

Chemistry in Context

Many diseases result from calcification. How is calcium measured by atomic spectroscopy?

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CH 8-10 Atomic Spectroscopy

Homework

1. For Na and Mg^+ ions, compare the ratios of the number of ions in the 3p excited state to the number in the ground state at 1800 K, 2950 K, and 7250 K.
2. A 5.00 mL sample of blood was treated with trichloroacetic acid to precipitate proteins. After centrifugation, the resulting solution was brought to a pH of 3 and was extracted with two 5 mL portions of methyl isobutyl ketone containing the organic lead complexing agent APCD. The extract was aspirated directly into an air-acetylene flame yielding an absorbance of 0.444 at 283.3 nm. Five, 1 mL aliquots of standard solutions containing 0.250 and 0.450 ppm Pb were treated in the same way and yielded absorbances of 0.396 and 0.599. Calculate the concentration of Pb in the sample assuming Beer's law is followed.
3. What is an internal standard and why is it used?
4. Describe three ways of introducing a sample into an ICP torch.
5. Why are ionization interferences less severe in ICP than in flame emission spectroscopy?

CH 8-10 Atomic Spectroscopy

Three common methods for identifying elements present in a sample:

(1) Atomic Absorption/emission Spectroscopy
Analysis of metals

(2) Mass Spectrometry
Analysis of metal complexes, particles, proteins,
organic molecules

(3) X-ray Spectroscopy
Analysis of particles and surfaces

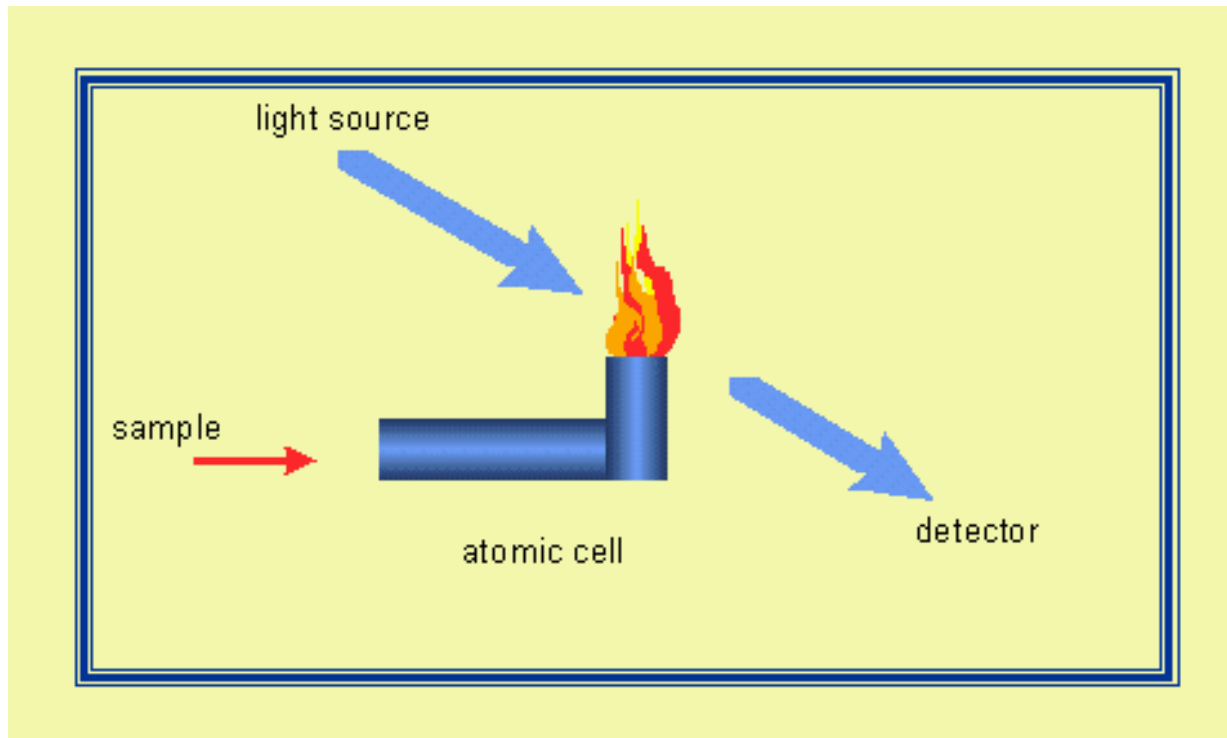
Atomic Absorption and Emission Spectroscopy

Sample is sprayed into a high-temperature atomizer to create gaseous atoms/ions, and then optical absorption/emission/fluorescence spectra are acquired.

AA: Absorption of light source is measured.

AF: Light source causes atomic fluorescence.

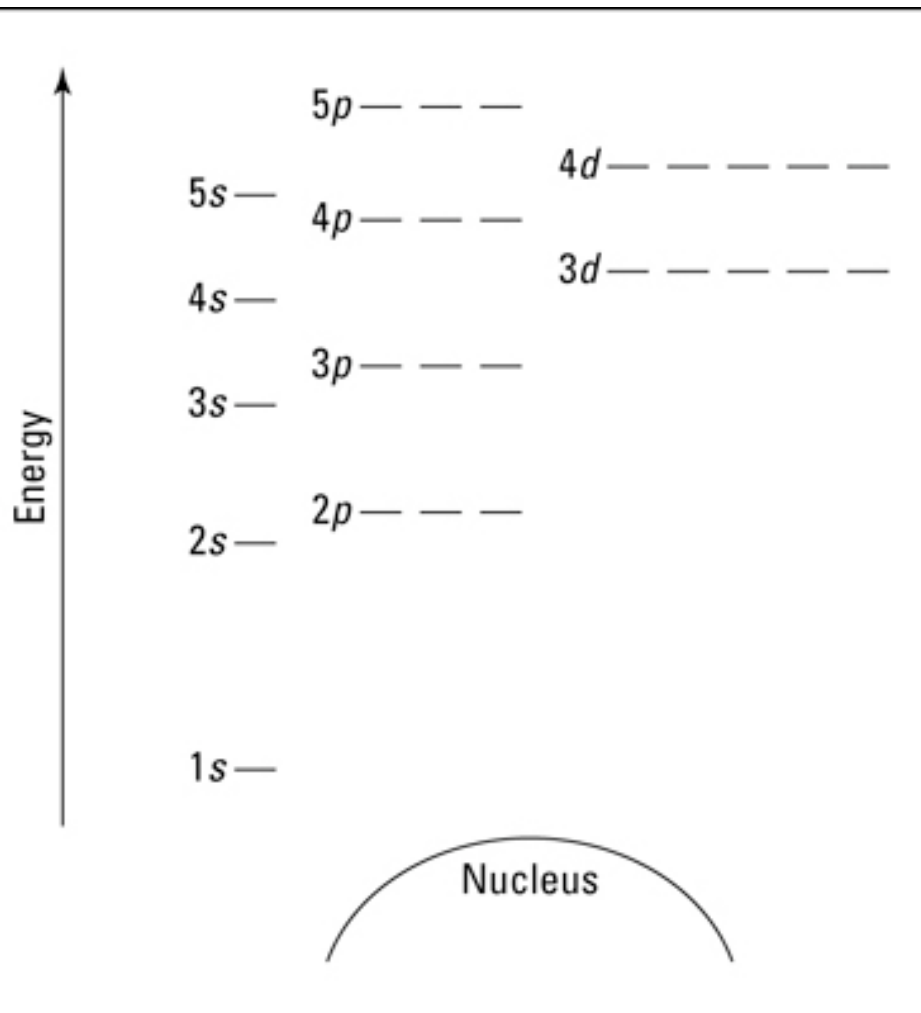
AE: High T flame/plasma excites atoms which then emit.



What are the atomic-level details behind this experiment?⁵

CH 8-10 Atomic Spectroscopy

Atomic Energy Level Diagrams



Recall the basic atomic energy level diagram.

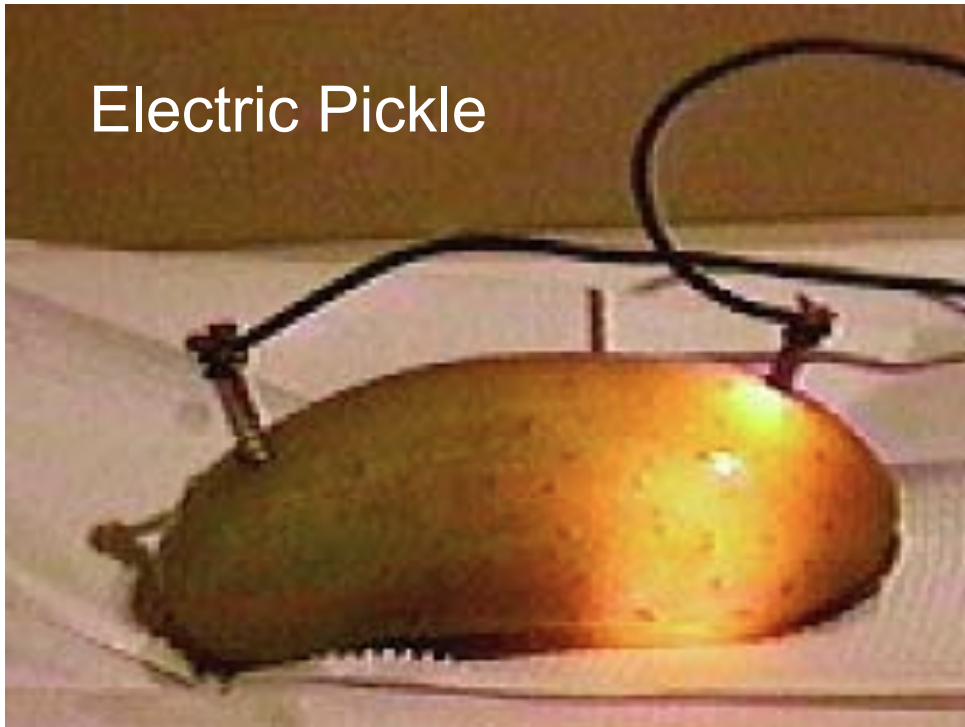
This diagram might lead one to believe that light-induced electronic transitions are very simple. They should be:

- (1) Narrow in wavelength.
- (2) Exactly equal to the differences in energy levels shown in the diagram.

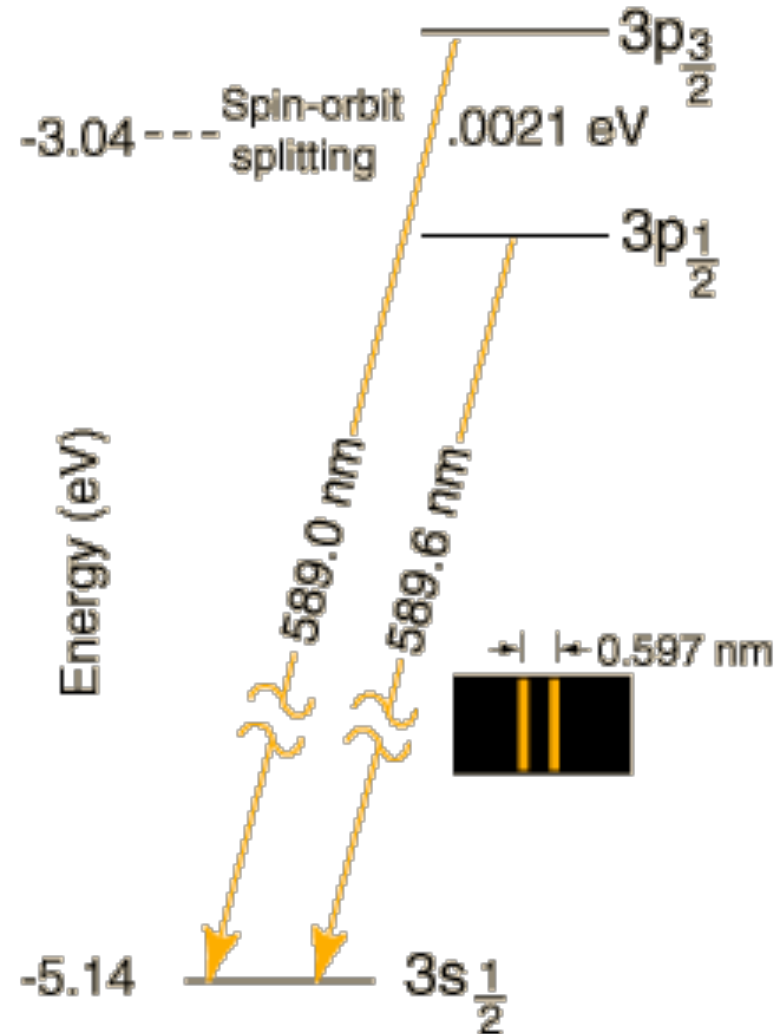
CH 8-10 Atomic Spectroscopy

In reality, atomic absorptions are always broad (more than a single wavelength absorbed), and there are more absorptions than one would expect from the energy level diagram.

Na Doublet from an Electric Pickle



Atomic Spectroscopy



Note the splitting of the p level into a doublet. This is a magnetic field effect that occurs because electrons have spin, and any oscillating electric field produces a magnetic field. A single electron spins as it “orbits” the nucleus. Both the spin and orbit create magnetic fields. The direction of spin changes the way the spin magnetic field interacts with the orbital magnetic field. In fact, the observation of this “fine structure” was the first evidence of electron spin.

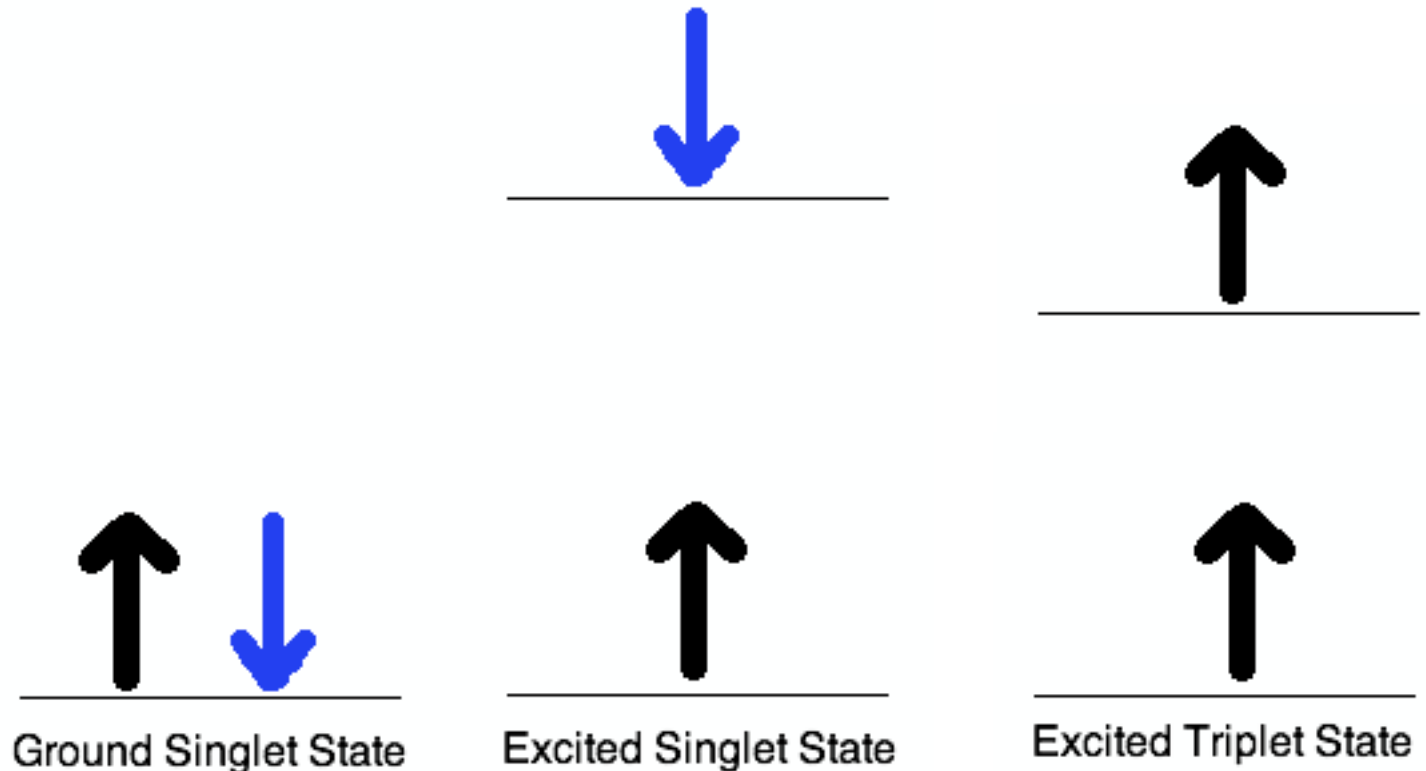


An applied magnetic field can split the levels even further, creating even more emission lines. This is the [Zeeman Effect](#).

Atomic Spectroscopy

Key Concept*: When an atom has two electrons in its ground state, two different excited states may be generated that differ in energy.

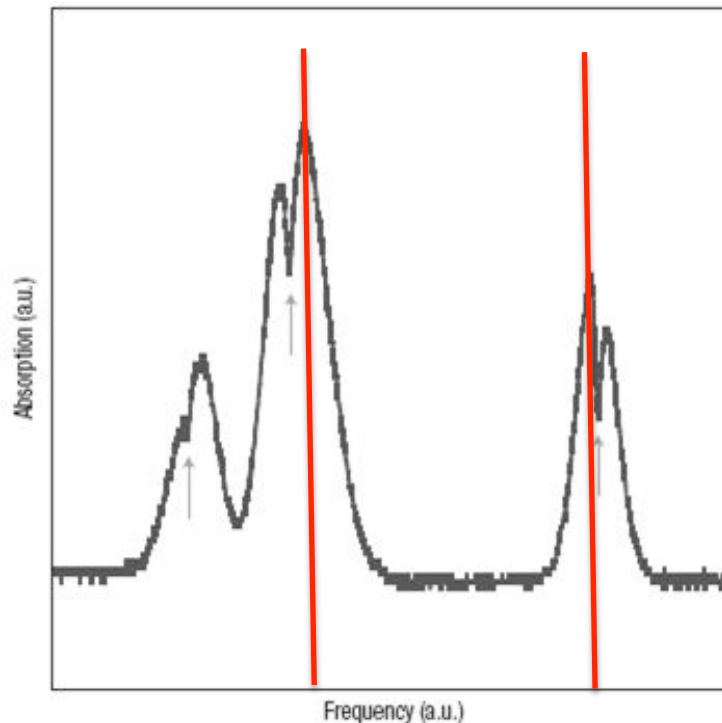
These are determined by the formula $2s + 1$, where s is the sum of the electron spins. This is called the spin multiplicity.



Atomic Spectroscopy

Atomic Line Widths

Atomic absorption and emission line widths are not completely narrow as one might expect from transitions between two discrete energy states.

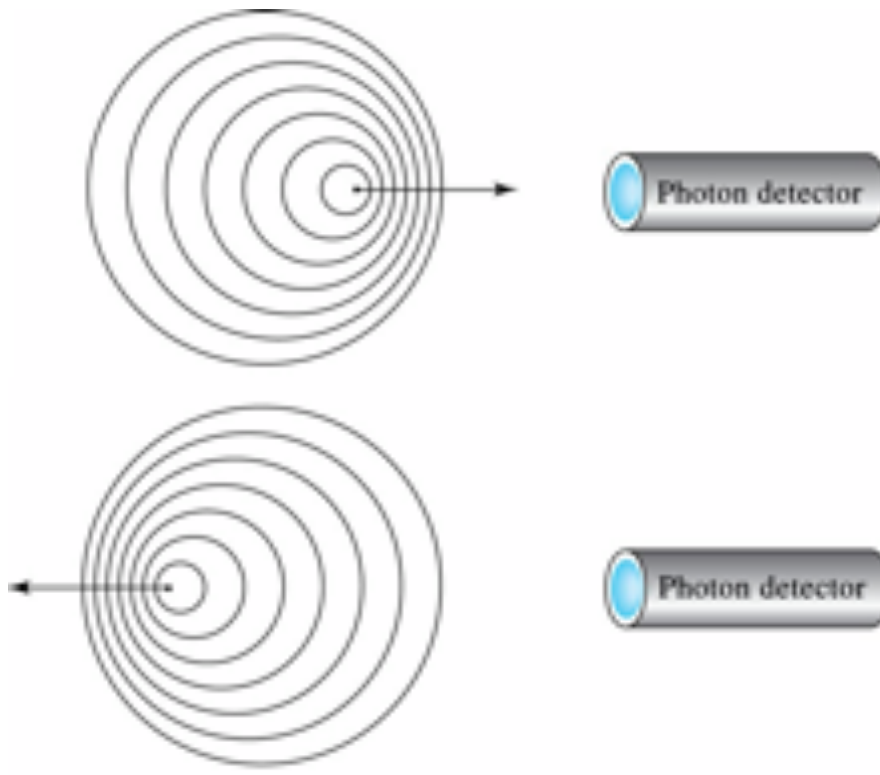


Atomic Spectroscopy

Sources of broadening

Doppler Broadening

Observed for all EM and sound waves.



For a collection of atoms moving in all directions with different velocities, wavelengths absorbed/emitted are shifted.

Doppler Broadening increases with T .

Wavelength in direction of detector is shortened.
Wavelength away from detector is lengthened.

***Key Concept**

Atomic Spectroscopy

Sources of broadening

Pressure or Collisional Broadening

Collisions between atoms in the sample can change the electronic energy levels.

In high-pressure Hg lamps, pressure broadening is so great that radiation is emitted throughout the UV-visible spectrum.

Concept Test

Which of the following statements concerning the effect of T on broadening are true?

- (A) Pressure broadening increases with T but Doppler broadening does not
- (B) Doppler broadening increases with T but pressure broadening does not
- (C) Both increase with T
- (D) Neither increases with T

The Heisenberg Uncertainty Principle is another source of line broadening called “natural broadening”.

Heisenberg Uncertainty Principle: We cannot know both the position and momentum of a particle with infinite precision. We also cannot know the precise energy of a particle in a finite amount of time.

$$\Delta x \Delta p > \hbar/2$$

x is position, p is momentum

$$\Delta E \Delta t > \hbar$$

E is energy, t is time

$$\Delta t > 1/\Delta \nu$$



The width of a line resulting from a transition between two states would approach zero only if the lifetime of the excited state approached infinity. We cannot know the E of a state that has an infinitesimally small lifetime.

Δt = lifetime; $\Delta \nu$ = linewidth; h = Planck's constant; “ \hbar bar” = $h/2\pi$

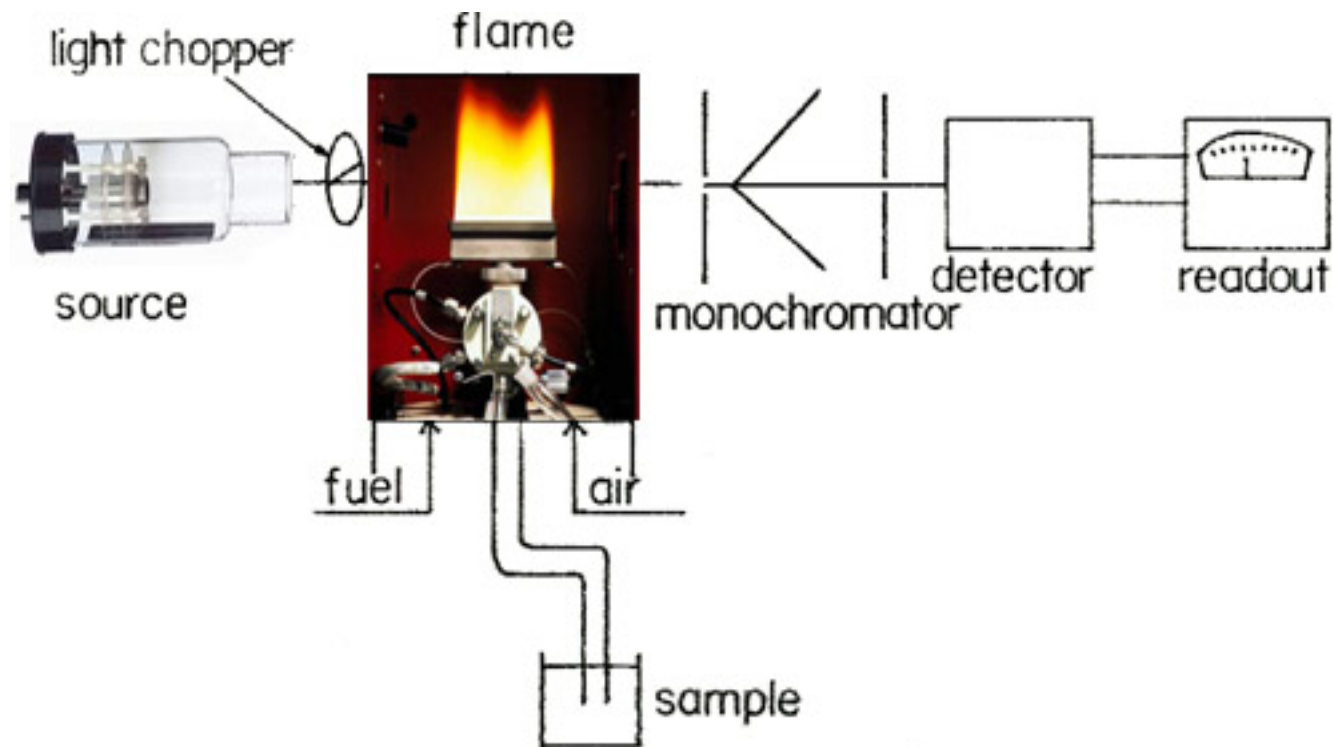
Fast decaying excited states have broader lines, slow decaying states have narrower lines.

Concept Test

Which of the following statements concerning the Heisenberg uncertainty principle are true?

- (A) The better you know the position of a particle the less you know its momentum.
- (B) The better you know the energy of an excited state the less you know its lifetime.
- (C) The shorter the excited state lifetime the broader the absorption spectrum.
- (D) All are true.
- (E) A and B are true.

Atomic Absorption Instrumentation



Sample Introduction and Atomization Methods

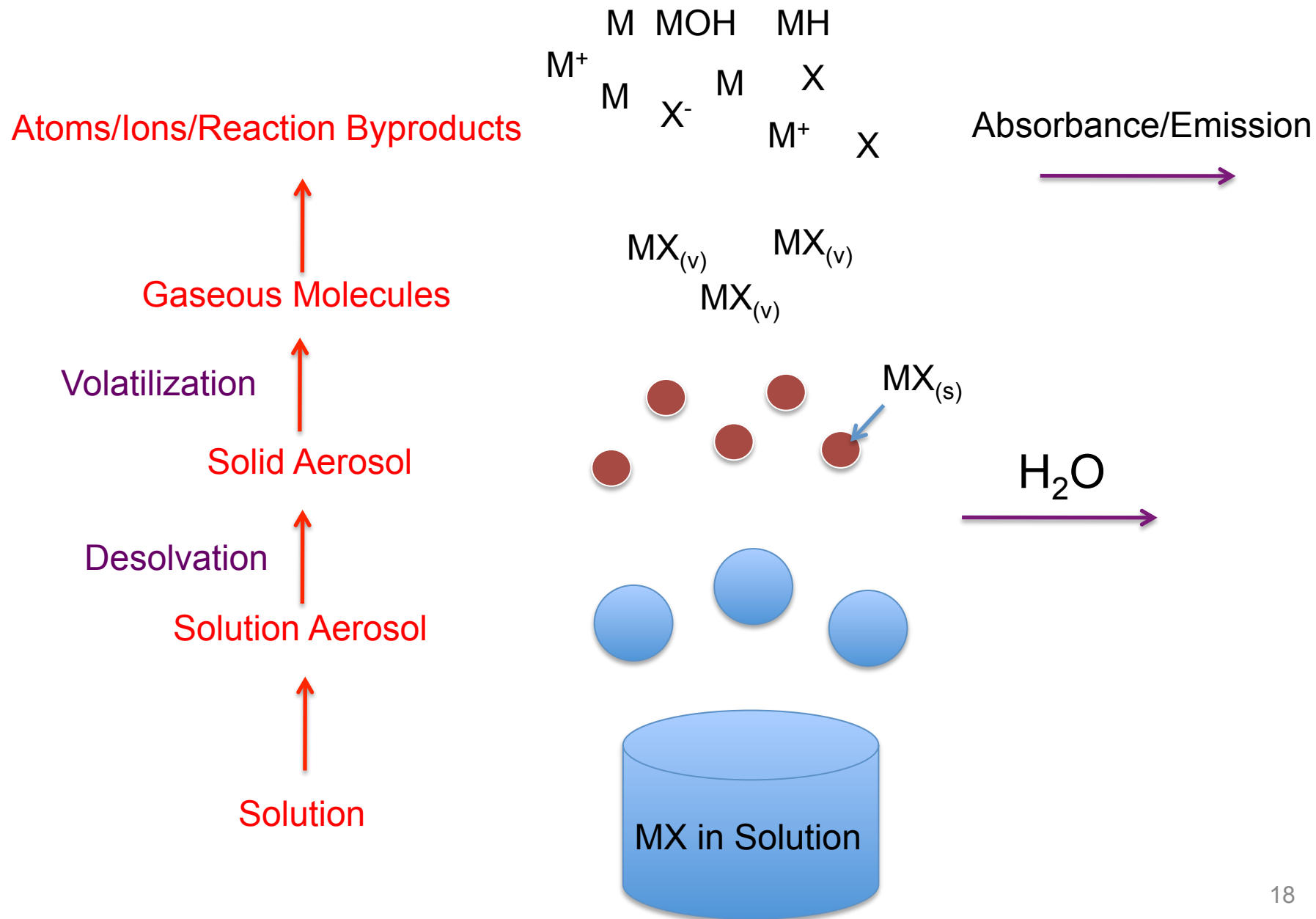
Samples may be introduced as solids, solutions, or gases. Solids are the least reproducible samples.

Nebulizers are typically used to introduce solutions. These devices create a spray of tiny droplets called an aerosol.

Solids can be introduced directly into the flame, or by vaporization with electrical discharge or Lasers.

Solids are frequently prepared by first “digesting” particulates to release the atoms of interest. A common digesting treatment is oxidation with strong acids (sulfuric, nitric, perchloric).

Fate of the Sample



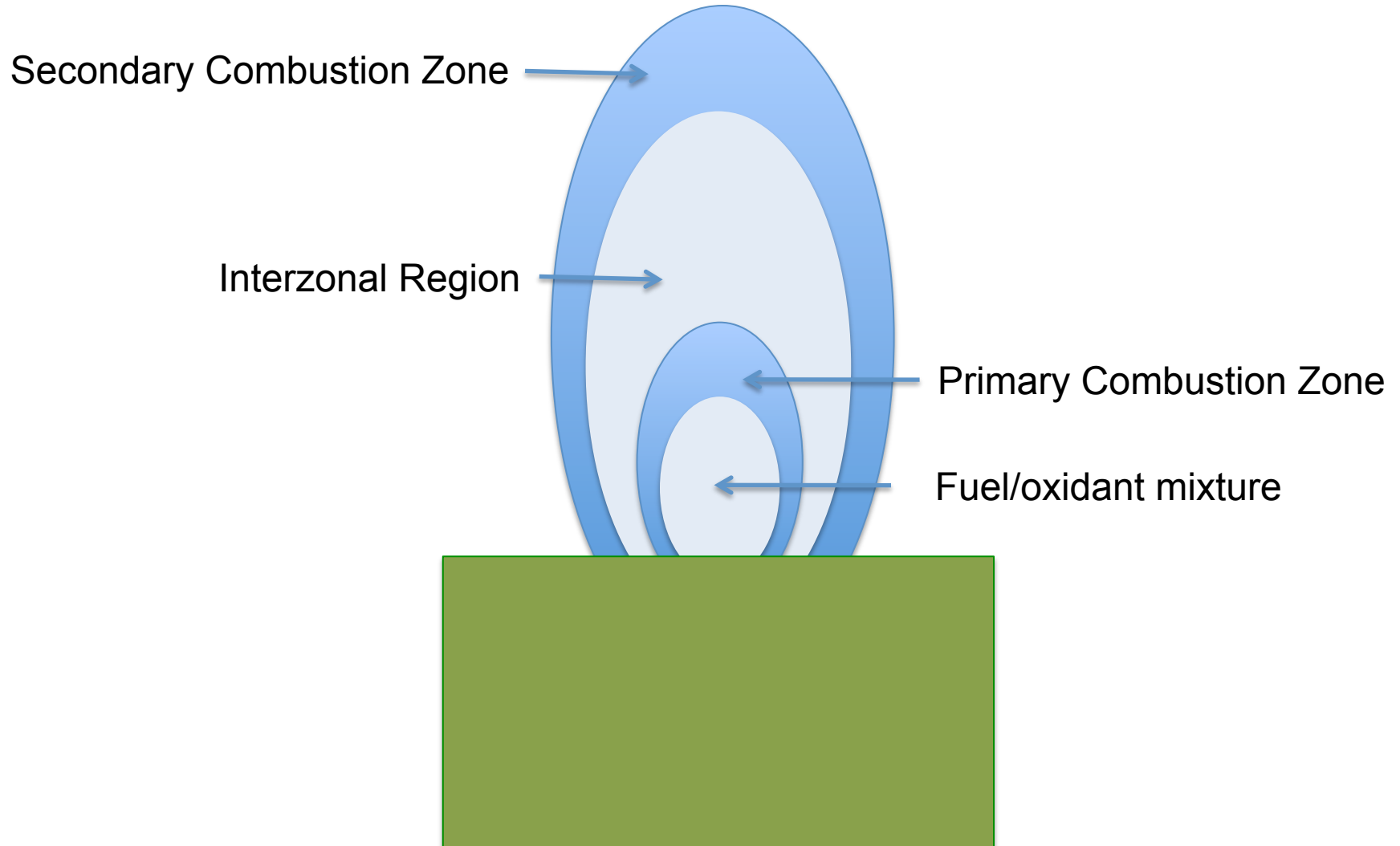
Sample Introduction and Atomization Methods

The temperature of the atomizer and the temperature profile are important in making sensitive measurements.

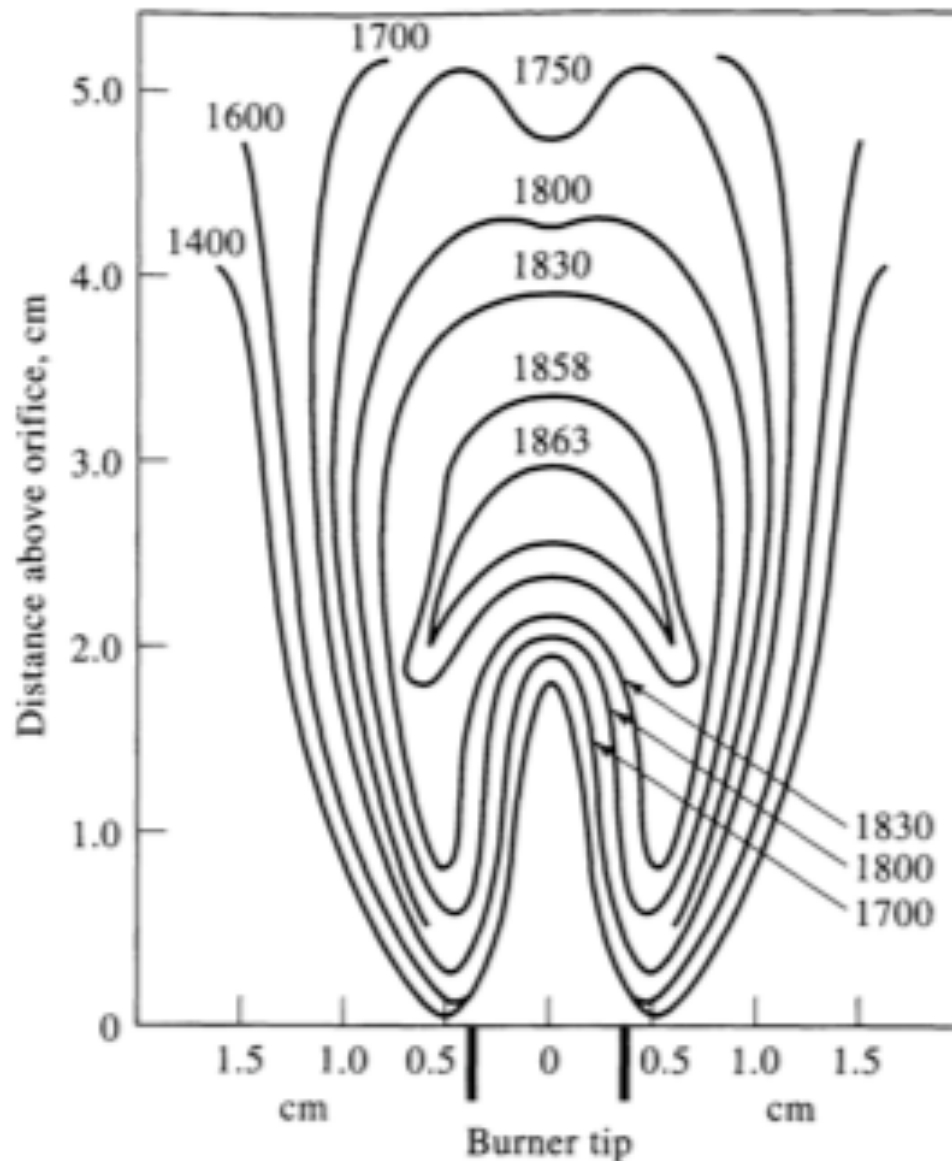
Atomizers

	<u>Temp, °C</u>
Flame (Air/Acetylene)	1700-3150
Electrothermal	1200-3000
Inductively coupled argon plasma (ICP)	4000-10,000
Microwave-induced argon plasma	2000-3000
Electric arc	4000-5000
Electric spark	40,000

Sample Introduction and Atomization Methods



Flame Atomizer-Temperature Profile



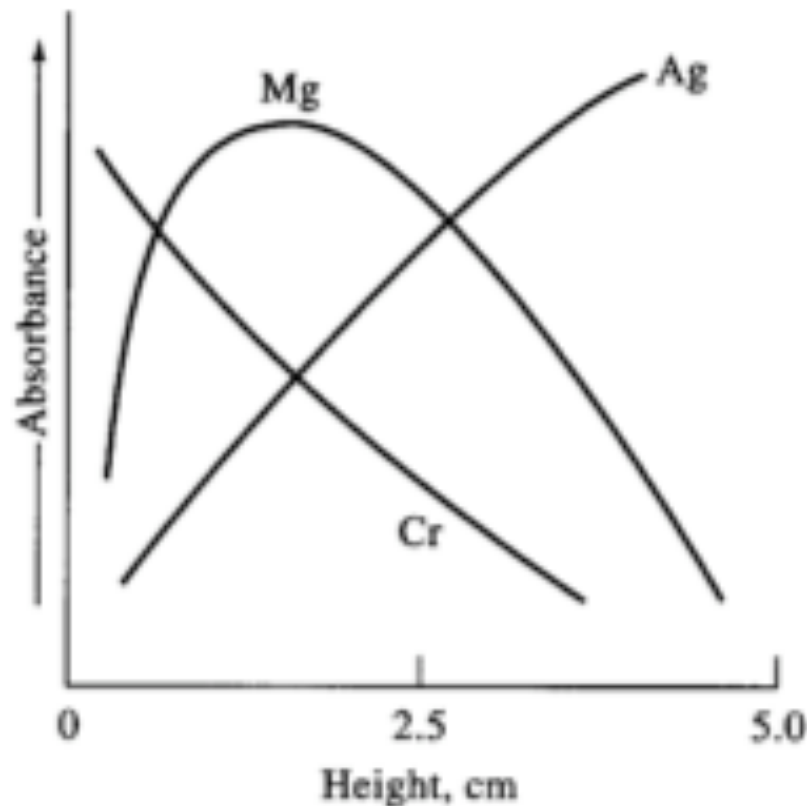
Hottest part of the flame is 2.5 cm above primary combustion zone.

Sample may be focused to different positions in the flame-must keep the position constant for standards and samples.

Different elements will respond better in different positions.

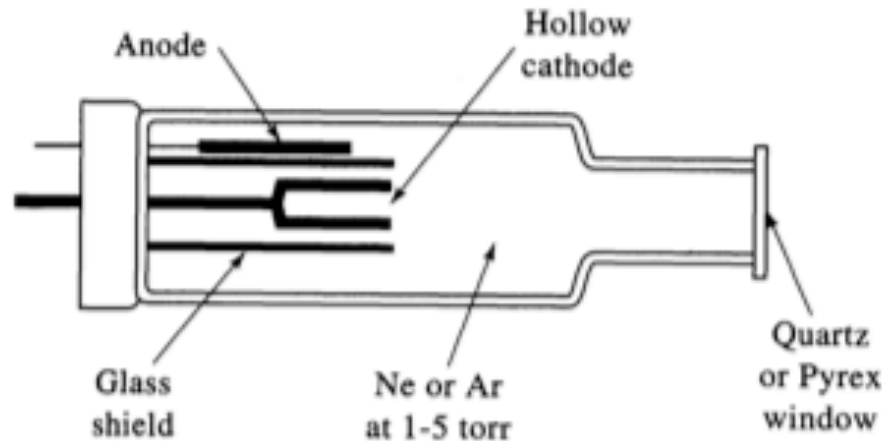
Flame Atomizer-Temperature Profile

Most sensitive position for sample introduction varies with element. One reason is that some elements will form oxides that do not absorb at the observation wavelength. Cr forms an oxide very quickly, anywhere in the flame, while Ag does not form an oxide.



Radiation Sources

Hollow Cathode Lamp



- 300 V applied between anode (+) and metal cathode (-)
- Ar ions bombard cathode and sputter cathode atoms
- Fraction of sputtered atoms excited, then fluoresce
- Cathode made of metal of interest (Na, Ca, K, Fe...)

different lamp for each element
restricts multielement detection

***Key Limitations**

Interferences in AA Spectroscopy

Spectral: atomic spectral lines overlap or are too close to resolve (rare)

Matrix: scattering of radiation during atomization (smoke).

Chemical: reactions that alter the analyte

Let's Do an AA Experiment

Before you even introduce your sample, what might your signal look like? There is a fuel that is combusting. What does that mean?



Concept Test

A complete combustion reaction would produce:

- (A) $\text{CO} + \text{OH}^- + \text{H}_2$ (B) $\text{CO} + \text{H}_2\text{O}$ (C) $\text{CO}_2 + \text{H}_2$ (D) $\text{CO}_2 + \text{H}_2\text{O}$

Spectral Interferences

Combustion reactions are rarely complete, however.

Particles or other products that scatter or absorb light will attenuate the beam-**Spectral Interference**.

Correct by making absorption measurements on a blank aspirated into the flame (background correction).

Spectral Interferences

Ok, now let's analyze a sample. Imagine you were working on the team that developed an X-ray contrast agent for imaging the GI tract. You find that Ba provides excellent contrast, and you now want to measure the rate of clearance from the body. Having been well trained in the art of instrumental methods of chemical analysis at CU, you choose AA as the detection method.

Interferences in AA Spectroscopy

Problem:

Ca (the most abundant element in the body) interferes with the Ba signal because the Ba absorption line appears in the middle of a broad absorbance from CaOH that can form as a stable species at the temperatures of air/acetylene flames-
Chemical Interference.

Solution:

Replacing air with nitrous oxide creates a higher temperature flame that decomposes the CaOH to produce Ca ions that do not absorb the same wavelengths.

Interferences in AA Spectroscopy

Chemical Interference

Dissociation equilibria. Metal atoms/ions will form small clusters that do not absorb/emit at the observation wavelength. Metal oxides, hydroxides, and even salt clusters (NaCl) can form, reducing the signal at the observation wavelength. Changing the fuel mixture or oxidant can help solve these problems.

<u>Mixture</u>	<u>°C</u>
Acetylene/Air	2400
Acetylene/O ₂	2800
Acetylene/NO	3140
H ₂ /O ₂	2660

Interferences in AA Spectroscopy

Now you are on a team that has developed a drug that dissolves CaPO_4 deposits in the body. You need to measure the rate of dissolution of these clots. You once again choose AA as your technique.

Interferences in AA Spectroscopy

Problem:

Formation of compounds with low volatility-results in a lower amount of analyte that is atomized.

In the presence of anions such as phosphate and sulfate, Ca is difficult to atomize. Absorbance signals can be 30% to 50% less than in the absence of these anions.

Solution:

Adding another cation to the sample can help tie up these anions (Sr will tie up phosphate). These are called “releasing agents”.

CH 10 Atomic Emission Spectroscopy

The most common type of AES instrument is the inductively coupled plasma-AES.

Advantages and Disadvantages Compared to AAS

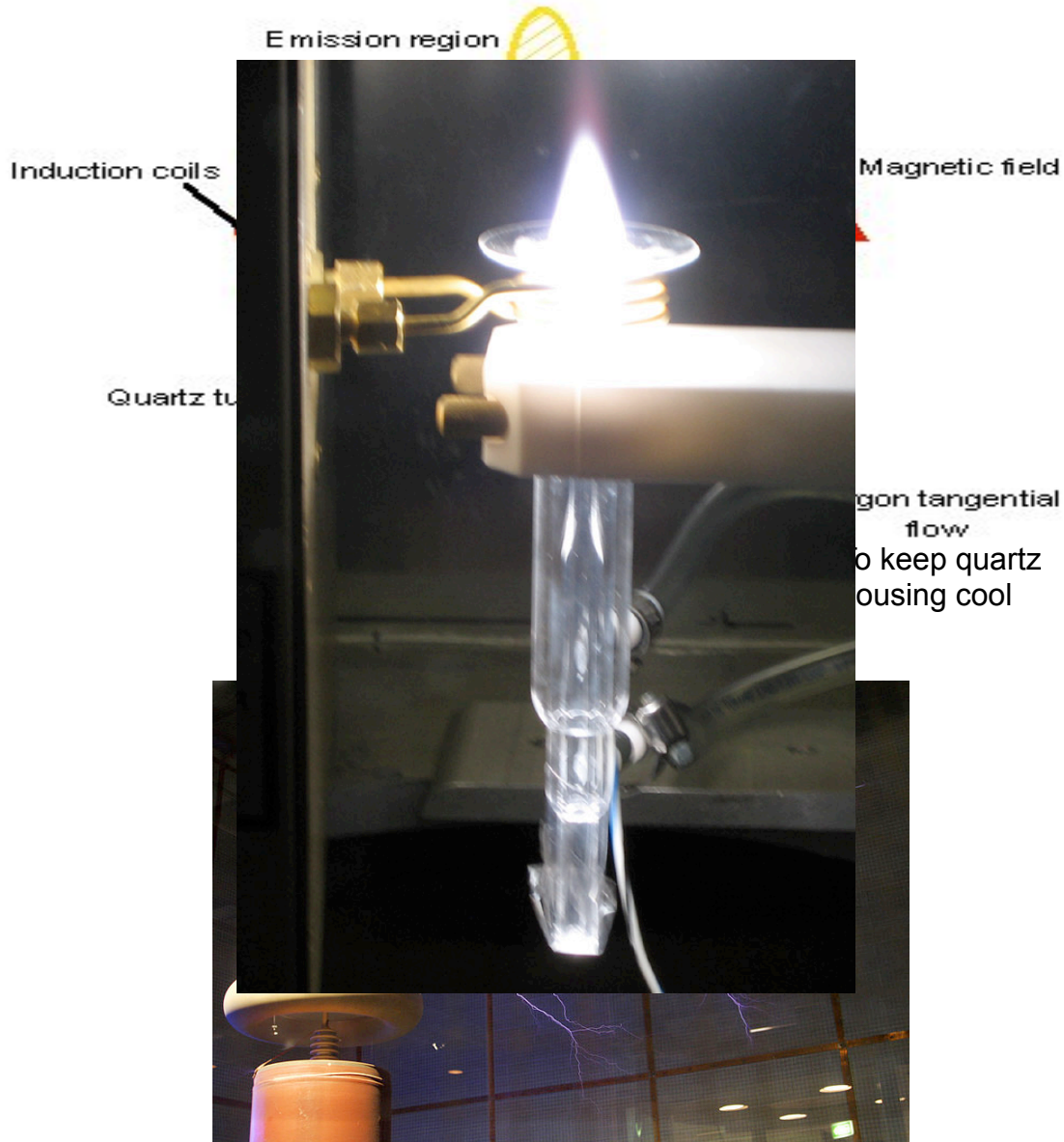
Higher temperatures decrease chemical interferences

Strong emission signals for most elements under a single set of conditions

More expensive

Many emission lines observed means good monochromator must be used

The Inductively Coupled Plasma Torch



Gaseous mixture of Ar cations and electrons

A Tesla coil is used as a “spark” (an electrical discharge) that ionizes the Ar atoms.

(Tesla coils turn 120V AC into extremely high voltages.)

The magnetic field stirs the pot, and the collisions between ions and electrons raises the T.

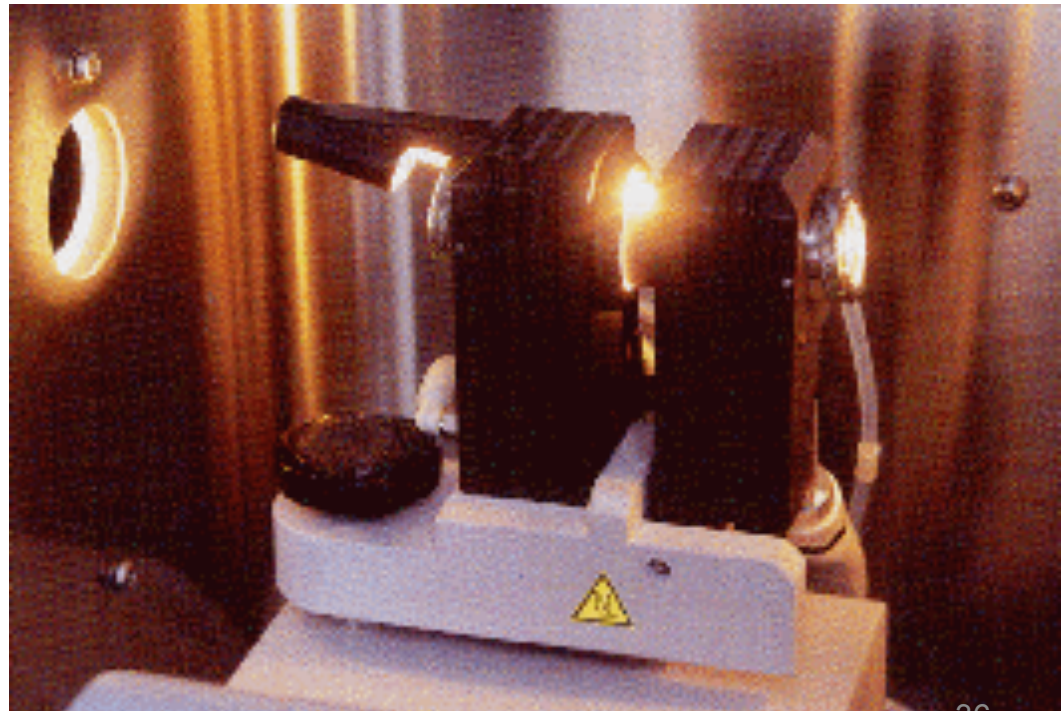
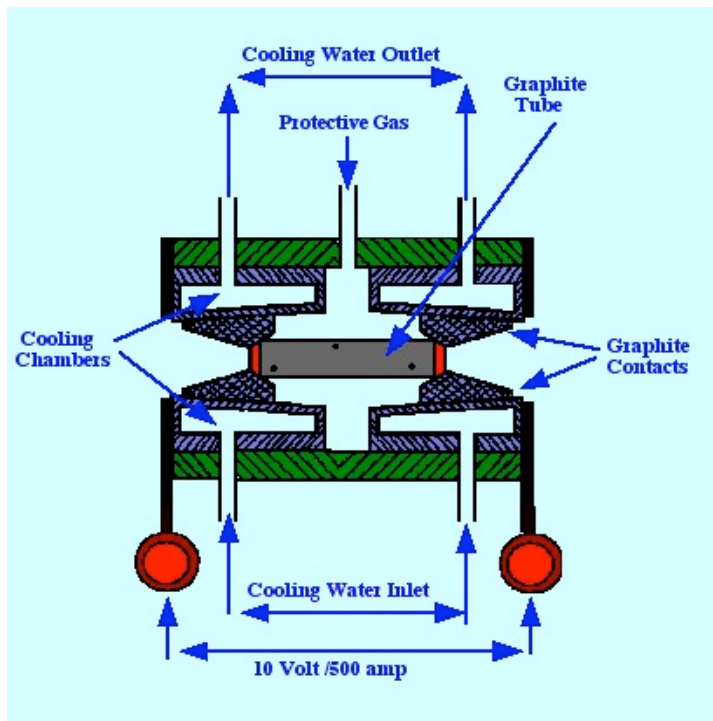
Temps can reach 10,000 K.

Concept Test

Which of the following is a light source for atomic emission spectroscopy?

Electrothermal Methods: The Graphite Furnace

With Graphite Furnace Atomic Absorption (GFAA), the sample is introduced directly into a graphite tube, which is then heated to remove the solvent and major matrix components and to atomize the remaining sample. Heating is accomplished by applying a voltage (10V, 500A) across the tube. Nearly 100% of the analyte is atomized, and the atoms are retained within the tube (and the light path, which passes through the tube) for an extended period of time.



The Graphite Furnace

Advantages

Small sample volumes (20 μL)

Solids and liquids

Rapid heating yields more efficient atomization

Atoms spend longer times in the tube (signal averaging)

TABLE 1. Summary of common techniques used atomic spectroscopy.

	ICP ¹	FAA ²	GFAA ³	MIP ⁴	Arc ⁵
Temp (K)	4000–8000	1500–2500	2000	1000–2000	3000–8000
e ⁻ /cm ³	5 × 10 ¹⁴	3–9 × 10 ¹³		7 × 10 ¹³	10 ¹⁴ –10 ¹⁵
gas	argon	air/acetylene	argon	helium	argon
LOD (conc) ⁶	2 ppb	10ppb	0.1 ppb		8 ppb
LOD (mass) ⁷	4 ng	20 ng	5 ng		16 ng
SME ⁸	ME	SE	SE	ME	ME
Heating Method	Induction	combustion	voltage across graphite tube	magnetron	voltage across graphite tube
λ Range ⁹	120–900	190–900	190–900	190–900	190–900
Range ¹⁰	4–6	3–4	2–3	3–4	3–4
AA source		HCL	HCL		
Common Application	ppb of numerous metals in solution	ppm of 1 metal (high volume)	single element low volume (ppb, pg)	halogens (Cl, Br, etc.)	Replaced by ICP
Price ¹¹	\$100,000	\$35,000	\$55,000	\$65,000	
Sample size	Flow (mL)	Flow (mL)	Static (μL)	Flow (mL)	Flow (mL)
Interfer. Instrum. System ¹²	argon emis ¹³ contin.	molecul. ¹⁴	molecul., scatter ¹⁵	He emis ¹⁶ contin.	elect ¹⁷ Ar emis., contin.
Frequency	27.12, 40 MHz			2450 MHz	DC
Power	1–2 kW			0.2–1 kW	<100 W

¹ Inductively Coupled Plasma-Atomic Emission Spectrometer.² Flame Atomic Absorption.³ Graphite Furnace Atomic Absorption.⁴ Microwave Induced Plasma.⁵ DC plasma arc.⁶ The limit of detection for iron by concentration (MIP-AES is used primarily for nonmetals).⁷ The limit of detection for iron by absolute mass (for ICP, FAA, DCP assumes 2 mL volume, GFAA assumes 50 μL).⁸ Single or multielement analysis possible on a single sample. For example, a commercial ICP can simultaneously detect 20 elements but a graphite furnace atomic absorption system is only capable of single element detection with a single "shot."⁹ The linear dynamic range (orders of magnitude).¹⁰ The wavelength range of the technique. These values can vary with sources, dispersing element, and detector chosen.¹¹ Varies with vendor, model, accessories, etc..¹² Interferences from instrumental system.¹³ Ar emission; continuum background.¹⁴ Molecular emission; absorbance from gas species (e.g., C₂, N₂, CO, etc.).¹⁵ Scattering from particulate matter.¹⁶ Helium emission.¹⁷ Electrode degradation (e.g., W, WC, emission etc.).

Concept Test

An environmental analytical chemist is asked to analyze a water sample for the presence of Pb^{2+} ions. The best technique to use for the analysis is (where best means it accomplishes the analysis at the cheapest price):

- (A) IR spectroscopy
- (B) Atomic emission spectroscopy
- (C) Atomic Absorption spectroscopy
- (D) Atomic fluorescence spectroscopy

Nanomedicine and Instrumental Analysis

Nanomedicine is the use of nanometer-sized matter in the diagnosis and treatment of disease.

Nanomedicine and Instrumental Analysis

When gold absorbs light, it heats up, killing any nearby cells.

ICP of Mice Treated with a Gold Nanoparticle Pancreatic Cancer Therapeutic

Tissues heated and digested with HNO_3 .

Mice Treated with a Gold Nanoparticle Antibiotic