INSTRUMENTAL METHODS OF ANALYSIS

ATOMIC ABSORPTION SPECTROSCOPY

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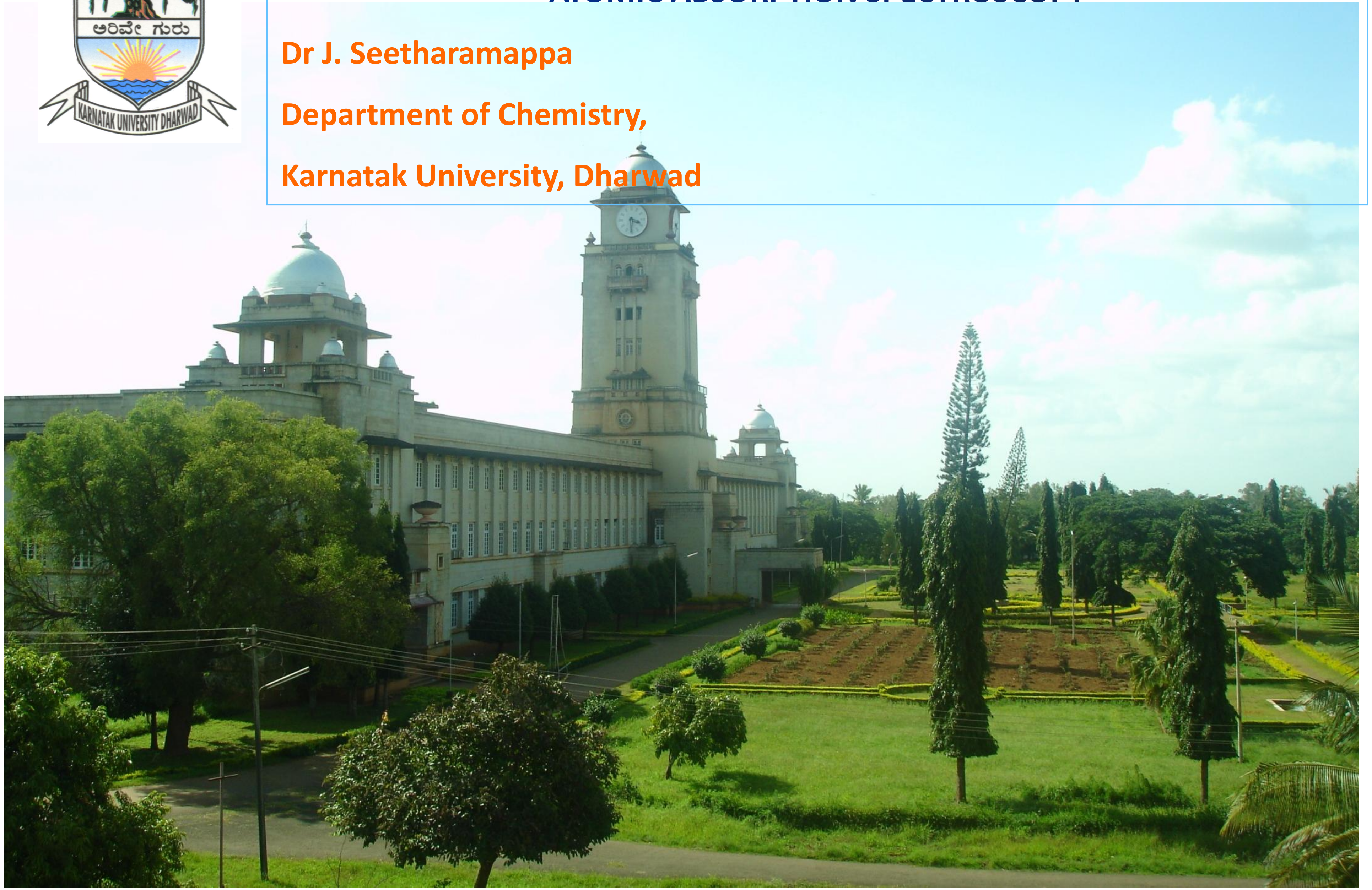


Main analytical tecniques used to determine heavy metals in environmental matrices are:

Atomic Absorption Spectrometry (AAS)

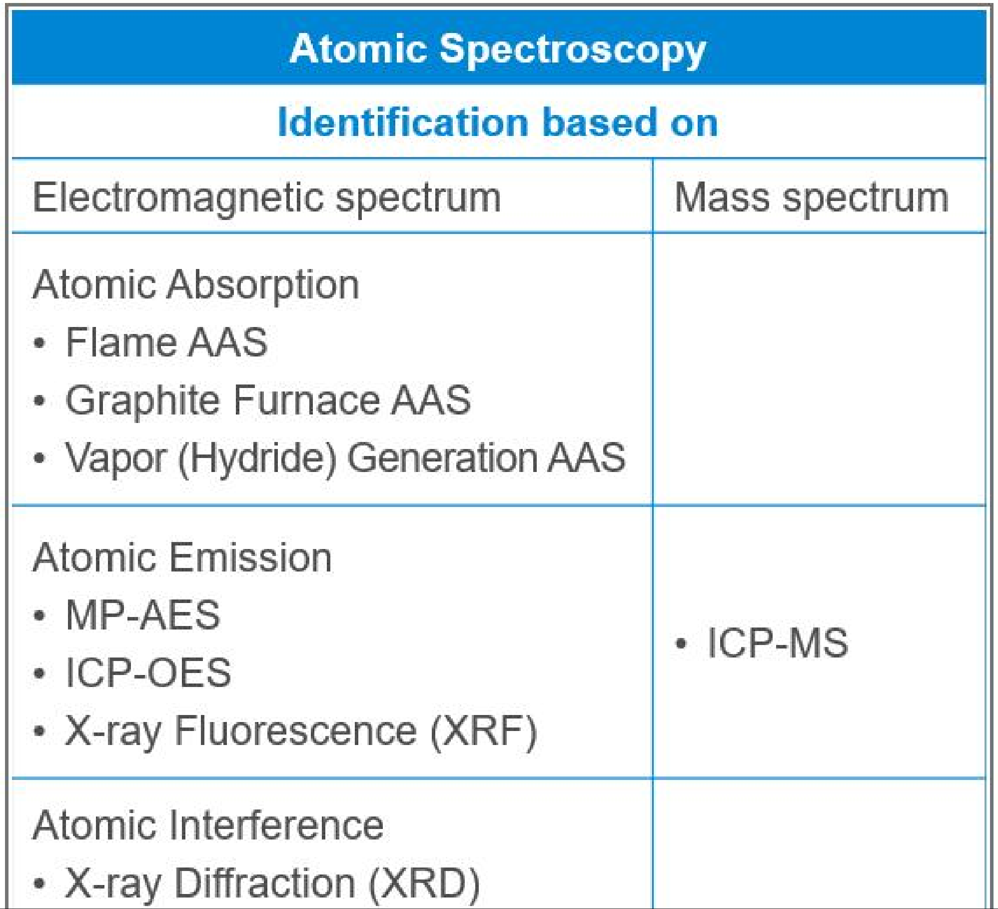
Inductively Coupled Plasma Atomic Emission Spectrometry (ICP/AES)

Inductively Coupled Plasma Mass Spectrometry (ICP/MS)

Neutron Activation Analysis (NAA)

X-ray fluorescence (XRF)

Ion Chromatography (IC)



Atomic Spectroscopy

Identification based on

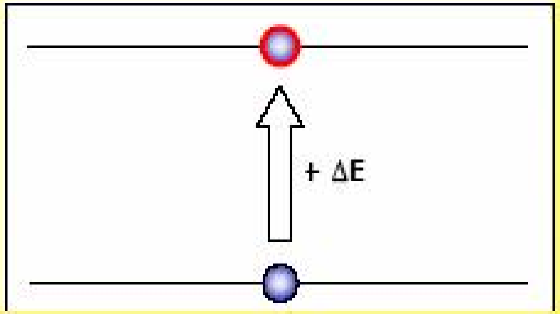
Electromagnetic spectrum	Mass spectrum
Atomic Absorption • Flame AAS • Graphite Furnace AAS • Vapor (Hydride) Generation AAS	
Atomic Emission • MP-AES • ICP-OES • X-ray Fluorescence (XRF)	• ICP-MS
Atomic Interference • X-ray Diffraction (XRD)	

References:

1. Instrumental Analysis-Douglas A Skoog, F. James Holler & S.R. Crouch Cengage Learning(5th Indian Reprint, 2010).

2. Vogel’s Text book of Quantitative Chemical Analysis- J. Mendham, R.C. Denney, J. D. Barnes &M. J. K. Thomas, 6th Edition, Pearson Education,2007.

Atomic Absorption Spectrometry (AAS) is an analytical technique that measures the concentrations of elements. Atomic absorption spectroscopy can be used to analyze the concentration of over 62 different metals in a solution and is so sensitive that it can measure down to parts per billion of a gram (ug/dm^{-3}) in a sample. The technique makes use of the wavelengths of light specifically absorbed by an element. They correspond to the energies needed to promote electrons from one energy level to another, higher, energy level.

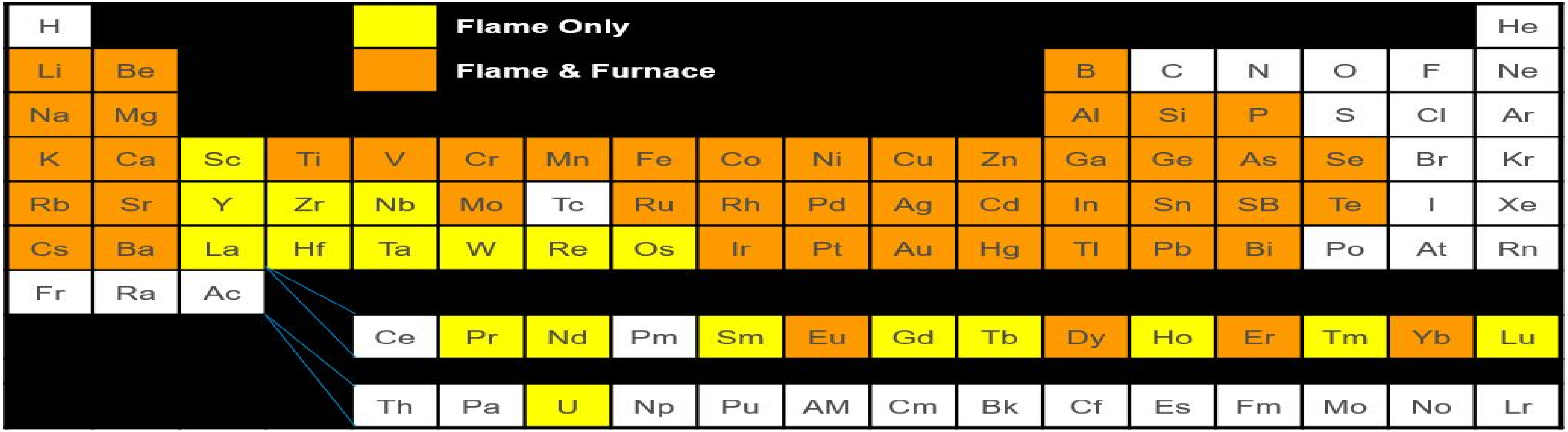


ABSORPTION

$E=h\nu=hc/\lambda$

Atomic Absorption Spectroscopy

Elemental Coverage in AAS



🟨 Flame Only

🟧 Flame & Furnace

H																	He
🟧 Li	🟧 Be											🟧 B	C	N	O	F	Ne
🟧 Na	🟧 Mg											🟧 Al	🟧 Si	🟧 P	S	Cl	Ar
🟧 K	🟧 Ca	🟨 Sc	🟧 Ti	🟧 V	🟧 Cr	🟧 Mn	🟧 Fe	🟧 Co	🟧 Ni	🟧 Cu	🟧 Zn	🟧 Ga	🟧 Ge	🟧 As	🟧 Se	Br	Kr
🟧 Rb	🟧 Sr	🟨 Y	🟨 Zr	🟨 Nb	🟧 Mo	Tc	🟧 Ru	🟧 Rh	🟧 Pd	🟧 Ag	🟧 Cd	🟧 In	🟧 Sn	🟧 SB	🟧 Te	I	Xe
🟧 Cs	🟧 Ba	🟨 La	🟨 Hf	🟨 Ta	🟨 W	🟨 Re	🟨 Os	🟧 Ir	🟧 Pt	🟧 Au	🟧 Hg	🟧 Tl	🟧 Pb	🟧 Bi	Po	At	Rn
Fr	Ra	Ac															
				Ce	🟨 Pr	🟨 Nd	Pm	🟨 Sm	🟧 Eu	🟨 Gd	🟨 Tb	🟧 Dy	🟨 Ho	🟧 Er	🟨 Tm	🟧 Yb	🟨 Lu
				Th	Pa	🟨 U	Np	Pu	AM	Cm	Bk	Cf	Es	Fm	Mo	No	Lr

PRINCIPLE: The sample solution is aspirated into a flame and the analyte element is converted to atomic vapor. The flame then contains atoms of that element. Some are thermally excited by the flame, but most remain in the ground state. These ground-state atoms can absorb radiation emitted by the source that is deliberately composed of that element so its characteristic lines are emitted.

Atomic absorption spectrophotometry is identical in principle to absorption spectrophotometry. The absorption follows Beer’s law. That is, the absorbance is directly proportional to the pathlength in the flame and to the concentration of atomic vapor in the flame.

Atomization Methods

To obtain both atomic optical and atomic mass spectra, the constituents of a sample must be converted to gaseous atoms or ions, which can then be determined by emission, absorption, fluorescence, or mass spectral measurements. The precision and accuracy of atomic spectrometric methods depend critically on the atomization step and the method of introduction of the sample into the atomization region. The common types of atomizers are listed in Table 8-1

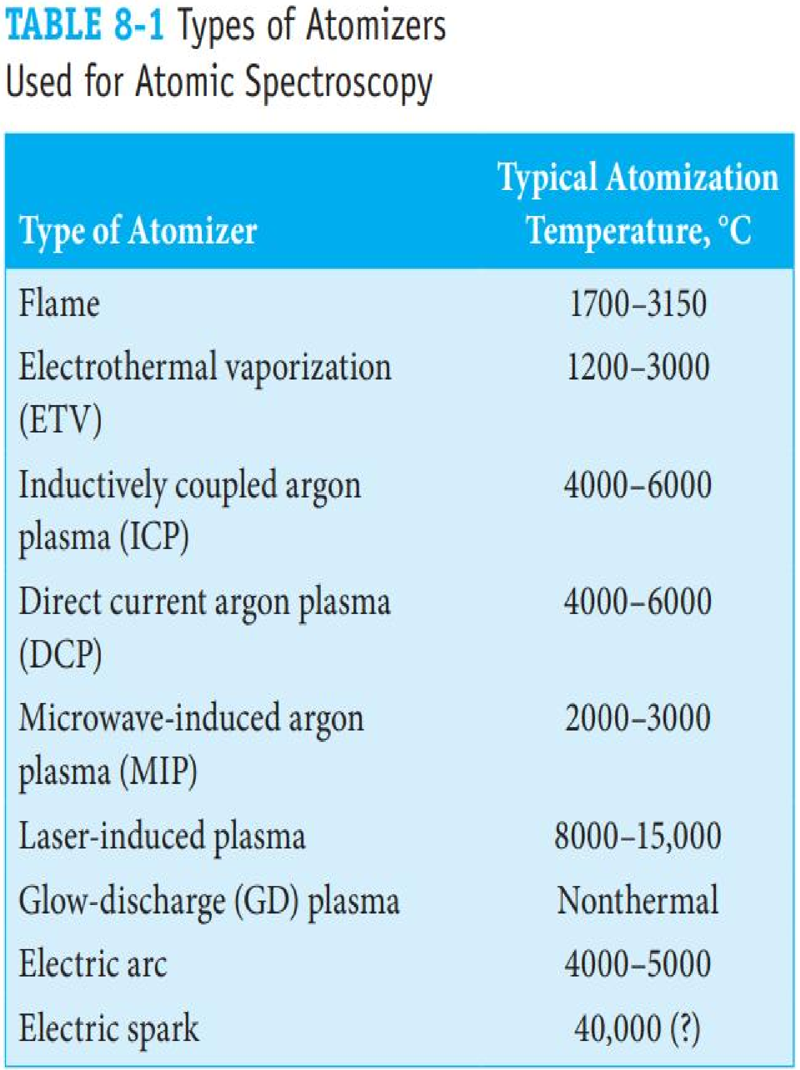
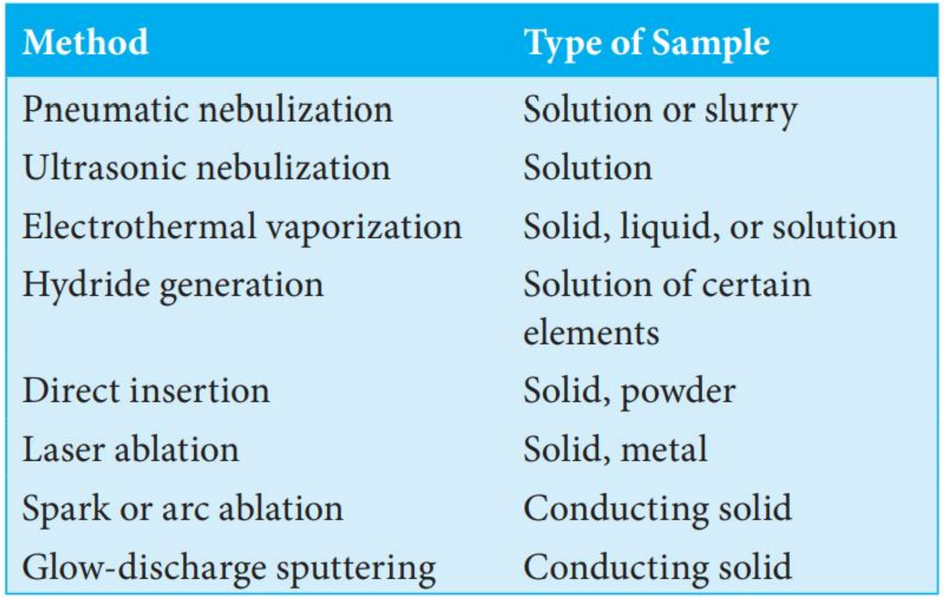


TABLE 8-1 Types of Atomizers Used for Atomic Spectroscopy

Type of Atomizer	Typical Atomization Temperature, °C
Flame	1700–3150
Electrothermal vaporization (ETV)	1200–3000
Inductively coupled argon plasma (ICP)	4000–6000
Direct current argon plasma (DCP)	4000–6000
Microwave-induced argon plasma (MIP)	2000–3000
Laser-induced plasma	8000–15,000
Glow-discharge (GD) plasma	Nonthermal
Electric arc	4000–5000
Electric spark	40,000 (?)

Introduction of Solution Samples

General methods to introduce solution samples into plasmas and flames include nebulization. Direct nebulization is most often used. In this case, the nebulizer constantly introduces the sample in the form of a fine spray of droplets, called an aerosol. Continuous sample introduction into a flame or plasma produces a steady-state population of atoms, molecules, and ions. Solutions are generally introduced into the atomizer by one of the first three methods listed in Table 8-2



Method	Type of Sample
Pneumatic nebulization	Solution or slurry
Ultrasonic nebulization	Solution
Electrothermal vaporization	Solid, liquid, or solution
Hydride generation	Solution of certain elements
Direct insertion	Solid, powder
Laser ablation	Solid, metal
Spark or arc ablation	Conducting solid
Glow-discharge sputtering	Conducting solid

Pneumatic Nebulizers

The most common kind of nebulizer is the concentric tube pneumatic type, shown in Fig.8-11a, in which the liquid sample is drawn through a capillary tube by a high-pressure stream of gas flowing around the tip of the tube (the Bernoulli effect). This process of liquid transport is called aspiration. The high-velocity gas breaks up the liquid into droplets of various sizes, which are then carried into the atomizer.

Cross-flow nebulizers,in which the high pressure gas flows across a capillary tip at right angles, are illustrated in Fig. 8-11b.

Fig. 8-11c is a schematic of a fritted-disk nebulizer in which the sample solution is pumped onto a fritted surface through which a carrier gas flows. This type of nebulizer produces a much finer aerosol than do the first two.

Fig.8-11d shows a Babington nebulizer, which consists of a hollow sphere in which a high-pressure gas is pumped through a small orifice in the sphere's surface. The expanding jet of gas nebulizes the liquid sample flowing in a thin film over the surface of the sphere. This type of nebulizer is less subject to clogging than other devices, and it is therefore useful for samples that have a high salt content or for slurries with a significant particulate content.

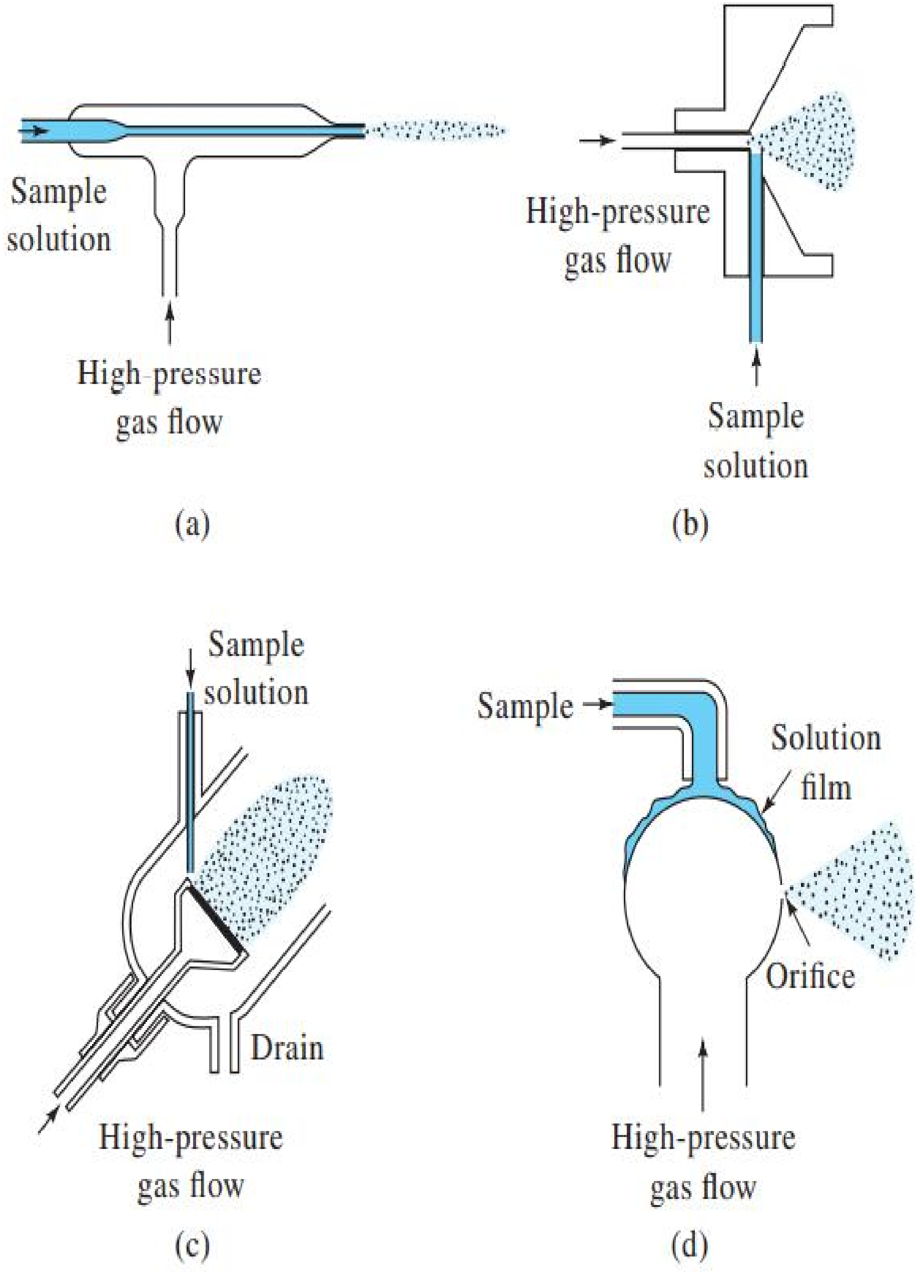
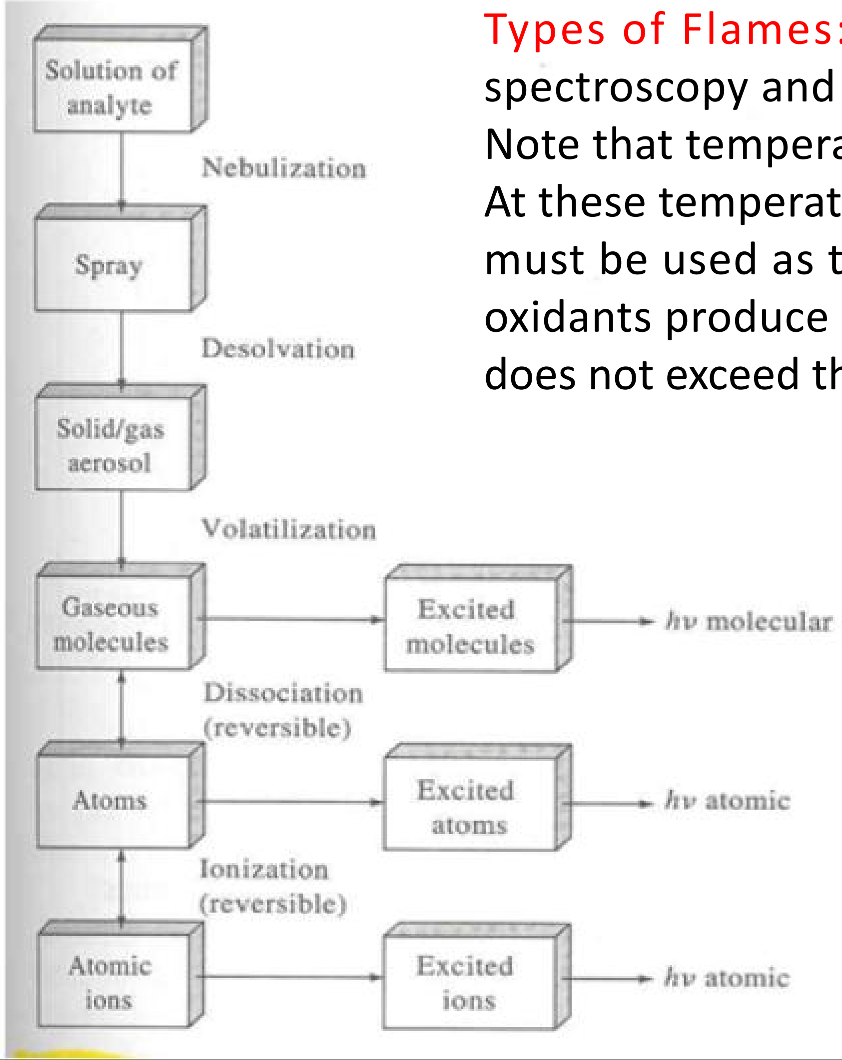


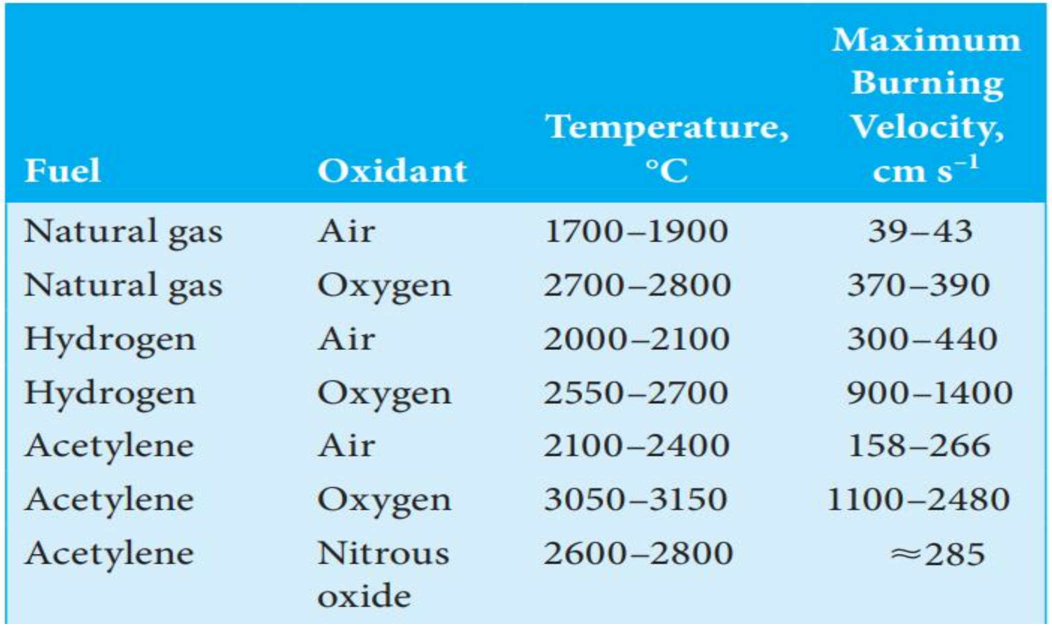
FIGURE 8-11 Types of pneumatic nebulizers: (a) concentric tube, (b) cross-flow, (c) fritted disk, (d) Babington.

Flame Atomization

Atomization is the process that converts a liquid sample into free atoms.In a flame atomizer, a solution of the sample is nebulized by a flow of gaseous oxidant, mixed with a gaseous fuel, and carried into a flame where atomization occurs. The first step is desolvation, in which the solvent evaporates to produce a finely divided solid molecular aerosol. The aerosol is then volatilized to form gaseous molecules. Dissociation of most of these molecules produces an atomic gas. Some of the atoms in the gas ionize to form cations and electrons.



Types of Flames: Table shown below lists the common fuels and oxidants used in flame spectroscopy and the approximate range of temperatures realized with each of these mixtures. Note that temperatures of 1700°C to 2400°C occur with the various fuels when air is the oxidant. At these temperatures, only easily decomposed samples are atomized, so oxygen or nitrous oxide must be used as the oxidant for more difficult to atomize samples (refractory samples). These oxidants produce temperatures of 2500°C to 3100°C with the common fuels. If the gas flow rate does not exceed the burning velocity, the flame propagates back into the burner, giving flashback.



Fuel	Oxidant	Temperature, °C	Maximum Burning Velocity, cm s^{-1}
Natural gas	Air	1700–1900	39–43
Natural gas	Oxygen	2700–2800	370–390
Hydrogen	Air	2000–2100	300–440
Hydrogen	Oxygen	2550–2700	900–1400
Acetylene	Air	2100–2400	158–266
Acetylene	Oxygen	3050–3150	1100–2480
Acetylene	Nitrous oxide	2600–2800	≈285

Flame atomizers are used for atomic absorption, fluorescence, and emission spectroscopy. Figure 9-5 is a diagram of a typical commercial laminar-flow burner that uses a concentric-tube nebulizer, similar to that shown in Figure 8-11a. The aerosol, formed by the flow of oxidant, is mixed with fuel and passes a series of baffles that remove all but the finest solution droplets. The baffles cause most of the sample to collect in the bottom of the mixing chamber where it drains to a waste container. The aerosol, oxidant, and fuel are then burned in a slotted burner to provide a 5- to 10-cm high flame. Laminar-flow burners produce a relatively quiet flame and a long path length for maximizing absorption. These properties tend to enhance sensitivity and reproducibility in AAS.

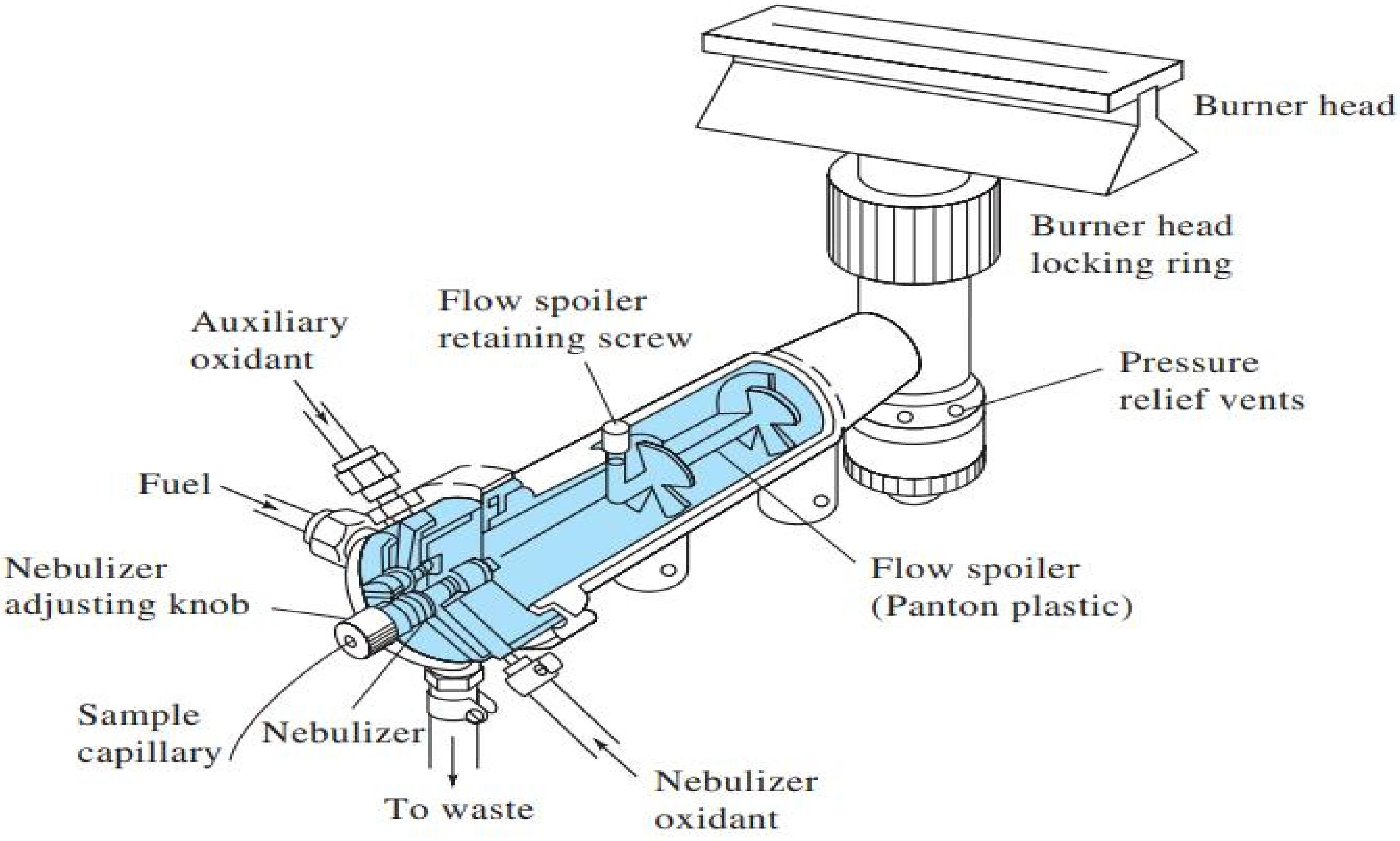
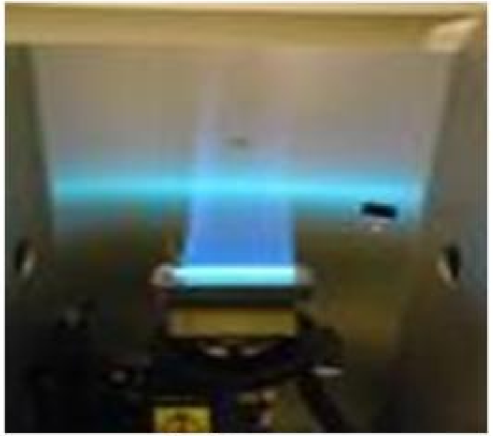
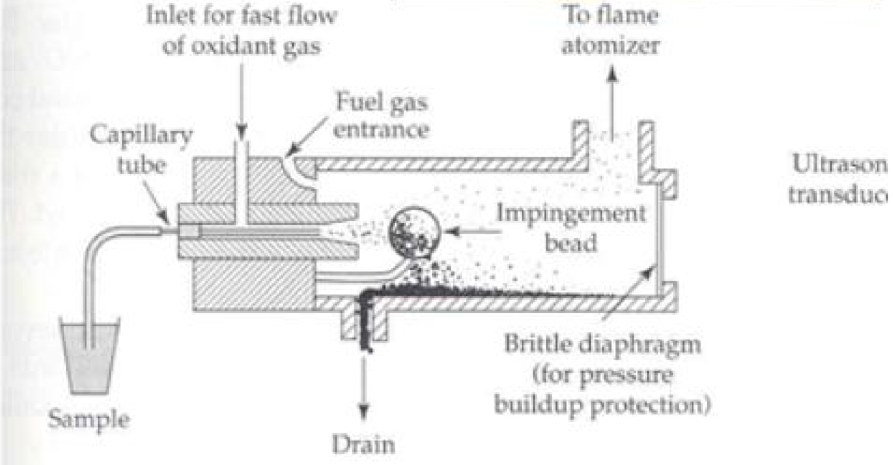


FIGURE 9-5 A laminar-flow burner. (Courtesy of Perkin-Elmer Corporation, Norwalk, CT.)

Flame :“Sample Introduction”

Nebulizer

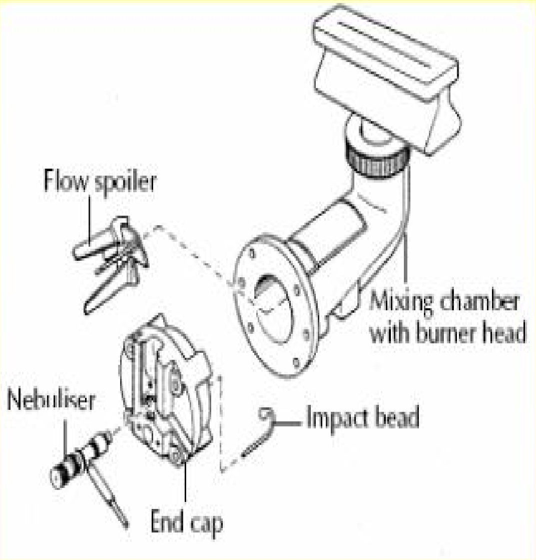




Atomisation of the sample

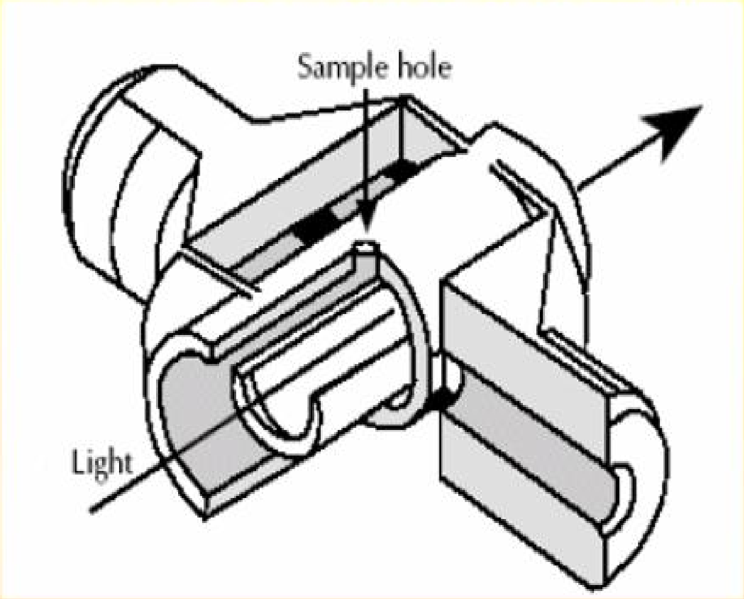
Two systems are commonly used to produce atoms from the sample. Aspiration involves sucking a solution of the sample into a flame; and electrothermal atomisation is where a drop of sample is placed into a graphite tube that is then heated electrically. Some instruments have both atomisation systems but share one set of lamps. Once the appropriate lamp has been selected, it is pointed towards one or other atomisation system.

Ethyne/air (giving a flame with a temperature of 2200–2400 °C) or ethyne/dinitrogen oxide (2600–2800 °C) are often used. A flexible capillary tube connects the solution to the nebuliser. At the tip of the capillary, the solution is 'nebulised' – *ie* broken into small drops. The larger drops fall out and drain off while smaller ones vaporise in the flame. Only *ca* 1% of the sample is nebulised.



Electrothermal atomisation

The figure shows a hollow graphite tube with a platform. 20 µl of sample (*ca* 1/100th of a raindrop) is placed through the sample hole and onto the platform from an automated micropipette and sample changer. The tube is heated electrically by passing a current through it in a pre-programmed series of steps. The details will vary with the sample but typically they might be 30–40 seconds at 150 °C to evaporate the solvent, 30 seconds at 600 °C to drive off any volatile organic material and char the sample to ash, and with a very fast heating rate (*ca* 1500 °C s-1) to 2000–2500 °C for 5–10 seconds to vaporise and atomise elements (including the element being analysed). Finally heating the tube to a still higher temperature – *ca* 2700 °C – cleans it ready for the next sample. During this heating cycle the graphite tube is flushed with argon gas to prevent the tube burning away. **In electrothermal atomisation almost 100% of the sample is atomised. This makes the technique much more sensitive than flame AAS.**



Atomic Absorption Spectroscopy

Graphite Furnace AAS Atomizer

Dissolution of sample into a liquid form is required in most cases.

Sample is injected into a graphite tube and electrothermally heated in different stages to atomize the analyte.

In graphite furnace atomic absorption (GFAAS) the atomization happens in three stages:

- Drying
- Ashing
- Atomization

Graphite furnace operation is a complementary technique to conventional flame AA and adds some advantages to the analysis.

Graphite furnace

Advantages

- High sensitivity due to
  - entire sample is atomized at one time
  - free atoms remain in the optical path longer
- Reduced sample volume
- Ultra trace analysis possible
- Can run unattended, even overnight

Limitations

- Very slow
- Fewer elements can be analyzed
- Poorer precision
- More chemical interferences (compared to flame AA)
- Method development requires skill
- Standard additions calibration required more frequently (compared to flame AA)
- Expensive consumables (graphite tubes)

Atomic Absorption Spectroscopy

Other Atomizers

Hydride generation technique

Suitable for elements forming volatile hydrides (As, Sn, Bi, Sb, Te, Ge and Se) when reacted with a reducing agent, such as sodium

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

Advantages

- Separation of specific elements as hydrides which can eliminate matrix interference
- Good sensitivity due to 100% sampling efficiency
- Good precision
- Faster than graphite furnace AA

Limitations

- Limited to specific elements
- Some chemical interferences
- Requires specific sample preparation (analyte must be converted to a specific oxidation state)

Cold vapor technique

Used specifically for mercury (has a large enough vapor pressure at ambient temperature) which can be reduced to atomic state by a strong reducing agent, such as sodium borohydride, tin (II) chloride).

Advantages

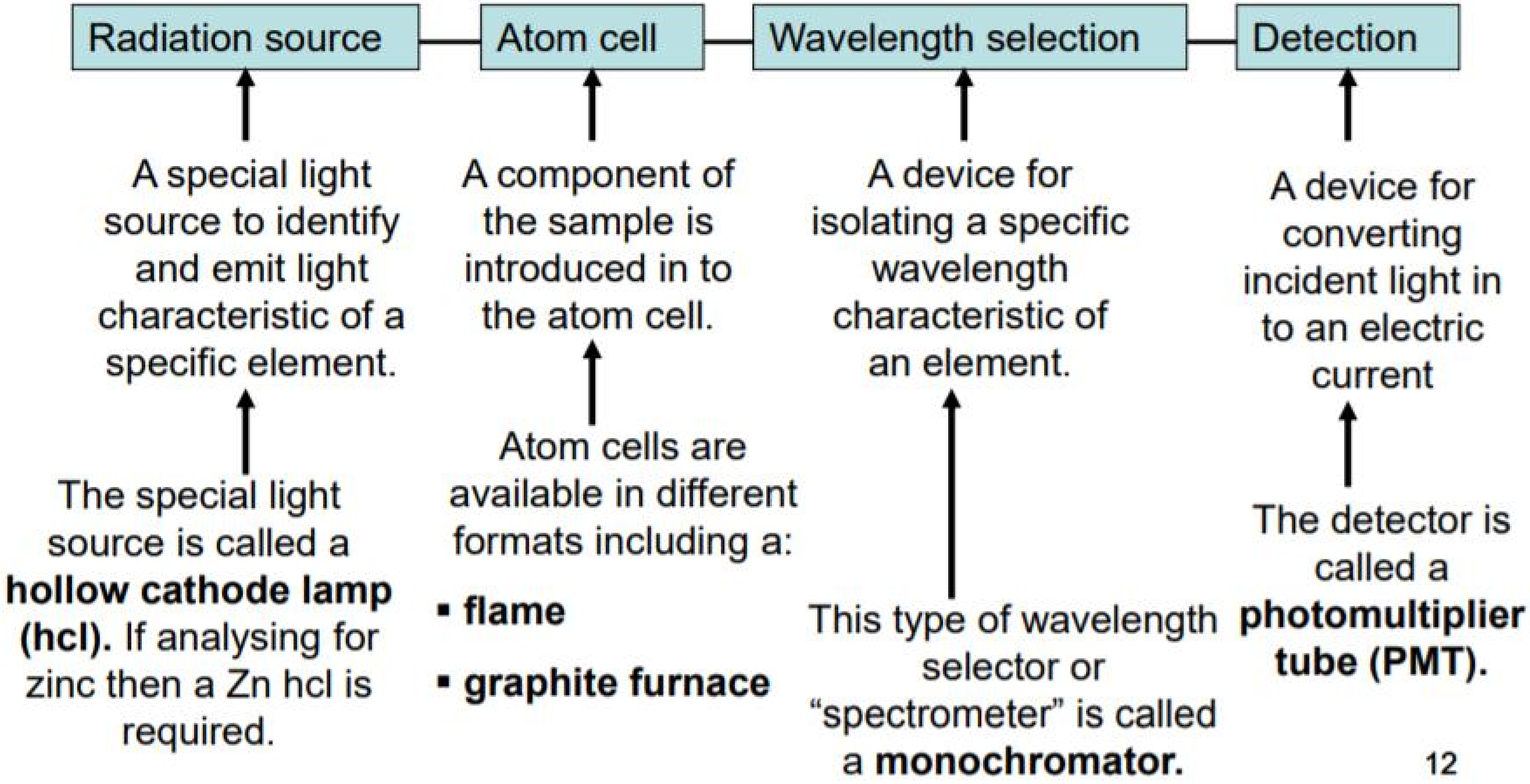
- Eliminates many matrix interferences
- Good sensitivity due to 100% sampling efficiency
- Good precision
- Faster than graphite furnace AA

Limitations

- Limited to mercury only
- Mercury must be stabilized in solution

Atomic Absorption Spectroscopy (AAS)

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



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

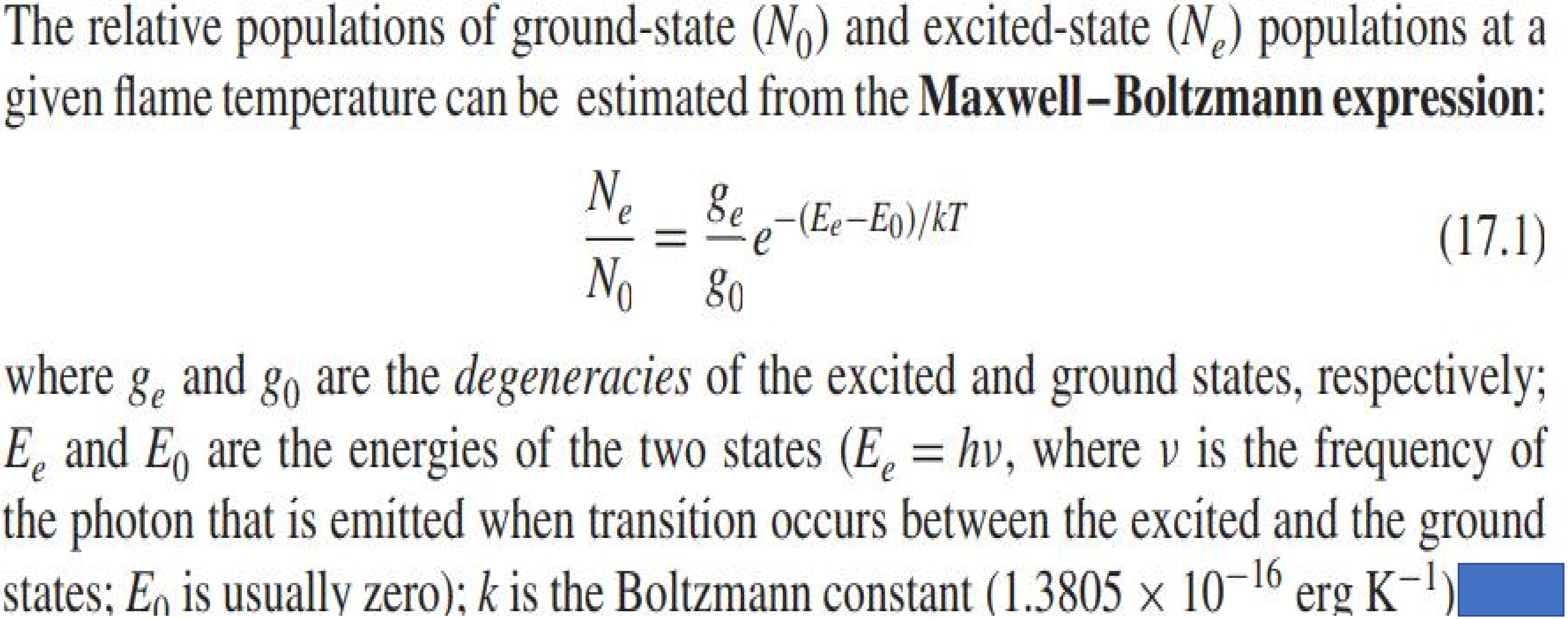
A device for isolating a specific wavelength characteristic of an element.

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

Detection

A device for converting incident light in to an electric current

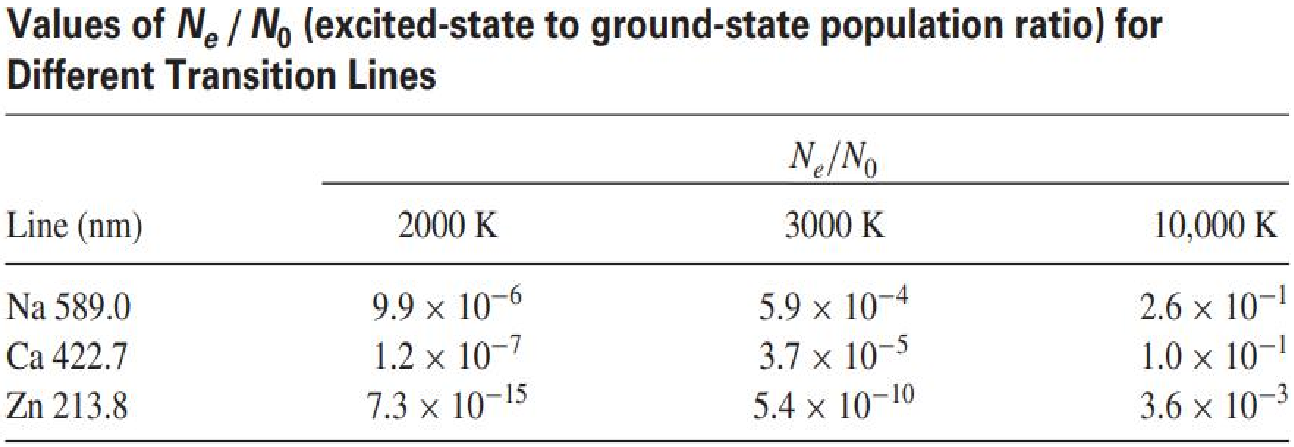
The detector is called a **photomultiplier tube (PMT).**



The relative populations of ground-state (N_0) and excited-state (N_e) populations at a given flame temperature can be estimated from the **Maxwell–Boltzmann expression**:

$$\frac{N_e}{N_0} = \frac{g_e}{g_0} e^{-(E_e - E_0)/kT} \tag{17.1}$$

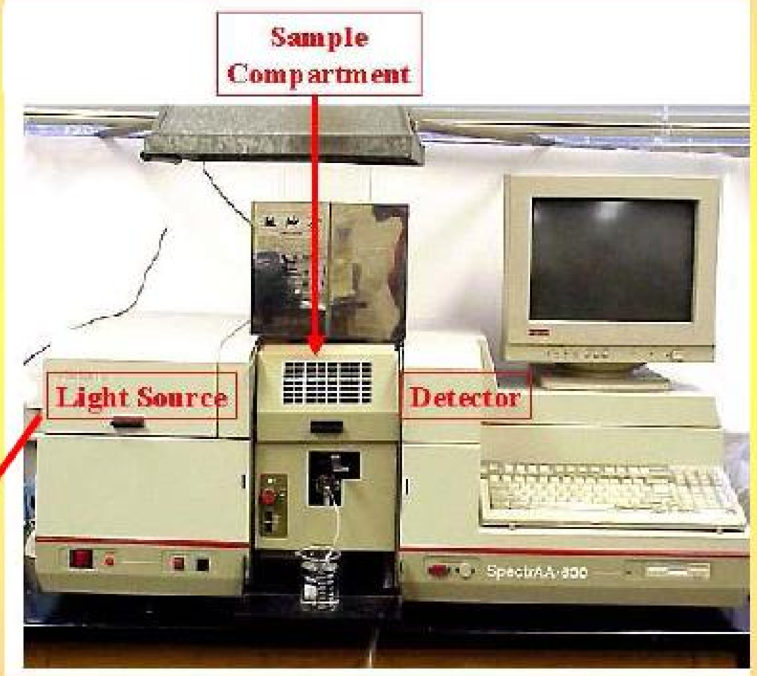
where g_e and g_0 are the *degeneracies* of the excited and ground states, respectively; E_e and E_0 are the energies of the two states ($E_e = h\nu$, where ν is the frequency of the photon that is emitted when transition occurs between the excited and the ground states; E_0 is usually zero); k is the Boltzmann constant (1.3805×10^{-16} erg K^{-1})[redacted]

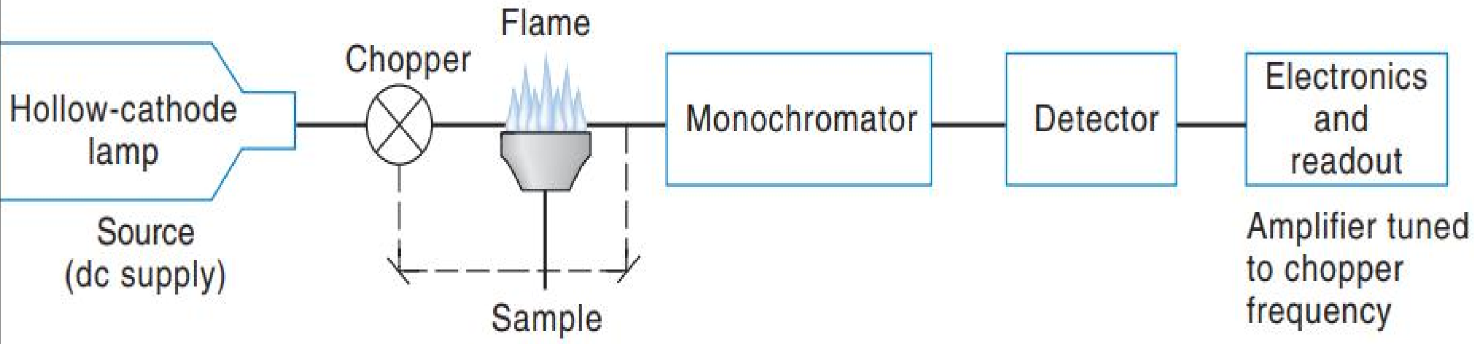


Values of N_e / N_0 (excited-state to ground-state population ratio) for Different Transition Lines

	N_e/N_0		
Line (nm)	2000 K	3000 K	10,000 K
Na 589.0	9.9×10^{-6}	5.9×10^{-4}	2.6×10^{-1}
Ca 422.7	1.2×10^{-7}	3.7×10^{-5}	1.0×10^{-1}
Zn 213.8	7.3×10^{-15}	5.4×10^{-10}	3.6×10^{-3}

An atomic absorption spectrophotometer consists of a light source, a sample compartment and a detector. In this method, light from a source is directed through the sample to a detector. The source of light is a lamp whose cathode is composed of the element being measured. Each element requires a different lamp.





PRINCIPLE: The sample solution is aspirated into a flame and the analyte element is converted to atomic vapor. The flame then contains atoms of that element. Some are thermally excited by the flame, but most remain in the ground state. These ground-state atoms can absorb radiation emitted by the source that is deliberately composed of that element so its characteristic lines are emitted.
Atomic absorption spectrophotometry is identical in principle to absorption spectrophotometry described in the previous chapter. The absorption follows Beer's law. That is, the absorbance is directly proportional to the pathlength in the flame and to the concentration of atomic vapor in the flame.

Working of AAS: Radiation from the hollow-cathode lamp is chopped and mechanically split into two beams, one of which passes through the flame and the other around the flame. A half-silvered mirror returns both beams to a single path by which they pass alternatively through the monochromator to the detector. The signal processor then separates the ac signal generated by the chopped light source from the dc signal produced by the flame. The logarithm of the ratio of the reference and sample components of the ac signal ($\log P_0/P$) is then computed and sent to a readout device for display as absorbance. Absorbance is linearly related to concn. Using the absorbance V_s concn. of standard solutions plot, it is possible to determine the concn of a unknown solution.

Radiation source: hollow cathode lamp (hcl)

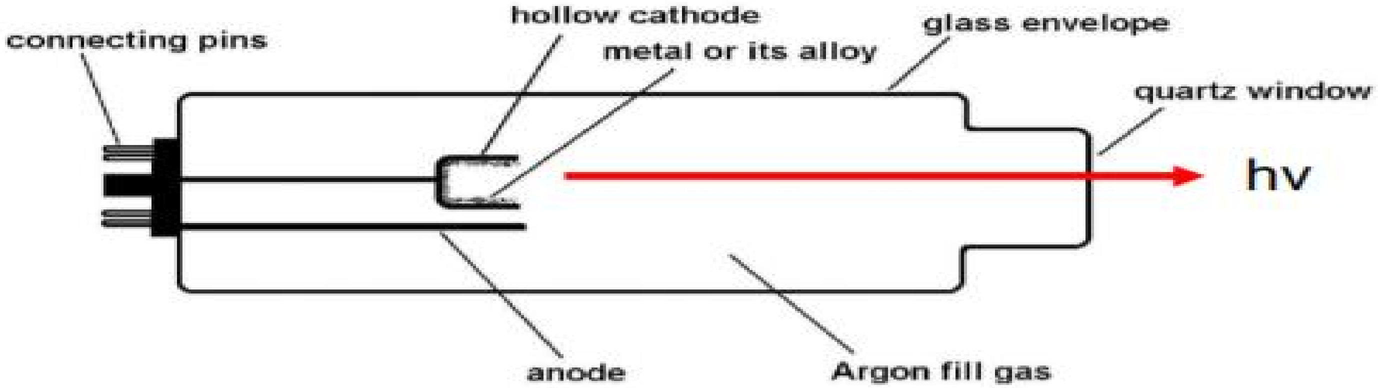


Figure 12.7. - schematic diagram of an hcl

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).

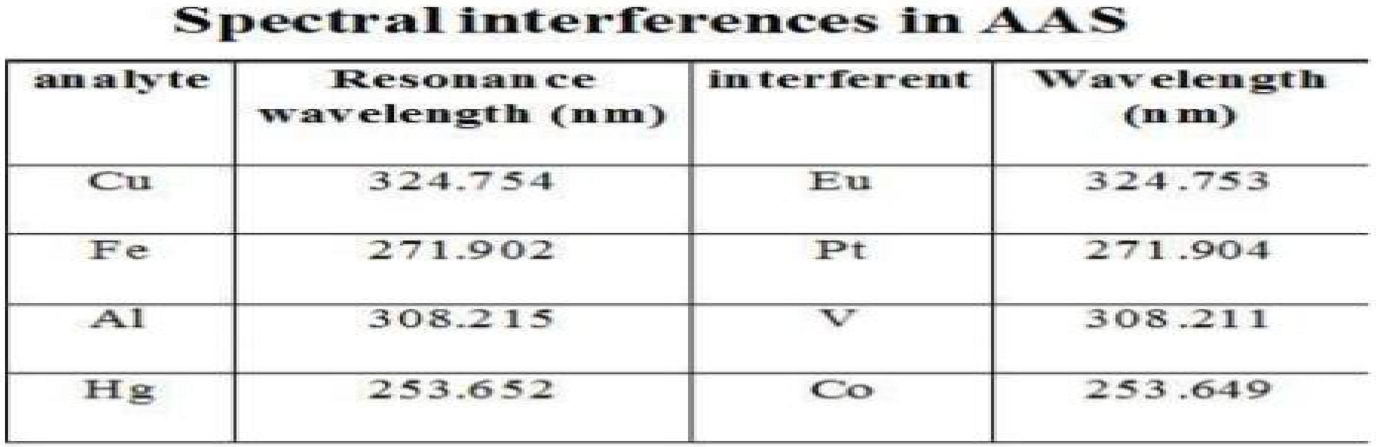
Principle of operation of an hcl:

- 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).

Electrodeless discharge lamps (EDLs) are useful sources of atomic line spectra and provide radiant intensities usually one to two orders of magnitude greater than hollow-cathode lamps. A typical lamp is constructed from a sealed quartz tube containing a few torr of an inert gas such as argon and a small quantity of the metal (or its salt) whose spectrum is of interest. The lamp contains no electrode but instead is energized by an intense field of radio-frequency or microwave radiation. Ionization of the argon occurs to give ions that are accelerated by the high frequency component of the field until they gain sufficient energy to excite the atoms of the metal whose spectrum is sought.

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.

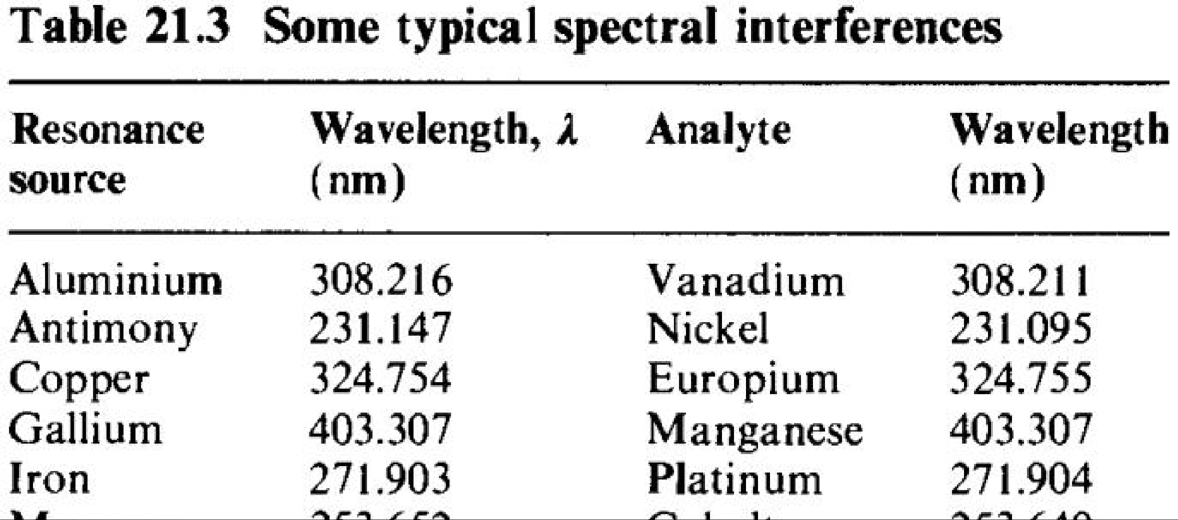


Table 21.3 Some typical spectral interferences

Resonance source	Wavelength, λ (nm)	Analyte	Wavelength (nm)
Aluminium	308.216	Vanadium	308.211
Antimony	231.147	Nickel	231.095
Copper	324.754	Europium	324.755
Gallium	403.307	Manganese	403.307
Iron	271.903	Platinum	271.904

Chemical interferences (also known as refractory compound formation)

This results from the formation of **stable compounds 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.

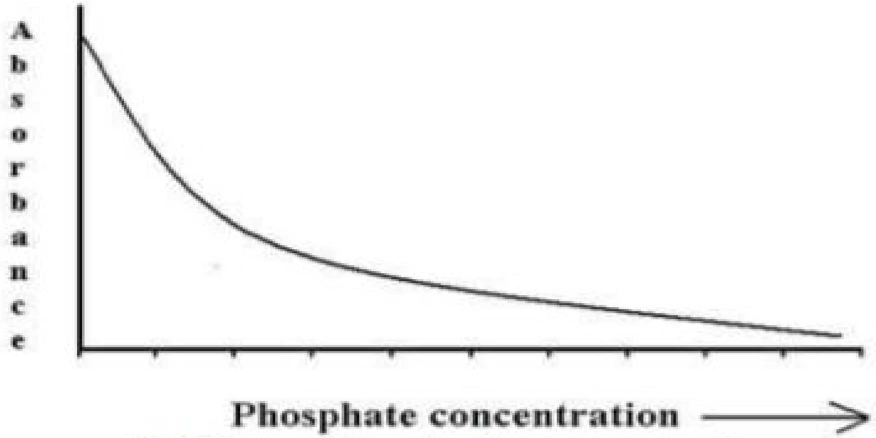


Figure 12.24 - effect of phosphate on The analysis of calcium

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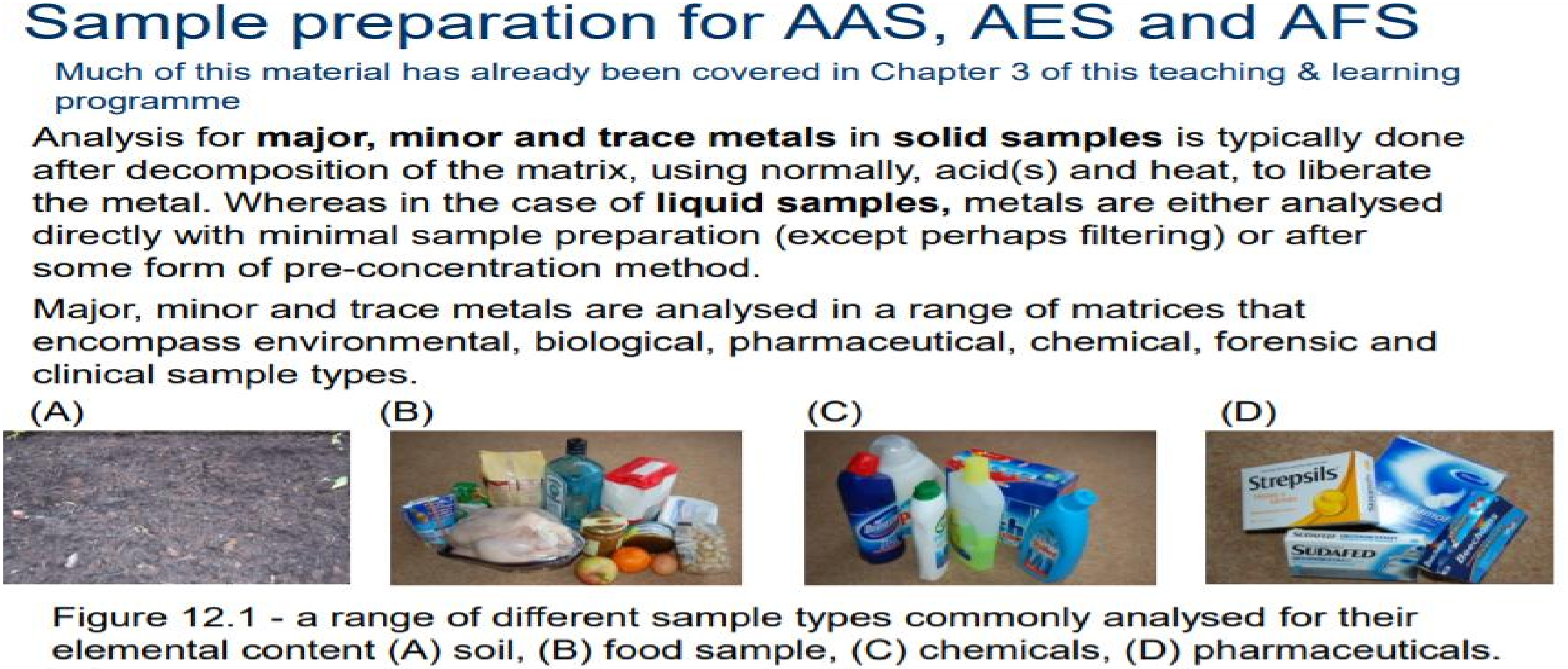
The addition of either a chelating or releasing agent can reduce or eliminate this type of chemical interference. For instance in the case of the analysis or calcium in the presence of phosphate, the addition of a chelating agent, [e.g. ethylenediaminetetraacetic acid (EDTA)], preferential chelation 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 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.

For example, in the determination of sodium (Na), it is necessary to add excess cesium (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

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.



Sample preparation for AAS, AES and AFS

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

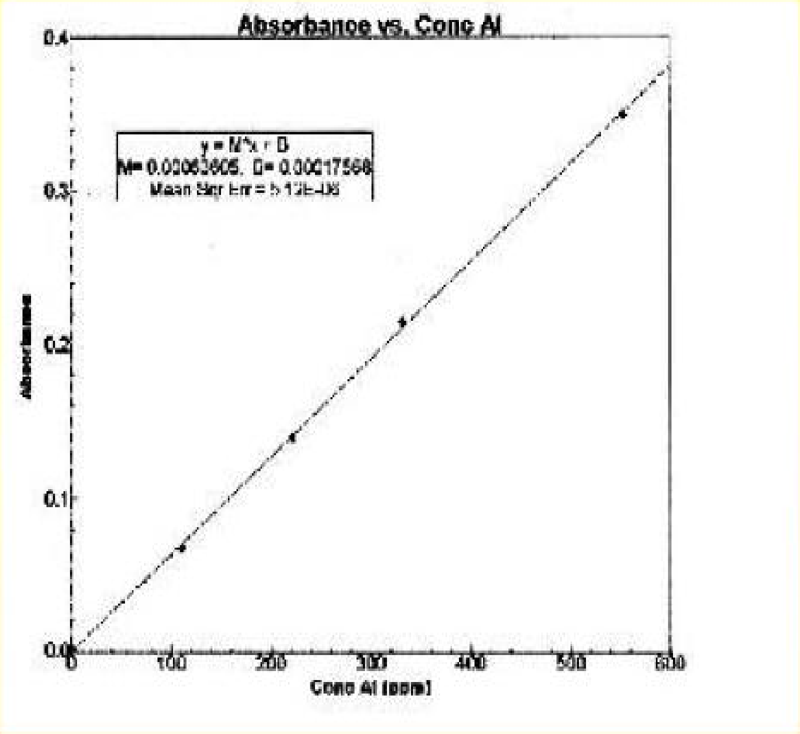
Analysis for **major, minor and trace metals** in **solid samples** is typically done after decomposition of the matrix, using normally, acid(s) and heat, to liberate the metal. Whereas in the case of **liquid samples,** metals are either analysed directly with minimal sample preparation (except perhaps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

Quantitative analysis

Quantitative analysis can be achieved by measuring the absorbance of a series of solutions of known concentration. A calibration curve and the equation for the line can be used to determine an unknown concentration based on its absorbance.



DETERMINATION OF MAGNESIUM AND CALCIUM IN TAP WATER

Determination of magnesium:

Preparation of the standard solutions- A magnesium stock solution (1000 mg L^{-1}) is prepared by dissolving 1.0 g magnesium metal in 50 mL of 5M hydrochloric acid and diluted to 1.0 L with distilled water. Prepare working standard solutions in the concentration range of 0.1-0.4 µg/ml or ppm of Mg^{2+}).

Place a magnesium hollow cathode lamp in the operating position, adjust the current to the recommended value (usually 2-3 mA), and select the magnesium line at 285.2 nm using the appropriate monochromator slit width. Adjust the operating conditions to give a fuel-lean acetylene-air flame. Starting with the least concentrated solution, aspirate in turn the standard magnesium solutions into the flame, and absorbance is noted down. Aspirate de-ionised water into the burner between measurements. Finally read the absorbance of the sample of tap water. Plot the calibration curve (Absorbance Vs concentration) and use this to determine the magnesium concentration of the tap water.

Determination of calcium.

Prepare a calcium stock solution (1000 ppm) by dissolving 2.497 g of dried calcium carbonate in a minimum volume of 1 M hydrochloric acid(about 50 mL). When dissolution is complete, transfer the solution to a 1 L graduated flask and make up to the mark with distilled water. The working standard solutions have conn. In the range of 1-5 ppm Ca^{2+} . Prepare five standard solutions (1.0,2.0, 3.0, 4.0, and 5.0 mL), add 10 mL of releasing agent (50,000 ppm of La^{3+} solution) or 5 mL of either reagent (76 g of strontium chloride dissolved in 500 ml or 75 g of EDTA dissolved in 1.0 L distilled water). A blank solution is similarly prepared but without the addition of any of the intermediate calcium stock solution.

Set up a calcium hollow cathode lamp selecting the resonance line of wavelength 422.7 nm, and a fuel-lean acetylene-air flame. Note down the absorbance of each standard solution and construct the calibration curve. Under similar reaction condition, note down the absorbance of unknown tap water. Using the calibration plot, the concentration of unknown Tap water can be readily determined.

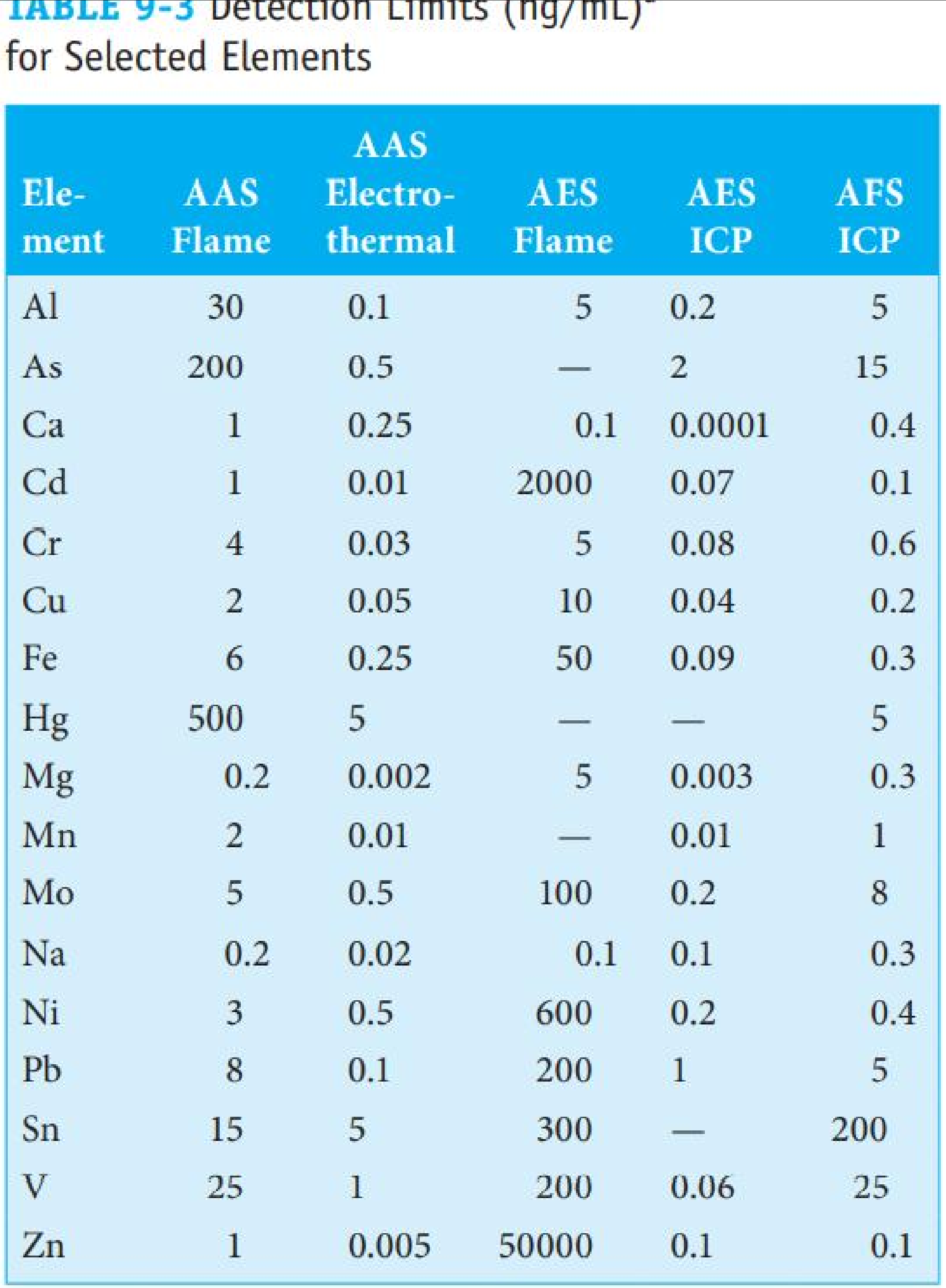


TABLE 9-3 Detection Limits (ng/mL)^a for Selected Elements

Element	AAS Flame	AAS Electrothermal	AES Flame	AES ICP	AFS ICP
Al	30	0.1	5	0.2	5
As	200	0.5	—	2	15
Ca	1	0.25	0.1	0.0001	0.4
Cd	1	0.01	2000	0.07	0.1
Cr	4	0.03	5	0.08	0.6
Cu	2	0.05	10	0.04	0.2
Fe	6	0.25	50	0.09	0.3
Hg	500	5	—	—	5
Mg	0.2	0.002	5	0.003	0.3
Mn	2	0.01	—	0.01	1
Mo	5	0.5	100	0.2	8
Na	0.2	0.02	0.1	0.1	0.3
Ni	3	0.5	600	0.2	0.4
Pb	8	0.1	200	1	5
Sn	15	5	300	—	200
V	25	1	200	0.06	25
Zn	1	0.005	50000	0.1	0.1

The term 'sensitivity' in atomic absorption spectroscopy is defined as the concentration of an aqueous solution of the element which absorbs 1 per cent of the incident resonance radiation; in other words, it is the concentration which gives an absorbance of 0.0044.

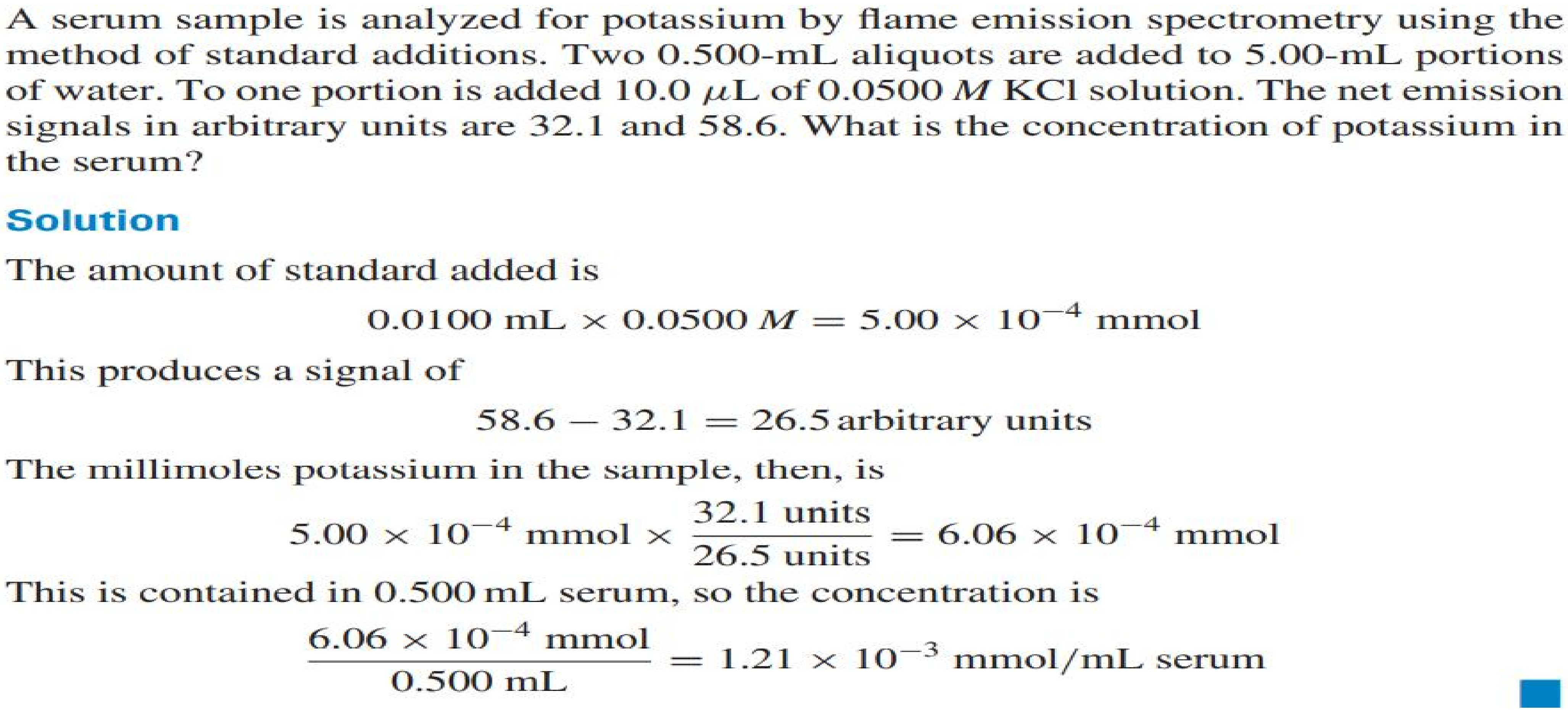
A comparison of the analytical performance of AAS and FES reveals that the two methods complement each other in many respects. FES is better for the determination of alkali, alkaline earth metals, rare earth elements as well as Ga, In and Tl.

AAS permits detn of Ag, Al, Au, Cd, Cu, Hg, Te, Pb, Sb, Se and Sn with high sensitivity.

FES permits simultaneous quantitative multielement analyses.

Electrothermal AAS is more sensitive compared to AAS and FES since the spectral radiance of the lamp is much greater and 100% atomization is achieved.

When compared to AAS, FES and AFS, ICPAES is more sensitive



A serum sample is analyzed for potassium by flame emission spectrometry using the method of standard additions. Two 0.500-mL aliquots are added to 5.00-mL portions of water. To one portion is added 10.0 μL of 0.0500 *M* KCl solution. The net emission signals in arbitrary units are 32.1 and 58.6. What is the concentration of potassium in the serum?

Solution

The amount of standard added is

$$0.0100 \text{ mL} \times 0.0500\ M = 5.00 \times 10^{-4} \text{ mmol}$$

This produces a signal of

$$58.6 - 32.1 = 26.5 \text{ arbitrary units}$$

The millimoles potassium in the sample, then, is

$$5.00 \times 10^{-4} \text{ mmol} \times \frac{32.1 \text{ units}}{26.5 \text{ units}} = 6.06 \times 10^{-4} \text{ mmol}$$

This is contained in 0.500 mL serum, so the concentration is

$$\frac{6.06 \times 10^{-4} \text{ mmol}}{0.500 \text{ mL}} = 1.21 \times 10^{-3} \text{ mmol/mL serum}$$

OR

Concentration of K = $i_1 v\, C_s / (i_2 - i_1)\, V$ where v is the volume of standard soln. added (10 micro Liter = 0.01 ml), i_1 and i_2 net signals(32.1 and 58.6), V is the volume of the aliquot soln(0.5 ml) and C_s is the concn.of standard added. Substituting these values, we get

Concentration of K = (32.1 X 0.01 X 0.05)/(58.6-32.1X 0.5) = 1.21 X10^{-3} mmol/ml serum