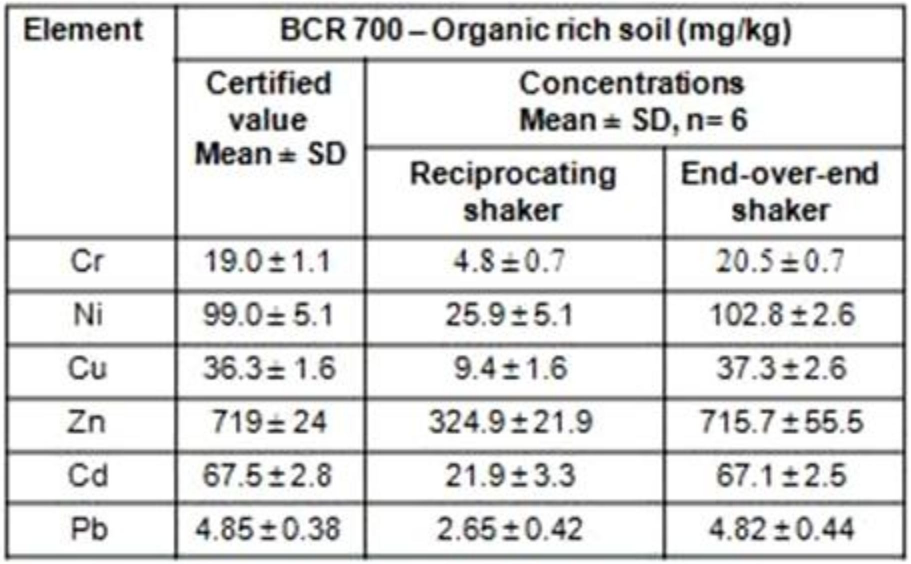
end-over-end

reciprocating

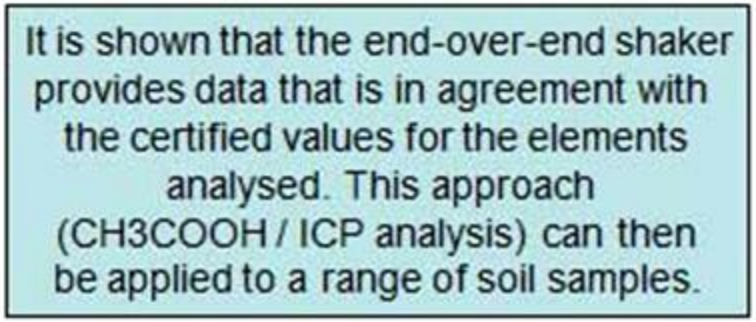
centrifuge at 3000 rpm for 10 mins.

filter the supernatant

ICP analysis



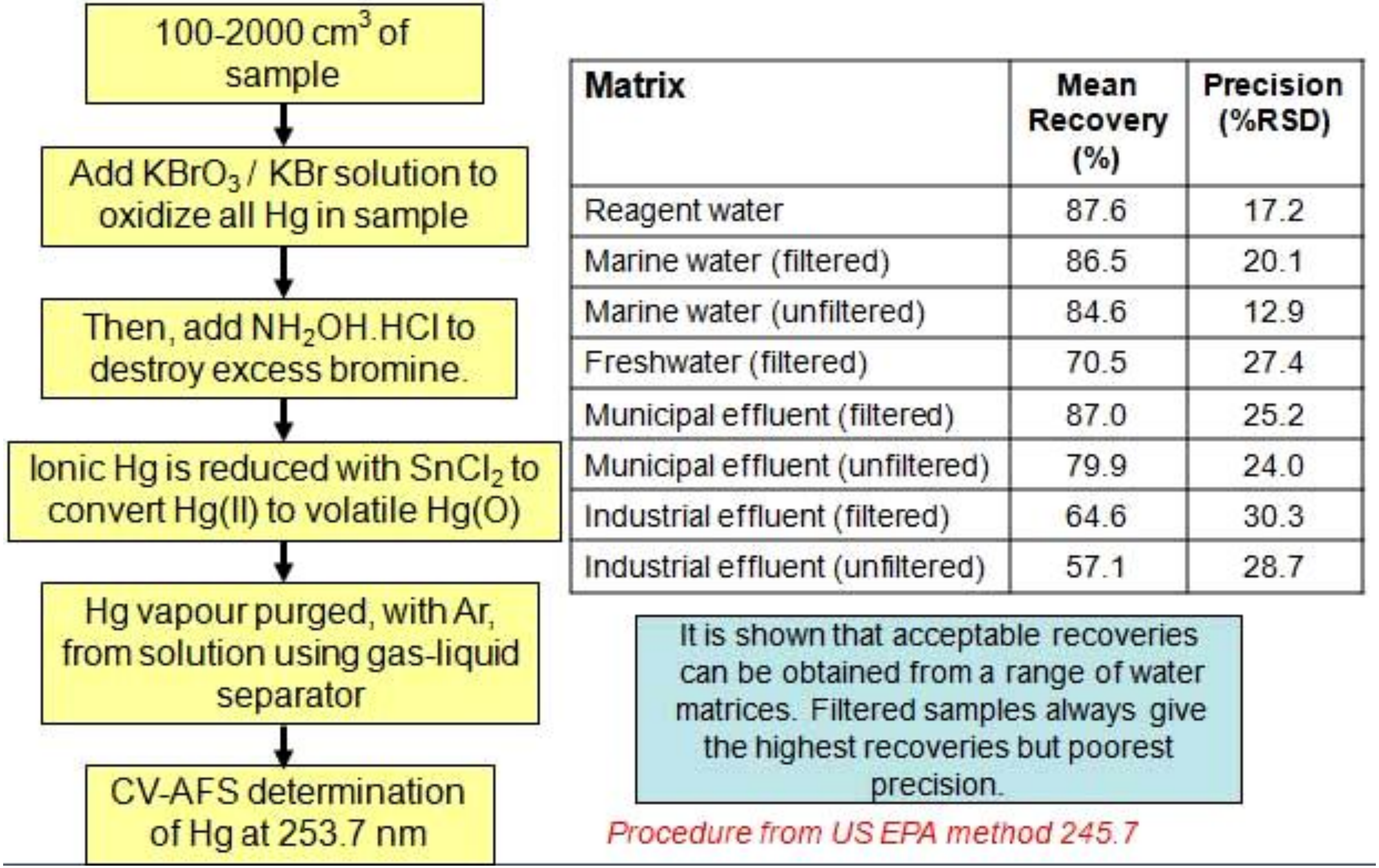
Element	BCR 700 – Organic rich soil (mg/kg)		
	Certified value Mean ± SD	Concentrations Mean ± SD, n= 6	
		Reciprocating shaker	End-over-end shaker
Cr	19.0 ± 1.1	4.8 ± 0.7	20.5 ± 0.7
Ni	99.0 ± 5.1	25.9 ± 5.1	102.8 ± 2.6
Cu	36.3 ± 1.6	9.4 ± 1.6	37.3 ± 2.6
Zn	719 ± 24	324.9 ± 21.9	715.7 ± 55.5
Cd	67.5 ± 2.8	21.9 ± 3.3	67.1 ± 2.5
Pb	4.85 ± 0.38	2.65 ± 0.42	4.82 ± 0.44



It is shown that the end-over-end shaker provides data that is in agreement with the certified values for the elements analysed. This approach (CH3COOH / ICP analysis) can then be applied to a range of soil samples.

Case study 12.5: mercury in water samples using cold vapour AFS.

A water sample is collected, filtered and preserved using 0.5% concentrated HCl. The minimum level of quantitation is assessed as 5.0 ng/dm^3.



100-2000 cm^3 of sample

↓

Add $KBrO_3$ / KBr solution to oxidize all Hg in sample

↓

Then, add $NH_2OH.HCl$ to destroy excess bromine.

↓

Ionic Hg is reduced with $SnCl_2$ to convert Hg(II) to volatile Hg(O)

↓

Hg vapour purged, with Ar, from solution using gas-liquid separator

↓

CV-AFS determination of Hg at 253.7 nm

Matrix	Mean Recovery (%)	Precision (%RSD)
Reagent water	87.6	17.2
Marine water (filtered)	86.5	20.1
Marine water (unfiltered)	84.6	12.9
Freshwater (filtered)	70.5	27.4
Municipal effluent (filtered)	87.0	25.2
Municipal effluent (unfiltered)	79.9	24.0
Industrial effluent (filtered)	64.6	30.3
Industrial effluent (unfiltered)	57.1	28.7

It is shown that acceptable recoveries can be obtained from a range of water matrices. Filtered samples always give the highest recoveries but poorest precision.

Procedure from US EPA method 245.7

Ultraviolet-Visible Spectroscopy (UV-Vis)

The instrumentation for UV/Vis spectroscopy or spectrophotometry can be described by considering **four** major, but inter-related components.

Radiation Source

A special light source that emits light over a continuous range of wavelengths

The special light source is either a **tungsten filament lamp** for the visible region or a **hydrogen or deuterium discharge tube** for the UV region.

Sample cell

A component of the sample is introduced in to the sample cell.

The cell or cuvette is made of either quartz (UV) or glass (visible).

Wavelength selection

A device for isolating a specific wavelength characteristic of an element.

This type of wavelength selector or “spectrometer” is called a **monochromator.**

Detection

A device for converting incident light in to an electric current

The detector is either a **photomultiplier tube (PMT)** or **photo diode array (PDA).**

In UV/Visible spectroscopy elemental species are measured in solution in the sample cell or cuvette. The elemental species absorb a portion of the incident radiation from an external source (e.g. tungsten filament lamp for the visible region or a hydrogen or deuterium discharge tube for the UV region); the remaining unabsorbed radiation is transmitted to a detector [e.g. a photomultiplier tube (**see slide 23**) or photodiode array (**see Chapter 11**)] where it is measured.

Liquid samples are introduced into the sample cuvette which has a typical path length of 1 cm. The cuvette is made of a material that will not absorb radiation in the region of interest. For work in the ultraviolet and visible region of the electromagnetic spectrum a quartz is used; quartz can transmit radiation from 190 to over 750 nm. For work in the visible region (i.e. 350-750 nm) plastic cuvettes are often used.

Please refer to Chapter 11 of this teaching and learning programme, where coverage of this topic was also considered

Applications

UV/Visible spectroscopy can be used to determine elements in a range of sample matrices.

Selected **case studies** to exemplify the role of UV/visible spectroscopy are now described:

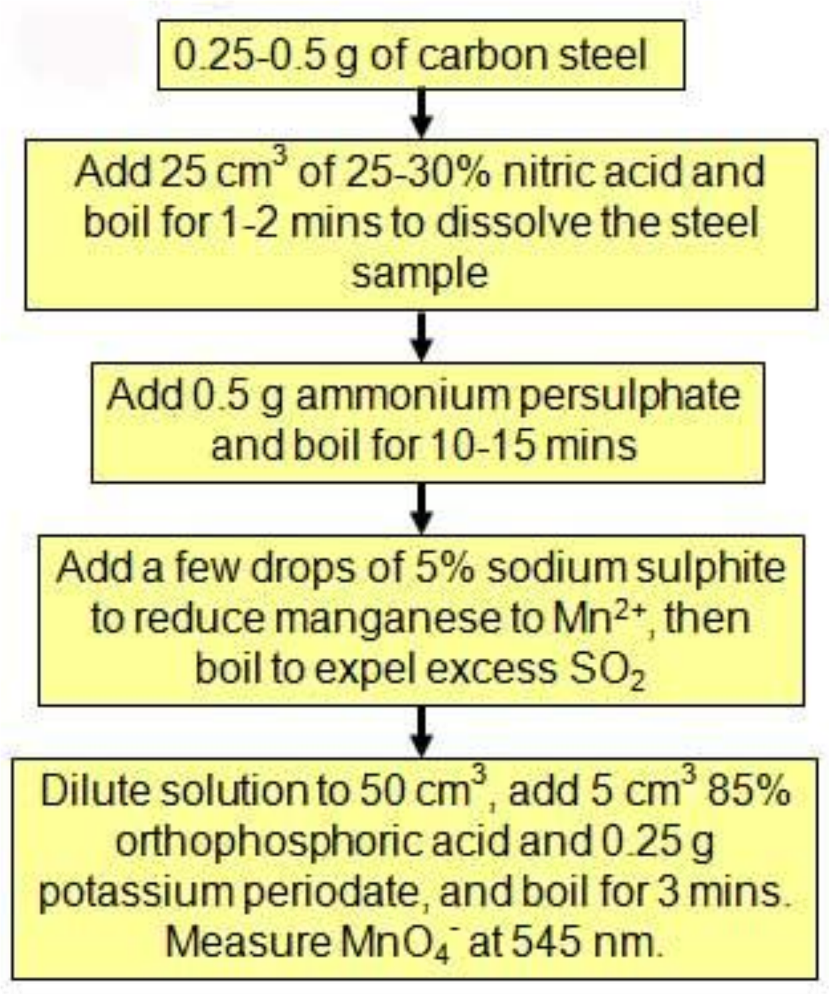
- Determination of manganese in carbon steel by visible spectroscopy
- Determination of magnesium in Water by Visible Spectroscopy

In addition, further examples can be found in Chapter 14 of this teaching and learning programme – 'Introduction to automation and process analysis', where UV/Visible spectroscopy is used as a detector for flow injection analysis (FIA). Case studies there include:

- **Spectrophotometric determination of chloride**
- **Determination of sulfite in brine by FIA**
- **On-line determination of residual aluminium in potable and treated waters by FIA.**

Case study 12.6: Determination of manganese in carbon steel by visible spectroscopy

The high absorption (ε ~2500 L / mol / cm) of the manganate (VII) ion, MnO_4^-, in the visible region can be used to determine trace quantities of manganese in carbon steel.



0.25-0.5 g of carbon steel

Add 25 cm^3 of 25-30% nitric acid and boil for 1-2 mins to dissolve the steel sample

Add 0.5 g ammonium persulphate and boil for 10-15 mins

Add a few drops of 5% sodium sulphite to reduce manganese to Mn^{2+}, then boil to expel excess SO_2

Dilute solution to 50 cm^3, add 5 cm^3 85% orthophosphoric acid and 0.25 g potassium periodate, and boil for 3 mins. Measure MnO_4^- at 545 nm.

This method requires:

1. Dissolution of steel sample in nitric acid.
2. Oxidation of carbon compounds present by ammonium persulphate
3. Oxidation of manganese (II) by the periodate ion:

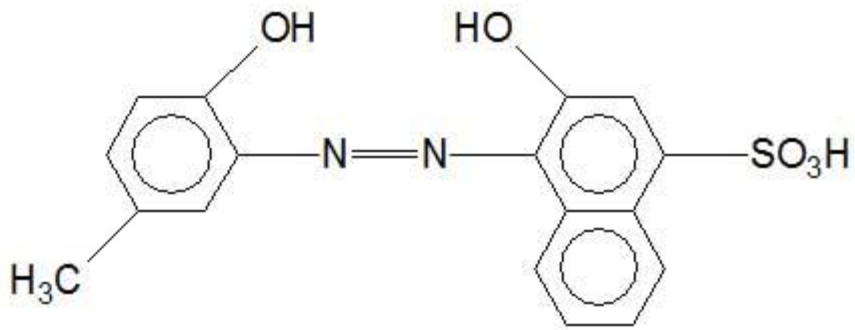
$$2Mn^{2+} + 5IO_4^- + 9H_2O \Longrightarrow 2MnO_4^- + 5IO_3^- + 6H^+$$

Orthophosphoric acid, H_3PO_4, must be present in solution to prevent precipitation of iron(III) periodate and iodate, and to decolourise Fe^{3+} by complex formation.

Case study 12.7: Determination of magnesium in Water by Visible Spectroscopy

Magnesium ions (Mg^{2+}) are determined in water by selective binding with a dye (calmagite), which exhibits a broad absorption band in aqueous solution. Calmagite appears blue in alkaline solution (pH 10) but on binding to Mg^{2+}, a purple coloured complex is formed and measured at 532 nm.

Figure 12.48 - Chemical structure of Calmagite



at pH 10 the sulphonate and one hydroxyl are ionised

Calmagite also forms a complex with calcium ions (Ca^{2+}) and so a preferential calcium chelator, ethyleneglycol-*bis*-(g-aminoethyl ether)-N,N,N',N'-tetra acetic acid (EGTA) is added to reduce this potential interference.

Typical conditions are as follows:

- Standard Mg^{2+} solutions (0.05, 1.00, 1.50 and 2.00 X 10^{-3} mol/dm^3)
- Mineral waters containing unknown amounts of magnesium
- Calmagite dye solution (0.4 g/dm^3 dye in water)
- EGTA solution (0.01 mol/dm^3 in carbonate buffer, pH 10)

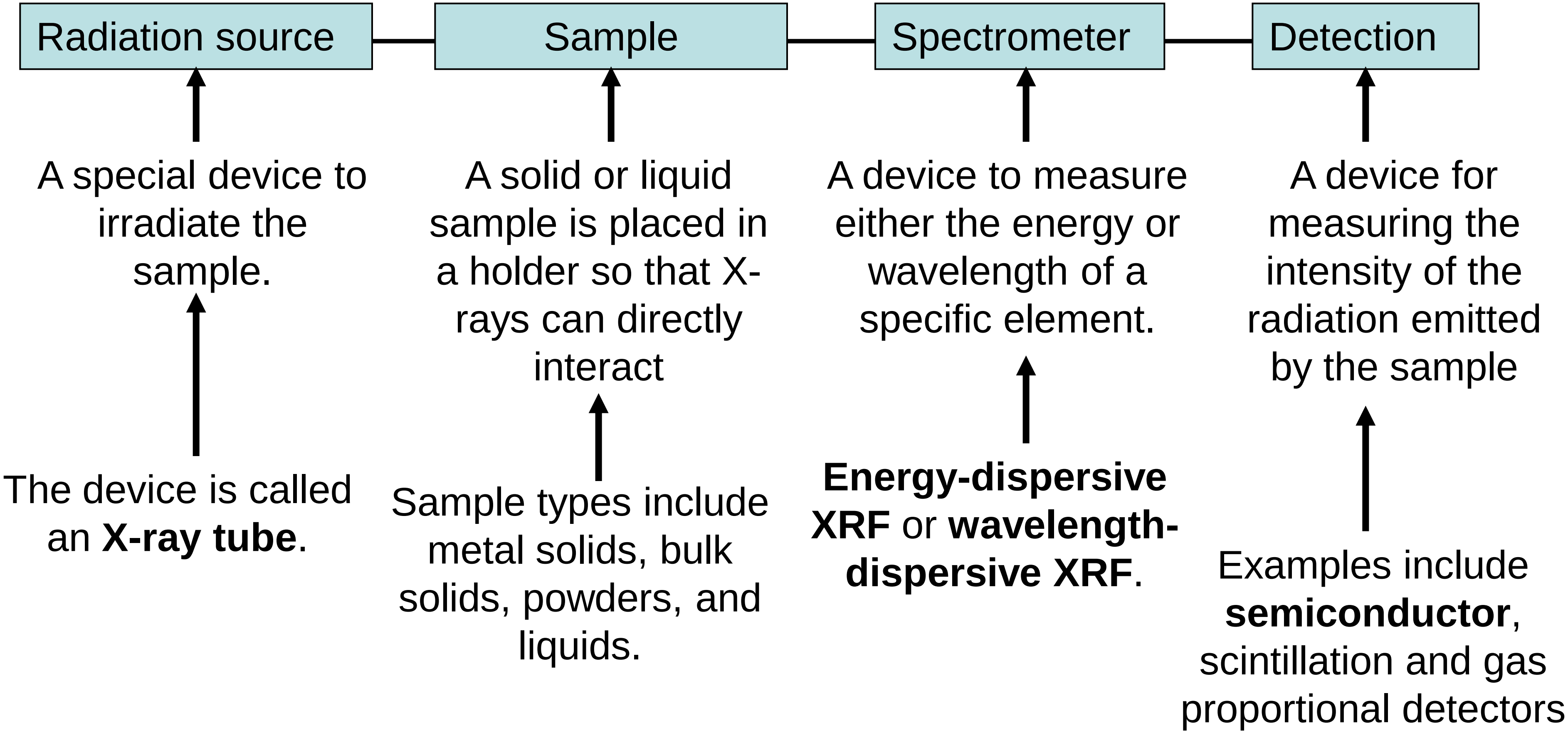
X-Ray Methods – An Introduction

X-rays are a form of electro-magnetic radiation with extremely high energies. Most practical X-ray experiments use wavelengths in the range ca. 0.01 – 2.5 nm. A wavelength of 1 nm corresponds to an energy of about 100 million Joules per mole: this is of course why X-ray experiments require a range of safety precautions. Such energies are usually obtained by the interactions of extremely high energy electrons with electrons in the inner orbitals of atoms, the latter having very high binding energies. X-rays produced in this way can be used to generate **secondary** X-rays from other atoms. In practice X-rays are also obtained from radioactive materials or, more rarely, from synchrotrons and similar high energy beam sources. Like other forms of electromagnetic radiation, X-rays can be absorbed or scattered, or generate fluorescence. In the analytical sciences X-rays thus have a range of applications, of which two are of outstanding importance:

- **X-Ray Fluorescence**, in which a sample irradiated by X-rays emits X-rays with longer wavelengths, the latter being characteristic of the atoms involved.
- **X-Ray Diffraction**, which results from the scattering of X-rays by crystals, and thus gives information about the structures of the latter.

X-ray fluorescence spectroscopy (XRF)

The instrumentation for XRF can be described by considering **four** major, but inter-related components.



Radiation source — Sample — Spectrometer — Detection

Radiation source

A special device to irradiate the sample.

The device is called an **X-ray tube**.

Sample

A solid or liquid sample is placed in a holder so that X-rays can directly interact

Sample types include metal solids, bulk solids, powders, and liquids.

Spectrometer

A device to measure either the energy or wavelength of a specific element.

Energy-dispersive XRF or **wavelength-dispersive XRF**.

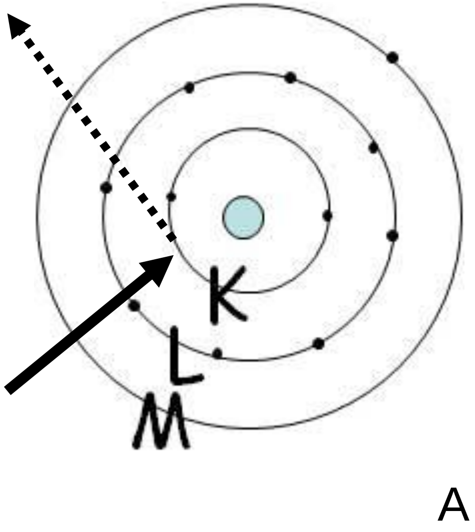
Detection

A device for measuring the intensity of the radiation emitted by the sample

Examples include **semiconductor**, scintillation and gas proportional detectors

Principle of X-ray Fluorescence Spectroscopy

An atom can be described as consisting of shells of electrons i.e. K, L, M, N etc. If a high speed X-ray photon, from the X-ray source, hits a sample atom and has sufficient energy it will dislodge an electron from one of the shells e.g. K shell. This results in a “hole” being produced making the atom an unstable ion. See figure (12.49A)



Within 10^{-4} s, an electron from an outer shell drops into the hole. This transition causes the emission of a characteristic X-ray (i.e. a photon of definite wavelength). See figure (12.49B)

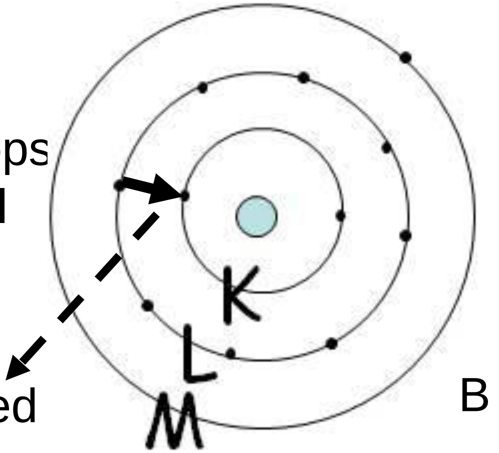


Figure 12.49 – production of X-rays

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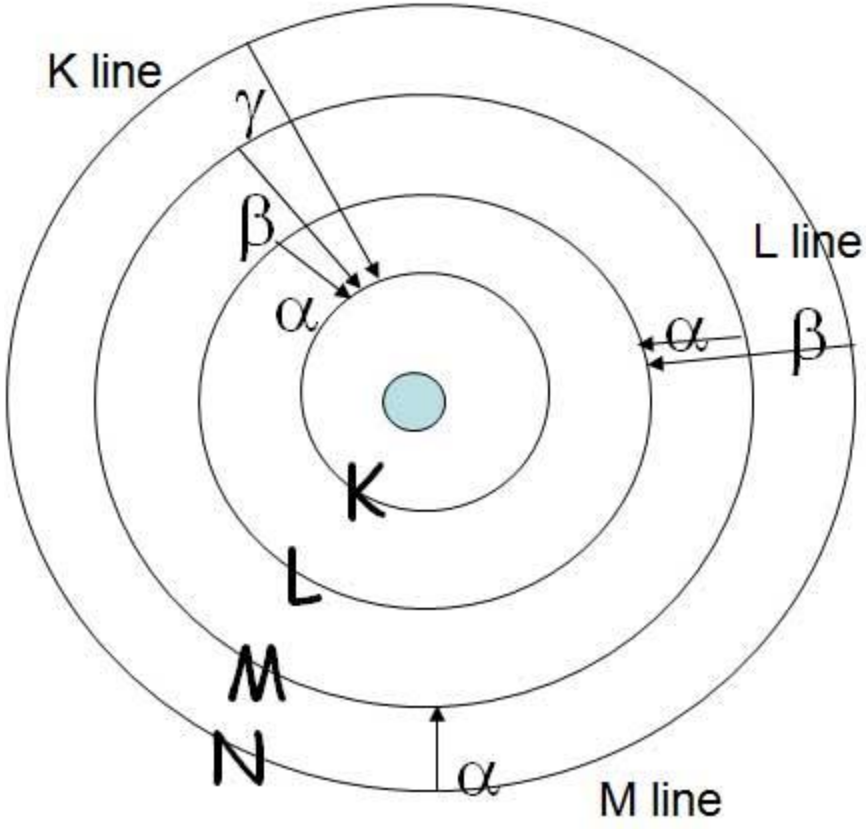

Figure 12.50 – nomenclature of X-ray lines

Nomenclature:

Transitions of electrons to the K shell are identified as Kα, Kβ, Kγ for L→K, M →L, N →M, respectively.

Whereas for the L shell are identified as Lα, Lβ for M →L, N →M, respectively.

And, for the M shell are identified as Mα for N →M.

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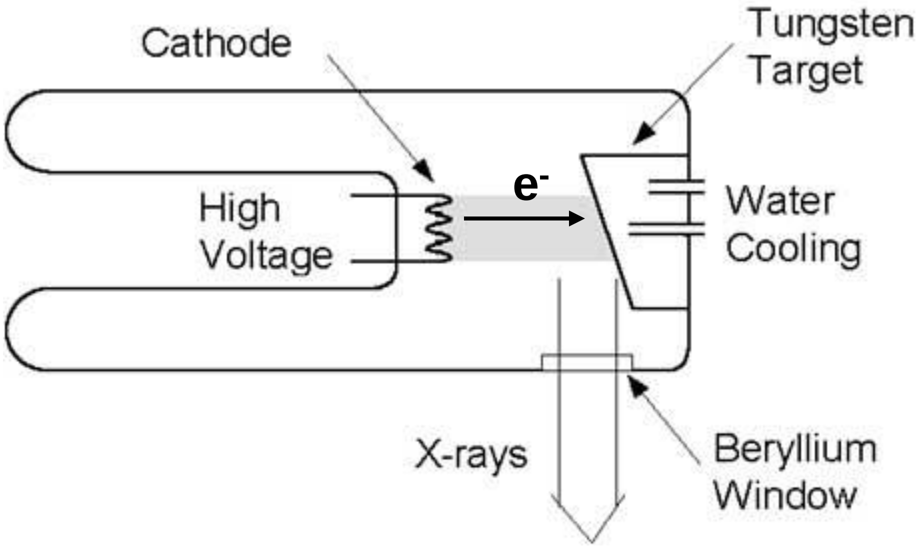
X-ray Tube

The desirable properties of an X-ray source include: a variable X-ray energy output; long term power stability; long life; and, small size. Two types of X-ray tube are available: a side window type and an end window type.

The X-ray tube (Figure 12.51) is energised by a high-voltage power supply (0.5 to 50 kV). The vacuum tube consists of a tungsten (or chromium) **target** (the anode – which is electrically positive). As accelerated electrons, from the cathode (the electrically negative terminal), strike the target X-rays are produced. The generated X-rays exit the tube via a Beryllium window.

Figure 12.51 - side-window X-ray tube



If the **target** used is tungsten (atomic number of 74) then it is used to excite the K and L lines of elements with higher atomic numbers. For lighter elements the **target** is chromium (atomic number of 24) which is used to excite elements of lower atomic number.

Spectral Output of X-ray tube

Two types of spectral output are produced by the X-ray tube:

- **Continuum Radiation**: results from deceleration of electrons by the atoms in the target. The intensity and energy range are dependent on the operating voltage of the X-ray tube;
- **Characteristic Radiation**: provided the accelerating potentials are sufficiently high then characteristic peaks Kα and Kβ are produced.

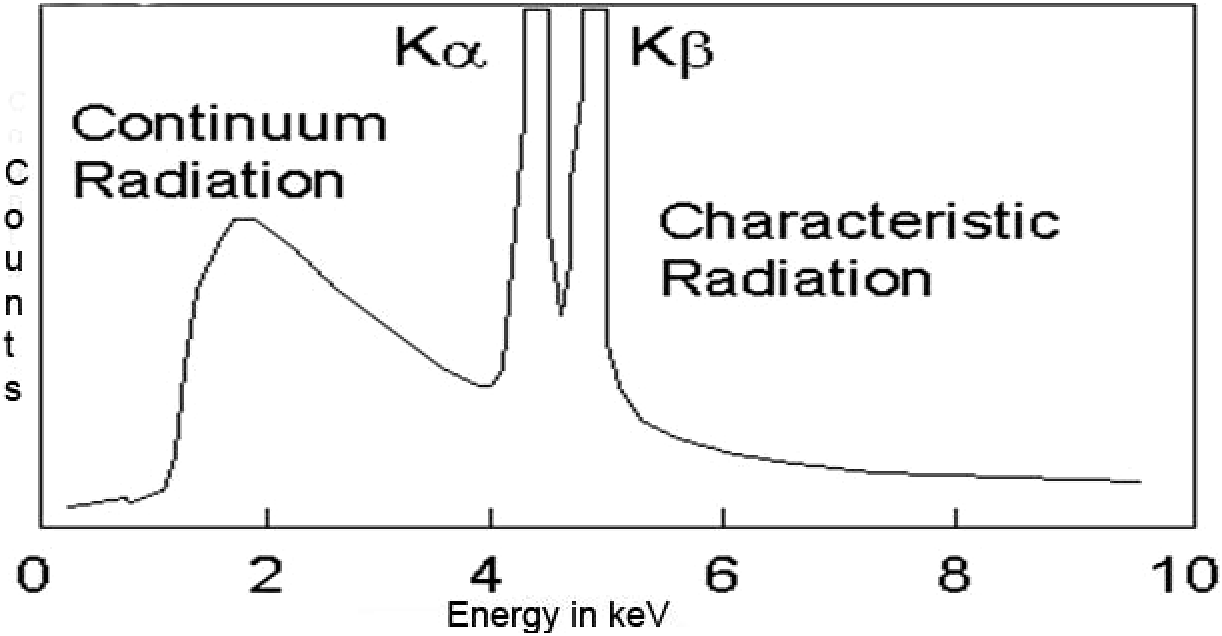


Figure 12.52 - a typical spectral output produced by electron bombardment of a tungsten target

Samples

A range of sample types can be analysed by placing either the flat surface of the sample in direct contact with the X-rays or by placing the sample in a holder. The sample cup holder is an open tube. On one end is placed Mylar™ film which allows X-rays to pass (and retain the sample in the cup) while the other end is either left open or covered. The use of covers is important for solution or powder samples to prevent contamination and/or loss of sample. Sample types include:

Solids (important that the surface is smooth and polished)

- metal solids (e.g. steel samples)
- bulk solids (e.g. geological samples)
- loose powders (e.g. soil) (place in a sample holder)

Liquids (aqueous and organic) (place in a sample holder)

Problems can arise due to the liquid sample evaporating, stratifying (forming layers) and/or precipitating. volatility under vacuum conditions.

Figure 12.53 - sample holder

Pre-concentrated samples

Sample has previously undergone some form of pre-concentration such that it has become immobilized on a support media e.g. filter or ion-exchange membrane. Alternatively addition of a solidifying agent to the liquid sample e.g. cellulose, alumina or gelatin.

Solid Powder Samples

In the case of powder samples they must be in a form that is similar to available standards in terms of matrix, density and particle size. A powder sample can be prepared as follows:

- **Fused beads** (cast or pressed into a disc) with a flux (1:5 to 1:10, w/w) using either tetraborate ($Na_2B_4O_7$ or $Li_2B_4O_7$) or potassium pyrophosphate ($K_2P_2O_7$) .
- **Pressed pellets** with a binding agent such that the sample is flat, homogeneous and infinitely thick with respect to the X-rays.

A **pressed pellet** is prepared by mixing the fine powder sample (4.0 g, accurately weighed) with polystyrene co-polymer binder (0.9 g) and then pressing the resultant mixture under a pressure of 12 tons for 1 minute [Figure (12.54)] to produce a smooth surfaced disc [Figure (12.55)].

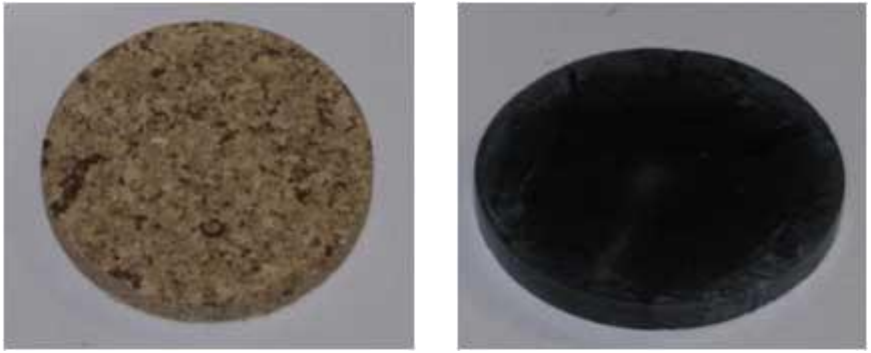


Figure 12.55 Different pressed pellet samples

Figure 12.54 - a hydraulic press

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XRF - instrumentation

There are two forms of instrumentation used to obtain XRF spectra:

- Wavelength dispersive
- Energy dispersive

Wavelength dispersive X-ray fluorescence

In wavelength-dispersive XRF or WD-XRF the emitted X-rays from the sample are angularly dispersed by a diffracting crystal on the basis of wavelength. The detector receives only one wavelength at a time: either single channel (sequential) or multi channel (simultaneous) – see figure (12.56)

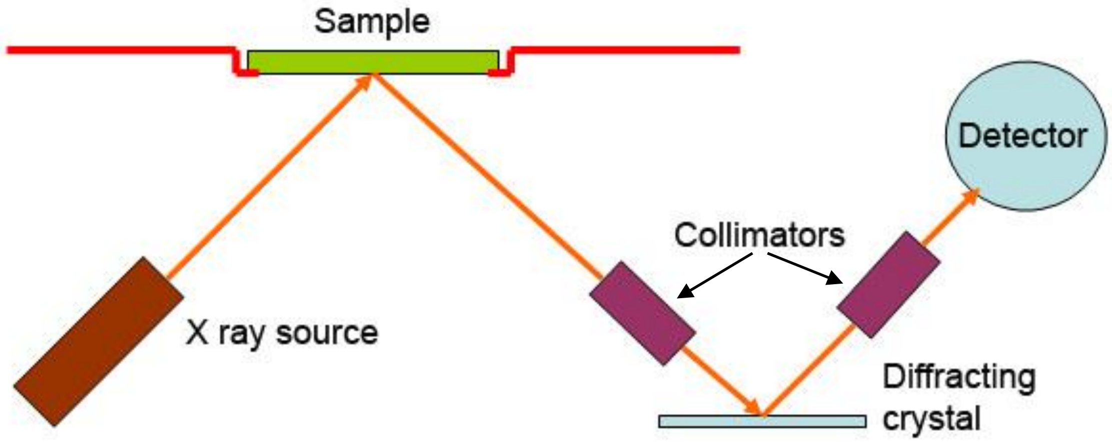


Figure 12.56 - diagram of a WD-XRF instrument

Energy Dispersive X-ray fluorescence

In energy-dispersive XRF or ED-XRF the energy of all X-rays are measured simultaneously using a solid-state semiconductor detector (Si(Li) detector). The detector registers an electric current having a height proportional to the photon energy. These pulses are then separated electronically, using a pulse analyser (counting time typically between 100-10,000 s) – see figure (12.57)

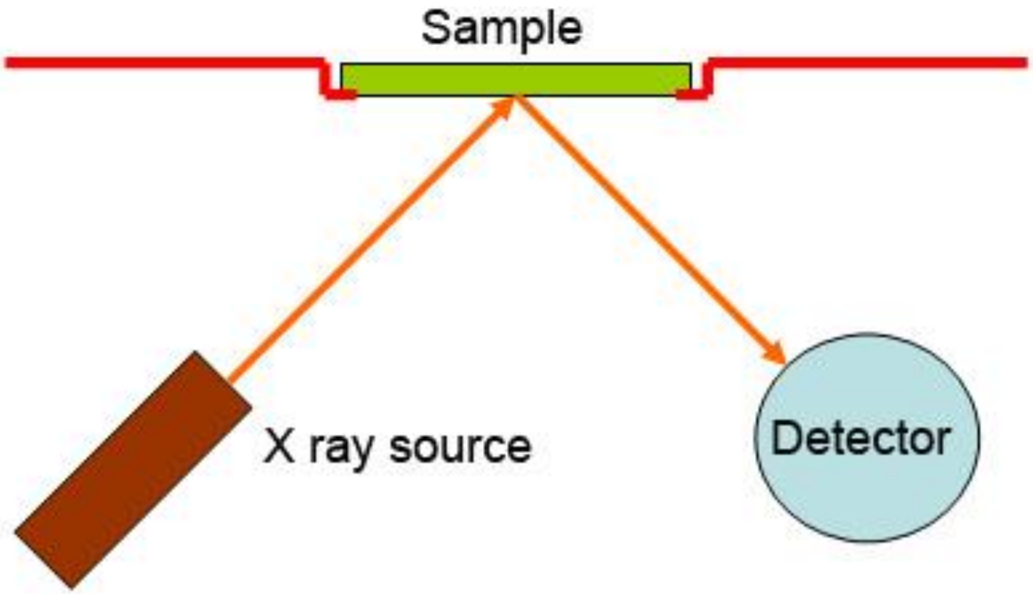


Figure 12.57 - diagram of a ED-XRF instrument

The spectrum shown as figure (12.58) on the next slide is a typical XRF spectrum from a sample containing a number of elemental species http://en.wikipedia.org/wiki/File:XRFScan.jpg

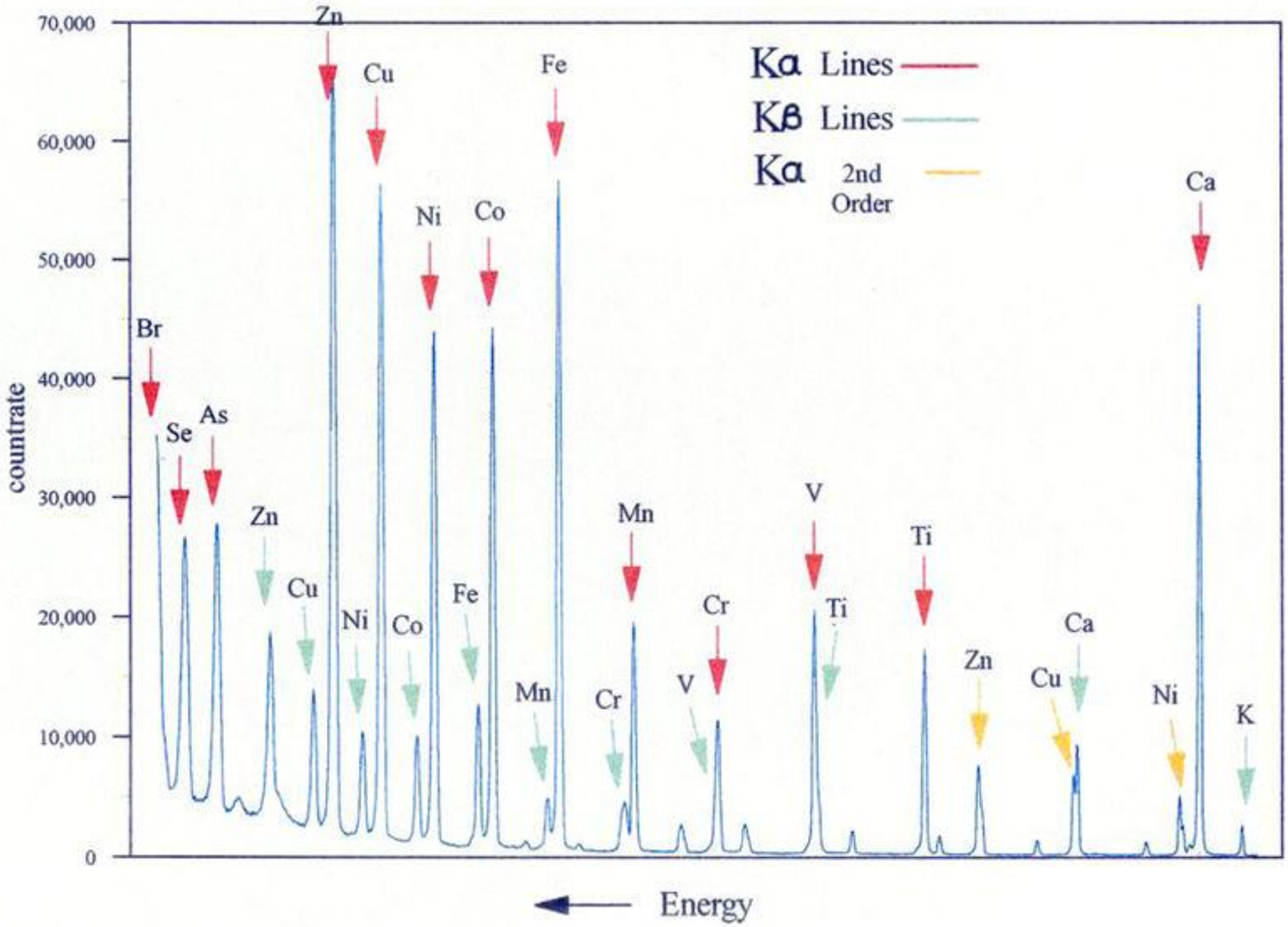


Figure 12.58 – typical energy dispersive XRF spectrum

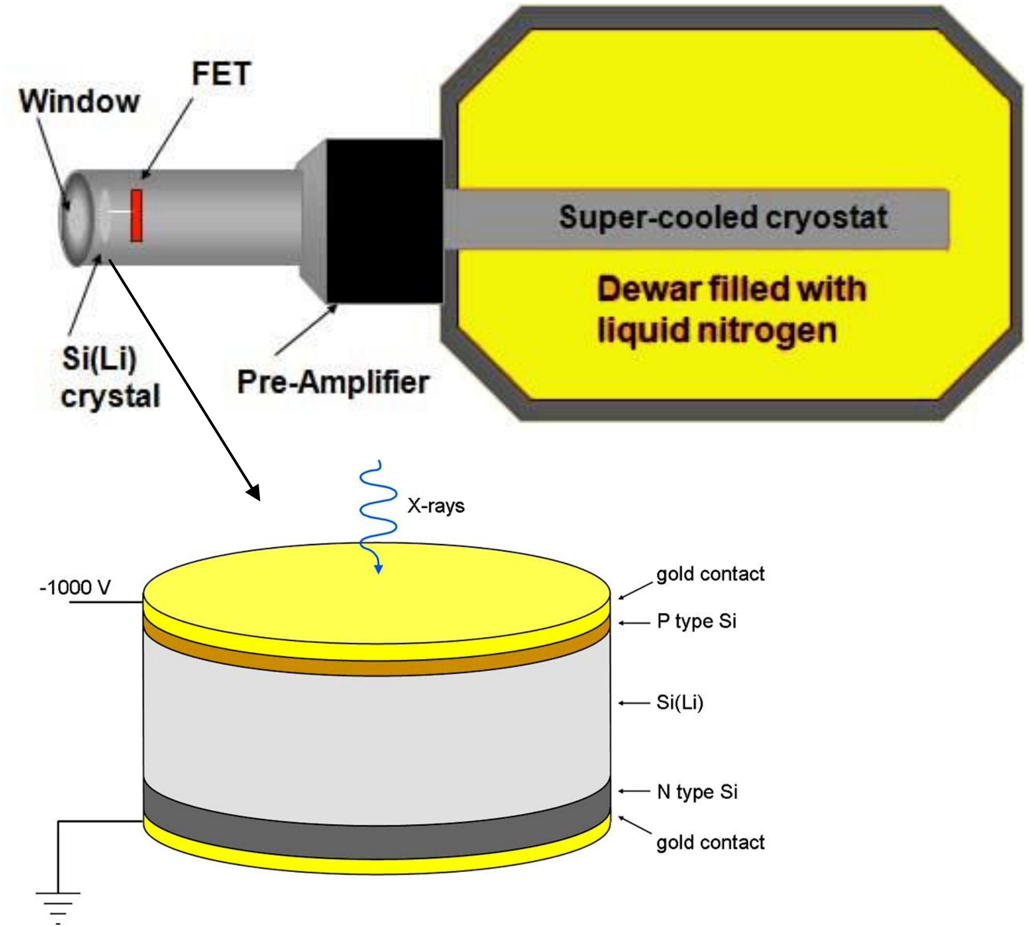
Detectors for XRF

The principle of operation of a detector for XRF is as follows:

- A detector is composed of a non-conducting or semi-conducting material between two charged electrodes.
- X-ray radiation ionizes the detector material causing it to become conductive, momentarily.
- The newly freed electrons are accelerated towards the detector anode to produce an output pulse.
- The ionized semiconductor produces electron-hole pairs, the number of pairs produced is proportional to the X-ray photon energy.

A range of detectors are available for XRF and include:

- A semiconductor detector (e.g. Si(Li)) which registers a current pulse from the formation of electron-hole pairs (*see next slide*).
- A gas-proportional counter which registers a current pulse from the collection of electron-ion pairs formed.
- A scintillation detector counts light pulses created when an X-rays passes through a phosphor.



http://en.wikipedia.org/wiki/File:DmedxrfSiLiDetector.jpg

Figure 12.59 - diagram of a Si(Li) detector

Window: Beryllium or Polymer; Counts Rates: 3000 – 50000 cps; Resolution: 120 -170 eV at Mn Kα.

When a photon enters the crystal, it ejects a high-energy photoelectron which ultimately dissipates its energy in multiple interactions which promote valence band electrons to the conduction band, leaving holes in the valence band. The electron-hole pairs are then collected by biasing the detector at -1000 V, giving rise to a current pulse for each X-ray entering the detector. Charge collection is much more efficient than in a gas.

Additional information on this type of X-ray detector may be found at:
http://en.wikipedia.org/wiki/X-ray_fluorescence

Interferences in XRF

Interferences in XRF occur as a result of:

- Matrix (inter-element) effects;
- Spectral coincidence:
- Environmental effects.

Matrix interferences

Two types, can result in **absorption** or enhancement effects [Figure (12.60)]. In absorption, any element can absorb or scatter the fluorescence of the element of interest whereas in **enhancement**, characteristic X-rays of one element can excite another element in the same sample resulting in signal enhancement. These matrix interferences can be mathematically corrected, by the use of influence coefficients, or alpha corrections.

The incoming source X-ray causes iron in the sample to fluoresce. The resultant iron fluorescence is sufficient in energy to cause calcium to fluoresce. In this situation calcium is detected, but iron is not. The resultant signal responses are proportional to the concentrations of both calcium and iron.

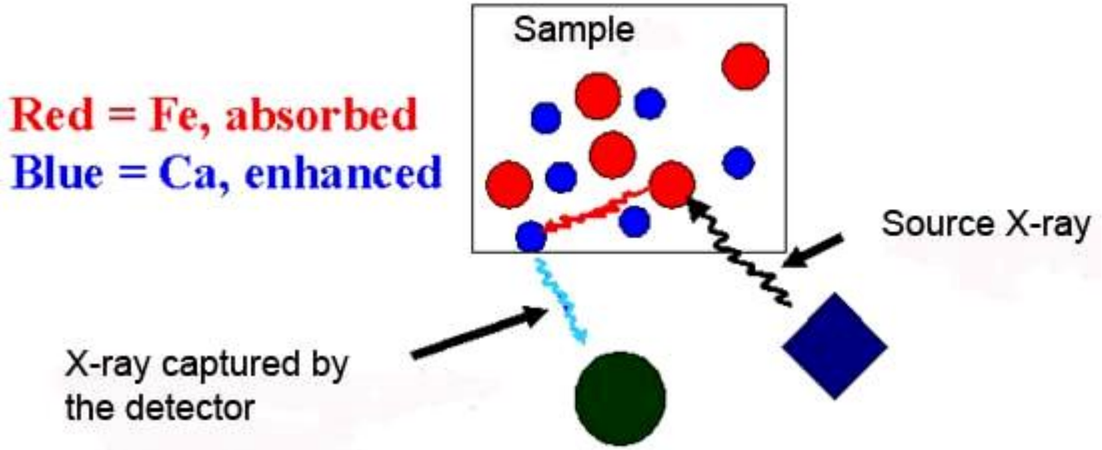


Figure 12.60 - matrix interferences in XRF

Spectral interferences

These are peaks in the spectrum that overlap with the spectral peak of the element to be analyzed. Examples include K and L line overlap for sulphur and molybdenum, chlorine and rhodium, and arsenic and lead. In addition, adjacent element overlap can occur, examples include aluminium and silicon, sulphur and chlorine, and potassium and calcium. In these situations it is the resolution of the detector that determines the extent of the overlap.

Environmental interferences

Lighter elements, such as those between sodium and chlorine in the Periodic Table emit weak X-rays, whose signal can be reduced by air. The remedy is to (a) purge the instrument with an inert gas e.g. helium, thereby removing the air. As helium is less dense than air, it results in less attenuation of the signal, or (b) evacuate air from the sample chamber via a vacuum pump. The removal of air from the sample chamber also has additional benefits, such as the elimination of spectral interferences resulting from argon present in small quantities in air. Argon has a spectral overlap with chlorine.

Qualitative and quantitative analysis

XRF is capable of both qualitative and quantitative analysis. In **qualitative analysis** the spectral positions are independent of the chemical state of the element, such that qualitative analysis is made by observing the energy or wavelength of the characteristic X-rays. In **quantitative analysis** a measurement is made by recording the X-ray intensity at the characteristic energy or wavelength for a particular element. Using this approach may require the elimination of sample inhomogeneity, particle size and surface effects. Also matrix (inter-element) effects may be substantial and require mathematical correction.

Approaches for **quantitative analysis** include:

- **Standard Calibration Method:** The analyte-line intensity from samples is compared with that from standards having the same form and the same matrix as the samples.
- **Internal Standardisation Method:** The standard calibration method is improved by quantitative addition to all samples and standards of an internal standard element having excitation, absorption and enhancement characteristics similar to those of the analyte in the particular matrix. The calibration function involves measuring the intensity ratio of the analyte and internal standard lines.

Continued on the next slide

- **Standard Addition Method**: The element concentration is altered quantitatively in the sample itself. The sample is subjected to one or more quantitative incremental concentrations or dilutions of the element. The intensity of the element lines is measured for effectively the same matrix in each case.

- **Matrix Dilution Method:** The matrix of all samples is diluted to a composition such that the effect of the matrix is determined by the diluent rather than the matrix.

- **Thin Film Method:** The samples are made so thin that absorption-enhancement effects substantially disappear.

- **Mathematical Correction Method:** Absorption-enhancement effects are corrected mathematically by the use of *influence coefficients* for each element present (these are derived experimentally from reference samples).

- **Fundamental Parameter Method:** The fundamental parameters calibration is a ‘standardless’ calibration that relies on the spectrometer’s response to pure elements and uses built-in mathematical algorithms to compensate for matrix effects.

- **Empirical Coefficient Method:** An empirical calibration can be performed using specific standards that closely match the sample matrix. Mathematical algorithms are used to compensate for matrix effects.

Applications

XRF offers the following advantages:

- Non-destructive analysis;
- Minimal sample preparation (no digestion of solid samples);
- Multi-element analysis;
- A relatively simple spectrum;
- Applicable over a wide range of element concentrations (covering major, minor and trace elements);
- Detection limits down to low µg/g (parts per million);
- Low running costs.

Figure 12.61 An ED-XRF Instrument

Element	**DL (µg/g)**
Ti	2.0
Cr	0.8
Mn	1.4
Fe	2.4
Co	5.0
Ni	1.8
Cu	0.9
Zn	0.9
As	0.2
Se	0.7
Cd	0.4
Hg	0.5
Pb	1.2

Table 12.3 ED-XRF detection limits (DL) using a beam diameter of 2 cm and X-ray tube power of 400 W

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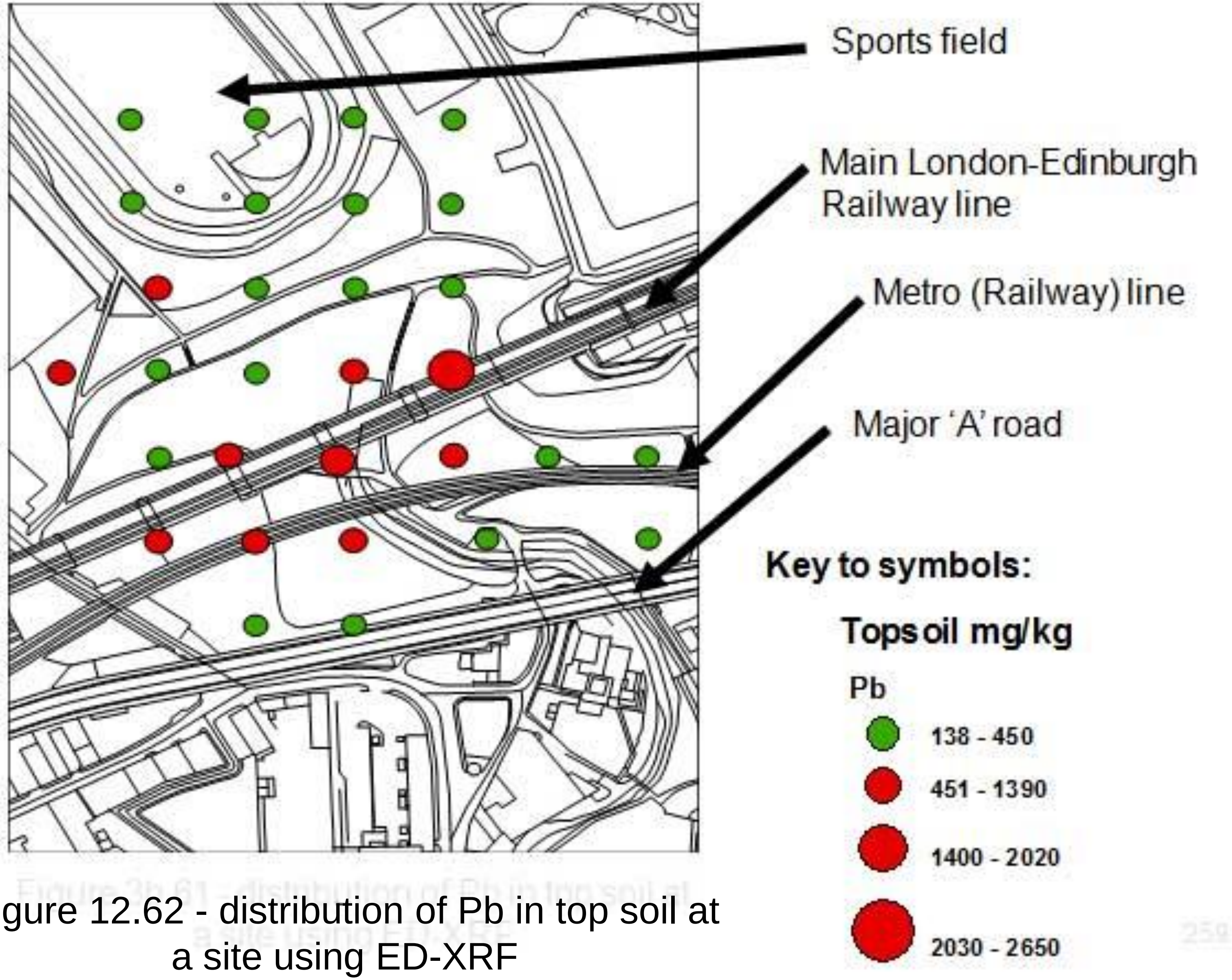
Case study 12.8: Determination of metals, using ED-XRF, in top soil collected from a site in Newcastle upon Tyne

Soil samples were analysed using ED-XRD for their elemental composition. Of particular interest was the level of lead on the site due to its former historic use as a lead smelting plant.

A total of 29 topsoil sample were collected, oven dried to constant weight and then pressed in to pellets with polystyrene co-polymer binder (**see slide 78**) prior to analysis.

The results, **shown on the next slide**, indicate the high levels of lead on the whole site with the highest lead level being found underneath the main London-Edinburgh (East Coast) main railway line.

The ease of use of ED-XRF with minimal sample preparation allows rapid screening of multiple samples effectively and efficiently for major and minor elements.



Sports field

Main London-Edinburgh Railway line

Metro (Railway) line

Major ‘A’ road

Key to symbols:

Topsoil mg/kg

Pb

● 138 - 450

● 451 - 1390

● 1400 - 2020

● 2030 - 2650

Figure 12.62 - distribution of Pb in top soil at a site using ED-XRF

X-Ray Diffraction

As already noted, X-rays can be scattered according to their wavelengths in the same way as UV-visible or infra-red light is diffracted by gratings, by using the regular lattice structure of crystals. This principle can also be used in reverse – the structures of crystals can be determined by measuring the effects they have on the diffraction of X-rays. This was discovered by Max von Laue in 1912, and is now the basis of a crucial method of determining molecular structures.

The fundamental equation in X-ray scattering is the **Bragg equation** [equation (12.1) below]. If an X-ray beam strikes a crystal at an angle θ to the surface, constructive interference, leading to intense scattering of the radiation, occurs when:

$$2d\sin\theta = \mathrm{n}\lambda \qquad \text{Equation (12.1)}$$

Where n is an integer, λ is the X-ray wavelength, and d is the spacing between the successive layers of atoms in the crystal.

In the simplest approach to structure determination a crystalline sample is ground to a fine homogeneous powder. In an X-ray beam the randomly oriented particles will allow the fulfilment of the Bragg condition for all the different regular planes in the crystal structure, allowing d values to be found from observed θ values and the crystal structure deduced. This is known as **X-ray powder diffraction**.

Instrumental components

The simplest device for measurement of a powder diffraction diagram for XRD consists of **three** major, but inter-related components.

Radiation source — **Sample** — **Debye-Scherrer powder camera**

A special device to irradiate the sample (**X-ray tube**).

A microcrystalline solid powder is placed in a holder so that X-rays can directly interact

Powder sample diffracts X-rays

Diffracted X-rays from sample are detected on photographic film

The main components of a powder diffraction XRD spectrometer is shown as figure (12.63). A typical instrument is shown as figure (12.65) on the slide 95.

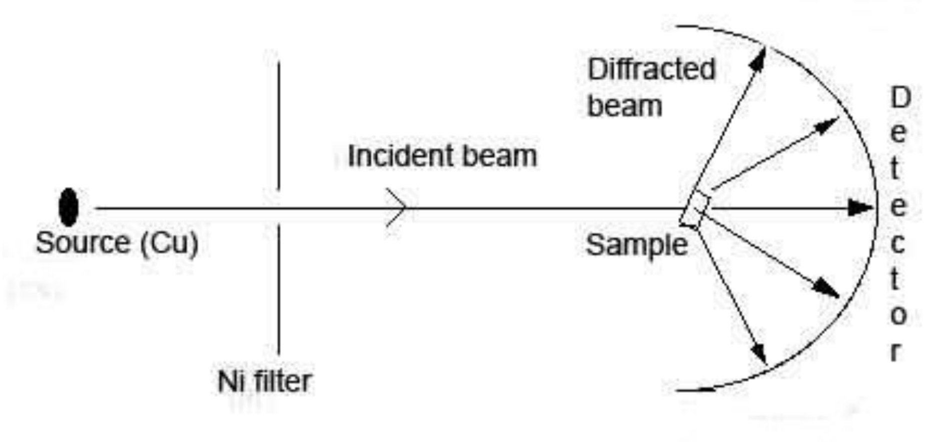
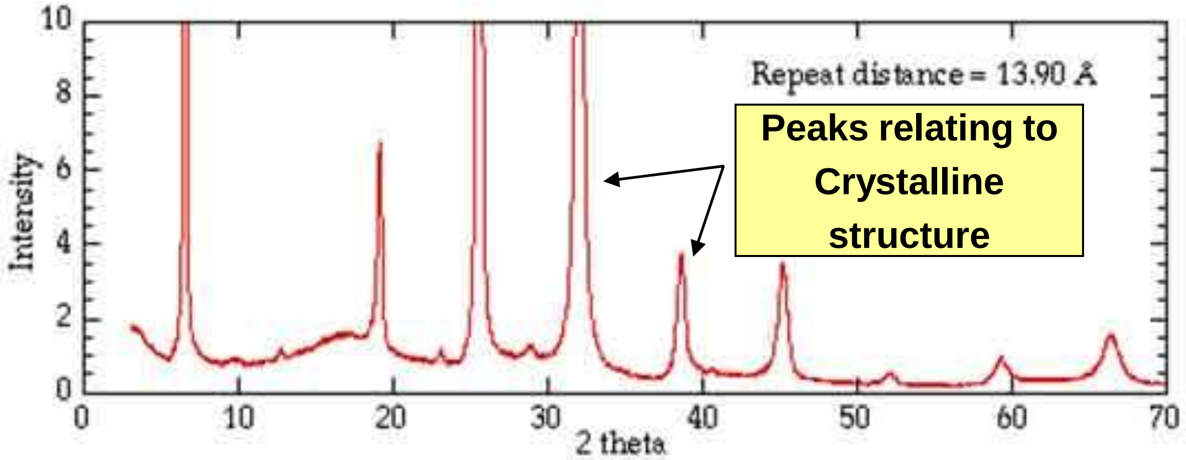


Figure 12.63 – schematic diagram of a basic XRD spectrometer

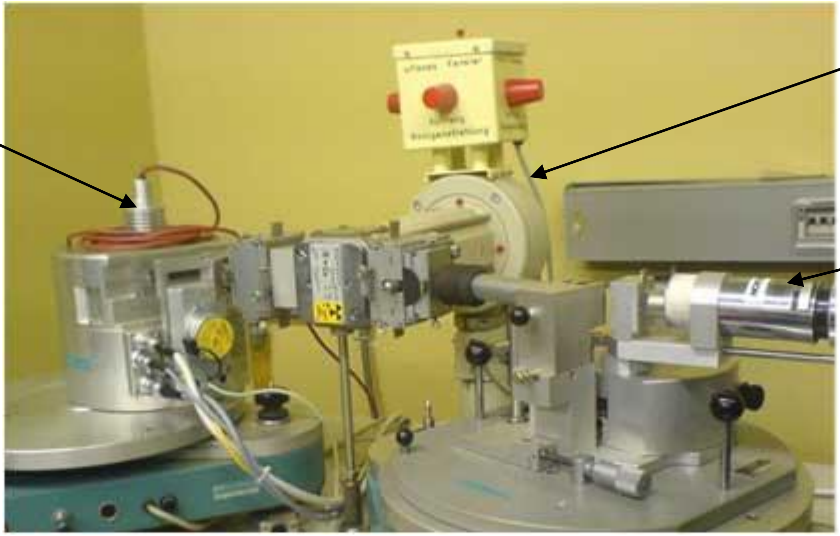
The X-ray radiation most commonly used is that emitted by copper, whose characteristic wavelength for the K radiation (see next slide) is =1.5418Å. When the incident beam strikes a powder sample, diffraction occurs in every possible orientation of 2theta. The diffracted beam may be detected by using a moveable detector such as a **Geiger** or **Scintillation** counter, which is connected to a chart recorder. In normal use, the counter is set to scan over a range of 2theta values at a constant angular velocity. Routinely, a 2theta range of 5 to 70 degrees is sufficient to cover the most useful part of the powder pattern. The scanning speed of the counter is usually 2theta of 2 degrees min^{-1} and therefore, about 30 minutes are needed to obtain a trace. A typical output from this analysis is shown as figure (12.64) on the next slide.



Peaks relating to Crystalline structure

Figure 12.64 – recorded output from a powder XRD of a clay mineral

The diffraction pattern as illustrated in figure (11.41) is typical of that obtained by subjecting a crystalline powder to XRD examination. Each peak relates to a different diffraction of the incident beam and from a set of diffraction tables may be used to identify crystalline materials present in the sample. A typical XRD instrument is shown as figure (12.65) below.



Detector

Sample compartment

X-ray gun

Figure 12.65 – powder diffraction spectrometer

Application

Unlike all the other analytical techniques discussed in this Chapter, X-ray diffraction is not normally used for quantitative analysis, but instead to obtain qualitative structural elucidation information.

XRD provides a fast and accurate method for identifying crystalline phases [for example, Figure (12.66)] in a range of materials. For example the use of XRD can differentiate between the different polymorphic forms of carbon i.e. diamond and graphite. Also, different oxides of iron e.g. FeO, Fe_2O_3 and Fe_3O_4 can be differentiated by XRD, whereas a simple chemical analysis would only determine the quantity of iron present and provide no information with regard to chemical structure.

Figure 12.66 - a natural crystalline mineral for which XRD could identify the structure and minerology

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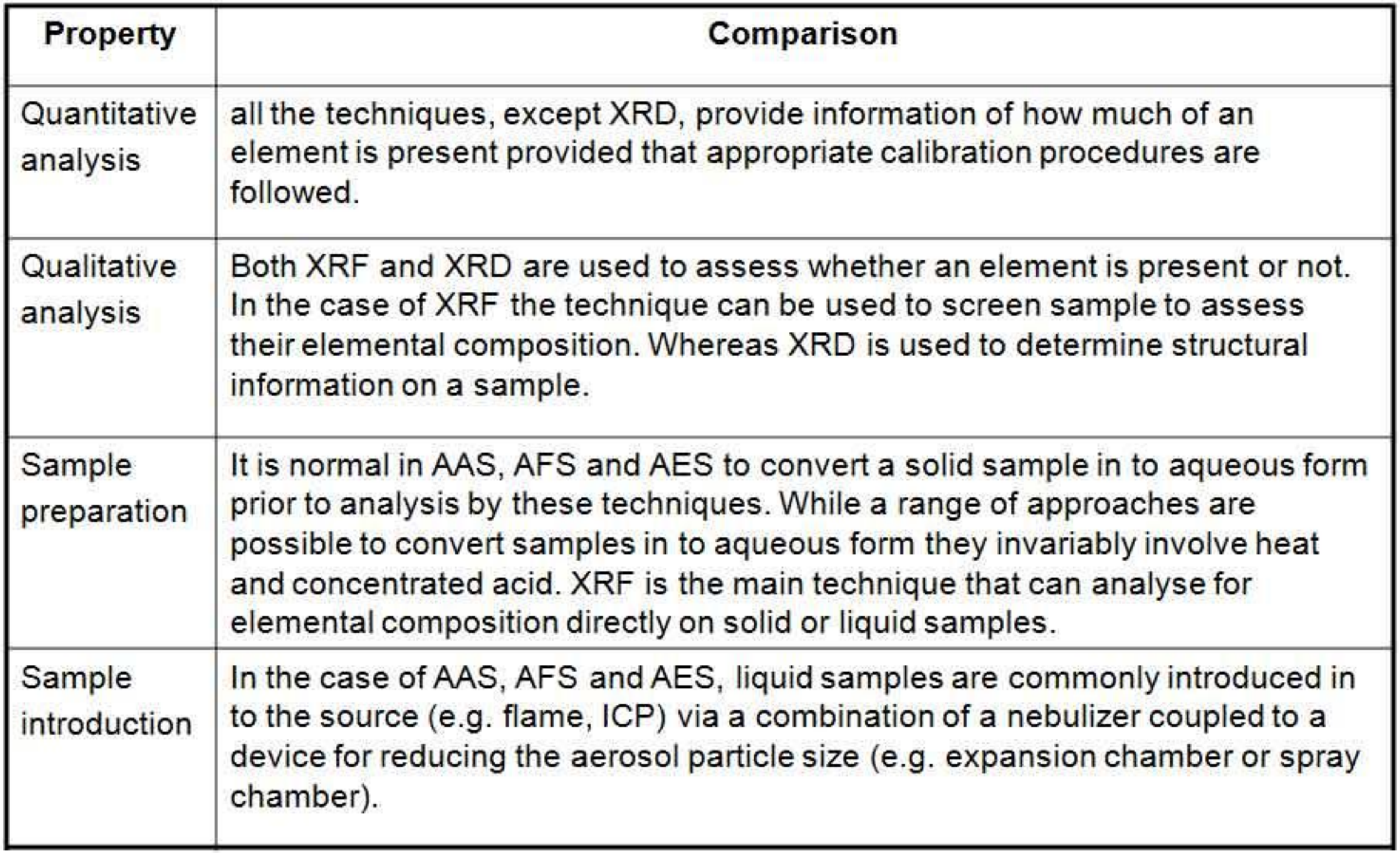
Comparison of elemental techniques



Property	Comparison
Quantitative analysis	all the techniques, except XRD, provide information of how much of an element is present provided that appropriate calibration procedures are followed.
Qualitative analysis	Both XRF and XRD are used to assess whether an element is present or not. In the case of XRF the technique can be used to screen sample to assess their elemental composition. Whereas XRD is used to determine structural information on a sample.
Sample preparation	It is normal in AAS, AFS and AES to convert a solid sample in to aqueous form prior to analysis by these techniques. While a range of approaches are possible to convert samples in to aqueous form they invariably involve heat and concentrated acid. XRF is the main technique that can analyse for elemental composition directly on solid or liquid samples.
Sample introduction	In the case of AAS, AFS and AES, liquid samples are commonly introduced in to the source (e.g. flame, ICP) via a combination of a nebulizer coupled to a device for reducing the aerosol particle size (e.g. expansion chamber or spray chamber).

Table 12.4 – comparison of atomic spectroscopic techniques

Question 12.1 The local council has recently acquired a new site for development in to a business park. Unfortunately, the site has been used for manufacturing over the past 100 years for a range of hazardous materials and specific details have been lost. You have successfully been awarded the contract to survey the site for metals contaminants. Describe the procedures to follow indicating your chosen sampling strategy, sample preparation methods and analytical techniques to provide a comprehensive survey of this site. Include details of an appropriate sample preparation method for your chosen analytical technique. Suggest reasons for your choice of sample preparation method.

Question 12.2(a) The principle of atomic absorption spectroscopy is sometimes referred to as the “lock and key” effect. Describe this principle using diagrams to assist the explanation.

Question 12.2(b) Describe the construction and operation of a hollow cathode lamp, and explain why this device is important as a light source in analytical atomic absorption spectroscopy.

Question 12.2(c) With the aid of sketches, describe and explain the operation of the device used to convert a liquid sample into an aerosol suitable for flame atomic absorption spectroscopy.

Question 12.2(d) Flame atomic absorption spectroscopy (FAAS) is prone to interferences. Briefly outline possible sources of interference in FAAS and their remedies. Flame atomic absorption spectrometry was used to analysis a solution of 20 mg ml-1 Ca2+ solution in the presence of phosphate ions. Explain how the absorbance value would change if the concentration of phosphate ions progressively increased and propose a method to alleviate this problem.

Question 12.2(e) The sensitivity of atomic absorption spectroscopy can be improved using a graphite furnace (GF) as the atom cell:
(i) Describe the operation of the graphite furnace;
(ii) Why is the method of matrix modification important in GFAAS?

Question 12.3(a) Draw the typical arrangement for an inductively coupled plasma torch. Indicate typical gas flow rates, input power levels, normal frequency of operation and viewing height. The plasma is a self-sustaining ionized gas. Comment on its formation and nature.

Question 12.3(b) Outline the main components of a monochromator system used for sequential ICP atomic emission spectroscopy.

Question 12.3(c) What benefits are achievable using an Echelle spectrometer over a conventional spectrometer

Question 12.3(d) A common detector in atomic emission spectroscopy is the photomultiplier tube (PMT). Describe the mode of operation of a PMT.

Question 12.4(a) What are the desirable attributes of a sample prepared for X-ray fluorescence analysis? Describe two methods of preparing solid samples for XRF analysis. Illustrate each method by means of an appropriate example.

Question 12.4(b) Describe the process giving rise to the emission of Kα and Kβ fluorescent X-rays from a sample exposed to an incident beam of X-rays.

Question 12.4 (c) Using a suitable diagram, explain the operation of an X-ray tube

Question 12.4 (d) Discuss the analytical advantages and disadvantages of energy-dispersive XRF compared with wavelength-dispersive XRF?

Question 12.4 (e) Describe what is meant by the term “interelement effects” in XRF spectrometry. Include in your answer examples of both positive and negative effects.

Question 12.4(f) Several methodologies can be utilised to overcome the matrix effects in quantitative analysis by XRF. Explain the principles of two such methods

Question 12.5(a) An accurately weighed (0.5235 g) soil sample is digested in 25 ml of concentrated nitric acid, cooled and then quantitatively transferred to a 100 ml volumetric flask and made up to the mark in high purity water. This solution is then diluted by taking 10 ml of the solution and transferring to a further 100 ml volumetric flask where it is made up to the mark with high purity water.

(i) What is the dilution factor?

(ii) If the concentration of an element in the solution is 15 g ml^{-1}, what is the abundance of the element in the original soil sample? [assuming that the solution analysed was found to be within the linear portion of the graph]. Express the answer in terms of mg kg^{-1}.

Question 12.5(b) A flame atomic absorption instrument is to be used for the determination of caesium in an industrial sample containing elevated concentrations of sodium, phosphate, and a silicate mineral. The detection limit for the instrument is quoted as 0.8 mg mL^{-1}. Explain the procedures to be adopted in carrying out this analysis, and for ensuring that the results are carefully validated.

Question 12.5 (c) A sample of river water was analysed for Pb, Cu and Fe by direct calibration using an ICP-AES instrument. The signal (mV) for each element at the appropriate wavelength was 25000, 520000 and 1500, respectively. Standard curves for Pb, Cu and Fe were obtained by placing 0, 10, 20, 30 and 50 ml of a multi-element stock solution containing 100 ng ml^{-1} Pb, 50 ng ml^{-1} Cu and 200 ng ml^{-1} Fe into 100 ml volumetric flasks. After making up to volume, the solutions were nebulised and the following readings obtained:

Stock Solution (ml)	signal (mV) obtained		
	Pb	Cu	Fe
0	0	0	0
10	18 000	122 500	600
20	36 000	250 000	1 200
30	54 000	375 000	1 800
50	90 000	620 000	3 000

Calculate the concentration (ng ml^{-1}) of Pb, Cu and Fe in the sample

Question 12.6 A 1.0500 g sample of river sediment was digested in approximately 30 ml of nitric acid and made up to 100 ml in a volumetric flask. This sample was analysed for cadmium by AAS and compared with values obtained for standard calibration solutions. Below are the absorbances recorded. Construct a calibration graph and determine the concentration of cadmium in the sediment.

Concentration (ppm)	Absorbances		
0	0	0	0
2	0.127	0.124	0.130
4	0.250	0.251	0.253
6	0.382	0.379	0.384
8	0.513	0.515	0.520
10	0.698	0.700	0.701

The absorbances of unknown samples were 0.217, 0.215 and 0.212. Accuracy and precision are two terms that are often applied to analytical data. From your knowledge of their use in analytical science:

(i) comment on the accuracy of the data obtained and

(ii) calculate the precision of the data.

Question 12.7 0.5465 g of solid sample containing two elements (nickel and lead) were dissolved in 25 ml of nitric acid and transferred to a 100 ml volumetric flask. Once made up to the mark, 5 ml of this solution was analysed by XRF. Below is a table showing the results obtained for the two sets of calibration standards along with the results for the two elements in the sample solution. Draw a calibration graph for each of the two elements (can be on the same axes) and calculate the concentration of the two unknowns.

Concentration (ppm)	Nickel (CTS)	Lead (CTS)
2	722	1052
4	984	1359
6	1156	1687
8	1348	1998
10	1575	2200
Unknown	834	1557

Outline answer to question 12.1

The answer to this question can be found on slides 4 – 11 and throughout Chapter 2 of this teaching & learning programme .

It is obvious that this is a difficult question to consider and requires extensive knowledge. However, it is possible to break it down in to its component parts as follows.

Sampling strategy: Initial work should use historical maps to establish the background of the site and likely metal contaminants. The sampling scheme should use this information to create an appropriate sampling strategy that allows representative samples to be taken from a large area. Also, it is necessary to consider the selection of sampling devices and their contamination risk. Another important consideration is the depth from which samples will be taken.

Sample preparation methods: After sampling it is necessary to prepare the sample. This might involve drying of the sample, grinding and sieving, and storage of the soil prior to treatment. Sample treatment might range from acid digestion (using conventional or microwave heating sources) in the presence of acid(s) through to direct analysis of the powdered samples.

Analytical techniques: A range of analytical techniques could be used. Consider the options that AAS, AES and XRF offer in terms of their sensitivity, linear dynamic range and ability to determine metals either sequentially or simultaneously.

Outline answer to question 12.2(a)

The answer to this question can be found on slide 24.

A diagram explaining the “lock and key” effect is shown on the slide. First of all it is important to appreciate that the hollow cathode lamp is an emission source that produces a range of wavelengths for a specific element. Initially the monochromator will be tuned to one of the emission wavelengths emitted by the hollow cathode lamp (often it is the resonance wavelength for maximum sensitivity). Then, the introduction of a sample in to the atom cell e.g. flame, graphite furnace or silica tube, produces a broad absorption profile for the element under investigation. By then having the monochromator tuned to the specific wavelength for the selected element allows the selected emission from the hollow cathode lamp to be coincident with the broad absorption from the sample in the atom cell. The difference between the absorption and emission profile produces the absorbance signal. It should be noted that as the amount of element (and hence sample) in the atom cell varies so does the corresponding absorbance signal.

Outline answer to question 12.2(b)

The answer to this question can be found on slides 13/4

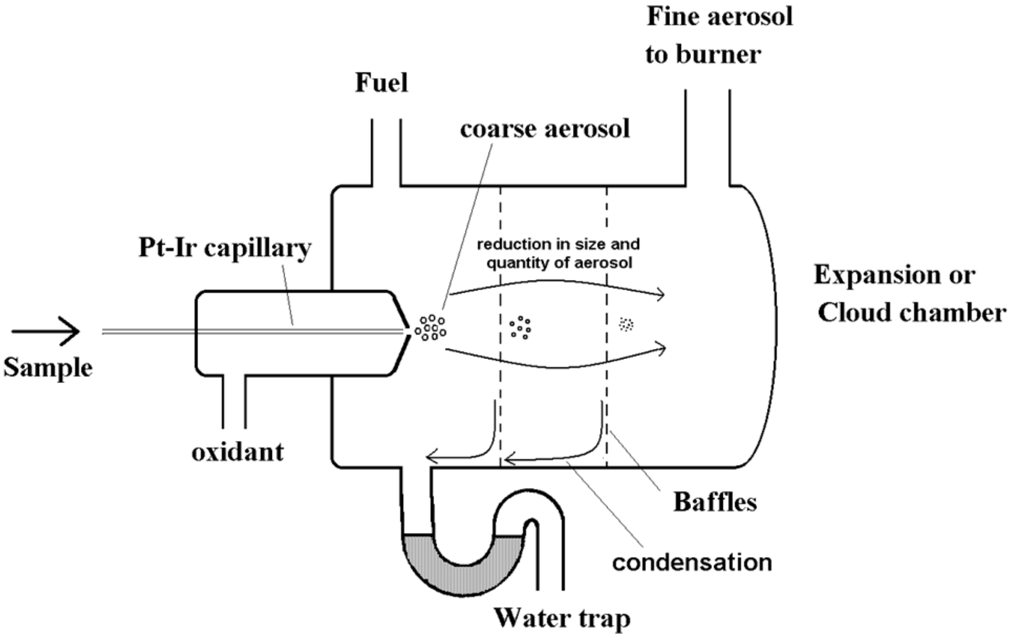
The hollow cathode lamp or (hcl) consists of a cylindrical hollow **cathode**, containing the metal (or its alloy) of interest, and a tungsten **anode**. They are enclosed in a sealed glass vessel with a **quartz window** to allow ultraviolet light (the main part of the electromagnetic spectrum for observing atomic wavelengths) to escape. The lamp is under reduced pressure and filled with an **inert gas**, usually argon (Ar) or neon (Ne). The principal of operation of an hcl is as follows: by applying a high voltage across the terminals (i.e. cathode and anode) causes the fill gas atoms e.g. argon, to ionise ($Ar \rightarrow Ar^+ + e^-$). The argon ion ($Ar^+$) is then attracted to the negative terminal (i.e. cathode) causing some of the metal to be “sputtered” and become vaporized. The vaporized metal is excited to higher electronic levels by collision with the fill gas ions (Ar^+) resulting in characteristic emission light of the metal (and also the fill gas).

The hollow cathode lamp (or hcl) is essential for atomic absorption spectroscopy. It emits light characteristic of a specific element (the same element as that which is used on the internal surface of the hollow cathode).

Outline answer to question 12.2(c)

The answer to this question can be found on slide 19

An aqueous sample is introduced in to an expansion (or cloud) chamber via a pneumatic nebulizer. The nebulizer is able, via the Venturi effect, to create a coarse aerosol. The role of the expansion chamber is two fold: (a) to reduce the particle size of the aerosol, and (b) to allow the fuel and oxidant for the flame to be pre-mixed.



Outline answer to question 12.2(d)

The answer to this question can be found on slides 26 - 31

Possible sources of interferences in FAAS include: **Ionization** - prevent by use of an ionization suppressor or buffer; **Chemical** - the formation of stable complexes e.g. calcium + phosphate. Remedies include use of a hotter flame or addition of a releasing agent or protective chelating agent; **Spectral** line overlap – in the case of atomic line interferences the solution is to choose another wavelength for the analysis. In the case of molecular band interferences use a background correction technique.

The calcium absorbance value in the presence of increasing amounts of phosphate ion would decrease due to the formation of a stable complex species between the calcium ions and the anion, which resists decompositon in an air-acetylene flame. This interference may be identified by the method of standard additions, involving the addition of known amounts of a stock solution of the analyte element to portions of the sample solution. To alleviate this problem either use a hotter flame (e.g. N_20- C_2H_2) or add a protective chelating agent (e.g. EDTA) to the solution prior to analysis.

Outline answer to question 12.2(e)

The answer to this question can be found on slides 18

A graphite furnace atomizer (also known as electrothermal atomizer) can be used to replace the flame burner in AAS. It consists of a graphite tube in to which are placed small quantities (5 – 50 µL) of (normally) aqueous sample and standards. The aqueous sample and standards are heated through a cycle as follows: 1 = **drying** (typically 105^{o}C for 40 s to allow removal of water); 2 = **ashing** (typically 1500^{o}C for 20 s to allow removal of the sample matrix, but not the element of interest); 3 = **atomisation** (typically 2200^{o}C for 2 s. This is the time when the signal absorbance is measured); 4 = **cleaning** (typically 2300^{o}C for 3 s to allow removal of any residual sample); and, 5 = **cooling** (typically 40 s to allow the graphite tube to cool in readiness for the next sample).

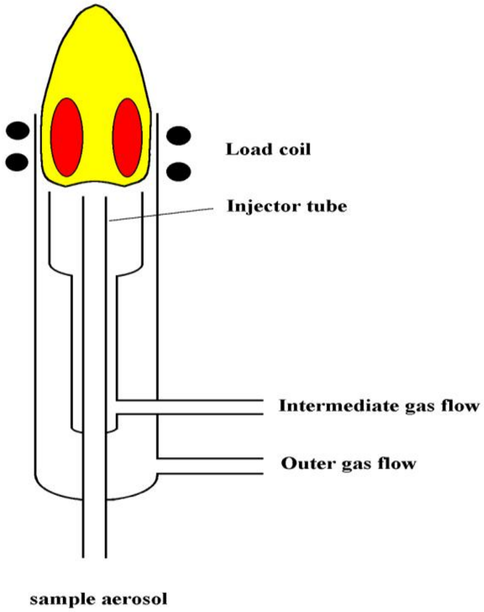
Matrix modification is required in GFAAS to allow premature atomization that occurs when a “volatile” element is analysed e.g. when analysing the volatile element selenium it is necessary to add excess nickel (as a matrix modifier). This allows formation of a ‘nickel selenide’ complex that is stable enough to remain on the graphite surface until the atomization stage when selenium atoms will be released.

Outline answer to question 12.3(a)

The answer to this question can be found on slides 36 - 38

The ICP torch operates at a frequency of either 27 or 40 MHz with an input power of 0.5-1.5 kW. The plasma is located within the confines of a torch, situated within the load coil, and consisting of three concentric quartz tubes in a tangentially flowing outer or coolant gas (12 L/min) which prevents the outer quartz tube from melting; a tangentially flowing intermediate gas (0.5 L/min) to sustain the plasma; and, a laminarly flowing injector gas (1.0 mL/min) by means of which the sample is introduced into the plasma. The typical viewing height above load coil is 10-15 mm.

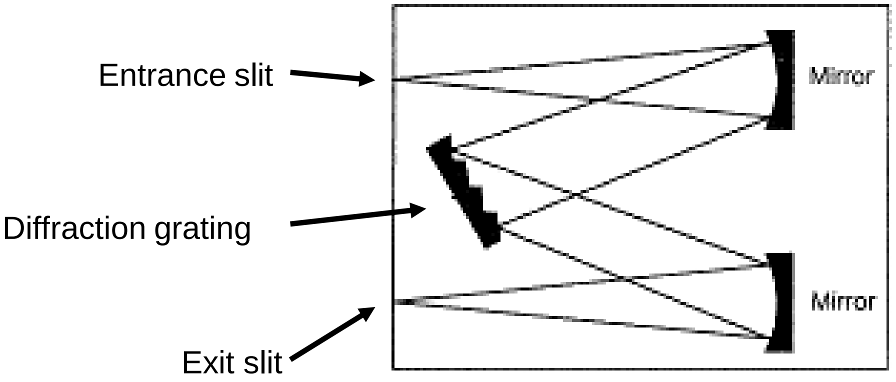
The plasma is formed by ‘seeding’ the flowing argon gas with free electrons from an external source i.e. a high voltage spark or ***Tesla discharge***. A magnetic field, formed by the high frequency current flowing in the load coil, generates oscillating magnetic fields. This induced axial oscillating magnetic field interacts with the free electrons from the Tesla discharge causing them to be accelerated as they flow in closed annular paths, inside the quartz plasma torch. These accelerated electrons meet resistance to their flow causing Joule or Ohmic heating which leads to ionization of the argon gas. As this entire process takes place in a very short time scale (milliseconds) a plasma is formed within the torch almost instantaneously.



Outline answer to question 12.3(b)

The answer to this question can be found on slides 46/7

In sequential ICP atomic emission spectroscopy the light emitted from the sample is measured at one wavelength at a time, each wavelength being appropriate for a particular element of interest. A typical optical arrangement for a sequential spectrometer (monochromator) is based on the Czerny-Turner configuration. The spectrometer consists of entrance and exit optics, a diffraction grating and a single detector. This type of spectrometer provides flexibility in terms of wavelength coverage e.g. from Al at 167 nm to Cs at 852 nm. Selection of the desired wavelength (and hence specific element) is achieved by computer-controlled rotation of the grating within its spectrometer mounting.



Entrance slit

Diffraction grating

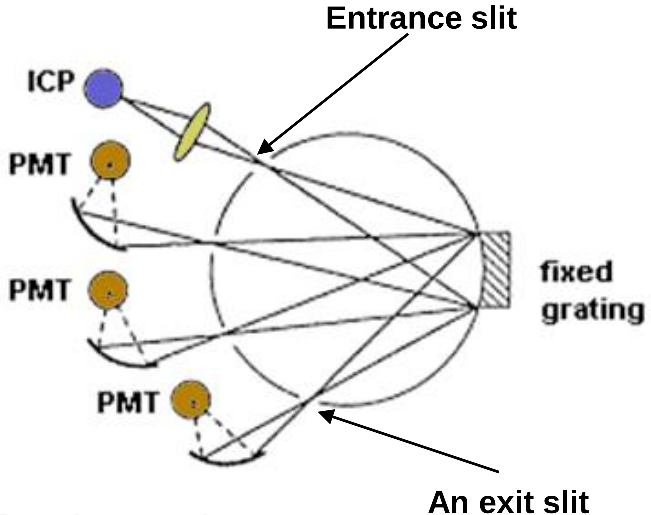
Exit slit

Outline answer to question 12.3(c)

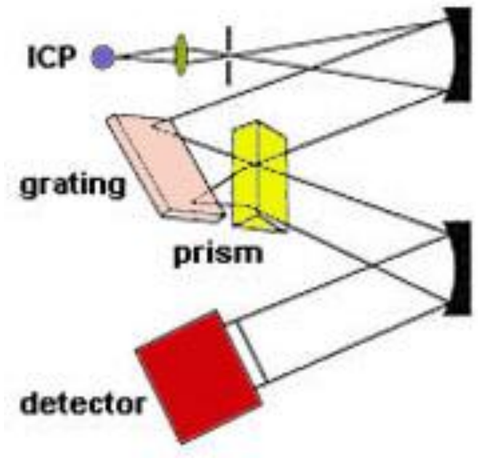
The answer to this question can be found on slides 48/9

Both an Echelle spectrometer and a conventional polychromator spectrometer offer the ability for simultaneous multi-element analysis. The mode of operation of the Echelle spectrometer allows (a) higher resolution to be achieved by a combination of the number of grooves (lines) ruled on the grating and spectral order and (b) flexibility in the choice of element wavelength.

A polychromator spectrometer



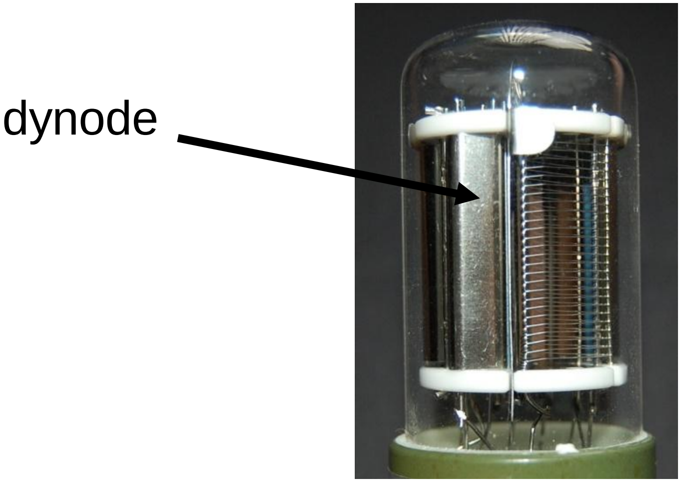
An Echelle spectrometer



Outline answer to question 12.3(d)

The answer to this question can be found on slides 23/4

A photomultiplier tube (or PMT) allows incident light to be converted in to an electric signal. By a process called the ‘photoelectric effect’ a photon of light is converted to an electron. The generated electron is then focused on to a dynode. As one electron hits the first dynode, it generates two electrons. The generated two electrons then hit the next dynode producing 4 electrons and so on. At the end all the generated electrons are collected at an anode and converted to a measurable electric current. The PMT is located behind the exit slit of the spectrometer.



A photograph of a side window photomultiplier tube

Outline answer to question 12.4(a)

The answer to this question can be found on slides 72/3, 77/8, 87 -89

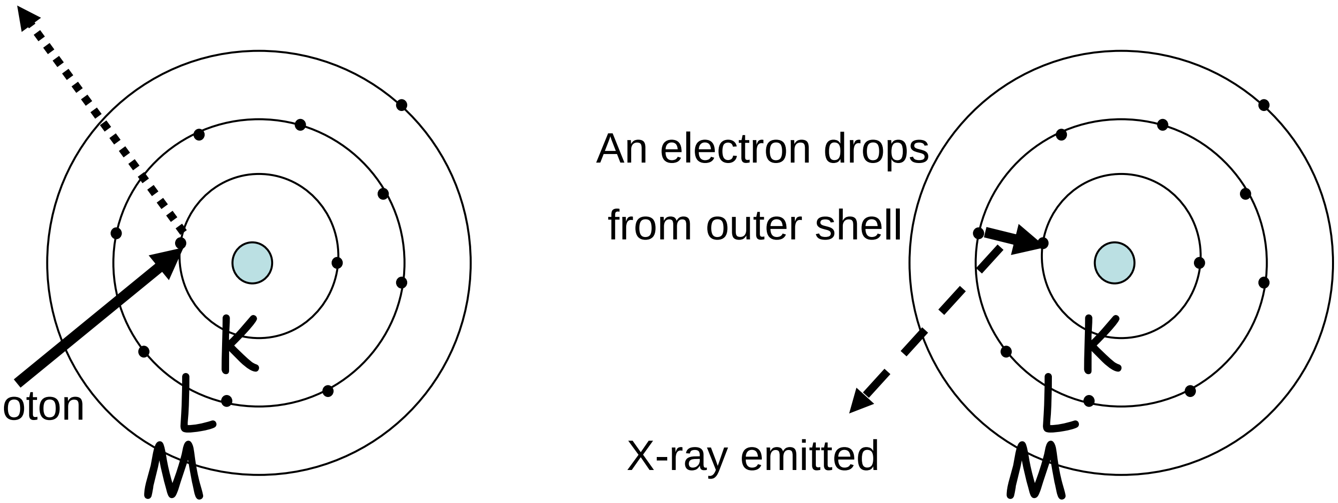
It is important that the sample taken is representative of the whole. The surface of the bulk solid may have been subject to oxidation or weathering effects and therefore the surface will have a different composition to the bulk. It is therefore important to sample a core from the bulk to ensure that the sample taken is representative of the whole.

Two methods for preparing a solid sample for XRF are: (1) make a fused bead (cast or pressed into a disc) with a flux (1:5 to 1:10, w/w) using either tetraborate ($Na_2B_4O_7$ or $Li_2B_4O_7$) or potassium pyrophosphate ($K_2P_2O_7$) or (2) grind the sample to a homogeneous powder then press into a pellet to make the smoothest surface. A pressed pellet is prepared by mixing the fine powder sample (4.0 g, accurately weighed) with polystyrene co-polymer binder (0.9 g) and then pressing the resultant mixture under a pressure of 12 tons for 1 minute to produce a smooth surfaced disc or pellet.

Outline answer to question 12.4(b)

The answer to this question can be found on slides 73 -76

An atom can be described as consisting of shells of electrons i.e. K, L, M, N etc. If a high speed X-ray photon, from the X-ray source, hits a sample atom and has sufficient energy it will dislodge an electron from one of the shells e.g. K shell. This results in a "hole" being produced making the atom an unstable ion. Within 10^{-4} s, an electron from an outer shell drops into the hole. This transition causes the emission of a characteristic X-ray (i.e. a photon of definite wavelength). Transitions of electrons to the K shell are identified as Kα, Kβ, Kγ for L$\rightarrow$K, M $\rightarrow$L, N $\rightarrow$M, respectively.



Ejected photoelectron

high speed X-ray photon

An electron drops

from outer shell

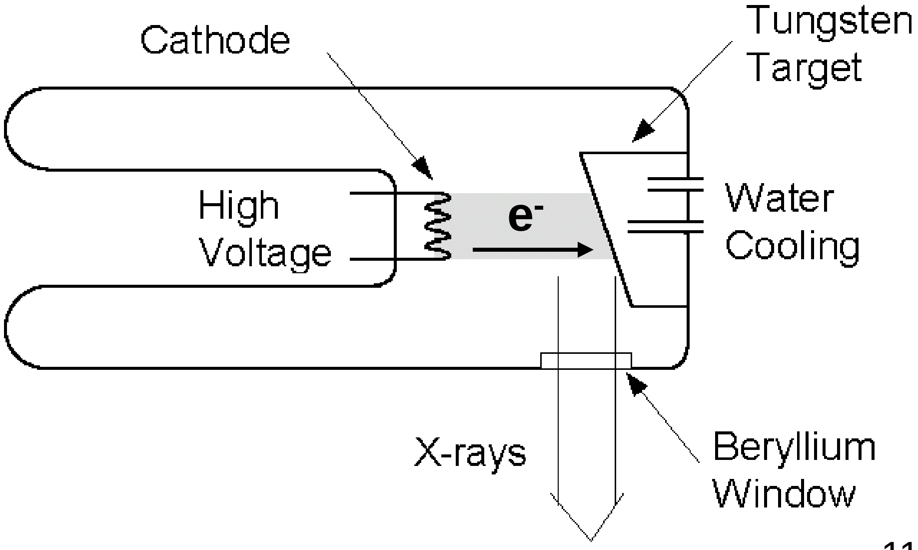
X-ray emitted

Outline answer to question 12.4(c)

The answer to this question can be found on slides 75

The X-ray tube is energised by a high-voltage power supply (0.5 to 50 kV). The vacuum tube consists of a tungsten (or chromium) **target** (the anode – which is electrically positive). As accelerated electrons, from the cathode (the electrically negative terminal), strike the target X-rays are produced. The generated X-rays exit the tube via a Beryllium window. If the **target** used is tungsten (atomic number of 74) then it is used to excite the K and L lines of elements with higher atomic numbers. For lighter elements the **target** is chromium (atomic number of 24) which is used to excite elements of lower atomic number.

A side-window X-ray tube

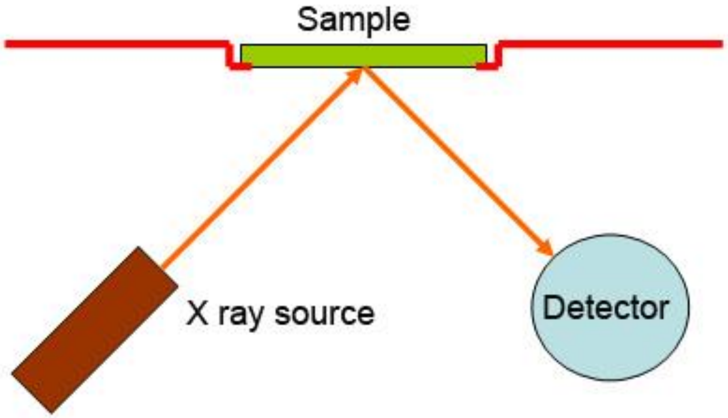


Outline answer to question 12.4(d)

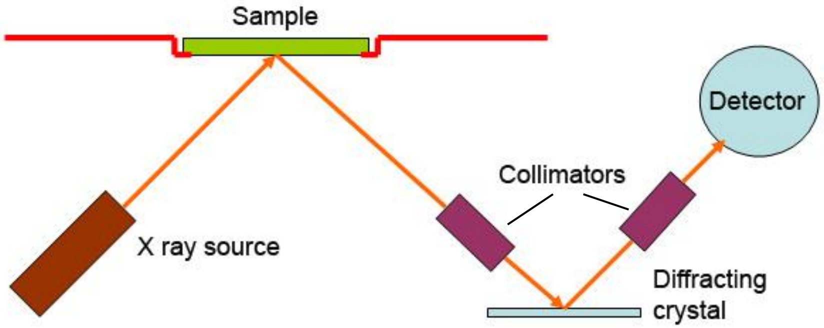
The answer to this question can be found on slides 79 & 80

In wavelength-dispersive XRF or WD-XRF the emitted X-rays from the sample are angularly dispersed by a diffracting crystal on the basis of wavelength. The detector receives only one wavelength at a time: either single channel (sequential) or multi channel (simultaneous). Whereas in energy-dispersive XRF or ED-XRF the energy of all X-rays are measured simultaneously using a solid-state semiconductor detector (Si(Li) detector). The detector registers an electric current having a height proportional to the photon energy. These pulses are then separated electronically, using a pulse analyser (counting time typically between 100-10,000 s).

An ED-XRF instrument



An WD-XRF instrument



Outline answer to question 12.4(e)

The answer to this question can be found on slides 84 - 86

Absorption-enhancement effects occur in three ways: matrix (inter-element) effects, spectral coincidence or environmental effects. **Matrix interferences** can result in absorption or enhancement effects. In absorption, any element can absorb or scatter the fluorescence of the element of interest whereas in enhancement, characteristic X-rays of one element can excite another element in the same sample resulting in signal enhancement. These matrix interferences can be mathematically corrected by the use of influence coefficients, or alpha corrections. **Spectral interferences** are peaks in the spectrum that overlap with the spectral peak of the element to be analyzed. Examples include K and L line overlap for sulphur and molybdenum, chlorine and rhodium, and arsenic and lead. In these situations it is the resolution of the detector that determines the extent of the overlap. In **Environmental interferences** lighter elements, such as those between sodium and chlorine in the Periodic Table emit weak X-rays, whose signal can be reduced by air. The remedy is to (a) purge the instrument with an inert gas e.g. helium, thereby removing the air. As helium is less dense than air, it results in less attenuation of the signal, or (b) evacuate air from the sample chamber via a vacuum pump.

Outline answer to question 12.4(f)

The answer to this question can be found on slides 87/8

Approaches for quantitative analysis include:

Standard Calibration Method: The analyte-line intensity from samples is compared with that from standards having the same form and the same matrix as the samples.

Standard Addition Method: The element concentration is altered quantitatively in the sample itself. The sample is subjected to one or more quantitative incremental concentrations or dilutions of the element. The intensity of the element lines is measured for effectively the same matrix in each case.

Outline answer to question 12.5(a)

(i) The dilution factor is calculated as follows:

$$(100\ \text{cm}^3 / 0.5120\ \text{g}) \times (100\ \text{cm}^3 / 10\ \text{cm}^3) = 1953.1\ \text{cm}^3/\text{g}$$

(ii) As the concentration of an element in the solution is determined as 8.6 µg/cm^3 the concentration of the element in the original soil sample is calculated as follows:

Dilution factor multiplied by the element concentration in the solution i.e.

$$(1953.1\ \text{cm}^3/\ \text{g}) \times (8.6\ \mu\text{g} / \text{cm}^3) = 16{,}797\ \mu\text{g} / \text{g}$$

Or 16,797 µg g^{-1} or in the specified units **16,797 mg kg^{-1}**.

Outline answer to question 12.5(b)

Guidance on the answer to this question can be found on slides 34/5 & in Chapter 15 of this teaching & learning programme.

The analysis of caesium (Cs) in an industrial sample will require the following to be considered:

- How to digest the sample? Digestion of the sample can be done by heating an accurately known quantity in concentrated mineral acids e.g. HCl-HNO_3 (3:1, v/v).

- What calibration range is appropriate for analysis of Cs by FAAS? A calibration over a typical working range of 0.8 $\mu g/cm^3$ to 10 $\mu g/cm^3$ would seem to be appropriate. (0.8 $\mu g/cm^3$ selected as the lowest concentration as this is the quoted detection limit of Cs).

- Potential interferences are identified: an ionization interference, from sodium ions, requires correction by addition of excess Na+ to all standards; a chemical interference due to the presence of PO_4^{3-} can be eliminated by addition of a releasing agent such as EDTA (if an air- acetylene flame is used).

- Validation requires the use of the method of standard additions, involving spiking the sample solution with various amounts of added Cs stock solution, and deriving the sample concentration from the extrapolated calibration graph, and, if possible, the incorporation of an appropriate certified reference material (CRM) within the sample run procedure.

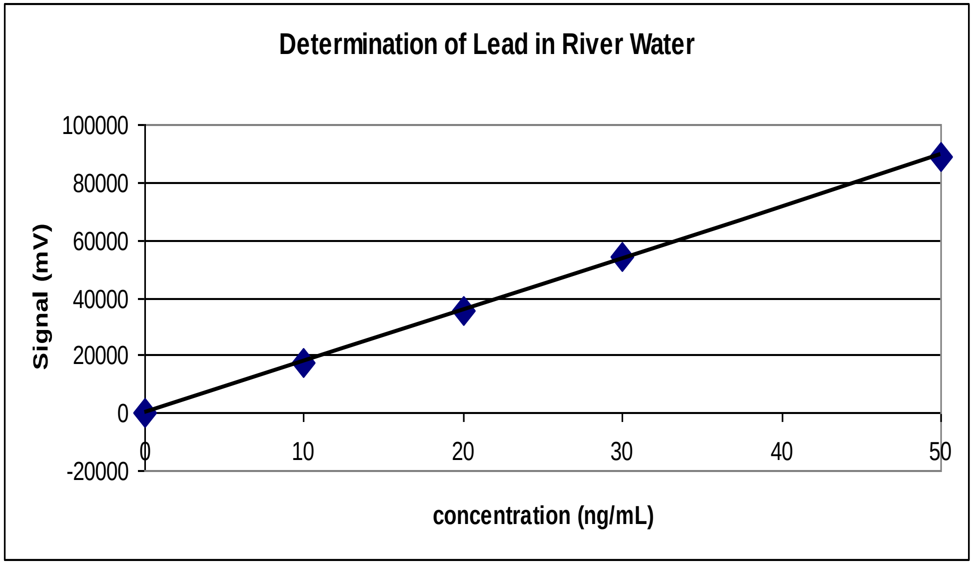
Outline answer to question 12.5(c)

Firstly it is necessary to calculate the concentration of each element (Pb, Cu and Fe) in the 100 mL volumetric flasks.

For example, what is the concentration of Fe if 30 mL of the stock solution (200 ng mL^{-1}) is quantitatively transferred to the 100 mL volumetric flask and making up to volume with ultrapure water.

Concentration of Fe is: (200 ng/cm^3) x (30 cm^3/100 cm^3) = 60 ng/cm^3.

Using this process all metal concentrations can be determined. Then, plot calibration graphs for each element against signal (mV) using Excel.



Using the derived equation:

$$Y = (1788.4\,x) - 30.5$$

It is possible to determine the Pb concentration in the river water sample as:

$$(24567 + 30.5) / 1788.4 = x$$

X = 13.8 ng/cm^3 Pb

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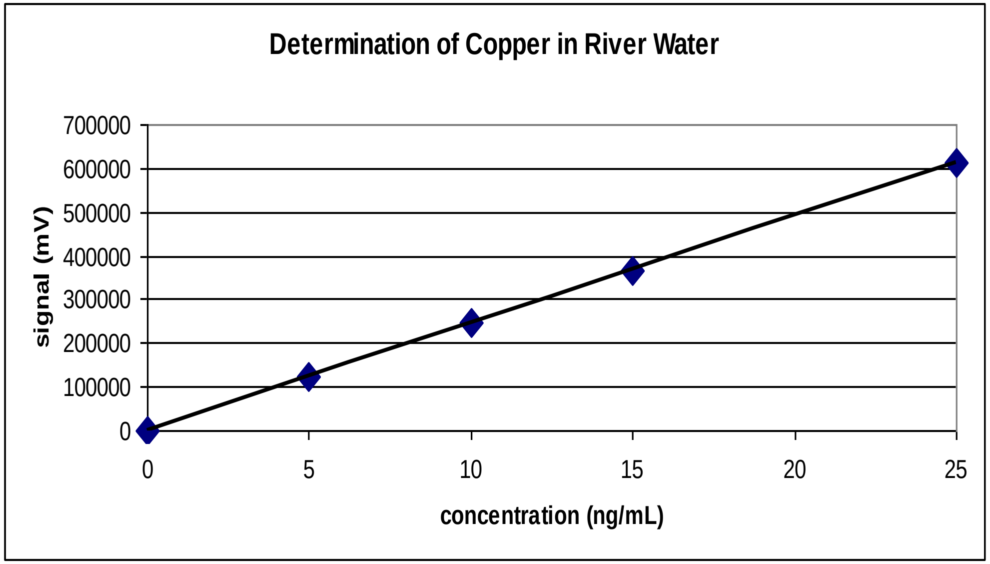


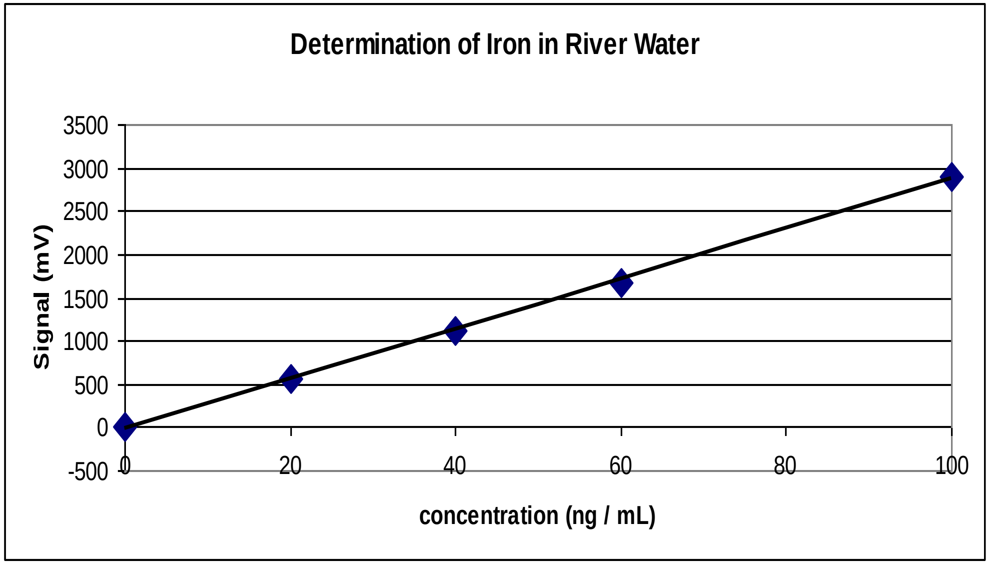
Using the derived equation:

$$Y = (24507\ x) + 562.7$$

It is possible to determine the Cu concentration in the river water sample as:

$$(534563 – 562.7) / 24507 = x$$

X = 21.8 ng/cm^3 Cu



Using the derived equation:

$$Y = (28.9\ x) – 17.6$$

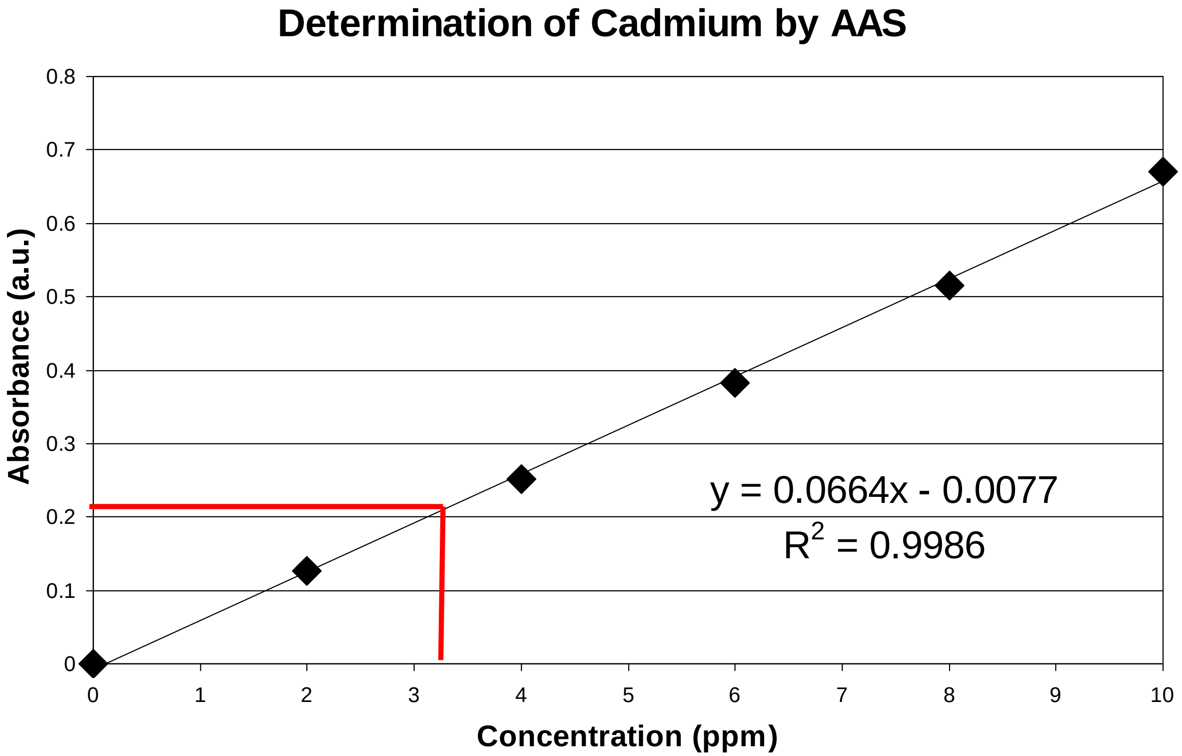
It is possible to determine the Fe concentration in the river water sample as:

$$(1364 + 17.6) / 28.9 = x$$

X = 47.8 ng/cm^3 Fe

Outline answer to question 12.6

Firstly, plot the calibration graph based on the averages of the three absorbance's obtained for each calibration standard. Calculate the concentration of the unknown by either reading off the graph or using the calculated equation for a straight line.



Value obtained from graph is 3.35 ppm or 3.35 µg/cm^3.

The dilution factor is calculated as 100 cm^3 / 1.0556 g = 94.73 cm^3 / g

Therefore the concentration of Cd in the river sediment is **317.3 µg /g.**

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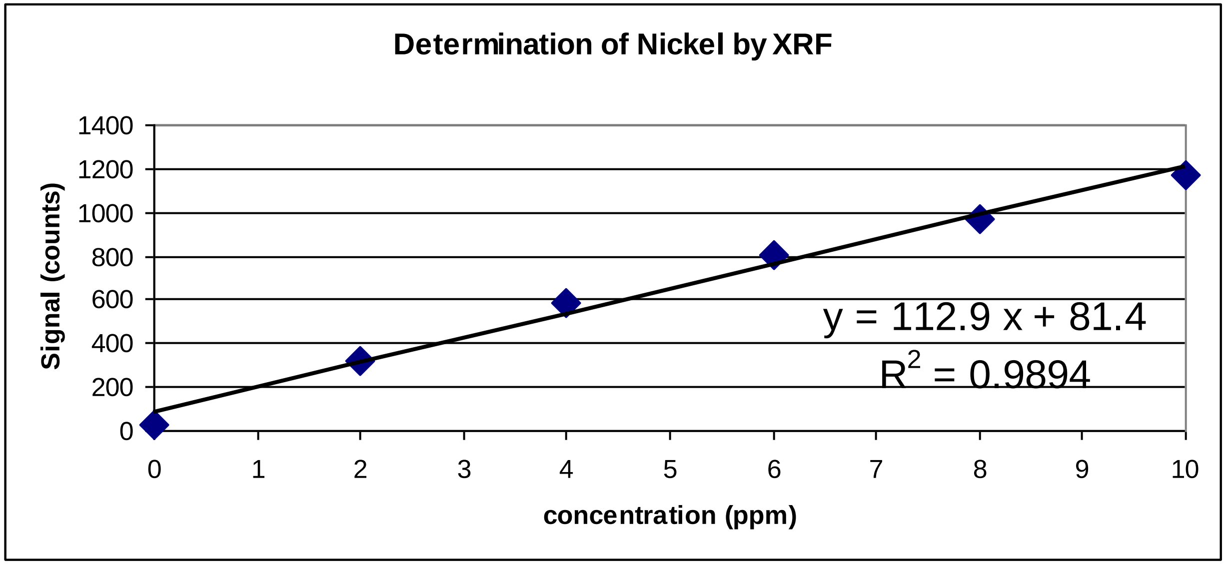
It is not possible to make any comment on the accuracy of this data since there is no information provided of “real values” or recoveries from certified reference materials. However, it is possible to calculate an average and percentage relative standard deviation for each calibration standard and the unknown.

concentration (ppm)	**Absorbance**				
	Run 1	**Run 2**	**Run 3**	**Average**	**%RSD**
0	0	0	0	0	0
2	0.127	0.124	0.130	0.127	1.93
4	0.250	0.251	0.253	0.251	0.50
6	0.382	0.379	0.384	0.382	0.54
8	0.513	0.515	0.520	0.516	0.57
10	0.698	0.700	0.701	0.700	0.18
Unknown	0.217	0.215	0.212	0.215	0.96

From the %RSD values it is possible to see that in all cases the value is below 2%. This indicates a very high precision.

Outline answer to question 12.7

Firstly, plot the calibration graph for each element based on the signals obtained for each calibration standard. Calculate the concentration of each unknown by using the calculated equation for a straight line.



Using the derived equation: Y = (112.9 x) + 81.4 it is possible to determine the Ni concentration in the sample as: (434 – 81.4) / 112.9 = x; x = **3.12 ppm Ni.**

Value obtained from graph is 3.12 ppm or 3.12 µg/cm^3. The dilution factor is calculated as 100 cm^3/0.5465 g = 183.0 cm^3/g. Therefore the concentration of Ni in the solid sample is **571 µg /g.**

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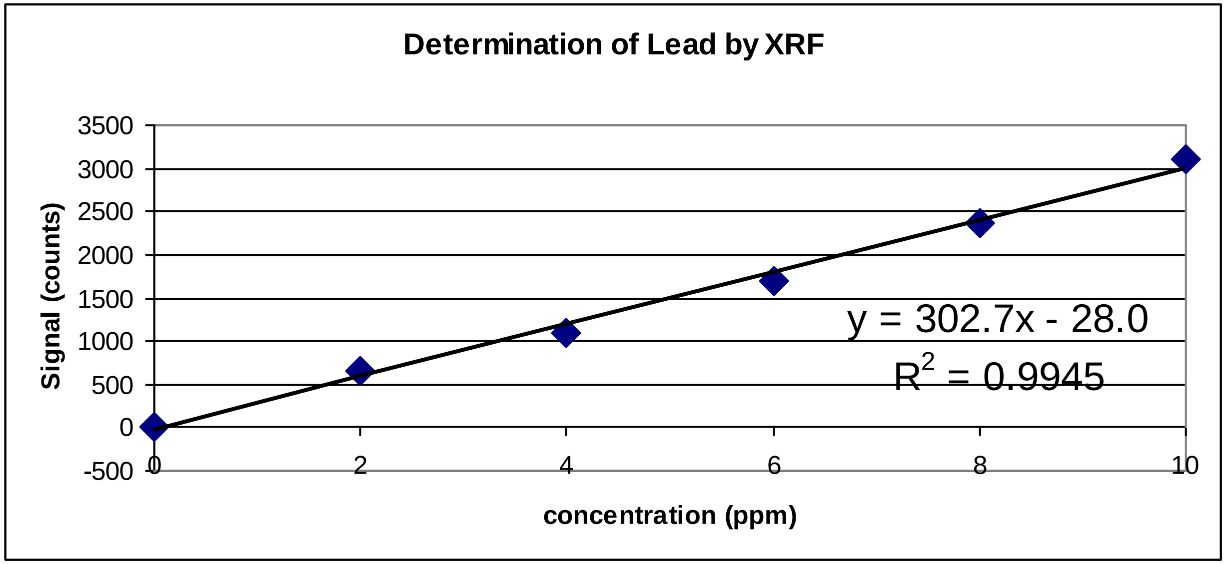

Using the derived equation: Y = (302.7 x) – 28.0 it is possible to determine the Pb concentration in the sample as: (1557 + 28.0) / 302.7 = x; x = **5.24 ppm Pb.**

Value obtained from graph is 5.24 ppm or 5.24 µg/cm^3. The dilution factor is calculated as 100 cm^3/ 0.5465 g = 183.0 cm^3/g. Therefore the concentration of Pb in the solid sample is **959 µg /g.**