Chapter 8

An Introduction to Optical Atomic Spectroscopy

- **Atomic Spectroscopic methods** are used for elemental analysis for identification and quantitation.
- Need free atoms in the gas phase for atomic analysis.
- The elements present in the sample are converted to gaseous atoms or elementary ions by a process called **atomization**.
- The ultraviolet/visible absorption, emission or fluorescence of the atomic species in the vapor is measured.
- no vibrational levels, much sharper absorbance, emission and fluorescence bands
- position of bands are well defined and characteristic of a given element
- Qualitative analysis is easy in atomic spectroscopy.

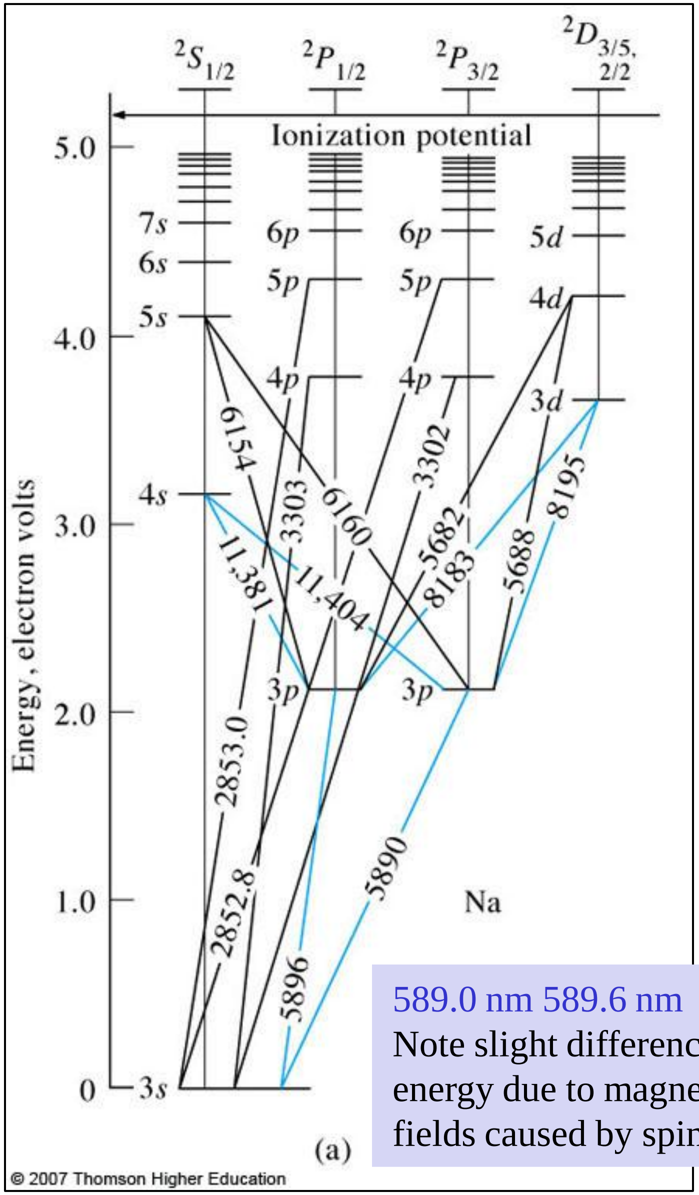
Optical Atomic Spectra

Energy Level Diagrams

- A value of zero electron volts (eV) is arbitrarily assigned to orbital 3s.
- A horizontal line represents the energy of an atomic orbital.
- The scale extends up to 5.14 eV, the energy required to remove the single 3s electron to produce a sodium ion.
  5.14eV is the ionization energy.
- “p” orbitals are split into two levels which differ slightly in energy:

3s → 3p λ= 5896 Å or 5890 Å
3s → 4p λ = 3303 Å or 3302
3s → 5p λ = 2853.0 Å or 2852.8 Å

- There are similar differences in the d and f orbitals, but their magnitudes are usually so small that are undetectable, thus only a single level is shown for orbitals d.



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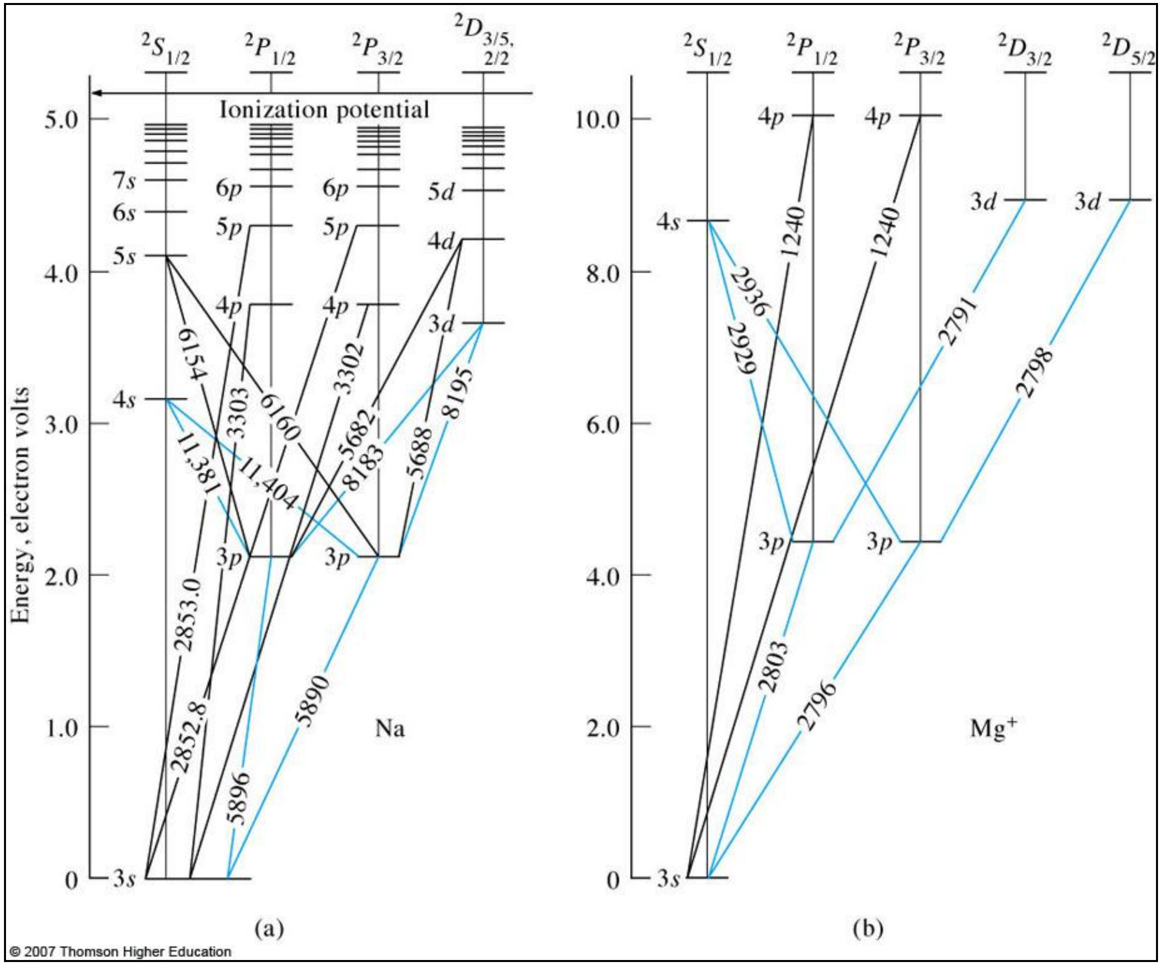
589.0 nm 589.6 nm
Note slight differences in energy due to magnetic fields caused by spin

Figure 8-1a Energy level diagram for sodium.

Mg+ and sodium atom.



- Even though Na and Mg+ species are isoelectronic, the energy differences between the 3p and 3s states are different in each case as a result of the different nuclear charges.

- Separations measured in electronvolts (eV)

  1eV =1.602×10^{-19}J

  = 96. 484 kJ ×mol^{-1}

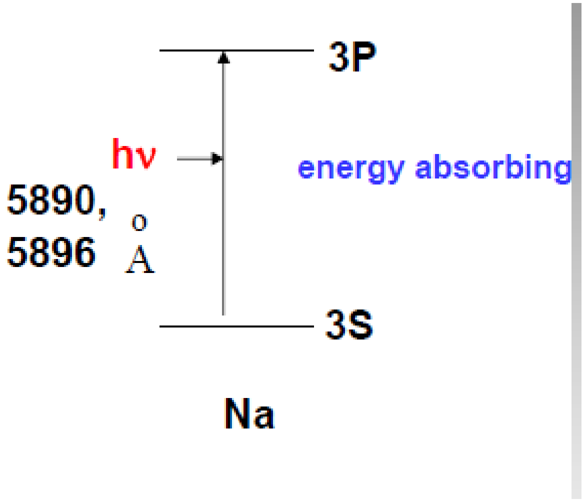
- As # of electrons increases, # of levels increases, Emission spectra become more complex. Li 30 lines, Cs 645 lines, Cr 2277 lines.

* *quantum mechanical selection rules permit prediction of which transitions are likely to occur and which are not.*

Atomic spectroscopy are of 3 types

✓atomic absorption (AA), atomic emission (AE) and atomic fluorescence (AF) methods

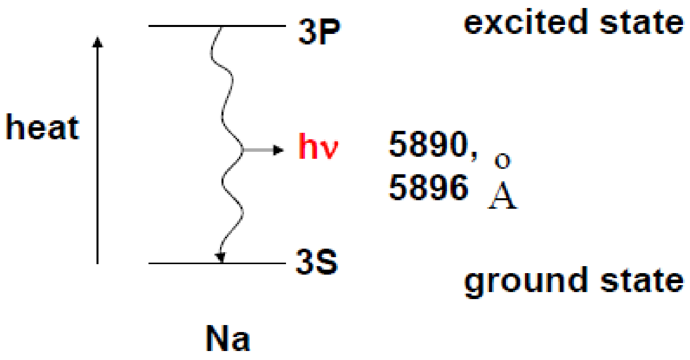
1. Atomic Absorption(AA):



- In a hot gaseous medium, atoms are capable of absorbing radiation of wavelengths characteristic of electronic transitions from ground to higher excited states.
- Typically atomic absorption spectrum consists of resonance lines which are the result of transitions from the ground to upper levels.

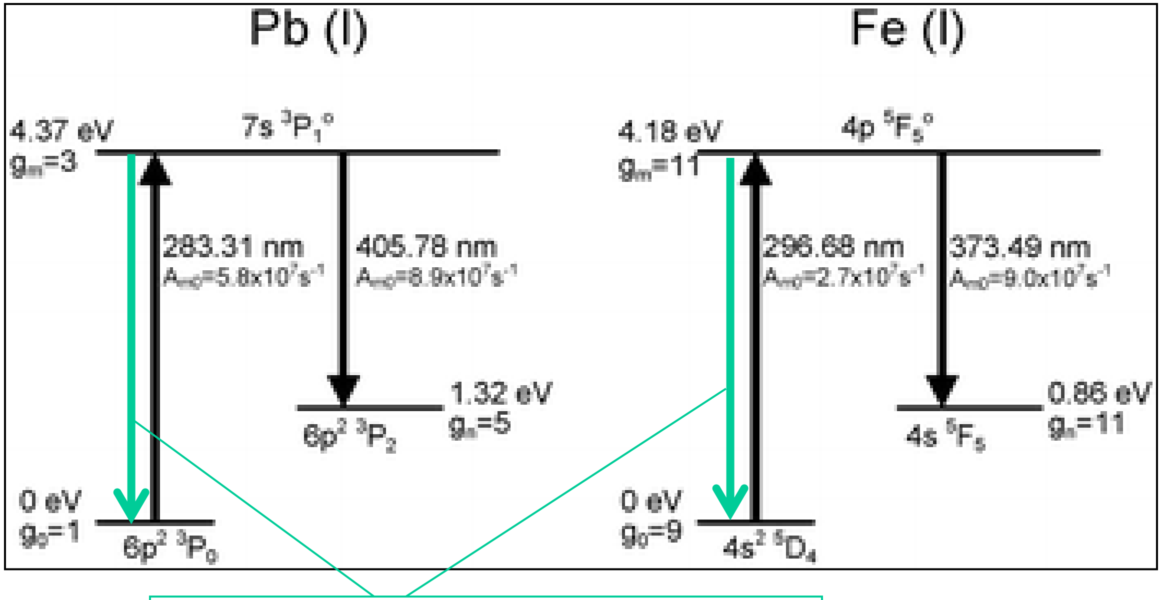
2. Atomic Emission (AE):

At room temperature, essentially all of the atoms of a sample of matter are in the ground state. Excitation to higher orbitals can be brought about by the *heat of a flame, a plasma, an electric arc or spark*. Its return to the ground state is accompanied by emission of a photon of radiation.



3. Atomic Fluorescence (AF):

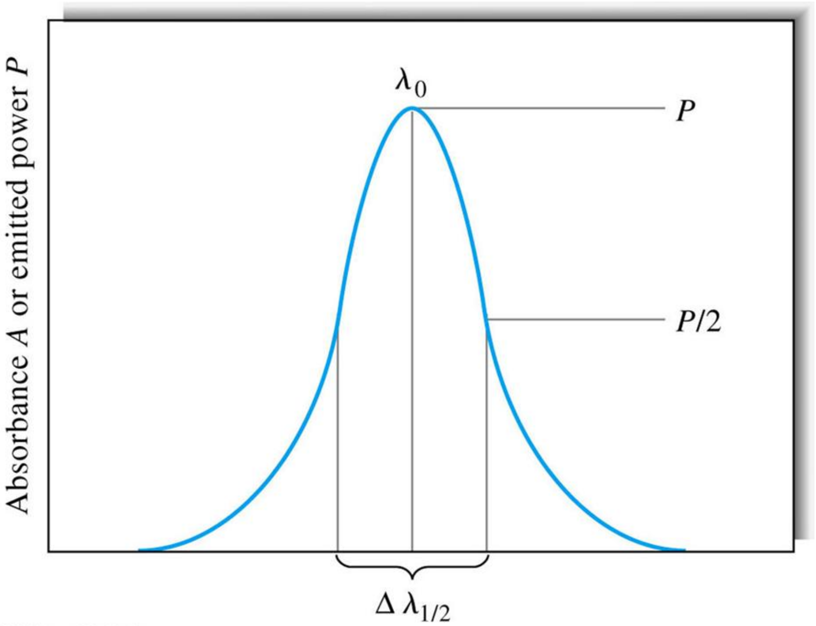
- Atoms or ions in a flame/plasma can be made to fluoresce by irradiation with an *intense source* containing wavelengths that are absorbed by the element.
- The observed radiation is most commonly the result of resonance fluorescence involving transitions from excited states returning to the ground state.



Resonance Fluorescence

Atomic Line Widths

- The widths of atomic lines are of considerable importance in atomic spectroscopy.
- Narrow lines are highly desirable for both absorption and emission because they reduce the possibility of interference due to overlapping spectra.
- A transition between two discrete, single valued energy states should be a line with line-width equal to zero.
- The line width $\Delta\lambda_{1/2}$ of an atomic absorption or emission line is defined as its width in wavelength units when measured at one half the maximum signal



Sources of broadening:
(1) Uncertainty effect
(2) Doppler effect
(3) Pressure effects due to collisions
(4) Electric and magnetic field effects

Line broadening arises from four sources:

1. The uncertainty effect (because of uncertainties in the transition times)
2. The Doppler effect (because of rapid movement of atoms)
3. Pressure effect due to collision between atoms of the same kind and with foreign atoms
4. Electric and magnetic field effects

Uncertainty Effect

- The uncertainty effect (because of uncertainties in the transition times)
- It results from the **uncertainty principle** postulated in 1927 by **Werner Heisenberg.**
- One of several ways of formulating the Heisenberg uncertainty principle is shown in the following equations:

$$\Delta t \ \mathrm{x} \ \Delta E = h \qquad E = hv \qquad \Delta t \ \mathrm{x} \ \Delta v \geq 1$$

The meaning in words of this equation is:

If the energy E of a particle or system of particles – photons, electrons, neutrons or protons – is measured for an exactly known period of time Δt, then this energy is uncertain by at least $h/\Delta t$.

- Therefore, the energy of a particle can be known with zero uncertainty only if it is observed for an infinite period of time.
- For finite periods, the energy measurement can never be more precise then $h/\Delta t$.
- The lifetime of a ground state is typically long, but the lifetimes of excited states are generally short, typically 10^{-7} to 10^{-8} seconds.
- Line widths due to uncertainty broadening are called **natural line widths and are generally 10^{-5}nm or 10^{-4}Å.**

Example

Lifetime of Hg*=2x10-8 s. What is uncertainty broadening for 254 nm line?

$$\Delta t \cdot \Delta \nu = 1 \qquad \Delta \nu = \frac{1}{\Delta t} = \frac{1}{2\text{x}10^{-8}\ \text{s}} = 5\text{x}10^{7}\ \text{Hz}$$

$$\nu = c \cdot \lambda^{-1}$$

Note that $\Delta\lambda = \Delta\lambda_{1/2}$

Differentiating wrt to frequency

$$d\nu = -c\lambda^{-2}d\lambda \qquad d\nu \approx \Delta\nu \text{ and } d\lambda \approx \Delta\lambda$$

$$\Delta\lambda = \frac{\Delta\nu \cdot \lambda^{2}}{c} = \frac{5\text{x}10^{7}\ \text{s}^{-1} \cdot \left(254\text{x}10^{-9}\ \text{m}\right)^{2}}{3\text{x}10^{8}\ \text{m} \cdot \text{s}^{-1}} = 1.1\text{x}10^{-4}\ \text{Å}$$

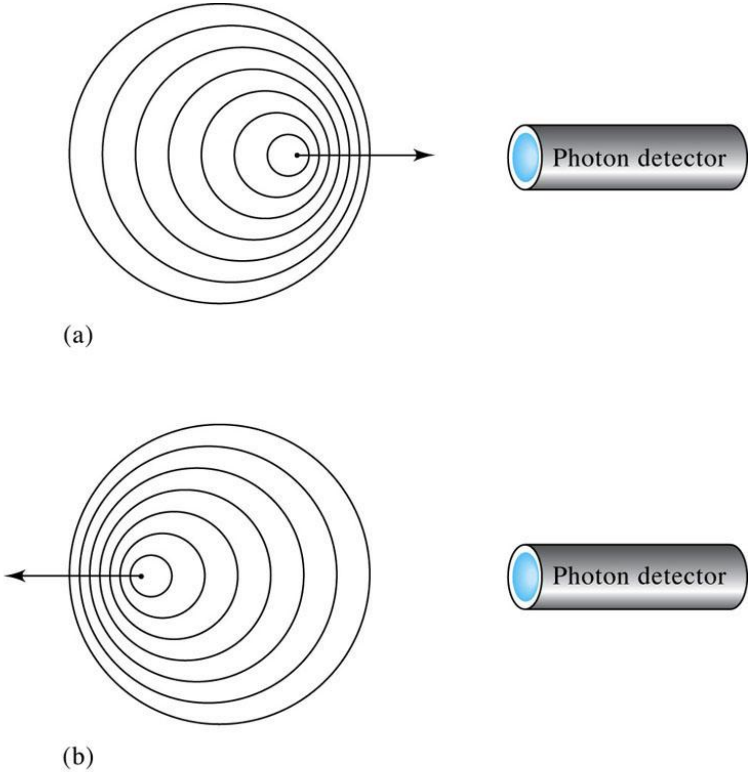
Doppler Effect:

* In a collection of atoms in a hot environment, such as an atomizer, atomic motions occur in every direction.

- The magnitude of the Doppler shift increases with the velocity at which the emitting or absorbing species approaches or recedes the detector.
- For relatively low velocities, the relationship between the Doppler shift ($\Delta\lambda$) and the velocity (v) of an approaching or receding atom is given by:

$$\Delta\lambda / \lambda_0 = v / c$$

Where λ_0 is the wavelength of an un-shifted line of a sample of an element at rest relative to the transducer, and c is the speed of light.



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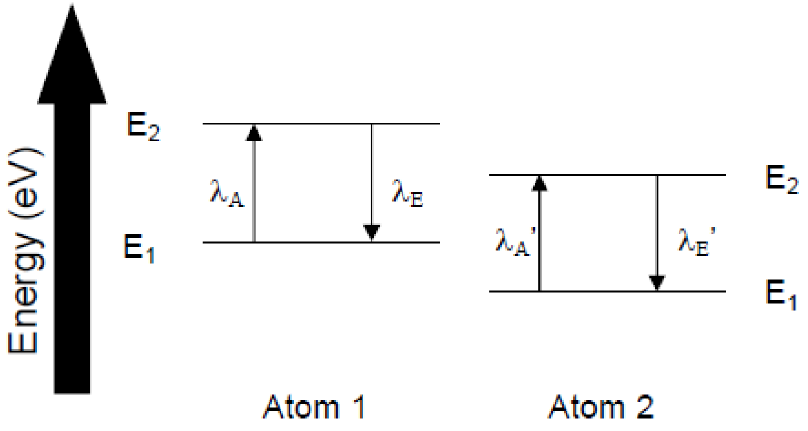
Emitting atom moving: (a) towards a photon detector, the detector sees wave crests more often and detect radiation of higher frequency; (b) away from the detector, the detector sees wave crests less frequently and detects radiation at lower frequency. The result is an statistical distribution of frequencies and thus a broadening of spectral lines.

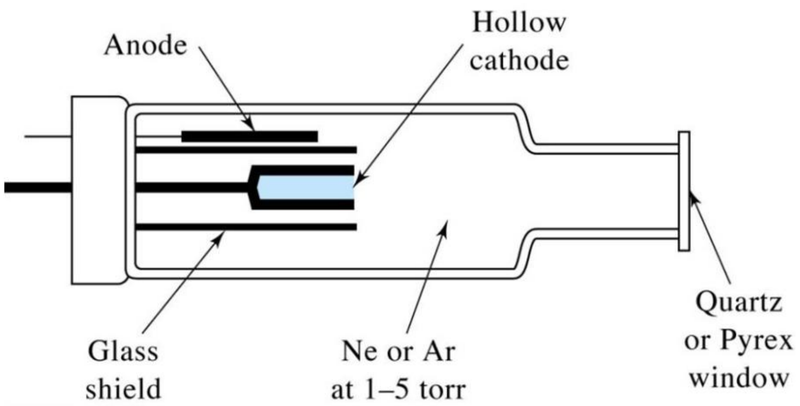
Pressure Effects Due to Collisions

Pressure or collisional broadening is caused by collisions of the emitting or absorbing species with other atoms or ions in the heated medium.

- These collisions produce small changes in energy levels and hence a range of absorbed or emitted wavelengths.
- These collisions produce broadening that is two to three orders of magnitude grater than the natural line widths.
    - Example: Hollow-cathode lamps (HCL)
- Pressure in these lamps is kept really low to minimize collisional broadening.
- Glass tube is filled with neon or argon at a pressure of 1 to 5 torr.

* In high-pressure mercury and xenon lamps, pressure broadening of this type is so extensive that continuum radiation is produced throughout the ultraviolet and visible region.





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The Effect of Temperature

- Temperature exerts a profound effect upon the ratio between the number of excited and unexcited atomic particles in an atomizer which can be derived from the Boltzmann equation, i.e.

$$N_j / N_0 = (g_j / g_0) \times [\exp(-E_j/kT)]$$

where,

N_j = number of atoms in an excited state

N_o = number of atoms ground state

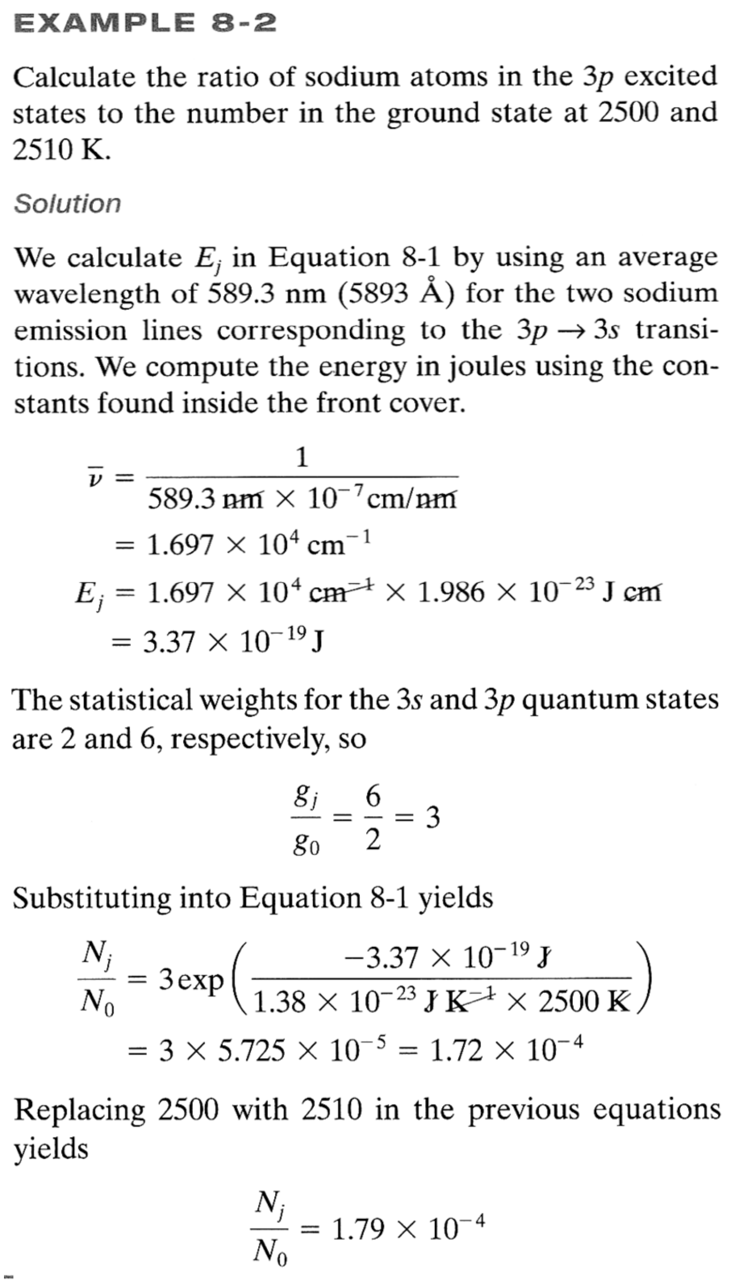
k = Boltzmann constant (1.38×10^{-23}J/K)

T = temperature in Kelvin

E_j = energy difference in joules between N_j and N_o

g_i and g_0 = statistical factors depend on quantum level , determined by the number of states having equal energy at each quantum level.

- Example shows that a temperature fluctuation of only 10K results in a 4% increase in the number of excited sodium atoms. A corresponding increase in emitted power by the two lines would result.
- An analytical method based on the measurement of emission requires close control of atomization temperature.a



EXAMPLE 8-2

Calculate the ratio of sodium atoms in the 3*p* excited states to the number in the ground state at 2500 and 2510 K.

Solution

We calculate E_j in Equation 8-1 by using an average wavelength of 589.3 nm (5893 Å) for the two sodium emission lines corresponding to the $3p \rightarrow 3s$ transitions. We compute the energy in joules using the constants found inside the front cover.

$$\begin{aligned}\bar{\nu} &= \frac{1}{589.3\,\cancel{\text{nm}} \times 10^{-7}\,\text{cm}/\cancel{\text{nm}}}\\ &= 1.697 \times 10^{4}\,\text{cm}^{-1}\\ E_j &= 1.697 \times 10^{4}\,\cancel{\text{cm}^{-1}} \times 1.986 \times 10^{-23}\,\text{J}\,\cancel{\text{cm}}\\ &= 3.37 \times 10^{-19}\,\text{J}\end{aligned}$$

The statistical weights for the 3*s* and 3*p* quantum states are 2 and 6, respectively, so

$$\frac{g_j}{g_0} = \frac{6}{2} = 3$$

Substituting into Equation 8-1 yields

$$\begin{aligned}\frac{N_j}{N_0} &= 3\exp\left(\frac{-3.37 \times 10^{-19}\,\cancel{\text{J}}}{1.38 \times 10^{-23}\,\cancel{\text{J}}\,\cancel{\text{K}^{-1}} \times 2500\,\cancel{\text{K}}}\right)\\ &= 3 \times 5.725 \times 10^{-5} = 1.72 \times 10^{-4}\end{aligned}$$

Replacing 2500 with 2510 in the previous equations yields

$$\frac{N_j}{N_0} = 1.79 \times 10^{-4}$$

-

Atomization Methods

➢In order to obtain atomic spectra, the constituents of a sample must be converted to gaseous atoms which can then be determined by emission, absorption or fluorescence measurements. The process by which the sample is converted into an atomic vapor is called **atomization**. The precision and accuracy of atomic methods are dependent upon the atomization step.

➢ Atomizers "fit" into two classes: continuous and discrete atomizers. Continuous atomizers: flames and plasmas. Samples are introduced in a steady manner. Discrete Atomizers: electro-thermal atomizers. Sample introduction is discontinuous and made with a syringe or an auto-sampler.

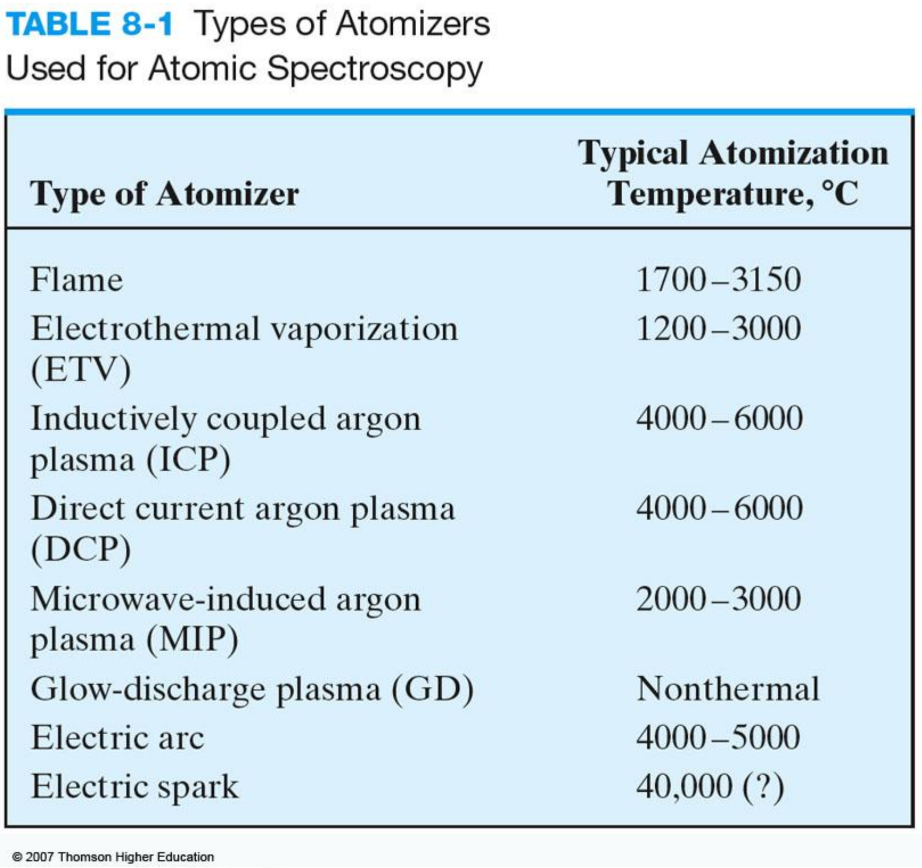
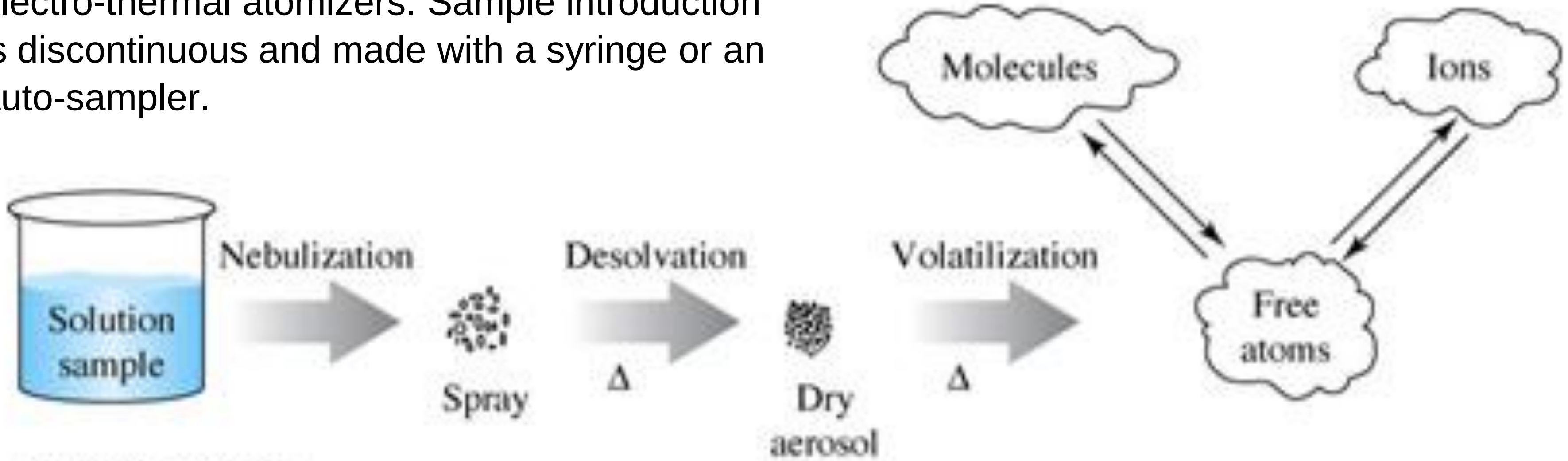


TABLE 8-1 Types of Atomizers Used for Atomic Spectroscopy

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
Glow-discharge plasma (GD)	Nonthermal
Electric arc	4000–5000
Electric spark	40,000 (?)



Sample Introduction Methods

✓ The goal of sample introduction is to transfer a reproducible and representative portion of a sample into the atomizer with

* high efficiency and

*no adverse interference effects.

✓Sample introduction limits the accuracy,precision and detection limits of atomic spectroscopic measurements.

✓Samples are most commonly introduced in the form of solutions.

✓Samples are introduced in the form of solids or finely dispersed powder if it is difficult to dissolve.

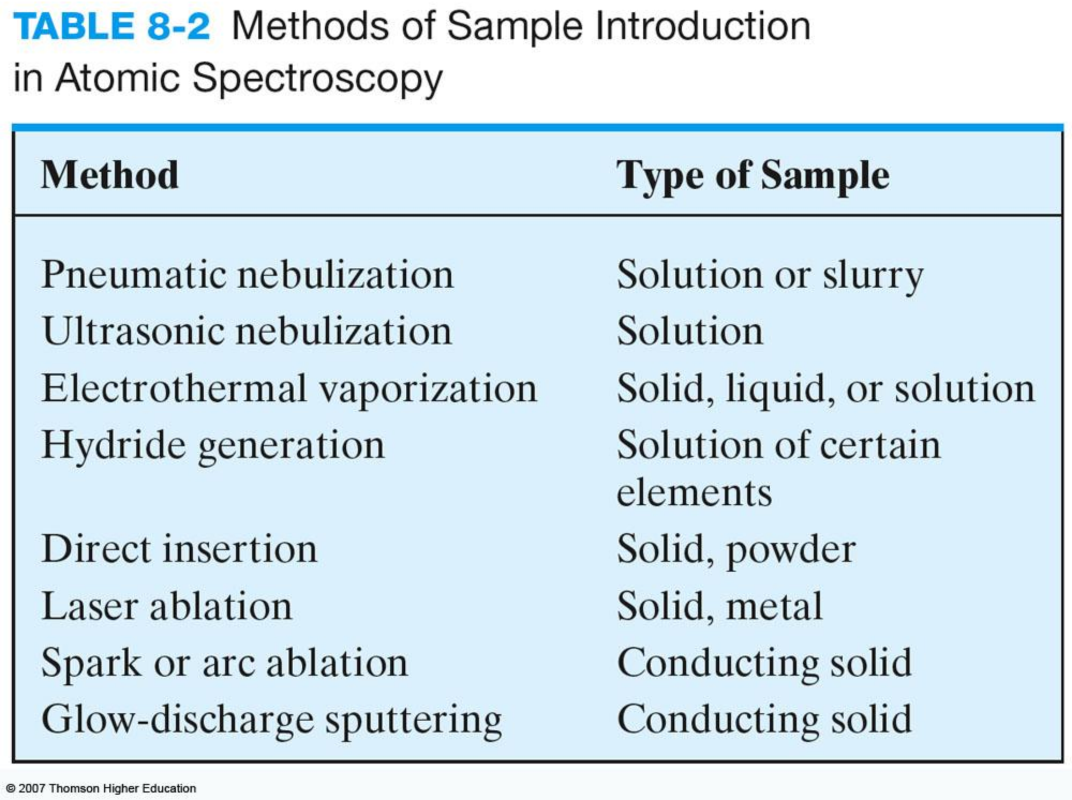


TABLE 8-2 Methods of Sample Introduction in Atomic Spectroscopy

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

Introduction of solution samples:

- *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. When flow injection or liquid chromatography is used a time-varying plug of sample is nebulized producing a time-dependent vapor population.*

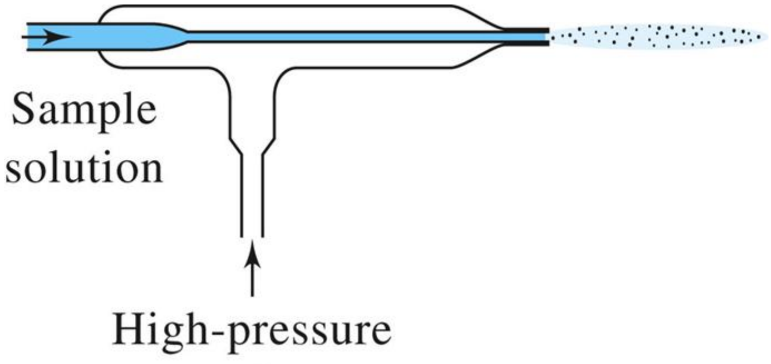
1. Pneumatic Nebulizers:

Samples are dissolved in an aqueous medium and then introduced into the atomizer by means of a nebulizer that converts the liquid into a fine mist or aerosol.

(a) Concentric tube pneumatic nebulizer

in which liquid sample is sucked through a capillary tube by a high pressure stream of gas flowing around the tip of the tube. The high velocity gas breaks the liquid up into fine droplets of various sizes which then carried into the atomizer.

This process of liquid transport is called aspiration.



(a)

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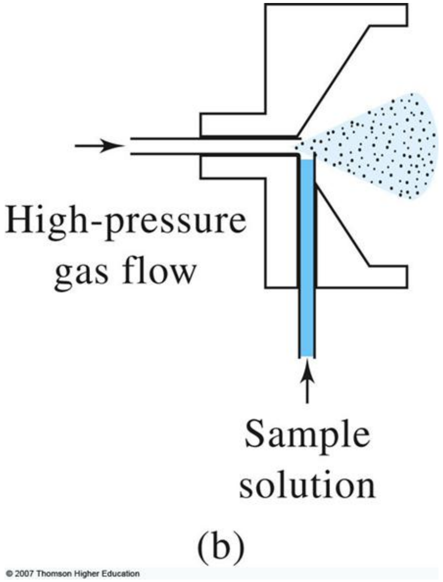
1. Pneumatic Nebulizers cont'd...

(b) Cross flow nebulizer; in which the high pressure gas flows across a capillary tip at right angles. Liquid is pumped through the capillary.



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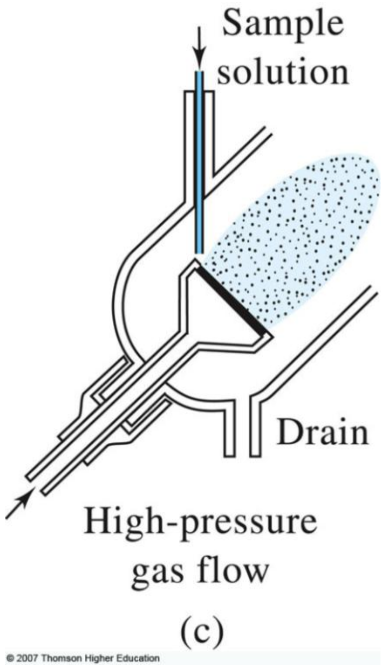

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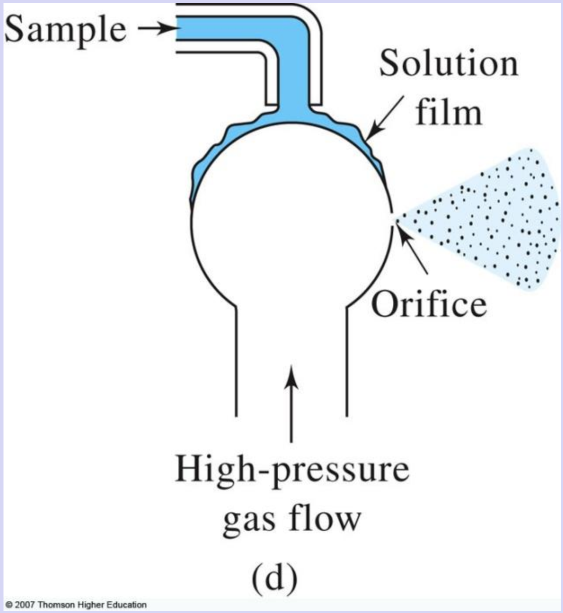
(c) Fritted disk nebulizer; in which the sample solution is pumped onto a fritted surface through which a carrier gas flows. It produces a much finer aerosol than do the first two.

(d) Babington nebulizer which consists of hollow sphere in which high pressure gas is pumped through a small orifice in the sphere surface. Liquid flowing in a thin film over the sphere surface is nebulized by the expanding jet of gas.



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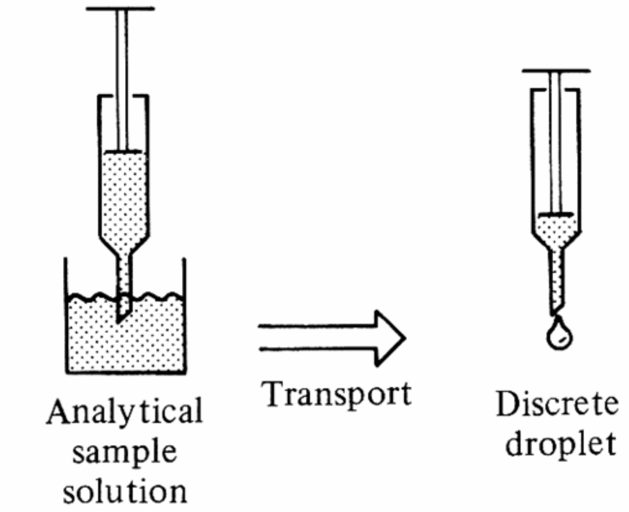
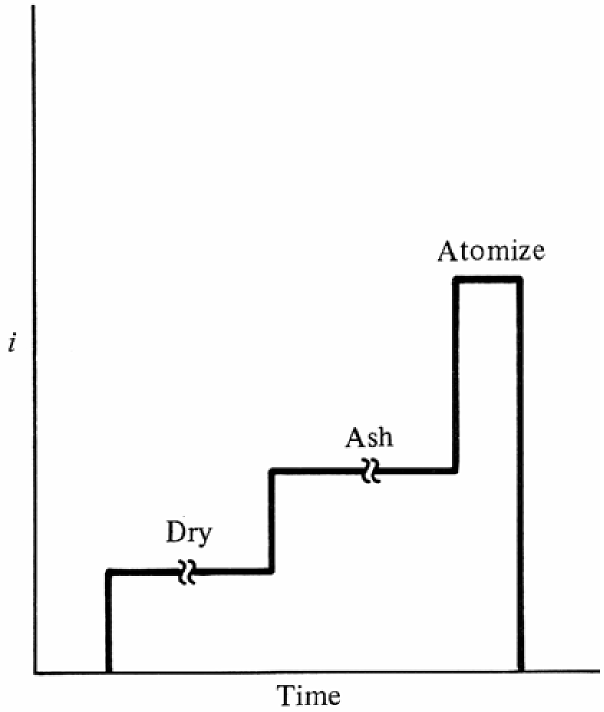
2. Ultrasonic Nebulizers:

- The sample is pumped onto the surface of a piezoelectric crystal that vibrates at a frequency of 20 kHz to several MHz.
- Such nebulizer produce more dense and more homogeneous aerosols than pneumatic nebulizers do.
- These devices have low efficiencies with viscous solutions and solutions containing particulates.

3. Electrothermal Vaporizers:

- ➢The most common type of discrete atomizer is the electro-thermal atomizer.
- ➢ It is an evaporator located in a closed chamber through which an inert gas such as argon flows to carry the vaporized sample into the atomizer.
- ➢ A small liquid or solid sample is placed on a conductor, such as a carbon rod or tantalum filament. An electric current then evaporates the sample rapidly and completely into the argon gas.
- ➢ An electro-thermal atomizer is a small furnace tube heated by passing a current through it from a programmable power supply.
- • The furnace is heated in stages. The drying and ashing steps removes water and organic or volatile inorganic matter, respectively.
- • The atomization step produces a pulse of atomic vapor that is probed by the radiation beam from the hollow-cathode lamp (HCL).





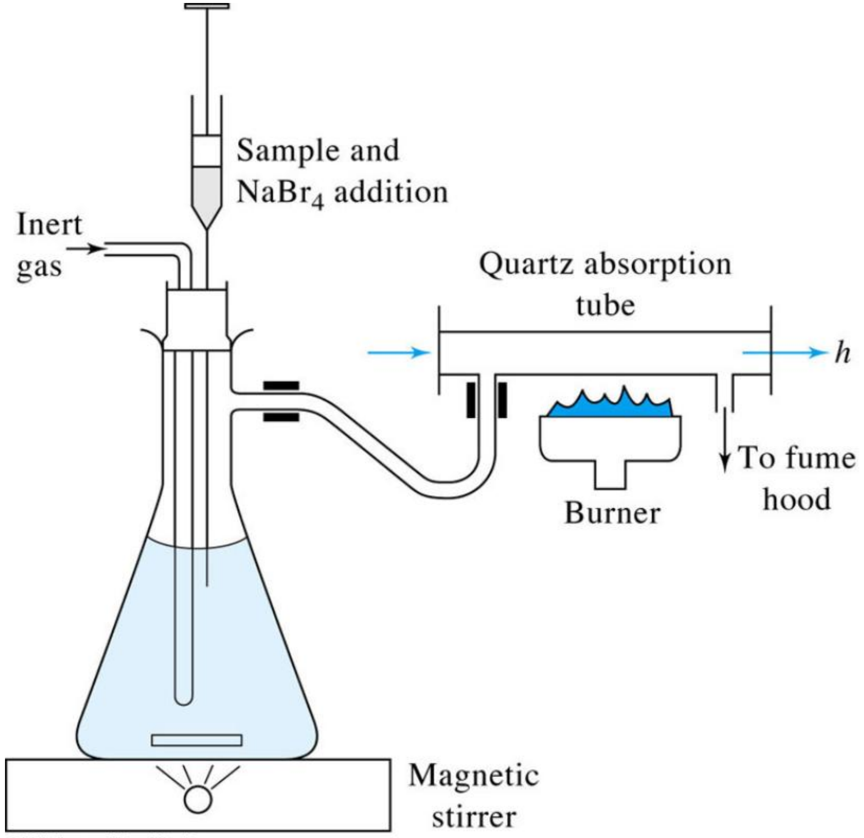
4. Hydride Generation Techniques:

- It provides a method for introducing samples containing arsenic, antimony, tin, selenium, bismuth, and lead into an atomizer as a gas.
- Volatile hydrides can be generated by addition of an acidified aqueous solution of a sample to a small volume of a 1% aqueous solution of sodium borohydride:

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

The volatile hydride – in this case, arsine – is swept into the atomization chamber by an inert gas.

- Such a procedure enhances the detection limits for these elements by a factor of 10 to 100. Because several of these species arc highly toxic, determining them at low concentration levels is quite important.



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Introduction of Solid Samples:

The introduction of solids in the form of powders, metals, or particulates into plasma and flame atomizers has the considerable advantage of avoiding the often tedious and time-consuming step of sample decomposition and dissolution. however, often suffer from severe difficulties with calibration, sample conditioning, precision, and accuracy.

Several techniques have been proposed during the last two decades for the direct introduction of solids into atomizers, thus avoiding the need to dissolve or decompose the sample.

(I) direct manual insertion of the solid into the atomization device,
(2) electrothermal vaporization of the sample and transfer of the vapor into the atomization region,
(3) arc. spark. or laser ablation of the solid to produce a vapor that is then swept into the atomizer,
(4) slurry nebulization in which the finely divided solid sample is carried into the atomizer as an aerosol consisting of a suspension of the solid in a liquid medium, and
(5) sputtering in a glow-discharge device.