Analytical chemistry

Lecture № 29

Emission spectroscopy
Part II

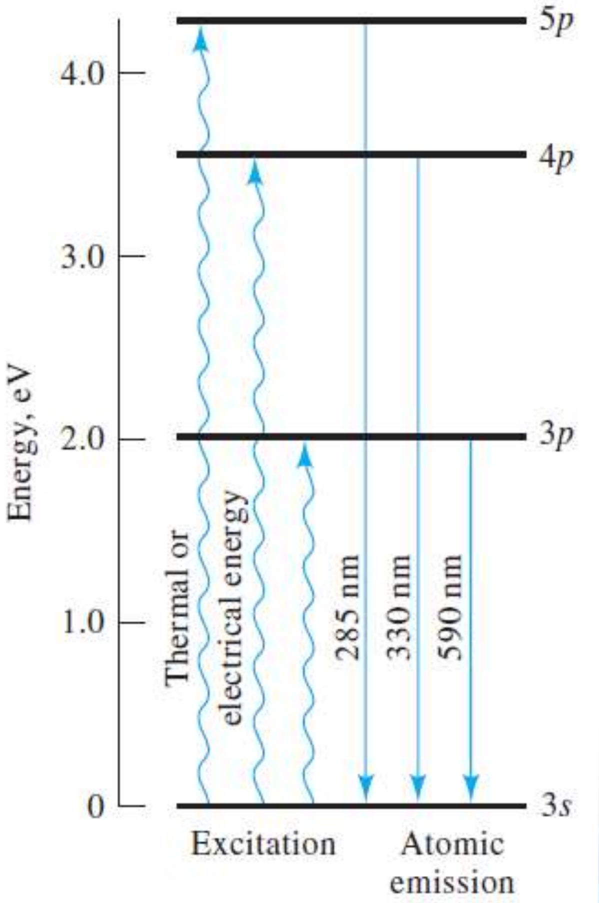
Similar to molecular luminescence, atomic luminescence can be produced by excitation of atoms by photons; this represents the technique of **atomic fluorescence spectrometry (AFS).** Also, unlike molecules that thermally decompose long before they can be thermally excited sufficiently to emit light, atoms can be heated to high enough temperatures to emit their characteristic radiation. While atoms undergo true thermoluminescence, this term is not used to describe the relevant measurement techniques, rather they are always described with reference to the specific means of exciting the atoms. Examples are the techniques of **flame emission spectrometry** (in practical use today, the desired wavelengths are selected using interference filters—hence, the technique is more accurately called **flame photometry), arc/spark** source emission spectrometry, direct current plasma (DCP) emission spectrometry, and **induction coupled plasma (also called inductively coupled plasma) atomic (or optical) emission spectrometry (ICP-AES or ICP-OES).**

Atomic emission spectroscopy

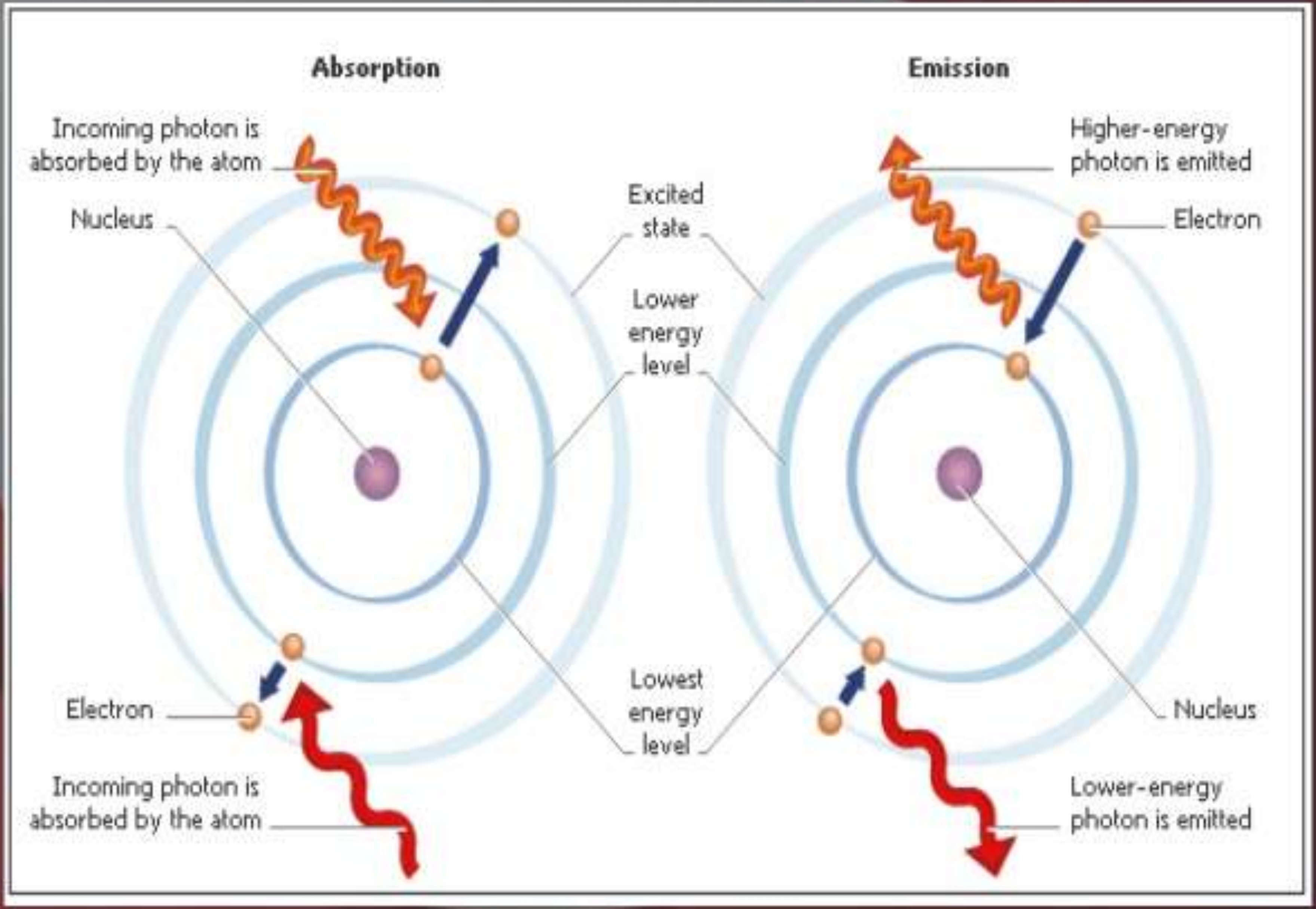
The focus of this section is the emission of ultraviolet and visible radiation following thermal or electrical excitation of atoms. Atomic emission spectroscopy has a long history. Qualitative applications based on the color of flames were used in the smelting of ores as early as 1550 and were more fully developed around 1830 with the observation of atomic spectra generated by flame emission and spark emission. Quantitative applications based on the atomic emission from electrical sparks were developed by Norman Lockyer (1836–1920) in the early 1870s, and quantitative applications based on flame emission were pioneered by H. G. Lundegardh in 1930. Atomic emission based on emission from a plasma was introduced in 1964.

In principle, emission spectroscopy can be applied to both atoms and molecules. Molecular infrared emission, or blackbody radiation played an important role in the early development of quantum mechanics and has been used for the analysis of hot gases generated by flames and rocket exhausts. Although the availability of FT–IR instrumentation extended the application of IR emission spectroscopy to a wider array of samples, its applications remain limited. Molecular UV/Vis emission spectroscopy is of little importance since the thermal energies needed for excitation generally result in the sample's decomposition.

In atomic emission spectroscopy, analyte atoms are excited by heat or electrical energy. The energy typically is supplied by a plasma, a flame, a low-pressure discharge, or by a high-powered laser. Before the external energy source is applied, the sodium atoms are usually in their lowest-energy or **ground state.** The applied energy then causes the atoms to be momentarily in a higher-energy or **excited state.**

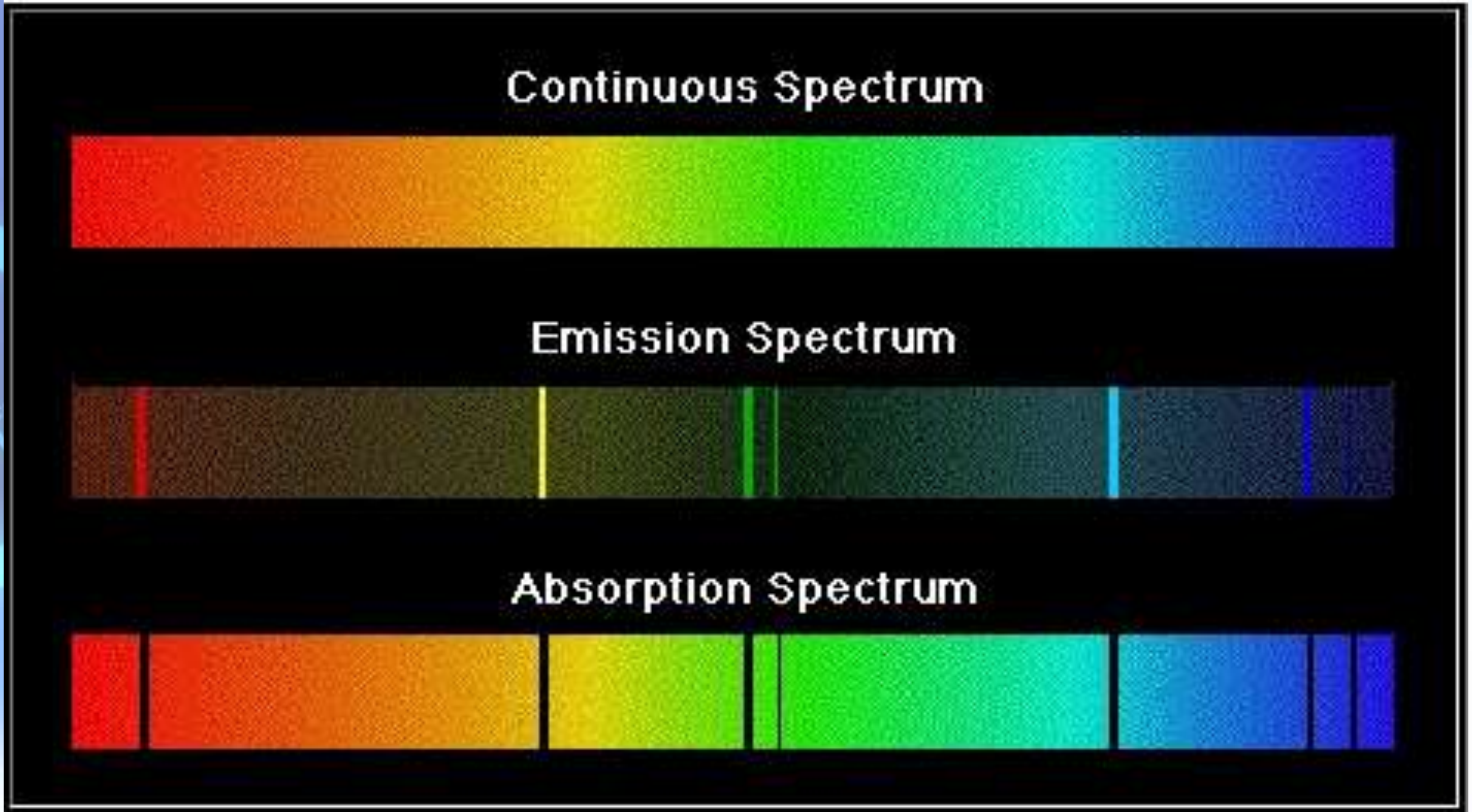


With sodium atoms, for example, in the ground state, the single valence electrons are in the 3*s orbital. External energy* promotes the outer electrons from their ground state 3*s orbitals to 3p, 4p, or 5p* excited-state orbitals. After a few nanoseconds, the excited atoms relax to the ground state giving up their energy as photons of visible or ultraviolet radiation. The wavelength of the emitted radiation is 590, 330, and 285 nm. A transition to or from the ground state is called a **resonance transition, and the** resulting spectral line is called a **resonance line.**



Absorption

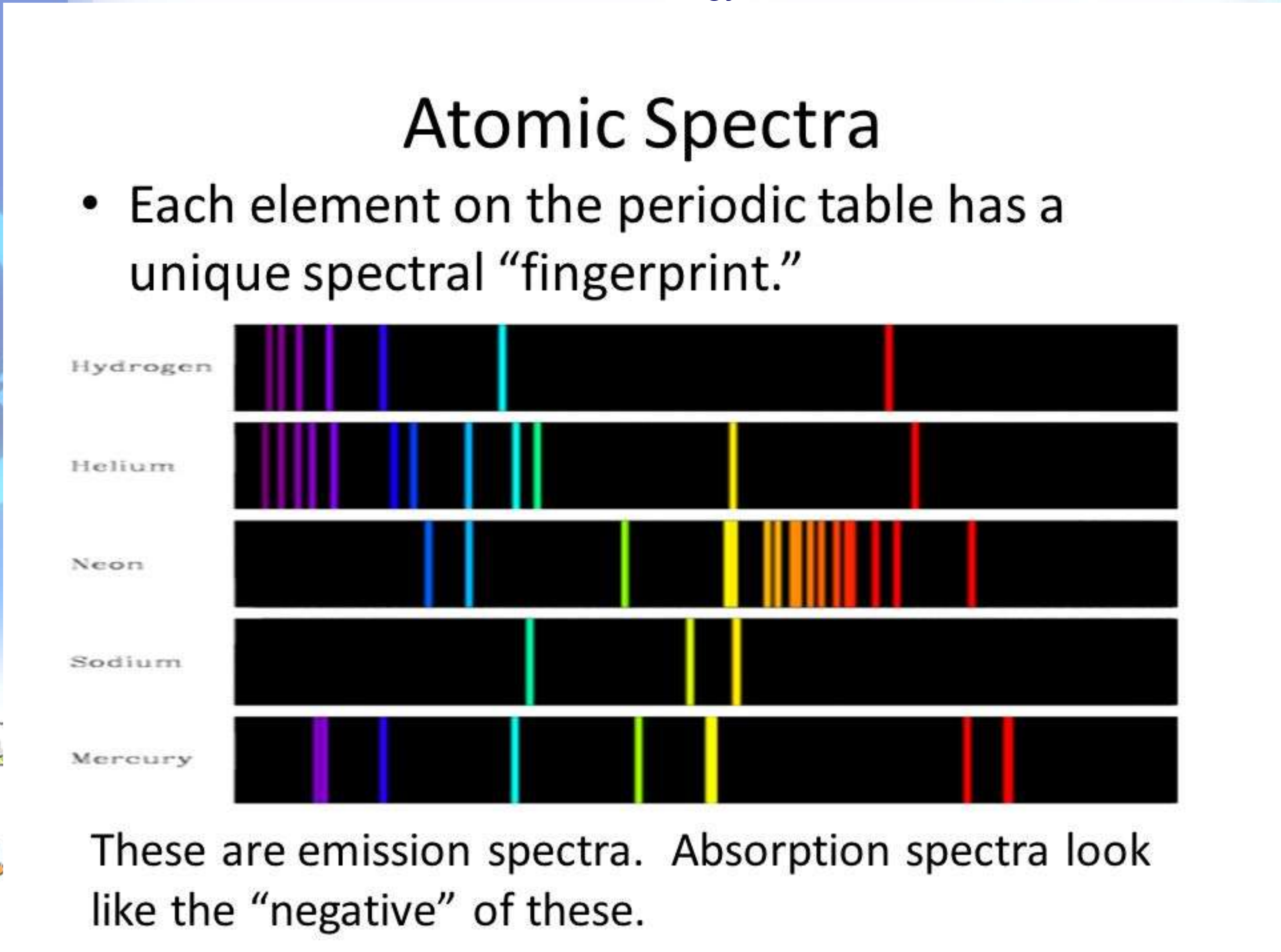
Emission



Continuous, emission, and absorption spectra

Atomic Emission Spectra

Atomic emission occurs when a valence electron in a higher-energy atomic orbital returns to a lower-energy atomic orbital.



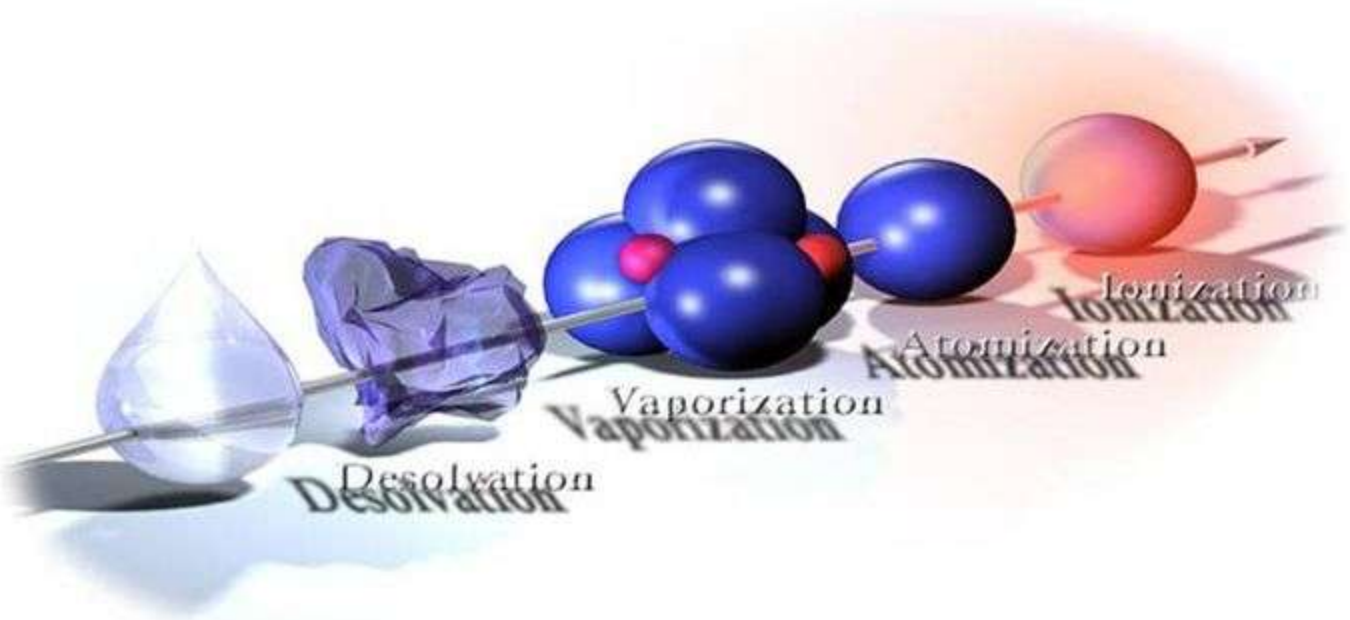
Atomic Spectra

- Each element on the periodic table has a unique spectral “fingerprint.”

These are emission spectra. Absorption spectra look like the “negative” of these.

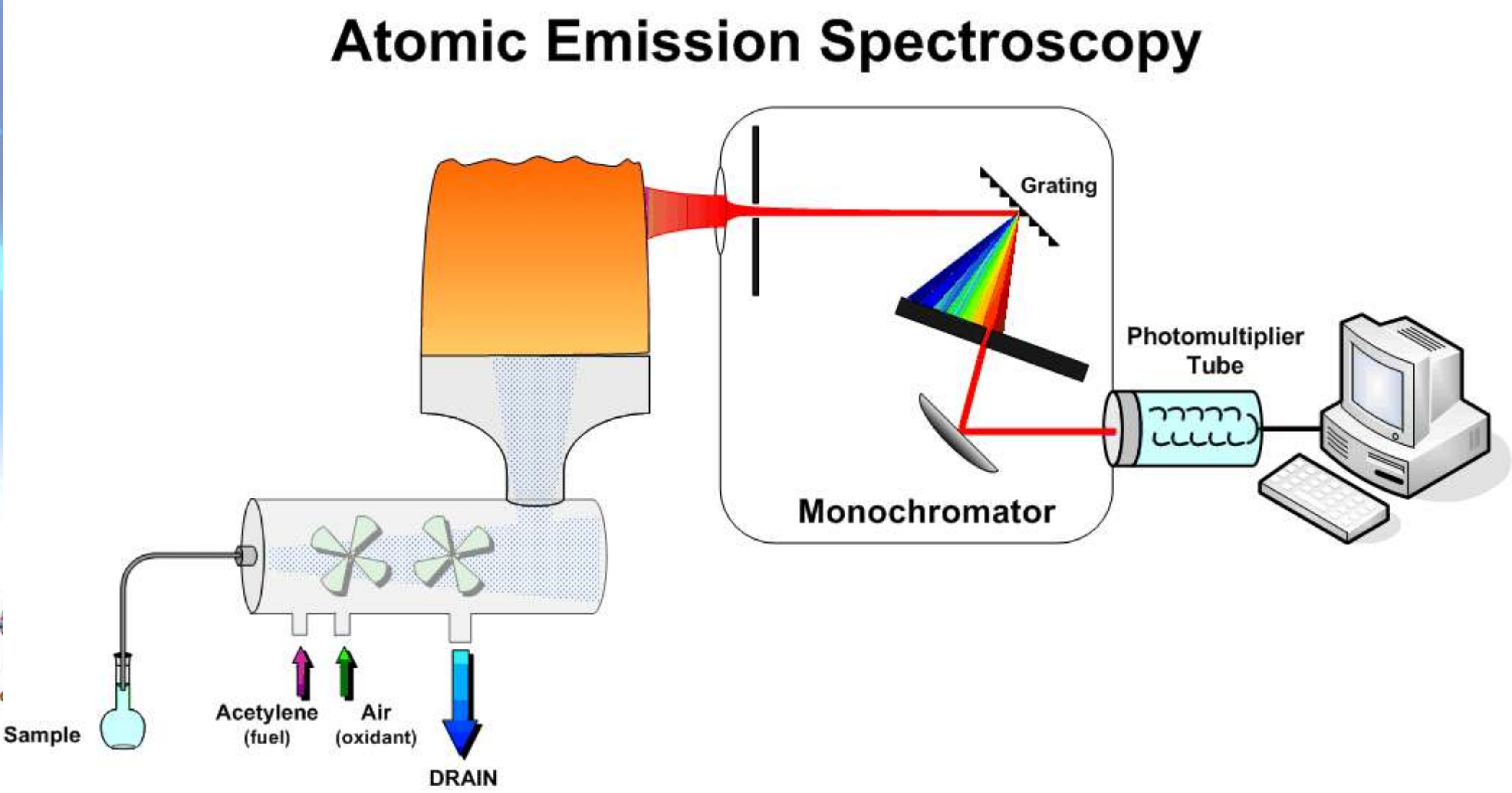
Atomic Emission Theory

- Atomic emission spectroscopy (AES or OES) uses quantitative measurement of the optical emission from excited atoms to determine analyte concentration
- Analyte atoms in solution are aspirated into the excitation region where they are desolvated, vaporized, and atomised by a plasma



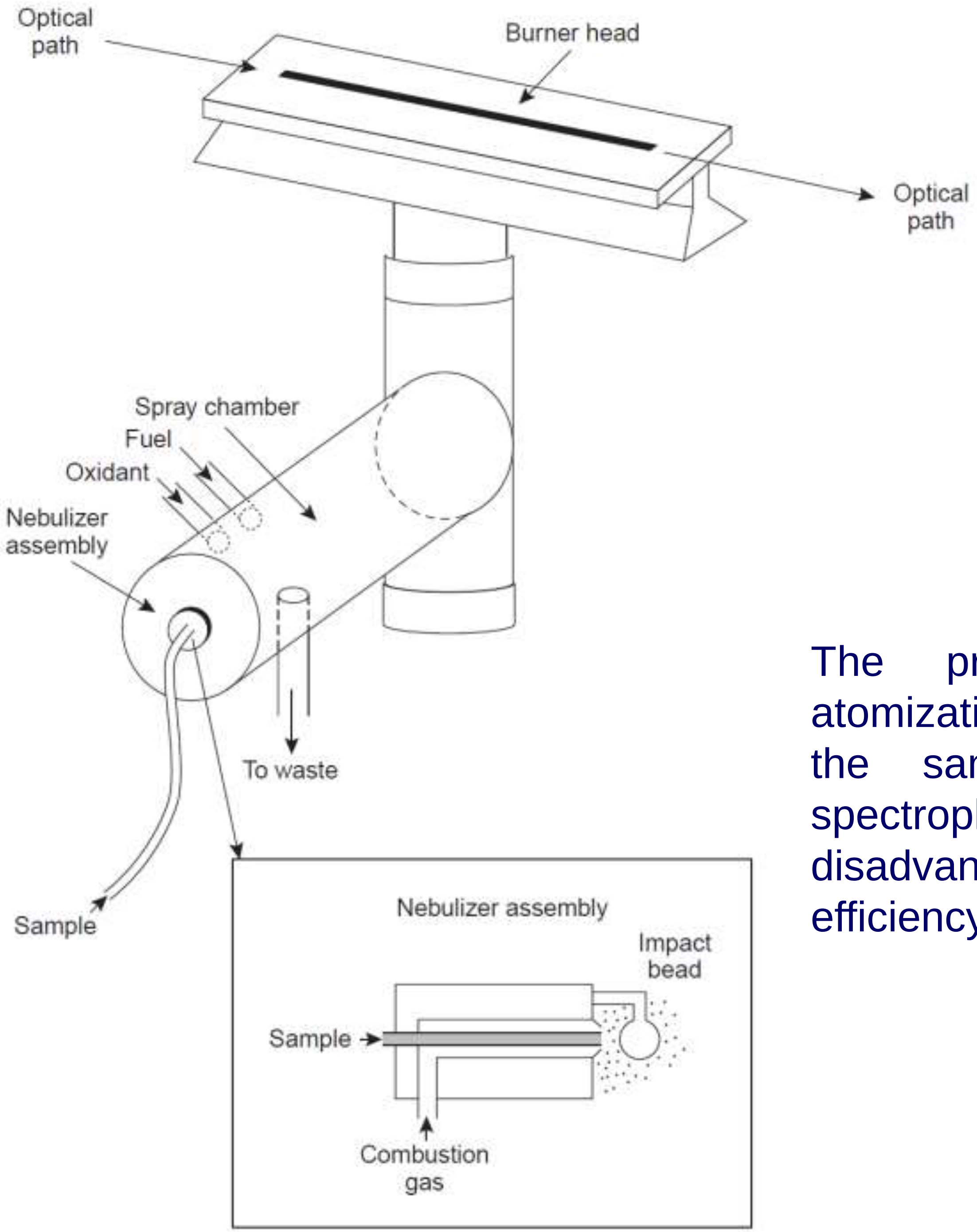
Equipment

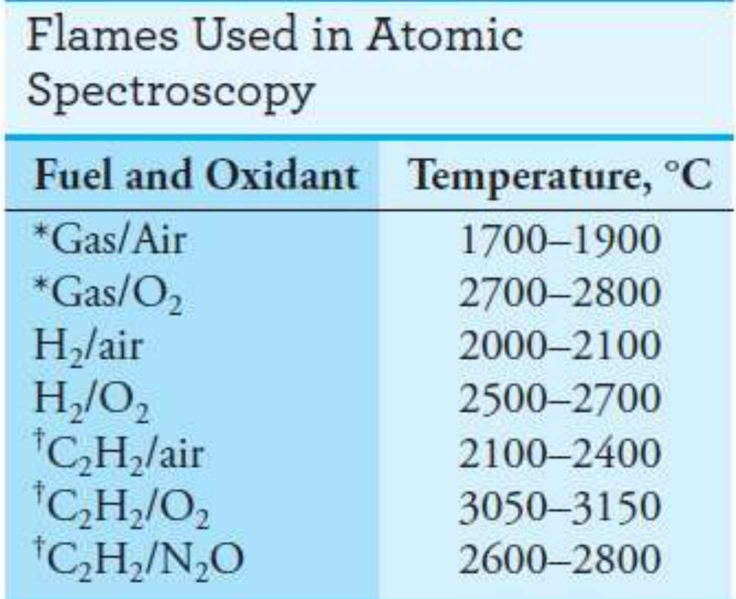
Instrumentation for atomic emission spectroscopy is similar in design to that used for atomic absorption. In fact, most flame atomic absorption spectrometers are easily adapted for use as flame atomic emission spectrometers by turning off the hollow cathode lamp and monitoring the difference between the intensity of radiation emitted when aspirating the sample and that emitted when aspirating a blank. Many atomic emission spectrometers, however, are dedicated instruments designed to take advantage of features unique to atomic emission, including the use of plasmas, arcs, sparks, and lasers, as atomization and excitation sources and have an enhanced capability for multielemental analysis.



Atomization and Excitation Atomic emission requires a means for converting an analyte in solid, liquid, or solution form to a free gaseous atom. The same source of thermal energy usually serves as the excitation source. The most common methods are flames and plasmas, both of which are useful for liquid or solution samples. Solid samples may be analyzed by dissolving in solution and using a flame or plasma atomizer.

- **Flame Sources** Atomization and excitation in flame atomic emission is accomplished using the same nebulization and spray chamber assembly used in atomic absorption. The burner head consists of single or multiple slots or a Meker-style burner. Older atomic emission instruments often used a total consumption burner in which the sample is drawn through a capillary tube and injected directly into the flame.



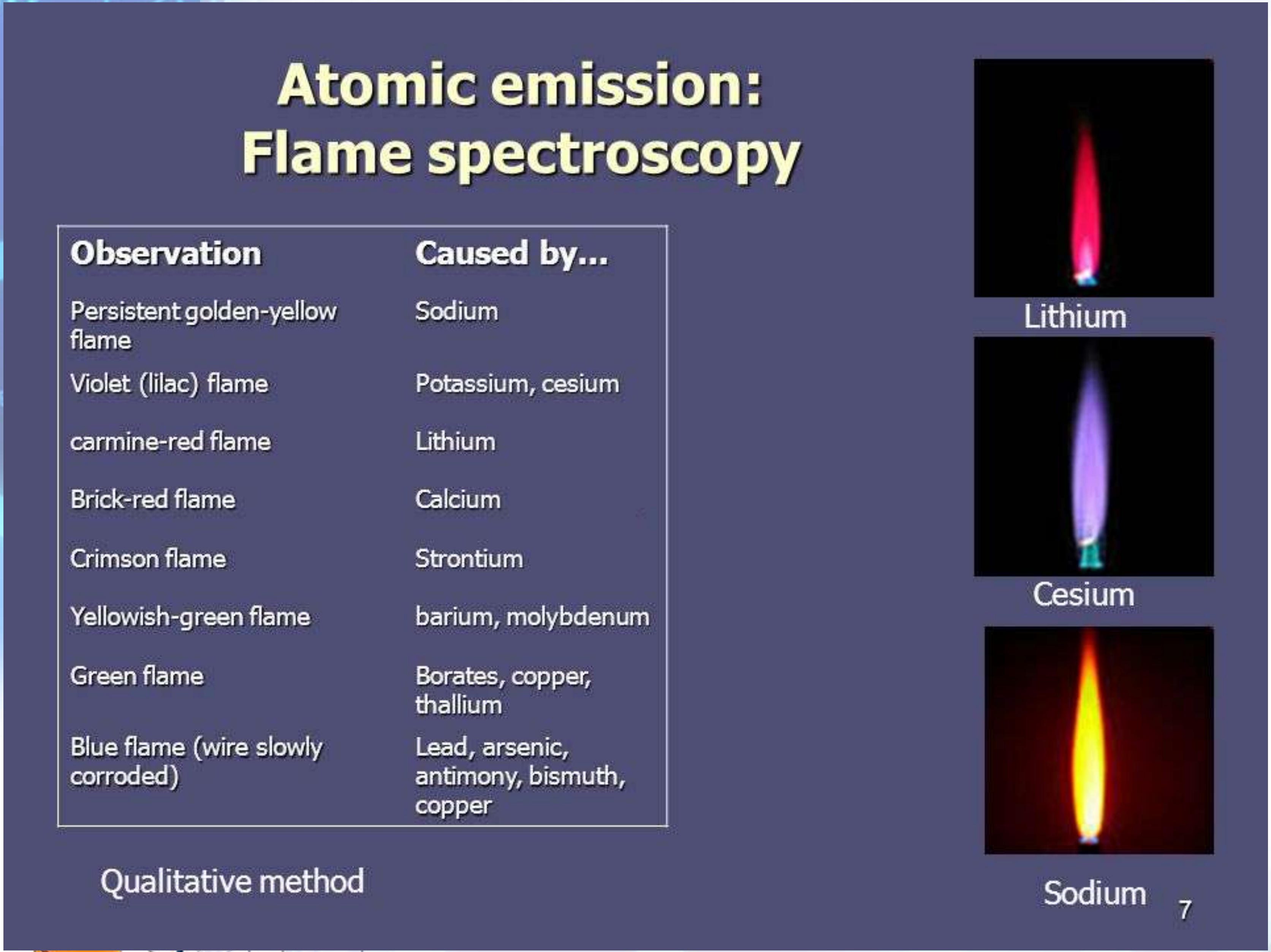


Flames Used in Atomic Spectroscopy

Fuel and Oxidant	Temperature, °C
*Gas/Air	1700–1900
*Gas/O_2	2700–2800
H_2/air	2000–2100
H_2/O_2	2500–2700
†C_2H_2/air	2100–2400
†C_2H_2/O_2	3050–3150
†C_2H_2/N_2O	2600–2800

The principal advantage of flame atomization is the reproducibility with which the sample is introduced into the spectrophotometer. A significant disadvantage to flame atomizers is that the efficiency of atomization may be quite poor.

Flame Emission Spectrometry



Atomic emission: Flame spectroscopy

Observation	Caused by...
Persistent golden-yellow flame	Sodium
Violet (lilac) flame	Potassium, cesium
carmine-red flame	Lithium
Brick-red flame	Calcium
Crimson flame	Strontium
Yellowish-green flame	barium, molybdenum
Green flame	Borates, copper, thallium
Blue flame (wire slowly corroded)	Lead, arsenic, antimony, bismuth, copper

Qualitative method

Lithium

Cesium

Sodium

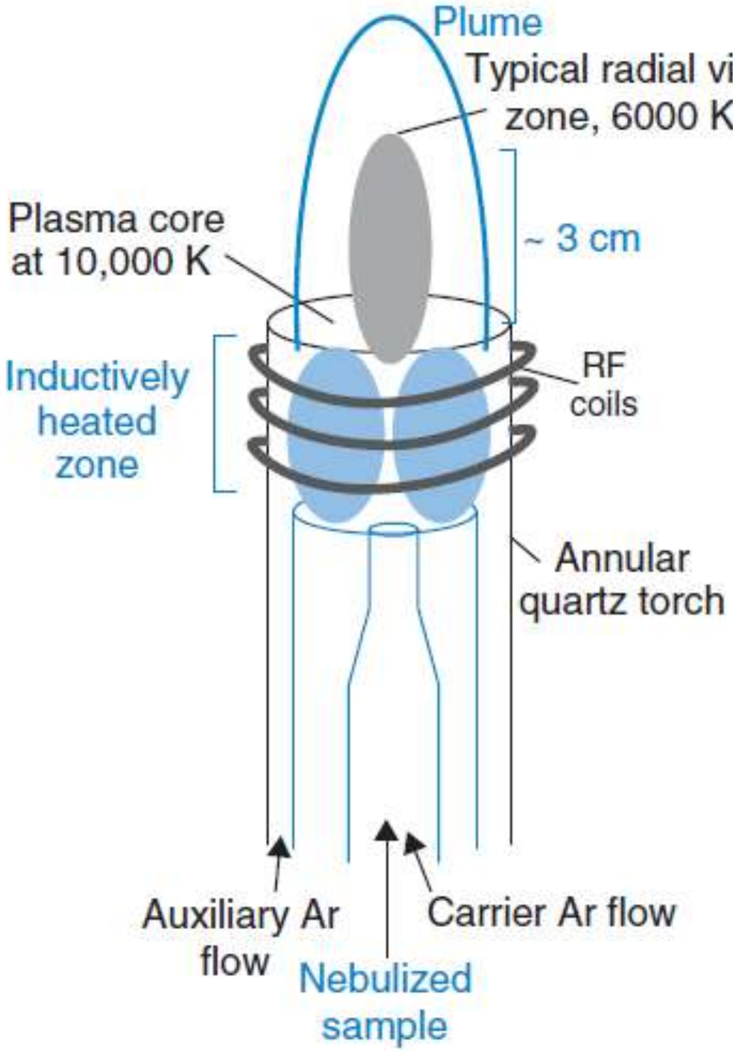
Many other types of atomization devices have been used in atomic spectroscopy. Gas discharges operated at reduced pressure have been investigated as sources of atomic emission. The **glow discharge** is generated between two planar electrodes in a cylindrical glass tube filled with gas to a pressure of a few torr. High-powered lasers have been employed to vaporize samples and to cause **laser-induced breakdown.** In the latter technique, dielectric breakdown of a gas occurs at the laser focal point. A laser-induced breakdown spectrometer (LIBS) is part of the Mars Science Laboratory aboard the rover Curiosity which arrived on Mars in August 2012.

In the early days of atomic spectroscopy, dc and ac arcs and high-voltage sparks were popular sources for exciting atomic emission. Such sources have almost entirely been replaced by the ICP.

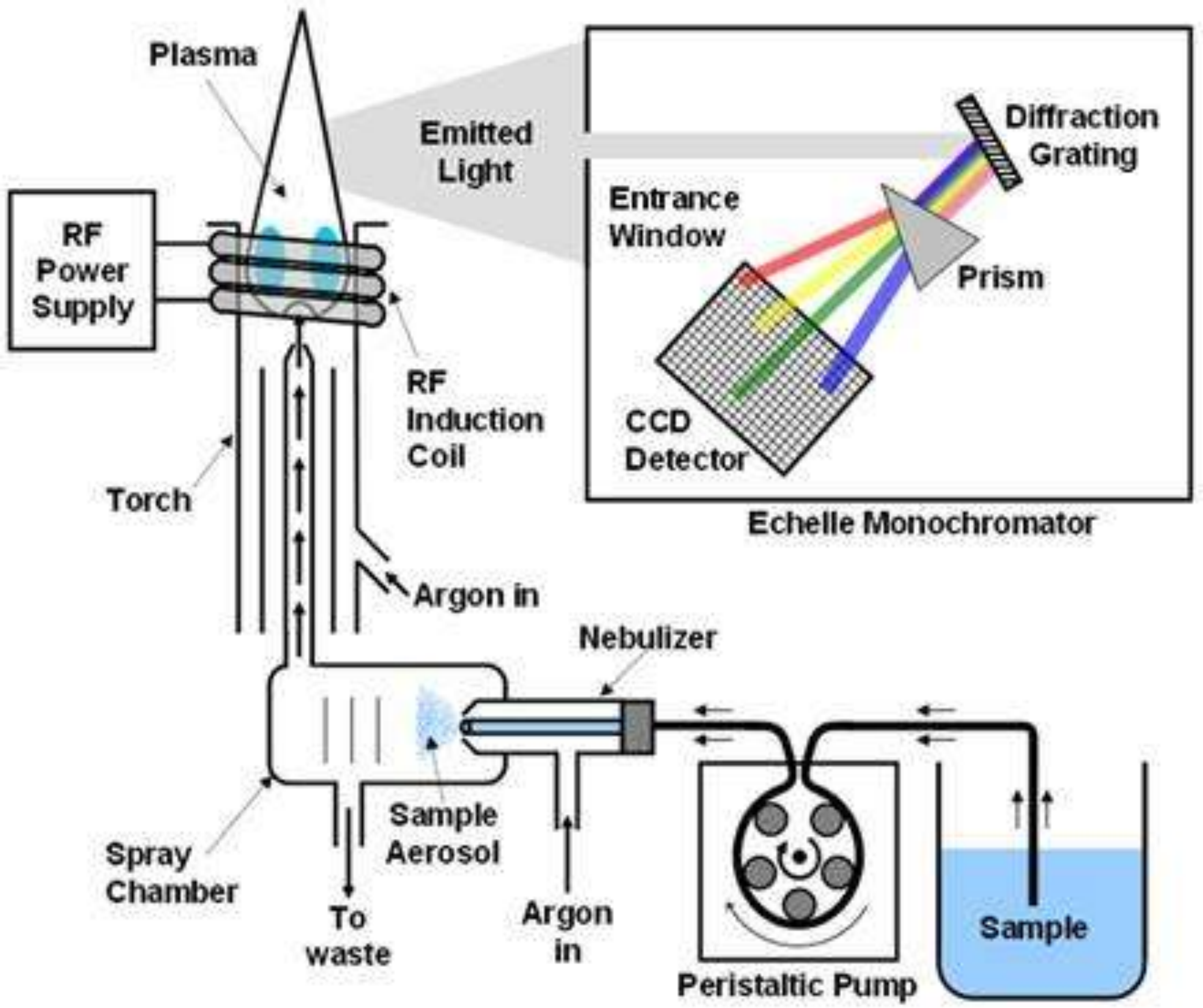
- **Plasma Sources**

Plasma atomizers, which became available commercially in the mid-1970s, offer several advantages for analytical atomic spectrosocopy. Plasma atomization has been used for atomic emission, atomic fluorescence, and atomic mass spectrometry.

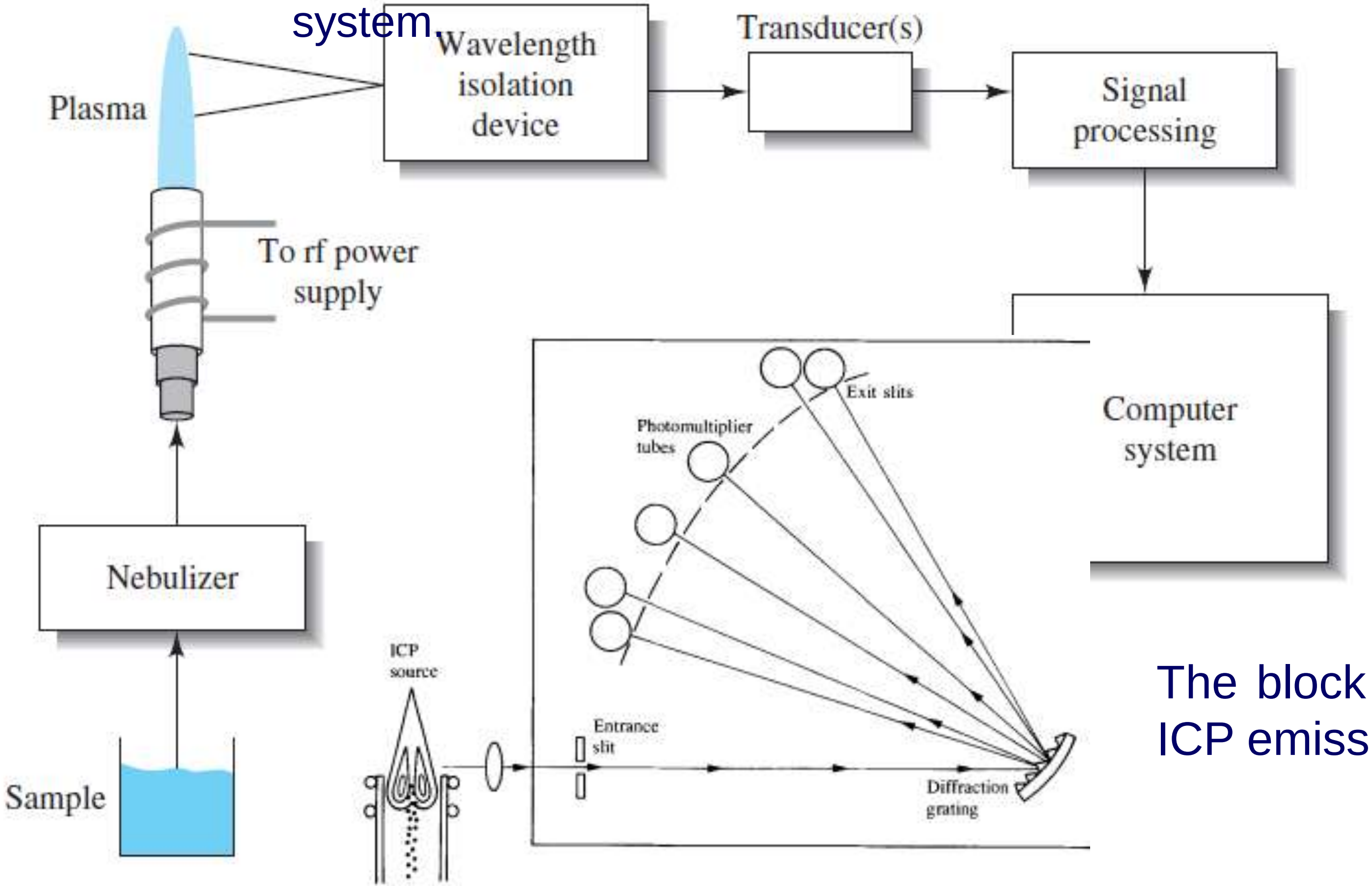
A **plasma is a hot, partially ionized** gas. It contains relatively high concentrations of ions and electrons.



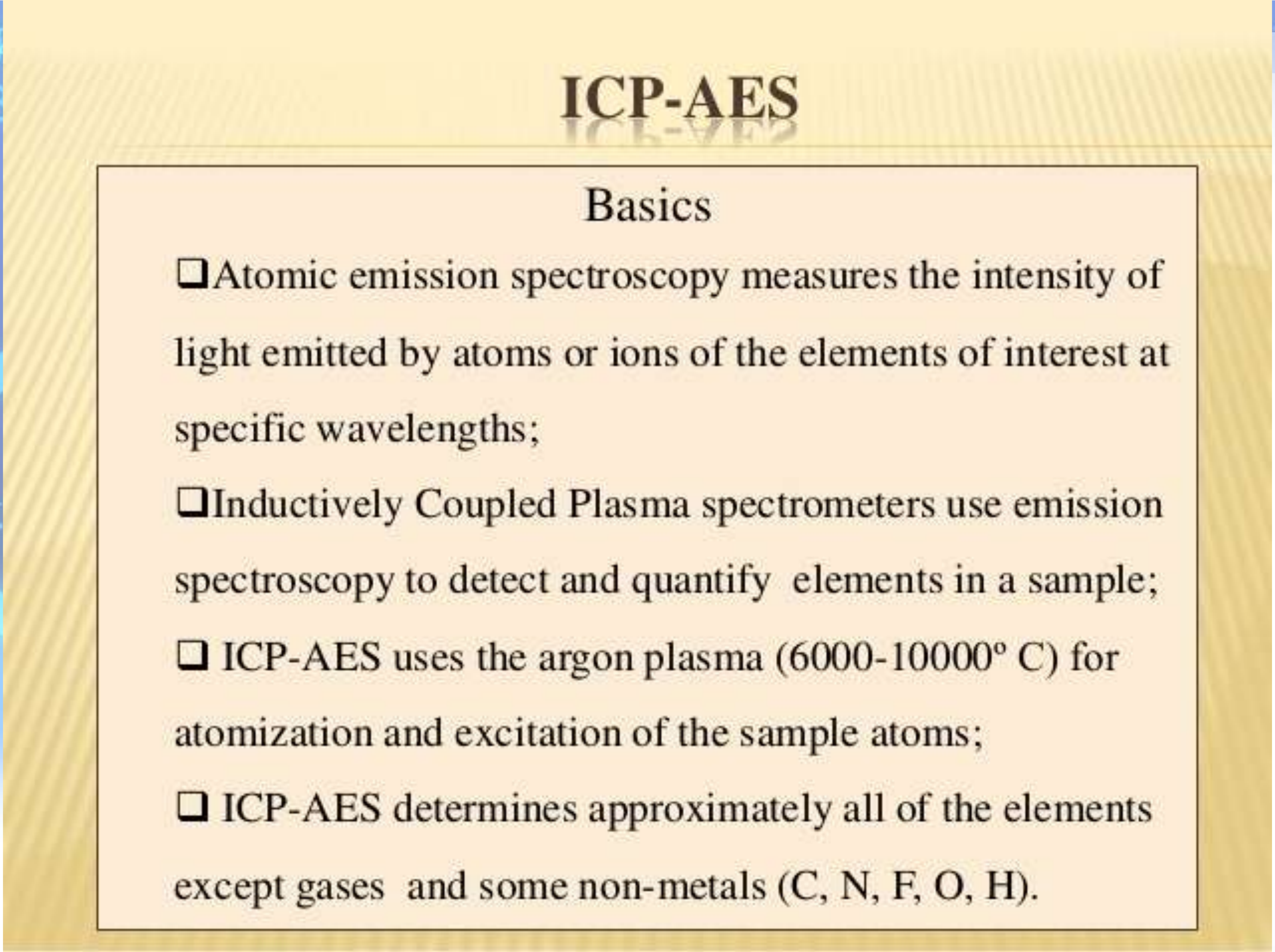
The ICP torch consists of three concentric quartz tubes, surrounded at the top by a radio-frequency induction coil. The sample is mixed with a stream of Ar using a spray chamber nebulizer similar to that used for flame emission and is carried to the plasma through the torch’s central tube. Plasma formation is initiated by a spark from a Tesla coil. An alternating radiofrequency current in the induction coils creates a fluctuating magnetic field that induces the argon ions and electrons to move in a circular path. The resulting collisions with the abundant unionized gas give rise to resistive heating, provid ing temperatures as high as 10,000 K at the base of the plasma, and between 6000 and 8000 K at a height of 15–20 mm above the coil, where emission is usually measured. At these high temperatures the outer quartz tube must be thermally isolated from the plasma. This is accomplished by the tangential flow of argon shown in the schematic diagram.


Plasma
Emitted Light
RF Power Supply
RF Induction Coil
Torch
Argon in
Diffraction Grating
Entrance Window
Prism
CCD Detector
Echelle Monochromator
Nebulizer
Spray Chamber
Sample Aerosol
To waste
Argon in
Peristaltic Pump
Sample

Atomic or ionic emission from the plasma is separated into its constituent wavelengths by the wavelength isolation device. This separation can take place in a **monochromator,** a **polychromator, or a spectrograph.** The monochromator isolates one wavelength at a time at a single exit slit, while a polychromator isolates several wavelengths simultaneously at multiple exit slits. The spectrograph provides a large aperture at its output to allow a range of wavelengths to exit. The isolated radiation is then converted into electrical signals by a single transducer, multiple transducers, or an array detector. The electrical signals are then processed and provided as input to the computer system.



The block diagram of a typical ICP emission spectrometer



ICP-AES

Basics

❑Atomic emission spectroscopy measures the intensity of light emitted by atoms or ions of the elements of interest at specific wavelengths;

❑Inductively Coupled Plasma spectrometers use emission spectroscopy to detect and quantify elements in a sample;

❑ ICP-AES uses the argon plasma (6000-10000° C) for atomization and excitation of the sample atoms;

❑ ICP-AES determines approximately all of the elements except gases and some non-metals (C, N, F, O, H).

Quantitative Applications

Atomic emission is used for the analysis of the same types of samples that may be analyzed by atomic absorption.

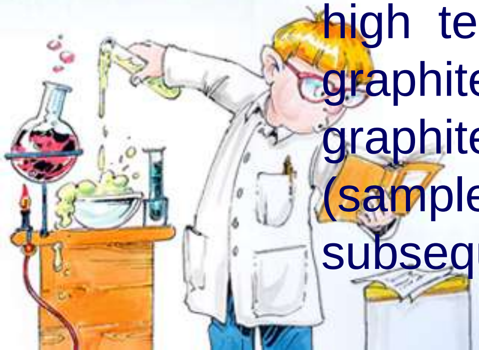
Quantitative Applications

Atomic emission is widely used for the analysis of trace metals in a variety of sample matrices. The development of a quantitative atomic emission method requires several considerations, including choosing a source for atomization and excitation, selecting a wavelength and slit width, preparing the sample for analysis, minimizing spectral and chemical interferences, and selecting a method of standardization.

PREPARING THE SAMPLE

Flame and plasma sources are best suited for samples in solution and liquid form. Although a solid sample can be analyzed by directly inserting it into the flame or plasma, they usually are first brought into solution by digestion or extraction.

Solid samples can be sub-divided into two categories, such as: (*i*) *Those possessing* good conductance characteristics and can withstand high temperatures: it can be achieved by making electrodes with the material directly to be used for the electrical discharge; (*ii*) *Those* having poor conductance and cannot withstand high temperatures: it can be powdered mixed with the powdered graphite (known as buffer) and placed in the depression of the lower graphite electrode. On passing the electrical discharge the material (sample) is first vaporised into the body of the discharge and subsequently the spectrographic emission occurs.



Evaluation

- **Scale of Operation** The scale of operations for atomic emission is ideal for the direct analysis of trace and ultratrace analytes in macro and meso samples. With appropriate dilutions, atomic emission also can be applied to major and minor analytes.
- **Accuracy** When spectral and chemical interferences are insignificant, atomic emission is capable of producing quantitative results with accuracies of 1–5%. Accuracy in flame emission frequently is limited by chemical interferences. Because the higher temperature of a plasma source gives rise to more emission lines, accuracy when using plasma emission often is limited by stray radiation from overlapping emission lines.
- **Precision** For samples and standards in which the concentration of analyte exceeds the detection limit by at least a factor of 50, the relative standard deviation for both flame and plasma emission is about 1–5%. Perhaps the most important factor affecting precision is the stability of the flame's or plasma's temperature.
- **Sensitivity** Sensitivity in flame atomic emission is strongly influenced by the temperature of the excitation source and the composition of the sample matrix. Normally, sensitivity is optimized by aspirating a standard solution and adjusting the flame's composition and the height from which emission is monitored until the emission intensity is maximized. Chemical interferences, when present, decrease the sensitivity of the analysis. With plasma emission, sensitivity is less influenced by the sample matrix.
- **Selectivity** The selectivity of atomic emission is similar to that of atomic absorption. Atomic emission has the further advantage of rapid sequential or simultaneous analysis.

- **Time, Cost, and Equipment** Sample throughput with atomic emission is very rapid when using automated systems capable of multielemental analysis. For example, sampling rates of 3000 determinations per hour have been achieved using an ICP with simultaneous analysis, and 300 determinations per hour with a sequential ICP. Flame emission is often accomplished using an atomic absorption spectrometer, which typically costs $10,000–50,000. Sequential ICPs range in price from $55,000 to $150,000, whereas an ICP capable of simultaneous multielemental analysis costs $80,000–200,000. Combination ICPs that are capable of both sequential and simultaneous analysis range in price from $150,000 to $300,000. The cost of Ar, which is consumed in significant quantities, cannot be overlooked when considering the expense of operating an ICP.

The blue color of the sky during the day and the red color of the sun at sunset result from the scattering of light by small particles of dust, molecules of water, and other gases in the atmosphere. The efficiency of a photon’s scattering depends on its wavelength. We see the sky as blue during the day because violet and blue light scatter to a greater extent than other, longer wavelengths of light. For the same reason, the sun appears red at sunset because red light is less efficiently scattered and is more likely to pass through the atmosphere than other wavelengths of light.

Summary

The spectrophotometric methods of analysis covered in this chapter include those based on the absorption, emission, or scattering of electromagnetic radiation. When a molecule absorbs UV/Vis radiation it undergoes a change in its valence shell configuration. A change in vibrational energy results from the absorption of IR radiation. Experimentally we measure the fraction of radiation transmitted, T, *by the sample. Instrumentation* for measuring absorption requires a source of electromagnetic radiation, a means for selecting a wavelength, and a detector for measuring transmittance. Beer's law relates absorbance to both transmittance and to the concentration of the absorbing species ($A = -\log T = \varepsilon bC$).

In atomic absorption we measure the absorption of radiation by gas phase atoms. Samples are atomized using thermal energy from either a flame or a graphite furnace. Because the width of an atom's absorption band is so narrow, the continuum sources common for molecular absorption can not be used. Instead, a hollow cathode lamp provides the necessary line source of radiation. Atomic absorption suffers from a number of spectral and chemical interferences. The absorption or scattering of radiation from the sample's matrix are important spectral interferences that may be minimized by background correction. Chemical interferences include the formation of nonvolatile forms of the analyte and ionization of the analyte. The former interference is minimized by using a releasing agent or a protecting agent, and an ionization suppressor helps minimize the latter interference.

When a molecule absorbs radiation it moves from a lower energy state to a higher energy state. In returning to the lower energy state the molecule may emit radiation. This process is called photoluminescence. One form of photoluminescence is fluorescence in which the analyte emits a photon without undergoing a change in its spin state. In phosphorescence, emission occurs with a change in the analyte’s spin state. For low concentrations of analyte, both fluorescent and phosphorescent emission intensities are a linear function of the analyte’s concentration. Thermally excited atoms also emit radiation, forming the basis for atomic emission spectroscopy. Thermal excitation is achieved using either a flame or a plasma.